

Causal versus noncausal description of nonlinear wave mixing: Resolving the damping-sign controversy

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(Received 19 June 2007; published 30 August 2007)

Frequency-domain nonlinear wave mixing processes may be described either using response functions, whereby the signal is generated after all interactions with the incoming fields, or in terms of scattering amplitudes where all fields are treated symmetrically with no specific time ordering. Closed Green's function expressions derived for the two types of signals have different analytical properties. The recent controversy regarding the sign of radiative damping in the linear (Kramers-Heisenberg) formula is put in a broader context.

DOI: 10.1103/PhysRevA.76.021803

PACS number(s): 42.65.An, 32.80.-t, 42.50.Ct, 32.70.Jz

A lively debate is currently going on with regard to the correct sign that should be introduced in the Kramers-Heisenberg expression for the (linear) optical polarizability. Both opposite-sign and constant-sign formulas have been derived by various authors. Perturbative QED calculations have been carried out to include radiative damping [1–8]. In an insightful recent article, Bialynicki-Birula and Sowiński [9] pointed out that this issue is fundamentally connected with the linear response vs scattering points of view for Rayleigh scattering. In this Rapid Communication we extend this argument to nonlinear wave mixing of arbitrary order. Closed formal expressions are derived that reveal the analytical properties of both retarded (response) and nonretarded (scattering) signals. The linear response results are recovered to lowest order. Our microscopic derivation could serve as the starting point for a full QED calculation. However, this is not required in order to pinpoint the analytical properties that should hold for other types of nonradiative damping as well.

The following derivation applies for processes of arbitrary order. However, for clarity we focus on four-wave mixing. Consider a system (atom, molecule) interacting with four modes of the radiation field. The states of the system will be denoted a, b, c, \dots . The j th mode has a frequency ω_j and initial occupation number n_j . To simplify the notation we hereafter consider sum frequency generation whereby $\omega_4 = \omega_1 + \omega_2 + \omega_3$; however, the results can be easily extended to any combination of frequencies $\omega_4 = \pm\omega_1 \pm \omega_2 \pm \omega_3$. For the process of interest, the initial state of the system+field is $|i\rangle = |a, n_1 n_2 n_3 n_4\rangle$, and the final state is $|f\rangle = |a, n_1 - 1, n_2 - 1, n_3 - 1, n_4 + 1\rangle$, with energies E_i and E_f , respectively.

The coupling of an atom located at point \mathbf{r} with the radiation field is

$$H_{int} = -VE(\mathbf{r}, t). \quad (1)$$

We shall divide the electric field into its positive and negative frequency components

$$E(\mathbf{r}, t) = \varepsilon(\mathbf{r}, t) + \varepsilon^\dagger(\mathbf{r}, t), \quad (2)$$

$$\varepsilon(\mathbf{r}, t) = \sum_j \left(\frac{2\pi\hbar\omega_j}{\Omega} \right)^{1/2} \exp(ik_j\mathbf{r} - i\omega_j t) a_j, \quad (3)$$

where a_j is the photon annihilation operator of mode j , V is the dipole operator, and Ω is the quantization volume.

We first assume that the system is prepared in a nonequilibrium steady state with the four fields and consider the entire process as a single four-photon scattering event. This is a *noncausal* process whereby all four modes are treated on the same footing. This implies that the interaction with mode 4 need not be the last, and all time orderings are allowed and should be summed over. The process is described by the S matrix element

$$S_{fi} = A_{fi} T_{fi}(E_i) \delta(E_i - E_f), \quad (4)$$

where T_{fi} is the matrix element of the T matrix $T = V + VG(E)V$, and

$$G(E) = \frac{1}{E - H + i\varepsilon} \quad (5)$$

is the retarded Green's function. The scattering amplitude for this process is given by

$$S_{fi}^{(4)} = A_{fi} \sum_{p_4} \langle a | VG(E_a + \omega_1 + \omega_2 + \omega_3) VG(E_a + \omega_1 + \omega_2) \times VG(E_a + \omega_1) V | a \rangle \delta(\omega_1 + \omega_2 + \omega_3 - \omega_4) \quad (6)$$

where

$$A_{fi} = \left(\frac{2\pi\hbar}{\Omega} \right)^2 \sqrt{n_1 n_2 n_3 (n_4 + 1)} \sqrt{\omega_1 \omega_2 \omega_3 \omega_4}. \quad (7)$$

\sum_{p_4} denotes the sum over all 4! permutations of $\omega_1, \omega_2, \omega_3$, and $-\omega_4$. The sign convention for ω_j in Eq. (6) is as follows: an absorbed photon gives $+\omega_j$ whereas an emitted photon gives $-\omega_j$. In the process considered here, ω_1, ω_2 , and ω_3 are absorbed and ω_4 is emitted. Other processes can be calculated by simply changing the signs of ω_j , as warranted in each case. H is the Hamiltonian for the atom+all modes of the radiation field excluding the four modes of interest, since those were treated perturbatively.

We next turn to the standard semiclassical description of four-wave mixing whereby the system first interacts with modes 1, 2, and 3 to generate third-order polarization, which then serves as a source for mode 4 [10]. This is a *causal* response where mode 4 is special since its interaction with

the system must be the very last. We shall calculate the n th order polarization as the expectation value of V [11],

$$P^{(n)} = \sum_{m=0}^n \langle \Psi^{(m)} | V | \Psi^{(n-m)} \rangle, \quad (8)$$

where $\Psi^{(m)}$ is the perturbed wave function to m th order in V . The m th term represents the $(n-m)$ th order for the ket and m th order for the bra. Overall there are $(n+1)$ terms. For $n=3$ we have four terms corresponding to $m=0, 1, 2, 3$, respectively, in Eq. (8). We then get $P^{(3)} = A_{fi} \chi_{fi}^{(3)}$, where

$$\begin{aligned} \chi_{fi}^{(3)} = & - \sum_{P_3} [\langle a | VG(E_a + \omega_1 + \omega_2 + \omega_3) VG(E_a + \omega_1 + \omega_2) VG(E_a + \omega_1) V | a \rangle \\ & - \langle a | VG^\dagger(E_a + \omega_1 + \omega_2 - \omega_4) VG(E_a + \omega_1 + \omega_2) VG(E_a + \omega_1) V | a \rangle \\ & + \langle a | VG^\dagger(\omega_1 - \omega_4 + \omega_2) VG^\dagger(E_a + \omega_1 - \omega_4) VG(E_a + \omega_1) V | a \rangle \\ & - \langle a | VG^\dagger(E_a - \omega_4 + \omega_1 + \omega_2) VG^\dagger(E_a - \omega_4 + \omega_1) VG^\dagger(E_a - \omega_4) V | a \rangle] \delta(\omega_1 + \omega_2 + \omega_3 - \omega_4), \end{aligned} \quad (9)$$

is the susceptibility and

$$G^\dagger(E) = \frac{1}{E - H - i\varepsilon} \quad (10)$$

is the advanced Green's function. \sum_{P_3} denotes the sum over all $3!$ permutations of the *incoming* modes ω_1, ω_2 , and ω_3 . In this expression the sign convention for ω_j is the same as in Eq. (6) (+ sign for absorbed photons, - for emitted). Each coupling with the ket is accompanied by a retarded Green's function G , whereas an advanced Green's function G^\dagger is accompanied by bra interactions. Equation (8) will thus yield $(n-m)$ G and m G^\dagger factors. An analogous expression may be obtained using superoperators in Liouville space. The present Hilbert space form is more suitable for comparison with the scattering amplitudes.

The extension of Eqs. (6) and (9) to arbitrary order is straightforward. $S^{(n+1)}$ will have a single basic term with $(n+1)$ V factors, and n retarded Green's functions G with arguments $E_a + \omega_1, \dots, E_a + \omega_1 + \omega_2 + \dots + \omega_n$. In addition, it contains a sum over the $(n+1)!$ permutations of $\omega_1, \dots, \omega_{n+1}$. Each ω_j may be changed to $-\omega_j$ in order to describe different processes. $\chi^{(n)}$ has $(n+1)$ basic terms, each containing $(n+1)$ V factors, and a $(G^+)^m (G^-)^{n-m}$ factor with $m=0, \dots, n$ [see Eq. (8)]. The retarded Green's functions will depend only on the incoming frequencies, $\omega_1, \dots, \omega_n$. All advanced Green's functions also depend on the signal frequency $-\omega_{n+1}$. Each basic term yields $n!$ terms upon the permutation over $\omega_1, \dots, \omega_n$. Altogether both $S^{(n+1)}$ and $\chi^{(n)}$ contain $(n+1)!$ terms. For $S^{(n+1)}$ these come from the $(n+1)!$ permutations of the $(n+1)$ frequencies over a single term. $\chi^{(n)}$ has $(n+1)$ basic terms, each containing $n!$ permutations of the n "incoming" frequencies. Unlike $\chi^{(n)}$, $S^{(n+1)}$ is symmetric with respect to all $(n+1)$ modes; the interaction with the signal field ω_{n+1} need not be chronologically the last. $S^{(n+1)}$ contains only retarded Green's functions and all propagations proceed forward in time. The $(n+1)!$ permutations take care of the possible time orderings of interactions with the various modes. $\chi^{(n)}$, in contrast, depends on both retarded and ad-

vanced Green's functions, which correspond to forward and backward propagations, respectively, along the Keldysh-Schwinger loop [12–14].

Both expressions (6) and (9) can serve as a starting point for a full QED perturbative calculation, where the coupling with all modes of the electromagnetic field is included in the Hamiltonian H . This will result in damping terms. However, the analytical properties of the two signals are completely determined by Eq. (6) or (9), and will be invariant to the level of approximation used for the radiative damping. When all frequencies are tuned off resonance, we can neglect the $\pm i\varepsilon$ terms in the Green's functions, setting $G = G^\dagger$. The causal and noncausal expressions then become identical.

The ongoing damping-sign controversy was restricted to the linear response of a two-level system with ground state a and an excited state b [1–9]. This may be immediately resolved by our general formulation. For Rayleigh (elastic) scattering, we have one absorbed and one emitted photon with the same frequency. We thus set $\omega_1 = \omega$ and $\omega_2 = -\omega$. The second-order analog of Eq. (6) reads

$$S_{fi}^{(2)} \sim \langle a | VG(E_a + \omega) V | a \rangle + \langle a | VG(E_a - \omega) V | a \rangle. \quad (11)$$

This is obtained from a single term + two permutations of ω and $-\omega$. Writing the matrix elements explicitly for the system Hamiltonian (neglecting coupling with other radiation modes), this gives

$$S_{fi}^{(2)} \sim |V_{ab}|^2 \left(\frac{1}{E_a + \omega - E_b + i\varepsilon} + \frac{1}{E_a - \omega - E_b + i\varepsilon} \right). \quad (12)$$

This is known as the constant-sign prescription (both terms have a $+i\varepsilon$ factor) [1–9]. A linear response expression similar to Eq. (9) gives, on the other hand,

$$\chi_{fi}^{(1)} \sim \langle a | VG(E_a + \omega) V | a \rangle + \langle a | VG^\dagger(E_a - \omega) V | a \rangle. \quad (13)$$

This comes from two basic terms with no permutation (there is only one incoming field, which is absorbed and has

frequency ω). Taking the matrix elements we recover the opposite-sign prescription

$$\chi_{fi}^{(1)} \sim |V_{ab}|^2 \left(\frac{1}{E_a + \omega - E_b + i\varepsilon} + \frac{1}{E_a - \omega - E_b - i\varepsilon} \right). \quad (14)$$

The origin of the different damping signs of $S^{(2)}$ and $\chi^{(1)}$ was clearly pointed out by Bialynicki-Birulya and Sowinski [9], who further carried out a fourth-order QED calculation of damping using both expressions. The present results extend these arguments to nonlinear processes of arbitrary order. It should be emphasized that the fundamental principle

of causality must always hold and is never in doubt. The terms “causal” and “noncausal” in this Rapid Communication refer to different observables. The traditional semiclassical formulation of nonlinear optics imposes a certain time ordering by singling out one of the fields. This response is causal. The scattering description is noncausal since it allows for arbitrary time ordering of interactions with the various fields.

The support of the National Science Foundation (Grant No. CHE-0446555) and NIRT (Grant No. EEC0303389) is gratefully acknowledged. I wish to thank Professor Bialynicki-Birula for useful discussions.

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