Resonant scattering of light by small particles

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An investigation is reported of the scattering of electromagnetic radiation by a small particle when the radiation frequency is close to one of the eigenfrequencies of the particle in the incident field. It is shown that, when the imaginary part of the relative permittivity of the scattering particle is not too high, the main effect restricting the amplitude of the scattered wave is nondissipative damping due to the nonuniform electric-field distribution within the particle (departure from quasistationarity of the scattering process). The partial scattering amplitudes corresponding to resonant excitation of electric dipole, or any other electric multipole, moments are then of the same order of magnitude.

1. It is well-known that the problem of scattering of electromagnetic radiation by spherical particles has an exact solution, obtained in the classic paper by Mie.[1] For a small particle, the partial scattering amplitudes corresponding to the excitation of the 2^l-pole electric moment ${}^eB_l$ are then found to be proportional to q^{2l+1}, whereas for the 2^l-pole magnetic moment ${}^mB_l \sim q^{2l+3}$ where $q = ak^{\mathrm{I}} \ll 1$, a is the radius of the particle, $k^{\mathrm{I}} = n^{\mathrm{I}}\omega/c$ is the wavenumber of the scattered wave, and $n^{\mathrm{I}} > 0$ is the refractive index of the medium in which the particle is localized. From this it is concluded that, for small particles, the main contribution to the scattering process is provided by the excitation of the electric dipole moment: $|{}^eB_1| \gg |{}^{e,m}B_l|$ for $l \geqslant 2$ (Ref. 2).

It will be shown below that this is not always the case. In fact, when q is small enough, the only universal inequality is $|{}^eB_1| \geqslant |{}^mB_l|$. As for the amplitudes ${}^eB_l$, these quantities contain "resonance denominators" of the form $\hat{n}^2 + (l+1)/l$ where $\hat{n}$ is the complex refractive index of the particle relative to the ambient medium: $n \equiv n^{\mathrm{II}}/n^{\mathrm{I}}$. It follows that the corresponding scattering amplitude diverges when the frequency of the incident radiation is equal to one of the resonance frequencies $\omega = \omega_l$, where ω_l satisfies the condition $\hat{n}^2(\omega_l) = -(l+1)/l$. Since the poles of the scattering amplitude determine the oscillation-mode spectrum, it is clear that the reason for the divergence is the resonant excitation of field oscillation modes by the scattered wave. When dissipative losses are low enough, the inhomogeneity of the electric-field distribution within the particle (departure from the quasistationarity of the scattering process) begins to play a significant role, so that the simple scattering-theory formulas that are normally used to describe the phenomenon[3] lose their validity.

2. We now turn to the exact solution to the problem. According to this solution[2]

$$ {}^eB_l = i^{l+1}\frac{2l+1}{l(l+1)}\frac{\hat{n}\psi_l'(q)\psi_l(\hat{n}q)-\psi_l(q)\psi_l'(\hat{n}q)}{\hat{n}\zeta_l^{(1)\prime}(q)\psi_l(\hat{n}q)-\zeta_l^{(1)}(q)\psi_l'(\hat{n}q)}, \quad (1) $$

where

$$ \psi_l(z) = (\pi z/2)^{1/2}J_{l+1/2}(z); \qquad \zeta_l^{(1)}(z) = (\pi z/2)^{1/2}H_{l+1/2}^{(1)}(z), $$

where $J_{l+1/2}(z)$ and $H_{l+1/2}^{(1)}(z)$ are, respectively, the Bessel and Hankel functions. Next, we use the well-known representations of these functions[4]

$$ J_\nu(z) = \left(\frac{z}{2}\right)^\nu \sum_{m=0}^{\infty}\frac{(-z^2/4)^m}{m!\,\Gamma(\nu+m+1)}, \quad (2) $$

$$ H_\nu^{(1)}(z) = -\frac{i}{\sin\pi\nu}\{J_{-\nu}(z) - e^{-i\pi\nu}J_\nu(z)\}. \quad (3) $$

The essential point is that the coefficients of the series given by (2) are real numbers. Hence, for small q, it is sufficient to retain only the first term in this series, since the inclusion of the higher-order terms merely gives rise to a small change in the resonance frequency ω_l.

As for (3), we see that, despite the fact that the order of magnitude of the term in the expansion for $J_{l+1/2}(z)$ in powers of z is lower than the order of the discarded terms in the expansion for $J_{-l-1/2}(z)$, it is essential to take it into account because the complex factor $\exp[-i\pi(l+1/2)]$ is present in (3). In view of the foregoing, equation (1) can be readily reduced to the form

$$ {}^eB_l = i^l q^{2l+1}\frac{\hat{n}^2-1}{[(2l-1)!!]^2}\left\{l^2\left(\hat{n}^2+\frac{l+1}{l}\right) - iq^{2l+1}\frac{\hat{n}^2-1}{[(2l-1)!!]^2}\frac{l(l+1)}{2l+1}\right\}^{-1}. \quad (4) $$

3. We known that the second term in braces, which distinguishes (4) from the usual formula for ${}^eB_l$ (Ref. 2), can be interpreted as nondissipative damping that restricts the amplitude of the scattered wave for purely real $\hat{n}^2$. In particular, for the l th frequency ($\hat{n}^2(\omega_l) = -(l+1)/l$), we have from (4) [cf. (1)]

$$ {}^eB_l = i^{l+1}(2l+1)/l(l+1). \quad (5) $$

When the rise in the scattered amplitude in the neighborhood of resonance is due to the excitation of the corresponding normal modes, i.e., to the transformation of the incident electromagnetic wave into volume plasmons, the physical meaning of nondissipative damping is, clearly, connected with the reverse transformation, namely, the transformation of the plasmon into the scattered electromagnetic wave. The amplitude of the electromagnetic field excited in the scattering particle then settles down to the self-consistent value for which the number of plasmons excited by the incident electromagnetic wave per unit time is equal to the

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number of plasmons transformed into the scattered wave per unit time.

We note that expression (5) does not contain any small quantities. This means that the scattered amplitude for reasonance of any order (i.e., for any l) is of the same order of magnitude and is independent of the geometrical size of the scattering particle. This conclusion is also valid for other quantities characterizing the scattering process. For example, the partial extinction cross section $\sigma_l(\omega)(\sigma_l = \sigma_{ls} + \sigma_{la}$, where $\sigma_{ls,a}$ are the partial cross sections for scattering and absorption, respectively), which is related to the scattering amplitude by the optical theorem[2]

$$\sigma_l(\omega) = \frac{2\pi}{(k^{\mathrm{I}})^2} l(l+1)\,\mathrm{Re}\{(-i)^{l+1}[{}^eB_l + {}^mB_l]\}, \qquad (6)$$

is given by the following expression at the point of resonance [this follows from (5) and (6)]:

$$\sigma_l(\omega_l) \approx {}^e\sigma_l(\omega_l) = 2\pi(2l+1)/(k_l^{\mathrm{I}})^2,$$

where $k_l^{\mathrm{I}} = k^{\mathrm{I}}(\omega_l)$ and ${}^e\sigma_l$ is the "electrical" part of the partial extinction cross section, which is related to the quantity ${}^eB_l$. Therefore, $2l+1$ is the degeneracy of the l th resonance (the number of independent modes corresponding to the excitation of the $2l$-pole electric moment). It follows from the expression obtained above that, in resonance scattering, each resonance mode provides the same contribution to the extinction cross section:

$${}^e\sigma_l^{\,1}(\omega_l) = 2\pi/(k_l^{\mathrm{I}})^2.$$

The complete partial cross section for resonance extinction is then given by

$$\sigma_l(\omega_l) \approx {}^e\sigma_l(\omega_l) = \sum {}^e\sigma_l^{\,1}(\omega_l) = (2l+1)\,{}^e\sigma_l^{\,1}(\omega_l).$$

It is interesting to note that, as follows from the optical theorem, for purely real $\hat{n}^2(\omega)$ $(\omega \neq \omega_l)$, the use of the standard approximation[2] $q \ll 1$ for ${}^eB_l$ without the inclusion of nondissipative damping (4) leads to $\sigma_l \equiv 0$ for all l, whereas the substitution of (4) in (6) gives the correct result for the scattering cross section of a small particle.[3]

The results presented above have a simple physical explanation: the requirement that the scattering amplitude at the point of resonance be large but finite is consistent with q being the only small parameter of the problem, but only in the case where ${}^eB_l$ is independent of q.

4. The range of validity of the results obtained above is obviously restricted by the condition

$$\mathrm{Im}\,\hat{n}^2(\omega_l) \ll q^{2l+1}\frac{l+1}{l^2[(2l-1)!!]^2}, \qquad (7)$$

which becomes increasingly stringent as l increases.

5. As a specific example, let us consider the scattering of light by a small metallic particle localized in a dielectric host. The function $\hat{n}^2(\omega)$ is then of the form (see, for example, Ref. 5)

$$\hat{n}^2 = \frac{1}{(n^{\mathrm{I}})^2}\left\{1 - \frac{\omega_p^2}{\omega^2+\nu^2}\right\} + \frac{i}{(n^{\mathrm{I}})^2}\frac{\nu}{\omega}\frac{\omega_p^2}{\omega^2+\nu^2}, \qquad (8)$$

where ω_p is the plasma frequency of the metal and ν is the effective electron collision frequency. For a small particle, the latter frequency is determined by collisions between conduction electrons and the boundary, and its order of magnitude is $\nu \sim v_F/a$ where v_F is the velocity of Fermi electrons.

When the foregoing is taken into account, expression (7) can be rewritten in the form of a condition for a. Combining this with the condition $|\hat{n}|q \ll 1$, and assuming that in the region of the resonance

$$-\mathrm{Re}\,\hat{n}(\omega_l) \approx (1+1/l)^{1/2} \sim 1 \gg \mathrm{Im}\,\hat{n}(\omega_l),$$

we finally obtain

$$\frac{n^{\mathrm{I}}v_F}{c}\left\{\frac{1}{(n^{\mathrm{I}})^2} + \frac{l+1}{l}\right\}\frac{l^2[(2l-1)!!]^2}{l+1} \ll (ak_l^{\mathrm{I}})^{2(l+1)} \ll 1. \qquad (9)$$

6. Let us now consider some numerical estimates. Additively colored (i.e., containing an excess of the metal component) alkali-halide crystals are convenient objects for investigating the scattering of light by small particles. At high temperatures, the excess metal in such crystals exists in the form of isolated point defects (F-centres). As the temperature is reduced, the "F-center gas" condenses into macroscopic metallic particles (colloids). The essential point is that, at a late stage in the condensation process (the coalescence stage), the size distribution of the colloids has a specific universal form for which the characteristic size of the colloids increases as $t^{1/3}$ where t is the coalescence time[6] (see also Ref. 7 where this process is examined in connection with problems of laser radiation damage to alkali-halide crystals).

Estimates shown that, for potasium particles localized in KCl crystals, the resonance frequency lies in the red and near infrared. As an example, Figs, 1–3 show that total extinction cross sections ($\sigma = \Sigma\sigma_l$) of such particles as functions of the frequency of incident radiation for a few values of a. The following values were used in the calculations: $\omega_p = 5.77\times10^{15}\ \mathrm{s}^{-1}$, $v_F = 10^8$ cm/s, and $n^{\mathrm{I}} \simeq 1.5$ throughout the frequency range under consideration. These calculations have shown that, in all these cases, the corrections to σ

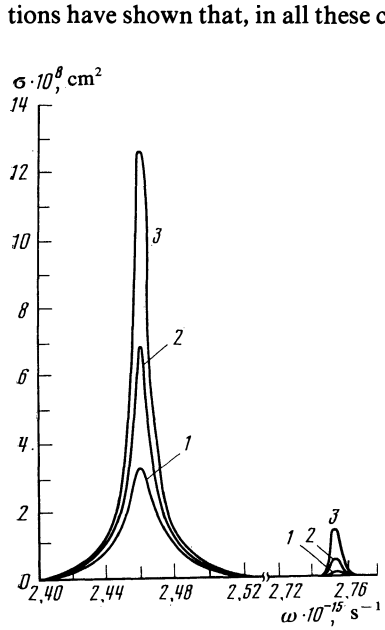

FIG. 1. Extinction cross section of small particles of potassium localized in a KCl crystal as a function of the frequency of incident radiation, without taking into account nondissipative damping ($Q \ll 1$, Ref. 2), for three values of the particle size $1 - a = 5.2\times10^{-6}$ cm; $2 - a = 6.2\times10^{-6}$ cm $3 - a = 7.2\times10^{-6}$ cm.

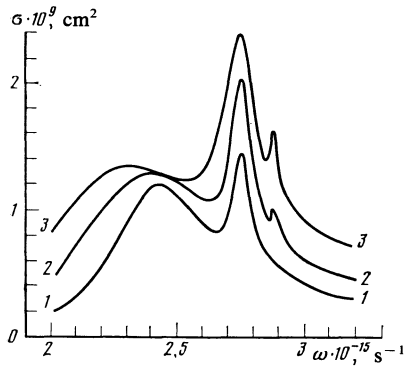

FIG. 2. Same as Fig. 1, but with allowance for nondissipative damping [see (4) and (6)].

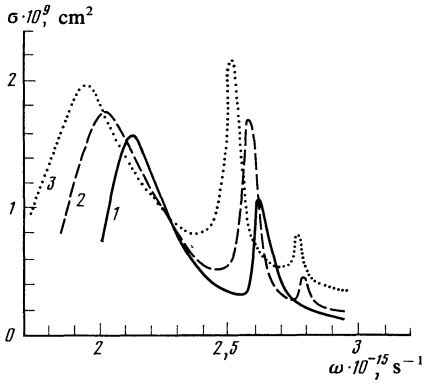

FIG. 3. Same as Fig. 1. Exact solution.

that are connected with ${}^{m}B_l$ do not exceed a fraction of a per cent, so that the function $\sigma(\omega)$ is wholly determined by the amplitudes ${}^{e}B_l$ [see (6)]. The data shown in the figures correspond to different approximations used in the calculations. Thus, Fig. 1 corresponds to the Rayleigh approximation,[3] i.e., calculations in which the standard approximation[2] $q \ll 1$ was used for ${}^{e}B_l$ with nondissipative damping (4), and Figs. 2 and 3 correspond to calculations based on (4) and the exact solution, i.e. equation (1), respectively. It is clear that the curves shown in Figs. 2 and 3 are very close to each other, and are qualitatively different from the Rayleigh scattering curves (cf. Fig. 1), despite the fact that the scattered particles were small. The reasons for the discrepancy between the resonance values ω_l calculated from the (4) and (6) and the true values is explained in Section 2 above. If necessary, the precision of (4) can readily be increased by including a larger number of terms in the expansion of the Bessel functions in powers of z [see (2) and (3)].

We note that, for all the above values of a, the exctinction cross section with the quadrupole resonance [second peak on the function $\sigma(\omega)$] is found to be comparable with the corresponding value of ω for the dipole resonance [first peak on $\sigma(\omega)$], or is even greater (see Fig. 3). Higher-order resonances and supressed by dissipative damping. The relatively early ($l \geqslant 3$) supression of resonance peaks is a special feature of the above example in which dissipative losses are found to be related to the geometrical size of the particles through the frequency of collisions between free electrons and the boundary, and are quite high for small particles. On the other hand, when dissipation is due to microscopic effects (radiationless transitions etc.), it may be expected that octupole and other higher-order resonances will also contribute significantly to $\sigma(\omega)$.

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