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

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Abstract

Using first principles, it is demonstrated that radiative damping alone cannot lead to a nonvanishing 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 electrooptic effect, but with a strength sufficiently weak that it is unlikely to be observable under realistic laboratory conditions.
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:

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

\[
\frac{\partial \rho_{ij}}{\partial t} = -i\omega_{ij}\rho_{ij} - \Gamma_{ij}\rho_{ij} + \text{different field terms} \Rightarrow (2)
\]

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 new effects such as collision-induced resonances which have been subsequently been observed experimentally [7]. 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 (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 (2) which take into account various damping processes in the medium. The nonlinear susceptibility is shown to have contributions of the form

\[
X \equiv \frac{2i\gamma_{ng}}{(\omega_{ng} - i\gamma_{ng})(\omega_{ng} + i\gamma_{ng})(\omega + \omega + i\gamma_{mg})}. \quad (3)
\]

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

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

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

\[
X \equiv \frac{1}{(\omega_{mg} +\omega + i\gamma_{mg})(\omega_{ng} - i\gamma_{ng}(0))} - \frac{1}{(\omega_{ng} + i\gamma_{ng}(0))}. \quad (5)
\]
Note that the frequency dependence of $\gamma$ 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 which 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 (2) has been derived. This need necessitates an examination of the microscopic theory leading to the derivation of the result (2). It may also be noted that, in recent times, one has discovered a number of other interesting situations which cannot be described by equations like (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 (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 $\omega_0$. Let the medium interact with an external electromagnetic field of frequency $\omega$ described by

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

The equation of motion with a phenomenological damping constant $\Gamma$ is

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

The response of the medium can then be expressed as

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

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

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 $\Gamma$ 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 $\Gamma$ 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
\[ H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2_0 x^2 - e x E(t) -xF(t), \]  

(10)

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

\[ F(t) = \sum_j (g_j a_j e^{-i\omega_j t} + h.c.). \]  

(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 (10):

\[ \dot{x} = p/m, \quad \dot{p} = -m\omega^2_0 x + e E(t) + F(t), \]

\[ \dot{a}_j = ig_j^* e^{i\omega_j t} x(t). \]  

(12)

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

\[ \dot{p} = -m\omega^2_0 x + e E(t) + F_0(t) + \int_0^t K(t - \tau)x(\tau)d\tau, \]  

(13)

where

\[ F_0(t) = \sum_j g_j a_j(0) e^{-i\omega_j t} + h.c., \]  

(14)

\[ K(t - \tau) = (i \sum_j |g_j|^2 e^{-i\omega_j(t-\tau)} + c.c.). \]  

(15)

Note that Eq. (13) is derived without any approximation. The further simplification will depend on the values of \( |g_j|, \omega_j, \omega \) etc. Let us examine the average response for the case in which \( E(t) = E e^{-i\omega t} + c.c. \) 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 \( \omega \) is positive. Using Eqs. (13) and (14), taking quantum mechanical expectation values and the long-time limit \( t \to \infty \), we obtain

\[ \langle x \rangle = \frac{e E e^{-i\omega t}}{m(\omega^2_0 - \omega^2)} - K(\omega) + c.c., \]  

(16)

where

\[ K(\omega) = \lim_{\epsilon \to 0} \sum_j |g_j|^2 \left\{ \frac{1}{\epsilon + i(\omega_j - \omega)} - \frac{1}{\epsilon - i(\omega_j + \omega)} \right\} \]

\[ = K'(\omega) + iK''(\omega), \]  

(17)

\[ K''(\omega) = \sum_j |g_j|^2 \pi \delta(\omega_j - \omega). \]  

(18)

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

\[
K''(\omega) \approx \sum_j |g_j|^2 \pi \delta(\omega_j - \omega_0).
\]

Clearly this can be done if the frequency \( \omega_0 \) of the system oscillator is very close to the applied frequency, i.e., essentially in the resonance region. If the frequency \( \omega \) 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 like (2) and (7) can give rise to incorrect nonlinear optical response for applied frequencies far away from the transition frequencies.

We also find from (18) that for static response

\[
\lim_{\omega \to 0} K''(\omega) \rightarrow \pi |g_j|^2 \mid_{\omega_j=0} \rightarrow 0,
\]

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 wavefunction approach. Let us write the interaction Hamiltonian of a two level system interacting with the field and undergoing radiative damping, as

\[
H = \hbar \omega_0 |e\rangle \langle e| - \hbar [G(t)|e\rangle \langle g| + \text{ h.c.}] - \hbar \sum_k (g_k a_k e^{-i\omega_k t}|e\rangle \langle g| + \text{ h.c.)},
\]

where we sum over all field modes labelled by the index \( k \) and where,

\[
G(t) = \frac{\vec{d} \cdot \vec{E}(t)}{\hbar} = G_0 e^{-i\omega t} + \text{ c.c. .}
\]

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

\[
|\psi\rangle = \psi_e |e, \{0\}\rangle + \psi_g |g, \{0\}\rangle + \sum_k \psi_k |g, \{k\}\rangle,
\]

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

\[
\dot{\psi}_g = iG^*(t)\psi_e, \\
\dot{\psi}_e = -i\omega_0 \psi_e + iG(t)\psi_g + i \sum_k g_k e^{-i\omega_k t} \psi_k, \\
\dot{\psi}_k = ig_k^* \psi_e e^{i\omega_k t}.
\]
The initial conditions are $\psi_e = \psi_k = 0, \psi_g = 1$. 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, $\rho_{eg}$ is

$$
\rho_{eg}^{(1)}(t) = \psi_e^{(1)}(t) \psi_g^{* (0)}(t) + \psi_e^{(0)}(t) \psi_g^{* (1)}(t) = \psi_e^{(1)}(t)
$$

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

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

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

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

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

In terms of Laplace transforms we have the result

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

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

$$
\psi^{(+)} = \left( i(\omega_0 - \omega) + \sum_k |g_k|^2 (i\omega_k - i\omega)^{-1} \right)^{-1} G_0,
$$

$$
\psi^{(-)} = \left( i(\omega_0 + \omega) + \sum_k |g_k|^2 (i\omega_k + i\omega)^{-1} \right)^{-1} G_0^*.
$$

The induced polarization can now be calculated

$$
\vec{p}(t) = (\rho_{eg} \vec{d}_{eg} + \text{c.c.})
\equiv \vec{p}_0 e^{-i\omega t} + \text{c.c.},
$$

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

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

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 (30) are positive. The radiative corrections enter the response function through the quantity

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

(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 counter-rotating 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 response. 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 occurrence 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 non-vanishing it must be extremely small; in particular it must exponentially small in a large quantity.

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

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

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

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

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

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

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

$$
\langle \sigma \rangle = iG \int_0^\infty d\tau e^{-i\Delta \tau} \exp \left\{ -\frac{f_0^2}{\Gamma} \left( \tau - \frac{(1-e^{-\Gamma \tau})}{\Gamma} \right) \right\}
\approx iG \int_0^\infty d\tau e^{-i\Delta \tau} e^{-\frac{1}{2}f_0^2 \tau^2}.
$$
Note that the square bracket in Eq. (4) is just the real part of $\int_0^\infty d\tau e^{-i\omega_n g \tau - \gamma_n g \tau}$, and thus if we had treated the damping properly it has to be replaced by

$$[\ ] \rightarrow \operatorname{Real} \int_0^\infty d\tau e^{-i\omega_n g \tau - \frac{1}{2}f_{n g}^{2}\tau^2}$$

$$= \sqrt{\frac{\pi}{2f_{n g}^{2}}} \exp \left(-\frac{\omega_{n g}^{2}}{2f_{n g}^{2}}\right). \quad (38)$$

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 $\omega_{n g}$ i.e., $\omega_{n g} \sim f_{n g}$.

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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