Nonlinear sum rules: The three-level and the anharmonic-oscillator models

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Recently derived sum rules for nonlinear optics are shown to be relevant to a number of experiments in atomic and solid-state physics. To interpret the experiments on atomic transitions and exciton transitions in solids, we analyze the three-level model and examine the modification of the optical spectrum induced on a probe light by the presence of an additional intense light beam. We show that the nonlinear sum rules explain the known experimental data and predict anomalous asymmetry in the nonlinear line shape. We also consider the cases of vibrational states of diatomic molecules and of optical modes of polar crystals and treat them with the model of the anharmonic oscillator. The nonlinear sum rules are shown to be obeyed, thus clarifying the processes of nonlinear absorption.

I. INTRODUCTION

In a recent paper, we have shown that dispersion relations and sum rules are obeyed by the nonlinear optical response of a system.[1] Among the many sum rules obtained, we consider those which involve the nonlinear optical absorption at frequency ω, in the presence of a laser beam of intensity $|\mathcal{E}_2|^2$ and frequency ω_2. In terms of the nonlinear contributions to the imaginary part of the dielectric function we have

$$\int_0^\infty \omega\epsilon_2^{\mathrm{NL}}(\omega,\omega_2,\mathcal{E}_2)d\omega=0 \ , \tag{1}$$

$$\int_0^\infty \omega^3\epsilon_2^{\mathrm{NL}}(\omega,\omega_2,\mathcal{E}_2)d\omega=\frac{\pi}{2}c(\omega_2,\mathcal{E}_2) \ , \tag{2}$$

c being an appropriate constant which has to be determined case by case.

It is to be expected that such rules can be useful in a large number of nonlinear optical processes, as the linear sum rules have been in the traditional optical studies of atoms, molecules, and solids.[2,3]

The main purpose of this paper is to correlate the sum rules to some experimental findings, such as the Autler-Townes splitting of spectral lines,[4] the population trapping observed in resonant Raman scattering in atoms,[5] and the dynamical Stark effect on exciton lines.[6] This is done by studying the optical transitions to all orders in a three-level approximation, as functions of the frequency ω of the probe beam.

We also consider the possibility of nonlinear optical effects on the vibrational states of dipolar molecules, and on the vibrational states of dipolar crystals. Multiphoton transitions have been observed in these cases,[7] but their frequency dependence has not been displayed in sufficient detail to display sum-rule-dependent effects. We show, however, by an anharmonic-oscillator model, that in this case the constraints imposed by the sum rules also influence the nonlinear line shape.

In Sec. II, we describe the optical transitions in a three-level model at a frequency near a resonance condition, and display sum-rule effects on the optical line shapes. In Sec. III, we give a classical and a quantum-mechanical treatment of the anharmonic oscillator. Also in this case, the oscillator strengths of the various nonlinear effects combine to verify the sum rules and introduce asymmetries in the nonlinear line shapes. In Sec. IV, we give our conclusions.

II. NONLINEAR OPTICAL TRANSITIONS IN THE THREE-LEVEL MODEL

The three-level model provides the simplest scheme to treat nonlinear processes, particularly in near-resonance conditions. Depending on the frequency range considered, we have two situations, referred to as the ladder configuration and the lambda configuration. They are shown in Fig. 1. The energies of the levels are denoted by E_0, E_1, and E_2, for the ground state, the intermediate state, and the final state, respectively. The interaction of an electron with the two radiation fields of frequency ω_1 and ω_2 is given by the dipole matrix elements between the states $|0\rangle$, $|1\rangle$, and $|2\rangle$, and are expressed in terms of the Rabi frequencies $\alpha_1=\langle 0|\mu\mathcal{E}_1|1\rangle/2\hbar$ and $\alpha_2=\langle 1|\mu\mathcal{E}_2|2\rangle/2\hbar$, $\mathcal{E}_1$ and $\mathcal{E}_2$ being the amplitudes of the two radiation fields and $\mu=ex$. The lifetimes of the two excited states are expressed by $\tau_1=1/2\gamma_1$ and $\tau_2=1/2\gamma_2$, where γ_1 and γ_2 are treated as phenomenological constants, introducing in this way the possibility of other states and of nonradiative decays.

The polarizability of the system can be computed by using the density-matrix formalism.[8] We do not repeat the calculation, which for the three-level system has first been carried out by Hänsch.[9] Considering the polarizability $P=N\mu$, where N is the number of atoms per unit volume, and taking the Fourier transform at frequency ω, at near-resonance conditions we have

$$\epsilon(\omega,\omega_2,\mathcal{E}_2)=1+\frac{4\pi N|\langle 0|\mu|1\rangle|^2/\hbar}{\omega_{10}-\omega-i\gamma_1-\dfrac{\alpha_2^2}{\omega_{20}-\omega\pm\omega_2-i\gamma_2}} \ , \tag{3}$$

where $\omega_{10}=(E_1-E_0)/\hbar$ and $\omega_{20}=(E_2-E_0)/\hbar$ are the

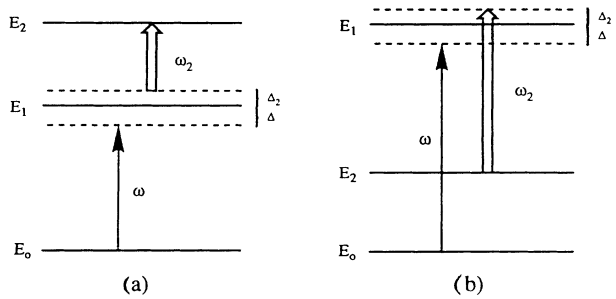

FIG. 1. Three-level system resonantly interacting with two radiation beams of frequency ω and ω_2. (a) Ladder configuration; (b) lambda configuration.

frequencies at the resonance conditions, and the + (−) sign in (3) refers to the ladder (lambda) configuration.

We wish to point out, in agreement with Bigot and Hönerlage,[10] that expression (3) is appropriate only for positive values of ω and cannot be extended for mathematical purposes to negative ω values, because this would violate the necessary condition $\epsilon(-\omega,\omega_2,\mathcal{E}_2)=\epsilon^*(\omega,\omega_2,\mathcal{E}_2)$. This is due to the fact that expression (3) is valid only near the resonance condition. To extend it far from resonance, we must add an antiresonant contribution, which is required to satisfy the above condition. Formula (3) is then modified into

$$\epsilon(\omega,\omega_2,\mathcal{E}_2)=1+\frac{4\pi N|\langle 0|\mu|1\rangle|^2/\hbar}{\omega_{10}-\omega-i\gamma_1-\dfrac{\alpha_2^2}{\omega_{20}\pm\omega_2-\omega-i\gamma_2}}+\frac{4\pi N|\langle 0|\mu|1\rangle|^2/\hbar}{\omega_{10}+\omega+i\gamma_1-\dfrac{\alpha_2^2}{\omega_{20}\pm\omega_2+\omega+i\gamma_2}}\ . \quad (4)$$

The importance of the nonlinear effects can be inferred from the dependence of (4) or (3) on the intensity α_2^2 and on the detunings $\Delta=\omega-\omega_{10}$ and $\Delta_2=\pm\omega_2-\omega_{20}$. When $\Delta_2=0$ and $\alpha_2\gg\gamma_1,\gamma_2$, we obtain the Autler-Townes doubling of the absorption line.[4] In the case of the lambda configuration, when $\gamma_2\ll\alpha_2\ll\gamma_1$, and $\alpha_2^2\gg\gamma_1\gamma_2$, we obtain population trapping.[5] The two effects are illustrated in Figs. 2 and 3, respectively, for different values of the external beam intensity.

When the additional beam is relatively far from resonance ($|\Delta_2|\gg\gamma_1,\gamma_2,\alpha_2$), by varying the frequency of the probe beam we can separately observe two-photon absorption and resonant Raman absorption at $\Delta+\Delta_2\simeq 0$, and a shift and lowering of the $0\rightarrow 1$ transition with respect to the linear result. This is clearly shown in Fig. 4.

Separating in (4) the linear and the nonlinear contributions, we can prove immediately that the sum rule (1) is satisfied. The nonlinear part $\epsilon^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)$ of (4), in fact, has poles only on the lower half of the complex plane, and goes to zero at infinity as $|\omega|^{-4}$. Then the integral of its product by ω vanishes because of Cauchy theorem. Since $\epsilon_2^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)$ is odd under the $\omega\rightarrow-\omega$ transformation, we immediately obtain that the sum rule (1) is verified.

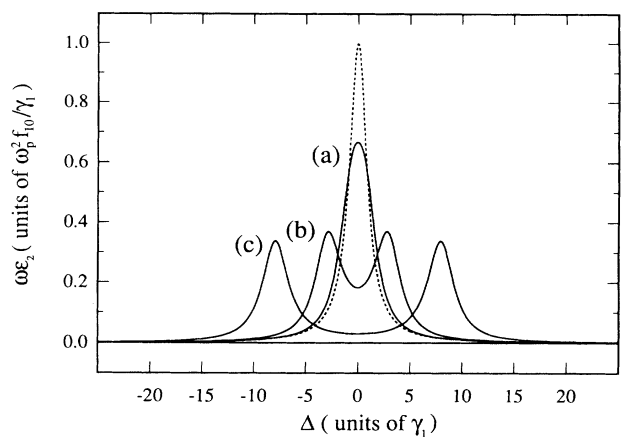

FIG. 2. (*Three-level system*). Absorption coefficient of a probe beam of frequency $\omega=\Delta+(E_1-E_0)/\hbar$ for three different values of the intensity of an external beam tuned at the exact resonance with the $1\rightarrow 2$ transition ($\Delta_2=0$). (a) $\alpha_2=1$; (b) $\alpha_2=3$; (c) $\alpha_2=8$; the dotted line refers to the linear absorption ($\alpha_2=0$). For the three cases, $\gamma_2=2$. All quantities are expressed in units of γ_1.

In a recent paper on the three-level model, Saikan *et al.*[11] stated that the integral of $\epsilon_2^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)$ vanishes, which is at variance with our sum rules. This in fact occurs only by extending Eq. (3) to negative frequencies, which is not correct because it neglects the contributions of the antiresonances, which are instead included in expression (4). Of course, the discrepancy between their result and our correct sum rule (1) is difficult to verify with experiments carried out only at near resonance, but it should be evident as a more extended frequency range is explored, or when the frequency ω_2 is far from resonance.

Effects due to our sum rule (1) can be observed in all the line shapes of Figs. 2, 3, and 4. In the case of the Autler-Townes splitting, the two lines obtained have an

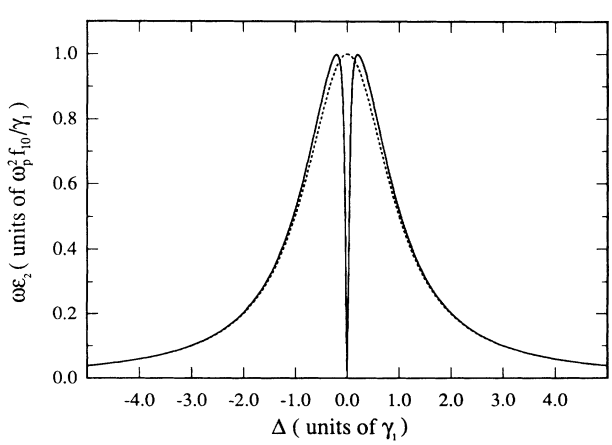

FIG. 3. (*Three-level system*). Absorption coefficient of a probe beam of frequency $\omega=\Delta+(E_1-E_0)/\hbar$ under the conditions of population trapping ($\alpha_2=0.2$, $\gamma_2=10^{-3}$). The dotted line refers to the linear absorption ($\alpha_2=0$). All quantities are expressed in units of γ_1.

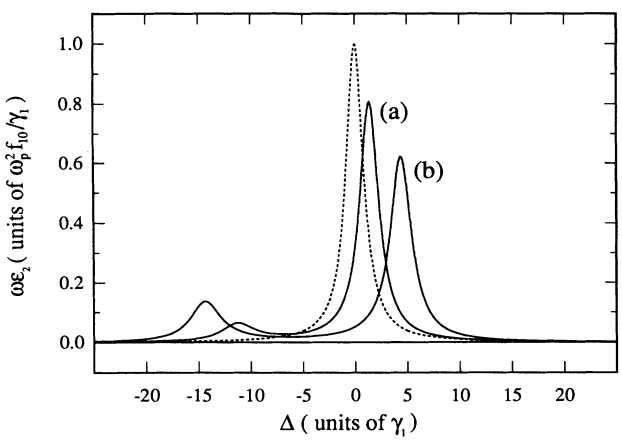

FIG. 4. (*Three-level system*). Absorption coefficient of a probe beam of frequency $\omega=\Delta+(E_1-E_0)/\hbar$ for three different values of the intensity of an external beam tuned slightly away from the resonance at the $1\rightarrow 2$ transition ($\Delta_2=10$). (a) $\alpha_2=3$; (b) $\alpha_2=8$; the dotted line refers to the linear absorption ($\alpha_2=0$). For the two cases, $\gamma_2=2$. All quantities are expressed in units of γ_1.

oscillator strength which is one-half that of the linear transition. In the case of population trapping (Fig. 3), the dip at the center of the line implies a lateral increase of the absorption. In the case of Fig. 4 (nonresonant external beam), an asymmetry occurs in the nonlinear line shape due to the fact that the two-photon absorption must be compensated by a prevailing negative contribution about $\Delta=0$. This is accomplished by a shift (dynamical Stark effect) and a lowering of the resonance.

To compute the constant $c(\omega_2,\mathcal{E}_2)$ in the sum rule (2), we cannot proceed in the simple way discussed above, because the Cauchy theorem cannot be applied since $\omega^3\epsilon^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)$ decreases at ∞ as $1/|\omega|$ only. We then proceed as indicated in Ref. 1, and compare the asymptotic behavior obtained from the dispersion relations and the superconvergence theorem

$$\omega^2\epsilon_1^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)=-\frac{2}{\pi\omega^2}\int_0^\infty d\omega'\omega'^3\epsilon_2^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)+o(\omega^{-2}) \tag{5}$$

with the asymptotic behavior

$$\omega^2\epsilon_1^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)=-\frac{4\pi N|\langle 0|\mu|1\rangle|^2}{\hbar}\times\alpha_2^2\frac{2\omega_{10}+\omega_{20}\mp\omega_2}{\omega^2}+o(\omega^{-2}) \tag{6}$$

obtained from Eq. (4). The comparison between (5) and (6) gives the typical nonlinear sum rule with the explicit value for the c constant

$$\int_0^\infty\omega^3\epsilon_2(\omega,\omega_2,\mathcal{E}_2)d\omega=\frac{2\pi^2N|\langle 0|\mu|1\rangle|^2}{\hbar}\times\alpha_2^2(2\omega_{10}+\omega_{20}\mp\omega_2)=\frac{\pi}{2}c\ . \tag{7}$$

We may observe that the c constant on the right-hand side of Eq. (7), when ω_2 is near the resonance between states E_1 and E_2, can be written very simply in terms of the plasma frequency ω_p, of the oscillator strength f_{10}, and of the Rabi frequency α_2, as

$$c\simeq\tfrac{3}{2}\omega_p^2f_{10}\alpha_2^2\ . \tag{8}$$

The sum rule (7) is the nonlinear counterpart of the Thomas-Reiche-Kuhn sum rule, because it can be taken as a measure of the importance of nonlinear processes. It would be of great interest to verify the sum rule (8) in real experiments. The most interesting experiments in this respect are those of Fröhlich, Nöthe, and Reimann on the dynamic Stark effect on the Cu_2O exciton[12] and on semiconductor quantum-well excitons.[13] The experimental points are given only near the resonance where the three-level model seems to be obeyed,[6] and the sum rules experimentally verified. Of course, far from resonance the model itself breaks down. Other experiments with a probe and pump light in quantum wells imply a population readjustment, and their interpretation requires the consideration of higher-energy states.[14]

III. ANHARMONIC OSCILLATOR

The model of the Lorentz-Drude oscillator has been of great help in the interpretation of the linear optical spectra of polar molecules and polar crystals, its quantum-mechanical counterpart giving analogous results.

To introduce nonlinear optical properties, we must improve the model by introducing anharmonic terms in the Hamiltonian, as done by many authors.[8] The Hamiltonian can be written as

$$H=\frac{p^2}{2m}+\tfrac{1}{2}m\omega_0^2x^2+ax^3+bx^4\ , \tag{9}$$

where the constants a and b are different for each specific case. The solution for a density N of particles of charge e, with a damping coefficient γ, gives a susceptibility which can be computed to all orders. The linear term gives the usual expression

$$\epsilon(\omega)=1+\frac{4\pi Ne^2}{mD(\omega)}\ , \tag{10}$$

with

$$D(\omega)=\omega_0^2-\omega^2-i\gamma\omega\ . \tag{11}$$

In the nonlinear case, we obtain for the contribution coming from the third-order susceptibility[15]

$$\epsilon^{\rm NL}(\omega,\omega_2,\mathcal{E}_2)=\frac{4\pi Ne^4\mathcal{E}_2^2}{m^4D^2(\omega)|D(\omega_2)|^2}\times\left[\frac{3}{2}\frac{a^2}{m}\left[\frac{1}{\omega_0^2}+\frac{1}{D(\omega+\omega_2)}+\frac{1}{D(\omega-\omega_2)}\right]-6b\right]\ . \tag{12}$$

We observe that, besides the resonance at $\omega=\omega_0$, which

is a correction to the linear resonance, we have additional resonances at $\omega+\omega_2=\omega_0$ (two-photon absorption) and at $|\omega-\omega_2|=\omega_0$ (Raman processes). For illustrative purposes, we report in Fig. 5 the total susceptibility and its nonlinear contribution, showing the asymmetry of the nonlinear line shape required by the sum rule.

We can easily verify that our sum rules (1) and (2) are obeyed. For the sum rule (1), for instance, the two additional resonances are compensated for by a decrease of the absorption with respect to the linear term, as shown in Fig. 5. The exact compensation can be proved directly by integration of the function $\omega\epsilon^{\mathrm{NL}}$ on the real axis of the complex plane, and application of the Cauchy theorem, considering that the function is holomorphic in the upper half-plane, its asymptotic behavior is $|\omega|^{-3}$, and it satisfies the condition $\epsilon^{\mathrm{NL}}(-\omega,\omega_2,\mathcal{E}_2)=\epsilon^{\mathrm{NL}}(\omega,\omega_2,\mathcal{E}_2)^*$. The constant c of the sum rule (2) can be computed with the same procedure shown at the end of Sec. II, to obtain

$$c(\omega_2,\mathcal{E}_2)=\frac{4\pi Ne^4}{m^4}\left[6b-\frac{3}{2}\frac{a^2}{m\omega_0^2}\right]\mathcal{E}_2^2\frac{1}{(\omega_0^2-\omega_2^2)^2+\gamma^2\omega_2^2}\ . \tag{13}$$

We wish to observe that the sum rule (1) had already been demonstrated for the case of the anharmonic oscillator by Peiponen.[16] We have introduced here an additional sum rule (2), which may be more susceptible to experimental verification.

While the harmonic-oscillator model does not display any difference between the classical and the quantum treatment because of the optical selection rule $\Delta n=\pm 1$, the quantum treatment of the anharmonic oscillator introduces some additional effects, which are simply displayed by perturbation theory.

First of all, we may notice that a number of additional transitions with $\Delta n\neq 1$ become allowed in first order. In nonlinear optics, besides the three resonances discussed in the classical model and displayed in Fig. 5, nonlinear transitions to a large number of states become possible, because the energies and dipole matrix elements of the anharmonic oscillator are modified with respect to the harmonic case.

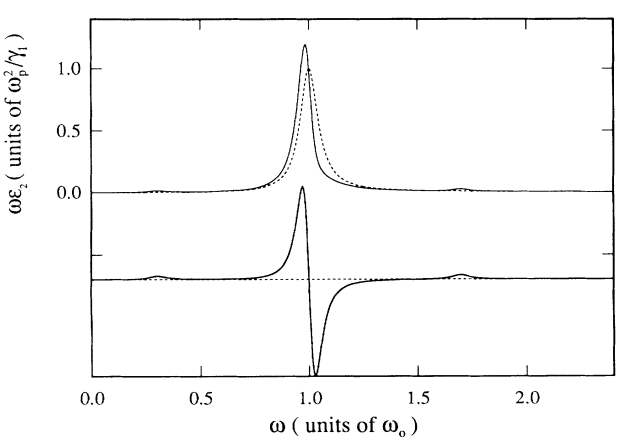

FIG. 5. (*Classical anharmonic oscillator*). Absorption coefficient of a probe beam of frequency ω in the presence of an external beam of frequency $\omega_2=0.7\omega_0$. The damping constant is $\gamma=0.1\omega_0$. The dotted line refers to the linear absorption, and the difference between the two is plotted below.

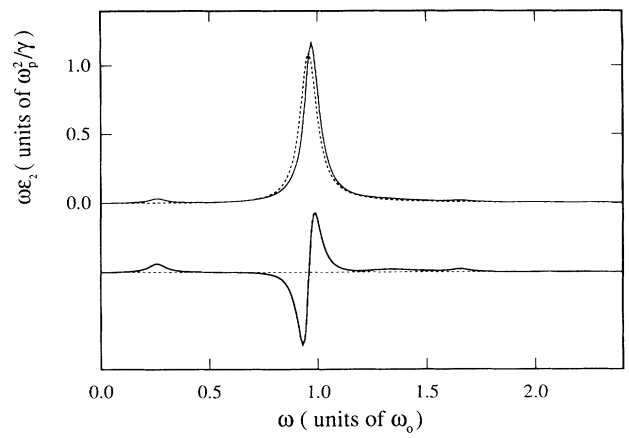

FIG. 6. (*Quantum anharmonic oscillator*). Absorption coefficient of a probe beam of frequency ω in the presence of an external beam of frequency $\omega_2=0.7\omega_0$. The damping constants are taken to be the radiative widths. The dotted line refers to the linear absorption, and the difference between the two is plotted below.

We have calculated the energies and dipole elements up to the second order of perturbation theory, using the same parameters adopted for the classical model, and we have then computed the third-order dielectric susceptibility, making use of Eq. (236) of Ref. 15. We report in Fig. 6 the absorption coefficient (first- plus third-order contributions). Comparison with Fig. 5 shows the nonlinear resonances introduced by quantum theory; for instance, the resonance at $\omega=2\omega_0-\omega_2$, due to the two-photon absorption from the ground state to the $n=2$ level. It also clearly appears that the dynamical Stark shift has a different sign in the two models.

The asymmetry of the nonlinear absorption line shape implied by the sum rules is more pronounced in the quantum-mechanical treatment, because of the larger two-photon contribution.

IV. CONCLUSIONS

We have investigated the role of the sum rules of nonlinear optics in specific experiments by using two soluble models: the three-level optical model with finite lifetimes, and the anharmonic oscillator with damping.

In the three-level optical model, it is found that the nonlinear sum rules are obeyed, provided the correct behavior is adopted for the optical function with consideration of the antiresonance. Specific effects are obtained on the nonlinear line shapes, in particular an asymmetry around the first-order resonance.

In the anharmonic-oscillator model, the optical sum rules are verified both in the classical and in the quantum-mechanical treatment. Additional transitions appear, however, in the latter treatment, and the asymmetric modifications of the linear resonance absorption are more evident.

ACKNOWLEDGMENTS

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