Comment on ''Phenomenological damping in optical response tensors''

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Damping factors arise from static as well as dynamic perturbations. These must appear with constant sign in the perturbation theory denominators for compatibility with quantum mechanics, conformity with time-reversal symmetry, and agreement with experiment.

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I. INTRODUCTION

In the course of an analysis of electro-optic rotation in fluids, a paper by Buckingham and Fischer [1] (which we refer to as BF) gives a perspective on the phenomenological damping of optical response tensors differing from our earlier work [2] (which we refer to as ANS) on the same topic. Both groups of authors agree on the final result and its directly measurable implications, namely that a linear electro-optical response cannot occur in an isotropic liquid, whether chiral or not (see also Dávila-Romero *et al.* [3]). However, there are several open issues.

At the heart of these issues is the basic question of whether the fully quantum-mechanical or the semiclassical polarization (optical susceptibility tradition) formulation of the problem is correct. BF simply states that our fully quantum-electrodynamical formula for the Pockels effect, for example, is incorrect. The history of confrontations between quantum theory and semiclassical theory is remarkably one-sided and it would be strange if at this stage a fully quantum-based theory were to prove vulnerable to a semiclassical analysis. In fact, we can identify the origin of such conflicts as intrinsic within the semiclassical polarization formalism. The latter is not demonstrably in agreement with observation, and is not directly related to quantum-theoretic observables. This much is obvious when the optical states are number states (see ANS). We show here, *inter alia*, that even for coherent states, when quantum and semiclassical formalisms most often make equivalent predictions, the polarization formalism adopted by BF and some others is inadequate.

II. ANALYSIS

The primary issue is the correct prescription for assigning the damping terms in optical response tensors. Here we emphasize that the variable-sign rule favored by BF can be appropriate only within the semiclassical polarization or susceptibility theory used in BF, and that the constant-sign (or equal-sign) rule which ANS verified is essential for physical results within a fully quantum-mechanical formalism. In particular connection with the current matters, we show that the BF choice of sign for damping factors fails to satisfy time-reversal symmetry, while the quantum formalism honors it through its constant-sign rule. We also give reasons why the removal by BF of damping terms for low-frequency fields (which has the effect of short-circuiting the matter under discussion) is unjustified.

As a context for addressing the major points, we first note that in all of quantum theory, formally imaginary constants can have physical importance. The *ad hoc* phenomenological damping of excited states for a molecule mediating an optical process reflects the interaction of that molecule with its local radiative and material surroundings, or *bath*. Phenomenological damping is the pragmatic means of representing the stochastic influence of the bath, in particular the effects of higher-order perturbations including radiative and nonradiative decay. None of the eigenstates of the unperturbed molecular Hamiltonian is a stationary state. Time-evolution factors thereby acquire dissipative corrections which, although formally imaginary in frequency or energy space, are associated physically with exponential decay. We also note that it is legitimate to require time-reversal symmetry in the fundamental quantum amplitudes (matrix elements, whose square modulus is directly related by the Fermi golden rule to the corresponding observable transition rates) when a subsystem is damped through contact with a thermal reservoir. The requirement for temporal symmetry remains valid, despite the *de facto* violation of time reversal invariance by the system itself (through molecular interaction with the bath and ensuing state decay) by explicit accommodation of the imaginary damping factors as above.

The equality of amplitudes for processes related by time-reversal was proved by ANS from this time-reversal invariance of the matrix elements; see their Eq. (11). These invariances are honored by the constant-sign rule and not by the variable-sign convention. They should not be confused with such reciprocity relations as Eq. (6) of BF, which are not in general true. To prove this we simply note, writing the evolution operator for the full system as $U=\exp(-i\hbar^{-1}\int H dt)$, that from Hermitian conjugation $\langle F|U|I\rangle = \langle I|\exp(i\hbar^{-1}\int H dt)|F\rangle^*$. Since the second operator is not equal to U, the associated matrix element is not a physically meaningful (time-forward) transition amplitude. Hence a reciprocity relation of the form $|\langle F|U|I\rangle| = |\langle I|U|F\rangle|$ does

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not hold in general. Berger [4] states that no special reason is needed for microscopic inversibility (our reciprocity) violation and exhibits several such violations, noting that when damping is neglected the Fermi golden rule delivers expressions that satisfy reciprocity—but that this is an exceptional case, not the rule.

In Eq. (1) of BF, semiclassical expressions for nonlinear electric polarization are assumed. Such expressions are not derived from quantum field theory, and can be inconsistent with it. The electric polarization represents the oscillating moment of a semiclassical radiating dipole which, when coupled with the electric-field vector of the ensuing radiation, casts the signal amplitude in the form of a sum of contributions associated with physically distinct processes. This is fundamentally incompatible with quantum theory; it would violate the superposition principle to sum the amplitudes of transitions between nonidentical sets of initial and final radiation states. Also the polarization formalism by its nature fails to honor the symmetry of the full theory when incident and emergent radiation fields are exchanged, as for example the symmetry between second-harmonic generation and parametric down-conversion. Similarly, the constant-sign rule is needed to give the relationship $\alpha^{uu}=-\alpha^{00}$ between the optical polarizabilities of two-level molecules in their ground and excited states, 0 and *u*, respectively—a form of relationship which equally applies to all higher-order (nonlinear) polarizabilities, but only under the jurisdiction of the constant-sign rule. Again, the semiclassical polarization formalism does not allow the full incorporation of magnetic and diamagnetic interactions. For example, in a general three-wave interaction mediated by a molecular species which supports $E1^2M1$ but not $E1^3$ channels, the magnetic dipole interaction in the former can be associated with each of the three waves, yet for obvious reasons only two are accommodated in the electric polarization. Any prescription with variable assignment of signs can also introduce significant ambiguities in connection with processes entailing two or more outgoing waves, as for example in four-wave mixing.

Although this discussion centers on parametric processes, the same issues have been rehearsed in the more general context of inelastic processes. Accepted quantum theories of Raman and hyper-Raman scattering [5–9] deliver the correct form of the associated scattering tensors with constant signing of the damping terms. These expressions respect time-reversal symmetry and subsume the expressions for molecular polarizability and hyperpolarizability which follow as the corresponding inelastic counterparts. In particular, Behringer's detailed work [7] on the relationship between resonance Raman scattering and resonance fluorescence vindicates the application of constant signing in every case.

The semiclassical polarization formalism obviously fails to correctly describe nonlinear optical phenomena when the optical input takes the form of photon number states. For example, it predicts a finite probability of second-harmonic generation when a one-photon state is incident (see ANS). In some situations, when optical input is closer in form to a quantum coherent state $|\alpha\rangle$, a semiclassical description can emerge as an asymptotic limit (as $|\alpha|$ tends to infinity) of the fully quantum approach. However, even for coherent states, the semiclassical polarization approach is inadequate in the problem which is at the center of the present discussion. Following ANS, the fully quantum electrodynamical picture will involve electronic Green's functions of the form $\langle T\{a_i(\tau)a_i^\dagger(0)\}\rangle$ (T here represents the time-ordered product, and a_i the fermion annihilation operator for electronic state i). Upon expansion of the Heisenberg operators in an uncoupled basis, the perturbation effects appear through the insertion of evolution or S-matrix operators $U(\tau)=T\exp[-i\hbar^{-1}\int_0^\tau V(t')\mathrm{d}t']$. Photon annihilation and creation operators $b_k, b_k^\dagger$ appear in such expressions within the perturbation Hamiltonian V, in bilinear form for linear coupling and in higher-order form for nonlinear effects. When the numerator operators in each matrix element are manipulated by commutation to normal ordered form, the effect of using coherent radiation states $|\{\alpha_k\}\rangle$ is to discharge all photon annihilation operators as the corresponding c numbers α_k, and the corresponding creation operators as α_k^* throughout. This substitution will not affect the requirements of the spectral theorem of ANS, that the observable be the discontinuity of the Green's function across the real axis, so delivering the constant-sign rule and fixing the signs of all imaginary factors in the perturbation denominators. Hence, because the polarization formalism has to violate this sign rule to predict real observables, even its transposition into a quantum description cast in terms of coherent states is inadequate.

The abstract of BF states that the ANS constant-sign rule is ''inconsistent'' and ''yields an unphysical material response.'' This seems to reflect a twofold misunderstanding. We have never proposed that the constant-sign rule should be incorporated in the polarization formalism; that would clearly make that formalism unusable, as already indicated in ANS and for the reasons indicated in BF. But far less should a sign convention that is required to salvage the physical credibility of a deficient formalism be deemed obligatory in the full quantum-mechanical formalism. The quantum spectral theorem of ANS allows no freedom of choice or convention in the matter; quantum amplitudes for optical processes must use the constant-sign rule for damping factors. It is only then that the observables are real and that rigorous time-reversal symmetry is satisfied. In particular, only then can it be proved (see ANS) that, in the presence of damping effects, electro-optic rotation is forbidden in isotropic fluids. By discarding any damping from static field effects, BF has failed to provide any such proof.

We now address the consequent issue, which can be posed as the following question: should denominators associated with static field effects have finite damping factors, of whatever sign? In the ansatz of BF this damping factor is totally removed for static fields. This dramatically short circuits the debate in ANS on electro-optical rotation in fluids, because selective removal of the damping factor permits the BF optical tensor to display the same index symmetry as that revealed by our fixed sign convention for nonzero damping. BF gives several arguments in support of this approach. First, BF states that ''care has to be taken to correct the corresponding relaxation terms'' for low-frequency fields,

and they refer to Van Vleck and Weisskopf [10] and to Bloembergen [11]. Van Vleck and Weisskopf discuss the higher-order effects of the perturbation (on state population in thermal equilibrium) for low-frequency fields. However, the differing approaches to electro-optical rotation under discussion here are all of lowest order in perturbation. The effects discussed by Van Vleck and Weisskopf do not pertain to the signs of damping in denominators, but to the effects of static fields in higher order upon the numerators. Bloembergen generally subjects applications to a semiclassical analysis, on account of its familiarity. Although the questions central to the present discussion did not arise in those applications, similar questions are nonetheless discussed; Bloembergen enlarges on Van Vleck and Weisskopf's work and comments in several places on the unphysical assumptions of the semiclassical model in regard to assumed temperature and equilibrium. We note that, when Bloembergen points out that his expression 2-28 becomes real for zero frequency, his damping terms still contribute in that limit. His analysis therefore does not support the notion that damping factors with constant sign introduce unphysical imaginary parts into observables, or that damping must be neglected for zero-frequency fields. When Bloembergen uses a quantum density-matrix approach, in each analysis of nonlinear optical effects the results are compatible with the constant sign damping rule, and incompatible with BF. Other independent quantum developments also deliver this constant sign rule (see ANS).

Next, BF argues that in the presence of a static electric field, nondegenerate states can be chosen to have real eigenfunctions, and that this leads to an inconsistency if we allow an imaginary part within a perturbation denominator. The possibility of choosing a nondegenerate wave function of a real and static (i.e., time-reversal-symmetric) Hamiltonian itself to be real (i.e., its own time reverse) is a simple application of time-reversal symmetry. In amplifying this argument, BF states that ''the lifetime of the excited state cannot be relevant to the (perturbed) state $|g_F\rangle$—we could use any complete basis set. . . .'' This position fails to recognize that damping is inevitable from any perturbation, including a static field. Indeed this would deny the relevance of damping in any perturbation theoretic context. The crux of the matter is this: any perturbation (including a static one) which engenders an interaction Hamiltonian that does not commute with the unperturbed Hamiltonian necessarily renders eigenstates of the unperturbed Hamiltonian no longer stationary states. As with bath-induced damping, the unperturbed states acquire a finite lifetime and, insofar as the received phenomenological treatment of damping admits only time-independent rates, a corresponding damping. In short, all unperturbed eigenstates are damped by any perturbative coupling to any other state. A static field perturbation is perfectly effective in generating time-dependent transitions (as in the Fermi golden rule) between virtual states and so limiting their lifetimes. Such a lifetime is constrained to a time scale determined by the inverse of the energy mismatch (for a static perturbation, the inverse of the state frequency change). On that time scale there is a finite probability for the decay of those levels.

The attempted proof in BF that damping vanishes for a static electric-field perturbation fails because BF has overplayed the reality requirement on the wave functions. Reality of an eigenstate under the conditions stated in BF is a possible choice, as is indeed stated in BF, but reality of a damped state is not the requirement that BF assumes will follow in practice. By definition of the problem we must treat the static field as a perturbation; otherwise there would be no possibility of finding a transition rate associated with an electro-optic response as such. In that case even a static real field limits the lifetime of the basis states (i.e., it damps them). In the context of a damping formalism, once this field is switched on and its physical effects incorporated in the formalism, these states are no longer eigenstates of the unperturbed Hamiltonian; their algebraic expression is changed. This change to the eigenstates of the unperturbed Hamiltonian should not be confused with the perturbative construction of new eigenstates of the combined Hamiltonian, which are not of concern here and which in fact have a different algebraic form. The damped states cannot be identified with even the first-order perturbation approximation to these combined-Hamiltonian eigenstates; rather, they represent the effect, on the eigenstates of the unperturbed Hamiltonian, of the correspondingly finite lifetime those states acquire. In brief, an eigenstate, which has an infinite lifetime, should not be confused with a damped state, which has a finite lifetime. This distinction is fundamental to the introduction of damping terms in a perturbation-theoretic context. Hence damped states are not constrained by the proof of reality offered by BF. For these various reasons, the BF analysis has not advanced the matter, and there remains no justification for intentionally disregarding these associated damping factors.

It may be helpful to explain more fully, from a quantum field-theoretic viewpoint, why static perturbations induce damping. All electromagnetic interactions are fundamentally mediated through the exchange of virtual photons (the gauge bosons). A static field involved in an electro-optical process in any given molecule is mediated in the same way. It owes its origin to the coupling between the charges within that molecule and those comprising the source of the static field [3]. This coupling is expressed through the accommodation of interactions with virtual photons from modes of an infinite range, as with any electrodynamic interaction, and summation over the virtual photon wave vectors and polarizations thereby ensures a result which properly reflects the conservation of energy. Consequently, the case of a static field is no different in type from a time-varying field—except that, whilst causality is of course satisfied, explicit retardation features disappear. Hence the damping associated with any molecular excited state, whose wave function contributes to the perturbed state vector of the system, must be vulnerable to damping irrespective of the frequency of the electric field responsible for the perturbation. Damping factors are not frequency dependent in this sense; each excited state has a damping of a characteristic magnitude, irrespective of the frequency of the perturbation with which it is associated.

III. CONCLUSION

In summary, the BF analysis based on the polarization formalism has made a number of untenable assertions, electing the variable-sign convention for excited-state damping and assuming that virtual states coupled by the static field in linear electro-optic response are undamped. That strategy places the static field on a different footing from the electromagnetic fields, illegitimately disengaging it from full involvement in the dynamics of scattering, and so rendering the offered proof invalid. Rather, proof that linear electro-optic effects vanish in fluids requires the full quantum theory, including its constant-sign rule for the damping factors.

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