Solid State Communications, Vol. 80, No. 1, pp. 85–88, 1991.
Printed in Great Britain.

0038–1098/91 $3.00 + .00
Pergamon Press plc

NOTE ON RETARDATION EFFECTS IN THE DIELECTRIC OPTICAL RESPONSE

Vladimir Agranovich* and Shaul Mukamel†

Center for Photoinduced Charge Transfer, University of Rochester, Rochester, NY 14627, USA

*Institute of Spectroscopy, Academy of Sciences USSR, Troitsk, Moscow obl. 142092, USSR

†Department of Chemistry, University of Rochester, Rochester, NY 14627. USA

(*Received* 14 *May* 1991 *by E. Burstein*)

An exact, fully retarded formal expression for the dielectric function is derived in terms of a ratio of two-time correlation functions of the Maxwell field and the polarization operators. The present expression incorporates properly spontaneous emission and polariton effects. To the lowest order the radiation-matter coupling, reduces to the conventional (unretarded) expression involving the two-time correlation function of the polarization.

MOST CALCULATIONS of linear and nonlinear optical susceptibilities in condensed phases neglect the effects of retarded radiative intermolecular interactions [1, 2]. Consequently, the optical susceptibilities are expressed in terms of equilibrium material correlation functions which are calculated in the absence of the transverse electromagnetic field. These theories do not incorporate, therefore, spontaneous emission properly. In addition, in low temperature crystals or monolayers the radiation field and matter (polarization) modes are strongly correlated, and form new quasiparticles, polaritons. The conventional theories of optical susceptibilities completely neglect polariton effects, and in many cases fail to give an adequate description of dissipation processes. As an example consider the linear susceptibility in the vicinity of an exciton resonance (neglecting spatial dispersion).

$$4\pi\chi^{(1)}(\omega) \equiv \frac{\omega_p^2 f/\omega_0}{\omega_0 - \omega - i\gamma(\omega)}. \qquad (1)$$

Here ω_p and ω_0 denote the plasma and the $k = 0$ exciton frequency, respectively, f is the oscillator strength, and $\gamma(\omega)$ is the dissipative width of the $k = 0$ exciton state resulting from exciton–phonon scattering. Since expression (1) is usually calculated without taking into account the retarded interactions, the function $\gamma(\omega)$ depends only on exciton dispersion $\omega_0(k)$. That is why the resulting function $\gamma(\omega)$ fails to give a correct description of the long-wavelength edge of excitonic absorption lines (see [3] and references there). In the region $\omega \leqslant \omega_0$ for excitonic transitions with sufficiently large oscillator strength f, retarded interactions strongly modify the exciton dispersion and for $\omega \leqslant \omega_0$ this effect may be very important. The same effect for the same frequencies takes place also for two or three photon absorption [4]. The correct calculation of the exciton–phonon scattering rate requires the incorporation of polariton effects. A microscopic treatment of polariton effects in the nonlinear optical response was developed by Knoester and Mukamel [5]. Another problem arises in calculating linear and nonlinear susceptibilities of monolayers. As was shown by Hopfield [6] and Agranovich [7], in perfect 3-D crystals, the spontaneous emission rate of polaritons vanishes, so in calculating the imaginary part of the susceptibilities, only damping mechanisms due to exciton–phonon scattering contribute to the dissipative rate $\gamma(\omega)$. This is not the case, however, for systems with restricted geometries such as monolayers. Even for perfect monolayers, as was shown by Agranovich and Dubovsky [8] (see also [9] and reference therein), polaritons in some branches have a radiative width. Theoretical estimates and experiments in anthracene crystal surfaces indicate that this width may be of the order of a few tenths of a wavenumber [10], which of course should be taken into account in the calculation of susceptibilities at sufficiently low temperatures. Retardation and polariton effects are also important in the radiative decay in semiconductor quantum wells [11] and molecular microstructures [12].

An interesting demonstration of the necessity of properly incorporating retardation, is provided by the decay kinetics of excitonic gratings for large exciton transition oscillator strength [13, 14]. In this case, the description of diffraction of the probe pulse requires the calculation of $\chi^{(3)}(-k_p - \omega_p; k_1, \omega_1, -k_2 - \omega_2, k_1, \omega_1)$, where ω_1 is the grating frequency, ω_2 is the

frequency of the probe pulse and $\omega_p = 2\omega_1 - \omega_2$ is the diffracted wave frequency. k_1, k_2 and $k_p = 2k_1 - k_2$ are the corresponding wavevectors. At low temperatures, and for grating excitation with $\omega_1 > \omega_0$, following a fast relaxation ($\tau \sim 1$ ps) a lattice of density of polaritons is created. The decay of this grating is related to the diffusion of polaritons rather than the diffusion of excitons and, therefore, polariton zero order states, and not the excitons should be incorporated in the calculation of $\chi^{(3)}$ [13–15].

These comments suggest that for calculating linear and nonlinear optical susceptibilities in the region of an excitonic transition ($\omega \sim \omega_0$), it would be desirable to derive an exact formal expression for the optical susceptibilities in the terms of equilibrium correlation functions, which properly takes into account the retarded electromagnetic interactions [15]. An example of such an expression is provided by the formula for the dielectric tensor $\varepsilon_{ij}(\omega)$, obtained by Dzyaloskinski and Pitaevski [16], and the expressions for the second order susceptibilities $\chi^{(2)}_{ijl}$, obtained by Agranovich, Ovander, and Toshich [17], and by Obukhovsky and Strizhevsky [18]. Since in the deriviation of these results the Maxwell equation was used, and not only the material relation between the displacement vector D and the electric field E, the resulting formulas were expressed through correlation functions of the type $\langle EE\rangle$, $\langle EEE\rangle$, etc., E being the Maxwell field operator. The result of [16] was later used by Agranovich and Konobeev [19] to calculate the tensor $\varepsilon_{ij}(\omega)$ in the excitonic region. The resulting expressions for $\chi^{(1)}$ and $\chi^{(2)}$ are given in terms of the total Maxwell field E. In order to use these expressions, the E field operator needs to be expressed in terms of the dynamical variables of the system. This is in general a complicated problem, particularly for an inhomogeneous medium, which can be solved only for special systems. For a dipolar lattice this calculation was made by Ewald.

In the present note, a new exact formula for the linear dielectric response including retardation is developed. Our theory relates to the cross correlation function of the polarization and electric field operators, and it naturally reduces to the conventional (non-retarded) theories when the radiation-matter interaction is treated perturbatively. The present theory gives the response to an arbitrary field E. When the calculations of the E operator is complex, we can restrict it to the transverse part of E. This is particularly simple using the Coulomb gauge, and results in the transverse dielectric response (see equations (9)).

We consider a general material system whose Hamiltonian is

$$H = H_0 + H_{\text{int}}, \tag{1a}$$

where

$$H_0 = H_M + H_R. \tag{1b}$$

is the Hamiltonian of the free matter (H_M) and radiation field (H_R) and H_{int} denotes the radiation-matter coupling. The precise form of these Hamiltonians depends on the choice of gauge [21]. For the sake of the following derivation, the gauge need not be specified. We start by writing the linear casual relationship:

$$\tilde{P}_i(\mathbf{r}, t) = \int d\mathbf{r}' \int_{-\infty}^{t} dt' K_{ij}(r - r', t - t')\tilde{E}_j(\mathbf{r}', t') + \tilde{R}_i(\mathbf{r}', t). \tag{2}$$

Here $\tilde{A}$ denotes an operator in the Heisenberg picture

$$\tilde{A} \equiv \exp(iHt)A \exp(-iHt), \tag{3}$$

$\tilde{P}$ is the polarization operator and E_i is the electric field, K_{ij} is a linear response kernel and $\tilde{R}_i$ is a random force whose statistical properties will be specified below. The subscripts i, j denote tensorial components. The conjecture given by equation (2) is expected to hold for any equilibrium quantum system in the linear approximation with respect to interaction of the system with an internal macroscopic electric field. If we adopt a classical description of the matter in the presence of some external electromagnetic radiation, all operators in (3) should be replaced by classical quantities: $\tilde{E}_i \to E_i$, $\tilde{P}_i \to P_i$, $\tilde{R}_i \to R_i$ and for the monochromatic wave $E_i(\mathbf{r}, t) = E_i(\mathbf{k}, \omega)\exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)$, we obtain using equation (3), that the polarization is given by $P_i(\mathbf{r}, t) = P_i(\omega, \mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)$, where $P_i(\omega, \mathbf{k}) = \chi^{(1)}_{ij}(\mathbf{k}, \omega)E_j(\mathbf{k}, \omega)$, and the linear susceptibility $\chi^{(1)}$ is given by

$$\chi^{(1)}_{ij}(\mathbf{k}, \omega) = \int d\mathbf{r} \int_0^{\infty} d\tau K_{ij}(\mathbf{r}, \tau)\exp(-i\mathbf{k}\cdot\mathbf{r} + i\omega\tau). \tag{4}$$

We now return to the quantum mechanical description. We assume that in the infinite past, the radiation-matter interaction is switched off. The total density matrix is then given by a direct product of a material and radiation parts:

$$\rho 0 = \rho^0_M \rho^0_R \equiv |0\rangle\langle 0|,$$

where $|0\rangle$ denotes the ground vacuum state. We further introduce the following notation, $\langle A\rangle \equiv \text{Tr}(A\rho_0)$, for any operator a. The equilibrium expectation value of the random force vanishes i.e. $\langle\tilde{R}(\mathbf{r}, t)\rangle = 0$. Also $\langle\tilde{R}(\mathbf{r}, t)\tilde{E}_j(\mathbf{r}', t')\rangle = 0$. Note, however, that $\langle\tilde{R}_i(r, t)\tilde{P}_j(\mathbf{r}', t')\rangle$ does not vanish, since the random force represents equilibrium fluctuations of the polarization in the absence of the electric field E. Taking a commutator of equation (2) with $\tilde{E}(r_0, t_0)$, multiplying by the

equilibrium distribution of the noninteracting system ρ_0 and taking a trace we get

$$\langle[\tilde{P}_i(\mathbf{r}, t), \tilde{E}_l(\mathbf{r}_0, t_0)]\rangle = \int d\mathbf{r}' \int_{-\infty}^{t} dt' K_{ij}(\mathbf{r} - \mathbf{r}', t - t') \times \langle[\tilde{E}_j(\mathbf{r}', t'), \tilde{E}_l(\mathbf{r}_0, t_0)]\rangle. \quad (5)$$

We now introduce the Fourier decompositions

$$\langle[\tilde{P}_i(\mathbf{r}, t), \tilde{E}_l(\mathbf{r}_0, t_0)]\rangle = \frac{1}{(2\pi)^4} \int d\mathbf{k} \int d\omega\, M_{il}(\mathbf{k}, \omega) \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) - i\omega t], \quad (6)$$

$$\langle[\tilde{E}_j(\mathbf{r}, t), \tilde{E}_l(\mathbf{r}_0, t_0)]\rangle = \frac{1}{(2\pi)^4} \int d\mathbf{k} \int d\omega\, N_{jl}(\mathbf{k}, \omega) \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) - i\omega t]. \quad (7)$$

Equation (5) then results in

$$M_{il}(k, \omega) = \chi_{ij}^{(1)}(k, \omega) N_{jl}(k, \omega).$$

The dielectric function $\varepsilon(\mathbf{k}, \omega) \equiv 1 + 4\pi\chi^{(1)}(\mathbf{k}, \omega)$ is finally given by

$$\varepsilon_{ij}(\mathbf{k}, \omega) = \delta_{ij} + 4\pi M_{il}(k, \omega)[N(\mathbf{k}, \omega)]_{lj}^{-1}, \quad (8a)$$

where

$$M_{il}(\mathbf{k}, \omega) = \int d\mathbf{r} \int_{\infty}^{\infty} dt \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) + i\omega t] \times \langle[\tilde{P}_i(\mathbf{r}, t), \tilde{E}_l(\mathbf{r}_0, t_0)]\rangle, \quad (8b)$$

$$N_{jl}(\mathbf{k}, \omega) = \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) + i\omega t] \times \langle[\tilde{E}_j(\mathbf{r}, t), \tilde{E}_l(\mathbf{r}_0, t_0)]\rangle. \quad (8c)$$

Equations (8) constitute the main result of this note. Since the time evolution in the correlation functions appearing in equations (8a) and (8b), defined in equation (3), is given by the full Hamiltonian H which includes the radiation–matter interaction H_{int}, retardation effects are fully accounted for by this formal expression.

In the deviation of equation (8) we have taken the commutation of equation (2) with $\tilde{E}(\mathbf{r}_0, t_0)$. Alternatively we could have just multiplied it by $\tilde{E}(\mathbf{r}_0, t_0)$ and taken a trace. We would have then obtained equation (8a) with M and N defined in terms of $\langle\tilde{P}(\mathbf{r}_1, t_1)\tilde{E}(\mathbf{r}_0, t_0)\rangle$ and $\langle\tilde{E}(\mathbf{r}_1, t_1)\tilde{E}(\mathbf{r}_0, t_0)\rangle$ respectively (rather than the commutators). This alternative expression is also correct. In practice, the evaluation of the commutators involves a calculation of a combination of the advanced and the retarded Green functions, which is much simpler [22]. This is why we have derived the present expressions involving commutators. It is easy to shown that equation (8) for 3-D crystals is equivalent to the expression for $\varepsilon_{ij}(\mathbf{k}, \omega)$ which was obtained in [19] by using Dzyaloskinski and Pitaevski approach [16, 22].

Equation (8) represents the dielectric function which relates the displacement vector to the total Maxwell field. The same method can also be used to calculate $\varepsilon_{ij}^{\perp}$ which represents the response to a transverse field $E^{\perp}$. In this case we have

$$\varepsilon_{ij}^{\perp}(\mathbf{k}, \omega) = \delta_{ij} + 4\pi M_{il}^{\perp}(\mathbf{k}, \omega)[N^{\perp}(\mathbf{k}, \omega)]_{lj}^{-1}, \quad (9a)$$

where

$$M_{il}^{\perp}(\mathbf{k}, \omega) = \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) + i\omega t] \times \langle[\tilde{P}_i(\mathbf{r}, t), \tilde{E}_l^{\perp}(\mathbf{r}_0, t_0)]\rangle, \quad (9b)$$

and

$$N_{jl}^{\perp}(\mathbf{k}, \omega) = \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) + i\omega t] \times \langle[\tilde{E}_j^{\perp}(\mathbf{r}, t), \tilde{E}_l^{\perp}(\mathbf{r}_0, t_0)]\rangle. \quad (9c)$$

Equation (8) reduces naturally to the conventional (nonretarded) expressions [1, 2, 23]. This may be shown as follows. We introduce a transformation $S(t)$ from the Heisenberg to the interaction picture

$$\tilde{A}(t) = S^{-1}(t)A(t)S(t),$$

where $A(t)$ is the operator A in the interaction representation [22]

$$A(t) = \exp(iH_0 t)A \exp(-iH_0 t),$$

and

$$S(t) \equiv s(t, -\infty) = T \exp\left[-i \int_{-\infty}^{t} H_{int}(t')\, dt\right].$$

To first order in H_{int} we have

$$S(t) \cong 1 - i \int_{-\infty}^{t} H_{int}(t_1)\, dt_1. \quad (10)$$

In the dipole approximation, the radiation-matter coupling is given by

$$H_{int}(t) = -\int d\mathbf{r} P_i(\mathbf{r}, t) \cdot E_i(\mathbf{r}, t). \quad (11)$$

Using equations (10) and (13) it is easy to show that to first order in H_{int}

$$\langle 0|[\tilde{P}_i(\mathbf{r}, t), \tilde{E}_l(\mathbf{r}_0 t_0)]|0\rangle \equiv \langle 0|\tilde{P}_i(\mathbf{r}, t)\tilde{E}_l(\mathbf{r}_0, t_0) - \tilde{E}_l(\mathbf{r}_0, t_0)\tilde{P}_i(\mathbf{r}, t)|0\rangle = -i \int d\mathbf{r}_1 \int_{t_0}^{t} dt_1 \langle 0|[P_i(\mathbf{r}, t), P_j(\mathbf{r}_1, t_1)]|0\rangle \times \langle 0|[E_j(\mathbf{r}_1, t_1), E_l(\mathbf{r}_0, t_0)]|0\rangle. \quad (12)$$

In the derivation of equation (12) we used the relations

$$\langle 0|P_i(\mathbf{r}, t), E_j(\mathbf{r}_0, t_0)|0\rangle = \langle 0|P_i(\mathbf{r}, t)|0\rangle \times \langle 0|E_j(\mathbf{r}_0, t_0)|0\rangle = 0,$$

which hold for a medium with no permanent dipole moment. Up to this point the time t_0 was arbitrary. Taking $t_0 = -\infty$ and evaluating equation (4) to the lowest order in H_{int}, we obtain:

$$\langle 0|[\tilde{P}_i(\mathbf{r}, t), \tilde{E}_j(\mathbf{r}_0, t_0)]|0\rangle$$

$$\cong \int \frac{d\mathbf{k}}{(2\pi)^4} \int_{-\infty}^{\infty} d\omega \chi_{ij}^{(1)}(\mathbf{k}, \omega) N_{ji}(i, \mathbf{k}, \omega)$$

$$\times \exp[i, \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0) - i\omega t],$$

where

$$\chi_{ij}^{(1)}(\mathbf{k}, \omega) = -i \int d\mathbf{r}_1 \int_{-\infty}^{t} dt_1 \langle 0|[P_i(\mathbf{r}, t), P_j(\mathbf{r}_1, t_1)]|0\rangle$$

$$\times \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}) - i\omega(t_1 - t)].$$

Using equation (8a) we have:

$$M_{ij}(\mathbf{k}, \omega) = \chi_{ij}^{(1)}(\mathbf{k}, \omega) N_{ji}(\mathbf{k}, \omega).$$

Thus we get:

$$\varepsilon_{ij}(\mathbf{k}, \omega) = \delta_{ij} + 4\pi \int d\mathbf{r} \int_0^{\infty} d\tau K_{ij}(\mathbf{r}, \tau)$$

$$\times \exp[-i\mathbf{k} \cdot \mathbf{r} + i\omega\tau], \quad (13)$$

with

$$K_{ij}(\mathbf{r}, \tau) = -i\langle 0|[P_i(\mathbf{r}, \tau), P_j(\mathbf{0}, 0)]|0\rangle \quad (14)$$

which is the conventional (nonretarded) expression for the dielectric response [2, 23]. The present approach may be also extended for calculating nonlinear optical susceptibilities and also for calculating optical susceptibilities of monolayers and clusters.

Acknowledgements – The support of the Center for Photoinduced Charge Transfer sponsored by the National Science Foundation, The Air Force Office of Scientific Research, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

REFERENCES

1. *The Dielectric Function of Condensed Systems* (Edited by L.V. Keldysh, D.A. Kirzhnitz & A.A. Maradudin), North-Holland, Amsterdam (1989).
2. C. Flytzanis, in *Quantum Electronics V.I.* (Edited by H. Rabin & C.L. Tang), p. 1, Academic Press, New York (1975); P. Maden & D. Kivelson, *Adv. Chem. Phys.* **56**, 467 (1984).
3. V.M. Agranovich & V.L. Ginzburg, *Crystal Optics with Spatial Dispersion and Excitons*, Springer, Berlin, (1984).
4. S.H. Stevenson, M.A. Connolly & G.J. Small, *Chem. Phys.* **128**, 157 (1988); G.M. Gale, F. Vallée & C. Flytzanis, *Phys. Rev. Lett.* **57**, 1867 (1986); D. Fröhlich, S. Kirchhoff, P. Köhler & W. Nieswand, *Phys. Rev.* **B40**, 1976 (1989); V.N. Denisov, B.N. Mavrin & V.B. Podobedov, *Phys. Rep.* **151**, 1 (1987).
5. J. Knoester & S. Mukamel, *J. Chem. Phys.* **91**, 989 (1989).
6. J.J. Hopfield, *Phys. Rev.* **112**, 1555 (1958).
7. V.M. Agranovich, *Ah. Eksp. Teor. Fiz.* **37**, 340 (159); [*Sov. Phys. JETP* **10**, 307 (1960)].
8. V.M. Agranovich & O.A. Dubovsky, *Pisma Zh. Eksp. Teor. Fiz.* **3**, 345 (1966); [*JEPT Lett.* **3**, 223 (1966)].
9. V.M. Agranovich & S. Mukamel, *Phys. Lett.* **A147**, 155 (1990).
10. J.M. Turlett, Ph. Kottis & M.R. Philpott, *Adv. Chem. Phys.* **54**, 303 (1983).
11. L.C. Andreani & F. Bassani, *Phys. Rev.* **B41**, 7536 (1990); E. Hanamura, *Phys. Rev.* **B38**, 1228 (1988).
12. F.C. Spano & S. Mukamel, *J. Chem. Phys.* (in press).
13. V.M. Agranovich, A.M. Ratner, M. Salieva, *Solid State Commun.* **63**, 329 (1987); V.M. Agranovich & T.A. Leskova, *Solid State Commun.* **68**, 1029 (1988); Proc. US-USSR Condensed Matter Symposium (Irvine, 1990).
14. J. Knoester & S. Mukamel, *Phys. Rep.* (1991) in press.
15. J. Knoester & S. Mukamel, *Phys. Rev.* **A39**, 1899 (1989); J. Knoester & S. Mukamel, *Phys. Rev.* **A40**, 7065 (1989); J. Knoester & S. Mukamel, *Phys. Rev.* **A41**, 3812 (1990).
16. I.E. Dzyaloskinski & L.P. Pitaevski, *Ah. Eksp. Teor. Fiz.* **36**, 1979 (1959); [*Sov. Phys. JETP* **9**, 1282 (1959)].
17. V.M. Agranovich, L.N. Ovander & B.C. Toshich, *Zh. Eksp. Teor. Fiz.* **50**, 1332 (1966); [*Sov. Phys. JETP* **23**, 885 (1966)].
18. V.V. Obukhovsky & V.L. Strizhevsky, *Zh. Eksp. Teor. Fiz.* **50**, 135 1332 (1966) [*Sov. Phys. JETP* **23**, 91 (1966))].
19. V.M. Agranovich & Yu.V. Konobeev, *Fiz. Tverd. Tela.* **5**, 2544 (1963) [*Sov. Phys. Solid States* **5**, 1858 (1963)].
20. M. Born & K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford, London (1954).
21. D.P. Craig & T. Thirunamachandran, *Molecular Quantum Electrodynamics*, Adademic Press, London (1984).
22. A.A. Abrikosov, L.P. Gorkov & I.E. Dzyaloskinski, *Methods of Quantum Field Theory in Statistical Physics*, Prentice-Hall, Englewood Cliffs, New York (1963).
23. R.F. Loring & S. Mukamel, *J. Chem. Phys.* **87**, 1272 (1987).