Influence of damping on the vanishing of the linear electro-optic effect in chiral isotropic media

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Using first principles, it is demonstrated that radiative damping alone cannot lead to a nonvanishing linear electro-optic effect in a chiral isotropic medium. This conclusion is in contrast with that obtained by a calculation in which damping effects are included using the standard phenomenological model. We show that these predictions differ because the phenomenological damping equations are valid only in regions where the frequencies of the applied electromagnetic fields are nearly resonant with the atomic transitions. We also show that collisional damping can lead to a nonvanishing linear electro-optic effect, but with a strength sufficiently weak, it is unlikely to be observable under realistic laboratory conditions.

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Several recent papers [1,2] have discussed the question of properly taking into account various relaxation processes while calculating the nonlinear response of an optical system. Even the existence of certain nonlinear optical processes is thought to be closely linked to the existence of a damping mechanism [3–5]. In this connection, it is especially important to incorporate in a consistent manner the effects of relaxation processes. Very often, the nonlinear response [6] is calculated by modifying the equation for the off-diagonal elements of the density matrix (coherences) by introducing phenomenological relaxation terms as follows:

$$\frac{\partial \rho_{ij}}{\partial t} = -i\omega_{ij}\rho_{ij} + (\text{field terms}) \Rightarrow \tag{1}$$

$$\frac{\partial \rho_{ij}}{\partial t} = -i\omega_{ij}\rho_{ij} - \Gamma_{ij}\rho_{ij} + (\text{different field terms}). \tag{2}$$

The equations for the populations are also modified appropriately. Such modifications have been extensively used in nonlinear optics and even have led to the prediction of phenomena such as collision-induced resonances that have been subsequently observed experimentally [7].

The importance of relaxation processes in establishing the existence of certain nonlinear optical processes has recently been raised in the context of the linear electo-optic effect [1,2,5]. For reasons of symmetry, the linear electro-optic effect must vanish in an isotropic nonchiral material. However, in a chiral material, symmetry arguments alone cannot rule out the possibility of the existence of a linear electro-optic effect. Thus, the question of the existence of such an effect must be decided by means of an explicit quantum-mechanical calculation of the electro-optic response. Several calculations of this sort have recently been reported, and have led to conflicting results. Buckingham and Fischer [1] and Stedman *et al.* [2] have concluded that the linear electro-optic effect much vanish. However, Kauranen and Persoons [4] have recently presented a theoretical argument that predicts the existence of a linear electro-optic effect (EOE) in chiral isotropic media provided material damping is taken into account. Their result follows by using Eq. (2). However, it is not clear *a priori* if Eq. (2) can be used to describe the linear electro-optic effect. In order to see the origin of this uncertainty, let us examine the expression for the nonlinear susceptibility describing the electro-optic effect in a chiral isotropic medium. The derivation given in Ref. [4] is based on the standard phenomenological equations Eq. (2) which take into account various damping processes in the medium. The nonlinear susceptibility is shown to have contributions of the form

$$X \equiv \frac{2i\gamma_{ng}}{(\omega_{ng}-i\gamma_{ng})(\omega_{ng}+i\gamma_{ng})(\omega_{mg}+\omega+i\gamma_{mg})}. \tag{3}$$

The authors of Ref. [4] have suggested that this damping-dependent contribution is the one which can lead to a nonvanishing electro-optic effect in a chiral isotropic medium. Let us examine this contribution further. We note first that the usual expression for the second-order susceptibility consists of two energy denominators, whereas the above contribution consists of three. Clearly, such a term arises from the combination of two contributions as X can be written as

$$X = \frac{1}{(\omega_{mg}+\omega+i\gamma_{mg})}\left[\frac{1}{\omega_{ng}-i\gamma_{ng}} - \frac{1}{\omega_{ng}+i\gamma_{ng}}\right]. \tag{4}$$

We note also that denominators such as $(\omega_{ng}-i\gamma_{ng})$ do not have an optical frequency contribution. Such denominators arise from the interaction of the system with a zero-frequency field. We show below that in a correct treatment of radiative damping, the denominator should be replaced by ones that involve frequency-dependent damping coefficients. Thus, a first-principles treatment would lead to

$$X \equiv \frac{1}{[\omega_{mg}+\omega+i\gamma_{mg}(\omega)]}\left[\frac{1}{[\omega_{ng}-i\gamma_{ng}(0)]} - \frac{1}{[\omega_{ng}+i\gamma_{ng}(0)]}\right]. \tag{5}$$

Note that the frequency dependence of γ in each denominator depends on the frequency component of the electromagnetic field responsible for such a denominator. Thus, the denominators corresponding to the static field have dampings evaluated at zero frequency. As discussed below, for the case of radiative damping, $\gamma_{ng}(0)$ vanishes identically, which implies that $X=0$. Thus, a first principles (and correct) treatment of radiative damping does *not* lead to any electro-optic effect in a chiral isotropic medium. We also show below that X is at most very small for the case of collisional damping. The nonvanishing of the EOE effect reported earlier is due to inappropriate use of equations that are not valid for the calculation of the EOE effect. Thus, when using the modification (2) in the calculation of the nonlinear optical response, one has to keep in view the conditions under which Eq. (2) has been derived. This need necessitates an examination of the microscopic theory leading to the derivation of result (2). It may also be noted that, in recent times, one has discovered a number of other interesting situations that cannot be described by equations such as Eq. (2). For example, there are situations under which the coherences get coupled to the populations, and this situation has led to considerable work on quantum interferences [8]. In addition, there is the subject of inhibited spontaneous emission, where the modifications of Eq. (2) due to strong external fields play an important role [9].

In order to uncover the role of relaxation mechanisms on the response to external fields and to determine how relaxation depends on the frequency of the applied field, we consider first a very simple model. This model brings out the salient features of the problem and enables us to establish that the form of the damping operator depends on the various frequency scales in the system. We consider the case in which the medium can be described by a one-dimensional harmonic oscillator with displacement x and with frequency ω_0. Let the medium interact with an external electromagnetic field of frequency ω described by

$$E=\mathcal{E}e^{-i\omega t}+\mathcal{E}^{*}e^{i\omega t}. \tag{6}$$

The equation of motion with a phenomenological damping constant Γ is

$$\ddot{x}+\Gamma\dot{x}+\omega_0^2x=\frac{e\mathcal{E}}{m}e^{-i\omega t}+\text{c.c.} \tag{7}$$

The response of the medium can then be expressed as

$$ex(t)=\chi(\omega)\mathcal{E}e^{-i\omega t}+\text{c.c.}, \tag{8}$$

$$\chi(\omega)=\frac{e^2}{m(\omega_0^2-\omega^2-i\omega\Gamma)}. \tag{9}$$

In this manner, one obtains the familiar response function. We would like to examine whether the response $\chi(\omega)$, as given by Eq. (9), is valid for all frequencies. Thus, we would like to understand if the introduction of a *frequency-independent* damping constant Γ in Eq. (7) is justified for all frequencies of the applied electromagnetic field. For this purpose, we start from first principles. Let us consider the interaction of the system oscillator with a bath. The bath will be responsible for the relaxation processes described phenomenologically by the damping parameter Γ in Eq. (7). As usual, we model the bath by a set of harmonic oscillators. The Hamiltonian for the system oscillator interacting with a bath is given by

$$H=\frac{p^2}{2m}+\frac{1}{2}m\omega_0^2x^2-ex\mathcal{E}(t)-xF(t), \tag{10}$$

where $\mathcal{E}$(t) is the time-dependent electromagnetic field and $F(t)$ represents the effect of the bath terms

$$F(t)=\sum_j\ (g_ja_je^{-i\omega_jt}+\text{H.c.}). \tag{11}$$

Here, $\omega_j(>0)$ are the frequencies of the bath oscillators a_j and g_j are the coupling constants of the system oscillator with the bath oscillators. The Heisenberg equations can be easily derived from Eq. (10):

$$\dot{x}=p/m,\quad \dot{p}=-m\omega_0^2x+e\mathcal{E}(t)+F(t),$$

$$\dot{a}_j=ig_j^{*}e^{i\omega_jt}x(t). \tag{12}$$

We integrate formally the equation for a_j and substitute it into the equation for p to obtain

$$\dot{p}=-m\omega_0^2x+e\mathcal{E}(t)+F_0(t)+\int_0^tK(t-\tau)x(\tau)d\tau, \tag{13}$$

where

$$F_0(t)=\sum_j\ g_ja_j(0)e^{-i\omega_jt}+\text{H.c.}, \tag{14}$$

$$K(t-\tau)=\left(i\sum_j\ |g_j|^2e^{-i\omega_j(t-\tau)}+\text{c.c.}\right). \tag{15}$$

Note that Eq. (13) is derived without any approximation. The further simplification will depend on the values of $|g_j|$, ω_j, ω, etc. Let us examine the average response for the case in which $\mathcal{E}(t)=\mathcal{E}e^{-i\omega t}+\text{c.c.}$ Note that the mean value of the operator $a_j(0)$ is zero and hence, $\langle F_0(t)\rangle=0$. It should be borne in mind that ω is positive. Using Eqs. (13) and (14), taking quantum-mechanical expectation values and the long-time limit $t\rightarrow\infty$, we obtain

$$\langle x\rangle=\frac{e\mathcal{E}e^{-i\omega t}}{m(\omega_0^2-\omega^2)-K(\omega)}+\text{c.c.}, \tag{16}$$

where

$$K(\omega)=\lim_{\epsilon\rightarrow0}\sum_j\ |g_j|^2i\left\{\frac{1}{\epsilon+i(\omega_j-\omega)}-\frac{1}{\epsilon-i(\omega_j+\omega)}\right\}$$

$$=K'(\omega)+iK''(\omega), \tag{17}$$

$$K''(\omega)=\sum_j\ |g_j|^2\pi\delta(\omega_j-\omega). \tag{18}$$

The exact result (16) has the same structure as Eq. (9), except for the important difference that $\omega\Gamma$ is replaced by a function $K''(\omega)$ that is dependent on the frequency ω of the applied electromagnetic field. In addition, there is a dispersive contribution $\mathrm{Re}\,K(\omega)$. Note further that very often one replaces Eq. (18) by

$$K''(\omega)\approx\sum_j |g_j|^2\pi\delta(\omega_j-\omega_0). \tag{19}$$

Clearly, this can be done if the frequency ω_0 of the system oscillator is very close to the applied frequency, i.e., essentially in the resonance region. If the frequency ω happens to be far away from a resonance frequency, then the phenomenological equation (7) should not be used. This is the real reason why usage of equations such as Eqs. (2) and (7) can give rise to incorrect nonlinear optical response for applied frequencies far away from the transition frequencies. We also find from Eq. (18) that for static response

$$\lim_{\omega\to 0} K''(\omega)\to\pi|g_j|^2|_{\omega_j=0}\to 0 \tag{20}$$

for the usual radiative coupling. Thus, the static response functions would be independent of the damping term. More generally, no damping term can appear in the static response as long as the bath does not have a characteristic static frequency.

The features discussed above are valid rather generally. To see this, we consider the dynamical equations for a two-level system undergoing, say, radiative damping. The case of a two-level system is more involved because of the intrinsic nonlinearity of the two level system. However, the salient features can be uncovered by using the wave-function approach. Let us write the interaction Hamiltonian of a two level system interacting with the field and undergoing radiative damping, as

$$\begin{aligned}H=&\hbar\omega_0|e\rangle\langle e|-\hbar[G(t)|e\rangle\langle g|+\text{H.c.}]\\&-\hbar\sum_k (g_k a_k e^{-i\omega_k t}|e\rangle\langle g|+\text{H.c.}),\end{aligned} \tag{21}$$

where we sum over all field modes, labeled by the index k and where,

$$\begin{aligned}G(t)&=\vec{d}\cdot\vec{E}(t)/\hbar\\&=G_0e^{-i\omega t}+\text{c.c.}\end{aligned} \tag{22}$$

The last term in Eq. (21) is responsible for the radiative decay of the atom. The coupling to the mode k with frequency ω_k of the electromagnetic field is represented by g_k and a_k is the photon annihilation operator. The wave function of the whole system can be expressed as

$$|\psi\rangle=\psi_e|e,\{0\}\rangle+\psi_g|g,\{0\}\rangle+\sum_k \psi_k|g,\{k\}\rangle, \tag{23}$$

where $\{0\}(\{k\})$ represents the vacuum (one photon in mode k) state of the field. The Schrödinger equation leads to

$$\begin{aligned}\dot{\psi}_g&=iG^*(t)\psi_e,\\ \dot{\psi}_e&=-i\omega_0\psi_e+iG(t)\psi_g+i\sum_k g_k e^{-i\omega_k t}\psi_k,\\ \dot{\psi}_k&=ig_k^*\psi_e e^{i\omega_k t}.\end{aligned} \tag{24}$$

The initial conditions are $\psi_e=\psi_k=0$, and $\psi_g=1$. The induced polarization is to be obtained from the off-diagonal element $\rho_{eg}=\psi_e\psi_g^*$. Note that to first order in the applied electromagnetic field, ρ_{eg} is

$$\begin{aligned}\rho_{eg}^{(1)}(t)&=\psi_e^{(1)}(t)\psi_g^{*(0)}(t)+\psi_e^{(0)}(t)\psi_g^{*(1)}(t)\\&=\psi_e^{(1)}(t)\end{aligned} \tag{25}$$

$$\xrightarrow{t\to\infty}\quad \psi^{(+)}e^{-i\omega t}+\psi^{(-)}e^{i\omega t}. \tag{26}$$

To obtain the steady state response, we combine last two equations in Eq. (24)

$$\dot{\psi}_e=-i\omega_0\psi_e+iG(t)\psi_g-\sum_k |g_k|^2\int_0^t e^{-i\omega_k(t-\tau)}\psi_e(\tau)d\tau, \tag{27}$$

and thus, to first order in the external electromagnetic field, we obtain

$$\dot{\psi}_e^{(1)}=-i\omega_0\psi_e^{(1)}+iG(t)-\sum_k |g_k|^2\int_0^t e^{-i\omega_k(t-\tau)}\psi_e^{(1)}(\tau)d\tau. \tag{28}$$

In terms of Laplace transforms, we have the result

$$\begin{aligned}\hat{\psi}_e^{(1)}(z)=&\left\{z+i\omega_0+\sum_k |g_k|^2(z+i\omega_k)^{-1}\right\}^{-1}i\{G_0(z+i\omega)^{-1}\\&+G_0^*(z-i\omega)^{-1}\},\end{aligned} \tag{29}$$

where we have used the explicit form (22). From Eq. (29), we get the response in the long-time limit

$$\begin{aligned}\psi^{(+)}&=\left[i(\omega_0-\omega)+\sum_k |g_k|^2(i\omega_k-i\omega)^{-1}\right]^{-1}G_0,\\ \psi^{(-)}&=\left[i(\omega_0+\omega)+\sum_k |g_k|^2(i\omega_k+i\omega)^{-1}\right]^{-1}G_0^*.\end{aligned} \tag{30}$$

The induced polarization can now be calculated

$$\begin{aligned}\vec{p}(t)&=(\rho_{eg}\vec{d}_{eg}^*+\text{c.c.})\\&\equiv\vec{p}_0e^{-i\omega t}+\text{c.c.},\end{aligned} \tag{31}$$

where $\vec{p}_0$ is calculated, using Eq. (30), as

$$\vec{p}_0=\psi^{(+)}\vec{d}_{eg}^*+\psi_e^{(-)*}\vec{d}_{eg}. \tag{32}$$

This is the most general result for the linear response. No assumption has been made regarding the nature of the bath. It should be borne in mind that all frequencies in Eq. (30) are positive. The radiative corrections enter the response function through the quantity

$$K(z)=\sum_k |g_k|^2(z+i\omega_k)^{-1}. \tag{33}$$

It should be noted that the actual radiative correction terms depend on the frequencies of the applied fields rather than the atomic frequencies. It is only when the applied frequency is close to the atomic frequency that we can use the approximate replacement $\omega\rightarrow\omega_0$ in $\psi^{(+)}$ (this cannot be done in $\psi^{(-)}$). We thus find that the counterrotating contribution $\psi^{(-)*}$ in Eq. (32) does *not* depend on the radiative damping [10]. The rotating-wave contribution depends on the radiative damping; however, the radiative damping is to be evaluated at the applied frequency. If such an applied frequency is very far from the atomic transition, as, for example, for dc fields, then *no* radiative damping term appears in the response. Thus, the full quantum-mechanical calculation also leads to the same conclusion as we derived for the simple oscillator model. Further, the above analysis can be easily extended to the multilevel systems and to the calculation of second-order and higher-order responses. We find similar conclusions regarding the various denominators which appear in response functions. The argument given in the context of Eqs. (4) and (5) is correct and we rule out the possibility of the occurence of electro-optics effect due to radiative damping.

A pertinent question could be: can other damping mechanisms, such as phase changing collisions, possibly lead to the nonvanishing of the EOE in isotropic chiral medium? This question has to be examined by considering a detailed microscopic model for the collisional process. However, a simple model calculation, outlined below, suggests that even if the effect is nonvanishing, it must be extremely small; particularly, it must exponentially small in a large quantity.

Consider the equation for the optical coherence $\sigma\equiv\rho_{eg}$. Let $f(t)$ be a stochestic source that represents the effect of phase changing collisions. We model $f(t)$ to be a Gaussian stochastic process with correlations given by

$$\langle f(t)\rangle=0,\quad \langle f(t)f(\tau)\rangle=e^{-\Gamma|t-\tau|}f_0^2. \tag{34}$$

Here Γ^{-1} is the magnitude of the collision time. The equation for the optical coherence can be written in the form

$$\dot{\sigma}=-i\Delta\sigma-if(t)\sigma+iG, \tag{35}$$

where G represents the external field. If Γ^{-1} is the smallest time scale in the problem, then one can show using the standard methods [11] that

$$\langle\sigma\rangle=\left(\frac{f_0^2}{\Gamma}+i\Delta\right)^{-1}(iG). \tag{36}$$

Thus, one recovers the result of the phenomenological theory. However, for the response to a static field, Δ is of the order of the optical frequency whereas typical collisional process take place over a scale that is of the order of picosecond, or larger. Thus, Γ^{-1} is no longer the smallest time in the problem. The smallest time scale will instead be Δ^{-1}. In such a case, one can show that in the long-time limit

$$\langle\sigma\rangle=iG\int_0^\infty d\tau e^{-i\Delta\tau}\exp\left\{-\frac{f_0^2}{\Gamma}\left(\tau-\frac{(1-e^{-\Gamma\tau})}{\Gamma}\right)\right\}$$
$$\approx iG\int_0^\infty d\tau e^{-i\Delta\tau}e^{-(1/2)f_0^2\tau^2}. \tag{37}$$

Note that the square bracket in Eq. (4) is just the real part of $\int_0^\infty d\tau e^{-i\omega_{ng}\tau-\gamma_{ng}\tau}$, and thus, if we had treated the damping properly, it has to be replaced by

$$[\ ]\rightarrow \mathrm{Re}\int_0^\infty d\tau e^{-i\omega_{ng}\tau-(1/2)f_{ng}^2\tau^2}$$
$$=\sqrt{\pi 2 f_{ng}^2}\exp\left(-\frac{\omega_{ng}^2}{2f_{ng}^2}\right). \tag{38}$$

Thus, collisional damping can make the EOE in chiral isotropic medium nonzero. However, it would be extremely small unless the strength of collisions is comparable to ω_{ng}, i.e., $\omega_{ng}\sim f_{ng}$.

In conclusion, we have shown that radiative damping cannot lead to a nonvanishing EOE in a chiral isotropic material. For the case of collisional damping, a nonvanishing EOE is predicted, but the magnitude of this effect is expected to be so small that it is unlikely that this effect could be observed experimentally. These results are in contrast with recent suggestions that relaxation effects can lead to an EOE in chiral isotropic materials, with potentially important practical implications. More generally, we have shown that in general, it is not adequate to use a frequency-independent damping parameter in treating relaxation processes within the context of density-matrix calculations.

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