12

The Hyperfine Splitting in Hydrogen

12–1 Base states for a system with two spin one-half particles

In this chapter we take up the "hyperfine splitting" of hydrogen, because it is a physically interesting example of what we can already do with quantum mechanics. It's an example with more than two states, and it will be illustrative of the methods of quantum mechanics as applied to slightly more complicated problems. It is enough more complicated that once you see how this one is handled you can get immediately the generalization to all kinds of problems.

As you know, the hydrogen atom consists of an electron sitting in the neighborhood of the proton, where it can exist in any one of a number of discrete energy states in each one of which the pattern of motion of the electron is different. The first excited state, for example, lies 3/4 of a Rydberg, or about 10 electron volts, above the ground state. But even the so-called ground state of hydrogen is not really a single, definite-energy state, because of the spins of the electron and the proton. These spins are responsible for the "hyperfine structure" in the energy levels, which splits all the energy levels into several nearly equal levels.

The electron can have its spin either "up" or "down" and, the proton can also have *its* spin either "up" or "down." There are, therefore, *four* possible spin states for every dynamical condition of the atom. That is, when people say "the ground state" of hydrogen, they really mean the "four ground-states," and not just the very lowest state. The four spin states do not all have exactly the same energy; there are slight shifts from the energies we would expect with no spins. The shifts are, however, much, much smaller than the 10 volts or so from the ground state to the next state above. As a consequence, each dynamical state has its energy split into a set of very close energy levels—the so-called *hyperfine splitting*.

The energy differences among the four spin states is what we want to calculate in this chapter. The hyperfine splitting is due to the interaction of the magnetic moments of the electron and proton, which gives a slightly different magnetic energy for each spin state. These energy shifts are only about ten-millionths of an electron volt—really very small compared with 10 volts! It is because of this large gap that we can think about the ground state of hydrogen as a "four-state" system, without worrying about the fact that there are really many more states at higher energies. We are going to limit ourselves here to a study of the hyperfine structure of the ground state of the hydrogen atom.

For our purposes we are not interested in any of the details about the *positions* of the electron and proton because that has all been worked out by the atom so to speak—it has worked itself out by getting into the ground state. We need know only that we have an electron and proton in the neighborhood of each other with some definite spatial relationship. In addition, they can have various different relative orientations of their spins. It is only the effect of the spins that we want to look into.

The first question we have to answer is: What are the *base states* for the system? Now the question has been put incorrectly. There is no such thing as "*the*" base states, because, of course, the set of base states you may choose is not unique. New sets can always be made out of linear combinations of the old. There are always many choices for the base states, and among them, any choice is equally legitimate. So the question is not what is *the* base set, but what *could* a base set be? We can choose any one we wish for our own convenience. It is usually best to start with a base set which is *physically* the clearest. It may not be the solution to any problem, or may not have any *direct* importance, but it will generally make it easier to understand what is going on.

We choose the following four base states:

State 1: The electron and proton are both spin "up."
State 2: The electron is "up" and the proton is "down."
State 3: The electron is "down" and the proton is "up."
State 4: The electron and proton are both "down."

We need a handy notation for these four states, so we'll represent them this way:

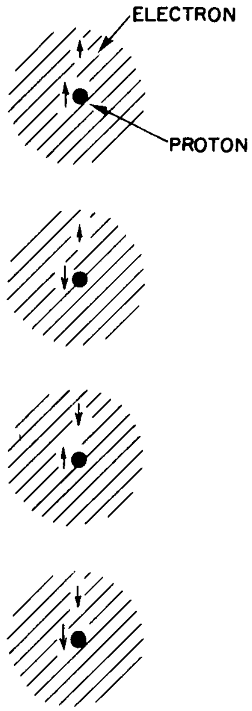

Fig. 12–1. A set of base states for the ground state of the hydrogen atom.

$$\begin{array}{ll}
\textit{State 1}: & |+\;+\rangle;\ \text{electron } \textit{up}\text{, proton } \textit{up}. \\
\textit{State 2}: & |+\;-\rangle;\ \text{electron } \textit{up}\text{, proton } \textit{down}. \\
\textit{State 3}: & |-\;+\rangle;\ \text{electron } \textit{down}\text{, proton } \textit{up}. \\
\textit{State 4}: & |-\;-\rangle;\ \text{electron } \textit{down}\text{, proton } \textit{down}.
\end{array} \tag{12.1}$$

You will have to remember that the *first* plus or minus sign refers to the electron and the *second*, to the proton. For handy reference, we've also summarized the notation in Fig. 12–1. Sometimes it will also be convenient to call these states $|\,1\rangle$, $|\,2\rangle$, $|\,3\rangle$, and $|\,4\rangle$.

You may say, "But the particles interact, and maybe these aren't the right base states. It sounds as though you are considering the two particles independently." Yes, indeed! The interaction raises the problem: what is the *Hamiltonian* for the system, but the interaction is not involved in the question of how to *describe* the system. What we choose for the base states has nothing to do with what happens next. It may be that the atom cannot ever *stay* in one of these base states, even if it is started that way. That's another question. That's the question: How do the amplitudes change with time in a particular (fixed) base? In choosing the base states, we are just choosing the "unit vectors" for our description.

While we're on the subject, let's look at the general problem of finding a set of base states when there is more than one particle. You know the base states for a single particle. An electron, for example, is completely described in real life—not in our simplified cases, but in real life—by giving the amplitudes to be in each of the following states:

$$|\,\text{electron "up" with momentum } \boldsymbol{p}\rangle$$

or

$$|\,\text{electron "down" with momentum } \boldsymbol{p}\rangle.$$

There are really two infinite sets of states, one state for each value of $\boldsymbol{p}$. That is to say that an electron state $|\,\psi\rangle$ is completely described if you know all the amplitudes

$$\langle +, \boldsymbol{p}\,|\,\psi\rangle \qquad \text{and} \qquad \langle -, \boldsymbol{p}\,|\,\psi\rangle,$$

where the $+$ and $-$ represent the components of angular momentum along some axis—usually the z-axis—and $\boldsymbol{p}$ is the vector momentum. There must, therefore, be two amplitudes for every possible momentum (a multi-infinite set of base states). That is all there is to describing a single particle.

When there is more than one particle, the base states can be written in a similar way. For instance, if there were an electron and a proton in a more complicated situation than we are considering, the base states could be of the following kind:

$$|\,\text{an electron with spin "up," moving with momentum } \boldsymbol{p}_1 \text{ and}$$
$$\text{a proton with spin "down," moving with momentum } \boldsymbol{p}_2\rangle.$$

And so on for other spin combinations. If there are more than two particles—same idea. So you see that to write down the *possible* base states is really very easy. The only problem is, what is the Hamiltonian?

For our study of the ground state of hydrogen we don't need to use the full sets of base states for the various momenta. We are specifying particular momentum states for the proton and electron when we say "the ground state." The details of the configuration—the amplitudes for all the momentum base states—can be calculated, but that is another problem. Now we are concerned only with the effects of the spin, so we can take only the four base states of (12.1). Our next problem is: What is the Hamiltonian for this set of states?

12–2 The Hamiltonian for the ground state of hydrogen

We'll tell you in a moment what it is. But first, we should remind you of one thing: *any* state can always be written as a linear combination of the base states. For any state $|\,\psi\rangle$ we can write

$$\begin{aligned}|\,\psi\rangle = |+\,+\rangle\langle+\,+\,|\,\psi\rangle + |+\,-\rangle\langle+\,-\,|\,\psi\rangle + |-\,+\rangle\langle-\,+\,|\,\psi\rangle \\ + |-\,-\rangle\langle-\,-\,|\,\psi\rangle.\end{aligned} \tag{12.2}$$

Remember that the complete brackets are just complex numbers, so we can also write them in the usual fashion as C_i, where $i = 1, 2, 3$, or 4, and write Eq. (12.2) as

$$|\,\psi\rangle = |+\,+\rangle C_1 + |+\,-\rangle C_2 + |-\,+\rangle C_3 + |-\,-\rangle C_4. \tag{12.3}$$

By giving the four amplitudes C_i we completely describe the spin state $|\,\psi\rangle$. If these four amplitudes change with time, as they will, the rate of change in time is given by the operator $\hat{H}$. The problem is to find the $\hat{H}$.

Table 12–1

$\sigma_z\,|+\rangle = +\,|+\rangle$
$\sigma_z\,|-\rangle = -\,|-\rangle$
$\sigma_x\,|+\rangle = +\,|-\rangle$
$\sigma_x\,|-\rangle = +\,|+\rangle$
$\sigma_y\,|+\rangle = +\,i\,|-\rangle$
$\sigma_y\,|-\rangle = -i\,|+\rangle$

There is no general rule for writing down the Hamiltonian of an atomic system, and finding the right formula is much more of an art than finding a set of base states. We were able to tell you a general rule for writing a set of base states for any problem of a proton and an electron, but to describe the general Hamiltonian of such a combination is too hard at this level. Instead, we will lead you to a Hamiltonian by some heuristic argument—and you will have to accept it as the correct one because the results will agree with the test of experimental observation.

You will remember that in the last chapter we were able to describe the Hamiltonian of a single, spin one-half particle by using the sigma matrices—or the exactly equivalent sigma operators. The properties of the operators are summarized in Table 12–1. These operators—which are just a convenient, shorthand way of keeping track of the matrix elements of the type $\langle+\,|\sigma_z\,|+\rangle$—were useful for describing the behavior of a *single* particle of spin one-half. The question is: Can we find an analogous device to describe a system with two spins? The answer is yes, very simply, as follows. We invent a thing which we will call "sigma electron," which we represent by the vector operator $\boldsymbol{\sigma}^{\text{e}}$, and which has the x-, y-, and z-components, σ_x^{e}, σ_y^{e}, σ_z^{e}. We now make the *convention* that when one of these things operates on any one of our four base states of the hydrogen atom, it acts only on the *electron* spin, and in exactly the same way as if the electron were all by itself. Example: What is $\sigma_y^{\text{e}}\,|-\,+\rangle$? Since σ_y on an electron "down" is $-i$ times the corresponding state with the electron "up",

$$\sigma_y^{\text{e}}\,|-\,+\rangle = -i\,|+\,+\rangle.$$

(When σ_y^{e} acts on the combined state it flips over the electron, but does nothing to the proton and multiplies the result by $-i$.) Operating on the other states, σ_y^{e} would give

$$\begin{aligned}\sigma_y^{\text{e}}\,|+\,+\rangle &= i\,|-\,+\rangle,\\ \sigma_y^{\text{e}}\,|+\,-\rangle &= i\,|-\,-\rangle,\\ \sigma_y^{\text{e}}\,|-\,-\rangle &= -i\,|+\,-\rangle.\end{aligned}$$

Just remember that the operators $\boldsymbol{\sigma}^{\text{e}}$ work only on the *first* spin symbol—that is, on the *electron* spin.

Next we define the corresponding operator "sigma proton" for the proton spin. Its three components σ_x^{p}, σ_y^{p}, σ_z^{p} act in the same way as $\boldsymbol{\sigma}^{\text{e}}$, only on the *proton* spin. For example, if we have σ_x^{p} acting on each of the four base states, we get—always using Table 12–1—

$$\begin{aligned}\sigma_x^{\text{p}}\,|+\,+\rangle &= |+\,-\rangle,\\ \sigma_x^{\text{p}}\,|+\,-\rangle &= |+\,+\rangle,\\ \sigma_x^{\text{p}}\,|-\,+\rangle &= |-\,-\rangle,\\ \sigma_x^{\text{p}}\,|-\,-\rangle &= |-\,+\rangle.\end{aligned}$$

As you can see, it's not very hard.

Now in the most general case we could have more complex things. For instance, we could have products of the two operators like $\sigma_y^{\text{e}}\sigma_z^{\text{p}}$. When we have such a product we do first what the operator on the right says, and then do what the other one says.† For example, we would have that

$$\sigma_x^{\text{e}}\sigma_z^{\text{p}}\,|+\,-\rangle = \sigma_x^{\text{e}}(\sigma_z^{\text{p}}\,|+\,-\rangle) = \sigma_x^{\text{e}}(-\,|+\,-\rangle) = -\sigma_x^{\text{e}}\,|+\,-\rangle = -\,|-\,-\rangle.$$

Note that these operators don't do anything on pure numbers—we have used this fact when we wrote $\sigma_x^{\text{e}}(-1) = (-1)\sigma_x^{\text{e}}$. We say that the operators "commute" with pure numbers, or that a number "can be moved through" the operator. You can practice by showing that the product $\sigma_x^{\text{e}}\sigma_z^{\text{p}}$ gives the following results for the four states:

$$\begin{aligned}\sigma_x^{\text{e}}\sigma_z^{\text{p}}\,|+\,+\rangle &= +\,|-\,+\rangle,\\ \sigma_x^{\text{e}}\sigma_z^{\text{p}}\,|+\,-\rangle &= -\,|-\,-\rangle,\\ \sigma_x^{\text{e}}\sigma_z^{\text{p}}\,|-\,+\rangle &= +\,|+\,+\rangle,\\ \sigma_x^{\text{e}}\sigma_z^{\text{p}}\,|-\,-\rangle &= -\,|+\,-\rangle.\end{aligned}$$

If we take all the possible operators, using each kind of operator only once, there are sixteen possibilities. Yes, *sixteen*—provided we include also the "unit operator" $\hat{1}$. First, there are the three: $\sigma_x^{\text{e}}, \sigma_y^{\text{e}}, \sigma_z^{\text{e}}$. Then the three $\sigma_x^{\text{p}}, \sigma_y^{\text{p}}, \sigma_z^{\text{p}}$—that makes six. In addition, there are the nine possible products of the form $\sigma_x^{\text{e}}\sigma_y^{\text{p}}$, which makes a total of 15. And there's the unit operator which just leaves any state unchanged. Sixteen in all.

Now note that for a four-state system, the Hamiltonian matrix has to be a four-by-four matrix of coefficients—it will have sixteen entries. It is easily demonstrated that any four-by-four matrix—and, therefore, the Hamiltonian matrix in particular—can be written as a linear combination of the sixteen double-spin matrices corresponding to the set of operators we have just made up. Therefore, for the interaction between a proton and an electron that involves only their spins, we can expect that the Hamiltonian operator can be written as a linear combination of the same 16 operators. The only question is, how?

Well, first, we know that the interaction doesn't depend on our choice of axes for a coordinate system. If there is no external disturbance—like a magnetic field—to determine a unique direction in space, the Hamiltonian can't depend on our choice of the direction of the x-, y-, and z-axes. That means that the Hamiltonian can't have a term like σ_x^{e} all by itself. It would be ridiculous, because then somebody with a different coordinate system would get different results.

The only possibilities are a term with the unit matrix, say a constant a (times $\hat{1}$), and some combination of the sigmas that doesn't depend on the coordinates—some "invariant" combination. The only *scalar* invariant combination of two vectors is the dot product, which for our σ's is

$$\boldsymbol{\sigma}^{\text{e}}\cdot\boldsymbol{\sigma}^{\text{p}} = \sigma_x^{\text{e}}\sigma_x^{\text{p}} + \sigma_y^{\text{e}}\sigma_y^{\text{p}} + \sigma_z^{\text{e}}\sigma_z^{\text{p}}. \tag{12.4}$$

This operator is invariant with respect to any rotation of the coordinate system.

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† For these *particular* operators, you will notice it turns out that the sequence of the operators doesn't matter.

So the only possibility for a Hamiltonian with the proper symmetry in space is a constant times the unit matrix plus a constant times this dot product, say,

$$\hat{H} = E_0 + A\,\boldsymbol{\sigma}^{\text{e}}\cdot\boldsymbol{\sigma}^{\text{p}}. \tag{12.5}$$

That's our Hamiltonian. It's the only thing that it can be, by the symmetry of space, *so long as there is no external field.* The constant term doesn't tell us much; it just depends on the level we choose to measure energies from. We may just as well take $E_0 = 0$. The second term tells us all we need to know to find the level splitting of the hydrogen.

If you want to, you can think of the Hamiltonian in a different way. If there are two magnets near each other with magnetic moments $\boldsymbol{\mu}_{\text{e}}$ and $\boldsymbol{\mu}_{\text{p}}$, the mutual energy will depend on $\boldsymbol{\mu}_{\text{e}}\cdot\boldsymbol{\mu}_{\text{p}}$—among other things. And, you remember, we found that the classical thing we call $\boldsymbol{\mu}_{\text{e}}$ appears in quantum mechanics as $\mu_{\text{e}}\boldsymbol{\sigma}_{\text{e}}$. Similarly, what appears classically as $\boldsymbol{\mu}_{\text{p}}$ will usually turn out in quantum mechanics to be $\mu_{\text{p}}\boldsymbol{\sigma}_{\text{p}}$ (where μ_{p} is the magnetic moment of the proton, which is about 1000 times smaller than μ_{e}, and has the opposite sign). So Eq. (12.5) says that the interaction energy is like the interaction between two magnets—only not quite, because the interaction of the two magnets depends on the radial distance between them. But Eq. (12.5) could be—and, in fact, *is*—some kind of an average interaction. The electron is moving all around inside the atom, and our Hamiltonian gives only the average interaction energy. All it says is that for a prescribed arrangement in space for the electron and proton there is an energy proportional to the cosine of the angle between the two magnetic moments, speaking classically. Such a classical qualitative picture may help you to understand where it comes from, but the important thing is that Eq. (12.5) is the correct quantum mechanical formula.

The order of magnitude of the classical interaction between two magnets would be the product of the two magnetic moments divided by the cube of the distance between them. The distance between the electron and the proton in the hydrogen atom is, speaking roughly, one half an atomic radius, or 0.5 angstrom. It is, therefore, possible to make a crude estimate that the constant A should be about equal to the product of the two magnetic moments μ_{e} and μ_{p} divided by the cube of 1/2 angstrom. Such an estimate gives a number in the right ball park. It turns out that A can be calculated accurately once you understand the complete quantum theory of the hydrogen atom—which we so far do not. It has, in fact, been calculated to an accuracy of about 30 parts in one million. So, unlike the flip-flop constant A of the ammonia molecule, which couldn't be calculated at all well by a theory, our constant A for the hydrogen *can* be calculated from a more detailed theory. But never mind, we will for our present purposes think of the A as a number which could be determined by experiment, and analyze the physics of the situation.

Taking the Hamiltonian of Eq. (12.5), we can use it with the equation

$$i\hbar\dot{C}_i = \sum_j H_{ij}C_j \tag{12.6}$$

to find out what the spin interactions do to the energy levels. To do that, we need to work out the sixteen matrix elements $H_{ij} = \langle i\,|\,H\,|\,j\rangle$ corresponding to each pair of the four base states in (12.1).

We begin by working out what $\hat{H}\,|\,j\rangle$ is for each of the four base states. For example,

$$\hat{H}\,|+\,+\rangle = A\boldsymbol{\sigma}^{\text{e}}\cdot\boldsymbol{\sigma}^{\text{p}}\,|+\,+\rangle = A\{\sigma_x^{\text{e}}\sigma_x^{\text{p}} + \sigma_y^{\text{e}}\sigma_y^{\text{p}} + \sigma_z^{\text{e}}\sigma_z^{\text{p}}\}\,|+\,+\rangle. \tag{12.7}$$

Using the method we described a little earlier—it's easy if you have memorized Table 12–1—we find what each pair of σ's does on $|+\,+\rangle$. The answer is

$$\begin{aligned}\sigma_x^{\text{e}}\sigma_x^{\text{p}}\,|+\,+\rangle &= +\,|-\,-\rangle,\\ \sigma_y^{\text{e}}\sigma_y^{\text{p}}\,|+\,+\rangle &= -\,|-\,-\rangle,\\ \sigma_z^{\text{e}}\sigma_z^{\text{p}}\,|+\,+\rangle &= +\,|+\,+\rangle.\end{aligned} \tag{12.8}$$

So (12.7) becomes

$$\hat{H}\,|+\,+\rangle = A\{|-\,-\rangle - |-\,-\rangle + |+\,+\rangle\} = A\,|+\,+\rangle. \tag{12.9}$$

Since our four base states are all orthogonal, that gives us immediately that

$$\begin{aligned}
\langle +\,+\,|\,H\,|+\,+\rangle &= A\langle +\,+\,|+\,+\rangle = A,\\
\langle +\,-\,|\,H\,|+\,+\rangle &= A\langle +\,-\,|+\,+\rangle = 0,\\
\langle -\,+\,|\,H\,|+\,+\rangle &= A\langle -\,+\,|+\,+\rangle = 0,\\
\langle -\,-\,|\,H\,|+\,+\rangle &= A\langle -\,-\,|+\,+\rangle = 0.
\end{aligned} \tag{12.10}$$

Remembering that $\langle j\,|\,H\,|\,i\rangle = \langle i\,|\,H\,|\,j\rangle^*$, we can already write down the differential equation for the amplitudes C_1:

$$i\hbar\dot{C}_1 = H_{11}C_1 + H_{12}C_2 + H_{13}C_3 + H_{14}C_4$$

or

$$i\hbar\dot{C}_1 = AC_1. \tag{12.11}$$

Table 12–2

Spin operators for the hydrogen atom

$$\begin{aligned}
\sigma_x^{\mathrm{e}}\sigma_x^{\mathrm{p}}\,|+\,+\rangle &= +\,|-\,-\rangle\\
\sigma_x^{\mathrm{e}}\sigma_x^{\mathrm{p}}\,|+\,-\rangle &= +\,|-\,+\rangle\\
\sigma_x^{\mathrm{e}}\sigma_x^{\mathrm{p}}\,|-\,+\rangle &= +\,|+\,-\rangle\\
\sigma_x^{\mathrm{e}}\sigma_x^{\mathrm{p}}\,|-\,-\rangle &= +\,|+\,+\rangle
\end{aligned}$$

$$\begin{aligned}
\sigma_y^{\mathrm{e}}\sigma_y^{\mathrm{p}}\,|+\,+\rangle &= -\,|-\,-\rangle\\
\sigma_y^{\mathrm{e}}\sigma_y^{\mathrm{p}}\,|+\,-\rangle &= +\,|-\,+\rangle\\
\sigma_y^{\mathrm{e}}\sigma_y^{\mathrm{p}}\,|-\,+\rangle &= +\,|+\,-\rangle\\
\sigma_y^{\mathrm{e}}\sigma_y^{\mathrm{p}}\,|-\,-\rangle &= -\,|+\,+\rangle
\end{aligned}$$

$$\begin{aligned}
\sigma_z^{\mathrm{e}}\sigma_z^{\mathrm{p}}\,|+\,+\rangle &= +\,|+\,+\rangle\\
\sigma_z^{\mathrm{e}}\sigma_z^{\mathrm{p}}\,|+\,-\rangle &= -\,|+\,-\rangle\\
\sigma_z^{\mathrm{e}}\sigma_z^{\mathrm{p}}\,|-\,+\rangle &= -\,|-\,+\rangle\\
\sigma_z^{\mathrm{e}}\sigma_z^{\mathrm{p}}\,|-\,-\rangle &= +\,|-\,-\rangle
\end{aligned}$$

That's all! We get only the one term.

Now to get the rest of the Hamiltonian equations we have to crank through the same procedure for $\hat{H}$ operating on the other states. First, we will let you practice by checking out all of the sigma products we have written down in Table 12–2. Then we can use them to get:

$$\begin{aligned}
\hat{H}\,|+\,-\rangle &= A\{2\,|-\,+\rangle - |+\,-\rangle\},\\
\hat{H}\,|-\,+\rangle &= A\{2\,|+\,-\rangle - |-\,+\rangle\},\\
\hat{H}\,|-\,-\rangle &= A\,|-\,-\rangle.
\end{aligned} \tag{12.12}$$

Then, multiplying each one in turn on the left by all the other state vectors, we get the following Hamiltonian matrix, H_{ij}:

$$H_{ij} = \begin{array}{cc} & \xrightarrow{j} \\ i\downarrow & \begin{pmatrix} A & 0 & 0 & 0\\ 0 & -A & 2A & 0\\ 0 & 2A & -A & 0\\ 0 & 0 & 0 & A \end{pmatrix} \end{array}. \tag{12.13}$$

It means, of course, nothing more than that our differential equations for the four amplitudes C_i are

$$\begin{aligned}
i\hbar\dot{C}_1 &= AC_1,\\
i\hbar\dot{C}_2 &= -AC_2 + 2AC_3,\\
i\hbar\dot{C}_3 &= 2AC_2 - AC_3,\\
i\hbar\dot{C}_4 &= AC_4.
\end{aligned} \tag{12.14}$$

Before solving these equations we can't resist telling you about a clever rule due to Dirac—it will make you feel that you are really advanced—although we don't need it for our work. We have—from the equations (12.9) and (12.12)—that

$$\begin{aligned}
\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}\,|+\,+\rangle &= |+\,+\rangle,\\
\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}\,|+\,-\rangle &= 2\,|-\,+\rangle - |+\,-\rangle,\\
\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}\,|-\,+\rangle &= 2\,|+\,-\rangle - |-\,+\rangle,\\
\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}\,|-\,-\rangle &= |-\,-\rangle.
\end{aligned} \tag{12.15}$$

Look, said Dirac, I can also write the first and last equations as

$$\begin{aligned}\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}\,|+\,+\rangle &= 2\,|+\,+\rangle-|+\,+\rangle,\\ \boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}\,|-\,-\rangle &= 2\,|-\,-\rangle-|-\,-\rangle;\end{aligned}$$

then they are all quite similar. Now I invent a new operator, which I will call $P_{\text{spin exch}}$ and which I *define* to have the following properties:†

$$\begin{aligned}P_{\text{spin exch}}\,|+\,+\rangle &= |+\,+\rangle,\\ P_{\text{spin exch}}\,|+\,-\rangle &= |-\,+\rangle,\\ P_{\text{spin exch}}\,|-\,+\rangle &= |+\,-\rangle,\\ P_{\text{spin exch}}\,|-\,-\rangle &= |-\,-\rangle.\end{aligned}$$

All the operator does is interchange the spin directions of the two particles. Then I can write the whole set of equations in (12.15) as a simple operator equation:

$$\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}} = 2P_{\text{spin exch}} - 1. \tag{12.16}$$

That's the formula of Dirac. His "spin exchange operator" gives a handy rule for figuring out $\boldsymbol{\sigma}^{\mathrm{e}}\cdot\boldsymbol{\sigma}^{\mathrm{p}}$. (You see, you can do everything now. The gates are open.)

12–3 The energy levels

Now we are ready to work out the energy levels of the ground state of hydrogen by solving the Hamiltonian equations (12.14). We want to find the energies of the stationary states. This means that we want to find those special states $|\psi\rangle$ for which each amplitude $C_i = \langle i\,|\,\psi\rangle$ in the set belonging to $|\psi\rangle$ has the same time dependence—namely, $e^{-i\omega t}$. Then the state will have the energy $E = \hbar\omega$. So we want a set for which

$$C_i = a_i e^{(-i/\hbar)Et}, \tag{12.17}$$

where the four coefficients a_i are independent of time. To see whether we can get such amplitudes, we substitute (12.17) into Eq. (12.14) and see what happens. Each $i\hbar\, dC/dt$ in Eq. (12.14) turns into EC, and—after cancelling out the common exponential factor—each C becomes an a; we get

$$\begin{aligned}Ea_1 &= Aa_1,\\ Ea_2 &= -Aa_2 + 2Aa_3,\\ Ea_3 &= 2Aa_2 - Aa_3,\\ Ea_4 &= Aa_4,\end{aligned} \tag{12.18}$$

which we have to solve for a_1, a_2, a_3, and a_4. Isn't it nice that the first equation is independent of the rest—that means we can see one solution right away. If we choose $E = A$,

$$a_1 = 1, \qquad a_2 = a_3 = a_4 = 0,$$

gives a solution. (Of course, taking all the a's equal to zero also gives a solution, but that's no state at all!) Let's call our first solution the state $|\,I\rangle$:‡

$$|\,I\rangle = |\,1\rangle = |+\,+\rangle. \tag{12.19}$$

Its energy is

$$E_I = A.$$

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† This operator is now called the "Pauli spin exchange operator."

‡ The state is really $|\,I\rangle e^{-(i/\hbar)E_I t}$; but, as usual we will identify the states by the constant vectors which are equal to the complete vectors at $t = 0$.

With that clue you can immediately see another solution from the last equation in (12.18):

$$a_1 = a_2 = a_3 = 0, \qquad a_4 = 1,$$
$$E = A.$$

We'll call that solution state $|\,II\rangle$:

$$|\,II\rangle = |\,4\rangle = |\,-\,-\rangle, \qquad E_{II} = A. \tag{12.20}$$

Now it gets a little harder; the two equations left in (12.18) are mixed up. But we've done it all before. Adding the two, we get

$$E(a_2 + a_3) = A(a_2 + a_3). \tag{12.21}$$

Subtracting, we have

$$E(a_2 - a_3) = -3A(a_2 - a_3). \tag{12.22}$$

By inspection—and remembering ammonia—we see that there are two solutions:

$$a_2 = a_3, \qquad E = A$$

and

$$a_2 = -a_3, \qquad E = -3A. \tag{12.23}$$

They are mixtures of $|\,2\rangle$ and $|\,3\rangle$. Calling these states $|\,III\rangle$ and $|\,IV\rangle$, and putting in a factor $1/\sqrt{2}$ to make the states properly normalized, we have

$$|\,III\rangle = \frac{1}{\sqrt{2}}(|\,2\rangle + |\,3\rangle) = \frac{1}{\sqrt{2}}(|\,+\,-\rangle + |\,-\,+\rangle), \qquad E_{III} = A \tag{12.24}$$

and

$$|\,IV\rangle = \frac{1}{\sqrt{2}}(|\,2\rangle - |\,3\rangle) = \frac{1}{\sqrt{2}}(|\,+\,-\rangle - |\,-\,+\rangle), \qquad E_{IV} = -3A. \tag{12.25}$$

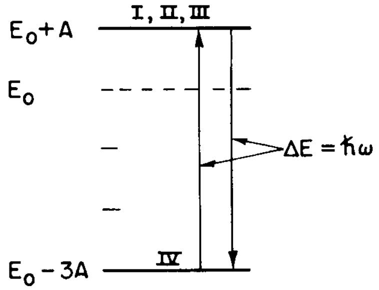

Fig. 12–2. Energy-level diagram for the ground state of atomic hydrogen.

We have found four stationary states and their energies. Notice, incidentally, that our four states are orthogonal, so they also can be used for base states if desired. Our problem is completely solved.

Three of the states have the energy A, and the last has the energy $-3A$. The average is zero—which means that when we took $E_0 = 0$ in Eq. (12.5), we were choosing to measure all the energies from the average energy. We can draw the energy-level diagram for the ground state of hydrogen as shown in Fig. 12–2.

Now the difference in energy between state $|\,IV\rangle$ and any one of the others is $4A$. An atom which happens to have gotten into state $|\,I\rangle$ could fall from there to state $|\,IV\rangle$ and emit light. Not optical light, because the energy is so tiny—it would emit a microwave quantum. Or, if we shine microwaves on hydrogen gas, we will find an absorption of energy as the atoms in state $|\,IV\rangle$ pick up energy and go into one of the upper states—but only at the frequency $\omega = 4A/\hbar$. This frequency has been measured experimentally; the best result, obtained very recently,† is

$$f = \omega/2\pi = (1{,}420{,}405{,}751.800 \pm 0.028)\text{ cycles per second.} \tag{12.26}$$

The error is only two parts in 100 billion! Probably no basic physical quantity is measured better than that—it's one of the most remarkably accurate measurements in physics. The theorists were very happy that they could compute the energy to an accuracy of 3 parts in 10^5, but in the meantime it has been measured to 2 parts in 10^{11}—a million times more accurate than the theory. So the experimenters are

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† Crampton, Kleppner, and Ramsey; *Physical Review Letters*, Vol. **11**, page 338 (1963).

way ahead of the theorists. In the theory of the ground state of the hydrogen atom *you* are as good as anybody. You, too, can just take your value of A from experiment—that's what everybody has to do in the end.

You have probably heard before about the "21-centimeter line" of hydrogen. That's the wavelength of the 1420 megacycle spectral line between the hyperfine states. Radiation of this wavelength is emitted or absorbed by the atomic hydrogen gas in the galaxies. So with radio telescopes tuned in to 21-cm waves (or 1420 megacycles approximately) we can observe the velocities and the location of concentrations of atomic hydrogen gas. By measuring the intensity, we can estimate the amount of hydrogen. By measuring the frequency shift due to the Doppler effect, we can find out about the motion of the gas in the galaxy. That is one of the big programs of radio astronomy. So now we are talking about something that's very real—it is not an artificial problem.

12–4 The Zeeman splitting

Although we have finished the problem of finding the energy levels of the hydrogen ground state, we would like to study this interesting system some more. In order to say anything more about it—for instance, in order to calculate the rate at which the hydrogen atom absorbs or emits radio waves at 21 centimeters—we have to know what happens when the atom is disturbed. We have to do as we did for the ammonia molecule—after we found the energy levels we went on and studied what happened when the molecule was in an electric field. We were then able to figure out the effects from the electric field in a radio wave. For the hydrogen atom, the electric field does nothing to the levels, except to move them all by some constant amount proportional to the square of the field—which is not of any interest because that won't change the energy *differences.* It is now the *magnetic* field which is important. So the next step is to write the Hamiltonian for a more complicated situation in which the atom sits in an external magnetic field.

What, then, is the Hamiltonian? We'll just tell you the answer, because we can't give you any "proof" except to say that this is the way the atom works.

The Hamiltonian is

$$\hat{H} = A(\boldsymbol{\sigma}^{\mathrm{e}} \cdot \boldsymbol{\sigma}^{\mathrm{p}}) - \mu_{\mathrm{e}}\boldsymbol{\sigma}^{\mathrm{e}} \cdot \boldsymbol{B} - \mu_{\mathrm{p}}\boldsymbol{\sigma}^{\mathrm{p}} \cdot \boldsymbol{B}. \tag{12.27}$$

It now consists of three parts. The first term $A\boldsymbol{\sigma}^{\mathrm{e}} \cdot \boldsymbol{\sigma}^{\mathrm{p}}$ represents the magnetic interaction between the electron and the proton—it is the same one that would be there if there were no magnetic field. This is the term we have already had; and the influence of the magnetic field on the constant A is negligible. The effect of the external magnetic field shows up in the last two terms. The second term, $-\mu_{\mathrm{e}}\boldsymbol{\sigma}^{\mathrm{e}} \cdot \boldsymbol{B}$, is the energy the electron would have in the magnetic field if it were there alone.† In the same way, the last term $-\mu_{\mathrm{p}}\boldsymbol{\sigma}^{\mathrm{p}} \cdot \boldsymbol{B}$, would have been the energy of a proton alone. Classically, the energy of the two of them together would be the sum of the two, and that works also quantum mechanically. In a magnetic field, the energy of interaction due to the magnetic field is just the sum of the energy of interaction of the electron with the external field, and of the proton with the field—both expressed in terms of the sigma operators. In quantum mechanics these terms are not really the energies, but thinking of the classical formulas for the energy is a way of remembering the rules for writing down the Hamiltonian. Anyway, the correct Hamiltonian is Eq. (12.27).

Now we have to go back to the beginning and do the problem all over again. Much of the work is, however, done—we need only to add the effects of the new terms. Let's take a constant magnetic field $\boldsymbol{B}$ in the z-direction. Then we have to

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† Remember that classically $U = -\boldsymbol{\mu} \cdot \boldsymbol{B}$, so the energy is lowest when the moment is along the field. For positive particles, the magnetic moment is parallel to the spin and for negative particles it is opposite. So in Eq. (12.27), μ_{p} is a *positive* number, but μ_{e} is a *negative* number.

add to our Hamiltonian operator $\hat{H}$ the two new pieces—which we can call $\hat{H}'$:

$$\hat{H}' = -(\mu_e\sigma_z^e + \mu_p\sigma_z^p)B.$$

Using Table 12–1, we get right away that

$$\begin{aligned} \hat{H}'\,|+\,+\rangle &= -(\mu_e + \mu_p)B\,|+\,+\rangle,\\ \hat{H}'\,|+\,-\rangle &= -(\mu_e - \mu_p)B\,|+\,-\rangle,\\ \hat{H}'\,|-\,+\rangle &= -(-\mu_e + \mu_p)B\,|-\,+\rangle,\\ \hat{H}'\,|-\,-\rangle &= (\mu_e + \mu_p)B\,|-\,-\rangle. \end{aligned} \tag{12.28}$$

How very convenient! The $\hat{H}'$ operating on each state just gives a number times that state. The matrix $\langle i\,|\,H'\,|\,j\rangle$ has, therefore, only *diagonal* elements—we can just add the coefficients in (12.28) to the corresponding diagonal terms of (12.13), and the Hamiltonian equations of (12.14) become

$$\begin{aligned} i\hbar dC_1/dt &= \{A - (\mu_e + \mu_p)B\}C_1,\\ i\hbar dC_2/dt &= -\{A + (\mu_e - \mu_p)B\}C_2 + 2AC_3,\\ i\hbar dC_3/dt &= 2AC_2 - \{A - (\mu_e - \mu_p)B\}C_3,\\ i\hbar dC_4/dt &= \{A + (\mu_e + \mu_p)B\}C_4. \end{aligned} \tag{12.29}$$

The form of the equations is not different—only the coefficients. So long as B doesn't vary with time, we can continue as we did before. Substituting $C_i = a_i e^{-(i/\hbar)Et}$, we get—as a modification of (12.18)—

$$\begin{aligned} Ea_1 &= A\,\{-\,(\mu_e + \mu_p)B\}a_1,\\ Ea_2 &= -\{A + (\mu_e - \mu_p)B\}a_2 + 2Aa_3,\\ Ea_3 &= 2Aa_2 - \{A - (\mu_e - \mu_p)B\}a_3,\\ Ea_4 &= \{A + (\mu_e + \mu_p)B\}a_4. \end{aligned} \tag{12.30}$$

Fortunately, the first and fourth equations are still independent of the rest, so the same technique works again.

One solution is the state $|\,I\rangle$ for which $a_1 = 1$, $a_2 = a_3 = a_4 = 0$, or

$$|\,I\rangle = |\,1\rangle = |+\,+\rangle,$$

with

$$E_I = A - (\mu_e + \mu_p)B. \tag{12.31}$$

Another is

$$|\,II\rangle = |\,4\rangle = |-\,-\rangle,$$

with

$$E_{II} = A + (\mu_e + \mu_p)B. \tag{12.32}$$

A little more work is involved for the remaining two equations, because the coefficients of a_2 and a_3 are no longer equal. But they are just like the pair we had for the ammonia molecule. Looking back at Eq. (9.20), we can make the following analogy (remembering that the labels 1 and 2 there correspond to 2 and 3 here):

$$\begin{aligned} H_{11} &\to -A - (\mu_e - \mu_p)B,\\ H_{12} &\to 2A,\\ H_{21} &\to 2A,\\ H_{22} &\to -A + (\mu_e - \mu_p)B. \end{aligned} \tag{12.33}$$

The energies are then given by (9.25), which was

$$E = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H_{12}H_{21}}\,. \tag{12.34}$$

Making the substitutions from (12.33), the energy formula becomes

$$E = -A \pm \sqrt{(\mu_e - \mu_p)^2 B^2 + 4A^2}.$$

Although in Chapter 9 we used to call these energies E_I and E_{II}, and we are in this problem calling them E_{III} and E_{IV},

$$\begin{aligned} E_{III} &= A\{-1 + 2\sqrt{1 + (\mu_e - \mu_p)^2 B^2/4A^2}\}, \\ E_{IV} &= -A\{1 + 2\sqrt{1 + (\mu_e - \mu_p)^2 B^2/4A^2}\}. \end{aligned} \tag{12.35}$$

So we have found the energies of the four stationary states of a hydrogen atom in a constant magnetic field. Let's check our results by letting B go to zero and seeing whether we get the same energies we had in the preceding section. You see that we do. For $B = 0$, the energies E_I, E_{II}, and E_{III} go to $+A$, and E_{IV} goes to $-3A$. Even our labeling of the states agrees with what we called them before. When we turn on the magnetic field though, all of the energies change in a different way. Let's see how they go.

First, we have to remember that for the electron, μ_e is negative, and about 1000 times larger than μ_p—which is positive. So $\mu_e + \mu_p$ and $\mu_e - \mu_p$ are both negative numbers, and nearly equal. Let's call them $-\mu$ and $-\mu'$:

$$\mu = -(\mu_e + \mu_p), \qquad \mu' = -(\mu_e - \mu_p). \tag{12.36}$$

(Both μ and μ' are positive numbers, nearly equal to magnitude of μ_e—which is about one Bohr magneton.) Then our four energies are

$$\begin{aligned} E_I &= A + \mu B, \\ E_{II} &= A - \mu B, \\ E_{III} &= A\{-1 + 2\sqrt{1 + \mu'^2 B^2/4A^2}\}, \\ E_{IV} &= -A\{1 + 2\sqrt{1 + \mu'^2 B^2/4A^2}\}. \end{aligned} \tag{12.37}$$

The energy E_I starts at A and increases linearly with B—with the slope μ. The

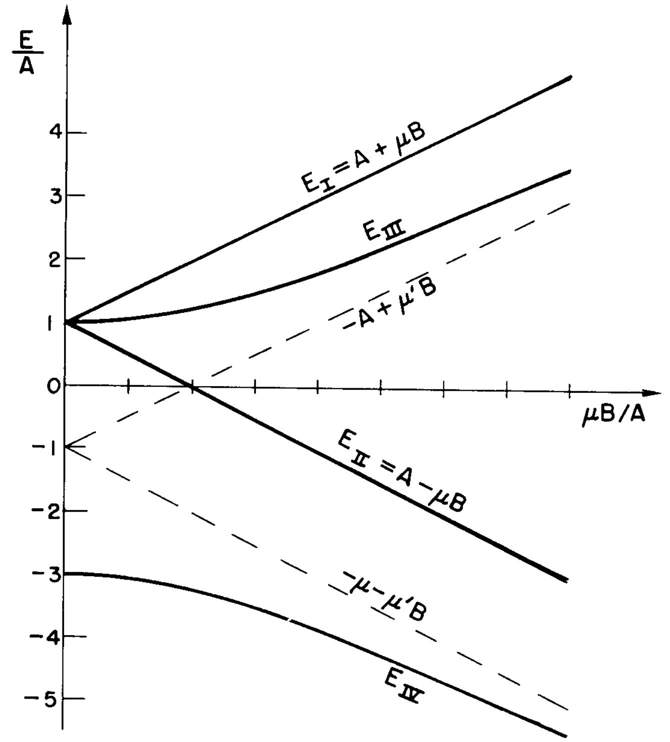

Fig. 12–3. The energy levels of the ground state of hydrogen in a magnetic field ***B***.

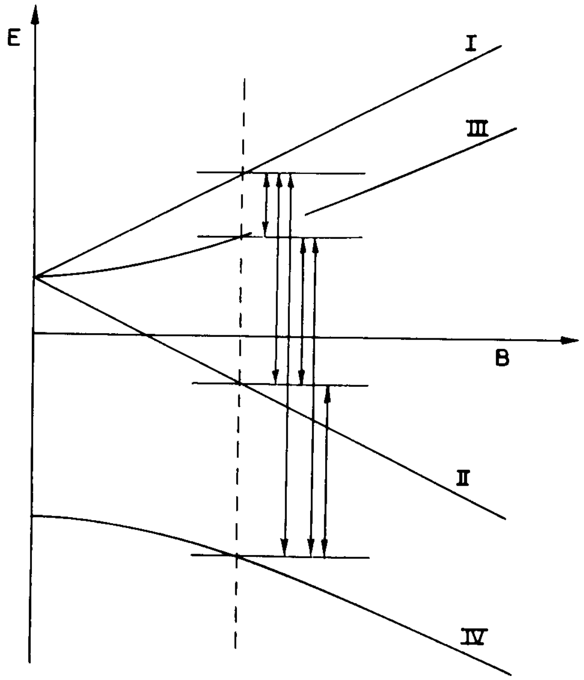

Fig. 12–4. Transitions between the levels of ground state energy levels of hydrogen in some particular magnetic field ***B***.

energy E_{II} also starts at A but *decreases* linearly with increasing B—its slope is $-\mu$. These two levels vary with B as shown in Fig. 12–3. We show also in the figure the energies E_{III} and E_{IV}. They have a different B-dependence. For small B, they depend quadratically on B, so they start out with horizontal slopes. Then they begin to curve, and for *large* B they approach straight lines with slopes $\pm\mu'$, which are nearly the same as the slopes of E_I and E_{II}.

The shift of the energy levels of an atom due to a magnetic field is called the *Zeeman effect*. We say that the curves in Fig. 12–3 show the *Zeeman splitting* of the ground state of hydrogen. When there is no magnetic field, we get just one spectral line from the hyperfine structure of hydrogen. The transitions between state $|\,IV\rangle$ and any one of the others occurs with the absorption or emission of a photon whose frequency 1420 megacycles is $1/h$ times the energy difference $4A$. When the atom is in a magnetic field $\boldsymbol{B}$, however, there are many more lines. There can be transitions between any two of the four states. So if we have atoms in all four states, energy can be absorbed—or emitted—in any one of the six transitions shown by the vertical arrows in Fig. 12–4. Many of these transitions can be observed by the Rabi molecular beam technique we described in Volume II, Section 35–3 (see Appendix).

What makes the transitions go? The transitions will occur if you apply a small disturbing magnetic field that varies with time (in addition to the steady strong field B). It's just as we saw for a varying electric field on the ammonia molecule. Only here, it is the magnetic field which couples with the magnetic moments and does the trick. But the theory follows through in the same way that we worked it out for the ammonia. The theory is the simplest if you take a perturbing magnetic field that rotates in the xy-plane—although any horizontal oscillating field will do. When you put in this perturbing field as an additional term in the Hamiltonian, you get solutions in which the amplitudes vary with time—as we found for the ammonia molecule. So you can calculate easily and accurately the probability of a transition from one state to another. And you find that it all agrees with experiment.

12–5 The states in a magnetic field

We would like now to discuss the shapes of the curves in Fig. 12–3. In the first place, the energies for large fields are easy to understand, and rather interesting. For B large enough (namely for $\mu B/A \gg 1$) we can neglect the 1 in the formulas of (12.37). The four energies become

$$\begin{aligned} E_I &= A + \mu B, & E_{II} &= A - \mu B,\\ E_{III} &= -A + \mu' B, & E_{IV} &= -A - \mu' B. \end{aligned} \tag{12.38}$$

These are the equations of the four straight lines in Fig. 12–3. We can understand these energies physically in the following way. The nature of the stationary states in a *zero* field is determined completely by the interaction of the two magnetic moments. The mixtures of the base states $|\,+\,-\rangle$ and $|\,-\,+\rangle$ in the stationary states $|\,III\rangle$ and $|\,IV\rangle$ are due to this interaction. In *large external* fields, however, the proton and electron will be influenced hardly at all by the field of the other; each will act as if it were alone in the external field. Then—as we have seen many times—the electron spin will be either parallel to or opposite to the external magnetic field.

Suppose the electron spin is "up"—that is, along the field; its energy will be $-\mu_e B$. The proton can still be either way. If the proton spin is also "up," its energy is $-\mu_p B$. The sum of the two is $-(\mu_e + \mu_p)B = \mu B$. That is just what we find for E_I—which is fine, because we are describing the state $|\,+\,+\rangle = |\,I\rangle$. There is still the small additional term A (now $\mu B \gg A$) which represents the interaction energy of the proton and electron when their spins are parallel. (We originally took A as positive because the theory we spoke of says it should be, and experimentally it is indeed so.) On the other hand, the proton can have its spin down. Then its energy in the external field goes to $-\mu_p B$, so it and the electron have the energy $-(\mu_e - \mu_p)B = \mu' B$. And the interaction energy becomes $-A$.

The sum is just the energy E_{III} in (12.38). So the state $| \, III \rangle$ must for large fields become the state $| + - \rangle$.

Suppose now the electron spin is "down." Its energy in the external field is $\mu_e B$. If the proton is also "down," the two together have the energy $(\mu_e + \mu_p)B = \mu B$, *plus* the interaction energy A—since their spins are parallel. That makes just the energy E_{II} in (12.38) and corresponds to the state $| - - \rangle = | \, II \rangle$—which is nice. Finally if the electron is "down" and the proton is "up," we get the energy $(\mu_e - \mu_p)B - A$ (*minus* A for the interaction because the spins are opposite) which is just E_{IV}. And the state corresponds to $| - + \rangle$.

"But, wait a moment!", you are probably saying, "The states $| \, III \rangle$ and $| \, IV \rangle$ *are not* the states $| + - \rangle$ and $| - + \rangle$; they are *mixtures* of the two." Well, only slightly. They are indeed mixtures for $B = 0$, but we have not yet figured out what they are for large B. When we used the analogies of (12.33) in our formulas of Chapter 9 to get the energies of the stationary states, we could also have taken the amplitudes that go with them. They come from Eq. (9.23), which is

$$\frac{a_2}{a_3} = \frac{E - H_{22}}{H_{11}}.$$

The ratio a_2/a_3 is, of course, just C_2/C_3. Plugging in the analogous quantities from (12.33), we get

$$\frac{C_2}{C_3} = \frac{E + A - (\mu_e - \mu_p)B}{2A}$$

or

$$\frac{C_2}{C_3} = \frac{E + A + \mu' B}{2A}, \tag{12.39}$$

where for E we are to use the appropriate energy—either E_{III} or E_{IV}. For instance, for state $| \, III \rangle$ we have

$$\left(\frac{C_2}{C_3}\right)_{III} \approx \frac{\mu' B}{A}. \tag{12.40}$$

So for large B the state $| \, III \rangle$ has $C_2 \gg C_3$; the state becomes almost completely the state $| \, 2 \rangle = | + - \rangle$. Similarly, if we put E_{IV} into (12.39) we get $(C_2/C_3)_{IV} \ll 1$; for high fields state $| \, IV \rangle$ becomes just the state $| \, 3 \rangle = | - + \rangle$. You see that the coefficients in the linear combinations of our base states which make up the stationary states depend on B. The state we call $| \, III \rangle$ is a 50–50 mixture of $| + - \rangle$ and $| - + \rangle$ at very low fields, but shifts completely over to $| + - \rangle$ at high fields. Similarly, the state $| \, IV \rangle$, which at low fields is also a 50–50 mixture (with opposite signs) of $| + - \rangle$ and $| - + \rangle$, goes over into the state $| - + \rangle$ when the spins are uncoupled by a strong external field.

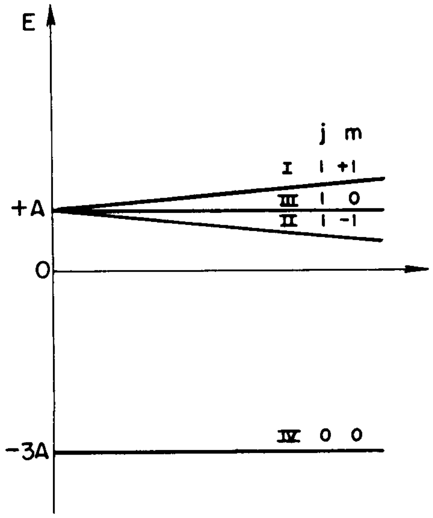

Fig. 12–5. The states of the hydrogen atom for small magnetic fields.

We would also like to call your attention particularly to what happens at *very low* magnetic fields. There is one energy—at $-3A$—which *does not change* when you turn on a small magnetic field. And there is another energy—at $+A$—which splits into three different energy levels when you turn on a small magnetic field. For weak fields the energies vary with B as shown in Fig. 12–5. Suppose that we have somehow selected a bunch of hydrogen atoms which all have the energy $-3A$. If we put them through a Stern-Gerlach experiment—with fields that are not too strong—we would find that they just go straight through. (Since their energy doesn't depend on B, there is—according to the principle of virtual work—no force on them in a magnetic field gradient.) Suppose, on the other hand, we were to select a bunch of atoms with the energy $+A$, and put them through a Stern-Gerlach apparatus, say an S apparatus. (Again the fields in the apparatus should not be so great that they disrupt the insides of the atom, by which we mean a field small enough that the energies vary linearly with B.) We would find *three beams*. The states $| \, I \rangle$ and $| \, II \rangle$ get opposite forces—their energies vary linearly with B with the slopes $\pm\mu$ so the *forces* are like those on a dipole with $\mu_z = \mp\mu$; but the state $| \, III \rangle$ goes straight through. So we are right back in Chapter 5. *A hydrogen atom with the energy $+A$ is a spin-one particle.* This energy state is a "particle" for which $j = 1$, and it can be described—with respect to some set of axes in space—in terms of the base states $|\,+S\rangle$, $|\,0\,S\rangle$, and $|\,-S\rangle$ we used in Chapter 5. On the other hand, when a hydrogen atom has the energy $-3A$, it is a spin-zero particle. (Remember, what we are saying is only strictly true for infinitesimal magnetic fields.) So we can group the states of hydrogen in zero magnetic field this way:

$$\left.\begin{aligned} |\,I\rangle &= |+\,+\rangle \\ |\,III\rangle &= \frac{|+\,-\rangle + |-\,+\rangle}{\sqrt{2}} \\ |\,II\rangle &= |-\,-\rangle \end{aligned}\right\}\text{ spin 1 }\left\{\begin{aligned} &|\,+S\rangle \\ &|\,0\,S\rangle \\ &|\,-S\rangle \end{aligned}\right. \tag{12.41}$$

$$|\,IV\rangle = \frac{|+\,-\rangle - |-\,+\rangle}{\sqrt{2}} \quad \text{spin 0.} \tag{12.42}$$

We have said in Chapter 35 of Volume II (Appendix) that for any particle its component of angular momentum along any axis can have only certain values always $\hbar$ apart. The z-component of angular momentum J_z can be $j\hbar$, $(j-1)\hbar$, $(j-2)\hbar, \dots, (-j)\hbar$, where j is the spin of the particle (which can be an integer or half-integer). Although we neglected to say so at the time, people usually write

$$J_z = m\hbar, \tag{12.43}$$

where m stands for one of the numbers $j, j-1, j-2, \dots, -j$. You will, therefore, see people in books label the four ground states of hydrogen by the so-called *quantum numbers j* and *m* [often called the "total angular momentum quantum number" (j), and "magnetic quantum number" (m)]. Then, instead of our state symbols $|\,I\rangle$, $|\,II\rangle$, and so on, they will write a state as $|\,j, m\rangle$. So they would write our little table of states for zero field in (12.41) and (12.42) as shown in Table 12-3. It's not new physics, it's all just a matter of notation.

Table 12-3

Zero field states of the hydrogen atom

State $\|\,j, m\rangle$	j	m	Our notation
$\|\,1, +1\rangle$	1	+1	$\|\,I\rangle = \|\,+S\rangle$
$\|\,1, 0\rangle$	1	0	$\|\,III\rangle = \|\,0\,S\rangle$
$\|\,1, -1\rangle$	1	−1	$\|\,II\rangle = \|\,-S\rangle$
$\|\,0, 0\rangle$	0	0	$\|\,IV\rangle$

12-6 The projection matrix for spin one †

We would like now to use our knowledge of the hydrogen atom to do something special. We discussed in Chapter 5 that a particle of *spin one* which was in one of the base states (+, 0, or −) with respect to a Stern-Gerlach apparatus of a particular orientation—say an S apparatus—would have a certain amplitude to be in each of the three states with respect to a T apparatus with a different orientation in space. There are nine such amplitudes $\langle jT\,|\,iS\rangle$ which make up the projection matrix. In Section 5-7 we gave without proof the terms of this matrix for various orientations of T with respect to S. Now we will show you one way they can be derived.

In the hydrogen atom we have found a spin-one system which is made up of two spin one-half particles. We have already worked out in Chapter 6 how to transform the spin one-half amplitudes. We can use this information to calculate the transformation for spin one. This is the way it works: We have a system—a hydrogen atom with the energy $+A$—which has spin one. Suppose we run it through a Stern-Gerlach filter S, so that we know it is in one of the base states with respect to S, say $|\,+S\rangle$. What is the amplitude that it will be in one of the base states, say $|\,+T\rangle$, with respect to the T apparatus? If we call the coordinate system of the S apparatus the x, y, z system, the $|\,+S\rangle$ state is what we have been calling the state $|+\,+\rangle$. But suppose another guy took his z-axis along the axis of T. He will be referring his states to what we will call the x', y', z' frame. His "up" and "down" states for the electron and proton would be different from ours. *His* "plus-plus" state—which we can write $|+'\,+'\rangle$, referring to the "prime" frame—is the $|\,+T\rangle$ state of the spin-one particle. What we want is $\langle +T\,|\,+S\rangle$ which is just another way of writing the amplitude $\langle +'\,+'\,|\,+\,+\rangle$.

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† Those who chose to jump over Chapter 6 should skip this section also.

We can find the amplitude $\langle +'\,+' \mid +\,+\rangle$ in the following way. In *our* frame the *electron* in the $\mid +\,+\rangle$ state has its spin "up". That means that it has some amplitude $\langle +' \mid +\rangle_e$ of being "up" in *his* frame, and some amplitude $\langle -' \mid +\rangle_e$ of being "down" in that frame. Similarly, the *proton* in the $\mid +\,+\rangle$ state has spin "up" in our frame and the amplitudes $\langle +' \mid +\rangle_p$ and $\langle -' \mid +\rangle_p$ of having spin "up" or spin "down" in the "prime" frame. Since we are talking about two distinct particles, the amplitude that *both* particles will be "up" *together* in *his* frame is the product of the two amplitudes,

$$\langle +'\,+' \mid +\,+\rangle = \langle +' \mid +\rangle_e \langle +' \mid +\rangle_p. \tag{12.44}$$

We have put the subscripts e and p on the amplitudes $\langle +' \mid +\rangle$ to make it clear what we were doing. But they are both just the transformation amplitudes for a spin one-half particle, so they are really identical numbers. They are, in fact, just the amplitude we have called $\langle +T \mid +S\rangle$ in Chapter 6, and which we listed in the tables at the end of that chapter.

Now, however, we are about to get into trouble with notation. We have to be able to distinguish the amplitude $\langle +T \mid +S\rangle$ for a *spin one-half* particle from what we have *also* called $\langle +T \mid +S\rangle$ for a *spin-one* particle—yet they are completely different! We hope it won't be too confusing, but *for the moment* at least, we will have to use some different symbols for the spin one-half amplitudes. To help you keep things straight, we summarize the new notation in Table 12-4. We will continue to use the notation $\mid +S\rangle$, $\mid 0\,S\rangle$, and $\mid -S\rangle$ for the states of a spin-one particle.

Table 12-4

Spin one-half amplitudes

This chapter	Chapter 6
$a = \langle +' \mid +\rangle$	$\langle +T \mid +S\rangle$
$b = \langle -' \mid +\rangle$	$\langle -T \mid +S\rangle$
$c = \langle +' \mid -\rangle$	$\langle +T \mid -S\rangle$
$d = \langle -' \mid -\rangle$	$\langle -T \mid -S\rangle$

With our new notation, Eq. (12.44) becomes simply

$$\langle +'\,+' \mid +\,+\rangle = a^2,$$

and this is just the spin-*one* amplitude $\langle +T \mid +S\rangle$. Now, let's suppose, for instance, that the other guy's coordinate frame—that is, the T, or "primed," apparatus—is just rotated with respect to *our* z-axis by the angle ϕ; then from Table 6-2,

$$a = \langle +' \mid +\rangle = e^{i\phi/2}.$$

So from (12.44) we have that the spin-one amplitude is

$$\langle +T \mid +S\rangle = \langle +'\,+' \mid +\,+\rangle = (e^{i\phi/2})^2 = e^{i\phi}. \tag{12.45}$$

You can see how it goes.

Now we will work through the general case for all the states. If the proton and electron are both "up" in *our* frame—the S-frame—the amplitudes that it will be in *any one of the four* possible states in the other guy's frame—the T-frame—are

$$\begin{aligned}
\langle +'\,+' \mid +\,+\rangle &= \langle +' \mid +\rangle_e \langle +' \mid +\rangle_p = a^2,\\
\langle +'\,-' \mid +\,+\rangle &= \langle +' \mid +\rangle_e \langle -' \mid +\rangle_p = ab,\\
\langle -'\,+' \mid +\,+\rangle &= \langle -' \mid +\rangle_e \langle +' \mid +\rangle_p = ba,\\
\langle -'\,-' \mid +\,+\rangle &= \langle -' \mid +\rangle_e \langle -' \mid +\rangle_p = b^2.
\end{aligned} \tag{12.46}$$

We can, then, write the state $\mid +\,+\rangle$ as the following linear combination:

$$\mid +\,+\rangle = a^2 \mid +'\,+'\rangle + ab\{\mid +'\,-'\rangle + \mid -'\,+'\rangle\} + b^2 \mid -'\,-'\rangle. \tag{12.47}$$

Now we notice that $\mid +'\,+'\rangle$ is the state $\mid +T\rangle$, that $\{\mid +'\,-'\rangle + \mid -'\,+'\rangle\}$ is just $\sqrt{2}$ *times* the state $\mid 0\,T\rangle$—see (12.41)—and that $\mid -'\,-'\rangle = \mid -T\rangle$. In other words, Eq. (12.47) can be rewritten as

$$\mid +S\rangle = a^2 \mid +T\rangle + \sqrt{2}\,ab \mid 0\,T\rangle + b^2 \mid -T\rangle. \tag{12.48}$$

In a similar way you can easily show that

$$\mid -S\rangle = c^2 \mid +T\rangle + \sqrt{2}\,cd \mid 0\,T\rangle + d^2 \mid -T\rangle. \tag{12.49}$$

For $|\,0\,S\rangle$ it's a little more complicated, because

$$|\,0\,S\rangle = \frac{1}{\sqrt{2}}\{|\,+\,-\rangle + |\,-\,+\rangle\}.$$

But we can express each of the states $|\,+\,-\rangle$ and $|\,-\,+\rangle$ in terms of the "prime" states and take the sum. That is,

$$|\,+\,-\rangle = ac\,|\,+'\,+'\rangle + ad\,|\,+'\,-'\rangle + bc\,|\,-'\,+'\rangle + bd\,|\,-'\,-'\rangle \tag{12.50}$$

and

$$|\,-\,+\rangle = ac\,|\,+'\,+'\rangle + bc\,|\,+'\,-'\rangle + ad\,|\,-'\,+'\rangle + bd\,|\,-'\,-'\rangle. \tag{12.51}$$

Taking $1/\sqrt{2}$ times the sum, we get

$$|\,0\,S\rangle = \frac{2}{\sqrt{2}}\,ac\,|\,+'\,+'\rangle + \frac{ad+bc}{\sqrt{2}}\{|\,+'\,-'\rangle + |\,-'\,+'\rangle\} + \frac{2}{\sqrt{2}}\,bd\,|\,-'\,-'\rangle.$$

It follows that

$$|\,0\,S\rangle = \sqrt{2}\,ac\,|\,+T\rangle + (ad+bc)\,|\,0\,T\rangle + \sqrt{2}\,bd\,|\,-T\rangle. \tag{12.52}$$

We have now all of the amplitudes we wanted. The coefficients of Eqs. (12.48), (12.49), and (12.52) are the matrix elements $\langle jT\,|\,iS\rangle$. Let's pull them all together:

$$\langle jT\,|\,iS\rangle = \begin{array}{cc} & \xrightarrow{iS} \\ jT\downarrow & \begin{pmatrix} a^2 & \sqrt{2}\,ac & c^2 \\ \sqrt{2}\,ab & ad+bc & \sqrt{2}\,cd \\ b^2 & \sqrt{2}\,bd & d^2 \end{pmatrix} \end{array} \tag{12.53}$$

We have expressed the spin-one transformation in terms of the spin one-half amplitudes a, b, c, and d.

For instance, if the T-frame is rotated with respect to S by the angle α about the y-axis—as in Fig. 5–6—the amplitudes in Table 12–4 are just the matrix elements of $R_y(\alpha)$ in Table 6–2.

$$\begin{aligned} a &= \cos\frac{\alpha}{2}, & b &= -\sin\frac{\alpha}{2}, \\ c &= \sin\frac{\alpha}{2}, & d &= \cos\frac{\alpha}{2}. \end{aligned} \tag{12.54}$$

Using these in (12.53), we get the formulas of (5.38), which we gave there without proof.

What ever happened to the state $|\,IV\rangle$?! Well, it is a spin-zero system, so it has only one state—it is the *same in all coordinate systems.* We can check that everything works out by taking the difference of Eq. (12.50) and (12.51); we get that

$$|\,+\,-\rangle - |\,-\,+\rangle = (ad-bc)\{|\,+'\,-'\rangle - |\,-'\,+'\rangle\}.$$

But $(ad-bc)$ is the determinant of the spin one-half matrix, and so is equal to 1. We get that

$$|\,IV'\rangle = |\,IV\rangle$$

for any relative orientation of the two coordinate frames.