PHYSICAL REVIEW B VOLUME 14, NUMBER 12 15 DECEMBER 1976

Sum rule for the polarizability of small particles*

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(Received 7 June 1976)

A sum rule is derived which is useful for verifying the accuracy of calculated optical properties of arbitrarily shaped particles or powders.

The optical absorption of a particle or collection of particles composed of an isotropic material with a complex dielectric susceptibility $\chi(\omega)$, and having a size much smaller than the wavelength of light, is determined by a susceptibility tensor $\langle\chi_{\alpha\beta}(\omega)\rangle$, which relates the Cartesian components of the induced dipole moment and the applied field. One can write[1,2]

$$\langle\chi_{\alpha\beta}(\omega)\rangle = \sum_m \frac{C_{\alpha\beta}(m)}{\chi^{-1}(\omega)+4\pi n_m}. \tag{1}$$

The depolarization factors n_m in the denominators of Eq. (1) determine the frequencies ω_m of the optical-absorption peaks, whereas the constants $C_{\alpha\beta}(m)$ in the numerators determine the strengths of the absorption peaks.

It has been shown previously[1] that the $C_{\alpha\beta}(m)$ satisfy the sum rule

$$\sum_m C_{\alpha\beta}(m) = \delta_{\alpha\beta}. \tag{2}$$

The purpose of this communication is to derive a second sum rule,

$$\sum_{\alpha=1}^{3}\sum_m n_m C_{\alpha\alpha}(m) = 1. \tag{3}$$

Since the result of a calculation of the polarizability of any particle or group of particles is contained entirely in the values of the quantities $C_{\alpha\beta}(m)$ and n_m, these sum rules are a useful test of the accuracy of the calculations in the sense that numerical inaccuracy or an incorrect treatment of interaction between particles should lead to a violation of the sum rules. The new sum rule (3) corresponds roughly to the statement that the centroid of the optical absorption of an arbitrary particle or group of particles, averaged over all possible orientations, is the same as that of a sphere. (A sphere has $C_{xx}=C_{yy}=C_{zz}=1$ and the depolarization factors are all $n=\frac{1}{3}$.)

From Eqs. (15)–(17) of Ref. 1, we have

$$\sum_m n_m C_{\alpha\beta}(m) = \tfrac{1}{2}\delta_{\alpha\beta} - \frac{1}{4\pi v}\sum_{mij}(x_i)_\alpha (n_j)_\beta U_{im}\lambda_m U^{-1}_{mj}\Delta S_j. \tag{4}$$

The λ_m can be eliminated using $\underline{U}^{-1}\underline{R}\,\underline{U}=\underline{\Lambda}$. If we set $\alpha=\beta$, sum over α, and use Eq. (5) of Ref. 1 for R_{ij}, Eq. (4) becomes

$$\sum_{\alpha m} n_m C_{\alpha\alpha}(m) = \frac{3}{2} - \frac{1}{4\pi v}\sum_{ij}{}' \vec{r}_i\cdot\hat{n}_j(\vec{r}_i-\vec{r}_j)\cdot\hat{n}_i|\vec{r}_i-\vec{r}_j|^{-3} \times\Delta S_i\Delta S_j. \tag{5}$$

The discrete sums in Eq. (5) can be converted to surface integrals:

$$\sum_{\alpha m} n_m C_{\alpha\alpha}(m) = \frac{3}{2} - \frac{1}{4\pi v} I, \tag{6}$$

where

$$I = \int\int (\vec{r}\cdot\hat{n}')\left(-\hat{n}\cdot\vec{\nabla}_r \frac{1}{|\vec{r}-\vec{r}'|}\right) dS\, dS'. \tag{7}$$

First, suppose that we have a single particle of arbitrary shape. Since the points $i=j$ are excluded in Eq. (5), the double surface integral (7) is a principal-value integral which can be written

$$I = \lim_{\epsilon\to 0}\tfrac{1}{2}(I_1+I_2), \tag{8}$$

where

$$I_1 = \int_{S-\epsilon} dS \int_S dS' (\vec{r}\cdot\hat{n}')\left(-\hat{n}\cdot\vec{\nabla}_r \frac{1}{|\vec{r}-\vec{r}'|}\right), \tag{9}$$

$$I_2 = \int_S dS \int_{S-\epsilon} dS' (\vec{r}\cdot\hat{n}')\left(-\hat{n}\cdot\vec{\nabla}_r \frac{1}{|\vec{r}-\vec{r}'|}\right). \tag{10}$$

In I_1, $\vec{r}'$ runs over the true surface S and $\vec{r}$ runs over a surface $S-\epsilon$ lying an infinitesimal distance inside S, whereas the reverse is true for I_2. Converting the surface integral $\int_{S-\epsilon} dS$ to a volume integral $\int_{v-\epsilon} d^3v$ and using the identity

$$\nabla^2 \frac{1}{|\vec{r}-\vec{r}'|} = -4\pi\delta(\vec{r}-\vec{r}'),$$

we find

$$I_1 = \int_{v-\epsilon} d^3r \int_S dS'\left(\hat{n}'\cdot\vec{\nabla}_{r'}\frac{1}{|\vec{r}-\vec{r}'|} + 4\pi(\vec{r}\cdot\hat{n}')\delta(\vec{r}-\vec{r}')\right). \tag{11}$$

Since $\vec{r}'$ is on S and $\vec{r}$ is inside $S-\epsilon$, the δ function does not contribute. Therefore

$$I_1 = \int_{v-\epsilon} d^3r \int_v d^3r' \, \nabla_{r'}^2 \frac{1}{|\vec{r}-\vec{r}'|} = -4\pi v \,. \qquad (12)$$

Similarly,

$$I_2 = \int_v d^3r \int_{S-\epsilon} dS' \left(\hat{n}' \cdot \vec{\nabla}_{r'} \frac{1}{|\vec{r}-\vec{r}'|} + 4\pi (\vec{r}\cdot\hat{n}')\delta(\vec{r}-\vec{r}') \right) . \qquad (13)$$

Now $\vec{r}$ and $\vec{r}'$ are both inside S, so the δ function contributes:

$$I_2 = -4\pi v + 4\pi \int_{S-\epsilon} dS' (\vec{r}'\cdot\hat{n}')$$

$$= -4\pi v + 4\pi \int_{v-\epsilon} d^3r' (\vec{\nabla}'\cdot\vec{r}') = 8\pi v \,. \qquad (14)$$

Therefore

$$I = 2\pi v \,,$$

and Eq. (6) becomes

$$\sum_{\alpha m} n_m C_{\alpha\alpha}(m) = 1 \,,$$

which is the desired sum rule.

If the system consists of N particles with surfaces S_μ and volumes v_μ, where $\mu = 1, 2, \ldots, N$, Eq. (7) can be written

$$I = \sum_{\mu\mu'} \int_{S_\mu} \int_{S_{\mu'}} f(\vec{r}, \vec{r}') \, dS \, dS' \,.$$

Here $f(\vec{r}, \vec{r}')$ denotes the integrand of Eq. (7). It can easily be shown that the contribution from terms $\mu \neq \mu'$ is zero, but if $\mu = \mu'$, the result is $2\pi v_\mu$. One gets

$$I = 2\pi \sum_\mu v_\mu = 2\pi v \,,$$

so the sum rule (3) is still valid.

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*Work performed for the U. S. ERDA under Contract No. W-7405-eng-82.

[1]R. Fuchs, Phys. Rev. B 11, 1732 (1975).
[2]R. Fuchs, Phys. Lett. A 48, 353 (1974).