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Phenomenological damping in optical response tensors

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Although perturbation theory applied to the optical response of a molecule or material system is only strictly valid far from resonances, it is often applied to ''near-resonance'' conditions by means of complex energies incorporating damping. Inconsistent signs of the damping in optical response tensors have appeared in the recent literature, as have errors in the treatment of the perturbation by a static field. The ''equal-sign'' convention used in a recent publication yields an unphysical material response, and Koroteev's intimation that linear electro-optical circular dichroism may exist in an optically active liquid under resonance conditions is also flawed. We show that the isotropic part of the Pockels tensor vanishes.

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I. INTRODUCTION

A time-varying induced electric polarization acts as a source of radiation, and it is therefore convenient to describe optical phenomena by expressing the polarization as a power series in the applied electric fields, $E_\alpha(\omega)$. In the frequency domain the polarization is then given by

$$P_\alpha(\omega)=\epsilon_0\chi^{(1)}_{\alpha\beta}(-\omega;\omega)E_\beta(\omega)+\epsilon_0K^{(2)}(-\omega;\omega_1,\omega_2)\chi^{(2)}_{\alpha\beta\gamma}\times(-\omega;\omega_1;\omega_2)E_\beta(\omega_1)E_\gamma(\omega_2)+\cdots, \tag{1}$$

where $K^{(n)}$ are numerical factors chosen such that the response tensors of order n converge to the same static limit [1].

The macroscopic susceptibility $\chi^{(n)}_{\alpha\beta\ldots\epsilon}$ can in turn be related to the nth molecular polarizability tensor, $\alpha^{(n)}_{\xi\eta\ldots\zeta}$, through a coordinate transformation from molecule-fixed axes to the frame of the incident radiation,

$$\chi^{(n)}_{\alpha\beta\ldots\epsilon}(-\omega;\omega_1,\ldots,\omega_n)=\frac{\mathcal{N}\alpha^{(n)}_{\xi\eta\ldots\zeta}(-\omega;\omega_1,\ldots,\omega_n)}{n!\,\epsilon_0}\times\langle a_{\xi\alpha}a_{\eta\beta}\ldots a_{\zeta\epsilon}\rangle, \tag{2}$$

where $\omega_1+\omega_2+\cdots+\omega_n=\omega$ and $a_{\xi\alpha}$ are direction cosines, $\mathcal{N}$ is the number density of molecules, and the angular brackets $\langle\cdots\rangle$ denote a statistical average over the orientational distribution. Time-dependent perturbation theory can be used to obtain the nth-order polarizability [2]. In particular the sum-over-states expression for the first-order complex polarizability is

$$\alpha^{(1)}_{\alpha\beta}(-\omega;\omega)=\frac{1}{\hbar}\sum_{k\neq g}\left(\frac{\langle g|\hat{\mu}_\alpha|k\rangle\langle k|\hat{\mu}_\beta|g\rangle}{\omega_{kg}-\omega}+\frac{\langle g|\hat{\mu}_\beta|k\rangle\langle k|\hat{\mu}_\alpha|g\rangle}{\omega_{kg}+\omega}\right), \tag{3}$$

where $\hat{\mu}$ is a dipole operator and ω_{kg} is the transition frequency between the upper level k and the ground state g. The summation is over all excited states $k\neq g$.

As $\omega\rightarrow\omega_{kg}$, Eq. (3) diverges and becomes unphysical. Strictly, the divergence only occurs because higher-order nonlinearities have been neglected [3]; in the presence of intense optical fields or very close resonance with the transition frequencies, a perturbation analysis is no longer valid, and a two-level system is a more appropriate model. Often, however, the resonant nonlinearities are dominated by various transition line-broadening processes, and a particular resonant process can then still be represented by a single order of nonlinearity derived by the small-perturbation analysis, as in the nonresonant case, but with the addition of appropriate damping terms [3]. The phenomenological damping terms represent the finite lifetime of a state due to spontaneous emission and collisions. The various damping mechanisms are usually combined in a single transition linewidth Γ.

In Sec. II we examine the form of the perturbation expressions under near-resonance conditions. Nonsingular versions of the sum over states for optical response tensors can be obtained by introducing a damping correction as in the Wigner-Weisskopf [4–6] extension of the Kramers-Heisenberg-Dirac dispersion formula [7,8], by allowing the transition frequency to be the complex quantity $\tilde{\omega}_{kg}\equiv\omega_{kg}-(i/2)\Gamma_{kg}$, where ω_{kg}, is the real transition frequency and Γ_{kg} is the population decay rate of the upper level k.

A more general treatment includes damping in the perturbation expansion of the density matrix [9,10] and correctly describes dephasing [11]. Diagrammatic techniques have been developed to facilitate the often laborious algebraic perturbation calculations. The initial schemes, which neglected damping [12,13], were later expanded by Yee and Gustafson [14] to distinguish between the evolution of bra- and ket-type state vectors and include damping. Concurrent evolution of bra and ket states allows the treatment of pure dephasing [11]. In these approaches the treatment of damping results in the inclusion of the linewidth through imaginary terms in the energy denominators of the sum-over-states expressions for optical response tensors. Both the complex transition frequency $\tilde{\omega}_{kg}$ and its complex conjugate appear in the energy denominators. Equation (3) becomes

$$\alpha^{(1)}_{\alpha\beta}(-\omega;\omega)=\frac{1}{\hbar}\sum_{k\neq g}\left(\frac{\langle g|\hat{\mu}_\alpha|k\rangle\langle k|\hat{\mu}_\beta|g\rangle}{\tilde{\omega}_{kg}-\omega}+\frac{\langle g|\hat{\mu}_\beta|k\rangle\langle k|\hat{\mu}_\alpha|g\rangle}{\tilde{\omega}^*_{kg}+\omega}\right). \tag{4}$$

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Recently, on the basis of time-reversal symmetry and quantum field theoretical arguments, Andrews *et al.* [15] proposed that the imaginary linewidths should all be of the same sign, i.e., the expressions for optical response tensors should only include the complex transition frequency or its complex conjugate, but not both in the same formula. We term this the equal-sign convention, and show that it yields unphysical results.

In Sec. III we discuss the form of the sum-over-states expressions for optical response tensors when the frequency of an electromagnetic field approaches zero. In this case care has to be taken to correct the corresponding relaxation terms [9,16]. This seems not to have been appreciated in a number of recent publications [15,17–21].

It has been intimated that linear electro-optical circular dichroism may exist in an optically active liquid under resonance conditions [17,18]. However, it has previously been shown, using time-reversal symmetry, that no electrical analog of the Faraday effect can exist in a nonconducting liquid [22]. We show that there is no contribution to the refractive index of a fluid, even at resonance, that is linear in an applied static electric field.

II. SIGN OF PHENOMENOLOGICAL DAMPING COEFFICIENTS

We require that a real time-dependent electric field induces a real polarization $P_\alpha(t)$ [23],

$$P_\alpha(t)=\epsilon_0\int_{-\infty}^{\infty}\chi^{(1)}_{\alpha\beta}(-\omega;\omega)E_\beta(\omega)e^{-i\omega t}d\omega, \tag{5}$$

where the susceptibility is defined by Eq. (1). It follows that

$$\begin{aligned}E_\beta(-\omega)&=E^*_\beta(\omega),\\ \chi^{(1)}_{\alpha\beta}(-\omega;\omega)&=\chi^{(1)*}_{\alpha\beta}(\omega;-\omega).\end{aligned} \tag{6}$$

This argument holds for susceptibilities (and consequently for polarizabilities) to all orders. It can be seen that in the equal-sign convention this requirement is not fulfilled [15,24,25], and a real electric field could give rise to an imaginary polarization.

III. POCKELS TENSOR IN OPTICALLY ACTIVE LIQUIDS

In incoherent light scattering from a gas, there is a small linear effect of an applied static electric field [26,27]. However, we limit our analysis to coherent scattering from an isotropic medium perturbed by a weak static electric field. We do not consider the application of external magnetic fields.

A stationary fluid medium in the absence of an external magnetic field is invariant under time reversal. This can easily be seen if the fluid is comprised of diamagnetic closed-shell molecules, but it applies equally to paramagnetic molecules, since in the bulk (in the absence of an external magnetic field) the magnetization of the liquid is zero. Time reversal inverts the direction of currents and spins, but leaves charges invariant. It follows that an electric field is symmetric under time reversal, whereas a magnetic field and a magnetic dipole are time antisymmetric.

Consider the application of a static electric field parallel to the propagation direction of the light beam in a nonconducting fluid [17,18] (an alternating electric field may lift time-reversal symmetry and induce optical activity in a chiral liquid [28]). Time reversal does not affect the fluid medium in the electric field, but it reverses the direction of propagation of the light beam relative to the field [29]. If there were a linear effect of the electric field, the refractive index of the fluid would depend on the direction of propagation, but this is not possible for a system that is time symmetric. It follows that the Pockels effect, electric-field-induced optical activity, and in particular circular electrodichroism, are zero in fluids.

Even powers of the static field may have an effect on the refractive index of a fluid. The Kerr effect is such an example, and there is also a contribution to the optical activity quadratic in a static field [30].

The absence of circular electrodichroism in liquids may also be seen to follow from the statistical averaging of the correct quantum-mechanical expression for the corresponding molecular property tensor, here the Pockels tensor. The quantum-mechanical expression may be found by time-dependent perturbation theory using electric-field-perturbed wave functions and energies [26,29]. The wave function of the ground state $|g\rangle$ of a nondegenerate system in an electrostatic field can be chosen to be real, for if it were complex it would differ from its complex conjugate and hence be degenerate. The ground state weakly perturbed by an electrostatic field F_γ is

$$|g\rangle_F=|g\rangle+\sum_{j\neq g}\frac{\langle j|\hat{\mu}_\gamma|g\rangle}{\hbar\omega_{jg}}|j\rangle F_\gamma. \tag{7}$$

The complete set of eigenfunctions $|j\rangle$ of the unperturbed Hamiltonian can be chosen to be real, since in this case $|g\rangle_F$ describes the ground state as slightly perturbed by the time-independent static field F_γ (the lifetime of the excited state $|j\rangle$ cannot be relevant to $|g\rangle_F$ and we could use any complete basis set to describe $|g\rangle_F$).

The time-dependent ground state perturbed by an optical field $E_\gamma=(1/2)E^{(0)}_\gamma(e^{-i\omega t}+e^{i\omega t})$ of angular frequency ω takes the form

$$|g\rangle_E=|g\rangle+\sum_{j\neq g}\frac{\langle j|\hat{\mu}_\gamma|g\rangle}{2\hbar}\left\{\frac{e^{-i\omega t}}{\omega_{jg}-\frac{i}{2}\Gamma_{jg}-\omega}+\frac{e^{i\omega t}}{\omega_{jg}-\frac{i}{2}\Gamma_{jg}+\omega}\right\}|j\rangle E^{(0)}_\gamma. \tag{8}$$

It can be seen that in the limit $\omega\rightarrow 0$ Eq. (8) is only equivalent to Eq. (7) if the associated damping term is also set to zero. The complex polarizability describing the Pockels effect is given by

$$\alpha^{(2)}_{\alpha\beta\gamma}(-\omega;\omega,0)=\frac{1}{\hbar^2}\sum_{k\neq g,j\neq g}\left(\frac{\hat{\mu}_{gk_\alpha}\overline{\mu}_{kj_\beta}\hat{\mu}_{jg_\gamma}}{\left(\omega_{kg}-\frac{i}{2}\Gamma_{kg}-\omega\right)\omega_{jg}}+\frac{\hat{\mu}_{gk_\beta}\overline{\mu}_{kj_\alpha}\hat{\mu}_{jg_\gamma}}{\left(\omega_{kg}+\frac{i}{2}\Gamma_{kg}+\omega\right)\omega_{jg}}+\frac{\hat{\mu}_{gk_\alpha}\overline{\mu}_{kj_\gamma}\hat{\mu}_{jg_\beta}}{\left(\omega_{kg}-\frac{i}{2}\Gamma_{kg}-\omega\right)\left(\omega_{jg}-\frac{i}{2}\Gamma_{jg}-\omega\right)}\right.$$
$$\left.+\frac{\hat{\mu}_{gk_\gamma}\overline{\mu}_{kj_\alpha}\hat{\mu}_{jg_\beta}}{\omega_{kg}\left(\omega_{jg}-\frac{i}{2}\Gamma_{jg}-\omega\right)}+\frac{\hat{\mu}_{gk_\beta}\overline{\mu}_{kj_\gamma}\hat{\mu}_{jg_\alpha}}{\left(\omega_{kg}+\frac{i}{2}\Gamma_{kg}+\omega\right)\left(\omega_{jg}+\frac{i}{2}\Gamma_{jg}+\omega\right)}+\frac{\hat{\mu}_{gk_\gamma}\overline{\mu}_{kj_\beta}\hat{\mu}_{jg_\alpha}}{\omega_{kg}\left(\omega_{jg}+\frac{i}{2}\Gamma_{jg}+\omega\right)}\right), \tag{9}$$

where $\hat{\mu}_{gk_\alpha}$ is the α component of a transition electric dipole moment $\langle g|\hat{\mu}_\alpha|k\rangle$, and $\overline{\mu}$ is the fluctuation dipole operator [31,32], $\overline{\mu}\equiv\hat{\mu}-\langle g|\hat{\mu}|g\rangle$. The transition frequencies describing the perturbation by an electrostatic field should be real, whereas they were taken to be complex in Refs. [15,17–21].

One can also deduce the static-field-perturbed polarizability from the corresponding dynamic polarizability by setting an optical frequency and the associated complex damping term to zero.

Statistical averaging in a liquid leaves only the isotropic susceptibility, i.e., $\langle\chi^{(2)}_{\alpha\beta\gamma}(-\omega;\omega,0)\rangle=\chi^{(2)}(-\omega;\omega,0)\epsilon_{\alpha\beta\gamma}$, where $\epsilon_{\alpha\beta\gamma}$ is the unit skew-symmetric tensor and the pseudoscalar.

$$\chi^{(2)}(-\omega;\omega,0)=\frac{\mathcal{N}}{2\epsilon_0}\frac{1}{6}\epsilon_{\xi\eta\nu}\alpha^{(2)}_{\xi\eta\nu}(-\omega;\omega,0). \tag{10}$$

In the absence of an external magnetic field the time-independent wave functions of Eq. (9) can be chosen to be real for a closed-shell molecule. It is then easy to show that the terms in Eq. (9) are pairwise symmetric in α and β, so that $\chi^{(2)}(-\omega;\omega,0)$ is zero in a fluid, as required by the above symmetry argument.

The antisymmetric polarizability $\alpha'^{(1)}_{\alpha\beta}(-\omega;\omega)=-\alpha'^{(1)}_{\beta\alpha}(-\omega;\omega)$ of a molecule in the state g exists only if the unperturbed wave function is complex, and that is possible only for systems that are not symmetric under time reversal (for example, a fluid in a magnetostatic field) [2]. If $\alpha'^{(1)}_{\alpha\beta}(-\omega;\omega)$ is perturbed by a static electric field, then this requirement remains in force, so that $\alpha'^{(2)}_{\alpha\beta\gamma}(-\omega;\omega,0)=-\alpha'^{(2)}_{\beta\alpha\gamma}(-\omega;\omega,0)\equiv 0$ for any frequency ω. We conclude that linear electro-optical circular dichroism will not be exhibited by any nonconducting fluid, even at resonance.

IV. CONCLUSION

Perturbation expressions describe near-resonance optical phenomena by including damping phenomenologically, but must ensure that a real electric field gives rise to a real polarization [2,9–11,14]. A sign convention used in a recent publication for damping coefficients in sum-over-states expressions for optical response tensors [15] violates this requirement. The correct zero-frequency limit of the dynamic susceptibilities ensures that the linear electrooptic effect is forbidden by symmetry in any nonconducting isotropic system, contrary to recent predictions [17,18]. It may further be shown that optical rectification $(0;\omega,-\omega)$ and difference-frequency mixing $(-\omega;2\omega,-\omega)$ are in principle allowed in optically active liquids when ω approaches resonance.

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