Linear polarizabilities of two- and three-level atoms

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Different expressions for the linear polarizability of a two-level atom with radiative corrections have been derived recently. We show that an expression said to differ from that obtained by the present authors is in fact consistent with it. The same-sign and opposite-sign prescriptions for linewidths are revisited with respect to the polarizability, the scattering amplitude, and the optical theorem. Both prescriptions represent approximations to more general expressions in the two-level case, and neither is correct for transitions between excited atomic states, as we demonstrate by calculating the linear polarizability of a three-level atom.

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I. INTRODUCTION

The linear response of an atom in state i to a field of frequency ω is described by the polarizability $\alpha_i(\omega)$: the electric dipole moment $\mathbf{p}(t)$ induced by the electric field $\mathbf{E}_0 \cos \omega t$ is

$$\mathbf{p}(t) = \frac{1}{2}[\alpha_i(\omega)\mathbf{E}_0 e^{-i\omega t} + \alpha_i(-\omega)\mathbf{E}_0 e^{i\omega t}]. \tag{1}$$

The imaginary part of the polarizability is due to damping effects such as spontaneous emission, and the reality of $\mathbf{p}(t)$ demands that the "crossing relation"

$$\alpha_i(-\omega) = \alpha_i^*(\omega) \tag{2}$$

be satisfied. The complex polarizability is generally written in terms of the atom's transition frequencies $\omega_{ji}=(E_j - E_i)/\hbar$ and transition electric dipole moments $\mathbf{d}_{ji}$ in one of two ways:

$$\alpha_i(\omega) = \frac{1}{3\hbar}\sum_j |\mathbf{d}_{ji}|^2 \left(\frac{1}{\omega_{ji} - \omega - i\gamma_{ji}} + \frac{1}{\omega_{ji} + \omega \pm i\gamma_{ji}} \right). \tag{3}$$

A similar formula applies in the more general case of Raman scattering, where two photon frequencies, those of the incident and scattered fields, appear in the denominators; again the scattering tensor is written with either a + sign or a − sign in the nonresonant term. The sign of the damping rate γ_{ji} with respect to the transition frequency ω_{ji} in the resonant and nonresonant terms defines the "opposite sign" (+) and "same sign" (−) prescriptions. The crossing relation obviously implies that the + sign in Eq. (3) is the correct choice, and this is consistent with the causality condition that $\alpha_i(\omega)$ must be analytic in the upper half of the complex ω plane; but the situation is not nearly so simple because the damping rates are in general frequency-dependent.

In the context of Raman scattering the + sign prescription has been used by Placzek [1] and Hassing and Svendsen [2], for instance. The latter authors state that the majority of authors use the − sign prescription, and Raman cross sections with the − sign are indeed found in various publications [3].

The recent interest in these different sign prescriptions was stimulated by Andrews *et al.* [4], who argued in favor of the − sign. Other authors [2,5–8] have presented arguments in favor of the + sign. The general case of frequency-dependent damping rates has not, to our knowledge, been analyzed. The special case of radiative damping, where $\gamma_{ji}(\omega) \propto \omega^3$, has been treated using the model in which the polarizable particle is a two-level atom [6–10]. Even in this simplified model the calculation is nontrivial because it requires a treatment of radiative corrections beyond the so-called rotating-wave approximation. The polarizability in this model has been calculated using the Heisenberg and Schrödinger pictures [6,8], time-dependent Green functions [7], and Feynman propagators [9].

The calculation in Ref. [6] supports the + sign convention, but small correction terms are required in order to satisfy the optical theorem in the case of Rayleigh scattering, where the incident and scattered field frequencies are identical [7,8]. From their elegant analysis for a two-level atom, Bialynicki-Birula and Sowiński [9], while concluding that the + sign prescription applies for the polarizability, obtain an expression "quite different from" that derived in Ref. [7], which is essentially the same as that obtained later by different methods in Ref. [8]. They also conclude that it is the − sign prescription that applies for the scattering amplitude.

In the following section we review the results obtained in Refs. [7–9] for the polarizability of a two-level atom with radiative damping, and show that they are identical in a weak-coupling approximation. The results are consistent with the opposite-sign prescription when an approximation is

made to a more general expression for the polarizability. We also consider briefly the scattering amplitude in this model, which was not considered in Refs. [6–8], and present a simple argument supporting the conclusion of Bialynicki-Birula and Sowiński [9] that the − sign applies in the lowest-order approximation to the scattering amplitude.

In Sec. III, we consider a three-level atom model in which transitions are allowed between the ground level and the first excited level and between the two excited levels. Following a time-dependent Green function approach used previously for the two-level model [7], we calculate the contribution to the polarizability from the transition between the two excited states. Whereas one could justifiably argue for the opposite-sign expression as an approximation to the two-level polarizability, we find that neither of the two sign prescriptions for the polarizability provide valid approximations in the three-level case. Our conclusions are summarized in Sec. IV. In the Appendix we briefly describe the calculation of the three-level polarizability using the Schrödinger picture.

Nonresonant contributions to resonant Rayleigh cross sections [11] and the natural line shape of the hydrogen atom [12] have recently been evaluated numerically for their possible relevance to the determination of atomic energy levels and fundamental constants from observed spectra. In evaluating such "problematic nonresonant contributions" [11] the effects of damping on them have been ignored, which is an excellent (and generally assumed) approximation, given the relative smallness of the nonresonant terms. The questions addressed in this and the earlier papers related to the frequency dependence of the decay parameters, while of fundamental theoretical interest, appear to be of no practical concern for even the most accurate of present spectroscopic studies.

II. TWO-LEVEL ATOM

The interaction Hamiltonian for a two-level atom and the quantized electromagnetic field is

$$\hat{H}' = i\hbar \int d\mathbf{k}(\hat{a}_{\mathbf{k}} - \hat{a}_{\mathbf{k}}^{\dagger}) j_{\mathbf{k}}(\hat{\sigma} + \hat{\sigma}^{\dagger}). \tag{4}$$

The coupling coefficient is defined by

$$\hbar j_{\mathbf{k}} = \left(\frac{\hbar\omega_k}{16\pi^3\epsilon_0}\right)^{1/2} \mathbf{e}_{\mathbf{k}} \cdot \mathbf{d}_{12}, \tag{5}$$

where $\hat{a}_{\mathbf{k}}$ and $\hat{a}_{\mathbf{k}}^{\dagger}$ are destruction and creation operators for mode $\mathbf{k}$, respectively, $\mathbf{e}_{\mathbf{k}}$ is the mode polarization and $\mathbf{d}_{12}$ is the transition dipole moment connecting the lower ($|1\rangle$) and upper ($|2\rangle$) states, and is assumed real [13]. The two transverse polarizations are not shown explicitly but are included in the wave-vector label $\mathbf{k}$, in order to simplify the notation. We follow here the notation of Refs. [6,8] for the lowering and raising operators for the two-level atom:

$$\hat{\sigma} = |1\rangle\langle 2|, \qquad \hat{\sigma}^{\dagger} = |2\rangle\langle 1|,$$

$$|2\rangle\langle 2| = \hat{\sigma}^{\dagger}\hat{\sigma}, \qquad |1\rangle\langle 1| = \hat{\sigma}\hat{\sigma}^{\dagger}. \tag{6}$$

The photon operator commutator is

$$[\hat{a}_{\mathbf{k}}, \hat{a}_{\mathbf{k}'}^{\dagger}] = \delta(\mathbf{k} - \mathbf{k}'). \tag{7}$$

A. Polarizability

We define

$$\Delta_{12}(\pm\omega) = \mathrm{P}\int d\mathbf{k} \frac{j_{\mathbf{k}}^2}{\omega_k \pm \omega} \tag{8}$$

and

$$\Gamma_{12}(\pm\omega) = \pi \int d\mathbf{k} j_{\mathbf{k}}^2 \delta(\omega_k \pm \omega)$$

$$= \frac{d_{12}^2}{6\pi\epsilon_0\hbar c^3} \int_0^{\infty} d\Omega \Omega^3 \delta(\Omega \pm \omega), \tag{9}$$

where P denotes the principal part of the integral, and $-\Delta_{12}(+\omega)$ and $-\Delta_{12}(-\omega)$ with $\omega > 0$ are, respectively, the (unrenormalized) radiative level shifts of the lower and upper states. Without an applied field of frequency ω the (vacuum) level shifts are $-\Delta_{12}(\omega_0)$ and $-\Delta_{12}(-\omega_0)$, where ω_0 (>0) is the atom's transition frequency. The quantity $\Gamma_{12}(-\omega)$ for $\omega > 0$ is half the spontaneous emission rate of the upper state, whereas $\Gamma_{12}(\omega)$ vanishes for $\omega > 0$. The notation here is consistent with that of the following section, where the expressions (8) and (9) are derived.

The ground-state polarizability $\alpha_1(\omega)$ obtained in Refs. [7,8] may be written in this notation as [14]

$$\alpha_1(\omega) = \frac{2d_{12}^2\omega_0}{\hbar} \frac{1}{\omega_0^2 - \omega^2 - 2i\omega[\gamma_{12}(\omega) - i\delta_{12}(\omega)]}$$

$$\times \left[1 + 2\frac{\Delta_{12}(-\omega) - \Delta_{12}(\omega_0) + i\Gamma_{12}(-\omega)}{\omega + \omega_0} + 2\frac{\Delta_{12}(\omega_0) - \Delta_{12}(\omega) + i\Gamma_{12}(\omega)}{\omega - \omega_0}\right], \tag{10}$$

with

$$\gamma_{12}(\omega) = \Gamma_{12}(-\omega) + \Gamma_{12}(\omega),$$

$$\delta_{12}(\omega) = \Delta_{12}(-\omega) - \Delta_{12}(\omega). \tag{11}$$

The expression (10) satisfies the crossing relation (2) as well as the optical theorem in the form

$$\mathrm{Im}\ \alpha_1(\omega) = \frac{1}{4\pi\epsilon_0}\left(\frac{2\omega^3}{3c^3}\right)|\alpha_1(\omega)|^2 \qquad (\omega > 0), \tag{12}$$

when terms up to fourth order are retained, consistent with the approximations made in obtaining Eq. (10) [7,8]. Equation (12) is simply the statement that the power lost by the applied field equals the power radiated by the atom. If the small, second, and third terms in brackets in Eq. (10) are neglected, we obtain the polarizability derived in Ref. [6]:

$$\alpha_1(\omega) \approx \frac{d_{12}^2}{\hbar}\left[\frac{1}{\omega_0 - \omega - \delta_{12}(\omega) - i\gamma_{12}(\omega)} + \frac{1}{\omega_0 + \omega + \delta_{12}(\omega) + i\gamma_{12}(\omega)}\right]. \tag{13}$$

This has the physically appealing feature that the radiative frequency shift $-\delta_{12}(\omega)$ in the denominators is the *difference* of the upper- and lower-state level shifts, and the damping terms are consistent with the opposite-sign prescription. As already noted, however, Eq. (13) does not satisfy the optical theorem.

If we retain the small terms in brackets in Eq. (10) but let them approach zero, we can bring them into the denominators $[1+x \approx 1/(1-x)]$ and write

$$\alpha_1(\omega) \approx \frac{2d_{12}^2\omega_0}{\hbar}\frac{1}{\omega_0^2 - \omega^2 - 2\omega_0[\tilde{\Delta}(\omega) + i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega) - 2\Delta_{12}(\omega_0)]}, \tag{14}$$

where $\mathrm{sgn}(\omega) \equiv |\omega|/\omega$ and

$$\tilde{\Gamma}(\omega) = \frac{d_{12}^2|\omega|^3}{6i\epsilon_0\hbar c^3}, \tag{15}$$

$$\tilde{\Delta}(\omega) = \Delta_{12}(-\omega) + \Delta_{12}(\omega). \tag{16}$$

The notation follows that of Bialynicki-Birula and Sowiński [9] except that we use a tilde instead of a circumflex, the latter used here to denote operators. Bialynicki-Birula and Sowiński employ a renormalization such that a mass $m_0 + \delta m = m$, which corresponds to $\omega_0/2$ in our notation, appears in the unperturbed Hamiltonian while a term $-\delta m$ is added to the interaction Hamiltonian, so that the effective free-atom Hamiltonian is $(m-\delta m)\hat{\psi}^\dagger\hat{\sigma}_z\hat{\psi}$, where $\hat{\sigma}_z = |2\rangle\langle 2| - |1\rangle\langle 1|$, $\hat{\psi}$ is the second-quantized fermion field describing the two-level atom, and $\hbar \equiv 1$. In our model the free-atom Hamiltonian is $\frac{1}{2}\hbar\omega_0\hat{\sigma}_z$. To compare our polarizability with that obtained by Bialynicki-Birula and Sowiński, therefore, we must replace $\frac{1}{2}\omega_0$ by $m-\delta m$, which is $\frac{1}{2}\omega_0 - \Delta_{12}(\omega_0)$ in our notation. Making the substitution

$$\omega_0 \to \omega_0 - 2\Delta_{12}(\omega_0) \tag{17}$$

in Eq. (14), we obtain

$$\alpha_1(\omega) \approx \frac{2\omega_0 d_{12}^2}{\hbar} \times \frac{1-\tilde{b}}{\omega_0^2 - \omega^2 - 2\omega_0(1-\tilde{b})[\tilde{\Delta}(\omega) + i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)]}, \tag{18}$$

where $\tilde{b} = 2\Delta_{12}(\omega_0)/\omega_0$. Expressing this result in the notation of Bialynicki-Birula and Sowiński, we see that it corresponds exactly to their *fourth-order* polarizability. [See Eq. (114) of Ref. [9].]

The second-order polarizability obtained by Bialynicki-Birula and Sowiński is obtained by setting $\tilde{b}=0$ [9]. To this order,

$$\frac{2\omega_0}{\omega_0^2 - \omega^2 - 2\omega_0[\tilde{\Delta}(\omega) + i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)]} \approx \frac{1}{\omega_0 - \omega - \tilde{\Delta}(\omega) - i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)} + \frac{1}{\omega_0 + \omega - \tilde{\Delta}(\omega) - i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)}. \tag{19}$$

This is consistent with the *same-sign* convention for the polarizability. For $\omega > 0$, for instance,

$$\frac{2\omega_0}{\omega_0^2 - \omega^2 - 2\omega_0[\tilde{\Delta}(\omega) + i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)]} \approx \frac{1}{\omega_0 - \omega - \tilde{\Delta}(\omega) - i\tilde{\Gamma}(\omega)} + \frac{1}{\omega_0 + \omega - \tilde{\Delta}(\omega) - i\tilde{\Gamma}(\omega)}. \tag{20}$$

Bialynicki-Birula and Sowiński, however, argue that "near both resonances,"when $\omega \approx \pm\omega_0$,

$$\frac{2\omega_0}{\omega_0^2 - \omega^2 - 2\omega_0[\tilde{\Delta}(\omega) + i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)]} \approx \frac{1}{\omega_0 - \omega - \tilde{\Delta}(\omega) - i\tilde{\Gamma}(\omega)} + \frac{1}{\omega_0 + \omega - \tilde{\Delta}(\omega) + i\tilde{\Gamma}(\omega)}. \tag{21}$$

This expression follows when $\omega > 0$ in the resonant part of Eq. (19) but $\omega < 0$ in the nonresonant part; but it is clear from Eq. (1) that this is an inappropriate juxtaposition of positive and negative frequencies in the expression for $\alpha_1(\omega)$: the argument of $\alpha_1(\omega)$ must be strictly positive or strictly negative. Note also that in Eq. (19) the effective frequency shift $\tilde{\Delta}(\omega)$ is actually the *sum* of the two level shifts.

Regarding this sum of level shifts, it is interesting to reconsider the calculations in Refs. [6,8] when the approximation $\hat{\sigma}_z \approx -1$ is made; this renders the two-level model effectively equivalent to a harmonic oscillator. In this approximation the equation of motion (14) in Ref. [8] yields the polarizability

$$\alpha_1(\omega) = \frac{2\omega_0 d^2}{\hbar}\frac{1}{\omega_0^2 - \omega^2 - 2\omega_0[\tilde{\Delta}(\omega) + i\ \mathrm{sgn}(\omega)\tilde{\Gamma}(\omega)]}, \tag{22}$$

the same as that implied by the left-hand side of Eq. (21). That is, if the two-level atom is approximated by a harmonic oscillator, we obtain the second-order polarizability of Bialynicki-Birula and Sowiński. The *difference* in the radiative level shifts appearing in Eq. (10) is traceable in Refs. [6,8] to the operator identity $\hat{\sigma}_z\hat{\sigma}^\dagger = +\hat{\sigma}^\dagger$, which is violated when $\hat{\sigma}_z$ is set to -1.

We can summarize our view of the situation as follows. The expression (10) for the linear polarizability of a two-level atom satisfies the crossing relation and the optical theorem. It was obtained by a calculation consistent to second order in the atom-field coupling, as exemplified in the calculation in the following section. If we approximate it by a sum of resonant and nonresonant terms [Eq. (13)], the crossing relation is still satisfied, the radiative frequency shift appears, as expected, as the difference of the two radiative level shifts, and the expression is consistent with the opposite-sign prescription. The optical theorem, however, is violated in this approximation. In a weak-coupling limit we can approximate Eq. (10) by the fourth-order result (18) of Bialynicki-Birula and Sowiński. This form satisfies the crossing relation but not the opposite-sign prescription, and moreover the radiative frequency shift that appears is the sum rather than the difference of the radiative level shifts. In other words, our expression (10) for the polarizability is consistent in a weak-coupling limit with that of Bialynicki-Birula and Sowiński, but if we replace Eq. (10) by that limiting form we forfeit two of its most desirable properties. On the other hand, Eq. (10) is to be taken as the correct expression to order $\tilde{\Gamma}(\omega)/\omega_0$ (assuming $\omega>0$); as a consequence, *neither* the same nor opposite sign prescription is strictly valid in describing the two-level polarizability.

B. Scattering amplitude

Consider now the scattering amplitude for the process $|i\rangle \rightarrow |f\rangle$ in which for both the initial state $|i\rangle$ and the final state $|f\rangle$ the two-level atom is in its lower state and there is a single photon in the field. The second-order scattering amplitude may be written as

$$a_{fi}(t) = -\frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2 \langle f|\hat{H}'(t_1)\hat{H}'(t_2)|i\rangle, \tag{23}$$

where $\hat{H}'(t)$ is the interaction Hamiltonian (4) in the Heisenberg picture and the atom and field operators are assumed to evolve approximately according to their free evolution except that the raising and lowering operators for the atom are damped at the rate $\tilde{\Gamma}(\omega)$:

$$\hat{a}_{\mathbf{k}}(t) \approx \hat{a}_{\mathbf{k}}(0)e^{-i\omega_{\mathbf{k}}t} \quad \text{and} \quad \hat{\sigma}(t) \approx \hat{\sigma}(0)e^{-i\omega_0 t}e^{-\tilde{\Gamma}(\omega)t}. \tag{24}$$

We ignore the radiative frequency shift here in order to focus on the damping. It follows from Eq. (23) that

$$a_{fi}(t) = -j_{\mathbf{k}_i}j_{\mathbf{k}_f}\int_0^t dt_1 \int_0^{t_1} dt_2 [e^{-i[\omega-\omega_0-i\tilde{\Gamma}(\omega)]t_1}e^{i[\omega-\omega_0+i\tilde{\Gamma}(\omega)]t_2} + e^{i[\omega+\omega_0+i\tilde{\Gamma}(\omega)]t_1}e^{-i[\omega+\omega_0-i\tilde{\Gamma}(\omega)]t_2}], \tag{25}$$

where $\mathbf{k}_i$ and $\mathbf{k}_f$ refer, respectively, to the initial and final photons, which are assumed to have the same frequency ω. Evaluating the integrals, and ignoring terms associated with an unphysical switching on of the interaction, we obtain, for $\tilde{\Gamma}(\omega)t \gg 1$,

$$a_{fi}(t) = \frac{-i}{2\tilde{\Gamma}(\omega)}j_{\mathbf{k}_i}j_{\mathbf{k}_f}\left(\frac{1}{\omega_0-\omega-i\tilde{\Gamma}(\omega)}+\frac{1}{\omega_0+\omega-i\tilde{\Gamma}(\omega)}\right), \tag{26}$$

which follows the same-sign prescription. We have used the approximations (24) and ignored radiative shifts in order to verify as simply as possible the conclusion of Bialynicki-Birula and Sowiński that this prescription is appropriate for the scattering amplitude. They obtain, in our notation, a scattering amplitude [see Eqs. (89) and (92) of Ref. [9]]

$$a_{fi} \propto \frac{2\omega_0}{\omega_0^2-\omega^2-2i\omega_0\tilde{\Gamma}(\omega)} \approx \frac{1}{\omega_0-\omega-i\tilde{\Gamma}(\omega)} + \frac{1}{\omega_0+\omega-i\tilde{\Gamma}(\omega)} \tag{27}$$

when radiative shifts are ignored.

For $\omega>0$, as assumed implicitly in scattering theory [15], the polarizability (18) with $\tilde{b}\approx 0$ and the scattering amplitude (27) have exactly the same frequency dependence to lowest order in the atom-field coupling. In other words, these expressions, like Eq. (10), are consistent with the optical theorem as expressed either in terms of the polarizability or the scattering amplitude. The optical theorem, though an exact consequence of unitarity, cannot, of course, be expected to be satisfied *exactly* when approximate formulas are derived for polarizabilities or scattering amplitudes.

Mukamel [16] has presented formal arguments supporting the same-sign prescription for the scattering amplitude and the opposite-sign prescription for the linear response (polarizability). We note, however, that in his Green-function formalism the linewidth $\tilde{\Gamma}(\omega)$ in our Eq. (26), for example, is replaced by the usual (frequency-independent) ϵ $(\rightarrow 0^+)$ that ensures advanced and retarded Green functions. As such his conclusions follow *ipso facto* from the assumption that the scattering amplitude is determined by a retarded Green function while the linear response is determined by the sum of advanced and retarded Green functions. In this connection it should be noted that the different signs of the ϵ's in the nonresonant parts of the scattering amplitude and the polarizability may already be found in the treatise of Berestetskii *et al.* [17]. They point out explicitly that "the expression for the [scattering amplitude] differs from [the expression for the polarizability] by a change in the sign of the imaginary part in the denominator of the [nonresonant] term."

The use of same sign and opposite sign prescriptions seems to serve little or no purpose when nonresonant contributions to the polarizability and scattering amplitude are included. For positive ω, the expressions for the two-level polarizability and scattering amplitude have *identical structure* to second order in the coupling,

$$\frac{2\omega_0}{\omega_0^2-\omega^2-2i\omega_0\tilde{\Gamma}(\omega)} \tag{28}$$

(neglecting radiative shifts) so it is not possible for one to be described by the same sign and the other by the opposite sign. The actual order of the calculation is somewhat confus-

ing since width and shift parameters appear both in resonance (and antiresonance) denominators, as well as in corrections to these terms. For example, in Eqs. (19) and (27), correction terms of order $\tilde{\Gamma}(\omega)/\omega_0$ are neglected, but these can be of the same order as the contribution from the $\tilde{\Gamma}(\omega)$ term in the antiresonance denominators in those equations. In other words,

$$\frac{2\omega_0}{\omega_0^2-\omega^2-2i\omega_0\tilde{\Gamma}(\omega)} \approx \left[\frac{1}{\omega_0-\omega-i\tilde{\Gamma}(\omega)}+\frac{1}{\omega_0+\omega-i\tilde{\Gamma}(\omega)}\right] \times\left(1-\frac{i\tilde{\Gamma}(\omega)}{\omega_0}\right) \tag{29}$$

and there is no justification for dropping the $\frac{i\tilde{\Gamma}(\omega)}{\omega_0}$ term since it can lead to corrections in the *denominators* of order $\tilde{\Gamma}(\omega)$. Instead of using same or opposite sign expressions, one is better off using the "exact" expression (28) for the polarizability or scattering amplitude.

III. THREE-LEVEL POLARIZABILITY

Consider now a three-level atom with ground state $|1\rangle$, lower and upper excited states $|2\rangle$ and $|3\rangle$, and energies $\hbar\omega_1=0$, $\hbar\omega_2$, and $\hbar\omega_3$. It is assumed that transitions are allowed from the lower excited state $|2\rangle$ to both the upper excited state $|3\rangle$ and to the ground state $|1\rangle$, with coupling coefficients $g_{\mathbf{k}}$ and $j_{\mathbf{k}}$, respectively, for the photon of wave vector $\mathbf{k}$. There are no allowed direct transitions between states $|1\rangle$ and $|3\rangle$. This configuration of energy levels provides radiative damping for the two excited states via the decay routes $|3\rangle\rightarrow|2\rangle$ and $|2\rangle\rightarrow|1\rangle$. The derived expression for the polarizability will thus include widths and shifts for both excited states.

The Hamiltonian of the interacting atom-photon system is $\hat{H}=\hat{H}_0+\hat{H}'$, where

$$\hat{H}_0=\hbar\omega_2\hat{\pi}\hat{\pi}^\dagger+\hbar\omega_3\hat{\pi}^\dagger\hat{\pi}+\int d\mathbf{k}\hbar\omega_k\hat{a}_{\mathbf{k}}^\dagger\hat{a}_{\mathbf{k}},$$

$$\hat{H}'=i\hbar\int d\mathbf{k}(\hat{a}_{\mathbf{k}}-\hat{a}_{\mathbf{k}}^\dagger)\{g_{\mathbf{k}}(\hat{\pi}^\dagger+\hat{\pi})+j_{\mathbf{k}}(\hat{\rho}^\dagger+\hat{\rho})\}. \tag{30}$$

The coupling coefficients are defined by

$$\hbar g_{\mathbf{k}}=\left(\frac{\hbar\omega_k}{16\pi^3\epsilon_0}\right)^{1/2}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{23},$$

$$\hbar j_{\mathbf{k}}=\left(\frac{\hbar\omega_k}{16\pi^3\epsilon_0}\right)^{1/2}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{12}, \tag{31}$$

where $\mathbf{d}_{23}$ and $\mathbf{d}_{12}$ are the dipole moments of the two allowed transitions, assumed real [13]. The projection operators in Eq. (30) are defined by

$$\hat{\pi}=|2\rangle\langle 3|,\quad \hat{\pi}^\dagger=|3\rangle\langle 2|,$$

$$\hat{\rho}=|1\rangle\langle 2|,\quad \hat{\rho}^\dagger=|2\rangle\langle 1|, \tag{32}$$

so that

$$|3\rangle\langle 3|=\hat{\pi}^\dagger\hat{\pi},\qquad |2\rangle\langle 2|=\hat{\pi}\hat{\pi}^\dagger=\hat{\rho}^\dagger\hat{\rho},\qquad |1\rangle\langle 1|=\hat{\rho}\hat{\rho}^\dagger, \tag{33}$$

and their nonvanishing commutators are

$$[\hat{\pi},\hat{\pi}^\dagger]=|2\rangle\langle 2|-|3\rangle\langle 3|,\quad [\hat{\rho},\hat{\rho}^\dagger]=|1\rangle\langle 1|-|2\rangle\langle 2|, \tag{34}$$

$$[\hat{\pi},\hat{\rho}]=-|1\rangle\langle 3|,\quad [\hat{\pi}^\dagger,\hat{\rho}^\dagger]=|3\rangle\langle 1|.$$

Since the calculation here will employ the Green-function approach of Ref. [7], we adopt the notation used there for the projection operators. The result obtained for the polarizability by this method may be shown to be the same as that obtained in the Heisenberg picture following the methods of Refs. [6,8].

The three bare atomic levels are perturbed by the interaction $\hat{H}'$ to form linear combinations given by second-order perturbation theory [18]. The calculations that follow use only expectation values for the form of state $|2\rangle$ as dressed by the vacuum field, denoted by $|2'\rangle$ and given by

$$|2'\rangle=\left\{1-\frac{1}{2}\int d\mathbf{k}\left[\frac{g_{\mathbf{k}}^2}{(\omega_{32}+\omega_k)^2}+\frac{j_{\mathbf{k}}^2}{|\omega_{21}-\omega_k+i\epsilon'|^2}\right]\right\}|2,0\rangle + i\int d\mathbf{k}\left\{\frac{g_{\mathbf{k}}}{\omega_{32}+\omega_k}|3,1_{\mathbf{k}}\rangle-\frac{j_{\mathbf{k}}}{\omega_{21}-\omega_k+i\epsilon'}|1,1_{\mathbf{k}}\rangle\right\}, \tag{35}$$

where $\omega_{ij}=\omega_i-\omega_j$ so that $\omega_2=\omega_{21}$ and $\omega_3=\omega_{31}$. The bare states are indicated by the unperturbed state labels 1, 2, and 3 for the atom and 0 and $1_{\mathbf{k}}$ for the field. The infinitesimal ϵ' represents the decay of field modes in a notional cavity and the photon frequency is written $\omega_k-i\epsilon'$ in terms that would otherwise diverge at $\omega_{21}=\omega_k$. The integral in the first term of Eq. (35) results from normalization of the perturbed wave function. Other, noncontributing, terms of second order in the radiative couplings are omitted. Expectation values with respect to state $|2'\rangle$ are indicated by angle brackets and given by

$$\langle[\hat{\pi},\hat{\pi}^\dagger]\rangle=1-\int d\mathbf{k}\left\{\frac{2g_{\mathbf{k}}^2}{(\omega_{32}+\omega_k)^2}+\frac{j_{\mathbf{k}}^2}{|\omega_{21}-\omega_k+i\epsilon'|^2}\right\}, \tag{36}$$

$$\langle\hat{a}_{\mathbf{k}}\hat{\pi}^\dagger\rangle=\langle\hat{a}_{\mathbf{k}}\hat{\rho}\rangle=0, \tag{37}$$

$$\langle\hat{a}_{\mathbf{k}}^\dagger\hat{\pi}^\dagger\rangle=-i\frac{g_{\mathbf{k}}}{\omega_{32}+\omega_k}\quad\text{and}\quad\langle\hat{a}_{\mathbf{k}}^\dagger\hat{\rho}\rangle=i\frac{j_{\mathbf{k}}}{\omega_{21}-\omega_k-i\epsilon'}, \tag{38}$$

all correct to second order in $g_{\mathbf{k}}$ and $j_{\mathbf{k}}$.

A. Green function method

The linear polarizability of the three-level system is given by

$$\alpha_1(\omega) = -\lim_{\epsilon\to 0^+} G_{\omega+i\epsilon}(d_{23}(\hat{\pi}+\hat{\pi}^\dagger)+d_{12}(\hat{\rho}+\hat{\rho}^\dagger), d_{23}(\hat{\pi}+\hat{\pi}^\dagger) + d_{12}(\hat{\rho}+\hat{\rho}^\dagger)). \tag{39}$$

The addition of a positive infinitesimal imaginary part to ω ensures that the Green function is retarded, with its poles in the negative-imaginary part of the complex plane, as is required by considerations of causality [19]. The Green function for general operators $\hat{A}$ and $\hat{B}$ is defined by

$$G_{\omega+i\epsilon}(\hat{A},\hat{B}) = \sum_{r,s} \frac{\exp(-E_r/k_BT)-\exp(-E_s/k_BT)}{\mathrm{Tr}\{\exp(-\hat{H}/k_BT)\}} \times \frac{\langle r|\hat{A}|s\rangle\langle s|\hat{B}|r\rangle}{\hbar(\omega+i\epsilon)+E_r-E_s}, \tag{40}$$

where $|r\rangle$, $|s\rangle$ and E_r, E_s are the exact eigenstates and eigenvalues, respectively, of the system Hamiltonian $\hat{H}$. The composite dipole operator that appears in the Green function of Eq. (39), here denoted $\hat{D}$, is Hermitian and it is not difficult to show from the definition in Eq. (40) that

$$G_{\omega+i\epsilon}(\hat{D},\hat{D}) = \{G_{-\omega+i\epsilon}(\hat{D},\hat{D})\}^* = G_{-\omega-i\epsilon}(\hat{D},\hat{D}). \tag{41}$$

The polarizability therefore satisfies the crossing relation (2) and it follows that $\alpha_1(0)$ must be real. Evaluations are usually made for positive or zero ω and the frequencies that appear in the Hamiltonian (30) are strictly positive.

The Green function in Eq. (39) contains contributions in the pairs of operators that refer to the two transitions separately and also interference terms that involve the operators of both transitions. The contribution to the polarizability from the transition between states $|2\rangle$ and $|3\rangle$ alone is

$$\alpha_2(\omega) = -d_{23}^2 \lim_{\epsilon\to 0^+}\{G_{\omega+i\epsilon}(\hat{\pi},\hat{\pi}^\dagger)+G_{\omega+i\epsilon}(\hat{\pi}^\dagger,\hat{\pi}^\dagger) + G_{\omega+i\epsilon}(\hat{\pi}^\dagger,\hat{\pi})+G_{\omega+i\epsilon}(\hat{\pi},\hat{\pi})\}, \tag{42}$$

and we restrict our attention to this partial polarizability. The individual Green functions are related by

$$G_{\omega+i\epsilon}(\hat{\pi}^\dagger,\hat{\pi}) = \{G_{-\omega+i\epsilon}(\hat{\pi},\hat{\pi}^\dagger)\}^* = G_{-\omega-i\epsilon}(\hat{\pi},\hat{\pi}^\dagger)$$

and

$$G_{\omega+i\epsilon}(\hat{\pi},\hat{\pi}) = \{G_{-\omega+i\epsilon}(\hat{\pi}^\dagger,\hat{\pi}^\dagger)\}^*, \tag{43}$$

again readily derived from the definition in Eq. (40). It is therefore necessary to calculate only the first two Green functions in Eq. (42).

The calculation proceeds via the Green-function equation of motion for general operators $\hat{A}$ and $\hat{B}$ in the form [20,21]

$$\hbar\omega G(\hat{A},\hat{B}) = \langle[\hat{A},\hat{B}]\rangle + G([\hat{A},\hat{H}],\hat{B}), \tag{44}$$

where ω is shorthand for $\omega+i\epsilon$ and this subscript on G is understood. Where appropriate, we use the technique of truncation of the hierarchy of equations for the Green functions generated by successive applications of Eq. (44). The calculations for the three-level system are approximated by neglect of terms of order higher than the second in $g_{\mathbf{k}}$ and $j_{\mathbf{k}}$ to give a closed set of equations that can be solved for the Green functions that appear in Eq. (42).

B. Approximate solutions for Green functions

It follows from Eqs. (30), (32), and (34) that

$$[\hat{\pi},\hat{H}] = \hbar\omega_{32}\hat{\pi} + i\hbar\int d\mathbf{k}(\hat{a}_{\mathbf{k}}-\hat{a}_{\mathbf{k}}^\dagger)\{g_{\mathbf{k}}[\hat{\pi},\hat{\pi}^\dagger]-j_{\mathbf{k}}\hat{\rho}\hat{\pi}\}. \tag{45}$$

The equation of motion from Eq. (44) is therefore

$$\hbar(\omega-\omega_{32})G(\hat{\pi},\hat{\pi}^\dagger) = \langle[\hat{\pi},\hat{\pi}^\dagger]\rangle + i\hbar\int d\mathbf{k}G\{(\hat{a}_{\mathbf{k}}-\hat{a}_{\mathbf{k}}^\dagger) \times(g_{\mathbf{k}}[\hat{\pi},\hat{\pi}^\dagger]-j_{\mathbf{k}}\hat{\rho}\hat{\pi}),\hat{\pi}^\dagger\}. \tag{46}$$

This is the first equation in the hierarchy and it brings in new Green functions.

It is convenient to separate the new Green functions into the four parts obtained from the product of factors in its first argument. The commutators needed for the new equations of motion are

$$\begin{aligned}[\hat{a}_{\mathbf{k}}[\hat{\pi},\hat{\pi}^\dagger],\hat{H}] &= \hbar\omega_k\hat{a}_{\mathbf{k}}[\hat{\pi},\hat{\pi}^\dagger] + i\hbar\int d\mathbf{k}'\{g_{\mathbf{k}'}[\hat{a}_{\mathbf{k}}(\hat{a}_{\mathbf{k}'}-\hat{a}_{\mathbf{k}'}^\dagger) \\ &\quad + (\hat{a}_{\mathbf{k}'}-\hat{a}_{\mathbf{k}'}^\dagger)\hat{a}_{\mathbf{k}}](\hat{\pi}-\hat{\pi}^\dagger) \\ &\quad + j_{\mathbf{k}'}[\hat{a}_{\mathbf{k}}(\hat{a}_{\mathbf{k}'}-\hat{a}_{\mathbf{k}'}^\dagger)\hat{\rho}^\dagger-(\hat{a}_{\mathbf{k}'}-\hat{a}_{\mathbf{k}'}^\dagger)\hat{a}_{\mathbf{k}}\hat{\rho}]\} \\ &\to \hbar\omega_k\hat{a}_{\mathbf{k}}[\hat{\pi},\hat{\pi}^\dagger] - i\hbar g_{\mathbf{k}}(\hat{\pi}-\hat{\pi}^\dagger) - i\hbar j_{\mathbf{k}}\hat{\rho}^\dagger,\end{aligned} \tag{47}$$

where the final expression results from the replacement of the photon operator products by their vacuum expectation values, with the use of Eq. (7) and $\langle\hat{a}_{\mathbf{k}}^\dagger\hat{a}_{\mathbf{k}}\rangle=0$. Similarly

$$[\hat{a}_{\mathbf{k}}^\dagger[\hat{\pi},\hat{\pi}^\dagger],H] \to -\hbar\omega_k\hat{a}_{\mathbf{k}}^\dagger[\hat{\pi},\hat{\pi}^\dagger] + i\hbar g_{\mathbf{k}}(\hat{\pi}-\hat{\pi}^\dagger) - i\hbar j_{\mathbf{k}}\hat{\rho}, \tag{48}$$

$$\begin{aligned}[\hat{a}_{\mathbf{k}}\hat{\rho}\hat{\pi},\hat{H}] &= \hbar(\omega_3+\omega_k)\hat{a}_{\mathbf{k}}\hat{\rho}\hat{\pi} + i\hbar\int d\mathbf{k}'\{\hat{a}_{\mathbf{k}}\hat{\rho}\hat{\pi}(\hat{a}_{\mathbf{k}'}-\hat{a}_{\mathbf{k}'}^\dagger) \\ &\quad \times[g_{\mathbf{k}'}(\hat{\pi}^\dagger+\hat{\pi}) + j_{\mathbf{k}'}(\hat{\rho}^\dagger+\hat{\rho})] \\ &\quad - (\hat{a}_{\mathbf{k}'}-\hat{a}_{\mathbf{k}'}^\dagger)[g_{\mathbf{k}'}(\hat{\pi}^\dagger+\hat{\pi}) + j_{\mathbf{k}'}(\hat{\rho}^\dagger+\hat{\rho})]\hat{a}_{\mathbf{k}}\hat{\rho}\hat{\pi}\} \\ &\to \hbar(\omega_3+\omega_k)\hat{a}_{\mathbf{k}}\hat{\rho}\hat{\pi} - i\hbar g_{\mathbf{k}}\hat{\rho},\end{aligned} \tag{49}$$

and

$$[\hat{a}_{\mathbf{k}}^\dagger\hat{\rho}\hat{\pi},\hat{H}] \to \hbar(\omega_3-\omega_k)\hat{a}_{\mathbf{k}}^\dagger\hat{\rho}\hat{\pi} - i\hbar j_{\mathbf{k}}\hat{\pi}. \tag{50}$$

The corresponding equations of motion (44) are

$$(\omega-\omega_k)G(\hat{a}_{\mathbf{k}}[\hat{\pi},\hat{\pi}^\dagger],\hat{\pi}^\dagger) = -ig_{\mathbf{k}}G(\hat{\pi}-\hat{\pi}^\dagger,\hat{\pi}^\dagger) - ij_{\mathbf{k}}G(\hat{\rho}^\dagger,\hat{\pi}^\dagger), \tag{51}$$

$$\hbar(\omega+\omega_k)G(\hat{a}_{\mathbf{k}}^\dagger[\hat{\pi},\hat{\pi}^\dagger],\hat{\pi}^\dagger) = -2\langle\hat{a}_{\mathbf{k}}^\dagger\hat{\pi}^\dagger\rangle + i\hbar g_{\mathbf{k}}G(\hat{\pi}-\hat{\pi}^\dagger,\hat{\pi}^\dagger) - i\hbar j_{\mathbf{k}}G(\hat{\rho},\hat{\pi}^\dagger), \tag{52}$$

$$(\omega - \omega_{31} - \omega_k)G(\hat{a}_\mathbf{k}\hat{\rho}\hat{\pi}, \hat{\pi}^\dagger) = -ig_\mathbf{k}G(\hat{\rho}, \hat{\pi}^\dagger), \tag{53}$$

and

$$\hbar(\omega - \omega_{31} + \omega_k)G(\hat{a}_\mathbf{k}^\dagger\hat{\rho}\hat{\pi}, \hat{\pi}^\dagger) = \langle\hat{a}_\mathbf{k}^\dagger\hat{\rho}\rangle - i\hbar j_\mathbf{k}G(\pi, \hat{\pi}^\dagger), \tag{54}$$

where expectation values that could appear on the right-hand sides of Eqs. (51) and (53) are omitted in accordance with Eq. (37). These four equations form the second level of the hierarchy and they again bring in new Green functions.

Evaluation of the Green functions $G(\hat{\rho}^\dagger, \hat{\pi}^\dagger)$ in Eq. (51) and $G(\hat{\rho}, \hat{\pi}^\dagger)$ in Eqs. (52) and (53) produces expressions of the first order in the coupling coefficients $g_\mathbf{k}$ and $j_\mathbf{k}$. These two Green functions can therefore be neglected in accordance with the restriction of the polarizability to terms of second order in the coupling. The new Green function $G(\hat{\pi}^\dagger, \hat{\pi}^\dagger)$ on the right-hand sides of Eqs. (51) and (52) is the second in the basic expression (42) for the polarizability. Its equation of motion is

$$(\omega + \omega_{32})G(\hat{\pi}^\dagger, \hat{\pi}^\dagger) = -i\int d\mathbf{k}G\{(\hat{a}_\mathbf{k} - \hat{a}_\mathbf{k}^\dagger)(g_\mathbf{k}[\hat{\pi}, \hat{\pi}^\dagger] - j_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger), \hat{\pi}^\dagger\}. \tag{55}$$

The Green function associated with the $[\hat{\pi}, \hat{\pi}^\dagger]$ term has already been evaluated in Eqs. (51) and (52). The remaining Green functions need the commutators

$$\begin{aligned}[\hat{a}_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger, \hat{H}] &= -\hbar(\omega_3 - \omega_k)\hat{a}_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger + i\hbar\int d\mathbf{k}'\{\hat{a}_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger \\ &\times(\hat{a}_{\mathbf{k}'} - \hat{a}_{\mathbf{k}'}^\dagger)[g_{\mathbf{k}'}(\hat{\pi}^\dagger + \hat{\pi}) + j_{\mathbf{k}'}(\hat{\rho}^\dagger + \hat{\rho})] \\ &- (\hat{a}_{\mathbf{k}'} - \hat{a}_{\mathbf{k}'}^\dagger)[g_{\mathbf{k}'}(\hat{\pi}^\dagger + \hat{\pi}) + j_{\mathbf{k}'}(\hat{\rho}^\dagger + \hat{\rho})]\hat{a}_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger\} \\ &\to -\hbar(\omega_3 - \omega_k)\hat{a}_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger - i\hbar j_\mathbf{k}\hat{\pi}^\dagger\end{aligned} \tag{56}$$

and

$$[\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\hat{\rho}^\dagger, \hat{H}] \to -\hbar(\omega_3 + \omega_k)\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\hat{\rho}^\dagger - i\hbar g_\mathbf{k}\hat{\rho}^\dagger. \tag{57}$$

The corresponding equations of motion are

$$(\omega + \omega_{31} - \omega_k)G(\hat{a}_\mathbf{k}\hat{\pi}^\dagger\hat{\rho}^\dagger, \hat{\pi}^\dagger) = -ij_\mathbf{k}G(\hat{\pi}^\dagger, \hat{\pi}^\dagger) \tag{58}$$

and

$$(\omega + \omega_{31} + \omega_k)G(\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\hat{\rho}^\dagger, \hat{\pi}^\dagger) = -ig_\mathbf{k}G(\hat{\rho}^\dagger, \hat{\pi}^\dagger). \tag{59}$$

The right-hand side of Eq. (59) can be set equal to zero in accordance with the remarks that precede Eq. (55).

The Green functions that appear in Eqs. (46), (51)–(55), (58), and (59) form a closed set and the functions needed for the polarizability (42) can be determined by the solution of these simultaneous equations. It is convenient to define

$$I(\omega) = \int d\mathbf{k}g_\mathbf{k}^2\left(\frac{1}{\omega_k - \omega} - \frac{1}{\omega_k + \omega}\right) = -I(-\omega) \tag{60}$$

and

$$J(\omega_{31} \pm \omega) = \int d\mathbf{k}\frac{j_\mathbf{k}^2}{\omega_{31} - \omega_k \pm \omega}, \tag{61}$$

where ω is shorthand for $\omega + i\epsilon$ throughout. Elimination of all except the required Green functions from the equations listed above then produces the pair of equations

$$\begin{aligned}&-\hbar\{\omega_{32} - \omega - I(\omega) - J(\omega_{31} - \omega)\}G(\hat{\pi}, \hat{\pi}^\dagger) - \hbar I(\omega)G(\hat{\pi}^\dagger, \hat{\pi}^\dagger) \\ &= \langle[\hat{\pi}, \hat{\pi}^\dagger]\rangle + i\int d\mathbf{k}\left\{\frac{2g_\mathbf{k}\langle\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\rangle}{\omega_k + \omega} - \frac{j_\mathbf{k}\langle\hat{a}_\mathbf{k}^\dagger\hat{\rho}\rangle}{\omega_{31} - \omega_k - \omega}\right\},\end{aligned} \tag{62}$$

$$\begin{aligned}&-\hbar I(\omega)G(\hat{\pi}, \hat{\pi}^\dagger) + \hbar\{\omega_{32} + \omega + I(\omega) - J(\omega_{31} + \omega)\}G(\hat{\pi}^\dagger, \hat{\pi}^\dagger) \\ &= -i\int d\mathbf{k}\frac{2g_\mathbf{k}\langle\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\rangle}{\omega_k + \omega}.\end{aligned} \tag{63}$$

The solutions of these simultaneous equations have the common denominator

$$\begin{aligned}\mathrm{D} &= \hbar[\omega_{32} - \omega - I(\omega) - J(\omega_{31} - \omega)][\omega_{32} + \omega + I(\omega) \\ &- J(\omega_{31} + \omega)] + \hbar[I(\omega)]^2 \\ &\approx \hbar\{\omega_{32}^2 - \omega^2 - 2\omega I(\omega) - (\omega_{32} - \omega)J(\omega_{31} + \omega) \\ &- (\omega_{32} + \omega)J(\omega_{31} - \omega)\},\end{aligned} \tag{64}$$

which is seen to be invariant under reversal of the sign of ω. The numerators are obtained from

$$\begin{aligned}G(\hat{\pi}, \hat{\pi}^\dagger)\mathrm{D} &= -[\omega_{32} + \omega + I(\omega) - J(\omega_{31} + \omega)]\langle[\hat{\pi}, \hat{\pi}^\dagger]\rangle \\ &- i(\omega_{32} + \omega)\int d\mathbf{k}\left\{\frac{2g_\mathbf{k}\langle\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\rangle}{\omega_k + \omega} - \frac{j_\mathbf{k}\langle\hat{a}_\mathbf{k}^\dagger\hat{\rho}\rangle}{\omega_{31} - \omega_k - \omega}\right\} \\ &\approx -(\omega_{32} + \omega)\langle[\hat{\pi}, \hat{\pi}^\dagger]\rangle - I(\omega) + J(\omega_{31} + \omega) \\ &- (\omega_{32} + \omega)\int d\mathbf{k}\left\{\frac{2g_\mathbf{k}^2}{(\omega_k + \omega)(\omega_{32} + \omega_k)}\right. \\ &\left. + \frac{j_\mathbf{k}^2}{(\omega_{31} - \omega_k - \omega)(\omega_{21} - \omega_k - i\epsilon')}\right\}\end{aligned} \tag{65}$$

and

$$\begin{aligned}G(\hat{\pi}^\dagger, \hat{\pi}^\dagger)\mathrm{D} &= -I(\omega)\langle[\hat{\pi}, \hat{\pi}^\dagger]\rangle - i(\omega_{32} - \omega)\int d\mathbf{k}\frac{2g_\mathbf{k}\langle\hat{a}_\mathbf{k}^\dagger\hat{\pi}^\dagger\rangle}{\omega_k + \omega} \\ &\approx -I(\omega) - (\omega_{32} - \omega)\int d\mathbf{k}\frac{2g_\mathbf{k}^2}{(\omega_k + \omega)(\omega_{32} + \omega_k)}.\end{aligned} \tag{66}$$

In each of these last three expressions, the second forms show approximations correct to order $g_{\mathbf{k}}^2$ and $j_{\mathbf{k}}^2$ in the denominator and numerators. It is easily shown with the use of Eq. (60) that the Green function in Eq. (66) is invariant under reversal of the sign of ω, a general property of Green functions with repeated arguments, $\hat{A}=\hat{B}$. The remaining Green functions are found by application of the relations in Eq. (43).

C. Partial polarizability $\alpha_2(\omega)$

The partial polarizability given by Eq. (42) is

$$\alpha_2(\omega) = -d_{23}^2 \frac{\mathrm{N}}{\mathrm{D}}, \tag{67}$$

where D is given by Eq. (64) and

$$\begin{aligned}\mathrm{N} = &-2\omega_{32}\langle[\hat{\pi},\hat{\pi}^{+}]\rangle + J(\omega_{31}+\omega) + J(\omega_{31}-\omega) \\ &-4\omega_{32}\int d\mathbf{k} g_{\mathbf{k}}^2 \left\{ \left(\frac{1}{\omega_{32}+\omega_k} - \frac{1}{\omega_k+\omega} \right) \frac{1}{\omega-\omega_{32}} \right. \\ &\left. - \left(\frac{1}{\omega_{32}+\omega_k} - \frac{1}{\omega_k-\omega} \right) \frac{1}{\omega+\omega_{32}} \right\} \\ &- \int d\mathbf{k} j_{\mathbf{k}}^2 \left\{ \left(\frac{1}{\omega_{31}-\omega_k-\omega} - \frac{1}{\omega_{21}-\omega_k-i\epsilon'} \right) \frac{\omega+\omega_{32}}{\omega-\omega_{32}} \right. \\ &\left. + \left(\frac{1}{\omega_{31}-\omega_k+\omega} - \frac{1}{\omega_{21}-\omega_k+i\epsilon'} \right) \frac{\omega-\omega_{32}}{\omega+\omega_{32}} \right\}. \end{aligned} \tag{68}$$

With ω replaced by $\omega+i\epsilon$, and in the limit $\epsilon\to 0^+$, it is convenient to use the separation into real and imaginary parts, following notation introduced in Sec. II:

$$\int d\mathbf{k} \frac{g_{\mathbf{k}}^2}{\omega_k \pm \omega \pm i\epsilon} \to \Delta_{23}(\pm\omega) \mp i\Gamma_{23}(\pm\omega), \tag{69}$$

so that, from Eq. (60),

$$\begin{aligned}\lim_{\epsilon\to 0^+} I(\omega+i\epsilon) &= \Delta_{23}(-\omega) + i\Gamma_{23}(-\omega) - \Delta_{23}(\omega) + i\Gamma_{23}(\omega) \\ &= \delta_{23}(\omega) + i\gamma_{23}(\omega),\end{aligned}$$

where

$$\delta_{23}(\omega) = \Delta_{23}(-\omega) - \Delta_{23}(\omega),$$

$$\gamma_{23}(\omega) = \Gamma_{23}(-\omega) + \Gamma_{23}(\omega). \tag{70}$$

Similarly

$$\begin{aligned}J(\omega_{31}\pm\omega) &= \int d\mathbf{k} \frac{j_{\mathbf{k}}^2}{\omega_{31}-\omega_k \pm \omega \pm i\epsilon} \\ &\to -\Delta_{12}(-\omega_{31}\mp\omega) \mp i\Gamma_{12}(-\omega_{31}\mp\omega)\end{aligned} \tag{71}$$

and, with $\epsilon'\to 0^+$,

$$\int d\mathbf{k} \frac{j_{\mathbf{k}}^2}{\omega_{21}-\omega_k \pm i\epsilon'} \to -\Delta_{12}(-\omega_{21}) \mp i\Gamma_{12}(-\omega_{21}). \tag{72}$$

The real parts are level shifts, given by principal-value integrals, and the imaginary parts are level widths or damping rates, with

$$\Gamma_{23}(\pm\omega) = \pi \int d\mathbf{k} g_{\mathbf{k}}^2 \delta(\omega_k \pm \omega), \tag{73}$$

$$\Gamma_{12}(-\omega_{31}\pm\omega) = \pi \int d\mathbf{k} j_{\mathbf{k}}^2 \delta(\omega_k - \omega_{31} \pm \omega) \tag{74}$$

and

$$\Gamma_{12}(-\omega_{21}) = \pi \int d\mathbf{k} j_{\mathbf{k}}^2 \delta(\omega_k - \omega_{21}). \tag{75}$$

The functions $-\Delta_{23}(-\omega)$ and $\Gamma_{23}(-\omega)$ are interpreted, respectively, as the level shift and damping of level $|3\rangle$, while $-\Delta_{23}(\omega)$ and $\Gamma_{23}(\omega)$ are the shift and damping of level $|2\rangle$ arising from its coupling to level $|3\rangle$, i.e., these quantities all result from the radiative coupling $g_{\mathbf{k}}$ between states $|3\rangle$ and $|2\rangle$. For positive ω, $\Gamma_{23}(\omega)=0$ for all ω, as expected on physical grounds from the absence of spontaneous emission in the upwards direction. While $\Gamma_{12}(-\omega_{31}-\omega)$ is nonzero for all ω, $\Gamma_{12}(-\omega_{31}+\omega)$ is nonzero only for $\omega<\omega_{31}$. The frequencies $\omega_{31}\pm\omega$, and therefore the damping rates $\Gamma_{12}(-\omega_{31}\mp\omega)$, appear through frequency mixing of the applied field and a source field that oscillates at ω_{31}. The latter results from the possibility of transitions between the states $|1\rangle$ and $|3\rangle$ via the allowed $|1\rangle\leftrightarrow|2\rangle$ and $|2\rangle\leftrightarrow|3\rangle$ transitions.

The partial polarizability (67) is quite complicated when these expressions are substituted. It is instructive to consider its form when all of the level shifts are neglected and only the damping terms are retained. The denominator is then

$$\begin{aligned}\mathrm{D} = &\hbar[\omega_{32}-\omega-i\gamma_{23}(\omega)-i\Gamma_{12}(-\omega_{31}+\omega)][\omega_{32}+\omega \\ &+i\gamma_{23}(\omega)+i\Gamma_{12}(-\omega_{31}-\omega)] + \hbar[I(\omega)]^2 \approx \hbar\{\omega_{32}^2-\omega^2 \\ &-2i\omega\gamma_{23}(\omega)+i(\omega_{32}-\omega)\Gamma_{12}(-\omega_{31}-\omega) \\ &-i(\omega_{32}+\omega)\Gamma_{12}(-\omega_{31}+\omega)\}\end{aligned} \tag{76}$$

and the numerator is

$$\begin{aligned}\mathrm{N} = &-2\omega_{32}\left\{ 1 + \frac{2i\Gamma_{23}(-\omega)}{\omega_{32}+\omega} - \frac{2i\Gamma_{23}(\omega)}{\omega_{32}-\omega} + \frac{i\Gamma_{12}(-\omega_{31}-\omega)}{\omega_{32}+\omega} \right. \\ &\left. - \frac{i\Gamma_{12}(-\omega_{31}+\omega)}{\omega_{32}-\omega} + \frac{2i\omega\Gamma_{12}(-\omega_{21})}{\omega_{32}^2-\omega^2} \right\}.\end{aligned} \tag{77}$$

The polarizability from Eq. (67) is therefore

$$\alpha_2(\omega) = \frac{2d_{23}^2\omega_{32}}{\hbar} \frac{1 + \frac{2i\Gamma_{23}(-\omega)}{\omega_{32}+\omega} - \frac{2i\Gamma_{23}(\omega)}{\omega_{32}-\omega} + \frac{i\Gamma_{12}(-\omega_{31}-\omega)}{\omega_{32}+\omega} - \frac{i\Gamma_{12}(-\omega_{31}+\omega)}{\omega_{32}-\omega} + \frac{2i\omega\Gamma_{12}(-\omega_{21})}{\omega_{32}^2-\omega^2}}{\omega_{32}^2 - \omega^2 - 2i\omega\gamma_{23}(\omega) + i(\omega_{32}-\omega)\Gamma_{12}(-\omega_{31}-\omega) - i(\omega_{32}+\omega)\Gamma_{12}(-\omega_{31}+\omega)}. \tag{78}$$

It is readily verified that this expression satisfies the crossing relation, and it shows the consequent property of a real value at $\omega=0$. The two terms in the product of square brackets on the right in the first line of Eq. (76) represent resonant and nonresonant contributions, respectively. Note the different structures of these terms with respect to the upper and lower transition functions. The latter results from the radiative coupling $j_{\mathbf{k}}$ between states $|2\rangle$ and $|1\rangle$ and makes only single contributions to the damping, as only state $|2\rangle$ is affected by spontaneous emission to state $|1\rangle$. There is no simple relation between the Γ_{12} magnitudes in the two terms, in contrast to the two upper-transition contributions contained in $\gamma_{23}(\omega)$.

The dominant feature in the polarizability is the resonance of the first term in Eq. (76) at $\omega=\omega_{32}$ and, for frequencies close to resonance, it is usually a good approximation to substitute ω_{32} for ω in the expressions for the level widths that occur in the first term. Then

$$\Gamma_{23}(-\omega_{32}) = \pi \int d\mathbf{k} g_{\mathbf{k}}^2 \delta(\omega_k - \omega_{32})$$

and

$$\Gamma_{12}(-\omega_{31}+\omega) \approx \Gamma_{12}(-\omega_{21}) = \pi \int d\mathbf{k} j_{\mathbf{k}}^2 \delta(\omega_k - \omega_{21}), \tag{79}$$

in agreement with the usual expressions for the decay rates of states $|3\rangle$ and $|2\rangle$.

IV. DISCUSSION

We note that the form (78) of the polarizability when the coupling $j_{\mathbf{k}}$ of level $|2\rangle$ to level $|1\rangle$ is set equal to zero, given by

$$\alpha_2(\omega) = -\frac{2d_{23}^2\omega_{32}}{\hbar} \frac{1 - \frac{2i\Gamma_{23}(\omega)}{\omega_{32}-\omega} + \frac{2i\Gamma_{23}(-\omega)}{\omega_{32}+\omega}}{\omega_{32}^2 - \omega^2 - 2i\omega\gamma_{23}(\omega)}, \tag{80}$$

agrees, apart from trivial changes in notation, with the two-level polarizability (10) when radiative shifts are ignored.

In our nonrelativistic approach without retardation or a high-frequency cutoff, the radiative level shifts are divergent. Nevertheless, whether they appear in a sum or a difference helps to determine the plausibility of various expressions for the polarizability, as discussed in Sec. II. In the three-level case the radiative level shifts of the states $|2\rangle$ and $|3\rangle$ appear, as expected, as the difference $\delta_{23}(\omega)$ determining a radiative frequency shift.

For our purposes the radiative widths are of much greater interest. Note that the widths of the upper and lower energy levels in the transition *add* in the polarizability denominator, in agreement with the line shape of the $|3\rangle \rightarrow |2\rangle$ transition in cascade emission given in Eqs. (C.44) and (C.45) of [22]. The two terms in the first line of Eq. (76) have the same damping term or level width $\gamma_{23}(\omega)$ in respect of the $|3\rangle \rightarrow |2\rangle$ transition alone. The signs of these terms essentially follow the signs of ω in the two denominators. Equivalently, they have opposite signs relative to the transition frequency ω_{32}, i.e., they follow the opposite-sign prescription.

However, any simple relation between the two terms is destroyed by the contributions from the decay and shift parameters appearing in the denominator of Eq. (78) that are associated with the $|2\rangle \rightarrow |1\rangle$ transition. In particular, the values of the damping functions $\Gamma_{12}(-\omega_{31}-\omega)$ and $\Gamma_{12}(-\omega_{31}+\omega)$ are different except at $\omega=0$. As stated above, $\Gamma_{12}(-\omega_{31}+\omega)$ is nonzero only for positive arguments while $\Gamma_{12}(-\omega_{31}-\omega)$ is nonzero for all positive ω. Both the simple forms of relation between the linewidths of the resonant and nonresonant terms, embodied in the opposite-sign and same-sign rules, are therefore incorrect for transitions between atomic excited states.

If we bring the small terms in the numerator of Eq. (78) into the denominator in the manner of Eq. (14), we obtain

$$\alpha_2(\omega) \approx \frac{2d_{23}^2\omega_{32}}{\hbar} \times \frac{1}{\omega_{32}^2 - \omega^2 - 2i\omega_{32}\,\mathrm{sgn}(\omega)\tilde{\Gamma}_{23}(\omega) - 2i\omega\Gamma_{12}(-\omega_{21})}, \tag{81}$$

where we define, analogously to Eq. (15),

$$\tilde{\Gamma}_{23}(\omega) = \frac{d_{23}^2|\omega|^3}{6\pi\epsilon_0\hbar c^3}. \tag{82}$$

We can use the simplification (81) to verify that the optical theorem,

$$\sigma_T(\omega) = \frac{\omega}{\epsilon_0 c}\mathrm{Im}\ \alpha_2(\omega) \qquad (\omega > 0), \tag{83}$$

is satisfied by the polarizability and the total cross section $\sigma_T(\omega)$ in our three-level model. We note first that, since we have considered only the partial polarizability $\alpha_2(\omega)$, the $|2\rangle \rightarrow |1\rangle$ transition in our model acts primarily as a decay channel for level $|2\rangle$. We have, from Eq. (81),

$$\frac{\omega}{\epsilon_0 c}\mathrm{Im}\ \alpha_2(\omega) = \sigma_{\mathrm{R}}(\omega) + \sigma_{\mathrm{A}}(\omega), \tag{84}$$

where

$$\sigma_{\mathrm{R}}(\omega) = \frac{1}{6\pi\epsilon_0^2}\left(\frac{\omega}{c}\right)^4 |\alpha_2(\omega)|^2 \tag{85}$$

and

$$\sigma_A(\omega) = \frac{\omega}{\epsilon_0 c}\frac{2d_{23}^2\omega_{32}}{\hbar} \times \frac{2\omega_{32}\Gamma_{12}(-\omega_{21})}{(\omega_{32}^2-\omega^2)^2+[2\omega_{32}\tilde{\Gamma}_{23}(\omega)+2\omega\Gamma_{12}(-\omega_{21})]^2}. \tag{86}$$

If $\omega \approx \omega_{32}$

$$\sigma_A(\omega) \approx \frac{\omega}{\epsilon_0 c}\frac{d_{23}^2}{\hbar}\frac{\Gamma_{12}(-\omega_{21})}{(\omega_{32}-\omega)^2+[\tilde{\Gamma}_{23}(\omega)+\Gamma_{12}(-\omega_{21})]^2}. \tag{87}$$

It is possible to give a physical interpretation to these terms in the limit that $\Delta=\omega_{32}-\omega \gg \tilde{\Gamma}_{23}(\omega)$, $\Gamma_{12}(-\omega_{21})$. To do so we first recall that light scattering from the *ground* state of an atom is Rayleigh scattering, to lowest order in the incident light intensity. That is, the scattering is *elastic,* with the frequency of the scattered radiation equal to that of the incident field. The elastic nature of the scattering can be understood in terms of a two-photon process in which a photon is scattered from the incident field into a previously unoccupied vacuum field mode having the same frequency but a different direction. Since the initial and final states of the atomic transition have zero width (the transition is from the ground state back to the ground state), the scattering is necessarily elastic. On the other hand, when one scatters from an excited state, the initial and final state width is that of the excited state. In this limit, one can show that radiation scattered by the atoms consists of *two* components, a component having width $2\Gamma_{12}(-\omega_{21})$ centered at the field frequency ω and a component having width $[\tilde{\Gamma}_{23}(\omega)+\Gamma_{12}(-\omega_{21})]$ centered at the transition frequency ω_{32}.

The radiation centered at the field frequency can be viewed as the analog of Rayleigh scattering. On integrating over all scattered frequencies centered at ω, one obtains the cross section $\sigma_R(\omega)$ [Eq. (85)] corresponding to Rayleigh scattering off an electric dipole scatterer having polarizability $\alpha_2(\omega)$, although in this case the scattering, while centered at ω, is not totally elastic. On integrating the component centered at the transition frequency ω_{32} over all scattered frequencies, one obtains the cross section $\sigma_A(\omega)$ [Eq. (87)] corresponding to absorption on the 2–3 transition. The absorption component occurs only if $\Gamma_{12}(-\omega_{21}) \neq 0$. In the limit that $\Gamma_{12}(-\omega_{21}) \ll \tilde{\Gamma}_{23}(\omega)$, the Rayleigh scattering is dominant. Thus the optical theorem is satisfied with a total optical cross section attributable to both Rayleigh scattering and absorption, a result that is quite general when one considers scattering from an excited state.

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APPENDIX: SCHRÖDINGER PICTURE

Since we are working to first order in the applied field, it is practical to use the Schrödinger picture to obtain an expression for the polarizability. This will allow us to get the frequency dependence of the decay parameters in a rather simple manner. To illustrate the method, we carry out the calculation in rotating wave approximation (RWA) and neglect any level shifts. Both amplitude and density matrix approaches may be used. They lead to slightly different results that are, nevertheless, consistent within the limits of the approximations. The results also agree with those of Sec. III, in the appropriate limits.

To proceed, we adopt a slightly different form for the Hamiltonian of our three-level system. Taking a classical, linearly polarized monochromatic field $\mathbf{E}(t)=E_0\hat{\mathbf{d}}_{23}\cos(\omega t)$ to drive the 2–3 transition and setting the energy of level 2 equal to zero, we write the RWA Hamiltonian as

$$\hat{H} = -\hbar\omega_{21}|1\rangle\langle 1| + \hbar\omega_{32}|3\rangle\langle 3| + \int d\mathbf{k}\hbar\omega_k\hat{a}_{\mathbf{k}}^\dagger\hat{a}_{\mathbf{k}} + i\hbar\int d\mathbf{k}[g_{\mathbf{k}}(|3\rangle\langle 2|\hat{a}_{\mathbf{k}} - |2\rangle\langle 3|\hat{a}_{\mathbf{k}}^\dagger) + j_{\mathbf{k}}(|2\rangle\langle 1|\hat{a}_{\mathbf{k}} - |1\rangle \times\langle 2|\hat{a}_{\mathbf{k}}^\dagger)] - \frac{d_{23}E_0}{2}(e^{i\omega t}|2\rangle\langle 3| + |3\rangle\langle 2|e^{-i\omega t}), \tag{A1}$$

where $g_{\mathbf{k}}$ and $j_{\mathbf{k}}$ are given in Eq. (31).

The state vector of the system is written in an interaction representation as

$$|\psi(t)\rangle = b_{20}(t)|20\rangle + b_{30}(t)e^{-i\omega t}|30\rangle + \int d\mathbf{k}[b_{2\mathbf{k}}(t)e^{-i\omega t}|2,1_{\mathbf{k}}\rangle + b_{1\mathbf{k}}|1,1_{\mathbf{k}}\rangle], \tag{A2}$$

which are the only states needed to first order in the external field. The first label in each state amplitude refers to the atomic state and the second to the state of the field. We can express the complex polarizability as

$$\alpha = \frac{d_{23}^2\rho_{32}^+}{\hbar\chi\rho_{22}}, \tag{A3}$$

where $\rho_{32}^+=\rho_{30,20}e^{i\omega t}$ is a density matrix element in an interaction representation and $\chi=d_{23}E_0/2\hbar$. We must divide ρ_{32}^+ by the steady-state population of level 2 to get a meaningful expression for the polarizability.

1. Amplitude approach

Since we use an amplitude approach and want a steady-state result, we use the trick of starting with the atom in state 2 at $t=t_0$, and eventually form density matrix elements which will depend on both t and t_0. At that point, we assume a (constant) pumping rate $\Lambda(t_0)=\Lambda$ and integrate the results from $-\infty$ to t. The equations for the amplitudes follow im-

mediately from Schrödinger's using the Hamiltonian (A1) as

$$\dot{b}_3 = -i(\omega_{32}-\omega)b_3 + i\chi b_2 + \int d\mathbf{k} g_{\mathbf{k}} b_{2\mathbf{k}}, \tag{A4a}$$

$$\dot{b}_2 = \int d\mathbf{k} j_{\mathbf{k}} b_{1\mathbf{k}}, \tag{A4b}$$

$$\dot{b}_{1\mathbf{k}} = -i(\omega_k-\omega_{21})b_{1\mathbf{k}'} - j_{\mathbf{k}} b_2, \tag{A4c}$$

$$\dot{b}_{2\mathbf{k}} = -i(\omega_k-\omega)b_{2\mathbf{k}} - g_{\mathbf{k}} b_3, \tag{A4d}$$

where $\omega_k = kc$ and we have suppressed the "0"in labeling amplitudes $b_{3,0}$ and $b_{2,0}$. By solving Eqs. (A4c) and (A4d) for $b_{1\mathbf{k}}$ and $b_{2\mathbf{k}}$ and substituting the solutions into Eqs. (A4a) and (A4b) using

$$\int d\mathbf{k} g_{\mathbf{k}}^2 e^{-i(\omega_k-\omega)(t-t')} = \Gamma_{23}(-\omega),$$

$$\int d\mathbf{k} j_{\mathbf{k}}^2 e^{-i(\omega_k-\omega)(t-t')} = \Gamma_{12}(-\omega) \tag{A5}$$

[consistent with Eqs. (69) and (72), neglecting radiative shifts], one finds

$$\dot{b}_3 = -i(\omega_{32}-\omega)b_{3,0} + i\chi b_2 - \gamma_3 b_3, \tag{A6a}$$

$$\dot{b}_2 = -\gamma_2 b_2, \tag{A6b}$$

where

$$\gamma_3 = \Gamma_{23}(-\omega); \qquad \gamma_2 = \Gamma_{12}(-\omega_{21}). \tag{A7}$$

The solutions then follow immediately

$$b_2(t,t_0) = e^{-\gamma_2(t-t_0)}, \tag{A8a}$$

$$b_3(t,t_0) = i\chi\int_{t_0}^{t} b_2(t')e^{-[\gamma_3+i(\omega_{32}-\omega)](t-t')}dt'$$
$$= \frac{i\chi}{\gamma_3-\gamma_2+i(\omega_{32}-\omega)}\left[e^{-\gamma_2(t-t_0)} - e^{-[\gamma_3+i(\omega_{32}-\omega)](t-t_0)}\right] \tag{A8b}$$

and the steady-state density matrix elements

$$\rho_{22} = \int_{-\infty}^{t} dt_0 \Lambda b_2(t,t_0) b_2^*(t,t_0) = \frac{\Lambda}{2\gamma_2}; \tag{A9}$$

$$\rho_{32}^+ = \int_{-\infty}^{t} dt_0 \Lambda b_3(t,t_0) b_2^*(t,t_0) = \frac{i\chi\Lambda}{\gamma_3-\gamma_2+i(\omega_{32}-\omega)}\left[\frac{1}{2\gamma_2} - \frac{1}{\gamma_3+\gamma_2+i(\omega_{32}-\omega)}\right] = \left(\frac{\Lambda}{2\gamma_2}\right)\frac{i\chi}{\gamma_3+\gamma_2+i(\omega_{32}-\omega)}. \tag{A10}$$

The result is as expected; Γ_{23} is evaluated at $-\omega$ and Γ_{12} at $-\omega_{21}$. The polarizability (A3) is

$$\alpha = \frac{d_{23}^2\rho_{32}^+}{\hbar\chi\rho_{22}} = \frac{d_{23}^2}{\hbar[(\omega_{32}-\omega)-i(\gamma_3+\gamma_2)]} \tag{A11}$$

and agrees with Eq. (81) in RWA with the neglect of level shifts.

2. Density matrix approach

The appropriate density matrix equations are

$$\dot{\rho}_{32}^+ = i\chi\rho_{22} - i(\omega_{32}-\omega)\rho_{32}^+ + \int d\mathbf{k} j_{\mathbf{k}}\rho_{3,1\mathbf{k}}^+ + \int d\mathbf{k} g_{\mathbf{k}}\rho_{2\mathbf{k},2}^+, \tag{A12a}$$

$$\dot{\rho}_{3,1\mathbf{k}}^+ \approx [-\epsilon + i(\omega_k+\omega-\omega_{31})]\rho_{3,1\mathbf{k}}^+ - j_{\mathbf{k}}\rho_{32}^+ + i\chi\rho_{2,1\mathbf{k}}^+, \tag{A12b}$$

$$\dot{\rho}_{2,1\mathbf{k}} \approx [i(\omega_k-\omega_{21}) - \epsilon']\rho_{2,1\mathbf{k}} - j_{\mathbf{k}}\rho_{22}, \tag{A12c}$$

$$\dot{\rho}_{2\mathbf{k},2}^+ \approx [-i(\omega_k-\omega) - \epsilon'']\rho_{2\mathbf{k},2}^+ - g_{\mathbf{k}}\rho_{32}^+, \tag{A12d}$$

$$\dot{\rho}_{22} = \Lambda + \int d\mathbf{k} j_{\mathbf{k}}(\rho_{1\mathbf{k},2} + \rho_{2,1\mathbf{k}}), \tag{A12e}$$

where

$$\rho_{32} = \rho_{32}^+ e^{-i\omega t}, \tag{A13a}$$

$$\rho_{3,1\mathbf{k}} = \rho_{3,1\mathbf{k}}^+ e^{-i\omega t}, \tag{A13b}$$

$$\rho_{2\mathbf{k},2} = \rho_{2\mathbf{k},2}^+ e^{-i\omega t}, \tag{A13c}$$

and decay rates ϵ, ϵ', and ϵ'' have been inserted into Eqs. (A12b)–(A12d) to account for the fact that $\rho_{3,1\mathbf{k}}^+$, $\rho_{2,1\mathbf{k}}$, and $\rho_{2\mathbf{k},2}^+$ decay to states involving additional photons in the field not contained in the basis states (A2). The steady state solution of Eq. (A12c), $\rho_{2,1\mathbf{k}} = j_{\mathbf{k}}\rho_{22}/[i(\omega_k-\omega_{21})-\epsilon]$, and its complex conjugate can be substituted into Eq. (A12e), and Eq. (72) used to obtain the steady-state solution $\rho_{22} = \Lambda/(2\gamma_2)$, in agreement with Eq. (A9).

To obtain ρ_{32}^+, one solves Eqs. (A12b) and (A12d) in steady state and substitutes the results in Eq. (A12a) to obtain the steady state equation

$$0 = i\chi\rho_{22} - i(\omega_{32}-\omega)\rho_{32}^+ + \int d\mathbf{k} j_{\mathbf{k}}\rho_{3,1\mathbf{k}}^+ + \int d\mathbf{k} g_{\mathbf{k}}\rho_{2\mathbf{k},2}^+$$
$$= i\chi\left(\frac{\Lambda}{2\gamma_2}\right) - i(\omega_{32}-\omega)\rho_{32}^+ - \int d\mathbf{k} j_{\mathbf{k}}\left[\frac{-j_{\mathbf{k}}\rho_{32}^+ + i\chi\rho_{2,1\mathbf{k}}^+}{i(\omega_k+\omega-\omega_{31})-\epsilon}\right]$$
$$- \int d\mathbf{k}\frac{g_{\mathbf{k}}^2\rho_{32}^+}{i(\omega_k-\omega)+\epsilon''} = i\chi\left(\frac{\Lambda}{2\gamma_2}\right) - i(\omega_{32}-\omega)\rho_{32}^+$$
$$- \int d\mathbf{k}\left[\frac{g_{\mathbf{k}}^2\rho_{32}^+}{i(\omega_k-\omega)+\epsilon''} + \frac{j_{\mathbf{k}}^2\rho_{32}^+}{i(\omega_k+\omega-\omega_{31})-\epsilon'}\right]$$
$$- \int d\mathbf{k}\frac{i\chi j_{\mathbf{k}}^2\left(\frac{\Lambda}{\Gamma_2}\right)}{[i(\omega_k+\omega-\omega_{31})-\epsilon][i(\omega_k-\omega_{21})-\epsilon']}. \tag{A14}$$

Using Eq. (69) and (72), one finds

$$0 = i\chi\left(\frac{\Lambda}{2\gamma_2}\right) + i(\omega_{32}-\omega)\rho_{32}^{+} - \gamma_3\rho_{32}^{+} - \gamma_2'\rho_{32}^{+} - i\chi\int d\mathbf{k} j_{\mathbf{k}}^2\left(\frac{\Lambda}{2\gamma_{22}}\right)\left[\frac{1}{i(\omega_{32}-\omega)-\epsilon'+\epsilon}\right] \times\left[\frac{1}{[i(\omega_k+\omega-\omega_{31})-\epsilon]} - \frac{1}{[i(\omega_k-\omega_{21})-\epsilon']}\right]$$
$$\approx i\chi\left(\frac{\Lambda}{2\gamma_2}\right) - i(\omega_{32}-\omega)\rho_{32}^{+} - \gamma_3\rho_{32}^{+} - \gamma_2'\rho_{32}^{+} + i\chi\left(\frac{\Lambda}{2\gamma_2}\right)\times\left[\frac{(\gamma_2'-\gamma_2)}{i(\omega_{32}-\omega)}\right] \tag{A15}$$

or

$$\rho_{32}^{+} = i\chi\left(\frac{\Lambda}{2\gamma_2}\right)\left[\frac{1}{i(\omega_{32}-\omega)+\gamma_2'+\gamma_3}\right]\left[1+\frac{\gamma_2'-\gamma_2}{i(\omega_{32}-\omega)}\right] \tag{A16}$$

where

$$\gamma_2' = \Gamma_{12}[-(\omega_{32}-\omega)-\omega_{21}]. \tag{A17}$$

For overall consistency of the result to this order, we replaced $[i(\omega_{32}-\omega)-\epsilon'+\epsilon]^{-1}$ by $[i(\omega_{32}-\omega)]^{-1}$ in the second line of Eq. (A15).

The polarizability

$$\alpha = \frac{d_{23}^2\rho_{32}^{+}}{\hbar\chi\rho_{22}} = \frac{d_{23}^2}{\hbar}\left[\frac{1}{(\omega_{32}-\omega)-i(\gamma_2'+\gamma_3)}\right]\left[1+\frac{\gamma_2'-\gamma_2}{i(\omega_{32}-\omega)}\right] \tag{A18}$$

agrees with Eq. (78) in RWA with the neglect of level shifts. If the second term in Eq. (A18) is brought into the denominator, the result agrees with Eq. (A11).

[1] G. Placzek, in *Handbuch der Radiologie*, edited by G. Marx (Akademische Verlagsgesellschaft, Leipzig, 1934), Vol. 6, p. 247.

[2] S. Hassing and E. N. Svendsen, J. Raman Spectrosc. **35**, 87 (2004).

[3] See, for instance, S.-Y. Lee and K.-S. Chow, J. Raman Spectrosc. **16**, 386 (1985).

[4] D. L. Andrews, S. Naguleswaran, and G. E. Stedman, Phys. Rev. A **57**, 4925 (1998); G. E. Stedman, S. Naguleswaran, D. L. Andrews, and L. C. Dávila Romero, *ibid.* **63**, 047801 (2001); D. L. Andrews, L. C. Dávila Romero, and G. E. Stedman, *ibid.* **67**, 055801 (2003).

[5] A. D. Buckingham and P. Fischer, Phys. Rev. A **61**, 035801 (2000); A. D. Buckingham and P. Fischer, *ibid.* **63**, 047802 (2001).

[6] P. W. Milonni and R. W. Boyd, Phys. Rev. A **69**, 023814 (2004).

[7] R. Loudon and S. M. Barnett, J. Phys. B **39**, S555 (2006).

[8] P. R. Berman, R. W. Boyd, and P. W. Milonni, Phys. Rev. A **74**, 053816 (2006).

[9] I. Bialynicki-Birula and T. Sowiński, Phys. Rev. A **76**, 062106 (2007).

[10] Other relevant literature has been mentioned in Refs. [4] and [6] and other papers cited herein. See also Ref. [5] and R. W. Boyd, J. E. Sipe, and P. W. Milonni, J. Opt. A, Pure Appl. Opt. **6**, S14 (2004) for remarks on the relevance of the damping terms to the question of the existence of a linear electro-optic effect in isotropic chiral media, and R. W. Boyd, *Nonlinear Optics*, 2nd ed. (Academic Press, San Diego, 2003), p. 158; D. A. Long, *The Raman Effect* (Wiley, New York, 2001). Here we are concerned primarily with the specific case of radiative damping.

[11] U. D. Jentschura and P. J. Mohr, Can. J. Phys. **80**, 633 (2002).

[12] L. N. Labzowsky, D. A. Solovyev, G. Plunien, and G. Soff, Phys. Rev. Lett. **87**, 143003 (2001).

[13] In general, only *one* component of the dipole matrix element can be taken as real—the phase of the other components is then determined uniquely. To simplify matters, we have taken all the components of $\mathbf{d}_{ij}$ to be real since this in no way changes the qualitative nature of the results.

[14] We have dropped the factor of (1/3) appearing in Eq. (3). For a true two level system, the polarizability must be represented as a tensor, since matrix elements of each component of **d** are not necessarily equal. The polarizabilities in this paper can be viewed as the diagonal element of the polarizability tensor in the direction of either $\mathbf{d}_{12}$ (two-level polarizabilty) or $\mathbf{d}_{23}$ (three-level polarizability). The factor of 1/3 is included in the equations for the polarizability in Refs. [6] and [9], for instance. Here we omit that factor in comparing our results with those of Ref. [9]. The factor of (1/3) affects the expression for the optical theorem. Without it, the optical theorem takes the form (12). With it, the right-hand side of Eq. (12) is multiplied by 3, as in Eq. (5) of Ref. [7].

[15] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Quantum Electrodynamics* (Pergamon Press, Oxford, 1982).

[16] S. Mukamel, Phys. Rev. A **76**, 021803(R) (2007).

[17] We quote the remark following Eq. (59.22), p. 227, of Ref. [15].

[18] L. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1955), Sec. 25.

[19] H. M. Nussenzveig, *Causality and Dispersion Relations* (Academic Press, New York, 1972).

[20] D. N. Zubarev, Sov. Phys. Usp. **3**, 320 (1960).

[21] E. R. Pike and S. Swain, J. Phys. A **4**, 555 (1971).

[22] C. Cohen–Tannoudji, J. Dupont–Roc, and G. Grynberg, *Atom–Photon Interactions* (Wiley, New York, 1992).