MODELLING MOLECULAR STRUCTURES

Second Edition

Alan Hinchliffe

Department of Chemistry, UMIST, Manchester, UK

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SERIES PREFACE

Theoretical chemistry is one of the most rapidly advancing and exciting fields in the natural sciences today. This series is designed to show how the results of theoretical chemistry permeate and enlighten the whole of chemistry together with the multifarious applications of chemistry in modern technology. This is a series designed for those who are engaged in practical research. It will provide the foundation for all subjects which have their roots in the field of theoretical chemistry.

How does the materials scientist interpret the properties of the novel doped-fullerene superconductor or a solid-state semiconductor? How do we model a peptide and understand how it docks? How does an astrophysicist explain the components of the interstellar medium? Where does the industrial chemist turn when he wants to understand the catalytic properties of a zeolite or a surface layer? What is the meaning of 'far-from-equilibrium' and what is its significance in chemistry and in natural systems? How can we design the reaction pathway leading to the synthesis of a pharmaceutical compound? How does our modelling of intermolecular forces and potential energy surfaces yield a powerful understanding of natural systems at the molecular and ionic level? All these questions will be answered within our series which covers the broad range of endeavour referred to as 'theoreitcal chemistry'.

The aim of the series is to present the latest fundamental material for research chemists, lecturers and students across the breadth of the subject, reaching into the various applications of theoretical techniques and modelling. The series concentrates on teaching the fundamentals of chemical structure, symmetry, bonding, reactivity, reaction mechanism, solid-state chemistry and applications in molecular modelling. It will emphasize the transfer of theoretical ideas and results to practical situations so as to demonstrate the role of theory in the solution of chemical problems in the laboratory and in industry.

D. Clary, A. Hinchliffe, D. S. Urch and M. Springborg
June 1994

PREFACE TO THE FIRST EDITION

In the beginning, quantum chemists had pencils, paper, slide rules and log tables. It is amazing that so much could have been done by so few, with so little.

My little book *Computational Quantum Chemistry* was published in 1988. In the Preface, I wrote the following:

> As a chemistry undergraduate in the 1960s . . . I learned quantum chemistry as a very 'theoretical' subject. In order to get to grips with the colour of carrots, I knew that I had to somehow understand
>
> $$\left| \int \Psi_k^* \sum \underline{\mathbf{r}}_i \Psi_0 \, \mathrm{d}\tau \right|^2$$
>
> but I really didn't know how to calculate the quantity, or have the slightest idea as to what the answer ought to be . . .

and I also drew attention to the new confidence of the late 1980s by quoting

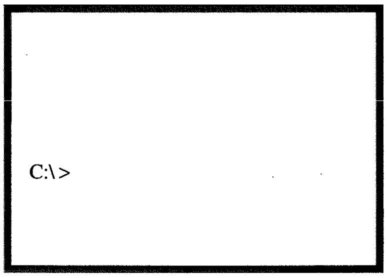
> Today we live in a world where everything from the chairs we sit in to the cars we drive are firstly designed by computer simulation and then built. There is no reason why chemistry should not be part of such a world, and why it should not be seen to be part of such a world by chemistry undergraduates.

The book seemed to capture the spirit of the 1980s, and it became accepted as a teaching text in many universities throughout the world. In those days, computing was done on mainframes, scientific programs were written in FORTRAN, and the phrase 'Graphical User Interface' (GUI) was unknown.

Personal computing had already begun in the 1980s with those tiny boxes called (for example) Commodore PETs, Apples, Apricots, Acorns, Dragons and so on. Most of my friends ignored the fact that PET was an acronym, and took one home in the belief that it would somehow change their life for the better and also become a family friend. Very few of them could have written a 1024 word essay describing the uses of a home computer. They probably still can't.

What they got was an 'entry level' machine with a simple operating system and the manufacturer's own version of BASIC. There were no application packages to speak of, and there was no industry standard in software. Anyone who wrote software in those days would have nightmares about printers and disk files.

IBM (the big blue giant) slowly woke up to the world of personal computing, and gave us the following famous screen, in collaboration with MICROSOFT.



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C:\>
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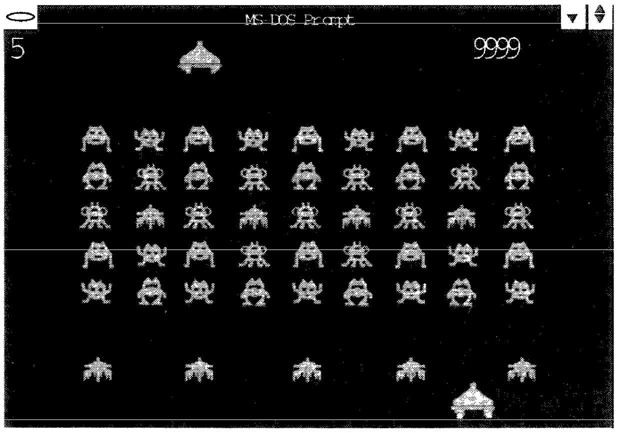
The DOS prompt

Not very user-friendly!

Then came the games, and most older readers will recognize the Space Invaders screen shown below ...



The Graphical User Interface was then born, courtesy of the the 'A' manufacturers such as Apple, Apricot, Amiga and Atari. Perhaps that is why so many of them went down the Games path. But they certainly left IBM behind.

These days we have Lemmings, Theme Park and SimCity. Many of them are modelling packages dressed up as games.

In the world of serious software, we soon saw the introduction of packages reflecting the three legs of the information technology trilogy

- word processing
- databases
- spreadsheets

and IT is now a well-established part of secondary education.

I don't want to bore you. As time went on, molecular modelling packages began to appear. Many ran under DOS (with the famous prompt screen above), but the more popular ran with GUIs on Apple Macs. Well, what happened is that MICROSOFT introduced WINDOWS, the famous graphical interface designed to protect users from DOS. There are now said to be more users of WINDOWS on IBM compatible PC's worldwide than all the other operating systems combined. But has all this actually changed out ability to understand molecules? Cynics will still argue that there have been no new major discoveries about molecular electronic structure theory since the heady days of the 1920s when Schrödinger, Pauli, Heisenberg and Dirac were active. Dirac said it all, in his oft-quoted statement.

Dirac's famous statement

> The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact application of these laws leads to equations much too complicated to be soluble.

But computers and computing have moved along apace. This is especially true for personal computing, whereby powerful modelling packages are now available for everyday use. Most of these packages use molecular mechanics, and these come with brilliant graphics and excellent user-interfaces. Conformational problems involving protein strands that have been tackled using these packages are becoming common-place in the primary literature.

It is interesting to note that all the simple theories (such as Hückel π-electron theory) have now reappeared as options in these very same packages! Thus, very many scientists now routinely use computational quantum chemistry as a futuristic tool for modelling the properties of pharmaceutical molecules, dyestuffs and biopolymers. I wrote the original *Computational Quantum Chemistry* text as an introduction for senior undergraduates and beginning postgraduates. True, the original edition had some flaws; reviewers pointed out that there was no need for a revision of the principles of quantum mechanics, however 'brief' and breakneck' (and I quote).

It seemed to me that the time was ripe for a new text that would focus on recent applications, especially those reflected in current modelling packages for PCs. Hence this book!

Alan Hinchliffe
UMIST,
Manchester, 1995

PREFACE TO THE SECOND EDITION

Molecular structure theory is a fast-moving subject, and a lot has happened since the First Edition was published in 1995. Chapters 3 (The Hydrogen Molecule-ion) and 4 (The Hydrogen Molecule) are pretty much as they were in the First Edition, but I have made changes to just about everything else in order to reflect current trends and the recent literature. I have also taken account of the many comments from friends and colleagues who read the First Edition.

Chapter 0 has been enhanced with a little background material on vector fields and vector calculus. I have significantly expanded Chapter 1 on molecular mechanics, and added a new chapter on molecular dynamics. The last ten years have seen the growth and growth of density functional theory, and I have therefore made significant improvements to my treatment. A 1976 paper in the (obscure) *Journal of Molecular Biology* has given us the cottage industry of 'Combined QM/MM methods' reflected in Chapter 15, and there has been exponential growth in derivative methods (reflected through the text).

A few topics have disappeared, and of course there are many gaps. One only has a finite number of pages and any text will naturally reflect the author's own experiences and preferences. Scattering theory and graph theory are both conspicuous by their absence, but there are several good texts on these subjects.

I have tried to remain true to my original brief, and produce a readable text for the more advanced consumer of molecular structure theory. The companion book *'Chemical Modelling: from Atoms to Liquids'* (John Wiley & Sons Ltd, Chichester, 1999) is more suitable for beginners.

Everyone has his or her favourite packages, and I have used a number for illustration. The commercial software packages mentioned can all be easily located on the Internet. I have made extensive use of screen grabs in order to illustrate points made in the text.

I welcome comments and suggestions, and can be reached at:

Alan.Hinchliffe@umist.ac.uk
UMIST
Manchester, 2000

0 PREREQUISITES

Welcome to the text. You are about to begin your study of molecular modelling. I must admit from the outset that this book is not quite as comprehensive as the title might suggest. You won't meet every model of molecular structure that has ever been tried, and you won't meet every molecule known to the chemical literature. I want to bring you up to speed on current molecular modelling techniques and applications, but I only have 300 pages in which to do it. My treatment of chemical reaction theories is skimpy, and we won't spend too much time on the solid state. Time dependence appears only briefly. But there are still an awful lot of exciting problems to be tackled and techniques to be learned.

The word 'model' has a special technical meaning: it implies that we have a set of mathematical equations that are capable of representing reasonably accurately the phenomenon under study. Thus, we can have a model of the UK economy just as we can have a model of a GM motor car, the Humber Road Bridge and a naphthalene molecule.

In the early days of chemical modelling, people did indeed construct models from plastic atoms and bonds, a ruler and a pair of scissors. The tendency now is to reach for the PC, and one aim of this book is to give you an insight into the bewitching acronyms that lie behind the keystrokes and mouse clicks of a sophisticated modelling package.

Why do we want to model molecules and chemical reactions? Chemists are interested in the distribution of electrons around the nuclei, and how these electrons rearrange in a chemical reaction; this is what chemistry is all about. Thomson tried to develop an electronic theory of valence in 1897. He was quickly followed by Lewis, Langmuir and Kössel, but their models all suffered from the same defect in that they tried to treat the electrons as classical point electric charges at rest.

The problem with moving charges is this: an accelerating electric charge generates electromagnetic radiation and so loses energy. According to all the theories of classical electromagnetism, a hydrogen atom should therefore be unstable. Bohr in 1916 solved the problem by postulating the existence of stable orbits (the so-called 'Bohr orbits') for the electron in a hydrogen atom. He was aware of de Broglie's hypothesis relating wave and particle properties, and he suggested that the electron's de Broglie waves had to fit precisely round circular orbits.

Bohr's treatment gave spectacularly good agreement with the observed fact that a hydrogen atom is stable, and also with the values of the spectral lines. This theory gave a single quantum number, n. Bohr's treatment failed miserably when it came to predictions of the intensities of the observed spectral lines, and more to the point, the stability (or otherwise) of a many-electron system such as He.

I should also mention Sommerfeld, who extended Bohr's theory to try and account for the extra quantum numbers observed experimentally. Sommerfeld allowed the electrons to have an elliptic orbit rather than a circular one.

The year 1926 was an exciting one. Schrödinger, Heisenberg and Dirac, all working independently, solved the hydrogen atom problem. Schrödinger's treatment, which we refer to as *wave mechanics*, is the version that you will be familiar with. The only cloud on the horizon was summarized by Dirac, in his famous statement:

> The underlying physical laws necessary for the mathematical description of a large part of physics and the whole of chemistry are thus completely known, and the only difficulty is that the exact application of these laws leads to equations much too difficult to be soluble.

If Dirac was warning us that solution of the equations of quantum mechanics was going to be horrendous for everyday chemical problems, then history has proved him right. Fifty years on from there, Enrico Clementi (1973) saw things differently:

> We can calculate everything

whilst Frank Boys (1950) saw things in a little more perspective when he said

> It has thus been established that the only difficulty which exists in the evaluation of the energy and wavefunction of any molecule . . . is the amount of computing necessary.

The kinds of problems that people could tackle successfully in the early days were very simple and semi-qualitative. For example:

- Why is the H atom stable, and what are its allowed energy levels?
- Why is the hydrogen molecule ion H_2^+ stable, and what should its bond length be?

- Why is methane tetrahedral?
- Why is the bond angle in water smaller than tetrahedral?

These days, even the simplest problems discussed in the primary journals are much more sophisticated, and I will give you a flavour as we progress through the text.

0.1 WHAT IS A CHAPTER 0?

Let me tell you how things were in the heady days of the late 1960s, when scientists (like me) and engineers first got their hands on computers. Computers were very large beasts, and they consumed very many kilojoules (kilocalories in those days, or if you are a North American reader) per unit time. If you believe in the law of conservation of energy, you will understand why such machines had a refrigeration plant, where the three resident engineers kept the milk for their coffee.

In those days, you wrote your own code or perished. There were no packages such as GAUSSIAN, all we had were rudimentary program libraries which contained procedures for matrix diagonalization, minimization of a function of many variables and the like. By 'we', I include the electrical and electronic engineers, the crystallographers and the weather forecasters who spent so many happy nights and weekends together watching our output being produced on five-track paper tape.

I wrote my first lines of code in Mercury Autocode; the problem was to find the Hückel bond orders in [18]-annulene, a fascinating compound that shows very unusual bond-length alternation. Mercury Autocode was originally developed for the Ferranti Mercury computer, which is how things were done in the late 1960s. The programming language was specific to a particular machine. FORTRAN II was just on the horizon. What you would recognize today as random-access memory was extremely limited on the early machines, and programs had to be segmented into units called 'chapters'.

Operating systems were still a gleam in computer scientists' eyes; you put your program into the paper-tape reader and pressed the Initial Transfer Button on the Engineers' Console. Compilation errors were indicated in binary on two cathode-ray tubes, and once you were past the stage of compilation errors, the first section of code to be executed was Chapter 0. If you know about program segmentation and overlays, then you will understand about Chapter 0. We used Chapter 0 to set up arrays, set constants and limits and generally prepare for the work ahead.

I hope you will regard this Chapter 0 in the same way. You really ought to read the entirety of this chapter before you begin the book in earnest, because it is a preparation for the work ahead. The reason is quite simple. I am going to have to assume some prerequisite knowledge, especially in mechanics, which is the branch of maths that deals with movement.

0.2 BRANCHES OF MECHANICS

There are three branches of mechanics. *Classical mechanics* normally deals with things in the everyday world: accelerating sports cars, bodies sliding down inclined planes and other related phenomena.

Relativistic mechanics normally deals with situations where one body is moving with respect to another one. If this relative motion is one of uniform velocity, then the subject is referred to as *special relativity*. Special relativity is well understood and has stood the test of experiment. If accelerations are involved, then we enter the realm of *general relativity*. It is fair comment to say that general relativity is still an active research field.

Finally we have *quantum mechanics*, which normally has to be invoked when dealing with situations where small particles (such as electrons, protons and neutrons) are involved.

In the following sections, I have tried to pick out some of the more familiar techniques and concepts that will form recurring themes throughout the text.

0.3 VECTORS, VECTOR FIELDS AND VECTOR CALCULUS

I assume that you are familiar with the elementary ideas of vectors and vector algebra. Thus if a point P has position vector $\mathbf{r}$ (I will use bold letters to denote vectors) then we can write $\mathbf{r}$ in terms of the unit Cartesian vectors $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ as:

$$\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z \tag{0.1}$$

The scalars x, y and z are called the *Cartesian components* (or coordinates) of point P.

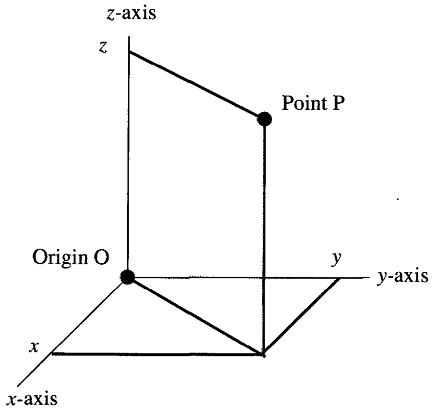


Figure 0.1 Cartesian coordinates

We normally solve problems in science by taking advantage of the symmetry of a given problem. In the case of spherical symmetry, it is advantageous to use the *spherical polar coordinates* r, θ and ϕ rather than Cartesian coordinates. The r coordinate is the distance of the point P from the origin O. The angle θ is the angle that the line OP makes with the positive z-axis system. The angle ϕ is the azimuthal angle measured in the $x-y$ plane from the positive x-axis.

The unit vectors in this system are $\mathbf{e}_r$, $\mathbf{e}_\theta$ and $\mathbf{e}_\phi$. The unit vector $\mathbf{e}_r$ is directed outwards from the coordinate origin O to point P, the unit vector $\mathbf{e}_\theta$ is normal to the line OP in the plane containing the z-axis and OP, and in the direction of increasing θ. The unit vector $\mathbf{e}_\phi$ is tangential to the circle shown in Figure 0.2 and points in the direction of increasing ϕ.

The coordinates (r, θ, ϕ) are related to Cartesian coordinates by

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

The values of r, θ and ϕ are restricted as follows:

$$r \geqslant 0$$
$$0 \leqslant \theta \leqslant \pi$$
$$0 \leqslant \phi < 2\pi$$

0.3.1 The Dot (or Scalar) Product

The *dot product* of two vectors $\mathbf{u}$ and $\mathbf{v}$ is

$$\mathbf{u} \cdot \mathbf{v} = |\mathbf{u}||\mathbf{v}|\cos\theta \qquad (0.2)$$

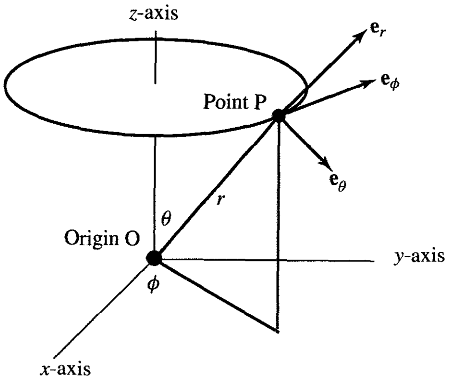


Figure 0.2 Spherical polar coordinates

where θ is the angle between $\mathbf{u}$ and $\mathbf{v}$, and $|\mathbf{u}|, |\mathbf{v}|$ are the magnitudes of the vectors. If $\mathbf{u} \cdot \mathbf{v} = 0$ and neither of $\mathbf{u}$ and $\mathbf{v}$ is a zero vector, then we say that $\mathbf{u}$ and $\mathbf{v}$ are *orthogonal.*

Dot products obey the rules:

$$\mathbf{u} \cdot \mathbf{v} = \mathbf{v} \cdot \mathbf{u}$$

$$\mathbf{u} \cdot (\mathbf{v} + \mathbf{w}) = \mathbf{u} \cdot \mathbf{v} + \mathbf{u} \cdot \mathbf{w}$$

and the Cartesian unit vectors satisfy

$$\mathbf{e}_x \cdot \mathbf{e}_x = \mathbf{e}_y \cdot \mathbf{e}_y = \mathbf{e}_z \cdot \mathbf{e}_z = 1$$

$$\mathbf{e}_x \cdot \mathbf{e}_y = \mathbf{e}_x \cdot \mathbf{e}_z = \mathbf{e}_y \cdot \mathbf{e}_z = 0$$

It follows that the dot product of $\mathbf{u}$ and $\mathbf{v}$ can be written

$$\mathbf{u} \cdot \mathbf{v} = u_x v_x + u_y v_y + u_z v_z$$

and the modulus of vector $\mathbf{v}$ is

$$|\mathbf{v}| = (\mathbf{v} \cdot \mathbf{v})^{1/2} = \left(v_x^2 + v_y^2 + v_z^2\right)^{1/2}$$

It also follows that the angle between the vectors $\mathbf{u}$ and $\mathbf{v}$ is given by

$$\cos\theta = \frac{u_x v_x + u_y v_y + u_z v_z}{\left(u_x^2 + u_y^2 + u_z^2\right)^{1/2} \left(v_x^2 + v_y^2 + v_z^2\right)^{1/2}} \tag{0.3}$$

0.3.2 The Cross (or Vector) Product

The *cross product* of two vectors $\mathbf{u}$ and $\mathbf{v}$ is

$$\mathbf{u} \times \mathbf{v} = |\mathbf{u}||\mathbf{v}| \sin\theta \mathbf{n} \tag{0.4}$$

where θ is the angle between $\mathbf{u}$ and $\mathbf{v}$ and $\mathbf{n}$ a unit vector normal to the plane containing the vectors $\mathbf{u}$ and $\mathbf{v}$. The direction of this unit normal is given by the direction in which a screw would advance if rotated from the direction of $\mathbf{u}$ to the direction of $\mathbf{v}$.

The cross product obeys the laws:

$$\mathbf{u} \times \mathbf{v} = -\mathbf{v} \times \mathbf{u}$$

$$\mathbf{u} \times (\mathbf{v} + \mathbf{w}) = \mathbf{u} \times \mathbf{v} + \mathbf{u} \times \mathbf{w}$$

The Cartesian unit vectors satisfy

$$\mathbf{e}_x \times \mathbf{e}_x = \mathbf{e}_y \times \mathbf{e}_y = \mathbf{e}_z \times \mathbf{e}_z = 0$$

$$\mathbf{e}_x \times \mathbf{e}_y = \mathbf{e}_z, \mathbf{e}_y \times \mathbf{e}_z = \mathbf{e}_x, \&\mathbf{e}_z \times \mathbf{e}_x = \mathbf{e}_y$$

and in terms of Cartesian components

$$\mathbf{u} \times \mathbf{v} = (u_y v_z - u_z v_y)\mathbf{e}_x + (u_z v_x - u_x v_z)\mathbf{e}_y + (u_x v_y - u_y v_x)\mathbf{e}_z \qquad (0.5)$$

If $\mathbf{u} \times \mathbf{v} = \mathbf{0}$ and neither **u** not **v** is a zero vector, then **u** and **v** are either parallel or antiparallel.

0.3.3 Scalar and Vector Fields

A field is a function that describes a physical property at points in space. In a *scalar field*, this physical property is completely described by a single value for each point (e.g. temperature, density, electrostatic potential). For *vector fields*, both a direction and a magnitude are required for each point (e.g. gravitation, electrostatic field intensity).

0.4 VECTOR CALCULUS

0.4.1 Differentiation of Fields

Suppose that the vector field $\mathbf{u}(t)$ is a continuous function of the scalar variable t. As t varies, so does **u** and if **u** denotes the position vector of a point P, then P moves along a continuous curve in space as t varies. For most of this book we will identify the variable t as time and so we will be interested in the trajectory of particles along curves in space.

By analogy with ordinary differential calculus, the ratio $\mathrm{d}\mathbf{u}/\mathrm{d}t$ is defined as the limit of the ratio $\delta\mathbf{u}/\delta t$ as the interval δt becomes progressively smaller.

$$\begin{aligned} \frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} &= \lim \frac{\delta\mathbf{u}}{\delta t} \\ &= \lim \left(\frac{\delta u_x}{\delta t}\mathbf{e}_x + \frac{\delta u_y}{\delta t}\mathbf{e}_y + \frac{\delta u_z}{\delta t}\mathbf{e}_z \right) \\ &= \frac{\mathrm{d}u_x}{\mathrm{d}t}\mathbf{e}_x + \frac{\mathrm{d}u_y}{\mathrm{d}t}\mathbf{e}_y + \frac{\mathrm{d}u_z}{\mathrm{d}t}\mathbf{e}_z \end{aligned} \qquad (0.6)$$

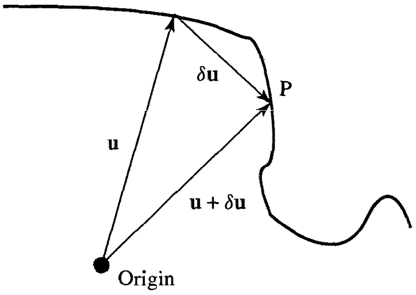


Figure 0.3 Movement along a curve in space

The derivative of a vector is the vector sum of the derivatives of its components. The usual rules for differentiation apply:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{u}+\mathbf{v}) = \frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} + \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(k\mathbf{u}) = k\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(f\mathbf{u}) = \frac{\mathrm{d}f}{\mathrm{d}t}\mathbf{u} + f\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t}$$

where k is a scalar and f a scalar field.

0.4.2 The Gradient

Suppose that $f(x, y, z)$ is a scalar field, and we wish to investigate how f changes between the points $\mathbf{r}$ and $\mathbf{r} + \mathrm{d}\mathbf{r}$. Here

$$\mathrm{d}\mathbf{r} = \mathbf{e}_x\,\mathrm{d}x + \mathbf{e}_y\,\mathrm{d}y + \mathbf{e}_z\,\mathrm{d}z$$

We know from elementary calculus that

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y + \left(\frac{\partial f}{\mathrm{d}z}\right)\mathrm{d}z$$

so we write $\mathrm{d}f$ as a scalar product,

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\mathbf{e}_x + \frac{\partial f}{\partial y}\mathbf{e}_y + \frac{\partial f}{\partial z}\mathbf{e}_z\right)\cdot(\mathbf{e}_x\,\mathrm{d}x + \mathbf{e}_y\,\mathrm{d}y + \mathbf{e}_z\,\mathrm{d}z)$$

The first vector on the right-hand side is called the *gradient of* f, and it is written 'grad f' in this text.

$$\text{grad } f = \frac{\partial f}{\partial x}\mathbf{e}_x + \frac{\partial f}{\partial y}\mathbf{e}_y + \frac{\partial f}{\mathrm{d}z}\mathbf{e}_z \tag{0.7}$$

An alternative notation involves the use of the so-called gradient operator ∇ (pronounced 'del'),

$$\nabla = \frac{\partial}{\partial x}\mathbf{e}_x + \frac{\partial}{\partial y}\mathbf{e}_y + \frac{\partial}{\partial z}\mathbf{e}_z \tag{0.8}$$

and so the gradient of f is ∇f.

In spherical polar coordinates, the corresponding expression for grad f is

$$\text{grad } f = \frac{\partial f}{\partial r}\mathbf{e}_r + \frac{1}{r}\frac{\partial f}{\partial \theta}\mathbf{e}_\theta + \frac{1}{r\sin\vartheta}\frac{\partial f}{\partial \phi}\mathbf{e}_\phi \tag{0.9}$$

grad f is a vector field whose direction at any point is the direction in which f is increasing most rapidly and whose magnitude is the rate of change of f in that direction. The spatial rate of change of the scalar field f in the direction of an arbitrary unit vector $\mathbf{e}$ is given by $\mathbf{e} \cdot \operatorname{grad} f$.

0.4.3 The Laplacian

It is worth noting at this point that the *Laplacian operator* $\nabla^2 = \nabla \cdot \nabla$ plays an important role in this text. In Cartesian coordinates,

$$\nabla^2 f \equiv (\nabla \cdot \nabla) f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \tag{0.10}$$

and in spherical polar coordinates

$$\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 f}{\partial \phi^2} \tag{0.11}$$

0.4.4 The Divergence

The *divergence* of a vector field $\mathbf{u}$, written div $\mathbf{u}$, is given in Cartesian coordinates by

$$\operatorname{div} \mathbf{u} \equiv \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \tag{0.12}$$

It is often written in terms of the ∇ operator as $\nabla \cdot u$.

0.4.5 The Curl

The *curl* of a vector field $\mathbf{u}$, written curl $\mathbf{u}$, is given in Cartesian coordinates by

$$\operatorname{curl} \mathbf{u} \equiv \left(\frac{\partial u_y}{\partial z} - \frac{\partial u_z}{\partial y}\right)\mathbf{e}_x + \left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z}\right)\mathbf{e}_y + \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right)\mathbf{e}_x \tag{0.13}$$

It is often written in terms of the ∇ operator as $\nabla \times \mathbf{u}$.

0.4.6 Flux

Figure 0.4 shows a vector field $\mathbf{u}$ on which I have drawn a surface S. The surface could correspond to a real physical boundary (such as a metallic surface, or the boundary between air and water), or it could just be an abstract entity. Lines of $\mathbf{u}$ cross the surface, and we speak colloquially of the *flux* of $\mathbf{u}$ through the surface. Again speaking colloquially, the more lines through S, the greater the flux. I will have cause to mention flux in this volume, so we need to investigate the concept in more detail.

Depending on $\mathbf{u}$ and its relation to the surface, the lines of $\mathbf{u}$ will not necessarily all have the same orientation with the surface, and the modulus of $\mathbf{u}$ will not necessarily be the same at all points on the surface. What I do is to divide the

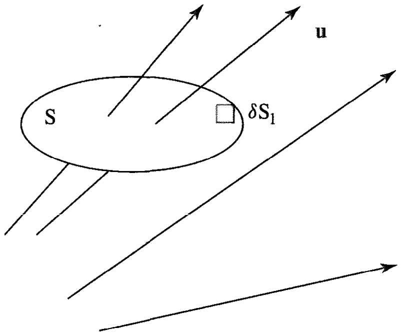


Figure 0.4 Flux of vector field through surface

surface S into small elements $\delta S_1, \delta S_2, \ldots$ as shown. On each of these small elements such as δS_1 I draw an outward normal as illustrated in Figure 0.5.

The flux of **u** through δS_1 is defined as $\mathbf{u} \cdot \mathbf{n}\ \delta S_1$, that is the projection of the vector field along the unit normal for δS_1 multiplied by the area of δS_1. It is usual to define a *surface element* $\delta \mathbf{S} = \mathbf{n}\ \delta S$.

If we calculate the sum of all such contributions

$$\sum_i \mathbf{u}_i \cdot \delta \mathbf{S}_i$$

and let the δS_i become infinitesimally small, then we get the flux of **u** through S:

$$\Phi = \int \mathbf{u} \cdot d\mathbf{S} \qquad (0.14)$$

I have used the accepted symbol Φ for flux. Obviously the evaluation of such integrals is no easy matter; it is discussed in all the advanced calculus texts.

There are a couple of interesting points. First of all, if the surface is a closed surface (an ellipsoid rather than the ellipse shown in Figure 0.4), then we often

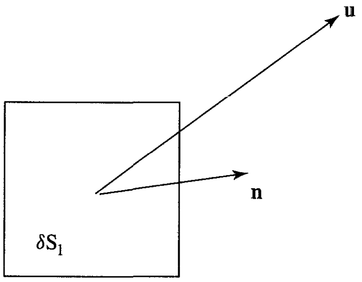


Figure 0.5 Construct needed to discuss flux

write the expression

$$\Phi = \oint \mathbf{u} \cdot \mathrm{d}\mathbf{S} \tag{0.15}$$

If the closed surface is such that it encloses neither sources nor sinks of **u**, then the flux of **u** entering the surface is exactly equal to the flux of **u** leaving the surface and so

$$\oint \mathbf{u} \cdot \mathrm{d}\mathbf{S} = 0$$

0.5 NEWTON'S LAWS OF MOTION

Problems in classical mechanics can be solved by the application of Newton's three laws, which can be stated as follows.

I Any body remains in a state of rest or of uniform motion unless an unbalanced force acts upon it.

II In order to make a body of mass m undergo an acceleration $\mathbf{a}$, a force $\mathbf{F}$ is required that is equal to the product of the mass times the acceleration. In symbols

$$\mathbf{F} = m\mathbf{a}. \tag{0.16}$$

III When two bodies A and B interact with each other, the force exerted by body A on body B, $\mathbf{F}_{\mathrm{A\ on\ B}}$, is equal and opposite to the force exerted by body B on body A, $\mathbf{F}_{\mathrm{B\ on\ A}}$

Bodies move under the influence of forces; we often use the term *statics* when dealing with situations where the resultant force on a body is zero.

0.5.1 The Force and the Potential

According to Newton's second law, a force $\mathbf{F}$ acts on a body of mass m to produce acceleration $\mathbf{a}$ according to the law

$$\mathbf{F} = m\mathbf{a}$$

which we can also write in terms of the position vector $\mathbf{r}$ of the body as

$$\mathbf{F} = m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} \tag{0.17}$$

You are probably *au fait* with the *principle of conservation of energy*, which introduces the idea of the potential energy U. The kinetic energy and the potential energy of the body can each vary, but their sum is a constant that I will write ε.

$$\tfrac{1}{2}mv^2 + U = \varepsilon \tag{0.18}$$

The problem now is to relate U to the force **F**. Suppose to start with that we are dealing with motion in the x direction, so that $v = \mathrm{d}x/\mathrm{d}t$. We then write

$$\frac{1}{2}m\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 + U = \varepsilon$$

Differentiating either side with respect to time, we find

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{2}m\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 + U\right) = 0$$

and so

$$m\frac{\mathrm{d}x}{\mathrm{d}t}\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{\mathrm{d}U}{\mathrm{d}t} = 0$$

This can be rewritten

$$m\frac{\mathrm{d}x}{\mathrm{d}t}\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{\mathrm{d}U}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}t} = 0$$

and so

$$\frac{\mathrm{d}x}{\mathrm{d}t}\left(m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{\mathrm{d}U}{\mathrm{d}x}\right) = 0$$

This means that $\mathrm{d}x/\mathrm{d}t = 0$ or

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{\mathrm{d}U}{\mathrm{d}x} = 0$$

Using Newton's second law, we see that

$$F = -\frac{\mathrm{d}U}{\mathrm{d}x} \tag{0.19}$$

which is the fundamental equation relating the force F and the potential energy U.

Forces are vector quantities and the potential energy U is a scalar quantity. For a three-dimensional problem, the link between the force **F** and the potential U can be found exactly as above. We have

$$\frac{1}{2}m\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\cdot\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} + U = \varepsilon$$

and following the above argument leads to

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} + \mathrm{grad}\ U = \mathbf{0}$$

which gives the more general link between force and mutual potential energy,

$$\mathbf{F} = -\mathrm{grad}\ U \tag{0.20}$$

0.6 BASIC ELECTROSTATICS

At various points throughout the text, I will have to refer to some of the basic concepts and results of classical electrostatics. This is the field of human endeavour that deals with the forces between electric charges at rest, the fields and electrostatic potentials produced by such charges, and the mutual potential energy of an array of such charges. To get us going, consider two point charges Q_A and Q_B as shown in Figure 0.6.

Point charge Q_A is located at vector position $\mathbf{r}_A$ and point charge Q_B is at vector position $\mathbf{r}_B$. The vector joining Q_A to Q_B is also shown: $\mathbf{r}_B - \mathbf{r}_A$ points in the direction from Q_A to Q_B.

The basic law of electrostatics is *Coulomb's law*, which relates the force between these point charges

$$\mathbf{F}(Q_A \text{ on } Q_B) = \frac{1}{4\pi\epsilon_0} Q_A Q_B \frac{\mathbf{r}_B - \mathbf{r}_A}{|\mathbf{r}_B - \mathbf{r}_A|^3} \tag{0.21}$$

Here ϵ_0 is a fundamental constant called the permittivity of free space. To three decimal places,

$$\epsilon_0 = 8.854 \times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}} \tag{0.22}$$

According to Newton's third law, this force should be exactly equal and opposite to the force exerted by Q_B on Q_A, and this is seen to be true from the elementary theory of vectors; $(\mathbf{r}_A - \mathbf{r}_B = -\mathbf{r}_B + \mathbf{r}_A)$ and so

$$\mathbf{F}(Q_B \text{ on } Q_A) = \frac{1}{4\pi\epsilon_0} Q_A Q_B \frac{\mathbf{r}_A - \mathbf{r}_B}{|\mathbf{r}_A - \mathbf{r}_B|^3}$$

0.6.1 Pairwise Additivity

If we add more and more point charges $Q_C, Q_D, \ldots$ then the forces between the existing point charges do not change, and so the total force acting on Q_A is given

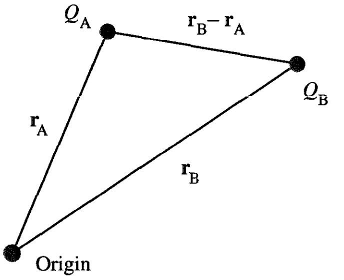


Figure 0.6 Construct needed to discuss the force between two point charges

by the *principle of superposition*:

$$\mathbf{F}(\text{All point charges on } Q_\text{A}) = \frac{1}{4\pi\epsilon_0} Q_\text{A} \sum_I Q_I \frac{\mathbf{r}_\text{A} - \mathbf{r}_I}{|\mathbf{r}_\text{A} - \mathbf{r}_I|^3} \tag{0.23}$$

0.6.2 The Mutual Potential Energy

Provided that the charge distribution does not change with time, then the derivation given above that links the force to the mutual potential energy also applies. We can therefore define a mutual potential energy U for two point charges Q_A and Q_B given by

$$\mathbf{F}(Q_\text{B} \text{ on } Q_\text{A}) = -\text{ grad } U$$

where the differentiation is with respect to the coordinates of Q_A. Algebraic manipulation shows that U is also given by

$$\mathbf{F}(Q_\text{A} \text{ on } Q_\text{B}) = -\text{grad } U$$

where the differentiation on the right-hand side is now with respect to the coordinates of Q_B and so U is truly the *mutual* potential energy of the point charges Q_A and Q_B. It is often written as U_AB, for that reason.

For a pair of point charges, U_AB is given by

$$U_\text{AB} = \frac{1}{4\pi\epsilon_0} Q_\text{A} Q_\text{B} \frac{1}{|\mathbf{r}_\text{A} - \mathbf{r}_\text{B}|} \tag{0.24}$$

The physical significance of U_AB is that it represents the work done in bringing up Q_B from infinity to the point whose position vector is $\mathbf{r}_\text{B}$, under the influence of Q_A which is fixed at $\mathbf{r}_\text{A}$. Because of the symmetry of the expression, it also represents the work done in bringing up point charge Q_A from infinity to the point with vector position $\mathbf{r}_\text{A}$, under the influence of point charge Q_B which is fixed in space at position $\mathbf{r}_\text{B}$.

0.6.3 The Electrostatic Field

The electrostatic force exerted by Q_A on Q_B (as discussed above) is

$$\mathbf{F}(Q_\text{A} \text{ on } Q_\text{B}) = \frac{1}{4\pi\epsilon_0} Q_\text{A} Q_\text{B} \frac{\mathbf{r}_\text{B} - \mathbf{r}_\text{A}}{|\mathbf{r}_\text{B} - \mathbf{r}_\text{A}|^3}$$

We can give this equation a different interpretation if we divide left- and right-hand sides by Q_B,

$$\frac{\mathbf{F}(Q_\text{A} \text{ on } Q_\text{B})}{Q_\text{B}} = \frac{1}{4\pi\epsilon_0} Q_\text{A} \frac{\mathbf{r}_\text{B} - \mathbf{r}_\text{A}}{|\mathbf{r}_\text{B} - \mathbf{r}_\text{A}|^3} \tag{0.25}$$

The right-hand side does not involve Q_B, and we say that Q_A generates an *electrostatic field* $\mathbf{E}$ at all points in space. The field is present at points in space

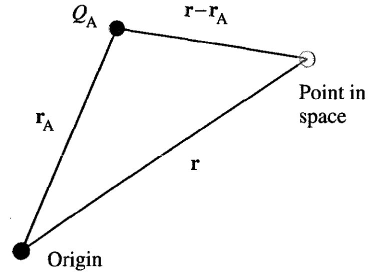


Figure 0.7 Electrostatic field

irrespective of the presence or absence of Q_B. For that reason, we define the ratio on the left-hand side of the equation as the electrostatic field, and remove all mention of Q_B according to Figure 0.7.

The point in space has position vector **r**, and the field exists because of the presence of Q_A. In order to measure the field at that point, we introduce a point test charge Q_B and measure the force exerted on it by Q_A. The ratio $\mathbf{F}/Q_B$ gives the field.

0.6.4 The Electrostatic Potential

Just as it is useful to replace the force between two point charges by their mutual potential energy U, so we can replace the electric field by a more general quantity called the *electrostatic potential* ϕ. This is related to **E** in the same way that U is related to **F**

$$\mathbf{E} = -\operatorname{grad} \phi$$

and for the point charge Q_A located at position vector $\mathbf{r}_A$ we find

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} Q_A \frac{1}{|\mathbf{r}_A - \mathbf{r}|} \tag{0.26}$$

For a set of point charges Q_A at $\mathbf{r}_A$, Q_B at $\mathbf{r}_B, \ldots$ the expression generalizes to

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_j Q_A \frac{1}{|\mathbf{r}_j - \mathbf{r}|} \tag{0.27}$$

0.6.5 Charge Distributions

When we have to deal with charge distributions rather than point charges, the definitions have to be generalized. What we do is to divide continuous charge distributions into differential charge elements $\rho(\mathbf{r})\,\mathrm{d}\tau$, and then apply the basic formula for the electrostatic field, and so on. Here, $\mathrm{d}\tau$ is a differential volume element. Finally, we would have to integrate over the coordinates of the charge

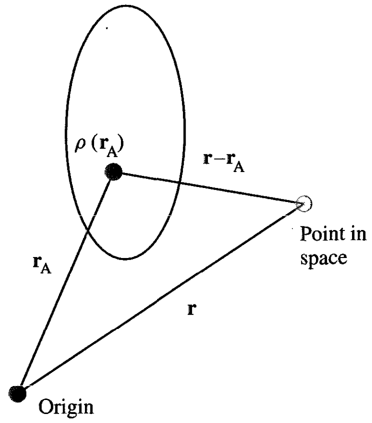


Figure 0.8 Field due to charge distribution

distribution in order to find the total electrostatic field, and so on.

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\int \rho_A(\mathbf{r})\frac{(\mathbf{r}-\mathbf{r}_A)}{|\mathbf{r}_A-\mathbf{r}|^3}\,d\tau \tag{0.28}$$

Likewise to find the mutual potential energy of two charge distributions $\rho_A(\mathbf{r}_A)$ and $\rho_B(\mathbf{r}_B)$ we would have to evaluate the integral

$$U(\rho_A, \rho_B) = \frac{1}{4\pi\epsilon_0}\iint \rho_A(\mathbf{r}_A)\rho_B(\mathbf{r}_B)\frac{1}{|\mathbf{r}_A-\mathbf{r}_B|}\,d\tau_A\,d\tau_B \tag{0.29}$$

The integration has to be done over the volumes of the charge distributions A and B.

0.7 THE SCHRÖDINGER EQUATION

If we have a single particle of mass m moving under the influence of a potential U, then we concern ourselves in quantum chemistry with solutions of the time-dependent Schrödinger equation

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+U\Psi = \frac{jh}{2\pi}\frac{\partial\Psi}{\partial t} \tag{0.30}$$

In this equation, the wavefunction $\Psi(x, y, z, t)$ depends on the spatial and time variables x, y, z and t. (I will use the symbol j for the square root of -1, $j^2 = -1$, throughout the text.)

In cases where the potential is time-independent, we find that the wavefunction can be factorized into space- and time-dependent parts

$$\Psi(x, y, z, t) = \psi(x, y, z)T(t) \tag{0.31}$$

which individually satisfy the time-independent Schrödinger equation

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\psi=\varepsilon\psi$$

and also

$$j\frac{h}{2\pi}\frac{\mathrm{d}t}{\mathrm{d}t}=\varepsilon T$$

In the theory of differential equations, the quantity ε is called a *separation constant*. Here it is equal to the energy of the system. The latter equation can be instantly solved to give

$$T=T_0\exp\left(-j\frac{2\pi\varepsilon}{h}\right). \tag{0.32}$$

Wavefunctions are often complex quantities, and we have to be careful to distinguish a wavefunction Ψ from its complex conjugate Ψ^*. For most of this text, wavefunctions will be real quantities and so we can drop the complex conjugate sign without lack of mathematical rigour.

Schrödinger's equations are usually written in a more succinct manner by invoking the Hamiltonian operator $\hat{H}$, so for example the time-dependent equation for a single particle

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+U\Psi=\frac{jh}{2\pi}\frac{\partial\Psi}{\partial t}$$

becomes

$$\hat{H}\Psi=\frac{jh}{2\pi}\frac{\partial\Psi}{\partial t}$$

and the time-independent equation for a single particle

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\psi=\varepsilon\psi$$

becomes

$$\hat{H}\psi=\varepsilon\psi$$

For almost this entire book, we will be concerned with cases where there is a discrete number of solutions to the equation above, when the equation is then usefully rewritten

$$\hat{H}\psi_i=\varepsilon_i\psi_i \tag{0.33}$$

The number of solutions can be finite or infinite. Other situations arise where the solutions form a continuum of values.

The Hamiltonian operator is the quantum-mechanical analogue of the energy, and we say that the allowed values of the energy, the ε_i above, are the *eigenvalues* of the operator. The ψ_i are called the *eigenvectors* or *eigenfunctions* of the operator.

In order to determine the operator, we first write down the classical energy expression in terms of the coordinates and momenta. For the electron in a hydrogen atom, the classical energy is the sum of the kinetic energy and the mutual potential energy of the electron and the nucleus (a proton)

$$\varepsilon = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} \tag{0.34}$$

We then replace the square of the momentum, now treated as an operator, as follows

$$p^2 \longrightarrow -\frac{h^2}{8\pi^2 m_e}\nabla^2 \tag{0.35}$$

giving the Hamiltonian operator

$$\hat{H} = -\frac{h^2}{8\pi^2 m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{0.36}$$

0.7.1 The Variation Principle

One of the great difficulties in molecular quantum mechanics is that of actually finding solutions to the Schrödinger time-independent equation. So whilst we might want to solve

$$\hat{H}\psi_i = \varepsilon_i\psi_i$$

in order to find all the energies ϵ_I and wavefunctions ψ_I, mother nature very often prevents us finding these solutions especially where three or more bodies are involved.

Suppose that ψ_0 is the lowest energy solution to the Schrödinger time-independent equation for the problem in hand. That is to say,

$$\hat{H}\psi_0 = \varepsilon_0\psi_0$$

If we multiply through from the left by the complex conjugate of ψ_0 we have

$$\psi_0^*\hat{H}\psi_0 = \varepsilon_0\psi_0^*\psi_0$$

and integration over all of space (represented as $\int\cdots\mathrm{d}\tau$) gives

$$\int \psi_0^*\hat{H}\psi_0\,\mathrm{d}\tau = \varepsilon_0\int \psi_0^*\psi_0\,\mathrm{d}\tau$$

This equation can be rearranged to give

$$\varepsilon_0 = \frac{\int \psi_0^*\hat{H}\psi_0\,\mathrm{d}\tau}{\int \psi_0^*\psi_0\,\mathrm{d}\tau} \tag{0.37}$$

which is at first sight an alternative formula for finding the eigenvalue ε_0. It isn't a very practical route to the eigenvalue, because an integration is involved, but if we have an approximation $\tilde{\psi}_0$ to the correct wavefunction ψ_0 then the variation principle says that the variational integral

$$\tilde{\varepsilon}_0 = \frac{\int \tilde{\psi}_0^* \hat{H} \tilde{\psi}_0 \, d\tau}{\int \tilde{\psi}_0^* \tilde{\psi}_0 \, d\tau} \tag{0.38}$$

is always greater than or equal to the true energy. The two wavefunctions ψ_0 and $\tilde{\psi}_0$ have to satisfy the same boundary conditions, and have to correspond to the lowest-energy solution for any given symmetry.

So, for example, you probably know that the lowest-energy solution for a hydrogen atom is

$$\psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right)$$

This satisfies the electronic Schrödinger equation exactly, giving

$$\hat{H}\psi_{1s} = -\left(\frac{m_e e^4}{8\epsilon_0^2 h^2}\right)\psi_{1s}$$

(The symbol a_0 is the first Bohr radius, approximately 52.9 pm, and ϵ_0 is the permittivity of free space.) As we will see in later chapters, Gaussian orbitals are

$$\psi_G = N_G \exp\left(-\alpha \frac{r^2}{a_0^2}\right)$$

which are often used instead of hydrogenic ones when dealing with molecular quantum-mechanical problems. The quantity α is called the Gaussian exponent. Gaussian orbitals have the correct boundary condition at $r = \infty$, but don't satisfy the electronic Schrödinger equation for a hydrogen atom. Calculation of the variational integral

$$\tilde{\varepsilon}_G = \frac{\int \psi_G^* \hat{H} \psi_G \, d\tau}{\int \psi_G^* \psi_G \, d\tau}$$

gives

$$\tilde{\varepsilon}_G(\alpha) = \frac{3h^2\alpha}{8\pi^2 m_e a_0^2} - \frac{2\sqrt{2}\, e^2 \sqrt{\alpha}}{4\pi\epsilon_0 \sqrt{\pi} a_0}$$

Every positive choice of α will give a variational energy higher than the true energy, and the best value of α occurs when

$$\frac{d\tilde{\varepsilon}_G(\alpha)}{d\alpha} = \frac{3h^2}{8\pi^2 m_e a_0^2} - \frac{1}{2}\frac{2\sqrt{2}\, e^2 \alpha^{-1/2}}{4\pi\epsilon_0 \sqrt{\pi}\, a_0} = 0$$

Simplification and evaluation gives the best exponent α as 0.283.

0.8 SYSTEMS OF UNITS

0.8.1 The Système International

It is usual these days to express all physical quantities in the system of units referred to as the *Système International*, SI for short. The International Unions of Pure and Applied Physics, and of Pure and Applied Chemistry both recommend SI units. The units are based on the metre, kilogram, second and the ampere as the fundamental units of length, mass, time and electric current. (There are three other fundamental units in SI, the kelvin, mole and candela which are the units of thermodynamic temperature, amount of substance and luminous intensity, respectively.)

Other SI electrical units are determined from the first four via the fundamental constants ϵ_0 and μ_0, the permittivity and permeability of free space respectively. The ampere is defined in terms of the force between two straight parallel infinitely long conductors placed a metre apart, and once this has been defined the coulomb must be such that one coulomb per second passes along a conductor if it is carrying a current of one ampere.

It turns out that the speed of light in vacuo c_0, ϵ_0 and μ_0 are interrelated by

$$c_0 = \frac{1}{\sqrt{\epsilon_0 \mu_0}} \tag{0.39}$$

and since 1983 the speed of light has been defined in terms of the distance that light travels per unit time. This speed of light in free space has the exact value

$$c_0 = 2.997\,924\,58 \times 10^8\,\mathrm{m\,s^{-1}} \tag{0.40}$$

We are going to be concerned with electrical and magnetic properties in this text, so I had better put on record the fundamental force laws for stationary charges and steady currents. These are as follows.

$$\mathbf{F}(Q_\mathrm{A} \text{ on } Q_\mathrm{B}) = \frac{1}{4\pi\epsilon_0} Q_\mathrm{A} Q_\mathrm{B} \frac{\mathbf{r}_\mathrm{B} - \mathbf{r}_\mathrm{A}}{|\mathbf{r}_\mathrm{B} - \mathbf{r}_\mathrm{A}|^3}$$

is the electrostatic force exerted *by* point charge Q_A *on* point charge Q_B, where $\mathbf{r}_\mathrm{A}$ is the position vector of Q_A and $\mathbf{r}_\mathrm{B}$ is the position vector of Q_B. I discussed this above, and you should be aware that this force is exactly equal and opposite to the force exerted by Q_B on Q_A.

The corresponding force between two complete electrical circuits A and B is

$$\mathbf{F}(\text{Circuit A on Circuit B}) = I_\mathrm{A} I_\mathrm{B} \frac{\mu_0}{4\pi} \oint\!\!\oint d\mathbf{l}_\mathrm{B} \times \left(d\mathbf{l}_\mathrm{A} \times \frac{\mathbf{r}_\mathrm{B} - \mathbf{r}_\mathrm{A}}{|\mathbf{r}_\mathrm{B} - \mathbf{r}_\mathrm{A}|^3} \right) \tag{0.41}$$

This is a much more complicated force law, because the integrations have to be done around the complete electrical circuits A and B. The details of the integration do not matter, the point being this. Because ϵ_0 and μ_0 are interrelated, we are free to give one of them an arbitrary value. In SI we choose arbitrarily to make

$$\mu_0 = 4\pi \times 10^{-7}\,\mathrm{H\,m^{-1}} \tag{0.42}$$

0.8.2 Gaussian Units

The most commonly used system apart from SI is the cgs system based on the centimetre, gram and second as the only base units. The unit of force is the dyne, and the unit of energy is the erg. In electromagnetism, SI is associated with an independent base quantity of current, whereas cgs is associated with current as a derived quantity.

The system of quantities usually associated with cgs units is called the Gaussian system; that associated with SI is often called 4D.

There is usually no problem in converting between 4D and Gaussian quantities until we have to consider electrical and magnetic phenomena. In the Gaussian system we take the proportionality constant in Coulomb's law to be unity (a number),

$$\mathbf{F}_{\mathrm{cgs}}(Q_{\mathrm{A}} \text{ on } Q_{\mathrm{B}}) = Q_{\mathrm{A}}Q_{\mathrm{B}}\frac{\mathbf{r}_{\mathrm{B}} - \mathbf{r}_{\mathrm{A}}}{|\mathbf{r}_{\mathrm{B}} - \mathbf{r}_{\mathrm{A}}|^3}$$

and this means that derived equations have a different form. The unit of charge is called the *electrostatic unit* (esu). If we have two charges each of magnitude 1 esu separated by a distance of 1 cm, then each charge experiences a force of 1 dyne. The electric field is measured in statvolts cm^{-1}.

As a rule of thumb, be wary of equations that have a $(-e)^2$ but no $4\pi\epsilon_0$, and of equations that relate to highly symmetrical charge distributions but seem to have a 4π too many.

It gets worse with magnetic properties, and the Lorentz force

$$\mathbf{F} = Q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \tag{0.43}$$

is written in such a way as to make the magnetic induction **B** have the same dimensions as the electric field **E**, namely force per length. In the Gaussian system, the Lorentz force law becomes

$$\mathbf{F} = Q\left(\mathbf{E} + \frac{1}{c_0}\mathbf{v} \times \mathbf{B}\right) \tag{0.44}$$

So, as a final *aide-mémoire*, beware of magnetic equations that have a c_0 in them.

A quick conversion table is given in Table 0.1. It isn't comprehensive, but you should find it useful. Unfortunately, many texts dealing with molecular modelling still use the cgs system.

0.8.3 Hartree's System

One problem in molecular modelling calculations is that large powers of 10 tend to appear in all the calculated quantities. Thus, for example, molecules have

Table 0.1 Conversion factors between SI and cgs units (taking the speed of light in free space as $3 \times 10^8\,\mathrm{m\,s^{-1}}$ instead of $2.997\,924\,58 \times 10^8\,\mathrm{m\,s^{-1}}$

Quantity	SI unit	cgs unit	No. of cgs units in one SI unit
Force	newton	dyne	10^5
Energy	joule	erg	10^7
Charge	coulomb	esu	3×10^9
Current	ampere	esu $\mathrm{s^{-1}}$	3×10^9
Potential	volt	statvolt	1/300
Electric field **E**	volt $\mathrm{metre^{-1}}$	statvolt $\mathrm{cm^{-1}}$	$1/(3 \times 10^4)$
Magnetic induction **B**	tesla	gauss	10^4

masses of typically 10^{-26} kg, ions have charges in multiples of 1.6×10^{-19} C, and so on. In many engineering applications it is normal to reduce an equation to dimensionless form and this is in essence what I will now describe. It is not mandatory that you should understand Hartree's system of units, but you will understand the output from many molecular modelling packages a lot more easily if you study this section.

The 'atomic unit of length' a_0 is equal to the radius of the first Bohr orbit for a hydrogen atom (and is usually called the bohr), whilst the 'atomic unit of energy', the hartree E_h, is twice the magnitude of the energy of a ground-state hydrogen atom. This also works out as the mutual potential energy of a pair of electrons at distance a_0 apart.

In terms of the electron rest mass m_e and the electron charge we find

$$a_0 = \frac{\epsilon_0 h^2}{\pi m_\mathrm{e} e^2} \tag{0.45}$$

and

$$E_\mathrm{h} = \frac{e^2}{4\pi\epsilon_0 a_0} \tag{0.46}$$

Table 0.1 shows such 'atomic units'. The accepted values of the SI constants are themselves subject to minor experimental improvements, so authors generally report the results of molecular modelling calculations as (e.g.) $R = 50a_0$ and give the conversion factor to SI somewhere in their paper, usually as a footnote.

As I mentioned above, it is conventional in many engineering applications to seek to rewrite basic equations in dimensionless form. This also applies in quantum-mechanical applications. For example, consider the time-independent electronic Schrödinger equation for a hydrogen atom

$$\left(-\frac{h^2}{8\pi^2 m_\mathrm{e}}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi_\mathrm{el}(\mathbf{r}) = \varepsilon_\mathrm{el}\psi_\mathrm{el}(\mathbf{r})$$

(Notice that I have been very careful to use the symbol ϵ_0 for the permittivity of free space and the symbol ε to denote an energy.)

Table 0.2 Hartree atomic units

Physical quantity	Symbol	X	Value of X
length	l, x, y, z, r	a_0	$5.2918 \times 10^{-11}\,\mathrm{m}$
mass	m	m_e	$9.1094 \times 10^{-31}\,\mathrm{kg}$
energy	ε	E_h	$4.3598 \times 10^{-18}\,\mathrm{J}$
charge	Q	e	$1.6022 \times 10^{-19}\,\mathrm{J}$
electric dipole moment	p_e	ea_0	$8.4784 \times 10^{-30}\,\mathrm{C\,m}$
electric quadrupole moment	θ_e	ea_0^2	$4.4866 \times 10^{-40}\,\mathrm{C\,m^2}$
electric field	E	$E_h e^{-1} a_0^{-1}$	$5.1422 \times 10^{11}\,\mathrm{V\,m^{-1}}$
electric field gradient	$-V_{zz}$	$E_h e^{-1} a_0^{-2}$	$9.7174 \times 10^{21}\,\mathrm{V\,m^{-2}}$
magnetic induction	B	$(h/2\pi)e^{-1}a_0^{-2}$	$2.3505 \times 10^{5}\,\mathrm{T}$
electric dipole polarizability	α	$e^2 a_0^2 E_h^{-1}$	$1.6488 \times 10^{-41}\,\mathrm{C^2\,m^2\,J^{-1}}$
magnetizability	ξ	$e^2 a_0^2 m_e^{-1}$	$7.8910 \times 10^{-29}\,\mathrm{J\,T^{-2}}$

The energy ε and the distance r are both real physical quantities, with a measure and a unit. If we define the variables $r_{\mathrm{red}} = r/a_0$ and $\varepsilon_{\mathrm{red}} = \varepsilon/E_h$, then both r_{red} and $\varepsilon_{\mathrm{red}}$ are dimensionless. The idea is to rewrite the electronic Schrödinger equation in terms of the dimensionless variables, giving a much simpler dimensionless equation,

$$\left(-\frac{1}{2}\nabla_{\mathrm{red}}^2 - \frac{1}{r_{\mathrm{red}}}\right)\psi_{\mathrm{el,red}}(\mathbf{r}_{\mathrm{red}}) = \varepsilon_{\mathrm{el,red}}\,\psi_{\mathrm{el,red}}(\mathbf{r}_{\mathrm{red}})$$

I am afraid that it is common practice for people to forget about all the considerations above, write down the equation as

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\psi_{\mathrm{el}}(\mathbf{r}) = \varepsilon_{\mathrm{el}}\psi_{\mathrm{el}}(\mathbf{r}) \qquad (0.47)$$

and quote the results of their calculations as if they were true distances, energies and so on. They are *reduced* quantities and so are dimensionless.

Even worse is the confusion regarding the wavefunction itself. The Born interpretation of quantum mechanics tells us that $\psi^*(\mathbf{r})\psi(\mathbf{r})\,d\tau$ represents the probability of finding the particle with spatial coordinates $\mathbf{r}$, described by the wavefunction $\psi(\mathbf{r})$, in volume element $d\tau$. Probabilities are real numbers, and so the dimensions of $\psi(\mathbf{r})$ must be of $(\text{length})^{-3/2}$. In the atomic system of units, we take the unit of wavefunction to be $a_0{}^{-3/2}$.

For your guidance, Table 0.2 will help you convert between the results of some molecular modelling packages and SI. The first column gives the physical quantity. The second column shows the usual symbol. The third column gives X, the collection of physical constants that correspond to each quantity. This collection is not unique, but the value given in the fourth column *is* unique.

1 MOLECULAR MECHANICS

You were probably taught very early in your professional career that skills in quantum chemistry are a prerequisite for the study of atomic and molecular phenomena. I must tell you that this isn't completely true. Some molecular phenomena can be modelled very accurately indeed using classical mechanics, and to get us started in our study of molecular modelling, we are going to study molecular mechanics. This aims to treat the vibrations of complex molecules by the methods of classical mechanics, and as we shall see, it does so very successfully.

Molecular mechanics is known by the acronym MM.

1.1 VIBRATIONAL MOTION

Consider first of all a very simple classical model for vibrational motion. We have a particle of mass m attached to a spring, which is anchored to a wall. The particle is initially at rest, with an equilibrium position x_e along the x-axis. If we displace the particle in the $+x$ direction, then experience teaches us that there is a restoring force exerted by the spring. Likewise, if we displace the particle in the $-x$ direction and so compress the spring, then there is also a restoring force. In either case the force acts so as to restore the particle to its rest position x_e.

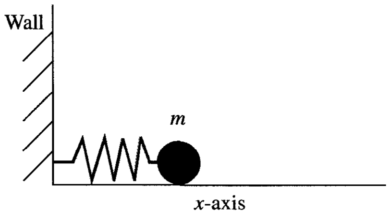


Figure 1.1 Simple harmonic motion

For very many springs, the restoring force turns out to be directly proportional to the displacement $x - x_e$:

$$F_s = -k_s(x - x_e)$$

and this is known as *Hooke's law*. The proportionality constant k_s is called the *force constant*. Not all materials obey Hooke's law, and even those materials that do, show deviations for a large extension. It is a good place to start our study of molecular modelling as it turns out that molecules vibrate in much the same way as particles attached to springs, especially when they make small excursions from their equilibrium positions. We therefore set the particle in motion along the horizontal (x) axis.

According to Newton's second law, force is mass times acceleration

$$F = m\frac{d^2x}{dt^2} \tag{1.1}$$

and so the motion of the particle is described by the second-order differential equation

$$m\frac{d^2x}{dt^2} = -k_s(x - x_e) \tag{1.2}$$

This differential equation has solution

$$x = x_e + A\sin\left(\sqrt{\frac{k_s}{m}}t\right) + B\cos\left[\sqrt{\left(\frac{k_s}{m}\right)}\,t\right] \tag{1.3}$$

where A and B are constants that have to be determined from the so-called boundary conditions. These constants need not concern us here; we find them by substituting known values of x at known times and so on.

The quantity $\sqrt{k_s/m}$ occurs again and again in the treatment of vibrational motion. It has dimension units of $(\text{time})^{-1}$ and so it is an angular frequency. It is often called the (angular) vibration frequency of the system. You might have been expecting me to write angle $(\text{time})^{-1}$ for the dimension of $\sqrt{k_s/m}$, but angles are dimensionless quantities, being defined as the ratio of arc length to circumference; the SI unit of angle is the radian.

We call

$$\nu_{cl} = \frac{1}{2\pi}\sqrt{\frac{k_s}{m}} \tag{1.4}$$

the classical vibration frequency of the system.

1.1.1 The Potential Energy

I explained the connection between force and potential energy in Chapter 0. For a one-dimensional problem

$$F = -\frac{dU}{dx} \tag{1.5}$$

In the case of a Hooke's law spring where

$$F_s = -k_s(x - x_e)$$

you should be able to prove that

$$U = U_0 + \tfrac{1}{2}k_s(x - x_e)^2 \tag{1.6}$$

where U_0 is a constant of integration. If we can define $U = 0$ when $x = 0$, then this constant of integration is zero.

1.1.2 A Diatomic

The next step is to consider a more obvious model of a vibrating diatomic, where we have particles of masses m_1 and m_2 joined by a spring that obeys Hooke's law. The horizontal axis is the x-axis, and the x coordinates of the two particles are x_1 and x_2. The equilibrium spring length is R_e. If we now pull the two particles away from each other such that the length of the spring is R (which is given by $x_2 - x_1$), then the spring exerts a restoring force on both atoms. In particular, the spring exerts a restoring force of magnitude $k_s(x_2 - x_1 - R_e)$ in the direction of increasing x_1 on particle 1, and a force of magnitude $k_s(x_2 - x_1 - R_e)$ in the direction of decreasing x on particle 2.

According to Newton's second law we have

$$m_1\frac{d^2x_1}{dt^2} = k_s(x_2 - x_1 - R_e)$$

and

$$m_2\frac{d^2x_2}{dt^2} = -k_s(x_2 - x_1 - R_e)$$

If we subtract and rearrange, we get a more interesting equation,

$$\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = -\frac{k_s}{m_2}(x_2 - x_1 - R_e) - \frac{k_s}{m_1}(x_2 - x_1 - R_e) \tag{1.7}$$

which can be rewritten in terms of the bond length $R = x_2 - x_1$,

$$\frac{d^2R}{dt^2} = -k_s\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(R - R_e) \tag{1.8}$$

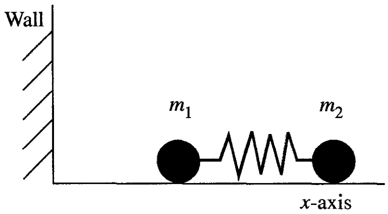


Figure 1.2 Simple harmonic vibrations of diatomic

This equation has exactly the same form as the equation of motion for the single particle, except that the reduced mass μ replaces the mass of the single particle, where

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{1.9}$$

The general solution is

$$R = R_e + A \sin\left[\sqrt{\left(\frac{k_s}{\mu}\right)}t\right] + B \cos\left[\sqrt{\left(\frac{k_s}{\mu}\right)}t\right] \tag{1.10}$$

and a diatomic molecule undergoing such simple harmonic motion has an angular frequency of $\sqrt{k_s/\mu}$, which is exactly what we would expect for a single particle with mass equal to the reduced mass.

1.1.3 The Mutual Potential Energy

The total energy, kinetic plus potential, of the system is easily shown to be

$$\varepsilon = \frac{1}{2}m_1\left(\frac{dx_1}{dt}\right)^2 + \frac{1}{2}m_2\left(\frac{dx_2}{dt}\right)^2 + \frac{1}{2}k_s(x_2 - x_1 - R_e)^2 \tag{1.11}$$

To check that the equation for ε really does obey the law of conservation of energy, we differentiate with respect to time as follows:

$$\varepsilon = \frac{1}{2}m_1\left(\frac{dx_1}{dt}\right)^2 + \frac{1}{2}m_2\left(\frac{dx_2}{dt}\right)^2 + \frac{1}{2}k_s(x_2 - x_1 - R_e)^2$$

$$\frac{d\varepsilon}{dt} = m_1\frac{dx_1}{dt}\frac{d^2x_1}{dt^2} + m_2\frac{dx_2}{dt}\frac{d^2x_2}{dt^2} + k_s(x_2 - x_1 - R_e)\left(\frac{dx_2}{dt} - \frac{dx_1}{dt}\right)$$

Collecting terms in dx_1/dt and dx_2/dt we find

$$\frac{d\varepsilon}{dt} = \left(m_1\frac{d^2x_1}{dt^2} - k_s(x_2 - x_1 - R_e)\right)\frac{dx_1}{dt} + \left(m_2\frac{d^2x_2}{dt^2} + k_s(x_2 - x_1 - R_e)\right)\frac{dx_2}{dt}$$

and each term in the large brackets is zero, showing that the energy is a constant. The term

$$\begin{aligned} U &= \tfrac{1}{2}k_s(x_2 - x_1 - R_e)^2 \\ &= \tfrac{1}{2}k_s(R - R_e)^2 \end{aligned} \tag{1.12}$$

is *the mutual potential energy* of the two particles. It is related to the forces acting on each particle as follows:

$$\begin{aligned} \text{Force on } 1 &= -\frac{\partial U}{dx_1} \\ \text{Force on } 2 &= -\frac{\partial U}{dx_2} \end{aligned} \tag{1.13}$$

This gives us the general rule for relating force to mutual potential energy: you differentiate the force with respect to the coordinates of the particle of interest.

1.2 NORMAL MODES OF VIBRATION

Consider now two particles connected by two springs, as shown in Figure 1.3. Let's call the force constant of the left-hand spring k_1 and the force constant of the right-hand spring k_2. The equilibrium position corresponds to the two masses having x coordinates $x_{1,\mathrm{e}}$ and $x_{2,\mathrm{e}}$. When we stretch the system, the two springs extend and I will call the instantaneous positions of the particles x_1 and x_2.

The left-hand spring exerts a restoring force on particle 1 of

$$-k_1(x_1 - x_{1\mathrm{e}})$$

The right-hand spring is stretched by an amount $(x_2 - x_1)$ and so it exerts a force

$$k_2(x_2 - x_{2\mathrm{e}} - x_1 + x_{1\mathrm{e}})$$

This force acts to the left on particle 2 and to the right on particle 1. For the sake of neatness, I can write

$$X_1 = x_1 - x_{1\mathrm{e}}$$
$$X_2 = x_2 - x_{2\mathrm{e}}$$

and so

$$\begin{aligned} k_2(X_2 - X_1) - k_1X_1 &= m_1\frac{\mathrm{d}^2X_1}{\mathrm{d}t^2} \\ -k_2(X_2 - X_1) &= m_2\frac{\mathrm{d}^2X_2}{\mathrm{d}t^2} \end{aligned} \tag{1.14}$$

There are many different solutions for X_1 and X_2 to this pair of coupled equations, but it proves possible to find two particularly simple ones called *normal modes of vibration*. These have the property that both particles execute simple harmonic motion at the same angular frequency. Not only that, every possible vibrational motion of the two particles can be described in terms of the normal modes, so they are obviously very important.

Having said that, it proves possible to find such solutions where both particles vibrate with the same frequency; let me assume that there exist such solutions to

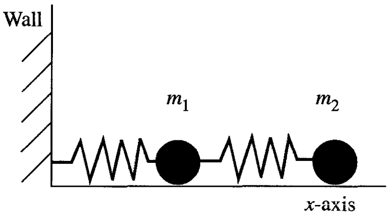


Figure 1.3 Figure for discussion of normal modes of vibration

the equations of motion such that

$$\begin{aligned} X_1(t) &= A\sin(\omega t + \phi_1) \\ X_2(t) &= B\sin(\omega t + \phi_2) \end{aligned} \tag{1.15}$$

where A, B, ϕ_1 and ϕ_2 are constants that have to be determined from the boundary conditions.

Differentiating each of these two equations twice with respect to time gives

$$\begin{aligned} \frac{\mathrm{d}^2X_1(t)}{\mathrm{d}t^2} &= \omega^2 A\sin(\omega t + \phi_1) \\ \frac{\mathrm{d}^2X_2(t)}{\mathrm{d}t^2} &= \omega^2 B\sin(\omega t + \phi_2) \end{aligned} \tag{1.16}$$

and substituting these expressions into the equations of motion gives

$$\begin{aligned} -\frac{k_1+k_2}{m_1}X_1 + \frac{k_2}{m_1}X_2 &= -\omega^2 X_1 \\ \frac{k_2}{m_2}X_1 - \frac{k_2}{m_2}X_2 &= -\omega^2 X_2 \end{aligned} \tag{1.17}$$

It turns out that these two equations are valid only when ω has one of two possible values called the normal-mode angular frequencies. In either case, both particles oscillate with the same angular frequency.

In order to find the normal modes of vibration, I am going to write the above equations in matrix form, and then find the eigenvalues and eigenvectors of a certain matrix. In matrix form, we write

$$\begin{pmatrix} -\dfrac{(k_1+k_2)}{m_1} & \dfrac{k_2}{m_1} \\ \dfrac{k_2}{m_2} & -\dfrac{k_2}{m_2} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = -\omega^2 \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \tag{1.18}$$

which is obviously a matrix eigenvalue problem. We have to find the two values of $-\omega^2$ for which these equations hold, and then for each value of $-\omega^2$ we need to find the relevant ratios of the coordinates. The results are rather complicated and won't be stated here.

There are thus two frequencies at which the two particles will show simple harmonic motion at the same frequency.

1.3 THE QUANTUM-MECHANICAL TREATMENT

We now need to investigate the quantum-mechanical treatment of vibrational motion. Consider then a diatomic molecule with reduced mass μ. The time-independent Schrödinger equation is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{8\pi^2\mu}{h^2}(\varepsilon - U)\psi = 0 \tag{1.19}$$

where ψ is the vibrational wavefunction and U the vibrational potential energy. The obvious place to start the discussion is with the Hooke's law model, where

$$U = U_0 + \tfrac{1}{2}k_s(x - x_e)^2$$

We normally take the constant of integration U_0 to be zero. Solution of the time-independent Schrödinger equation can be done exactly. We don't need to concern ourselves with the details, I will just give you the results.

First of all, the vibrational energy is quantized, and we write the single quantum number v. This quantum number can take values $0, 1, 2, \ldots$

The vibrational energy levels are given by

$$\varepsilon_v = \frac{h}{2\pi}\left(v + \frac{1}{2}\right)\sqrt{\frac{k_s}{\mu}} \tag{1.20}$$

The normalized vibrational wavefunctions are given by the general expression

$$\psi_v(\xi) = \left(\frac{\sqrt{\beta/\pi}}{2^v v!}\right)^{1/2} H_v(\xi)\exp(-\xi^2/2) \tag{1.21}$$

where $\beta = (2\pi\sqrt{\mu k_s})/h$ and $\xi = \sqrt{\beta}x$. The polynomials H_v are called the Hermite polynomials. They are solutions of the differential equation

$$\frac{d^2H}{d\xi^2} - 2\xi\frac{dH}{d\xi} + 2vH = 0 \tag{1.22}$$

and they are most easily found explicitly from the recursion formula

$$H_{v+1}(\xi) = 2\xi H_v(\xi) - 2vH_{v-1}(\xi) \tag{1.23}$$

The first few are shown in Table 1.1.

The Hermite polynomials are well known in science and engineering.

Vibrational wavefunctions for the states $v = 0$ and $v = 1$ are shown in Figures 1.4 and 1.5. For the sake of illustration, I have taken numerical values appropriate to $^{12}C^{16}O$. The x-axis legend 'variable' is ξ. Note that the $v = 0$ wavefunction has a maximum in the middle of the spring. The $v = 1$ wavefunction has a node at the midpoint.

Table 1.1

	$H_v(\xi)$
$v = 0$	1
$v = 1$	2ξ
$v = 2$	$4\xi^2 - 2$
$v = 3$	$8\xi^3 - 12\xi$
$v = 4$	$16\xi^4 - 48\xi^2 + 12$
$v = 5$	$32\xi^5 - 160\xi^3 + 120\xi$

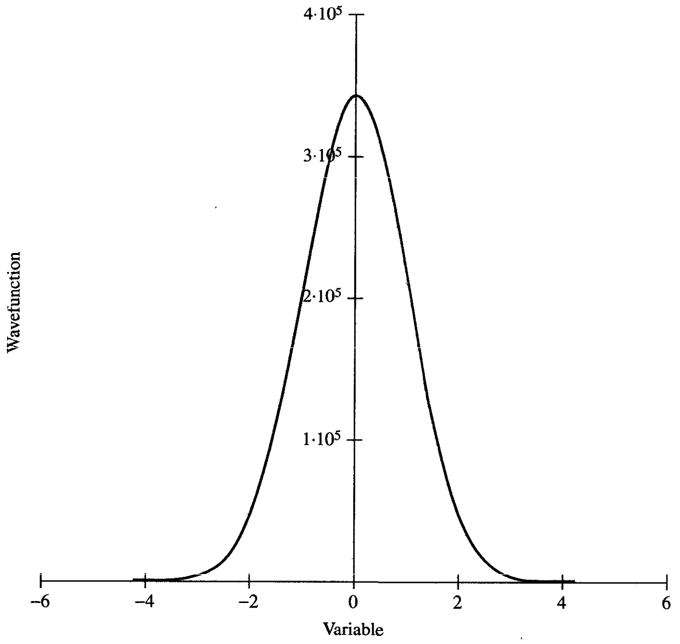


Figure 1.4 Vibrational wavefunction, $v = 0$

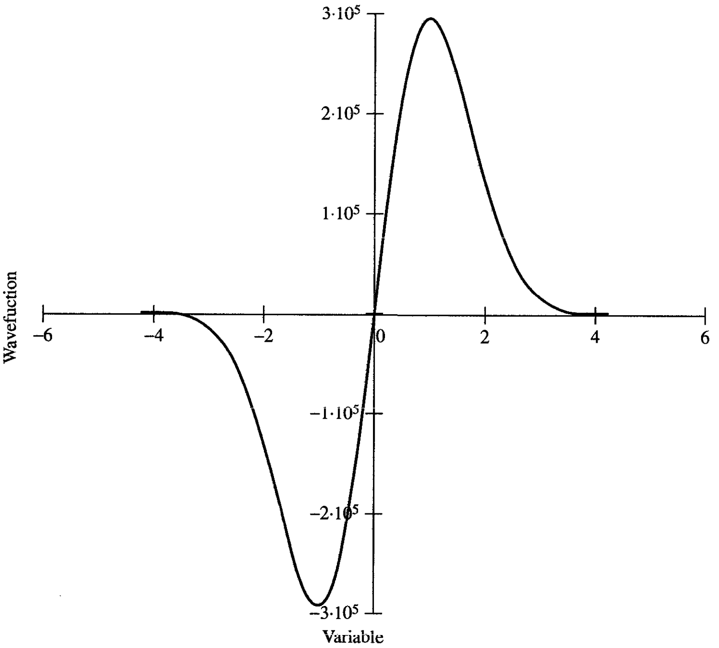


Figure 1.5 Vibrational wavefunction, $v = 1$

Wavefunctions by themselves can be very beautiful objects, but they do not have any particular physical interpretation. Of more importance is the Born interpretation of quantum mechanics, which relates the square of a wavefunction to the probability of finding a particle (in this case a particle of reduced mass μ vibrating about the centre of mass) in a certain differential region of space. This probability is given by the square of the wavefunction times dx and so we should concentrate on the square of the wavefunction rather than on the wavefunction itself.

The square of the wavefunction for $v = 0$ is shown in Figure 1.6. And the square of the wavefunction for $v = 5$ is shown in Figure 1.7.

The classical model predicts that the largest probability of finding a particle is when it is at the endpoints of the vibration. The quantum-mechanical picture is quite different. In the lowest vibrational state, the maximum probability is at the midpoint of the vibration. As the quantum number v increases, then the maximum probability approaches the classical picture. This is called the *correspondence principle*. Classical and quantum results have to agree with each other as the quantum numbers get large.

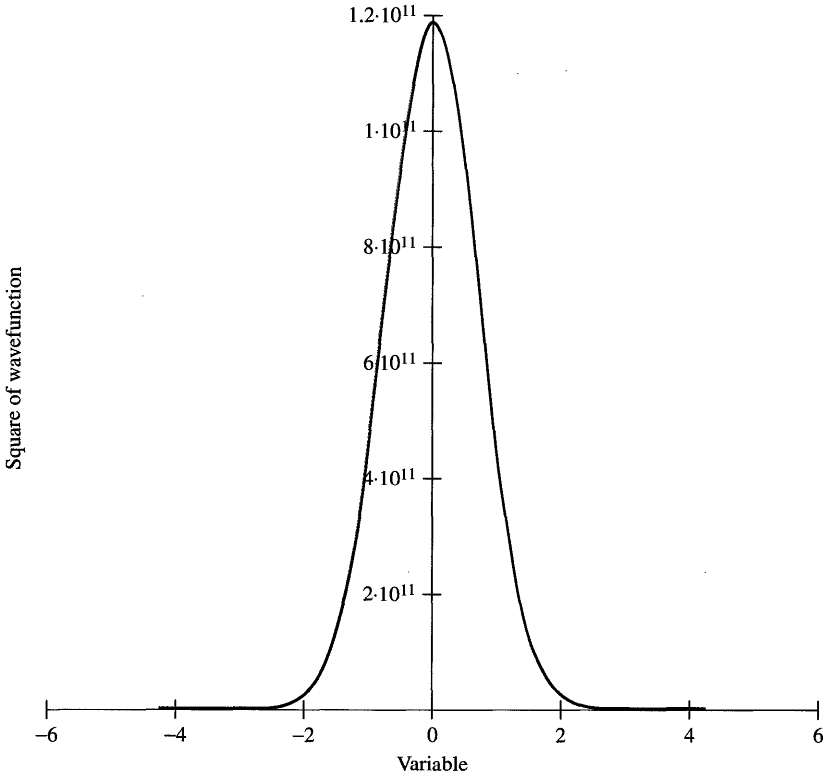


Figure 1.6 Square of wavefunction for $v = 0$

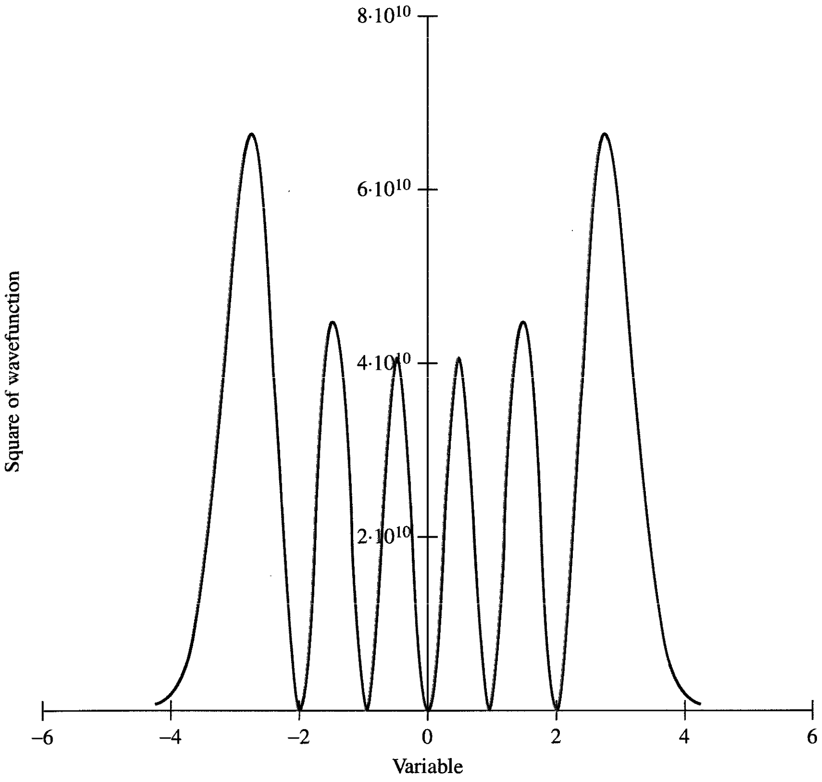


Figure 1.7 Square of wavefunction with $v = 5$

A plot of the square of the vibrational wavefunction with $v = 30$ is shown in Figure 1.8.

The square of the wavefunction is finite beyond the classical turning points of the motion, and this is referred to as *quantum-mechanical tunnelling*. There is a further point worth noticing about the quantum-mechanical solutions. The harmonic oscillator is not allowed to have zero energy. The smallest allowed value of vibrational energy is $(h/2\pi)\sqrt{k_s/\mu}(0 + \frac{1}{2})$ and this is called the *zero point energy*. Even at a temperature of 0 K, molecules have this residual energy.

Spectroscopists usually talk in terms of wavenumbers rather than frequencies or energies. A wavenumber is an energy divided by hc_0, or a frequency divided by c_0, and so we refer to the classical vibrational wavenumber ω_e given by

$$\omega_e = \frac{1}{2\pi c_0}\sqrt{\frac{k_s}{\mu}} \tag{1.24}$$

Analysis of a vibrational spectrum gives ω_e and hence the force constant k_s.

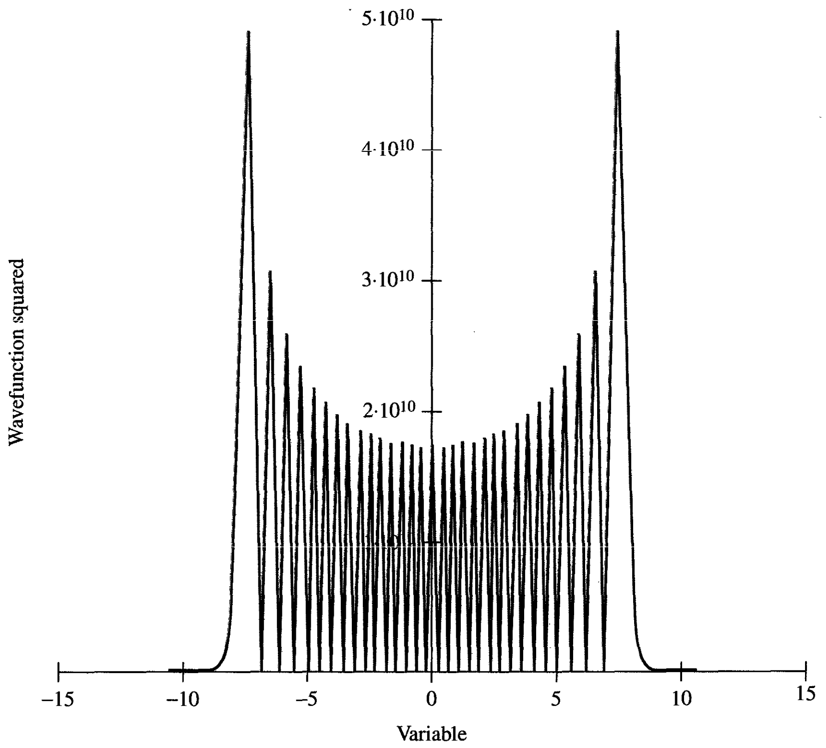


Figure 1.8 Square of wavefunction for $v = 30$

Table 1.2

D_0	11.092 eV
ω_c	2169.8 cm^{-1}
$\omega_e x_e$	13.3 cm^{-1}
$\omega_e y_e$	0.0308 cm^{-1}
B_e	1.9313 cm^{-1}
α_e	0.01748 cm^{-1}
R_e	112.81 pm

To take a typical diatomic molecule such $^{12}C^{16}O$ in its electronic ground state, Table 1.2 gives data from Herzberg and Huber's compilation (1979).

The simple harmonic model gives a force constant of $4\pi^2 c_0^2 \omega_e^2 \mu$ and since the reduced mass $\mu = 1.139 \times 10^{-27}$ kg, $k_s = 1901.5\,\mathrm{Nm}^{-1}$. The potential energy is therefore

$$U_{CO} = \frac{1}{2} \times 1901.5\,\mathrm{Nm}^{-1}(R_{CO} - 112.81\,\mathrm{pm})^2 \qquad (1.25)$$

and this is shown in Figure 1.9.

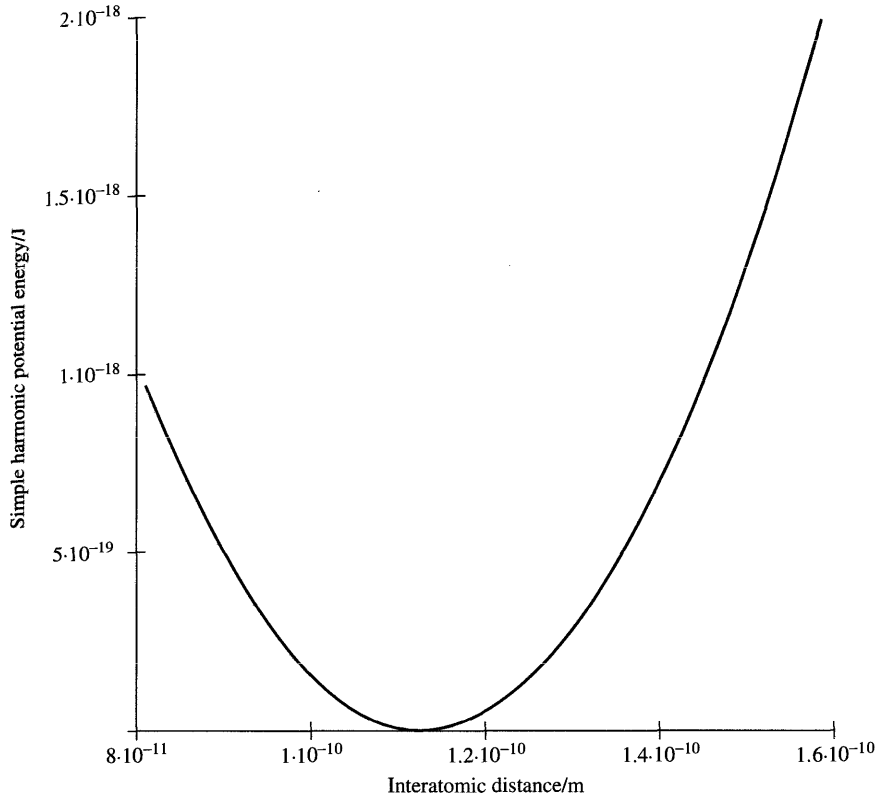


Figure 1.9 Hooke's law plot for CO

1.4 THE TAYLOR EXPANSION

It is useful at this point if we examine the Taylor expansion for a general diatomic potential $U(R)$ about the equilibrium bond length R_e.

$$U(R) = U(R_\mathrm{e}) + \left(\frac{\mathrm{d}U}{\mathrm{d}R}\right)_{R_\mathrm{e}} (R - R_\mathrm{e}) + \frac{1}{2}\left(\frac{\mathrm{d}^2U}{\mathrm{d}R^2}\right)_{R_\mathrm{e}} (R - R_\mathrm{e})^2 + \cdots \quad (1.26)$$

where the point R is close to R_e. Symbols such as $(\mathrm{d}U/\mathrm{d}R)_{R_\mathrm{e}}$ mean that we calculate the first derivative and then evaluate it at the point R_e.

If R_e is a minimum point then

$$\left(\frac{\mathrm{d}U}{\mathrm{d}R}\right)_{R_\mathrm{e}} = 0$$

and

$$\left(\frac{d^2U}{dR^2}\right)_{R_e} > 0$$

We often choose the zero of potential such that $U(R_e) = 0$ and the term

$$\frac{1}{2}\left(\frac{d^2U}{dR^2}\right)_{R_e}$$

is called the harmonic force constant. As we shall see, we can include terms beyond the quadratic term in the energy expression.

1.5 THE MORSE POTENTIAL

The harmonic potential is a good starting place for a discussion of vibrating molecules, but analysis of the vibrational spectrum shows that real diatomic

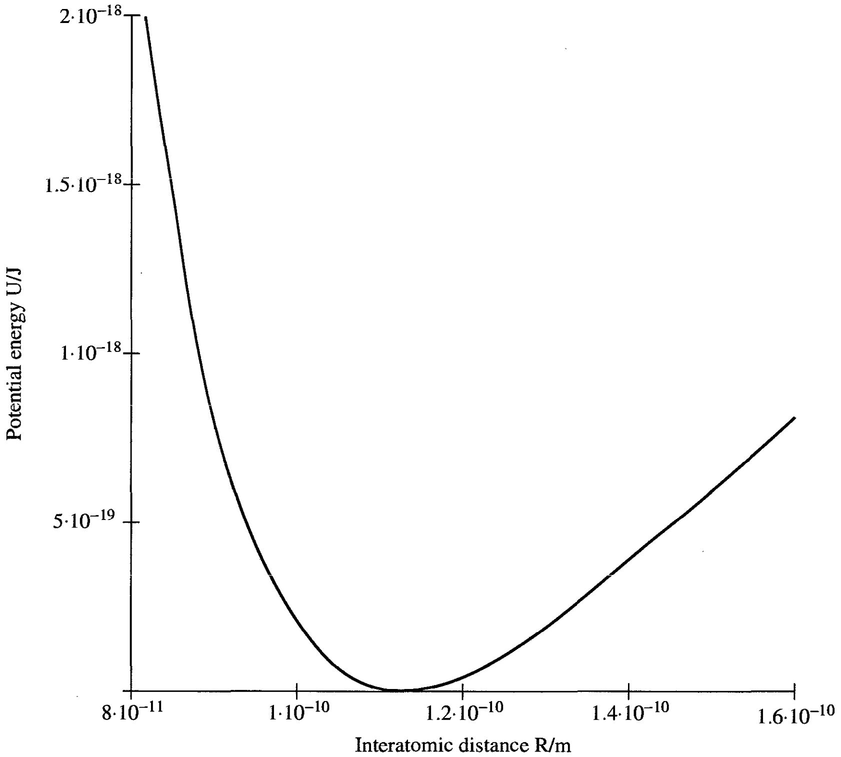


Figure 1.10 Morse potential for CO

molecules do not vibrate as if they were simple particles at the ends of classical springs. Professional spectroscopists would scoff at the idea of using Hooke's law as a model for the vibration. They would be more concerned with matching the experimental energy levels with a more accurate potential. Many such potentials have been used over the years, with that due to Morse being widely quoted. The Morse potential is as follows:

$$U = D_e(1 - \exp(-\beta x))^2 \tag{1.27}$$

where D_e is the depth of the potential well, i.e. the dissociation energy, and

$$\beta = \frac{\omega_e}{2}\sqrt{\frac{2\mu}{D_e}}$$

This potential actually contains three parameters, D_e, k_s and R_e, and so should be capable of giving a better representation to the potential energy curve than the simple harmonic, which contains just the two parameters k_s and R_e.

In the case of $^{12}C^{16}O$, a simple calculation shows that the dissociation energy

$$D_e = D_0 + \tfrac{1}{2}h(2\pi c_0 \omega_e)$$

is $11.092 + 0.134$ eV. The Morse potential for $^{12}C^{16}O$ is shown in Figure 1.10.

1.6 MORE ADVANCED EMPIRICAL POTENTIALS

More often than not, the following spectroscopic constants are available for a diatomic molecule:

R_e	the equilibrium internuclear separation
D_e	the dissociation energy
k_s	the force constant
$\omega_e x_e$	the anharmonicity constant (sometimes equated to x_e only)
α_e	the vibration–rotation coupling constant

and usually these five constants can be found to good experimental accuracy.

There are a number of three- to five-parameter potential functions in the literature, of which the Morse potential is the most popular; a typical five-parameter potential is the Linnett function (Linnett, 1940, 1942):

$$U(x) = \frac{K}{x^m} - b\exp(-tx)[1 + g_1(x-1) + g_2(x-1)^2] \tag{1.28}$$

The five parameters K, b, t, g_1 and g_2 can be related to the molecular constants.

1.7 MOLECULAR MECHANICS

At this point, spectroscopists and molecular modellers part company because they have very different aims. Spectroscopists want to describe the vibrations of a molecule to the last possible decimal point, and their problem is how a *force field* should be determined as accurately as possible from a set of experimental vibrational frequencies and absorption intensities. This problem is well understood, and is discussed in definitive textbooks such as that by Wilson, Decius and Cross (1955).

Molecular modellers want to be able to start from a given molecule and make predictions about the geometries of related molecules. We saw above the harmonic potential for $^{12}C^{16}O$,

$$U_{CO} = \frac{1}{2} \times 1901.5\,\mathrm{N m^{-1}}(R_{CO} - 112.81\,\mathrm{pm})^2$$

Similar considerations can be applied to $^{12}C^{32}S$ to give

$$U_{CS} = \frac{1}{2} \times 849.0\,\mathrm{N m^{-1}}(R_{CS} - 153.5\,\mathrm{pm})^2$$

and we might imagine that a sum of these two would describe the vibrations of the linear triatomic molecule $^{16}O^{12}C^{32}S$ (so long as we discount the possibility of vibrations that bend the molecule). That is,

$$U(\mathrm{OCS}) = U(\mathrm{CO}) + U(\mathrm{CS}) \tag{1.29}$$

or

$$\begin{aligned} U_{OCS} &= \frac{1}{2} \times 849.0\,\mathrm{N m^{-1}}(R_{CS} - 153.5\,\mathrm{pm})^2 \\ &\quad + \frac{1}{2} \times 1901.9\,\mathrm{N m^{-1}}(R_{CO} - 112.81\,\mathrm{pm})^2 \end{aligned}$$

where the mutual potential energy now depends on the two independent variables R_{CO} and R_{CS}.

The minimum of U_{OCS} corresponds to the equilibrium geometry, and it is very easy to see that it corresponds to $R_{CS} = 153.5\,\mathrm{pm}$ and $R_{CO} = 112.8\,\mathrm{pm}$. We might have suspected from our study of normal modes of vibration that the two vibrations would not be independent of each other, so our first guess at a triatomic potential is not very profitable.

We refer to models where we write the total potential energy in terms of chemical entities such as bond lengths, bond angles, dihedral angles and so on as *valence force field* models.

A *Urey–Bradley force field* is similar to a valence force field, except that we include non-bonded interactions.

Even for such a simple molecule, which I deliberately constrained to be linear and where I assumed that the harmonic approximation was applicable, the potential energy function will have cross-terms.

$$\begin{aligned} U(\mathrm{OCS}) &= \frac{1}{2}k_{CO}(R_{CO} - R_{e,CO})^2 + \frac{1}{2}k_{CS}(R_{CS} - R_{e,CS})^2 \\ &\quad + k_{CO,CS}(R_{CO} - R_{e,CO})(R_{CS} - R_{e,CS}) \end{aligned} \tag{1.30}$$

where the *off-diagonal* force constant $k_{\mathrm{CO,CS}}$ couples together the CO and the CS vibrations.

For a non-linear molecule of N atoms, there are $3N - 6$ ($3N - 5$ if the molecule is linear) internal vibrational coordinates. If we wish to include the off-diagonal force constants then there are $(3N - 6)$ diagonal and $(3N - 6)^2 - (3N - 6)$ off-diagonal terms. Only half of the off-diagonal force constants are unique, since (for example) $k_{\mathrm{CO,CS}}$ must equal $k_{\mathrm{CS,CO}}$. In other words, the force constant matrix has to be symmetric. This gives $1/2(3N - 6)(3N - 5)$ independent force constants, a number that usually far exceeds the available experimental vibration frequencies. A complete determination of all force constants requires analysis of the spectra of many isotopically substituted molecules. Many of the off-diagonal terms turn out to be very small, and spectroscopists have developed systematic simplifications to the force field in order to make as many of the off-diagonal terms as possible, vanish.

The key study for our development of molecular mechanics was that by Schachtschneider and Snyder (1969), who showed that transferable force constants can be obtained provided that a few off-diagonal terms are *not* neglected. These authors found that off-diagonal terms are usually largest when neighbouring atoms are involved. A final point for consideration is that the C atom in OCS is obviously chemically different from a C atom in ethane and from a C atom in ethyne. It is necessary to take account of the chemical environment of a given atom.

In molecular mechanics, then, we have to take account of non-bonded interactions, and the chemical sense of each atom. The idea is to treat the force constants, the reference equilibrium geometry and just about everything else as parameters that have to be fixed by reference to some molecular properties. You can imagine the difficulty of trying to set up a system of reliable and transferable parameters for large molecules containing many different types of atoms, and it should come as no surprise to find that the original molecular mechanics calculations were performed on saturated hydrocarbons. The aim of the calculations was invariably to predict an equilibrium geometry by minimizing the intramolecular potential energy. Over the years, the original parameter sets were extended to include different atoms with varied hybridizations, and attention was also given to the problem of intermolecular interactions.

So, consider a typical molecule such as aspirin (acetylsalicylic acid), shown in Figure 1.11. Such two-dimensional drawings can be made using ChemDraw or ISISDraw, but all the features needed to construct a molecular mechanics force field are apparent.

First of all, we have to take account of every bond-stretching motion. We could write a simple harmonic potential for each bond, as discussed above. For a bond A–B, we would therefore write

$$U_{\mathrm{AB}} = \frac{1}{2}k_{\mathrm{s,AB}}(R_{\mathrm{AB}} - R_{\mathrm{e,AB}})^2 \tag{1.31}$$

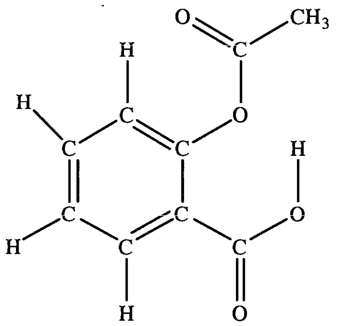


Figure 1.11

where the force constant $k_{s,AB}$ and the reference equilibrium bond length $R_{e,AB}$ would be appropriate for the atom pairs AB with their given hybridizations.

Next we have to consider the bond angles. It is usual to write these vibrational terms as harmonic ones, typically for the connected atoms A–B–C

$$U_{ABC} = \frac{1}{2}k_{ABC}(\theta_{ABC} - \theta_{e,ABC})^2 \tag{1.32}$$

where k_{ABC} is a harmonic bending force constant and $\theta_{e,ABC}$ the reference equilibrium angle for that particular grouping of atoms.

Next come the *dihedral angles* (or *torsions*), and the contribution that each makes to the total intramolecular potential energy depends on the local symmetry. We distinguish between torsion where full internal rotation is chemically possible, and torsion where we would not normally expect full rotation. Full rotation about the C–C bond in ethane is normal behaviour at room temperature (although I have yet to tell you why), and the two CH_3 groups would clearly need a threefold potential, such as

$$U(CH_3 - CH_3) = \frac{U_0}{2}(1 + \cos(3\omega)) \tag{1.33}$$

where ω gives the dihedral angles between the corresponding C–H groups on the two C atoms. For systems of lower symmetry we must seek a potential that depends on the local axis of symmetry; for an n-fold axis, we would write

$$U = \frac{U_0}{2}(1 + \cos(n\omega - \omega_0)) \tag{1.34}$$

where the phase angle ω_0 shifts the potential curve to the right or left. For $n = 1$ and $\omega_0 = 0$, the equation represents a minimum for the *trans* conformation, with an energy U_0 lower than the *cis* conformation.

Some authors refer to *improper dihedrals* when discussing dihedral torsion where we would not normally expect full rotation, for example, any of the C–C–C–C linkages in the benzene ring of aspirin. Many MM force fields treat improper dihedrals in the same way as bond-bending, and take a contribution to the force field as

$$U_{\mathrm{ABCD}} = \tfrac{1}{2}k_{\mathrm{ABCD}}(\xi_{\mathrm{ABCD}} - \xi_{\mathrm{e,ABCD}})^2 \tag{1.35}$$

where ξ is the dihedral angle between the planes defined by the atoms ABC and the atoms BCD. The dihedral force constant is taken as an empirical parameter.

I mentioned earlier that molecular-mechanics force fields have to be transferable from molecule to molecule, and that it was found many years ago that extra terms were needed apart from the pure valence ones. Non-bonded interactions are usually taken as the Lennard-Jones 12–6 potential

$$U_{\mathrm{AB}} = \frac{C_{12}}{R_{\mathrm{AB}}^{12}} - \frac{C_6}{R_{\mathrm{AB}}^{6}} \tag{1.36}$$

where the coefficients C_{12} and C_6 depend on the nature of the atoms A and B. The Lennard-Jones 12–6 potential is sometimes written in terms of the depth of the potential well ε and the parameter σ which is related to the equilibrium distance R_e by

$$\begin{aligned} R_e &= 2^{1/6}\sigma \\ U_{\mathrm{AB}} &= 4\varepsilon\left(\left(\frac{\sigma}{R_{\mathrm{AB}}}\right)^{12} - \left(\frac{\sigma}{R_{\mathrm{AB}}}\right)^{6}\right) \end{aligned} \tag{1.37}$$

Lennard-Jones 12–6 parameters have been deduced over the years, initially for the interactions between identical pairs of inert gas atoms. Over the years, authors have extended such studies to include simple molecules and some examples are given in Table 1.3.

For molecular species, the interaction is to be interpreted as some kind of average over all the possible geometries. A typical plot for the van der Waals benzene–benzene interaction is shown in Figure 1.12.

For interactions between different atom pairs, we should ideally try to deduce experimental parameters for the interactions of these atoms. What is done instead is to use *combination rules*, which allow us to relate the parameters for unlike atom pairs A···B to those for the two like pairs A···A and B···B. If we use symbols i and j to label the two atoms, then there are a number of different such

Table 1.3 Sample Lennard-Jones parameters

	ε/J mol^{-1}	σ/pm
He	84.97	258
Ne	296.8	279
Ar	1031.0	342
H_2	276.9	297
CO_2	1580.0	400
C_6H_6	3658.0	527

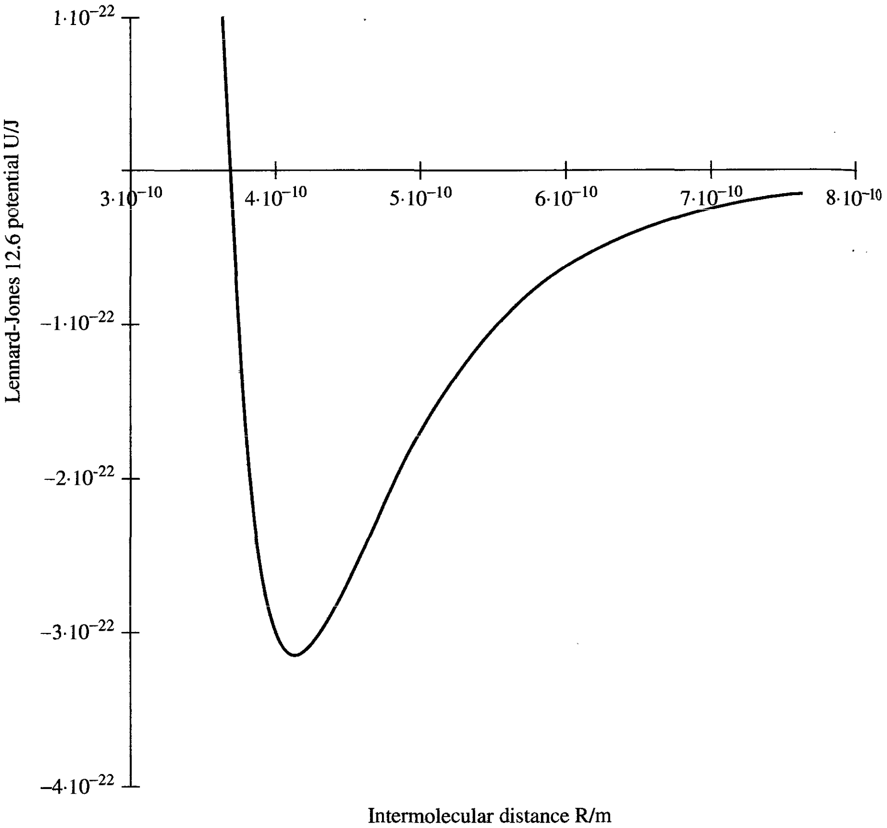


Figure 1.12 L-J 12–6 potential for benzene–benzene

combination rules in the literature such as the following three.

1
$$C_{12,ij} = \left(\frac{r_i^*}{2} + \frac{r_j^*}{2}\right)^{12} \sqrt{\varepsilon_i \varepsilon_j}$$
$$C_{6,ij} = 2\left(\frac{r_i^*}{2} + \frac{r_j^*}{2}\right)^{6} \sqrt{\varepsilon_i \varepsilon_j} \tag{1.38}$$

where $r_i^*/2$ is half the minimum energy separation for two atoms of type i and ε_i the well depth.

2
$$C_{12,ij} = 4(\sigma_i \sigma_j)^6 \sqrt{\varepsilon_i \varepsilon_j}$$
$$C_{6,ij} = 4(\sigma_i \sigma_j)^3 \sqrt{\varepsilon_i \varepsilon_j} \tag{1.39}$$

and finally

$$C_{6,ij} = C\frac{\alpha_i\alpha_j}{\sqrt{\frac{\alpha_i}{N_i}}+\sqrt{\frac{\alpha_j}{N_j}}}$$

3

$$C_{12,ij} = \tfrac{1}{2}C_{6,ij}(R_i + R_j)^6 \tag{1.40}$$

where α_i is the dipole polarizability of atom i, N_i the number of valence electrons and R_i the van der Waals radius. C is a constant.

1.7.1 Hydrogen Bonding

Some force fields make special provision for hydrogen-bonded atoms A–H $\cdots$ B, and modify the Lennard-Jones 12–6 potential to a 12–10 model:

$$U_{AB} = \frac{C_{12}}{R_{AB}^{12}} - \frac{C_{10}}{R_{AB}^{10}} \tag{1.41}$$

1.7.2 Electronegativity Differences

Some force fields make special provision for the mutual electrostatic potential energy of pairs of atoms that have different electronegativities. If atom A has a formal charge of Q_A and atom B (distant R_{AB} from Q_A) has a formal charge of Q_B, then their mutual potential energy is

$$U_{AB} = \frac{1}{4\pi\epsilon_0}\frac{Q_AQ_B}{R_{AB}} \tag{1.42}$$

The Q's are treated as parameters, and these terms are sometimes included in molecular-mechanics force fields.

1.7.3 United Atoms

Some force fields use the so-called united atom approach where (for example) a methyl group is treated as a single pseudo-atom. They arose historically in order to save computer resource when dealing with large systems such as amino-acid chains.

1.7.4 Cut-offs

For a given large molecule, there are very many more non-bonded interactions than bonded ones. Molecular-mechanics force fields often truncate the non-bonded interactions at some finite distance, in order to save on computer resource. A number of ingenious algorithms have been proposed in order to ensure the continuity of the potential at the cut-off point.

1.7.5 Conjugated Subsystems

The aspirin molecule given above contains a single conjugated ring. Smart molecular mechanics packages note the presence of conjugated systems, and cut down on the computation time needed by recognizing that such subsystems are invariably planar. They sometimes use quantum-mechanically based models in order to treat the conjugated system — see later.

1.8 PROFESSIONAL MOLECULAR MECHANICS FORCE FIELDS

The original molecular-mechanics force field was developed by Allinger, and is generally referred to as MM. You should read the definitive text by Burkert and Allinger (1982) for more details. This model was followed by the MM2 model (Allinger, 1977), and I thought that you might like to read the synopsis.

> Conformational Analysis 130
> MM2. A Hydrocarbon Force Field Utilizing V_1 and V_2 Torsional Terms
> Norman L. Allinger
> *Journal of the American Chemical Society*, **99** (1977) 8127
>
> An improved force field for molecular mechanics calculations of the structures and energies of hydrocarbons is presented. The problem of simultaneously obtaining a sufficiently large gauche butane interaction energy whilst keeping the hydrogens small enough for good structural predictions was solved with the aid of onefold and twofold rotational barriers. The structural results are competitive with the best of currently available force fields, while the energy calculations are superior to any previously reported. For a list of 42 selected diverse types of hydrocarbons, the standard deviation between the calculated and experimental heats of formation is 0.42 kcal/mol, compared with an average reported experimental error for the same group of compounds of 0.40 kcal/mol.

The following additional force fields are currently available in serious professional modelling packages.

1.8.1 MM+

This is an extension of MM2, and it was designed primarily for small organic molecules. It uses a cubic stretching potential

$$U_{\mathrm{AB}} = \frac{1}{2}k_{\mathrm{s,AB}}(R_{\mathrm{AB}} - R_{\mathrm{e,AB}})^2(1 + \alpha(R_{\mathrm{AB}} - R_{\mathrm{e,AB}})) \qquad (1.43)$$

where α is a constant which depends on the atom types of A and B, rather than the Hooke's law expression

$$U_{\rm AB} = \tfrac{1}{2}k_{\rm s,AB}(R_{\rm AB} - R_{\rm e,AB})^2$$

Also, the angle-bending term is modified from

$$U_{\rm ABC} = \tfrac{1}{2}k_{\rm ABC}(\theta_{\rm ABC} - \theta_{\rm e,ABC})^2$$

by inclusion of a higher-order angle term to give

$$U_{\rm ABC} = \tfrac{1}{2}k_{\rm ABC}(\theta_{\rm ABC} - \theta_{\rm e,ABC})^2 \left(1 + \beta(\theta_{\rm ABC} - \theta_{\rm e,ABC})^2\right) \qquad (1.44)$$

Here β is a constant that depends on the nature of atoms A, B and C. Not only that, both MM+ and MM2 allow for coupling between bond-stretching and angle-bending. Electrostatic interactions are accounted for by the interaction of bond dipoles rather than point charges.

1.8.2 AMBER (Assisted Model Building and Energy Refinement)

This force field was developed primarily for protein and nucleic acid applications. It is a united atom force field, and there are many versions. Once again, you might like to see the Abstract of the original Paper.

> A New Force Field for Molecular Mechanics Simulation of Nucleic Acids and Proteins
> Scott J. Weiner, Peter A. Kollman, David A. Case, U. Chandra Singh, Caterina Ghio, Guiliano Alagona, Salvatore Profeta, Jr and Paul Weiner
> *Journal of the American Chemical Society* **106** (1984) 765
>
> We present the development of a force field for simulation of nucleic acids and proteins. Our approach began by obtaining bond lengths and angles from microwave spectroscopy, neutron diffraction, and prior molecular mechanical calculations, torsional constants from microwave, NMR, and molecular mechanical studies, nonbonded parameters from crystal packing calculations and atomic charges from the fit of a partial charge model to electrostatic potentials calculated by Ab Initio quantum mechanical theory. The parameters were then refined with molecular mechanics studies on the structures and energies of model compounds. For nucleic acids ...

An interesting feature of this force field is that it adds lone pairs to all sulfur atoms.

1.8.3 OPLS (Optimized Potentials for Liquid Simulations)

> The OPLS Potential Function for Proteins. Energy Minimization for
> Crystals of Cyclic Peptides and Crambin
> William L. Jorgensen and Julian Tirado-Rives
> *Journal of the American Chemical Society* **110** (1988) 1657
>
> A complete set of intermolecular potential functions has been developed for use in computer simulations of proteins in their native environment. Parameters have been reported for 25 peptide residues as well as the common neutral and charged terminal groups. The potential functions have the simple Coulomb plus Lennard-Jones form and are compatible with the widely used models for water, TIP4P, TIP3P and SPC. The parameters were obtained and tested primarily in conjunction with Monte Carlo statistical mechanics simulations of 36 pure organic liquids and numerous aqueous solutions of organic ions representative of subunits in the side chains and backbones of proteins...
>
> Improvement is apparent over the AMBER united-atom force field which has previously been demonstrated to be superior to many alternatives.

OPLS is designed for calculations on proteins and nucleic acids; the non-bonded interactions have been carefully developed from liquid simulations on small molecules. There are many more force fields in the literature, but the ones given above are representative.

1.9 A SAMPLE MM CALCULATION: ASPIRIN

Molecular mechanics calculations generally aim to find energy minima. They need a starting geometry, corresponding to a starting point on the potential energy surface. In the early days of molecular modelling, people had lots of fun taking X-ray pictures of macroscopic models, or projecting shadows of such models onto screens and then measuring their Cartesian coordinates. Many of the available molecular modelling packages have libraries of fragments or full molecules, and they can make a rough attempt at converting two-dimensional representations of simple molecules produced by drawing packages such as ChemDraw and ISISDraw, into three-dimensional structures.

So, back then to aspirin. Very often, X-ray data is available for the molecule of interest or related molecules. The *lingua franca* for molecular modelling purposes is a file of Cartesian coordinates such as the following .pdb (Protein Database) file, Figure 1.13, for aspirin.

```
HETATM   1  C          1       1.083   3.125   0.000
HETATM   2  C          2       1.083   1.875   0.000
HETATM   3  C          3       2.167   1.250   0.000
HETATM   4  C          4       3.250   1.875   0.000
HETATM   5  C          5       3.250   3.125   0.000
HETATM   6  C          6       2.167   3.750   0.000
HETATM   7  H          7       2.167   0.000   0.000
HETATM   8  H          8       0.000   1.250   0.000
HETATM   9  H          9       0.208   4.000   0.000
HETATM  10  H         10       2.167   5.000   0.000
HETATM  11  O         11       4.333   3.750   0.000
HETATM  12  C         12       4.333   1.250   0.000
HETATM  13  O         13       4.333   0.000   0.000
HETATM  14  O         14       5.417   1.875   0.000
HETATM  15  C         15       4.333   5.000   0.000
HETATM  16  C         16       3.250   5.625   0.000
HETATM  17  O         17       5.417   5.625   0.000
HETATM  18  H         18       5.417   3.125   0.000
HETATM  19  H         19       2.679   5.361   0.890
HETATM  20  H         20       2.679   5.361  -0.890
HETATM  21  H         21       3.449   6.697   0.000
CONECT   1    2    6    9
CONECT   2    1    3    8
CONECT   3    2    4    7
CONECT   4    3    5   12
CONECT   5    4    6   11
CONECT   6    5    1   10
CONECT   7    3
CONECT   8    2
CONECT   9    1
CONECT  10    6
CONECT  11    5   15
CONECT  12    4   13   14
CONECT  13   12
CONECT  14   12   18
CONECT  15   11   16   17
CONECT  16   15   19   20   21
CONECT  17   15
CONECT  18   14
CONECT  19   16
CONECT  20   16
CONECT  21   16
END
```

Figure 1.13

The format is self-explanatory; each `HETATM` line gives the Cartesian coordinates of the atoms, and lines such as

```
CONECT  1  2  6  9
```

give connectivity data. Atom 1 is joined to atoms 2, 6 and 9. A .pdb file from the Internet or from the Brookhaven Protein Data Bank will also have lots of 'comment' lines and literature references.

1.10 THE GRAPHICAL USER INTERFACE

In the good old days of the 1960s, we had to try and make sense of a numerical table of atomic Cartesian coordinates. We did this by plotting points on graph paper and then trying to see how things would look in three dimensions. Plastic model-building kits were the height of technology by the 1970s.

Figure 1.14 is a screen grab from HyperChem, after geometry optimization (energy minimization). I'll explain later how energy minimization works. I have deliberately given the output as a screen grab so that you can see some of the options available in such a sophisticated modelling package.

There are many ways of representing molecules on screen, and most modelling packages will have a selection. The screen grab in Figure 1.14 shows the 'line' representation of aspirin. Figures 1.15 to 1.17 give a few of the options from WebLab Viewer.

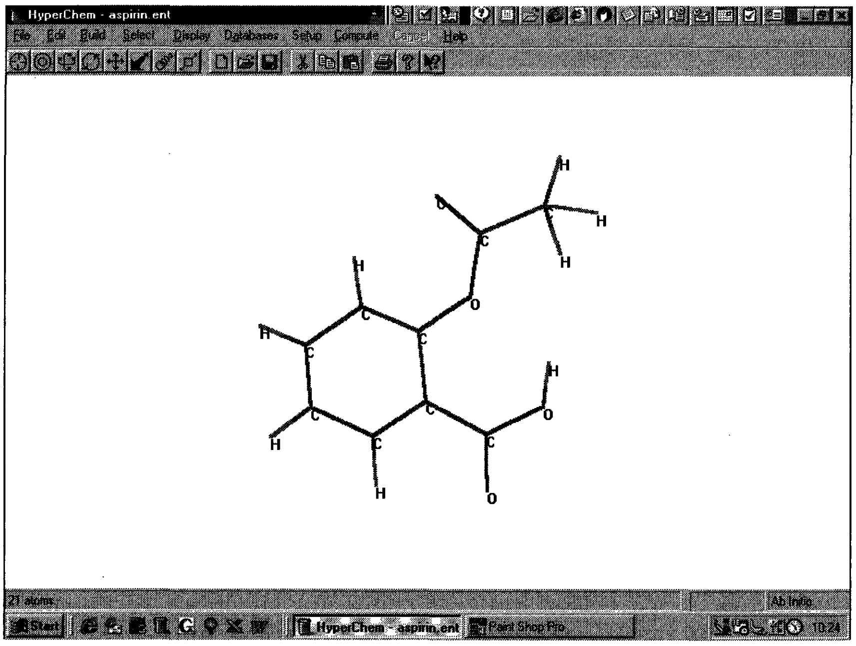


Figure 1.14 Aspirin after geometry optimization

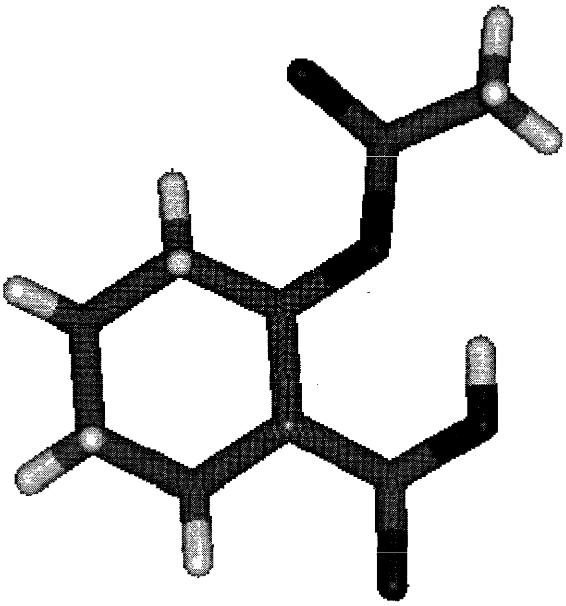


Figure 1.15 Stick representation of aspirin

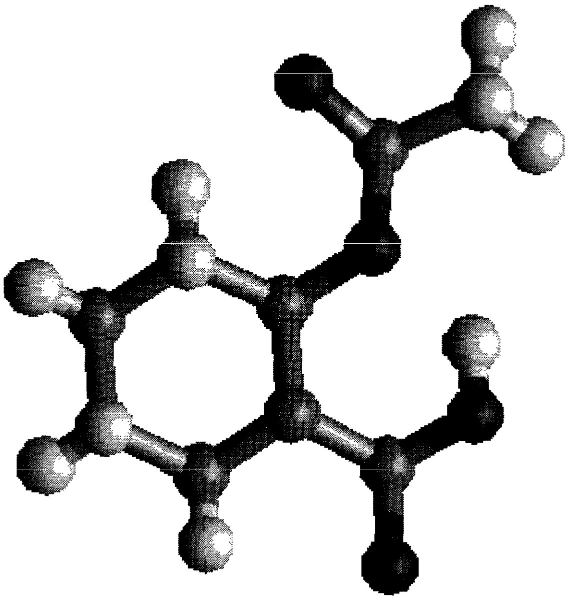


Figure 1.16 Aspirin ball and stick

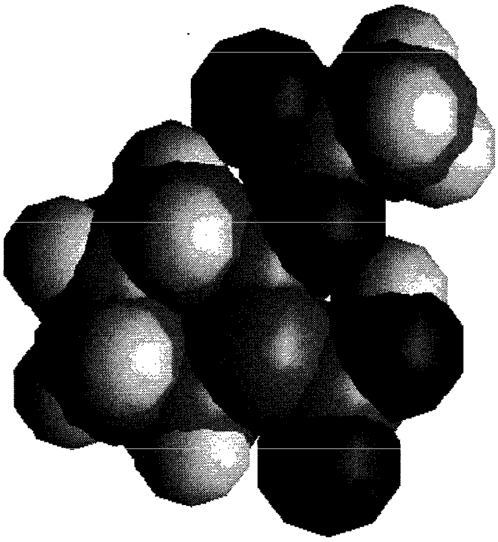


Figure 1.17 Aspirin CPK representation

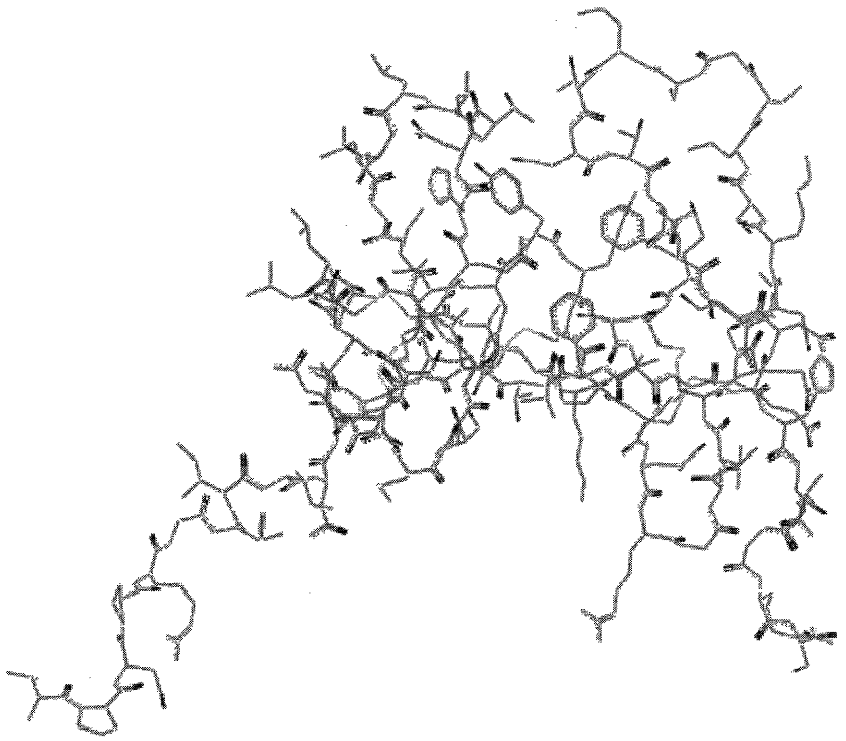


Figure 1.18 Procolipase from the Protein DataBank

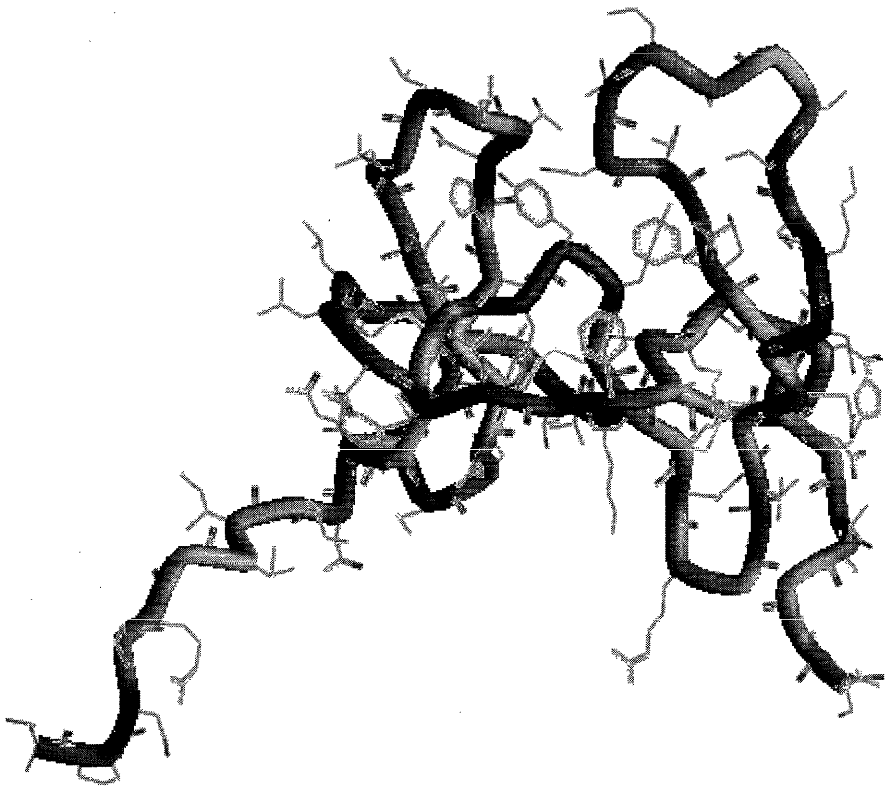


Figure 1.19 Tube representation of protein

Taking a larger number of pixels can smooth the jagged borders.

Different methods have been devised to represent proteins. A structure for porcine pancreatic procolipase is reported in the Protein Databank, as determined by NMR spectroscopy. Many such structures are reported without the hydrogen atoms, since their positions often cannot be determined experimentally. Most MM packages will add hydrogens. Figure 1.18 gives the hydrogen-free procolipase structure in line representation.

Such large amino acid strands are usually presented in terms of *ribbons*, or *tubes*, where attention focuses on the backbone of the protein. Figure 1.19 gives a tube view of procolipase.

1.11 GENERAL FEATURES OF POTENTIAL ENERGY SURFACES

Most people use MM in order to find potential energy minima, which correspond to equilibrium geometries at 0 K.

A little experimentation shows that there are very many stationary points, depending on the starting geometry. For example, I quickly generated the aspirin energy stationary point in Figure 1.20 by starting from a different geometry and then minimizing the energy.

This structure has a lower energy than the one we first found. Both structures are true stationary points, and a detailed investigation shows that they are both minima on the *potential energy surface*. For large molecules there will be very many minima. How can I say with confidence that a given stationary-point structure corresponds to a minimum (rather than a maximum), how do I go about finding these stationary points and which is the 'real' minimum? What do the other stationary points mean chemically? In order to answer such questions, we need to take a look at the general features exhibited by potential energy surfaces.

1.11.1 Multiple Minima

Even potential energy curves that depend on a single variable can show interesting properties. Consider, for example, a model (Figure 1.21) of ethane composed of two rigid CH_3 fragments which are joined through the C atoms but are free to rotate about the internuclear C–C axis. The potential energy curve is then a function of the single variable describing the azimuthal angle, and there are three identical minima separated by intervals of 120°. In this case, the minima are all equivalent to each other.

Figure 1.22 shows a typical energy calculation, to illustrate the point.

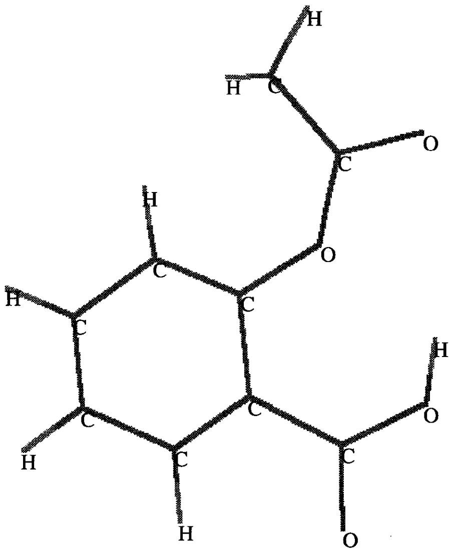


Figure 1.20 A second stationary energy point for aspirin

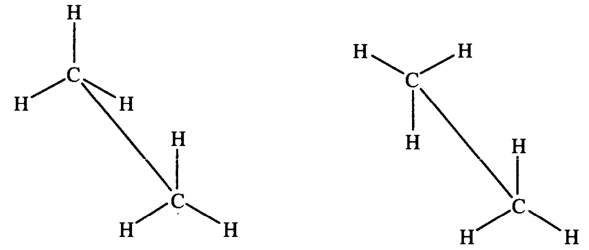


Figure 1.21

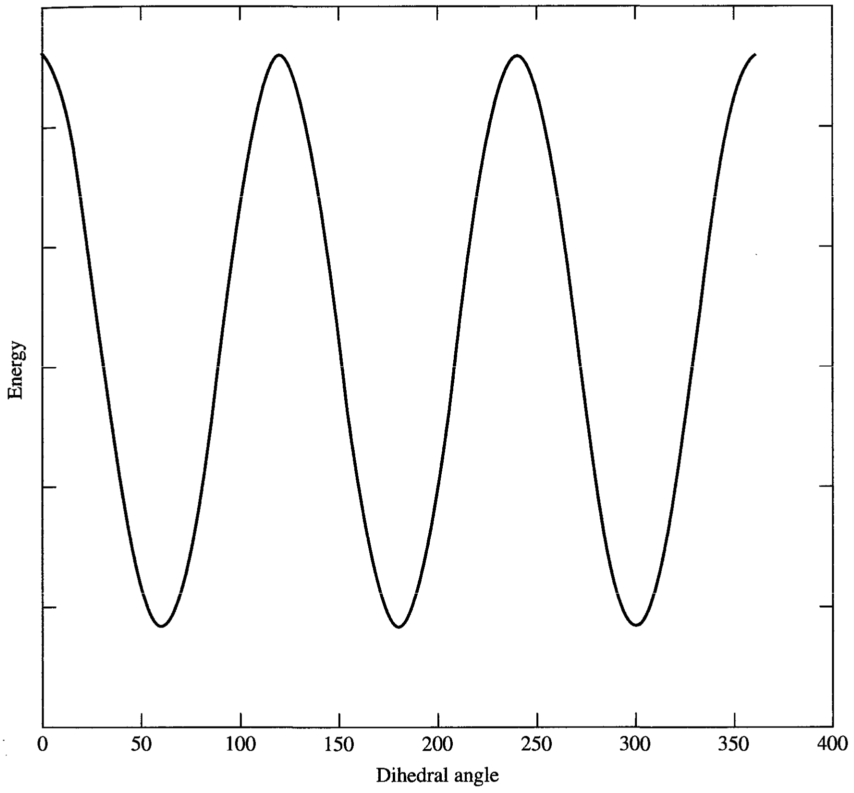


Figure 1.22 Potential energy curve for rotation about C–C bond of ethane

Now consider the disubstituted molecule CH_2FCH_2Cl. The potential energy curve has a new feature. There are three minima, corresponding to the three conformations of Figure 1.23. A potential energy curve is shown in Figure 1.24. The conformation with the F and the Cl atoms *trans* is the *global minimum*. The other two conformations correspond to *local minima*.

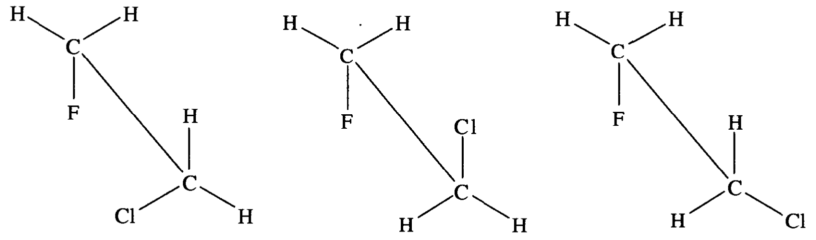


Figure 1.23

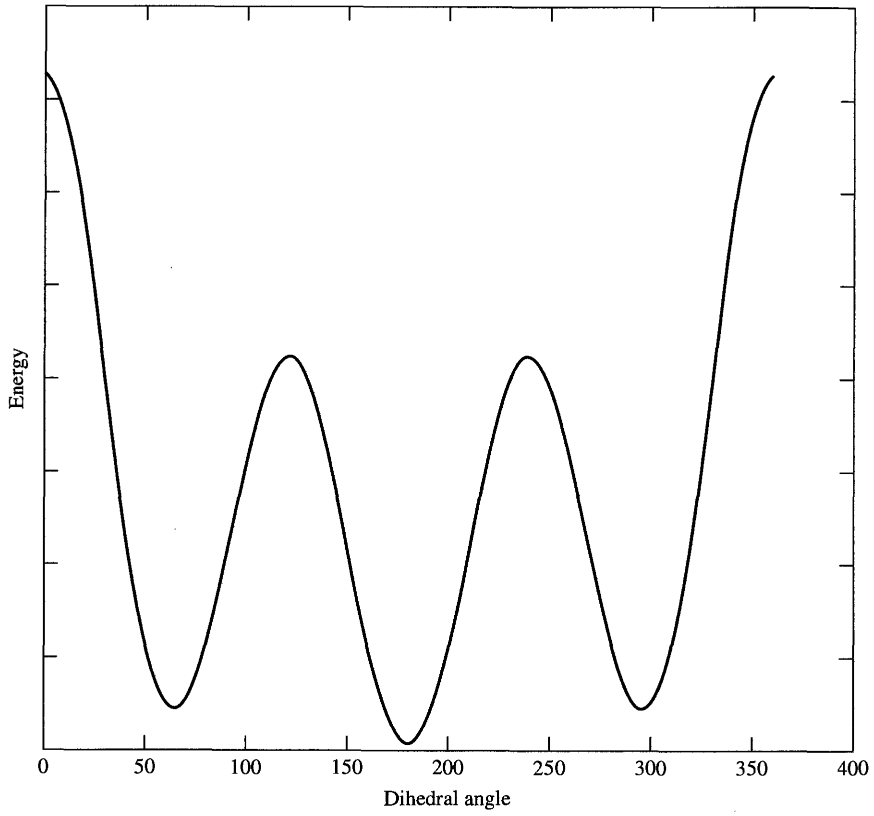


Figure 1.24 Potential energy curve for rotation about C–C bond

The next step is a function of two variables, when we begin to talk about *potential energy surfaces* rather than *potential energy curves*. Such functions are often represented as *surface plots* such as the one in Figure 1.25 which shows the variation of energy of the water molecule (the vertical axis) against the two bond lengths (assumed equal) and the bond angle.

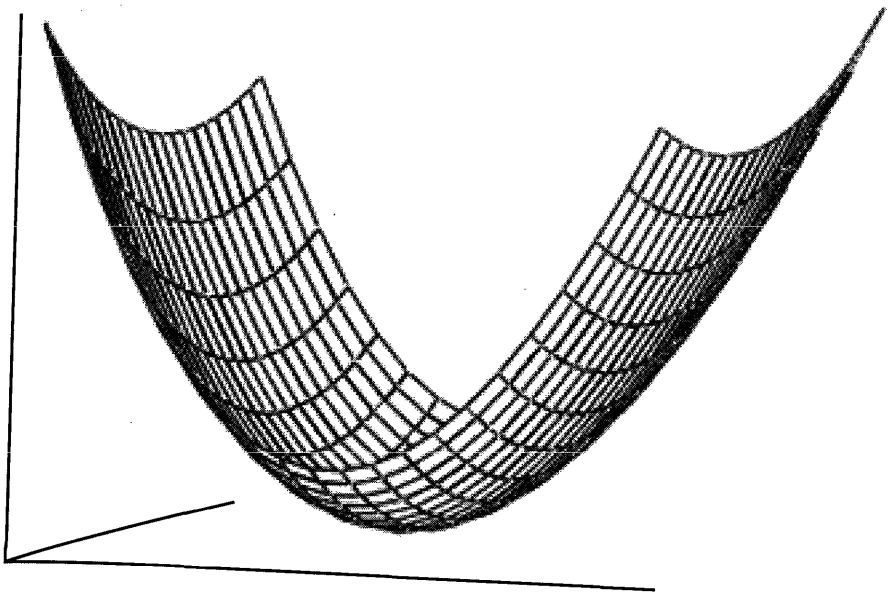


Figure 1.25 A function of two variables

This particular potential energy surface seems very clean-cut, because there is a single minimum in the range of variables scanned. The chances are that this minimum is a local one, and a more careful scan of the potential surface with a wider range of variables would reveal many other potential minima.

Potential energy surfaces show many fascinating features, of which the most important for chemists is a *saddle point*. At any stationary point, both $\partial f/\partial x$ and $\partial f/\partial y$ are zero. For functions of two variables $f(x, y)$ such as that above, elementary calculus texts rarely go beyond the simple observation that if the quantity

$$\frac{\partial^2 f}{\partial x^2}\frac{\partial^2 f}{\partial y^2} - \left(\frac{\partial^2 f}{\partial x \partial y}\right)^2 \qquad (1.45)$$

is greater than zero at a certain point, then that point is either a maximum or a minimum. If the quantity is less than zero then there is neither a maximum nor a minimum, and if the quantity is zero then the case is undecided.

I'll explain later how we characterize such surfaces; you might have noticed that (1.45) can be written as the determinant of a matrix **H** called the *Hessian*

$$\mathbf{H} = \begin{pmatrix} \dfrac{\partial^2 f}{\partial x^2} & \dfrac{\partial^2 f}{\partial x \partial y} \\ \dfrac{\partial^2 f}{\partial y \partial x} & \dfrac{\partial^2 f}{\partial y^2} \end{pmatrix} \qquad (1.46)$$

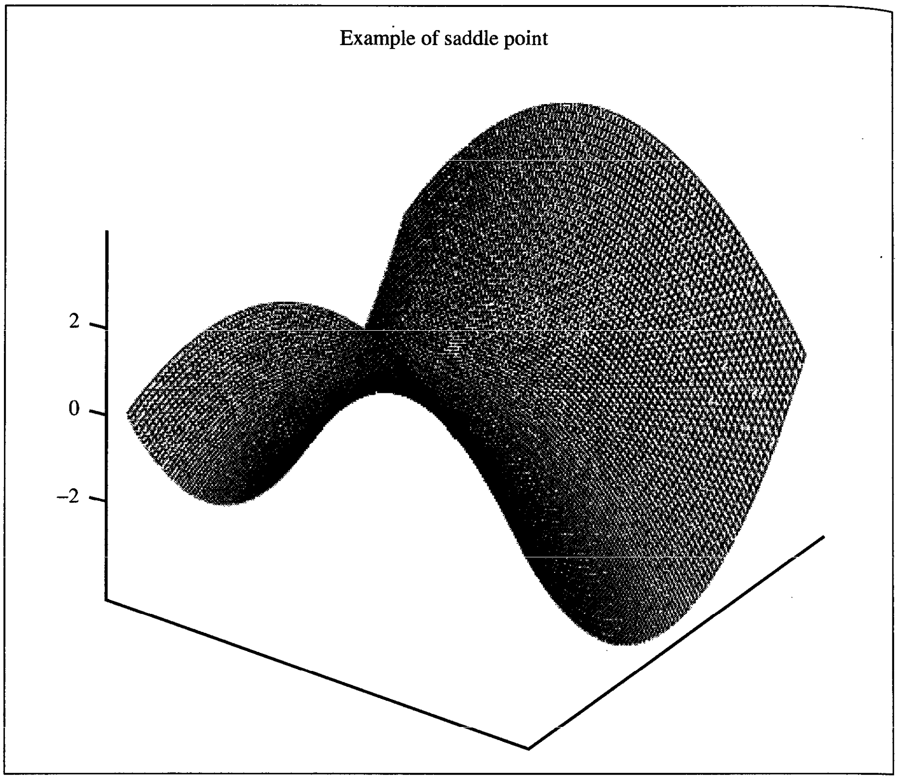


Figure 1.26 Example of a saddle point

Saddle points are important in chemistry because they correspond to transition states.

1.12 OTHER PROPERTIES

Apart from finding structures that give energy minima, most molecular mechanics packages will calculate structural features such as the surface area or the molecular volume. Quantities such as these are often used to investigate relationships between molecular structure and pharmacological activity. This field of human endeavour is called QSAR (quantitative structure and activity relations).

1.13 PROTEIN DOCKING

One great advantage of the molecular mechanics model is that it can be applied to large molecules on your average PC. Apart from single molecular structure

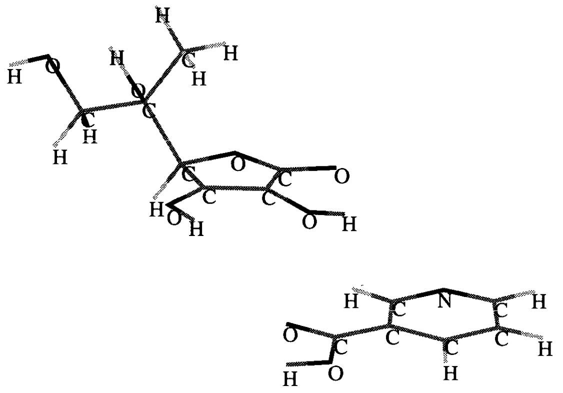


Figure 1.27 Protein docking: niacin and vitamin C

calculations, many researchers in the life sciences are concerned with the interaction between proteins, and we normally refer to *protein docking* when we study this phenomenon. Let me give you a very simple example, with which to end the chapter.

Figure 1.27 represents *a protein docking* study of the interaction between niacin and vitamin C. It is widely believed that such interactions can help stabilize proteins because of the strong electrostatic interactions. The idea of protein docking is to investigate the way such amino acids interact with each other as they approach an equilibrium separation. In *vector docking* we choose an atomic position in either fragment and then study the energy variation as the two fragments approach along the line joining these two points. In *unconstrained docking*, we simply let the fragments interact as best they can. In either case, we would normally keep the geometry of the fragments constant.

1.14 UNANSWERED QUESTIONS

The molecular mechanics calculations discussed so far have been concerned with predictions of the possible equilibrium geometries of molecules *in vacuo* and at 0 K. Because of the classical treatment, there is no zero-point energy (which is a pure quantum-mechanical effect), and so the molecules are completely at rest at 0 K. There are therefore two problems that I have carefully avoided. First of all, I have not treated dynamical processes. Neither have I mentioned the effect of temperature, and for that matter, how do molecules know the temperature? Secondly, very few scientists are interested in isolated molecules in the gas phase. Chemical reactions usually take place in solution and so we should ask how to tackle the solvent. We will pick up these problems in future chapters.

2 DYNAMICS

I mentioned temperature at the end of the last chapter. The concept of temperature has a great deal to do with thermodynamics, and at first sight very little to do with microscopic systems such as atoms or molecules. The Zeroth Law of Thermodynamics states that 'If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is also in thermal equilibrium with system C'. This statement indicates the existence of a property that is common to systems in thermal equilibrium, irrespective of their nature or composition. The property is referred to as the *temperature* of the system.

That's fine in the macroscopic world, but how does the concept of temperature translate to the microscopic world?

Consider the vibrating diatomic of Chapter 1, where we wrote the total energy as

$$\varepsilon = \frac{1}{2}m_1\left(\frac{\mathrm{d}x_1}{\mathrm{d}t}\right)^2 + \frac{1}{2}m_2\left(\frac{\mathrm{d}x_2}{\mathrm{d}t}\right)^2 + \frac{1}{2}k_\mathrm{s}(x_2 - x_1 - R_\mathrm{e})^2 \tag{2.1}$$

For pedantic reasons, I am going to rewrite this energy expression in terms of so-called *generalized coordinates*, which in this simple case are exactly the Cartesian ones

$$q_1 = x_1$$

$$q_2 = x_2$$

and also their corresponding *generalized momenta*

$$p_1 = m_1\frac{\mathrm{d}q_1}{\mathrm{d}t}$$

$$p_2 = m_2\frac{\mathrm{d}q_2}{\mathrm{d}t}$$

to give a quantity called the Hamiltonian H.

$$H = \frac{1}{2m_1}\left(\frac{\mathrm{d}p_1}{\mathrm{d}t}\right)^2 + \frac{1}{2m_2}\left(\frac{\mathrm{d}p_2}{\mathrm{d}t}\right)^2 + \frac{1}{2}k_\mathrm{s}(q_2 - q_1 - R_\mathrm{e})^2 \tag{2.2}$$

H is of immense importance in classical mechanics; it is seen by inspection to be a sum of the kinetic and potential energies, and it is easily proved that H is constant with time provided that the potential energy does not contain time-dependent terms.

Although I do not intend to progress the idea here, there is a set of first-order differential equations called *Hamilton's equations of motion* that are fully equivalent to Newton's laws. Hamilton's equations are:

$$\begin{aligned}\frac{\partial H}{\partial p_i} &= \frac{\mathrm{d}q_i}{\mathrm{d}t}\\ \frac{\partial H}{\partial q_i} &= -\frac{\mathrm{d}p_i}{\mathrm{d}t}\end{aligned} \tag{2.3}$$

where the subscript i runs over the generalized coordinates. We have to integrate these equations to study the time evolution of the system. Hamilton's equations are first-order differential equations, which are usually easier to solve than second-order ones.

The state of any particle at any instant is given by its position vector $\mathbf{q}$ and its linear momentum vector $\mathbf{p}$, and we say that the state of a particle can be described by giving its location in *phase space*. For a system of N atoms, this space has $6N$ dimensions: three components of $\mathbf{p}$ and the three components of $\mathbf{q}$ for each atom. If we use the symbol $\boldsymbol{\Gamma}$ to denote a particular point in this six-dimensional phase space (just as we would use the vector $\mathbf{r}$ to denote a point in three-dimensional coordinate space) then the value of a particular property A (such as the mutual potential energy, the pressure and so on) will be a function of $\boldsymbol{\Gamma}$ and is often written as $A(\boldsymbol{\Gamma})$. As the system evolves in time then $\boldsymbol{\Gamma}$ will change and so will $A(\boldsymbol{\Gamma})$.

Computer simulation generates information at the microscopic level, and the conversion of this information into macroscopic terms is the province of *statistical thermodynamics*. An experimentally observable property A is just the *time average* of $A(\boldsymbol{\Gamma})$ taken over a long time interval,

$$A = \langle A(\Gamma)\rangle_{\text{time}}$$

2.1 EQUIPARTITION OF ENERGY

According to the *law of equipartition of energy*, the average energy of each different degree of freedom is $\frac{1}{2}\,k_\text{B}T$ and this gives us a clear link between energy and temperature. In the case of a monatomic gas, there are three translational modes of motion along three perpendicular axes and so the internal energy ought to be $\frac{3}{2}\,k_\text{B}T$ per atom. The law applies pretty well to rotating molecules, and so the mean rotational energy of methane ought to be $\frac{3}{2}\,k_\text{B}T$. The law also suggests that the mean vibrational energy of a bond ought to be $\frac{1}{2}\,k_\text{B}T$ for the kinetic energy and $\frac{1}{2}\,k_\text{B}T$ for the potential energy, but this is hardly ever found in practice because of the finite spacing of vibrational energy levels compared to k_BT. We can use k_BT as a yardstick for assessing the magnitude of thermal effects at room temperature, and these considerations give us a second clue as to the molecular meaning of temperature. Roughly speaking, provided the temperature is sufficiently high that we can ignore zero-point vibrations, and that the Boltzmann populations of vibrational states are all significant then the laws of classical mechanics are fine and the law of equipartition of energy is valid.

2.2 ENSEMBLES

Because of the complexity of dealing with the time evolution for very large numbers of molecules, Gibbs suggested that we replace the time average by the *ensemble average*. There are at least three ensembles in common use, and for each one certain thermodynamic variables are fixed. In the *microcanonical ensemble*, N, V and the internal energy U are held constant, where N is the number of particles. In the *canonical ensemble*, N, V and T are held constant. In the *grand canonical ensemble*, the chemical potential, V and T are held constant. For each ensemble, the quantities mentioned are fixed and other quantities of interest have to be determined by averaging over the members of the ensemble.

Thus we have an alternative route to the experimentally observable property A; it is the statistical average of the results of measurement on very many identical systems. The *ergodic hypothesis* tells us that this interpretation and the time-dependent interpretation are equivalent.

The simulation of a molecular system at a finite temperature requires the generation of a statistically significant set of points in phase space (so-called *configurations*), and the properties of a system can be obtained as averages over these points. For a many-particle system, the averaging usually involves integration over many degrees of freedom.

2.3 THE BOLTZMANN DISTRIBUTION

Suppose now that we have an ensemble of N non-interacting particles in a thermally insulated enclosure of constant volume. This statement means that the number of particles, the internal energy and the volume are constant and so we are dealing with a microcanonical ensemble. Suppose that each of the particles has quantum states with energies given by $\varepsilon_1, \varepsilon_2, \ldots$ and that, at equilibrium there are: N_1 particles in quantum state ε_1, N_2 particles in quantum state ε_2, and so on.

Since the number of particles is constant,

$$N = N_1 + N_2 + \cdots$$

and since the internal energy U is constant (because the particles do not interact with each other)

$$U = N_1\varepsilon_1 + N_2\varepsilon_2 + \cdots$$

According to Boltzmann's law, the average fraction of particles in quantum state i with energy with energy ε_i is

$$\frac{N_i}{N} = \frac{\exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)}{\sum\limits_{\text{states}} \exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)} \tag{2.4}$$

The sum in the denominator relates to the quantum states. The formula is often written in terms of energy levels rather than quantum states; in the case that some of the energy levels are degenerate, with degeneracy factors g_i then the formula can be modified to refer to energy-level populations directly:

$$\frac{N_i'}{N} = \frac{g_i \exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)}{\sum\limits_{\text{levels}} g_i \exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)} \tag{2.5}$$

The numbers N_i and N_i' are only equal if there are no degeneracies. The sum in the denominator runs over all available molecular energy levels and it is called *the molecular partition function*. It is a quantity of immense importance in statistical thermodynamics, and it is given the special symbol q (sometimes z). We have

$$q = \sum_{\text{levels}} g_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \tag{2.6}$$

The sum runs over all possible energy levels: transitional, rotational, vibrational and electronic. q can be related to thermodynamic quantities such as the Helmholtz energy and the entropy. Don't confuse this q with the generalized coordinate discussed above. It often happens that some particular states are sufficiently close together that we can replace the sum on the right-hand side by an integral. It is usually the case that the kinetic-energy part of the Hamiltonian does not depend on the coordinates, and that the potential-energy part does not depend on the momenta. In this case we can divide the integral into a product of momentum integrals and coordinate integrals.

If we deal with N isolated non-interacting entities such as the molecules in a gas at low density, we can further divide up molecular energies with reasonable accuracy into their electronic, vibrational and rotational contributions

$$\varepsilon = \varepsilon_{\text{elec}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}}$$

If we replace the single molecule energy ε_i in q by the energy of the complete ensemble of molecules E_i and sum over the ensemble states, we create the *system* *partition function* Q. This can be related to the molecular partition function q by

$$Q = q^N \tag{2.7}$$

provided that the N particles are distinguishable, or

$$Q = \frac{q^N}{N!} \tag{2.8}$$

if the N particles are indistinguishable. To look ahead a little, molecular partition functions are usually written as a product of electronic, vibrational, rotational and translational contributions

$$q = q_{\mathrm{el}}\, q_{\mathrm{vib}}\, q_{\mathrm{rot}}\, q_{\mathrm{trans}}$$

where for example

$$q_{\mathrm{vib}} = \sum_i \exp\left(-\frac{\varepsilon_i}{k_{\mathrm{B}}T}\right)$$

with the sum running over all molecular vibrational energy levels.

2.4 MOLECULAR DYNAMICS

In Chapter 1, I discussed the concept of mutual potential energy and demonstrated its relationship to that of force. So, for example, the mutual potential energy of the diatomic molecule discussed in Section 1.1.2 is

$$U = \tfrac{1}{2}k_{\mathrm{s}}(x_2 - x_1 - R_{\mathrm{e}})^2$$

This is related to the forces on particles 1 and 2 by

$$\text{Force on particle 1} = -\frac{\partial U}{\partial x_1}$$

$$\text{Force on particle 2} = -\frac{\partial U}{\partial x_2}$$

This is a general rule: we differentiate U by the coordinates of the particle in question in order to recover the force on that particle, from the expression for the mutual potential energy. Knowing the force $\mathbf{F}$, we can use Newton's second law

$$\mathbf{F} = m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2}$$

to study the trajectory of each particle in space, and this is the basis of *molecular dynamics* (MD). We do not attempt an algebraic solution to Newton's equations; rather we look for numerical solutions at discrete time steps Δt. A suitable Δt is usually a femtosecond (10^{-15} s). So in order to make progress with an

MD simulation, we need a reliable numerical algorithm for integrating Newton's equations.

2.4.1 Integration

If the position (**r**), velocity (**v**), acceleration (**a**) and time derivative of the acceleration (**b**) are known at time t, then these quantities can be obtained at $t + \delta t$ by a Taylor expansion:

$$\begin{aligned}
\mathbf{r}^{\mathrm{p}}(t+\delta t) &= \mathbf{r}(t) + \delta t\mathbf{v}(t) + \tfrac{1}{2}(\delta t)^2\mathbf{a}(t) + \tfrac{1}{6}(\delta t)^3\mathbf{b}(t) + \cdots \\
\mathbf{v}^{\mathrm{p}}(t+\delta t) &= \mathbf{v}(t) + \delta t\mathbf{a}(t) + \tfrac{1}{2}(\delta t)^2\mathbf{b}(t) + \cdots \\
\mathbf{a}^{\mathrm{p}}(t+\delta t) &= \mathbf{a}(t) + \delta t\mathbf{b}(t) + \cdots \\
\mathbf{b}^{\mathrm{p}}(t+\delta t) &= \mathbf{b}(t) + \cdots
\end{aligned} \tag{2.9}$$

One way to do this is afforded by the *predictor–corrector* method. We ignore terms higher than those shown explicitly, and calculate the 'predicted' terms starting with $\mathbf{b}^{\mathrm{p}}(t)$. However, this procedure will not give the correct trajectory because we have not included the force law. This is done at the 'corrector' step. We calculate from the new position $\mathbf{r}^{\mathrm{p}}$ the force at time $t + \delta t$ and hence the correct acceleration $\mathbf{a}^{\mathrm{c}}(t + \delta t)$. This can be compared with the predicted acceleration $\mathbf{a}^{\mathrm{p}}(t + \delta t)$ to estimate the size of the error in the prediction step

$$\Delta\mathbf{a}(t+\delta t) = \mathbf{a}^{\mathrm{c}}(t+\delta t) - \mathbf{a}^{\mathrm{p}}(t+\delta t)$$

This error, and the results from the predictor step, are fed into the corrector step to give

$$\begin{aligned}
\mathbf{r}^{\mathrm{c}}(t+\delta t) &= \mathbf{r}^{\mathrm{p}}(t+\delta t) + c_0\Delta\mathbf{a}(t+\delta t) \\
\mathbf{v}^{\mathrm{c}}(t+\delta t) &= \mathbf{v}^{\mathrm{p}}(t+\delta t) + c_1\Delta\mathbf{a}(t+\delta t) \\
\mathbf{a}^{\mathrm{c}}(t+\delta t) &= \mathbf{a}^{\mathrm{p}}(t+\delta t) + c_2\Delta\mathbf{a}(t+\delta t) \\
\mathbf{b}^{\mathrm{c}}(t+\delta t) &= \mathbf{b}^{\mathrm{p}}(t+\delta t) + c_3\Delta\mathbf{a}(t+\delta t)
\end{aligned} \tag{2.10}$$

These values are now better approximations to the true position, velocity and so on, hence the generic term 'predictor–corrector' for the solution of such differential equations. Values of the constants c_0 through c_3 are available in the literature.

There are many algorithms in the literature, many of which date from the early days of the science of numerical analysis. I simply haven't space to review them all, so I will end this section with the famous *Verlet algorithm*.

If we start from the Taylor expansion about $\mathbf{r}(t)$ then

$$\begin{aligned}
\mathbf{r}(t+\delta t) &= \mathbf{r}(t) + \delta t\mathbf{v}(t) + \tfrac{1}{2}(\delta t)^2\mathbf{a}(t) + \cdots \\
\mathbf{r}(t-\delta t) &= \mathbf{r}(t) - \delta t\mathbf{v}(t) + \tfrac{1}{2}(\delta t)^2\mathbf{a}(t) + \cdots
\end{aligned}$$

Adding these two equations gives the Verlet algorithm, which is used to advance the position vector **r** from its value at time t to time $t + \delta t$

$$\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + (\delta t)^2\mathbf{a}(t)$$

The acceleration is calculated from the force on the atom at time t. The velocity does not appear in this expression, but it may be obtained from the formula

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)}{2\delta t} \tag{2.11}$$

There are many other algorithms in the literature and all have their adherents.

2.5 COLLECTION OF STATISTICS

A molecular dynamics (MD) calculation collects statistical information as it progresses. So, for example, if the calculated position vector of atom A at times $t_1, t_2, \ldots, t_n$ is $\mathbf{r}_A(t_1), \mathbf{r}_A(t_2), \ldots, \mathbf{r}_A(t_n)$, then the statistical-mechanical average is

$$\langle \mathbf{r}_A \rangle = \frac{1}{n}\sum_{i=1}^{n} \mathbf{r}_A(t_i) \tag{2.12}$$

We can also calculate the standard deviation if we want to investigate fluctuations from the mean. The total kinetic energy can be calculated as the sum of the kinetic energies of the individual atoms, whilst the total mutual potential energy is evaluated by summing over pairs of atoms. We can also collect information about individual geometric parameters such as bond lengths and angles.

We normally begin an MD simulation with a molecular structure optimized by (e.g.) molecular mechanics, but with all the atoms at rest. The first step in the simulation is the *heating* step, and it is usual to increase the temperature in small increments from the starting temperature (0 K) to the desired one (e.g. 300 K). At each step, the velocity of each atom is scaled so that its kinetic energy is $\frac{3}{2}\,k_BT$. Next we identify the *data collection* step, and finally we may wish to let the molecule cool, which gives of course the *cooling step*. One advantage of using the cooling step is that we may well overcome potential energy barriers and so force a molecule into a different conformation from the starting point.

A typical plot of total energy and temperature vs time (for aspirin, with the temperature constrained to be constant) is shown in Figure 2.1.

The three phases of the run can be seen clearly; the heating step corresponds to the sharp rise on the left-hand side, the data collection step corresponds to the flat part of the curve, and the cooling step is seen as the final part of the curve.

2.6 SIMULATION OF SYSTEMS

Simulating the dynamical properties of single molecules is all very interesting, but molecular dynamics (MD) was originally developed to study systems of particles

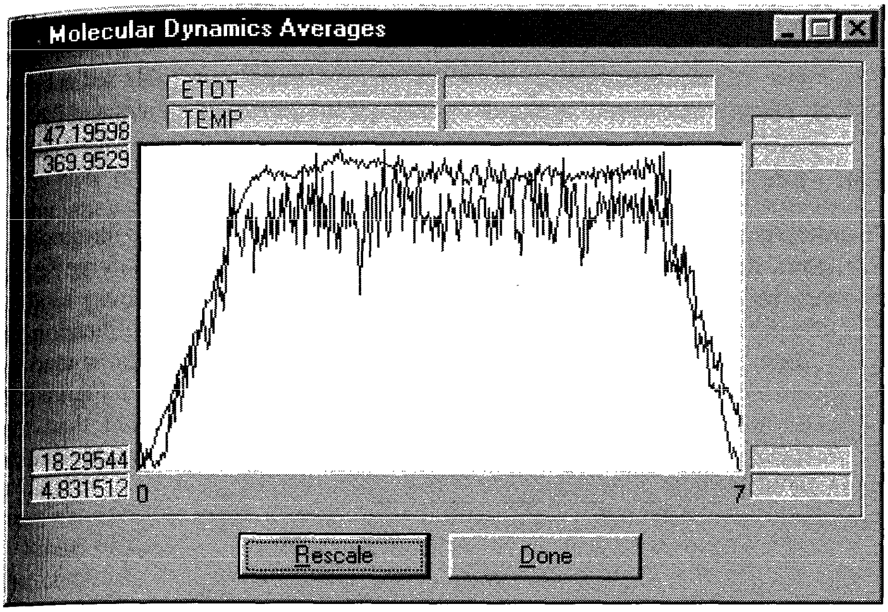


Figure 2.1 Molecular dynamics run on aspirin

rather than individual molecules. The MD method was pioneered by Alder and Wainwright using model systems with very simple pair potentials, and you might like to read one of their key papers:

Studies in Molecular Dynamics I General Method
B. J. Alder and T. E. Wainwright
The Journal of Chemical Physics **31** (1959) 459–466

A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computer are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

Alder and Wainwright gave MD treatments of particles whose pair potential was very simple, typically the square well potential and the hard sphere potential. Rahman (1964) simulated liquid argon in 1964, and the subject has shown exponential growth since then. The 1970s saw a transition from atomic systems to molecular ones, and biological systems are now widely studied using MD. We have to balance the number of particles against the cost of the calculation. Figure 2.2 shows a typical box of 216 water molecules suitable for solvent studies. The box has side 18.70 Å and the density is 1 gm cm^{-3} at 1 atm and 25 °C.

2.6.1 Site–Site Interactions

Potential functions such as MM+ discussed in Chapter 1 are fine for intramolecular interactions. MD was developed long before such sophisticated force fields became available, and in any case the aims of MM and MD simulations tend to be quite different. MM studies tend to be concerned with the identification of equilibrium geometries of individual molecules whilst MD calculations tend to be concerned with the simulation of bulk properties. Inspection of Figure 2.2 suggests that the intramolecular details ought to be less important than the intermolecular ones, and early MD studies concentrated on the intermolecular potential rather than the intramolecular one.

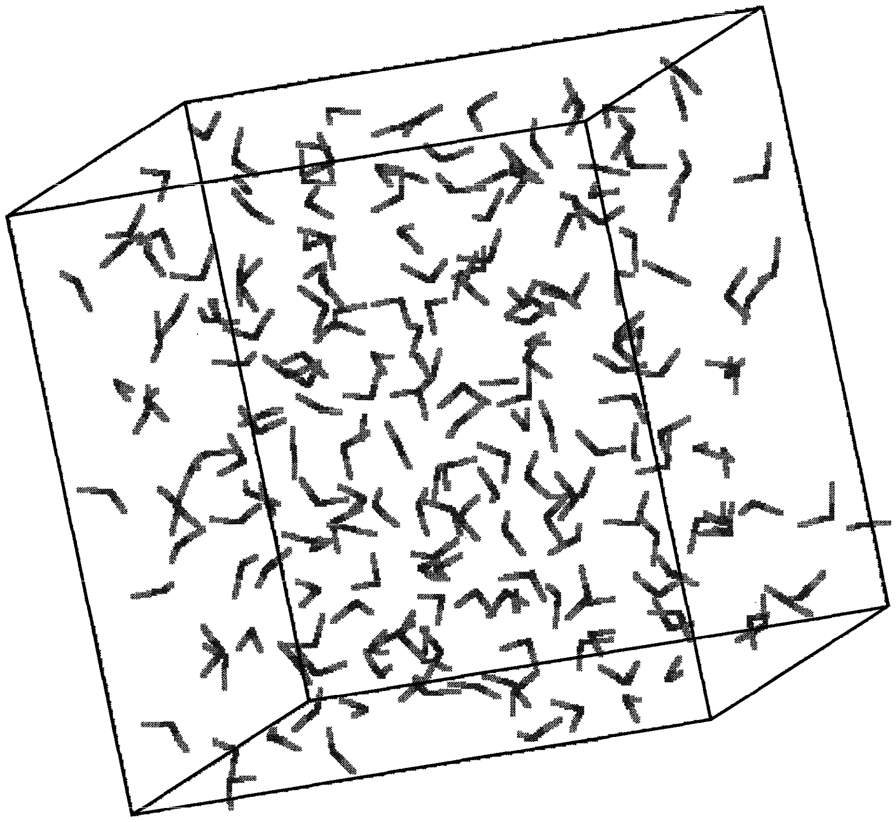


Figure 2.2 Box of water molecules

A number of intermolecular potentials have been developed over the years that treat molecules as collections of point charges. The intermolecular electrostatic potential is taken as a sum of the mutual electrostatic interaction of these point charges, summed over interacting pairs of molecules. Occasionally, extra van der Waals terms are added to the potential.

In view of the importance of water in chemistry and biology, there have been many attempts to construct simple yet effective intramolecular potentials for water molecules. Water monomers are traditionally left rigid. The early three-site model for water took positive charges on the hydrogens (q_H) and a negative charge ($q_O = -2q_H$) on the oxygen, and wrote the pair potential between two H_2O molecules A and B as

$$U_{AB} = \sum_{i \,\mathrm{on}\, A} \sum_{j \,\mathrm{on}\, B} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \frac{C_{12}}{r(O_A \cdots O_B)^{12}} - \frac{C_6}{r(O_A \cdots O_B)^6} \tag{2.13}$$

a Coulomb interaction between all charges, and a further Lennard–Jones 12–6 term between the oxygen atoms. This is illustrated in Figure 2.3

Some of the site–site interactions are shown on the figure. We count both the electrostatic interaction and the Lennard–Jones 12–6 interaction for the oxygen–oxygen interaction.

In the five-site water model, negative charges were also taken to represent the lone pairs. The magnitude of these charges is sometimes found by attempting to fit a molecular charge density feature such as the molecular dipole moment, whilst other authors simply treat them as parameters, along with the Lennard-Jones constants C_{12} and C_6. These parameters are then adjusted until the simulation gives good agreement with experiment.

Here is an extract from the synopsis to the original paper by Rahman and Stillinger:

> Molecular Dynamics Study of Liquid Water
> Aneesur Rahman and Frank H. Stillinger
> *The Journal of Chemical Physics* **55** (1972) 3336–3359
>
> A sample of water, consisting of 216 rigid molecules at mass density 1 gm/cm^3, has been simulated by computer using the molecular dynamics technique. The system evolves in time by the laws of classical dynamics, subject to an effective pair potential that incorporates the principal structural effects of many body interactions in real water. Both static structural properties and the kinetic behaviour have been examined in considerable detail for a dynamics 'run' at nominal temperature 34.3 °C. In those few cases where direct comparison with experiment can be made, agreement is moderately good; a simple energy rescaling of the potential (using a factor 1.06) however improves the closeness of agreement considerably ...

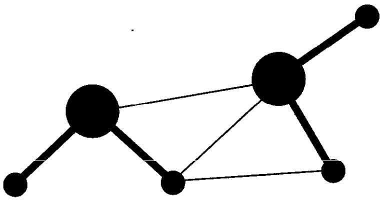


Figure 2.3 Site–site interaction for water

2.6.2 The Effective Pair Potential

Notice that Rahman and Stillinger make use of the concept of an effective pair potential. The potential energy of any substance may always be resolved systematically into pair, triplet, quadruplet, ... contributions. If we consider N particles each with position vector $\mathbf{R}_i$ then formally we can write

$$U_N(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} U^{(2)}(\mathbf{R}_i, \mathbf{R}_j) + \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} \sum_{k=j+1}^{N} U^{(3)}(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \cdots \tag{2.14}$$

In the case of fluids which consist of simple non-polar particles, such as liquid argon, it is widely believed that U_N is nearly pairwise additive. In other words, the functions $U^{(n)}$ for $n > 2$ are small. Water fails to conform to this simplification, and if we truncate the series after the $U^{(2)}$ term, then we have to understand that the potential involved is an *effective pair potential* which takes into account the higher order-terms.

2.6.3 The Periodic Box

There are two difficulties that arise in trying to model an (essentially) infinite system in terms of a representative box of particles such as the one above. First of all, particles near the walls of the box experience very different forces compared to molecules in the middle of the box. Secondly, as the simulation progresses, molecules can leave the box and so the density can change.

Both of these problems can be solved by the introduction of a periodic box; I can explain this idea by Figure 2.4, which shows a much smaller two-dimensional box than the one discussed above.

The box in Figure 2.4 is to be thought of as a very limited part of an infinite set of identical boxes, all joined together. I have illustrated this in two dimensions in Figure 2.5.

This box is embedded in an infinite array of boxes, all with the same geometrical arrangement of particles.

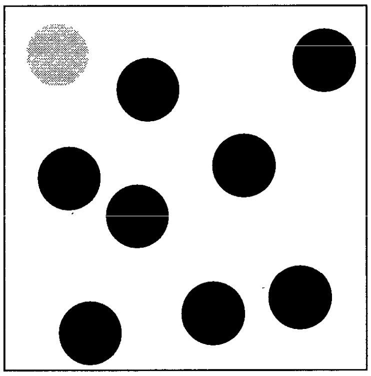


Figure 2.4 Box of particles

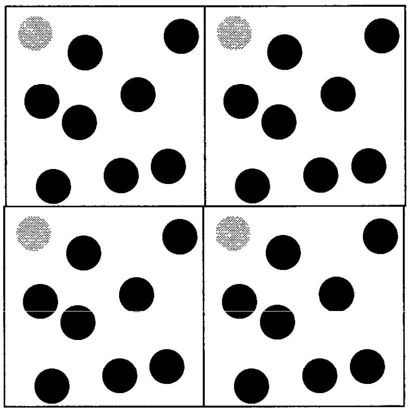


Figure 2.5 Ensemble of boxes of particles

Focus attention on the top left-hand box. As the position and momentum of each particle in this box change, then so do the position and momentum vectors of all the image particles in all the other boxes. In particular, if the grey particle in the top left-hand box leaves its box during a dynamics run, then it is replaced by the movement of its image particle from a corresponding neighbouring box. This is a well-known technique in statistical mechanics, which acts to preserve the density.

2.7 THE MONTE CARLO METHOD

The method of molecular dynamics gives information about the time evolution of a microscopic system, and permits the evaluation of macroscopic properties as time averages. The alternative Monte Carlo method was developed at the end of the Second World War to study the diffusion of neutrons in fissionable material. The name 'Monte Carlo' was chosen because of the extensive use of random numbers.

Consider the two-dimensional box in Figure 2.5. If we know the positions of each of the N particles in the square and their pair potential, then we can calculate the total mutual potential energy

$$U = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{N} U_{ij}$$

and this configuration has a statistical weight of $\exp(-U/k_{\mathrm{B}}T)$.

In order to calculate an equilibrium property A of the system, we have to evaluate the integral

$$\langle A\rangle = \frac{\displaystyle\int_{\text{momenta}}\int_{\text{positions}} A\exp\left(\frac{-U}{k_{\mathrm{B}}T}\right)\mathbf{dp}\,\mathbf{dq}}{\displaystyle\int_{\text{momenta}}\int_{\text{positions}} \exp\left(\frac{-U}{k_{\mathrm{B}}T}\right)\mathbf{dp}\,\mathbf{dq}} \qquad (2.15)$$

where the integration is over all the momenta and all the generalized spatial coordinates. It is impractical to carry out a several-hundred-dimensional integral by standard numerical techniques, so we resort to the Monte Carlo method. This consists of integrating over a random selection of points.

We therefore have to generate a significant number of configurations, and we might (for example) envisage moving each of the particles in succession according to the prescription

$$X \rightarrow X + \alpha\xi_1$$
$$Y \rightarrow Y + \alpha\xi_2$$

where α is the maximum allowed displacement and ξ_1 and ξ_2 are random numbers between -1 and $+1$. After we move a particle, it is equally likely to be anywhere within a square of side 2α centred about its original position. For a densely packed configuration, there is a high probability that some of the particles will now be very close to each other, and so the weight of the new configuration $\exp(-U/k_{\mathrm{B}}T)$ will be vanishingly small. The method normally employed is the Metropolis Monte Carlo scheme; instead of choosing configurations randomly and then weighting them with $\exp(-U/k_{\mathrm{B}}T)$, we choose configurations with a probability $\exp(-U/k_{\mathrm{B}}T)$ and weight them evenly.

We do this as follows. The N particles are placed in a starting configuration, for example a regular lattice. Each particle is then tentatively moved at random. For each move, we calculate the change in the mutual potential energy, ΔU. If ΔU is negative, then we allow the move. If ΔU is positive, we allow the move with a probability of $\exp(-U/k_{\mathrm{B}}T)$.

To decide whether to allow the move or not, we generate a random number between 0 and 1. If this random number is less than $\exp(-U/k_{\mathrm{B}}T)$, we allow the move. If the random number is greater than $\exp(-U/k_{\mathrm{B}}T)$ we leave the particle in its old position.

After each particle move, we increment $\langle A \rangle$ and then proceed to the next particle, continuing until a predetermined number of moves have been made.

The following paper is of great historical significance in the field.

Equation of State Calculations by Fast Computing Machines
Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth,
Augusta H. Teller and Edward Teller
Journal of Chemical Physics **21** (1953) 1087

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient of expansion.

3 THE HYDROGEN MOLECULE ION

In Chapter 1, we dealt at length with molecular mechanics. MM is a classical model where atoms are treated as composite but interacting particles. In the MM model, we assume a simple mutual potential energy for the particles making up a molecular system, and then look for stationary points on the potential energy surface. Minima correspond to equilibrium structures.

Classical descriptions of molecular phenomena can be remarkably successful, but we have to keep our eye on the intrinsic quantum nature of microscopic systems.

The traditional place to begin a quantum-mechanical study of molecules is with the hydrogen molecule ion $H_2{}^+$. Apart from being a prototype molecule, it reminds us that molecules consist of nuclei and electrons. We often have to be aware of the nuclear motion in order to understand the electronic ones. The two are linked.

Potential energy surfaces are also central to our quantum-mechanical studies, and we are going to meet them again and again in subsequent chapters. Let's start then with Figure 3.1, which shows $H_2{}^+$. We are not going to be concerned with the overall translational motion of the molecule. For simplicity, I have drawn a local axis system with the centre of mass as the origin. By convention, we label the internuclear axis the z-axis.

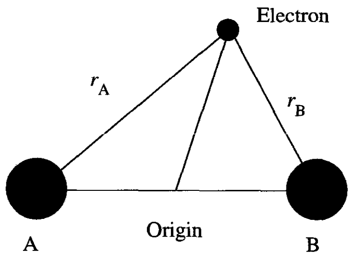


Figure 3.1 Coordinates used in the discussion

We need to be clear about the various coordinates, and about the difference between the various vector and scalar quantities. The electron has position vector $\mathbf{r}$ from the centre of mass, and the length of the vector is r. The scalar distance between the electron and nucleus A is r_A, and the scalar distance between the electron and nucleus B is r_B. I will write R_{AB} for the scalar distance between the two nuclei A and B. The position vector for nucleus A is $\mathbf{R}_A$ and the position vector for nucleus B is $\mathbf{R}_B$. The wavefunction for the molecule as a whole will therefore depend on the vector quantities $\mathbf{r}$, $\mathbf{R}_A$ and $\mathbf{R}_B$.

It is an easy step to write down the Hamiltonian operator for the problem

$$\hat{H}_{\text{tot}} = -\frac{h^2}{8\pi^2 M}\nabla_A^2 - \frac{h^2}{8\pi^2 M}\nabla_B^2 + \frac{e^2}{4\pi\epsilon_0 R_{AB}} - \frac{h^2}{8\pi^2 m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} \tag{3.1}$$

The first two terms represent the kinetic energy of the nuclei A and B (each of mass M), whilst the fourth term represents the kinetic energy of the electron (of mass m). The fifth and sixth (negative) terms give the Coulomb attraction between the nuclei and the electron. The third term is the Coulomb repulsion between the nuclei. I have used the subscript 'tot' to mean nuclei plus electron, and used a capital Ψ.

As is often the case in quantum chemistry, we are interested in solutions of the time-independent Schrödinger equation

$$\hat{H}_{\text{tot}}\Psi_{\text{tot}}(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}) = \varepsilon_{\text{tot}}\Psi_{\text{tot}}(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}) \tag{3.2}$$

and I have written explicitly the dependence of the wavefunction on the position vectors of both the nuclei and the electron.

3.1 THE BORN-OPPENHEIMER APPROXIMATION

The first thing to note is that the nuclei are very much more massive than the electron (by a factor of 1836). If they were classical particles, we might argue that their velocities would be very much less than the velocity of the electron, and so to a first approximation the motion of the electron should be the same as if the nuclei were fixed in space.

If the motions of the electron and of the two nuclei are indeed independent of one another, the total wavefunction should be a product of an electronic one and a nuclear one,

$$\Psi_{\text{tot}} = \psi_n(\mathbf{R}_A, \mathbf{R}_B)\psi_e(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}) \tag{3.3}$$

We might reasonably expect that the electronic wavefunction would depend on the particular values of R_A and R_B at which the nuclei were fixed, and I have indicated this in the expression above.

Born and Oppenheimer tackled the problem quantum-mechanically in 1927; their treatment is pretty involved, but the basic physical idea is as outlined above. To simplify the notation, I will write the total Hamiltonian as follows:

$$\begin{aligned}\hat{H}_{\mathrm{tot}} &= \left[-\frac{h^2}{8\pi^2 M}\nabla_{\mathrm{A}}^2 - \frac{h^2}{8\pi^2 M}\nabla_{\mathrm{B}}^2 + \frac{e^2}{4\pi\epsilon_0 R_{\mathrm{AB}}}\right] \\ &+ \left[-\frac{h^2}{8\pi^2 m_{\mathrm{e}}}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_{\mathrm{A}}} - \frac{e^2}{4\pi\epsilon_0 r_{\mathrm{B}}}\right] \\ &= \hat{H}_{\mathrm{n}} + \hat{H}_{\mathrm{e}}\end{aligned} \tag{3.4}$$

where I have collected the pure nuclear terms symbolized as $\hat{H}_{\mathrm{n}}$ into the first bracket [...] and the remaining terms symbolized $\hat{H}_{\mathrm{e}}$ into the second square bracket. The latter operator depends on the coordinates of the electron and on the nuclei (through the r_{A} and r_{B} terms).

Had we been dealing with a polyelectron system, there would have been extra terms in the total Hamiltonian to take account of the electron–electron repulsion. These would have also been collected into $\hat{H}_{\mathrm{e}}$.

Thus we wish to solve the time-independent Schrödinger equation

$$\hat{H}_{\mathrm{tot}}\Psi_{\mathrm{tot}}(\mathbf{R}_{\mathrm{A}}, \mathbf{R}_{\mathrm{B}}, \mathbf{r}) = \varepsilon_{\mathrm{tot}}\Psi_{\mathrm{tot}}(\mathbf{R}_{\mathrm{A}}, \mathbf{R}_{\mathrm{B}}, \mathbf{r})$$

or

$$(\hat{H}_{\mathrm{n}} + \hat{H}_{\mathrm{e}})\Psi_{\mathrm{tot}}(\mathbf{R}_{\mathrm{A}}, \mathbf{R}_{\mathrm{B}}, \mathbf{r}) = \varepsilon_{\mathrm{tot}}\Psi_{\mathrm{tot}}(\mathbf{R}_{\mathrm{A}}, \mathbf{R}_{\mathrm{B}}, \mathbf{r})$$

If we can indeed write the total wavefunction as the product of an electronic and a nuclear one

$$\Psi_{\mathrm{tot}} = \psi_{\mathrm{n}}(\mathbf{R}_{\mathrm{A}}, \mathbf{R}_{\mathrm{B}})\psi_{\mathrm{e}}(\mathbf{R}_{\mathrm{A}}, \mathbf{R}_{\mathrm{B}}, \mathbf{r})$$

then these two wavefunctions would be separately solutions of the 'nuclear' and 'electronic' time-independent Schrödinger equations

$$\begin{aligned}\hat{H}_{\mathrm{n}}\psi_{\mathrm{n}} &= \varepsilon_{\mathrm{n}}\psi_{\mathrm{n}} \\ \hat{H}_{\mathrm{e}}\psi_{\mathrm{e}} &= \varepsilon_{\mathrm{e}}\psi_{\mathrm{e}}\end{aligned} \tag{3.5}$$

We need to investigate the conditions under which this is true, and to do this we make use of a technique called 'separation of variables'. We substitute the product wavefunction (3.3) into (3.2) to give

$$(\hat{H}_{\mathrm{n}} + \hat{H}_{\mathrm{e}})\psi_{\mathrm{e}}\psi_{\mathrm{n}} = \varepsilon_{\mathrm{tot}}\psi_{\mathrm{e}}\psi_{\mathrm{n}}$$

Dividing left- and right-hand sides by the product wavefunction gives

$$\frac{1}{\psi_{\mathrm{e}}\psi_{\mathrm{n}}}(\hat{H}_{\mathrm{n}} + \hat{H}_{\mathrm{e}})\psi_{\mathrm{e}}\psi_{\mathrm{n}} = \varepsilon_{\mathrm{tot}}$$

and we must now investigate the conditions under which the two terms on the left-hand side are constant.

The nuclear operator $\hat{H}_{\mathrm{n}}$ contains differentials with respect to the nuclear coordinates; the electronic operator $\hat{H}_{\mathrm{e}}$ contains differentials with respect to the electron. The nuclear wavefunction does not involve the coordinates of the electron, but the electronic wavefunction does involve the coordinates of the nuclei. This means that

$$\nabla^2 \psi_e \psi_n = \psi_n \nabla^2 \psi_e$$
$$\nabla_A^2 \psi_e \psi_n = \psi_e \nabla_A^2 + \text{extra terms}$$

Born and Oppenheimer showed that, to a very good approximation, these extra terms were of the order of m_e/M and so the motions of the electron and the nuclei could indeed be considered separately for many purposes.

There *are* phenomena such as the Renner and the Jahn–Teller effects where the Born–Oppenheimer approximation breaks down, but for the vast majority of chemical applications the Born–Oppenheimer approximation is a vital one. It has a great conceptual importance in chemistry; without it we could not speak of a molecular geometry.

The electronic wavefunction is thus given as solution of $\hat{H}_e \psi_e = \varepsilon_e \psi_e$ and the total energy is given by

$$\varepsilon_{\text{tot}} = \varepsilon_e + \frac{e^2}{4\pi\epsilon_0 R_{AB}} \tag{3.6}$$

The final term on the right-hand side is just the Coulomb repulsion between the stationary nuclei. We think of the nuclei as being clamped in position for the purpose of calculating the electronic energy and the electronic wavefunction. We then change the nuclear positions and recalculate the energies and the electronic wavefunction. Should we be interested in the nuclear motions (vibrational and rotational), we have to solve the relevant nuclear Schrödinger equation. Don't get this confused with MM calculations; the nuclear Schrödinger equation is a full quantum-mechanical equation, which has to be solved by standard techniques. You might like to read Eyring, Walter and Kimball (EWK)'s classic text *Quantum Chemistry* (1944) to see how it is done.

The nuclei move under the influence of a potential that is generated by the electrons, so once again we meet the concept of a potential energy curve (or surface, for more complicated systems).

The Born–Oppenheimer approximation shows us the way ahead for a polyelectronic molecule comprising n electrons and N nuclei; for most chemical applications we want to solve the electronic time-independent Schrödinger equation

$$\hat{H}_e \Psi_e(r_1, r_2, \ldots, r_n) = \varepsilon_e \Psi_e(r_1, r_2, \ldots, r_n)$$

at some fixed nuclear geometry, with the N nuclei clamped at points in space. If we repeat the calculation for a range of nuclear geometries, we get the potential energy surface.

I am going to generally write wavefunctions that depend on the coordinates of many particles as capitals from now on, and wavefunctions that depend on the coordinates of a single particle in lower-case.

You will find the detailed solution of the electronic Schrödinger equation for $H_2{}^+$ in any rigorous and old-fashioned quantum mechanics text (such as EWK), together with the potential energy curve. If you are particularly interested in the method of solution, the key reference is Bates, Lodsham and Stewart (1953). Even for such a simple molecule, solution of the electronic Schrödinger equation is far from easy and the problem has to be solved numerically. Burrau (1927) introduced the so-called elliptic coordinates

$$\begin{aligned} \mu &= \frac{r_A + r_B}{R_{AB}} \\ \nu &= \frac{r_A - r_B}{R_{AB}} \end{aligned} \tag{3.7}$$

and the angle ϕ which measures rotation about the internuclear axis. He was then able to separate into three equations. The ϕ equation is algebraically soluble but the remaining two need numerical solution.

The best solution to date for the electronic ground state is that of Wind (1965) who found an electronic energy (relative to infinitely separated nuclei and electrons) of $-0.602\,634\,2\ E_h$, which corresponds to a dissociation energy of $0.102\,634\,2\ E_h$.

There is very little experimental data available for $H_2{}^+$, apart from the dissociation energy and equilibrium bond distance.

3.2 THE LCAO MODEL

The *exact* solution of the electronic Schrödinger equation is no mean feat, even for such a simple molecule as $H_2{}^+$. The electronic Schrödinger equation is

$$\left(-\frac{h^2}{8\pi^2 m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}\right)\psi_e = \varepsilon_e \psi_e$$

Let's examine the limiting behaviour when the electron is in the vicinity of nucleus A but far away from nucleus B. In this case the electronic Schrödinger equation is

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A}\right)\psi_e = \varepsilon_e \psi_e$$

which is just a hydrogen atom problem. This sort of conclusion holds when the electron is in the vicinity of nucleus B. So, near each nucleus, the molecular hydrogen molecule-ion electronic wavefunction must resemble an atomic orbital centred on that particular nucleus. This suggests that it might be profitable to investigate the approximate wavefunction

$$\psi_{LCAO} = c_A 1s_A + c_B 1s_B$$

where I have written $1s_A$ to represent a hydrogen atom 1s orbital centred on nucleus A, and $1s_B$ to represent a 1s orbital centred on nucleus B. These atomic orbitals have the algebraic form exemplified by

$$1s_A = \sqrt{\frac{\zeta^3}{\pi a_0^3}} \exp\left(-\zeta \frac{r_A}{a_0}\right) \tag{3.8}$$

where ζ is called the *orbital exponent.* In the case of a hydrogen atom, $\zeta = 1$. We refer to this treatment as the *linear combination of atomic orbitals* (LCAO) model.

From simple symmetry arguments concerning the electron density, we can deduce that $c_A = \pm c_B$ and we label the two molecular orbitals by symmetry; $1\sigma_g = 1s_A + 1s_B$ and $1\sigma_u = 1s_A - 1s_B$. Neither is a solution of the electronic Schrödinger equation, but each has the correct boundary conditions and so they are possible approximate solutions.

In order to test the accuracy of the LCAO approximations, we use the variation principle; if ψ_{LCAO} is an approximate solution then the variational integral

$$\varepsilon_{LCAO} = \frac{\int \psi_{LCAO} \hat{H}_e \psi_{LCAO} \, d\tau}{\int \psi_{LCAO}^2 \, d\tau} \tag{3.9}$$

gives an upper bound to the true ground-state energy. In this particular case, evaluation of the variational integral is straightforward, and after a little algebraic manipulation you will find

$$\varepsilon_{LCAO} = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} \tag{3.10}$$

where the + sign goes with the $1s_A + 1s_B$ combination, the − sign with the $1s_A - 1s_B$ combination. The integrals are

$$\begin{aligned} H_{AA} &= \int 1s_A \hat{H}_e 1s_A \, d\tau \\ H_{AB} &= \int 1s_A \hat{H}_e 1s_B \, d\tau \\ S_{AB} &= \int 1s_A 1s_B \, d\tau \end{aligned} \tag{3.11}$$

3.3 INTEGRAL EVALUATION

One of the biggest headaches in computational quantum chemistry is the problem of integral evaluation, so let's spend a few minutes with this very simple problem.

The physical quantities h, e and m_e all tend to get in the way, so the first task is to write the Hamiltonian in dimensionless form (each variable is now the true variable divided by the appropriate atomic unit). I showed you how to do this in Chapter 0. The electronic Hamiltonian

$$\hat{H}_e = -\frac{h^2}{8\pi^2 m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}$$

becomes, in reduced form

$$\hat{H}_e = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B}$$

The variational energy expression for the $1s_A + 1s_B$ combination is

$$\begin{aligned}(1 + S_{AB})\varepsilon_{LCAO} = &\int 1s_A\left(-\frac{1}{2}\nabla^2\right)1s_A\,d\tau \\ &+ \int 1s_A\left(-\frac{1}{2}\nabla^2\right)1s_B\,d\tau + \int 1s_A\left(-\frac{1}{r_A}\right)1s_A\,d\tau \\ &+ \int 1s_A\left(-\frac{1}{r_B}\right)1s_A\,d\tau + 2\int 1s_A\left(-\frac{1}{r_A}\right)1s_B\,d\tau\end{aligned}$$

which I am going to write as

$$\varepsilon_{LCAO} = \frac{1}{1 + S_{AB}}(T_{AA} + T_{AB} - V_{AARA} - V_{AARB} - 2V_{ABRA}) \qquad (3.12)$$

In deriving the expression, I have made use of the symmetry of the problem and the equality of certain integrals, for example

$$\int 1s_A\left(-\frac{1}{2}\nabla^2\right)1s_A\,d\tau = \int 1s_B\left(-\frac{1}{2}\nabla^2\right)1s_B\,d\tau$$

Let's look at the overlap integral in detail.

$$S_{AB} = \int 1s_A(\mathbf{r})1s_B(\mathbf{r})\,d\tau \qquad (3.13)$$

where the integration has to be done over the coordinates of the electron whose vector position is **r**. For the sake of generality, I will take the atomic orbitals to have exponent ζ so that their normalizing factors are $(\zeta^3/\pi)^{1/2}$. The first step in integral evaluation is to choose an appropriate coordinate system. In this instance, it is the so-called elliptic system mentioned above. The ranges for integration are $[1, \infty]$, $[-1, +1]$ and $[0, 2\pi]$. The volume element

$$d\tau = \frac{R_{AB}^3}{8}(\mu^2 - \nu^2)\,d\mu\,d\nu\,d\phi \qquad (3.14)$$

Thus

$$S_{AB} = \frac{\zeta^3}{\pi}\frac{R_{AB}^3}{8}\int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi}(\mu^2 - \nu^2)\exp(-\zeta\mu R_{AB})\,d\mu\,d\nu\,d\phi$$

and we find

$$S_{AB} = \exp(-\zeta R_{AB})\left(1 + \zeta R_{AB} + \frac{\zeta^3 R_{AB}^3}{3}\right) \tag{3.15}$$

It is conventional to write $p = \zeta R_{AB}$.

For the sake of completeness, I have summarized all the $H_2{}^+$ integrals in Table 3.1.

Figure 3.2 shows the potential energy curve.

Table 3.1 Energy integrals for the hydrogen molecule-ion LCAO problem. Reduced units are used throughout. ζ is the orbital exponent, and R_{AB} the internuclear separation. $p = \zeta R_{AB}$

S_{AA}	1
S_{AB}	$\exp(-p)(1 + p + p^2/3)$
T_{AA}	$1/2\zeta^2$
T_{AB}	$\zeta^2\exp(-p)(1/2 + p/2 - (1/6)p^2)$
V_{AARA}	ζ
V_{ABRA}	$\zeta\exp(-p)(1 + p)$
V_{AARB}	$(1/R_{AB})[1 - \exp(-2p)(1 + p)]$

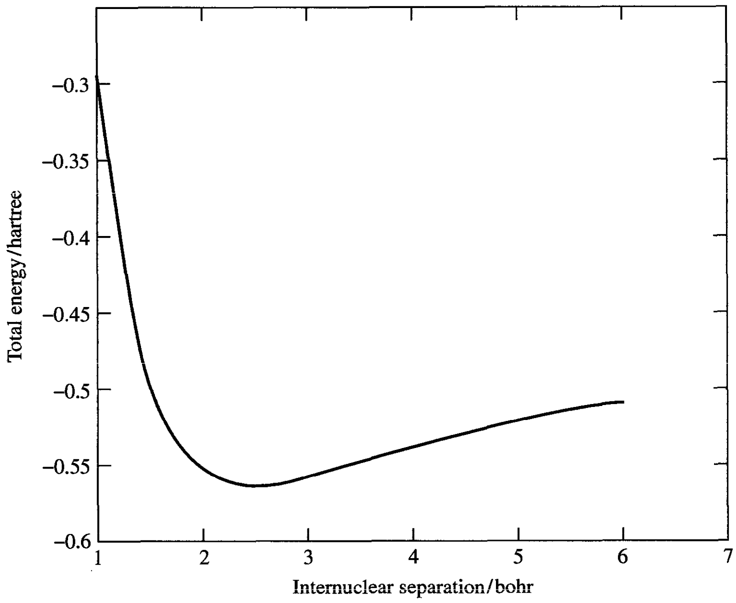


Figure 3.2 Potential energy curve for hydrogen molecule-ion

At large internuclear separation, the $1s_A + 1s_B$ combination gives a good description of the dissociation of H_2^+ into $H + H^+$ (which together have energy $-\frac{1}{2}E_h$). Electronic band spectra of the electronic ground state indicate a dissociation energy of $D_e = 2.791\,\text{eV}$ ($0.010\,26\ E_h$) and equilibrium bond length $R_e = 106\,\text{pm}$ ($2.003\ a_0$). Our simple LCAO model predicts $0.006\,47\ E_h$ and $2.495\ a_0$ in qualitative agreement with experiment. A more detailed comparison with the 'true' potential energy curve shows that the $1s_A + 1s_B$ LCAO combination gives a poor representation for small internuclear separations. One reason is that, at small R_{AB}, the limiting model should really be a helium cation He^+ for which the 1s atomic orbital has an exponent of 2 rather than 1.

3.4 IMPROVING THE ATOMIC ORBITAL

With the above in mind, it is sensible to modify the atomic orbital by treating the orbital exponent ζ as a variational parameter. What we could do is vary ζ for each value of the internuclear separation R_{AB}, and for each value of R_{AB} calculate the energy with that particular orbital exponent. Just for illustration, I have calculated the energies for a range of orbital exponent and internuclear distance pairs, and my results are shown as energy contours in Figure 3.3.

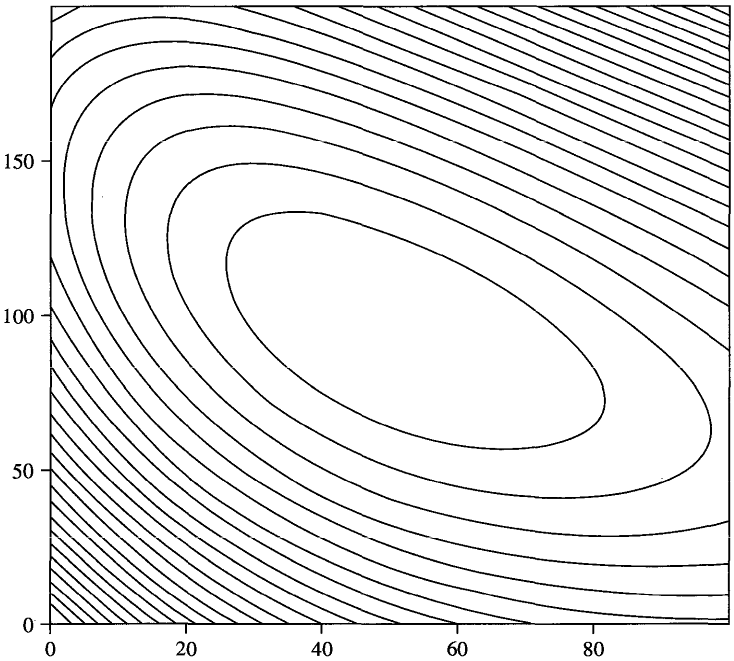


Figure 3.3 Energy vs internuclear distance and orbital exponent

The horizontal axis corresponds to an internuclear separation running from 1.5 to 2.5 a_0 and the vertical axis corresponds to an orbital exponent running from 1.0 to 1.4. The potential energy minimum corresponds to an exponent of 1.238, and we note the contraction of the atomic 1s orbital on molecule formation.

Table 3.2 records historically significant calculations for the electronic ground state of $H_2{}^+$.

3.5 MORE ADVANCED CALCULATIONS

Why stop with a single hydrogenic 1s orbital on either centre? A little thought shows that the 2s and 2pσ orbitals might also make a contribution to the bonding, and so we could write

$$\psi_{\mathrm{LCAO}} = c_{\mathrm{A}}1\mathrm{s}_{\mathrm{A}} + c_{\mathrm{B}}1\mathrm{s}_{\mathrm{B}} + d_{\mathrm{A}}2\mathrm{s}_{\mathrm{A}} + d_{\mathrm{B}}2\mathrm{s}_{\mathrm{B}} + e_{\mathrm{A}}2\mathrm{p}\sigma_{\mathrm{A}} + e_{\mathrm{B}}2\mathrm{p}\sigma_{\mathrm{B}} \qquad (3.16)$$

It is obvious by symmetry that the coefficients are related: $c_{\mathrm{A}} = \pm c_{\mathrm{B}}$, $d_{\mathrm{A}} = \pm d_{\mathrm{B}}$ and $e_{\mathrm{A}} = \pm e_{\mathrm{B}}$, but what about the ratios of c_{A} to d_{A} to e_{A}? I'll just mention for now that there is a systematic procedure called the *Hartree–Fock self consistent field method* for solving this problem. In the special case of the hydrogen molecular ion, which only has a single electron, we can calculate the variational integral and find the LCAO expansion coefficients by requiring that the variational integral is a minimum. Dickinson (1933) first did this calculation using 1s and 2pσ orbitals. He found the best orbital exponents to be $\zeta_{1\mathrm{s}} = 1.246$ and $\zeta_{2\mathrm{p}\sigma} = 2.965$ (See Table 3.2.)

The best orbitals for this simple system are those which exploit its symmetry. James and Coolidge (1935) found that a good approximation to the $1\sigma_{\mathrm{g}}$ orbital was

$$\psi = \exp(-\delta\mu)(1 + c\nu^2) \qquad (3.17)$$

where δ and c are parameters that have to be determined by the variation principle. The big advantage of James's approach is that the integrals are straightforward,

Table 3.2 Historically significant calculations for the electronic ground state of the hydrogen molecular ion

Description	Reference	D_e/eV	R_e/pm
Experiment		2.791	106.0
Numerical	Wind (1965)	2.792	105.8
LCAO with exponent of 1.0		1.763	132.3
LCAO with best exponent of 1.238	Finkelstein and Horowitz (1928)	2.354	106.8
LCAO with optimized exponents, 1s and 2pσ	Dickinson (1933)	2.716	106.1

since the wavefunction exploits the natural coordinate system. For the observed internuclear separation, the dissociation energy comes out as 2.772 eV, in good agreement with experiment.

3.6 VISUALIZATION

These days, we place a deal of emphasis on the visualization of quantum chemical calculations. I have already emphasized the importance of a graphical user interface in earlier chapters. There are several ways of representing molecular orbitals graphically. Figures 3.4 through 3.6 all refer to the simple LCAO treatment of the ground-state hydrogen molecule-ion, which has algebraic form

$$\psi_{\mathrm{LCAO}} = \frac{1}{\sqrt{2(1+S_{\mathrm{AB}})}}(1\mathrm{s}_{\mathrm{A}} + 1\mathrm{s}_{\mathrm{B}})$$

The orbital is correctly normalized. I have taken a bond length of 106 pm, and fixed the orbital exponent at 1.

First of all, it is traditional to plot values of the wavefunction along the internuclear axis, and this is shown in Figure 3.4.

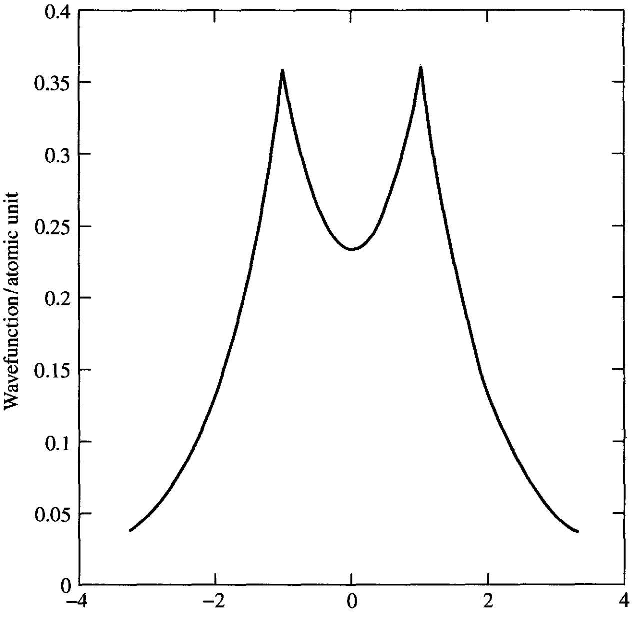


Figure 3.4 LCAO wavefunction along internuclear axis

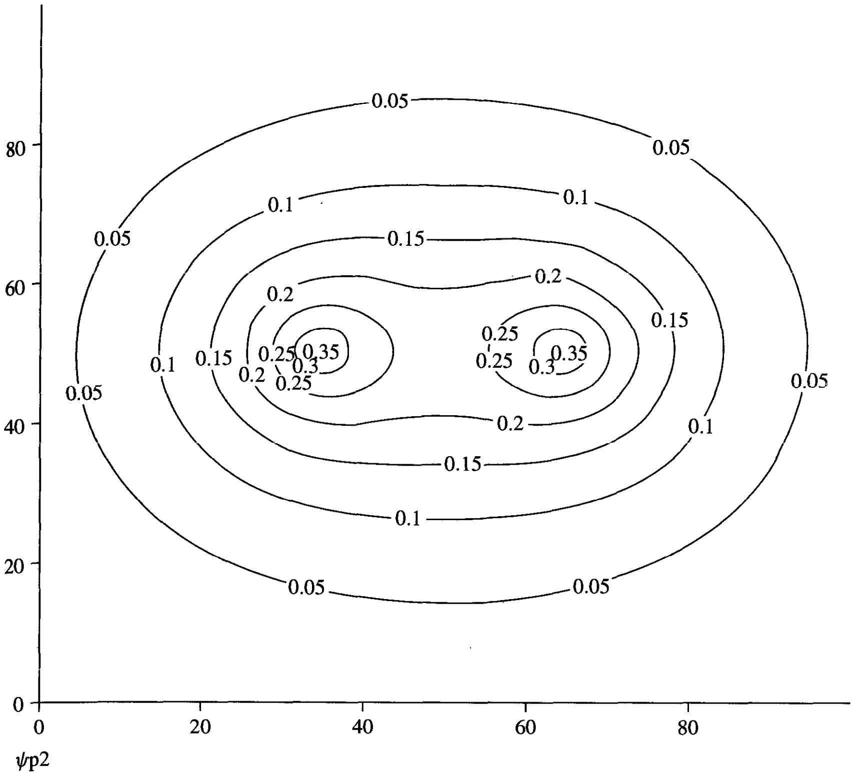


Figure 3.5 LCAO wavefunction, contour plot

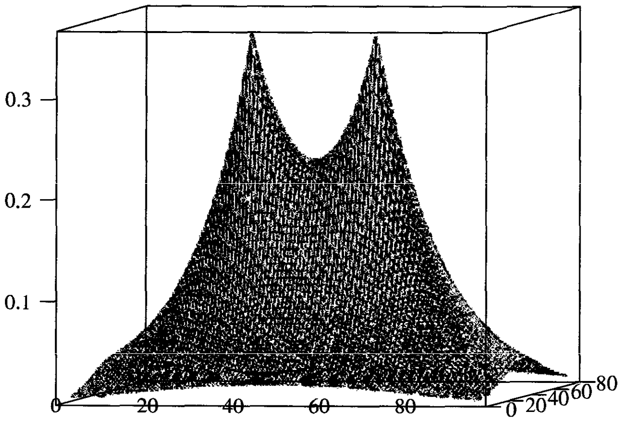


Figure 3.6 LCAO wavefunction, surface plot

As an alternative, we might want to plot the square of the wavefunction rather than the wavefunction itself, on the physical grounds that such quantities have a direct interpretation. The form of the graph is very similar to Figure 3.4, and I haven't shown it.

Many graphics packages allow for contour diagrams and surface plots. These are given above for the square of the LCAO plus combination, for any plane containing the internuclear axis.

4 THE HYDROGEN MOLECULE

I dealt with the simplest possible molecule, the hydrogen molecule ion H_2^+, in Chapter 3. The hydrogen molecule is also one of great historical interest, and it is shown schematically in Figure 4.1. The naming convention for particles and distances should be self-evident, despite the fact that I have not indicated all possible distances in the diagram. Once again, I intend to ignore the overall translational motion of the molecule. The coordinate origin is taken to be the centre of mass.

To solve the time-independent Schrödinger equation for the nuclei plus electrons, we need an expression for the Hamiltonian operator. It is

$$\begin{aligned}\hat{H}_{\text{tot}} = &\left[-\frac{h^2}{8\pi^2 M}\nabla_A^2 - \frac{h^2}{8\pi^2 M}\nabla_B^2 + \frac{e^2}{4\pi\epsilon_0 R_{AB}}\right] \\ &- \frac{h^2}{8\pi^2 m_e}\nabla_1^2 - \frac{h^2}{8\pi^2 m_e}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} \\ &- \frac{e^2}{4\pi\epsilon_0 r_{B1}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\end{aligned} \tag{4.1}$$

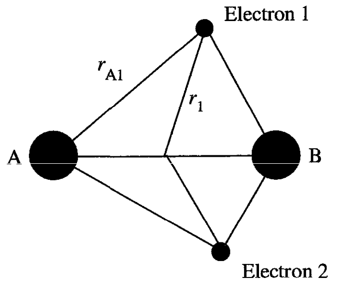


Figure 4.1 Hydrogen molecule

The terms in square brackets are to do with the nuclear motion; the first two of these represent the kinetic energy of the nuclei labelled A and B (each of mass M), and the third term in the square brackets is the Coulomb repulsion between the two nuclei. The fourth and fifth terms give the kinetic energy of the two electrons. The next four negative terms give the mutual Coulomb attraction between the two nuclei A, B and the two electrons labelled 1, 2. The final term is the Coulomb repulsion between electrons 1 and 2, with r_{12} the distance between them. As in Chapter 3, I have used the subscript 'tot' to mean nuclear plus electron.

The first step is to make use of the Born–Oppenheimer approximation, so I separate the nuclear and the electronic terms:

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{n}} + \hat{H}_{\text{e}}$$

where $\hat{H}_{\text{n}}$ is the term in square brackets. Note that the 'electronic' contribution $\hat{H}_{\text{e}}$ contains terms that refer to electron 1, electron 2 and a cross-term involving r_{12}.

For large molecules, very many terms contribute to the electronic Hamiltonian. To simplify the notation, I am going to collect together all those terms that depend explicitly on the coordinates of a single electron and write them as

$$\hat{h}(\mathbf{r}_i) = -\frac{h^2}{8\pi^2 m_{\text{e}}}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0 r_{\text{A}i}} - \frac{e^2}{4\pi\epsilon_0 r_{\text{B}i}} \tag{4.2}$$

Such operators which collect together all the variable terms involving a particular electron are called *one-electron operators*. The $1/r_{12}$ term is a typical *two-electron operator*, which we often write

$$\hat{g}(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{4.3}$$

It represents the Coulomb repulsion between a pair of electrons.

You have probably come across the idea of electron spin, know that it can be represented by a single variable s, and are probably wondering where spin is going to appear in the discussion. Bear with me for a little while yet.

Using the notation given above for the one- and two-electron operators, the electronic Hamiltonian is

$$\hat{H}_{\text{e}} = \hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2) + \hat{g}(\mathbf{r}_1, \mathbf{r}_2) \tag{4.4}$$

The total wavefunction will depend on the spatial coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ of the two electrons 1 and 2, and also the spatial coordinates $\mathbf{R}_{\text{A}}$ and $\mathbf{R}_{\text{B}}$ of the two nuclei A and B. I will therefore write the total wavefunction as $\Psi_{\text{tot}}(\mathbf{R}_{\text{A}}, \mathbf{R}_{\text{B}}, \mathbf{r}_1, \mathbf{r}_2)$. The time-independent Schrödinger equation is

$$\hat{H}_{\text{tot}}\Psi_{\text{tot}}(\mathbf{R}_{\text{A}}, \mathbf{R}_{\text{B}}, \mathbf{r}_1, \mathbf{r}_2) = \varepsilon_{\text{tot}}\Psi_{\text{tot}}(\mathbf{R}_{\text{A}}, \mathbf{R}_{\text{B}}, \mathbf{r}_1, \mathbf{r}_2) \tag{4.5}$$

But we can carry forward the knowledge of the Born–Oppenheimer approximation gained from Chapter 2 and focus attention on the *electronic* problem. Thus we want to solve

$$\hat{H}_\mathrm{e}\Psi_\mathrm{e}(\mathbf{R}_\mathrm{A}, \mathbf{R}_\mathrm{B}, \mathbf{r}_1\mathbf{r}_2) = \varepsilon_\mathrm{e}\Psi_\mathrm{e}(\mathbf{R}_\mathrm{A}, \mathbf{R}_\mathrm{B}, \mathbf{r}_1, \mathbf{r}_2)$$

or, in our new notation,

$$[\hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2) + \hat{g}(\mathbf{r}_1, \mathbf{r}_2)]\Psi_\mathrm{e}(\mathbf{R}_\mathrm{A}, \mathbf{R}_\mathrm{B}, \mathbf{r}_1, \mathbf{r}_2) = \varepsilon_\mathrm{e}\Psi_\mathrm{e}(\mathbf{R}_\mathrm{A}, \mathbf{R}_\mathrm{B}, \mathbf{r}_1, \mathbf{r}_2) \quad (4.6)$$

As before, the nuclei are to be thought of as being clamped in position for the purpose of evaluating the electronic energy and electronic wavefunction. The electronic wavefunction depends implicitly on the nuclear coordinates, which is why I have shown the functional dependence.

If we want to calculate the potential energy curve, then we have to change the internuclear separation and rework the electronic problem at the new A–B distance, as in the H_2^+ calculation. Once again, should we be so interested, the nuclear problem can be studied by solving the appropriate nuclear Schrödinger equation. This is a full quantum-mechanical equation, not to be confused with the MM treatment.

You will see shortly that an exact solution of the electronic Schrödinger equation is impossible, because of the electron–electron repulsion term $g(\mathbf{r}_1, \mathbf{r}_2)$. What we have to do is investigate approximate solutions based on chemical intuition, and then refine these models, typically using the variation principle, until we attain the required accuracy. This means in particular that any approximate solution will not satisfy the electronic Schrödinger equation, and we will not be able to calculate the energy from an eigenvalue equation. First of all, let's see why the problem is so difficult.

4.1 THE NON-INTERACTING ELECTRON MODEL

Imagine a model hydrogen molecule with non-interacting electrons, such that their Coulomb repulsion is zero. Each electron in our model still has kinetic energy and is still attracted to both nuclei, but the electron motions are completely independent of each other because the electron–electron interaction term is zero. We would, therefore, expect that the electronic wavefunction for the pair of electrons would be a product of the wavefunctions for two independent electrons in H_2^+ (Figure 4.1), which I will write $X(\mathbf{r}_1)$ and $Y(\mathbf{r}_2)$. Thus $X(\mathbf{r}_1)$ and $Y(\mathbf{r}_2)$ are molecular orbitals which describe independently the two electrons in our non-interacting electron model.

In order to investigate whether the wavefunction can indeed be written in this way, we use the 'separation of variables' technique and so write a wavefunction of the form

$$\Psi_\mathrm{e}(\mathbf{r}_1, \mathbf{r}_2) = X(\mathbf{r}_1)Y(\mathbf{r}_2)$$

We then substitute this wavefunction into the electronic Schrödinger equation, and study the consequences. Do the substitution yourself, divide either side by

$\Psi_e(\mathbf{r}_1, \mathbf{r}_2)$ and you will find

$$\frac{1}{X(\mathbf{r}_1)}\hat{h}(\mathbf{r}_1)X(\mathbf{r}_1) + \frac{1}{Y(\mathbf{r}_2)}\hat{h}(\mathbf{r}_2)Y(\mathbf{r}_2) = \varepsilon_e$$

Each term on the left-hand side separately involves the coordinates of one of the two electrons, and as the sum has to be a constant for all values of the coordinates of these two electrons, the terms must individually be constants which I can write as ε_x and ε_y so

$$\begin{aligned}\hat{h}(\mathbf{r}_1)X(\mathbf{r}_1) &= \varepsilon_x X(\mathbf{r}_1)\\ \hat{h}(\mathbf{r}_2)Y(\mathbf{r}_2) &= \varepsilon_y Y(\mathbf{r}_2)\end{aligned} \tag{4.7}$$

and in the case where the two electrons don't interact with each other we just solve the $H_2{}^+$ problem twice over (once for each electron). The solution I have given is exact, even for two atoms at a chemical bond length. If you substitute the solution into the electronic Schrödinger equation then you will find that it fits exactly, and you can calculate the energy that way if you so wish (or just add ε_x and ε_y).

You are probably used to this idea from descriptive chemistry, where we build up the configurations for many-electron atoms in terms of atomic wavefunctions, and where we would write an electronic configuration for Ne as

$$\text{Ne: } (1\text{s})^2(2\text{s})^2(2\text{p})^6$$

The orbital model would be exact were the electron repulsion terms negligible or equal to a constant. Even if they were negligible, we would have to solve an electronic Schrödinger equation appropriate to $C_{10}H_8{}^{67+}$ in order to make progress with the solution of the electronic Schrödinger equation for naphthalene. Every molecular problem would be different.

We will actually use the idea that the interaction between electrons can somehow be averaged; in a later chapter you will see how this idea forms the basis for the self-consistent field (SCF) model.

4.2 THE VALENCE BOND MODEL

So, let's get a bit more chemical and imagine the formation of an H_2 molecule from two separated hydrogen atoms, H_A and H_B, initially an infinite distance apart. Electron 1 is associated with nucleus A, electron 2 with nucleus B, and the terms in the electronic Hamiltonian R_{AB}, r_{A2} and r_{B1} are all negligible when the nuclei are at infinite separation. Thus the electronic Schrödinger equation becomes

$$\left(-\frac{h^2}{8\pi^2 m_e}\nabla_1^2 - \frac{h^2}{8\pi^2 m_e}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}}\right)\Psi_e(\mathbf{r}_1, \mathbf{r}_2) = \varepsilon_e\Psi_e(\mathbf{r}_1, \mathbf{r}_2) \tag{4.8}$$

I am going to leave you to prove for yourself that the wavefunction corresponding to this infinite-distance H_2 problem is a product of two hydrogen atom wavefunctions. Physically, you might have expected this: the two atoms are independent and so the electronic wavefunctions multiply to give the molecular electronic wavefunction.

If I write possible atomic orbitals for hydrogen atom A as χ_A and possible atomic orbitals for hydrogen atom B as χ_B, the molecular electronic wavefunction will be

$$\Psi_e(\mathbf{r}_1, \mathbf{r}_2) = \chi_A(\mathbf{r}_1)\chi_B(\mathbf{r}_2)$$

The χ's can individually be 1s, 2s, 2p, ... atomic orbitals. The lowest-energy solution will be when the χ's correspond to 1s orbitals on each of the two hydrogen atoms, the next-highest-energy solution will be when one of the χ's is a 1s, the other a 2s atomic orbital, and so on. Possible solutions of the electronic problem, with the two H atoms at infinity, are shown in Table 4.1.

In this table, ε_{1s} is the energy of a hydrogenic 1s orbital, ε_{2s} the energy of a hydrogenic 2s orbital. Before we worry about comparison with experiment, there are a couple of loose ends that have to be tidied up.

4.3 INDISTINGUISHABILITY

I live in a country park, which has a lake, ducks, geese and rabbits. One rabbit looks very much like another one, but each of them is actually different (if you happen to be a rabbit). The one I caught eating my runner beans is quite different from the others because it is now dead, but we could paint one rabbit red, one blue, one green if we wanted to distinguish between them. Despite that fact that they all look alike, they are *distinguishable*. All similar things in our macroscopic world are distinguishable.

Electrons are *indistinguishable*, they simply cannot be labelled. This means that an acceptable electronic wavefunction has to treat all electrons on an equal footing. Thus, although I have so far implied that electron 1 is to be associated with nucleus H_A, and electron 2 with nucleus H_B, I must also cater for the alternative description where electron 1 is associated with nucleus H_B and electron 2 with nucleus H_A. I therefore have to modify Table 4.1 to Table 4.2.

Table 4.1 Hydrogen molecule with infinite atomic separation; electron 1 associated with nucleus A, electron 2 associated with nucleus B

$\Psi_e(\mathbf{r}_1, \mathbf{r}_2)$	Electronic energy ε_e
$1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2)$	$2\varepsilon_{1s}$
$1s_A(\mathbf{r}_1)2s_B(\mathbf{r}_2)$	$\varepsilon_{1s} + \varepsilon_{2s}$
$2s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2)$	$\varepsilon_{1s} + \varepsilon_{2s}$
$2s_A(\mathbf{r}_1)2s_B(\mathbf{r}_2)$	$2\varepsilon_{2s}$

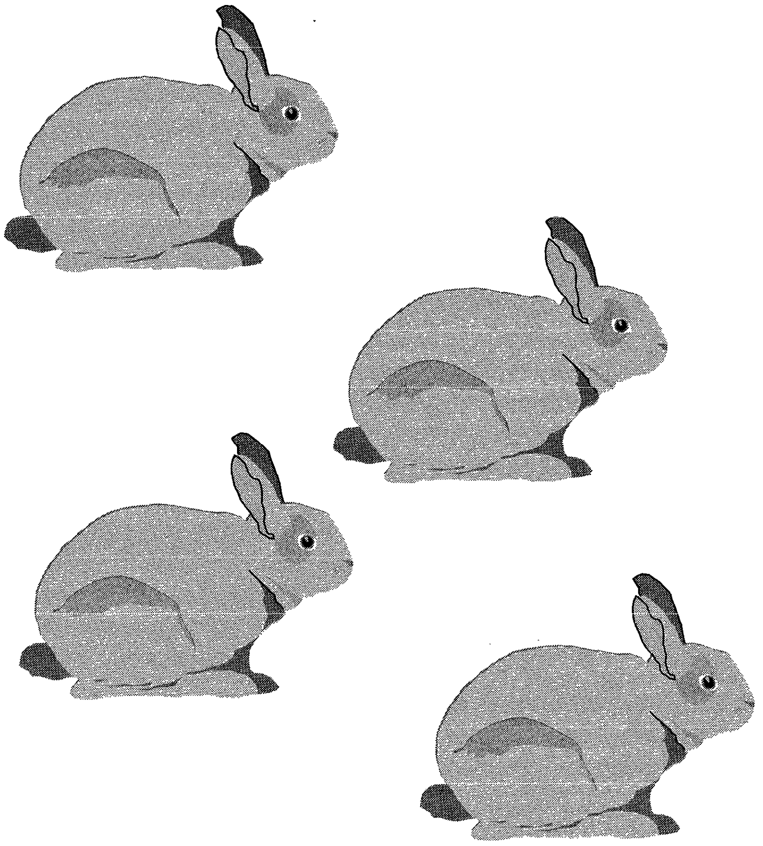


Figure 4.2 Distinguishable rabbits

Table 4.2 Hydrogen molecule with infinite atomic separation; allowance made for indistinguishability

$\Psi_e(\mathbf{r}_1, \mathbf{r}_2)$		Electronic energy ε_e
$1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2)$	$1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)$	$2\varepsilon_{1s}$
$1s_A(\mathbf{r}_1)2s_B(\mathbf{r}_2)$	$1s_A(\mathbf{r}_2)2s_B(\mathbf{r}_1)$	$\varepsilon_{1s} + \varepsilon_{2s}$
$2s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2)$	$2s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)$	$\varepsilon_{1s} + \varepsilon_{2s}$
$2s_A(\mathbf{r}_1)2s_B(\mathbf{r}_2)$	$2s_A(\mathbf{r}_2)2s_B(\mathbf{r}_1)$	$2\varepsilon_{2s}$

The extra column allows for indistinguishability. Each entry in the table is a distinct quantum state, and the ground state of the molecule is described equally by the two quantum states $1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2)$ and $1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)$, and each quantum state has the same energy. Any linear combination of these two quantum states also has the same energy, and so we ought to consider a linear combination

$$a1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) + b1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)$$

Symmetry arguments tell us that we have to take $a = \pm b$, so we write possible spatial wavefunctions as

$$1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) \pm 1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1). \tag{4.9}$$

These combinations both allow for the indistinguishability of the two electrons.

4.4 ELECTRON SPIN

So far, I have ignored the existence of spin. Spin is an internal angular momentum that some particles have and others do not. Electron spin is a two-valued quantity; we denote the spin variable for a single electron s, and the spin states are written $\alpha(s)$ and $\beta(s)$, or just α and β for short when the meaning is obvious. The notation I am going to use is that $\alpha(s_1)$ means electron 1 in spin state α. With an eye to the discussion above about indistinguishability, we consider the following four combinations of spin states for two electrons:

$$\begin{gathered}\alpha(s_1)\beta(s_2) \pm \alpha(s_2)\beta(s_1) \\ \alpha(s_1)\alpha(s_2) \\ \beta(s_1)\beta(s_2)\end{gathered} \tag{4.10}$$

All four of these combinations allow for the indistinguishability of the electrons.

4.5 THE PAULI PRINCIPLE

We can construct a total electronic wavefunction as the product of a spatial part and a spin part. For the electronic ground state of H_2 we can consider combinations of the two spatial terms

$$1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) \pm 1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)$$

with the four spin terms

$$\begin{gathered}\alpha(s_1)\beta(s_2) \pm \alpha(s_2)\beta(s_1) \\ \alpha(s_1)\alpha(s_2) \\ \beta(s_1)\beta(s_2)\end{gathered}$$

to give eight possible candidates for the total (space and spin) wavefunction. The *generalized Pauli principle* (Pauli, 1925) guides us in our choice: for electrons, the total wavefunction has to be antisymmetric to the exchange of electron names, and so only the following four combinations out of the eight are acceptable:

$$\begin{aligned}
&(1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) + 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2))(\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)) \\
&(1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) - 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2))(\alpha(s_1)\beta(s_2) + \alpha(s_2)\beta(s_1)) \\
&(1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) - 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2))\alpha(s_1)\alpha(s_2) \\
&(1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) - 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2))\beta(s_1)\beta(s_2)
\end{aligned} \qquad (4.11)$$

In the limit of infinite atom separations, or if we switch off the Coulomb repulsion between two electrons, all four wavefunctions have the same energy. But they correspond to different eigenvalues of the electron spin operator: the first combination describes the singlet electronic ground state, and the other three combinations give an approximate description of the components of the first triplet excited state.

4.6 THE DIHYDROGEN MOLECULE

For a real-life dihydrogen molecule around the equilibrium bond length, we cannot ignore the electron repulsion term $\hat{g}(\mathbf{r}_1, \mathbf{r}_2)$ in the Hamiltonian. The simple atomic orbital product wavefunctions in Table 4.2 are no longer solutions of the electronic problem. They have the right physical characteristics, and so are acceptable models. As the two H atoms approach from infinity, the energy will decrease. As the two H atoms approach, we expect that the energy will increase rapidly because as the two unscreened nuclei approach they repel strongly. Heitler and London first tried this approach in 1927. The singlet electronic ground state is written

$$\Psi_{\mathrm{HL}} = (1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) + 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2))(\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)) \qquad (4.12)$$

and the electronic energy is evaluated with the exact Hamiltonian as

$$\varepsilon_{\mathrm{HL}} = \frac{\int \Psi_{\mathrm{HL}} \hat{H}_e \Psi_{\mathrm{HL}}\, d\tau}{\int \Psi_{\mathrm{HL}}^2\, d\tau}$$

Here the integration $\int \cdots d\tau$ is over the coordinates of both electrons. Such integrals are therefore eight-dimensional (three spatial variables and one spin variable per electron). Integration over the spin variables is straightforward, but the spatial variables are far from easy; a particular source of trouble arises from the electron repulsion term.

In the case of the hydrogen molecule-ion $H_2{}^+$, we defined certain integrals S_{AA}, T_{AA}, $T_{AB}, \ldots V_{ABRA}$. The electronic part of the energy appropriate to the Heitler–London (singlet) ground-state wavefunction, after doing the integrations over the spin variables, is found to be

$$\varepsilon_{\mathrm{HL}}(\mathrm{Singlet}) = \frac{2T_{\mathrm{AA}} + 2S_{\mathrm{AB}}T_{\mathrm{AB}} - 2V_{\mathrm{AARA}} - 2V_{\mathrm{AARB}} - 4S_{\mathrm{AB}}V_{\mathrm{ABRA}} + E_{\mathrm{AABB}} + E_{\mathrm{ABAB}}}{\left(1 + S_{\mathrm{AB}}^2\right)} \tag{4.13}$$

where E_{AABB} and E_{ABAB} are additional integrals given by

$$\begin{aligned} E_{\mathrm{AABB}} &= \iint 1\mathrm{s}_{\mathrm{A}}^2(\mathbf{r}_1) g(\mathbf{r}_1, \mathbf{r}_2) 1\mathrm{s}_{\mathrm{B}}^2(\mathbf{r}_2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 \\ E_{\mathrm{ABAB}} &= \iint 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_1) 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_1) g(\mathbf{r}_1, \mathbf{r}_2) 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_2) 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 \end{aligned} \tag{4.14}$$

The integrals $\iint \cdots \mathrm{d}\tau_1\, \mathrm{d}\tau_2$ are called *two-electron integrals*, and they are hard to evaluate. Expressions for these integrals are given in (for example) Slater (1965, 1974). They are often given classical electrostatic interpretations. The first one represents the mutual potential energy of two charge clouds with densities $-e1\mathrm{s}_{\mathrm{A}}^2(\mathbf{r}_1)$ and $-e1\mathrm{s}_{\mathrm{B}}^2(\mathbf{r}_2)$. It is often called a *Coulomb integral*. The second represents the mutual potential energy of a charge distribution $-e1\mathrm{s}_{\mathrm{A}}(\mathbf{r})1\mathrm{s}_{\mathrm{B}}(\mathbf{r})$ with itself. It is often called an *exchange integral*.

Finally we have to remember to add on the nuclear repulsion and, if we repeat the calculation for a range of values of the internuclear separation, we arrive at the potential energy curves shown in Figure 4.3 for the ground-state (singlet)

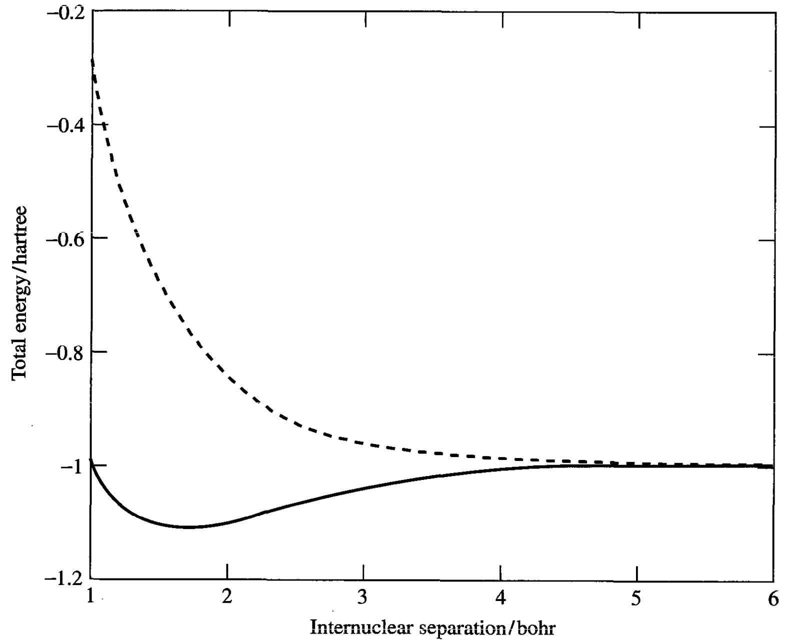


Figure 4.3 Valence bond treatment of singlet and triplet states

Table 4.3 Significant calculations on dihydrogen

Description	Reference	D_e/eV	R_e/pm
Experiment		4.72	74.1
Single hydrogenic 1s valence bond	Heitler and London $\zeta = 1$	3.156	86.8
Best exponent for above	$\zeta = 1.12$	3.592	
Single hydrogenic 1s VB-CI	$\zeta = 1$	3.238	88.4
Single hydrogenic 1s LCAO	$\zeta = 1$	2.694	84.7
Best exponent for above	$\zeta = 1.14$	3.292	
Simple LCAO including $2p_\sigma$ orbitals	Rosen (1931)	4.02	

and excited-state (triplet) wavefunctions. The triplet state is repulsive, whilst the singlet state curve shows a minimum at 88.4 pm.

We often refer to Heitler and London's method as the *valence bond* (VB) model. A comparison between the experimental and the valence bond potential energy curves shows excellent agreement at large R_{AB} but poor quantitative agreement in the valence region (Table 4.3). The cause of this lies in the method itself: the VB model starts from atomic wavefunctions and adds as a perturbation the fact that the electron clouds of the atoms are polarized when the molecule is formed.

A slight improvement in the predicted dissociation energy occurs if the 1s orbital exponent is treated as a variational parameter.

4.7 CONFIGURATION INTERACTION

The simple VB treatment of dihydrogen uses a wavefunction

$$\Psi_{HL} = (1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) + 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2))(\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1))$$

and it is usual to give a physical interpretation to each of the spatial terms. We say that $1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2)$ represents a situation where electron 1 is associated with nucleus A and electron 2 with nucleus B. The term $1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)$ represents a situation where electron 2 is associated with nucleus A and electron 2 with nucleus B. We talk about *covalent structures* and recognize that *ionic structures* such as $1s_A(\mathbf{r}_1)1s_A(\mathbf{r}_2)$ and $1s_B(\mathbf{r}_1)1s_B(\mathbf{r}_2)$ should also be considered. Here, the two electrons are both associated with nucleus A or nucleus B. So, an improved VB wavefunction would have spatial part

$$a(1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) + 1s_A(\mathbf{r}_2)1s_B(\mathbf{r}_1)) + b(1s_A(\mathbf{r}_1)1s_A(\mathbf{r}_2) + 1s_B(\mathbf{r}_1)1s_B(\mathbf{r}_2)) \tag{4.15}$$

where the parameters a and b would have to be determined by the variation principle. We would expect on physical grounds that $a > b$, that is to say the covalent terms would outweigh the ionic ones.

This is a simple example of valence bond *configuration interaction*.

4.8 THE LCAO–MOLECULAR ORBITAL MODEL

In Chapter 3, I discussed the construction of simple LCAO–MOs for the hydrogen molecule-ion, starting from 1s atomic orbitals on the hydrogen centres. Thus, we constructed LCAO–MO approximations to the two lowest energy molecular orbitals as

$$1\sigma_g = \frac{1}{\sqrt{2(1+S_{AB})}}(1s_A + 1s_B)$$

$$1\sigma_u = \frac{1}{\sqrt{2(1-S_{AB})}}(1s_A - 1s_B)$$

and we noted how to calculate energies. We now have to deal with the case of two electrons, and we must seriously consider the consequences of spin and antisymmetry. Table 4.3 summarized the possible allowed space and spin parts of the total wavefunction formed by allowing either electron to occupy the $1\sigma_g$ or the $1\sigma_u$ molecular orbital.

In Table 4.4, I have ignored overall normalization.

Calculation of the potential energy curve for the ground state gives poor agreement with experiment on three counts. The predicted equilibrium distance is poor and the dissociation energy is only about one-half of its experimental value. This is not dissimilar to the simple VB calculation. Much more serious is that the molecular orbital wavefunction shows the wrong behaviour for large R_{AB}. The asymptotic energy ought to be $-1E_h$. The simple VB calculation gets the energy of the dissociated state (relative to four separated particles) right.

A careful analysis shows that the dissociation process corresponds to

$$H_2 \rightarrow \tfrac{1}{2}(H + H + H^+ + H^-)$$

rather than the lower-energy reaction

$$H_2 \rightarrow H + H$$

This is a near-universal failure of molecular orbital calculations.

Table 4.4 Possible LCAO–MO wavefunctions for dihydrogen

Spatial function	Spin function	Electronic state	
		Symmetry	Configuration
$1\sigma_g(\mathbf{r}_1)1\sigma_g(\mathbf{r}_2)$	$\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)$	$^1\Sigma_g$	$1\sigma_g^2$
$1\sigma_g(\mathbf{r}_1)1\sigma_u(\mathbf{r}_2) - 1\sigma_g(\mathbf{r}_2)1\sigma_u(\mathbf{r}_1)$	$\alpha(s_1)\alpha(s_2)$	$^3\Sigma_u$	$1\sigma_g^1 1\sigma_u^1$
$1\sigma_g(\mathbf{r}_1)1\sigma_u(\mathbf{r}_2) - 1\sigma_g(\mathbf{r}_2)1\sigma_u(\mathbf{r}_1)$	$\alpha(s_1)\beta(s_2) + \alpha(s_2)\beta(s_1)$	$^3\Sigma_u$	$1\sigma_g^1 1\sigma_u^1$
$1\sigma_g(\mathbf{r}_1)1\sigma_u(\mathbf{r}_2) - 1\sigma_g(\mathbf{r}_2)1\sigma_u(\mathbf{r}_1)$	$\beta(s_1)\beta(s_2)$	$^3\Sigma_u$	$1\sigma_g^1 1\sigma_u^1$
$1\sigma_g(\mathbf{r}_1)1\sigma_u(\mathbf{r}_2) + 1\sigma_g(\mathbf{r}_2)1\sigma_u(\mathbf{r}_1)$	$\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)$	$^1\Sigma_u$	$1\sigma_g^1 1\sigma_u^1$
$1\sigma_u(\mathbf{r}_1)1\sigma_u(\mathbf{r}_2)$	$\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)$	$^1\Sigma_g$	$1\sigma_u^2$

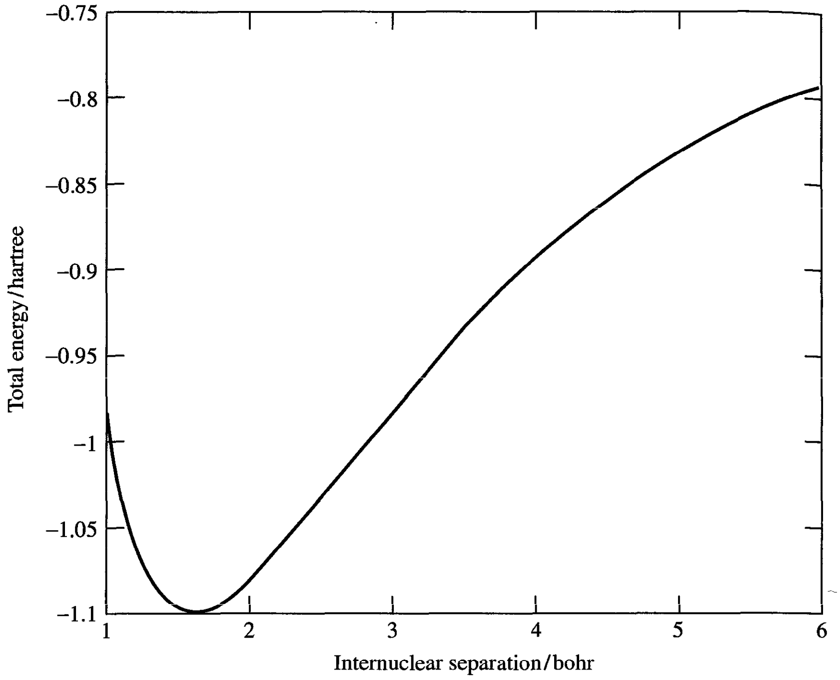


Figure 4.4 Molecular orbital treatment

4.8.1 Configuration Interaction

In molecular orbital language, we write $1\sigma_g^2$ for the ground-state electronic configuration (corresponding to a single state), $1\sigma_g^1\sigma_u^1$ for a singly excited configuration (corresponding to both a triplet and a singlet state) and $1\sigma_u^2$ for the first available doubly excited configuration (again corresponding to a single state). In the spirit of the variation technique, we would seek to improve our description of the electronic ground state by writing a 'better' wavefunction as a linear combination of all three singlet-spin states:

$$\Psi_{\mathrm{CI}} = a\Psi(1\sigma_g^2) + b\Psi(1\sigma_g^1 1\sigma_u^1) + c\Psi(1\sigma_u^2) \qquad (4.16)$$

where a, b and c can be determined using the variation principle. Table 4.4 shows that the ground state and the doubly excited state have the same symmetry, different from that of the first excited singlet state. This shows immediately that $b = 0$, since only states of the same symmetry can mix.

Once the calculation is done, we get a better prediction of the equilibrium bond length and dissociation energy, but most important of all we recover the correct behaviour for large R_{AB}.

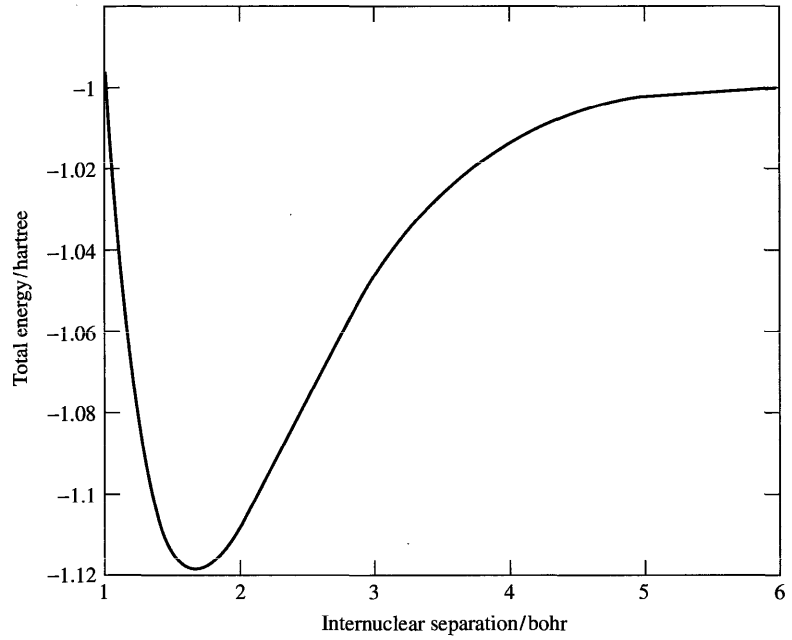


Figure 4.5 Simple CI treatment

4.9 COMPARISON OF SIMPLE VB AND LCAO TREATMENTS

It is instructive to compare the simple LCAO and VB (valence bond) treatments, and especially to enquire why the LCAO treatment fails so disastrously at large R.

It is easily shown that the LCAO wavefunction can be written

$$\Psi_{\mathrm{MO}} = \Psi_{\mathrm{HL}} + \Psi_{\mathrm{ionic}}$$

and so it gives equal weights to the 'covalent' and 'ionic' valence bond structures. The simple VB treatment gives zero weighting to the ionic structures. In their simplest forms, the LCAO and VB models give very different descriptions of the dihydrogen covalent bond. Once configuration interaction is taken into account, they give exactly the same answers.

4.10 SLATER DETERMINANTS

The simplest possible LCAO building block for the ground state of dihydrogen is

$$1\sigma_g(\mathbf{r}_1)1\sigma_g(\mathbf{r}_2)(\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1))$$

This simple wavefunction is antisymmetric to the exchange of electron names, and treats both space and spin.

By inspection, it can be written as a determinant

$$\begin{vmatrix} 1\sigma_g(\mathbf{r}_1)\alpha(s_1) & 1\sigma_g(\mathbf{r}_2)\alpha(s_2) \\ 1\sigma_g(\mathbf{r}_1)\beta(s_1) & 1\sigma_g(\mathbf{r}_2)\beta(s_2) \end{vmatrix} \tag{4.17}$$

Determinants have the useful property that they change sign when we interchange two columns, and this is equivalent to interchanging the names of the two electrons:

$$\begin{vmatrix} 1\sigma_g(\mathbf{r}_1)\alpha(s_1) & 1\sigma_g(\mathbf{r}_2)\alpha(s_2) \\ 1\sigma_g(\mathbf{r}_1)\beta(s_1) & 1\sigma_g(\mathbf{r}_2)\beta(s_2) \end{vmatrix} = - \begin{vmatrix} 1\sigma_g(\mathbf{r}_2)\alpha(s_2) & 1\sigma_g(\mathbf{r}_1)\alpha(s_1) \\ 1\sigma_g(\mathbf{r}_2)\beta(s_2) & 1\sigma_g(\mathbf{r}_{12})\beta(s_1) \end{vmatrix}$$

Such a determinantal wavefunction is called a *Slater determinant*, after Slater (1929), and you should appreciate that a

Slater determinant = smallest logical building block for electronic wavefunctions

I don't mean that such a wavefunction is necessarily very accurate; you saw a minute ago that the LCAO treatment of dihydrogen is rather poor. I mean that, in principle, a Slater determinant has the correct spatial and spin symmetry to represent an electronic state. It very often happens that we have to take combinations of Slater determinants in order to make progress; for example, the first excited states of dihydrogen cannot be represented adequately by a single Slater determinant such as

$$\begin{vmatrix} 1\sigma_g(\mathbf{r}_1)\alpha(s_1) & 1\sigma_g(\mathbf{r}_2)\alpha(s_2) \\ 1\sigma_u(\mathbf{r}_1)\beta(s_1) & 1\sigma_u(\mathbf{r}_2)\beta(s_2) \end{vmatrix}$$

we have to take combinations of determinants such as

$$\begin{vmatrix} 1\sigma_g(\mathbf{r}_1)\alpha(s_1) & 1\sigma_g(\mathbf{r}_2)\alpha(s_2) \\ 1\sigma_u(\mathbf{r}_1)\beta(s_1) & 1\sigma_u(\mathbf{r}_2)\beta(s_2) \end{vmatrix} \text{ and } \begin{vmatrix} 1\sigma_g(\mathbf{r}_1)\beta(s_1) & 1\sigma_g(\mathbf{r}_2)\beta(s_2) \\ 1\sigma_u(\mathbf{r}_1)\alpha(s_1) & 1\sigma_u(\mathbf{r}_2)\alpha(s_2) \end{vmatrix}$$

We cannot ignore one of them at the expense of the other.

So, we have learned that a single Slater determinant can adequately describe some electronic configurations, but others can only be described by a linear combination of Slater determinants, even at the lowest level of accuracy.

5 THE ELECTRON DENSITY

As computational facilities improve, electronic wavefunctions tend to become more and more complicated. A configuration interaction (CI) calculation on a medium-sized molecule might be a linear combination of a million Slater determinants, and it is very easy to lose sight of the 'chemistry' and the 'chemical intuition', to say nothing of the visualization of the results. Such wavefunctions seem to give no simple physical picture of the electron distribution, and so we must seek to find ways of extracting information that is chemically useful.

In Chapter 3, I showed you how to write a simple LCAO wavefunction for the electronic ground state of the hydrogen molecule-ion, $H_2{}^+$

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{2(1+S_{AB})}}(1s_A(\mathbf{r}) + 1s_B(\mathbf{r})) \tag{5.1}$$

S_{AB} is the overlap integral between atomic orbitals $1s_A$ and $1s_B$, and the factor $1/\sqrt{2(1+S_{AB})}$ is often called a *normalization coefficient* or the *normalizing factor*. It is introduced to make sure that

$$\int |\psi(\mathbf{r})|^2 \, d\tau = 1$$

where the integration is over the spatial variables of the electron.

I have included the modulus bars in $|\psi(\mathbf{r})|^2$ because wavefunctions can be complex quantities. For most of this and subsequent chapters, I will assume that we are dealing with real wavefunctions.

The total electronic wavefunction is the product of a spatial part and a spin part; it is $\psi(\mathbf{r})$ times $\alpha(s)$ or $\beta(s)$ for this one-electron molecule. There are thus two different quantum states having the same spatial part $\psi(\mathbf{r})$. In the absence of a magnetic field, these are degenerate.

Some authors write $\mathbf{x} = \mathbf{r}\ s$ to denote the 'total' variables of the electron, and write the total wavefunction as $\Psi(\mathbf{x})$ or $\Psi(\mathbf{r}, s)$. I have used a capital Ψ here to emphasize that the total wavefunction depends on both the space and spin variables. I will use the symbol $d\tau$ to denote a differential space element, and ds to denote a differential spin element.

The Born interpretation of quantum mechanics tells us that $\Psi^2(\mathbf{r}, \mathrm{s})\,\mathrm{d}\tau\,\mathrm{ds}$ gives the chance of finding the electron in the spatial volume element $\mathrm{d}\tau$ and with spin coordinate between s and s + ds. Since probabilities have to sum to 1, we have

$$\int \Psi^2(\mathbf{r}, \mathrm{s})\,\mathrm{d}\tau\,\mathrm{ds} = 1$$

where the integration has to be over the spatial variables and the spin variable. A short calculation will show you that a wavefunction such as

$$\psi(\mathbf{r})\alpha(\mathrm{s}) = \frac{1}{\sqrt{2(1+S_{\mathrm{AB}})}}(1\mathrm{s}_{\mathrm{A}}(\mathbf{r}) + 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}))\alpha(\mathrm{s}) \tag{5.2}$$

does indeed satisfy this requirement. (You should recall that the spin functions $\alpha(\mathrm{s})$ and $\beta(\mathrm{s})$ are orthonormal.)

Many physical properties such as the electrostatic potential, the dipole moment and so on, do not depend on electron spin and so we can ask a slightly different question: what is the chance that we will find the electron in a certain region of space $\mathrm{d}\tau$ irrespective of spin? To find the answer, we integrate over the spin variable, and to use the example 5.2 above

$$\left[\int \psi^2(\mathbf{r})\alpha^2(\mathrm{s})\,\mathrm{ds}\right]\mathrm{d}\tau$$

gives the chance of finding the electron in $\mathrm{d}\tau$, irrespective of spin. A short calculation shows that this is

$$\frac{1}{2(1+S_{\mathrm{AB}})}\left[1\mathrm{s}_{\mathrm{A}}^2(\mathbf{r}) + 1\mathrm{s}_{\mathrm{B}}^2(\mathbf{r}) + 2 \times 1\mathrm{s}_{\mathrm{A}}(\mathbf{r})1\mathrm{s}_{\mathrm{B}}(\mathbf{r})\right]\mathrm{d}\tau \tag{5.3}$$

This is usually written $P(\mathbf{r})\,\mathrm{d}\tau$ where $P(\mathbf{r})$ is the *electron density*.

What happens when we have a many-electron wavefunction, such as the one below which relates to the simple valence-bond treatment of dihydrogen?

$$\begin{aligned}\Psi_{\mathrm{VB}}(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2) &= \frac{1}{\sqrt{2\left(1+S_{\mathrm{AB}}^2\right)}}(1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_1)1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_2) + 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_2)1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_1))\\ &\quad\times \frac{1}{\sqrt{2}}(\alpha(\mathrm{s}_1)\beta(\mathrm{s}_2) - \alpha(\mathrm{s}_2)\beta(\mathrm{s}_1))\end{aligned} \tag{5.4}$$

As noted above, many of the common molecular properties don't depend on electron spin. The first step is to average-out the effect of electron spin, and we do this by integrating with respect to s_1 and s_2 to give the purely spatial wavefunction

$$\Psi_{\mathrm{VB}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2\left(1+S_{\mathrm{AB}}^2\right)}}(1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_1)1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_2) + 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_2)1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_1)) \tag{5.5}$$

The Born interpretation of quantum mechanics tells us that

$$\left\lfloor \Psi_{\mathrm{VB}}^2(\mathbf{r}_1, \mathbf{r}_2) \right\rfloor \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \tag{5.6}$$

is the probability of finding electron 1 in $\mathrm{d}\tau_1$ and simultaneously finding electron 2 in $\mathrm{d}\tau_2$. The quantity in square brackets comes to

$$\begin{aligned} &\frac{1}{2\left(1 + S_{\mathrm{AB}}^2\right)} \left(1\mathrm{s}_{\mathrm{A}}^2(\mathbf{r}_1) 1\mathrm{s}_{\mathrm{B}}^2(\mathbf{r}_2) + 1\mathrm{s}_{\mathrm{A}}^2(\mathbf{r}_2) 1\mathrm{s}_{\mathrm{B}}^2(\mathbf{r}_1)\right. \\ &\qquad \left. + 2 \times 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_1) 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_1) 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_2) 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_2)\right) \end{aligned} \tag{5.7}$$

Irrespective of electron spin, many simple molecular electronic properties depend only on the probability of finding either electron in a region of space $\mathrm{d}\tau$. The region $\mathrm{d}\tau$ is to be regarded as a fixed region of space that could from time to time be occupied by either of the electrons. To find this probability, we focus attention on one of the electrons (say 1), and then average over the coordinates of the other. In the simple VB case, Eq. 5.4, we average-out electron 2 to give a probability

$$\frac{1}{2(1 + S_{\mathrm{AB}}^2)} \left(1\mathrm{s}_{\mathrm{A}}^2(\mathbf{r}_1) + 1\mathrm{s}_{\mathrm{B}}^2(\mathbf{r}_1) + 2S_{\mathrm{AB}} \times 1\mathrm{s}_{\mathrm{A}}(\mathbf{r}_1) 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}_1)\right) \mathrm{d}\tau \tag{5.8}$$

Electrons are indistinguishable, and this probability is exactly equal to the chance of finding electron 2 in $\mathrm{d}\tau$. The chance of finding either electron in $\mathrm{d}\tau$ is therefore twice the above expression.

We could therefore define the electron density $P(\mathbf{r}_1)$ as

$$P(\mathbf{r}_1) = 2 \int \Psi_{\mathrm{VB}}^2(\mathbf{r}_1, \mathbf{r}_2) \, \mathrm{d}\tau_2 \tag{5.9}$$

where the integration has to be carried out with respect to the second electron. There is a further simplification, due to the indistinguishability of the electrons. We normally drop all reference to electron 1 and write simply

$$P(\mathbf{r}) = 2 \int \Psi_{\mathrm{VB}}^2(\mathbf{r}_1, \mathbf{r}_2) \, \mathrm{d}\tau_2 \tag{5.10}$$

where it is understood that we replace the variable $\mathbf{r}_1$ with $\mathbf{r}$ after integration. $P(\mathbf{r})\,\mathrm{d}\tau$ gives the chance that the differential volume of space $\mathrm{d}\tau$ is occupied by one electron, no matter which.

Integration of $P(\mathbf{r})$ with respect to the coordinates of this electron (now written $\mathbf{r}$) gives the number of electrons, 2 in this case. In the case of a many-electron wavefunction that depends on the spatial coordinates of electrons $1, 2, \ldots, m$, we define the electron density as

$$P(\mathbf{r}) = m \int \Psi^2(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m) \, \mathrm{d}\tau_2 \, \mathrm{d}\tau_2 \cdots \mathrm{d}\tau_m \tag{5.11}$$

with the understanding that we replace $\mathbf{r}_1$ by $\mathbf{r}$ after the integration. Again, integration of the electron density yields the number of electrons, m.

When working with atomic orbitals, it is usual to write the electron density in terms of a certain matrix called (not surprisingly) the *electron density matrix*. For the simple dihydrogen VB wavefunction, we have

$$P(\mathbf{r}) = (1s_A(\mathbf{r})1s_B(\mathbf{r}))\begin{pmatrix} \dfrac{1}{1+S_{AB}^2} & \dfrac{S_{AB}}{1+S_{AB}^2} \\ \dfrac{S_{AB}}{1+S_{AB}^2} & \dfrac{1}{1+S_{AB}^2} \end{pmatrix}\begin{pmatrix} 1s_A(\mathbf{r}) \\ 1s_B(\mathbf{r}) \end{pmatrix} \tag{5.12}$$

For the simple LCAO case, it turns out to be

$$P(\mathbf{r}) = (1s_A(\mathbf{r})1s_B(\mathbf{r}))\begin{pmatrix} \dfrac{1}{1+S_{AB}} & \dfrac{1}{1+S_{AB}} \\ \dfrac{1}{1+S_{AB}} & \dfrac{1}{1+S_{AB}} \end{pmatrix}\begin{pmatrix} 1s_A(\mathbf{r}) \\ 1s_B(\mathbf{r}) \end{pmatrix} \tag{5.13}$$

5.1 THE GENERAL LCAO CASE

In later chapters we will be concerned with the LCAO model. Suppose we have a set of n atomic orbitals $\chi_1(\mathbf{r}), \chi_2(\mathbf{r}), \ldots, \chi_n(\mathbf{r})$, and a normalized LCAO orbital

$$\psi_A(\mathbf{r}) = \sum_{i=1}^{n} a_i \chi_i(\mathbf{r}) \tag{5.14}$$

I will assume that the atomic orbitals χ_i are normalized, but not generally orthogonal. That is to say,

$$\int \chi_i^2(\mathbf{r})\,\mathrm{d}\tau = 1$$

$$\int \chi_i(\mathbf{r})\chi_j(\mathbf{r})\,\mathrm{d}\tau \neq 0$$

By analogy with the discussion of the previous section, the electron density for a single electron in ψ_A is given by

$$P(\mathbf{r}) = (\chi_1(\mathbf{r})\chi_2(\mathbf{r})\ldots\chi_n(\mathbf{r}))\begin{pmatrix} a_1^2 & a_1a_2 & \ldots & a_1a_n \\ a_2a_1 & a_2^2 & \ldots & a_2a_n \\ \ldots & \ldots & \ldots & \ldots \\ a_na_1 & a_na_2 & \ldots & a_n^2 \end{pmatrix}\begin{pmatrix} \chi_1(\mathbf{r}) \\ \chi_2(\mathbf{r}) \\ \ldots \\ \chi_n(\mathbf{r}) \end{pmatrix} \tag{5.15}$$

and the matrix

$$\mathbf{P} = \begin{pmatrix} a_1^2 & a_1a_2 & \ldots & a_1a_n \\ a_2a_1 & a_2^2 & \ldots & a_2a_n \\ \ldots & \ldots & \ldots & \ldots \\ a_na_1 & a_na_2 & \ldots & a_n^2 \end{pmatrix} \tag{5.16}$$

is the electron density matrix associated with the single LCAO ψ_A. If the electronic state of the molecule in question could be written (for example) $\psi_A^2\psi_B^2\psi_C^1$, where the three LCAO orbitals were linear combinations of the same atomic orbitals, we would calculate an electron density matrix whose (i, j)th element is

$$\mathbf{P}_{ij} = 2a_ia_j + 2b_ib_j + 1c_ic_j \tag{5.17}$$

The 2's and the 1 are called *occupation numbers*. In standard molecular orbital theory, occupation numbers are 0, 1 or 2 and they tell us the occupancy of a given orbital.

Since

$$\int \psi_A^2(\mathbf{r})\,d\tau = 1$$

we have

$$1 = a_1^2 \int \chi_1^2(\mathbf{r})\,d\tau + 2a_1a_2 \int \chi_1(\mathbf{r})\chi_2(\mathbf{r})\,d\tau + \cdots + a_n^2 \int \chi_n^2(\mathbf{r})\,d\tau$$

The integrals involving atomic orbitals are often collected together into a matrix called the *overlap matrix* **S**

$$\mathbf{S} = \begin{pmatrix} \int \chi_1^2(\mathbf{r})\,d\tau & \int \chi_1(\mathbf{r})\chi_2(\mathbf{r})\,d\tau & \dots & \int \chi_1(\mathbf{r})\chi_n(\mathbf{r})\,d\tau \\ \int \chi_2(\mathbf{r})\chi_1(\mathbf{r})\,d\tau & \int \chi_2^2(\mathbf{r})\,d\tau & \dots & \int \chi_2(\mathbf{r})\chi_n(\mathbf{r})\,d\tau \\ \dots & \dots & \dots & \dots \\ \int \chi_n(\mathbf{r})\chi_1(\mathbf{r})\,d\tau & \int \chi_n(\mathbf{r})\chi_2(\mathbf{r})\,d\tau & \dots & \int \chi_n^2(\mathbf{r})\,d\tau \end{pmatrix} \tag{5.18}$$

The matrix **S** is of course symmetric. The normalization condition for a single LCAO wavefunction can be written in a compact notation as

$$\sum_{i=1}^{n}\sum_{j=1}^{n} \mathbf{P}_{ij}\mathbf{S}_{ji} = 1 \tag{5.19}$$

In the more general case of several LCAOs, where **P** has been calculated according to the occupation numbers, we have

$$\sum_{i=1}^{n}\sum_{j=1}^{n} \mathbf{P}_{ij}\mathbf{S}_{ji} = \text{number of electrons} \tag{5.20}$$

5.2 POPULATION ANALYSIS

Once an approximation to the wavefunction of a molecule has been found, it can be used to calculate the probable result of many physical measurements and hence to predict properties such as a molecular hexadecapole moment or the electric field gradient at a quadrupolar nucleus. For many workers in the field, this is the primary objective for performing quantum-mechanical calculations. But from the early days of quantum chemistry, others have repeatedly tackled the problem of interpreting the wavefunction itself, attempting to understand why it takes a particular form for a particular molecule, and how the form of the wavefunction affects the expectation values calculated from it.

I have emphasized the electron density $P(\mathbf{r})$; it turns out that the expectation values of operators such as the dipole moment operator can be determined directly from $P(\mathbf{r})$ itself without recourse to the wavefunction. The density function $P(\mathbf{r})$ has a simple physical meaning; $P(\mathbf{r})\,\mathrm{d}\tau$ gives the probability of finding an electron of either spin in the spatial volume element $\mathrm{d}\tau$. Authors often speak about $P(\mathbf{r})$ as if it were some kind of time average, and state that electrons 'spend so much of their time associated with nucleus A', etc. This interpretation is quite wrong. First of all, we have only considered the time-independent Schrödinger equation, so you should be wary about any arguments based on time. Time does not appear in the time-independent Schrödinger equation!

Secondly, making measurements on atomic and molecular systems generally interferes with the system. If we were to repeatedly make measurements on a single system, we would change the system at each measurement and so would not be dealing necessarily with the same system. The correct interpretation is a statistical one. We would have to prepare a very large number of systems all in the same electronic state, and then do the measurements on all of them.

For a preliminary survey of the electron density, it is usual to make a pictorial representation as we did in previous chapters. Whilst such diagrams do not carry much information, they do provide a theoretical measure which can be compared to the results of X-ray diffraction studies. A whole volume of the *Transactions of the American Chemical Society* (1972) was devoted to the Symposium 'Experimental and Theoretical Studies of Electron Densities'.

For the purposes of a purely theoretical analysis of molecular electronic structure, we need more detailed information. The term *population analysis* was introduced in a series of papers by Mulliken in 1955, but the basic ideas had already been anticipated by Mulliken himself, and by other authors. The technique has been widely applied since Mulliken's 1955 papers, because it is very simple and has the apparent virtue of being 'quantitative'. The word 'quantitative' seems to mean two different things to different authors:

- an analytical description of the charge distribution in a molecule
- a measure of the strength and nature of the bonding in a molecule.

Most users of population analysis seem to be concerned with the first meaning. Take the LCAO–MO treatment of dihydrogen as an example. We focus on the electron density

$$P(\mathbf{r}) = (1s_{\mathrm{A}}(\mathbf{r})1s_{\mathrm{B}}(\mathbf{r}))\begin{pmatrix} \dfrac{1}{1+S_{\mathrm{AB}}} & \dfrac{1}{1+S_{\mathrm{AB}}} \\ \dfrac{1}{1+S_{\mathrm{AB}}} & \dfrac{1}{1+S_{\mathrm{AB}}} \end{pmatrix}\begin{pmatrix} 1s_{\mathrm{A}}(\mathbf{r}) \\ 1s_{\mathrm{B}}(\mathbf{r}) \end{pmatrix} \tag{5.21}$$

Electronic Population Analysis on LCAO-MO Molecular Wave Functions I
R. S. Mulliken
Journal of Chemical Physics **23** (1955) 1833–1840

With increasing availability of good all-electron LCAO-MO wavefunctions for molecules, a systematic procedure for obtaining maximum insight from such data has become desirable. An analysis in quantitative form is given here in terms of breakdowns of the electronic population into partial and total 'gross atomic populations' or into partial and total 'net atomic populations' together with 'overlap populations'. 'Gross atomic populations' distribute the electrons almost perfectly among the various AOs of the various atoms in the molecule. From these numbers, a definite figure is obtained for the amount of promotion (e.g., from 2s to 2p) in each atom; and also for the gross charge Q on each atom if the bonds are polar. The total overlap population for any pair of atoms in a molecule is in general made up of positive and negative contributions.

and the matrix

$$\mathbf{P} = \begin{pmatrix} \frac{1}{1+S_{AB}} & \frac{1}{1+S_{AB}} \\ \frac{1}{1+S_{AB}} & \frac{1}{1+S_{AB}} \end{pmatrix} \tag{5.22}$$

Atomic orbital $1s_A$ is associated with nucleus H_A and atomic orbital $1s_B$ with nucleus H_B. The first term in the electron density $\left(1s_A^2(\mathbf{r})\right)/(1+S_{AB})$ is taken to represent the amount of electron density associated with nucleus H_A. The corresponding term $\left(1s_B^2(\mathbf{r})\right)/(1+S_{AB})$ represents the electron density associated with nucleus H_B and the remainder $2(1s_A(\mathbf{r})1s_B(\mathbf{r}))/(1+S_{AB})$ is taken to represent the amount shared by the two nuclei. Mulliken's first idea was to integrate these contributions, which gives the values $1/(1+S_{AB})$, $1/(1+S_{AB})$ and $(2S_{AB})/(1+S_{AB})$. These values are assumed to contain some chemical information. Note that they sum to 2, the number of electrons in H_2.

The values are called the *net atomic populations* and the *overlap population*. Chemists speak of the charges on atoms in molecules, and Mulliken's second contribution was to propose a method of partitioning the overlap population between contributing atoms. He proposed that the overlap populations be divided equally between participating atoms, so giving the *gross atomic populations* of

$$\frac{1}{1+S_{AB}} + \frac{1}{2}\frac{2S_{AB}}{1+S_{AB}} \tag{5.23}$$

and hence atomic (nuclear plus electronic) charges of 0 in this particular case.

For a homonuclear diatomic, there is no argument that this sharing is equitable, but other authors have produced different sharing schemes for heteronuclear

Table 5.1 Mulliken atomic charges for water as function of quality of LCAO–MO

Quality	Total energy/E_h	Charge on O/e	Charge on H/e
STO–3G	−74.959 835	−0.382 4	+0.191 2
STO/6G	−75.675 842	−0.400 0	+0.200 0
STO/6–31G	−75.984 303	−0.792 5	+0.396 3
STO/6–31G*	−76.010 703	−0.869 8	+0.434 9
STO/6–31G**	−76.023 615	−0.670 7	+0.335 4

systems depending on atomic electronegativity differences, bond dipoles and so on.

5.2.1 Dependence on Quality

Population analysis is a deceptively simple process for obtaining a rough and ready account of the charge distribution in a molecule. Caution is needed when quoting population analysis indices, for the following reason. I have looked ahead a little, and the calculations above are more sophisticated versions of the LCAO treatment of water. I will explain the jargon such as 'HF/STO-3G' in later chapters; all we need to know for now is that I have added more and more atomic orbitals in order to get a lower energy. The presence of a * means that I have added d-type orbitals to oxygen, the presence of ** means that I have taken both p-type orbitals on hydrogen and d-type orbitals on oxygen.

The first two charges obviously resemble each other, despite the large change in energy; the overall 'agreement' between the calculated charges is non-existent, other than that oxygen is predicted to carry a negative charge. The numbers calculated depend critically on the quality of the wavefunction. Nevertheless, it is found that the Mulliken population analysis indices do carry useful chemical information, provided that comparisons are made between wavefunctions of equal quality.

5.3 DENSITY FUNCTIONS

I now want to generalize the concept of the charge density, and in particular treat spin explicitly rather than averaging it out. I told you earlier that, for a one-electron wavefunction $\Psi(\mathbf{r}, s)$, $\Psi^2(\mathbf{r}, s)\,d\tau\,ds$ gives the chance of finding the electron in the spatial volume element $d\tau$ with spin coordinate between s and s + ds. In Cartesian coordinates, $d\tau = dx\,dy\,dz$. Some authors write $\mathbf{x}$ for the space and spin variables and I am going to follow this notation where appropriate.

In order to calculate the total probability (which comes to 1), we have to integrate over both space $d\tau$ and spin ds. In the case of the hydrogen molecule-ion, we would write LCAO wavefunctions

$$\Psi(\mathbf{r}, \mathrm{s}) = \frac{1}{\sqrt{2(1 + S_{AB})}}(1\mathrm{s_A}(\mathbf{r}) + 1\mathrm{s_B}(\mathbf{r}))\alpha(\mathrm{s})$$

and

$$\Psi(\mathbf{r}, \mathrm{s}) = \frac{1}{\sqrt{2(1+S_{\mathrm{AB}})}}(1\mathrm{s}_{\mathrm{A}}(\mathbf{r}) + 1\mathrm{s}_{\mathrm{B}}(\mathbf{r}))\beta(\mathrm{s})$$

Both correspond to the same energy, in the absence of an external magnetic field. In either case, $\int \Psi^2(\mathbf{r}, s)\,\mathrm{d}\tau\,\mathrm{ds} = 1$ and we call $\Psi^2(\mathbf{r}, \mathrm{s})$ the *density function* $\rho_1(\mathbf{x})$.

For a many-electron system with wavefunction $\Psi(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \dots, \mathbf{r}_m, s_m)$ then

$$\Psi^2(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \dots, \mathbf{r}_m, \mathrm{s}_m)\,\mathrm{d}\tau_1\,\mathrm{d}s_1\,\mathrm{d}\tau_2\,\mathrm{d}s_2 \cdots \mathrm{d}\tau_m\,\mathrm{d}s_m \qquad (5.24)$$

gives the probability of finding simultaneously electron 1 in $\mathrm{d}\tau_1\,\mathrm{ds}_1$, electron 2 in $\mathrm{d}\tau_2\,\mathrm{ds}_2, \dots$, electron m in $\mathrm{d}\tau_m\,\mathrm{ds}_m$. The probability that electron 1 is in $\mathrm{d}\tau_1\,\mathrm{ds}_1$ with the other electrons anywhere is found by averaging over the remaining electrons. To find this we integrate

$$\left(\int \cdots \int \Psi^2(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \dots, \mathbf{r}_n, \mathrm{s}_n)\,\mathrm{d}\tau_2\,\mathrm{ds}_2 \cdots \mathrm{d}\tau_m\,\mathrm{ds}_m\right)\mathrm{d}\tau_1\,\mathrm{ds}_1$$

and, because electrons are indistinguishable, the probability must be the same for all electrons. We therefore define the *one-electron density function* as

$$\rho_1(\mathbf{r}_1, \mathrm{s}_1) = m\left(\int \cdots \int \Psi^2(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \dots, \mathbf{r}_m, \mathrm{s}_m)\,\mathrm{d}\tau_2\,\mathrm{ds}_2 \cdots \mathrm{d}\tau_m\,\mathrm{ds}_m\right) \qquad (5.25)$$

It is sometimes written

$$\rho_1(\mathbf{r}, \mathrm{s}) = m\left(\int \cdots \int \Psi^2(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \dots, \mathbf{r}_m, \mathrm{s}_m)\,\mathrm{d}\tau_2\,\mathrm{ds}_2 \cdots \mathrm{d}\tau_m\,\mathrm{ds}_m\right) \qquad (5.26)$$

with the convention that **r**,s refers to a point in spin-space. We evaluate ρ_1 from expression 5.25 above, but then drop the subscript.

The one-electron density function is the first of a series of density functions which relate to clusters of any numbers of electrons. The second member of the series is

$$\rho_2(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2) = m(m-1)\left(\int \cdots \int \Psi^2(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \mathbf{r}_3, \mathrm{s}_3 \dots, \mathbf{r}_m, \mathrm{s}_m) \times \mathrm{d}\tau_3\,\mathrm{ds}_3 \cdots \mathrm{d}\tau_m\,\mathrm{ds}_m\right)$$

which is related to the probability that any two electrons will be found simultaneously at points $\mathbf{r}_1, \mathrm{s}_1$ and $\mathbf{r}_2, \mathrm{s}_2$.

For every electronic wavefunction that is an eigenfunction of the electron spin operator $\hat{S}_z$, the one-electron density function always comprises an α^2 spin part and a β^2 spin part, with no cross-term involving $\alpha\beta$.

$$\rho_1(\mathbf{r}_1, s_1) = P^{\alpha}(\mathbf{r}_1)\alpha^2(s_1) + P^{\beta}(\mathbf{r}_1)\beta^2(s_1)$$

The electron densities for α spin electrons and for β spin electrons are always equal in a singlet spin state, but in non-singlet spin states the densities may be different, giving a resultant *spin density*. If we evaluate the spin density function at the position of certain nuclei, it gives a value proportional to the isotropic hyperfine coupling constant that can be measured from electron spin resonance experiments.

We note that the charge density discussed earlier is given by

$$P(\mathbf{r}_1) = P^{\alpha}(\mathbf{r}_1) + P^{\beta}(\mathbf{r}_1)$$

6 THE HARTREE–FOCK MODEL

In Chapter 4, I discussed the concept of an idealized dihydrogen molecule where the electrons did not repel each other. After making the Born–Oppenheimer approximation, we found that the electronic Schrödinger equation separated into two independent equations, one for either electron. These equations are the ones appropriate to the hydrogen molecule ion.

Once electron repulsion is taken into account, this separation of a many-electron wavefunction into a product of one-electron wavefunctions (orbitals) is no longer possible. This is not a failing of quantum mechanics; scientists and engineers reach similar conclusions whenever they have to deal with problems involving three or more mutually interacting particles. We speak of the *three-body problem.*

Thus, astronomers also suffer from the three-body problem when they try to study the motion of the planets round the sun. They are lucky in that the gravitational force between bodies A and B goes as

$$\mathbf{F}_{\mathrm{AB}} = -\frac{GM_{\mathrm{A}}M_{\mathrm{B}}\mathbf{R}_{\mathrm{AB}}}{R_{\mathrm{AB}}^{3}} \tag{6.1}$$

where G is the gravitation constant, M_{A} and M_{B} the masses of bodies A and B and $\mathbf{R}_{\mathrm{AB}}$ the vector joining A and B. In the case of our solar system, the sun is massive compared to the planets, and the gravitational attraction between the planets can be treated as a small perturbation on the motion of the planets round the sun.

The electrostatic force between two point charges Q_{A} and Q_{B} is

$$\mathbf{F}_{\mathrm{AB}} = \frac{Q_{\mathrm{A}}Q_{\mathrm{B}}\mathbf{R}_{\mathrm{AB}}}{4\pi\epsilon_{0}R_{\mathrm{AB}}^{3}} \tag{6.2}$$

and the charges on an electron and a proton are exactly equal and opposite. The forces between electrons are therefore comparable in magnitude to the forces between electrons and nuclei.

The orbital model is a very attractive one, and it can obviously be used to successfully model atoms, molecules and the solid state because it is now part of the language of elementary descriptive chemistry. In this chapter, I will show you how we go about recovering the orbital model when dealing with many-electron systems. The essence of this *Hartree–Fock* (HF) model is to solve the electronic Schrödinger equation for a single electron moving in a potential that averages out the effects of the nuclei and the remaining electrons. Electron repulsion is certainly not taken to be zero, but the HF model cannot treat the finer details of electronic structure theory that are caused by the instantaneous repulsion between electrons. So, dispersion forces cannot be treated at the HF level of theory.

The basic physical idea of HF theory is a simple one and can be tied in very nicely with our discussion of the electron density given in Chapter 5. We noted the physical significance of the density function $\rho_1(\mathbf{r}, s)$; $\rho_1(\mathbf{r}, s)\,\mathrm{d}\tau\,\mathrm{d}s$ gives the chance of finding any electron simultaneously in the spin-space volume elements $\mathrm{d}\tau$ and $\mathrm{d}s$, with the other electrons anywhere in space and with either spin. $P(\mathbf{r})\,\mathrm{d}\tau$ gives the corresponding chance of finding any electron with either spin in the spatial volume element $\mathrm{d}\tau$.

There are several ways in which we can proceed with the derivation of the HF equations. The traditional one is to look for an eigenvalue equation for the HF orbitals

$$\hat{h}^{\mathrm{F}}\psi_i = \varepsilon_i\psi_i \tag{6.3}$$

where the HF operator $\hat{h}^{\mathrm{F}}$ depends only on the coordinates of any one of the electrons, but allows for the averaging over their interactions. I am going to follow tradition, but link the discussion back to the electron density of Chapter 5.

The vast majority of known molecules are organic, totally lacking in symmetry and having singlet electronic ground states which can be written in the language of elementary descriptive chemistry as configurations $\psi_{\mathrm{A}}^2\psi_{\mathrm{B}}^2\ldots\psi_{\mathrm{M}}^2$.

This is shown schematically in Figure 6.1. For such molecules, the only degeneracies that occur are accidental ones and all the ψ's have the same spatial symmetry (their irreducible representation is a).

There are m doubly occupied molecular orbitals, and the number of electrons is $2m$ because we have allocated an α and a β spin electron to each. In the original Hartree model, the many-electron wavefunction was written as a straightforward product of one-electron orbitals ψ_{A}, ψ_{B} and so on

$$\Psi_{\mathrm{e}}(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_{2m}, s_{2m}) = \psi_{\mathrm{A}}(\mathbf{r}_1)\alpha(s_1)\psi_{\mathrm{A}}(\mathbf{r}_2)\beta(s_2)\ldots\psi_{\mathrm{M}}(\mathbf{r}_{2m})\beta(s_{2m}) \tag{6.4}$$

I will refer to the Hartree model from time to time in the text. Hartree's energies were in poor agreement with experiment. With the benefit of hindsight he should have allowed for indistinguishability and the Pauli principle. This was Fock's contribution to the field; he wrote the wavefunction as what we would now recognize as a Slater determinant. Such a wavefunction automatically satisfies the Pauli principle.

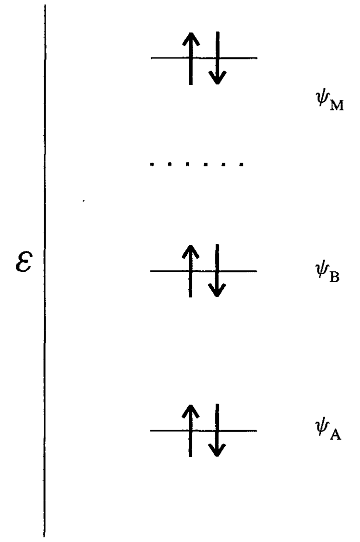


Figure 6.1 Orbital energy-level diagram for a typical organic molecule

$$\Psi_e(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_{2m}, s_{2m}) = \begin{vmatrix} \psi_A(\mathbf{r}_1)\alpha(s_1) & \psi_A(\mathbf{r}_1)\beta(s_1) & \cdots & \psi_M(\mathbf{r}_1)\beta(s_1) \\ \psi_A(\mathbf{r}_2)\alpha(s_2) & \psi_A(\mathbf{r}_2)\beta(s_2) & \cdots & \psi_M(\mathbf{r}_2)\beta(s_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_A(\mathbf{r}_{2m})\alpha(s_{2m}) & \psi_A(\mathbf{r}_{2m})\beta(s_{2m}) & \cdots & \psi_M(\mathbf{r}_{2m})\beta(s_{2m}) \end{vmatrix} \tag{6.5}$$

I am assuming that this particular electronic state is the lowest-energy one of that given spatial symmetry, and that the ψ's are orthonormal. The first assumption is a vital one, the second just makes the algebra a little easier. The aim of HF theory is to find the best 'form' of the one-electron functions $\psi_A, \ldots, \psi_M$ and to do this we minimize the variational energy

$$\varepsilon_e = \frac{\int \Psi_e \hat{H}_e \Psi_e \, d\tau}{\int \Psi_e^2 \, d\tau} \tag{6.6}$$

The integration is over the coordinates of all of the electrons, and I have assumed that the wavefunction is a real quantity. In the case of a complex wavefunction we are concerned with

$$\varepsilon_e = \frac{\int \Psi_e^* \hat{H}_e \Psi_e \, d\tau}{\int \Psi_e^* \Psi_e \, d\tau}$$

where Ψ^* is the complex conjugate of Ψ.

The first step is to work out ε in terms of the one- and two-electron operators and the orbitals $\psi_{\mathrm{A}}, \dots, \psi_{\mathrm{M}}$. For a polyatomic, polyelectron molecule, the electronic Hamiltonian is a sum of terms representing

- the kinetic energy of each of the electrons (which I will denote with subscript i);
- the mutual potential energy of each of the N nuclei with every electron. Nuclei are given a subscript α, which is not to be confused with the spin variable;
- the mutual potential energy of each distinct pair of electrons. I say 'distinct' because we have to avoid the double counting of the interaction between electron 1 with electron 2, and the interaction between electrons 2 and 1.

In symbols, we have

$$\hat{H}_{\mathrm{e}} = \left(-\frac{h^2}{8\pi^2 m_{\mathrm{e}}} \sum_{i=1}^{2m} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{2m} \sum_{\alpha=1}^{N} \frac{Z_\alpha}{R_{\alpha,i}} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{2m-1} \sum_{j=i+1}^{2m} \frac{1}{r_{ij}} \tag{6.7}$$

I have grouped the terms on the right-hand side together for a reason. We normally simplify the notation along the lines discussed for dihydrogen in Chapter 4, and write the electronic Hamiltonian as a sum of the one-electron and two-electron operators already discussed,

$$\hat{H}_{\mathrm{e}} = \sum_{i=1}^{m} \hat{h}(\mathbf{r}_i) + \sum_{i=1}^{2m-1} \sum_{j=i+1}^{2m} \hat{g}(\mathbf{r}_i, \mathbf{r}_j) \tag{6.8}$$

where

$$\hat{h}(\mathbf{r}_i) = -\frac{h^2}{8\pi^2 m_{\mathrm{e}}} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha=1}^{N} \frac{Z_\alpha}{R_{\alpha i}}$$

and

$$\hat{g}(\mathbf{r}_i, \mathbf{r}_j) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}}$$

The energy expression can be found using a set of rules known as the Slater–Condon–Shortley rules. These rules are discussed in all the classic texts, the idea being that the energy expression which involves integration over the coordinates of all the electrons can be reduced to a much simpler sum of terms involving the coordinates of one and (at most) two electrons. The variational energy works out as

$$\begin{aligned} \varepsilon_{\mathrm{e}} = {} & 2 \sum_{R=\mathrm{A}}^{\mathrm{M}} \int \psi_R(\mathbf{r}_1) \hat{h}(\mathbf{r}_1) \psi_R(\mathbf{r}_1) \, \mathrm{d}\tau_1 \\ & + \sum_{R=\mathrm{A}}^{\mathrm{M}} \sum_{S=\mathrm{A}}^{\mathrm{M}} \left(2 \iint \psi_R^2(\mathbf{r}_1) \hat{g}(\mathbf{r}_1, \mathbf{r}_2) \psi_S^2(\mathbf{r}_1) \, \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \right. \\ & \left. - \iint \psi_R(\mathbf{r}_1) \psi_S(\mathbf{r}_1) \hat{g}(\mathbf{r}_1, \mathbf{r}_2) \psi_R(\mathbf{r}_2) \psi_S(\mathbf{r}_2) \, \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \right) \end{aligned} \tag{6.9}$$

The subscripts R and S run over the orbital labels as in ψ_{A}, $\psi_{\mathrm{B}}, \dots$

The first of the two-electron integrals has a simple physical significance. The charge density of the electron labelled 1 is $-e\psi_R^2(\mathbf{r}_1)$ and the charge density of the electron labelled 2 is $-e\psi_S^2(\mathbf{r}_2)$. The integral therefore gives the mutual potential energy of the pair of electrons.

The second two-electron integral is a little more difficult to understand: formally, it represents the mutual potential energy of the 'overlap' charge distribution $-e\psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)$ due to electron 1 with an identical density $-e\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)$ due to electron 2.

We next find the minimum of the electronic energy by varying the form of the orbitals $\psi_\mathrm{A}, \psi_\mathrm{B}, \dots, \psi_\mathrm{M}$.

At the energy minimum, each electron moves in an average field due to the other electrons and the nuclei. Small variations in the form of the orbitals at this point do not change the energy or the electric field, and so we speak of a *self-consistent field (SCF)*. Many authors use the acronyms HF and SCF interchangeably, and I will do so from time to time. These HF orbitals are found as solutions of the HF eigenvalue problem

$$\hat{h}^\mathrm{F}\psi_i = \varepsilon_i\psi_i \tag{6.10}$$

and the occupied orbitals correspond to the m lowest eigenvalues.

All the early work was concerned with atoms, with Sir William Hartree regarded as the father of the technique. His son, Douglas R. Hartree, published the definitive book, *The Calculation of Atomic Structures*, in 1957, and in this he derived the atomic HF equations and described numerical algorithms for their solution. Charlotte Froese Fischer was a research student working under the guidance of D. R. Hartree, and she published her own definitive book, *The Hartree–Fock Method for Atoms: A Numerical Approach* in 1977. The Appendix lists a number of freely available atomic structure programs. Most of these can be obtained from the Computer Physics Communications Program Library.

Solution of the numerical HF equations to full accuracy is routine in the case of atoms. We say that such calculations are at the *Hartree–Fock limit*. These represent the best solution possible within the orbital model. For large molecules, solutions at the HF limit are not possible, which brings me to my next topic.

6.1 THE LCAO PROCEDURE

In fact, the HF procedure leads to a complicated set of integro-differential equations that can only be solved for a one-centre problem. If your interest lies in atomic applications, you should read the classic books mentioned above. What we normally do for molecules is to use the LCAO procedure; each HF orbital is expressed as a linear combination of n atomic orbitals $\chi_1, \chi_2, \dots, \chi_n$ so that (for example)

$$\psi_\mathrm{A}(\mathbf{r}) = a_1\chi_1(\mathbf{r}) + a_2\chi_2(\mathbf{r}) + \cdots + a_n\chi_n(\mathbf{r})$$

Here the a_i are the LCAO coefficients, which have to be determined. The formulation of HF theory where we use the LCAO approximation is usually attributed to Roothaan (1951a). His formulation applies only to electronic configurations of the type $\psi_{\mathrm{A}}^2, \psi_{\mathrm{B}}^2, \ldots, \psi_{\mathrm{M}}^2$. Following the discussion of Chapter 5, the charge density matrix has elements

$$P_{ij} = 2\sum_{r=a}^{m} r_i r_j \tag{6.11}$$

If we collect the LCAO coefficients into an $n \times m$ matrix

$$\mathbf{U} = \begin{pmatrix} a_1 & b_1 & \cdots & m_1 \\ a_2 & b_2 & \cdots & m_2 \\ \ldots & \ldots & \ldots & \ldots \\ a_n & b_n & \cdots & m_n \end{pmatrix}$$

then it is evident that

$$\mathbf{P} = 2\mathbf{U}\mathbf{U}^{\mathrm{T}} \tag{6.12}$$

where $\mathbf{U}^{\mathrm{T}}$ is the transpose of $\mathbf{U}$. Just to remind you how to calculate the product of two matrices, if $\mathbf{A}$ has n rows and l columns, and $\mathbf{B}$ has l rows and p columns, then the i, j^{th} element of $\mathbf{AB}$ is

$$(\mathbf{AB})_{ij} = \sum_{k=1}^{l} A_{ik} B_{kj}$$

Most authors refer to the χ's as *basis functions*. These usually overlap each other, and I will collect their overlap integrals into the $n \times n$ matrix $\mathbf{S}$ as in Chapter 5:

$$\mathbf{S} = \begin{pmatrix} \int \chi_1^2(\mathbf{r})\,\mathrm{d}\tau & \int \chi_1(\mathbf{r})\chi_2(\mathbf{r})\,\mathrm{d}\tau & \cdots & \int \chi_1(\mathbf{r})\chi_n(\mathbf{r})\,\mathrm{d}\tau \\ \int \chi_2(\mathbf{r})\chi_{12}(\mathbf{r})\,\mathrm{d}\tau & \int \chi_2^2(\mathbf{r})\,\mathrm{d}\tau & \cdots & \int \chi_2(\mathbf{r})\chi_n(\mathbf{r})\,\mathrm{d}\tau \\ \ldots & \ldots & \ldots & \ldots \\ \int \chi_n(\mathbf{r})\chi_1(\mathbf{r})\,\mathrm{d}\tau & \int \chi_n(\mathbf{r})\chi_2(\mathbf{r})\,\mathrm{d}\tau & \cdots & \int \chi_n^2(\mathbf{r})\,\mathrm{d}\tau \end{pmatrix}$$

In the unlikely event that none of the basis functions overlap, then $\mathbf{S}$ is a unit matrix. We usually require the LCAO orbitals $\psi_{\mathrm{A}}, \psi_{\mathrm{B}}, \ldots, \psi_{\mathrm{M}}$ to be orthonormal and this fact can be summarized in a single matrix statement. A little manipulation will show that $\mathbf{U}^{\mathrm{T}}\mathbf{S}\mathbf{U}$ is then a unit matrix (with m rows and m columns), and also that

$$\mathbf{PSP} = 4\mathbf{P} \tag{6.13}$$

We now need to use the variation principle to seek the best possible values of the LCAO coefficients. To do this, I have to find ε_{e} as above, and set its first derivative to zero. I keep track of the requirement that the LCAO orbitals are orthonormal by making sure that the electron density **P** satisfies equation 6.13 above.

If I collect together all integrals involving the basis functions $\chi_1, \chi_2, \ldots, \chi_n$ and a one-electron operator into an $n \times n$ matrix $\mathbf{h}_1$ with elements

$$(\mathbf{h}_1)_{ij} = \int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

then it turns out that the one-electron operators make a contribution

$$\sum_{i=1}^{n}\sum_{j=1}^{n}(\mathbf{h}_1)_{ij}(\mathbf{P})_{ji} \tag{6.14}$$

to the variational energy. This double sum can be written a little more neatly as the *trace* of the matrix product $\mathbf{h}_1\mathbf{P}$, symbolized Tr $(\mathbf{h}_1\mathbf{P})$. (The trace of an $n \times n$ matrix is the sum of its diagonal elements. The product $\mathbf{h}_1$ **P** is $n \times n$ and the diagonal elements of the product are $\sum_{j=1}^{n}(\mathbf{h}_1)_{ij}(\mathbf{P})_{ji}$.)

The two-electron contribution to the energy can be written as 1/2 Tr (**P G**) where the elements of the $n \times n$ matrix **G** depend on **P** in a complicated manner,

$$\begin{aligned} G_{ij} &= \sum_{k=1}^{n}\sum_{l=1}^{n} P_{kl} \iint \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\quad - \frac{1}{2}\sum_{k=1}^{n}\sum_{l=1}^{n} P_{kl} \iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \end{aligned} \tag{6.15}$$

The electronic energy comes out as

$$\varepsilon_{\mathrm{e}} = \mathrm{Tr}(\mathbf{P}\mathbf{h}_1) + \tfrac{1}{2}\mathrm{Tr}(\mathbf{PG}) \tag{6.16}$$

The next step is to examine how ε_{e} changes when the electron density changes (equivalent to varying the LCAO coefficients). We let $\mathbf{P} \to \mathbf{P} + \delta\mathbf{P}$ and after a little manipulation find that the first-order change in the electronic energy is

$$\delta\varepsilon_{\mathrm{e}} = \mathrm{Tr}(\delta\mathbf{P}\mathbf{h}_1) + \mathrm{Tr}(\delta\mathbf{PG}) \tag{6.17}$$

Note that the factor of 1/2 has disappeared from the energy expression; this is because the **G** matrix itself depends on **P**, which has to be taken into account. We write $\delta\varepsilon_{\mathrm{e}}$ in terms of the *Hartree–Fock Hamiltonian* matrix $\mathbf{h}^{\mathrm{F}}$, where

$$\mathbf{h}^{\mathrm{F}} = \mathbf{h}_1 + \mathbf{G}$$

so that $\delta\varepsilon_{\mathrm{e}} = \mathrm{Tr}(\delta\mathbf{P}\mathbf{h}^{\mathrm{F}})$. We want to find $\delta\mathbf{P}$ such that $\delta\varepsilon_{\mathrm{e}}$ is zero. We know that $\mathbf{PSP} = 4\mathbf{P}$, and $P + \delta\mathbf{P}$ must also satisfy the same condition

$$(\mathbf{P} + \delta\mathbf{P})\mathbf{S}(\mathbf{P} + \delta\mathbf{P}) = 4(\mathbf{P} + \delta\mathbf{P})$$

A little manipulation will show you that, at the energy minimum

$$\mathbf{h}^{\mathrm{F}}\mathbf{P} = \mathbf{P}\mathbf{h}^{\mathrm{F}} \tag{6.18}$$

This shows that, when we have found the correct electron density matrix and correctly calculated the Hartree–Fock Hamiltonian matrix from it, the two matrices will satisfy the condition given. (When two matrices **A** and **B** are such that **AB** = **BA**, we say that they *commute*.) This doesn't help us to actually find the electron density, but it gives us a condition for the minimum.

Roothaan actually solved the problem by allowing the LCAO coefficients to vary, subject to the LCAO orbitals remaining orthonormal. He showed that the LCAO coefficients are given from the following *matrix eigenvalue equation*:

$$\mathbf{h}^{\mathrm{F}}\mathbf{c} = \varepsilon\mathbf{S}\mathbf{c} \tag{6.19}$$

Here, **c** is a column vector of LCAO coefficients and ε is called the *orbital energy*. If we start with n basis functions, then there are exactly n different **c**'s (and ε's) and the m lowest-energy solutions of the eigenvalue problem correspond to the doubly occupied HF orbitals. The remaining $n - m$ solutions are called the *virtual orbitals*. They are unoccupied.

Once again, this doesn't help us to find the HF orbitals, because we have to know the LCAO coefficients before we know the Hamiltonian matrix. For the record, and because we will refer to them many times, the elements of the HF matrix for a closed shell system are

$$\begin{aligned} h_{ij}^{\mathrm{F}} &= \int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau \\ &+ \sum_{k=1}^{n}\sum_{l=1}^{n} P_{kl} \iint \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &- \frac{1}{2}\sum_{k=1}^{n}\sum_{l=1}^{n} P_{kl} \iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \end{aligned} \tag{6.20}$$

A lot of effort has gone into devising procedures for solving the problem. You might like to read about direct procedures for finding **P** in McWeeny and Sutcliffe (1969). Roughly, what we do is this:

- have a guess at the electron density **P**;
- calculate $\mathbf{h}^{\mathrm{F}}$ from it;
- check on the condition for a minimum energy; and
- improve **P** if the condition is not met, and move back two steps.

In terms of the LCAO coefficients, the procedure is very similar:

- have a guess at the LCAO coefficients and calculate **P**;
- calculate $\mathbf{h}^{\mathrm{F}}$ from it;

- check for a minimum energy; and
- solve the eigenvalue problem to give (hopefully) a better estimate of the LCAO coefficients, and then move back two steps.

Many authors refer to the HF–LCAO procedure, when discussing HF calculations made within the LCAO approximation.

6.2 THE ELECTRONIC ENERGY

Suppose then that we have successfully solved the HF equations for a molecule with $2m$ electrons as shown in Figure 6.1, and that the occupied orbitals have energies $\varepsilon_A, \varepsilon_B, \ldots, \varepsilon_M$. The LCAO coefficients are also collected in the column vectors $\mathbf{a}, \mathbf{b}, \ldots, \mathbf{m}$ and the electronic energy is given by

$$\varepsilon_e = \mathrm{Tr}(\mathbf{Ph}_1) + \tfrac{1}{2}\mathrm{Tr}(\mathbf{PG})$$

The sum of the orbital energies is

$$\varepsilon_{\mathrm{orb}} = 2(\varepsilon_A + \varepsilon_B + \cdots + \varepsilon_M)$$

Now the orbital energies are given by

$$\mathbf{h}^F\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_i$$

and so $\mathbf{c}_i^T\mathbf{h}^F\mathbf{c}_i = \varepsilon_i\mathbf{c}_i^T\mathbf{S}\mathbf{c}_i$. This gives ε_i and after a little manipulation you will find that

$$\varepsilon_e = \varepsilon_{\mathrm{orb}} - \tfrac{1}{2}\,\mathrm{Tr}\,(\mathbf{PG}) \tag{6.21}$$

The orbital energies do not sum to the electronic energy.

6.3 THE KOOPMANS THEOREM

The orbital energies for such an HF wavefunction therefore don't bear any simple relationship to the electronic energy, but they do have an interesting significance that is of immense importance to workers in the field of photoelectron spectroscopy. Suppose we remove a single electron from orbital ψ_X, and ask about the energy required for the process. Koopmans proved that this ionization energy is related very simply to the HF orbital energy ε_X by

$$\text{Ionization energy} = -\varepsilon_X$$

There is some small print to the derivation: the orbitals must not change during the ionization process. In other words, the orbitals for the cation produced must be the same as the orbitals for the parent molecule. Koopmans (1934) derived the result for an exact HF wavefunction in the numerical Hartree–Fock sense. It turns out that the result is also valid for wavefunctions calculated using the LCAO version of HF theory.

The fact is that the molecular orbitals describing the resulting cation may well be quite different from those of the parent molecule. We speak of *electron relaxation*, and so we need to examine the problem of calculating accurate HF wavefunctions for open-shell systems.

6.4 OPEN-SHELL SYSTEMS

As mentioned above, the vast majority of organic molecules have electronic singlet ground states, which can be described adequately by the HF procedure detailed above. But a great deal of chemistry is concerned with electronically excited states and with cations and anions, and the procedure outlined is not appropriate. The HF approach is very attractive, since it gives an orbital picture and it turns out that several classes of open-shell electronic states can still be treated using the HF principles. The simplest case is that shown in Figure 6.2, where we have removed an electron from the highest occupied orbital ψ_M and we could have a number of doubly occupied orbitals together with more than one singly occupied orbital, with the proviso that the singly occupied orbitals all have spins parallel. We often speak of the *closed shell* (where all the electrons are paired) and the *open shell* (where all the electrons have parallel spins). Figure 6.2 shows an open shell with a single electron; we could treat the first excited triplet state of dihydrogen by this technique, but not the first excited singlet state (whose wavefunction has to be written as a combination of two Slater determinants). The algebraic treatment is very similar to the closed-shell case, except that we need to consider electron density matrices for the closed-shell and the open-shell electrons.

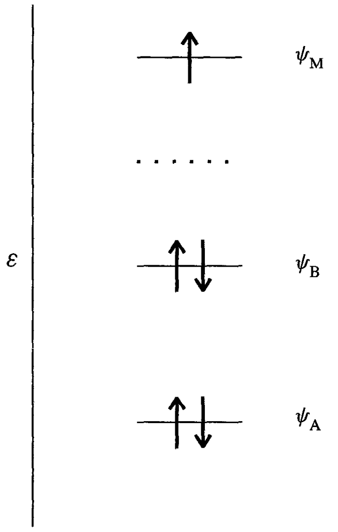


Figure 6.2 An ROHF open-shell configuration

So, for the sake of argument, consider the case where there is a closed shell of n_1 doubly occupied orbitals, and an open shell of n_2 orbitals, all of which are singly occupied with parallel spins. The LCAO–MOs of the closed shell and the open shell can be collected in the matrices $\mathbf{U}_1$ and $\mathbf{U}_2$, with n_1 and n_2 columns respectively, and we define density matrices $\mathbf{R}_1$ and $\mathbf{R}_2$ for each shell as

$$\begin{aligned}\mathbf{R}_1 &= \mathbf{U}_1\mathbf{U}_1^+ \\ \mathbf{R}_2 &= \mathbf{U}_2\mathbf{U}_2^+\end{aligned} \tag{6.22}$$

We would have $\mathbf{P} = 2\mathbf{R}_1$ and $\mathbf{R}_2 = \mathbf{0}$ for a closed-shell singlet state. The closed-shell electronic energy expression given earlier,

$$\begin{aligned}\varepsilon_{\mathrm{e}} = 2\sum_{R=\mathrm{A}}^{\mathrm{M}} \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ + \sum_{R=\mathrm{A}}^{\mathrm{M}}\sum_{S=\mathrm{A}}^{\mathrm{M}}\Bigg(2\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_S^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ - \iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\Bigg)\end{aligned}$$

is modified as follows. If we use R, S, … for general closed-shell orbitals and U, V, … for general open-shell orbitals then

$$\begin{aligned}\varepsilon_{\mathrm{e}} = \nu_1 &\left(\begin{aligned}&\sum_R \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ &\quad +\frac{1}{2}\nu_1\sum_R\sum_S\Bigg(\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_S^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\quad -\frac{1}{2}\iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\Bigg)\end{aligned}\right) \\ + \nu_2 &\left(\begin{aligned}&\sum_U \int \psi_U(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_U(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ &\quad +\frac{1}{2}\nu_2\sum_U\sum_V\Bigg(\iint \psi_U^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_V^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\quad -\iint \psi_U(\mathbf{r}_1)\psi_V(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_U(\mathbf{r}_2)\psi_V(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\Bigg)\end{aligned}\right) \\ + \nu_1\nu_2 &\Bigg(\sum_R\sum_U\Bigg(\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_U^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &-\frac{1}{2}\iint \psi_R(\mathbf{r}_1)\psi_U(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_U(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\Bigg)\Bigg)\end{aligned} \tag{6.23}$$

I have introduced the *occupation numbers* ν_1 and ν_2 (where $\nu_1 = 2$ and $\nu_2 = 1$ in this simple case) to emphasize the symmetry of the electronic energy expression.

For closed-shell states, we found an energy expression

$$\varepsilon_e = \mathrm{Tr}(\mathbf{P}\mathbf{h}_1) + \tfrac{1}{2}\mathrm{Tr}(\mathbf{P}\mathbf{G})$$

The corresponding expression for an open-shell state is

$$\varepsilon_e = \nu_1 \mathrm{Tr}\left(\mathbf{R}_1\left(\mathbf{h}_1 + \tfrac{1}{2}\mathbf{G}_1\right)\right) + \nu_2 \mathrm{Tr}\left(\mathbf{R}_2\left(\mathbf{h}_1 + \tfrac{1}{2}\mathbf{G}_2\right)\right) \tag{6.24}$$

where the two **G** matrices are similar to that defined by equation 6.15 for the closed-shell case.

We then allow $\mathbf{R}_1$ and $\mathbf{R}_2$ to vary, subject to orthonormality, just as in the closed-shell case. Just as in the closed-shell case, Roothaan (1960) showed how to write a Hamiltonian matrix whose eigenvectors give the columns $\mathbf{U}_1$ and $\mathbf{U}_2$ above.

6.5 UNRESTRICTED HARTREE–FOCK THEORY

A more general way to treat systems having an odd number of electrons, and certain electronically excited states of other systems, is to let the individual HF orbitals become singly occupied, as in Figure 6.3. In standard HF theory, we constrain the wavefunction so that every HF orbital is doubly occupied. The idea of *unrestricted Hartree–Fock (UHF) theory* is to allow the α and β electrons to have different spatial wavefunctions. In the LCAO variant of UHF theory, we seek LCAO coefficients for the α spin and β spin orbitals separately. These are determined from coupled matrix eigenvalue problems that are very similar to the closed-shell case.

There are several points to note about UHF wavefunctions:

- The α and β electrons are considered separately, and there is an electron density matrix for each set. These add to give the electron density, whilst the difference is the spin density.
- The resulting wavefunction is not necessarily an eigenfunction of the spin operator $\hat{S}^2$. This may or may not matter, depending on the application.

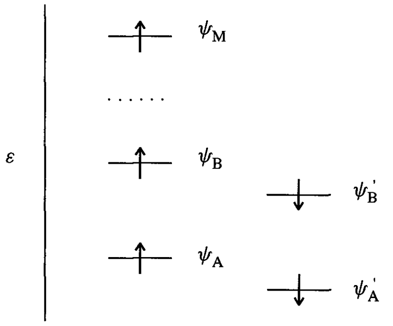


Figure 6.3 A UHF open-shell configuration

- The only electronic states that can be treated are those that correspond to the highest spin multiplet of a given orbital configuration.

6.6 THE $\hat{J}$ AND $\hat{K}$ OPERATORS

We saw earlier that the variational energy for a closed-shell state formed from electron configurations such as

$$\psi_A^2\psi_B^2\cdots\psi_M^2$$

can be written

$$\begin{aligned}\varepsilon_e = {} & 2\sum_{R=A}^{M}\int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ & + \sum_{R=A}^{M}\sum_{S=A}^{M}\left(2\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_S^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right. \\ & \left. - \iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right)\end{aligned}$$

The sums run over the occupied orbitals; note that we have not made any reference to the LCAO approximation. The energy expression is correct for a determinantal wavefunction irrespective of whether the orbitals are of LCAO form or not.

It is sometimes useful to recast the equation as the expectation value of a sum of one-electron and pseudo one-electron operators

$$\varepsilon_c = 2\int\sum_{R=A}^{M}\psi_R(\mathbf{r}_1)\left(\hat{h}_1(\mathbf{r}_1)+\hat{J}(\mathbf{r}_1)-\frac{1}{2}\hat{K}(\mathbf{r}_1)\right)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \tag{6.25}$$

The operator $\hat{h}_1$ is a one-electron operator, representing the kinetic energy of an electron and the nuclear attraction. The operators $\hat{J}$ and $\hat{K}$ are called the *Coulomb* and *exchange operators*. They can be defined through their expectation values as follows.

$$\int \psi_R(\mathbf{r}_1)\hat{J}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 = \sum_{S=A}^{M}\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_S^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \tag{6.26}$$

and

$$\int \psi_R(\mathbf{r}_1)\hat{K}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 = \sum_{S=A}^{M}\iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \tag{6.27}$$

We will meet these two operators again when we study density functional theory in Chapter 13.

7 THE HÜCKEL MODEL

Molecules with extensive π bonding systems, like benzene and pyridine, are not well described by classical valence bond theory. Such molecules are often planar, or largely planar, and two types of bond contribute to their structure: σ and π bonds. The σ bonds are to be thought of as localized between atoms, whilst the π bonds are to be thought of as being delocalized over large portions of the molecule. Much of the interesting chemistry of such compounds appears to relate to the so-called π-electrons. Chemists believe that the σ-electrons and the nuclei generate a potential for the π-electrons, and that this potential is roughly a constant. From the early days of quantum theory, chemists have focused on the π-electrons by themselves, almost as if the σ-electrons were not present, and these π-electron models have been remarkably successful.

One of the earliest models for treating conjugated molecules is afforded by the Hückel π-electron model. This dates from the work of E. Hückel in 1931. The ideas are simple and appealing, and the model enjoyed many years of successful application to individual molecules, molecular clusters and solids.

Hückel's model was not originally presented in terms of the HF model, but I want you to think in HF–LCAO terms for the remainder of the chapter. So, imagine a simple π-electron molecule such as ethene (Figure 7.1).

There are 16 electrons in total, 14 σ and 2 π and so our total wavefunction will be some complicated function of their spatial $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{16})$ and spin variables $(s_1, s_2, \ldots, s_{16})$. The electronic state wavefunction for the molecule can therefore be written

$$\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_{16}, s_{16})$$

or, if I use the shorthand that $\mathbf{x}$ is a space-and-spin variable,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{16}) \tag{7.1}$$

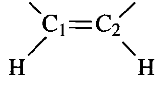


Figure 7.1

Don't confuse the state wavefunction with a molecular orbital; we might well want to build the state wavefunction, which describes all the 16 electrons, from molecular orbitals each of which describe a single electron. But the two are not the same. We would have to find some suitable one-electron wavefunctions and then combine them into a slater determinant in order to take account of the Pauli principle.

Where might these one-electron wavefunctions come from? I explained the basic ideas of HF and HF–LCAO theory in Chapter 6; we could find the molecular orbitals as linear combinations of appropriate atomic orbitals by solving the HF eigenvalue problem

$$\hat{h}^{\mathrm{F}}\psi_i = \varepsilon_i\psi_i$$

You should remember the basic physical idea behind the HF model: each electron experiences an average potential due to the other electrons (and of course the nuclei), so that the HF Hamiltonian operator contains within itself the averaged electron density due to the other electrons. In the LCAO version, we seek to expand the HF orbitals ψ in terms of a set of fixed basis functions $\chi_1, \chi_2, \ldots, \chi_n$, and write

$$\psi = \sum_{i=1}^{n} c_i\chi_i$$

The LCAO expansion coefficients are found from the matrix eigenvalue problem

$$\mathbf{h}^{\mathrm{F}}\mathbf{c}_i = \varepsilon_i\mathbf{S}\mathbf{c}_i$$

where the matrices $\mathbf{h}^{\mathrm{F}}$ and $\mathbf{S}$ have elements

$$h_{ij}^{\mathrm{F}} = \int \chi_i(\mathbf{r}_1)\hat{h}^{\mathrm{F}}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

and

$$S_{ij} = \int \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

For the minute, imagine an HF–LCAO treatment of just the π-electrons in ethene where each carbon atom contributes just one electron and one atomic orbital of the correct symmetry to the conjugated system. Without any particular justification except chemical intuition, we make the following assumptions.

1 The atomic orbitals are normalized and orthogonal.

This means that the overlap matrix is a unit matrix, in this case

$$\mathbf{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Not only that, the elements of the HF–LCAO matrix are taken to be constants that depend only on the nature of atoms and atom pairs as follows.

2 Diagonal elements of the HF matrix depend only on the nature of the atom on which χ is centred.
3 Off-diagonal elements of the HF matrix are zero for non-bonded atoms.
4 Off-diagonal elements for bonded pairs of atoms depend only on the types of atom involved.

We generally write α for a diagonal element and β for a bonded off-diagonal element; in particular α_C and β_{CC} for carbon atoms and carbon–carbon conjugated bonds. The physical interpretation is that each of the π-electrons experiences an average field due to the nuclei, the σ-electrons and the remaining π-electrons.

7.1 EXAMPLES

7.1.1 Ethene

In the Hückel π-electron model, ethene is a two-electron problem. I have numbered the carbon atoms C_1 and C_2, and χ_1 is centred on C_1 with χ_2 on C_2. The HF matrix becomes

$$\mathbf{h}^{F} = \begin{pmatrix} \alpha_C & \beta_{CC} \\ \beta_{CC} & \alpha_C \end{pmatrix} \tag{7.2}$$

and matrix diagonalization, followed by normalization of the HF–LCAO orbitals, gives the results in Table 7.1.

It turns out that β_{CC} is a negative quantity, so the electronic ground state of ethene corresponds to orbital configuration ψ_A^2 where

$$\psi_A = 0.7071\chi_1 + 0.7071\chi_2$$

The π-electron density matrix is

$$\mathbf{P} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \tag{7.3}$$

I should mention that matrix diagonalization can be easily done with any commercially available mathematics package such as Mathcad.

Table 7.1 Hückel π-electron calculation on ethene

Orbital energy ε	LCAO coefficients	
$\alpha_C + \beta_{CC}$	0.7071	0.7071
$\alpha_C - \beta_{CC}$	0.7071	−0.7071

7.1.2 Hexatriene

Hexatriene (Figure 7.2) is a six-electron problem, and we write the HF–LCAO orbitals in terms of the basis functions $\chi_1, \chi_2, \ldots, \chi_6$, one per carbon atom. The HF matrix is

$$\mathbf{h}^F = \begin{pmatrix} \alpha_C & \beta_{CC} & 0 & 0 & 0 & 0 \\ \beta_{CC} & \alpha_C & \beta_{CC} & 0 & 0 & 0 \\ 0 & \beta_{CC} & \alpha_C & \beta_{CC} & 0 & 0 \\ 0 & 0 & \beta_{CC} & \alpha_C & \beta_{CC} & 0 \\ 0 & 0 & 0 & \beta_{CC} & \alpha_C & \beta_{CC} \\ 0 & 0 & 0 & 0 & \beta_{CC} & \alpha_C \end{pmatrix} \tag{7.4}$$

The zeros arise because (for example) atom 1 is bonded to atom 2 but not to atom 3, 4, 5 or 6. Diagonalization gives the orbital energies and normalized LCAO coefficients shown in Table 7.2.

Notice molecular symmetry at work. The Hückel π-electron model is in many ways a blunt instrument, because we would get exactly the same answers for either of the following possible conformers of hexatriene (Figure 7.3).

The Hückel π-electron model uses information about what is bonded to what (i.e. the connectivity) but does not cater for molecular geometries.

In the electronic ground state, the six π-electrons occupy the three lowest-energy orbitals (the first three from Table 7.2). The Hückel π-electron charge density matrix is

$$\mathbf{P} = \begin{pmatrix} 1.0000 & 0.8711 & 0.0000 & -0.3877 & 0.0000 & 0.3014 \\ 0.8711 & 1.0000 & 0.4834 & 0.0000 & -0.0863 & 0.0000 \\ 0.0000 & 0.4834 & 1.0000 & 0.7849 & 0.0000 & -0.3877 \\ -0.3877 & 0.0000 & 0.7849 & 1.0000 & 0.4834 & 0.0000 \\ 0.0000 & -0.0863 & 0.0000 & 0.4834 & 1.0000 & 0.8711 \\ 0.3014 & 0.0000 & -0.3877 & 0.0000 & 0.8711 & 1.0000 \end{pmatrix} \tag{7.5}$$

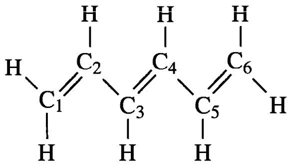


Figure 7.2

Table 7.2 Hückel π-electron calculation on hexatriene

Orbital energy ε	LCAO coefficients					
$\alpha_C + 1.802\beta_{CC}$	0.2319	0.4179	0.5211	0.5211	0.4179	0.2319
$\alpha_C + 1.247\beta_{CC}$	−0.4179	−0.5211	−0.2319	0.2319	0.5211	0.4179
$\alpha_C + 0.445\beta_{CC}$	0.5211	0.2319	−0.4179	−0.4179	0.2319	0.5211
$\alpha_C - 0.445\beta_{CC}$	−0.5211	0.2319	0.4179	−0.4179	−0.2319	0.5211
$\alpha_C - 1.247\beta_{CC}$	−0.4179	0.5211	−0.2319	−0.2319	0.5211	−0.4179
$\alpha_C - 1.802\beta_{CC}$	−0.2319	0.4179	−0.5211	0.5211	−0.4179	0.2319

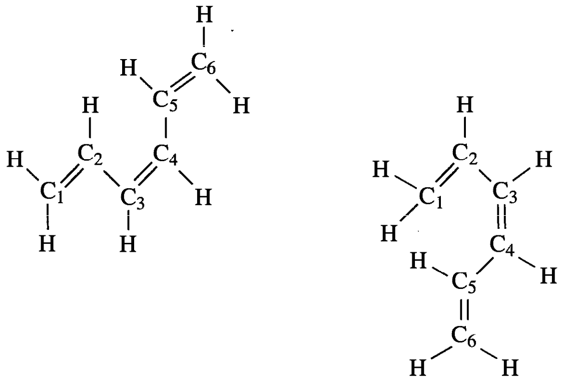


Figure 7.3

The off-diagonal elements of **P** corresponding to directly bonded atoms are referred to as (π-electron) *bond orders*. Hexatriene shows *bond-length alternation*: there are distinct single and double bonds. Notice that the bond orders for the bonded atom pairs show a related alternation.

7.1.3 Benzene

A similar calculation on benzene gives the following:

$$\mathbf{P} = \begin{pmatrix} 1.0000 & 0.6667 & 0.0000 & -0.3333 & 0.0000 & 0.6667 \\ 0.6667 & 1.0000 & 0.6667 & 0.0000 & -0.3333 & 0.0000 \\ 0.0000 & 0.6667 & 1.0000 & 0.6667 & 0.0000 & -0.3333 \\ -0.3333 & 0.0000 & 0.6667 & 1.0000 & 0.6667 & 0.0000 \\ 0.0000 & -0.3333 & 0.0000 & 0.6667 & 1.0000 & 0.6667 \\ 0.6667 & 0.0000 & -0.3333 & 0.0000 & 0.6667 & 1.0000 \end{pmatrix} \tag{7.6}$$

Experimentally, all the C–C bonds in benzene are of equal length, and this is mirrored by the C–C bond orders.

7.2 BOND LENGTHS AND THE HÜCKEL MODEL

It was noted many years ago that the π-electron bond orders correlated well with experimental bond lengths. Simple relationships such as

$$R_{ij}/\mathrm{pm} = 150 - 16P_{ij} \tag{7.7}$$

were found to be useful, and you might like to read Streitwieser's book (1961) for more details.

Off-diagonal elements of **P** corresponding to non-bonded atoms can be negative. They arise because **P** has to satisfy the orthonormality constraint **PSP** = 4**P**. They are not assigned any deep physical meaning.

7.3 MOLECULAR MECHANICS OF π-ELECTRON SYSTEMS

Many MM packages now give special consideration to π-electron systems for the following reason. MM force fields are usually parameterized according to the classical valence description of a given 'heavy' atom: for example, C(sp), C(sp^2) or C(sp^3) depending on the local symmetry of the carbon atom. It was found that this gave a poor representation to the enthalpies of formation of conjugated systems and so a correction is usually made. We test for the presence of a conjugated system, perform a Hückel calculation on the input geometry and then adjust the bond lengths in accordance with the calculated bond orders. The MM calculation is then made on this adjusted geometry, in a self-consistent fashion.

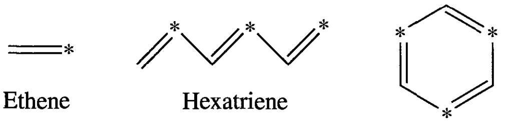
7.4 ALTERNANT HYDROCARBONS

An important distinction for conjugated hydrocarbons is the classification into *alternant* and *non-alternant* hydrocarbons. Alternant hydrocarbons are those like ethene, hexatriene, benzene and naphthalene where we can divide the carbon atoms into two sets called 'starred' and 'unstarred', such that no member of one set is directly bonded to another member (Figure 7.4).

This division is not possible for other hydrocarbons such as fulvene and heptafulvene (Figure 7.5).

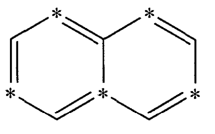
Hückel calculations on alternant hydrocarbons have the following characteristics:

- Hückel orbital energies come in pairs, $\alpha \pm k\beta$ The MO with positive k is a bonding orbital, that with negative k is an antibonding one.
- In each pair, provided there are no degeneracies, the LCAO coefficients for the 2p$_\pi$ orbital on each carbon atom has the same modulus.
- The coefficients of the starred (or unstarred) atoms change sign in each pair.



Ethene Hexatriene

Benzene



Naphthalene

Figure 7.4

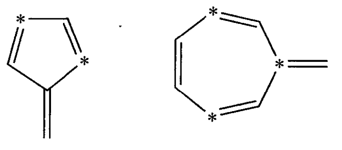

Fulvene Heptafulvene

Figure 7.5

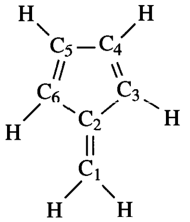


Figure 7.6

Table 7.3 Hückel π-electron calculation on fulvene

Orbital energy ε	LCAO coefficients					
$\alpha_C + 2.115\beta_{CC}$	0.2473	0.5230	0.4294	0.3851	0.3851	0.4294
$\alpha_C + 1.000\beta_{CC}$	−0.5000	−0.5000	0	0.5000	0.5000	0
$\alpha_C + 0.618\beta_{CC}$	0	0	−0.6015	−0.3717	0.3717	0.6015
$\alpha_C - 0.254\beta_{CC}$	0.7495	−0.1904	−0.3505	0.2795	0.2795	−0.3505
$\alpha_C + 1.618\beta_{CC}$	0	0	0.3717	−0.6015	0.6015	−0.3718
$\alpha_C + 1.861\beta_{CC}$	−0.3566	0.6635	−0.4390	0.1535	0.1535	−0.4390

A consequence of these findings is that the π-electron charges are all exactly equal to 1, for the ground state of every alternant hydrocarbon. (Coulson and Rushbrooke, 1940).

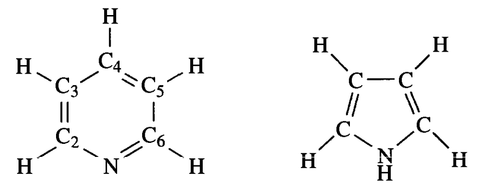
For the record, a Hückel calculation on fulvene gives the results in Table 7.3. I leave you to verify that the π-electron **P** matrix diagonal elements are 0.6223, 1.0470, 1.0923, 1.0730, 1.0730 and 1.0923.

7.5 TREATMENT OF HETEROATOMS

How does the Hückel π-electron model deal with pyridine? Nitrogen is more electronegative than carbon, so the N atom ought to have a higher (more negative) π-electron charge than a carbon atom in benzene. It is conventional to write the heteroatom (X and Y are used to denote heteroatoms such as N and O) parameters in terms of the standard α_C and β_{CC} as

$$\begin{aligned} \alpha_X &= \alpha_C + h_X\beta_{CC} \\ \beta_{XY} &= k_{XY}\beta_{CC} \end{aligned} \tag{7.8}$$

A trial calculation shows that h_N must be positive, and different authors recommend values ranging from 0.5 to 1.2. The value of k_{CN} is sometimes taken as 0.8,



Pyridine Pyrrole

Figure 7.7

Table 7.4 Heteroatom parameters for CX

Atom X	h_X	k_{CX}
C	0	1
N (donates one π-electron)	0.5	0.8
N (donates two π-electrons)	1.5	1.0
B	−1.0	0.7
O (donates one π-electron)	1.0	0.8
CH_3	2.0	0.7

sometimes as 1. There is a certain subjectivity to the choice. Not only that, the nitrogen atom in pyridine formally contributes one π-electron to the conjugated system, but the nitrogen atom in pyrrole formally contributes two π-electrons and so should have different parameters (Figure 7.7):

Some suggested values of the h and k parameters are shown in Table 7.4.

A calculation on pyridine using the values suggested above gives a **P** matrix

$$\mathbf{P} = \begin{pmatrix} 1.2452 & 0.6380 & -0.0268 & -0.3528 & -0.0268 & 0.6380 \\ 0.6380 & 0.9065 & 0.6866 & 0.0767 & -0.3134 & -0.0935 \\ -0.0268 & 0.6866 & 1.0047 & 0.6554 & 0.0046 & -0.3134 \\ -0.3528 & 0.0767 & 0.6554 & 0.9326 & 0.6554 & 0.0767 \\ -0.0268 & -0.3134 & 0.0046 & 0.6554 & 1.0047 & 0.6866 \\ 0.6380 & -0.0935 & -0.3134 & 0.0767 & 0.6866 & 0.9065 \end{pmatrix} \tag{7.9}$$

which gives the nitrogen atom a formal charge of $(1.2452 - 1)$ electrons, the 1 subtraction arising from the net charge of the nucleus and σ-electrons.

Contrary to popular belief, Hückel π-electron theory is not dead and buried. Papers appear from time to time dealing with topics such as dielectric susceptibilities (McIntyre and Hameka, 1978) and soliton dynamics (Su and Schrieffer, 1980).

7.6 EXTENDED HÜCKEL THEORY

Hückel's calculations on planar conjugated systems were extensively exploited, and I refer you once again to Streitwieser's classic book, *Molecular Orbital Theory for Organic Chemists*. What few calculations that had been done at that time on the σ framework had used the method of linear combination of bond orbitals.

The pioneering calculations of Wolfsberg and Helmholtz on MnO_4^-, CrO_4^- and ClO_4^- are usually cited as the first applications of 'extended' Hückel theory.

The Spectra and Electronic Structure of the Tetrahedral Ions MnO_4^-, CrO_4^{2-} and ClO_4^-
Max Wolfsberg and Lindsay Helmholtz
Journal of Chemical Physics, **20** (1952) 837–843

We have made use of a semiempirical treatment to calculate the energies of the molecular orbitals for the ground state and the first few excited states of permanganate, chromate and perchlorate ions. The calculation of the excitation energies is in agreement with the qualitative features of the observed spectra, i.e. absorption in the far ultraviolet for ClO_4^- with two strong maxima in the visible or near ultraviolet for MnO_4^- and CrO_4^{2-} with the chromate spectrum displaced towards higher energies. An approximate calculation of the relative f-values for the first two transitions in CrO_4^{2-} and MnO_4^- is also in agreement with experiment.

The data on the absorption spectra of permanganate ion in different crystalline fields is interpreted in terms of the symmetries of the excited states predicted by our calculations.

The Extended Hückel model treats all valence electrons within the spirit of the π-electron model. Each molecular orbital is written as an LCAO expansion of the valence orbitals, which can be thought of as being Slater-type orbitals (to look ahead to Chapter 9). Slater-type orbitals are very similar to hydrogenic ones except that they do not have radial nodes. Once again we can understand the model best by considering the HF–LCAO equations

$$\mathbf{h}^{\mathrm{F}}\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_i$$

For H and He, the atomic basis set consists of a single 1s orbital. For Li through Ne, the inner-shell electrons are treated as part of the nucleus and the basis functions used are atomic 2s, $2p_x$, $2p_y$ and $2p_z$. For Na through Al, the inner shell is treated as part of the nucleus and we consider only 3s, $3p_x$, $3p_y$ and $3p_z$ orbitals. For Si through Cl we have to decide on whether or not to include the atomic 3d-orbitals in addition, and practice varies. Most authors include them.

The diagonal elements of the HF–LCAO matrix are taken to be the negatives of the valence shell ionization energy for the orbital in question. These can be determined from a study of atomic spectra.

The off-diagonal elements of the HF–LCAO matrix are usually taken to be

$$h_{ij}^{\mathrm{F}} = kS_{ij}\frac{h_{ii}^{\mathrm{F}} + h_{jj}^{\mathrm{F}}}{2} \tag{7.10}$$

where S_{ij} is the overlap integral between the two basis functions χ_i and χ_j. The k is a 'constant' that has to be adjusted to give agreement with experiment, and common experience is that $k = 1.75$ is a reasonable choice

To use the chlorate ion example cited by Wolfsberg and Helmholtz, we would use a basis set comprising 2s and 2p orbitals on oxygen with 3s, 3p and 3d orbitals on chlorine, giving a total of 25 basis functions. That gives 16 doubly occupied valence shell molecular orbitals (made up as follows: 6 valence electrons from each oxygen, 7 from chlorine and 1 from the excess negative charge). A standard extended Hückel calculation (using HyperChem) with a tetrahedral geometry and bond length of 145 pm gave the results, in Table 7.5.

The oxygen atoms carry a formal charge of −0.7854 whilst the chlorine carries a charge of 2.1411.

An isosurface plot of the electron density is shown in Figure 7.8.

A key part to an extended Hückel treatment is the calculation of overlap integrals. You might like to read the classic work:

Formulas and Numerical Tables for Overlap Integrals
R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff
The Journal of Chemical Physics **17** (1949) 1248–1267

Explicit formulas and numerical tables for the overlap integral S between AOs (atomic orbitals) of two overlapping atoms a and b are given. These cover all the most important combinations of AO pairs involving ns, npσ and npπ AOs. They are based on approximate AOs of the Slater type, each containing two parameters μ [equal to $Z/(n - \delta)$], and $n - \delta$, where $n - \delta$ is an effective principal quantum number. The S formulas are given as functions of two parameters p and t, where $p = \frac{1}{2}(\mu_A + \mu_B)R/a_0$, R being the interatomic distance, and $t = (\mu_A - \mu_B)/(\mu_A + \mu_B)$. Master tables of computed values of S are given over wide ranges of p and t values corresponding to actual molecules, and also including the case $p = 0$ (intra-atomic overlap integrals). In addition, tables of computed S values are given for several cases involving 2-quantum s, p hybrid AOs.

Table 7.5 LCAO molecular orbitals for the chlorate ion

Summetry	Orbital energy/eV
$1a_1$	−39.983
$1t_2$	−32.839
$2a_1$	−19.361
$2t_2$	−16.900
1e	−15.554
$3t_2$	−15.007
$1t_1$	−14.543

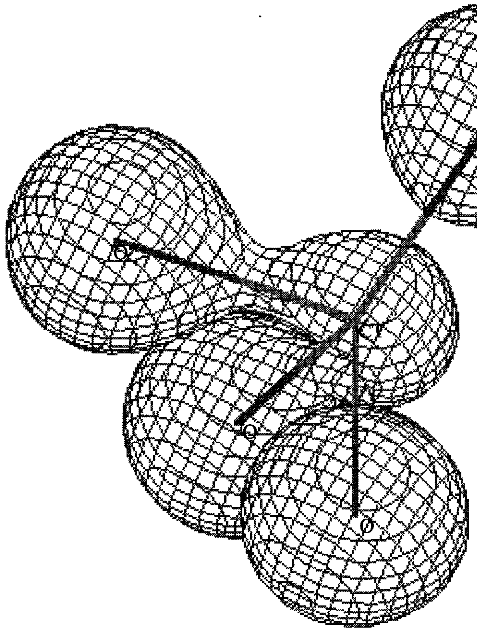


Figure 7.8 Isosurface grid of chlorate anion

The systematic application of extended Hückel theory to organic molecules comes with the work of Hoffmann.

An Extended Hückel Theory. I Hydrocarbons
Roald Hoffmann
The Journal of Chemical Physics **39** (1963) 1397–1412

The Hückel theory, with an extended basis set consisting of 2s and 2p carbon and 1s hydrogen orbitals, with inclusion of overlap and all interactions, yields a good qualitative solution of most hydrocarbon conformational problems. Calculations have been performed within the same parameterization for nearly all simple saturated and unsaturated compounds, testing a variety of geometries for each. Barriers to internal rotation, ring conformations, and geometrical isomerism are among the topics treated. Consistent σ and π charge distributions and overlap populations are obtained for aromatice and their relative roles discussed. For alkanes and alkenes charge distributions are also presented. Failures include overemphasis on steric factors, which leads to some incorrect isomerization energies; also the failure to predict strain energies, It is stressed that the geometry of a molecule appears to be its most predictable property.

7.7 THE NIGHTMARE OF THE INNER SHELLS

At the beginning of this chapter, I introduced the notion that the 16 electrons in ethene could be divided conceptually into two sets, the 14 σ and the 2 π electrons. Let me refer to the space and spin variables as $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{16}$, and for the minute I will formally label electrons 1 and 2 as the π-electrons, with 3 through 16 the σ-electrons. Methods such as Hückel π-electron theory aim to treat the π-electrons in an effective field due to the nuclei and the remaining σ electrons. To see how this might be done, let's look at the electronic Hamiltonian and see if it can be sensibly partitioned into a π-electron part (electrons 1 and 2) and a σ part (electrons 3 through 16). We have

$$\hat{H}_e = -\frac{h^2}{8\pi^2 m_e}\sum_{i=1}^{16}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{16}\sum_{\alpha=1}^{6}\frac{Z_\alpha}{R_{\alpha,i}} + \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{15}\sum_{j=i+1}^{16}\frac{1}{r_{ij}} \tag{7.11}$$

If we were to write

$$\hat{H}_e = \hat{H}_\sigma + \hat{H}_\pi + \hat{H}_{\text{int}} \tag{7.12}$$

where $\hat{H}_\sigma$ contains only the coordinates of the σ-electrons, $\hat{H}_\pi$ contains the coordinates of the π-electrons and $\hat{H}_{\text{int}}$ contains all the terms left over, then we would have for example

$$\hat{H}_\sigma = -\frac{h^2}{8\pi^2 m_e}\sum_{i=3}^{16}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{16}\sum_{\alpha=1}^{6}\frac{Z_\alpha}{R_{\alpha,i}} + \frac{e^2}{4\pi\epsilon_0}\sum_{i=3}^{15}\sum_{j=i+1}^{16}\frac{1}{r_{ij}} \tag{7.13}$$

If it weren't for the interaction terms such as

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{1,15}}$$

then we would be able to concentrate on each set of electrons independently.

There is actually a further problem to do with the Pauli principle. Suppose that we had been able to calculate a wavefunction for the σ-electron and the π-electron parts, written

$$\Psi_\sigma(\mathbf{x}_3, \mathbf{x}_4, \ldots, \mathbf{x}_{16}) \text{ and } \Psi_\pi(\mathbf{x}_1, \mathbf{x}_2)$$

Each of them will have to satisfy the Pauli principle. We might be tempted to write a total wavefunction for the 16 electrons as

$$\Psi_\sigma(\mathbf{x}_3, \mathbf{x}_4, \ldots, \mathbf{x}_{16})\Psi_\pi(\mathbf{x}_1, \mathbf{x}_2) \tag{7.14}$$

but we would then run into a problem. The total wavefunction has to change sign if we interchange the names of two of the π-electrons (which it does) and if we interchange the names of two of the σ-electrons (which it does). Finally it has to change sign if we interchange the name of one of the σ-electrons with that of one of the π-electrons (which it doesn't). We have to allow for this shortcoming in constructing the total wavefunction.

A full analysis shows that it is indeed possible to treat either group of electrons as if they were experiencing an average field due to the nuclei and the other group. The subject is dealt with in more advanced texts, such as McWeeny and Sutcliffe (1969).

Hückel theory goes way beyond this and approximates entire matrix elements to constants. But during the early days of quantum chemistry, it soon became customary to simplify the problem of molecular binding between many-electron atoms by treating the valence electrons alone, regarding the atomic nuclei and inner shells as simple localized positive charges. This simple valence electron approximation gave remarkably satisfactory results, yet at first sight there seemed no justifiable mathematical grounds for the approximation. Van Vleck and Sherman (1935) referred to the problem as the 'nightmare of the inner shells'.

7.8 BUT WHAT *IS* THE HÜCKEL HAMILTONIAN?

A basic tenet of the Hückel π-electron theory is that the orbital energies add to give the π-electron energy. Yet I demonstrated earlier that HF orbital energies do not add in this way, so the Hückel Hamiltonian cannot be strictly identified with the HF Hamiltonian.

The accepted wisdom is that the Hückel Hamiltonian matrix should be identified with the matrix $(\mathbf{h}^{\mathrm{F}} - \frac{1}{2}\mathbf{G})$ where $\mathbf{G}$ is the electron repulsion matrix of Chapter 6. The basis for this belief is that that the matrix $(\mathbf{h}^{F} - \frac{1}{2}\mathbf{G})$ has eigenvalues that do sum correctly to the electronic energy.

8 NEGLECT OF DIFFERENTIAL OVERLAP MODELS

Hückel models of molecular electronic structure enjoyed many years of popularity, particularly the π-electron variants. Authors sought to extract the last possible amount of information from these models, perhaps because nothing more refined was technically feasible at the time. Thus, for example, the inductive effect was studied. The inductive effect is a key concept in organic chemistry: a group R should show a +I or a −I effect (according to the nature of the group R) when it is substituted into a benzene ring.

Wheland and Pauling (1959) tried to explain the inductive effect in terms of π-electron theory by varying the α_X and β_{XY} parameters for nearest-neighbour atoms, then for next-nearest-neighbour atoms and so on. But, as many authors have also pointed out, it is always easy to introduce yet more parameters into a simple model, obtain agreement with an experimental finding and then claim that the model represents some kind of absolute truth.

A great failing of the Hückel models is their treatment of electron repulsion. Electron repulsion is not treated explicitly; it is somehow averaged within the spirit of Hartree–Fock theory. I gave you a Hückel π-electron treatment of pyridine in Chapter 7. Orbital energies are shown in Table 8.1.

Table 8.1 Hückel orbital energies for pyridine

Orbital ψ_i	ε_i
1	$\alpha_C + 1.954\,\beta_{CC}$
2	$\alpha_C + 1.062\,\beta_{CC}$
3	$\alpha_C + 1.000\,\beta_{CC}$
4	$\alpha_C - 0.667\,\beta_{CC}$
5	$\alpha_C - 1.000\,\beta_{CC}$
6	$\alpha_C - 1.849\,\beta_{CC}$

The electronic ground state corresponds to a configuration $\psi_1^2\psi_2^2\psi_3^2$ and the lowest excited states, both singlet and triplet, correspond to $\psi_1^2\psi_2^2\psi_3^1\psi_4^1$. Because electron repulsion is not treated explicitly, these two excited states have the same energy, $(\alpha_{\mathrm{C}} - 0.667\,\beta_{\mathrm{CC}}) - (\alpha_{\mathrm{C}} + 1.000\,\beta_{\mathrm{CC}}) = -1.667\,\beta_{\mathrm{CC}}$ above the electronic ground state (recall that β_{CC} is a negative quantity). Experimentally, triplet excited states are usually lower in energy than the corresponding singlet ground state. A second failure of the simple π-electron models is that they cannot treat $\mathrm{n} \rightarrow \pi^*$ excitations, only $\pi \rightarrow \pi^*$.

8.1 THE π-ELECTRON ZERO DIFFERENTIAL OVERLAP MODELS

The next step came in the 1950s, with more serious attempts to include formally the effect of electron repulsion between the valence electrons. First came the π-electron models associated with the name of Pople, and with Pariser and Parr. You might like to read the synopses of their first papers.

Electron Interaction in Unsaturated Molecules
J. A. Pople
Transactions of the Faraday Society **49** (1953) 1375–1385

An approximate form of the molecular orbital theory of unsaturated hydrocarbon molecules in their ground states is developed. The molecular orbital equations rigorously derived from the correct many-electron Hamiltonian are simplified by a series of systematic approximations and reduce to equations comparable with those used in the semi-empirical method based on an incompletely defined one-electron Hamiltonian. The two sets of equations differ, however, in that those of this paper include certain important terms representing electronic interactions. The theory is used to discuss the resonance energies, ionization potentials, charge densities, bond orders and bond lengths of some simple hydrocarbons. The electron interaction terms introduced in the theory are shown to play an important part in determining the ionization potentials. It is also shown that the uniform charge density theorem, proved by Coulson and Rushbrooke for the simpler theory, holds also for the self consistent orbitals derived by the method of this paper.

A Semi-Empirical Theory of the Electronic Spectra and Electronic Structure of Complex Unsaturated Molecules
R. Pariser and R. G. Parr
The Journal of Chemical Physics **21** (1953) 466–471

A semi-empirical theory is outlined which is designed for the correlation and prediction of the wavelengths and intensities of the first main visible

> or ultraviolet bands and other properties of complex unsaturated molecules, and preliminary application of the theory is made to ethylene and benzene.
>
> The theory is formulated in the language of the purely theoretical method of the antisymmetrized products of molecular orbitals (in LCAO approximation) including configuration interaction, but departs from this theory in several essential respects. First, atomic orbital integrals involving the core Hamiltonian are expressed in terms of quantities which may be regarded as semi-empirical. Second, an approximation of zero differential overlap is employed and an optionally uniformly charged sphere representation of atomic π-orbitals is introduced, which greatly simplify the evaluation of electronic repulsion integrals and make applications to complex molecules containing heteroatoms relatively simple. Finally, although the theory starts from the π-electron approximation, in which the unsaturated electrons are treated apart from the rest, provision is included for the adjustment of the σ-electrons to the π-electron distribution in a way which does not complicate the mathematics.

We often speak of the PPP (Pariser–Parr–Pople) model in honour of these three authors. Thinking of the pyridine example above, we still divide the 42 electrons into two groups, the 6 π-electrons and the 36 σ-electrons. The spirit of the PPP model is that the σ-electrons and the atomic nuclei provide a potential for the π-electrons. Attention focuses on the π-electrons.

You probably noted that the original papers were couched in terms of HF–LCAO theory. From Chapter 6, the defining equation for a Hamiltonian matrix element (in the usual doubly occupied molecular orbital, closed-shell case) is

$$\begin{aligned}
h^{\mathrm{F}}_{ij} &= \int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\
&\quad + \sum_{k=1}^{n}\sum_{l=1}^{n} P_{kl} \iint \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\
&\quad - \frac{1}{2}\sum_{k=1}^{n}\sum_{l=1}^{n} P_{kl} \iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2
\end{aligned} \qquad (8.1)$$

In the PPP model, each first-row atom such as carbon and nitrogen contributes a single basis function to the π system. Just as in Hückel theory, the orbitals χ_i are not rigorously defined but we can visualize them as $2\mathrm{p}_\pi$ atomic orbitals. Each first-row atom contributes a certain number of π-electrons — in the pyridine case, one electron per atom just as in Hückel π-electron theory.

It is usual to assume that the basis functions are normalized and orthogonal. Unnormalized basis functions can easily be normalized, but ordinary atomic $2\mathrm{p}_\pi$

orbitals are *not* orthogonal. Just live with this apparent contradiction for the minute.

8.1.1 The ZDO Approximation

The two-electron integrals in equation 8.1 above pose an immense problem. There are potentially very many of them; for n basis functions there are roughly $n^{3.5}$ unique integrals. As six-dimensional singular integrals, they can also be difficult to evaluate. The PPP model makes the *zero differential overlap* (ZDO) approximation: whenever a product of two basis functions $\chi_i(\mathbf{r})\chi_j(\mathbf{r})\,\mathrm{d}\tau$ appears under an integral sign in a two-electron integral, the integral is taken to be zero unless $i = j$. So for example

$$\begin{aligned}&\iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\\ &\quad = \delta_{ik}\delta_{jl}\iint \chi_i^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \qquad (8.2)\end{aligned}$$

where the Kronecker δ is defined as 0 when the subscripts are different, 1 when the subscripts are the same. Note that I have used the ZDO approximation twice in this equation, once for the coordinates of each electron.

This approximation has the immense advantage of reducing the number of integrals to be calculated, and we could in principle calculate the remainder of them exactly if we knew which basis functions were involved. When Pariser and Parr first tried to calculate the excitation energies of unsaturated hydrocarbons on the assumption that the basis functions χ_i were ordinary $2\mathrm{p}_\pi$ orbitals, they got very poor agreement with experiment. But when they treated the integrals as parameters that had to be fixed by appeal to experiment, they got much better agreement.

Many simple schemes have been put forward for these repulsion integrals, which are usually written γ_{ij}. They are taken to depend on the type of atoms that basis function χ_i and χ_j are centred on, and on the distance between the atomic centres. Pariser and Parr made use of the *uniformly charged sphere representation* illustrated in Figure 8.1.

The spheres represent (roughly) the $2\mathrm{p}_\pi$ atomic orbitals on C and N, and half an electron resides in each sphere. The mutual potential energy of this charge distribution can be easily calculated from elementary electrostatics. For small distances, a polynomial fit was used instead.

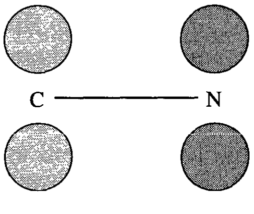


Figure 8.1 A pair of atoms

The simplest formula used over the years for the γ_{ij} is probably that due to Nishimito and Forster (1966), who wrote

$$\gamma_{ij} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{R_{ij} + a_{ij}} \tag{8.3}$$

which corresponds to the mutual potential energy of a pair of (point) electrons separated by distance $R_{ij} + a_{ij}$. In the spirit of PPP theory, a_{ij} is treated as a parameter.

8.1.2 The One-Electron Terms

Now for the one-electron terms in the HF Hamiltonian matrix

$$\int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

For bonded atoms, the 'off-diagonal' terms (where $i \neq j$) are taken to depend on the type and length of the bond joining the atoms on which the basis functions χ_i and χ_j are centred. The entire integral is written as a constant, β_{ij}, which is not the same as the β_{XY} in Hückel π-electron theory. The β_{ij} are taken to be parameters, fixed by calibration against experiment. It is usual to set β_{ij} to zero when the pair of atoms are not formally bonded.

The 'diagonal' terms (where $i = j$) need a little more consideration. They are taken to depend on the nature of the atom on which basis function χ_i is centred, but they also depend on the nature of the neighbouring atoms.

We have, from Chapter 6

$$\hat{h}(\mathbf{r}_i) = -\frac{h^2}{8\pi^2 m_{\mathrm{e}}}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha=1}^{N}\frac{Z_\alpha}{R_{\alpha i}}$$

where N is the number of nuclei. Thus,

$$\int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1 = \int \chi_i(\mathbf{r}_1)\left(-\frac{h^2}{8\pi^2 m_{\mathrm{e}}}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha=1}^{N}\frac{Z_\alpha}{R_{\alpha 1}}\right)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

and we separate out the kinetic energy term and the contribution from the nucleus on which χ_i is centred. If basis function χ_i is centred on nucleus I which has charge Z_I, these terms are

$$\int \chi_i(\mathbf{r}_1)\left(-\frac{h^2}{8\pi^2 m_{\mathrm{e}}}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z_{\mathrm{I}}}{R_{\mathrm{I},1}}\right)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1 \tag{8.4}$$

This is taken to be the atomic *valence state ionization energy*, invariably written ω_i and treated as an empirical parameter to be determined by fitting an experimental result.

The remaining terms such as

$$\int \chi_i(\mathbf{r}_1)\left(-\frac{e^2}{4\pi\epsilon_0}\frac{Z_J}{R_{J,1}}\right)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1 \tag{8.5}$$

are given values of $-Z_J\gamma_{ij}$, according to the approximations introduced by Goeppert-Mayer and Sklar (1938).

To collect up terms and summarize, the HF Hamiltonian matrix has elements

$$\begin{aligned} h_{ii}^{\mathrm{F}} &= \omega_i + \frac{1}{2}P_{ii}\gamma_{ii} + \sum_{j\neq i}(P_{jj} - Z_J)\gamma_{ij} \\ h_{ij}^{\mathrm{F}} &= \beta_{ij} - \frac{1}{2}P_{ij}\gamma_{ij} \end{aligned} \tag{8.6}$$

The calculation usually proceeds along the traditional lines of HF–LCAO theory. We make an initial estimate of the electron density matrix **P**, calculate a revised $\mathbf{h}^{\mathrm{F}}$ and iterate until the electron density and the HF matrix are self-consistent.

In order to perform PPP calculations, we need a molecular geometry because integral evaluation depends on interatomic separations. In the early days, no one addressed the possibility of geometry optimization and very few accurate X-ray structures were known. For that reason, one tended to adopt a cavalier approach and treat conjugated structures as regular figures with reasonable bond lengths. So for pyridine I would have assumed a regular hexagon with equal bond lengths of 140 pm. Output from a 1960s-style PPP calculation consisted of a table of HF–LCAO orbital coefficients, energies and the **P** matrix. Table 8.2 gives the first two of these for pyridine. Atom number 1 is the N atom, as in Chapter 6.

In HF–LCAO theory, the electronic ground state of pyridine is $\psi_1^2\psi_2^2\psi_3^2$. We would write this as a single Slater determinant which I will denote Ψ_0. Electron configurations such as $\psi_1^2\psi_2^2\psi_3^1\psi_4^1$ are called *singly excited states*, and they give a rough and ready treatment of the genuine spectroscopic excited states of such a molecule. I will denote these as $\Psi_{\mathrm{A}}^{\mathrm{X}}$ where we have promoted an electron from a doubly occupied orbital ψ_{A} to the virtual (unoccupied) orbital ψ_{X}.

We have to take account of electron spin. It is necessary to write a combination of two Slater determinants in order to correctly describe the excited singlet states.

Table 8.2 Pariser–Parr–Pople HF–LCAO treatment of pyridine

Orbital ψ_i	Orbital energy ε_i/eV	LCAO coefficients c_1	c_2	c_3	c_4	c_5	c_6
1	−13.988	−0.562	−0.424	−0.337	−0.313	−0.337	−0.424
2	−11.127	0.539	0.165	−0.371	−0.617	−0.371	0.165
3	−10.394	0	−0.495	−0.505	0	0.505	0.495
4	−1.275	0.518	−0.349	−0.267	0.588	−0.267	−0.349
5	−0.907	0	0.505	−0.495	0	0.495	−0.505
6	1.965	0.353	−0.415	0.422	−0.420	0.422	−0.415

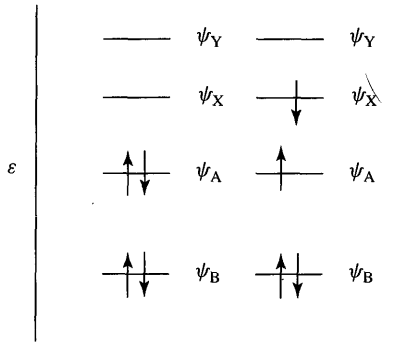


Figure 8.2 Electronic ground and singly excited state

There are 9 possible singly excited singlet states in our π-electron PPP treatment of pyridine, formed by promoting an electron from any one of the three filled orbitals to any of the three virtual ones. Their relative energies can be calculated using the Slater–Condon–Shortley rules. Relative to the energy of the ground state, the singly excited state Ψ_A^X has energy

$$\begin{aligned}\int \Psi_A^X \hat{H}_e \Psi_A^X \,d\tau = \varepsilon_X - \varepsilon_A \\ - \iint \psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_X(\mathbf{r}_2)\psi_X(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \\ + 2\iint \psi_A(\mathbf{r}_1)\psi_X(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_A(\mathbf{r}_2)\psi_X(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \qquad (8.7)\end{aligned}$$

where ε_X and ε_A are the orbital energies. In the Hückel model, the excited state energies depend only on differences of orbital energies whilst the PPP model gives an explicit treatment of electron repulsion.

The two-electron integrals over LCAO orbitals have to be evaluated from the LCAO coefficients and the γ_{ij}. In general, a two-electron integral

$$\iint \psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_X(\mathbf{r}_2)\psi_Y(\mathbf{r}_2)\,d\tau_1\,d\tau_2$$

is given by

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n}\iint a_i b_j c_k d_l \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,d\tau_1\,d\tau_2$$

which at first sight contains 6^4 contributions. The beauty of the ZDO approximation is that all but 36 of the integrals over the basis functions are zero and the calculation is pretty simple (in fact, there are only $\frac{1}{2}n(n+1)$ distinct two-electron integrals). The energies work out as shown in Table 8.3.

Table 8.3 Relative pyridine singly excited state singlet energies in the PPP model

State	Energy/eV
Ψ_0	0
Ψ_3^4	5.697
Ψ_2^5	6.544
Ψ_3^5	6.591
Ψ_2^4	6.897
Ψ_3^6	8.689
Ψ_1^4	9.095
Ψ_1^5	9.253
Ψ_2^6	9.327
Ψ_1^6	11.977

The next step might be to perform a configuration interaction calculation, in order to get a more accurate representation of the excited states. We touched on this for dihydrogen in an earlier chapter. To do this, we take linear combinations of the 10 states given above, and solve a 10 × 10 matrix eigenvalue problem to find the expansion coefficients. The diagonal elements of the Hamiltonian matrix are given above (equation 8.7), and it turns out that there is a simplification.

Brillouin's theorem (Brillouin, 1933) tells us that the singly excited states do not interact with the HF ground state. This theorem is true for all HF wavefunctions, and does not depend on the ZDO or LCAO approximations. This means that

$$\int \Psi_0 \hat{H}_e \Psi_A^X \, d\tau = 0 \tag{8.8}$$

and so we need not include Ψ_0 in the calculation. The remaining matrix elements are given by

$$\int \Psi_A^X \hat{H}_e \Psi_B^Y \, d\tau = -\iint \psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_X(\mathbf{r}_2)\psi_Y(\mathbf{r}_2)\, d\tau_1 \, d\tau_2$$
$$+ 2\iint \psi_A(\mathbf{r}_1)\psi_X(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_B(\mathbf{r}_2)\psi_Y(\mathbf{r}_2)\, d\tau_1 \, d\tau_2 \tag{8.9}$$

I won't give you the results in full, but on matrix diagonalization we find a description of the first excited singlet state as

$$-0.8288\Psi_3^4 + 0.5570\Psi_2^5 + 0.0203\Psi_3^6 - 0.0489\Psi_1^5$$

with an excitation energy of 4.984 eV, which is to be compared to an experimental transition energy of 4.90 eV. This is actually a very weakly allowed transition. The first strong singlet $\pi \rightarrow \pi^*$ transition is observed experimentally at 6.94 eV, to be compared with the value of 6.897 eV obtained from the configuration interaction calculation.

Notice that certain states (such as Ψ_3^5) don't appear in this particular excited state. This is because they have the wrong symmetry; only states of the same symmetry mix. I could have saved myself a great deal of unnecessary calculation by deciding which states correspond to which symmetry, and treating each symmetry species separately.

8.2 THE IDENTITY OF THE BASIS FUNCTIONS

Looking back, I seem to have made two contradictory statements about the basis functions χ_i used in the PPP model. On the one hand, I appealed to your chemical intuition and prior knowledge by suggesting that the basis functions should be regarded as 'ordinary' atomic orbitals of the correct symmetry (i.e. $2p_\pi$ orbitals). On the other hand, I told you that the basis functions used in such calculations are taken to be orthonormal and so

$$\int \chi_i(\mathbf{r})\chi_j(\mathbf{r})\,d\tau = 0$$

when $i \neq j$. How can we reconcile these two statements?

Think of ethene, where we use π basis functions χ_1 and χ_2. If we identify these as ordinary atomic $2p_\pi$ orbitals, then we can calculate the overlap matrix using the methods described earlier. I will write it as

$$\mathbf{S} = \begin{pmatrix} 1 & p \\ p & 1 \end{pmatrix} \tag{8.10}$$

where p is typically 0.25. The eigenvalues of $\mathbf{S}$ are $1 + p$ and $1 - p$, and the eigenvectors are

$$\mathbf{v}_1 = \sqrt{\frac{1}{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ and } \mathbf{v}_2 = \sqrt{\frac{1}{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

A short calculation will show you that $\mathbf{S}$ can be written in terms of its eigenvalues and eigenvectors as

$$\mathbf{S} = (1 + p)\mathbf{v}_1\mathbf{v}_1^{\mathrm{T}} + (1 - p)\mathbf{v}_2\mathbf{v}_2^{\mathrm{T}} \tag{8.11}$$

Other powers of $\mathbf{S}$ can be calculated in this way, for example the inverse

$$\mathbf{S}^{-1} = (1 + p)^{-1}\mathbf{v}_1\mathbf{v}_1^{\mathrm{T}} + (1 - p)^{-1}\mathbf{v}_2\mathbf{v}_2^{\mathrm{T}}$$

(although I should tell you that there are more practical ways of inverting such matrices than this) and the negative square root

$$\mathbf{S}^{-1/2} = (1 + p)^{-1/2}\mathbf{v}_1\mathbf{v}_1^{\mathrm{T}} + (1 - p)^{-1/2}\mathbf{v}_2\mathbf{v}_2^{\mathrm{T}} \tag{8.12}$$

The negative square root has the property that

$$(\mathbf{S}^{-1/2})^2 = \mathbf{S}^{-1}$$

It is widely accepted that the basis functions used in ZDO π-electron theory (which I will write for clarity χ^{ZDO}) are related to 'ordinary' $2\mathrm{p}_\pi$ atomic orbitals (which I will write χ^{A}) by the matrix transformation

$$(\chi_1^{\mathrm{ZDO}}\chi_2^{\mathrm{ZDO}}) = (\chi_1^{\mathrm{A}}\chi_2^{\mathrm{A}})\mathbf{S}^{-1/2} \tag{8.13}$$

These new basis functions can easily be shown to be orthonormal. It also turns out that two-electron integrals calculated using these orthogonalized basis functions do indeed satisfy the ZDO approximation much more closely than the ordinary basis functions.

Although I used the example of ethene, where $n = 2$, the same considerations apply to ZDO calculations on all conjugated molecules. All overlap matrices are real symmetric, positive definite and so have eigenvalues > 0.

8.3 THE 'ALL VALENCE ELECTRON' NDO MODELS

Prior to 1965, all we had in our armoury were the σ and π Hückel theories, and a very small number of rigorous calculations designated *ab initio* (to be discussed later). The aims of quantum chemistry in those days were to give total energies and charge distributions for 'real' molecules, and the seventh decimal place in the calculated properties of LiH. Practical chemists wanted things like reliable enthalpy changes for reactions, reaction paths, and so on. It should come as no surprise to learn that the practical chemists therefore treated theoreticians with scepticism.

Theoreticians did little to improve their case by proposing yet more complicated and obviously unreliable parameter schemes. For example, it is usual to call the C_2 axis of the water molecule the z-axis. The molecule doesn't care, it must have the same energy, electric dipole moment and enthalpy of formation no matter how we label the axes. I have to tell you that some of the more esoteric versions of extended Hückel theory did not satisfy this simple criterion. It proved possible to calculate different physical properties depending on the arbitrary choice of coordinate system.

To look ahead a little, there *are* properties that depend on the choice of coordinate system: the electric dipole moment of a charged species is origin-dependent in a well-understood way. But not the charge density or the electronic energy! Quantities that have the same value in any coordinate system are sometimes referred to as *invariants*, a term borrowed from the theory of relativity.

Pople and Santry seem to have been the first authors to give a systematic treatment of this problem. They identified two important types of transformation amongst the basis functions:

- transformations which mix those orbitals on the same atom that share common principal and azimuthal quantum numbers. For example, a rotation of axes would mix together the three 2p orbitals on a carbon atom;

transformations that can mix any of the atomic orbitals on the same atom. For example, descriptive organic chemistry emphasizes the carbon sp^3 hybrid atomic orbitals at the expense of the more usual 2s, $2p_x$, $2p_y$ and $2p_z$ ones.

In either case, the invariant physical property has to be the same before and after the transformation. Pople and coworkers proceeded to examine the consequences in the context of the 'all valence electron' NDO models. I write NDO rather than ZDO because the more sophisticated of these models retain many two-electron integrals that would be set to zero under the ZDO prescription.

8.3.1 CNDO/1 and CNDO/2

The most elementary 'all valence electron' NDO model is that known as 'complete neglect of differential overlap' (CNDO). Segal and Pople introduced this in 1966. Only valence electrons are explicitly treated, the inner shells being taken as part of the atomic core. The ZDO approximation is applied to the two-electron integrals, so that

$$\iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

$$= \delta_{ik}\delta_{jl}\iint \chi_i^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

In the π-electron theories, each first-row atom contributes a single basis function. For the 'all valence electron' models there is now an additional complication in that some of the basis functions could be on the same atomic centre. So how should we treat integrals involving basis functions all on the same atomic centre such as

$$\iint 2s^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)2s^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

$$\iint 2p_x^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)2s^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

$$\iint 2p_x^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)2p_y^2(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

And what if the basis functions are centred on different atoms? The CNDO solution to the problem is to take all possible integrals such as those above to be equal, and to assume that they depend only on the atoms A and B on which the basis functions are centred. This satisfies the rotational invariance requirement. In CNDO theory, we write the two-electron integrals as γ_{AB} and they are taken to have the same value irrespective of the basis functions on atom A and/or atom B. They are usually calculated exactly, but assuming that the orbital in question is a 1s orbital (for hydrogen) or a 2s orbital (for a first row atom).

Once again, I can explain the features of the model in terms of Hartree–Fock theory. The next step is therefore to investigate the one-electron integrals

$$\int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

The only difference from our discussion about π-electron systems is that there may be many basis functions on the same atomic centre.

The diagonal terms (where $i = j$) are conveniently divided into those contributions that refer to a given atomic centre (atom A), and those that refer to other atomic centres. In the following discussion, assume that basis function χ_i is centred on nucleus A. We have

$$\int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1 = \int \chi_i(\mathbf{r}_1)\left(-\frac{h^2}{8\pi^2 m_\mathrm{e}}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha=1}^{N}\frac{Z_\alpha}{R_{\alpha 1}}\right)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

and the term

$$\int \chi_i(\mathbf{r}_1)\left(-\frac{h^2}{8\pi^2 m_\mathrm{e}}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z_\mathrm{A}}{R_{\mathrm{A}1}}\right)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

looks like an 'atomic' quantity, since it only involves a basis function χ_i centred on atom A and the nuclear charge of that atom, Z_A. It is usually written U_{ii} and is determined from atomic spectroscopic data. The remaining terms are of the type

$$\int \chi_i(\mathbf{r}_1)\left(-\frac{e^2}{4\pi\epsilon_0}\frac{Z}{R_{\mathrm{B}1}}\right)\chi_i(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

and they represent physically the interaction of an electron in orbital χ_i with nucleus B. We call such terms *penetration integrals*, and they are usually denoted $-V_\mathrm{AB}$.

The off-diagonal terms ($i \neq j$) are treated to a similar analysis. Each penetration term involving different basis functions that are on the same atomic centre are given a value of $-V_\mathrm{AB}$ to maintain invariance. Suppose now that χ_i is centred on nucleus A and χ_j on nucleus B. We have

$$\int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1 = \int \chi_i(\mathbf{r}_1)\left(-\frac{h^2}{8\pi^2 m_\mathrm{e}}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{\alpha=1}^{N}\frac{Z_\alpha}{R_{\alpha 1}}\right)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1$$

and so

$$\begin{aligned}\int \chi_i(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\chi_{ji}(\mathbf{r}_1)\,\mathrm{d}\tau_1 = \int \chi_i(\mathbf{r}_1)&\left(-\frac{h^2}{8\pi^2 m_\mathrm{e}}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z_\mathrm{A}}{R_{\mathrm{A}1}}\right.\\ &\left.-\frac{e^2}{4\pi\epsilon_0}\frac{Z_\mathrm{B}}{R_{\mathrm{B}1}}\right)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1\\ &+\int \chi_i(\mathbf{r}_1)\left(-\sum_{\alpha\neq\mathrm{A,B}}\frac{e^2}{4\pi\epsilon_0}\frac{Z_\alpha}{R_{\alpha 1}}\right)\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1\end{aligned}$$

The final terms involve three atomic centres, and we neglect them. The two-centre terms are written $\beta^0_{\mathrm{AB}}S_{ij}$ where β^0_{AB} depends only on the nature of the atoms A and B, and S_{ij} is the overlap integral between orbitals χ_i (centred on atom A) and χ_j (centred on atom B). The overlap integrals are calculated as if the basis functions were 'ordinary' atomic orbitals.

A CNDO all-valence-electron HF–LCAO Hamiltonian matrix has elements

$$\begin{aligned} h^{\mathrm{F}}_{ii} &= U_{ii} + \left(P_{\mathrm{AA}} - \frac{1}{2}P_{ii}\right)\gamma_{\mathrm{AA}} + \sum_{\mathrm{B}\neq\mathrm{A}}(P_{\mathrm{BB}}\gamma_{\mathrm{AB}} - V_{\mathrm{AB}}) \\ h^{\mathrm{F}}_{ij} &= \beta^0_{\mathrm{AB}}S_{ij} - \frac{1}{2}P_{ij}\gamma_{\mathrm{AB}} \end{aligned} \tag{8.14}$$

I have collected together all the electron density terms involving basis functions on atom A into P_{AA}. These expressions are correct even if χ_i and χ_j are both centred on the same atom.

The original parameter scheme was called CNDO/1 (Pople and Segal, 1965), and allowed treatment of molecules containing hydrogen and all first-row atoms. The basis set was taken as Slater-type orbitals, and an orbital exponent of 1.2 was used for hydrogen. Overlap integrals were calculated exactly, but the basis functions were assumed orthogonal for the purpose of solving the HF–LCAO equations. Electron repulsion integrals γ_{AB} were calculated exactly, and the penetration integral was calculated exactly in CNDO/1 theory. The U_{ii} were found from a study of atomic energy levels. That leaves the 'bonding' parameter β^0_{AB}. In order to help minimize the number of parameters in the theory, the bonding parameters were estimated from atomic ones (denoted by a single subscript below) by a very simple additive scheme,

$$\beta^0_{\mathrm{AB}} = \beta^0_{\mathrm{A}} + \beta^0_{B} \tag{8.15}$$

In a fascinating variation on the usual theme of comparing with experiment, the atomic β values were chosen by comparison with matrix elements of accurate HF–LCAO Hamiltonians.

It turned out that CNDO/1 calculations gave poor predictions of molecular equilibrium geometries, and this failing was analysed as being due to the treatment of the U_{ii} and the penetration terms V_{AB}.

The CNDO/2 model came next (Pople and Segal, 1966). It differs from CNDO/1 in the way it handles U_{ii} and V_{AB}. The penetration term V_{AB} is no longer calculated exactly, but taken as $-Z_{\mathrm{B}}\gamma_{\mathrm{AB}}$. The atomic terms become

$$U_{ii} = -\frac{1}{2}(I_i + A_i) - \left(Z_{\mathrm{A}} - \frac{1}{2}\right)\gamma_{aa} \tag{8.16}$$

where I_i is the ionization energy of an appropriate valence state orbital and A_i the corresponding electron affinity. The basic HF–LCAO Hamiltonian matrix elements for the CNDO/2 model are.

$$h_{ii}^{\mathrm{F}} = -\frac{1}{2}(I_i + A_i) + \left((P_{\mathrm{AA}} - Z_{\mathrm{A}}) - \frac{1}{2}(P_{ii} - 1)\right)\gamma_{\mathrm{AA}} + \sum_{B \neq A}(P_{\mathrm{BB}}\gamma_{\mathrm{AB}} - V_{\mathrm{AB}}) \tag{8.17}$$

$$h_{ij}^{\mathrm{F}} = \beta_{\mathrm{AB}}^{0} S_{ij} - \frac{1}{2}P_{ij}\gamma_{\mathrm{AB}}$$

At this point, it is wise to see an example, and I will take H_2O with a bond length of 95.6 pm and bond angle of 104.5°. If I take the coordinate system such that the molecule lies in the *yz*-plane with coordinate origin given by the centre of mass, and the *z*-axis as the symmetry axis, then the Cartesian coordinates are given in Table 8.4.

The repulsion integrals can be calculated from standard formulae, and they come to the values shown in Table 8.5.

The overlap integrals (Table 8.6) were calculated from the master formulae of Mulliken *et al.* (1949).

Table 8.4 Cartesian coordinates for H_2O

Atom	x/pm	y/pm	z/pm
O	0	0	11.71
H_1	0	75.59	−46.82
H_2	0	−75.99	−46.82

Table 8.5 Electron repulsion integrals $\gamma_{\mathrm{AB}}/E_{\mathrm{h}}$ for H_2O

	O	H_1	H_2
O	0.8265	0.5013	0.5013
H_1		0.7500	0.3422
H_2			0.7500

Table 8.6 Overlap integrals S_{ij} for H_2O

	O(2s)	O(2p$_x$)	O(2p$_y$)	O(2p$_z$)	H_1(1s)	H_2(1s)
O(2s)	1	0	0	0	0.4803	0.4803
O(2p$_x$)		1	0	0	0	0
O(2p$_y$)			1	0	0.3031	−0.3031
O(2p$_z$)				1	−0.2347	−0.2347
H_1(1s)					1	0.2708
H_2(1s)						1

Table 8.7 CNDO/2 orbital energies and LCAO coefficients for H_2O

ε_i/E_h	O(2s)	O (2p$_x$)	O (2p$_y$)	O (2p$_z$)	H_1 (1s)	H_2 (1s)
−1.488	−0.8617	0	0	0.0696	−0.3554	−0.3554
−0.788	0	0	0.7589	0	0.4605	−0.4605
−0.713	−0.3164	0	0	−0.8480	0.3006	0.3006
−0.655	0	1	0	0	0	0
0.336	−0.3966	0	0	0.5254	0.5323	0.5323
0.351	0	0	−0.6512	0	0.5366	−0.5366

A CNDO/2 calculation gives the HF orbital energies and LCAO coefficients shown in Table 8.7.

8.3.2 CNDO/S

As I hinted earlier, a major objective for practitioners of ZDO π-electron theories was the treatment of molecular electronic spectra. These calculations were almost always made at the 'HF–LCAO plus singly excited configuration interaction' level of theory. Consumers of CNDO models had different goals, often the prediction of ground-state electronic properties, molecular geometries, reaction mechanisms, atomization energies, etc. When the CNDO models were applied to the prediction of electronic spectra, it was found that both CNDO/1 and CNDO/2 grossly overestimated electronic excitation energies, especially the singlet $n \rightarrow \pi^*$ states, and often predicted the wrong ordering for excited states. These models had the immense advantage of being able to treat both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within a sound theoretical framework, but something was obviously wrong somewhere.

The most significant treatment of excited states within the CNDO approach is that of Del Bene and Jaffé, who made three modifications to the original CNDO parameterization scheme. Two of the modifications were just minor tinkering with the integral evaluation, and need not concern us. The key point in their method was the treatment of the β parameters. Think of a pair of bonded carbon atoms in a large molecule. Some of the p-type basis functions on C_A will be aligned to those on C_B in a σ-type local fashion, some will be aligned in a π-type fashion. Del Bene and Jaffé introduced a new parameter κ such that the π-type interaction was reduced. They wrote

$$\begin{aligned} \beta_{ij}^{\sigma} &= \tfrac{1}{2}(\beta_A^0 + \beta_B^0)S_{ij} \\ \beta_{ij}^{\pi} &= \tfrac{1}{2}\kappa(\beta_A^0 + \beta_B^0)S_{ij} \end{aligned} \tag{8.18}$$

depending whether the atomic orbital pair χ_i (on atom A) and χ_j (on atom B) were locally σ or π to each other. Variation of κ over a range showed that $\kappa = 0.585$ gave the best agreement with experiment for many conjugated molecules.

The following is a key paper:

Use of the CNDO Method in Spectroscopy: I Benzene, Pyridine and the Diazines
Janet E. Del Bene and H. H. Jaffe
The Journal of Chemical Physics, **48** (1968) 1807–1813

The CNDO method has been modified by substitution of semiempirical Coulomb integrals similar to those used in the Pariser–Parr–Pople method, and by the introduction of a new empirical parameter to differentiate resonance integrals between σ orbitals and π orbitals. The CNDO method with this change in parameterization is extended to the calculation of electronic spectra and applied to the isoelectronic compounds benzene, pyridine, pyridazine, pyrimidine and pyrazine. The results obtained were refined by a limited CI calculation, and compared with the best available experimental data. It was found that the agreement was quite satisfactory for both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ singlet transitions. The relative energies of the π and the lone pair orbitals in pyridine and the diazines are compared and an explanation proposed for the observed orders. Also, the nature of the 'lone pairs' in these compounds is discussed.

8.3.3 INDO

The CNDO model makes a draconian assumption about the two-electron integrals

$$\iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,d\tau_1\,d\tau_2$$

$$= \delta_{ik}\delta_{jl}\iint \chi_i^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\chi_j^2(\mathbf{r}_2)\,d\tau_1\,d\tau_2$$

In the case that (for example) χ_i and χ_k are centred on the same atom, these integrals are far from zero. In any case, it is exactly these integrals that give the correct ordering between atomic spectroscopic states. Thus, for example, the CNDO model cannot distinguish energetically between the ^{3}P, ^{1}D and ^{1}S states arising from the orbital configuration

$$\mathrm{C} : (1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^2$$

and gives a zero spin density at all the atoms in a planar π-radical such as CH_3.

Pople, Beveridge and Dobosh introduced the *intermediate neglect of differential overlap* model (INDO) in 1967. INDO is CNDO/2 with a more realistic treatment of the one-centre two-electron integrals. In the spirit of such models, the non-zero integrals were calibrated against experiment rather than being calculated from first principles. The authors concluded that, although INDO was a little better than

CNDO/2 for predicting molecular geometries, it gave a vastly superior treatment of singlet–triplet splittings and spin densities.

8.3.4 NDDO

Just to finish this train of thought, the next logical step in the argument would be to retain all integrals of the type

$$\iint \chi_i(\mathbf{r}_1)\chi_k(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_j(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

where orbitals χ_i and χ_k are on one nuclear centre, with χ_j and χ_l on another. This is the essence of the *neglect of diatomic differential overlap* model (NDDO). For one reason or another, it never caught on.

8.3.5 MINDO

At this point, enter stage-left Michael Dewar and the *modified intermediate neglect of differential overlap* (MINDO) model. Dewar's objective was very simple: to develop a CNDO-style parameter scheme that would give a genuine working model for experimentalists, particularly organic chemists and biochemists. This is a very worthwhile goal, but there are certain implications. Any such model has to be capable of making chemical predictions to chemical accuracy: bond lengths of 0.1 pm, bond angles of 0.1°, enthalpies of formation that are correct to 0.1%, and so on. The model has to be parameterized for a range of atoms, not just carbon, nitrogen and hydrogen.

As a practical point, any computer code has to be transferable between platforms, so there is little point writing code in esoteric but obsolete languages such as French ALGOL.

I am conscious that I have missed many sets of acronyms from my guided tour of the differential overlap models, and I will just tell you that MINDO, MINDO/1, MINDO/2 all appeared but have now been consigned to oblivion. With MINDO/3, Dewar thought that he had at last developed a reliable model for use by organic chemists. The abstract to the landmark MINDO/3 paper is terse:

> Ground States of Molecules XXV MINDO/3. An Improved Version of the MINDO Semiempirical SCF-MO Method
> Richard C. Bingham, Michael J. S. Dewar and Donald H. Lo
> *Journal of the American Chemical Society* **97** (1975) 1285–1293
>
> The problems involved in attempts to develop quantitative treatments of organic chemistry are discussed. An improved version (MINDO/3) of the MINDO semiempirical SCF-MO treatment is described. Results obtained for a large number of molecules are summarized.

However, the 'Summary and Conclusions' section is more revealing:

> Summary and Conclusions
>
> MINDO/3 has thus proved to be an extraordinarily versatile procedure, giving good results for every ground state property so far studied and apparently offering hope of equal extension to excited states and photochemistry. Whilst it has not yet achieved 'chemical' accuracy, the average error in the calculated heats of atomization being ca. 6 kCal mol^{-1} instead of 1 kCal mol^{-1}, it has given no unreasonable results except in one area where the MINDO approximation would be expected to fail. The errors in the heats of atomization are in any case less by orders of magnitude than those (given by non-empirical) calculations or other semiempirical MO procedures. Moreover, the results for activation energies of reactions and for heats of formation of 'non-classical' ions seem definitely superior to those from (non-empirical) calculations, although admittedly there are few examples for comparison since few meaningful (non-empirical) calculations have been reported.

8.3.6 MNDO

The *modified neglect of differential overlap* (MNDO) model should probably come next; MNDO is like INDO except that MNDO treats the diatomic two-electron integrals more accurately. It retains all two-electron integrals involving 'monatomic' differential overlap, and the paper to read is probably:

> Ground States of Molecules 39 MNDO Results for Molecules containing
> Hydrogen, Carbon, Nitrogen and Oxygen
> Michael J. S. Dewar and Walter Thiel
> *Journal of the American Chemical Society* **99** (1977) 4907–4917
>
> Heats of formation, molecular geometries, ionization potentials and dipole moments are calculated by the MNDO method for a large number of molecules. The MNDO results are compared with the corresponding MINDO/3 results on a statistical basis. For the properties investigated, the mean absolute errors in MNDO are uniformly smaller than those in MINDO/3 by a factor of about 2. Major improvements of MNDO over MINDO/3 are found for the heats of formation of unsaturated systems and molecules with NN bonds, for bond angles, for higher ionization potentials, and for dipole moments of compounds with heteroatoms.

8.3.7 AM1

Again, let Dewar give the summary for the *Austin Model 1* (AM1):

> AM1: A New General Purpose Quantum Mechanical Molecular Model
> Michael J. S. Dewar, Eve G. Zoebisch, Eamonn F. Healey and James J. P. Stewart
> *Journal of the American Chemical society* **107** (1985) 3902–3909
>
> A new parametric quantum mechanical model AM1 (Austin model 1), based on the NDDO approximations, is described. In it the major weakness of MNDO, in particular the failure to reproduce hydrogen bonds, have been overcome without any increase in computer time. Results for 167 molecules are reported. Parameters are currently available for C, H, O and N.

According to Dewar, MNDO had a common tendency to overestimate repulsion between atoms at their van der Waals distances, and attempts to rectify this bad behaviour usually involved changing the core repulsion integrals. In AM1, these core repulsion integrals are modified by multiplying them by a sum of Gaussian functions, whose coefficients and exponents were all optimized. Dewar concluded, 'The main gains are the ability of AM1 to reproduce hydrogen bonds and the promise of better estimates of activation energies for reactions'.

Readers of this book from Austin, TX, will appreciate the significance of the acronym.

8.3.8 PM3

Parameterized Model 3 was developed by Stewart (1989) and is a reparameterization of AM1. PM3 differs from AM1 only in the values of the parameters used. PM3 has been parameterized for many main group elements.

8.3.9 ZINDO and ZINDO/S

These models were developed by Zerner and coworkers (Zerner, Anderson, and Edwards, 1986). ZINDO/1 is a variant of INDO, and ZINDO/S is an INDO method designed to predict spectroscopic transitions.

9 BASIS SETS

We must now consider the choice of a basis set. I have already made reference to hydrogenic orbitals and Slater orbitals without any real explanation. I have also hinted at the integrals problem: variational calculations almost always involve the calculation of a number of two-electron integrals over the basis functions

$$\iint \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2$$

These integrals can be terrifyingly difficult; they involve the spatial coordinates of a pair of electrons and so are six-dimensional. They are singular, in the sense that the integrand becomes infinite as the distance r_{12} between the electrons tends to zero. Each basis function could be centred on a different atom, and there is no obvious choice of coordinate origin in such a case.

Not only that, there are usually a lot of them. An HF–LCAO calculation with n basis functions requires the calculation and manipulation of about $n^4/8$ such integrals.

Then there is the question of quality. The variation principle only tells us about energies; we might calculate the variational integral

$$\varepsilon = \frac{\displaystyle\int \Psi^* \hat{H} \Psi\, \mathrm{d}\tau}{\displaystyle\int \Psi^* \Psi\, \mathrm{d}\tau}$$

to get a rough and ready criterion for the quality of a wavefunction and therefore a basis set. Suppose we have two different basis sets for carbon, nitrogen and hydrogen, and we perform HF–LCAO calculations on pyridine using both basis sets. At first sight, the basis set that gave the lower energy would seem to be the better one. Unfortunately, a basis set that is good for calculating the energy may be disastrous for calculating the electric dipole moment, and if your interest in life is electric dipole moments you would not be helped by the variation principle. The variation principle only 'works' for energy, there are no corresponding principles for the more chemically interesting properties.

So, back to the beginning.

9.1 HYDROGENIC ORBITALS

The time-independent electronic Schrödinger equation for a one-electron atom such as H or C^{5+} is

$$\left(-\frac{h^2}{8\pi^2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi_e = \varepsilon_e\psi_e \tag{9.1}$$

where μ is the reduced mass of the electron and the nucleus and Ze the nuclear charge.

Atoms are spherical objects, and what we do is to write the electronic Schrödinger equation in spherical polar coordinates, to mirror the symmetry of the problem.

$$\begin{aligned}&\frac{1}{r^2}\frac{\partial^2}{\partial r^2}\left(r^2\frac{\partial\psi_e}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi_e}{\partial\phi^2}\right)\\ &\quad + \frac{8\pi^2\mu}{h^2}\left(\varepsilon + \frac{Ze^2}{4\pi\epsilon_0}\right)\psi_e = 0\end{aligned} \tag{9.2}$$

The electronic Hamiltonian $\hat{H}_e$ commutes with both the square of the angular momentum operator $\hat{l}^2$ and its z-component $\hat{l}_z$ and so the three operators have simultaneous eigenfunctions. Solution of the electronic Schrödinger problem gives the well-known *hydrogenic atomic orbitals*

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{nl}(r)Y_{l,m_l}(\theta,\phi) \tag{9.3}$$

where the $Y_{l,m_l}(\theta,\phi)$ are eigenfunctions of the two angular momentum operators, and are known as 'spherical harmonics'. The radial function $R(r)$ satisfies the *radial equation*

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{8\pi^2\mu}{h^2}\left(\varepsilon + \frac{Ze^2}{4\pi\epsilon_0 r}\right) - \frac{l(l+1)}{r^2}\right]R = 0 \tag{9.4}$$

The bound states (where $\varepsilon < 0$) are characterized by the three quantum numbers n (the principal quantum number), l (the azimuthal quantum number) and m_l (the magnetic quantum number).

There are also *unbound states* for which the energy is positive. The unbound states are quite different from the bound ones, in that they are finite at infinity and at the origin. There is a continuous range of positive energies, and these correspond to ionization of the hydrogen atom. We will not need to consider the unbound states in this text.

The electronic energy of a free one-electron atom depends only on n:

$$\varepsilon_n = -\frac{\mu e^4 Z^2}{8\pi^2\epsilon_0^2}\frac{1}{n^2} \tag{9.5}$$

and these energies are in essential agreement with the results of simple experimental measurements.

In summary,

$$\begin{aligned} \hat{H}_e \psi_{nlm_l} &= \varepsilon_n \psi_{nlm_l} \\ \hat{l}^2 \psi_{nlm_l} &= l(l+1)\frac{h^2}{4\pi^2}\psi_{nlm_l} \\ \hat{l}_z \psi_{nlm_l} &= m_l \frac{h}{2\pi}\psi_{nlm_l} \end{aligned} \tag{9.6}$$

For $l = 1$, there are three possible values of m_l, namely $m_l = -1$, $m_l = 0$ and $m_l = +1$, which I can designate as the p_{-1}, p_0 and p_{+1} states. Their associated angular factors $Y_{l,m_l}(\theta, \phi)$ are (apart from any numerical factors)

$$\begin{aligned} &\sin(\theta)\exp(-j\phi) \text{ for } p_{-1} \\ &\cos(\theta) \text{ for } p_0 \\ &\sin(\theta)\exp(+j\phi) \text{ for } p_{+1} \end{aligned} \tag{9.7}$$

where j is the square root of -1. For many purposes in chemistry it is convenient to work with the so-called *real equivalents*,

$$\begin{aligned} p_x &= \frac{p_{+1} + p_{-1}}{\sqrt{2}} \\ p_z &= p_0 \\ p_y &= -j\left(\frac{p_{+1} - p_{-1}}{\sqrt{2}}\right) \end{aligned} \tag{9.8}$$

In order to get real equivalents for the d-orbitals, we take

$$\begin{aligned} d_{z^2} &= d_0 \\ d_{xz} &= \frac{d_{+1} + d_{-1}}{\sqrt{2}} \\ d_{yz} &= -j\left(\frac{d_{+1} - d_{-1}}{\sqrt{2}}\right) \\ d_{x^2-y^2} &= \frac{d_{+2} + d_{-2}}{\sqrt{2}} \\ d_{xy} &= -j\left(\frac{d_{+2} - d_{-2}}{\sqrt{2}}\right) \end{aligned} \tag{9.9}$$

Table 9.1 The 1s, 2s and 3s hydrogenic orbitals

n, l, m_l	Symbol	Expression
1,0,0	1s	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp(-\rho)$
2,0,0	2s	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)\exp\left(-\frac{\rho}{2}\right)$
3,0,0	3s	$\frac{2}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)\exp\left(-\frac{\rho}{3}\right)$

It is instructive to look at the form of the 1s, 2s and 3s orbitals (Table 9.1). By convention, we use the dimensionless variable $\rho = Zr/a_0$ rather than r. Here Z is the nuclear charge number and a_0 the first Bohr radius (approximately 52.9 pm). The quantity Z/n is usually called the *orbital exponent*, written ζ. These exponents have an increasing number of radial nodes, and they are orthonormal.

9.2 SLATER'S RULES

Exact solutions to the electronic Schrödinger equation are not possible for many-electron atoms, but atomic HF calculations have been done both numerically and within the LCAO model. In approximate work, and for molecular applications, it is desirable to use basis functions that are simple in form. A polyelectron atom is quite different from a one-electron atom because of the phenomenon of *shielding*: for a particular electron, the other electrons partially screen the effect of the positively charged nucleus. Both Zener (1930) and Slater (1930) used very simple hydrogen-like orbitals of the form

$$Nr^{(n^*-1)}\exp\left(-\left(\frac{Z-s}{n^*}\right)\frac{r}{a_0}\right)Y_{lm_l}(\theta,\phi) \tag{9.10}$$

where the *effective principal quantum number* n^* and the *screening constant* s are adjustable constants. Here, N is a normalizing constant. Such orbitals differ from the hydrogenic orbitals in that they have no radial nodes. They are actually solutions of an electronic one-electron Schrödinger equation with mutual potential energy

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{(Z-s)e^2}{r} + \frac{n^*(n^*-1)h^2}{8\pi^2 m_e r^2} \tag{9.11}$$

By varying n^* and s so as to minimize the energy, Slater was able to give the following rules for the determination of these constants.

Table 9.2 Slater orbital exponents

Atom	ζ_{1s}	$\zeta_{2s} = \zeta_{2p}$
H	1	
He	1.700	
Li	2.700	0.650
Be	3.700	0.975
B	4.700	1.300
C	5.700	1.625
N	6.700	1.950
O	7.700	2.275
F	8.700	2.600
Ne	9.700	2.925

1 n^* is assigned a value as follows, according to the value of the 'real' quantum number n.

$n = 1$	2	3	4	5	6
$n^* = 1$	2	3	3.7	4.0	4.2

2 For determining s, the electrons are divided into the following shells: (1s); (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d, 4f).

3 The shielding constant s is calculated, for any of the sets of orbitals, from the following contributions:

- nothing from any shell outside the one considered;
- 0.35 from each other electron in the set considered (except in the 1s case, where 0.30 is used);
- if the shell considered is an s or a p shell, an amount 0.85 from each electron with principal quantum number less by 1, and an amount 1.00 from each electron still farther in. If the shell is a d or f shell, an amount of 1.00 from each electron inside it.

In honour of J. C. Slater, we refer to such basis functions as *Slater-type orbitals* (STOs). Slater orbital exponents ($\zeta = (Z - s)/n^*$) for atoms through neon are given in Table 9.2.

Various other sets of screening constants have been proposed, for example those by Pauling and Sherman (1932).

9.3 CLEMENTI AND RAIMONDI

Clementi and Raimondi refined these results by performing atomic HF–LCAO calculations, treating the orbital exponents as variational parameters. A selection of their results for H through Ne is given in Table 9.3.

Table 9.3 Clementi and Raimondi orbital exponents

Atom	ζ_{1s}	ζ_{2s}	ζ_{2p}
H	1		
He	1.6875		
Li	2.6906	0.6396	
Be	3.6848	0.9560	
B	4.6795	1.2881	1.2107
C	5.6727	1.6083	1.5679
N	6.6651	1.9237	1.9170
O	7.6579	2.2458	2.2266
F	8.6501	2.5638	2.5500
Ne	9.6421	2.8792	2.8792

Atomic Screening Constants from SCF Functions
E. Clementi and D. L. Raimondi
The Journal of Chemical Physics **38** (1963) 2686–2689

The self-consistent field function for atoms with 2 to 36 electrons are computed with a minimum basis set of Slater-type orbitals. The orbital exponents of the atomic orbitals are optimized so as to ensure the energy minimum. The analysis of the optimized orbital exponents allows us to obtain simple and accurate rules for the 1s, 2s, 3s, 4s, 2p, 3p, 4p and 3d electronic screening constants. These rules are compared with those proposed by Slater and reveal the need for the screening due to the outside electrons. The analysis of the screening constants (and orbital exponents) is extended to the excited states of the ground state configuration and the positive ions.

Notice that the 2s and 2p orbitals have a slightly different exponent. Such basis sets, where we simply use the same number of atomic orbitals that we would use in everyday descriptive chemistry, are referred to as *minimal* basis sets.

The next step on the road to quality is to expand the size of the atomic orbital basis set, and I hinted in Chapters 3 and 4 how we might go about this. To start with, we double the number of basis functions and then optimize their exponents by systematically repeating atomic HF–LCAO calculation. This takes account of the so-called *inner* and *outer* regions of the wavefunction, and Clementi puts it nicely.

Simple Basis Set for Molecular Wavefunctions Containing First- and Second-Row Atoms
E. Clementi
The Journal of Chemical Physics **40** (1964) 1944–1945

The self-consistent field functions for the ground state of the first- and second-row atoms (from He to Ar) are computed with a basis set in

> which two Slater-type orbitals (STO) are chosen for each atomic orbital. The reported STOs have carefully optimized orbital exponents. The total energy is not far from the accurate Hartree–Fock energy given by Clementi, Roothaan and Yoshimine for the first-row atoms and unpublished data for the second-row atoms. The obtained basis sets have sufficient flexibility to be a most useful starting set for molecular computations, as noted by Richardson. With the addition of 3d and 4f functions, the reported atomic basis sets provide a molecular basis set which duplicates quantitatively most of the chemical information derivable by the more extended basis sets needed to obtain accurate Hartree–Fock molecular functions.

We refer to such a basis set as a *double zeta* basis set. Where the minimal basis set for atomic lithium had a 1s exponent of 2.6906, the double zeta basis set has two 1s orbitals with exponents 2.4331 and 4.5177 (the outer and inner orbitals).

A selection of Clementi's double zeta basis sets is given in Table 9.4.

That accounts for atoms. The general view is that STOs, which are given by the general formula

$$Nr^{(n^*-1)}\exp\left(-\left(\frac{Z-s}{n^*}\right)\frac{r}{a_0}\right)Y_{lm_l}(\theta,\phi) \qquad (9.12)$$

are the correct ones to use for accurate descriptions of atomic charge densities.

Table 9.4 A selection from Clementi's double zeta basis set

	ζ_{1s}	ζ_{2s}	ζ_{2p}
He	1.4461		
	2.8622		
Li	2.4331	0.6714	
	4.5177	1.9781	
Be	3.3370	0.6040	
	5.5063	1.0118	
B	4.3048	0.8814	1.0037
	6.8469	1.4070	2.2086
C	5.2309	1.1678	1.2557
	7.9690	1.8203	2.7263
N	6.1186	1.3933	1.5059
	8.9384	2.2216	3.2674
O	7.0623	1.6271	1.6537
	10.1085	2.6216	3.6813
F	7.9179	1.9467	1.8454
	11.0110	3.0960	4.1710
Ne	8.9141	2.1839	2.0514
	12.3454	3.4921	4.6748

9.3.1 Polarization Functions

There is a second point to note in Clementi's paper above where he speaks of 3d and 4f functions. These atomic orbitals play no part in the description of atomic electronic ground states for first- and second-row atoms, but on molecule formation the atomic electron density distorts and such *polarization functions* are needed to accurately describe the distortion.

9.4 GAUSSIAN ORBITALS

Atoms are special, because of their high symmetry. How do we proceed to molecules? The orbital model dominates chemistry, and at the heart of the orbital model is the HF–LCAO procedure. The main problem is integral evaluation. Even in simple HF–LCAO calculations we have to evaluate a large number of integrals in order to construct the HF Hamiltonian matrix, especially the notorious two-electron integrals

$$\iint \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,d\tau_1\,d\tau_2$$

The breakthrough for molecular applications came with Boys's classic paper (1950) on the use of Gaussian-type orbitals (GTOs). These basis functions have an exponential dependence of $\exp\left(-\left(\alpha r^2/a_0^2\right)\right)$ rather than $\exp(-(\zeta r/a_0))$.

The quantity α is called the *Gaussian exponent.* Normalized 1s and 2p GTOs are

$$G_{1s} = \left(\frac{2\alpha}{\pi a_0^2}\right)^{3/4} \exp\left(-\frac{\alpha r^2}{a_0^2}\right) \tag{9.13}$$

$$G_{2p_x} = \left(\frac{128\alpha^5}{\pi^3 a_0^{10}}\right)^{1/4} x \exp\left(-\frac{\alpha r^2}{a_0^2}\right) \tag{9.14}$$

and so are analogous to the corresponding STO. When dealing with d-type (and higher) GTOs, we often work with the so-called *Cartesian* GTO; these have pre-exponential factors

$$x^l y^m z^n$$

In the case of d-type orbitals, there are six Cartesian GTOs with pre-exponential factors of x^2, xy, y^2, xz, yz and z^2. Only five are linearly independent, the combination $\left(x^2 + y^2 + z^2\right)$ actually gives an s-orbital. Software packages sometimes allow a choice of five or six d-type orbitals.

Similar considerations apply to the f, g, h, ... GTOs.

GTOs owe their popularity to one key fact: integrals involving GTOs are much simpler than those involving STOs. The reason is as follows. Figure 9.1 shows a pair of s-type GTOs, which I will refer to as $\chi_A (= G_A(\mathbf{r}_A, \alpha_A))$ and χ_B. The

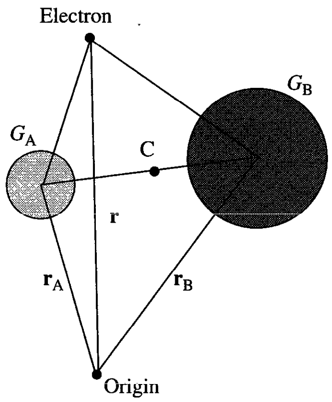


Figure 9.1 Two s-type GTO

centre of GTO A is at $\mathbf{r}_A$ and it has exponent α_A. The centre of G_B is at position vector $\mathbf{r}_B$ and it has exponent α_B.

Suppose we wish to evaluate the overlap integral

$$S_{AB} = \int \chi_A \chi_B \, d\tau \tag{9.15}$$

We see from the figure that the position vector of the electron relative to the centre of χ_A is $\mathbf{r} - \mathbf{r}_A$, so we need a factor of

$$G_A(\mathbf{r} - \mathbf{r}_A, \alpha_A) = \left(\frac{2\alpha_A}{\pi a_0^2}\right)^{3/4} \exp\left(-\frac{\alpha_A(\mathbf{r} - \mathbf{r}_A)^2}{a_0^2}\right) \tag{9.16}$$

under the integral sign where I have written χ_A, and a corresponding factor

$$G_A(\mathbf{r} - \mathbf{r}_B, \alpha_B) = \left(\frac{2\alpha_B}{\pi a_0^2}\right)^{3/4} \exp\left(-\frac{\alpha_B(\mathbf{r} - \mathbf{r}_B)^2}{a_0^2}\right) \tag{9.17}$$

where I have written χ_B.

The product of these two exponentials is equal to a third GTO situated at point C along the line of centres AB, as shown in Figure 9.1. The resultant GTO $G_C(\mathbf{r}_C, \alpha_C)$ is situated at the point C with position vector $\mathbf{r}_C$ such that

$$\mathbf{r}_C = \frac{1}{\alpha_A + \alpha_B}(\alpha_A \mathbf{r}_A + \alpha_B \mathbf{r}_B) \tag{9.18}$$

and the exponent of this new GTO is

$$\alpha_C = \alpha_A + \alpha_B \tag{9.19}$$

Apart from the normalizing factor, the two-centre overlap integral then reduces to a simple one-centre integral of the form

$$S_{AB} = \int \exp\left(-\frac{\alpha_C(\mathbf{r} - \mathbf{r}_C)^2}{a_0^2}\right) d\tau \qquad (9.20)$$

The simplification is even more dramatic for a two-electron integral, which can involve GTOs on four different centres. Formulae for integrals involving Cartesian GTOs of p, d, ... types can be deduced from those involving s orbitals by simple differentiation. Here is the famous synopsis.

Electronic Wave Functions
A General Method of Calculation for the Stationary States of
any Molecular System
S. F. Boys
Proceedings of the Royal Society of London Series A, **200** (1950) 542–554

This communication deals with the general theory of obtaining numerical electronic wavefunctions for the stationary states of atoms and molecules. It is shown that by taking Gaussian functions, and functions derived from these by differentiation with respect to the parameters, complete systems of functions can be constructed appropriate to any molecular problem, and that all the necessary integrals can be explicitly evaluated. These can be used in connection with the molecular orbital treatment, or localized bond method, or the general method of linear combinations of many Slater determinants by the variation procedure. This general method of obtaining a sequence of solutions converging to the accurate solution is examined. It is shown that the only obstacle to the evaluation of wavefunctions of any required degree of accuracy is the labour of computation. A modification of the general method applicable to atoms is discussed and considered to be extremely practicable.

One problem that concerned the early workers is that GTOs do not give terribly good energies. If we use a single GTO for a hydrogen atom,

$$G_A(\alpha) = \left(\frac{\alpha}{\pi a_0^2}\right)^{3/4} \exp\left(-\alpha\frac{r^2}{a_0^2}\right) \qquad (9.21)$$

and calculate the best orbital exponent using the variation principle, we find $\alpha_{\text{opt}} = 0.283$ and the variational energy is $-0.424\,41\ E_h$. This has to be compared with the 'experimental' value of $-\frac{1}{2}\ E_h$, and is therefore in error by some 15%.

In addition, GTOs have the wrong behaviour at nuclear positions. A comparison of the 1s GTO and the corresponding 1s STO for a H atom is shown in Figure 9.2.

The full plot is the STO, and the dotted plot is the corresponding GTO. The atomic unit of wavefunction is $a_0^{-3/2}$. The GTO shows incorrect behaviour at the

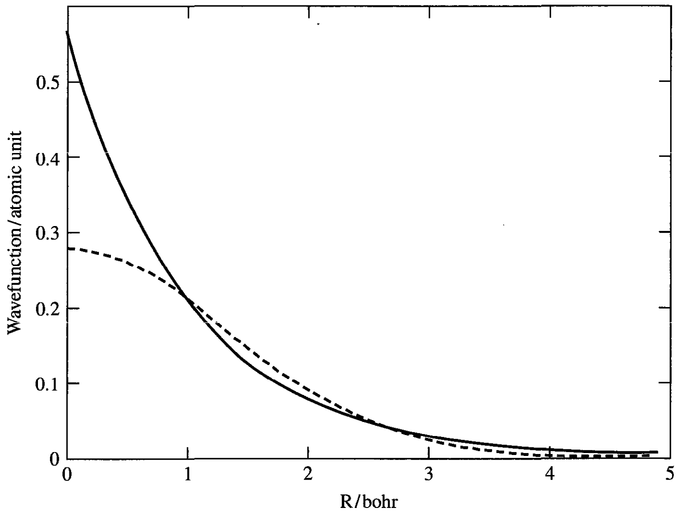


Figure 9.2 1s Slater and 1s Gaussian

nucleus, where it is flat rather than having a cusp. It also falls off too quickly with distance from the nucleus.

9.5 THE STO/nG PHILOSOPHY

The next step was to represent each Slater atomic orbital as a fixed linear combination of Gaussian orbitals; so a Slater-type orbital with exponent ζ is written as a sum of GTOs with exponents α_1, α_2, and so on. For example, in the case of three *primitive* GTOs we might write

$$\mathrm{STO}(\zeta) = d_1\mathrm{GTO}(\alpha_1) + d_2\mathrm{GTO}(\alpha_2) + d_3\mathrm{GTO}(\alpha_3) \qquad (9.22)$$

where STO(ζ) represents a 1s STO with exponent ζ, which is to be represented as a linear combination of the three 1s GTOs with exponents α_1, α_2 and α_3. The values of the d's and the exponents are usually found by least-squares fitting (Hehre, Stewart and Pople, 1969). If we choose to fit the entire minimal basis set STO as a linear combination of n GTOs, then we speak of the STO-nG model. Here is the synopsis for a key paper.

Self Consistent Molecular-Orbital Methods
I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals
W. J. Hehre, R. F. Stewart and J. A. Pople
The Journal of Chemical Physics **51** (1969) 2657–2665

Least squares representations of Slater-type atomic orbitals as a sum of Gaussian-type orbitals are presented. These have the special feature that

> common Gaussian exponents are shared between Slater-type 2s and 2p functions. Use of these atomic orbitals in self-consistent molecular-orbital calculations is shown to lead to values of atomization energies, atomic populations, and electric dipole moments which converge rapidly (with increasing size of the Gaussian expansion) to the values appropriate for pure Slater-type orbitals. The ζ exponents (or scale factors) for the atomic orbitals which are optimized for a number of molecules are also shown to be nearly independent of the number of Gaussian functions. A standard set of ζ values for use in molecular calculations is suggested on the basis of this study and is shown to be adequate for the calculation of total and atomization energies, but less appropriate for studies of the charge distribution.

To take a concrete example, the fit for a 1s atomic orbital with $\zeta = 1$ gives the values of d and α shown in Table 9.5, as we increase the number of GTO in the expansion.

We therefore regard each fixed linear combination as a single basis function made up from the *n primitive* Gaussians, for the purposes of (e.g.) HF–LCAO calculations. But of course we have to do integral evaluation over all the primitive GTOs and so we don't escape the necessity of calculating integrals over the primitive GTOs. The STO–nG method uses the same primitives (but with different

Table 9.5 STO–nG expansion coefficients for fitting a 1s STO with exponent $\zeta = 1$

	Gaussian exponents α	Linear expansion coefficients d
STO–2G	0.151 623	0.067 8914
	0.851 819	0.430 129
STO–3G	0.109 818	0.444 635
	0.405 771	0.535 328
	2.227 66	0.154 329
STO–4G	0.088 0187	0.291 626
	0.265 204	0.532 846
	0.954 620	0.260 141
	5.216 86	0.056 7523
STO–5G	0.074 4527	0.193 572
	0.197 572	0.482 570
	0.578 648	0.331 816
	2.071 73	0.113 541
	11.305 6	0.022 1406
STO–6G	0.065 1095	0.130 334
	0.158 088	0.416 492
	0.407 099	0.370 563
	1.185 06	0.168 538
	4.235 92	0.049 3615
	23.310 30	0.009 16360

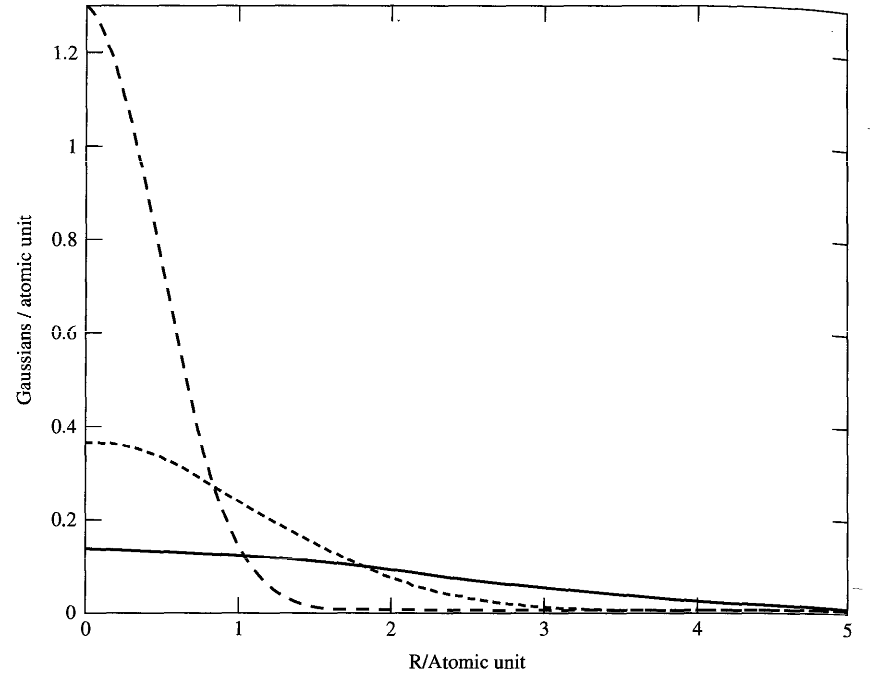


Figure 9.3 Primitive Gaussians in the STO–3G expansion

linear expansion coefficients) for the 2s and the 2p STOs; this helps integral evaluation because there are many common integrals over the primitives.

Thus, to give an STO–3G fit to a 1s orbital with exponent $\zeta = 1$ we have to take the three primitive 1s GTOs with exponents $\alpha_1 = 0.109\,818$, $\alpha_2 = 0.405\,771$ and $\alpha_3 = 2.227\,66$. Their individual variations with distance is shown in Figure 9.3.

The atomic unit of wavefunction is $a_0^{-3/2}$. The dashed plot is the primitive with exponent 2.227 66, the dotted plot is the primitive with exponent 0.405 771 and the full plot is the primitive with exponent 0.109 818. The idea is that each primitive describes a part of the STO. If we combine them together using the expansion coefficients from Table 9.5, we get a very close fit to the STO, except in the vicinity of the nucleus. The full curve in Figure 9.4 is the contracted GTO, the dotted curve the STO.

For an atomic STO with exponent ζ different from 1, the d's remain the same but the exponents of the primitives have to be multiplied by $\zeta^{3/2}$.

The original literature reference contains coefficients and expansion coefficients for 2s and 2p orbitals. For computational efficiency, the 2s and 2p orbitals are taken to have the same exponents.

The STO–3G wavefunction does not have a cusp at the nucleus. Very few molecular properties depend on the exact shape of the wavefunction at the nucleus;

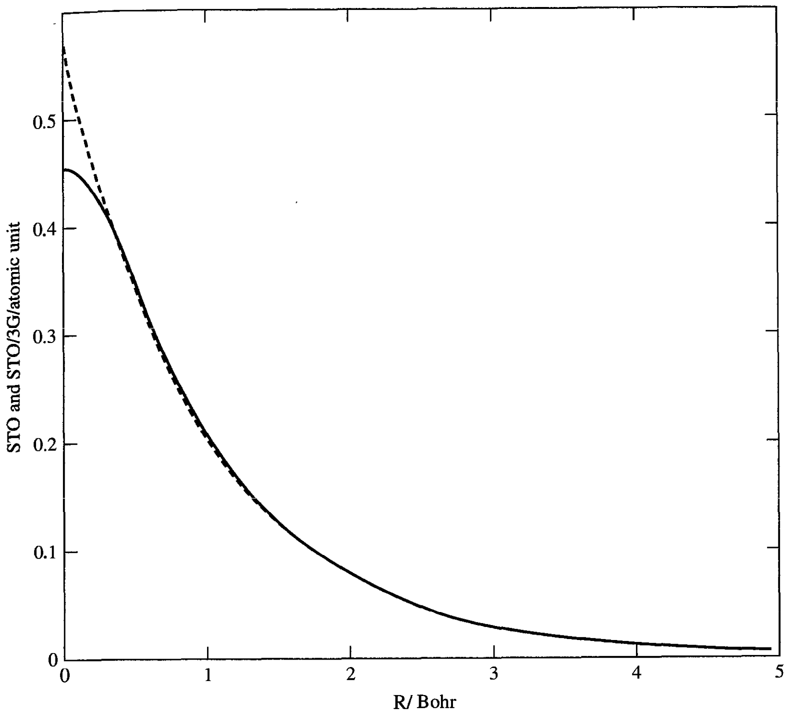


Figure 9.4 STO vs STO-3G

the only common exception being hyperfine coupling constants, to be discussed in Chapter 18. We say that we have *contracted* the primitive GTOs into a basis function, and we often speak about the d coefficients as *contraction coefficients*.

9.6 THE STO/4-31G STORY

It became apparent that these STO-nG minimal basis sets were not particularly adequate for the accurate prediction of molecular geometries, and this failing was attributed to their lack of flexibility in the valence region. The next step was to give a little more flexibility to the STO-nG basis sets, whilst retaining their computational attractiveness. The classic paper is that by Ditchfield, Hehre and Pople.

Self-Consistent Molecular-Orbital Methods IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules
R. Ditchfield, W. J. Hehre and J. A. Pople
The Journal of Chemical Physics **54** (1971) 724–728

An extended basis set of atomic functions expressed as fixed linear combinations of Gaussian functions is presented for hydrogen and the first row atoms carbon to fluorine. In this set, described as 4–31G, each inner shell is represented by a single basis function taken as a sum over four Gaussians and each valence orbital is split into inner and outer parts described by three and one Gaussian function respectively. The expansion coefficients and Gaussian exponents are determined by minimizing the total calculated energy of the electronic ground state. This basis set is then used in single-determinant molecular-orbital studies of a group of small polyatomic molecules. Optimization of valence-shell scaling factors shows that considerable rescaling of atomic functions occurs in molecules, the largest effects being observed for hydrogen and carbon. However, the range of optimum scale factors for each atom is small enough to allow the selection of a standard molecular set. The use of this standard basis gives theoretical equilibrium geometries in reasonable agreement with experiment.

Thus a hydrogen atom is represented by two basis functions, the first of which is a fixed linear combination of three primitives, and the other one a more diffuse primitive as shown in Table 9.6.

To remind you, for an atomic STO with exponent ζ different from 1, the d's remain the same but the exponents of the primitives have to be multiplied by $\zeta^{3/2}$.

For a carbon atom, the 1s STO is represented as a combination of four primitive GTOs, whilst the 2s and 2p STO are represented by two basis functions, one consisting of three primitives and the other of one.

9.7 EXTENDED BASIS SETS

Other workers followed a different line of attack, which I can illustrate using Dunning's basis sets. The idea is to start out with a reasonable (large) set of atomic GTOs, and then look for a contraction scheme that will give accuracy but computational economy. So we search for groupings of the primitives that are more or less constant in a molecular calculation. Dunning concentrated on energy-optimized GTOs where each exponent had been variationally optimized in an atomic HF–LCAO calculation. The GTO set used was that of Huzinaga, which consists of ten primitive s-type GTO and six primitive GTO for each first-row atom.

Table 9.6 STO/4–31G treatment of H (^{2}S)

Exponent α	Contraction coefficient d
13.007 73	0.334 960
1.962 079	0.224 727 20
0.444 529 0	0.813 757 3
0.121 949 2	1

First, the synopsis:

Gaussian Basis Functions for use in Molecular Calculations III Contraction of (10s, 6p) Atomic Basis Sets for the First-Row Atoms
T. H. Dunning, Jr
The Journal of Chemical Physics **55** (1975) 716–723

Contracted [5s3p] and [5s4p] Gaussian basis sets for the first-row atoms are derived from the (10s6p) primitive basis sets of Huzinaga. Contracted [2s] and [3s] sets for the hydrogen atom obtained from primitive sets ranging from (4s) to (6s) are also examined. Calculations on the water and nitrogen molecules indicate that such basis sets when augmented with suitable polarization functions should yield wavefunctions near the Hartree–Fock limit.

Take note of Dunning's notation. He writes the primitives (10s6p) and the contracted basis functions in square brackets [5s3p]. To give a detailed example, consider the oxygen atom set in Table 9.7.

The primitive GTOs with exponents 18 050.0 through 0.2558 are 1s type, and the remainder are 2p type. The two most diffuse s functions (those with exponents 0.7736 and 0.2558) are the main components of the 2s STO, and they are allowed to vary freely in molecular calculations. The 1s primitive with exponent 2.077 turns out to make substantial contributions to both the atomic 1s and 2s orbitals, so that one is also left free. The remaining seven distinct primitive 1s GTOs describe the atomic 1s orbital, and a careful examination of the ratios of their

Table 9.7 Dunning's [5s3p] contraction scheme for Huzinaga's (10s6p) GTO set

1805.0	s	0.000 757
2660.0		0.006 066
585.7		0.032 782
160.9		0.132 609
51.16		0.396 839
17.90		0.542 572
17.90	s	0.262 490
6.639		0.769 828
2.077	s	1
0.7736	s	1
0.2558	s	1
49.83	p	0.016 358
11.49		0.106 453
3.609		0.349 302
1.321		0.657 183
0.4821	p	1
0.1651	p	1

contributions to the atomic orbitals led Dunning to conclude that the primitive with exponent 17.90 should be counted twice. Similar considerations apply to the 2p primitives.

9.8 DIFFUSE AND POLARIZATION FUNCTIONS

We would normally write the electronic ground state electron configuration of a carbon atom as $1s^2 2s^2 2p^2$. Despite the intellectual activity that has gone into defining mythical 'valence states' for carbon atoms in different bonding situations, no one would include a d-orbital in the description of ground state carbon.

Carbon atoms in free space have spherical symmetry, but a carbon 'atom' in a molecule is a quite different entity because its charge density may well distort from spherical symmetry. To take account of the finer points of this distortion, we very often need to include d, f, ... atomic orbitals in the basis set. Such atomic orbitals are referred to as *polarization functions* because their inclusion would allow a free atom to take account of the polarization induced by an external electric field or by molecule formation. I mentioned polarization functions briefly in Section 9.3.1.

Let's see what Pople and coworkers have to say about polarization functions.

> Self-Consistent Molecular Orbital Methods. XVII Geometries and Binding Energies of Second-Row Molecules. A Comparison of Three Basis Sets
> J. B. Collins, P. von R. Schleyer, J. S. Binkley and J. A. Pople
> *The Journal of Chemical Physics* **64** (1976) 5142–5151
>
> Three basis sets (minimal s-p, extended s-p and minimal s-p with d functions on the second row atoms) are used to calculate geometries and binding energies of 24 molecules containing second row atoms. d functions are found to be essential in the description of both properties for hypervalent molecules and to be important in the calculations of two-heavy-atom bond lengths even for molecules of normal valence.

The presence of a single polarization function (either a full set of the six Cartesian Gaussians $d_{xx}, d_{xy}, d_{xz}, d_{yy}, d_{yz}$ and d_{zz}, or five spherical harmonic ones) on each first row atom in a molecule is denoted by the addition of a *. Thus, STO/3G* means the STO/3G basis set with a set of six Cartesian Gaussians per heavy atom. A second star as in STO/3G** implies the presence of 2p polarization functions on each hydrogen atom. Details of these polarization functions are usually stored internally within the software package.

Sometimes it turns out that we need to include a number of polarization functions, not just one of each type. The notation 4–31G(3d, 2p) indicates a standard 4–31G basis set augmented with three d-type primitive Cartesian Gaussians per centre and two p-type primitives on every hydrogen atom. Again, details of the

Gaussian exponents are usually stored internally; it isn't necessary to know the details.

In order to deal with atoms and molecules that carry a formal negative charge, it is necessary to treat the outer regions of the charge density with some respect. Anions have extended electron densities compared to neutral species. These outer regions can best be described by atomic orbitals whose maxima are far from the associated nucleus, and we speak about *diffuse functions*. It is necessary to add diffuse functions to the standard basis sets when dealing with anions, with molecular properties that give a measure of the response to external electric fields and so on. Once again, there have been a number of studies to optimize exponents, and details are usually stored internally in sophisticated packages like GAUSSIAN.

So, finally, a Gaussian basis set denoted

$$\mathrm{STO/6{-}311{+}{+}G(3d, 2p)}$$

means that inner shells are represented as fixed linear combinations of six GTOs. The valence shells are represented as combinations of inner and outer orbitals. The inner orbitals are represented as three fixed-combination GTOs and two GTOs are left free to vary in LCAO calculations. The ++ shows that extra diffuse functions have been added to both the hydrogens and the heavy atoms and the (3d, 2p) means that three sets of (probably Cartesian) d-orbitals have been added to each heavy atom, whilst two sets of p orbitals have been added to each H atom.

9.9 EFFECTIVE CORE POTENTIALS

The chemical similarities of periodic elements arise because the valence electrons determine most of the chemical properties of molecules. The core electrons are only slightly affected by their chemical environment and act primarily to shield the nuclei. They also provide an effective field for the valence electrons.

Effective core potentials (ECP) replace the atomic core electrons in valence-only *ab initio* calculations, and they are often used when dealing with compounds containing elements from the second row of the periodic table and above.

These ECPs were traditionally presented as a linear combination of functions of the type

$$r^{-n} \exp\left(-ar^2\right)$$

with coefficients and exponents determined by least-squares fits to the potential generated from accurate HF–LCAO wavefunctions. Typically, ten such functions would be needed and for this reason ECPs offered no competitive advantage for molecular calculations involving only first-row atoms. In recent years, it has become fashionable to represent these core potentials by compact one- and two-term Gaussian expansions obtained directly from the appropriate atomic eigenvalue equation.

Ab initio ECPs are derived from atomic all-electron calculations, and they are then used in valence-only molecular calculations where the atomic cores are chemically inactive. We start with the atomic HF equation for valence orbital $\chi_{l,i}$ whose angular momentum quantum number is l:

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2R}{\mathrm{d}r^2}-\frac{1}{r}\frac{\mathrm{d}R}{\mathrm{d}r}-\frac{Ze^2}{4\pi\epsilon_0 r}+\frac{l(l+1)}{2r^2}+\hat{U}_{\mathrm{val}}+\hat{U}_{\mathrm{core}}\right)\chi_{l,i}=\varepsilon_{l,i}\chi_{l,i} \qquad (9.23)$$

Here, U_{val} and U_{core} are the Coulomb and exchange operators summed over the core and other occupied valence orbitals, respectively.

Valence orbital $\chi_{l,i}$ is the lowest energy solution of equation 9.23 only if there are no core orbitals with the same angular momentum quantum number. Equation 9.23 can be solved using standard atomic HF codes. Once these solutions are known, it is possible to construct a valence-only HF-like equation that uses an effective potential to ensure that the valence orbital is the lowest energy solution. The equation is written

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2R}{\mathrm{d}r^2}-\frac{1}{r}\frac{\mathrm{d}R}{\mathrm{d}r}-\frac{Z_{\mathrm{eff}}e^2}{4\pi\epsilon_0 r}+\frac{(l+1)}{2r^2}+\hat{U}'_{\mathrm{val}}+\hat{U}^{\mathrm{eff}}_{\mathrm{core}}\right)\omega_{l,i}=\varepsilon_{l,i}\omega_{l,i} \qquad (9.24)$$

Here $\hat{U}^{\mathrm{eff}}_{\mathrm{core}}$ is the effective potential and $\omega_{l,i}$ is a nodeless *pseudo-orbital* that can be derived from $\chi_{l,i}$ in several different ways. For first-row atoms, Christiansen, Lee and Pitzer (1979) suggest

$$\begin{aligned}\omega_{l,i}(r)&=\sum_{k=0}^{4}c_k r^{N+k} \text{ if } r\leqslant R_l\\ \omega_{l,i}(r)&=\chi_{l,i} \text{ if } r\geqslant R_1\end{aligned} \qquad (9.25)$$

So, for some match point R_l to infinity, the atomic pseudo-orbital is identical to the valence HF atomic orbital. For radial distances less than R_l the pseudo-orbital is defined by a polynomial expansion that goes to zero. The values of the polynomial are found by matching the value and first three derivatives of the HF orbital at R_l.

10 *AB INITIO* PACKAGES

It is traditional to divide quantum-mechanical molecular models into three broad bands depending on their degree of sophistication. There are sublevels within each band, and a great deal of jargon accompanied by acronyms. Many authors speak of the 'level of theory'. The Hückel independent electron model of Chapter 7 typifies the lowest level of theory, and authors sometimes refer to these models as '*empirical*'. The Hamiltonian is not rigorously defined, and neither are the basis functions. Nevertheless, these models have been able to produce impressive predictions and rationalizations.

At the other end of the spectrum are the *ab initio* ('from first principles') methods, such as the calculations already discussed for H_2 in Chapter 4. I am not trying to imply that these calculations are 'correct' in any strict sense, although we would hope that the results would bear some relation to reality. An *ab initio* HF calculation of the potential energy curve for a diatomic A_2 will generally give incorrect dissociation products, and so cannot possibly be 'right' in the absolute sense. The phrase *ab initio* simply means that we have started with a certain Hamiltonian and a set of basis functions, and then done all the intermediate calculations with full rigour and no appeal to experiment.

In between come the *semi-empirical* models such as PPP or ZINDO. Here we start with a rigorous Hamiltonian and perhaps a well-defined basis set, but we then calibrate the difficult integrals against experiment.

I have deliberately restricted the discussion to quantum-mechanical models, so molecular mechanics is excluded from the classification.

Over the last thirty years, international collaboration and cooperation on a scale rarely witnessed in science has led to the development of several very sophisticated software packages for *ab initio* molecular electronic structure calculations. In the early days, such packages were freely distributed amongst workers in the field. Today, you buy executable code, a licence and professional documentation just as with any software package.

Source code for the early packages such as POLYATOM, HONDO and GAUSSIAN70 are still available from the Quantum Chemistry Program Exchange, for a handling fee. Set your web browser to find QCPE (based at the University of Indiana) if you want more details.

At its very simplest, a 1970s package would consist 20 000 lines of FORTRAN to calculate one- and two-electron integrals over Gaussian orbitals, perform HF–LCAO calculations on closed-shell states and a few possible open-shell states, and finally give a Mulliken population analysis together with the electric dipole moment. Think of input on punched cards and output on a Teletype, and you have got the idea. Visualization was done (by hand) with a pencil and sheets of graph paper. The graphical user interface had still to be born.

We have moved along since then and a modern *ab initio* package will do very much more. 'Visualization' is the key word. Some packages are strong on visualization and some are rather poor. Third-party packages proliferate. I am going to use the output from two well-known packages, Gaussian 98W and HyperChem5.1 in order to illustrate this chapter. Both run under MS-Windows98, and I did all the calculations on my office PC. It may be that you prefer a different package, or that you do all your calculations on a workstation or supercomputer. The principles are the same.

10.1 LEVEL OF THEORY

We need two things to get going, a molecular geometry and a decision as to the 'level of theory'. I am going to concentrate on HF–LCAO molecular orbital calculations using GTOs for this chapter, which together with my choice of basis set defines the level of theory. Everyone in the field understands acronyms such as HF/4–31G*. Most *ab initio* packages have the common basis sets stored internally. In addition several basis sets have been developed for certain specific purposes. Table 10.1 gives a selection.

10.2 GEOMETRY INPUT

Apart from editing a screen image, there are two ways to input a molecular geometry: the Cartesian coordinates and the *Z-matrix*. The Z-matrix defines the nuclear geometry in terms of bond lengths, bond angles and dihedral angles. In recent years, Cartesian coordinates have displaced the Z-matrix, but it is as well to know about the Z-matrix. In any case, the packages sometimes translate a screen image into a Z-matrix. Some examples will make things plain (Figure 10.1).

The first case is H_2O. I will take a bond length of 95.6 pm and an H_1–O–H_2 bond angle of 104.5°.

We start the Z-matrix with an atom — it doesn't matter too much which. I have chosen to start with oxygen (Figure 10.2). The next Z-matrix record says that

Table 10.1 Some common basis sets, and some special-purpose ones

Basis set	Atoms	Comment and reference
STO/3G	H to Xe	General-purpose minimal basis set. Hehre, Stewart and Pople(1969)
3-21G	H to Xe	General-purpose compact extended basis set. Binkley, Pople and Hehre, (1980)
4-31G	H to Ne	General-purpose extended basis set. Ditchfield, Hehre and Pople (1971)
6-311G	H to Kr	Krishnan *et al.* (1980); McLean and Chandler (1980)
D95V	H to Ne	Dunning valence double zeta Dunning (1975); Dunning and Hay (1976)
D95	H to Cl	Dunning full double zeta. References as above
SHC	H to Cl	Shape and Hamiltonian consistent basis set. Rappé, Smedley and Goddard (1981)
CEP-4G	H to Rn	Stevens, Basch and Krauss (1984) Used for ECP (effective core potential) calculations
cc-pVDZ through cc-pV6Z	H, He, B-Ne, Al-Ar	Dunning's correlation consistent basis sets (double, triple, quadruple, quintuple and sextuple zeta respectively). Used for correlation calculations Woon and Dunning (1993)

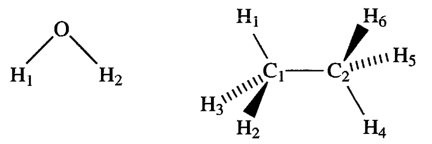


Figure 10.1

```
OXYGEN
H1 OXYGEN ROH
H2 OXYGEN ROH H1 ANGLE

ROH 0.956
ANGLE 104.5
```

Figure 10.2

H_1 is joined to OXYGEN with a bond distance of ROH. The third record says that H_2 is joined to OXYGEN with a bond length of ROH and the bond angle H_2-O-H_1 is ANGLE.

The final two records give values to the two variables ROH and ANGLE.

For a molecule having more than three atoms, we have to define dihedral angles in addition to the bond lengths and bond angles. For such a molecule, each Z-matrix record after the first three usually has a format

E N1 L N2 A N3 D

where, in the words of one user manual 'E is the elemental symbol of the atom, N1 is a previously defined atom to which the new atom is bonded and L is the length of the bond. N2 is another atom and B the bond angle between the atom being defined (N1) and N2. N3 is another atom and D the dihedral angle between the EN1N2 and N1N2N3 planes'.

In the case of staggered ethane, I have started at C_1 (Figure 10.3). The next record says that C_2 is joined to C_1 with a bond length RCC. H_1 is joined to C_1 with bond length RCH and makes a bond angle $H_1C_1C_2$. H_2 is obviously related to H_1 by a 120° rotation about the C–C axis, so the dihedral angle is $+120°$. H_3 is related to H_1 by a 120° rotation about the C–C bond in the opposite direction, giving a dihedral angle of $-120°$.

To define H_4, I make use of the dihedral angle H4C2C1H1 = 180°, and the same reasoning applied to the two remaining H atoms.

There are a couple of simple tricks of the trade when writing Z-matrices. The first point concerns linear molecules. Many packages run into difficulty at some stage when bond angles of 180° occur. These problems can be avoided by introducing dummy atoms (which are invariably given the symbol X). The Z-matrix for the linear CO···HF hydrogen-bonded complex is shown in Figure 10.4. I have added two dummy centres, X_1 and X_2 with the aim of creating off-axis centres. The first dummy atom is joined to O with an arbitrary bond distance, and the second is joined to H. See Figure 10.5 for the Z-matrix.

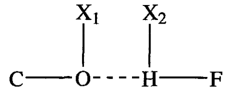
The second point concerns cyclic structures in molecules of high symmetry. Think of furan (Figure 10.6) and you might define the Z-matrix by starting

```
C1
C2 C1 RCC
H1 C1 RCH C2 ANG
H2 C1 RCH C2 ANG H1 +120.0
H3 C1 ROH C2 ANG H1 -120.0
H4 C2 RCH C1 ANG H1 +180.0
H5 C2 RCH C1 ANG H2 +180.0
H6 C2 RCH C1 ANG H3 +180.

RCC 1.5272
RCH 1.0862
ANG 111.1184
```

Figure 10.3

Figure 10.4



```
C
O  C  RCO
X1 O 1.0   C   90.0
H  O  ROH X1  90.0 C  180.0
X2 H  1.0  O   90.0  X1 0.0
F  H  RHF  X2  90.0 O  180.0

RCO  1.1306
ROH  1.9606
RHF  0.9234
```

Figure 10.5

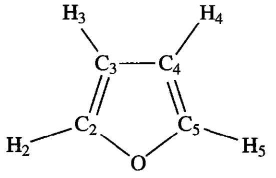


Figure 10.6

from O and working round to the last C atom joined to O. The problem is that by the time you get round to the final C atom, arithmetic rounding errors will have reduced the symmetry. A difference of 10^{-5} Å is enough to break the symmetry, unless your package is sufficiently smart to prevent this kind of behaviour.

A solution to the problem is to define an axis of symmetry through the use of dummy atoms. To take the case of furan, the Z-matrix of Figure 10.7 will retain C_{2v} symmetry.

```
X
C3  X  HALF34
O  X  ROX  C3  90.
C4 X   HALF34  O  90.  C3  180.
C2  C3  R23  X  A23X  O  0.0
C5  C4  R23  X  A23X  O  0.0
H2  C2  RCH  O  AA  X  180.
H3  C3  RCH  C2  BB  H2  0.
H5  C5  RCH  O  AA  X  180.
H4  C4  RCH  C5  BB  O  180.

HALF34  0.72119
ROX  2.0933
R23  1.3395
RCH  1.0632
A23X  106.676
AA  116.4592
BB  126.685
```

Figure 10.7

What I have done is to take a dummy centre halfway along the C_3-C_4 bond, defined the oxygen atom by its distance from the dummy atom and work from there. The lengths and angles used in a Z-matrix do not have to correspond to chemical bond distances or angles, although the normal valence variables are said to be the best choice for geometry optimization.

Most packages will happily take Cartesian coordinates or Z-matrices, but you ought to be aware of the Z-matrix. The point is that Cartesian coordinates can be obtained from sources such as the Protein Data Bank (these come in files with .pdb or .ent extensions).

10.3 AN *AB INITIO* HF-LCAO CALCULATION

Consider then a HF/STO-3G calculation on aspirin (acetylsalicylic acid)—Figure 10.8.

In chapter 2 I gave you the .pdb file which contains the Cartesian coordinates. We just add a couple of records to define the level of theory (HF/STO-3G), the charge (0) and spin multiplicity (1).

Extracts from the Gaussian 98 output file follow.

The first extract (Figure 10.9) reminds us that such packages have been developed over a number of years by a large team of people.

Gaussian 98 is a complex program with very many options. It is possible to take standard routes through the program (as I have done in this case) or to design your own route. Lines such as

```
1/38=1/1;
```

shown in the second extract (Figure 10.10) are to do with the route to be taken through the program.

Of interest is the `SCF=Direct` option. There are three ways of dealing with two-electron integrals over the basis functions in *ab initio* HF-LCAO calculations. The *Conventional* way is to calculate them once and store them on a

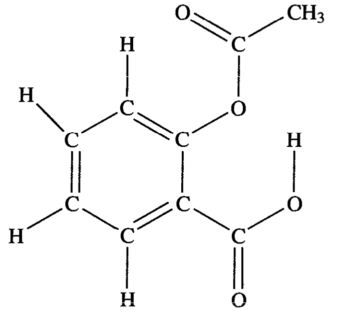
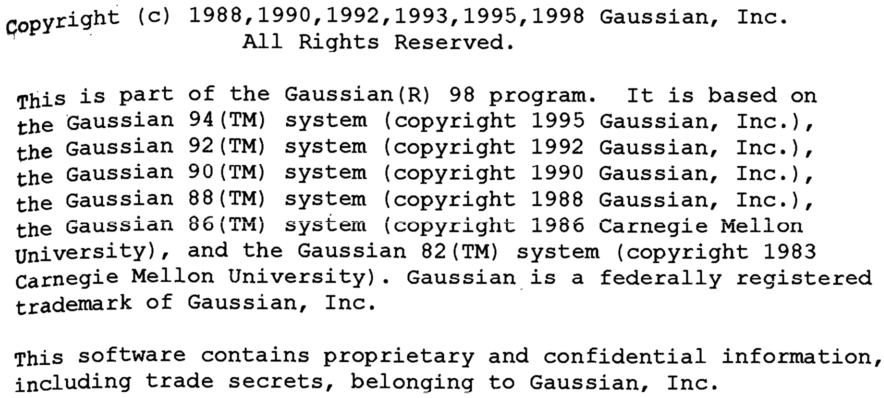


Figure 10.8

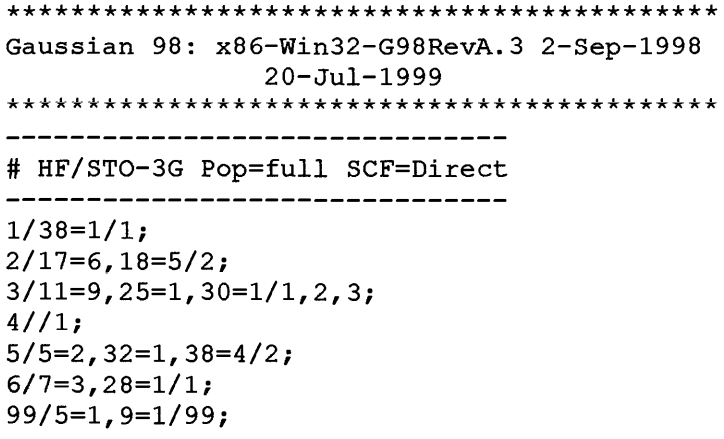


```
Copyright (c) 1988,1990,1992,1993,1995,1998 Gaussian, Inc.
                  All Rights Reserved.

This is part of the Gaussian(R) 98 program.  It is based on
the Gaussian 94(TM) system (copyright 1995 Gaussian, Inc.),
the Gaussian 92(TM) system (copyright 1992 Gaussian, Inc.),
the Gaussian 90(TM) system (copyright 1990 Gaussian, Inc.),
the Gaussian 88(TM) system (copyright 1988 Gaussian, Inc.),
the Gaussian 86(TM) system (copyright 1986 Carnegie Mellon
University), and the Gaussian 82(TM) system (copyright 1983
Carnegie Mellon University). Gaussian is a federally registered
trademark of Gaussian, Inc.

This software contains proprietary and confidential information,
including trade secrets, belonging to Gaussian, Inc.
```

Figure 10.9



```
******************************************
Gaussian 98: x86-Win32-G98RevA.3 2-Sep-1998
                20-Jul-1999
******************************************
------------------------------
# HF/STO-3G Pop=full SCF=Direct
------------------------------
1/38=1/1;
2/17=6,18=5/2;
3/11=9,25=1,30=1/1,2,3;
4//1;
5/5=2,32=1,38=4/2;
6/7=3,28=1/1;
99/5=1,9=1/99;
```

Figure 10.10

medium such as magnetic tape or a fixed disk. At each cycle of the HF–LCAO procedure, the list of integrals has to be read back into memory and processed in order to construct the HF–LCAO matrix.

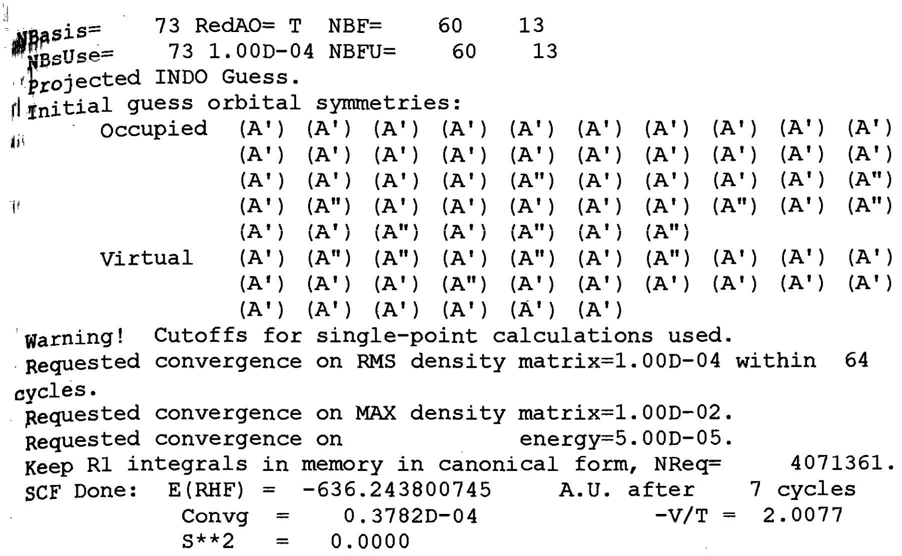
The *In-Core* method is to calculate all the integrals over the basis functions and keep them all in memory. Given that a set of n basis functions will lead to roughly $n^4/8$ unique integrals, you will appreciate that the memory requirements will be enormous. For 1000 basis functions, there will be about 2×10^{11} possible non-zero integrals. If each integral requires 4 bytes of storage (for 32-bit precision), this implies a memory requirement of about 10^{12} bytes. In fact very many of the integrals will be negligible, and we normally store the basis set indices i, j, k and l, together with the value of the integral.

In the *Direct* SCF method, we do not store the two-electron integrals over the basis functions, we recalculate them on demand every cycle of the HF procedure. At first sight, this may seem wasteful, but Conventional methods rely on disk input/output transfer rates whilst Direct methods rely on processor power. There is obviously a balance between processor speed and disk I/O. Just for the record, my calculation on aspirin (73 basis functions) took 363 s using the Direct method and 567 s using the Conventional method.

The next part of the output illustrates the interconversion between a Z-matrix and Cartesian coordinates, and shows the internal use of molecular symmetry. Aspirin as written above belongs to the C_s point group, and the two irreducible representations are A′ and A″.

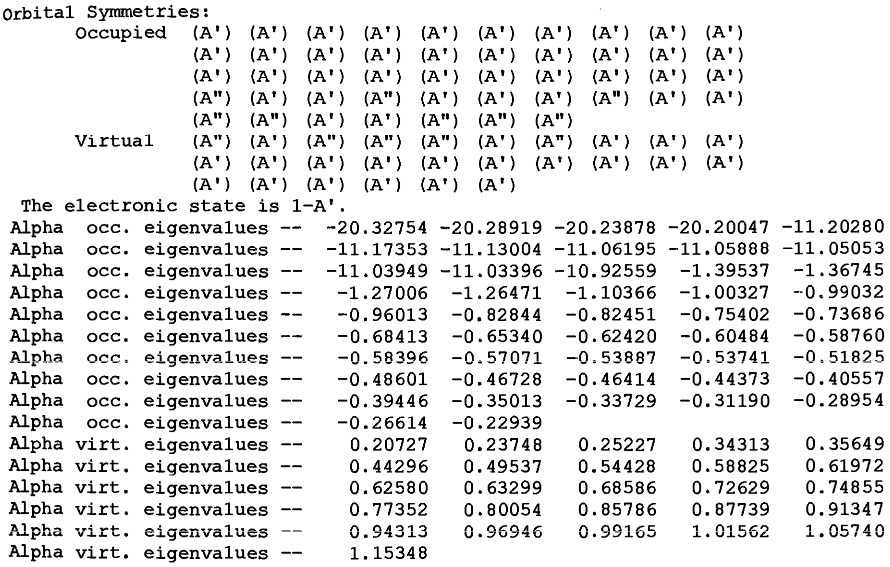
```
Stoichiometry    C9H8O4
 Framework group  CS[SG(C9H8O4)]
 Deg. of freedom   39
 Full point group                CS       NOp   2
 Largest Abelian subgroup        CS       NOp   2
 Largest concise Abelian subgroup C1      NOp   1
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number      Type               X           Y           Z
 ---------------------------------------------------------------------
    1          6          0        -1.428383    2.498520    0.000000
    2          6          0        -2.543396    1.753807    0.000000
    3          6          0        -0.116280    1.845891    0.000000
    4          1          0        -1.494894    3.546991    0.000000
    5          6          0        -2.440009    0.292180    0.000000
    6          6          0         0.000000    0.499220    0.000000
    7          1          0        -3.487840    2.214115    0.000000
    8          1          0         0.728893    2.465226    0.000000
    9          6          0        -1.240174   -0.333599    0.000000
   10          1          0        -3.332825   -0.264241    0.000000
   11          8          0         1.208109   -0.133455    0.000000
   12          6          0        -1.237527   -1.821254    0.000000
   13          6          0         2.494909    0.331263    0.000000
   14          8          0        -2.308522   -2.430781    0.000000
   15          8          0        -0.138012   -2.612651    0.000000
   16          6          0         3.680034   -0.591191    0.000000
   17          8          0         2.755492    1.533783    0.000000
   18          1          0         2.910506   -1.379933    0.000000
   19          1          0         4.053206   -1.630788    0.000000
   20          1          0         4.733745   -0.366119    0.000000
   21          1          0         0.737625   -2.289446    0.000000
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      1.0711540      0.6654936      0.4104725
 Isotopes: C-12,C-12,C-12,H-1,C-12,C-12,H-1,H-1,C-12,H-1,O-16,C-12,C-
12,O-16,O-16
 ,C-12,O-16,H-1,H-1,H-1,H-1
 Standard basis: STO-3G (5D, 7F)
 There are    60 symmetry adapted basis functions of A'  symmetry.
 There are    13 symmetry adapted basis functions of A"  symmetry.
```

Figure 10.11



```
NBasis=    73 RedAO= T  NBF=    60    13
NBsUse=    73 1.00D-04 NBFU=    60    13
Projected INDO Guess.
Initial guess orbital symmetries:
      Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')
                (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')
                (A') (A') (A') (A') (A") (A') (A') (A') (A') (A")
                (A') (A") (A') (A') (A') (A') (A') (A") (A') (A")
                (A') (A') (A") (A') (A") (A') (A")
      Virtual   (A') (A") (A") (A') (A") (A') (A") (A') (A') (A')
                (A') (A') (A') (A") (A') (A') (A') (A') (A') (A')
                (A') (A') (A') (A') (A') (A')
Warning!  Cutoffs for single-point calculations used.
Requested convergence on RMS density matrix=1.00D-04 within  64
cycles.
Requested convergence on MAX density matrix=1.00D-02.
Requested convergence on             energy=5.00D-05.
Keep R1 integrals in memory in canonical form, NReq=     4071361.
SCF Done:  E(RHF) =  -636.243800745     A.U. after    7 cycles
            Convg  =    0.3782D-04             -V/T =  2.0077
            S**2   =    0.0000
```

Figure 10.12



```
Orbital Symmetries:
      Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')
                (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')
                (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')
                (A") (A') (A') (A") (A') (A') (A') (A") (A') (A')
                (A") (A") (A') (A') (A") (A") (A")
      Virtual   (A") (A') (A") (A") (A") (A') (A") (A') (A') (A')
                (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')
                (A') (A') (A') (A') (A') (A')
  The electronic state is 1-A'.
 Alpha  occ. eigenvalues --  -20.32754 -20.28919 -20.23878 -20.20047 -11.20280
 Alpha  occ. eigenvalues --  -11.17353 -11.13004 -11.06195 -11.05888 -11.05053
 Alpha  occ. eigenvalues --  -11.03949 -11.03396 -10.92559  -1.39537  -1.36745
 Alpha  occ. eigenvalues --   -1.27006  -1.26471  -1.10366  -1.00327  -0.99032
 Alpha  occ. eigenvalues --   -0.96013  -0.82844  -0.82451  -0.75402  -0.73686
 Alpha  occ. eigenvalues --   -0.68413  -0.65340  -0.62420  -0.60484  -0.58760
 Alpha  occ. eigenvalues --   -0.58396  -0.57071  -0.53887  -0.53741  -0.51825
 Alpha  occ. eigenvalues --   -0.48601  -0.46728  -0.46414  -0.44373  -0.40557
 Alpha  occ. eigenvalues --   -0.39446  -0.35013  -0.33729  -0.31190  -0.28954
 Alpha  occ. eigenvalues --   -0.26614  -0.22939
 Alpha virt. eigenvalues --    0.20727   0.23748   0.25227   0.34313   0.35649
 Alpha virt. eigenvalues --    0.44296   0.49537   0.54428   0.58825   0.61972
 Alpha virt. eigenvalues --    0.62580   0.63299   0.68586   0.72629   0.74855
 Alpha virt. eigenvalues --    0.77352   0.80054   0.85786   0.87739   0.91347
 Alpha virt. eigenvalues --    0.94313   0.96946   0.99165   1.01562   1.05740
 Alpha virt. eigenvalues --    1.15348
```

Figure 10.13

Then comes the HF–LCAO calculation (Figure 10.12). The procedure starts with an INDO run (Chapter 8) for the initial estimate of the electron density. Notice once again the internal use of molecular symmetry. In early packages such as POLYATOM, the use of molecular symmetry was essential for fast execution but had to be explicitly included by the user.

The item S**2 = 0.0000 is the expectation value of the spin operator $\hat{S}^2$. For a singlet state, the value should be 0 as it is.

Next (Figure 10.13) come the results in numerical form: orbital energies, LCAO–MO coefficients and the like.

Here, '`occ`' means occupied and '`virt`' means virtual. In the restricted Hartree–Fock model, each orbital can be occupied by at most one α spin and one β spin electron. That is the meaning of the (redundant) `Alpha` in the output. In the unrestricted Hartree–Fock model, the α spin electrons have a different spatial part to the β spin electrons and the output consists of the HF–LCAO coefficients for both the α spin and the β spin electrons.

There is very little point in trying to obtain information from the 73 × 47 = 3431 numbers that constitute the HF–LCAO coefficients for the occupied orbitals. Mulliken population indices are given next, together with Mulliken atomic charges (Figure 10.14).

```
Total atomic charges:
              1
  1  C   -0.050486
  2  C   -0.075257
  3  C   -0.098742
  4  H    0.078064
  5  C   -0.040957
  6  C    0.153293
  7  H    0.073339
  8  H    0.102517
  9  C   -0.041052
 10  H    0.095825
 11  O   -0.315261
 12  C    0.317285
 13  C    0.366709
 14  O   -0.256523
 15  O   -0.338841
 16  C   -0.563162
 17  O   -0.303240
 18  H    0.265387
 19  H    0.240602
 20  H    0.155675
 21  H    0.234826
 Sum of Mulliken charges=   0.00000
```

Figure 10.14

```
Charge=      0.0000 electrons
Dipole moment (Debye):
   X=      2.4644    Y=     -0.6049    Z=      0.0000  Tot=      2.5375
Quadrupole moment (Debye-Ang):
   XX=   -62.3974   YY=   -74.3387   ZZ=   -68.9444
   XY=   -22.4504   XZ=     0.0000   YZ=     0.0000
Octapole moment (Debye-Ang**2):
  XXX=    54.6261  YYY=    12.0293  ZZZ=     0.0000  XYY=    25.5933
  XXY=   -38.3246  XXZ=     0.0000  XZZ=     0.2697  YZZ=    -8.9088
  YYZ=     0.0000  XYZ=     0.0000
Hexadecapole moment (Debye-Ang**3):
 XXXX= -1574.8336 YYYY= -1160.7386 ZZZZ=   -49.8971 XXXY=  -209.9827
 XXXZ=     0.0000 YYYX=   -98.4096 YYYZ=     0.0000 ZZZX=     0.0000
 ZZZY=     0.0000 XXYY=  -487.0756 XXZZ=  -334.7616 YYZZ=  -192.3609
 XXYZ=     0.0000 YYXZ=     0.0000 ZZXY=    17.9459
```

Figure 10.15

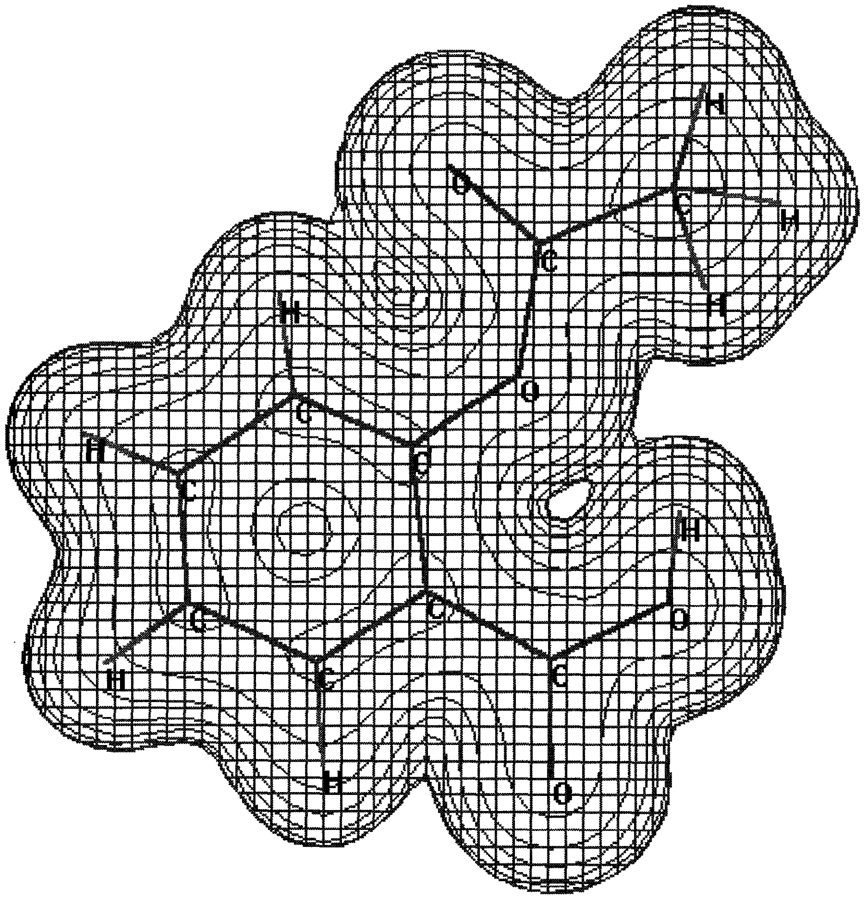


Figure 10.16 Aspirin isosurface electron density

Finally, the package gives us skeletal information about molecular properties in the form of electric moments (Figure 10.15).

10.4 VISUALIZATION

Some of the major packages are better at visualization than others. In any case, there are a host of third-party providers with software on offer. Here then is what you might like to do with the results of the calculations above (and I used HyperChem to produce the following screen grabs). First of all an isosurface plot of the electron density (Figure 10.16). Next are isosurface densities for the highest

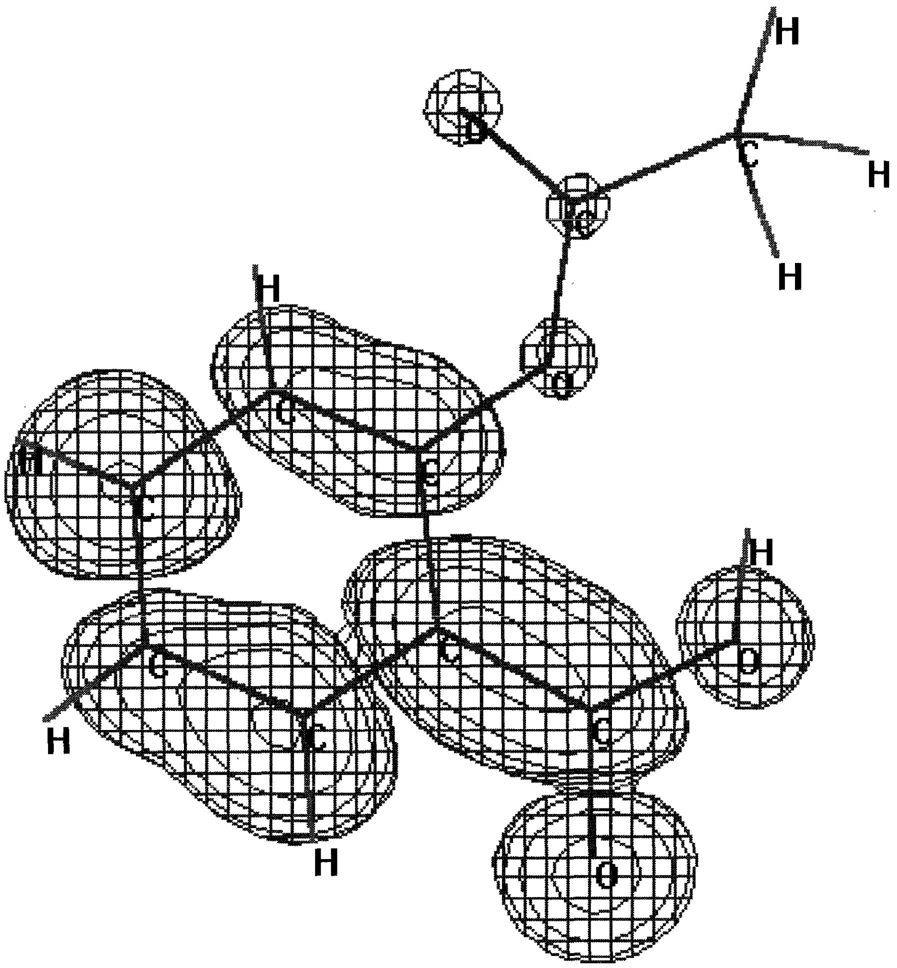


Figure 10.17 Aspirin LUMO density isosurface

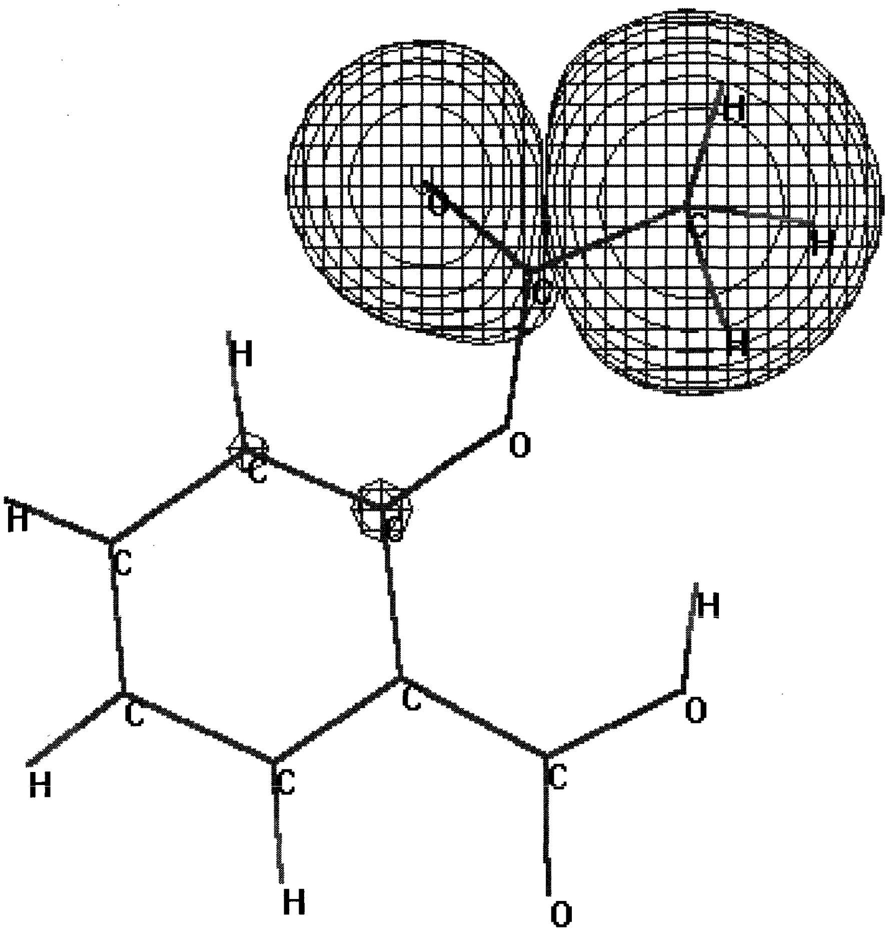


Figure 10.18 Aspirin HOMO density isosurface

occupied molecular orbital (the HOMO) and the lowest unoccupied molecular orbital (the LUMO).

11 ELECTRON CORRELATION

In our discussion of the electron density in Chapter 5, I mentioned the density functions $\rho_1(\mathbf{x}_1)$ and $\rho_2(\mathbf{x}_1, \mathbf{x}_2)$. I have used the composite space–spin variable $\mathbf{x}$ to include both the spatial variables $\mathbf{r}$ and the spin variable s. These density functions have a probabilistic interpretation: $\rho_1(\mathbf{x}_1)\,\mathrm{d}\tau_1\,\mathrm{d}s_1$ gives the chance of finding an electron in the element $\mathrm{d}\tau_1\,\mathrm{d}s_1$ of space and spin, whilst $\rho_2(\mathbf{x}_1, \mathbf{x}_2)\,\mathrm{d}\tau_1\,\mathrm{d}s_1\,\mathrm{d}\tau_2\,\mathrm{d}s_2$ gives the chance of finding simultaneously electron 1 in $\mathrm{d}\tau_1\,\mathrm{d}s_1$ and electron 2 in $\mathrm{d}\tau_2\,\mathrm{d}s_2$. The two-electron density function gives information as to how the motion of any pair of electrons is correlated. For independent particles, these probabilities are independent and so we would expect

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho_1(\mathbf{x}_1)\rho_2(\mathbf{x}_2) \qquad (11.1)$$

In such a case we say that there is no *correlation* between the particles. This would certainly be the case if there were no electrostatic interaction between electrons, but it also holds for the electrons in Hartree's original SCF model. This is because each electron experiences an average potential due to the remaining electrons and the nuclei. Electrons repel each other, and we would certainly expect the probability of finding two of them close together would be reduced compared to the value expected for independent particles.

- In the Hartree–Fock model, where we take account of antisymmetry, it turns out that there is no correlation between the positions of electrons of opposite spin, yet,
- there is a correlation between the position of electrons of like spin.

The second bullet point describes a special type of correlation that prevents two electrons of like spin being found at the same point in space, and it applies whenever the particles are fermions. For that reason, it is described as *Fermi correlation.*

It should therefore be clear that energies calculated by the HF procedure will always be greater than the true energy because of the correlation defect.

HF–LCAO calculations must give poorer energies still, because we have to use a finite basis set. I have illustrated these ideas in Figure 11.1. The difference between the 'true' HF energy and the 'experimental' energy is called the *correlation energy*. It is typically 1% of the total energy, which often works out as the order of magnitude of the energy of a chemical bond.

There is a nice point as to what we mean by the 'experimental' energy. All the calculations so far have been based on non-relativistic quantum mechanics. A measure of the importance of relativistic effects for a given atom is afforded by its spin–orbit coupling parameter. This parameter can be easily determined from spectroscopic studies, and it is certainly not zero for first-row atoms. We should strictly compare the HF limit to an experimental energy that refers to a non-relativistic molecule. This is a moot point; we can neither calculate molecular energies at the HF limit, nor can we easily make measurements that allow for these relativistic effects.

The remarkable thing is that the HF model is so reliable for the calculation of very many molecular properties, as I will discuss in Chapters 16 and 17. But for many simple applications, a more advanced treatment of electron correlation is essential and in any case there are very many examples of spectroscopic states that cannot be represented as a single Slater determinant (and so cannot be treated using the standard HF model). In addition, the HF model can only treat the lowest-energy state of any given symmetry.

Let me give you a couple of simple examples to show where the HF model is inadequate.

1 Consider the electronic ground state of dicarbon C_2. Elementary arguments would suggest a ground state configuration

$$C_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 \quad {}^1\Sigma_g^+$$

which could certainly be treated using the HF model. But two other electronic configurations also have states that are also possible contenders to be the

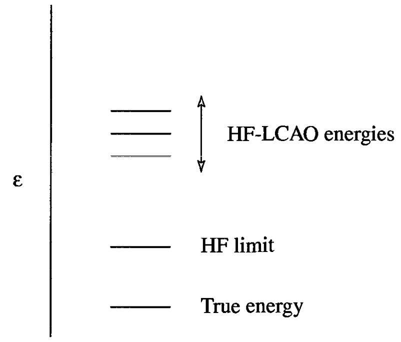


Figure 11.1 Relationships between energies

electronic ground state;

$$\mathrm{C_2}: 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^1 \quad {}^1\Pi_u, {}^3\Pi_u \qquad \text{and}$$

$$\mathrm{C_2}: 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2 \quad {}^1\Sigma_g^+, {}^3\Sigma_g^-, {}^1\Delta_g$$

Even at the equilibrium geometry, it is necessary to treat both of the ${}^1\Sigma_g^+$ states in order to get a reasonable description of the electronic wavefunction for the ground state.

2 In Chapter 4, we considered a simple LCAO treatment of dihydrogen and calculated the potential energy curve reproduced in Figure 11.2. The LCAOs we deduced correspond to HF–LCAO MOs for a minimal basis set.
The lowest-energy process for bond-breaking is

$$\mathrm{H_2} \rightarrow 2\mathrm{H}\,(^2\mathrm{S})$$

In the atomic system of units, the energy of a ground-state hydrogen atom is $-\frac{1}{2}\,E_h$ and so we would expect the potential curve to tend asymptotically to $-1E_h$. This is obviously not the case, and analysis of the results shows that the HF wavefunction describes the following process, for large R:

$$\mathrm{H_2} \rightarrow \tfrac{1}{2}\left(2\mathrm{H}\,(^2\mathrm{S}) + \mathrm{H}^+ + \mathrm{H}^-\right).$$

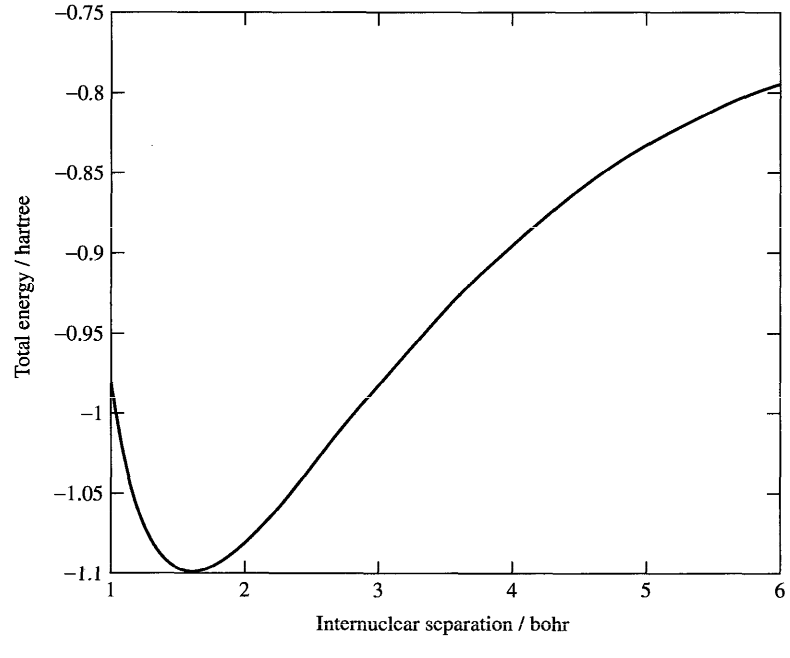


Figure 11.2 Dihydrogen potential energy curve HF–LCAO model

This turns out to be common behaviour for HF wavefunctions; wherever strong bonds are made or broken, the HF wavefunction will tend to give incorrect dissociation products.

In fact, I showed you how to solve this problem using configuration interaction. We write suitable singlet spin wavefunctions corresponding to the electronic configurations $1\sigma_g^2$, $1\sigma_g^1 1\sigma_u^1$ and $1\sigma_u^2$. According to the Brillouin theorem, singly excited states don't mix with the ground state in the HF model. In any case, the singly excited state has the wrong spatial symmetry for mixing with the ground state, so we mix together just the ground state and the doubly excited state.

This simple treatment is of great historical interest, but for a real molecule there will be a vast number of possible excited states and we obviously need to develop a systematic treatment in order to make sensible CI calculations on large systems.

11.1 CONFIGURATION INTERACTION

In Chapter 8, I discussed a ZDO treatment of the $\pi \rightarrow \pi^*$ transitions in pyridine using configuration interaction. I used singly excited states (sometimes referred to as *singles*), and explained the key steps in the calculation. I showed that a Hamiltonian matrix element between two singlet spin, singly excited states formed by promoting an electron from ψ_A to ψ_X (written Ψ_A^X) and from ψ_B to ψ_Y (written Ψ_B^Y) was given by

$$\int \psi_A^X \hat{H}_e \Psi_B^Y \, d\tau = - \iint \psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_X(\mathbf{r}_2)\psi_Y(\mathbf{r}_2)\, d\tau_1 \, d\tau_2$$
$$+ 2 \iint \psi_A(\mathbf{r}_1)\psi_X(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_B(\mathbf{r}_2)\psi_Y(\mathbf{r}_2)\, d\tau_1 \, d\tau_2 \qquad (11.2)$$

The two-electron integrals involve the LCAO orbitals, and the time-consuming part of a traditional CI calculation is the transformation of these to integrals involving the basis functions. This is often referred to as the *four-index transformation*. Not only that, it turns out that traditional CI calculations are very slowly convergent; we have to add a vast number of excited states in order to improve the energy significantly.

The reason usually advanced is that whilst the occupied orbitals are determined variationally within the HF–LCAO procedure, the virtual orbitals are not. Consequently, the virtual orbitals give a very poor description of excited states.

Nevertheless, CI is an important tool for addressing electron correlation. It is used in two different ways:

- to give a description of excited states;
- to improve the ground-state wavefunction and energy;

and a good place to start is with the 1992 paper of Foresman *et al.*

Towards a Systematic Molecular Orbital Theory for Excited States
James B. Foresman, Martin Head-Gordon, John A. Pople
and Michael J. Frisch
Journal of Physical Chemistry **96** (1992) 135

This work reviews the methodological and computational considerations necessary for the determination of the *ab initio* energy, wavefunction and gradient of a molecule in an electronically excited state using molecular orbital theory. In particular, this paper re-examines a fundamental level of theory which was employed several years ago for the interpretation of the electronic spectra of simple organic molecules: configuration interaction (CI) among all singly substituted determinants using a Hartree Fock reference state. This investigation presents several new enhancements to this general theory. First, it is shown how the CI singles wavefunction can be used to compute efficiently the analytic first derivative of the energy .... Second, a computer program is described which allows these computations to be done in a 'direct' fashion.

Part of this paper deals with energy gradients, a subject for a later chapter. You should recognize the phrase from Chapter 1, and realize that it is concerned with geometry optimization.

The basic idea is to take a single determinant ground-state HF wavefunction, and produce excited-state wavefunctions from it by replacing each occupied orbital in turn by each of the virtual orbitals. The variation principle is invoked in order to find linear combinations of the resulting Slater determinants. These linear combinations describe the excited states; some CI implementations allow for the fact that just the first few lowest-energy states will be of interest, and only calculate these explicitly. If all possible singly excited states are used, then we reach a level of theory known variously as *single-excitation configuration interaction* (SECI), *monoexcited* CI, *CIS* (CI singles), or the *Tamm–Dancoff* approximation.

The basis functions are kept constant throughout the calculation, as are the LCAO coefficients.

The treatment follows my discussion of the $\pi \rightarrow \pi^*$ spectra in Chapter 8. I actually performed a CIS calculation on pyridine within the ZDO scheme. If the ground state configuration is

$$\psi_A^2 \psi_B^2 \cdots \psi_M^2$$

with (unnormalized) Slater determinant

$$\Psi_0 = \begin{vmatrix} \psi_A(\mathbf{r}_1)\alpha(s_1) & \psi_A(\mathbf{r}_1)\beta(s_1) & \cdots & \psi_M(\mathbf{r}_1)\beta(s_1) \\ \psi_A(\mathbf{r}_2)\alpha(s_2) & \psi_A(\mathbf{r}_2)\beta(s_2) & \cdots & \psi_M(\mathbf{r}_2)\beta(s_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_A(\mathbf{r}_{2M})\alpha(s_{2M}) & \psi_A(\mathbf{r}_{2M})\beta(s_{2M}) & \cdots & \psi_M(\mathbf{r}_{2M})\beta(s_{2M}) \end{vmatrix} \qquad (11.3)$$

then single replacements such as

$$\psi_{\mathrm{A}}^{1}\psi_{\mathrm{X}}^{1}\psi_{\mathrm{B}}^{2}\cdots\psi_{\mathrm{M}}^{2}$$

can be represented by the two Slater determinants,

$$\begin{vmatrix} \psi_{\mathrm{A}}(\mathbf{r}_1)\alpha(s_1) & \psi_{X}(\mathbf{r}_1)\beta(s_1) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_1)\beta(s_1) \\ \psi_{\mathrm{A}}(\mathbf{r}_2)\alpha(s_2) & \psi_{X}(\mathbf{r}_2)\beta(s_2) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_2)\beta(s_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{\mathrm{A}}(\mathbf{r}_{2\mathrm{M}})\alpha(s_{2\mathrm{M}}) & \psi_{X}(\mathbf{r}_{2\mathrm{M}})\beta(s_{2\mathrm{M}}) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_{2\mathrm{M}})\beta(s_{2\mathrm{M}}) \end{vmatrix} \tag{11.4}$$

and

$$\begin{vmatrix} \psi_{\mathrm{X}}(\mathbf{r}_1)\alpha(s_1) & \psi_{\mathrm{A}}(\mathbf{r}_1)\beta(s_1) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_1)\beta(s_1) \\ \psi_{\mathrm{X}}(\mathbf{r}_2)\alpha(s_2) & \psi_{\mathrm{A}}(\mathbf{r}_2)\beta(s_2) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_2)\beta(s_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{\mathrm{X}}(\mathbf{r}_{2\mathrm{M}})\alpha(s_{2\mathrm{M}}) & \psi_{\mathrm{A}}(\mathbf{r}_{2\mathrm{M}})\beta(s_{2\mathrm{M}}) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_{2\mathrm{M}})\beta(s_{2\mathrm{M}}) \end{vmatrix} \tag{11.5}$$

In my discussion of pyridine, I took a combination of these determinants that had the correct singlet spin symmetry (that is, the combination that represented a singlet state). I could equally well have concentrated on the triplet states. In modern CI calculations, we simply use all the raw Slater determinants. Such single determinants by themselves are not necessarily spin eigenfunctions, but provided we include them all we will get correct spin eigenfunctions on diagonalization of the Hamiltonian matrix.

11.1.1 An *Ab Initio* CIS Calculation

Let's now look at an *ab initio* CIS calculation on pyridine. As a routine first step, I optimized the molecular geometry (yet to be discussed) at the HF/6–31G* level of theory. It is interesting to examine the *ab initio* orbital configuration (Figure 11.3).

The highest occupied a_2 and b_1 orbitals are of π type and MO number 19 (which is of a_1 type) is best thought of as the *n* orbital (i.e, a σ orbital more or

```
Orbital Symmetries:
      Occupied  (A1) (B2) (A1) (A1) (B2) (A1) (A1) (A1) (B2) (B2)
                (A1) (A1) (B2) (A1) (B2) (A1) (B1) (B2) (A1) (B1)
                (A2)
      Virtual   (B1) (A2) (A1) (B2) (A1) (A1) (B2) (B1) (A1) (B2)
                (A1) (B2) (B2) (A1) (B1) (B2) (A1) (A1) (A2) (B1)
                (B2) (A1) (A2) (A1) (B1) (B2) (A1) (B2) (A1) (B2)
                (A1) (B1) (B2) (A1) (A1) (B2) (B2) (A1) (A1) (B2)
                (A2) (A1) (B1) (B2) (A2) (B1) (B1) (A2) (A1) (A1)
                (A1) (B2) (A1) (B2) (A1) (A2) (B2) (B1) (B2) (A1)
                (B1) (A2) (B1) (A1) (B2) (A1) (A1) (A2) (B2) (B2)
                 .......
```

Figure 11.3

less localized on nitrogen). MO number 17 (b_1) is of π type and the remainder of the occupied orbitals are of σ type. The LUMO (orbital 22 of b_1 symmetry) is π^*, as is MO number 23, whilst MOs number 24 and 25 are of σ^* type. MO number 29 is π^*. There is an interesting overlap between the sets of σ, π and n orbitals.

On, then, to the CIS calculation. I ran the Gaussian98 job of Figure 11.5. The %chk record refers to the 'checkpoint' file, where I have stored all my pyridine Gaussian results. I studied the first 15 singlet excited states, and the `Symmetry=Loose` directive was included in order to make the package recognize C_{2v} symmetry (this is needed because of tiny rounding errors in the nuclear geometry). So we find Figure 11.6.

The phrase `symmetry adapted basis functions` refers to those linear combinations of basis functions (on several atoms) that transform like the particular irreducible representation of the appropriate point group. Molecular symmetry is used at various points in these calculations; twenty years ago I would have had to write several chapters on molecular symmetry, point groups, constructing symmetry-adapted combinations of basis functions, factoring a Hamiltonian matrix using symmetry and related topics. The point is that twenty

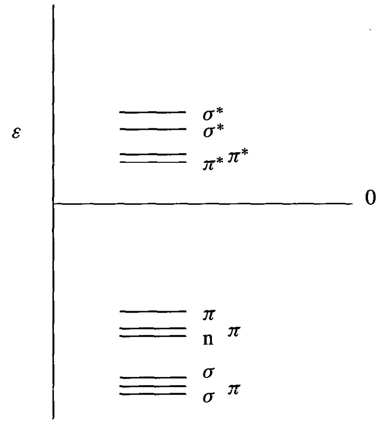


Figure 11.4 Orbital energy diagram

```
*********************************************
 Gaussian 98:  x86-Win32-G98RevA.3 2-Sep-1998
                29-Jul-1999
*********************************************
%chk=f:\modmol2\pyridine.chk
-----------------------------------------------------------------------
# RCIS=(NStates=15,Singlets)/6-31G* Guess=Read Geom=Check CIS=Direct #
Symmetry=Loose
-----------------------------------------------------------------------
```

Figure 11.5

```
Stoichiometry     C5H5N
 Framework group  C2V[C2(NCH),SGV(C4H4)]
 Deg. of freedom   10
 Full point group               C2V     NOp   4
 Largest Abelian subgroup       C2V     NOp   4
 Largest concise Abelian subgroup C2    NOp   2
Standard basis: 6-31G(d) (6D, 7F)
 There are    44 symmetry adapted basis functions of A1  symmetry.
 There are    10 symmetry adapted basis functions of A2  symmetry.
 There are    14 symmetry adapted basis functions of B1  symmetry.
 There are    32 symmetry adapted basis functions of B2  symmetry.
```

Figure 11.6

years ago one invariably studied simple molecules with high degrees of symmetry and it was necessary to manually include symmetry information in the molecule's dataset. Today, the emphasis has moved to large systems where there is essentially no molecular symmetry, but in any case the input is transparent.

It is usual to make the *frozen core* approximation in calculations of this type. This means that the seven inner shells are left frozen and not included in the CI calculation.

There are 100 basis functions and 21 electron pairs, giving a total of $(100 - 22 + 1) \times (21 - 7 + 1) = 1264$ possible singly excited configurations. We do not need to include the electronic ground state, which does not mix with singly excited states according to the Brillouin theorem. The intermediate details of the calculation are not of relevance to our discussion. The final output (Figure 11.7) consists of transition electric dipole moment vectors (which give measures of optical transition probabilities) followed by the velocity dipole transition

```
**********************************************************************
 Excited states from <AA,BB:AA,BB> singles matrix:
**********************************************************************

 Ground to excited state Transition electric dipole moments (Au):
       state          X           Y           Z          Osc.
         1          0.2132      0.0000      0.0000      0.0016
         2          0.0000     -0.6755      0.0000      0.0160
         3          0.0000      0.0000      0.3127      0.0037
         4          0.0000      0.0000      0.0000      0.0000
         5          0.0000      0.0000     -1.5520      0.1477
         6          0.0000     -1.5060      0.0000      0.1424
         7          0.0000      0.0000      0.0000      0.0000
         8          0.0000      0.0000      0.0000      0.0000
         9          0.1937      0.0000      0.0000      0.0035
        10          0.0159      0.0000      0.0000      0.0000
        11         -0.0727      0.0000      0.0000      0.0005
        12          0.0000      0.0000     -0.0025      0.0000
        13         -0.0339      0.0000      0.0000      0.0001
        14          0.0000      0.0000      0.0000      0.0000
        15         -0.0473      0.0000      0.0000      0.0003
```

Figure 11.7

```
Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-B1     6.1593 eV  201.29 nm  f=0.0016
      19 -> 22         0.62353
      19 -> 29         0.17224

 Excited State   2:   Singlet-B2     6.2393 eV  198.71 nm  f=0.0160
      20 -> 23        -0.43901
      21 -> 22         0.71451

 Excited State   3:   Singlet-A1     6.4810 eV  191.30 nm  f=0.0037
      20 -> 22         0.51178
      21 -> 23         0.61081

 Excited State   4:   Singlet-A2     7.4309 eV  166.85 nm  f=0.0000
      19 -> 23         0.68673

 Excited State   5:   Singlet-A1     8.2523 eV  150.24 nm  f=0.1477
      20 -> 22         0.43344
      21 -> 23        -0.32914

 Excited State   6:   Singlet-B2     8.3504 eV  148.48 nm  f=0.1424
      20 -> 23         0.52127
      21 -> 22         0.22250

 Excited State   7:   Singlet-A2     9.5874 eV  129.32 nm  f=0.0000
      13 -> 29        -0.11048
      18 -> 22         0.66163

 Excited State   8:   Singlet-A2     9.8517 eV  125.85 nm  f=0.0000
      17 -> 25         0.11413
      21 -> 24         0.66494

 Excited State   9:   Singlet-B1    10.2384 eV  121.10 nm  f=0.0035
      18 -> 23         0.63474
      20 -> 24        -0.13901
      21 -> 25        -0.15090

 Excited State  10:   Singlet-B1    10.3730 eV  119.52 nm  f=0.0000
      16 -> 22         0.28974
      17 -> 24         0.12749
      18 -> 23         0.17177
      19 -> 29         0.11827
      20 -> 24         0.48694
      21 -> 25         0.26104

 Excited State  11:   Singlet-B1    10.5776 eV  117.21 nm  f=0.0005
      16 -> 22         0.55320
      19 -> 22        -0.10156
      19 -> 29         0.15972
      20 -> 24        -0.24304
      21 -> 25        -0.17777

 Excited State  12:   Singlet-A1    11.1073 eV  111.62 nm  f=0.0000
      17 -> 22         0.61381
      19 -> 24         0.13502
      20 -> 29        -0.21363
```

Figure 11.8 *(continued)*

```
Excited State  13:   Singlet-B1    11.2926 eV  109.79 nm  f=0.0001
     17 -> 26         0.11306
     20 -> 24        -0.34991
     20 -> 27         0.11588
     21 -> 25         0.55600

Excited State  14:   Singlet-A2    11.4545 eV  108.24 nm  f=0.0000
     13 -> 22         0.27183
     14 -> 23        -0.14972
     15 -> 22        -0.37389
     16 -> 23         0.37982
     18 -> 29        -0.24753

Excited State  15:   Singlet-B1    11.5322 eV  107.51 nm  f=0.0003
     12 -> 29         0.10325
     13 -> 23         0.17548
     14 -> 22         0.11632
     15 -> 23         0.56037
     18 -> 23        -0.11083
     19 -> 29         0.23168
```

Figure 11.8

moments, transition magnetic dipole moments, excitation energies and oscillator strengths for the 15 lowest-energy singlet states.

The largest coefficients in the CI expansion are also given. A nice feature is that all transitions, $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and so on are treated on an equal footing with no 'calibration' against experiment. The agreement with experiment is not spectacular; no one would claim that CIS is a reliable tool for the accurate treatment of electronic spectra. Rather, it offers a low-level means of studying excited states with minimal inclusion of electron correlation.

11.1.2 CISD

The CIS procedure was designed to give a computationally inexpensive way of dealing with excited states. The next logical step is to include all doubly excited states. This can be done together with the singly excited ones (in which case we speak of *configuration interaction with all single and double substitutions*, CISD), or without the singly excited ones (in which case we speak of *configuration interaction with double substitutions*, CID).

The Brillouin theorem still applies (singly excited states do not interact with the ground state), but doubly excited states interact with the ground state and with the singly excited states (if present), so lowering the ground-state energy. This means that the singly excited states couple with the ground state via the doubly excited states. If we write Ψ^{HF} for the Hartree–Fock wavefunction and Ψ^{CISD} for the new ground-state wavefunction, then

$$\Psi^{\mathrm{CISD}} = \Psi^{\mathrm{HF}} + \sum_{\mathrm{A,X}} c_{\mathrm{A}}^{\mathrm{X}} \Psi_{\mathrm{A}}^{\mathrm{X}} + \sum_{\mathrm{A,B,X,Y}} c_{\mathrm{AB}}^{\mathrm{XY}} \Psi_{\mathrm{AB}}^{\mathrm{XY}} \tag{11.6}$$

where Ψ_A^X is a singly excited state formed by promoting from orbital ψ_A to virtual orbital ψ_X, Ψ_{AB}^{XY} a doubly excited state formed by promoting two electrons from ψ_A and ψ_B to ψ_X and ψ_Y. The c's are the expansion coefficients, and in order to normalize the wavefunction we would have to divide by

$$1 + \sum_{A,X} (c_A^X)^2 + \sum_{A,B,X,Y} (c_{AB}^{XY})^2 \tag{11.7}$$

To illustrate the CISD technique, consider dineon (Figure 11.9). HF theory cannot hope to give an accurate description of the dispersion interaction between two neon atoms, so an electron correlation treatment is vital. Here are the results for a separation of 300 pm.

The HF–LCAO calculation follows the usual lines (Figure 11.10) and the frozen core approximation is invoked by default for the CISD calculation. CISD is iterative, and eventually we arrive at the improved ground-state energy and normalization coefficient (as given by equation 11.7)—Figure 11.11.

```
*******************************************
Gaussian 98:  x86-Win32-G98RevA.3 2-Sep-1998
               30-Jul-1999
*******************************************
-------------
#CISD/6-311G*
-------------
-------------
Neon ... Neon
-------------
```

Figure 11.9

```
Requested convergence on RMS density matrix=1.00D-08 within  64
cycles.
 Requested convergence on MAX density matrix=1.00D-06.
 Keep R1 integrals in memory in canonical form, NReq=
714311.
 SCF Done:  E(RHF) =  -257.045191385     A.U. after    7 cycles
            Convg  =     0.2525D-08           -V/T =  1.9997
            S**2   =   0.0000
 Range of M.O.s used for correlation:    3    36
```

Figure 11.10

```
Iteration   Nr.   7
 **********************
 DE(CI)=   -0.40155306D+00        E(CI)=       -0.25744674445D+03
 NORM(A)=   0.10248950D+01
```

Figure 11.11

Table 11.1 Dineon 6–311G* calculations

Method	5000 pm	Atom energy
HF–LCAO	−257.045 106 1	−128.522 553 05
CISD	−257.446 614 7	−128.728 395 6

Table 11.1 shows an interesting point about CISD. The energy of the dineon pair at the arbitrarily large separation of 5000 pm is exactly twice the energy of two free atoms at the HF–LCAO level of theory, but this is not the case at the CISD level of theory. We say that HF theory *scales* correctly, whilst CISD does not.

More rigorously, if we have an ensemble of n particles and their energy at a certain level of theory is related to the energy of a single particle (at the same level of theory) by $\varepsilon(n) = n\varepsilon(1)$, then we say that the theory scales correctly.

In calculating a pair potential for dineon, we have to take the 'separated atom' energy as one half of the pair energy for an arbitrarily large distance.

11.2 PERTURBATION THEORY

The number of problems that can be solved exactly in mechanics is not large. Once we have to treat three interacting bodies, life becomes very difficult indeed. This comment applies to classical mechanics just as to quantum mechanics. What we often do is to look for a simple, idealized problem that we can solve exactly, and then treat the real problem in hand as some kind of perturbation on the idealized one.

Suppose then that our problem is to solve

$$\hat{H}\Psi_i = \varepsilon_i\Psi_i \tag{11.8}$$

which at first sight does not seem to be capable of solution, whilst the simpler problem

$$\hat{H}_i^0\Psi_i^0 = \varepsilon_i^0\Psi_i^0 \tag{11.9}$$

can be solved on the back of a postcard. For example, $\hat{H}$ might be the Hamiltonian for a helium atom whilst the simpler Hamiltonian $\hat{H}^0$ might refer to two superimposed deuterium atoms with non-interacting electrons. We can solve the $\hat{H}^0$ problem very easily: the wavefunction is just a product of hydrogenic orbitals.

In perturbation theory, we write the 'true' Hamiltonian $\hat{H}$ in terms of $\hat{H}^0$ and a perturbation $\hat{H}^{(1)}$

$$\hat{H} = \hat{H}^0 + \lambda\hat{H}^{(1)} \tag{11.10}$$

I have included the arbitrary parameter λ in order to keep track of orders of magnitude. I will later set it to unity. In the case of the helium problem above, the perturbation would be just the Coulomb repulsion between the electrons.

Very occasionally, we might need to add more than one perturbation; for example, if we wanted to study a molecule subject to external electric and magnetic fields, we might write something like

$$\hat{H} = \hat{H}^{00} + \lambda \hat{H}^{(10)} + \eta \hat{H}^{(01)} \tag{11.11}$$

where the double superscript refers to the double perturbation. 00 indicates a molecule in the absence of the perturbation, 01 might indicate the presence of the electric field and the absence of the magnetic one, 10 the presence of the magnetic field and the absence of the electric one, and so on. I am assuming that we can solve the field-free problem $\hat{H}^{00}\Psi^{00} = \varepsilon^{00}\Psi^{00}$ to chemical accuracy.

Back now to the simpler case of a single perturbation. Perturbation theory aims to write solutions for

$$\hat{H}\Psi_i = \varepsilon_i \Psi_i$$

in terms of the known solutions for the zero-order problem

$$\hat{H}^0 \Psi_i^0 = \varepsilon_i^0 \Psi_i^0$$

where $\hat{H} = \hat{H}^0 + \lambda \hat{H}^{(1)}$

To this end we make a *perturbation expansion* of the wavefunctions and energies

$$\begin{aligned} \Psi_i &= \Psi_i^0 + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \cdots \\ \varepsilon_i &= \varepsilon_i^0 + \lambda \varepsilon_i^{(1)} + \lambda^2 \varepsilon_i^{(2)} + \cdots \end{aligned} \tag{11.12}$$

If we substitute these series into equation 11.8, we find

$$\begin{aligned} &\hat{H}_0 \Psi_i^0 + \lambda \left(\hat{H}^{(1)} \Psi_i^0 + \hat{H}^0 \Psi_i^{(1)} \right) + \lambda^2 \left(\hat{H}^{(1)} \Psi_i^{(1)} + \hat{H}^0 \Psi_i^{(2)} \right) + \cdots \\ &\quad = \varepsilon_i^0 \Psi_i^0 + \lambda \left(\varepsilon_i^{(1)} \Psi_i^0 + \varepsilon_i^{(0)} \Psi_i^{(1)} \right) + \lambda^2 \left(\varepsilon_i^{(2)} \Psi_i^0 + \varepsilon_i^{(1)} \Psi_i^{(1)} + \varepsilon_i^0 \Psi_i^{(2)} \right) + \cdots \end{aligned} \tag{11.13}$$

In order that this equation may be satisfied for all values of λ the coefficients of the various powers of λ on the two sides of the equation must be equal. We find

$$\begin{aligned} \hat{H}_0 \Psi_i^0 &= \varepsilon_i^0 \Psi_i^0 \\ \hat{H}^{(1)} \Psi_i^0 + \hat{H}^0 \Psi_i^{(1)} &= \varepsilon_i^{(1)} \Psi_i^0 + \varepsilon_i^{(0)} \Psi_i^{(1)} \\ \hat{H}^{(1)} \Psi_i^{(1)} + \hat{H}^0 \Psi_i^{(2)} &= \varepsilon_i^{(2)} \Psi_i^0 + \varepsilon_i^{(1)} \Psi_i^{(1)} + \varepsilon_i^0 \Psi_i^{(2)} \end{aligned} \tag{11.14}$$

The first of these is already solved, by assumption. If the second can be solved, we can find the first-order corrections to the wavefunction $\Psi_i^{(1)}$ and the energy $\varepsilon_i^{(1)}$. Solution of the third equation gives the second-order corrections, and so on. It is shown in the standard textbooks (e.g. Eyring, Walter and Kimball, 1944) that the solutions are

$$\varepsilon_i = \varepsilon_i^0 + \lambda H_{ii}^{(1)} + \lambda^2 \sum_{j \neq i} \frac{H_{ij}^{(1)} H_{ji}^{(1)}}{\varepsilon_i^0 - \varepsilon_j^0} + \lambda^3 (\cdots) + \cdots \tag{11.15}$$

$$\Psi_i = \Psi_i^0 + \lambda \sum_{j \neq i} \frac{H_{ij}^{(1)}}{\varepsilon_i^0 - \varepsilon_j^0} \Psi_j^0$$

$$+ \lambda^2 \sum_{k \neq i} \left(\sum_{m \neq i} \frac{H_{km}^{(1)} H_{mi}^{(1)}}{\left(\varepsilon_i^0 - \varepsilon_k^0\right)\left(\varepsilon_i^0 - \varepsilon_m^0\right)} - \frac{H_{ii}^{(1)} H_{ki}^{(1)}}{\left(\varepsilon_i^0 - \varepsilon_k^0\right)^2} \right) \Psi_k^0 + \lambda^3(\cdots) + \cdots \tag{11.16}$$

where (for example)

$$H_{ij}^{(1)} = \int \left(\Psi_i^0\right)^* \hat{H}^{(1)} \Psi_j^0 \, \mathrm{d}\tau$$

or, if the wavefunctions are all real quantities,

$$H_{ij}^{(1)} = \int \Psi_i^0 \hat{H}^{(1)} \Psi_j^0 \, \mathrm{d}\tau$$

The first-order energy involves only the perturbation operator and the unperturbed wavefunction. In an HF–LCAO treatment, the integrals would be over the LCAOs, and this implies a four-index transformation to integrals over the basis functions.

11.3 MØLLER–PLESSET PERTURBATION THEORY

Until the advent of density functional theory (Chapter 13), thinking centred around means of circumventing the two-electron integral transformation, or at least partially circumventing it. The Møller–Plesset method is one of immense historical importance, and you might like to read the original paper.

> Note on an Approximate Treatment for Many-Electron Systems
> Chr. Møller and M. S. Plesset
> *Physical Review* **46** (1934) 618
>
> A Perturbation Theory is developed for treating a system of n electrons in which the Hartree–Fock solution appears as the zero-order approximation. It is shown by this development that the first order correction for the energy and the charge density of the system is zero. The expression for the second order correction for the energy greatly simplifies because of the special property of the zero order solution. It is pointed out that the development of the higher order approximation involves only calculations based on a definite one-body problem.

The idea is simple. We take the zero-order problem as the HF (or HF–LCAO) one, where each electron moves in an average field due to the nuclei and the remaining electrons. The perturbation is the difference between the true Hamiltonian and the HF Hamiltonian. Because of the special features of the zero-order problem, it is not necessary to fully transform all the two-electron integrals; all that is needed is a partial transformation. Depending on the order of perturbation theory, we speak of *MP2*, *MP3*, *MP4*, ... or generically *MPn* calculations.

Pople, Binkley and Seeger (amongst others) have made a systematic study of the MP method. Here is their summary.

> Theoretical Models Incorporating Electron Correlation
> John A. Pople, J. Stephen Binkley and Rolf Seeger
> *International Journal of Quantum Theory*, Symp. No. **10** (1976) 1
>
> Some methods of describing electron correlation are compared from the point of view of requirements for theoretical chemical models. The perturbation approach originally introduced by Møller and Plesset, terminated at finite order, is found to satisfy most of these requirements. It is size consistent, that is applicable to an ensemble of isolated systems in an additive manner. On the other hand, it does not provide an upper bound for the electronic energy ... .
>
> Equilibrium geometries, dissociation energies, and energy separations between electronic states of different spin multiplicities are described substantially better by Møller–Plesset theory to second or third order than by Hartree–Fock theory.

As a simple example, let's return to the dineon problem discussed above. Here are the salient points from a Gaussian run at 300 pm. Figure 11.12 shows the standard HF–LCAO calculation.

Next come the integral transformations (not shown) and then (Figure 11.13) the various contributions to the second, third and fourth order MPn energies. The

```
 ------------
 #MP4/6-311G*
 ------------
 -------------
 Neon ... Neon
 -------------

Requested convergence on RMS density matrix=1.00D-08 within  64
cycles.
 Requested convergence on MAX density matrix=1.00D-06.
 Keep R1 integrals in memory in canonical form, NReq=
714311.
 SCF Done:  E(RHF) =  -257.045191385     A.U. after    7 cycles
            Convg  =     0.2525D-08            -V/T =  1.9997
            S**2   =   0.0000
```

Figure 11.12

```
spin components of T(2) and E(2):
     alpha-alpha T2 =       0.7548320174D-02 E2=      -
0.5726319677D-01
     alpha-beta  T2 =       0.4048023368D-01 E2=      -
0.3035686778D+00
     beta-beta   T2 =       0.7548320174D-02 E2=      -
0.5726319677D-01
 ANorm=     0.1027412709D+01
 E2=        -0.4180950714D+00 EUMP2=       -0.25746328645640D+03
 R2 and R3 integrals will be kept in memory, NReq=      979822.
 DD1Dir will call FoFMem   1 times, MxPair=        72
 NAB=    36 NAA=      0 NBB=      0.
 MP4(D)= -0.32010852D-02
 MP4(S)= -0.15655063D-02
 MP4(R+Q)=  0.92129416D-03
 Time for triples=       22.00 seconds.
 MP4(T)=   -0.47497314D-02
 E3=        0.51230403D-03        EUMP3=       -0.25746277415D+03
 E4(DQ)=   -0.22797910D-02        UMP4(DQ)=    -0.25746505394D+03
 E4(SDQ)=  -0.38452973D-02        UMP4(SDQ)=   -0.25746661945D+03
 E4(SDTQ)= -0.85950287D-02        UMP4(SDTQ)= -0.25747136918D+03
 Largest amplitude= 1.90D-02
```

Figure 11.13

notation is that (for example) `E4(SDTQ)` is the contribution to the fourth-order energy made by single, double, triple and quadruple excitations. It is `UMP4` rather than `RMP4` because the code was written for the UHF case.

11.4 THE DINEON PAIR POTENTIAL

I have used dineon as an example in this chapter; you might like to compare the various models for the dineon pair potential. This is done for the HF/6–311G*, MP2/6–311G* and CISD/6–311G* levels of theory in Figure 11.14. The potential minima and distances are shown in Table 11.2, together with two 'experimental' values that have been deduced from studies using Lennard–Jones potentials. The two experimental results differ significantly: we have to distinguish results that are appropriate to an isolated pair of particles in the gas phase (I), and experimental results that refer to condensed phases such as liquids (II). In the latter case, the pair potential is an 'effective' one, since it absorbs the effects of three, four and higher many-body interactions.

Electron correlation studies demand basis sets that are capable of very high accuracy, and the 6–311G* set I used for the examples above is not truly adequate. A number of basis sets have been carefully designed for correlation studies, for example the *correlation consistent basis sets* of Dunning. These go by the acronyms cc–pVDZ, cc–pVTZ, cc–pVQZ, cc–pV5Z and cc–pV6Z (double, triple, quadruple, quintuple and sextuple-zeta respectively). They include polarization functions by definition, and (for example) the cc–pV6Z set consists of 7s, 6p, 4d, 3f, 2g and 1h basis functions.

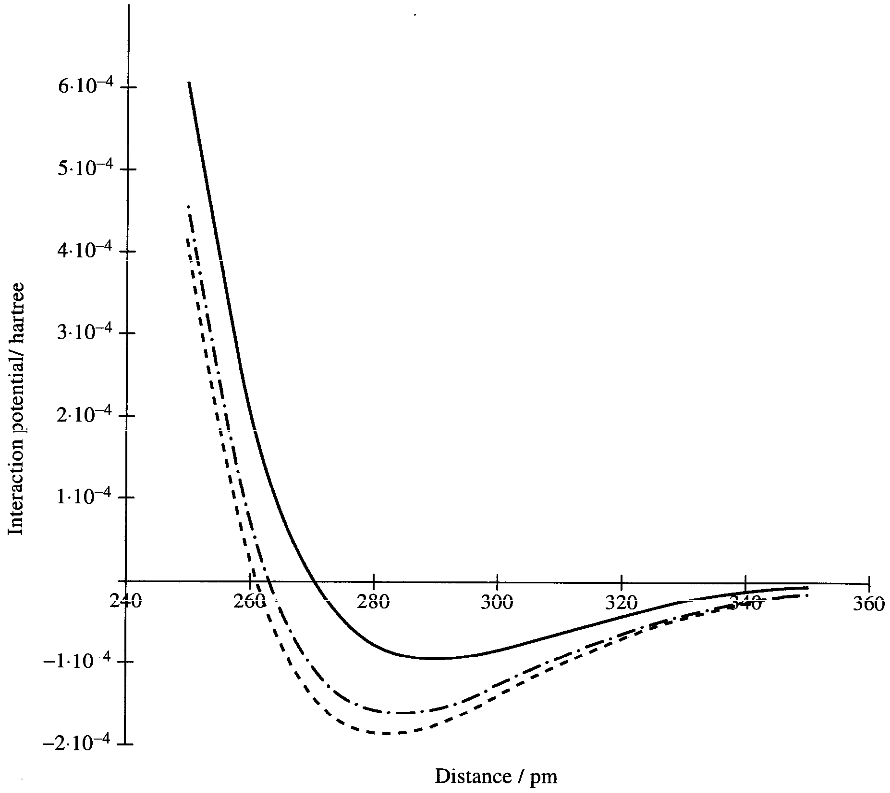


Figure 11.14 Dineon pair potential HF–LCAO, MP2 and CISD/6–311G*

Table 11.2 Dineon potential energy parameters

Level of theory	R/pm	$\varepsilon_{\text{min}}/J\ \text{mol}^{-1}$
HF/6–311G*	289.3	257.6
MP2/6–311G*	282.1	545.1
CISD/6–311G*	283.8	436.9
HF/cc–pVTZ	312.2	140.8
MP2/cc–pVTZ	298.3	445.8
CISD/cc–pVTZ	300.7	362.1
Lennard-Jones (I) Maitland, *et al.* (1981)	272.0	391
Lennard-Jones (II) Hirschfelder, Curtiss and Bird (1900)	279.0	297

I have included some representative results in the table, using the cc-pVTZ basis set.

If the neon-neon interaction were a pure dispersion one, then the HF-LCAO calculation would give a fully repulsive curve. The fact that the HF-LCAO calculation gives a shallow minimum implies an element of covalency.

Most of the calculations cited give qualitative agreement with 'experiment', but none agrees quantitatively.

11.5 MULTICONFIGURATION SCF

In Chapter 6, I discussed the open-shell HF-LCAO model. I considered the simple case where we had n_1 doubly occupied orbitals and n_2 orbitals all singly occupied by parallel spin electrons. The ground-state wavefunction was a single Slater determinant. I explained that it was possible to derive an expression for the electronic energy

$$
\begin{aligned}
\varepsilon_e = \nu_1 & \left(\begin{array}{l} \displaystyle\sum_R \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,d\tau_1 \\ \displaystyle +\frac{1}{2}\nu_1 \sum_R \sum_S \left(\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_S^2(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \right. \\ \displaystyle \left. -\frac{1}{2}\iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \right) \end{array} \right) \\
+ \nu_2 & \left(\begin{array}{l} \displaystyle\sum_U \int \psi_U(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_U(\mathbf{r}_1)\,d\tau_1 \\ \displaystyle +\frac{1}{2}\nu_2 \sum_U \sum_V \left(\iint \psi_U^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_V^2(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \right. \\ \displaystyle \left. -\iint \psi_U(\mathbf{r}_1)\psi_V(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_U(\mathbf{r}_2)\psi_V(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \right) \end{array} \right) \\
+ \nu_1\nu_2 & \left(\sum_R \sum_U \left(\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_U^2(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \right. \right. \\
& \left. \left. -\frac{1}{2}\iint \psi_R(\mathbf{r}_1)\psi_U(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_U(\mathbf{r}_2)\,d\tau_1\,d\tau_2 \right) \right)
\end{aligned}
\tag{11.17}
$$

where R and S run over the doubly occupied orbitals and U, V run over the singly occupied orbitals (which contain electrons with parallel spins) I have followed common practise and introduced the *occupation numbers* ν_1 and ν_2, to demonstrate the symmetry of the result. In this case, $\nu_1 = n_1$ and $\nu_2 = n_2$ but more general cases are possible.

It turns out that certain electronic states of atoms and linear molecules, even those requiring many-determinant wavefunctions, may have an energy expression of the form

$$\begin{aligned}\varepsilon_{\mathrm{e}} = 2 &\left(\begin{aligned} &\sum_{R} \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ &+\sum_{R}\sum_{S}\left(\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_S^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \right.\\ &\left. -\frac{1}{2}\iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right) \end{aligned} \right) \\ + \nu_2 &\left(\begin{aligned} &\sum_{U} \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ &+\frac{1}{2}\nu_2\sum_{U}\sum_{V}\left(a\iint \psi_U^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_V^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \right.\\ &\left. -\frac{1}{2}b\iint \psi_U(\mathbf{r}_1)\psi_V(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_U(\mathbf{r}_2)\psi_V(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right) \end{aligned} \right) \\ + 2\nu_2 &\left(\sum_{R}\sum_{U}\left(\iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_U^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right.\right. \\ &\left.\left. -\frac{1}{2}\iint \psi_R(\mathbf{r}_1)\psi_U(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_U(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right)\right)\end{aligned} \tag{11.18}$$

The constants ν_1, ν_2, a and b depend on the particular electronic state under consideration, and they have been listed by Roothaan (1960). Open-shell HF theory can deal with such states.

There are, however, many electronic states for which a linear combination of determinants is essential, but which cannot by treated using HF theory.

It is also a common experience that traditional CI calculations converge very poorly, because the virtual orbitals produced from an HF (or HF–LCAO) calculation are not determined by the variation principle and turn out to be very poor for representations of excited states.

Multiconfiguration self-consistent field (MCSCF) theory aims to optimize simultaneously the LCAO coefficients and the CI expansion coefficients in a wavefunction such as

$$\Psi = c_0\Psi_0 + \sum c_{\mathrm{A}}^{\mathrm{X}}\Psi_{\mathrm{A}}^{\mathrm{X}} + \cdots \tag{11.19}$$

discussed above. I have written the wavefunction emotively as if it were dominated by a ground state Ψ_0, but this may not be the case. In the singlet dihydrogen excited state example, we would have to include two Slater determinants of equal weight corresponding to the electron configuration $1\sigma_g^1 1\sigma_u^1$, together with a number of less important higher excited configurations.

MCSCF theory is a specialist branch of quantum modelling. Over the years it has become apparent that there are computational advantages in treating all possible excitations arising by promoting electron(s) from a (sub)set of the occupied orbitals to a (sub)set of the virtual orbitals. We then speak of *complete active space* MCSCF, or CASSCF.

```
*******************************************
Gaussian 98:  x86-Win32-G98RevA.3 2-Sep-1998
                  15-Aug-1999
*******************************************
%chk=f:\modmol2\ethene.chk
---------------------------------------------------------
# CASSCF(2,2)/cc-pVTZ Symmetry=Loose Guess=Read Geom=Check
---------------------------------------------------------
```

Figure 11.15

```
ENTER MCSCF PROGRAM
 NO. OF ORBITALS =116    NO. OF CORE-ORBITALS =  7
 NO. OF VALENCE-ORBITALS =  2     NO. OF VIRTUAL-ORBITALS =107
 USED ACCURACY IN CHECKING CONVEGERGENCE =  1.00D-05
 InCore calculation needs more space:   37926342
 In this calculation the integrals will be calculated in every iteration
 and Contracted with The Density Matrices
Do  4 iterations with Incremental Fock Matrices and then one Full.
IBUJAK length=       68120
Symmetry not used in FoFDir.
MinBra= 0 MaxBra= 3 Meth= 1.
IRaf=    -5 NMat=  4 IRICut=       1 DoRegI=T DoRafI=F ISym2E= 0 JSym2E=0.
Defining IBUGAM
2ND ORD PT ENERGY    CV   0.000000  CU  -0.000016  UV  -0.007902
TOTAL                    -78.085413
ITN=  1 MaxIt= 64 E=   -78.0774944659 DE=-7.81D+01 Acc= 1.00D-05 Lan=  0
ITN=  2 MaxIt= 64 E=   -78.0898795485 DE=-1.24D-02 Acc= 1.00D-05 Lan=  0
ITN=  3 MaxIt= 64 E=   -78.0907919941 DE=-9.12D-04 Acc= 1.00D-05 Lan=  0
ITN=  4 MaxIt= 64 E=   -78.0909381754 DE=-1.46D-04 Acc= 1.00D-05 Lan=  0
ITN=  5 MaxIt= 64 E=   -78.0909656422 DE=-2.75D-05 Acc= 1.00D-05 Lan=  0
ITN=  6 MaxIt= 64 E=   -78.0909710896 DE=-5.45D-06 Acc= 1.00D-05 Lan=  0
... DO AN EXTRA-ITERATION FOR FINAL PRINTING
Final one electron symbolic density matrix:
          1            2
 1  0.191968D+01
 2  0.000000D+00  0.803168D-01
MCSCF converged.
```

Figure 11.16

To give a numerical example, consider ethene. In the traditional HF–LCAO treatment there are eight doubly occupied orbitals, and descriptive chemistry leads us to believe that both the HOMO and the LUMO will be of π type. An HF–LCAO calculation using the cc–pVTZ basis set does indeed give such an ordering. The salient features from a CASSCF calculation using an active space comprising just the HOMO and the LUMO are shown in Figure 11.15. The `(2,2)` means that I have included the highest two electrons, and enough virtual orbitals to make a total of two orbitals. I optimized the geometry in a previous calculation, and saved the results on the checkpoint file.

The main output is shown in Figure 11.16. The energy of the ground state is given, together with the 'one-electron symbolic density matrix'.

11.6 QUADRATIC CONFIGURATION INTERACTION

A full configuration interaction calculation is only possible for very small systems. Limited CI expansions (CID and CISD) are widely used; they give energies that are upper bounds to the correct energy (they are said to be *variational*) but they are not size-consistent. Langhoff and Davidson (1974) gave a simple correction to the CISD method that makes the energies approximately size-consistent but no longer variational. The CISD method also omits the effects of triple substitutions.

The MP*n* method treats the correlation part of the Hamiltonian as a perturbation on the Hartree–Fock part, and truncates the perturbation expansion at some order, typically $n = 4$. MP4 theory incorporates the effect of single, double, triple and quadruple substitutions. The method is size-consistent but not variational. It is commonly believed that the series MP1, MP2, MP3, ... converges very slowly.

Quadratic Configuration Interaction. A general technique for determining electron correlation energies
John A. Pople, Martin Head-Gordon and Krishnan Raghavachari
Journal of Chemical Physics **87** (1987) 5968–5975

A general procedure is introduced for calculation of the electron correlation energy, starting from a single Hartree–Fock determinant. The normal equations of (linear) configuration interaction theory are modified by introducing new terms which are quadratic in the configuration coefficients and which ensure size consistency in the resulting total energy. When used in the truncated configuration space of single and double substitutions, the method termed QCISD, leads to a tractable set of quadratic equations. The relation of this method to coupled cluster (CCSD) theory is discussed. A simplified method of adding corrections for triple substitutions is outlined, leading to a method termed QCISD(T). Both of these new procedures are tested (and compared with other procedures) by application to some small systems for which full configuration interaction results are available.

Suppose we have an HF determinantal wavefunction Ψ_0 constructed from singly occupied spin orbitals $\psi_1, \psi_2, \ldots, \psi_n$ (that is, a UHF wavefunction). Other determinantal wavefunctions are derived from Ψ_0 by substitution of occupied spin orbitals by virtual spin orbitals. If we use indices A, B, ... for the occupied spin orbitals and X, Y, ... for the virtual spin orbitals, then we define complete single, double, triple, ... substitution operators

$$\begin{aligned}\hat{T}_1 &= \sum_{\mathrm{A,X}} a_{\mathrm{A}}^{\mathrm{X}} \hat{t}_{\mathrm{A}}^{\mathrm{X}} \\ \hat{T}_2 &= \frac{1}{4} \sum_{\mathrm{A,B,X,Y}} a_{\mathrm{AB}}^{\mathrm{XY}} \hat{t}_{\mathrm{AB}}^{\mathrm{XY}} \\ \hat{T}_3 &= \frac{1}{36} \sum_{\mathrm{A,B,C,X,Y,Z}} a_{\mathrm{ABC}}^{\mathrm{XYZ}} \hat{t}_{\mathrm{ABC}}^{\mathrm{XYZ}}\end{aligned} \tag{11.20}$$

where the t's are elementary substitution operators and the a's are coefficients that have to be determined.

Various types of antisymmetric wavefunction can be obtained by applying different functions of the T operators to Ψ_0, and the unknown coefficients together with the energy can be determined from the *projection equations*

$$\begin{aligned}\int \Psi_0(\hat{H} - \varepsilon)\Psi \, \mathrm{d}\tau &= 0 \\ \int \Psi_{\mathrm{A}}^{\mathrm{X}}(\hat{H} - \varepsilon)\Psi \, \mathrm{d}\tau &= 0 \\ \int \Psi_{\mathrm{AB}}^{\mathrm{XY}}(\hat{H} - \varepsilon)\Psi \, \mathrm{d}\tau &= 0\end{aligned} \tag{11.21}$$

The simplest choice for the T operators is linear, and so we have

$$\begin{aligned}\Psi_{\mathrm{CID}} &= (1 + \hat{T}_2)\Psi_0 \\ \Psi_{\mathrm{CISD}} &= (1 + \hat{T}_1 + \hat{T}_2)\Psi_0\end{aligned} \tag{11.22}$$

The projection equations are then identical with those obtained by minimizing the energy and so the CID and CISD energies are truly variational (they give upper bounds to the full CI result).

If we define

$$\begin{aligned}\hat{H} &= \hat{H}^{\mathrm{HF}} + \hat{V} \\ \varepsilon &= \varepsilon^{\mathrm{HF}} + \varepsilon^{\mathrm{correlation}}\end{aligned} \tag{11.23}$$

where the superscript HF refers to the Hartree–Fock wavefunction, the projection equations become

$$\begin{aligned}
\int \Psi_0 \hat{H} T_2 \Psi_0 \,\mathrm{d}\tau &= \varepsilon^{\text{correlation}} \\
\int \Psi_{\mathrm{A}}^{\mathrm{X}} \left(\hat{H} - \varepsilon^{\mathrm{HF}}\right) \left(\hat{T}_1 + \hat{T}_2\right) \Psi_0 \,\mathrm{d}\tau &= a_{\mathrm{A}}^{\mathrm{X}} \varepsilon^{\text{correlation}} \\
\int \Psi_{\mathrm{AB}}^{\mathrm{XY}} \left(\hat{H} - \varepsilon^{\mathrm{HF}}\right) \left(1 + \hat{T}_1 + \hat{T}_2\right) \Psi_0 \,\mathrm{d}\tau &= a_{\mathrm{AB}}^{\mathrm{XY}} \varepsilon^{\text{correlation}}
\end{aligned} \tag{11.24}$$

and the CISD energy is not size-consistent. The energy can be made size-consistent by introducing quadratic T terms as follows:

$$\begin{aligned}
\int \Psi_0 \hat{H} T_2 \Psi_0 \,\mathrm{d}\tau &= \varepsilon^{\text{correlation}} \\
\int \Psi_{\mathrm{A}}^{\mathrm{X}} \left(\hat{H} - \varepsilon^{\mathrm{HF}}\right) \left(\hat{T}_1 + \hat{T}_2 + \hat{T}_1\hat{T}_2\right) \Psi_0 \,\mathrm{d}\tau &= a_{A}^{X} \varepsilon^{\text{correlation}} \\
\int \Psi_{\mathrm{AB}}^{\mathrm{XY}} \left(\hat{H} - \varepsilon^{\mathrm{HF}}\right) \left(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2\right) \Psi_0 \,\mathrm{d}\tau &= a_{AB}^{XY} \varepsilon^{\text{correlation}}
\end{aligned} \tag{11.25}$$

and these equations form the basis of the QCISD method.

QCISD still takes inadequate account of the triple substitutions. If their effect is small, they may be added as a perturbation after calculation of the singles plus doubles. This is the basis of the QCISD(T) method.

11.7 RESOURCE CONSUMPTION

Many authors have drawn attention to the resource implications of *ab initio* calculations. Schlegel and Frisch (1990) give a particularly comprehensive review. The two resources to be considered are CPU usage and disk usage. A small subset of Schlegel and Frisch's tables are given in Table 11.3; n is the number of basis functions and O is the number of occupied orbitals.

Table 11.3 Resource consumption

	CPU usage	Disk usage
Conventional HF–LCAO	$n^{3.5}$	$n^{3.5}$
Direct HF–LCAO	$n^{2.7}$	n^2
Conventional MP2	On^4	n^4
Direct MP2	O^2n^3	n^2
CISD	O^2n^4	n^4

12 SLATER'S Xα MODEL

I have dealt at length with the Hartree and the Hartree–Fock models. The father of this field, Sir William Hartree, was concerned with the atomic problem where it is routinely possible to integrate numerically the HF integro-differential equations in order to produce (numerical) wavefunctions that correspond to the Hartree–Fock limit. For molecular applications the LCAO variant of HF theory assumes a dominant role because of the reduced symmetry of the problem.

Briefly, we write the atomic orbitals for a one-electron atom as

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \tag{12.1}$$

and separate out the radial and angular variables, by making use of the standard separation-of-variables technique. This gives the radial equation

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \left[\frac{8\pi^2\mu}{h^2}(\varepsilon - U(r)) - \frac{l(l+1)}{r^2}\right]R(r) = 0 \tag{12.2}$$

$R(r)$ is called the *radial function*, and $Y_{l,m_l}(\theta, \phi)$ is a spherical harmonic. $U(r)$ is the mutual potential energy of the nucleus and the electron.

In order to retain the orbital model for a many-electron atom, Hartree assumed that each electron came under the influence of the nuclear charge and an average potential due to the remaining electrons. He therefore retained the form of the radial equation for a one-electron atom, equation 12.2, but assumed that the mutual potential energy U was the sum of

- that between the electron and the nucleus, and
- an average between the same electron and the remaining electrons in the atom.

Sir William Hartree developed ingenious ways of solving the radial equation, and they are documented in Douglas R. Hartree's book (1957). By the time this book was published, the SCF method had been well developed, and its connection with the variation principle was finally understood. It is interesting to note that Chapter 2 of Douglas R. Hartree's book deals with the variation principle.

So, if we consider a closed-shell singlet state with m electron pairs and electronic configuration

$$\psi_{\mathrm{A}}^2 \psi_{\mathrm{B}}^2 \cdots \psi_{\mathrm{M}}^2$$

then we can write either a simple product wavefunction

$$\Psi_{\mathrm{e}}(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \ldots, \mathbf{r}_n, \mathrm{s}_n) = \psi_{\mathrm{A}}(\mathbf{r}_1)\alpha(\mathrm{s}_1)\psi_{\mathrm{A}}(\mathbf{r}_2)\beta(\mathrm{s}_2) \cdots \psi_{\mathrm{M}}(\mathbf{r}_{2m})\beta(\mathrm{s}_{2m}) \tag{12.3}$$

for which the electronic energy is

$$\begin{aligned} \varepsilon_{\mathrm{e}} = {} & 2\sum_{R=\mathrm{A}}^{\mathrm{M}} \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ & + \sum_{R=A}^{\mathrm{M}} \sum_{S=\mathrm{A}}^{\mathrm{M}} 2 \iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_S^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \end{aligned} \tag{12.4}$$

or an (unnormalized) Slater determinant

$$\Psi_{\mathrm{e}}(\mathbf{r}_1, \mathrm{s}_1, \mathbf{r}_2, \mathrm{s}_2, \ldots, \mathbf{r}_{2m}, \mathrm{s}_{2m}) = \begin{vmatrix} \psi_{\mathrm{A}}(\mathbf{r}_1)\alpha(\mathrm{s}_1) & \psi_{\mathrm{A}}(\mathbf{r}_1)\beta(\mathrm{s}_1) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_1)\beta(\mathrm{s}_1) \\ \psi_{\mathrm{A}}(\mathbf{r}_2)\alpha(\mathrm{s}_2) & \psi_{\mathrm{A}}(\mathbf{r}_2)\beta(\mathrm{s}_2) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_2)\beta(\mathrm{s}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{\mathrm{A}}(\mathbf{r}_{2m})\alpha(\mathrm{s}_{2m}) & \psi_{\mathrm{A}}(\mathbf{r}_{2m})\beta(\mathrm{s}_{2m}) & \cdots & \psi_{\mathrm{M}}(\mathbf{r}_{2m})\beta(\mathrm{s}_{2m}) \end{vmatrix} \tag{12.5}$$

which automatically takes account of the Pauli antisymmetry principle. The electronic energy then works out as

$$\begin{aligned} \varepsilon_{\mathrm{e}} = {} & 2\sum_{R=A}^{\mathrm{M}} \int \psi_R(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\psi_R(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ & + \sum_{R=\mathrm{A}}^{\mathrm{M}} \sum_{S=\mathrm{A}}^{\mathrm{M}} \left(2 \iint \psi_R^2(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_S^2(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \right. \\ & \left. - \iint \psi_R(\mathbf{r}_1)\psi_S(\mathbf{r}_1)\hat{g}(\mathbf{r}_1, \mathbf{r}_2)\psi_R(\mathbf{r}_2)\psi_S(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \right) \end{aligned} \tag{12.6}$$

Notice that I haven't made any mention of the LCAO procedure; Hartree produced numerical tables of radial functions. The atomic problem is quite different from the molecular one because of the high symmetry of atoms. The theory of atomic structure is simplified (or complicated, according to your viewpoint) by angular momentum considerations. The Hartree–Fock limit can be easily reached by numerical integration of the HF equations, and it is not necessary to invoke the LCAO method.

There has been a resurgence of interest in atomic HF calculations because astrophysicists want to study highly ionized atomic species in the interstellar medium. They look to theory for their energy-level data rather than earth-bound experiments where the species are hard to prepare and study.

12.1 THE EXCHANGE POTENTIAL

There was initially a great deal of confusion about the extra term in the Hartree–Fock energy equation 12.6 above, compared to the straightforward Hartree model energy equation 12.4. The extra term in the energy expression was called the 'exchange term', and some authors tried to describe it in terms of a mysterious force called the 'exchange potential'. Attention focused on the exchange phenomenon, and a great deal of effort was spent in finding an effective model potential that mimicked exchange.

In the meantime, solid-state physics had been developing along a quite different direction. Wigner and Seitz (1934) suggested what is now called the 'cellular method' for handling the problem of computing crystal orbitals. These orbitals have energies ε that form continuous bands and for this reason their models are known as *energy band theories*. Wigner and Seitz made valuable observations about the exchange terms.

In order to give you some background to Slater's Xα method, I would like to describe some very simple models that were used many years ago in order to understand the behaviour of electrons in metallic conductors.

12.2 THE DRUDE MODEL

The simplest picture of a metallic conductor is one where we have a rigid lattice of metal (M) atoms, each of which has lost one or more electrons to form a surrounding sea of electrons.

Figure 12.1 shows a slice through such a solid; the cations are to be thought of as a rigid lattice, and the electrons form a gas. I have deliberately drawn the cations as large objects for two reasons. First, the very early models such as that due to Drude tried to treat the electron sea as a perfect gas. It was eventually recognized that the electrons would collide with the cations and with each other an uncomfortable number of times. In any case, many of the predictions of the Drude model turned out to be demonstrably flawed.

Secondly, the influence of the cations on their surrounding space is not negligible. The cations produce strong non-uniform electrostatic fields and the electron density in such a model is far from constant, or even slowly varying. The free electrons experience a very strong attraction when they approach the cations.

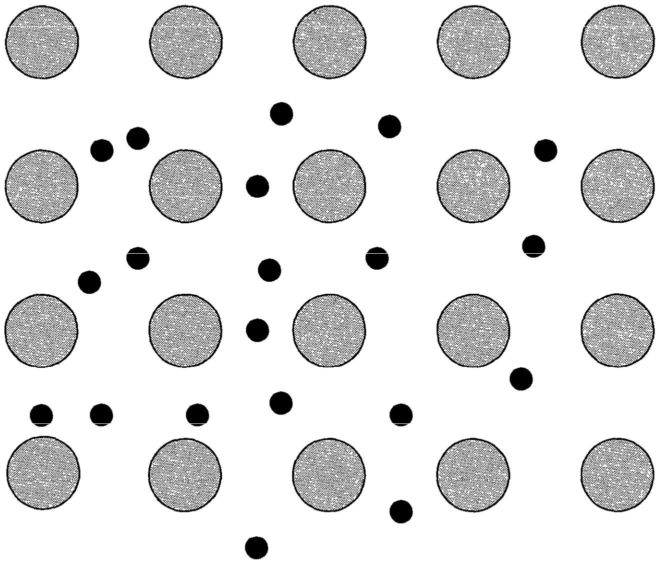


Figure 12.1 The Drude model: small circles are electrons, large circles cations

12.3 PAULI'S MODEL

In Pauli's model, we still envisage a core of rigid cations (metal atoms that have lost electrons), surrounded by a sea of electrons. The electrons are treated as non-interacting particles just as in the Drude model, but the analysis is done according to the rules of quantum mechanics.

The electrons are treated as independent particles constrained to a three-dimensional box, treated here for simplicity as a cube of side L. The box contains the metallic sample. The potential U is infinite outside the box, and a constant U_0 inside the box. We focus attention on a single electron whose electronic Schrödinger equation is

$$\left(-\frac{h^2}{8\pi^2 m_e}\nabla^2 + U\right)\psi = \varepsilon\psi \tag{12.7}$$

It is easily demonstrated that the solutions are

$$\begin{aligned}\psi_{n,k,l} &= \left(\sqrt{\frac{2}{L}}\right)^3 \sin\left(\frac{n\pi}{L}x\right)\sin\left(\frac{k\pi}{L}y\right)\sin\left(\frac{l\pi}{L}z\right)\\ \varepsilon_{n,k,l} &= U_0 + (n^2+k^2+l^2)\frac{h^2}{8m_e L^2}\end{aligned} \tag{12.8}$$

where the three quantum numbers n, k and l can each take values 1, 2, 3, ... Each orbital can hold at most two electrons, one of either spin.

A simple pen and paper calculation for the metallic sample shows that quantum numbers can be very large, typically 10^9. For large quantum numbers, very many of the individual quantum states are degenerate. This is for two reasons. First of all, there are six possible quantum states for every set of different values of n, k and l. Secondly, there are many combinations of $n^2 + k^2 + l^2$ that sum to the same value. Not only that, the high-energy quantum states crowd together and essentially form a continuum rather than a discrete set of levels. For these reasons, we focus attention on the number of quantum states having energy between ε and $\varepsilon + d\varepsilon$. This is written $D(\varepsilon)\,d\varepsilon$ where $D(\varepsilon)$ is the *density of states*. For the 'electron-in-a-box' model of a metal, it turns out that

$$D(\varepsilon) = \frac{4\pi L^3}{h^3}(2m_e)^{3/2}\varepsilon^{1/2} \tag{12.9}$$

and so the density of states depends on the square root of the energy.

In Pauli's model, the sea of electrons, known as the *conduction electrons* are taken to be non-interacting and so the total wavefunction is just a product of individual one-electron wavefunctions. The Pauli model takes account of the exclusion principle: each conduction electron has spin and so each available spatial quantum state can accommodate a pair of electrons, one of either spin.

If we wish to investigate the lowest-energy configuration of the metal, we have to fill up the available quantum states with pairs of electrons, starting with the lowest-energy quantum state $\psi_{1,1,1}$. The highest occupied energy level is referred to as the *Fermi level*, and the corresponding energy is called the *Fermi energy*. The number N of conduction electrons can be related to the Fermi energy, and we find

$$\varepsilon_F = \frac{h^2}{8m_e}\left(\frac{3N}{L^3\pi}\right)^{2/3} \tag{12.10}$$

Now, N/L^3 is the number density of conduction electrons and so Pauli's model gives a simple relationship between the Fermi energy and the number density of electrons. If I follow normal practice and write the number density ρ_0 then we have

$$\varepsilon_F = \frac{h^2}{8m_e}\left(\frac{3\rho_0}{\pi}\right)^{2/3} \tag{12.11}$$

(Unfortunately, some authors use the same symbol ρ for a number density and for volume charge distributions; the electron density is $(-e)$ times the number density.) The number density is a constant in this simple model.

12.4 THE THOMAS–FERMI MODEL

We now switch on an external potential $U(\mathbf{r})$ that is slowly varying over the dimensions of the metallic box. This makes the conduction electron density inhomogeneous and a little analysis suggests that the number density should be

$$\rho(\mathbf{r}) = \frac{8\pi}{3h^3}(2m_e)^{3/2}(\varepsilon_F - U(\mathbf{r}))^{3/2} \tag{12.12}$$

which is called the *Thomas–Fermi relation*. It relates the number density of the conduction electrons at point **r** to the potential at that point.

Our treatment so far has dealt with non-interacting electrons, yet we know for sure that electrons do interact with each other. Dirac (1930b) studied the effects of exchange interactions on the Thomas–Fermi model, and he soon discovered that this effect could be modelled by adding an extra term

$$V_X = C\rho^{1/3} \tag{12.13}$$

where C is a constant given by

$$C = -E_h a_0 \left(\frac{3}{\pi}\right)^{1/3} \tag{12.14}$$

This result was rediscovered by Slater (1951) with a slightly different numerical coefficient of $\frac{2}{3}$ C. Authors often refer to a term V_X which is proportional to the one-third power of the electron density as a *Slater–Dirac exchange potential*.

Just to remind you, the electron density and therefore the exchange potential are both scalar fields; they vary depending on the position in space **r**. We often refer to models that make use of such exchange potentials as *local density models*. The disagreement between Slater's and Dirac's numerical coefficients was quickly resolved, and authors began to write the exchange potential as

$$V_{X\alpha} = \alpha C\rho^{1/3} \tag{12.15}$$

where α would take values between $\frac{2}{3}$ and 1. I will refer to this potential as the Xα exchange potential, and the idea is that you add it to the Hartree Hamiltonian in order to take account of electron exchange (i.e. antisymmetry).

12.5 THE ATOMIC Xα MODEL

By analogy with solid-state studies, Slater had the idea of writing the atomic Hartree–Fock eigenvalue equation

$$\hat{h}^F\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \tag{12.16}$$

as

$$(\hat{h}_1 + \hat{V}_C(\mathbf{r}) + \hat{V}_{X\alpha}(\mathbf{r}))\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \tag{12.17}$$

where $\hat{h}_1$ and $\hat{V}_C$ are the one-electron and Coulomb operators discussed in Chapter 6. Slater's suggestion does not make the atomic problem easier to solve, and it begs the question of the correct choice of α. The α values given by Schwarz

(1972) are normally used. Atomic Xα calculations are straightforward, and most workers use the computer code developed by Herman and Skillman (1963).

The orbitals and orbital energies produced by an atomic HF–Xα calculation differ in several ways from those produced by standard HF calculations. First of all, the Koopmans theorem is not valid and so the orbital energies do not give a direct estimate of the ionization energy. A key difference between standard HF and HF–Xα theories is the way we conceive the *occupation number* ν. In standard HF theory, we deal with doubly occupied, singly occupied and virtual orbitals for which $\nu = 2$, 1 and 0 respectively. In solid-state theory, it is conventional to think about the occupation number as a continuous variable that can take any value between 0 and 2.

In Xα theories, the relationship between the electronic energy ϵ_e, the orbital energy ϵ_i, and the occupation number ν_i of orbital i is

$$\frac{\partial \varepsilon_e}{\partial \nu_i} = \varepsilon_i \tag{12.18}$$

so that the ionization energy from a particular orbital ψ_i, assuming that all the other orbitals remain unchanged on ionization, is given by

$$\varepsilon_e(\nu_i = 0) - \varepsilon_e(\nu_i = 1) = \int_1^0 \varepsilon_i \, d\nu_i \tag{12.19}$$

If we make the assumption that the total energy is a quadratic function of occupation number ν_i, then a quick calculation shows that the ionization energy is given by the orbital energy calculated when that orbital is half occupied.

A separate HF–Xα calculation is therefore needed in order to calculate each ionization energy. What we do is to place half an electron in the orbital from which the electron is supposedly ionized and re-do the HF–Xα calculation. The hypothetical state with a fractional electron is sometimes called an *Xα transition state*, a phrase borrowed from chemical kinetics. We treat the transition state by UHF or ROHF methods according to personal preference.

The great advantage of such HF–Xα calculations over traditional HF ones is that they take account of electron reorganization on ionization, and so the Xα ionization energies were thought to be superior.

12.6 SLATER'S MULTIPLE SCATTERING Xα METHOD FOR MOLECULES

We can quickly and easily solve the HF–Xα equations for an atomic species because of the spherical symmetry. Molecules do not generally have spherical symmetry; in fact, the vast majority of organic molecules have no symmetry to speak of. The extension of HF–Xα models from atoms to molecules took many years, and most calculations in the literature relate to symmetrical inorganic species. The molecular version of the Xα model builds on a chemist's intuitive

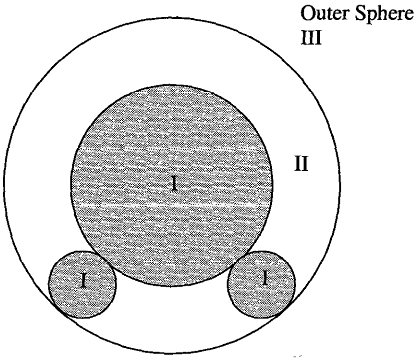


Figure 12.2 Atomic, outer and intersphere regions

idea that a molecule is a collection of perturbed atoms. To take a simple example, H_2O, we picture the three atoms as spheres, and inside these spheres we solve the atomic HF–Xα equations.

The atoms in Figure 12.2 belong to 'region I'. We solve the atomic Xα problem in region I.

It was found in pilot calculations that it is necessary to enclose the molecule by an *outer sphere* that includes the entire molecule. I have denoted the region from the outer sphere radius to infinity as region III. The wavefunction is assumed to be of an atomic type in region III.

The *intersphere region* II is more difficult, and Slater assumed that the potential was constant in this region (this region is shown as II in the figure). The wavefunction and its gradient have to be continuous at the region boundaries, and this requirement leads to an eigenvalue equation. Extensive use is made of molecular symmetry in locating the eigenvalues.

The molecular HF–Xα method has been reviewed by Connolly, and you might like to see how it works for the H_2O example.

12.6.1 An HF-Xα Calculation of the Ionization Energies of Water

The first step is to choose a molecular geometry, the atomic sphere radii and the exchange parameters for each atom and the outer sphere region. I have summarized these in Table 12.1.

Table 12.1 H_2O molecular HF–Xα calculation. $R_{OH} = 95.84\,\text{pm}$, HOH = 104.5°

Atom	Sphere radius/a_0	α
H	0.310 126	0.978 04
O	1.498 674	0.743 67
Outer sphere	1.903 608	0.899 92

Table 12.2 HF–Xα calculation on H_2O ROHF transition state, ionization energies/E_h

Orbital	Touching spheres	10% overlapped spheres	ESCA	Conventional HF–LCAO
$1b_1$	0.586	0.585	0.464	0.396
$3a_1$	0.606	0.599	0.540	0.458
$1b_2$	0.622	0.667	0.682	0.621
$2a_1$	1.149	1.140	1.181	1.277
O(1s) $1a_1$	20.10	20.10	19.89	20.43

The sphere radii were deduced from Slater's (1965) table based on crystal data. The basic molecular HF–Xα equations were originally derived on the basis that the spheres did not overlap (Schwarz and Connolly, 1971). But the equations remain valid when the spheres are allowed to overlap, provided that each sphere does not contain more than one nucleus and that none of the nuclei lie outside the outer sphere. A 10% overlap seems to be normal practice, and our results are given in Table 12.2.

In this particular example, the Xα orbital energies resemble those produced from a conventional HF–LCAO calculation. It often happens that the Xα ionization energies come in a different order than HF–LCAO Koopmans-theorem ones, due to electron relaxation.

13 DENSITY FUNCTIONAL THEORY

Electronic wavefunctions symbolized in this text as $\Psi_e(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_m, s_m)$ depend on the spatial ($\mathbf{r}$) and spin (s) variables of all the m electrons. The electron density on the other hand depends only on the coordinates of a single electron. I discussed the electron density in Chapter 5, and showed how it was related to the wavefunction. The argument proceeds as follows. The chance of finding electron 1 in the differential space element $d\tau_1$ and spin element ds_1 with the other electrons anywhere is given by

$$\left(\int \Psi^*(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_n, s_n)\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_n, s_n) \times d\tau_2\, ds_2 \ldots d\tau_m\, ds_m\right) d\tau_1\, ds_1 \qquad (13.1)$$

if Ψ is complex, or just

$$\left(\int \Psi^2(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_m, s_m)\, d\tau_2\, ds_2 \ldots d\tau_m\, ds_m\right) d\tau_1\, ds_1 \qquad (13.2)$$

if Ψ is a real quantity.

The integration is over all the space and spin coordinates of electrons $2, 3, \ldots, m$. Many of the operators that represent physical properties do not depend on spin, and so we often average-out over the spin variable when dealing with such properties. The chance of finding electron 1 in the differential space element $d\tau_1$ with either spin, and the remaining electrons anywhere and with either spin is

$$\left(\int \Psi^*(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_n, s_n)\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_n, s_n) \times ds_1\, d\tau_2\, ds_2 \ldots d\tau_n\, ds_n\right) d\tau_1 \qquad (13.3)$$

Here, the integration is now over the spin variable for electron 1, as well as the space and spin variables for all the remaining electrons.

Finally, many of the common molecular electronic properties depend only on the chance of finding any electron in $\mathrm{d}\tau_1$ and this is obviously m times the above quantities. We focus attention on points in space (written $\mathbf{r}$) and interest ourselves in the electron probability density

$$P(\mathbf{r}) = m\left(\int \Psi^*(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_n, s_n)\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_n, s_n) \right.$$

$$\left. \times\ \mathrm{d}s_1\,\mathrm{d}\tau_2\,\mathrm{d}s_2 \ldots \mathrm{d}\tau_m\,\mathrm{d}s_m\right) \tag{13.4}$$

where the convention is that we replace $\mathbf{r}_1$ by $\mathbf{r}$ after integration.

The actual electron density is $-eP(\mathbf{r})$, but authors speak about $P(\mathbf{r})$, which is strictly the electron number density, as if it were the same thing. I will follow this sloppy (but common) usage from time to time.

We know a number of things about the electron density $P(\mathbf{r})$. First of all, if we integrate it over space, we get the number of electrons, m. This follows simply from the definition

$$P(\mathbf{r}) = m\left(\int \Psi^2(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_m, s_m)\,\mathrm{d}s_1\,\mathrm{d}\tau_2\,\mathrm{d}s_2 \ldots \mathrm{d}\tau_m\,\mathrm{d}s_m\right) \tag{13.5}$$

whence

$$\int P(\mathbf{r})\,\mathrm{d}\tau = m$$

provided the wavefunction Ψ is normalized to unity.

Secondly, it can be shown (Davidson, 1976) that the so-called nuclear cusp condition for nucleus A with position vector $\mathbf{R}_\mathrm{A}$ gives

$$\frac{\partial}{\partial R_\mathrm{A}}\langle P(R_\mathrm{A})\rangle_{R_\mathrm{A}=0} = -2Z_\mathrm{A}\langle P(R_\mathrm{A} = 0)\rangle \tag{13.6}$$

In this equation, $\langle P(R_\mathrm{A})\rangle$ is the spherical average of the electron density at distance R_A from nucleus A. The symbol $\langle\ldots\rangle_{R=0}$ means that we have to evaluate the mean value of the quantity and then set R to zero in the result. The symbol $\langle\ldots(R_\mathrm{A} = 0)\rangle$ means that we have to evaluate the mean value of the quantity when it is measured at $R_\mathrm{A} = 0$.

Thirdly, Morrell, Parr and Levy (1975) have demonstrated that $P(\mathbf{r})$ behaves asymptotically as $r \to \infty$ as follows:

$$P(\mathbf{r}) \to \exp\left(-A\sqrt{\frac{I_\mathrm{min}}{E_\mathrm{h}}\frac{r}{a_0}}\right) \tag{13.7}$$

where I_min is the first ionization energy and A a constant.

Many atomic and molecular properties depend on the electron density, and some depend on the gradient of the electron density evaluated at certain positions in space.

It has become fashionable to talk about *density functional theory*, so we had better come to grips with the term *linear functional*. It is a highly specialized term in modern algebra with the following meaning (for the mathematicians amongst you, and paraphrased from Birkhoff and MacLane (1965: 182)):

> In elementary algebra, a 'linear function' of the coordinates x_i of a variable vector $\xi = (x_1, x_2, \ldots, x_n)$ of the finite-dimensional vector space $V = V_n(F)$ is a polynomial function of the special form
>
> $$f(\xi) = c_1x_1 + c_2x_2 + \cdots + c_nx_n$$
>
> where the c_i terms are arbitrary constants in the field F. One easily verifies that any such function satisfies the identities
>
> $$(\xi + \eta)f = \xi f + \eta f$$
> $$(a\xi)f = a(\xi f)$$
>
> for any vectors ξ and η in V and any scalar a in F...
>
> We ... therefore define a linear functional f on any vector space V over any field F as a function which satisfies the above identities.

A little explanation is in order. A set is a collection of elements with a defining formula: for example, the set of positive integers, the set of all integers, the set of all real numbers and so on. Figure 13.1 shows a mapping f between two sets;

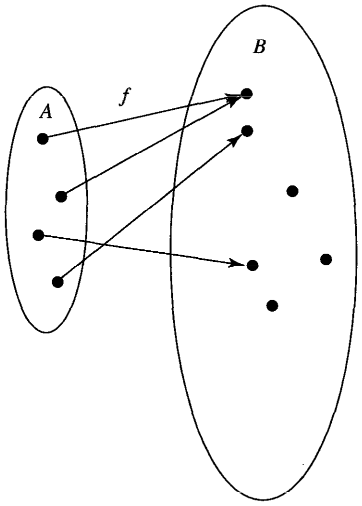


Figure 13.1 A many–one relationship (a function)

a mapping is just a rule whereby we can calculate an element in set B given an element in set A. The relationship illustrated is called a *many–one* relationship, since several elements in set A map into the same element in set B. Such a mapping f is called a *function*. Other mappings are possible, for example a one–many relationship.

A *vector space* is a set with very special properties, which I don't have time to discuss. Wavefunctions are members of vector spaces. If we identify set A with the set of all possible electron densities for the problem of interest, and set B as the set of all real energies, then f defines a density functional.

So, a function is a rule for mapping from a set of numbers to a set of numbers. A functional is a mapping from a set of functions to a set of numbers.

The familiar expectation value $\int \Psi^* \hat{H} \Psi \, d\tau$ is a functional because, given a wavefunction Ψ, one calculates the integral and so gets a number (in this context, we gloss over the difference between a number and a physical quantity such as energy, which has a measure and units). Similarly $\int \Psi^* \Psi \, d\tau$ is a mapping between a function and a number and so is a functional.

13.1 THE HOHENBERG–KOHN THEOREM

Slater's Xα method is now regarded as so much history, but it gave an important stepping stone towards modern density functional theory. In Chapter 12, I discussed the free-electron model of the conduction electrons in a solid. The electrons were assumed to occupy a volume of space that we identified with the dimensions of the metal under study, and the electrons were taken to be non-interacting.

I explained how the model could be extended to allow for the fermion nature of electrons (that is, the Pauli principle).

Electrons do of course interact with each other through their mutual Coulomb electrostatic potential, so an alternative step to greater sophistication might be to allow electron repulsion into the free-electron model. We therefore start again from the free-electron model but allow for the Coulomb repulsion between the electrons. We don't worry about the fermion nature of electrons at this point.

The Hamiltonian operator is now written

$$\hat{H}_e = \hat{T} + \hat{V} + \hat{U}$$

where the operators on the right-hand side are (reading from left to right) the kinetic energy, the potential energy due to any one-electron external perturbation $U(\mathbf{r})$ and the Coulomb repulsion between pairs of electrons. It is fashionable to denote density functionals by square brackets so we would write the energy expression as

$$\varepsilon_e[P] = T[P] + V[P] + U[P] \tag{13.8}$$

Hohenberg and Kohn's 1964 paper was widely regarded by physicists, but its true importance in chemistry has only become apparent during the last decade or so. During this time, density functional theory has become an increasingly important topic in chemistry. This culminated in the award of a half-part of the 1998 Chemistry Nobel Prize to Walter Kohn. (You might like to know that the other half-part of the award went to John A. Pople, whose name ought to be familiar to you by now.)

The paper deals with a gas of interacting metallic electrons, and examines the ground state of such a gas in the presence of an external potential $U(\mathbf{r})$.

The key papers in the field were written by physicists. They tend to write $n(\mathbf{r})$ for the electron number density, i.e. $P(\mathbf{r})$. I have kept to the original wording in the following abstract, but you should mentally switch to $P(\mathbf{r})$ for $n(\mathbf{r})$.

Inhomogeneous Electron Gas
P. Hohenberg and W. Kohn
Physical Review **136** (1964) B864

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r}), \tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas–Fermi methods and their limitations. Some new extensions of these methods are presented.

Part I of the paper develops an exact variational principle for the ground-state energy, in which the density $n(\mathbf{r})$ is the variable function (i.e. the one allowed to vary). The authors introduce a universal functional $F[n(\mathbf{r})]$ which applies to all electronic systems in their ground states no matter what the external potential is. This functional is used to develop a variational principle.

The authors essentially state and prove two theorems. These theorems are at the heart of modern density functional theory, so here they are. I have replaced the number density $n(\mathbf{r})$ beloved of physicists with $P(\mathbf{r})$, the electron density beloved of chemists.

Theorem 1
The electron density $P(\mathbf{r})$ determines the external potential.

Proof
Suppose there are two external potentials $v_1(\mathbf{r})$ and $v_2(r)$ arising from the same electron density $P(\mathbf{r})$. There will be two Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ with the same

electron density with different wavefunctions Ψ_1 and Ψ_2. If ϵ_1 and ϵ_2 are the ground-state energies for $\hat{H}_1$ and $\hat{H}_2$ respectively, then

$$\varepsilon_1 < \int \psi_2^* \hat{H}_1 \psi_2 \, \mathrm{d}\tau$$

I can rearrange the right-hand side as follows:

$$\int \psi_2^* \hat{H}_1 \psi_2 \, \mathrm{d}\tau = \int \psi_2^* \hat{H}_2 \psi_2 \, \mathrm{d}\tau + \int \psi_2^* \left(\hat{H}_1 - \hat{H}_2\right) \psi_2 \, \mathrm{d}\tau$$

which gives

$$\varepsilon_1 < \varepsilon_2 + \int P(\mathbf{r}) \left[v_1(\mathbf{r}) - v_2(\mathbf{r})\right] \mathrm{d}\tau$$

The above argument can be repeated with subscripts interchanged to give

$$\varepsilon_2 < \varepsilon_1 + \int P(\mathbf{r})[v_2(\mathbf{r}) - v_1(\mathbf{r})] \, \mathrm{d}\tau$$

Addition of these two inequalities gives

$$\varepsilon_1 + \varepsilon_2 < \varepsilon_2 + \varepsilon_1$$

which is a contradiction.

Thus $v(\mathbf{r})$ is a unique functional of the electron density; since $v(\mathbf{r})$ fixes the Hamiltonian we see that the full many-particle ground state is a unique functional of the electron density.

Note that the theorem is restricted to electronic ground states.

We next define a universal functional

$$F[P(\mathbf{r})] \equiv \int \Psi^* \left(\hat{T} + \hat{U}\right) \Psi \, \mathrm{d}\tau$$

and with its aid the energy functional

$$\varepsilon(P(\mathbf{r})) \equiv \int v(\mathbf{r}) P(\mathbf{r}) \, \mathrm{d}\tau + F[P(\mathbf{r})] \, \mathrm{d}\tau$$

Theorem 2

$\varepsilon(P(\mathbf{r}))$ assumes its minimum value for the correct $P(\mathbf{r})$, if the admissible functions $P(\mathbf{r})$ satisfy the condition

$$\int P(\mathbf{r}) \, \mathrm{d}\tau = m$$

where m is the number of electrons.

Proof

Any approximate density $\tilde{P}(\mathbf{r})$, by Theorem 1, determines the Hamiltonian and wavefunction $\tilde{\Psi}$. Using this wavefunction in the variational expression we obtain

$$\begin{aligned}\varepsilon\left[\tilde{P}(\mathbf{r})\right] &= \int v(\mathbf{r})\tilde{P}(\mathbf{r})\,\mathrm{d}\tau + T\left[\tilde{P}(\mathbf{r})\right] + U\left[\tilde{P}(\mathbf{r})\right] \\ &= \int \tilde{\Psi}^*\hat{H}\tilde{\Psi}\,\mathrm{d}\tau \geqslant \varepsilon[P(\mathbf{r})]\end{aligned}$$

The main problem relating to practical applications of the Hohenberg and Kohn theorems is obvious: the theorems are *existence theorems* and do not give us any clues as to the calculation of the quantities involved.

In Part 2 of their paper, Hohenberg and Kohn go on to investigate the form of the functional $F[P(\mathbf{r})]$ in the special cases of certain limiting charge densities. They find that $F[P(\mathbf{r})]$ can be expressed in terms of the correlation energy and electric polarizabilities.

13.2 THE KOHN-SHAM EQUATIONS

The next key paper is that of Kohn and Sham. Here is the abstract, which is self-explanatory.

Self-Consistent Equations Including Exchange and Correlation Effects
W. Kohn and L. J. Sham
Physical Review **140** (1965) A1133

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree–Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appears as additional effective potentials. (The exchange portion of our effective potential differs from the due to Slater by a factor of 2/3.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

The Kohn–Sham equations look like standard HF equations, except that the exchange term is replaced with an exchange–correlation potential whose form is unknown.

In order to bring the notation back into line with other chapters, I will write the electronic energy for a molecular species as

$$\varepsilon_e[P] = v[P] + h_1[P] + J[P] + V_{XC}[P] \qquad (13.9)$$

The first term on the right-hand side is a contribution from external fields, usually zero. The second term is the contribution from the kinetic energy and the nuclear attraction. The third term is the Coulomb repulsion between the electrons, and the final term is a composite exchange and correlation term.

All that is needed (in principle) in order to solve the KS–LCAO equations is a simple modification to standard HF–LCAO computer codes. The exchange contribution has to be replaced by the KS contribution.

We often split the exchange–correlation term into a sum of one part for exchange effects and one part for correlation effects.

13.3 THE LOCAL DENSITY APPROXIMATION

There is no systematic way in which the exchange correlation functional $V_{XC}[P]$ can be systematically improved; in standard HF–LCAO theory, we can improve on the model by increasing the accuracy of the basis set, doing configuration interaction or MP*n* calculations. What we have to do in density functional theory is to start from a model for which there is an exact solution, and this model is the uniform electron gas. Parr and Yang (1989) write

$$V_{XC}(P) = V_X(P) + V_C(P) \qquad (13.10)$$

The exchange part is given by the Dirac exchange-energy functional

$$V_X = CP^{1/3} \qquad (13.11)$$

Accurate values of the correlation functional are available thanks to the quantum Monte Carlo calculations of Ceperley and Alder (1980). These values have been interpolated in order to give an analytic form to the correlation potential (Vosko, Wilk and Nusair, 1980).

13.4 BEYOND THE LOCAL DENSITY APPROXIMATION

According to many authors (e.g. Handy, 1993), the local density approximation (LDA) is not adequate for useful predictions in computational chemistry.

13.5 THE BECKE EXCHANGE CORRECTION

One of the most important deficiencies of the LDA exchange is that is does not have the correct asymptotic behaviour. Becke (1988a) recognized that it was necessary to introduce both a logarithm and a term that included the gradient of the density. He found

$$V_{\mathrm{X}}^{\mathrm{B}} = -\beta P^{1/3} \frac{x^2}{1 + 6\beta x \sin\mathrm{h}^{-1} x}$$
$$x = \frac{|\mathrm{grad}\, P|}{P^{4/3}} \tag{13.12}$$

It has one adjustable parameter β which was chosen so that the sum of the LDA and Becke exchange terms accurately reproduce the exchange energies of six noble gas atoms.

13.6 THE LEE–YANG–PARR CORRELATION POTENTIAL

Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density
Chengteh Lee, Weitao Yang and Robert G. Parr
Physical Review **B 37** (1988) 785–789

A correlation-energy formula due to Colle and Salvetti [*Theor. Chim. Acta* 37 (1975) 329], in which the correlation energy density is expressed in terms of the electron density and a Laplacian of the second-order Hartree–Fock density matrix, is restated as a formula involving the density and local kinetic-energy density. On insertion of gradient expansions for the local kinetic-energy density, density functional formulas for the correlation energy and correlation potential are then obtained. Through numerical calculations on a number of atoms, positive ions, and molecules, of both open- and closed-shell type, it is demonstrated that these formulas, like the original Colle–Salvetti formulas, give correlation energies within a few percent.

The great challenge is to develop improved functionals for molecular studies, and a great deal of effort is currently going into such studies.

13.7 QUADRATURE

Implementation of the Kohn–Sham–LCAO procedure is quite simple: we replace the standard exchange term in the HF–LCAO expression by an appropriate V_{XC} that will depend on the local electron density and perhaps also its gradient. The new integrals involved contain fractional powers of the electron density and cannot be evaluated analytically. There are various ways forward, all of which involve numerical integration (or *quadrature*). All methods involve a grid of points in molecular three-dimensional space. A typical scheme is that discussed by Becke.

Multicenter Numerical Integration Scheme for Polyatomic Molecules
A. D. Becke
The Journal of Chemical Physics **88** (1988b) 2547–2553

We propose a simple scheme for decomposition of molecular functions into single-center components. The problem of three-dimensional integration in molecular systems thus reduces to a sum of one-centre, atomic-like integrations which are treated using standard numerical techniques in spherical polar coordinates. The resulting method is tested on representative diatomic and polyatomic systems for which we obtain five- or six-figure accuracy using a few thousand integration points per atom.

13.8 A TYPICAL IMPLEMENTATION

Gaussian98 gives a choice of six exchange functionals and seven correlation functionals, together with a number of so-called hybrid functionals. These latter

```
 -------------------------
 #BLYP/cc-pVTZ Pop=Regular
 -------------------------
 1/38=1/1;
 2/17=6,18=5/2;
 3/5=16,6=1,11=2,25=1,30=1/1,2,3;
 4//1;
 5/5=2,32=1,38=4,42=402/2;
 6/28=1/1;
 99/5=1,9=1/99;
 -----------------------------
 Water at experimental geometry
 -----------------------------
 Symbolic Z-matrix:
 Charge =  0 Multiplicity = 1
 O
 H1                    O    ROH
 H1                    O    ROH       H1    Angle
       Variables:
  ROH                    0.957
 Angle        104.5
```

Figure 13.2

include a mixture of HF exchange with density functional exchange correlation. There is a great deal of interest in hybrid functionals at present. It is interesting to see that the only local exchange functional used in Gaussian98 is the Slater one.

As mentioned above, a KS–LCAO calculation adds one additional step to each iteration of a standard HF–LCAO calculation: a quadrature to calculate the exchange and correlation functionals. The accuracy of such calculations therefore depends on the number of grid points used, and this has a memory resource implication. The Kohn–Sham equations are very similar to the HF–LCAO ones and most cases converge readily.

Here is a KS–LCAO calculation on water at the experimental geometry of 95.7 pm and 104.5°. I chose the BLYP functional; this comprises Becke's 1988

```
Rotational constants (GHZ):     822.4556261    437.8911976
285.7515664
 Isotopes: O-16,H-1,H-1
 Standard basis: CC-pVTZ (5D, 7F)
 There are    23 symmetry adapted basis functions of A1  symmetry.
 There are     7 symmetry adapted basis functions of A2  symmetry.
 There are    11 symmetry adapted basis functions of B1  symmetry.
 There are    17 symmetry adapted basis functions of B2  symmetry.
 Crude estimate of integral set expansion from redundant
integrals=1.074.
 Integral buffers will be    262144 words long.
 Raffenetti 2 integral format.
 Two-electron integral symmetry is turned on.
    58 basis functions       82 primitive gaussians
     5 alpha electrons        5 beta electrons
       nuclear repulsion energy         9.1969343804 Hartrees.
 One-electron integrals computed using PRISM.
 NBasis=    58 RedAO= T  NBF=    23     7    11    17
 NBsUse=    58 1.00D-04 NBFU=    23     7    11    17
 Projected INDO Guess.
 Initial guess orbital symmetries:
       Occupied  (A1) (A1) (B2) (A1) (B1)
       Virtual   (A1) (B2) (A1) (A1) (A1) (A1) (A1) (A1) (A1) (A1)
                 (A1) (A1) (A1) (A1) (A1) (A1) (A1) (A1) (A1) (A1)
                 (A1) (A2) (A2) (A2) (A2) (A2) (A2) (A2) (B1) (B1)
                 (B1) (B1) (B1) (B1) (B1) (B1) (B1) (B1) (B2) (B2)
                 (B2) (B2) (B2) (B2) (B2) (B2) (B2) (B2) (B2) (B2)
                 (B2) (B2) (B2)
 Warning!  Cutoffs for single-point calculations used.
 Requested convergence on RMS density matrix=1.00D-04 within  64
cycles.
 Requested convergence on MAX density matrix=1.00D-02.
 Requested convergence on             energy=5.00D-05.
 Keep R1 and R2 integrals in memory in canonical form, NReq=
5761857.
 SCF Done:  E(RB-LYP) =  -76.4411026287     A.U. after    6 cycles
             Convg  =    0.2791D-05             -V/T =  2.0040
             S**2   =   0.0000
```

Figure 13.3

```
Orbital Symmetries:
     Occupied  (A1) (A1) (B2) (A1) (B1)
     Virtual   (A1) (B2) (B2) (A1) (A1) (B1) (B2) (A1) (A2) (B1)
               (A1) (B2) (B2) (A1) (B1) (A2) (B2) (A1) (A1) (A1)
               (B2) (B1) (A1) (A2) (B1) (B2) (B2) (A1) (A2) (B1)
               (B2) (A1) (A2) (A1) (B2) (B1) (B2) (A1) (A1) (B2)
               (B1) (A1) (B1) (A2) (A1) (B1) (B2) (A1) (A2) (A1)
               (B2) (B2) (A1)
 The electronic state is 1-A1.
Alpha  occ. eigenvalues --  -18.76231  -0.91207  -0.46904  -0.32290  -0.24616
Alpha virt. eigenvalues --    0.00328   0.07608   0.33663   0.38177   0.45939
Alpha virt. eigenvalues --    0.54070   0.58491   0.59357   0.64622   0.74151
Alpha virt. eigenvalues --    0.87913   0.97494   1.24170   1.26731   1.71176
Alpha virt. eigenvalues --    1.73466   1.75416   1.83488   1.90195   2.17845
Alpha virt. eigenvalues --    2.53596   2.99038   3.13072   3.20401   3.28472
Alpha virt. eigenvalues --    3.29464   3.45557   3.51785   3.58143   3.61826
Alpha virt. eigenvalues --    3.63519   3.69604   3.93397   3.95737   4.17591
Alpha virt. eigenvalues --    4.20129   4.44204   4.66603   4.73489   4.99462
Alpha virt. eigenvalues --    5.51075   6.01502   6.29660   6.29910   6.39267
Alpha virt. eigenvalues --    6.43740   6.49235   6.54653   6.68312   6.84804
Alpha virt. eigenvalues --    7.19141   7.64739  12.01801
```

Figure 13.4

```
Total atomic charges:
               1
  1  O    -0.414266
  2  H     0.207133
  3  H     0.207133
  Sum of Mulliken charges=   0.00000
```

Figure 13.5

exchange functional and the Lee, Yang and Parr correlation functional. I also chose a large and sophisticated basis set.

Figure 13.2 shows the route and basis set choice.

Then Figure 13.3 shows what appears to be a standard HF–LCAO calculation. The calculated density functional KS–LCAO energy is denoted E(RB-LYP).

I drew attention in Chapter 12 to the fact that the Xα orbitals did not satisfy the nice properties of standard HF–LCAO ones: the Koopmans theorem is not valid, and so on. The same is true of all density functional KS–LCAO calculations. In practice, it usually turns out that the KS–LCAO orbitals are very similar to ordinary HF–LCAO ones, which must mirror the fact that exchange–correlation effects are only a minor part of the total electronic energy. So the orbitals are often analysed as if they were ordinary HF orbitals (Figure 13.4).

The KS–LCAO orbitals may be visualized by all the popular methods, or one may just focus on the Mulliken population analysis indices (Figure 13.5).

Density functional theory was originally developed by solid-state physicists for treating crystalline solids and almost all applications were in that field until the mid-1980s. It is a current hot topic in chemistry, with many papers appearing in the primary journals.

14 POTENTIAL ENERGY SURFACES

The concept of a potential energy surface has appeared in several chapters. Just to remind you, we make use of the Born–Oppenheimer approximation to separate the total (electron plus nuclear) wavefunction into a nuclear wavefunction and an electronic wavefunction. To calculate the electronic wavefunction, we regard the nuclei as being clamped in position. To calculate the nuclear wavefunction, we have to solve the relevant nuclear Schrödinger equation. The nuclei vibrate in the potential generated by the electrons. Don't confuse the nuclear Schrödinger equation (a quantum-mechanical treatment) with molecular mechanics (a classical treatment).

People are interested in potential energy surfaces for a variety of reasons. They might want to

- calculate molecular geometries, in which case they are interested in the local and global minima on the surface;
- fit an analytical expression to the potential energy surface for one reason or another. For example, to use the resulting curve as input to a 'scattering' calculation, or to test out the validity of some physical model such as the harmonic oscillator. In the latter case, the physical model will be represented as a (simple) equation containing a number of parameters and the aim of the calculation is to choose the best parameters in order to give a fit with experiment;
- give a very accurate representation of the potential energy surface, with the intention of interpolation, differentiation, integration and so on. In this case, the form of the fitting equation is usually irrelevant;
- investigate chemical reactions from a study of saddle points. Such data is of great interest in theories of reaction mechanisms, but virtually unobtainable from experimental measurements;

- calculate accurate force constants for a novel molecule. Such experimental data is hard to come by, even after making all possible isotopic substitutions.

All these problems are interrelated.

14.1 A DIATOMIC MOLECULE

Consider a diatomic molecule such as $^1H^{35}Cl$. Within the Born–Oppenheimer approximation, we focus attention on the electronic wavefunction and calculate enough data points to give a potential energy curve. Such a curve shows the variation of the electronic energy with internuclear separation. The nuclei vibrate in this potential.

You will easily reproduce Table 14.1 if you have access to an *ab initio* package. A more advanced calculation shows that the potential (defined by the data points) has a minimum at 127.34 pm with a corresponding energy of −460.244 0222 E_h.

Suppose for example that we want to test the validity of our data against the harmonic model

$$\varepsilon_{el} = \varepsilon_0 + \tfrac{1}{2}k_s(R - R_e)^2 \tag{14.1}$$

(I have written ε_{el} because we have calculated an electronic energy.) One way to do this is to fit the data points to a function such as

$$\varepsilon = a + b(R - c)^2 \tag{14.2}$$

Table 14.1

R/pm	MP2 Energy/E_h
110.0	−460.217 540
112.5	−460.225 580
115.0	−460.231 890
117.5	−460.236 680
120.0	−460.240 130
122.5	−460.242 410
125.0	−460.243 660
127.5	−460.244 020
130.0	−460.243 600
132.5	−460.242 490
135.0	−460.240 790
137.5	−460.238 580
140.0	−460.235 920
142.5	−460.232 890
145.0	−460.229 530
147.5	−460.225 890
150.0	−460.222 030
152.5	−460.217 970
155.0	−460.213 760

Table 14.2 HCl MP2/6-311G** calculation

Equation	k_s/N m^{-1}
14.2	459.3
14.3	355.9
14.4	403.1
14.5	484.5
Experimental value	516.3

where a, b and c can be determined by least squares techniques. Other strategies might be to fix the constant(s) a and/or c

$$\varepsilon = a + b(R - 127.34\,\mathrm{pm})^2 \tag{14.3}$$

$$\varepsilon = -460.244\,0222E_\mathrm{h} + b(R - 127.34\,\mathrm{pm})^2 \tag{14.4}$$

Alternatively, we might try to allow for anharmonicity and write a more general expression such as

$$\varepsilon = a + b(R - c)^2 + d(R - c)^4 + e(R - c)^6 \tag{14.5}$$

If for the minute we identify the constant b with $\frac{1}{2}k_\mathrm{s}$ in every case then we obtain Table 14.2.

On the other hand, the equation

$$\varepsilon = \varepsilon_0 + a\ln(R/\mathrm{pm}) + b(\ln(R/\mathrm{pm}))^2 + c(\ln(R/\mathrm{pm}))^3 + \cdots + g(\ln(R/\mathrm{pm}))^6 \tag{14.6}$$

gave the best fit to the data points out of the several thousand equations I tested, but it bears no relation to any simple physical model.

For the rest of the chapter, I am going to be concerned with two problems:

- characterizing stationary points on a potential energy surface, and
- locating stationary points on a potential energy surface.

14.2 CHARACTERIZING POINTS ON A POTENTIAL ENERGY SURFACE

In Chapter 1, I discussed the Taylor expansion for a general diatomic potential $U(R)$ about the equilibrium bond length R_e:

$$U(R) = U(R_\mathrm{e}) + \left(\frac{\mathrm{d}U}{\mathrm{d}R}\right)_{R_\mathrm{e}}(R - R_\mathrm{e}) + \frac{1}{2}\left(\frac{\mathrm{d}^2U}{\mathrm{d}R^2}\right)_{R_\mathrm{e}}(R - R_\mathrm{e})^2 + \cdots \tag{14.7}$$

where the point R is close to R_e. Symbols such as $(\mathrm{d}U/\mathrm{d}R)_{R_\mathrm{e}}$ mean that we calculate the first derivative and then evaluate it at the point R_e.

If R_e is a minimum point then

$$\left(\frac{\mathrm{d}U}{\mathrm{d}R}\right)_{R_e} = 0$$

and

$$\left(\frac{\mathrm{d}^2U}{\mathrm{d}R^2}\right)_{R_e} > 0$$

We often choose the zero of potential such that $U(R_e) = 0$ and the term

$$\frac{1}{2}\left(\frac{\mathrm{d}^2U}{\mathrm{d}R^2}\right)_{R_e}$$

is called the harmonic force constant.

So in order to calculate the harmonic force constant from equation 14.6 above,

$$\varepsilon = \varepsilon_0 + a\ln(R/\mathrm{pm}) + b(\ln(R/\mathrm{pm}))^2 + c(\ln(R/\mathrm{pm}))^3 + \cdots + g(\ln(R/\mathrm{pm}))^6$$

I would have to find the minimum and then calculate the second derivative at the minimum.

Suppose that our potential function U is now a function of many (p) variables. They could be bond lengths, bond angles, dihedral angles or the Cartesian coordinates of each atom in a molecule. I will write these variables $x_1, x_2, \ldots, x_p$ and so

$$U = U(x_1, x_2, \ldots, x_p)$$

I can collect the coordinates $x_1, x_2, \ldots, x_p$ into a column vector

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ \ldots \\ x_p \end{pmatrix}$$

and so $\mathbf{x}$ defines a vector in a p-dimensional space. If I write U as $U(\mathbf{x})$, then Taylor's expansion of U about point $\mathbf{x}_0$ is

$$\begin{aligned} U(\mathbf{x}) = U(\mathbf{x}_0) &+ \sum_{i=1}^{p}\left(\frac{\partial U}{\partial x_i}\right)_{x_i^0}\left(x_i - x_i^0\right) \\ &+ \frac{1}{2}\sum_{i=1}^{p}\sum_{j=1}^{p}\left(\frac{\partial^2 U}{\partial x_i \partial x_j}\right)_{x_i^0 x_j^0}\left(x_i - x_i^0\right)\left(x_j - x_j^0\right) + \cdots \end{aligned} \qquad (14.8)$$

The column vector with components $\partial U/\partial x_i$ is the *gradient* of U; it gives the negative of the force, when evaluated at a nuclear position. The $p \times p$ matrix with components $\partial^2 U/\partial x_i \partial x_j$ is called the *Hessian*. The Hessian is also called the force constant matrix. I will use the symbols **g** and **H**, so that

$$\mathbf{g} \equiv \operatorname{grad} U = \begin{pmatrix} \dfrac{\partial U}{\partial x_1} \\ \dfrac{\partial U}{\partial x_2} \\ \cdots \\ \dfrac{\partial U}{\partial x_p} \end{pmatrix} \text{ and } \mathbf{H} = \begin{pmatrix} \dfrac{\partial^2 U}{\partial x_1^2} & \dfrac{\partial^2 U}{\partial x_1 \partial x_2} & \cdots & \dfrac{\partial^2 U}{\partial x_1 \partial x_p} \\ \dfrac{\partial^2 U}{\partial x_2 \partial x_1} & \dfrac{\partial^2 U}{\partial x_2^2} & \cdots & \dfrac{\partial^2 U}{\partial x_2 \partial x_p} \\ \cdots & \cdots & \cdots & \cdots \\ \dfrac{\partial^2 U}{\partial x_p \partial x_1} & \dfrac{\partial^2 U}{\partial x_p \partial x_2} & \cdots & \dfrac{\partial^2 U}{\partial x_p^2} \end{pmatrix}.$$

I discussed stationary points in Chapter 1: a stationary point is one where the gradient vector is zero. For functions of a single variable, such points can be maxima, minima or points of inflection, as determined by the value of the second derivative. For functions of many variables, the points can be maxima, minima or *saddle points* and they are characterized by the eigenvalues of the Hessian matrix. If all the eigenvalues are positive, the point is a local minimum. If all are negative then the point is a local maximum. A first-order saddle point has one negative eigenvalue. An nth-order saddle point has n negative eigenvalues.

A minimum on a potential energy surface represents an equilibrium structure. There will invariably be a number of such local minima, and we can imagine a number of paths on the surface that connect one particular minimum to another. If the highest-energy point on each path is considered, the *transition structure* can be defined as the lowest of these maxima. The *reaction path* is the lowest-energy route between two minima.

An *intrinsic reaction coordinate (IRC)* is concerned with travel along the reaction path; it can be defined by the path taken by a classical particle sliding from a saddle point down to a minimum.

14.3 LOCATING STATIONARY POINTS

14.3.1 A Function of a Single Variable

A good place to start our study is with a function of a single variable $f(x)$. Consider the function

$$f(x) = x \exp(-x)$$

for which

$$\frac{\mathrm{d}f(x)}{\mathrm{d}x} = \exp(-x) - x\exp(-x)$$

It is obvious by inspection that the equation $f(x) = 0$ has a root at $x = 0$, and a graph of the function is shown in Figure 14.1.

A simple way of finding the roots of an equation, other than by divine inspiration, symmetry or guesswork is afforded by the Newton method. We start at some point denoted $x^{(1)}$ along the x-axis, and calculate the tangent to the curve at

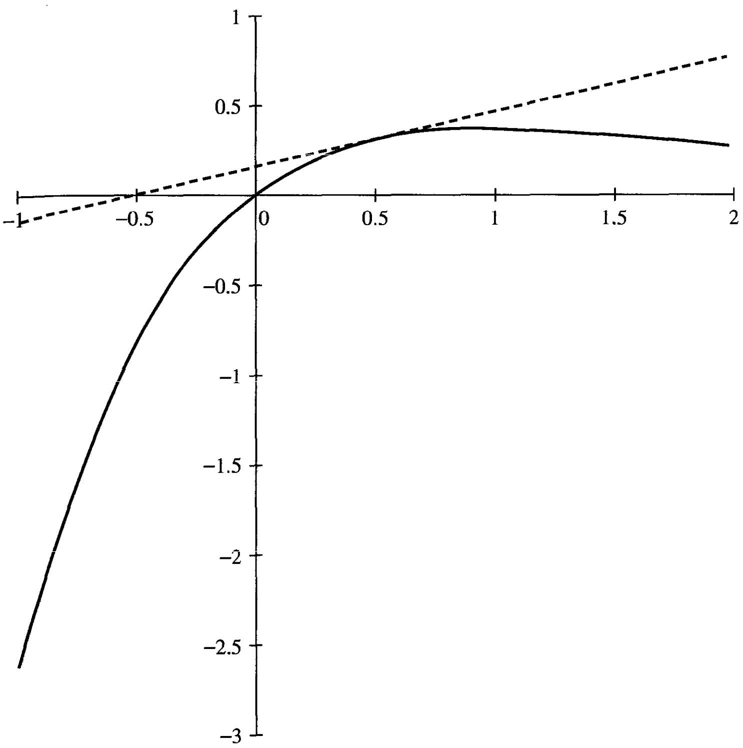


Figure 14.1 Newton's method. Dotted line is tangent at $x = 0.5$

this point. For the function in the figure, if we take $x^{(1)} = 0.5$, then the gradient at this point is 0.3033. I will write this as $(\mathrm{d}f/\mathrm{d}x)_{x^{(1)}}$. A simple calculation shows that this tangent line cuts the x-axis at the point

$$x^{(2)} = x^{(1)} - \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)^{-1}_{x^{(1)}} f\left(x^{(1)}\right) \tag{14.9}$$

which works out as −0.5. We take $x^{(2)} = -0.5$ as the next guess for the root of the equation and repeat the process until the required accuracy is achieved. We have to repeat the process for all of the roots, unless we are just interested in certain ones.

Newton's method can be easily re-written for the problem of finding stationary points, where $(\mathrm{d}f/\mathrm{d}x) = 0$ rather than $x = 0$. The formula 14.9 becomes

$$x^{(2)} = x^{(1)} - \left(\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\right)^{-1}_{x^{(1)}} \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x^{(1)}} \tag{14.10}$$

and so we need to know the first and second derivatives of $f(x)$ in order to apply the method.

Newton's method raises several issues. There is the ease of evaluating the function value (the energy, in our case), and this has to be balanced against the number of variables. A molecular mechanics calculation on a large molecule will typically have thousands of unknown bond lengths, bond angles and the like but the energy formula is particularly simple. An HF–LCAO calculation on a system of medium size might have 100 unknowns, but each energy evaluation (of the HF–LCAO energy) will take some time. For these reasons, minimization techniques for MM applications tend to be different from minimization techniques for quantum-chemical applications.

Finally, there is the question of availablity of analytical derivatives. Minima, maxima and saddle points can be characterized by their first and second derivatives. Over the last 25 years, there has been a rapid development in this area, and analytical gradient formulae are now known for most of the common techniques discussed in this volume. The great advantage is that those methods that use analytical gradients tend to out-perform in speed of execution those methods where gradients have to be estimated numerically.

14.3.2 Function-only Minimization Methods

Such algorithms can be found in any standard book on numerical analysis. These methods have the widest range of applicability, but they tend to be slower than those methods that make use of analytical formulae for the gradient. Two examples will give the gist.

14.3.3 The Sequential Univariate Search

Here we change one variable at a time, and cycle over all the variables until a minimum is reached. We proceed as follows:

1 Calculate the energy at the initial geometry.
2 Calculate the energy at two displacements along a coordinate.
3 Fit a quadratic to these three points.
4 Find the minimum of the quadratic and calculate the energy.
5 Choose the next coordinate, and go back to step 2.

We stop the calculation once the change in the coordinates is thought to be acceptable. In general, convergence is slow and the only way to check the accuracy is to carry through yet another cycle and observe the changes in predicted coordinates.

14.3.4 The Fletcher–Powell Algorithm

A more sophisticated version of the sequential univariate search, the Fletcher–Powell, is actually a derivative method where elements of the gradient vector **g** and the Hessian matrix **H** are estimated numerically.

1 Calculate the energy U^{k} for an initial geometry $\mathbf{x}^{\mathrm{k}}$ (with iteration count $k = 0$), and at positive and negative displacements for each of the coordinates. (Note that I have dropped the brackets from around the iteration count superscript, for clarity.)

2 Fit a quadratic for each of the coordinates according to the formula

$$U(\mathbf{x}) = U^k + \sum_{i=1}^{p}\left(g_i^k\left(x_i - x_i^k\right) + \frac{1}{2}H_{ii}^k\left(x_i - x_i^k\right)^2\right) \tag{14.11}$$

(which essentially gives numerical estimates of the gradient and the Hessian).

3 Find a minimum of this expression

$$\begin{aligned}\frac{\partial U}{\partial x_i} &= 0\\ g_i^k + H_{ii}^k\left(x_i - x_i^k\right) &= 0\\ p_i^k = x_i - x_i^k &= -\frac{g_i^k}{H_{ii}^k}\end{aligned} \tag{14.12}$$

The last term gives the correction to coordinate x_i; if the p's are small enough then stop. Otherwise we progress to the next point on the surface. To do this we:

4 Calculate the energy at points $\mathbf{x}^k$, $\mathbf{x}^k + \mathbf{p}^k$ and $\mathbf{x}^k + 2\mathbf{p}^k$.

5 Fit a quadratic to these three points as in step 2.

6 Find the energy minimum, as in step 3. This gives point $\mathbf{x}^{k+1}$ on the surface. Calculate the gradient $\mathbf{g}^{k+1}$ at this point.

7 Go back to step 3.

14.3.5 Gradient Methods

The term *gradient method* is often applied to algorithms that make use of a gradient to find stationary points. It is always possible to estimate the gradient numerically, for example by calculating the function value at points that are close together in space

$$\left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x=x_1} \approx \frac{f(x_1 + \Delta) - f(x_1)}{\Delta} \tag{14.13}$$

but such numerical estimations need sevaral energy evaluations and there is then little to choose between a gradient method with numerical estimates of the gradient and a non-gradient method.

I will use the term 'gradient method' to imply the existence of an analytical formula for the calculation of an energy gradient. In order to calculate an analytical formula, we have to be able to differentiate one- and two-electron integrals with respect to nuclear coordinates.

14.3.6 Newton's Method

The algorithm for a function of a single variable

$$x^{(2)} = x^{(1)} - \left(\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right)^{-1}_{x^{(1)}} \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x^{(1)}} \tag{14.14}$$

becomes

$$\mathbf{x}^{(2)} = \mathbf{x}^{(1)} - \left(\mathbf{H}^{(1)}\right)^{-1} \mathbf{g}^{(1)} \tag{14.15}$$

when we have to deal with a function of many variables. In *ab initio* calculations, the gradient vector involves first derivatives and the Hessian involves second derivatives of the basis functions with respect to the nuclear coordinates. First- and second-derivative expressions are known for a number of levels of theory.

14.4 GENERAL COMMENTS

Many gradient methods approximate the energy surface at step k by a quadratic expression in terms of the coordinate vector $\mathbf{x}^{(k)}$, the total energy $\varepsilon^{(k)}$, the gradient $\mathbf{g}^{(k)}$ and the Hessian $\mathbf{H}^{(k)}$

$$\varepsilon^{(k+1)}(\mathbf{x}) = \varepsilon^{(k)}(\mathbf{x}) + \left(\mathbf{g}^{(k)}\right)^{\mathrm{T}} \left(\mathbf{x} - \mathbf{x}^{(k)}\right) + \left(\mathbf{x} - \mathbf{x}^{(k)}\right)^{\mathrm{T}} \mathbf{H}^{(k)} \left(\mathbf{x} - \mathbf{x}^{(k)}\right) \tag{14.16}$$

Almost all optimization methods need a starting geometry and an initial estimate of the Hessian. The Hessian is improved as the optimization proceeds.

14.5 STEEPEST DESCENTS

The simplest gradient method is the steepest descents algorithm. The Hessian is taken as a multiplier of the unit matrix, and it is constant for the entire geometry optimization. The search is along the direction in which $\mathbf{x}^{(k)}$ decreases most rapidly. Experience suggests that the steepest descent algorithm quickly decreases the energy in the first few cycles, but that the final convergence is slow.

14.6 THE FLETCHER–REEVES ALGORITHM

The most frequently used methods fall between the Newton method and the steepest descents method. These methods avoid direct calculation of the Hessian (the matrix of second derivatives); instead they start with an approximate Hessian and update it at every iteration.

The *conjugate gradient method* is one of the oldest; in the Fletcher–Reeves approach, the search direction is given by

$$\mathbf{p}^{(k)} = -\mathbf{g}^{(k)} + \mathbf{p}^{(k-1)} \frac{\left(\mathbf{g}^{(k)}\right)^{\mathrm{T}} \left(\mathbf{g}^{(k)}\right)}{\left(\mathbf{g}^{(k-1)}\right)^{\mathrm{T}} \left(\mathbf{g}^{(k-1)}\right)} \tag{14.17}$$

A more detailed discussion of such methods can be found in specialist books dealing with optimization (Fletcher, 1981; Powell, 1985).

14.7 THE HELLMAN-FEYNMAN THEOREM

Suppose we have a wavefunction Ψ, which for the sake of argument I will assume to be real. The expectation value of the energy is

$$\varepsilon = \int \Psi \hat{H} \Psi \, d\tau$$

and the wavefunction is normalized if

$$\int \Psi \Psi \, d\tau = 1$$

I now differentiate these expressions with respect to some parameter 'a' that could be a Cartesian coordinate, the component of an applied electric field, or whatever. We then have

$$\frac{\partial \varepsilon}{\partial a} = \int \frac{\partial \Psi}{\partial a} \hat{H} \Psi \, d\tau + \int \Psi \frac{\partial \hat{H}}{\partial a} \Psi \, d\tau + \int \Psi \hat{H} \frac{\partial \Psi}{\partial a} \, d\tau \qquad (14.18)$$

The first and third terms on the right-hand side are equal for a real wavefunction. Differentiating the normalization condition gives

$$0 = \int \frac{\partial \Psi}{\partial a} \Psi \, d\tau + \int \Psi \frac{\partial \Psi}{\partial a} \, d\tau \qquad (14.19)$$

which shows that Ψ is orthogonal to its derivative. The two terms on the right-hand side are obviously equal. Repeated differentiation of expression 14.19 shows that Ψ is orthogonal to all its derivatives.

In the early days of quantum chemistry, it was argued that terms such as $\int (\partial \Psi / \partial a) \hat{H} \Psi \, d\tau$ were therefore zero, as substitution of $\hat{H}\Psi = \varepsilon \Psi$ into Equation 14.18 might suggest. Unfortunately, exact wavefunctions are very hard to come by and $\hat{H}\Psi = \varepsilon \Psi$ only for an exact wavefunction.

The result

$$\frac{\partial \varepsilon}{\partial a} = \int \Psi \frac{\partial \hat{H}}{\partial a} \Psi \, d\tau \qquad (14.20)$$

is referred to as the Hellman–Feynman theorem. It was widely used to investigate isoelectronic processes such as isomerizations X → Y, barriers to internal rotation, and bond extensions where the only changes in the energy are due to changes in the positions of the nuclei and so the energy change can be calculated from one-electron integrals.

Notice that the Hellman–Feynman theorem only applies to exact wavefunctions, not to variational approximations. All the enthusiasm of the 1960s and 1970s evaporated when it was realized that approximate wavefunctions themselves also depend on nuclear coordinates, since the basis functions are usually centred there. So the derivatives of Ψ with respect to the parameter 'a' are not necessarily negligible.

The Hellman–Feynman theorem deserves a place in history and in this text, but all attempts to make profitable use of the theorem failed because of the small print contained in the paragraph above.

14.8 THE COUPLED HARTREE–FOCK (CPHF) MODEL

To show the principles involved in finding an analytical gradient expression, consider an HF–LCAO calculation where the electronic energy comes to

$$\varepsilon_e = \text{trace}(\mathbf{Ph}_1) + \tfrac{1}{2}\text{trace}(\mathbf{PG}) \qquad (14.21)$$

The **P** matrix involves the HF–LCAO coefficients and the $\mathbf{h}_1$ matrix has elements that consist of the one-electron integrals (kinetic energy and nuclear attraction) over the basis functions $\chi_1, \ldots, \chi_n$. The **G** matrix contains two-electron integrals and elements of the **P** matrix. If we differentiate with respect to parameter 'a' which could be a nuclear coordinate or a component of an applied electric field, then we have to evaluate terms such as

$$\frac{\partial}{\partial a}\int \chi_i(\mathbf{r})\hat{h}(\mathbf{r})\chi_j(\mathbf{r})\,\mathrm{d}\tau \qquad (14.22)$$

$$\frac{\partial}{\partial a}\int \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \qquad (14.23)$$

and

$$\frac{\partial P_{ij}}{\partial a} \qquad (14.24)$$

The first two kinds of terms are called *derivative integrals*; they are the derivatives of integrals that are well known in molecular structure theory, and they are easy to evaluate. Terms of the third kind pose a problem, and we have to solve a set of equations called the *coupled Hartree–Fock* equations in order to find them. The coupled Hartree–Fock method is far from new; one of the earliest papers is that of Gerratt and Mills.

Force Constants and Dipole-Moment Derivatives of Molecules from
Perturbed Hartree–Fock Calculations I
J. Gerratt and I. M. Mills
Journal of Physical Chemistry **49** (1968) 1719

General expressions for the force constants and dipole derivatives of molecules are derived, and the problems arising from their practical application are reviewed. Great emphasis is placed on the use of the Hartree–Fock function as an approximate wavefunction, and a number of its properties are discussed and re-emphasized. The main content of this paper is the development of a perturbed Hartree–Fock theory that makes possible the direct calculation of force constants and dipole-moment derivatives from SCF–MO wavefunctions. Essentially the theory yields $\partial\phi_i/\partial R_j^{\alpha}$, the derivative of an MO with respect to a nuclear coordinate.

A pioneering paper in gradient evaluation is that of Pulay.

Ab Initio Calculation of Force Constants and Equilibrium Geometries
in Polyatomic Molecules. I. Theory
P. Pulay
Molecular Physics **2** (1969) 197–204

The general expression for the exact forces on the nuclei (negative derivatives of the total energy with respect to the nuclear coordinates) is applied for Hartree–Fock wavefunctions. It is suggested that force constants should be calculated by differentiating the forces numerically. This method, called the force method, is numerically more accurate and requires less computation than the customary one of differentiating the energy numerically twice. It permits the quick determination of the equilibrium geometry by relaxing the nuclear coordinates until the forces vanish. The unreliability of the methods using the Hellmann–Feynman forces is re-emphasized. The question of which force constants can be best calculated *ab initio* is discussed.

Note Pulay's mention of the Hellman–Feynman theorem. We have moved on since 1969, especially in the development and application of analytical methods for evaluating the gradients.

14.9 CHOICE OF VARIABLES

Ab initio packages are generally written to perform their minimizations using so-called *internal coordinates*. This means the bond lengths, bond angles and azimuthal angles discussed in Chapter 1. Such coordinates are often called 'valence coordinates' because they relate to chemists' way of thinking. MM packages often work directly with the Cartesian coordinates.

In the early days of *ab initio* geometry optimizations, everything was controlled by the Z-matrix discussed in Chapter 10. To give an example, consider ethene C_2H_4. There are $N = 6$ atoms and so the molecule has $3 \times 6 - 6 = 12$ degrees of vibrational freedom. A full geometry optimization should therefore include 12 independent bond lengths, bond angles and azimuthal angles. However most chemists would be interested in a planar D_{2h}-symmetry ethene, for which all HCC bond angles were equal and all the CH bond lengths were the same (Figure 14.2).

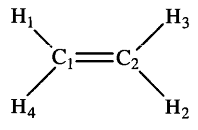


Figure 14.2

```
 ------------------------
 #HF/6-311G** Opt=Z-Matrix
 ------------------------
 ---------------------------------
 Ethene Optimization using Z-Matrix
 ---------------------------------
 Symbolic Z-matrix:
 Charge =  0 Multiplicity = 1
 C1
 C2                C1   RCC
 H1                C1   RCH     C2   Angle
 H2                C2   RCH     C1   Angle    H1    180.     0
 H3                C2   RCH     C1   Angle    H1    0.       0
 H4                C1   RCH     C2   Angle    H3    180.     0
      Variables:
  RCC                1.2
  RCH                1.08
  Angle            120.

 Berny optimization.
 Initialization pass.
                        ---------------------------
                        !   Initial Parameters    !
                        ! (Angstroms and Degrees) !
 ----------------------                           ----------------------
 !     Name          Value   Derivative information (Atomic Units)    !
 -----------------------------------------------------------------------
 !     RCC         1.2      estimate D2E/DX2
 !     RCH         1.08     estimate D2E/DX2
 !     Angle     120.       estimate D2E/DX2
```

Figure 14.3

Here are the salient features from a typical Gaussian98 run on ethene at the HF/6-311G** level of theory, using the Z-matrix option (Figure 14.3). I have forced D_{2h} symmetry by setting all the C–H bonds equal, all HCC bond angles equal and all azimuthal angles equal.

The three variables R(C–C), R(C–H) and the angle HCC are displayed, together with the Z-matrix. As the calculation progresses, the force on each nucleus is displayed as in Figure 14.4 and the optimization algorithm proceeds to find the values of these variables that lead to a local minimum on the potential energy surface. In Figure 14.5 we keep our eye on the second derivative (force constant) matrix, especially the eigenvalues.

Eventually, if all has gone well, we reach the local stationary point (Figure 14.6).

We still have to investigate the nature of the stationary point, especially in view of my assumption of D_{2h} symmetry. We do this by calculating the Hessian matrix at this point, and finding its eigenvalues. To repeat myself, an energy minimum corresponds to positive eigenvalues. A single negative eigenvalue tells us that we have a saddle point.

```
***** Axes restored to original set *****
-------------------------------------------------------------------
Center     Atomic              Forces (Hartrees/Bohr)
Number     Number            X              Y              Z
-------------------------------------------------------------------
   1          6          0.000000000    0.000000000   -0.014663036
   2          6          0.000000000    0.000000000    0.014663036
   3          1          0.000276006    0.000000000    0.002054343
   4          1         -0.000276006    0.000000000   -0.002054343
   5          1          0.000276006    0.000000000   -0.002054343
   6          1         -0.000276006    0.000000000    0.002054343
-------------------------------------------------------------------
Cartesian Forces:  Max     0.014663036 RMS     0.004984394
```

Figure 14.4

```
The second derivative matrix:
                          RCC        RCH        Angle
           RCC          1.04510
           RCH          0.00784    1.43953
           Angle        0.04066    0.00093    1.93653
     Eigenvalues ---    1.04310    1.43968    1.93838
RFO step:  Lambda=-2.11895882D-04.
Quartic linear search produced a step of  0.04333.
Variable        Old X    -DE/DX   Delta X   Delta X   Delta X      New X
                                  (Linear)   (Quad)    (Total)
  RCC         2.47097   0.01055   0.00881   0.00402   0.01283    2.48380
  RCH         2.03769  -0.00346  -0.00014  -0.00241  -0.00255    2.03514
 Angle        2.13539  -0.01535   0.00178  -0.00990  -0.00813    2.12726
        Item                Value      Threshold  Converged?
Maximum Force              0.015350     0.000450     NO
RMS     Force              0.010939     0.000300     NO
Maximum Displacement       0.012830     0.001800     NO
RMS     Displacement       0.008891     0.001200     NO
Predicted change in Energy=-1.501837D-04
```

Figure 14.5

```
-- Stationary point found.
                         ----------------------------
                         !   Optimized Parameters   !
                         ! (Angstroms and Degrees)  !
----------------------                              ----------------------
!      Name          Value   Derivative information (Atomic Units)      !
--------------------------------------------------------------------------
!       RCC          1.3163   -DE/DX =   -0.0001                          !
!       RCH          1.0767   -DE/DX =   -0.0001                          !
!      Angle       121.6939   -DE/DX =   -0.0002                          !
--------------------------------------------------------------------------
```

Figure 14.6

Over the years, geometry optimization has become an essential part of *ab initio* methodology. Research papers simply don't get published unless they report a geometry optimization. Almost all of the early *ab initio* packages made use of internal coordinates (bond lengths, bond angles and dihedral angles), as defined by the Z-matrix discussed in Chapter 1. The reason for the popularity of the

Z-matrix was that it mirrors the way chemists think. Molecular construction using the Z-matrix is not particularly difficult for a small molecule, and symmetry can be readily imposed, as in my ethene example above.

Molecular construction for a protein chain is just about impossible using the Z-matrix (unless you are particularly good at crossword puzzles). As I mentioned in Chapter 10, there are also immense practical difficulties associated with symmetric, cyclic and linear structures, and as time went by people began to question the use of the Z-matrix.

Finally, I should tell you that structural databases invariably contain Cartesian coordinates. A typical paper from the early 1990s addresses the problem.

Geometry Optimization in Cartesian Coordinates:
The End of the Z-Matrix?
Jon Baker and Warren J. Hehre
Journal of Computational Chemistry **12** (1991) 606–610

Geometry optimization directly in Cartesian coordinates using the EF and GDIIS algorithms with standard Hessian updating techniques is compared and contrasted with optimization in internal coordinates utilising thewell-known Z-matrix formalism. Results on a test set of 20 molecules show that, with an appropriate initial Hessian, optimization in Cartesians is just as efficient as optimization in internals, thus rendering it unnecessary to construct a Z-matrix in situations where Cartesians are readily available, for example from structural databases or graphical model builders.

Many modern computer codes (e.g. GAUSSIAN98) employ so-called *redundant internal coordinates*; this means that we use all possible internal coordinates, of which there will generally be more than $3N - 6$. Only a maximum of $3N - 6$ will be linearly independent, and we essentially throw away the remainder at the end of the full calculation. Here is ethene, done using redundant internal coordinates.

```
----------------
#HF/6-311G** Opt
----------------
-------------------------------------------------
Ethene Optimization, redundant internal coordinates
-------------------------------------------------
Symbolic Z-matrix:
Charge =  0 Multiplicity = 1
C1                  0.          0.        0.
C2                  0.          0.        1.2
H1                  0.93531     0.       -0.54
H2                 -0.93531     0.        1.74
H3                  0.93531     0.        1.74
H4                 -0.93531     0.       -0.54
```

Figure 14.7

```
Initialization pass.
                              --------------------------
                              !    Initial Parameters    !
                              ! (Angstroms and Degrees)  !
--------------------------                            ------------------------
! Name  Definition              Value         Derivative Info.              !
--------------------------------------------------------------------------------
! R1    R(1,2)                   1.2          estimate D2E/DX2              !
! R2    R(1,3)                   1.08         estimate D2E/DX2              !
! R3    R(1,6)                   1.08         estimate D2E/DX2              !
! R4    R(2,4)                   1.08         estimate D2E/DX2              !
! R5    R(2,5)                   1.08         estimate D2E/DX2              !
! A1    A(2,1,3)               120.           estimate D2E/DX2              !
! A2    A(2,1,6)               120.           estimate D2E/DX2              !
! A3    A(3,1,6)               120.           estimate D2E/DX2              !
! A4    A(1,2,4)               120.           estimate D2E/DX2              !
! A5    A(1,2,5)               120.           estimate D2E/DX2              !
! A6    A(4,2,5)               120.           estimate D2E/DX2              !
! D1    D(3,1,2,4)             180.           estimate D2E/DX2              !
! D2    D(3,1,2,5)               0.           estimate D2E/DX2              !
! D3    D(6,1,2,4)               0.           estimate D2E/DX2              !
! D4    D(6,1,2,5)             180.           estimate D2E/DX2              !
--------------------------------------------------------------------------------
```

Figure 14.8

First of all (Figure 14.7), the initial structure can be input using any coordinate system, or with a Z-matrix. I chose Cartesian coordinates, but could have used the Z-matrix.

The big difference is the internal coordinates: 15 in all, of which 3 are redundant (Figure 14.8).

Once again, we keep our eye on the matrix of force constants. Three eigenvalues are arbitrariliy given a large value (1000) and the variables are updated (Figure 14.9).

Eventually, we get exactly the same answer as before, and each calculation took about the same time on my office PC.

14.10 NORMAL COORDINATES

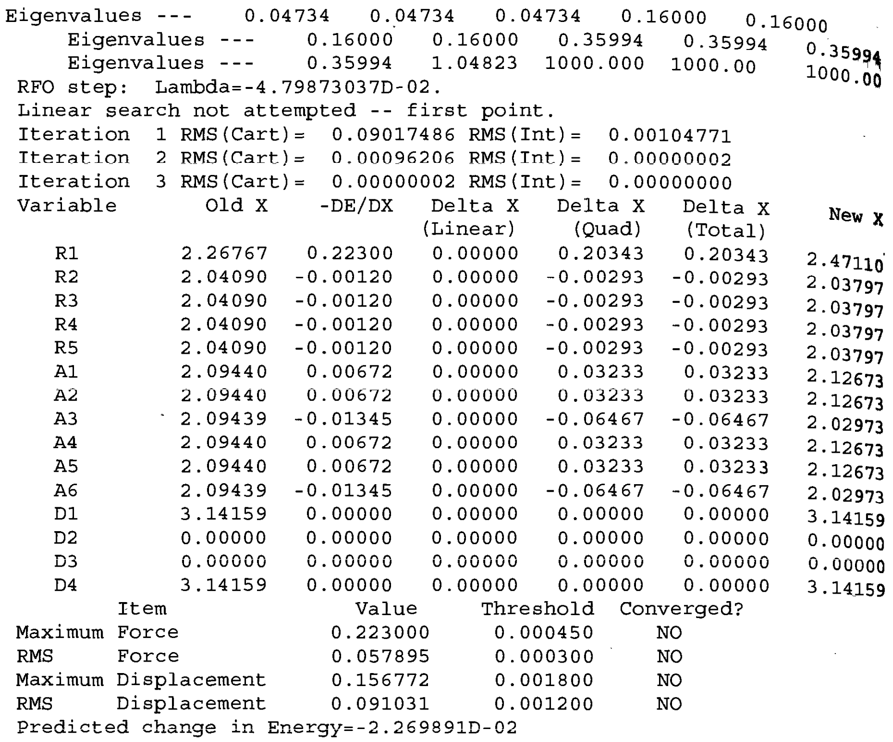
Force constant calculations are normally done in Cartesian coordinates. Suppose we have N atoms whose position vectors are $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$. Each of the atoms vibrates about its equilibrium position $\mathbf{R}_{1,\mathrm{e}}, \mathbf{R}_{2,\mathrm{e}}, \ldots, \mathbf{R}_{N,\mathrm{e}}$.

The first step in our treatment is to define *mass-weighted displacement coordinates*

$$\mathbf{Q}_i = \sqrt{m_i}(\mathbf{R}_i - \mathbf{R}_{i,\mathrm{e}}) \tag{14.25}$$

The total nuclear kinetic energy is therefore

$$T = \frac{1}{2}\sum_{i=1}^{N}\left|\frac{\mathrm{d}\mathbf{Q}_i}{\mathrm{d}t}\right|^2 \tag{14.26}$$



```
Eigenvalues ---    0.04734   0.04734   0.04734   0.16000   0.16000
     Eigenvalues ---    0.16000   0.16000   0.35994   0.35994   0.35994
     Eigenvalues ---    0.35994   1.04823  1000.000  1000.00   1000.00
 RFO step:  Lambda=-4.79873037D-02.
 Linear search not attempted -- first point.
 Iteration  1 RMS(Cart)=  0.09017486 RMS(Int)=  0.00104771
 Iteration  2 RMS(Cart)=  0.00096206 RMS(Int)=  0.00000002
 Iteration  3 RMS(Cart)=  0.00000002 RMS(Int)=  0.00000000
 Variable       Old X    -DE/DX   Delta X   Delta X   Delta X     New X
                                  (Linear)   (Quad)   (Total)
    R1        2.26767   0.22300   0.00000   0.20343   0.20343   2.47110
    R2        2.04090  -0.00120   0.00000  -0.00293  -0.00293   2.03797
    R3        2.04090  -0.00120   0.00000  -0.00293  -0.00293   2.03797
    R4        2.04090  -0.00120   0.00000  -0.00293  -0.00293   2.03797
    R5        2.04090  -0.00120   0.00000  -0.00293  -0.00293   2.03797
    A1        2.09440   0.00672   0.00000   0.03233   0.03233   2.12673
    A2        2.09440   0.00672   0.00000   0.03233   0.03233   2.12673
    A3        2.09439  -0.01345   0.00000  -0.06467  -0.06467   2.02973
    A4        2.09440   0.00672   0.00000   0.03233   0.03233   2.12673
    A5        2.09440   0.00672   0.00000   0.03233   0.03233   2.12673
    A6        2.09439  -0.01345   0.00000  -0.06467  -0.06467   2.02973
    D1        3.14159   0.00000   0.00000   0.00000   0.00000   3.14159
    D2        0.00000   0.00000   0.00000   0.00000   0.00000   0.00000
    D3        0.00000   0.00000   0.00000   0.00000   0.00000   0.00000
    D4        3.14159   0.00000   0.00000   0.00000   0.00000   3.14159
         Item               Value     Threshold  Converged?
 Maximum Force            0.223000     0.000450     NO
 RMS     Force            0.057895     0.000300     NO
 Maximum Displacement     0.156772     0.001800     NO
 RMS     Displacement     0.091031     0.001200     NO
 Predicted change in Energy=-2.269891D-02
```

Figure 14.9

It is convenient to define a set of $3N$ mass-weighted Cartesian displacement coordinates $q_1, q_2, \ldots, q_{3N}$ such that the first three q's are the components of $\mathbf{Q}_1$, the fourth, fifth and sixth q's are the components of $\mathbf{Q}_2$, and so on. The kinetic energy T can therefore be written

$$T = \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{\mathrm{d}q_i}{\mathrm{d}t}\right)^2 \tag{14.27}$$

The vibrational potential energy U will also be a function of the q's, so I can write it

$$U = U(q_1, q_2, \ldots, q_{3N}) \tag{14.28}$$

and we can re-write its expansion about the equilibrium position in a Taylor series as

$$U = U_\mathrm{e} + \sum_{i=1}^{3N}\left(\frac{\partial U}{\partial q_i}\right)_\mathrm{e} + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N}\left(\frac{\partial^2 U}{\partial q_i \partial q_j}\right)_\mathrm{e} q_i q_j + \cdots \tag{14.29}$$

the equilibrium position, the gradient is zero and provided the vibrations are t large we can write

$$U = U_\mathrm{e} + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N}\left(\frac{\partial^2 U}{\partial q_i \partial q_j}\right)_\mathrm{e} q_i q_j \tag{14.30}$$

$$U = U_\mathrm{e} + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} u_{ij} q_i q_j \tag{14.31}$$

The force on atom i is given by the negative of the gradient

$$\mathbf{F}_i = -\mathrm{grad} U \text{ which is } m_i \frac{\mathrm{d}^2\mathbf{R}_i}{\mathrm{d}t^2}.$$

Hence, each of the q's satisfies

$$\frac{\mathrm{d}^2 q_i}{\mathrm{d}t^2} + \frac{\partial U}{\partial q_i} = 0$$

Differentiating equation 14.31 shows that

$$\frac{\partial U}{\partial q_i} = \sum_{j=1}^{3N} u_{ij} q_j$$

and so, finally

$$\frac{\mathrm{d}^2 q_i}{\mathrm{d}t^2} + \sum_{j=1}^{3N} u_{ij} q_i = 0 \tag{14.32}$$

Normal modes are those motions where all the atoms are vibrating in phase; if we write

$$q_i = A_i \sin(\omega t + \phi_i)$$

as in Chapter 1, we have

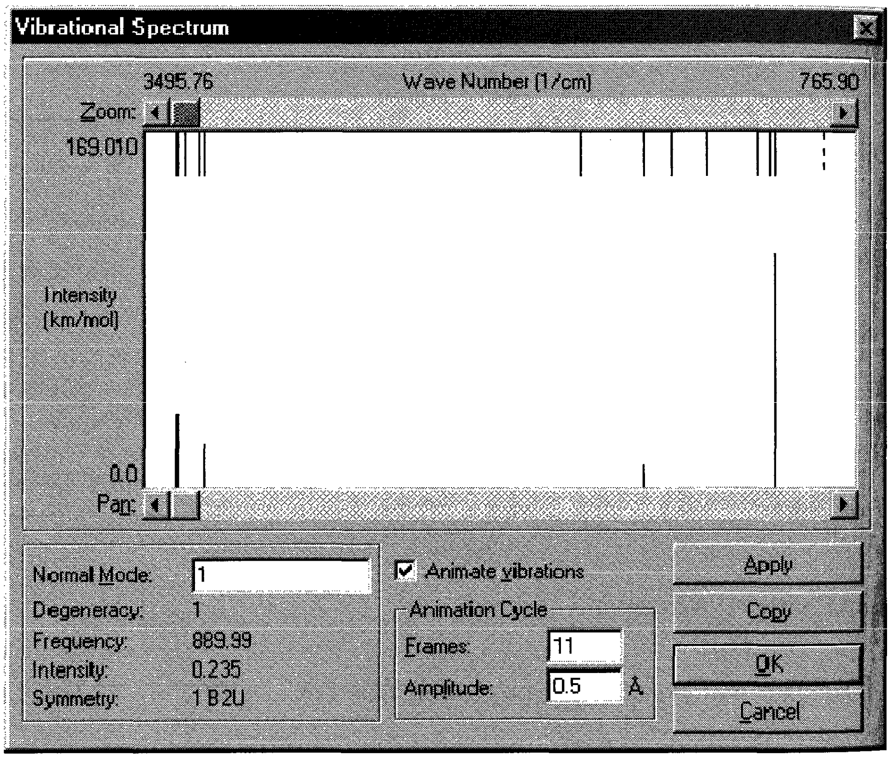
$$-\omega^2 q_i + \sum_{i=1}^{3N} u_{ij} q_j = 0 \text{ for } j = 1, 2, \ldots, 3N \tag{14.33}$$

or

$$\begin{pmatrix} u_{11} & u_{12} & \cdots & u_{1,3N} \\ u_{21} & u_{22} & \cdots & u_{2,3N} \\ \cdots & \cdots & \cdots & \cdots \\ u_{3N,1} & u_{3N,2} & \cdots & u_{3N,3N} \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \\ \cdots \\ q_{3N} \end{pmatrix} = \omega^2 \begin{pmatrix} q_1 \\ q_2 \\ \cdots \\ q_{3N} \end{pmatrix} \tag{14.34}$$

```
Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                        1                      2                      3
                       B2U                    B3U                    B2G
 Frequencies --     890.0098              1082.2465              1096.8653
 Red. masses --       1.0426                 1.1607                 1.5199
 Frc consts  --       0.4866                 0.8010                 1.0774
 IR Inten    --       0.2468               112.5680                 0.0000
 Raman Activ --       0.0000                 0.0000                 5.5215
 Depolar     --       0.0000                 0.0000                 0.7500
 Atom AN      X      Y      Z        X      Y      Z        X      Y      Z
   1   6     0.00   0.04   0.00     0.08   0.00   0.00     0.15   0.00   0.00
   2   6     0.00   0.04   0.00     0.08   0.00   0.00    -0.15   0.00   0.00
   3   1     0.00  -0.24   0.44    -0.50   0.00   0.00    -0.49   0.00   0.00
   4   1     0.00  -0.24   0.44    -0.50   0.00   0.00     0.49   0.00   0.00
   5   1     0.00  -0.24  -0.44    -0.50   0.00   0.00     0.49   0.00   0.00
   6   1     0.00  -0.24  -0.44    -0.50   0.00   0.00    -0.49   0.00   0.00
```

Figure 14.10



Normal Mode: 1
Degeneracy: 1
Frequency: 889.99
Intensity: 0.235
Symmetry: 1 B2U

☑ Animate vibrations

Frames: 11
Amplitude: 0.5 Å

Figure 14.11 Vibrational spectrum of ethene

This is clearly a matrix eigenvalue problem; the eigenvalues determine the vibrational frequencies and the eigenvectors are the normal modes of vibration. Typical output is shown in Figure 14.10, with the mass-weighted normal coordinates expressed as linear combinations of mass-weighted Cartesian displacements making up the bottom six lines.

HyperChem 5.1 has a nice graphical display (Figure 14.11) of calculated vibrational frequencies and it is also possible to animate the vibrations. The bottom part of the display shows the calculated intensities of the spectral lines.

14.11 SEARCHING FOR TRANSITION STATES

Maxima, minima and saddle points are stationary points on a potential energy surface characterized by a zero gradient. A (first-order) saddle point is a maximum along just one direction and in general this direction is not known in advance. It must therefore be determined during the course of the optimization. Numerous algorithms have been proposed, and I will finish this chapter by describing a few of the more popular ones.

14.12 SURFACE-FITTING

At first sight, the easiest approach is to fit a set of points near the saddle point to some analytical expression. Derivatives of the fitted function can then be used to locate the saddle point. This method has been well used for small molecules (see Sana, 1981). An accurate fit to a large portion of the potential energy surface is also needed for the study of reaction dynamics by classical or semi-classical trajectory methods.

The main disadvantage seems to be the lack of a standard, universally applicable method for fitting multidimensional non-quadratic surfaces. Each family of reactions is a special case.

14.12.1 Linear and Quadratic Synchronous Transit

The linear synchronous transit (LST) and quadratic synchronous transit (QST) methods first proposed by Halgren and Lipscomb (1977) make assumptions about the reaction path. The LST algorithm assumes that the path joining reactants and products is linear. The LST estimate of the transition state occurs at the energy maximum along this linear path. The QST algorithm is an improvement on LST, and searches for a maximum along a parabola connecting the reactants and the products.

The Synchronous-Transit Method for determining Reaction Pathways and Locating Molecular Transition States
Thomas A. Halgren and William N. Lipscomb
Chemical Physics Letters **49** (1977) 225–232

In the Synchronous-Transit method, a *linear synchronous transit* pathway is first constructed and is then refined by optimizing one or more intermediate structures subject to the constraint that the optimized structure retain the same relative position along the path (*orthogonal optimization*). The method yields a series of energy estimates, which progressively bound the energy of the transition state from above and from below. High computational efficiency is attainable, and sufficient flexibility is provided to deal with asynchronous processes. Comparisons are made to the alternative 'reaction-coordinate' approach, which is shown to be subject to several serious deficiencies. The method is applied to a model two-dimensional energy surface and to the allowed electrocyclic interconversions of the cyclopropyl and allyl cations and of cyclobutene and *cis*-butadiene.

In a recent version, the LST or QST algorithm is used to find an estimate of the maximum, and a Newton method is then used to complete the optimization (Peng and Schlegel, 1993).

14.12.2 Coordinate Driving

It often happens that the change from reactants to products is dominated by the change of one coordinate. A series of points along the reaction path can be obtained by stepping along the dominant coordinate and minimizing the energy of the remaining coordinates at each point.

14.12.3 Eigenvector Following

One of the earliest attempts to develop a transition-state search algorithm that could take corrective action when in the wrong region of the potential energy surface was due to Poppinger (1975). Poppinger suggested that, if the Hessian had all positive eigenvalues, the lowest Hessian eigenvector should be followed uphill. If the Hessian had two or more negative eigenvalues, the eigenvector corresponding to the least negative eigenvalue should be followed uphill. Baker has described an algorithm that makes use of these ideas.

An Algorithm for the Location of Transition States
Jon Baker
Journal of Computational Chemistry **7** (1986) 385–395

An algorithm for locating transition states designed for use in the *ab initio* program package GAUSSIAN 82 is presented. It is capable of locating transition states even if started in the wrong region of the energy surface, and, by incorporating the ideas on Hessian mode following due to Cerjan and Miller, can locate transition states for alternative rearrangement/dissociation reactions from the same initial starting point. It can also be used to locate minima.

14.12.4 The Synchronous Transit-Guided Quasi-Newton Method(s)

A recent development uses the quadratic synchronous transit approach to get close to a transition state, and then a Newton or eigenvector-following algorithm to complete the optimization. It performs optimizations in redundant internal coordinates. The key reference is due to Peng, Ayala and Schlegel.

Using Redundant Internal Coordinates to Optimize Equilibrium Geometries and Transition States
Chunyang Peng, Philippe Y. Ayala and H. Bernhard Schlegel
Journal of Computational Chemistry **17** (1996) 49–56

A redundant internal coordinate system for optimizing molecular geometries is constructed from all bonds, all valence angles between bonded atoms, and all dihedral angles between bonded atoms. Redundancies are removed by using the generalized inverse of the **G** matrix; constraints can be added by using an appropriate projector. For minimizations, redundant internal coordinates provide substantial improvements in optimization efficiency over Cartesian and nonredundant internal coordinates, especially for flexible and polycyclic systems. Transition structure searches are also improved when redundant coordinates are used and when the initial steps are guided by the quadratic synchronous transit approach.

15 DEALING WITH THE SOLVENT

Chemical reactions generally take place in condensed media. I have had very little to say so far about the presence or otherwise of a solvent, and many of our calculations refer to isolated molecules in the gas phase at 0 K.

Over the years, many models have been tried that aim to take account of the solvent. I will just discuss four basic types.

15.1 LANGEVIN DYNAMICS

In Chapter 2, I gave you a brief introduction to molecular dynamics. The idea is quite simple: we study the time evolution of our system according to classical mechanics. To do this, we calculate the force on each particle (by differentiating the potential) and then numerically solve Newton's second law

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \mathbf{F} \tag{15.1}$$

The calculation is advanced by a suitable timestep, typically a femtosecond, and statistical data is collected for comparison with experiment.

In Langevin dynamics, we simulate the effect of a solvent by making two modifications to equation 15.1. First of all, we take account of random collisions between the solute and the solvent by adding a random force **R**. It is usual to assume that there is no correlation between this random force and the particle velocities and positions, and it is often taken to obey a Gaussian distribution with zero mean.

Second, we take account of the frictional drag as the solute molecule moves through the solvent. The frictional force is taken to be proportional to the velocity of the particle, with a proportionality constant called the friction coefficient ξ:

$$\mathbf{F}_{\text{friction}} = -\xi\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \tag{15.2}$$

ξ is related to the collision frequency γ by $\gamma = \xi/m$ and for a spherical particle the friction coefficient γ can be related to the diffusion constant D of the solvent by the Einstein relation

$$\gamma = \frac{k_B T}{mD} \tag{15.3}$$

The quantity γ^{-1} is sometimes called the *velocity relaxation time*; it can be considered to be the time taken for the particle to forget its initial velocity. The Langevin equation of motion for a particle is therefore

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \mathbf{F} - m\gamma\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} + \mathbf{R} \tag{15.4}$$

No solvent molecules are actually included in the simulation. The integration proceeds along the lines discussed in Chapter 2. In the general case, where the integration timestep and the velocity relaxation time are of similar magnitudes, the integration algorithm is rather complicated (van Gunsteren and Berendsen, 1982). We can distinguish two limiting cases, as follows.

If the timestep is short relative to the velocity relaxation time, the solvent does not play much part in the motion. Indeed, if $\gamma = 0$, there are no solvent effects at all. A simple algorithm for advancing the position vector $\mathbf{r}$ and velocity $\mathbf{v}$ has been given by van Gunsteren (van Gunsteren, Berendsen and Rullmann, 1981):

$$\begin{aligned} \mathbf{r}(t+\delta t) &= \mathbf{r}(t) + \delta t\mathbf{v}(t) + \frac{1}{2}(\delta t)^2\left(-\gamma\mathbf{v}(t) + \frac{1}{m}(\mathbf{F}(t) + \mathbf{R}(t))\right) \\ \mathbf{v}(t+\delta t) &= \mathbf{v}(t) + \delta t\left(-\gamma\mathbf{v}(t) + \frac{1}{m}(\mathbf{F}(t) + \mathbf{R}(t))\right) \end{aligned} \tag{15.5}$$

The random force is taken from a Gaussian distribution with zero mean and variance

$$\frac{2mk_B T\gamma}{\delta t} \tag{15.6}$$

If the velocity relaxation time is short relative to the integration timestep, the following result is obtained:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \frac{\delta t}{m\gamma}\mathbf{F}(t) + \mathbf{X}(\delta t) \tag{15.7}$$

were $\mathbf{X}$ is a Gaussian distribution with zero mean and variance $2D\delta t$.

15.2 THE SOLVENT BOX

In Langevin dynamics studies, the solvent is simulated; no solvent molecules are included explicitly in the calculation. The beauty of such calculations is their consequent speed.

In Chapter 2, I mentioned that there was great interest in water as a solvent, and explained about the pioneering calculations of Rahman and Stillinger (1972). Many molecular mechanics (MM), Monte Carlo (MC) and molecular dynamics (MD) studies have been made based on their box of 216 water molecules. A good starting point is the work of Jorgensen and coworkers.

Comparison of Simple Potential Functions for Simulating Liquid Water
William L. Jorgensen, Jayaraman Chandresekhar and Jeffrey D. Madura
Journal of Physical Chemistry **79** (1983) 926

Classical Monte Carlo simulations have been carried out for liquid water in the NPT ensemble at 25 °C and 1 atm using six of the simpler intermolecular potential functions for the water dimer: Bernal–Fowler (BF), SPC, ST2, TIPS2, TIP3P and TIP4P. Comparisons are made with experimental thermodynamic and structural data including the recent neutron diffraction data of Thiessen and Narten. The computed densities and potential energies are in reasonable accord with experiment except for the original BF model, which yields an 18% overestimate of the density and poor structural results. The TIPS2 and TIP4P potentials yield oxygen–oxygen partial structure functions in good agreement with the neutron diffraction results. The accord with the experimental OH and HH partial structure functions is poorer; however, the computed results for these functions are similar for all the potential functions. Consequently, the discrepancy may be due to the correction terms needed in processing the neutron data or to an effect uniformly neglected in the computations. Comparisons are also made for self-diffusion coefficients obtained from molecular dynamics simulations. Overall, the SPC, SDT2, TIPS2 and TIP4P models give reasonable structural and thermodynamic descriptions of liquid water and they should be useful in simulations of aqueous solutions. The simplicity of the SPC, TIPS2, and TIP4P is also attractive from a computational standpoint.

The idea is to embed the molecule of interest in a solvent box as shown in Figure 15.1 (aspirin in water). After this MM, MD or MC calculations can be made. A periodic box should be added as needed.

15.3 THE ONSAGER MODEL

In their classic review on 'Continuous Distributions of the Solvent', Tomasi and Persico (1994) identify four groups of approaches to dealing with the solvent. First, there are methods based on the elaboration of physical functions; this includes approaches based on the virial equation of state and methods based on perturbation theory with particularly simple reference systems. For many years

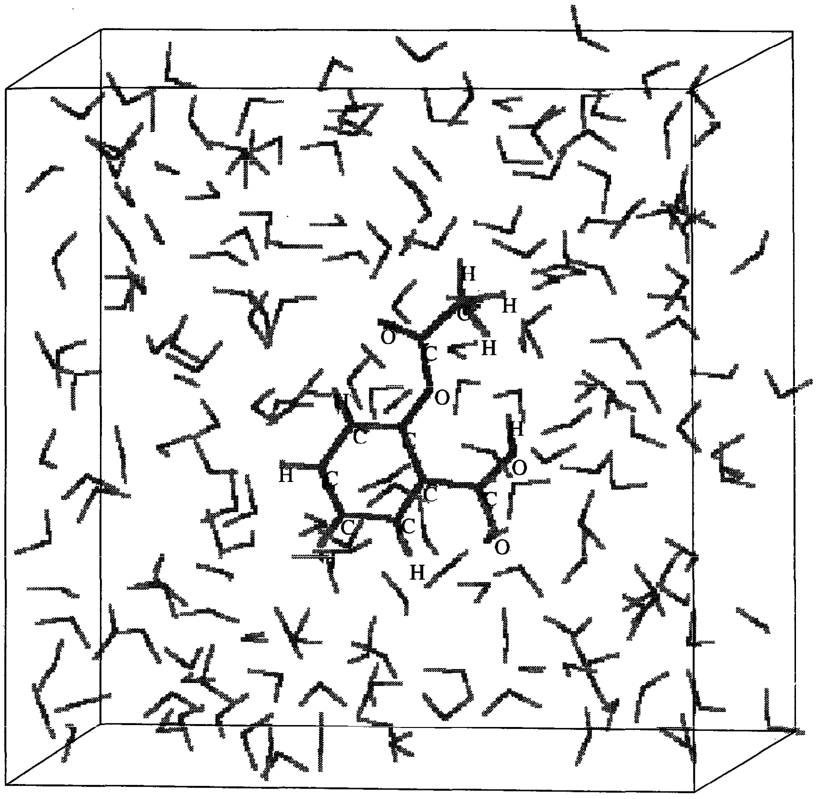


Figure 15.1 Aspirin in a solvent box

the evolution of such methods was based on a drastically simplified intermolecular potential.

In the second group come molecular dynamics and Monte Carlo simulations, especially those where the solvent is modelled without being explicitly included. Their fourth class is the related supermolecule class, where we actually include solvent molecules in the simulation, and treat the entire array of molecules according to the rules of quantum mechanics or whatever.

The third group is the *continuum models*, and these are based on simple concepts from classical electromagnetism. It is convenient to divide materials into two classes, electrical conductors and *dielectrics*. In a conductor such as metallic copper, the conduction electrons are free to move under the influence of an applied electric field. In a dielectric material such as glass, paraffin wax or paper, all the electrons are bound to the molecules as shown schematically in Figure 15.2. The black circles represent nuclei, and the electron clouds are represented as open circles.

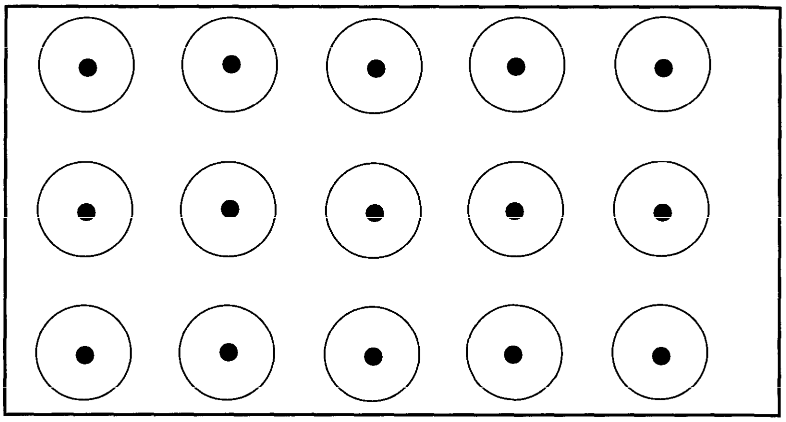


Figure 15.2 An unpolarized dielectric medium

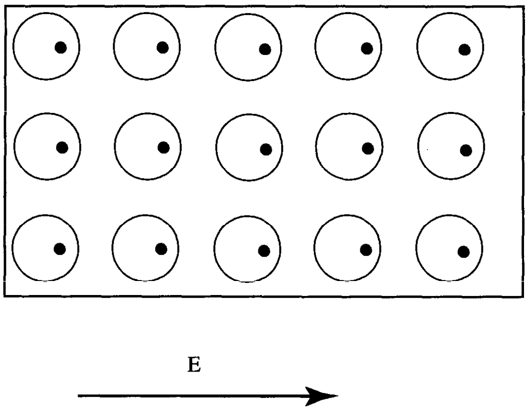


Figure 15.3 A polarized dielectric

If we apply an external electrostatic field **E** then the protons and electrons each experience a force. This force tends to cause charge separation in the dielectric. The positively charged nuclei move in the direction of the applied field, the negatively charged electrons move in the opposite direction. I have illustrated this behaviour in Figure 15.3.

The phenomenon is referred to as *dielectric polarization*. The induced dipole moment per volume is called the *polarization* **P**, and the charge reorganization always acts so as to reduce the field inside the dielectric. The phenomenon is treated in all elementary books on electromagnetism.

For very many materials, the polarization can be related to the applied field by

$$\mathbf{P} = \epsilon_0 \chi_e \mathbf{E} \tag{15.8}$$

where χ_e is the electric susceptibility.

Suppose now, that the material is a gas comprising N atoms each of polarizability α in a volume V. When an electric field $\mathbf{E}$ is applied, each atom acquires an induced dipole moment $\alpha\mathbf{E}$ and so the polarization is

$$\mathbf{P} = \frac{N\alpha\mathbf{E}}{V} \tag{15.9}$$

Comparison of the macroscopic and microscopic equations 15.8 and 15.9 gives

$$\chi_{\mathrm{e}} = \frac{N\alpha}{\epsilon_0 V} \tag{15.10}$$

The relative permittivity, the electric susceptibility and the refractive index n are related by

$$\begin{aligned} \epsilon_r &= 1 + \chi_{\mathrm{e}} \\ \epsilon_r &= n^2 \end{aligned} \tag{15.11}$$

and so we have

$$n = \left(1 + \frac{N\alpha}{\epsilon_0 V}\right)^{1/2} \tag{15.12}$$

which can be expanded by the binomial theorem to give

$$n = 1 + \frac{N\alpha}{2\epsilon_0 V} \tag{15.13}$$

Finally, if the gas is ideal we have

$$n = 1 + \frac{p\alpha}{2\epsilon_0 k_{\mathrm{B}} T} \tag{15.14}$$

which gives a means of deducing α, by measuring n at different pressures and temperatures.

In condensed phases, the separation between molecules is of the order of the molecular dimensions and the result is that each molecule is polarized not by just the ordinary applied electric field $\mathbf{E}$ but by a local field $\mathbf{F}$ consisting of $\mathbf{E}$ plus the fields of all the other dipoles. Once the local field is known, we can use equation 15.8 to find the polarization, simply by substituting αF for αE. The calculation of F is difficult because the dipoles that contribute to $\mathbf{F}$ are themselves determined by $\mathbf{F}$ and a self-consistent treatment is necessary. This is achieved by relating $\mathbf{F}$ to $\mathbf{P}$, ultimately giving an equation for χ_{e}.

We write the local field as

$$\mathbf{F} = \mathbf{E} + \frac{L\mathbf{P}}{\epsilon_0} \tag{15.15}$$

where L is the (dimensionless) *Lorentz structure tensor*. In cubic and isotropic phases the three principal values of the tensor are equal to $\frac{1}{3}$ and we then obtain the *Lorentz local field*

$$F = E + \frac{P}{3\epsilon_0} \tag{15.16}$$

After a little manipulation we derive the *Clausius–Mossotti equation*

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N}{3\epsilon_0 V}\alpha \tag{15.17}$$

At optical frequencies in non-magnetic materials we may replace ϵ_r by n^2 to give the *Lorenz–Lorentz equation*

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N}{3\epsilon_0 V} \tag{15.18}$$

In the case of a condensed phase comprising molecules with permanent dipole moment $\mathbf{p}_0$, the argument is more involved. Such a molecule will have an interaction energy

$$U = -\mathbf{p}_0 \cdot \mathbf{E} \tag{15.19}$$

with an external field, and this energy will achieve its minimum when the dipole is parallel to the field and so the molecules in a fluid will tend to orient themselves parallel to the field. This tendency will be opposed by random thermal agitation, but there will be some net orientation and hence a net *orientation polarization* $\mathbf{P}_0$.

This can be calculated by the methods of statistical thermodynamics, and we find

$$\mathbf{P}_0 = \frac{N p_0^2}{3 V k_B T} F \tag{15.20}$$

This orientation polarization has to be added to the distortion polarization considered above, giving a total polarization

$$\mathbf{P} = \frac{N}{V}\left[\alpha + \frac{p_0^2}{3k_B T}\right]\mathbf{F} \tag{15.21}$$

The derivation of the Clausius–Mossotti equation follows as above, except that the quantity in square brackets has to replace α, and we obtain finally

$$\frac{M}{\rho}\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N_A}{3\epsilon_0}\left[\alpha + \frac{p_0^2}{3k_B T}\right] \tag{15.22}$$

where M is the molar mass, N_A the Avogardo number and ρ the density.

A more thorough analysis shows that one should not expect the electric dipole moment to remain constant, because real molecules have polarizability. The polarization of the dielectric in the electric field of the molecule itself gives rise to a *reaction field*, which tends to enhance the electrical asymmetry.

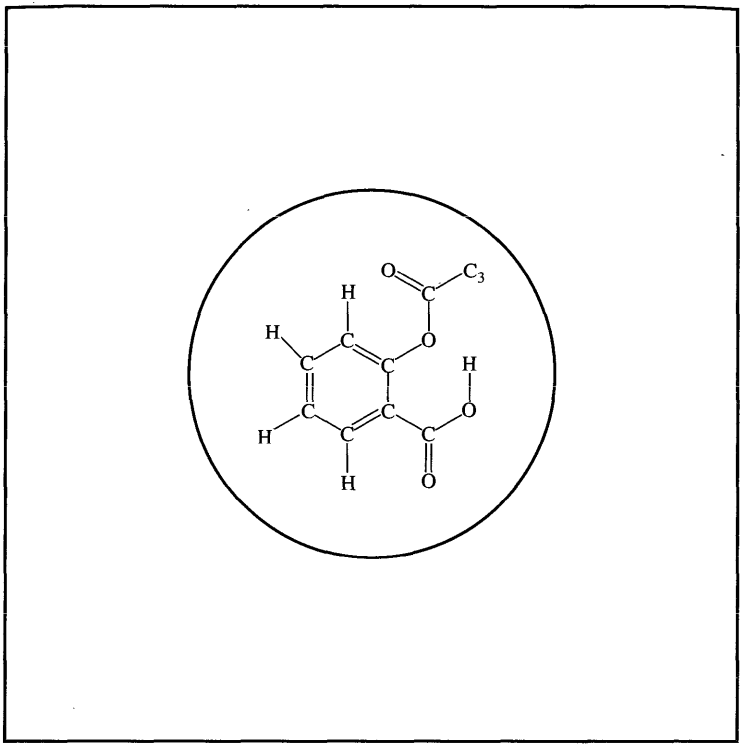


Figure 15.4 Molecule in cavity

Continuum models of solvation treat the solute microscopically, and the surrounding solvent macroscopically, according to the above principles. The simplest treatment is the Onsager (1936) model, where aspirin in solution would be modelled according to Figure 15.4. The solute is embedded in a spherical cavity, whose radius can be estimated by calculating the molecular volume. A dipole in the solute molecule induces polarization in the solvent continuum, which in turn interacts with the solute dipole, leading to stabilization.

One drawback of the original Onsager model is that molecules that have no dipole moment do not show any stabilization.

Over the years, many workers have addressed the problem of choice of cavity and the reaction field. Tomasi's polarized continuum model (PCM) defines the cavity as a series of interlocking spheres. The isodensity PCM (IPCM) defines the cavity as an isodensity surface of the molecule. This isodensity surface is determined iteratively. The self-consistent isodensity polarized continuum model (SCI-PCM) gives a further refinement in that it allows for a full coupling between the cavity shape and the electron density.

Figure 15.5 defines a SCI-PCM run on aspirin.

The relevant output is as in Figure 15.6.

```
*************************************************
Gaussian 98:  Sun-SVR4-Unix-G98RevA.5 21-Sep-1998
               26-Nov-1999
*************************************************
Default route:  MAXDISK=400MB
----------------------------------
# scrf/STO-3G Units=au scrf=iefpcm
----------------------------------
```

Figure 15.5

```
IN VACUO Dipole moment (Debye):
  X=  2.1145  Y= -3.1745  Z= -1.2549  Tot=  4.0154
 IN SOLUTION Dipole moment (Debye):
  X=  2.5047  Y= -3.5616  Z= -1.4632  Tot=  4.5934
 SCF Done:  E(RHF) =  -636.664451503     A.U. after    4 cycles
            Convg  =    0.3728D-04            -V/T =  2.0091
            S**2   =   0.0000
 ------------------------------------------------------
 ------------- VARIATIONAL  IEF  RESULTS ------------
 ------------------------------------------------------
    <Psi(0)| H |Psi(0)>        (a.u.) =   -636.654763
    <Psi(0)|H+V(0)/2|Psi(0)>   (a.u.) =   -636.663805
    <Psi(0)|H+V(f)/2|Psi(0)>   (a.u.) =   -636.664444
    <Psi(f)| H |Psi(f)>        (a.u.) =   -636.654035
    <Psi(f)|H+V(f)/2|Psi(f)>   (a.u.) =   -636.664452
    Total free energy in sol.
    (with non electrost.terms) (a.u.) =   -636.657233
 ------------------------------------------------------
    (Unpol.Solute)-Solvent (kcal/mol) =     -5.67
    (Polar.Solute)-Solvent (kcal/mol) =     -6.54
    Solute Polarization    (kcal/mol) =      0.46
    Total Electrostatic    (kcal/mol) =     -6.08
 ------------------------------------------------------
    Cavitation energy      (kcal/mol) =     23.67
    Dispersion energy      (kcal/mol) =    -22.66
    Repulsion energy       (kcal/mol) =      3.52
    Total non electr.      (kcal/mol) =      4.53
 ------------------------------------------------------
    DeltaG (solv)          (kcal/mol) =     -1.55
 ------------------------------------------------------
```

Figure 15.6

15.4 HYBRID QUANTUM-MECHANICAL AND MOLECULAR MECHANICAL METHODS

Studies of chemical reactions in solution and in enzymes present an enormous challenge because of the enormous size and complexity of these systems. MM force fields have made a tremendous impact in certain areas, but they cannot cope with chemical phenomena involving bond-forming and bond-breaking, nor with electronically excited states.

A combination of quantum mechanics and molecular mechanics, where one treats a small part of the system (e.g. the solute) by means of quantum mechanics and the remainder by MM, provides a powerful tool for studies of structure and reactivity. It all started with the classic paper due to Warshel and Levitt.

Theoretical Studies of Enzymic Reactions: Dielectric, Electrostatic and Steric Stabilizations of the Carbonium Ion in the Reaction of Lysozyme
A. Warshel and M. Levitt
Journal of Molecular Biology **103** (1976) 227–249

A general method for detailed study of enzymic reactions is presented. The method considers the complete enzyme–substrate complex together with the surrounding solvent and evaluates all the different quantum mechanical and classical energy factors that can affect the reaction pathway. These factors include the quantum mechanical energies associated with bond cleavage and charge redistribution of the substrate and the classical energies of steric and electrostatic interactions between the substrate and the enzyme. The electrostatic polarization of the enzyme atoms and the orientation of the dipoles of the surrounding water molecules are simulated by a microscopic dielectric model. The solvation energy resulting from this polarization is considerable and must be included in any realistic calculation of chemical reactions involving anything more than an isolated atom *in vacuo*. Without it, acidic groups can never become ionized and the charge distribution on the substrate will not be reasonable. The same dielectric model can also be used to study the reaction of the substrate in solution. In this way, the reaction is solution can be compared with the enzymic reaction.

In this paper, we study the stability of the carbonium ion intermediate formed in the cleavage of a glycosidic bond by lysozyme. It is found that the electrostatic stabilization is an important factor in increasing the rate of the reaction step that leads to the formation of the carbonium ion intermediate. Steric factors, such as the strain of the substrate on binding to lysozyme, do not seem to contribute significantly.

What the authors did was to combine a MM potential for the solvent with an early (MINDO/2) quantum-mechanical model for the solute. Perhaps because of the biological nature of the journal, the method did not become immediately popular with chemists. By 1998, such *hybrid methods* had become sufficiently well known to justify an American Chemical Society ACS Symposium (Gao and Thompson, 1998).

I can explain a *two-level* hybrid calculation by referring to Figure 15.1, where I divide the system into two parts, the solute (aspirin) and the solvent (water). I treat the solute quantum-mechanically and the solvent by molecular mechanics. The wavefunction for the solute depends on the coordinates of the electrons $\mathbf{r}$, the coordinates of the quantum-mechanical solute molecule $\mathbf{R}_{\mathrm{QM}}$ and the coordinates of all the molecular mechanics solvent molecules $\mathbf{R}_{\mathrm{MM}}$ (I have omitted specific electron and atom labels, such as $\mathbf{r}_i$, for clarity).

$$\Psi = \Psi(\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}}, \mathbf{r}) \tag{15.23}$$

The Hamiltonian is an effective electronic Hamiltonian that operates on Ψ:

$$\hat{H}_{\mathrm{eff}}\Psi(\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}}, \mathbf{r}) = \varepsilon\Psi(\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}}, \mathbf{r}) \tag{15.24}$$

and it can be divided into three terms: a completely quantum-mechanical term that describes the solute molecule, a completely molecular mechanics term that describes the solvent and an interaction term that describes the interaction between the quantum-mechanical particles and the classical particles.

The total energy of the system can also be written

$$\varepsilon = \varepsilon_{\mathrm{MM}} + \varepsilon_{\mathrm{QM}} + \varepsilon_{\mathrm{QM/MM}} \tag{15.25}$$

Here $\varepsilon_{\mathrm{MM}}$ is the energy of the MM part of the system, and this is calculated from a straightforward MM procedure. $\varepsilon_{\mathrm{QM}}$ is the quantum-mechanical energy of the solute and, in recent years, different authors have used semi-empirical, *ab initio* and density functional treatments for this part. The mixed term represents the interactions between the MM atoms with the quantum-mechanical electrons of the solute, as well as the repulsions between the MM atoms and the QM atomic nuclei.

In detail, if

- q_{M} is the atom point charge on the MM atom labelled M,
- R_{AM} is the distance from the quantum-mechanical atom A to the MM atom M,
- eZ_{A} is the core charge of the quantum-mechanical atom A, and
- $r_{i\mathrm{M}}$ is the distance between electron i in the quantum-mechanical system and the MM atom M, then

$$\hat{H}_{\mathrm{QM,MM}} = -\frac{e^2}{4\pi\epsilon_0}\sum_{i,\mathrm{M}}\frac{q_{\mathrm{M}}}{r_{i\mathrm{M}}} + \frac{e}{4\pi\epsilon_0}\sum_{\mathrm{A,M}}\frac{q_{\mathrm{M}}Z_{\mathrm{A}}}{R_{\mathrm{AM}}} \tag{15.26}$$

Finally, it was found necessary to add a Lennard-Jones (LJ) 12–6 intermolecular term between each pair of quantum-mechanical and MM atoms, in order to obtain good interaction energies as well as good geometries for intermolecular interactions.

The complete equation for the QM/MM interaction is therefore

$$\hat{H}_{\mathrm{QM,MM}} = -\frac{e^2}{4\pi\epsilon_0}\sum_{i,\mathrm{M}}\frac{q_{\mathrm{M}}}{r_{i\mathrm{M}}} + \frac{e}{4\pi\epsilon_0}\sum_{\mathrm{A,M}}\frac{q_{\mathrm{M}}Z_{\mathrm{A}}}{R_{\mathrm{AM}}} + \sum_{\mathrm{A,M}}\left(\frac{C_{12,\mathrm{AM}}}{R_{\mathrm{AM}}^{12}} - \frac{C_{6,\mathrm{AM}}}{R_{\mathrm{AM}}^{6}}\right) \tag{15.27}$$

where the C_{12} and the C_6 are the Lennard-Jones 12–6 parameters from Chapter 1.

The term that allows the quantum-mechanical region to see the MM region is the first term of equation 15.27, where the summation is over the quantum-mechanical electrons and the MM atoms.

There are no new concepts for us to study, so I will quickly deal with the three terms in the Hamiltonian.

15.4.1 The QM Region

In their original paper, Warshel and Levitt used MINDO/2 to treat the quantum-mechanical part of the system. Since then, different authors have tried all the most popular quantum-mechanical models. The quantum-mechanical part of the model tends to dominate resource consumption.

15.4.2 The MM Region

Typically a simple MM model is used.

15.4.3 Lennard-Jones (LJ) Parameters for the QM/MM Region

One of the more difficult decisions to be made is the proper value for the Lennard-Jones parameters. These relate to the interaction between the quantum mechanical atoms and the MM atoms. At the time of writing (1999), there does not appear to be a consensus amongst researchers. Some authors recommend a 10% scaling of the traditional 12–6 parameters. Some authors scale the MM atom charges.

15.4.4 Link Atoms

In the case of solution phase studies, it is clear where we should draw a boundary between the parts of a system that ought to be studied quantum-mechanically and those that can be treated by the techniques of molecular mechanics.

Biochemists have different problems in mind: they want to divide parts of a protein chain into regions of interest that ought to be treated quantum-mechanically and the remainder of the chain that can be treated according to the methods of molecular mechanics.

Consider, for example, the protein shown in Figure 15.7. The bottom left-hand amino acid is valine, which is linked to proline. Suppose for the sake of argument that we wanted to treat this valine quantum-mechanically and the rest of the protein chain according to the methods of molecular mechanics. We would have to draw a QM/MM boundary somewhere between valine and the rest of the protein. The *link atoms* define the boundary between the QM and the MM regions. A great deal of care has to go into this choice of boundary. The boundary should not give two species whose chemical properties are quite different from those implied by the structural formulae on either side of this boundary.

In order to achieve this aim, it is usual to 'cap' the exposed valency at the boundary by adding an extra quantum-mechanical atom. There are several reasons

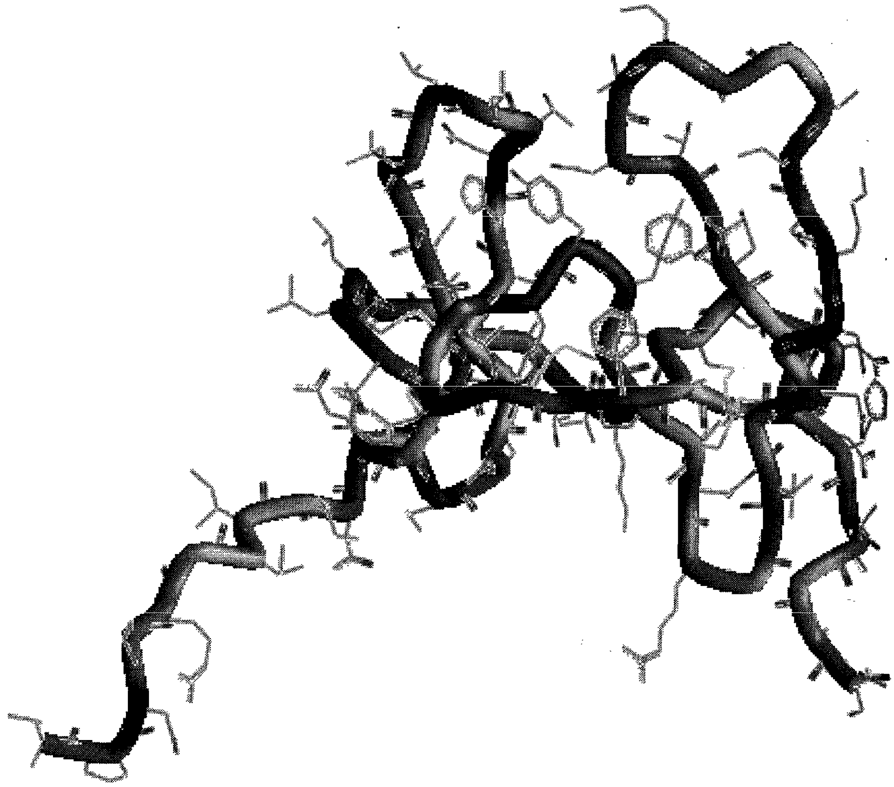


Figure 15.7 A typical protein

for doing this, not the least of which is that we do not want to be left with a radical for the quantum-mechanical part. The extra quantum-mechanical atom does not see any atoms within the MM region and the final atom of the MM region is attached to this quantum-mechanical atom by a harmonic molecular mechanics potential.

15.4.5 Three-Layer Studies

In a three-layer model, we represent one part of the system by MM, one part by a semi-empirical Hamiltonian and one part by an *ab initio* Hamiltonian.

16 PRIMARY PROPERTIES AND THEIR DERIVATIVES

In their classic paper 'Mathematical Problems in the Complete Quantum Predictions of Chemical Phenomena', Boys and Cook (1960) divided the determination of an *ab initio* electronic wavefunction into distinct logical stages which include the

- choice of atomic orbital basis set,
- calculation of one-electron integrals,
- calculation of two-electron integrals,
- choice of Slater determinants, and finally
- the calculation of the wavefunction.

This paper represented advanced thinking in 1960, and whilst we might now be interested to add extra steps such as

- post-HF calculations, and
- geometry optimizations,

their 1962 analysis is still useful. Once the electronic wavefunction Ψ_e has been determined, a number of molecular properties O (for example, the electric dipole moment) can be determined from an expression such as

$$O = O_\mathrm{nuc} + \int \Psi_\mathrm{e}^* \left(\sum_{i=1}^{m} \hat{O}_i \right) \Psi_\mathrm{e}\, \mathrm{d}\tau \tag{16.1}$$

where O_nuc is the contribution to the molecular property made by the nuclei (which are clamped in position according to the Born–Oppenheimer approximation), and the second term is the electronic contribution from the m electrons. The electronic contribution is the expectation value of a symmetric sum of m one-electron operators, and it can also be written in terms of the electron density, as discussed in Chapter 5.

Boys and Cook refer to these properties as *primary properties* because their electronic contributions can be obtained directly from the electronic wavefunction Ψ_e. As a matter of interest, they also classified the electronic energy as a primary property. It can't be calculated as the expectation value of a sum of true one-electron operators, but the Hartree–Fock operator is sometimes written as a sum of pseudo one-electron operators, which include the average effects of the other electrons.

Several other properties are given by the rate of change of a primary property with respect to the normal coordinates (or to some other quantity such as a component of an applied electric field). For example, the second derivative of the energy with respect to the normal coordinates gives the force constants, and the rate of change of the electric dipole moment with normal coordinates determines the intensities of the bands in vibrational infrared spectra. Boys and Cook refer to these as *derivative properties*. I have mentioned the importance of gradients in several chapters, particularly those concerned with geometry optimization. There has recently been a great deal of interest in the calculation of related derivative properties, and I will spend time on them later in this chapter.

Thirdly, *induced properties* are those that measure the response of a system to an applied field. I will concentrate on *polarizabilities* (for which the external field is electric) and *magnetizabilities* (for which the applied field is magnetic) in a later chapter.

Finally, Boys and Cook refer to *interactions between systems* as the fourth category of molecular property.

This is not a unique way of classifying molecular properties. For example, Dykstra *et al.* (1990) concentrate on the response of a system to an applied external field; the electric dipole moment can be defined as the first derivative of the energy with respect to the field, and so on. I will stick with the Boys and Cook nomenclature as a broad basis for discussion.

Much of our knowledge of molecules is obtained from experimental studies of the way they interact with electromagnetic radiation, and the recent growth in non-linear spectroscopies and molecular electronics has focused attention on our ability (or otherwise) to predict and rationalize the electric properties of molecules. The idea of an electric multipole is an important one, so let's begin the discussion there.

16.1 ELECTRIC MULTIPOLE MOMENTS

In Figure 16.1, we see a pair of point charges: Q_A at position vector $\mathbf{r}_A$ and Q_B at position vector $\mathbf{r}_B$. Q_A is not necessarily equal to Q_B, and one is not necessarily the negative of the other. Their *electric dipole moment* $\mathbf{p}_e$ is defined as

$$\mathbf{p}_e = Q_A\mathbf{r}_A + Q_B\mathbf{r}_B$$

This is consistent with the more elementary definition usually given: a pair of equal and opposite charges $\pm Q$ separated by distance d (in which case the

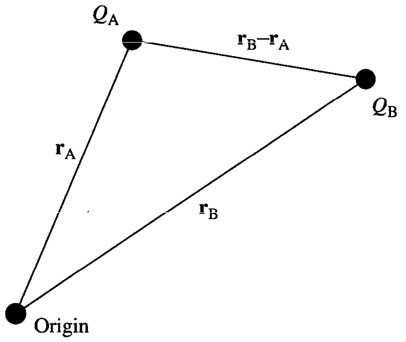


Figure 16.1 A simple electric dipole moment

dipole moment has magnitude Qd and a direction from $-Q$ to $+Q$). For the sake of generality, we take a set of point charges $Q_A, Q_B, \ldots, Q_N$ located at position vectors $\mathbf{r}_A, \mathbf{r}_B, \ldots, \mathbf{r}_N$. The general definition is

$$\mathbf{p}_e = \sum_{i=1}^{N} Q_i \mathbf{R}_i \tag{16.2}$$

The vector $\mathbf{p}_e$ thus has three components whose values are

$$\sum_{i=1}^{N} Q_i x_i, \sum_{i=1}^{N} Q_i y_i \quad \text{and} \quad \sum_{i=1}^{N} Q_i z_i$$

If we make a change of coordinate origin, so that

$$\mathbf{R}_i' = \mathbf{R}_i + \mathbf{A}$$

where $\mathbf{A}$ is a constant vector, then the dipole moment becomes

$$\begin{aligned} \mathbf{p}_e' &= \sum_{i=1}^{N} Q_i(\mathbf{R}_i + \mathbf{A}) \\ &= \mathbf{p}_e + \mathbf{A}\sum_{i=1}^{N} Q_i \end{aligned} \tag{16.3}$$

This definition is therefore independent of the choice of coordinate origin only when the charges sum to zero. The dipole moment of a charged species depends on the coordinate origin, which must be quoted when reporting such quantities.

At the molecular level, electric dipole moments are important because they give information about the charge distribution in a molecule. Examination of the experimental data for a few simple compounds reveals that the electric dipole moment is also a property associated with chemical bonds and their polarity. The literature is immense and you might like to consult the classic text by LeFèvre (1938) on this subject.

The six quantities

$$\sum_{i=1}^{N} Q_i x_i^2, \sum_{i=1}^{N} Q_i y_i^2, \sum_{i=1}^{N} Q_i z_i^2, \sum_{i=1}^{N} Q_i x_i y_i, \sum_{i=1}^{N} Q_i x_i z_i \text{ and } \sum_{i=1}^{N} Q_i y_i z_i$$

define *the electric second moments* and we usually collect them into a 3×3 symmetric matrix:

$$\mathbf{Q}_\mathrm{e} = \begin{pmatrix} \sum_{i=1}^{N} Q_i x_i^2 & \sum_{i=1}^{N} Q_i x_i y_i & \sum_{i=1}^{N} Q_i x_i z_i \\ \sum_{i=1}^{N} Q_i y_i x_i & \sum_{i=1}^{N} Q_i y_i^2 & \sum_{i=1}^{N} Q_i y_i z_i \\ \sum_{i=1}^{N} Q_i z_i x_i & \sum_{i=1}^{N} Q_i z_i y_i & \sum_{i=1}^{N} Q_i z_i^2 \end{pmatrix} \tag{16.4}$$

There are several different definitions relating to second moments in the literature, and it is necessary to take care when applying seemingly simple formulae that involve such quantities. Not only that, authors often use the same name for the different definitions.

Most authors prefer to work with a quantity Θ_e called the *electric quadrupole moment*. It is usually defined as

$$\Theta_\mathrm{e} = \frac{1}{2} \begin{pmatrix} \sum_{i=1}^{N} Q_i(3x_i^2 - r_i^2) & 3\sum_{i=1}^{N} Q_i x_i y_i & 3\sum_{i=1}^{N} Q_i x_i z_i \\ 3\sum_{i=1}^{N} Q_i y_i x_i & \sum_{i=1}^{N} Q_i(3y_i^2 - r_i^2) & 3\sum_{i=1}^{N} Q_i y_i z_i \\ 3\sum_{i=1}^{N} Q_i z_i x_i & 3\sum_{i=1}^{N} Q_i z_i y_i & \sum_{i=1}^{N} Q_i(3z_i^2 - r_i^2) \end{pmatrix} \tag{16.5}$$

The factor of 1/2 is thought conventional by some authors, but ignored by others. The diagonal elements of Θ_e always add together to zero, for any charge distribution. For a spherically symmetric charge distribution, each of the diagonal terms is individually zero, and so the electric quadrupole moment gives us a measure of the deviation of a charge distribution from spherical symmetry.

Depending on the orientation of the Cartesian axes, the matrix of quadrupole moments

$$\Theta_\mathrm{e} = \begin{pmatrix} \Theta_{xx} & \Theta_{xy} & \Theta_{xz} \\ \Theta_{yx} & \Theta_{yy} & \Theta_{yz} \\ \Theta_{zx} & \Theta_{zy} & \Theta_{zz} \end{pmatrix} \tag{16.6}$$

may or may not be diagonal. There is always one choice of coordinate axes, called the *principal axes*, for which the matrix is diagonal. We normally refer to these as the a, b and c directions and the diagonal components are referred to as the *principal values*. We find these by the usual process of matrix diagonalization. The largest of the three principal values

$$\Theta_e = \begin{pmatrix} \Theta_{aa} & 0 & 0 \\ 0 & \Theta_{bb} & 0 \\ 0 & 0 & \Theta_{cc} \end{pmatrix} \tag{16.7}$$

is usually referred to as 'the' electric quadrupole moment.

At the molecular level, electric quadrupoles can lead to useful structural information. Thus, whilst the absence of a permanent electric dipole in CO_2 simply means that the molecule is linear, the fact that the electric quadrupole moment is negative shows that our simple chemical intuition of $O^-C^+O^-$ is correct. The definition of quadrupole moment is only independent of the coordinate origin when the charges sum to zero and when the electric dipole moment is zero.

The definitions need to be generalized when dealing with continuous charge distributions. Sums such as

$$\sum_{i=1}^{N} Q_i(\ldots)$$

have to be replaced by integrals over the charge distribution $\rho(\mathbf{r})$,

$$\int \rho(\mathbf{r})(\ldots)\,\mathrm{d}\tau$$

so for example, the x^2 component of the electric quadrupole moment is

$$\Theta_{xx} = \int \rho(\mathbf{r}) x^2\,\mathrm{d}\tau \tag{16.8}$$

16.2 THE MULTIPOLE EXPANSION

Multipole moments are useful quantities in that they collectively describe an overall charge distribution. In Chapter 0, I explained how to calculate the electrostatic field (and electrostatic potential) due to a charge distribution, at an arbitrary point in space.

In principle, we can calculate the potential at the point in space $\mathbf{r}$ from

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}_A)\,\mathrm{d}\tau}{|\mathbf{r} - \mathbf{r}_A|} \tag{16.9}$$

but in practice this integral might be a difficult one to evaluate. The charge distribution will have a set of associated electric moments, and one might anticipate that it would be possible to evaluate $\phi(\mathbf{r})$ from the (simpler) potentials due to these moments. For example, the potential due to a dipole is shown in all the

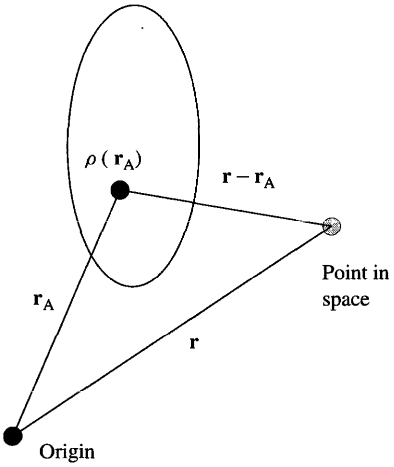


Figure 16.2 Potential at point in space, due to charge distribution

elementary electromagnetism texts to be

$$\phi_{\text{dip}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{\mathbf{p}_e \cdot (\mathbf{r} - \mathbf{r}_A)}{|\mathbf{r} - \mathbf{r}_A|^3} \tag{16.10}$$

The *multipole expansion* gives exactly that expression. If the charge distribution shown has an overall charge Q, an electric dipole $\mathbf{p}_e$, an electric quadrupole Θ_e, and so on, then we write

$$\phi(\mathbf{r}) = \phi_{\text{charge}}(\mathbf{r}) + \phi_{\text{dipole}}(\mathbf{r}) + \phi_{\text{quadrupole}}(\mathbf{r}) + \cdots \tag{16.11}$$

The potential due to a point charge falls off as $1/r$, the potential due to a dipole falls off as $1/r^2$, and so on, and the expectation in that the series will quickly terminate for chemical problems.

The equations become a little more compact if we take the point in space as the coordinate origin. The potential due to a dipole is then

$$\phi_{\text{dip}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{\mathbf{p}_e \cdot \mathbf{r}}{r^3} \tag{16.12}$$

It is conventional to write the multipole expansion as a series in $1/r$, and so we need to find alternative expressions for terms higher than the first. From elementary vector calculus we have

$$\text{grad}\left(\frac{1}{r}\right) = -\frac{\mathbf{r}}{r^3} \tag{16.13}$$

and so we write the multipole expansion as

$$4\pi\epsilon_0\phi(\mathbf{r}) = \frac{Q}{r} - \mathbf{p}_e \cdot \text{grad}\left(\frac{1}{r}\right) + \cdots \tag{16.14}$$

where each term on the right-hand side is a product of an electrical moment with an expression involving $1/r$.

For a long time, the multipole expansion was widely regarded as giving the correct starting point for a study of intermolecular forces. The hope is that the major contributions to the potential around a molecule will be those associated with its overall charge, dipole and quadrupole (if any). It is interesting to note that all the classic texts on intermolecular forces begin with a discussion of electromagnetism and the multipole expansion. Historically, such studies were also used as an indirect route to molecular quadrupole moments.

16.3 CHARGE DISTRIBUTION IN AN EXTERNAL FIELD

It is often useful to know the energy of interaction U of a charge distribution in the presence of an external electrostatic field $\mathbf{E}$. It is

$$U = Q\phi - \mathbf{p}_\mathrm{e} \cdot \mathbf{E} - \frac{1}{3}\sum_{i=x}^{z}\sum_{j=x}^{z} \Theta_{ij}E'_{ij} - \cdots \tag{16.15}$$

where $\mathbf{E}'$ is the electrostatic field gradient matrix

$$\mathbf{E}' = \begin{pmatrix} \dfrac{\partial E_x}{\partial x} & \dfrac{\partial E_x}{\partial y} & \dfrac{\partial E_x}{\partial z} \\ \dfrac{\partial E_y}{\partial x} & \dfrac{\partial E_y}{\partial y} & \dfrac{\partial E_y}{\partial z} \\ \dfrac{\partial E_z}{\partial x} & \dfrac{\partial E_z}{\partial y} & \dfrac{\partial E_z}{\partial z} \end{pmatrix} \tag{16.16}$$

Just like the electric quadrupole moment, the electric field gradient matrix can be written in diagonal form for a suitable choice of coordinate axes.

16.4 IMPLICATIONS OF BRILLOUIN'S THEOREM

I mentioned the Brillouin theorem in earlier chapters; if Ψ_0 is a closed-shell HF wavefunction and $\Psi_\mathrm{A}^\mathrm{X}$ represents a singly excited state, then

$$\int \Psi_0^* \hat{H}_\mathrm{e} \Psi_\mathrm{A}^\mathrm{X}\, \mathrm{d}\tau = 0 \tag{16.17}$$

If we were to seek an improvement on Ψ_0 using configuration interaction, we could write

$$\Psi_0 \to c_0\Psi_0 + \sum_{\mathrm{A,X}} c_\mathrm{A}^\mathrm{X}\Psi_\mathrm{A}^\mathrm{X} + \sum_{\mathrm{A,B}}\sum_{\mathrm{X,Y}} c_\mathrm{AB}^\mathrm{XY}\Psi_\mathrm{AB}^\mathrm{XY} + \cdots \tag{16.18}$$

If we used perturbation theory to estimate the expansion coefficients c_A^X etc., then all the singly excited coefficients would be zero by Brillouin's theorem. This led authors to make statements that 'HF calculations of primary properties are correct to second order of perturbation theory', because substitution of the perturbed wavefunction into

$$O = O_\mathrm{nuc} + \int \Psi_\mathrm{e}^* \left(\sum_{i=1}^{m} \hat{O}_i \right) \Psi_\mathrm{e} \,\mathrm{d}\tau \tag{16.19}$$

suggests that the first correction terms ought to be typically

$$c_0 c_\mathrm{AB}^\mathrm{XY} \int \Psi_0^* \left(\sum_{i=1}^{M} \hat{O}_i \right) \Psi_\mathrm{AB}^\mathrm{XY} \,\mathrm{d}\tau$$

If we were to use CISD to calculate the expansion coefficients, then the c_A^X need not be zero; they couple in to the ground state through the higher-order excitations.

In any case, the argument ignores the fact that molecular HF calculations are invariably done at the HF–LCAO level and the choice of basis set often turns out to be the dominant source of error.

16.5 ELECTRIC DIPOLE MOMENTS

These can be determined experimentally to very high accuracy from the Stark effect and molecular beam studies. The experimental accuracy is far beyond the capabilities of *ab initio* studies. At the other extreme, the original route to these quantities was through studies of the dielectric polarization of species in solution, and there is currently interest in collision-induced dipole moments. In either case, the quantities deduced depend critically on the model used to interpret the experiment.

The electric dipole moment operator is

$$\hat{\mathbf{p}}_\mathrm{e} = e \sum_{\alpha=1}^{N} Z_\alpha \mathbf{R}_\alpha - e \sum_{i=1}^{M} \hat{\mathbf{r}}_i$$

In terms of the electron density P($\mathbf{r}$), the expectation value is therefore

$$\mathbf{p}_\mathrm{e} = e \sum_{\alpha=1}^{N} Z_\alpha \mathbf{R}_\alpha - e \int \hat{\mathbf{r}} P(\mathbf{r}) \,\mathrm{d}\tau \tag{16.20}$$

and the integrals involved are particularly easy to calculate. Dipole moments are usually routinely reported by *ab initio* packages, often in non-SI units. The debye

(D) is a relic from the days of cgs, defined as the dipole moment corresponding to a pair of equal and opposite charges of magnitudes 10^{-10} esu, separated by 1 Å. There are 2.998×10^9 esu per coulomb, and so $1\mathrm{D} = 10^{-10}$ esu × 1 Å = $3.336 \times 10^{-30}\,\mathrm{C\,m}$. Also, $ea_0 = 8.4784 \times 10^{-30}\,\mathrm{C\,m}$, which is 2.5418 D.

In recent years, a great deal of effort has been expended in seeking analytical first and second derivatives of the energy with respect to nuclear displacements, in order to calculate the gradient (i.e. the force) and force constants. Given such a gradient program, it is a simple matter to differentiate the interaction energy of a molecule in an external electrostatic field with respect to this field.

$$U = Q\varphi - \mathbf{p}_e \cdot \mathbf{E} - \frac{1}{3}\sum_{i=x}^{z}\sum_{j=x}^{z}\Theta_{ij}E'_{ij} - \cdots \tag{16.21}$$

The gradient gives the electric dipole, since

$$\frac{\partial U}{\partial E_x} = -p_x \text{ etc.}$$

Many *ab initio* packages use this route to calculate the dipole for wavefunctions where analytical derivatives are known.

It is usual to consider the following factors in discussions of one-electron properties:

- relativistic effects
- the Born–Oppenheimer approximation
- dependence upon basis set
- electron correlation.

Spin–orbit coupling is a relativistic effect that is well reported in tables of atomic energy levels, and this gives a guide. Relativistic effects are generally thought to be negligible for first-row elements.

Breakdown of the Born–Oppenheimer approximation is responsible for the small but non-zero permanent electric dipole moment of HD ($2 \times 10^{-33}\,\mathrm{C\,m}$, Trefler and Gush, 1968) but otherwise the effect is negligible to chemical accuracy.

Table 16.1 Modulus of the electric dipole moment vector of pyridine

Details	Value/10^{-30} C m
HF/STO-3G	6.9185
HF/4-31G	8.7901
HF/6-311G**	7.6070
MP2/6-311G**	7.4431
BLYP/6-311G**	7.1828
Experiment	7.31 ± 2%

Basis set dependence is important. The results in Table 16.1 were obtained for HF–LCAO calculations on pyridine. In each case, the geometry was optimized.

As a general rule, *ab initio* HF–LCAO calculations with small basis sets tend to underestimate the dipole moment, whilst extended basis sets overestimate it.

A treatment of electron correlation usually brings better agreement with experiment.

16.5.1 Dipole Derivatives

HF–LCAO calculations on molecules with small electric dipoles need to be treated with caution. The classic case is CO. Burrus (1958) determined the magnitude of the vector from a Stark experiment as 0.112 ± 0.005 D ($0.374 \pm 0.017 \times 10^{-30}$ C m).

Early *ab initio* HF–LCAO calculations using minimal basis sets were at first thought to have been unsuccessful, in that they gave the polarity C^-O^+, whilst HF–LCAO calculations with extended basis sets gave the polarity C^+O^-. That the polarity is indeed C^-O^+ was shown by Rosenblum, Nethercott and Townes (1958) from a molecular beam resonance experiment; it goes against all chemical intuition.

Table 16.2 shows typical results. In all cases, the bond length was optimized. It is of interest to consider the variation of electric dipole moment with internuclear separation, shown in Table 16.3.

At this level of theory, the calculated equilibrium bond length is 110.47 pm, and the dipole moment changes sign around R_e which may explain why one has to work so hard to achieve agreement with experiment. The dipole derivative can be found by numerical methods from the data points.

The variation of any diatomic property O with bond distance is usually studied in terms of the fractional extension

$$\xi = \frac{R - R_{eq}}{R_{eq}} \tag{16.22}$$

Table 16.2 Electric dipole moment of CO

Level of theory	R_e/pm	$p_e/10^{-30}$ C m	Polarity
HF/STO-3G	114.55	0.4147	C^-O^+
HF/4-31G	112.77	−2.0023	C^+O^-
HF/6-311G**	110.47	−0.5111	C^+O^-
MP2/6-311G**	113.87	1.0872	C^-O^+
MP2/cc-pVTZ	113.85	0.9808	C^-O^+
CID/6-311G**	112.16	0.2862	C^-O^+
CISD/6-311G**	112.43	0.2986	C^-O^+
BLYP/6-311G**	113.88	0.6435	C^-O^+
Experiment		0.374 0.017	

Table 16.3 Dipole moment vs internuclear separation for CO HF/6-311G**

R/pm	$p_e/10^{-30}$ C m
95	1.8308
100	1.1222
105	0.3646
$110.47 = R_e$	−0.5111
115	−1.2767
120	−2.1137
125	−2.9787

where R_{eq} is the equilibrium bond distance. If we write the vibrational potential energy as

$$U(\xi) - U_0 = a_0\xi^2\left(1 + a_1\xi + a_2\xi^2 + \cdots\right) \tag{16.23}$$

and property O as

$$O = O_{eq} + O_1\xi + \tfrac{1}{2}O_2\xi^2 + \cdots \tag{16.24}$$

the expectation value of the property for the vth vibrational and Jth rotational state of a diatomic molecule is (Buckingham, 1962)

$$O_{v,J} = O_{eq} + \left(v + \frac{1}{2}\right)\left(\frac{B_e}{\omega_e}\right)(O_2 - 3a_1O_1) + 4J(J+1)\left(\frac{B_e}{\omega_e}\right)^2 O_1 + \cdots \tag{16.25}$$

where B_e and ω_e are the equilibrium rotational constant (expressed as an inverse length) and fundamental vibrational wavenumber. Similar formulae exist for polyatomic molecules (Riley, Raynes and Fowler, 1979). The formulae are all based on perturbation theory, and it is often better to explicitly solve the nuclear Schrödinger equation and evaluate the expectation values by direct integration.

One of the most familiar uses of dipole derivatives is the calculation of infrared intensities. To relate the intensity of a transition between states with vibrational wavefunctions ψ_v and $\psi_{v'}$ it is necessary to evaluate the transition dipole moment

$$\int \psi_v \hat{\mathbf{p}}_e \psi_{v'}\,d\tau$$

If we write a Taylor expansion of p_e in normal coordinates about the equilibrium value $p_{e,eq}$

$$p_e = p_{e,eq} + \sum_i \left(\frac{\partial p_e}{\partial q_i}\right) q_i + \frac{1}{2}\sum_i\sum_j \left(\frac{\partial^2 p_e}{\partial q_i \partial q_j}\right) q_i q_j + \cdots \tag{16.26}$$

and truncate after the first derivatives, the transition moment becomes

$$\int \psi_v \hat{\mathbf{p}}_e \psi_{v'}\,d\tau = \sum_i \left(\frac{\partial \mathbf{p}_e}{\partial q_i}\right)\int \psi_v q_i \psi_{v'}\,d\tau \tag{16.27}$$

If we further assume that the vibrational wavefunctions associated with normal mode i are the usual harmonic oscillator ones, and $v' = v + 1$, then the integrated intensity of the infrared absorption band becomes

$$\frac{1}{4\pi\epsilon_0}\left(\frac{N_A\pi}{3c_0^2}\right) d_i \left|\frac{\partial \mathbf{p}_e}{\partial q_i}\right|^2 \tag{16.28}$$

where d_i is the degeneracy of the mode, N_A the Avogadro number and c_0 the speed of light in free space.

16.6 ANALYTICAL GRADIENTS

Analytical gradient energy expressions have been reported for many of the standard models discussed in this book. Analytical second derivatives are also widely available. The main use of analytical gradient methods is to locate stationary points on potential energy surfaces. So, for example, in order to find an expression for the gradient of a closed-shell HF–LCAO wavefunction we might start with the electronic energy expression from Chapter 6,

$$\varepsilon_e = \text{trace } (\mathbf{P}\mathbf{h}_1) + \tfrac{1}{2} \text{ trace } (\mathbf{P}\mathbf{G})$$

Differentiating with respect to some parameter 'a', we see that it is necessary to evaluate terms such as

$$\frac{\partial P_{ij}}{\partial a}, \frac{\partial h_{1,ij}}{\partial a} \text{ and } \frac{\partial G_{ij}}{\partial a}$$

in order to calculate the gradient. The terms involving G involve both differentiation of the electron density and differentiation of the two-electron integrals.

Similar considerations apply to the electric dipole moment; the derivatives of the dipole integrals can be easily obtained whilst the derivatives of the density matrix require the use of coupled Hartree–Fock theory (e.g. Gerratt and Mills, 1968).

16.7 ELECTRIC QUADRUPOLE MOMENTS

Molecular electric quadrupole moments are more elusive animals, and they are not particularly easy to determine experimentally. Prior to 1970, the only direct routes to these quantities were from the Kerr and Cotton–Mouton effects. They can now be obtained from microwave Zeeman spectroscopy, to fair accuracy. It is fair to say that direct calculation offers a faster and more reliable route to this property than experiment.

Basis-set sensitivity is important, as it was for the calculation of electric dipole moments. Several experimental values in the literature refer to measurements corrected neither for zero-point vibrations nor for centrifugal effects.

16.8 ELECTRIC FIELD GRADIENTS

Electron spin has appeared many times in this book; it is an intrinsic property of electrons. It is an angular momentum, usually written **s**. We know that

- the magnitude of **s** is $\sqrt{s(s+1)}\ h/2\pi$ where the spin quantum number $s = 1/2$;
- only the magnitude of **s** and one component (usually called the z component) can be measured simultaneously;
- the z component of the vector has magnitude $m_s\ h/2\pi$, where m_s, the magnetic spin quantum number $= \pm 1/2$.

We often say that an electron is a spin-1/2 particle. Many nuclei also have a corresponding internal angular momentum which we refer to as *nuclear spin*, and we use the symbol **I** to represent the vector. The nuclear spin quantum number I is not restricted to the value of 1/2: it can have both integral and half-integral values depending on the particular isotope of a particular element. All nuclei for which $I \geqslant 1$ also posses a *nuclear quadrupole moment*. It is usually given the symbol Q_N and it is related to the nuclear charge density $\rho_N(\mathbf{r})$ in much the same way as the electric quadrupole discussed earlier;

$$\mathbf{Q}_N = \frac{1}{e}\begin{pmatrix} \int \rho_N(\mathbf{r})\left(3x^2 - r^2\right)\mathrm{d}\tau & 3\int \rho_N(\mathbf{r})xy\,\mathrm{d}\tau & 3\int \rho_N(\mathbf{r})xz\,\mathrm{d}\tau \\ 3\int \rho_N(\mathbf{r})yx\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})\left(3y^2 - r^2\right)\mathrm{d}\tau & 3\int \rho_N(\mathbf{r})yz\,\mathrm{d}\tau \\ 3\int \rho_N(\mathbf{r})zx\,\mathrm{d}\tau & 3\int \rho_N(\mathbf{r})zy\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})\left(3z^2 - r^2\right)\mathrm{d}\tau \end{pmatrix} \tag{16.29}$$

although some authors prefer to work with the second moment

$$\frac{1}{e}\begin{pmatrix} \int \rho_N(\mathbf{r})x^2\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})xy\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})xz\,\mathrm{d}\tau \\ \int \rho_N(\mathbf{r})yx\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})y^2\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})yz\,\mathrm{d}\tau \\ \int \rho_N(\mathbf{r})zx\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})zy\,\mathrm{d}\tau & \int \rho_N(\mathbf{r})z^2\,\mathrm{d}\tau \end{pmatrix} \tag{16.30}$$

The context usually makes it clear which definition is in use.

In principle we could calculate the nuclear quadrupole moment from knowledge of the nuclear charge density distribution, but this knowledge is very hard to come by and so we determine the nuclear quadrupole experimentally. The charged particles in the nucleus are of course protons, and we can imagine them rotating about the local z-axis of the nuclear spin vector. If an average is made over a time that is long enough for the nuclear particles to rotate but so short that the electrons have not appreciably changed position, the nuclear charge distribution may be considered axial. Using a principal axis system which coincides with the nuclear spin, all non-diagonal components of $\mathbf{Q}_N$ will be zero and $Q_{\mathrm{N},xx} = Q_{\mathrm{N},yy} = -1/2\, Q_{\mathrm{N},zz}$. We normally speak of 'the' nuclear quadrupole $Q_\mathrm{N} = Q_{\mathrm{N},zz}$.

In a molecule, a given nucleus will generally experience an electric field gradient due to the surrounding electrons. The energy of interaction U between the nuclear quadrupole and the electric field gradient $\mathbf{E}'$ is given by

$$U = -\frac{e}{6}\sum_{i=x}^{z}\sum_{j=x}^{z} Q_{N,ij}E'_{ij} \tag{16.31}$$

It is usual to denote the electric field gradient at nuclear position N by $\mathbf{q}_\mathrm{N}$, which can be written as a 3×3 matrix

$$\mathbf{q}_\mathrm{N} = \begin{pmatrix} q_{xx} & q_{xy} & q_{xz} \\ q_{yx} & q_{yy} & q_{yz} \\ q_{zx} & q_{zy} & q_{zz} \end{pmatrix} \tag{16.32}$$

and this is usually defined in such a way that the sum of the diagonal elements is zero. In principal axes, we have

$$\mathbf{q}_\mathrm{N} = \begin{pmatrix} q_{aa} & 0 & 0 \\ 0 & q_{bb} & 0 \\ 0 & 0 & q_{cc} \end{pmatrix} \tag{16.33}$$

and $q_{aa} + q_{bb} + q_{cc} = 0$. The interaction is therefore characterized by $Q_{\mathrm{N},zz}$ and two of q_{aa}, q_{bb}, q_{cc}. The largest of the q's is just referred to as q. The quantity ν = (difference of smaller q's divided by the largest) is called the *asymmetry parameter*.

In order to find the correct quantum-mechanical energies for a nuclear quadrupole in an electric field gradient, we need to

- write down the classical energy expression,
- deduce the correct Hamiltonian operator, and
- solve the eigenvalue problem.

The interaction energy depends on Q_N, q and ν and the allowed energy levels turn out to depend on $eQ_\mathrm{N}q$. Division by h gives eqQ_N/h which we refer to as the *quadrupole coupling constant* (QCC).

16.8.1 Quadrupole Coupling Constants

Quadrupole coupling constants for molecules are usually determined from the hyperfine structure of pure rotational spectra or from electric-beam and magnetic-beam resonance spectroscopies. Nuclear magnetic resonance, electron spin resonance and Mossbäuer spectroscopies are also routes to the property. There is a large amount of experimental data for ^{14}N and halogen-substituted molecules. Less data is available for deuterium because the nuclear quadrupole is small.

The quadrupole coupling constant contains two unknowns, the electric field gradient at a given nucleus and the nuclear quadrupole moment. For a simple atom or an atomic anion, it is occasionally possible to make a realistic estimate of the field gradient, and so the quadrupole coupling constant has sometimes been used to give a measure of the nuclear quadrupole moment. In a molecule (charged or otherwise), the nuclei are embedded in the electron cloud, and the electric field gradient gives a measure of the departure from spherical symmetry of the electric charge distribution at the nucleus in question. It depends on the environment of the nucleus, and is thus intimately connected with bonding.

The chemical significance of quadrupole coupling constants has been summarized by Townes and Dailey (1949), and reviewed by Orville-Thomas (1957, 1965). Townes and Dailey argue that only p, d and f atomic orbitals can contribute to the field gradients, and since d and f orbitals do not penetrate near the nucleus, quadrupole coupling constants should be largely due to any p-electrons in the valence shell. An interesting discussion of the Townes and Dailey theory is given in Orville-Thomas's paper, which has both an intriguing title and abstract.

Clash between Experimental Parameters and Simple Theoretical Concepts
W. J. Orville-Thomas
Journal of Chemical Physics **43** (1965) S244–S247

Facts are better than Dreams — Winston Churchill

The author concerns himself with a comparison between theoretical and experimental studies of simple molecules containing the C $\equiv$ N linkage. A large number of spectroscopic studies have been made for XCN molecules, and in the majority of cases many isotopic species have been studied. The experimental data is very accurate. An interesting feature of such molecules is that the C $\equiv$ N distances are equal to within experimental error, and one might expect that the ^{14}N quadrupole coupling constants would be similar. This is not the case, as shown in Table 16.4.

16.9 THE ELECTROSTATIC POTENTIAL

One of the fundamental objectives of chemistry is the prediction and rationalization of molecular reactivity. In principle, this involves the construction of an

Table 16.4 ^{14}N quadrupole coupling constants (QCC)

Molecule	R (C $\equiv$ N)/pm	QCC/MHz
HCN	115.5	−4.58
FCN	115.9	−2.67
ClCN	115.9	−3.63

accurate potential energy surface and a study of the motion of reactants and products along this surface. Most of the traditional theories of chemical reactivity have been aimed at organic molecules, and these theories attempt to extract, from the electronic properties of isolated molecules, some useful information as to how molecules will interact with other molecules.

We can distinguish between *static theories*, which in essence give a description of the electron density, and *dynamic theories*, where an attempt is made to measure the response of a molecule to (e.g.) an approaching NO_2^+ ion. In recent years, the electrostatic potential has been used to give a simple representation of the more important features of molecular reactivity. It can be calculated quite easily at points in space:

$$\varphi(\mathbf{r}) = \frac{e}{4\pi\epsilon_0}\left(\sum_{\alpha=A}^{N}\frac{Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}|} - \int\frac{P(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\tau\right) \qquad (16.34)$$

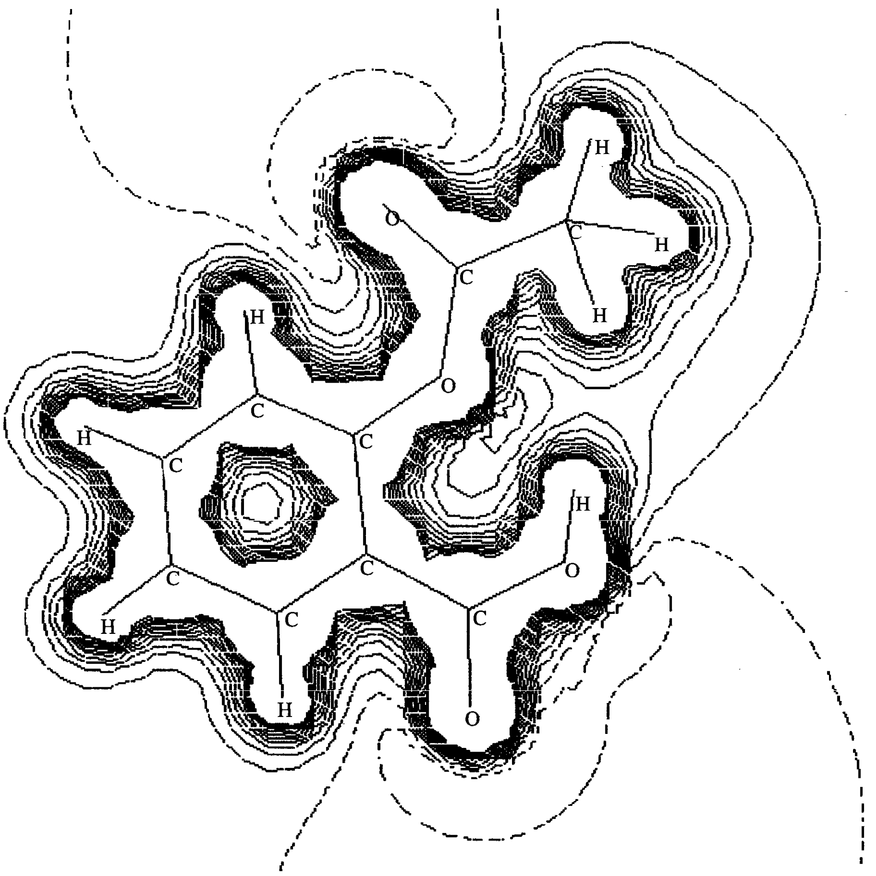


Figure 16.3 Electrostatic potential for aspirin HF/STO–3G

and the quantity $+1\ \mathrm{C}\ \varphi(\mathbf{r})$ is often used in discussion. (This quantity is actually the mutual potential energy of the molecule and a charge of 1 C at position **r**.)

The spirit of this kind of calculation is to give a rough and ready visualization to the potential reactivity of a molecule. For example, Figure 16.3 is a contour map for aspirin. These maps look much better in colour, and it is often possible to spot the route that an approaching charged reagent would take.

17 INDUCED PROPERTIES

In Chapter 16, we studied the so-called primary properties, which I defined as those that could be obtained by direct calculation from the electron density (or equivalently the wavefunction). We also touched on derivative or gradient properties. It is now time to turn our attention to those properties that measure the response of a system to an external field. In the language of Boys and Cook, these are the *induced properties*.

As I mentioned earlier, this classification is not unique and other authors concentrate on classification with respect to gradients. The electric dipole can be understood as the gradient of a certain interaction energy with respect to the components of an applied field, and so on.

17.1 INDUCED DIPOLES

Molecules do not consist of rigid arrays of point charges, and on application of an external electrostatic field the electrons and protons will rearrange themselves until the interaction energy is a minimum. In classical electrostatics, where we deal with macroscopic samples, the phenomenon is referred to as the *induced polarization*. I dealt with this in Chapter 15, when we discussed the Onsager model of solvation. The nuclei and the electrons will tend to move in opposite directions when a field is applied, and so the electric dipole moment will change. Again, in classical electrostatics we study the induced dipole moment per unit volume.

Both the permanent dipole and the applied field are vector quantities, and the direction of the induced dipole need not be the same as the direction of the applied field. Hence, we need a more general property than a vector to describe the polarizability.

Since we normally deal with electrostatic field perturbations that are small, we can profitably expand the electric moments as a Taylor series in the external field:

$$\mathbf{p}_e(\mathbf{E}) = \mathbf{p}_e(\mathbf{0}) + \alpha \cdot \mathbf{E} + \cdots \tag{17.1}$$

where $\mathbf{p}_e(\mathbf{0})$ is the permanent electric dipole. The property α is the *dipole polarizability*, and it can be written as a 3 × 3 symmetric matrix

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \tag{17.2}$$

The dipole polarizability, the field gradient and the quadrupole moment are all examples of *tensor properties*. A detailed treatment of tensors is outside the scope of the text, but you should be aware of the existence of such entities.

In terms of the components of $\mathbf{p}_e$ we write

$$p_{e,i}(\mathbf{E}) = p_{e,i}(\mathbf{0}) + \sum_{j=x}^{z} \alpha_{ij} E_j \tag{17.3}$$

For the special case of an axially symmetric molecule, the electric dipole moment lies along the axis of highest symmetry, which we usually call the z-axis. The induced dipole due to a field along the molecular axis is usually written

$$p_{e,z}(E) = p_e(0) + \alpha_{zz} E_z \tag{17.4}$$

whilst for a field perpendicular to the axis we have

$$p_{e,x}(E) = \alpha_{xx} E_x \tag{17.5}$$

The next terms in the series, denoted ... in equation 17.1 above, are called the *dipole hyperpolarizabilities*. The first one is β and this also is a tensor. It has three indices, and the corresponding formula for the induced dipole, equation 17.3, becomes

$$p_{e,i}(\mathbf{E}) = p_{e,i}(\mathbf{0}) + \sum_{j=x}^{z} \alpha_{ij} E_j + \sum_{j=x}^{z} \sum_{k=x}^{z} \beta_{ijk} E_j E_k \tag{17.6}$$

There are in fact an infinite number of hyperpolarizabilities, and one occasionally comes across terms higher than β.

17.2 ENERGY OF CHARGE DISTRIBUTION IN FIELD

The effect of the induced dipole on the energy of a charge distribution in a uniform electrostatic field can be deduced, and it is (Hinchliffe and Munn, 1985)

$$U = U_0 - \mathbf{p}_e(\mathbf{0}) \cdot \mathbf{E} - \frac{1}{2} \sum_{i=x}^{z} \sum_{j=x}^{z} \alpha_{ij} E_i E_j - \frac{1}{6} \sum_{i=x}^{z} \sum_{j=x}^{z} \sum_{k=x}^{z} \beta_{ijk} E_i E_j E_k - \cdots \tag{17.7}$$

The Cartesian components of the permanent dipole and the polarizability can therefore be written equivalently

$$\begin{aligned} p_{\mathrm{e},i} &= -\frac{\partial U}{\partial E_i} \\ \alpha_{ij} &= -\frac{\partial^2 U}{\partial E_i \partial E_j} \end{aligned} \tag{17.8}$$

with corresponding formulae for the hyperpolarizabilities. All the derivatives have to be evaluated at zero electrostatic field ($\mathbf{E} = \mathbf{0}$). The latter equation demonstrates that the dipole moment tensor is symmetric, and so there are no more than six independent components. As with all such properties, there is a set of Cartesian axes that are usually called a, b and c such that the matrix has diagonal form, and we speak of the 'principal axes of polarizability'. For a molecule with symmetry axes, the principal axes correspond to the symmetry axes. For a linear molecule, the matrix can be written in an even simpler way,

$$\alpha = \begin{pmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha \end{pmatrix}$$

and the parallel component is usually larger than the perpendicular one. Experimental measurements focus on the *mean value* $\langle \alpha \rangle = \frac{1}{3}(\alpha \ + 2\alpha_\perp)$ and the *anisotropy* $\gamma = \alpha \ - \alpha_\perp$. In the general case,

$$\langle \alpha \rangle = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

whilst some authors report an anisotropy γ given by

$$\gamma^2 = \sum_{i>j} \left((\alpha_{ii} - \alpha_{jj})^2 + 6\alpha_{ij}^2 \right)$$

Experimental determinations are far from straightforward, especially if the molecule has little or no symmetry. The mean value can be deduced from the refractive index of a gas, whilst Kerr effect experiments give some idea of the anisotropy.

17.3 MULTIPOLE POLARIZABILITIES

Just as the dipole changes in an external field, so do all the other moments, and we can develop a set of equations for the quadrupole polarizability (and hyperpolarizabilities), the octupole polarizability, and so on. These esoteric quantities are rarely met in chemistry.

17.4 POLARIZABILITY DERIVATIVES

Just as the derivatives of the electric dipole with respect to normal coordinates are important in infrared spectroscopy, so the same derivatives of the polarizability play a role in Raman spectroscopy.

17.5 A CLASSICAL MODEL OF DIPOLE POLARIZABILITY

Studying the response of a very simple 'atom' to an applied electric field can provide an insight into the physical mechanism of polarizability. Our model has a point positive charge $+Q$ surrounded by a uniform spherical distribution of negative charge. The radius of the atom is a. We now apply a uniform electric field as shown in Figure 17.1. The nucleus and the negative sphere will be displaced in opposite directions to create a displacement between centres of d. For simplicity, the sphere is not shown as displaced in the figure. At this point, there is on the nucleus a force due to the applied field and a force due to the electron density. This latter force can be shown (e.g. by Gauss's theorem) to be

$$\frac{Q^2 d}{4\pi\epsilon_0 a^3}$$

At equilibrium these two forces must be equal and so the displacement d satisfies

$$\frac{Q^2 d}{4\pi\epsilon_0 a^3} = QE$$

The induced dipole moment is Qd and the polarizability (here a scalar) is Qd/E so that

$$\alpha = 4\pi\epsilon_0 a^3 \tag{17.9}$$

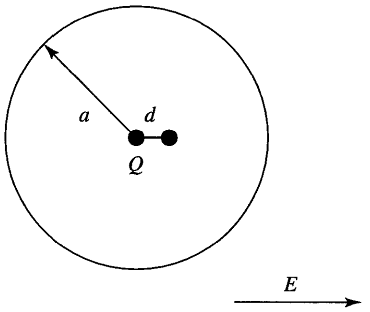


Figure 17.1 Construct needed to discuss polarizability

Apart from the factor of $4\pi\epsilon_0$, the polarizability of an atom is determined in this model by the volume. If we had been working in cgs (old-fashioned electromagnetic quantities) rather than SI (modern ones), we would have found $\alpha = a^3$ and for this reason people speak of the *polarizability volume*.

The SI units of polarizability are $\mathrm{F\,m^2}$. Alternatively, since $\mathrm{F\,m^{-1}} = \mathrm{C^2\,m^{-2}\,N^{-1}}$ we can quote polarizabilities as $\mathrm{C^2\,N^{-1}\,m}$ or $\mathrm{C^2\,m^2\,J^{-1}}$, which is the normal form. In the atomic system, it is usual to quote polarizabilities in multiples of $e^2 a_0^2 E_\mathrm{h}^{-1}$.

The polarizability of the inert gas atoms does indeed increase with their size, as can be seen from Table 17.1.

Atomic and molecular polarizabilities are usually determined by measuring the response of a system to monochromatic electromagnetic radiation. It turns out that the measured values depend on the frequency of the radiation used; they are said to be *frequency-dependent* properties. Roughly speaking, it is observed that the dipole polarizability increases as the frequency of the radiation increases. Eventually the energy of each photon is enough to cause an electronic transition, when a large change is observed in the polarizability. In order to account for the photon absorption, any model has to take account of the quantum nature of matter. For this reason, our simple model above does not explain the experimental findings.

Molecules respond to frequency-dependent fields in a quite different way than to static fields, and some care has to be exercised when comparing the results of theory and experiment.

To give a simple classical model for frequency-dependent polarizabilities, let me return to Figure 17.1 and now consider the positive charge as a point nucleus and the negative sphere as an electron cloud. In the static case, the restoring force on the displaced nucleus is $(Q^2 d)/(4\pi\epsilon_0 a^3)$ which corresponds to a simple harmonic oscillator with force constant

$$k = \frac{Q^2}{4\pi\epsilon_0 a^3}$$

Since nuclear masses are much greater than the electron mass we can treat the nucleus as if it were fixed in space. Taking the mass of the electron charge cloud as m, then $k = m\omega_0^2$ where ω_0 is the angular frequency of the oscillator.

Table 17.1 Some atomic polarizabilities

Atom	$\alpha/10^{-40}\,\mathrm{F\,m^2}$
He	0.23
Ne	0.44
Ar	1.83

Comparing equations, we find that

$$\alpha = \frac{Q^2}{m\omega_0^2}$$

where α is the static polarizability.

A simple time-dependent electric field is given by

$$\mathbf{E}(t) = \mathbf{E}_0 \exp(j\omega t)$$

where $\mathbf{E}_0$ is a constant, ω the angular frequency of the field and j the square root of minus 1 ($j^2 = -1$). Repeating the polarizability calculation above for a simple harmonic oscillator in such a field gives

$$\alpha(\omega) = \frac{Q^2}{m(\omega_0^2 - \omega^2)} \tag{17.10}$$

This simple model shows that the polarizability increases as ω increases, in agreement with experiment, but it cannot deal with the case where the frequency of the applied field is able to cause an electronic transition.

17.6 QUANTUM-MECHANICAL CALCULATIONS OF STATIC POLARIZABILITIES

Two key equations (17.6 and 17.7) for the following discussion are

$$p_{e,i}(\mathbf{E}) = p_{e,i}(\mathbf{0}) + \sum_{j=x}^{z} \alpha_{ij} E_j + \frac{1}{2} \sum_{j=x}^{z} \sum_{k=x}^{z} \beta_{ijk} E_j E_k + \cdots$$

$$U = U_0 - \sum_{i=x}^{z} p_{e,i}(\mathbf{0}) E_i - \frac{1}{2} \sum_{i=x}^{z} \sum_{j=x}^{z} \alpha_{ij} E_i E_j$$
$$- \frac{1}{6} \sum_{i=x}^{z} \sum_{j=x}^{z} \sum_{k=x}^{z} \beta_{ijk} E_i E_j E_k - \cdots$$

The external field $\mathbf{E}$ is taken to be uniform over the dimensions of an atom or a molecule so that there are no external electric field gradients, and I should remind you that these equations are classical ones: we have made no mention of quantization. Again to remind you, the dipole components are given by the first derivative of the energy, the polarizability components are given by either the first derivative of the dipole or the second derivative of the energy. The second derivatives of the dipole or the third derivatives of the energy give the hyperpolarizability, and so on. All derivatives are with respect to the external electric field, and they all have to be evaluated for a limiting zero field.

The first step in our quantum-mechanical calculation is the construction of an appropriate molecular Hamiltonian. For a weak constant static field **E** we have

$$U = U_0 - \mathbf{p}_e(\mathbf{0}) \cdot \mathbf{E} \tag{17.11}$$

and so we simply add an extra term to the corresponding field-free Hamiltonian operator to give

$$\hat{H} = \hat{H}_0 - \hat{\mathbf{p}}_e(\mathbf{0}) \cdot \mathbf{E}$$

I will write $\Delta = -\mathbf{p}_e \cdot \mathbf{E}$ as appropriate in the following few pages, for the sake of compactness.

17.6.1 Standard Perturbation Theory

If we know the solutions for the field-free problem

$$\hat{H}_0 \Psi_i = \varepsilon_i \Psi_i$$

then standard perturbation theory allows us to write solutions to the perturbed problem, as discussed in other chapters. I will write the electronic ground state as Ψ_0 and the excited states Ψ_i. The number of excited states might very well be infinite, and it is necessary to include any unbound states.

Examination of the energy expression 17.7 shows that the polarizability components are the second-order energies and a little analysis shows that (for example)

$$\alpha_{xx} = 2 \sum_{i=1}^{\infty} \frac{\left| \int \Psi_0^* \hat{p}_x \Psi_i \, \mathrm{d}\tau \right|^2}{\varepsilon_i - \varepsilon_0} \tag{17.12}$$

This expression is correct, but not useful because we need information about the excited states of the molecule. Such information is hard to come by. In the old days, we would try to make progress by taking some average energy difference $\Delta\varepsilon$ between the excited states and the ground state. We can then write

$$\alpha_{xx} = \frac{2}{\Delta\varepsilon} \sum_{i=1}^{\infty} \left| \int \Psi_0^* \hat{p}_x \Psi_i \, \mathrm{d}\tau \right|^2 \tag{17.13}$$

The sum runs over all excited states but not the ground state. It can also be written as a sum over all states (including the ground state) as

$$\alpha_{xx} = \frac{2}{\Delta\varepsilon} \left(\sum_{i=0}^{\infty} \left(\left| \int \Psi_0^* \hat{p}_x \Psi_i \, \mathrm{d}\tau \right|^2 \right) - \left| \int \Psi_0^* \hat{p}_x \Psi_0 \, \mathrm{d}\tau \right|^2 \right) \tag{17.14}$$

The summation can be simplified using an expression called the *closure relation*, to give finally

$$\alpha_{xx} = \frac{2}{\Delta\varepsilon} \left(\left| \int \Psi_0^* \hat{p}_x^2 \Psi_0 \, \mathrm{d}\tau \right| - \left| \int \Psi_0^* \hat{p}_x \Psi_0 \, \mathrm{d}\tau \right|^2 \right) \tag{17.15}$$

The first term in the brackets is the expectation value of the square of the dipole moment operator (i.e. the second moment) and the second term is the square of the expectation value of the dipole moment operator. This expression defines the *sum over states* model. A subjective choice of the average excitation energy $\Delta\varepsilon$ has to be made.

17.6.2 Self-Consistent Perturbation Theory

In the context of the HF–LCAO model, we seek a solution of the matrix eigenvalue equation

$$\mathbf{h}^{\mathrm{F}}\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_{\mathrm{i}}$$

If we add a perturbation Δ then the self-consistency is destroyed and we need to re-do the iterative HF–LCAO calculation. The idea of self-consistent perturbation theory is to seek solutions of the perturbed HF–LCAO equations

$$(\mathbf{h}^{\mathrm{F}} + \Delta)\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_{\mathrm{i}} \qquad (17.16)$$

using perturbation theory in a self-consistent way. There are various formulations, depending on whether or not the orders of perturbation need to be kept separate, and the dipole polarizability can be evaluated from a second-order energy.

17.6.3 The Finite Field Method

This is similar to self-consistent perturbation theory, except that we just solve the modified HF–LCAO equations

$$(\mathbf{h}^{\mathrm{F}} + \Delta)\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_{\mathrm{i}} \qquad (17.16)$$

for some arbitrary (and small) external electric field, without bothering to sort out the orders of perturbation theory. Imagine then a simple finite-field calculation on CH_3F. We would run a HF–LCAO calculation on the field-free molecule, and then include an external field along each of the Cartesian axes. The polarizability is calculated from the induced dipole moment or from the energy change. In the HF–LCAO model with basis functions $\chi_1, \chi_2, \ldots, \chi_n$ this involves calculating an extra matrix of dipole integrals over the basis functions, and adding it to the one-electron integral matrix.

In practice the finite-field calculation is not so simple because the higher-order terms in the induced dipole and the interaction energy are not negligible. Normally we use a number of applied fields along each axis, typically multiples of 10^{-4} a.u., and use the standard techniques of numerical analysis to extract the required data. Such calculations are not particularly accurate, because they use numerical methods to find differentials.

As an example, here is an output from Gaussian 98 on CH_3F (Figure 17.2). I forced the finite field method by choice of *Polar = Enonly* (Polar = Energy only) in the route. The geometry was first optimized and stored in a checkpoint file.

```
%chk=f:\modmol2\Chapter18\fmethane.chk
 Default route:  MaxDisk=2000MB
 ----------------------------------------------------
 # HF/6-311G** Polar=Enonly Guess=Read Geom=Check Nopop
 ----------------------------------------------------
```

Figure 17.2

```
The following finite field(s) will be applied:
 An electric field of              0.0010  0.0000  0.0000
 .....
 The following finite field(s) will be applied:
 An electric field of             -0.0010  0.0000  0.0000
 .....
 The following finite field(s) will be applied:
 An electric field of              0.0000  0.0010  0.0000
```

Figure 17.3

Various external electric fields are now switched on, in order to calculate the second derivatives (Figure 17.3).

The gradients are then evaluated to produce the polarizabilities.

17.7 DERIVATIVES

Many *ab initio* packages use the two key equations given above in order to calculate the polarizabilities and hyperpolarizabilities. If analytical gradients are available, as they are for many levels of theory, then the quantities are calculated from the first or second derivative (with respect to the electric field), as appropriate. If analytical formulae do not exist, then numerical methods are used.

An analytical gradient calculation is invariably faster than a numerical one. To repeat the argument from Chapter 14, with real wavefunction Ψ, Hamiltonian $\hat{H}$ (including the field terms) and 'parameter' a (where a is a component of the external electric field)

$$\varepsilon = \int \Psi \hat{H} \Psi \, \mathrm{d}\tau$$

$$\frac{\partial \varepsilon}{\partial a} = 2 \int \frac{\partial \Psi}{\partial a} \hat{H} \Psi \, \mathrm{d}\tau + \int \Psi \frac{\partial \hat{H}}{\partial a} \Psi \, \mathrm{d}\tau$$

$$\begin{aligned}\frac{\partial^2 \varepsilon}{\partial a^2} &= 2 \int \frac{\partial^2 \Psi}{\partial a^2} \hat{H} \Psi \, \mathrm{d}\tau + 4 \int \frac{\partial \Psi}{\partial a} \frac{\partial \hat{H}}{\partial a} \Psi \, \mathrm{d}\tau + 2 \int \frac{\partial \Psi}{\partial a} \hat{H} \frac{\partial \Psi}{\partial a} \, \mathrm{d}\tau \\ &\quad + \int \Psi \frac{\partial^2 \hat{H}}{\partial a^2} \Psi \, \mathrm{d}\tau\end{aligned}$$

```
%chk=f:\modmol2\Chapter18\fmethane.chk
 Default route:  MaxDisk=2000MB
 ----------------------------------------------
 # HF/6-311G** Polar Guess=Read Geom=Check Nopop
 ----------------------------------------------
```

Figure 17.4

```
Range of M.O.s used for correlation:      1     54
 NBasis=     54 NAE=       9 NBE=       9 NFC=      0 NFV=      0
 NROrb=      54 NOA=       9 NOB=       9 NVA=     45 NVB=     45
        Differentiating once with respect to electric field.
                with respect to dipole field.
```

Figure 17.5

```
Exact polarizability:  12.435   0.000  12.364   0.000   0.000  12.435
 Approx polarizability:   9.969   0.000  10.235   0.000   0.000   9.969
```

Figure 17.6

The first term is zero because Ψ and its derivatives are orthogonal. The fourth term involves second moments and we use the coupled Hartree–Fock procedure to find the terms requiring the first derivative of the wavefunction.

Figure 17.4 then is a typical Hartree–Fock analytical derivative calculation on fluoromethane.

The coupled Hartree–Fock equations are then solved (Figure 17.5).

In the older literature, the coupled Hartree–Fock part of the calculation was often ignored. Output in this case (Figure 17.6) gives the coupled and (so-called) uncoupled polarizabilities; these are the `Approx` polarizabilities. The output is in the order α_{xx}, α_{xy}, α_{yy}, α_{xz}, α_{yz}, α_{zz}.

17.7.1 Sensitivity to Level of Theory

Table 17.2 refers to various polarizability calculations on CH_3F. In every case, I optimized the geometry before calculating the polarizability.

Table 17.2 Polarizability calculations for fluoromethane

Level of Theory	α_{zz}	$\alpha_{xx} = \alpha_{yy}$	$\langle\alpha\rangle$
HF/STO-3G	1.182	0.938	1.019
HF/4-31G	1.914	1.789	1.831
HF/6-311G**	2.040	2.047	2.045
HF/6-311++G(3d,2p)	2.221	2.202	2.208
MP2/6-311G**	2.179	2.111	2.134
CID/6-311G**	2.113	2.071	2.092
CISD/6-311G**	2.123	2.075	2.091
BLYP/6-311G**	2.362	2.261	2.295

The STO–3G basis set is clearly inadequate for such calculations. The results demonstrate the importance of the diffuse functions and electron correlation. The density functional results are very attractive.

17.8 INTERACTION POLARIZABILITIES

The virial equation of state is sometimes written

$$\frac{pV_{\mathrm{m}}}{RT} = 1 + \frac{B}{V_{\mathrm{m}}} + \frac{C}{V_{\mathrm{m}}^2} + \cdots \tag{17.17}$$

This equation of state applies to all substances under all conditions of p, V_{m} and T. All of the virial coefficients B, C, ... are zero for a perfect gas. For other materials, the virial coefficients are finite and they give information about molecular interactions. The virial coefficients are temperature-dependent. Theoretical expressions for the virial coefficients can be found from the methods of statistical thermodynamics.

By analogy, the virial expansion of the bulk molecular property X (such as the dielectric polarization) is written

$$X = A_X + \frac{B_X}{V_{\mathrm{m}}} + \frac{C_X}{V_{\mathrm{m}}^2} + \cdots \tag{17.18}$$

where in this case all the constants A_X, B_X, ... are dependent on the temperature.

For static electric properties, the bulk property of interest is the dielectric polarization **P**. The magnitude of **P** can be estimated from (for example) the Clausius–Mossotti relation

$$P = \frac{\epsilon_{\mathrm{r}} - 1}{\epsilon_{\mathrm{r}} + 2} V_{\mathrm{m}} \tag{17.19}$$

where ϵ_{r} is the relative permittivity of the medium. The dielectric virial equation for the polarization is usually written

$$P = A_\epsilon + \frac{B_\epsilon}{V_{\mathrm{m}}} + \frac{C_\epsilon}{V_{\mathrm{m}}^2} + \cdots \tag{17.20}$$

and it is argued that A_ϵ gives the contribution of free molecules to the property, B_ϵ gives the contribution from pairwise interactions, and so on. Terms beyond B_ϵ are rarely encountered. The first dielectric virial coefficient can be estimated from the Clausius–Mossotti equation in its original form, as obtained by Debye (see Chapter 15 for a fuller discussion).

$$A_\epsilon = \frac{N_{\mathrm{A}}}{3\epsilon_0}\left(\alpha_0 + \frac{p_{\mathrm{e}}^2}{3k_{\mathrm{B}}T}\right) \tag{17.21}$$

Buckingham (1962) has given the (classical) statistical thermodynamic expression for B_ϵ as

$$\begin{aligned} B_\epsilon = \frac{4\pi N_\mathrm{A}^2}{3\epsilon_0} \int_0^\infty \Bigg(\left(\frac{1}{2}\alpha_{12}(r) - \alpha_0 \right) \\ + \frac{1}{3} k_\mathrm{B} T \left(\frac{1}{2} p_{\mathrm{e},12}^2(r) - p_{\mathrm{e},0}^2 \right) \exp\left(-\frac{U_{12}(r)}{k_\mathrm{B}T} \right) \Bigg) r^2 \,\mathrm{d}r \end{aligned} \tag{17.22}$$

Here, $\alpha_{12}(r)$ is the mean polarizability of a pair of species separated by distance r, while p_{12} is their electric dipole moment and U the potential energy. $p_{\mathrm{e},0}$ is the permanent electric dipole moment for the two species at infinity.

An important experimental quantity for studying molecular interactions in gases and liquids is the scattering of laser light. When polarized light is scattered by a fluid, both polarized and depolarized components are produced. The depolarized spectrum is several orders of magnitude less intense than the polarized spectrum and much more difficult to observe. A great deal of information has been obtained about molecular motions from such spectral analyses.

Gelbart (1974) has reviewed a number of theories of the origins of the depolarized spectrum. One of the simplest models is the isolated binary collision (IBC) model of McTague and Birnbaum (1968). All effects due to the interaction of three or more particles are ignored, and the scattering is due only to diatomic collision processes. In the case that the interacting particles A and B are atoms or highly symmetrical molecules then there are only two unique components of the pair polarizability tensor, and attention focuses on the anisotropy and the *incremental mean pair polarizability*

$$\langle \alpha^{(2)} \rangle = \tfrac{1}{3}(\alpha \;\; + 2\alpha_\perp) - (\alpha_\mathrm{A} + \alpha_\mathrm{B}) \tag{17.23}$$

where α_A and α_B are the polarizabilities of the interacting species A and B. In the IBC model, the polarized spectrum depends on the thermal average of this quantity over the assembly of interacting particles. The thermal average of the anisotropy is also responsible for the depolarized spectrum.

The first *ab initio* study of an interaction polarizability was that of O'Brien *et al.* (1973) on a pair of helium atoms. They obtained $\beta(r)$ for the range $r = 3.5a_0$ through $10a_0$. The experimentally determined value of B_ϵ is negative, which suggests that the incremental mean pair polarizability must be negative around the minimum in the potential curve.

A problem with studies on inert gas is that the interactions are so weak. Alkali halides are important commercial compounds because of their role in extractive metallurgy. A deal of effort has gone into corresponding calculations on alkali halides such as LiCl, with a view to understanding the structure and properties of ionic melts. Experience suggests that calculations at the Hartree–Fock level of theory are adequate, provided that a reasonable basis set is chosen. Figure 17.7 shows the variation of the anisotropy and incremental mean pair polarizability as a function of distance.

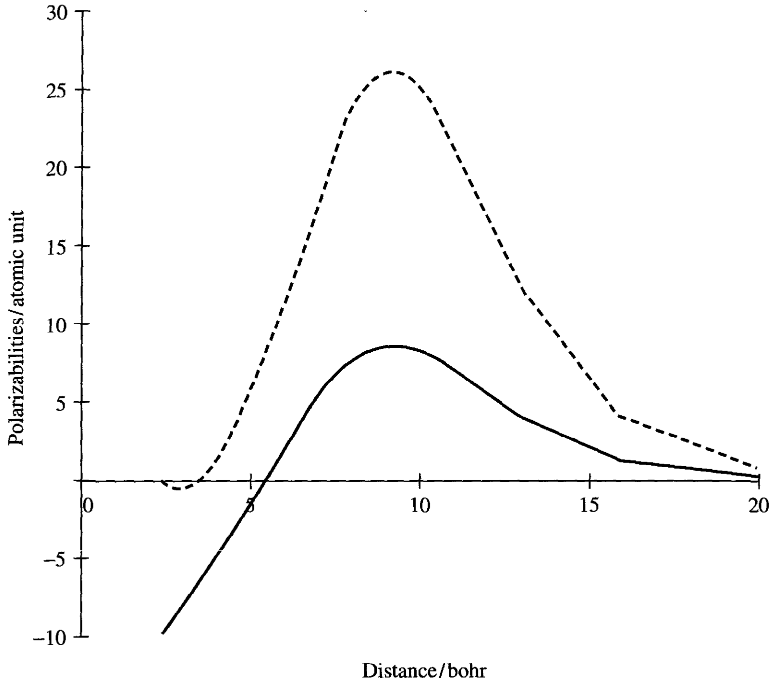


Figure 17.7 Anisotropy (dotted) and mean incremental pair polarizability

If one examines similar simple systems, then it turns out that these curves all have the same features provided one works with the reduced distance R/R_e.

17.9 THE HAMILTONIAN

I appealed to your good sense when I asked you to believe that the Hamiltonian for a particle in an external electric field could be written

$$\hat{H} = \hat{H}_0 - \hat{\mathbf{p}}_e(\mathbf{0}) \cdot \mathbf{E}$$

Derivation of this equation is actually far from straightforward. In electromagnetism, we describe static fields by the electric field **E** and the magnetic induction **B**. For our purposes, we need to enquire about the potentials rather than the fields, and these are defined by

$$\mathbf{E} = -\text{grad}\,\phi$$

$$\mathbf{B} = \text{curl}\,\mathbf{A}$$

We have met the electrostatic potential ϕ in earlier chapters. The *vector potential* **A** is a fundamental construct in electromagnetism (Hinchliffe and Munn, 1985).

Imagine a free particle with charge Q and mass m. The Hamiltonian is

$$\hat{H} = \frac{1}{2m}\hat{p}^2$$

where $\mathbf{p}$ is the linear momentum. In the presence of external fields defined by the potentials ϕ and $\mathbf{A}$, the correct Hamiltonian turns out to be (Hinchliffe and Munn, 1985)

$$\hat{H} = \frac{|\hat{\mathbf{p}} - Q\hat{\mathbf{A}}|^2}{2m} + Q\phi \tag{17.24}$$

The quantity $\mathbf{p} - Q\mathbf{A}$ is called a *generalised momentum.* It appears in both classical electromagnetism and quantum mechanics. In the Schrödinger picture, we make the substitution

$$\hat{\mathbf{p}} \rightarrow -\frac{jh}{2\pi}\nabla$$

After some manipulation the Hamiltonian turns out to be

$$\hat{H} = \hat{H}_0 + \frac{jhQ}{2\pi m}\mathbf{A}\cdot\nabla + \frac{Q^2A^2}{2m} + Q\phi \tag{17.25}$$

where $j^2 = -1$.

The vector potential $\mathbf{A}$ is defined by

$$\mathbf{B} = \operatorname{curl}\mathbf{A}$$

and by making use of the vector identity $\operatorname{curl}\operatorname{grad} \equiv 0$ we also have

$$\mathbf{B} = \operatorname{curl}(\mathbf{A} + \operatorname{grad} V)$$

where V is an arbitrary differentiable scalar field. The vector potential is therefore undetermined to within a constant field. In deriving the equation 17.25 above, I have made use of this freedom, and assumed that the vector potential satisfies

$$\operatorname{div}\mathbf{A} = 0$$

In the special case where the vector potential is zero and the electrostatic field is uniform along the z-axis we have

$$\hat{H} = \hat{H}_0 - QE\hat{z} \tag{17.26}$$

and you should recognize Qz as the z-component of the dipole moment operator $\hat{\mathbf{p}}_e$.

In the case of a uniform magnetic induction along the z-axis, $\mathbf{B} = B\mathbf{e}_z$, you will find that the vector field

$$\mathbf{A} = \tfrac{1}{2}(-By\mathbf{e}_x + Bx\mathbf{e}_y)$$

satisfies both of

$$\mathbf{B} = \operatorname{curl} \mathbf{A}$$

$$\operatorname{div} \mathbf{A} = 0$$

Substitution gives a Hamiltonian

$$\hat{H} = \hat{H}_0 + \frac{jhQB}{4\pi m}\left(-y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}\right) + \frac{Q^2B^2}{8m}\left(x^2 + y^2\right) + Q\phi \qquad (17.27)$$

The operator in the first brackets is related to the z-component of the angular momentum operator $\hat{l}_z$, giving finally

$$\hat{H} = \hat{H}_0 - \frac{QB}{2m}\hat{l}_z + \frac{Q^2B^2}{8m}\left(x^2 + y^2\right) + Q\phi \qquad (17.28)$$

17.10 MAGNETIZABILITIES

Magnetizabilities are the magnetic analogue of polarizabilities; they measure the response of the system to an applied magnetic induction. As a rule of thumb, magnetostatic phenomena are more complicated than their electrostatic analogues, and this turns out to be the case here. Apart from the pure electrostatic $Q\phi$, the Hamiltonian contains two extra terms involving B. In terms of perturbation theory, the first- and second-order corrections are therefore more complicated in the magnetic case. The first-order correction is

$$\Delta U^{(1)} = -\frac{QB}{2m}\int \psi_0^* \hat{l}_z \psi_0 \,\mathrm{d}\tau \qquad (17.29)$$

and the terms second-order in B give the magnetizability. These are

$$\Delta U^{(2)} = \frac{Q^2B^2}{2m}\int \psi_0^*\left(x^2 + y^2\right)\psi \,\mathrm{d}\tau - \frac{Q^2B^2}{4m^2}\sum_{i=1}^{\infty}\frac{\int |\psi_i^* \hat{l}_z \psi_0 \,\mathrm{d}\tau|^2}{\varepsilon_i - \varepsilon_0} \qquad (17.30)$$

The second-order terms give the magnetizability. The first term is known as the *diamagnetic part* and it is particularly easy to calculate since it is just the expectation value of the second moment operators. The second term is called the *paramagnetic part*.

The derivations given above related to a single particle in a constant magnetic induction. For a molecule within the Born–Oppenheimer approximation, the derivation is similar except that we take the nuclei to be fixed in space. There is a nuclear and an electronic contribution to each property.

17.11 GAUGE INVARIANCE

I mentioned above the magnetic vector potential $\mathbf{A}$. This is given in the static case by

$$\mathbf{B} = \operatorname{curl} \mathbf{A}$$

There is a vector identity

$$\mathrm{curl}\,(\mathrm{grad}\,F) = 0$$

which is true for any differentiable field F, and so if we add $\mathrm{grad}\,F$ to $\mathbf{A}$, the curl is still zero. In symbols,

$$\mathbf{B} = \mathrm{curl}\,(\mathbf{A} + \mathrm{grad}\,F) = 0$$

and so the vector potential is undefined to within a constant of integration.

Magnetic properties should be independent of the choice of coordinate origin. The term *choice of origin* is often translated into *choice of gauge*, and so we say that physical properties should be *gauge-invariant* (for a discussion, see Hameka, 1965).

In early work, Stevens, Pitzer and Lipscomb (1963) calculated magnetic shielding constants for a number of diatomics, using self-consistent perturbation theory. They achieved gauge invariance by using a very large basis set. An alternative is to use *gauge-invariant atomic orbitals* (GIAO). A GIAO is the product of an ordinary basis function $\chi(\mathbf{r})$ and a complex factor that depends on the origin of the vector potential

$$\chi^{\mathrm{GIAO}}(\mathbf{r}) = \chi(\mathbf{r}) \exp\left(-\frac{j}{c_0}\mathbf{A}\cdot\mathbf{r}\right) \tag{17.31}$$

London (1937) first made use of these functions in connection with ring currents in aromatic hydrocarbons. A key paper for the use of GIAO is that of Ditchfield.

Self-Consistent Perturbation Theory of Diamagnetism I. A Gauge-Invariant
LCAO
Method for N M R Chemical Shifts
Robert Ditchfield
Molecular Physics **27** (1974) 789–807

An *ab initio* gauge-invariant molecular orbital theory is developed for nuclear magnetic shielding. The molecular orbitals are written as linear combinations of gauge-invariant atomic orbitals, the wavefunction in the presence of an external magnetic field being determined by self-consistent field perturbation theory. The final magnetic shielding result is broken up into contributions which can be related to various features of electronic structure. Calculated magnetic shielding constants are presented using three sets of atomic orbitals, all of which are taken as contracted gaussian-type functions. The first two sets are minimal and the third is slightly extended. All three levels of theory give good descriptions of shielding at first row and hydrogen atoms. Carbon and hydrogen chemical shifts calculated at the extended level are in excellent agreement with experimental values.

17.12 NON-LINEAR OPTICAL PROPERTIES

There is a growing interest in the non-linear optical (NLO) properties of organic materials. Organic and polymeric materials with large non-linear optical coefficients can be used in principle in optoelectronic and photonic devices, and a great deal of research effort has been expended in efforts to design new compounds with optimal NLO properties.

Such efforts have met with limited success, and the reason usually advanced is our lack of understanding of the frequency dependence of molecular NLO properties. In classical electromagnetism, we refer to properties that depend on the frequency of radiation as *dispersive* and we say that (for example) *dispersion* is responsible for a rainbow. The blue colour of the sky is a dispersion effect, as is the red sky at night and morning. There is more to it than that, and you might like to read a more advanced text (Hinchliffe and Munn, 1985).

We have seen above how to calculate polarizabilities and hyperpolarizabilities for static electric fields. I will consider a simple oscillating electric field

$$\mathbf{E} = \mathbf{E}_0 \exp(j\omega t)$$

I should mention the convention that in electromagnetic studies we write oscillating fields as (e.g.) $\mathbf{E} = \mathbf{E}_0 \exp(j\omega t)$ rather than $\mathbf{E} = \mathbf{E}_0 \cos(j\omega t)$. There is nothing sinister in this — it just makes the maths simpler. A laboratory electric field is the real part of $\mathbf{E} = \mathbf{E}_0 \exp(j\omega t)$, and so we have to remember to take the real part of any result before comparison with experiment.

The polarizabilities $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are often calculated by the methods of time-dependent perturbation theory, which I shall now describe.

17.13 TIME-DEPENDENT PERTURBATION THEORY

Strictly speaking, all perturbations must be time-dependent: we cannot arrange for them to have been in existence since $t = -\infty$ and we must instead switch them on. As in an electrical circuit, such switching-on causes initial transient behaviour that eventually dies away to leave a steady state.

We now suppose that the perturbed system is described by

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \tag{17.32}$$

where the zero-order problem has solutions

$$\hat{H}_0 \psi_i^0 = \varepsilon_i^0 \psi_i^0$$

The corresponding zero-order time-dependent states are (from Chapter 0)

$$\Psi_i^0(t) = \psi_i^0 \exp\left(-j\frac{2\pi\varepsilon_i t}{h}\right) \tag{17.33}$$

In this section I will write Ψ for the time-dependent states and ψ for the time-independent ones. The ψ_i may themselves depend on the space and spin variables of all the particles present.

If I write the state of the perturbed system $\Psi_{\mathrm{v}}(t)$ then it must satisfy the time-dependent Schrödinger equation

$$\hat{H}\Psi_{\mathrm{v}}(t) = j\frac{h}{2\pi}\frac{\partial \Psi_{\mathrm{v}}(t)}{\partial t} \tag{17.34}$$

In the spirit of the time-independent perturbation treatment, I write Ψ_{v} as a linear combination of the unperturbed states

$$\Psi_{\mathrm{v}}(t) = \sum_i c_i(t)\Psi_i^0(t) \tag{17.35}$$

It is easily seen that

$$c_i(t) = \int \Psi_{\mathrm{v}}^*(t)\Psi_i^0\,\mathrm{d}\tau \tag{17.36}$$

and so $|c_i(t)|^2$ gives the fraction of the unperturbed state Ψ_i^0 in the perturbed state $\Psi_{\mathrm{v}}(t)$.

The expression 17.35 is substituted into the time-dependent Schrödinger equation to give, after a little rearrangement,

$$j\frac{h}{2\pi}\sum_i\left(\frac{\partial c_i(t)}{\partial t}\Psi_i^0(t) + c_i(t)\frac{\partial \Psi_i^0}{\partial t}\right) = \sum_i c_i(t)(\hat{H}_0 + \hat{V}(t))\Psi_i^0(t)$$

This equation contains the time-dependent Schrödinger equation for the unperturbed states

$$\hat{H}_0\Psi_i^0(t) = j\frac{h}{2\pi}\frac{\partial \Psi_i^0(t)}{\partial t}$$

leaving

$$j\frac{h}{2\pi}\sum_i\frac{\partial c_i(t)}{\partial t}\Psi_i^0(t) = \sum_i c_i(t)\hat{V}(t)\Psi_i^0(t) \tag{17.37}$$

The time derivative of the coefficient $c_k(t)$ for the particular state $\Psi_k^0(t)$ is found by multiplying either side of the equation by the complex conjugate of $\Psi_k^0(t)$ and integrating. After a little manipulation we find

$$j\frac{h}{2\pi}\frac{\partial c_k(t)}{\partial t} = \sum_i c_i(t)\int(\Psi_k^0(t))^*\hat{V}(t)\Psi_i^0(t)\,\mathrm{d}\tau \tag{17.38}$$

The integral on the right-hand side is over space and spin variables, and so can be written

$$\int(\Psi_k^0(t))^*\hat{V}(t)\Psi_i^0(t)\,\mathrm{d}\tau = \exp\left(j\frac{2\pi(\varepsilon_k^0 - \varepsilon_i^0)t}{h}\right)\int(\psi_k^0)^*\hat{V}(t)\psi_i^0\,\mathrm{d}\tau \tag{17.39}$$

For the sake of neatness, we can put

$$V_{ki} = \int (\psi_k^0)^* \hat{V}(t)\psi_i^0 \, d\tau$$

and

$$\frac{h}{2\pi}\omega_{ki} = \varepsilon_k^0 - \varepsilon_i^0$$

This gives the result

$$\frac{\partial c_k(t)}{\partial t} = \frac{2\pi}{jh}\sum_i c_i(t)V_{ki}(t)\exp(j\omega_{ki}t) \tag{17.40}$$

which is exact. This integral equation is generally hard to solve, but can often be found to successively higher orders of perturbation theory.

17.14 TIME-DEPENDENT HARTREE–FOCK THEORY

The time-dependent Hartree–Fock theory was first discussed by Dirac (1930b) and subsequently in perturbative form by Dalgarno and Victor (1966). Its relationship to time-dependent perturbation theory has been discussed by Langhoff, Epstein and Karplus (1972).

The standard Hartree–Fock LCAO equation from Chapter 6

$$\mathbf{h}^{\mathrm{F}}\mathbf{c}_i = \varepsilon_i\mathbf{S}\mathbf{c}_i$$

becomes

$$\left(\mathbf{h}^{\mathrm{F}} - j\frac{h}{2\pi}\frac{\partial}{\partial t}\mathbf{S}\right)\mathbf{c}_i = \varepsilon_i\mathbf{S}\mathbf{c}_i \tag{17.41}$$

where the LCAO coefficients are now time-dependent. The normalization condition

$$\mathbf{c}_i^{\mathrm{T}}\mathbf{S}\mathbf{c}_j = \delta_{ij}$$

becomes

$$\frac{\partial}{\partial t}\mathbf{c}_i^{\mathrm{T}}\mathbf{S}\mathbf{c}_j = 0 \tag{17.42}$$

The Hartree–Fock equations have to be solved by the coupled Hartree–Fock method. The following article affords a typical example.

Dispersion of Linear and Nonlinear Optical Properties of Benzene: An Ab Initio Time-Dependent Coupled-Perturbed Hartree–Fock Study
Shashi P. Karna, Gautam B. Talapatra and Paras N. Prasad
Journal of Chemical Physics **95** (1991) 5873–5881

Frequency-dependent polarizability α and second hyperpolarizability γ corresponding to various third-order nonlinear optical processes have been calculated by *ab initio* time-dependent coupled–perturbed Hartree–Fock method. The selection of proper diffuse functions in the basis set is made from a comparison of the calculated values of $\alpha(\omega)$ at two optical wavelengths ($\lambda = 589$ and 632.3 nm) and that of $\gamma(-2\omega, 0, \omega, \omega)$ at $\lambda = 1064$ nm with the reported experimental values at these wavelengths. It is found that a 4–31G basis with a diffuse p and diffuse d function, in addition to properly describing various elements, yields the values of α and γ which are, respectively, within 7% and 5% of the corresponding experimental results. The in-plane components of α show a larger frequency dispersion compared to the out-of-plane component. The calculated values of γ for the electric field-induced second harmonic generation (EFISH) at five optical wavelengths are within 5%–14% of the reported experimental results. However, a somewhat larger discrepancy between the calculated and measured values of γ for the third harmonic generation (THG) and γ for degenerate four wave mixing (DFWM) is found. The order of the γ values for various third-order processes is γ(THG) > γ(EFISH) > γ(DFWM) > γ(EFIKE) ≈ γ(EFIOR), where EFIKE and EFIOR, respectively, represent electric field-induced Kerr effects and electric field-induced optical rectification. The elements of γ show deviation from the Kleinmann symmetry even at lower optical frequencies.

18 MISCELLANY

To finish off, I want to describe four applications. They either illustrate or reinforce many of the themes discussed in this book. I hope they will interest you.

18.1 THE FLOATING SPHERICAL GAUSSIAN (FSGO) MODEL

In standard quantum-mechanical molecular structure calculations, we normally work with a set of nuclear-centred atomic orbitals $\chi_1, \chi_2, \ldots, \chi_n$. GTOs are a good choice for the χ's, if only because of the ease of integral evaluation. Procedures such as HF–LCAO then express the molecular electronic wavefunction in terms of these basis functions and at first sight the resulting HF–LCAO orbitals are delocalized over regions of molecules. It is often thought desirable to have a simple *ab initio* method that can correlate with chemical concepts such as bonds, lone pairs and inner shells. A theorem due to Fock (1930) enables one to transform the HF–LCAOs into localized orbitals that often have the desired spatial properties.

Another approach, the floating spherical Gaussian orbital (FSGO) model starts from a set of localized orbitals and uses the ideas of simple descriptive chemistry. Most chemists would describe ammonia as a nitrogen inner shell comprising a pair of 1s electrons, three equivalent pairs of electrons localized between the N and the H nuclei, and a nitrogen lone pair. In FSGO theory, each pair of electrons is allocated to a spherical (1s) GTO $\chi_1, \chi_2, \ldots, \chi_5$, as illustrated in Figure 18.1. For simplicity I have omitted the inner shell and two of the bond orbitals. In the simplest version of the FSGO model we just consider enough spherical (i.e. s-type) Gaussian orbitals to accommodate the number of electrons: if there are $2m$ electrons, we need m FSGOs. These basis functions need not be nuclear-centred, and indeed we let them float through space and change their size (the orbital exponent) until an energy minimum is reached.

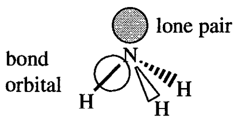


Figure 18.1 The FSGO model for ammonia

In the case of ammonia, which has ten electrons, we would choose five 1s-type GTOs $\chi_1, \chi_2, \ldots, \chi_5$ as appropriate and write an electronic wavefunction

$$\Psi = N \begin{vmatrix} \chi_1(\mathbf{r}_1)\alpha(s_1) & \chi_1(\mathbf{r}_2)\alpha(s_2) & \cdots & \chi_1(\mathbf{r}_{10})\alpha(s_{10}) \\ \chi_1(\mathbf{r}_1)\beta(s_1) & \chi_1(\mathbf{r}_2)\beta(s_2) & \cdots & \chi_1(\mathbf{r}_{10})\beta(s_{10}) \\ \ldots & \ldots & \ldots & \ldots \\ \chi_5(\mathbf{r}_1)\beta(s_1) & \chi_5(\mathbf{r}_2)\beta(s_2) & \cdots & \chi_5(\mathbf{r}_{10})\beta(s_{10}) \end{vmatrix} \tag{18.1}$$

A geometry optimization can be done if required, using any of the standard methods.

There are a few interesting points about the treatment. First of all, there is no variational HF–LCAO calculation (because every available χ is doubly occupied) and so the energy evaluation is straightforward. For a wavefunction comprising m doubly occupied orthonormal χ's the normalizing factor N is

$$N = \sqrt{\frac{1}{(2m)!}} \tag{18.2}$$

In the case that the χ's are individually normalized but not necessarily orthogonal then the overlap integrals between the basis functions have to be taken into account. If we write the matrix of overlap integrals $\mathbf{S}$ and its determinant $\det \mathbf{S}$ then

$$N = \sqrt{\frac{1}{(2m)!}\det \mathbf{S}} \tag{18.3}$$

The electronic energy formula turns out as

$$\begin{aligned} \varepsilon_{\text{el}} &= 2\sum_{i=1}^{m}\sum_{j=1}^{m} T_{ij} \int \chi_i(\mathbf{r}_1)\hat{h}_1\chi_j(\mathbf{r}_1)\,\mathrm{d}\tau_1 \\ &\quad + \sum_{i=1}^{m}\sum_{j=1}^{m}\sum_{k=1}^{m}\sum_{l=1}^{m} \iint \chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)\hat{g}(\mathbf{r}_1,\mathbf{r}_2)\chi_k(\mathbf{r}_2)\chi_l(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\quad \times (2T_{ij}T_{kj} - T_{ik}T_{jl}) \end{aligned} \tag{18.4}$$

where $\mathbf{T}$ is the inverse of the overlap matrix

$$\mathbf{T} = \mathbf{S}^{-1}$$

The overlap integrals are first calculated, and the matrix inverted. The one- and two-electron integral contributions to the electronic energy are summed as they

Table 18.1 Input and output from an FSGO calculation on ammonia

Nucleus	Charge	X/pm	Y/pm	Z/pm
N	7	0.0	0.0	0.0
H1	1	0.0	149.95	100.13
H2	1	129.86	−75.00	100.13
H3	1	−129.86	−75.00	100.13
Orbital	**Radius/pm**	**x/pm**	**y/pm**	**z/pm**
N 1s	27.69	0.0	0.0	0.08
N lone pair	154.93	0.0	0.0	0.08
Bond 1	150.07	0.0	57.12	40.00
Bond 2	150.07	49.46	−28.56	40.00
Bond 3	150.07	−49.46	−28.56	40.00

are calculated. Finally the nuclear repulsion is added. The positions and sizes of the χ's are determined, and a geometry optimization performed.

The final total energy in such calculations is typically 85% of that obtained in a standard HF–LCAO calculation.

The inner-shell orbitals for first-row atoms are almost invariably found to be very close to the nuclei, and so they were often assumed to be nuclear-centred. An interesting problem arises when trying to handle multiple bonds. It is natural to place a pair of doubly occupied FSGOs above and below the plane of the molecule. It is observed that the energy minimum occurs as these two FSGOs coalesce, which gives a singular overlap matrix. An *ad hoc* solution is to keep such a pair of FSGOs separated by a fixed amount.

Some authors also recommended that the inner-shell octet of a second-row atom should be represented by four doubly occupied FSGOs arranged tetrahedrally round the nucleus.

The FSGO model attracted a great deal of attention in the 1960s and 1970s. Bond lengths, bond angles, barriers to rotation, electric moments, force constants and electric dipole moments were all studied. According to Frost and Rouse (1968), the greatest computational achievement of the FSGO model was its ability to calculate bond lengths to within a few percent. Deviations occur for short bonds and long bonds, but hydrocarbons are particularly well represented.

18.2 HYPERFINE INTERACTIONS

Any particle with charge Q, mass m and non-zero angular momentum $\mathbf{l}$ is a magnetic dipole,

$$\mathbf{p}_{\mathrm{M}} = \frac{Q}{2m}\mathbf{l} \qquad (18.5)$$

In the presence of an external magnetic induction **B** this dipole $\mathbf{p}_\mathrm{M}$ has a potential energy given by the laws of classical electromagnetism as

$$U = -\mathbf{p}_\mathrm{M} \cdot \mathbf{B} \tag{18.6}$$

All possible alignments between the dipole and the magnetic induction are allowed, and the energies are continuous; there is no hint of quantization.

The Stern–Gerlach experiment demonstrated that electrons have an intrinsic angular momentum in addition to their orbital angular momentum, and the unfortunate term *'electron spin'* was coined to describe this pure quantum-mechanical phenomenon. Many nuclei also possess an internal angular momentum, referred to as *nuclear spin*. As in classical mechanics, there is a relationship between the angular momentum and the magnetic moment. For electrons, we write

$$\mathbf{p}_\mathrm{M} = g_\mathrm{e} \frac{-e}{2m_\mathrm{e}} \mathbf{s} \tag{18.7}$$

where g_e is approximately 2. The fact that g_e is different from 1 is a consequence of the quantum-mechanical nature of electron spin. It simply does not have a classical analogue.

Spin does not appear in the Schrödinger treatment, and essentially has to be postulated. There are more sophisticated versions of quantum theory where electron spin appears naturally, and where the magnetic dipole appears with the correct magnitude. I want to spend time discussing electron spin in more detail, before moving to the topic of electron spin resonance.

18.2.1 The Dirac Theory of the Electron

The version of quantum mechanics we have developed so far does not satisfy the requirements of the special theory of relativity. We can see this by noting the form of the time-dependent Schrödinger equation for a single electron

$$-\frac{h^2}{8\pi^2 m_\mathrm{e}} \nabla^2 \psi + U\psi = j\frac{h}{2\pi}\frac{\partial \psi}{\partial t} \tag{18.8}$$

It is a first-order differential equation in time, but second-order in the spatial variables. Space and time do not enter on an equal footing, as required by the special theory of relativity.

There are at least two ways forward, and the first was proposed by Schrödinger. Instead of the non-relativistic Hamiltonian for a free electron, he started from the correct relativistic expression

$$\varepsilon^2 = m_\mathrm{e}^2 c_0^4 + c_0^2 \mathbf{p}^2$$

where m_e is the electron mass and c_0 the speed of light in free space. He then made the operator replacements

$$\varepsilon \rightarrow j\frac{h}{2\pi}\frac{\partial}{\partial t}$$

$$\mathbf{p} \rightarrow -j\frac{h}{2\pi}\nabla$$

One then arrives at the Klein–Gordon equation

$$\left(\nabla^2 - \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2} - \frac{4\pi^2 m_e^2 c_0^2}{h^2}\right)\Psi(\mathbf{r}, t) = 0 \tag{18.9}$$

In going from the Schrödinger equation to the Klein–Gordon equation, we obtain the necessary symmetry between space and time by having second-order derivatives throughout. It is usually written in a form that brings out its relativistic invariance by using what is called *four-vector notation*. We define a four-vector $\mathbf{x}$ to have components

$$\mathbf{x} \equiv \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \\ jc_0 t \end{pmatrix} \tag{18.10}$$

(Don't confuse this with my earlier use of $\mathbf{x}$ for a space-spin variable; the notation is common usage in both applications.) The Klein–Gordon equation is therefore

$$\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} + \frac{\partial^2}{\partial x_4^2} - \frac{4\pi^2 m_e^2 c_0^2}{h^2}\right)\psi(x_1, x_2, x_3, x_4) = 0 \tag{18.11}$$

It turns out that the Klein–Gordon equation cannot describe electron spin; in the limit of small kinetic energy, it can be shown to reduce to the familiar Schrödinger equation.

Dirac (1930a) had the idea of working with a relativistic equation that was *linear* in the space and time derivatives. He wrote

$$\left(\gamma_1\frac{\partial}{\partial x_1} + \gamma_2\frac{\partial}{\partial x_2} + \gamma_3\frac{\partial}{\partial x_3} + \gamma_4\frac{\partial}{\partial x_4} + \frac{2\pi m_e c_0}{h}\right)\psi(x_1, x_2, x_3, x_4) = 0 \tag{18.12}$$

where the γ's have to be determined. They are certainly not ordinary scalars. This equation is called the Dirac equation.

The Schrödinger equation and the Klein–Gordon equation both involve second order partial derivatives, and to recover such an equation from the Dirac equation we can operate on equation 18.12 with the operator

$$\left(\gamma_1\frac{\partial}{\partial x_1} + \gamma_2\frac{\partial}{\partial x_2} + \gamma_3\frac{\partial}{\partial x_3} + \gamma_4\frac{\partial}{\partial x_4} - \frac{2\pi m_e c_0}{h}\right) \tag{18.13}$$

A little operator algebra shows that this gives exactly the Klein–Gordon equation if the γ's satisfy the relationship

$$\gamma_i\gamma_j + \gamma_j\gamma_i = 2\delta_{ij} \tag{18.14}$$

where the Kronecker δ is zero unless $i = j$, in which case it is 1.

Dirac's theory therefore leads to a Hamiltonian linear in the space and time variables, but with coefficients that do not commute. It turns out that these coefficients can be represented as 4 × 4 matrices, related in turn to the well-known *Pauli spin matrices*. I have focused on electrons in the discussion; it can be shown that any particle whose wavefunction satisfies the Dirac equation must have spin $\frac{1}{2}$. Not only that, the Dirac theory gave the correct value for the magnetic moment (if you accept that $2 = 2.0023\ldots$).

18.2.2 Many-Particle Systems

A charge density $\rho(\mathbf{r})$ generates an electrostatic potential $\phi(\mathbf{R})$ at the field point $\mathbf{R}$ according to the formula

$$\phi(\mathbf{R}) = \frac{1}{4\pi\epsilon_0}\int \frac{\rho(\mathbf{r})}{|\mathbf{R}-\mathbf{r}|}\,\mathrm{d}\tau$$

where the integration is over the coordinates of the charge distribution. Fields can only propagate through free space at the speed of light, and so if a change were made to the charge distribution $\rho(\mathbf{r})$ at time t, the effect of that change could only take an effect at field point $\mathbf{R}$ at a time

$$\frac{|\mathbf{R}-\mathbf{r}|}{c_0}$$

later. The contribution to the potential (or indeed, any other field) at time t made by the charge density thus depends on the charge density as it was at time

$$t - \frac{|\mathbf{R}-\mathbf{r}|}{c_0}$$

This potential is referred to in electromagnetism texts as the *retarded potential.* It gives a clue as to why a complete relativistic treatment of the many-body problem has never been given. A theory due to Darwin and Breit suggests that the Hamiltonian can indeed be written as a sum of nuclear–nuclear repulsions, electron–nuclear attractions and electron–electron repulsions. But these terms are only the leading terms in an infinite expansion.

Atomic and molecular magnetic dipoles have to obey the angular momentum laws of quantum mechanics, since they are proportional to angular momenta. Each dipole can therefore make just a number of orientations with an applied magnetic induction $\mathbf{B}$. Each allowed orientation corresponds to a different potential energy, and absorption of a photon with suitable energy may cause a change in orientation.

When discussing magnetic resonance phenomena, it is conventional to proceed along the lines of standard perturbation theory. If the field-free Hamiltonian is $\hat{H}_0$ then we write

$$\hat{H} = \hat{H}_0 + \hat{H}^{(1)}$$

where the perturbation represents the effect of external fields and the small internal fields that typically give rise to the fine structure shown in atomic spectra (for example, spin–orbit coupling and the Lamb shift).

According to McWeeny and Sutcliffe (1969) we should write the perturbation as

$$\hat{H}^{(1)} = \hat{H}_{\mathrm{E}} + \hat{H}_{\mathrm{B}} + \hat{H}_{\mathrm{SL}} + \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{SS}} + \hat{H}_{\mathrm{N}} \qquad (18.15)$$

The first term on the right-hand side arises from external electric fields. The second (B) term arises from external magnetic inductions interacting with electronic orbital motion. The SL term arises from electron spin–orbital motion interactions. The Z term arises from the Zeeman interaction between electron spin and the external electric field. $\hat{H}_{\mathrm{SS}}$ arises from electron spin–electron spin interactions and $\hat{H}_{\mathrm{N}}$ includes all hyperfine terms arising from nuclear spins.

$\hat{H}_{\mathrm{N}}$ includes a nuclear Zeeman term, a nuclear dipole–dipole term, an electron–nuclear dipole term and a term describing the interaction between the nuclear dipole and the electron orbital motion.

18.2.3 Spin Hamiltonians

Electron spin resonance (or electron paramagnetic resonance) is now a well-established analytical technique, which also offers a unique probe into the details of molecular structure. The energy levels involved are very close together and reflect essentially the properties of a single electronic state split by a small perturbation.

There are two terms of interest. First there is a classical electron spin–nuclear spin dipole–dipole interaction

$$g_{\mathrm{e}}\beta_{\mathrm{e}}\sum_{i}\sum_{\alpha} g_{\alpha}\beta_{\alpha}\frac{3\left(\mathbf{R}_{\alpha i}\cdot\hat{\mathbf{S}}_i\right)\left(\mathbf{R}_{\alpha i}\cdot\hat{\mathbf{I}}_{\alpha}\right)-R_{\alpha i}^2\left(\hat{\mathbf{S}}_i\cdot\hat{\mathbf{I}}_{\alpha}\right)}{R_{\alpha i}^5} \tag{18.16}$$

This interaction dominates the spectra for free radicals and radical ions in solids. It averages to zero for species in the gas phase or in solution.

Second, the *Fermi contact term*

$$\frac{4\pi}{3}g_{\mathrm{e}}\beta_{\mathrm{e}}\sum_{i}\sum_{\alpha} g_{\alpha}\beta_{\alpha}\hat{\mathbf{I}}_{\alpha}\cdot\hat{\mathbf{S}}_i\delta(R_{\alpha i}) \tag{18.17}$$

where $\delta(R_{\alpha i})$ is a Dirac delta function which is zero everywhere except when the separation $R_{\alpha i}$ between electron i and nucleus α is zero. g_{e} and g_{α} are the electron and nuclear g-values and β_{e}, β_{α} the electron and nuclear magnetons. This term gives rise to the *isotropic hyperfine coupling*.

Experimentalists work with a *spin Hamiltonian*, which in the latter case would be written

$$h\sum_{\alpha} a_{\alpha}\hat{S}_z\hat{I}_{\alpha z} \tag{18.18}$$

The spin Hamiltonian operates only on spin wavefunctions, and all details of the electronic wavefunction are absorbed into the *coupling constant* a_{α}. If we treat the Fermi contact term as a perturbation on the wavefunction Ψ_0, then use of standard perturbation theory gives a first-order energy

$$\int \Psi_0^*\left(\frac{4\pi}{3}g_{\mathrm{e}}\beta_{\mathrm{e}}\sum_{i}\sum_{\alpha} g_{\alpha}\beta_{\alpha}\hat{\mathbf{I}}_{\alpha}\cdot\hat{\mathbf{S}}_i\delta(R_{\alpha i})\right)\Psi\,\mathrm{d}\tau \tag{18.19}$$

This can be written neatly in terms of the spin density, introduced in Chapter 5. For nucleus α we have

$$a_\alpha = \frac{4\pi}{3} g_e \beta_e g_\alpha \beta_\alpha \frac{h}{\left\langle \hat{S}_z \right\rangle} Q(\mathbf{R}_\alpha) \tag{18.20}$$

where the spin density $Q(\mathbf{r})$ has to be evaluated at the position $\mathbf{R}_\alpha$ of nucleus α. The spin density is the difference between the α-spin electrons and the β-spin electrons, and it can have positive and negative regions. To look ahead a little, Figure 18.2 shows the spin density in the vinyl radical $H_2C{=}CH$, calculated at the UHF/4–31G level of theory.

The vinyl $H_2C{=}CH$ radical can be produced by cleavage of a C–H bond in ethene, and has been studied in the gas phase. The unpaired electron clearly occupies a carbon sp^2 hybrid orbital, to lapse into the language of descriptive organic chemistry, but there are regions of space where the β-spin electrons have

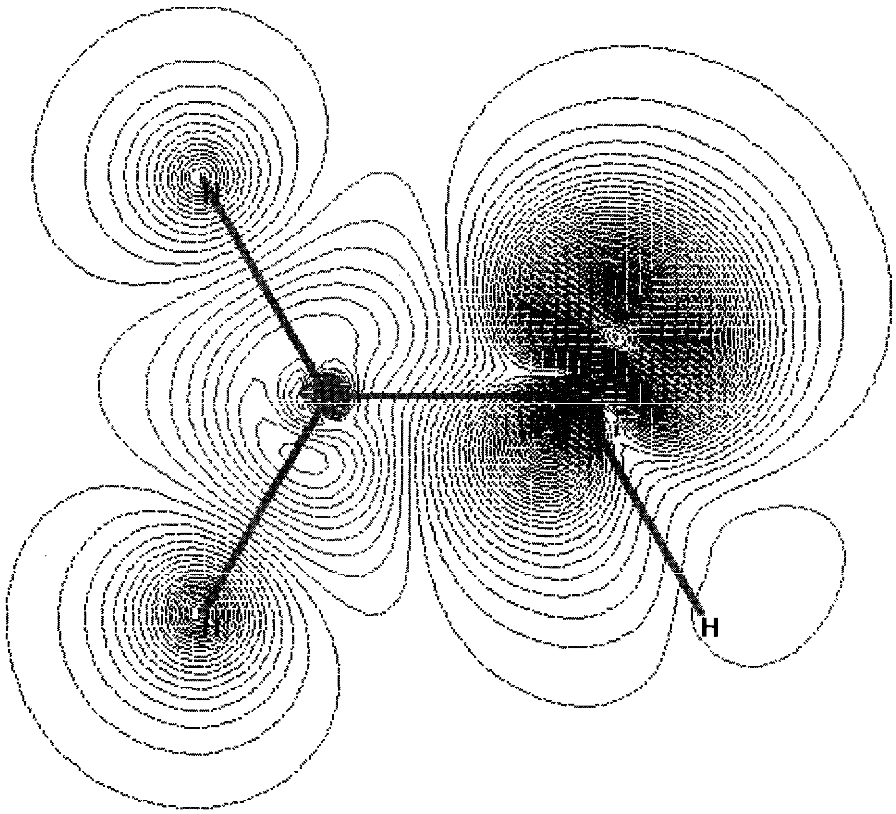


Figure 18.2 Spin density in the vinyl radical

a higher density than those of α spin and so the spin density is negative at these points. In particular, the spin density is negative at the CH_2 carbon and so the coupling constant must be negative.

The late 1960s and 1970s saw an immense wave of interest in the production and characterization of radicals and radical ions. Calculated coupling constants gave a useful guide to the assignment of ESR spectra, and the literature of that era abounds with semi-empirical (PPP, INDO, etc.) and a few rudimentary *ab initio* calculations. Attention focuses on the Fermi contact term. Analysis of an ESR spectrum yields the magnitude of the hyperfine coupling constant, but not the sign. The sign can be determined (in principle) by observing linewidth variations or from a single-crystal study. Few radicals are sufficiently stable for the latter studies. To be strictly comparable, theoretical studies should report calculated splittings averaged over all populated vibrational states.

The simplest place to start is with a hydrogen atom. The experimental ESR spectrum shows two lines separated by 1420.4 MHz (often reported as a magnetic induction, since transitions occur at the *resonance condition* $h\nu = g_e\beta_e B_z$. In which case it is 50.682 mT).

The spin density function is very simple, since there is only one electron

$$Q(\mathbf{r}) = \chi_{1s}^2(\mathbf{r}) \tag{18.21}$$

Substitution $r = 0$ gives a value of 1422.7 MHz (50.765 mT) and the small difference between theory and experiment is essentially due to the use of first-order perturbation theory in the derivation above.

GTOs are widely used in molecular structure calculations, but have the wrong behaviour at the nucleus. We might expect them to give poorer agreement with experiment. Table 18.2 shows a selection of calculations for the H atom. Standard GTO expansions were taken from the literature and left uncontracted.

Simple organic radicals such as the vinyl radical mentioned above were routinely treated using semi-empirical or rudimentary *ab initio* HF–LCAO techniques.

Table 18.2 Hyperfine coupling constant for a hydrogen atom when the 1s orbital is represented as an uncontracted sum of n primitives

n	ε/E_h	a_H/mT
2	−0.4858	27.95
3	−0.4970	37.55
4	−0.4993	42.86
5	−0.4998	45.84
6	−0.4999	47.61
7	−0.5000	48.68
8	−0.5000	49.34
9	−0.5000	49.78
10	−0.5000	50.09
Exact 1s orbital	$-\frac{1}{2}$	50.68

Table 18.3 illustrates some salient points for ROHF calculations. In each case, I optimized the geometry before calculating the hyperfine coupling constants.

Agreement with experiment is not particularly good, and the ROHF method cannot give regions of negative spin density, since the spin density is just the sum of the squares of the partially occupied orbitals in this model.

Corresponding calculations with the UHF method give Table 18.4.

A major problem with the UHF method is that it does not give a pure spin state, so that

$$\hat{S}^2\Psi_{\mathrm{UHF}} \neq s(s+1)\frac{h^2}{4\pi^2}\Psi_{\mathrm{UHF}} \qquad (18.22)$$

In general, if there are p α-spin electrons and q β-spin electrons, the UHF wavefunction can contain spin contributions ranging from $s = \frac{1}{2}(p - q)$ to $\frac{1}{2}(p + q)$. The expectation value

$$\langle S^2 \rangle = \int \Psi_{\mathrm{UHF}}^2 \hat{S}^2 \Psi_{\mathrm{UHF}}\, \mathrm{d}s\, \mathrm{d}\tau$$

gives a measure of the spin impurities. For the vinyl radical discussed above, this was typically 1.2308 (atomic units) rather than $\frac{3}{4}$ for each point in the geometry optimization.

Ideally one should remove all the unwanted spin components before minimizing the energy. In semi-empirical π-electron theory, Amos and Snyder (1965)

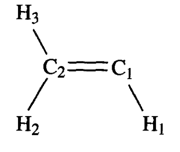


Figure 18.3

Table 18.3 Hyperfine coupling constants/mT for the vinyl radical. ROHF calculations

	H_1	H_2	H_3	C_1	C_2
Experiment	1.33	6.81	3.41	10.76	−0.86
ROHF/STO-3G	1.35	2.53	2.41	13.80	0.923
ROHF/4-31G	1.56	2.41	2.36	11.24	0.99
ROHF/6-311G**	1.32	2.01	2.38	11.49	1.19

Table 18.4 Hyperfine coupling constants/mT for the vinyl radical. UHF calculations

	H_1	H_2	H_3	C_1	C_2
Experiment	(−?)1.33	6.81	3.41	10.76	−0.86
UHF/STO-3G	−3.34	7.75	5.43	23.52	−8.31
UHF/4-31G	−3.06	8.01	6.53	20.38	−7.07
UHF/6-311G**	−1.33	6.53	4.59	17.77	−4.23

demonstrated that a reliable compromise was to remove the component corresponding to the next highest spin state to the one of interest (i.e. the quartet in this case). For the example above, this gave typically an expectation value of 0.7771, which is sufficiently close to the doublet value of $\frac{3}{4}$.

A good many early ESR studies were concerned with π-electron radicals and triplet states. A prototype π-electron system is the methyl radical, CH_3. This radical is planar, and according to the concepts of elementary structural chemistry the odd electron occupies a $2p_z$ orbital perpendicular to the molecular plane. A straightforward *ab initio* ROHF calculation gives exactly that, and the spin density is zero at all the nuclear positions. Experimental measurements show hyperfine couplings from all the nuclei, with negative coupling constants from the protons. A UHF calculation reveals the following spin density for a C–H plane perpendicular to the molecular plane.

Many early studies in ESR spectroscopy were concerned with anions, cations and triplet states derived from conjugated molecules. The unpaired electron(s)

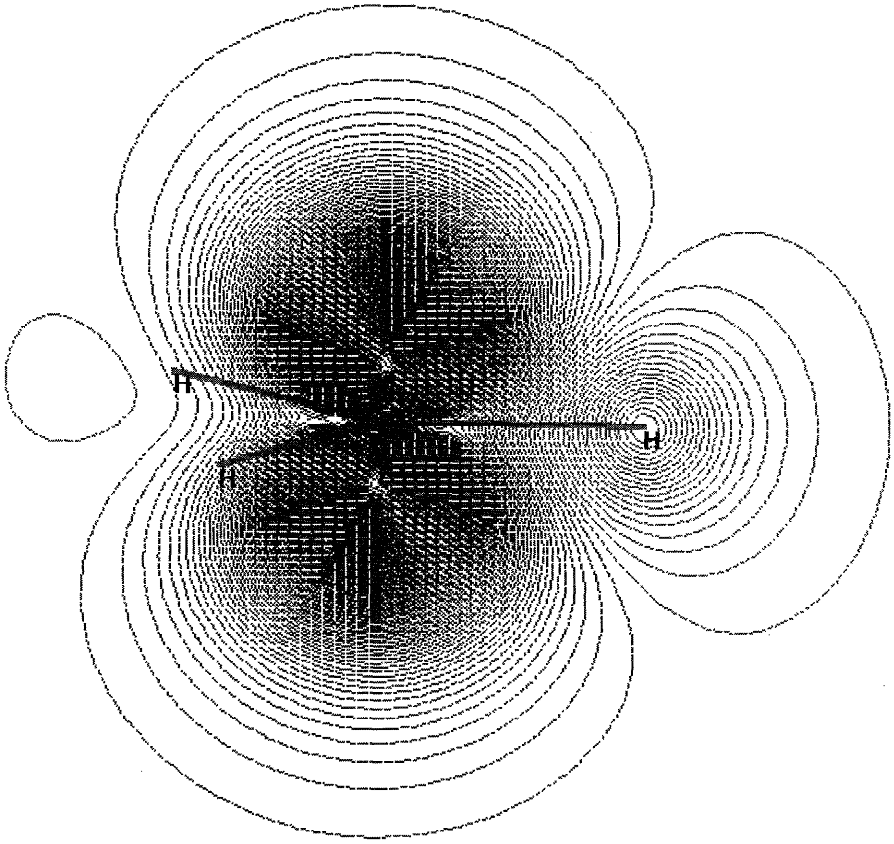


Figure 18.4 Spin density in the methyl radical

formally occupy π-type orbital, which have nodes at the nuclear positions. McConnell (1956) explained the non-zero hyperfine coupling constants in terms of a *spin polarization* mechanism: the spin due to the odd electron polarizes the electron spins in the C–H bond, and so the H nuclear spin can sense the electron spin at the C atom, through the CH bonding electron pair. Pictorially, the argument runs as shown in Figure 18.4 and so McConnell derived his well-known relationship

$$a_{\mathrm{H}}/mT = -2.3Q^{\pi} \tag{18.23}$$

relating the proton coupling constant to the π-electron spin density at the adjoining carbon atom. The spin density could then be calculated from standard π-electron models.

A large number of calculations have appeared in the literature for the methyl radical. It has a low out-of-plane vibrational frequency and the coupling constant is observed to vary with temperature. There have been a number of semi-empirical calculations of the temperature dependence, for example Chang, Davidson and Vincow (1970a). They considered just the symmetric out-of-plane vibration, and the normal coordinate for this vibration was approximated as the out-of-plane angle θ. The hyperfine coupling constant was calculated for a series of values of θ, and these values were then averaged over the nuclear motion using a harmonic oscillator which incorporated the experimental vibrational frequency.

18.2.4 The Cusp Condition

Chang, and Davidson and Vincow (1970b) also investigated the problem of making the wavefunction satisfy the cusp condition (Kato, 1957). A general conclusion appears to be that it makes little or no difference to the agreement with experiment of the hyperfine coupling constants, provided that a large enough basis set is used.

18.2.5 Density Functional Calculations

Barone's review is timely.

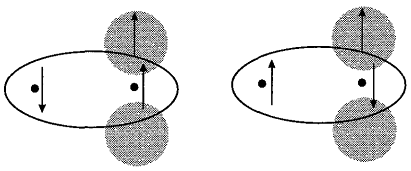


Figure 18.5 Spin polarization mechanism

Structure, Magnetic Properties and Reactivity of Open-Shell Species from Density Functional and Self-Consistent Hybrid Methods
Vincenzo Barone
in *Recent Advances in Density Functional Methods*, ed. D. P. Chong. World Scientific Publishing Co, Singapore, 1996

This contribution is devoted to the impact of density functional theory in the most important building blocks of a comprehensive theoretical characterization and analysis of processes involving open-shell species. After a discussion of the theoretical background, I report the essentials of a number of case studies selected to show the potentialities and limits of local and gradient corrected density functionals in dealing with structural, spectroscopic, thermochemical and kinetic aspects. At the same time I introduce self-consistent hybrid methods obtained by adding some Hartree–Fock exchange to gradient-corrected functionals ...

Barone also introduces two new basis sets, EPR-II and EPR-III. These are optimized for the calculation of hyperfine coupling constants by density functional methods. EPR-II is a double zeta basis set with a single set of polarization functions and an enhanced s part. EPR-III is a triple zeta set including diffuse functions, double d polarization functions and a single set off functions.

18.2.6 Typical Applications

In the following, all isotropic hyperfine coupling constants were calculated using the BLYP functional and the EPR-II basis set. A full geometry optimization was done in all cases.

A great deal is known about the methyl radical CH_3.

The effect of vibrational averaging is particularly significant for the carbon hyperfine coupling constant.

The allyl radical (Figure 18.6) has been the subject of very many studies. It has been prepared in the liquid phase by electron irradiation of cyclopropane. The sign of the CH proton coupling constant was deduced by comparison with a single-crystal study of the radical $CH(COOH)_2$ formed by γ-irradiation of a single crystal of malonic acid. A straightforward UHF calculation gives a wavefunction

Table 18.5 The methyl radical CH_3

Property	BLYP/EPR-II results	Experiment
Geometry	Planar	Planar
R(C–H)/pm	108.8	107.9
a_H/mT	−2.206	−2.309
a_C/mT	2.829	3.829

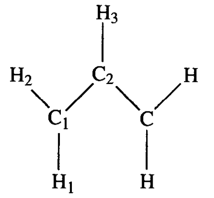


Figure 18.6

that has a totally unacceptable value of $\langle S^2 \rangle$ even after annihilation of the quartet spin contaminant. In addition, the radical exhibits the phenomenon of symmetry-breaking and ROHF studies fail to give a C_{2v} structure. This behaviour does not occur in DFT studies.

Experimental and theoretical studies on the benzyl radical (Figure 18.7) have long figured in the literature. The agreement with experiment is acceptable at the BLYP/EPR-II level of theory — much better than that produced by standard UHF calculations.

In standard Hückel π-electron theory, the highest occupied orbital has a node through the position of C_3 and so we might expect a zero proton hyperfine coupling constant, even after using McConnell's argument.

Table 18.6 The allyl radical C_3H_5

Property	BLYP/EPR-II result	Experiment
$R(C-C)$/pm	140.5	138.7
$R(C_1-H_1)$/pm	109.6	108.7
$R(C_1-H_2)$/pm	109.2	108.5
$R(C_2-H_3)$/pm	109.0	108.2
$C_1-C_2-H_3$/degrees	117.5	118.0
$C_1-C_2-H_3$/degrees	120.9	121.2
$C_1-C_2-H_3$/degrees	121.5	121.5
$a(H_1)$/mT	−1.320	−1.39
$a(H_2)$/mT	−1.393	−1.48
$a(H_3)$/mT	+0.289	+0.41
$a(C_1)$/mT	1.6909	
$a(C_2)$/mT	−1.407	

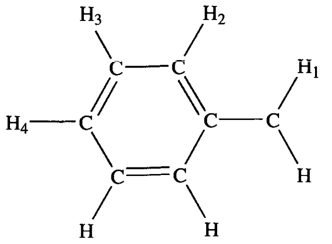


Figure 18.7

Table 18.7 Simple treatment of the benzyl radical

hfcc/mT	Calculated	Experiment
H_1	−1.497	−1.635
H_2	−0.470	−0.514
H_3	+0.138	+0.175
H_4	−0.567	−0.614

18.3 ATOMS IN MOLECULES

The atom and bond concepts dominate chemistry. Dalton postulated that atoms retained their identities even when in chemical combinations with other atoms. We know that their properties are sometimes transferable from one molecule to another; for example, the incremental increase in the standard enthalpy of formation of a normal hydrocarbon per CH_2 group is $-20.6 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$. We also know that more often there are subtle modifications to the electron density.

In Chapter 3, we studied the topic of population analysis. In population analysis, we attempt a rough-and-ready numerical division of the electron density into atom and bond regions. In Mulliken theory, the bond contributions are divided up equally between the contributing atoms, giving the net charges. The aim of the present section is to answer the questions 'Are there atoms in Molecules?', and if so, 'How can they be defined?'. According to Bader and coworkers (Bader, 1990) the answers to both questions are affirmative, and the boundaries of these atoms are determined by a particular property of the electron density.

In our study of the hydrogen molecule-ion $H_2{}^+$ in Chapter 3, we considered the electron density map shown in Figure 18.8. It is obvious by inspection that the

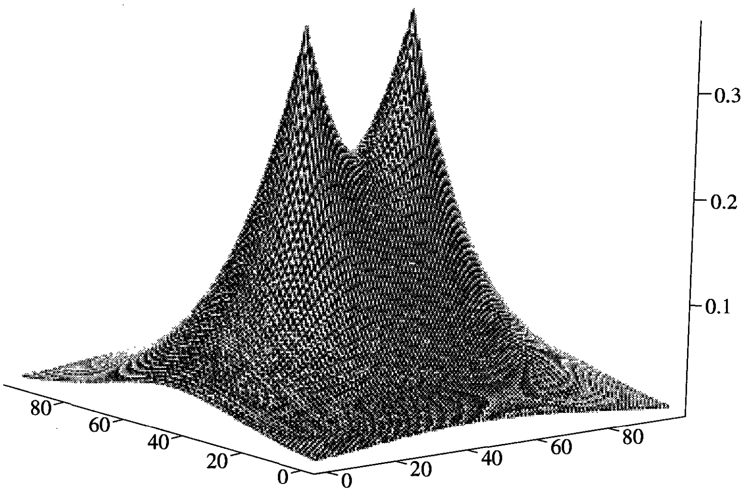


Figure 18.8 Electron density for hydrogen molecule ion

electron density has maxima at the positions of the nuclei. The mutual potential energy of a nucleus and an electron becomes singular as the electron approaches the nucleus, and the first derivative of the electronic wavefunction has to be zero at the nucleus. This is the reason for the so-called cusp condition (Kato, 1957).

These are local maxima: we would expect much higher maxima at the carbon atoms of ethene than at the hydrogen atoms.

The electron density also has a saddle point halfway between the two nuclei.

It should be clear from our discussion of potential energy surfaces that we have to examine the gradient of the electron density and the matrix of second derivatives, in order to make progress. The gradient of the electron density $P(\mathbf{r})$ is, in Cartesian coordinates,

$$\text{grad } P(\mathbf{r}) \equiv \frac{\partial P}{\partial x}\mathbf{e}_x + \frac{\partial P}{\partial y}\mathbf{e}_y + \frac{\partial P}{\partial z}\mathbf{e}_z \tag{18.24}$$

and the matrix of second derivatives (called the Hessian) $\mathbf{H}$ is

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 P}{\partial x^2} & \frac{\partial^2 P}{\partial x \partial y} & \frac{\partial^2 P}{\partial x \partial z} \\ \frac{\partial^2 P}{\partial y \partial x} & \frac{\partial^2 P}{\partial y^2} & \frac{\partial^2 P}{\partial y \partial z} \\ \frac{\partial^2 P}{\partial z \partial x} & \frac{\partial^2 P}{\partial z \partial y} & \frac{\partial^2 P}{\partial z^2} \end{pmatrix} \tag{18.25}$$

$\mathbf{H}$ is a real symmetric matrix, and its eigenvalues are therefore real. Its eigenvectors are referred to as the 'principal axes of curvature'.

The quantity

$$\nabla^2 P = \frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2} + \frac{\partial^2 P}{\partial z^2} \tag{18.26}$$

is called the *Laplacian* of P, and it is also equal to the sum of the eigenvalues of the Hessian.

18.3.1 Critical Points

Each maximum, minimum or saddle point occurs at a so-called *critical point* $\mathbf{r}_c$, where the gradient vanishes. The nature of the critical point is determined by the eigenvalues of the Hessian. All the eigenvalues are real at the critical point, but some of them may be zero. The *rank* ω of the critical point is defined to be the number of non-zero eigenvalues. The *signature* σ is the sum of the signs of the eigenvalues, and critical points are discussed in terms of the pair of numbers (ω, σ).

With few exceptions, the critical points for stable molecules usually have $\omega = 3$ and there are three possible signature values:

$\sigma = -3$: all curvatures are negative and the electron density is a local maximum at the critical point.

$\sigma = -1$: two curvatures are negative, so we have a saddle point.
$\sigma = +1$: two curvatures are positive, again corresponding to a saddle point.

Now imagine that we rotate the molecule about the internuclear axis. The curved contour will trace out a surface. If we draw a unit outward normal vector to this surface, it will be everywhere perpendicular to the gradient vector (because the gradient vector points along the trajectory).

In vector calculus, the flux Φ of an arbitrary vector field $\mathbf{A}$ through a surface S is given by the surface integral

$$\Phi = \int_S \mathbf{A} \cdot \hat{\mathbf{n}}\, \mathrm{d}S \tag{18.27}$$

If $\mathbf{A}$ is everywhere perpendicular to the unit normal then the flux through the surface is zero. We note that for all points on the curved trajectory in Figure 18.9, the gradient of the charge density is perpendicular to any unit normal. When we construct a plane by rotating the molecule about the axis, the charge density gradient is perpendicular to any outward normal on this plane and so the flux of the density gradient is zero through this plane.

For molecules with lower symmetry, we have to find this plane by numerical methods.

In AIM theory, this plane is used to divide up a molecule into atoms. The charge in either region can be calculated numerically, and many other properties calculated. The numbers resulting are quite different from those of conventional population analysis. In Table 18.8, for example, are HF/6–311G** results for LiCl and LiH. The interesting thing is that the Li charges are so similar, with an underlying chemical trend.

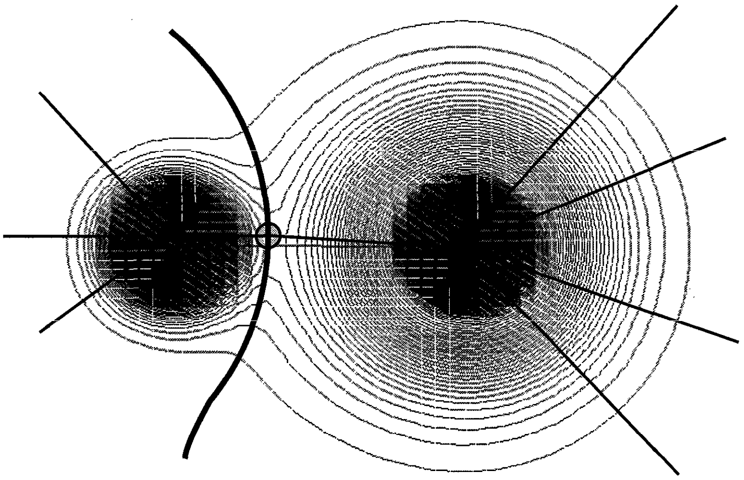


Figure 18.9 Electron density for LiCl with some gradient contours

Table 18.8 LiH and LiCl atom charges HF/6-311G** calculations

	Lithium charge	
	Mulliken	AIM
LiH	0.3571	0.9118
LiCl	0.6353	0.9321

18.4 THERMODYNAMIC QUANTITIES

It is reasonable to expect that models in chemistry should be capable of giving thermodynamic quantities to chemical accuracy. In this text, the phrase 'thermodynamic quantities' means enthalpy changes ΔH, internal energy changes ΔU, heat capacities C, and so on, for gas-phase reactions. Where necessary, the gases are assumed ideal. The calculation of equilibrium constants and transport properties is also of great interest, but I don't have the space to deal with them in this text. Also, the term 'chemical accuracy' means that we should be able to calculate the usual thermodynamic quantities to the same accuracy that an experimentalist would measure them ($\pm 10\,\mathrm{kJ\,mol^{-1}}$).

Our objective proved elusive in the early days of quantum chemistry. The major problem is electron correlation. As I have pointed out on several occasions through the text, the dissociation energy of dihydrogen into its lowest-energy products

$$\mathrm{H_2} \rightarrow 2\mathrm{H}\,(^2\mathrm{S})$$

is beyond the scope of Hartree–Fock theory, because HF wavefunctions dissociate into a mixture of ions and atoms according to

$$\mathrm{H_2} \rightarrow \tfrac{1}{2}\left(2\mathrm{H}\,(^2\mathrm{S}) + \mathrm{H^+} + \mathrm{H^-}\right)$$

Several authors have been more modest in their goals and attempted to calculate directly thermodynamic quantities for reactions involving closed-shell species, where there is some hope that the correlation errors will cancel. The two papers often quoted in this field are those of Snyder and Basch (1969) and Hehre *et al.* (1970).

Molecular Orbital Theory of the Electronic Structure of Organic Compounds V Molecular Orbital Theory of Bond Separation
W. J. Hehre, R. Ditchfield, L. Random and J. A. Pople
Journal of the American Chemical Society **92** (1970) 4796

The complete hydrogenation of an organic molecule is separated into two processes. In the first, termed *bond separation*, the molecule is separated into its simplest parents containing the same component bonds. The energy associated with such a reaction is then the *heat of bond separation*. The second step then consists of full hydrogenation of the products of bond separation. To study these two processes, we have performed Ab Initio molecular orbital calculations on a variety of polyatomic molecules. Both minimal and extended basis sets, taken as linear combinations of Gaussian-type functions, are shown to give heats of bond separation in good agreement with experiment. In contrast, only the extended basis set is successful in reproducing the heats of hydrogenation of the parents.

The aim is to predict the enthalpy change for a reaction such as

$$C_6H_6 + 9H_2 \rightarrow 6CH_4 \tag{18.28}$$

We use Hess's law to break down the equation into a composite of

$$\begin{aligned} C_6H_6 + 6CH_4 &\rightarrow 3C_2H_6 + 3C_2H_4 && \text{I} \\ C_2H_6 + H_2 &\rightarrow 2CH_4 && \text{II} \\ C_2H_4 + 2H_2 &\rightarrow 2CH_4 && \text{III} \end{aligned} \tag{18.29}$$

Weighted addition of the three equations gives the original equation.

Bond separation reactions such as (I) are examples of chemical changes in which there is a retention of the number of bonds of a given formal type, but with a change in their relationship to one another. Such reactions are often called *isodesmic*.

Table 18.9 shows the HF/6–311G** energies for the molecules of interest. Some care is needed when comparing these with thermodynamic data.

The values in the second column give internal energies (U) all relative to separated electrons and nuclei. For a reaction involving ideal gases with a change of Δn in the number of gaseous moles, we have

$$\Delta H = \Delta U + RT\Delta n$$

They take no account of the zero point vibrations. So for example, in the case of a diatomic molecule the dissociation constants D_e and D_0 are related by

$$D_e = D_0 + \frac{1}{2}hc_0\omega_e \tag{18.30}$$

Table 18.9 Molecular energy data calculated at the HF/6–311G** level of theory

Molecule	ε_{el}/E_h	Corrected to 298 K
H_2	−1.132 491	−1.119 664
CH_4	−40.209 012	−40.159 212
C_2H_4	−78.054 725	−77.997 729
C_2H_6	−79.251 708	−79.169 691
C_6H_6	−230.754 098	−230.643 386

We therefore need to calculate the vibrational frequencies, which means that we have to perform a geometry optimization.

The energies quoted are electronic energies, and we often have to take account of the translational, rotational and vibrational contributions of the nuclear framework. They also refer to a temperature of 0 K, and for a molecule at temperature T the kinetic energy is $\frac{3}{2}\,k_BT$ (i.e. $\frac{1}{2}\,k_BT$ per translational degree of freedom, where k_B is the Boltzmann constant). The rotational energy is also $\frac{1}{2}\,k_BT$ per degree of rotational freedom, and there are two such degrees of freedom for a linear molecule and three for a non-linear molecule. Many vibrational modes will be populated at temperature T; if the fundamental vibrational wavenumber of a given mode is ω_e then the associated energy is $hc_0\omega_e$ and in the harmonic approximation the energies of all vibrational states are

$$\varepsilon_v = \left(v + \tfrac{1}{2}\right) hc_0\omega_e \tag{18.31}$$

The fraction of molecules N_v/N having energy ε_v is given by the well-known Boltzmann formula

$$\frac{N_v}{N} = \frac{\exp\left(-\dfrac{\varepsilon_v}{k_BT}\right)}{\displaystyle\sum_v \exp\left(-\dfrac{\varepsilon_v}{k_BT}\right)} \tag{18.32}$$

With all this in mind, the molecular data in column 3 of Table 18.9 has been corrected to 298 K and 1 atm pressure. Like is compared to like in Table 18.10.

The agreement with experiment is reasonable, for both types of reaction. In the case of benzene, the bond separation energy refers to the energy of the molecule compared to fragments with pure single and double bonds and so the internal energy change should give a good estimate for the resonance energy.

18.4.1 G1 and G2

Things have moved on since the early papers given above. The development of Møller–Plesset perturbation theory (Chapter 11) marked a turning point in treatments of electron correlation, and made such calculations feasible for molecules of moderate size. The Møller–Plesset method is usually implemented up to MP4 but the convergence of the MPn series is sometimes unsatisfactory. The effect

Table 18.10 Internal energy changes at 298 K and 1 atm

Reaction	$\Delta U_{298\,\text{K}}$(calc)/kJ mol^{-1}	$\Delta U_{298\,\text{K}}$(expt)/kJ mol^{-1}
$CH_3{-}CH_3 + H_2 \rightarrow 2CH_4$	−76.17	−75.73
$CH_2{=}CH_2 + 2H_2 \rightarrow 2CH_4$	−213.63	−194.56
$C_6H_6 + 6CH_4 \rightarrow 3CH_2{=}CH_2 + 3CH_3{-}CH_3$	+253.09	+275.30

of extended basis sets is also important: d and even f orbitals make considerable contributions to the total energies of small first-row molecules. With these general thoughts in mind, Pople *et al.* (1989) introduced the *Gaussian-1* (G1) theory.

Gaussian-1 theory: A general procedure for prediction of molecular energies John A. Pople, Martin Head-Gordon, Douglas J. Fox, Krishnan Raghavachari and Larry A. Curtiss
Journal of Chemical Physics **90** (1989) 5622–5629

A general procedure is developed for the computation of the total energies of molecules at their equilibrium geometries. Ab Initio molecular orbital theory is used to calculate electronic energies by a composite method, utilizing large basis sets (including diffuse-sp, double-d and f-polarization functions) and treating electron correlation by the Møller Plesset perturbation theory and by quadratic configuration interaction. The theory is also used to compute zero-point vibrational energy corrections. Total atomization energies for a set of 31 molecules are found to agree with experimental thermochemical data to an accuracy of greater than 2 kcal mol^{-1} in most cases. Similar agreement is achieved for ionization energies, electron and proton affinities. Residual errors are assessed for the total energies of neutral atoms.

The G1 procedure consists of a number of standard calculation steps that aim to find an equilibrium geometry, an electronic energy and a set of harmonic force constants. The defects mentioned above are assumed additive, and they are investigated in turn.

There are eight distinct stages in the calculation:

1 An initial equilibrium structure is obtained at the HF/6–31G* level of theory.

2 The equilibrium structure is revised to the MP2/6–31G* level of theory. For operational reasons, all electrons are used in the perturbation expansion.

3 The geometry from step 2 is now used in a number of single-point calculations at higher levels of theory, starting with MP4/6–311G**. This energy is now systematically improved, and the improvements are assumed to be additive.

4 The first correction is that due to diffuse sp basis functions. These are known to be important for anions and molecules with lone pairs. The correction is obtained at MP4 level, comparing the energy of the 6–311 + G** and the 6–311G** basis sets.

5 The second correction takes account of polarization functions on non-hydrogens. This is done by comparing MP4/6–311G**(2df) and MP4/6–311G** energies.

6. The third correction allows for inadequacies in the MP4 treatment. The QCISD(T) method is equivalent to MP4 in fourth order and also correctly incorporates parts of the fifth and higher orders. We therefore make a quadratic CI correction using the 6–311G** basis set. This is a very expensive calculation for molecules of medium size.
7. The final correction is to add an empirical 'higher-level correction' which is chosen to give agreement between the G1 values for hydrogen atom, hydrogen molecule and experiment. In the original G1 theory, a value of $An_\beta - Bn_\alpha$ was used. Here n_α is the number of α-spin electrons, n_β the number of β-spin electrons, $A = 4.81 \times 10^{-3} E_\mathrm{h}$ and $\mathrm{B} = 0.19 \times 10^{-3}\ E_\mathrm{h}$.
8. Finally, the harmonic frequencies are obtained at the HF/6–31G* level and scaled uniformly by the well-accepted factor of 0.8929. That allows for Boltzmann contributions to the vibrational modes.

Typical output from a G1 calculation on HCN is shown in Figure 18.10. For '`Free Energy`' read Gibbs energy.

The MP4/6–311G** energy (not shown) works out at $-93.233\,84 E_\mathrm{h}$ and the final G1 energy at 0 K is $-93.285\,47 E_\mathrm{h}$. The final corrected G1 energy at 298.15 K is $-93.282\,95\ E_\mathrm{h}$.

18.4.2 G2 Theory

'G1 theory' was originally tested against experimental values of atomization energies, ionization energies, proton affinities and electron affinities for a wide range of simple molecules. For compounds containing first-row atoms, the agreement with experiment turned out as $\pm 2\,\mathrm{kcal\,mol^{-1}}$. For molecules containing second-row atoms, the agreement with experiment is $\pm 3\,\mathrm{kcal\,mol^{-1}}$.

G1 theory does badly with ionic molecules, with triplet-state molecules such as O_2 and S_2 and with hypervalent molecules. 'Gaussian-2' (G2) theory eliminates some of these difficulties by making the following three changes:

1. It eliminates the assumption of additivity of the diffuse sp (+) and 2df basis set used in G1 theory.
2. It adds a third d function on the non-hydrogen atoms and a second p function on the hydrogens.
3. The high-level correction (item 7 above) is determined by a least squares fit for 55 molecules rather than just hydrogen atom and hydrogen molecule.

```
Temperature=        298.150000 Pressure=                  1.000000
E(ZPE)=               0.016065 E(Thermal)=                0.018586
E(QCISD(T))=        -93.220833 E(Empiric)=               -0.030700
DE(Plus)=            -0.003008 DE(2DF)=                  -0.046991
G1(0 K)=            -93.285468 G1 Energy=               -93.282947
G1 Enthalpy=        -93.282003 G1 Free Energy=          -93.304798
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Figure 18.10

Gaussian-2 Theory for Molecular Energies of First- and Second-Row Compounds

Larry A. Curtiss, Krishnan Raghavachari, Gary W. Trucks and John A. Pople

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The Gaussian-2 theoretical (G2 theory), based on ab initio molecular orbital theory, for calculation of molecular energies (atomization energies, ionization potentials, electron affinities, and proton affinities) of compounds containing first- (Li–F) and second-row atoms (Na–Cl) is presented. This new theoretical procedure adds three features to G1 theory including a correction for nonadditivity of diffuse sp and 2df basis set extensions, a basis set extension containing a third d function on nonhydrogen atoms and a second p function on hydrogen atoms, and a modification of the high level correction. G2 theory is a significant improvement over G1 theory because it eliminates a number of deficiencies present in G1 theory. Of particular importance is the improvement in atomization energies of ionic molecules such as LiF and hydrides such as C_2H_6, NH_3, N_2H_4, H_2O_2 and CH_3SH.

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