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Chirality and polarization effects in nonlinear optics

Robert W Boyd[1], **John E Sipe**[2] **and Peter W Milonni**[3]

[1] Institute of Optics and Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, USA
[2] Department of Physics, University of Toronto, Toronto, ON, M5S 1A7, Canada
[3] Theoretical Division (T-TOC), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract
Polarization effects play an even more important role in nonlinear optics than in linear optics because of the richer set of phenomena describable by higher-order tensor relations. The present contribution surveys some recent research on polarization aspects of nonlinear optical interactions, paying special attention to nonlinear optical interactions in chiral isotropic optical materials. We especially address the question of the existence of a linear electro-optic effect in chiral isotropic materials and analyse some of the conflicting statements that have recently been made in the scientific literature.

Keywords: polarization, nonlinear optics, molecular optics, chirality

1. Introduction

Although polarization is an inherent property of light and plays a role in all optical phenomena, polarization effects manifest themselves in an especially dominant manner in nonlinear optical interactions. At a formal level, polarization effects become so important in nonlinear optics because the dielectric response is described by a tensor relation. In linear optics, the dielectric susceptibility is a second-rank tensor designated $\chi_{ij}^{(1)}$. In contrast, second-order nonlinear optical interactions (an example of which is the process of second-harmonic generation) are described by the third-rank tensor $\chi_{ijk}^{(2)}$, and third-order interactions (which, for instance, describe the intensity-dependent refractive index) are described by the fourth-rank tensor $\chi_{ijkl}^{(3)}$. The polarization of the material is given in terms of these susceptibilities by expressions of the form

$$P_i^{(1)} = \chi_{ij}^{(1)} E_j \qquad P_i^{(2)} = \chi_{ijk}^{(2)} E_j E_k \qquad P_i^{(3)} = \chi_{ijkl}^{(3)} E_j E_k E_l. \tag{1}$$

The increasing complexity of the nonlinear susceptibility for higher-order interactions leads to richer polarization phenomena for such interactions.

To make this point explicit, let us note that in linear optics it is often convenient to work in the scalar approximation by treating the polarization, electric field, and susceptibility as scalar quantities related by

$$P = \chi^{(1)} E. \tag{2}$$

For an isotropic, non-gyrotropic medium, the scalar approximation entails no loss of detail regarding the interaction. However, for such a medium the degenerate third-order nonlinear response is described most generally by the relation [1]

$$\mathbf{P} = A(\mathbf{E}\cdot\mathbf{E}^*)\mathbf{E} + \tfrac{1}{2}B(\mathbf{E}\cdot\mathbf{E})\mathbf{E}^* \tag{3}$$

where $A = 6\chi_{1122}^{(3)} = 3\chi_{1122}^{(3)} + 3\chi_{1212}^{(3)}$ and $B = 6\chi_{1221}^{(3)}$ denote the independent tensor elements of the nonlinear response tensor, assuming that the frequency dependence in each case is $\chi^{(3)}(\omega;\omega,\omega,-\omega)$. The first term is identified as the 'grating' contribution to the nonlinear response, and the second term as the 'phase conjugating' contribution to the nonlinear response. Thus we see that, even in an isotropic material, the nonlinear response depends in a nontrivial manner on the state of polarization of the incident light field.

The present contribution reviews some recent research involving polarization effects in nonlinear optics. One topic is the second-order nonlinear optical response of a liquid

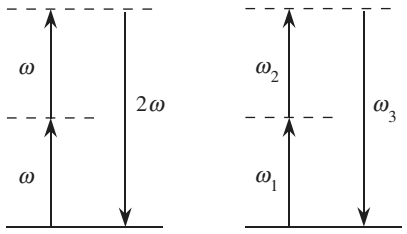

Figure 1. Illustration of the prototypical second-order nonlinear optical processes of second-harmonic generation (left) and sum-frequency generation (right).

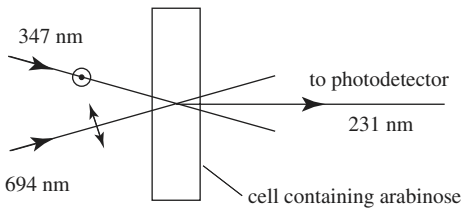

Figure 2. Experimental set-up used in one of the first laboratory studies of sum-frequency generation in a liquid of chiral molecules.

composed of chiral molecules[4]. Two examples of second-order nonlinear optical processes are second-harmonic generation and sum-frequency generation, which are illustrated in figure 1. The process of second-harmonic generation $\omega + \omega \rightarrow 2\omega$ is described by the second-order nonlinear optical susceptibility $\chi^{(2)}(2\omega, \omega, \omega)$. The more general process of sum-frequency generation $\omega_1 + \omega_2 \rightarrow \omega_3$ is described by the second-order nonlinear optical susceptibility $\chi^{(2)}(\omega_3, \omega_1, \omega_2)$. Fundamental symmetry considerations show that $\chi^{(2)}$ must vanish in a material that possesses inversion symmetry. For this reason, second-order nonlinear optical interactions are usually studied in crystals. But isotropic collections (e.g., liquids) of chiral molecules (that is, of molecules that 'look' different from their mirror images) also lack a centre of inversion symmetry and can also produce second-order interactions. But the symmetry properties of such interactions are extremely subtle. For example, second-harmonic generation cannot occur in such a material, although sum and difference frequency generation can occur, but only if the input waves are cross polarized and noncollinear [2], as illustrated in figure 2. There has recently been great debate in the scientific literature on the question of whether a linear electro-optic effect can exist in an isotropic collection of chiral molecules. Clearly, this question has some significant practical as well as conceptual implications, as the ability to use isotropic materials (liquids and polymers, for example) would be very helpful for many applications of electro-optics. There is no group theoretical reason why the linear electro-optic effect should vanish in such media. The question of the existence of such an effect thus rests on laboratory measurement or on detailed quantum mechanical calculation of the optical response [3–11]. Various authors are currently in disagreement regarding the correct means of performing such calculations. The status of these calculations is described in greater detail below.

[4] Note that $\chi\iota\epsilon\rho$ is Greek for hand. A chiral molecule is thus one that possesses handedness. More precisely, if the mirror image of a molecule cannot be superposed onto the original, the molecule is said to be chiral.

2. Nonlinear optical properties of chiral media

Recall that chiral materials possess the special linear optical property known as optical activity, that is, the rotation of the direction of linear polarization upon propagation through such a medium. Chiral media possess unique nonlinear optical properties. The second-order nonlinear optical response (to two applied fields of amplitudes $\mathbf{E}_1$ and $\mathbf{E}_2$) can be expressed as

$$\mathbf{P}_{\mathrm{NL}} = A_{123}\,\mathbf{E}_1 \times \mathbf{E}_2 \qquad \text{where } A_{ijk} = \tfrac{1}{2}(\chi^{(2)}_{ijk} - \chi^{(2)}_{ikj}). \quad (4)$$

Thus A_{ijk} is the antisymmetric (in the last two indices) part of the nonlinear susceptibility. Note that $\mathbf{P}_{\mathrm{NL}}$ vanishes for second-harmonic generation. Sum-frequency generation can occur only if the two input fields are orthogonally polarized and non-collinear.

3. Existence of a linear electro-optic (Pockels) effect in isotropic chiral media

As mentioned above, it would be very important technologically if a linear electro-optic effect could occur in isotropic media. Such an effect would be described by $\chi^{(2)}(\omega, \omega, 0)$.

There is no group-theoretical reason why such an effect cannot exist. However, for a lossless material, it can be shown that A must vanish, as can be demonstrated from the condition of full-permutation symmetry (which follows from the fact that the internal energy must be a function of state in a lossless material) or from explicit quantum mechanical calculation. On the other hand, for a lossy medium, there is no fundamental reason why such a linear electro-optic effect cannot exist. However, lossy materials are described quantum mechanically in terms of decay constants that are usually introduced phenomenologically. Whether or not a linear electro-optic effect is predicted to exist thus depends on the details of how decay is added to the model.

Various authors have treated the question of the existence of a linear electro-optic effect in isotropic chiral media, but have reached conflicting conclusions. Some of the representative papers treating this topic are as follows. Buckingham and Fischer [7] and Stedman *et al* [9] conclude that a linear electro-optic effect does not exist in chiral electro-optic materials. (But it is not clear whether their conclusions hold in general and in particular for lossy media.) Koroteev [3] and Kauranen and Persoons [6] conclude that a linear electro-optic effect does exist for lossy optical materials if decay is treated properly. Agarwal and Boyd [11] conclude that the linear electro-optic effect vanishes for radiative damping and is very small for other damping mechanisms.

In detail, Kauranen and Persoons [6] find that each term in the expression for $\chi^{(2)}$ is proportional to $\mathrm{i}\gamma_{nm}$, where γ_{nm} is the damping rate of the transition between levels n and m. Thus, the linear electro-optic effect is inherently dependent on the existence of decay phenomena. Consequently, the predictions of the calculation are critically dependent on the assumptions made in introducing decay into the calculation. Other examples are known within the field of nonlinear optics of processes that owe their existence to decay phenomena [16, 17].

Agarwal and Boyd [11] have recently performed a theoretical study of the manner in which decay phenomena influence the existence of a linear electro-optic effect in chiral isotropic materials. They explicitly treat the case of radiative broadening. Even though most material systems of interest are unlikely to be radiatively broadened, the case of radiative broadening is one in which the calculation can be performed starting from first principles. In a brief summary, Agarwal and Boyd agree with the formula of Kauranen and Persoons [6], but find that the damping rate γ_{nm} is really a function of frequency, and that the relevant damping rate for the electro-optic effect is $\gamma_{nm}(\omega = 0)$ which vanishes. This conclusion makes sense in that for radiative damping γ_{nm} is equal to the Einstein A coefficient, which scales with frequency as ω^3.

4. A controversy

Considerable controversy has developed because one of the early theoretical treatments of the linear electro-optic effect in isotropic chiral media [4] concludes that the resonance nature of the optical response (stated for simplicity for the linear resonse) is expressed by

$$\frac{1}{\omega_0 - \omega - \mathrm{i}\Gamma} + \frac{1}{\omega_0 + \omega - \mathrm{i}\Gamma} \qquad \text{(same-sign convention)} \tag{5}$$

rather than the more generally accepted result

$$\frac{1}{\omega_0 - \omega - \mathrm{i}\Gamma} + \frac{1}{\omega_0 + \omega + \mathrm{i}\Gamma} \qquad \text{(opposite-sign convention).} \tag{6}$$

These authors reach their conclusion as the result of a detailed quantum mechanical calculation. In support of their conclusion, these authors also state that Cohen-Tannoudji *et al* [12] agree with their result, and furthermore that Weisskopf [13, 15][5] agrees with their result. However, inspection of the book of Cohen-Tannoudji *et al* shows that only the resonant term is displayed, and thus the issue of the correct form of the antiresonant term is not addressed. Also, inspection of the Weisskopf paper shows that a simple sign error (perhaps just a misprint) was introduced into the calculation. Unfortunately, this form of the expression with the wrong sign of the damping term in the antiresonant contribution has been reproduced (with proper citation!) in many subsequent publications.

Buckingham and Fischer [7] have more recently argued that the analysis of Andrews *et al* [4] is necessarily incorrect in that it leads to non-physical behaviour, namely the following.

(1) The same-sign convention violates the reality condition $\chi(\omega) = \chi(-\omega)^*$. Thus the *physical* polarization created by a physical (real) electric field is complex.
(2) The same-sign convention violates causality in that it possesses poles in both the upper and lower half planes.

In response to this criticism, Stedman *et al* [9] respond that one obtains the opposite-sign convention when treating the problem semiclassically, but obtains the same-sign convention when treating the problem as a scattering problem using a fully quantum (and presumably correct) approach. The present authors reserve judgment on this point. But Stedman *et al* are entirely correct that response functions, such as susceptibilities, are semiclassical concepts.

It should also be noted that Long's well known textbook [18] on the Raman effect presents an appendix that reviews the history of the sign of the damping terms in the Raman susceptibility. He notes that Placzek had the signs correct (that is, used the opposite-sign convention) in his original treatment of the problem, but that the sign of the damping factor in the antiresonant term inexplicably was inverted in many subsequent papers that supposedly relied on the same calculation. Long now favours the opposite-sign convention.

[5] More precisely, Andrews *et al* [4] state and Hecht and Barron [15] arrive at this result in apparent agreement with Weisskopf [13].

5. What is the correct form for the linear susceptibility?

Since considerable confusion has developed already over this seemingly simple point, it is worthwhile to consider briefly the proper form of the damping terms in the linear susceptibility for several model systems.

We consider first the simple harmonic oscillator with phenomenological damping, which is described by the equation

$$\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x = (-e/m)E\mathrm{e}^{-\mathrm{i}\omega t}. \tag{7}$$

We also let $p(t) = -ex(t) = \alpha(\omega)E\mathrm{e}^{-\mathrm{i}\omega t}$ where $\alpha(\omega)$ is the polarizability. Then from the solution of equation (7) we find that

$$\alpha(\omega) = \frac{(e^2/m)}{\omega_0^2 - \omega^2 - 2\mathrm{i}\omega\gamma} = \frac{e^2}{2m\omega_0}\left(\frac{1}{\omega_0 - \omega - \mathrm{i}\gamma} + \frac{1}{\omega_0 + \omega + \mathrm{i}\gamma}\right). \tag{8}$$

The second form is approximate (as it assumes that $\gamma \ll \omega_0$), but the exact result can be cast into the same functional form through a redefinition of ω_0 (see below). This equation constitutes the standard result (the 'opposite-sign convention').

But in obtaining this standard result, we have introduced damping phenomenologically. For the case of radiative broadening, the form of the damping term can be calculated from first principles. Let us treat radiative damping in terms of radiation reaction. Let E_T denote the total field that the atom experiences, that is, the sum of the applied field and the radiation reaction field. The equation of motion is taken to be undamped, of the form

$$\ddot{x} + \omega_0^2 x = (-e/m)E_\mathrm{T}\mathrm{e}^{-\mathrm{i}\omega t}. \tag{9}$$

The solution can be expressed as

$$p(\omega) = -ex(\omega) = \alpha_0(\omega)E_\mathrm{T} \qquad \text{where } \alpha_0(\omega) = \frac{(e^2/m)}{\omega_0^2 - \omega^2}. \tag{10}$$

By the standard treatment of radiation reaction, we know that $E_\mathrm{T} = E_0 + \frac{2}{3}\mathrm{i}(\omega/c)^3 p$, and by definition we know that $p(\omega) = \alpha(\omega)E_0$. By combining these equations we find that

$$\alpha(\omega) = \frac{(e^2/m)}{\omega_0^2 - \omega^2 - \frac{2}{3}\mathrm{i}(e^2/mc^3)\omega^3}. \tag{11}$$

This is the exact (within the context of the present model) result. Note that the damping is explicitly frequency dependent. It is also non-causal. We can rewrite this result as follows:

$$\alpha(\omega) = \frac{e^2}{2m\omega_0'}\left[\frac{1}{\omega_0' - \omega - \mathrm{i}\gamma(\omega)} + \frac{1}{\omega_0' + \omega + \mathrm{i}\gamma(\omega)}\right], \quad (12)$$

where $\gamma(\omega) = \frac{1}{3}(e^2/mc^3)\omega^3$ and $\omega_0' = \sqrt{\omega_0^2 - \gamma^2}$. This result has the form of the opposite-sign convention, but with frequency-dependent damping.

6. Conclusions

In general, the damping factor γ that appears in quantum mechanical expressions for the optical susceptibility is frequency dependent. Only close to resonance can one take γ to be a constant. It is only in this case that phenomenological damping models are expected to be reliable. Leaving aside these theoretical issues, one should note that a linear electro-optic effect has not yet been observed in isotropic chiral materials. The analysis of Kauranen and Persoons [6] suggests that the best opportunity to observe such an effect is afforded by lossy materials. We also conclude that the generally accepted form of the susceptibility (the same-sign convention) is the correct form, at least under those circumstances in which the concept of the susceptibility has any meaning.

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