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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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1.Introduction

Induced time varying polarization can be represented as power series of applied electric field.

$$
\begin{aligned}
P_\alpha(\omega) = {} & \epsilon_0 \chi^{(1)}_{\alpha\beta}(-\omega;\omega) E_\beta(\omega) + \epsilon_0 K^{(2)}(-\omega;\omega_1,\omega_2) \chi^{(2)}_{\alpha\beta\gamma} \\
& \times(-\omega;\omega_1;\omega_2) E_\beta(\omega_1) E_\gamma(\omega_2) + \cdots, \qquad (1)
\end{aligned}
$$

Relation between n-th order Molecular polarizability and susceptibility depends on average of directional cosine, number density.

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

Proof>Derivation of first order polarizability, $\alpha^{(1)}{}_{\alpha\beta}$

From time-dependent schrodinger equation and wave function described as linear combination of eigen functions.

$$i\hbar \frac{\partial \psi_s(\vec{r},t)}{\partial t} = \hat{H}\,\psi_s(\vec{r},t)$$

$$\psi_s(\vec{r},t) = \sum_n C_n^s(t) u_n(\vec{r})$$

Wave function of statistical ensemble of system 'S'

$$i\hbar \sum_n \frac{\partial C_n^s(t)}{\partial t} u_n(\vec{r}) = \hat{H} \sum_n C_n^s(t) u_n(\vec{r}), \text{take} \int dr^3 u_m^*(\vec{r}) \text{ then,}$$

by orthonormalitiy condition, $\int dr^3 u_m^*(\vec{r}) u_n(\vec{r}) = \delta_{mn}$

$$set, H_{mn} = \int dr^3 u_m^*(\vec{r}) \hat{H} u_n(\vec{r})$$

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1.Introduction

$$i\hbar \frac{\partial C_m^s(t)}{\partial t} = \sum_n H_{mn} C_n^s(t)$$

And system have statistical probability of remain state 'S'

$$\rho_{nm} = \sum_s P(s) C_m^{s^*}(t) C_n^s(t)$$ Take time derivative,

$$\dot{\rho}_{nm} = \frac{i}{\hbar}\left(\sum_s P(s)\frac{dC_m^{s^*}(t)}{dt} C_n^s(t) + \sum_s P(s) C_m^{s^*}(t)\frac{dC_n^s(t)}{dt}\right)$$

Substitute the time derivation of $C_n^s(t)$

$$\dot{\rho}_{nm} = \frac{i}{\hbar}\sum_s P(s)\sum_v \left(C_n^s C_v^{s^*} H_{vm} - C_n^{s^*} C_v^s H_{nv}\right) = \frac{i}{\hbar}\sum_v \left(\rho_{nv} H_{vm} - H_{nv}\rho_{vm}\right) = \frac{i}{\hbar}\left[\hat{\rho}, \hat{H}\right]_{nm}$$

1.Introduction

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}$$

From time dependent perturbation theory.

ρ can be expanded as power series of λ

$$\Rightarrow \quad \rho_{nm} = \rho_{nm}^{(0)} + \lambda \rho_{nm}^{(1)} + \lambda^2 \rho_{nm}^{(2)} + \cdots$$

We can also consider about damping term, $H^{(0)}{}_{nm} = E_{nm}\delta_{nm}$

$$\Rightarrow \quad \dot{\rho}_{nm} = \frac{i}{\hbar}\left[\hat{\rho}, \hat{H}\right]_{nm} - \frac{\Gamma_{nm}}{2}(\rho_{nm} - \rho_{nm}^{eq})$$

Substitute and rearrange by order of lambda. Then
we can get the relation denoted as below,

$$\Rightarrow \quad \dot{\rho}_{nm}^{(N)} = -(i\omega_{nm} + \frac{\Gamma_{nm}}{2})\rho_{nm}^{(N)} - \frac{i}{\hbar}\left[\hat{V}, \hat{\rho}^{(n-1)}\right]_{nm}$$

1.Introduction

For first order,

$$\dot{\rho}_{nm}^{(1)} = -(i\omega_{nm} + \frac{\Gamma_{nm}}{2})\rho_{nm}^{(1)} - \frac{i}{\hbar}\left[\hat{V}, \hat{\rho}^{(0)}\right]_{nm} = -(i\omega_{nm} + \frac{\Gamma_{nm}}{2})\rho_{nm}^{(1)} - \frac{i}{\hbar}\sum_{v}(\rho_{nv}^{(0)} V(t)_{vm} - V(t)_{nv}\rho_{vm}^{(0)})$$

$$\rho_{nv}^{(0)} = \rho_{nv}^{(0)}\delta_{vn}$$

If the perturbing potential is response of the applied field,

$$\hat{V}(t) = -\hat{\mu} \bullet \vec{E}(t), \vec{E}(t) = \vec{E}(\omega_p)e^{-i\omega_p t}$$

Take integration about t,

$$\rho_{nm}^{(1)} = \frac{1}{\hbar}(\rho_{mm}^{(0)} - \rho_{nn}^{(0)})\frac{\left[\overrightarrow{\mu_{nm}} \bullet \vec{E}(\omega_p)e^{-i\omega_p t}\right]}{((\omega_{nm} - \omega_p) - i\frac{\Gamma_{nm}}{2})}$$

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1.Introduction

expectation value of operator A

$$< A >= \sum_{n,m} \rho_{nm} A_{mn} = \sum_{n} \sum_{m} \rho_{nm} A_{mn} = \sum_{n} (\rho A)_{nn} = tr(\hat{\rho} \hat{A})$$

So, expectation value of $\hat{\mu}$ is,

$$< \hat{\mu} >= \sum_{n,m} \rho_{nm}{}^{(1)} \mu_{mn} = \frac{1}{\hbar} \sum_{n,m} (\rho_{mm}{}^{(0)} - \rho_{nn}{}^{(0)}) \frac{\overrightarrow{\mu_{mn}} \left[\overrightarrow{\mu_{nm}} \bullet \vec{E}(\omega_p) e^{-i\omega_p t} \right]}{((\omega_{nm} - \omega_p) - i \frac{\Gamma_{nm}}{2})}$$

$$< \hat{\mu} >= \frac{1}{\hbar} \sum_{n,m} \rho_{mm}{}^{(0)} \frac{\overrightarrow{\mu_{mn}} \left[\overrightarrow{\mu_{nm}} \bullet \vec{E}(\omega_p) e^{-i\omega_p t} \right]}{((\omega_{nm} - \omega_p) - i \frac{\Gamma_{nm}}{2})} - \sum_{m,n} \rho_{mm}{}^{(0)} \frac{\overrightarrow{\mu_{mn}} \left[\hat{\mu}_{mn} \bullet \vec{E}(\omega_p) e^{-i\omega_p t} \right]}{((-\omega_{nm} - \omega_p) - i \frac{\Gamma_{nm}}{2})}$$

at initial state, energy level of system is ground state,

$$\rho_{mm}{}^{(0)} = \rho_{mm}{}^{(0)} \delta_{mg}$$

1.Introduction

At last, first order polarizability is,

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

If there is no damping process,

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

2.Sign of phenomenological damping coefficient

BRIEF REPORTS

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].

Apply time reversal potential

$$\hat{V}(-t) = -\hat{\mu}\bullet\vec{E}(-t), \vec{E}(-t) = \vec{E}(\omega_p)e^{i\omega_p t}$$

$$<\hat{\mu}> = \frac{1}{\hbar}\sum_{n,m}\rho_{mm}^{(0)}\frac{\overrightarrow{\mu_{mn}}\left[\overrightarrow{\mu_{nm}}\bullet\vec{E}(\omega_p)e^{-i\omega_p t}\right]}{((\omega_{nm}+\omega_p)-i\frac{\Gamma_{nm}}{2})} + \sum_{m,n}\rho_{mm}^{(0)}\frac{\overrightarrow{\mu_{mn}}\left[\hat{\mu}_{mn}\bullet\vec{E}(\omega_p)e^{-i\omega_p t}\right]}{((\omega_{nm}-\omega_p)+i\frac{\Gamma_{nm}}{2})}$$

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2.Sign of phenomenological damping coefficient

We require that real electric field induces real polarization

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

It follows that,

$$E_{\beta}(-\omega)=E^{*}_{\beta}(\omega),$$
$$\chi^{(1)}_{\alpha\beta}(-\omega;\omega)=\chi^{(1)*}_{\alpha\beta}(\omega;-\omega). \qquad (6)$$

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.

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3.Pockels tensor in optically active liquids

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].

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

The ground state weakly perturbed by electro static field is,

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

And the ground state perturbed by optical field $E_\gamma = \frac{E_\gamma^{(0)}(e^{-i\omega t} + e^{i\omega t})}{2}$ is,

(as shown in sec 1)

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3.Pockels tensor in optically active liquids

Derivation of Pockels tensor from second order polarization

$$\dot{\rho}_{nm}^{(2)} = -(i\omega_{nm} + \frac{\Gamma_{nm}}{2})\rho_{nm}^{(2)} - \frac{i}{\hbar}\left[\hat{V}, \hat{\rho}^{(1)}\right]_{nm}$$

$$\rho_{nm}^{(1)} = \frac{1}{\hbar}(\rho_{mm}^{(0)} - \rho_{nn}^{(0)})\frac{\hat{\mu}_{nm} \bullet \vec{E}(\omega_p)e^{-i\omega_p t}}{((\omega_{nm} - \omega_p) - i\frac{\Gamma_{nm}}{2})}$$

$$\left[\hat{V}, \hat{\rho}^{(1)}\right]_{nm} = -\frac{1}{\hbar}\sum_{v}(\rho_{mm}^{(0)} - \rho_{vv}^{(0)})\frac{\left[\hat{\mu}_{nv} \bullet \vec{E}(\omega_q)\right]\left[\hat{\mu}_{vm} \bullet \vec{E}(\omega_p)\right]e^{-i(\omega_p + \omega_q)t}}{((\omega_{vm} - \omega_p) - i\frac{\Gamma_{vm}}{2})}$$

$$+\frac{1}{\hbar}\sum_{v}(\rho_{vv}^{(0)} - \rho_{nn}^{(0)})\frac{\left[\hat{\mu}_{nv} \bullet \vec{E}(\omega_p)\right]\left[\hat{\mu}_{vm} \bullet \vec{E}(\omega_q)\right]e^{-i(\omega_p + \omega_q)t}}{((\omega_{nv} - \omega_p) - i\frac{\Gamma_{nv}}{2})}$$

3.Pockels tensor in optically active liquids

$$\rho_{nm}^{(2)} = \sum_{v}\sum_{p,q} e^{-i(\omega_p+\omega_q)t} \left\{ \frac{\rho_{mm}^{(0)} - \rho_{vv}^{(0)}}{\hbar^2} \frac{\left[\hat{\mu}_{nv}\bullet\vec{E}(\omega_q)\right]\left[\hat{\mu}_{vm}\bullet\vec{E}(\omega_p)\right]}{\left[(\omega_{nm}-\omega_p-\omega_q) - i\frac{\Gamma_{nm}}{2}\right]\left[(\omega_{vm}-\omega_p) - i\frac{\Gamma_{vm}}{2}\right]} - \frac{\rho_{vv}^{(0)} - \rho_{nn}^{(0)}}{\hbar^2} \frac{\left[\hat{\mu}_{nv}\bullet\vec{E}(\omega_p)\right]\left[\hat{\mu}_{vm}\bullet\vec{E}(\omega_q)\right]}{\left[(\omega_{nm}-\omega_p-\omega_q) - i\frac{\Gamma_{nm}}{2}\right]\left[(\omega_{nv}-\omega_p) - i\frac{\Gamma_{nv}}{2}\right]} \right\}$$

After doing same procedure as section 1(but lengthy….)

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

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3.Pockels tensor in optically active liquids

Statistical averaging in liquid leaves only the isotropic susceptibility

$$\langle \chi^{(2)}_{\alpha\beta\gamma}(-\omega;\omega,0)\rangle = \chi^{(2)}(-\omega;\omega,0)\,\epsilon_{\alpha\beta\gamma},$$

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

Because (9) is symmetric in α and β, (10) will be zero in any isotropic, non-conducting fluid.

Pockel effect doesn’t appear in isotropic, non-conducting fluid

4.Conclusion

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.