The Bohren Experiment

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How can a particle absorb more than the light incident on it?

Craig F. Bohren
Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania 16802

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A particle can indeed absorb more than the light incident on it. Metallic particles at ultraviolet frequencies are one class of such particles and insulating particles at infrared frequencies are another. In the former strong absorption is associated with excitation of surface plasmons; in the latter it is associated with excitation of surface phonons. In both instances the target area a particle presents to incident light can be much greater than its geometrical cross-sectional area. This is strikingly evident from the field lines of the Poynting vector in the vicinity of a small sphere illuminated by a plane wave.

I. INTRODUCTION

Several years ago a friend of mine was on the last leg of a long journey to a conference nearly halfway across the world from his home. Exhausted, disoriented, lost in thought, his reverie was suddenly and unexpectedly interrupted by a fellow conferee in the adjacent seat, who turned to him and asked anxiously: "How can a particle absorb more than the light incident on it?"

To those who first encountered in neutron physics the concept of the area that a target presents to a projectile (i.e., its cross section), it comes as no surprise that targets can sometimes extend beyond their strict geometrical boundaries, even greatly so. Indeed, the very unit for neutron cross sections, the barn, encourages one to think big. But pho-

by

$$\omega_p^2 = Ne^2/m\varepsilon_0, \qquad (1)$$

where e and m are the electronic charge and mass, and ε_0 is the permittivity of free space.

A plasma oscillation is longitudinal and originates from long-range correlations of the electrons caused by Coulomb forces. Such plasma oscillations in gaseous discharges were investigated theoretically and experimentally by Tonks and Langmuir.[1] Further refinements to the classical theory were added by Bohm and Gross[2]; this in turn led to a series of papers on the quantum theory of plasma oscillations by Bohm and Pines.[3]

The frequency of longitudinal oscillation in a medium sections, the barn, encourages one to think big. But photons are supposed to behave more soberly than neutrons; every physics student knows that photons travel through free space mostly in straight lines, although they do sometimes exhibit a bit of waywardness in the vicinity of edges. Notions about what photons can and cannot do are formed in traditional optics courses, which emphasize visible light interacting with large bodies, usually transparent. With time these notions become deep-seated prejudices and are often difficult to dislodge. Yet it is incontrovertible that there are many circumstances, by no means exotic, under which small particles (smaller than the wavelength) can absorb more than the light incident on them. My first task in this paper is to examine some of these circumstances. Then I shall give a pictorial representation of absorption of light by a particle in a way which, to the best of my knowledge, has not been done before.

II. PLASMONS AND PHONONS IN SMALL CRYSTALS

A. Bulk plasmons

Let us take as a simple model of a metal a gas of free electrons moving against a fixed background of immobile positive ions. The number density $\mathcal{N}$ of positive ions is therefore constant in space and time; in equilibrium the density of electrons is also $\mathcal{N}$. But if the electrons are somehow disturbed slightly from equilibrium the nonuniform charge distribution will set up an electric field which will tend to restore charge neutrality. The electrons, having acquired momentum from the field, will overshoot the equilibrium configuration: there will be an oscillation. This collective oscillation of the electron gas is called a plasma oscillation; its frequency, the plasma frequency ω_p is given

emerges from examination of the equations of the electromagnetic field; we need only the first of them [assuming harmonic time dependence $\exp(-i\omega t)$]:

$$\epsilon(\omega)\nabla\cdot\mathbf{E}(\omega) = 0,$$

where $\mathbf{E}$ is the electric field and the dielectric function[4] $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ is the permittivity of the medium relative to that of free space.

There are two cases to be considered. At frequencies where ϵ does not vanish the divergence of the electric field must; in this instance the field is transverse. But at frequencies where $\epsilon = 0$ the divergence of $\mathbf{E}$ need not vanish; such a field is longitudinal. The frequencies at which the medium can support longitudinal oscillations are therefore the roots of

$$\epsilon(\omega) = 0.$$

The dielectric function of a simple free-electron metal is given by the Drude formula

$$\epsilon(\omega) = 1 - \omega_p^2/(\omega^2 + i\gamma\omega), \tag{2}$$

where ω_p is as in (1) and γ is a damping coefficient. The frequency $\omega \simeq \omega_p - i\gamma/2$ (assuming $\omega_p \gg \gamma$) at which ϵ in (2) is zero is therefore complex; this just means that the plasma oscillation is damped.

In quantum-mechanical language excitation of a plasma oscillation is referred to as creation (or excitation) of a *plasmon*, the quantum of plasma oscillation, with energy $\hbar\omega_p$ and lifetime $\tau = 2/\gamma$. For a plasmon to be a well-defined entity it must be sufficiently long lived ($\omega_p\tau \gg 1$).

Up to this point I have tacitly assumed that the plasma is unbounded; that is to say, I have had in mind *bulk plasmons*. Because of the long-range nature of the organizing forces in a plasma oscillation, however, it is reasonable to

expect that for a sufficiently small system the electrons will sense the presence of the boundaries and modify their collective behavior accordingly. Indeed, following hard on the heels of the acceptance of bulk plasmons in metals came the realization that *surface plasmons* were possible in thin films.[5] Whereas the energy of a bulk plasmon is $\hbar\omega_p$, that of a surface plasmon in a thin film (in air) is $\hbar\omega_p/\sqrt{2}$. The next member in this family of plasmons is the surface plasmon in a sphere. The easiest route to its energy is classical; this route is followed below.

B. Surface plasmons

Suppose that a spherical particle of radius a is illuminated by a plane monochromatic wave with irradiance[6] I_i. The rates at which energy is absorbed by the particle and scattered in all directions are products of the irradiance and the cross sections—so named because they have the dimensions of area—for absorption and scattering:

$$W_{\text{abs}} = I_i C_{\text{abs}}, \quad W_{\text{sca}} = I_i C_{\text{sca}}.$$

It is customary, but by no means necessary, to normalize these cross-sectional areas:

$$Q_{\text{abs}} = C_{\text{abs}}/\pi a^2, \quad Q_{\text{sca}} = C_{\text{sca}}/\pi a^2. \tag{3}$$

The resulting dimensionless quantities are referred to as *efficiencies* (or efficiency factors) for absorption and scattering. This term is poorly chosen: the efficiencies in (3) are not bounded by unity, as the word efficiency implies. Normalized cross section would be a better term.

If the particle is sufficiently small compared with the wavelength then the approximate expressions for the absorption and scattering efficiencies are[7]

shifts to a lower value because of the presence of the boundaries. In the language of elementary excitations there is a bulk plasmon with energy $\hbar\omega_p$ in an unbounded metal and a surface plasmon with energy $\hbar\omega_F$ in a small metallic sphere.

Absorption at the Fröhlich frequency is not infinite, but it can be quite large depending on the value of ϵ'', the imaginary, or absorptive, part of the dielectric function. This dependence, however, is contrary to what one might expect: absorption is *inversely* proportional to ϵ'' at the frequency where ϵ' is approximately -2. That is, it follows from (4) that

$$Q_{\text{abs}}(\omega_F) = 12x/\epsilon''(\omega_F). \tag{5}$$

Note that, although x is small, Q_{abs} may be large because ϵ'' may also be small.

Up to this point I have tacitly assumed that the particles are in air. If they are not, as in many laboratory investigations, then the effect of a surrounding nonvacuous medium is to shift the Fröhlich frequency to lower values. This shift can be appreciable, so it is well to be cognizant of it.

It is reasonable to expect that if the frequency of collective oscillation of electrons changes in going from an infinite to a finite medium, then this frequency will depend on the shape of the medium as well. This is indeed true, but to discuss shape effects would lead us too far afield.

C. Surface phonons

Consider now collective oscillations of lattice ions in, say, an ionic solid like NaCl, which when quantized are called phonons. If the frequency of collective oscillation of

$$Q_{abs} \simeq 4x \, \text{Im}\left(\frac{\epsilon - 1}{\epsilon + 2}\right), \quad Q_{sca} \simeq \frac{8}{3} x^4 \left|\frac{\epsilon - 1}{\epsilon + 2}\right|^2 \quad \left.\begin{matrix} x \ll 1 \\ |\sqrt{\epsilon}|x \ll 1, \end{matrix}\right. \tag{4}$$

where the *size parameter* x is the particle's circumference divided by the wavelength ($2\pi a/\lambda$).

The conventional wisdom has it that because the size parameter is small, then small particles are "inefficient" absorbers and scatterers of light: an inappropriate noun spawns an even more inappropriate adjective. Let us leave aside the fact that because the term "efficiency" is really quite meaningless it is also meaningless to describe small particles as inefficient. In (4) there are expressions involving ϵ, often overlooked because they are small—sometimes. But it is difficult to stare at these expressions for long without an itch to set their denominators equal to zero and to ask: Are there any materials with the property that $\epsilon = -2$ at some frequency? For if there are, then such materials when fashioned into very small spheres will be strong absorbers and scatterers of light of this frequency. The answer to this question is that there are many such materials: free-electron metals, for example. The frequency at which the Drude dielectric function (2) is -2 is complex; but if $\gamma \ll \omega_p$, then the real part is approximately $\omega_p/\sqrt{3}$, which is sometimes denoted as the *Fröhlich frequency* ω_F.

We may interpret this as follows. In an unbounded metal the frequency of collective oscillation of the electrons is ω_p, the plasma frequency. But when the electrons are confined to a small sphere the frequency of collective oscillation electrons depends on the size and shape of their container then so does that of collective lattice oscillations. That is, if there are surface plasmons then there may be *surface phonons* as well. An excellent review of phonons in small crystals has been given by Ruppin and Englman.[8]

The starting point for a discussion of surface phonons is the Lorentz dielectric function for a system of identical oscillators

$$\epsilon(\omega) = \epsilon_\infty + \frac{\omega_p^2}{\omega_t^2 - \omega^2 - i\gamma\omega}. \tag{6}$$

Because the mass of an ion is so much greater than that of an electron the frequency ω_p in (6) is much lower—in the infrared—than plasma frequencies for metals, which are usually in the ultraviolet. The *transverse optical mode frequency* ω_t is the frequency at which ϵ'' is a maximum (approximately). Another frequency of importance is the *longitudinal optical mode frequency* ω_l, given by

$$\omega_l^2/\omega_t^2 = \epsilon_0/\epsilon_\infty,$$

where ϵ_0 and ϵ_∞ are low-frequency and high-frequency limits of (6); ω_l is the frequency at which ϵ is zero (approximately), hence the designation longitudinal.

For materials described to good approximation by (6)—alkali halides at infrared frequencies, for example—the Fröhlich frequency lies between ω_t and ω_l:

$$\omega_F^2 = \omega_t^2\left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\right).$$

On the basis of the results of the previous paragraphs there are two classes of small particles which, at some frequencies, are expected to appear larger to an incoming beam than their geometrical cross sections: metallic parti-

cles at ultraviolet frequencies and insulating particles at infrared frequencies. It is easy enough to compute absorption efficiencies for small spheres and note that, yes indeed, they can be greater than unity. But it seems more physically satisfying and visually appealing—as well as pedagogically more effective—to examine how the Poynting vector behaves in the vicinity of a small sphere, both at and away from the Fröhlich frequency; this is done in Sec. III.

III. FIELD LINES OF THE POYNTING VECTOR

A. Derivation of the basic equation

The magnitude and direction of energy flow in an electromagnetic field is specified by the Poynting vector. In the region outside a sphere illuminated by a plane harmonic wave the electric (magnetic) field is the sum of the incident field $\mathbf{E}_i$ ($\mathbf{H}_i$) and the scattered field $\mathbf{E}_s$ ($\mathbf{H}_s$). The total Poynting vector **S** (time-averaged) in this region may therefore be written as

$$\mathbf{S} = \mathbf{S}_i + \mathbf{S}_s + \mathbf{S}_{\text{ext}},$$

where

$$\mathbf{S}_i = \tfrac{1}{2}\,\mathrm{Re}(\mathbf{E}_i \times \mathbf{H}_i^*),$$

$$\mathbf{S}_s = \tfrac{1}{2}\,\mathrm{Re}(\mathbf{E}_s \times \mathbf{H}_s^*),$$

$$\mathbf{S}_{\text{ext}} = \tfrac{1}{2}\,\mathrm{Re}(\mathbf{E}_i \times \mathbf{H}_s^* + \mathbf{E}_s \times \mathbf{H}_i^*).$$

We may interpret $\mathbf{S}_{\text{ext}}$ as the term which arises because of interaction between the incident and scattered fields; the subscript ext indicates that the integral of $\mathbf{S}_{\text{ext}}$ over a surface surrounding the particle is, for unit incident irradiance, the extinction cross section—the sum of the absorption and scattering cross sections. $\mathbf{S}_s$ is associated solely with the scattered field. Of greater interest here

sphere.[11] Vector spherical harmonics are generated by solutions ψ of the scalar wave equation in spherical polar coordinates r, θ, ϕ:

$$\mathbf{M} = \nabla \times (\mathbf{r}\psi), \quad \mathbf{N} = \nabla \times \mathbf{M}/k,$$

where **r** is the radius vector. The generating functions for the vector harmonics in (7) are[12]

$$\psi_{e1n} = \cos\phi\, P_n^1(\cos\theta)\, h_n^{(1)}(kr),$$

$$\psi_{o1n} = \sin\phi\, P_n^1(\cos\theta)\, h_n^{(1)}(kr),$$

where P_n^1 is an associated Legendre function of the first kind and $h_n^{(1)}$ is a spherical Hankel function.

If the sphere is sufficiently small compared with the wavelength of the incident light then a_1 is the dominant coefficient, and in this instance

$$\mathbf{E}_s \simeq -\tfrac{3}{2} a_1 E_0 \mathbf{N}_{e11}^{(3)}, \quad \mathbf{H}_s \simeq \frac{3i}{2k\omega\mu}\, a_1 E_0 \mathbf{M}_{e11}^{(3)},$$

$$a_1 \simeq \frac{-i2x^3}{3}\,\frac{\epsilon - 1}{\epsilon + 2}.$$

The ϕ component of **A** is zero in the xz plane ($\phi = 0$). In this plane, therefore, the field lines are solutions to the differential equation

$$dr/d\theta = rA_r/A_\theta. \tag{8}$$

All the ingredients are at hand for writing (8) in explicit form, a laborious task the details of which are best omitted; the result is

$$d\rho/d\theta = -\rho\cos\theta/\sin\theta\,\{\rho^3 + [(x^2\rho^2\cos\theta + x^2\rho^2 - 1)(K_r\cos\xi + K_i\sin\xi) + (x\rho\cos\theta + x\rho)(K_r\sin\xi - K_i\cos\xi)]\}/\{\rho^3$$

solely with the scattered field. Of greater interest here, however, is the flow of electromagnetic energy exclusive of that scattered. Thus the Poynting vector under consideration (normalized by I_i, the magnitude of $\mathbf{S}_i$) is

$$\mathbf{A} = (\mathbf{S}_i + \mathbf{S}_{ext})/I_i.$$

Were it not for the particle, of course, $\mathbf{A}$ would just be a unit vector parallel to the direction of propagation of the incident wave, and the field lines would be parallel lines. At sufficiently large distances from the sphere the field lines are nearly parallel, but close to the sphere they are distorted. It is the nature of this distortion, and its relation to the properties of the sphere at the frequency of the incident wave, that I wish to investigate.

If the incident electric field is polarized along the x axis and propagating in the $+z$ direction, then the electric and magnetic fields [omitting the time-harmonic factor $\exp(-i\omega t)$] are

$$\mathbf{E}_i = E_0 e^{ikz}\hat{e}_x, \quad \mathbf{H}_i = (k/\omega\mu)E_0 e^{ikz}\hat{e}_y,$$

where $k = 2\pi/\lambda$ and μ is the permeability of the medium surrounding the particle (assumed to be free space). The field scattered by a sphere of arbitrary radius is an infinite series in vector spherical harmonics[9,10]

$$\mathbf{E}_s = \sum E_n (ia_n \mathbf{N}^{(3)}_{e1n} - b_n \mathbf{M}^{(3)}_{o1n}),$$

$$\mathbf{H}_s = \frac{k}{\omega\mu} \sum E_n (ib_n \mathbf{N}^{(3)}_{o1n} + a_n \mathbf{M}^{(3)}_{e1n}), \qquad (7)$$

$$E_n = i^n E_0 (2n+1)/n(n+1),$$

where the *scattering coefficients* a_n and b_n are complicated functions of the radius and optical properties of the

$$+ [(x^2\rho^2 \cos\theta + 2)(K_r \cos\xi + K_i \sin\xi)$$
$$+ (x\rho\cos\theta - 2x\rho)(K_r \sin\xi - K_i \cos\xi)]\}, \qquad (9)$$

where $K = K_r + iK_i = (\epsilon - 1)/(\epsilon + 2)$, $\xi = x\rho(\cos\theta - 1)$, and $\rho = r/a$. Subject to restrictions on the size of the particle, (9) is completely general: it gives the field lines of the Poynting vector right up to the boundary of the sphere.

Equation (9) was solved numerically with a fourth-order Runge–Kutta scheme. It was usually more convenient to recast (9) as a differential equation in the rectangular Cartesian coordinates; sometimes, however, the advantage was tipped in favor of the polar coordinates. The results given in the following section were obtained with a mixture of the two approaches.

B. Field lines

To good approximation, particularly in the far ultraviolet, the dielectric function of aluminum is given by the Drude formula (2). At a photon energy of about 8.8 eV—the surface plasmon energy—the real part of the dielectric function of aluminum[13] is -2; the corresponding imaginary part is about 0.2. It follows from (4) or (5), therefore, that the absorption efficiency of a small aluminum sphere (in air) with size parameter 0.3 is about 18: such a sphere presents to incident photons a target area 18 times greater than its geometrical cross-sectional area. This conclusion follows from a simple back-of-the-envelope calculation. More palpable evidence of the sphere's great size in this instance is provided by Fig. 1, which shows the field lines of the Poynting vector in the surrounding region. Note the strong convergence of field lines near the sphere; light that, from the point of view of ray optics, would have passed the

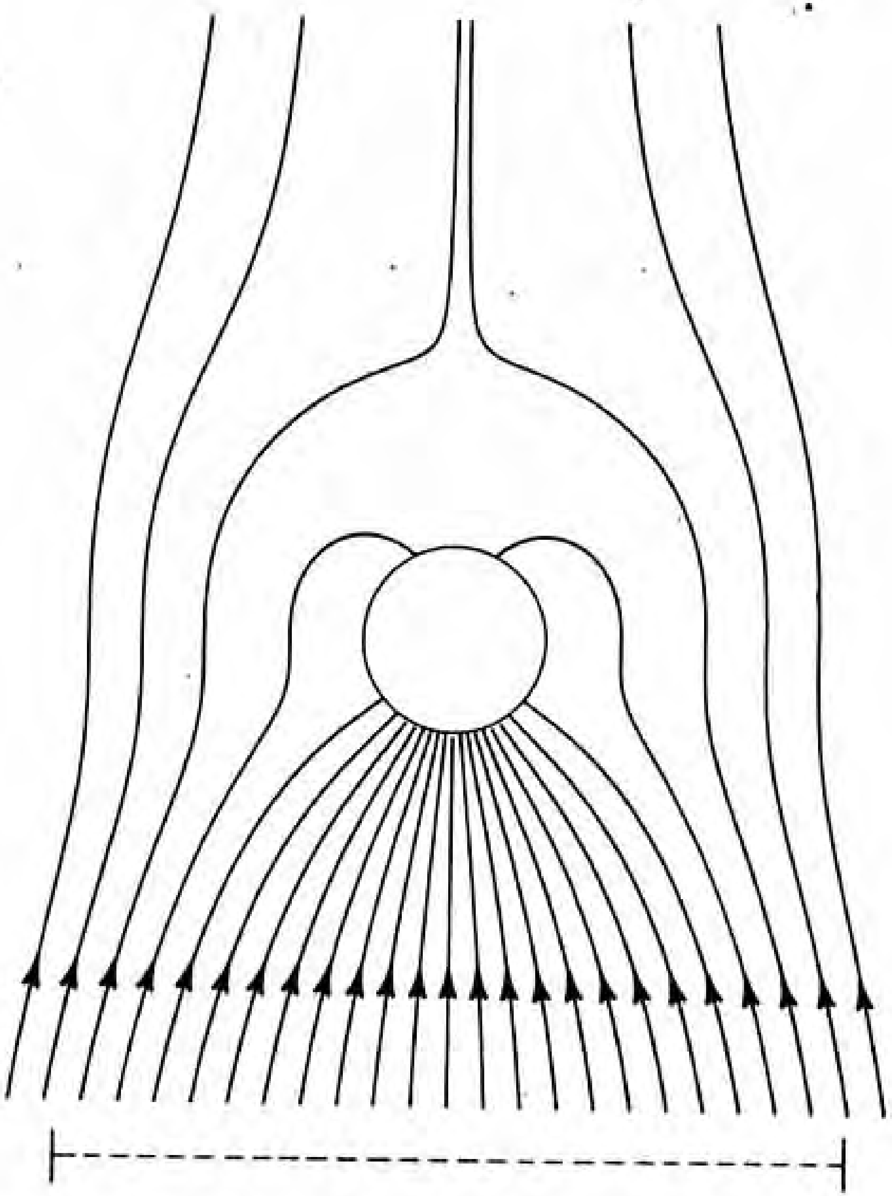

Fig. 1. Field lines of the total Poynting vector (excluding that scattered) around a small aluminum sphere illuminated by light of energy 8.8 eV. The dashed vertical line indicates the effective size of the sphere for absorption of incident light.

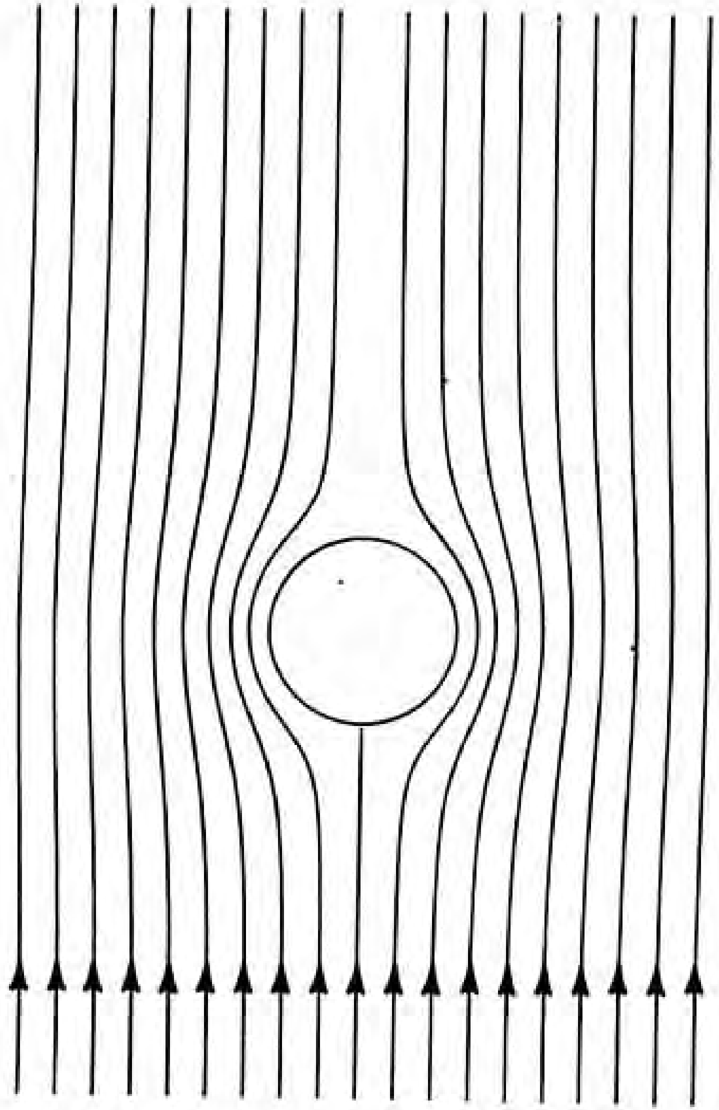

Fig. 2. Field lines of the total Poynting vector (excluding that scattered) around a small aluminum sphere illuminated by light of energy 5 eV.

IV. CONCLUDING REMARKS

sphere without impediment, is deflected toward it.

An absorption cross section 18 times greater than the geometrical cross section implies that the absorption radius—to coin a term—is about 4.2 times greater than the geometrical radius. This follows from the analytical expression (5), but it should also emerge from purely geometrical reasoning. And indeed it does: note in Fig. 1 that those field lines extending to about 3.9 times the particle radius converge onto the particle.

At other frequencies, on either side of 8.8 eV, a small aluminum sphere presents a much smaller target to incident photons. At 5 eV, for example, the absorption efficiency of a sphere with $x = 0.3$ is about 0.1; as far as absorption is concerned, the sphere is much smaller than its geometrical cross-sectional area. The field lines of the Poynting vector, shown in Fig. 2, are what are to be expected for such a small target; a few lines intersect the sphere, but most are deflected around it.

Silicon carbide is an insulating solid the infrared dielectric function of which is well approximated by the Lorentz formula (6).[14] The Fröhlich frequency $(1/\lambda_F)$ for SiC is about 932 cm^{-1} and its dielectric function at this frequency is quite close to that of aluminum at 8.8 eV. So Fig. 1 also shows the field lines of the Poynting vector around a small SiC sphere illuminated by light at the Fröhlich frequency. On either side of this frequency, however, the sphere is much less absorbing; at 900 cm^{-1}, for example, where the dielectric function of SiC is about $-4.8 + 0.3i$, the absorption efficiency (for $x = 0.3$) is about 0.13; in this instance the field lines are quite similar to those shown in Fig. 2 for aluminum at 5 eV.

No textbook on electromagnetic theory would be complete without a figure showing the field lines around a sphere in an electrostatic field. The reason, of course, is that this is a very effective way of presenting an idea—the sphere distorts the otherwise uniform field—in such a way that it can be grasped at a glance. But a small sphere illuminated by a plane wave also disturbs the flow of electromagnetic energy in its neighborhood. To the best of my knowledge, a graphic illustration of this has never been given. Yet the field lines of the Poynting vector (exclusive of the scattered Poynting vector) around the sphere help to elucidate how a particle can absorb more than the light incident on it.

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Scientific work hardly seems worth the effort unless at least one other person responds to it. I am grateful in this instance for the enthusiastic endorsement of my colleagues Sean Twomey, Alistair Fraser, Donald Huffman, John Olivero, and Timothy Nevitt, without which I would not have undertaken this work in good spirits. I also thank Peter Shaw for discussing some of the ideas in this paper with me.

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Comment on "How can a particle absorb more than the light incident on it?"

H. Paul and R. Fischer
Zentralinstitut für Optik und Spektroskopie, Akademie der Wissenschaften der DDR, DDR-1199 Berlin, Rudower Chaussee 6, German Democratic Republic

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Independently of the work by C. F. Bohren,[1] we investigated the same problem,[2] however, on the atomic scale. Specifically, we considered the following physical picture: In the presence of an intense (plane-wave-type) coherent resonant monochromatic electromagnetic field, an atom, being initially nonexcited, acquires an electric dipole moment—in the sense of the quantum-mechanical expectation value. This dipole moment, oscillating at the frequen-

the atom has taken up the energy of a single photon. Physically, the essential difference between our results and that of Bohren is that we found the effective absorption cross section of an atom to decrease with growing intensity of the incident field as the inverse of the field amplitude, while the corresponding quantity for a macroscopic particle (with dimensions still small compared with the wavelength) proved to be independent of the field in Ref. 1.

cy of the incident field, according to classical electrodynamics emits a wave which interferes with the incoming wave.

We found that the energy flux lines in the superposition field are bent, in a rather large neighborhood of the atom, in such a way as to direct energy into the atom. In fact, the corresponding curves in the x, z plane are very similar to those presented by Bohren.

In contrast to his paper, we had to deal with a transient phenomenon—the absorption process being finished when

From our study, it becomes evident that the wave picture quite naturally accounts for the well-known large effective absorption cross sections, compared to the geometrical ones, of atomic systems, while the particle picture certainly fails to do so.

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