DIELECTRIC PERMITTIVITY OF CRYSTALS TAKING RETARDED INTERACTION INTO ACCOUNT

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Abstract

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1. A quantum theory is developed for the dielectric permittivity of molecular crystals, determining the response of a medium to an external long-wavelength electromagnetic field. It is assumed that all interactions between molecules are effected only through the field. Owing to the spatial inhomogeneity of an ideal crystal, a long-wavelength field also gives rise in the crystal to a short-wavelength field. Below, taking account of the retardation of such short-wavelength fields, the tensors of the total $\varepsilon(\omega, \mathbf{k})$ and transverse $\varepsilon^{\perp}(\omega, \mathbf{k})$ dielectric permittivity are found, which relate the long-wavelength induction $\mathbf{D}(\omega, \mathbf{k})$, respectively, to the total $\mathbf{E}(\omega, \mathbf{k})$ and transverse $\mathbf{E}^{\perp}(\omega, \mathbf{k})$ long-wavelength fields.

2. Let us consider a model of a molecular crystal containing one molecule per elementary cell. The centers of mass of the molecules are located at the lattice sites

$$\mathbf{n} = \sum_{i=1}^{3} n_i \mathbf{a}_i, \quad \text{where } n_i = 0, \pm 1, \dots; \quad \mathbf{a}_i \text{ are the basis vectors of the lattice.}$$

We shall take into account dipole-allowed electronic transitions in the molecules. Let ω_f, $\mathbf{e}_f$, d_f be the frequency, polarization, and absolute magnitude of the dipole moment for the f-th transition.

We introduce Bose operators $^{(1)}$ $B_f^{+}(\mathbf{n}), B_f(\mathbf{n})$ for the creation and annihilation of the f-th excitation in molecule $\mathbf{n}$. The Hamiltonian of the electromagnetic field interacting with the electronic transitions of the crystal has the form

$$H = \sum_{f,\mathbf{n}} \hbar\omega_f B_f^{+}(\mathbf{n}) B_f(\mathbf{n}) - \frac{i}{c} \sum_{f,\mathbf{n}} \omega_f d_f (\mathbf{e}_f \cdot \mathbf{A}(\mathbf{n}))(B_f^{+}(\mathbf{n}) - B_f(\mathbf{n})) + \frac{e^2 S}{2mc^2} \sum_{n} \mathbf{A}^2(\mathbf{n}), \tag{1}$$

where S is the number of optically active electrons in the molecule; e, m are the charge and mass of the electron;

$$H_{\text{ph}} = \frac{1}{8\pi} \int \left\{ 16\pi^2 c^2 \Pi^2(\mathbf{r}) + (\operatorname{rot} \mathbf{A}(\mathbf{r}))^2 \right\} d^3 r$$

is the energy operator of the electromagnetic field; $\mathbf{A}(\mathbf{r})$ and $\Pi(\mathbf{r})$ are, respectively, the operators of the vector potential and of the canonically conjugate momentum.

On the basis of operator (1), one can obtain equations for the retarded Green’s functions $^{(2)}$

$$\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \left\langle\!\left\langle A_j(\mathbf{r}, t) \mid A_l(\mathbf{r}', t') \right\rangle\!\right\rangle + \operatorname{rot}_j \operatorname{rot} \left\langle\!\left\langle \mathbf{A}(\mathbf{r}, t) \mid A_l(\mathbf{r}', t') \right\rangle\!\right\rangle =$$

$$= 4\pi\hbar \delta_{jl} \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') + \frac{4\pi}{c} \frac{\partial}{\partial t} \left\langle\!\left\langle P_j(\mathbf{r}, t) \mid A_l(\mathbf{r}', t') \right\rangle\!\right\rangle, \tag{2}$$

$$\left(\frac{\partial^2}{\partial t^2} + \omega_f^2 \right) \left\langle\!\left\langle p_f(\mathbf{n}, t) \mid A_l(\mathbf{r}', t') \right\rangle\!\right\rangle = -\frac{e^2 F_f}{mc} e_{fj} \frac{\partial}{\partial t} \left\langle\!\left\langle A_j(\mathbf{n}, t) \mid A_l(\mathbf{r}', t') \right\rangle\!\right\rangle, \tag{3}$$

where $F_f = 2m\omega_f d_f^2 / e^2\hbar$ is the oscillator strength of the electronic transition in the molecule;

$$\mathbf{P}(\mathbf{r}, t) = \sum_{f, \mathbf{n}} \mathbf{e}_f p_f(\mathbf{n}, t) \delta(\mathbf{r} - \mathbf{n})$$

is the operator of the specific polarization of the crystal;

$$\mathbf{e}_f p_f(\mathbf{n}, t) = \mathbf{e}_f d_f \left[B_f^+(\mathbf{n}, t) + B_f(\mathbf{n}, t) \right]$$

is the operator of the dipole moment of the electronic transition. The Green’s functions entering expressions (2) and (3) are translationally invariant, for example

$$\left\langle\!\left\langle A_j(\mathbf{r} + \mathbf{n}, t) \mid A_l(\mathbf{r}' + \mathbf{n}, t') \right\rangle\!\right\rangle = \left\langle\!\left\langle A_j(\mathbf{r}, t) \mid A_l(\mathbf{r}', t') \right\rangle\!\right\rangle .$$

3. The electromagnetic field and polarization arise in the crystal under the influence of external perturbations. Suppose that such a perturbation is produced by an external macroscopic current

$$\mathbf{j}^{\text{ext}}(\mathbf{r},t) = \frac{1}{V}\,\mathbf{j}(\omega,\mathbf{Q})\exp\{i(\mathbf{Qr}-\omega t)\}, \qquad \mathbf{Qa}_i \ll 1,$$

which is switched on adiabatically at $t = -\infty$. Such switching-on is ensured by a formal addition to the frequency ω of a small positive imaginary quantity $i\eta$. In the final expressions one must pass to the limit $\eta \to +0$. The mean fields and polarizations induced by the current are related to the retarded Green' s functions by the relations (2)

$$\langle A_j(\mathbf{r},t)\rangle = -\frac{1}{\hbar c}\int \langle\langle A_j(\mathbf{r},t) \mid A_l(\mathbf{r}',t')\rangle\rangle\, j_l^{\text{ext}}(\mathbf{r}',t')\, d^3r'\, dt',$$

$$\langle p_f(\mathbf{n},t)\rangle = -\frac{1}{\hbar c}\int \langle\langle p_f(\mathbf{n},t) \mid A_l(\mathbf{r}',t')\rangle\rangle\, j_l^{\text{ext}}(\mathbf{r}',t')\, d^3r'\, dt'.$$

With the aid of these relations and equations (2) and (3) one can obtain equations for the mean values of the fields and the polarization

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \operatorname{rot}\operatorname{rot}\right)\langle \mathbf{A}(\mathbf{r},t)\rangle = 4\pi \mathbf{j}^{\text{ext}}(\mathbf{r},t) + \frac{4\pi}{c}\frac{\partial}{\partial t}\langle \mathbf{P}(\mathbf{r},t)\rangle, \tag{4}$$

$$\left(\frac{\partial^2}{\partial t^2} + \omega_f^2\right)\langle p_f(\mathbf{n},t)\rangle = -\frac{e^2F_f}{mc}\left(\mathbf{e}_f\cdot\frac{\partial}{\partial t}\langle \mathbf{A}(\mathbf{n},t)\rangle\right). \tag{5}$$

Let us perform Fourier transformations in equations (4) and (5), for example,

$$\langle \mathbf{A}(\mathbf{r},t)\rangle = \frac{1}{V}\sum_{\mathbf{k}}^{\infty}\mathbf{A}(\omega,\mathbf{k})\exp\{i(\mathbf{Qr}-\omega t)\}.$$

Taking into account the equality

$$\mathbf{P}(\mathbf{k},\omega) = \sum_f \mathbf{e}_f p_f(\mathbf{k},\omega),$$

where $p_f(\mathbf{k},\omega) = \sum_{\mathbf{n}}\langle p_f(\mathbf{n},t)\rangle\exp\{-i(\mathbf{kn}-\omega t)\}$, we find that the coefficients $p_f(\mathbf{k},\omega)$ possess the important property

$$p_f(\mathbf{k},\omega) = p_f(\mathbf{k}+\mathbf{g},\omega), \tag{6}$$

where $\mathbf{g}$ are reciprocal-lattice vectors multiplied by 2π. Equality (6) makes it possible to reduce all values $p_f(\mathbf{k},\omega)$ to their values in the first Brillouin zone. After passing to Fourier components and taking account of equality (6), equations (4) and (5) are transformed into the form

$$\left[\mathbf{k}^2-\omega^2/c^2\right]\mathbf{A}(\mathbf{k},\omega)-\mathbf{k}(\mathbf{k}\cdot\mathbf{A}(\mathbf{k},\omega))=4\pi\mathbf{j}(\mathbf{Q},\omega)\delta_{\mathbf{k},\mathbf{Q}}-i\frac{4\pi\omega}{c}\sum_f\mathbf{e}_f p_f(\mathbf{k},\omega),\tag{7}$$

$$(\omega_f^2-\omega^2)p_f(\mathbf{k},\omega)=\frac{ie^2\omega F_f}{mc\nu}\sum_{\mathbf{g}}\left(\mathbf{e}_f\cdot\mathbf{A}(\mathbf{k}+\mathbf{g},\omega)\right),\tag{8}$$

where ν is the volume of the elementary cell of the crystal.

In accordance with our formulation of the problem, the long-wavelength field $\mathbf{A}(\mathbf{Q},\omega)$, the polarization $p_f(\mathbf{Q},\omega)$, and the short-wavelength fields $\mathbf{A}(\mathbf{q},\omega)$ ($\mathbf{q}\equiv\mathbf{Q}+\mathbf{g},\mathbf{g}\neq 0$) are absent without an external current. It follows from equation (8) that the short-wavelength fields are expressed in terms of the polarization by means of the equality

$$\frac{\omega}{c}\mathbf{A}(\mathbf{q},\omega)=i4\pi\sum_f p_f(\mathbf{Q},\omega)\frac{\mathbf{q}(\mathbf{q}\cdot\mathbf{e}_f)-\mathbf{e}_f\omega^2/c^2}{\mathbf{q}^2-\omega^2/c^2},\tag{9}$$

which makes it possible to eliminate the microfields from equation (7). Thus we obtain

$$\left[(\omega_f^2-\omega^2)\delta_{ff'}+\Lambda_{ff'}(\mathbf{Q},\omega)\right]F_j^*(\mathbf{Q},\omega)=\frac{ie^2\omega}{mvc}(\mathbf{e}_f\cdot\mathbf{A}(\mathbf{Q},\omega)),\tag{10}$$

where

$$\Lambda_{ff'}(\mathbf{Q},\omega)=\omega_p^2F_f\sum_{g\neq 0}\frac{(\mathbf{Q}+\mathbf{g},\mathbf{e}_f)(\mathbf{Q}+\mathbf{g},\mathbf{e}_{f'})-\mathbf{e}_f\mathbf{e}_{f'}\omega^2/c^2}{(\mathbf{Q}+\mathbf{g})^2-\omega^2/c^2}\tag{11}$$

is the force matrix that takes into account the interactions of electronic transitions of molecules through microfields; $\omega_p^2\equiv 4\pi e^2/mv$. Eliminating the polarization $p_f(\mathbf{Q},\omega)$ from equations (10) and (7) (for $\mathbf{k}=\mathbf{Q}$), we obtain Maxwell' s equations for the macroscopic field in the crystal. In the approximation $\Lambda_{ff'}=\delta_{ff'}\Lambda_f$, this equation has the form

$$\left[-\frac{\omega^2}{c^2}\varepsilon_{lm}(\mathbf{Q},\omega)+Q^2\delta_{lm}-Q_{lQ}m\right]A_m(\mathbf{Q},\omega)=\frac{4\pi}{c}j_l(\mathbf{Q},\omega),\tag{12}$$

where

$$\varepsilon_{lm}(\mathbf{Q},\omega)=\delta_{lm}+\sum_f\omega_p^2F_f\frac{e_{f;l}e_{f;m}}{\omega_f^2-\omega^2+\Lambda_f(\mathbf{Q},\omega)}.\tag{13}$$

4. If the external current is transverse (i.e., $\rho^{\mathrm{st}} = 0$), then in equations (7), (8) one may eliminate the longitudinal part of the macroscopic field and obtain the equation

$$\left[-\frac{\omega^2}{c^2}\varepsilon^{\perp}(\mathbf{Q},\omega) + Q^2\right]\mathbf{A}^{\perp}(\mathbf{Q},\omega) = \frac{4\pi}{c}\mathbf{j}^{\perp}(\mathbf{Q},\omega),$$

where

$$\varepsilon^{\perp}_{lm}(\mathbf{Q},\omega) = \eta_{lm} + \sum_f \omega_p^2 F_f \frac{e^{\perp}_{f;l}(\mathbf{Q}) e^{\perp}_{f;m}(\mathbf{Q})}{\omega_f^2 - \omega^2 + \Gamma_f(\mathbf{Q},\omega)} \tag{14}$$

is the transverse tensor of dielectric permittivity; $\mathbf{e}^{\perp}_f(\mathbf{Q}) = \mathbf{e}_f - \mathbf{Q}(\mathbf{Q}\mathbf{e}_f)/Q^2$ is the transverse vector; $\eta_{lm} = \delta_{lm} - s_{ls}m$ is the transverse-projection tensor;

$$\Gamma_f(\mathbf{Q},\omega) = \omega_p^2 F_f (\mathbf{Q}\cdot\mathbf{e}_f)^2/Q^2 + \Lambda_f(\mathbf{Q},\omega) \tag{15}$$

is the force matrix that takes into account the interaction of molecular transitions through all microfields and the longitudinal macroscopic field. If retardation is neglected ($\omega/c \to 0$), then matrix (15) will take into account the complete Coulomb interaction between the charges composing neutral molecules. In this case the poles of the dielectric permittivity determine the energies of Coulomb excitons.

5. In our method of calculating the dielectric permittivity, the entire interaction between molecular transitions is taken into account through the field. In this case the matrices Λ_f and Γ_f contain nonphysical self-energies of dipole transitions. Their elimination is conveniently carried out by representing these matrices as sums over the nodes of the reciprocal lattice. For

of such a transformation, we introduce the auxiliary matrix

$$\frac{2\omega}{\hbar}L_f(\mathbf{Q},\omega) = \left\{\Lambda_f + \omega_p^2 F_f \frac{(\mathbf{Q}\cdot\mathbf{e}_f)^2 - \omega^2/c^2}{Q^2 - \omega^2/c^2}\right\} = \left\{\Gamma_f + \omega_p^2 F_f \frac{\left[(\mathbf{e}_f\cdot\mathbf{Q})^2/Q^2 - 1\right]\omega^2/c^2}{Q^2 - \omega^2/c^2}\right\}.$$

Then we obtain

$$L_f = -\left\{D_f \sum_n{}' \frac{e^{i\mathbf{Q}\mathbf{n}}}{|\mathbf{r}-\mathbf{n}|}\cos\left(\frac{\omega}{c}|\mathbf{r}-\mathbf{n}|\right)\right\}_{r=0}, \tag{16}$$

where

$$D_f = d_f\{\mathbf{e}_f\nabla + \omega^2/c^2\}.$$

The prime on the summation sign indicates that the terms with $n = 0$ are absent from the sums. This excludes the self-energy. In the absence of retardation ($\omega/c \to 0$), the matrix L_f goes over into the matrix of the resonance interaction ([3,4]) of exciton theory.

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Note: Figure translations are in progress. See original paper for figures.