THE ADIABATIC APPROXIMATION IN PROBLEMS IN NONLINEAR OPTICS

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The frequency dependence in the adiabatic approximation is examined for the third-rank polarizability tensors of a crystal lacking a center of symmetry. These tensors contain electronic, ionic, and mixed terms, the first type being independent of temperature.

1. Nonlinear optical effects in crystals [1, 2] raise the question of the processes responsible for these effects [3, 4]. Here I examine the contribution of the ion motion to the nonlinear-polarizability tensors by the method of [5] for the dielectric constant \( \varepsilon_{ik}(\omega) \). It is found that the electron and nuclear motion do not contribute additively, and the correlation between them gives rise to a mixed contribution \( P_{\alpha\beta\gamma}^{i} \) to the polarizability tensor \( P_{\alpha\beta\gamma} \). The contribution of \( P_{\alpha\beta\gamma}^{i} \) is considerable at frequencies such that the ionic contribution is negligible. The temperature dependence is of interest [6]. The electronic part \( P_{\alpha\beta\gamma}^{e} \) is not dependent on temperature, whereas \( P_{\alpha\beta\gamma}^{i} \) (ionic part) and \( P_{\alpha\beta\gamma}^{n} \) are temperature-dependent. Crystals with ionic and covalent bonds give [5] an effective potential energy for the nuclear motion. The same method may be applied to a van der Waals crystal via use of the adiabatic approximation for the motion of the ions within the molecule.

Nonstationary perturbation theory is used. This is applicable here because \((E/E_0)^2\) is small, in which \( E \) is the amplitude of the incident electric field (frequency \( \omega \)) and \( E_0 \) is the mean intraatomic field (see [3] for estimates). Here \( \pm \omega \) and \( \pm 2\omega \) should not coincide with quantized transitions, so \( \omega \) lies between the IR (ionic) and UV (electronic) absorption bands.

In the local approach we seek a relation between the polarization of a small volume and the actual (local) field. Consider the behavior of a molecular system lacking a center of symmetry in the electric field

\[
E(t) = E \cdot e^{-i\omega t} + E_0 \cdot e^{i\omega t}, \quad E^- = (E^+)^*.
\]

whose wavelength is much greater than the dimensions of the system, so the field may be considered as uniform. The Hamiltonian of the system is

\[
H(E) = H(0) - ME^- e^{-i\omega t} - ME^+ e^{i\omega t}.
\]

Here \( H(0) \) is the Hamiltonian in the absence of the field and \( M \) is the operator for the dipole moment. We disregard ferroelectric crystals and assume that the mean of \( M \) is zero in the absence of the external field. Then we have the induced dipole moment

\[
m(t) = \int \Psi_n^* M \Psi_n dx dy,
\]

in which \( \Psi_n \) is the solution of Schrodinger's equation with the Hamiltonian of (2). As unperturbed wave function we take the eigenfunction of the \( n \)-th stationary state. Formula (3) gives the ordinary polarizability in the first order with respect to the external field. The dipole moment in the second order is

\[
m^{(2)}(t) = \frac{1}{\hbar^2} \sum_{k,l} \langle n | M_\beta | k \rangle \langle k | M_\alpha | l \rangle \langle l | M_\gamma | n \rangle \times
\]

\[
\times \left[ \frac{E_\beta^+ E_\gamma^-}{(\omega_{kn} - \omega)(\omega_{ln} - \omega)} + \frac{E_\beta^- E_\gamma^+}{(\omega_{kn} + \omega)(\omega_{ln} + \omega)} \right] +
\]

\[
e^{-2i\omega t} \frac{E_\beta^+ E_\gamma^-}{(\omega_{kn} + \omega)(\omega_{ln} - \omega)} + e^{2i\omega t} \frac{E_\beta^- E_\gamma^+}{(\omega_{kn} - \omega)(\omega_{ln} + \omega)} +
\]

\[
+ \langle n | M_\alpha | k \rangle \langle k | M_\beta | l \rangle \langle l | M_\gamma | n \rangle \left[ \frac{E_\beta^+ E_\gamma^-}{\omega_{kn}(\omega_{ln} + \omega)} + \right.
\]

\[
\left. + \frac{E_\beta^+ E_\gamma^-}{\omega_{kn}(\omega_{ln} - \omega)} + e^{-2i\omega t} \frac{E_\beta^+ E_\gamma^-}{(\omega_{kn} - 2\omega)(\omega_{ln} - \omega)} + e^{2i\omega t} \times
\right]
\]
Here \( \hbar \omega_{kn} = E_k^0 - E_n^0 \); \( E_k^0, E_n^0 \) are the eigenvalues of the energy of the system in the stationary states \(|k\rangle \) and \(|n\rangle \); \( \hbar = 1.05 \cdot 10^{-34} \) J \cdot \text{sec}. The terms in \( \exp(-2i\omega t) \) and \( \exp(2i\omega t) \) on the right in (4) lead to second-harmonic generation. In addition, there are terms corresponding to a dipole moment constant in time. The tensors for the nonlinear polarizability are

\[
\begin{align*}
\mathcal{m}^{(2)}(t) &= P_{\Phi \Psi}(\pm 2\omega) E^\s_\beta E^\s_\gamma e^{-2i\omega t} + P_{\Phi \Psi}(2\omega) E^\s_\beta E^\s_\gamma e^{2i\omega t} + P_{\Phi \Psi}(\omega), \\
&\qquad \times E^\s_\beta E^\s_\gamma + P_{\Phi \Psi}(\omega, \omega) E^\s_\beta E^\s_\gamma.
\end{align*}
\]

(5)

The definition of \( P_{\Phi \Psi}(\pm 2\omega) \), \( P_{\Phi \Psi}(\pm \omega, \pm \omega) \) will be clear from comparison of (4) and (5). Formula (4) provides the frequency dependence of these tensors, for which we need to consider the intermediate states involved in the summation.

The wave function in the Born-Oppenheimer adiabatic approximation may [5] be put as

\[
\Psi_{\alpha \nu}(x, y) = \chi_{\alpha \nu}(y) \varphi_{\alpha}(x, y).
\]

(6)

Here \( x \) and \( y \) are the sets of coordinates for the electrons and nuclei; \( \varphi_{\alpha}(x, y), n, \) and \( \Phi_{\alpha}(y) \) are the wave function quantum number, and eigenvalue of the energy for the electron motion with the nuclei fixed in an arbitrary position \( y \) (\( y^0 \) is the equilibrium position). The nuclei move in an effective potential \( \Phi_{\alpha}(y) - \Phi_{\alpha}(y^0) \), \( \chi_{\alpha \nu}(y) \) being their wave function, \( \nu \) the quantum number and \( \varphi_{\alpha} \) the energy. The energy of the whole system in state \(|\nu \alpha \rangle \) is \( \Phi_{\alpha}(y^0) + \chi_{\alpha \nu}(y) \). In what follows we assume that \( \varphi_{\alpha} \) is small relative to \( |\Phi_{\nu'}(y^0_{\alpha}) - \Phi_{\alpha}(y^0)\rangle \) for \( \nu' \neq \nu \). If the nuclei are in position \( y \), then

\[
M(y) = \int \varphi^*_\alpha(x, y) M^\s(x, y) \varphi_{\alpha}(x, y) \, dx
\]

is the dipole-moment operator averaged over the ground electronic state. We put

\[
R^\s_{\Phi \psi}(\omega, y) = \frac{1}{\hbar} \sum_{n=0} \left[ \frac{1}{(\omega_{n0} \pm \omega)^{-1}} \int \varphi^*_\alpha(x, y) \times \\
\times M_{n}(x, y) \varphi_{\alpha}(x, y) \, dx \right] \chi_{\alpha \nu}(y) \varphi_{\alpha}(x', y) M_{\nu'}(x', y) \varphi_{\alpha}(x', y) \, dx'.
\]

(3)

The linear polarizability due only to the electrons (nuclei fixed) in the lowest electronic state is expressed in terms of \( R^\s_{\Phi \psi}(\omega, y) \)

\[
\mathcal{P}_{\Phi \psi}(\omega, y) = R^\s_{\Phi \psi}(\omega, y) + R^\s_{\Phi}(\omega, y).
\]

(9)

We need also the tensors for the nonlinear polarizability of electronic origin with the nuclei fixed:

\[
\mathcal{P}_{\Phi \psi}(\pm 2\omega, y) = \frac{1}{\hbar^2} \sum_{n', n'' \neq 0} \left( \frac{\langle 0, y | M_\beta | n', y \rangle \langle n', y | M_\alpha | n'' \rangle \langle n'', y | M_\gamma | 0, y \rangle}{(\omega_{n0} \pm \omega)(\omega_{n''0} \pm \omega)} \right) + \mathcal{P}_{\Phi}(\pm 2\omega, y).
\]

(10)