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LETTER TO THE EDITOR

Unified theory for collisional dephasing in strong radiation fields. A generalisation of the Karplus–Schwinger formula

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Abstract. An expansion is presented for the absorption lineshape of a two-level system in a strong radiation field being perturbed by dephasing collisions, within the binary collision approximation. No dynamical assumptions regarding the time scale of the collisions (relative to the broadening) need to be made and the present theory interpolates smoothly between the impact and the quasistatic limits. The present solution reduces in weak radiation fields to the linear unified theory of spectral lineshapes and in the impact limit (fast collisions) we recover the Karplus–Schwinger formula. The only molecular information necessary for the exact evaluation of the absorption lineshape in a strong field is the same single-particle correlation function $g(\tau)$ which appears in the linear (weak field) unified theory.

We consider a two-level molecular system ($|a\rangle$ and $|b\rangle$) which interacts with a strong monochromatic radiation field and with a bath of foreign perturbers in the low-pressure gas phase. We assume that the perturbers do not induce relaxation of population (T_1) but have only diagonal interactions with the two-level system. The total Hamiltonian within the rotating-wave approximation is

$$H = H_0 + V \tag{1}$$

where

$$H_0 = \tfrac{1}{2}\Delta(|a\rangle\langle a| - |b\rangle\langle b|) + |a\rangle F_a(Q_B)\langle a| + |b\rangle F_b(Q_B)\langle b| \tag{1a}$$

and

$$V = \mu(|a\rangle\langle b| + |b\rangle\langle a|). \tag{1b}$$

Here $\Delta = \omega_L - \omega_{ba}$ is the detuning of the radiation frequency (ω_L) from the two-level frequency ω_{ba}, and μ is the Rabi frequency (the transition dipole times the field amplitude). The second term in H_0 describes the two-level system interacting with the bath. Within the binary collision approximation we assume additive interactions of our system with the νth bath particle i.e.

$$F_i(Q_B) = \sum_\nu F_{i\nu}(Q_{B\nu}) \qquad i = a, b. \tag{2}$$

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The eigenstates of F_a and F_b (normalised in a box with volume Ω) are therefore

$$|a\alpha\rangle = |a\rangle \prod_{\nu} |\alpha_\nu\rangle \tag{3a}$$

and

$$|b\beta\rangle = |b\rangle \prod_{\nu} |\beta_\nu\rangle \tag{3b}$$

with eigenvalues E_α and E_β respectively.

The time evolution of the density matrix for the entire system + bath + the radiation field is given by the Liouville equation

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mathrm{i}L\rho - \mathrm{i}\tilde{L}\rho \tag{4}$$

where $L \equiv [H, \ ]$ is the Liouville operator (commutator) corresponding to H. (Similarly we define $L_0 \equiv [H_0, \ ]$ and $v \equiv [V, \ ]$). $\tilde{L}$ is a T_1 relaxation matrix $\tilde{L}_{aa,aa} = -\tilde{L}_{bb,aa} = -\mathrm{i}\gamma_a$, $\tilde{L}_{bb,bb} = -\tilde{L}_{aa,bb} = -\mathrm{i}\gamma_b$ and $\tilde{L}_{ab,ab} = \tilde{L}_{ba,ba} = -\frac{1}{2}\mathrm{i}\gamma$, where $\gamma = \gamma_a + \gamma_b$. $\tilde{L}$ guarantees the relaxation of the two-level system (in the absence of driving, $\mu = 0$) to thermal equilibrium where $\rho_{aa}^{\mathrm{eq}} = \gamma_b/\gamma$ and $\rho_{bb}^{\mathrm{eq}} = \gamma_a/\gamma$.

The absorption lineshape $I(\Delta)$ for the system described by the Liouville equation (4) may be solved making use of the tetradic scattering formalism (Fano 1963, Ben-Reuven 1975, Ben-Reuven and Mukamel 1975, Ben-Reuven and Rabin 1979, Mukamel 1979 a, b). The final result is

$$I(\Delta) = (\rho_{aa}^{\mathrm{eq}} - \rho_{bb}^{\mathrm{eq}}) S(\Delta) \tag{5}$$

where

$$S(\Delta) = \frac{R(\Delta)}{1 + 2R(\Delta)/\gamma} \tag{6}$$

and where

$$R(\Delta) = \mu^2 R^{(2)}(\Delta) - \mu^4 R^{(4)}(\Delta) + \mu^6 R^{(6)}(\Delta) \ldots . \tag{7}$$

The nth term in equation (7) is given by

$$R^{(2n)}(\Delta) = 2^{n-1} \int_0^\infty \mathrm{d}\tau_1 \int_0^\infty \mathrm{d}\tau_2 \ldots \int_0^\infty \mathrm{d}\tau_{2n-1} K^{(2n)}(\tau_1, \ldots, \tau_{2n-1}) \times \exp[-\tfrac{1}{2}\gamma(\tau_1 + 2\tau_2 + \tau_3 + 2\tau_4 + \ldots)] \tag{8}$$

where $K^{(2n)}$ is a $2n$th-order cumulant given formally by

$$K^{(2n)}(\tau_1, \tau_2, \ldots, \tau_{2n-1}) = \frac{1}{\mu^{2n}} \mathrm{Tr}_{\mathrm{bath}} \langle\langle aa|v(t_1)v(t_2)Dv(t_3)v(t_4)D \ldots Dv(t_{2n-1})v(0)|aa\rangle\rangle \rho_{\mathrm{B}}^0 \tag{9}$$

where

$$t_1 = \tau_1 + \tau_2 + \ldots + \tau_{2n-1} \qquad t_2 = \tau_2 + \tau_3 + \ldots + \tau_{2n-1} \qquad \ldots \qquad t_{2n-1} = \tau_{2n-1} \tag{10}$$

and

$$v(\tau) = \exp(\mathrm{i}L_0\tau)\, v \exp(-\mathrm{i}L_0\tau). \tag{11}$$

The projection operator D is defined by

$$D \equiv |aa\rangle\rangle\langle\langle aa|(1 - \rho_{\mathrm{B}}^0 \mathrm{Tr}_{\mathrm{bath}}) \tag{12}$$

and ρ_B^0 is the canonical equilibrium distribution function for the bath

$$\rho_B^0 = \sum_\alpha |\alpha\rangle P(\alpha)\langle\alpha| \tag{13a}$$

and

$$P(\alpha) = \exp(-E\alpha/kT)/\mathrm{Tr}\exp(-F_a/kT). \tag{13b}$$

We may further define $2n$th-order moments $M^{(2n)}(\tau_1, \tau_2, \ldots, \tau_{2n-1})$ by an expression similar to (9) whereby each projection D is replaced by $D_a = |aa\rangle\rangle\langle\langle aa|$. From these definitions we see that each cumulant $K^{(2n)}$ may be expressed in terms of the lower moments $M^{(j)}$ $j = 2, 4, \ldots, 2n$ i.e.

$$K^{(2)}(\tau_1) = M^{(2)}(\tau_1) \tag{14a}$$

$$K^{(4)}(\tau_1, \tau_2, \tau_3) = M^{(4)}(\tau_1, \tau_2, \tau_3) - M^{(2)}(\tau_1)M^{(2)}(\tau_3) \tag{14b}$$

$$\begin{aligned} K^{(6)}(\tau_1, \ldots, \tau_5) &= M^{(6)}(\tau_1, \ldots, \tau_5) \\ &\quad - M^{(4)}(\tau_1, \tau_2, \tau_3)M^{(2)}(\tau_5) - M^{(2)}(\tau_1)M^{(4)}(\tau_3, \tau_4, \tau_5) \\ &\quad - M^{(2)}(\tau_1)M^{(2)}(\tau_3)M^{(2)}(\tau_5) \qquad \text{etc.} \end{aligned} \tag{14c}$$

The molecular information relevant for the absorption lineshape in a strong field is thus expressed in terms of the hierarchy of moments $M^{(2n)}$ which are used to construct $R^{(2n)}$. This is a common feature to multiphoton processes in general (Mukamel 1979a, b). The evaluation of $M^{(2)}$ is equivalent to the solution of the ordinary (weak field) lineshape (Jablonski 1945, Baranger 1958, Szudy and Baylis 1975) so that we have

$$K^{(2)}(\tau) = M^{(2)}(\tau) = \exp(-\mathrm{i}\Delta\tau - g(\tau)) + \mathrm{CC} \tag{15}$$

where

$$g(\tau) = \frac{N}{\Omega}\sum_{\alpha,\beta} P(\alpha)|\langle\alpha|\beta\rangle|^2[1 - \exp(\mathrm{i}\,\omega_{\beta\alpha}\tau)] \tag{16}$$

and $\omega_{\beta\alpha} = E_\beta - E_\alpha$. Substitution of (16) in (8) results in

$$R^{(2)} = 2\,\mathrm{Re}\int_0^\infty \mathrm{d}\tau \exp[-\mathrm{i}\Delta\tau - \tfrac{1}{2}\gamma\tau - g(\tau)]. \tag{17}$$

We note that $g(\tau)$ is a single-particle correlation function involving the Franck–Condon overlap factors $\langle\alpha|\beta\rangle$ of the F_a and F_b potential surfaces and is proportional to the number density of perturbers N/Ω (where N is the number of perturber molecules and Ω is the volume of the system).

All the moments $M^{(2n)}$ may be evaluated rigorously using a systematic density expansion (Mukamel 1979a) resulting in

$$\begin{aligned} R^{(4)} = 2\int_0^\infty \mathrm{d}\tau_1 \int_0^\infty \mathrm{d}\tau_2 \int_0^\infty \mathrm{d}\tau_3 \exp[(-\mathrm{i}\Delta - \tfrac{1}{2}\gamma)\tau_1 - g(\tau_1) + (-\mathrm{i}\Delta - \tfrac{1}{2}\gamma)\tau_3 - g(\tau_3) - \gamma\tau_2] \\ \times\{\exp[g(\tau_1+\tau_2) - g(\tau_2) + g(\tau_2+\tau_3) - g(\tau_1+\tau_2+\tau_3)] - 1\} \\ + 2\int_0^\infty \mathrm{d}\tau_1 \int_0^\infty \mathrm{d}\tau_2 \int_0^\infty \mathrm{d}\tau_3 \\ \times\exp[(\mathrm{i}\Delta - \tfrac{1}{2}\gamma)\tau_1 - g(\tau_1) + (-\mathrm{i}\Delta - \tfrac{1}{2}\gamma)\tau_3 - g(\tau_3) - \gamma\tau_2] \\ \times\{\exp[-g(\tau_1+\tau_2) + g(\tau_2) - g(\tau_2+\tau_3) + g(\tau_1+\tau_2+\tau_3)] - 1\} + \mathrm{CC}. \end{aligned} \tag{18}$$

The general expression for the $2n$th moment is

$$M^{(2n)}(\tau_1, \tau_2, \ldots, \tau_{2n-1}) = \sum_{v_1=\pm1} \sum_{v_2=\pm1} \sum_{v_n=\pm1} \left[\exp\left(\sum_{k=1,3}^{2n-1} \phi_k(v_k) \right) \times \exp\left(\sum_{k=1,3}^{2n-1} \sum_{l=k+2,k+4}^{2n-1} \xi_{kl}(v_k, v_l) \right) \right] \qquad n \geqslant 2 \tag{19}$$

where

$$\phi_k(+1) = -i\Delta\tau_k + g(\tau_k) \qquad \phi_k(-1) = \phi_k^*(+1) = i\Delta\tau_k + g(\tau_k) \tag{20}$$

and where

$$\xi_{k,l}(+1, +1) = \xi_{k,l}(-1, -1) = -\xi(-1, +1) = -\xi(+1, -1) = g(t_k - t_l) - g(t_k - t_{l-1}) - g(t_{k-1} - t_l) + g(t_{k-1} - t_{l-1}). \tag{21}$$

In conclusion we note the following.

(i) We have presented a general solution to the absorption lineshape in a strong field in the presence of dephasing collisions of an arbitrary nature. The only molecular information required for the evaluation of the lineshape (6) is contained in the line broadening function $g(\tau)$ which appears in ordinary (weak field) lineshapes. All moments $M^{(2n)}$ may be expressed in terms of $g(\tau)$.

(ii) In the weak radiation field limit we may expand $S(\Delta)$ to lowest order in μ resulting in

$$S(\Delta) = \mu^2 R^{(2)}(\Delta) \tag{22}$$

where $R^{(2)}$ is given by equation (17). This is the well known expression of the linear unified theory of lineshapes (Szudy and Baylis 1975).

(iii) In the impact (Markovian) limit of fast collisions (relative to the line broadening) we take $g(\tau)$ (on a coarse-grained time scale) to be linear in τ i.e. (Szudy and Baylis 1975, Mukamel 1979a)

$$g(\tau) \equiv \int_0^\tau d\tau_1 (\tau - \tau_1) g''(\tau_1) \simeq \tau \int_0^\infty d\tau_1 g''(\tau_1) = \hat{\Gamma}\tau \tag{23}$$

where $g''(\tau_1)$ is the second derivative of g. From equation (21) we note that in this case all $\xi(v_k, v_l) = 0$ so that the moments factorise

$$M^{(2n)}(\tau_1, \ldots \tau_{2n-1}) = M^{(2)}(\tau_1) M^{(2)}(\tau_3) \ldots M^{(2)}(\tau_{2n-1}) \tag{24}$$

(such a factorisation was assumed recently for other multiphoton processes (Mukamel 1979b) without rigorous proof).

Using (24) we immediately obtain

$$K^{(4)} = K^{(6)} = \ldots = 0. \tag{25}$$

So that

$$R(\Delta) = \mu^2 R^{(2)}(\Delta) = \frac{2\mu^2 \Gamma}{\Delta^2 + \Gamma^2} \tag{26}$$

where

$$\Gamma = \tfrac{1}{2}\gamma + \hat{\Gamma}. \tag{27}$$

Upon substitution of (26) in (6) we recover the Karplus–Schwinger formula (Karplus and Schwinger 1948)

$$S(\Delta)=\frac{2\mu^2\Gamma}{\Delta^2+\Gamma^2+4\mu^2\Gamma/\gamma}. \tag{28}$$

It should be noted that Lisitsa and Yakovlenko (1975) have recently suggested phenomenologically an expansion for $S(\Delta)$ based on equation 28, by taking Γ to depend on the Rabi frequency and the detuning i.e. $\Gamma=\Gamma(\mu,\Delta)$. Such an expansion is convenient near the impact limit but becomes very tedious in the quasistatic limit even for weak fields.

(iv) In the non-Markovian case (when $g(\tau)$ is not linear in τ) we may use the expansion (7) to obtain the lineshape. Simple arguments based on equation (8) show that $R^{(2n)}\simeq R^{(2)}(\mu^2\tau_c/\gamma)^{n-1}$ where τ_c is a duration of a collision. To lowest order in τ_c we thus have the approximate relation:

$$S(\Delta)\simeq\frac{\mu^2R^{(2)}(\Delta)}{1+2\mu^2R^{(2)}(\Delta)/\gamma}. \tag{29}$$

(v) The present formalism may be easily extended to other processes (resonance Raman etc) which also require the evaluation of cumulants similar in form to equation (9) (Rabin and Mukamel 1980).

Note added in proof. In general the $|aa\rangle\!\rangle\langle\!\langle aa|$ factor in D (equation (12)) should be $[\eta|aa\rangle\!\rangle\langle\!\langle aa|+(1-\eta)|bb\rangle\!\rangle\langle\!\langle bb|-\eta|bb\rangle\!\rangle\langle\!\langle aa|-(1-\eta)|aa\rangle\!\rangle\langle\!\langle bb|]/2$, where $\eta=\rho_{bb}^{eq}$. Equations (14)–(21) are given in the high-temperature limit where $kT\gg$ linewidth, and $g(\tau)$ is real. This limit is usually expected to hold for collisional line broadening. In this case the complicated factor above reduces simply to $|aa\rangle\!\rangle\langle\!\langle aa|$.

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