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Nonimpact theory of absorption line broadening in strong radiation fields

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We develop an expansion for the absorption line shape of a two-level system in a strong radiation field being perturbed by dephasing collisions with a thermal bath of foreign atoms. We assume that the bath atoms do not interact with the radiation field and with each other. The microscopic information relevant for line broadening in a strong field is expressed in terms of a hierarchy of dipole correlation functions. The latter may be calculated with the use of the Franck-Condon factors for the nuclear wave functions. The present theory reduces in the weak-field limit to the well-known linear unified theory of line broadening and in the impact limit we recover the Karplus-Schwinger formula.

I. INTRODUCTION

The problem of pressure broadening of spectral lines in weak electromagnetic fields has a long history and was attacked by a variety of theoretical techniques.[1-13] The theory is relatively simple in the two limits of very fast or very slow collisions (relative to the inverse line broadening). In the former case (the impact, Markovian limit), the observed line shape $S(\Delta)$ of a two-level system interacting with the radiation field and with a bath of perturbers assumes a Lorentzian form

$$S(\Delta)=\frac{2\mu^2\Gamma}{\Delta^2+\Gamma^2} . \tag{1}$$

Here μ is the Rabi frequency which measures the strength of the interaction with the electromagnetic field, $\Delta=\omega_L-\omega_{ba}$ is the detuning of the incident frequency ω_L from the two-level separation ω_{ba}, and Γ is the linewidth given by

$$\Gamma=\tfrac{1}{2}(\gamma_a+\gamma_b)+\hat{\Gamma}\equiv\tfrac{1}{2}\gamma+\hat{\Gamma} . \tag{2}$$

$\tau_a\equiv\gamma_a^{-1}$ and $\tau_b\equiv\gamma_b^{-1}$ are the total lifetimes of the two levels a and b, respectively, and $\hat{\Gamma}$ is the proper dephasing rate which is linear in the pressure at low pressures. The calculation of $\hat{\Gamma}$ is the basic goal of the theories of line broadening in the impact limit. In the reverse (quasistatic, statistical limit) collisions are assumed to be slow and the line is inhomogeneously broadened so that the line-shape problem reduces to the evaluation of certain static averages over molecular interactions. By now there exists a unified theory, hereafter denoted LUT (linear unified theory), which interpolates between the two limits.

The problem of line broadening in the presence of strong radiation fields is usually treated in the impact limit, resulting in the famous expression of Karplus and Schwinger[14,15]:

$$S(\Delta)=\frac{2\mu^2\Gamma}{\Delta^2+\Gamma^2+(4\Gamma/\gamma)\mu^2} . \tag{3}$$

Equation (3) differs from Eq. (1) by the saturation factor $(4\Gamma/\gamma)\mu^2$ appearing in the denominator. Lisitsa and Yakovlenko[16] have attempted to generalize phenomenologically the Karplus-Schwinger expression Eq. (3) by replacing Γ by $\Gamma(\Delta,\mu)$ so that it includes some nonimpact contributions. However, at the moment a nonlinear unified theory (NUT) which holds for strong fields and reduces to the LUT in the weak-field limit is not available.

In this paper we utilize the tetradic scattering formalism to develop a microscopic nonlinear unified theory (NUT) which reduces in the weak-field limit to the LUT and in the impact limit to the Karplus-Schwinger formula. The present work is an extension and application of techniques that were recently developed, for multiphoton processes in general.[17,18]

In Sec. II we construct the model Hamiltonian corresponding to a two-level system interacting with foreign perturbers and with a strong radiation field. In Sec. III we present the expressions for the absorption line shape and in Sec. IV we discuss our results and present some numerical calculations.

II. MODEL HAMILTONIAN

We consider a two-level system $|a\rangle$ and $|b\rangle$ which are coupled by a strong monochromatic radiation field with frequency ω_L. Our two-level system is also interacting with a thermal bath containing many degrees of freedom. The bath is assumed to have only diagonal interactions with the system, i.e., it cannot induce relaxation of population (T_1). The total Hamiltonian for the system bath + the radiation field within the rotating wave approximation [RWA (Ref. 12)] has the form

$$H=H_0+V\ , \tag{4}$$

where

$$H_0=|a\rangle[\Delta+H_a(Q_B)]\langle a| + |b\rangle H_b(Q_B)\langle b|\ , \tag{4a}$$

and

$$V=\mu(|a\rangle\langle b|+|b\rangle\langle a|)\ . \tag{4b}$$

Here $|a\rangle$ and $|b\rangle$ denote the two-level system, $H_a(Q_B)$ and $H_b(Q_B)$ are the Hamiltonians for the bath degrees of freedom (Q_B), and μ is the Rabi frequency (transition dipole times the radiation field amplitude) denoting the coupling of the system to the radiation field. Within the rotating wave approximation, V is time independent and Δ includes the radiation field frequency, i.e.,

$$\Delta=E_a-E_b+\omega_L\ , \tag{5}$$

where E_a and E_b are the energies of the "bare" two-level system (without the field). In addition to the above Hamiltonian we assume the existence of an independent T_1 relaxation mechanism (for example, radiative in nature or due to coupling with another bath with a short correlation time). This mechanism assures the relaxation of our two-level system (in the absence of the field) to thermal equilibrium. The inclusion of a T_1 relaxation is necessary in order to define a line shape in a strong field. In the absence of a T_1 relaxation mechanism the populations of the two levels will be equalized at steady state and there will be no absorption of radiation. The time evolution of the entire (system + bath) density matrix ρ is thus given by the Liouville equation

$$\frac{d\rho}{dt}=-iL\rho\ , \tag{6}$$

where L is the Liouville operator

$$L\equiv[H,\ ]+\tilde{L}\ . \tag{7}$$

$\tilde{L}$ is the T_1 relaxation matrix given by[20]

$$\tilde{L}_{aa,aa}=-\tilde{L}_{bb,aa}=-i\gamma_a\ , \tag{8a}$$

$$\tilde{L}_{bb,bb}=-\tilde{L}_{aa,bb}=-i\gamma_b\ , \tag{8b}$$

$$\tilde{L}_{ab,ab}=\tilde{L}_{ba,ba}=-\frac{i}{2}\gamma\ , \tag{8c}$$

where

$$\gamma=\gamma_a+\gamma_b\ . \tag{8d}$$

$\tilde{L}$ is responsible for the relaxation of our two-level system (in the absence of driving, $\mu=0$) to thermal equilibrium, i.e.,

$$\rho_{bb}^0=\gamma_a/\gamma\equiv\eta\ , \tag{9a}$$

$$\rho_{aa}^0=\gamma_b/\gamma\equiv1-\eta\ . \tag{9b}$$

The line-shape problem defined by the Hamiltonian (4)–(8) in a strong field was solved recently[19] for a general type of H_0 of the form (4a). The solution was perturbative in $\lambda U\equiv H_b-H_a$ which is the operator responsible for the line broadening (when $\lambda U=0$ the bath does not induce any line broadening). In this paper we shall consider a specific form for H_a and H_b which is relevant for collisional line broadening. This form is simple enough and allows to solve the line-shape problem nonperturbatively in λ. In the present model we take the system atom to be stationary in a macroscopic spherical box of volume Ω containing N foreign perturber atoms (the bath). We further assume that the bath atoms do not interact with the radiation field or with each other but merely exhibit diagonal interactions with the system atom. This assumption may be relaxed by adopting a general cluster expansion for the line shape as was shown recently for the LUT.[12] The present theory provides the exact solution for the line shape when the bath atoms do not interact with each other. The solution is correct to first order in bath density (N/Ω) for the more general model where these interactions are included.[12] We thus have

$$H_i(Q_B)=\sum_v \bar{H}_i(Q_{Bv}),\quad i=a,b,c \tag{10}$$

where

$$\bar{H}_i(Q_{Bv})=\frac{-1}{2M_v}\frac{\partial^2}{\partial Q_{Bv}^2}+V_i(Q_{Bv}),\quad i=a,b\ . \tag{11}$$

Here $V_i(Q_{Bv})$ are the adiabatic potentials of interaction of the vth perturber with the system in the ith state. We have also ignored any nonadiabatic coupling with the bath (i.e., the bath cannot change the population of the two levels). The eigenstates of H_a and H_b will be denoted $|a\alpha\rangle$ and $|b\beta\rangle$ with eigenvalues E_α and E_β, respectively. Since H_i are separable in Q_{Bv}, the eigenstates are products of single-particle states

$$|a\alpha\rangle=|a\rangle\prod_v|\alpha_v\rangle\ , \tag{12a}$$

$$|b\beta\rangle=|b\rangle\prod_v|\beta_v\rangle\ , \tag{12b}$$

and

$$E_\alpha=\sum_v E_{\alpha_v}\ , \tag{13a}$$

$$E_\beta=\sum_v E_{\beta_v}\ . \tag{13b}$$

We further adopt a box normalization for our eigenstates so that

$$\langle\alpha_v|\alpha'_v\rangle=\delta_{\alpha\alpha'}\ , \tag{14a}$$

$$\langle\beta_v|\beta'_v\rangle=\delta_{\beta\beta'}\ . \tag{14b}$$

III. ABSORPTION LINE SHAPE IN A STRONG RADIATION FIELD

Making use of the tetradic scattering formalism[6,9,21–23] the absorption line shape for the system described by the Hamiltonian (4) is given by[19] (see Appendix A)

$$I(\Delta)=(\rho^0_{aa}-\rho^0_{bb})S(\Delta)=(1-2\eta)S(\Delta)\ , \tag{15}$$

where

$$S(\Delta)=\frac{\chi(\Delta)}{1+(2/\gamma)\chi(\Delta)} \tag{16}$$

and where

$$\chi(\Delta)=\mu^2\chi^{(2)}(\Delta)-\mu^4\chi^4(\Delta)+\mu^6\chi^{(6)}(\Delta)+\cdots\ . \tag{17}$$

Here

$$\chi^{(2n)}(\Delta)=\int_0^\infty d\tau_1\int_0^\infty d\tau_2\cdots\int_0^\infty d\tau_{2n-1}K^{(2n)}(\tau_1,\tau_2,\ldots,\tau_{2n-1})\times\exp\left[-\frac{\gamma}{2}(\tau_1+2\tau_2+\tau_3+2\tau_4+\cdots)\right]. \tag{18}$$

Each $K^{(2n)}(\tau)$ is a $2n$th order cumulant and may be expressed as a combination of $2k$ time-correlation functions of the dipole operator, where $k=1,2,\ldots,n$. The formal expressions for $K^{(2n)}(\tau)$ which are common to multiphoton processes in general[17] are given in Appendix A. We shall give here the explicit expressions for $\chi^{(2)}$ and for $\chi^{(4)}$:

$$\chi^{(2)}(\Delta)=\int_0^\infty d\tau\exp[-i\Delta\tau-\tfrac{1}{2}\gamma\tau-g(\tau)]+\text{c.c.}\ , \tag{19}$$

where

$$g(\tau)=\frac{N}{\Omega}\sum_{\alpha\beta}P(\alpha)|\langle a\alpha|b\beta\rangle|^2\times[\exp(-i\omega_{\alpha\beta}\tau)-1]\ . \tag{20}$$

The two-time correlation function $g(\tau)$ contains the complete information necessary for the evaluation of ordinary (weak-field) line shapes within the LUT. Formally it is given by

$$g(\tau)=\frac{1}{\mu^2}\langle V_{ab}(0)V_{ba}(\tau)\rangle_s-1 \equiv\text{Tr}[\rho^0_a\exp(i\bar{H}_b\tau)\exp(-i\bar{H}_a\tau)]\ , \tag{21}$$

where $\langle\cdots\rangle_s$ denotes a single-particle correlation function in which the trace is taken over single-perturber states, and

$$\rho^0_a=\frac{\exp(-\bar{H}_a/kT)}{\text{Tr}\exp(-\bar{H}_a/kT)}\equiv\sum_\alpha|a\alpha\rangle P(\alpha)\langle a\alpha| \tag{22}$$

is the equilibrium canonical distribution function of the bath when the system is in the $|a\rangle$ state. The evaluation of $K^{(4)}(\tau_1,\tau_2,\tau_3)$ is much more complicated than the evaluation of $K^{(2)}$. It is shown in Appendix B that it may be written as[16]

$$K^{(4)}(\tau_1,\tau_2,\tau_3)=\exp(-i\Delta\tau_1-i\Delta\tau_3)\bar{K}^{(4)}(\tau_1,\tau_2,\tau_3)+\exp(i\Delta\tau_1-i\Delta\tau_3)\bar{K}^{(4)}(-\tau_1,\tau_1+\tau_2,\tau_3)+\text{c.c.} \tag{23}$$

The complete expression for $\bar{K}^{(4)}$ is given in Appendix B. We shall give here $K^{(4)}$ only in two limiting cases where it is greatly simplified.

A. Perturbative (weak-coupling) limit

The quantity responsible for the line broadening in the present model is

$$\lambda U \equiv H_b - H_a \ , \tag{24}$$

where λ is a dimensionless parameter introduces for bookkeeping purposes and at the end of the calculation we set $\lambda=1$. $\bar{K}^{(4)}$ was recently evaluated perturbatively in λ resulting in[19]:

$$\begin{aligned}\chi^{(4)}(\Delta)=&\ 2\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\exp(-i\Delta\tau_1-i\Delta\tau_3)\\&\times\exp[-\tfrac{1}{2}\gamma(\tau_1+2\tau_2+\tau_3)]f(\tau_1)f(\tau_3)[F(\tau_1,\tau_2,\tau_3)-1]\\&+2\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\exp(i\Delta\tau_1-i\Delta\tau_3)\exp[-\tfrac{1}{2}\gamma(\tau_1+2\tau_2+\tau_3)]\\&\times f(-\tau_1)f(\tau_3)[F(-\tau_1,\tau_1+\tau_2,\tau_3)-1]+\text{c.c.}\ ,\end{aligned} \tag{25}$$

where

$$f(\tau)=\exp[-\lambda^2\bar{g}(\tau)]\ , \tag{26a}$$

$$F(\tau_1,\tau_2,\tau_3)=\exp\{\lambda^2[-\bar{g}(\tau_2)+\bar{g}(\tau_2+\tau_3)+\bar{g}(\tau_1+\tau_2)-\bar{g}(\tau_1+\tau_2+\tau_3)]+O(\lambda^3)\}\ , \tag{26b}$$

where

$$\bar{g}(\tau)=\frac{N}{\Omega}\int_0^\infty d\tau_1(\tau-\tau_1)\langle U(0)U(\tau_1)\rangle_s \tag{27a}$$

and

$$\langle U(0)U(\tau_1)\rangle_s=\Omega\sum_{\substack{\alpha\alpha'\\(\alpha\neq\alpha')}}P(\alpha)\,|\langle a\alpha\,|\,U\,|\,a\alpha'\rangle|^2\exp(-i\omega_{\alpha\alpha'}\tau_1)\ . \tag{27b}$$

The function $\bar{g}(\tau)$ may be obtained by expanding $g(\tau)$, Eq. (20), to second oreder in λ.[16]

B. Static (classical) limit

In this limit we ignore the kinetic energy terms of H_a and H_b appearing in the general expression for $\bar{K}^{(4)}$ [Eq. (B2)]. In this case $\bar{K}^{(4)}$ simplifies considerably and assumes the form

$$\bar{K}^{(4)}(\tau_1,\tau_2,\tau_3)=2\{\langle\exp[iU(\tau_1+\tau_3)]\rangle-\langle\exp(iU\tau_1)\rangle\langle\exp(iU\tau_3)\rangle\}\ , \tag{28}$$

where

$$\langle\exp(iU\tau)\rangle\equiv\int dQ\exp[iU(Q)\tau]\exp[-V_a(Q)/kT]\Big/\int dQ\exp[-V_a(Q)/kT]\ . \tag{29}$$

Using Eqs. (18), (23), and (28) we get

$$\begin{aligned}\chi^{(4)}=&\ 2\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\exp[-\tfrac{1}{2}\gamma(\tau_1+2\tau_2+\tau_3)]\exp[-i\Delta(\tau_1+\tau_3)]\\&\times\{\langle\exp[iU(\tau_1+\tau_3)]\rangle-\langle\exp(iU\tau_1)\rangle\langle\exp(iU\tau_3)\rangle\}\\&+2\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\exp[-\tfrac{1}{2}\gamma(\tau_1+2\tau_2+\tau_3)]\exp[i\Delta(\tau_1-\tau_3)]\\&\times\{\langle\exp[iU(\tau_3-\tau_1)]\rangle-\langle\exp(-iU\tau_1)\rangle\langle\exp(iU\tau_3)\rangle\}+\text{c.c.}\end{aligned} \tag{30a}$$

In the same limit $\chi^{(2)}$ assumes the form

$$\chi^{(2)}=\int_0^\infty d\tau \exp(-i\Delta\tau-\tfrac{1}{2}\gamma\tau)\langle\exp(iU\tau)\rangle + \text{c.c.} \tag{30b}$$

IV. DISCUSSION AND LIMITING CASES

In the preceding sections we have developed a general expansion for the absorption line shape of a collisionally perturbed two-level system in a strong radiation field. The main approximations involved in the present approach are the following: (i) Low density of perturbers. In this limit we may assume that the perturbers do not interact with each other. This assumption may be relaxed by using a cluster expansion.[12] (ii) T_1 processes were treated phenomenologically by introducing the relaxation rate γ. Within a cluster expansion it is possible to take a microscopic model for T_1. (iii) Space degeneracy was not explicitly introduced and we assumed that each level contains one state only. This assumption may be also relaxed but is not expected to lead to drastic changes as long as we do not observe polarization effects.[24] (iv) The Rabi frequency μ may not exceed the inverse duration of a collision so that our expansion in μ will hold. μ may, however, still be much larger than γ thus allowing for saturation. We shall now discuss our result [Eqs. (16) and (17)] and consider some limiting cases. We first note that in weak radiation fields (to lowest order in μ) Eqs. (16) and (17) reduce to

$$S(\Delta)=\mu^2\chi^{(2)}(\Delta)\ , \tag{31}$$

where $\chi^{(2)}(\tau)$ is given by Eqs. (19) and (20), i.e.:

$$\chi^{(2)}(\Delta)=\int_0^\infty d\tau \exp\left[i\Delta\tau-\frac{\gamma}{2}\tau-g(\tau)\right] + \text{c.c.}\ , \tag{32}$$

with the normalization

$$\int \chi^{(2)}(\Delta)d\Delta=2\pi\ . \tag{33}$$

This is the well-known expression of the LUT.[10–12]

Our more general expression for the line shape is, however,

$$S(\Delta)=\frac{\mu^2\chi^{(2)}(\Delta)-\mu^4\chi^{(4)}(\Delta)+\cdots}{1+(2/\gamma)[\mu^2\chi^{(2)}(\Delta)-\mu^4\chi^{(4)}(\Delta)+\cdots]}\ . \tag{34}$$

If we truncate the expansion in (34) and retain only $\chi^{(2)}$ we get an expression for the line shape in a strong field expressed in terms of the ordinary, weak-field line shape $\chi^{(2)}(\Delta)$, i.e.,

$$S(\Delta)=\frac{\mu^2\chi^{(2)}(\Delta)}{1+(2/\gamma)\mu^2\chi^{(2)}(\Delta)}\ . \tag{35}$$

In general, however, the line shape depends also on $\chi^{(4)}$, $\chi^{(6)}$, etc., which contain higher-order dipole correlation functions [see Eqs. (18), (A30), and Appendix B]. Thus the nonlinear line shape contains more detailed information regarding the collisions than the ordinary weak-field line.

For the sake of illustration we have calculated the line-shape function (35), where $\chi^{(2)}(\Delta)$ is given by Eq. (32) and $g(\tau)$ was taken from the stochastic theory of line shapes developed by Kubo,[7] i.e.,

$$g(\tau)=\frac{\delta^2}{\Lambda^2}[\exp(-\Lambda\tau)-1+\Lambda\tau]\ . \tag{36}$$

δ is a measure of the coupling strength responsible for the line broadening and Λ^{-1} is a correlation time which measures the typical time scale of $g(\tau)$ (i.e., the duration of a collision). The nature of the line-shape function $\chi^{(2)}(\Delta)$ is dominated by the dimensionless parameter

$$\kappa\equiv\frac{\Lambda}{\delta}\ . \tag{37}$$

When $\kappa>>1$ we are in the Markovian (impact) limit,

$$\exp[-g(\tau)]\simeq\exp\left[-\frac{\delta^2}{\Lambda}\tau\right] \quad (\kappa>>1) \tag{38}$$

and

$$\chi^{(2)}(\Delta)=\frac{2\Gamma}{\Delta^2+\Gamma^2}\ , \tag{39}$$

where

$$\Gamma=\tfrac{1}{2}\gamma+\delta^2/\Lambda\ . \tag{40}$$

Whereas when $\kappa<<1$ we are in the static limit,

$$\exp[-g(\tau)]=\exp(-\tfrac{1}{2}\delta^2\tau^2) \quad (\kappa<<1) \tag{41}$$

and the line shape assumes the Voigt profile

$$\chi^{(2)}(\Delta)=\frac{1}{\sqrt{2\pi}\delta}\int d\Delta'\frac{\gamma}{(\Delta-\Delta')^2+\frac{1}{4}\gamma^2}\times\exp\left[-\frac{\Delta'^2}{2\delta^2}\right]\ , \tag{42}$$

where $\gamma<<\delta$, (42) becomes a Gaussian.

$$\chi^{(2)}(\Delta)=\frac{\sqrt{2\pi}}{\delta}\exp\left[-\frac{\Delta^2}{2\delta^2}\right]. \tag{43}$$

We have calculated the line-shape function Eq. (35), where $\chi^{(2)}(\Delta)$ was evaluated using Eqs. (32) and (36). The results are given in Figs. 1–3 for various values of the Rabi frequency μ. Figure 1 shows the impact line shape ($\kappa=10$), Fig. 2 gives an intermediate case ($\kappa=1$), whereas Fig. 3 uses the Gaussian line shape (43). In the impact limit we get, upon substituting Eq. (39) in (35),

$$S(\Delta)=\frac{2\mu^2\Gamma}{\Delta^2+\Gamma^2+4\mu^2\Gamma/\gamma}. \tag{44}$$

This is the well-known formula describing a Lorentzian line in a weak field ($\mu\to 0$) which is power broadened at strong fields when μ is comparable to $\sqrt{\Gamma\gamma}$. Equation (44) may be obtained directly from the Bloch equations[15,20] and was first derived in the context of pressure broadening by Karplus and Schwinger.[14] As is clearly seen from Fig. 1, $S(\Delta)$ remains a Lorentzian in this case even for strong saturating fields μ. We should note further that in the perturbative limit, if we substitute $g(\tau)=(\delta^2/\Lambda)\tau$ in Eqs. (24) and (21) we get $K^{(4)}=0$. It may be easily verified that the higher cumulants ($K^{(6)}$, $K^{(8)}$, etc.) also vanish in this case so that

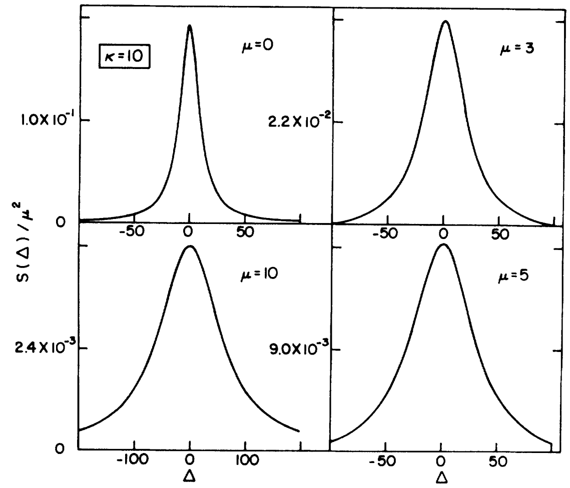

FIG. 1. Saturation behavior of the absorption line shape [Eqs. (36), (32), and (35)] in the Markovian limit $\kappa=10$. The energy scale is set by taking $\gamma=1$. In units of γ we have $\delta=100$, $\Lambda=1000$.

$$K^{(4)}=K^{(6)}=\cdots=0\,. \tag{45}$$

In Figs. 2 and 3 the line shape changes its form significantly as μ increases. Regarding the higher cummulants in the static limit, if we substitute Eq. (41) in (24) and (26) we get

$$K^{(2)}(\tau)=\exp(-i\bar{\Delta}\tau-\tfrac{1}{2}\delta^2\tau^2)+\text{c.c.}\,, \tag{46}$$

$$\begin{aligned}K^{(4)}(\tau_1,\tau_2,\tau_3)= {}&\exp(-i\bar{\Delta}\tau_1-i\bar{\Delta}\tau_3)\{\exp[-\tfrac{1}{2}\delta^2(\tau_1+\tau_3)^2]-\exp[-\tfrac{1}{2}\delta^2(\tau_1^2+\tau_3^2)\}\\ &+\exp(i\bar{\Delta}\tau_1-i\bar{\Delta}\tau_3)\{\exp[-\tfrac{1}{2}\delta^2(\tau_1-\tau_3)^2]-\exp[-\tfrac{1}{2}\delta^2(\tau_1^2+\tau_3^2)]\}\,.\end{aligned} \tag{47}$$

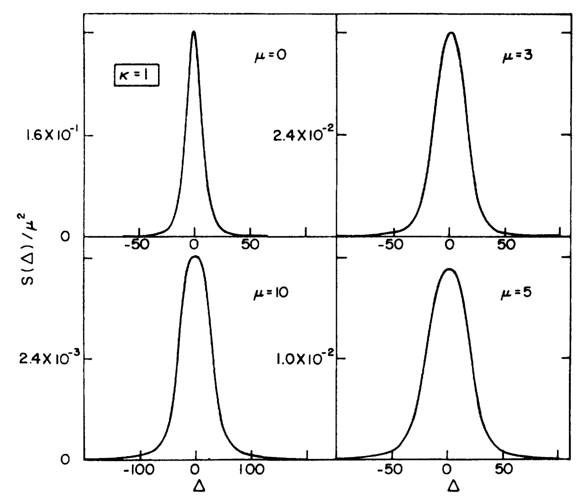

FIG. 2. Same as Fig. 1 but in the intermediate case $\kappa=1$ ($\delta=10$, $\gamma=10$).

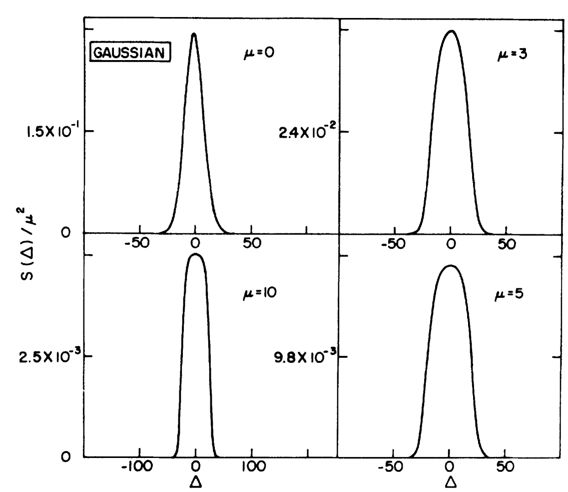

FIG. 3. Same as Fig. 1 but for $\chi^{(2)}$ we have taken the Gaussian line (43) $\delta=8.49$ (so that the FWHM$=10$ of the $\mu=0$ line is the same as in Fig. 1).

None of the cumulants $K^{(2n)}$ [Eq. (18)] vanish in this case. It should be pointed out that in the static limit, the condition

$$\mu\tau_c >> 1 \tag{48}$$

is easily satisfied for moderate laser intensities. Hence, instead of using the present expansion [Eqs. (16) and (17)], one can calculate the collision potential surfaces in the dressed-atom representation and obtain the optical collision cross section nonperturbatively in μ.[16,25–27]

ACKNOWLEDGMENTS

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APPENDIX A: FORMAL DERIVATION OF THE LINE SHAPE

The present derivation proceeds along the lines developed in Ref. 16. We start with the following expression for the absorption line shape:

$$I(\Delta)=i\,\mathop{\mathrm{Tr}}_{\mathrm{bath}}\langle\langle aa\,|\,\mathcal{T}(0)\,|\,\rho(-\infty)\rangle\rangle\;, \tag{A1}$$

where $\mathcal{T}(\omega)$ is the tetradic scattering T matrix[6,9,18,19]

$$\mathcal{T}(\omega)=\mathcal{V}+\mathcal{V}\frac{1}{\omega-L}\mathcal{V}\,, \tag{A2}$$

and v is the tetradic operator corresponding to V, i.e.,

$$\mathcal{V}=[V,\ ]\ . \tag{A3}$$

The initial density matrix $\rho(-\infty)$ is given by

$$\rho(-\infty)=\frac{\exp(-H_a/kT)}{\mathrm{Tr}[\exp(-H_a/kT)]}\times[(1-\eta)\,|\,a\rangle\langle a\,|+\eta\,|\,b\rangle\langle b\,|\,]\;, \tag{A4}$$

where η is defined in Eq. (9) and Tr stands for trace over the bath. Since

$$\mathcal{V}\,|\,aa\rangle\rangle=\mu(\,|\,ab\rangle\rangle-|\,ba\rangle\rangle)=-\mathcal{V}\,|\,bb\rangle\rangle\;, \tag{A5}$$

we may rearrange Eq. (A1) together with Eq. (A4) in the form

$$I(\Delta)=(\rho^0_{aa}-\rho^0_{bb})S(\Delta)=(1-2\eta)S(\Delta)\ . \tag{A6}$$

At this stage we introduce the tetradic projection operator

$$P=(\,|\,aa\rangle\rangle\langle\langle aa\,|+|\,bb\rangle\rangle\langle\langle bb\,|\,)\rho^0_B\mathrm{Tr} \tag{A7a}$$

and the complementary projection

$$Q=1-P\;, \tag{A7b}$$

in terms of which we may write

$$S(\Delta)=i\,\mathrm{Tr}\langle\langle aa\,|\,P\mathcal{T}(0)P\,|\,aa\rangle\rangle\rho^0_B\ . \tag{A8}$$

For any projection operator P we have

$$P\mathcal{T}(\omega)P=P\mathcal{R}(\omega)P[1-P\mathcal{G}(\omega)P\mathcal{R}(\omega)P]^{-1}\;, \tag{A9}$$

where

$$\mathcal{R}(\omega)=\mathcal{V}+\mathcal{V}Q\frac{1}{\omega-QLQ}Q\mathcal{V}\ . \tag{A10}$$

Here

$$G(\omega)=\frac{1}{\omega-L_1} \tag{A11}$$

is the tetradic Green's function and

$$L_1=[H_0,\ ]+\tilde{L}\equiv L_0+\tilde{L}\ . \tag{A11a}$$

Equation (A9) is analogous to a similar equation in ordinary (Hilbert space) scattering theory where $\mathcal{T}$, $\mathcal{G}$, $\mathcal{R}$, and P are replaced by their dyadic analogs. P converts $\mathcal{T}$, $\mathcal{R}$, and $\mathcal{G}$ to 2×2 matrices in the $|\,aa\rangle\rangle, |\,bb\rangle\rangle$ space.

Using Eqs. (A5) and (A10) it is clear that

$$(P\mathcal{R}P)_{aa,aa}=(P\mathcal{R}P)_{bb,bb}=-(P\mathcal{R}P)_{bb,aa}=-(P\mathcal{R}P)_{aa,bb}\ . \tag{A12}$$

We thus have

$$P\mathcal{R}(\omega)P=\mathcal{R}(\omega)_{aa,aa}\begin{bmatrix}1&-1\\-1&1\end{bmatrix}\ . \tag{A13}$$

Regarding $P\mathcal{G}P$ we have

$$P\mathcal{G}(\omega)P=\begin{bmatrix}\omega+i\gamma_a&-i\gamma_b\\-i\gamma_a&\omega+i\gamma_b\end{bmatrix}^{-1}=\frac{1}{\omega(\omega+i\gamma)}\begin{bmatrix}\omega+i\gamma_b&i\gamma_b\\i\gamma_a&\omega+i\gamma_a\end{bmatrix}\ . \tag{A14}$$

Using Eqs. (A13) and (A14) we get:

$$P\mathscr{G}(0)P\mathscr{R}(0)P=\frac{\mathscr{R}(0)_{aa,aa}}{i\gamma}\begin{bmatrix}1 & -1\\ -1 & 1\end{bmatrix} . \quad (A15)$$

Upon substitution of Eqs. (A9), (A13), and (A15) in Eq. (A8) we finally get

$$S(\Delta)=i[P\mathscr{T}(0)P]_{aa,aa}=\frac{\chi(\Delta)}{1+(2/\gamma)\chi(\Delta)} , \quad (A16)$$

where

$$\chi(\Delta)=i\mathscr{R}(0)_{aa,aa} . \quad (A17)$$

We have proven Eq. (16).

$\chi(\Delta)$ may be expanded in μ, resulting in

$$\chi(\Delta)=\mu^2\chi^{(2)}-\mu^4\chi^{(4)}+\mu^6\chi^{(6)}+\cdots , \quad (A18)$$

where

$$\chi^{(2n)}=\int_0^\infty d\tau_1\int_0^\infty d\tau_2\cdots\int_0^\infty d\tau_{2n-1}\,\mathrm{Tr}\langle\langle aa\,|\,\mathscr{V}\exp(-iQL_1Q\tau_1)\mathscr{V}\exp(-iQL_1Q\tau_2)\mathscr{V}\cdots \times\exp(-iQL_1Q\tau_{2n-1})\mathscr{V}\,|\,aa\rangle\rangle\rho_B^0 , \quad (A19)$$

where L_1 was defined in Eq. (A11a). Since for our choice of projection operator P [Eq. (A7a)] we have

$$PL_0=L_0P=0 , \quad (A20)$$

we may write:

$$QL_1Q=L_0+Q\tilde{L}Q . \quad (A21)$$

For the odd times variables in Eq. (A19), $\tau_1,\tau_3,\ldots$, etc., we may then replace $\exp(-iQL_1Q\tau_j)$ by $\exp(-iL_0\tau_j-\frac{1}{2}\gamma\tau_j)$.

Regarding the even times, $\exp(-iQL_1Q\tau_j)$, $j=2, 4$, etc., may be replaced by $Q\exp(-i\tilde{L}\tau_j)$ since L_0 does not act in the subspace of populations $|aa\rangle\rangle$ and $|bb\rangle\rangle$. $\exp(-i\tilde{L}\tau)$ in this subspace may be evaluated by finding its right- and left-hand eigenstates. We may then write

$$\exp(-i\tilde{L}\tau)=\mathscr{G}^+ +\mathscr{G}^-\exp(-\gamma\tau) , \quad (A22)$$

where

$$\mathscr{G}^+=(1-\eta)\,|\,aa\rangle\rangle\langle\langle aa\,|+\eta\,|\,bb\rangle\rangle\langle\langle bb\,|+(1-\eta)\,|\,aa\rangle\rangle\langle\langle bb\,|+\eta\,|\,bb\rangle\rangle\langle\langle aa\,| , \quad (A23)$$

$$\mathscr{G}^-=\eta\,|\,aa\rangle\rangle\langle\langle aa\,|+(1-\eta)\,|\,bb\rangle\rangle\langle\langle bb\,|-\eta\,|\,bb\rangle\rangle\langle\langle aa\,|-(1-\eta)\,|\,aa\rangle\rangle\langle\langle bb\,| . \quad (A24)$$

It is clear that $\mathscr{G}^+$ does not contribute in Eq. (A19) since it always acts on the vector $(1,-1)$ and

$$\mathscr{G}^+\begin{bmatrix}1\\ -1\end{bmatrix}=0 , \quad (A25)$$

so we may replace $\exp(-i\tilde{L}\tau_j)$ by

$$\mathscr{G}^-\exp(-\gamma\tau_j),\quad j=2,4,\ldots . \quad (A26)$$

We then get

$$\chi^{(2n)}=\int_0^\infty d\tau_1\cdots\int_0^\infty d\tau_{2n-1} \times\mathop{\mathrm{Tr}}_{\mathrm{bath}}\langle\langle aa\,|\,\mathscr{V}\exp(-iL_0\tau_1)\mathscr{V}Q\mathscr{G}^-\mathscr{V}\exp(-iL_0\tau_3)\mathscr{V}Q\mathscr{G}^-\cdots\mathscr{V} \times\exp(-iL_0\tau_{2n-1})\mathscr{V}\,|\,aa\rangle\rangle\rho_B^0\exp\left[-\frac{\gamma}{2}(\tau_1+2\tau_2+\tau_3+2\tau_4+\cdots)\right] . \quad (A27)$$

Acting with all $\exp(-iL_0\tau_j)$ to the left and introducing the definitions

$$\mathscr{V}(\tau)\equiv\exp(iL_0\tau)\mathscr{V}\exp(-iL_0\tau) , \quad (A28)$$

and

$$D \equiv Q\mathcal{G}^- \,, \tag{A29}$$

we finally get Eq. (18), where the $2n$th order cummulant $K^{(2n)}$ is given by

$$K^{(2n)}(\tau_1, \ldots, \tau_{2n-1}) = \frac{1}{\mu^{2n}} \operatorname*{Tr}_{\text{bath}} [\langle \langle aa \mid \nu(t_1)\nu(t_2) D \nu(t_3)\nu(t_4) D \cdots D\nu(t_{2n-1})\nu(0) \mid aa \rangle \rangle \rho_B^0] \,, \tag{A30}$$

where

$$\begin{aligned} t_1 &= \tau_1 + \tau_2 + \cdots + \tau_{2n-1} \,, \\ t_2 &= \tau_2 + \tau_3 + \cdots + \tau_{2n-1} \,, \\ &\vdots \\ t_{2n-1} &= \tau_{2n-1} \,. \end{aligned} \tag{A31}$$

APPENDIX B: EVALUATION OF $K^{(4)}$

The tetradic correlation function of $K^{(4)}$ [Eq. (A30)] may be expressed in terms of dyadic correlation functions as follows[16]:

$$\begin{aligned} K^{(4)}(\tau_1,\tau_2,\tau_3) &= \exp(-i\Delta\tau_1 - i\Delta\tau_3)\bar{K}^{(4)}(\tau_1,\tau_2,\tau_3) \\ &\quad + \exp(i\Delta\tau_1 - i\Delta\tau_3)\bar{K}^{(4)}(-\tau_1,\tau_1+\tau_2,\tau_3) + \text{c.c.} \,, \end{aligned} \tag{B1}$$

where

$$\begin{aligned} &\mu^4 \bar{K}^{(4)}(\tau_1,\tau_2,\tau_3) \\ &\quad = [\langle V_{ab}(0)V_{ba}(\tau_3)V_{ab}(\tau_2+\tau_3)V_{ba}(\tau_1+\tau_2+\tau_3)\rangle - \langle V_{ab}(0)V_{ba}(\tau_1\rangle\langle V_{ab}(0)V_{ba}(\tau_3)\rangle] \\ &\quad + [\langle V_{ab}(0)V_{ba}(\tau_1+\tau_2+\tau_3)V_{ab}(\tau_2+\tau_3)V_{ba}(\tau_3)\rangle - \langle V_{ab}(0)V_{ba}(\tau_1)\rangle\langle V_{ab}(0)V_{ba}(\tau_3)\rangle] \\ &\quad + \left[\frac{1}{\mu^2}\langle V_{av}(0)V_{ba}(\tau_3)V_{ab}(0)V_{ba}(\tau_1+\tau_2+\tau_3)V_{ab}(\tau_2+\tau_3)V_{ba}(0)\rangle - \langle V_{ab}(0)V_{ba}(\tau_1)\rangle\langle V_{ab}(0)V_{ba}(\tau_3)\rangle \right] \\ &\quad + [\langle V_{ab}(\tau_2+\tau_3)V_{ba}(\tau_1+\tau_2+\tau_3)V_{ab}(0)V_{ba}(\tau_3)\rangle - \langle V_{ab}(0)V_{ba}(\tau_1)\rangle\langle V_{ab}(0)V_{ba}(\tau_3)\rangle] \,. \end{aligned} \tag{B2}$$

Here

$$V_{ab}(\tau) = \exp(iH_a\tau)V_{ab}\exp(-iH_b\tau) \tag{B3}$$

and

$$\langle V_{ab}(0)V_{ba}(t_1)V_{ab}(t_2)V_{ba}(t_3)\rangle \equiv \text{Tr}[V_{ab}(0)V_{ba}(t_1)V_{ab}(t_2)V_{ba}(t_3)\rho_a^0] \,. \tag{B4}$$

Using Eq. (B2) we note that the evaluation of $\bar{K}^{(4)}$ requires the calculation of four- and six-time dipole correlation functions of the form (B4). The microscopic evaluation of (B4) is a generalization of the method used for two-time correlation functions and goes as follows.

(i) We first note that due to the *separability* of our Hamiltonian [Eq. (10)] we have

$$\langle V_{ab}(0)V_{ba}(t_1)V_{ab}(t_2)V_{ba}(t_3)\rangle = \langle V_{ab}(0)V_{ba}(t_1)V_{ab}(t_2)V_{ba}(t_3)\rangle_s^N \,, \tag{B5}$$

where $\langle \cdots \rangle_s$ is a *single-particle* correlation function obtained by considering a single perturber in the macroscopic box.

(ii) Since V_a and V_b are finite only in a microscopic volume $O(1/\Omega)$ and vanish in most of the box, $V_{ba}(\tau)$ exhibits a diagonal singularity property, i.e.,[10,12,18]

$$\begin{aligned} V_{ba}(\tau) &= 1 + \hat{f}_{ba}(\tau) \,, \\ \hat{f}_{ba}(\tau) &= \sum_{\beta\alpha} \mid b\beta\rangle\langle b\beta \mid a\alpha\rangle\langle a\alpha \mid [\exp(i\omega_{\beta\alpha}\tau) - 1] \,. \end{aligned} \tag{B6}$$

Here $\hat{f}_{ba}(\tau)$, includes only "nondiagonal" elements which are $O(1/\Omega)$ due to the Franck-Condon overlap factor $\langle b\beta \mid a\alpha \rangle$. Similarly we have

$$V_{ab}(\tau)=1+\hat{f}_{ab}(\tau) , \tag{B7}$$

where

$$\hat{f}_{ab}=\hat{f}_{ba}^{\dagger} . \tag{B8}$$

Using Eqs. (B6) and (B7) we may write

$$\langle V_{ab}(0)V_{ba}(t_1)V_{ab}(t_2)V_{ba}(t_3)\rangle = \left[1-\frac{1}{\Omega}W(t_1,t_2,t_3)\right]^N \xrightarrow[N/\Omega(\text{finite})]{N\to\infty,\Omega\to\infty} \exp\left[-\frac{N}{\Omega}W(t_1,t_2,t_3)\right] , \tag{B9}$$

where

$$W(t_1,t_2,t_3)=\Omega[\langle \hat{f}_{ba}(t_1)\rangle+\langle \hat{f}_{ab}(t_2)\rangle+\langle \hat{f}_{ba}(t_3)\rangle+\langle \hat{f}_{ba}(t_1)\hat{f}_{ab}(t_2)\rangle+\langle \hat{f}_{ba}(t_1)\hat{f}_{ba}(t_3)\rangle$$
$$+\langle \hat{f}_{ab}(t_2)\hat{f}_{ba}(t_3)\rangle+\langle \hat{f}_{ba}(t_1)\hat{f}_{ab}(t_2)\hat{f}_{ba}(t_3)\rangle] . \tag{B10}$$

Each of the terms in the brackets of Eq. (B10) is $O(1/\Omega)$ so that W is $O(1)$.[12,18]

APPENDIX C: LIMITING CASES OF $\bar{K}^{(4)}$

A. Weak coupling

$\bar{K}^{(4)}$ may be expanded to lowest order in λ. The result is (for details see Ref. 16)

$$\bar{K}^{(4)}(\tau_1,\tau_2,\tau_3)=\eta f(\tau_1)f(\tau_3)[F_1(\tau_1,\tau_2,\tau_3)-1]+(1-\eta)[f(-\tau_1)f(\tau_3)F_2(\tau_1,\tau_2,\tau_3)-f(\tau_1)f(\tau_3)]$$
$$+\eta[f(-\tau_1)f(\tau_3)F_3(\tau_1,\tau_2,\tau_3)-f(\tau_1)f(\tau_3)]+(1-\eta)f(\tau_1)f(\tau_3)[F_4(\tau_1,\tau_2,\tau_3)-1] , \tag{C1}$$

and

$$f(\tau)=\exp[-\lambda^2\bar{g}(\tau)] , \tag{C2}$$

$$F_1(\tau_1,\tau_2,\tau_3)=\exp\{\lambda^2[-\bar{g}(\tau_2)+\bar{g}(\tau_2+\tau_3)+\bar{g}(\tau_1+\tau_2)-\bar{g}(\tau_1+\tau_2+\tau_3)]+O(\lambda^3)\} , \tag{C3}$$

$$F_2(\tau_1,\tau_2,\tau_3)=\exp\{\lambda^2[-\bar{g}^*(\tau_2)+\bar{g}(\tau_2+\tau_3)+\bar{g}^*(\tau_1+\tau_2)-\bar{g}(\tau_1+\tau_2+\tau_3)]+O(\lambda^3)\} , \tag{C4}$$

$$F_3(\tau_1,\tau_2,\tau_3)=\exp\{\lambda^2[-\bar{g}(\tau_2)+\bar{g}(\tau_2+\tau_3)+\bar{g}(\tau_1+\tau_2)-\bar{g}(\tau_1+\tau_2+\tau_3)]$$
$$+[\bar{g}^*(\tau_1+\tau_2+\tau_3)-\bar{g}(\tau_1+\tau_2+\tau_3)+\bar{g}(\tau_2+\tau_3)-\bar{g}^*(\tau_2+\tau_3)]+O(\lambda^3)\} , \tag{C5}$$

$$F_4(\tau_1,\tau_2,\tau_3)=\exp\{\lambda^2[-\bar{g}^*(\tau_2)+\bar{g}^*(\tau_2+\tau_3)+\bar{g}^*(\tau_1+\tau_2)-\bar{g}^*(\tau_1+\tau_2+\tau_3)]+O(\lambda^3)\} , \tag{C6}$$

$$\bar{g}(\tau)=\frac{N}{\Omega}\Omega\sum_{\alpha\alpha'}P(\alpha)\,|\langle a\alpha \mid U \mid a\alpha'\rangle|^2[\exp(i\omega_{\alpha\alpha'}\tau)-1] , \tag{C7}$$

$$\bar{g}(\tau)=\int_0^\infty d\tau_1(\tau-\tau_1)\tilde{g}(\tau_1) ,$$

$$\tilde{g}(\tau)=\frac{N}{\Omega}\Omega\sum_{\alpha\alpha'}P(\alpha)\omega_{\alpha\alpha'}^2\,|\langle a\alpha \mid U \mid a\alpha'\rangle|^2\exp(i\omega_{\alpha\alpha'}\tau) . \tag{C8}$$

B. Static (statistical) limit

In the static limit we neglect the kinetic energy terms in Eq. (B2) and get

$$\langle V_{ab}(0)V_{ba}(t_1)V_{ab}(t_2)V_{ba}(t_3)\rangle=\langle \exp[iU(t_1+t_3-t_2)]\rangle \tag{C9}$$

substituting (9) in (B10) we get

$$\bar{K}^{(4)}(\tau_1,\tau_2,\tau_3)=2[\langle \exp[iU(\tau_1+\tau_3)]\rangle-\langle \exp(iU\tau_1)\rangle\langle \exp(iU\tau_3)\rangle] .$$

[1]A. Jablonski, Phys. Rev. 68, 78 (1945).
[2]M. Baranger, Phys. Rev. 111, 481 (1958).
[3]H. Margenau, Phys. Rev. 48, 755 (1935); *ibid.* 82, 156 (1951).
[4]J. H. van Vleck and V. F. Weisskopf, Rev. Mod. Phys. 17, 227 (1945).
[5]For a review see D. Mihalas, *Stellar Atmospheres* (Freeman, San Francisco, 1978).
[6]U. Fano, Phys. Rev. 13, 259 (1963).
[7](a) R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems,* edited by D. Ter Haar (Oliver & Boyd, Edinburgh, 1962); (b) R. Kubo, Adv. Chem. Phys. 15, 101 (1969).
[8]R. P. Futrelle, Phys. Rev. A 5, 2162 (1972).
[9]A. Ben-Reuven, Adv. Chem. Phys. 33, 235 (1975).
[10]J. Szudy and W. E. Baylis, J. Quant. Spectrosc. Radiat. Transfer 15, 641 (1975).
[11](a) A. Royer, Phys. Rev. A 6, 1741 (1972). (b) A. Royer, Phys. Rev. A 22, 1625 (1980).
[12](a) S. Mukamel, Phys. Rev. A 26, 617 (1982); (b) D. Grimbert and S. Mukamel, J. Chem. Phys. 76, 834 (1982).
[13]R. G. Breene, *Theories of Spectral Line Shapes* (Wiley, New York, 1981).
[14]R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).
[15]L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975).
[16]V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 68, 479 (1975) [Sov. Phys.—JETP 41, 233 (1975)].
[17]S. Mukamel, J. Chem. Phys. 70, 5834 (1979); 71, 2012 (1979); Adv. Chem. Phys. 47, 509 (1981).
[18]S. Mukamel, J. Chem. Phys. 71, 2884 (1979).
[19]S. Mukamel, J. Chem. Phys. 73, 5322 (1980).
[20]A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961).
[21]A. Ben-Reuven and S. Mukamel, J. Phys. A 8, 1313 (1975).
[22]A. Ben-Reuven and Y. Rabin, Phys. Rev. A 19, 2056 (1979).
[23]Y. Rabin and S. Mukamel, J. Phys. B 13, L331 (1980).
[24]K. Burnett, J. Cooper, R. J. Ballagh, and E. W. Smith, Phys. Rev. A 22, 2005 (1980); K. Burnett and J. Cooper, *ibid.* 22, 2027 (1980); 22, 2044 (1980).
[25]S. Yeh and P. R. Berman, Phys. Rev. A 19, 1106 (1979).
[26]M. Crance and S. Stenholm, J. Phys. B 13, 1563 (1980).
[27]Y. Rabin and A. Ben-Reuven, J. Phys. B 13, 2011 (1980).