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On the semiclassical calculation of molecular absorption and fluorescence spectra

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A semiclassical expansion is developed for the direct calculation of molecular electronic (absorption and fluorescence) spectra without having to calculate the molecular vibrational eigenstates. The expansion is based on expressing the necessary dipole correlation functions (which do not have a straightforward classical analog) in terms of a hierarchy of other intramolecular correlation functions which do have a simple semiclassical expansion. To lowest order in $\hbar$ the spectra may be calculated by running classical trajectories on a zero-order Hamiltonian H_c. The present semiclassical expansion is not unique and depends on our choice of H_c. This arises since the spectra are not analytic functions of $\hbar$. Applications are made to the absorption and to the fluorescence spectra of polyatomic molecules (single- and two-photon processes). The present method may be easily generalized to other multiphoton processes.

I. INTRODUCTION

It is well known that molecular spectra may be calculated using the molecular eigenstates and their dipole matrix elements. Conversely, the experimental spectra are often used to extract individual level spacings and transition dipoles.[1] The analysis of the optical spectra of small molecules (diatomics, triatomics) as well as the infrared vibrational spectra of larger polyatomic molecules[2] goes along these lines. The spectroscopist's traditional dream is to end up with a large table containing level positions, symmetry assignments of these levels, and oscillator strengths.

Recent progress in spectroscopic techniques gives us information regarding the dynamics of highly vibrationally excited polyatomic molecules either in the ground electronic state or in electronically excited states. Examples are the studies of absorption and dispersed fluorescence spectra of supercooled molecules in a beam,[3-5] overtone spectra,[6,7] coherent transients,[8,9] and molecular multiphoton processes using high power infrared lasers.[10] In these studies the calculation of properties of individual states is neither feasible nor desirable. The number of states involved is way too large and the amount of experimental information is too small to allow for such a detailed analysis. It is thus necessary to develop a theoretical framework which will enable us to calculate the molecular spectra and the relevant molecular motions directly from the Hamiltonian, without going through the exact molecular eigenstates. This subject has drawn recently a considerable theoretical attention due to the open debate regarding the nature of highly vibrationally excited polyatomic molecules. It is believed that at low energies the molecular vibrational motions are quasiperiodic and they change to a stochastic behavior at higher energies.[11-17] This has important implications regarding our understanding the mechanisms of chemical reactions. It is therefore crucial to develop a workable scheme where experimental spectra may be calculated microscopically and the nature of the molecular motions may be deduced.

Methods of nonequilibrium statistical mechanics were introduced recently to study molecular multiphoton processes[18] and the fluorescence of supercooled molecules.[4(b)] It has been shown how reduced equations of motion for molecular multiphoton processes may be expressed in terms of a hierarchy of n-time intramolecular dipole correlation functions. The explicit evaluation of these correlation functions is the key problem in all molecular radiative phenomena and is the main subject of the present work. The application of methods of classical mechanics seem most appropriate for that purpose. Since the vibrational motions of highly vibrationally excited molecules are almost classical, it is tempting to try to simulate molecular spectra by running classical trajectories in the same way that cross sections for molecular scattering processes and unimolecular reaction rates may be obtained.[19] The simplest example is the calculation of molecular infrared spectra. Here the electronic degrees of freedom merely provide the potential surface for the nuclear motions and need not be considered explicitly. The formulation of the quantum mechanical line-shape function in terms of classical mechanics is straightforward in this case. Basically, the absorption line shape of a photon ω is given by

$$I(\omega) \equiv \pi \sum_{\alpha\beta} P(\alpha) |\mu_{\alpha\beta}|^2 \delta(E_\alpha + \omega - E_\beta)$$

$$\equiv \mathrm{Re} \int_0^\infty d\tau \langle \mu(0)\mu(\tau)\rangle \exp(i\omega\tau) , \qquad (1)$$

where the transition dipole operator μ is a function of the nuclear coordinates Q,

$$\mu(\tau) \equiv \exp[(i/\hbar)H\tau]\mu \exp[(-i/\hbar)H\tau] , \qquad (2)$$

and

$$\langle \mu(0)\mu(\tau)\rangle = \mathrm{Tr}\,[\mu^\dagger(0)\mu(\tau)\rho_0] . \qquad (3)$$

Here $|\alpha\rangle$ and $|\beta\rangle$ are the eigenstates of the molecular Hamiltonian H and $\langle\mu(0)\mu(\tau)\rangle$ is the intramolecular dipole correlation function. $P(\alpha)$ is the equilibrium population of the $|\alpha\rangle$ state, i.e.,

$$P(\alpha) = \langle \alpha | \rho_0 | \alpha\rangle , \qquad (4)$$

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and ρ_0 is the molecular canonical density matrix

$$\rho_0 = \exp(-H/kT)/\mathrm{Tr}\,\exp(-H/kT) \ . \tag{5}$$

The dipole correlation function [Eq. (3)] may be semi-classically expanded in powers of $\hbar$. To zero order in $\hbar$ we have the classical dipole operator

$$\mu(\tau) \to \mu_c(\tau) \equiv \mu(Q_\tau|Q_0 P_0) \ , \tag{6}$$

where Q_τ is the solution of Hamilton's equations (classical trajectories) with the initial conditions $Q = Q_0$, $P = P_0$ at $\tau = 0$. The classical limit of the correlation function (3) is thus

$$\langle \mu(\tau)\mu(0)\rangle_c = \int dP_0\,dQ_0\,\mu_c(Q_0)\mu_c(Q_\tau|Q_0\,P_0)\rho_c(Q_0,P_0)\ , \tag{7}$$

where ρ_c is the classical distribution function. The Wigner representation[20] allows us to go beyond the classical limit by a systematic $\hbar$ expansion of the Wigner equation of motion, resulting in

$$\langle \mu(\tau)\mu(0)\rangle = \langle \mu(\tau)\mu(0)\rangle_c + \hbar^2\langle \mu(\tau)\mu(0)\rangle_2 + \cdots \ . \tag{8}$$

We shall not consider the higher terms $\langle \mu(\tau)\mu(0)\rangle_2$, etc., here. Marcus and co-workers[12] have extensively developed and applied classical mechanics to obtain the spectra of model Hamiltonians.

The procedure for evaluating semiclassically molecular *optical* spectra involving two electronic states is less straightforward. Here we have two Hamiltonians H_a and H_b corresponding to both potential surfaces and $\mu(\tau)$ in Eq. (3) should be replaced by

$$\mu_{ba}(\tau) = \exp[(i/\hbar)H_b\tau]\mu_{ba}\exp[(-i/\hbar)H_a\tau] \ . \tag{9}$$

The fact that the evolution of μ_{ba} from the right and the left is with different Hamiltonians [unlike Eq. (2)] makes it difficult to define an obvious classical analog to Eq. (9). The problem arises since the electronic degrees of freedom are quantum mechanical (a two-level system) whereas the nuclear ones are treated classically. It is thus not at all obvious how to expand Eq. (9) semiclassically in analogy with Eq. (7). Heller and co-workers[13] have developed a semiclassical theory of molecular scattering and photodissociation, based on propagating classically Gaussian wave packets. Recently they have extended this technique towards the calculation of molecular electronic spectra. For the absorption spectrum they write[13]

$$I(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} d\tau\,\exp(i\omega\tau)\langle\psi(0)\,|\,\psi(\tau)\rangle \ , \tag{10}$$

where $|\psi(0)\rangle$ is the doorway state[21] for the optical transition [$|\psi(0)\rangle = \mu\,|\psi_a\rangle$, $|\psi_a\rangle$ being the initial molecular state] and $|\psi(\tau)\rangle$ is obtained by propagating $|\psi(0)\rangle$ with H_b. Provided $|\psi(0)\rangle$ is Gaussian and the potential in H_b is locally quadratic they give a receipe to obtain $|\psi(\tau)\rangle$ by running classical trajectories on H_b.

It is our purpose in this paper to develop a systematic way for the semiclassical evaluation of molecular electronic spectra using classical trajectories. The basic idea is to express the spectra in terms of a hierarchy of n-time intramolecular correlation functions ϕ^n which have a direct classical analog and may be thus evaluated classically. Our procedure is based on a *double expan-*

sion of the optical spectrum. First an expansion in a coupling strength λ is made and the spectrum is expressed in terms of ϕ^n. We then expand ϕ^n in powers of $\hbar$ and obtain the final semiclassical expansion for the molecular spectrum. The present formulation may be also easily applied to multiphoton processes, e.g., fluorescence and Raman spectra which are two photon processes etc.

In Sec. II we consider the absorption line shape of polyatomic molecules and present the general λ expansion, using an arbitrary zero-order Hamiltonian H_c. We then consider three different choices of H_c, i.e., $H_c = H_a$, $H_c = H_b$, and $H_c = H_s \equiv (H_a + H_b)/2$. In Sec. III we demonstrate the applicability of the present formulation for a simple model Hamiltonian of displaced harmonic surfaces where the line shape problem is analytically solvable. In Sec. IV we extend our expansion towards the evaluation of fluorescence and Raman spectra. Finally in Sec. V we summarize our results.

II. THE CALCULATION OF ELECTRONIC ABSORPTION SPECTRA

We consider a polyatomic molecule with two electronic states, the ground state $|a\rangle$ and an excited state $|b\rangle$. The molecular Hamiltonian within the Born–Oppenheimer approximation is

$$H = |a\rangle\left[H_a(Q) - \frac{i}{2}\gamma_a\right]\langle a| + |b\rangle\left[\omega_{ba} + H_b(Q) - \frac{i}{2}\gamma_b\right]\langle b|\ , \tag{11}$$

where

$$H_a = T_Q + V_a(Q)\ , \tag{12a}$$

and

$$H_b = T_Q + V_b(Q)\ . \tag{12b}$$

Here Q are the nuclear coordinates, T_Q is the nuclear kinetic energy operator, and V_a and V_b are the two adiabatic potential surfaces for the electronic states $|a\rangle$ and $|b\rangle$, respectively. ω_{ba} is the electronic energy difference of the origins of the two surfaces and γ_a and γ_b are the inverse lifetimes of the molecule in both states (which may be radiative or nonradiative in nature). The molecule is assumed to be initially at thermal equilibrium within the $|a\rangle$ electronic state with temperature T, and its density matrix is

$$\rho_0 = \exp(-H_a/kT)/\mathrm{Tr}\,\exp(-H_a/kT)\ . \tag{13}$$

The absorption line shape for our model Hamiltonian is given by[22]

$$I(\Delta) = \mathrm{Re}\int_0^{\infty} d\tau\,\exp[-i\Delta\tau - \tfrac{1}{2}(\gamma_a + \gamma_b)\tau]M^{(2)}(\tau)\ , \tag{14}$$

where $\Delta = \omega - \omega_{ba}$ is the photon detuning from the electronic transition frequency ω_{ba}, μ_{ba} is the electronic transition dipole, and

$$\mu_{ba}(\tau) = \exp[(i/\hbar)H_b\tau]\mu_{ba}\exp[-(i/\hbar)H_a\tau]\ . \tag{15}$$

$M^{(2)}(\tau)$ is the two-time dipole correlation function

$$M^{(2)}(\tau) \equiv \langle\mu_{ab}(0)\mu_{ba}(\tau)\rangle\ , \tag{16}$$

where the correlation function of two operators is defined as

$$\langle AB \rangle \equiv \mathrm{Tr}\,(A^\dagger B \rho_0) \ . \tag{17}$$

Here $\mu_{ba} = D(Q)\,|b\rangle\langle a|$ and $\mu_{ab} = D(Q)\,|a\rangle\langle b|$, where $D(Q)$ is the electronic transition dipole. We assume that $D(Q)$ is normalized such that $\langle D^2 \rangle = 1$. We thus have

$$M^{(2)}(\tau) = \mathrm{Tr}\{D\exp[(i/\hbar)H_b\tau]D\exp[-(i/\hbar)H_a\tau]\rho_0\} \ . \tag{18}$$

We are now in a position to transform Eq. (18) to a form convenient for a semiclassical expansion. It should be emphasized that the semiclassical expansion of Eq. (18) is not unique and depends on our choice of a zero-order Hamiltonian H_c on which the classical trajectories will be finally evaluated. The choice of H_c is formally arbitrary but need to be made using some physical insight. We shall discuss this choice later. For the moment suffice it to write

$$H_c \equiv T_Q + V_c(Q) \ , \tag{19}$$

where $V_c(Q)$ is an arbitrary potential. We shall further introduce the definitions

$$H_a \equiv H_c + \lambda_0 V_{ac}(Q) \ , \tag{20a}$$

$$H_b \equiv H_c + \lambda_0 V_{bc}(Q) \ , \tag{20b}$$

where

$$\lambda_0 V_{ac}(Q) \equiv V_a(Q) - V_c(Q) \ , \tag{21a}$$

$$\lambda_0 V_{bc}(Q) \equiv V_b(Q) - V_c(Q) \ , \tag{22b}$$

and where λ_0 is a dimensionless parameter introduced for bookkeeping purposes; at the end we set $\lambda_0 = 1$. It is clear that when $\lambda_0 = 0$, then $H_a = H_b$ and if in addition we set $\gamma_a = \gamma_b = 0$ we get

$$I(\Delta) = \pi\delta(\Delta) \ . \tag{22}$$

λ_0 is thus a measure of the coupling of the electronic and nuclear degrees of freedom which is responsible for the line broadening in the present model.

We now make use of the following identities:

$$\exp\left(-\frac{i}{\hbar}H_a\tau\right) = \exp\left(-\frac{i}{\hbar}H_c\tau\right)\exp_+\left[-i\lambda\int_0^\tau d\tau_1 V_{ac}(\tau_1)\right], \tag{23}$$

$$\exp(iH_b\tau) = \exp_-\left[i\lambda\int_0^\tau d\tau_1 V_{bc}(\tau_1)\right]\exp\left(\frac{i}{\hbar}H_c\tau\right) \ , \tag{24}$$

where

$$A(\tau_1) \equiv \exp[(i/\hbar)H_c\tau_1]\,A\,\exp[-(i/\hbar)H_c\tau_1] \ ,$$

$$A = V_{ac}, V_{bc}, D \ , \tag{25}$$

$$\lambda = \lambda_0/\hbar \ . \tag{26}$$

The positive and negative time ordered exponentials $\exp_+$ and $\exp_-$ are defined as follows[23]:

$$\exp_-\left[i\int_0^\tau d\tau_1 A(\tau_1)\right] \equiv 1 + i\int_0^\tau d\tau_1 A(\tau_1)$$
$$+ (i)^2\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2 A(\tau_2)A(\tau_1) + \cdots \tag{27}$$

and

$$\exp_+\left[-i\int_0^\tau d\tau_1 A(\tau)\right] \equiv 1 - i\int_0^\tau d\tau_1 A(\tau_1)$$
$$+ (-i)^2\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2 A(\tau_1)A(\tau_2) + \cdots \ . \tag{28}$$

We then have, upon substitution of Eq. (23) and Eq. (24) in Eq. (18)

$$M^{(2)}(\tau) = \left\langle D(0)\exp_-\left[i\lambda\int_0^\tau d\tau_1 V_{bc}(\tau_1)\right]D(\tau) \right.$$
$$\left. \times \exp_+\left[-i\lambda\int_0^\tau d\tau_1 V_{ac}(\tau_1)\right]\right\rangle \ . \tag{29}$$

We next introduce the ansatz

$$M^{(2)}(\tau) = \exp[i\lambda m^{(1)}(\tau) + (i\lambda)^2 m^{(2)}(\tau) + \cdots] \ . \tag{30}$$

The various terms $m^{(1)}(\tau)$, $m^{(2)}(\tau)$, etc. may be obtained by expanding Eqs. (29) and (30) in λ and comparing term by term. The result is

$$m^{(1)}(\tau) = \int_0^\tau d\tau_1[\langle D(0)V_{bc}(\tau_1)D(\tau)\rangle - \langle D(0)D(\tau)V_{ac}(\tau_1)\rangle] \ , \tag{31a}$$

$$m^{(2)}(\tau) = \int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2[\langle D(0)V_{bc}(\tau_2)V_{bc}(\tau_1)D(\tau)\rangle + \langle D(0)D(\tau)V_{ac}(\tau_1)V_{ac}(\tau_2)\rangle]$$
$$- \int_0^\tau d\tau_1\int_0^\tau d\tau_2\,\langle D(0)V_{bc}(\tau_1)D(\tau)V_{ac}(\tau_2)\rangle - \tfrac{1}{2}[m^{(1)}(\tau)]^2 \ , \tag{31b}$$

$$m^{(3)}(\tau) = \int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2\int_0^{\tau_2} d\tau_3[\langle D(0)V_{bc}(\tau_3)V_{bc}(\tau_2)V_{bc}(\tau_1)D(\tau)\rangle - \langle D(0)D(\tau)V_{ac}(\tau_1)V_{ac}(\tau_2)V_{ac}(\tau_3)\rangle]$$
$$- \int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2\int_0^\tau d\tau_3\,[\langle D(0)V_{bc}(\tau_2)V_{bc}(\tau_1)D(\tau)V_{ac}(\tau_3)\rangle - \langle D(0)V_{bc}(\tau_3)D(\tau)V_{ac}(\tau_1)V_{ac}(\tau_2)\rangle]$$
$$- \tfrac{1}{6}[m^{(1)}(\tau)]^3 - m^{(1)}(\tau)m^{(2)}(\tau) \ . \tag{31c}$$

$$\vdots$$

etc.

Equations (30) and (31) provide us with a convenient starting point for a semiclassical expansion of the absorption line shape. The relevant molecular information is put in the form of the hierarchy of *intramolecular correlation functions* of V_{ac} and V_{bc} [Eqs. (31)]. The

choice of H_c is formally completely arbitrary but the usefulness of the expansion (31) and our ability to truncate it at low order is crucially dependent on that choice. To demonstrate the type of flexibility that the present formulation gives us, let us consider now three explicit

choices of H_c, i.e., $H_c = H_a$, $H_c = H_b$, and $H_c = H_s \equiv (H_a + H_b)/2$. In all three choices we are left with self-correlation functions of the operator

$$\lambda_0 U \equiv V_b - V_a \ . \tag{32}$$

We shall see that the resulting expansions, when truncated at any finite order, will depend on the choice of H_c. If, however, U is small enough, then all three choices will be practically equivalent. For simplifying the forthcoming manipulations we shall hereafter assume that $D(Q)$ is weakly dependent on Q so that we may set $D(0) = D(\tau) = 1$ in Eqs. (31). This assumption is usually justified and arises from the weak dependence of the electronic wave functions on nuclear coordinates (The Franck–Condon principle). As is seen from Eqs. (31) the generalization to the case when $D(Q)$ depends on Q is straightforward.

A. Expansion around H_a

Choosing $H_c = H_a$ we have

$$V_{ac} = 0 \ , \tag{33a}$$

$$\lambda_0 V_{bc} = \lambda U = V_b - V_a \ . \tag{33b}$$

Defining

$$U_a(\tau) = \exp(iH_a\tau)\, U \exp(-iH_a\tau) \tag{34}$$

we get

$$M^{(2)}(\tau) = \exp[i\lambda m_a^{(1)}(\tau) + (i\lambda)^2 m_a^{(2)}(\tau) + \cdots] \ . \tag{35}$$

Using Eqs. (31) and (35) we then get

$$m_a^{(1)} = \int_0^\tau d\tau_1 \langle U_a(\tau_1)\rangle = \langle U_a\rangle \tau \ . \tag{36}$$

The last equality holds since H_a commutes with ρ_0. Without loss of generality we may then modify ω_{ba} to include $\langle U_a\rangle$ and take $\langle U_a\rangle = 0$. We then get

$$m_a^{(1)} = 0 \ , \tag{37a}$$

$$m_a^{(2)} = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \, \langle U_a(\tau_2)U_a(\tau_1)\rangle$$

$$= \int_0^\tau d\tau_1\, (\tau - \tau_1)\langle U_a(0)U_a(\tau_1)\rangle \ , \tag{37b}$$

$$m_a^{(3)} = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \, \langle U_a(\tau_3)U_a(\tau_2)U_a(\tau_1)\rangle \ , \tag{37c}$$

where

$$\langle U_a(\tau_1)U_a(\tau_2)\cdots U_a(\tau_n)\rangle$$
$$\equiv \mathrm{Tr}\,[U_a(\tau_1)U_a(\tau_2)\cdots U_a(\tau_n)\rho_0] \ . \tag{38}$$

B. Expansion around H_b

Alternatively we may choose $H_c \equiv H_b$. We then have

$$V_{bc} = 0 \ , \tag{39a}$$

$$\lambda_0 V_{ac} = -\lambda_0 U = V_a - V_b \ , \tag{39b}$$

$$U_b(\tau) = \exp(iH_b\tau)\, U \exp(-iH_b\tau) \ . \tag{40}$$

Equation (30) then assumes the form

$$M^{(2)}(\tau) = \exp[i\lambda m_b^{(1)} + (i\lambda)^2 m_b^{(2)} + \cdots] \ , \tag{41}$$

where

$$m_b^{(1)} = \int_0^\tau d\tau_1 \langle U_b(\tau_1)\rangle \tag{42a}$$

$$m_b^{(2)} = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 [\langle U_b(\tau_1)U_b(\tau_2)\rangle - \langle U_b(\tau_1)\rangle\langle U_b(\tau_2)\rangle] \ . \tag{42b}$$

C. Expansion around $(H_a + H_b)/2$

A more symmetric expansion, which treats H_a and H_b along the same footing, is obtained by the choice

$$H_c \equiv H_s \equiv (H_a + H_b)/2 \ , \tag{43}$$

i.e., we set

$$\lambda_0 V_{ac} = -\tfrac{1}{2}\lambda_0 U = V_a - V_c \ , \tag{44a}$$

$$\lambda_0 V_{bc} = \tfrac{1}{2}\lambda_0 U = V_b - V_c \ , \tag{44b}$$

$$U_s(\tau) = \exp(iH_s\tau)\, U \exp(-iH_s\tau) \ . \tag{45}$$

Introducing the *ansatz*

$$M^{(2)}(\tau) = \exp[i\lambda m_s^{(1)} + (i\lambda)^2 m_s^{(2)} + \cdots] \ , \tag{46}$$

and using Eqs. (31) we get

$$m_s^{(1)} = \int_0^\tau d\tau_1 \langle U_s(\tau_1)\rangle \ , \tag{47a}$$

$$m_s^{(2)} = \frac{1}{2}\int_0^\tau d\tau_1 \int_0^\tau d\tau_2 [\langle U_s(\tau_1)U_s(\tau_2)\rangle$$

$$- \langle U_s(\tau_1)\rangle\langle U_s(\tau_2)\rangle] \ . \tag{47b}$$

To summarize this section we note that we were able to express the electronic absorption line shape of polyatomic molecules in terms of a hierarchy of intramolecular correlation functions

$$\phi^n(\tau_1, \tau_2, \ldots, \tau_n) \equiv \langle V_\alpha(\tau_1)V_\beta(\tau_2)\cdots V_\gamma(\tau_n)\rangle \ ,$$
$$n = 1, 2 \ldots, \quad \alpha, \beta, \ldots, \gamma = ac, bc \ , \tag{48}$$

where

$$V_\alpha(\tau) = \exp(iH_c\tau)V_\alpha \exp(-iH_c\tau) \tag{49}$$

and H_c is a chosen zero-order Hamiltonian. This goal was achieved in the following steps:

(1) The absorption cross section was written in terms of the two-time dipole correlation function $M^{(2)}(\tau)$ [Eq. (14)].

(2) $M^{(2)}$ was expanded using time-ordered exponential functions around a chosen zero-order Hamiltonian H_c [Eq. (19)].

(3) An *ansatz* was introduced which expressed $M^{(2)}$ as an exponential of a power series in λ and the various terms m_α [Eqs. (30)] were calculated by comparing the *ansatz*, term by term, with the time-ordered exponential expansion [Eq. (29)].

As a result, the dipole correlation functions $M^{(2)}$ were expressed in terms of the correlation functions of V_α, Φ^n [Eq. (48)]. Unlike $\mu_{ba}(\tau)$ whose time evolution from the left and from the right is governed by different Hamiltonians [Eq. (15)], $V_\alpha(\tau)$ evolves in time according

to our chosen zero-order Hamiltonian H_c [Eq. (25)]. Consequently, $V_\alpha(\tau)$ has a straightforward semiclassical expansion whose leading term is the classical one, exactly as was done in the introduction, for infrared spectra. For the particular choices $c = a$, b, or s we need only self-correlation functions of $\lambda_0 U \equiv V_b - V_a$, i.e.,

$$\Phi_\alpha^n(\tau_1, \tau_2, \ldots, \tau_n) \equiv \langle U_\alpha(\tau_1) U_\alpha(\tau_2) \cdots U_\alpha(\tau_n) \rangle$$

$$\equiv \mathrm{Tr}\left[U_\alpha(\tau_1) U_\alpha(\tau_2) \cdots U_\alpha(\tau_n) \rho_0 \right],$$

$$n = 1, 2 \ldots, \quad \alpha = a, b, s \ , \quad (50a)$$

where

$$U_\alpha(\tau) = \exp(iH_\alpha \tau) U \exp(-iH_\alpha \tau) \ . \quad (50b)$$

The classical limit of ϕ^n is a straightforward generalization of Eq. (48), i.e.,

$$\phi_c^n(\tau_1, \ldots, \tau_n) = \int dP_0 \, dQ_0 \, V_\alpha(Q_{\tau_1} | Q_0 P_0) V_\beta(Q_{\tau_2} | Q_0 P_0) \cdots$$

$$V_\gamma(Q_{\tau_n} | Q_0 P_0) \rho_c(Q_0, P_0) \ , \quad (51)$$

where Q_τ, P_τ are the solutions of Hamilton's equations (10) with the Hamiltonian H_c. Using Eq. (51) we are able to evaluate the cross sections for photon absorption, using classical trajectories. All we have to do is to choose enough points P_0, Q_0 to sample ρ_0, solve Hamilton's equations for P_t, Q_t and using $H = H_c$, and perform the integration (51) to obtain Φ^n. The latter are then substituted in Eqs. (30) and (31) to obtain the absorption spectrum. If we wish to go beyond the fully classical limit [i.e., to expand the rhs of Eq. (50) to higher order in $\hbar$] we have to solve the Wigner equation of motion for $V_\alpha(\tau)$.[20] Our final expressions for the molecular line shape thus involve a double expansion: an expansion in λ to obtain Φ^n and then a semiclassical expansion of Φ^n in powers of $\hbar$. An important question which we have not yet discussed is the choice of the zero-order Hamiltonian H_c ($c = a$, b, s or any other choice). As a rule, H_c is treated nonperturbatively, whereas λV_{ac} and λV_{bc} are treated perturbatively, and the different expansions put the emphasis on a different H_c.

Formally it is most convenient to expand around H_a [i.e., to use Eqs. (37)], since H_a commutes with ρ_0 [Eq. (13)] and $\rho_0(\tau) = \rho_0(0)$. As a result, one time variable may be eliminated from Φ_a^n which are invariant to translation in time. Physically, however, when considering the absorption spectrum of a supercooled large molecule,[3-5] we expect the spectrum to be mostly determined by H_b. H_a is important only for determining ρ_0. It is thus desirable to expand around H_b in this case and use Eqs. (42). It is interesting to note that in the wave packet formalism of Heller[13] the trajectories are calculated on H_b, whereas here we have the formal flexibility to choose our zeroth order Hamiltonian on which the trajectories are calculated.

III. A SOLVABLE EXAMPLE—LINEARLY DISPLACED HARMONIC SURFACES

In order to demonstrate the formalism developed in Sec. II let us consider the following illustrative example of a simple harmonic oscillator which is linearly dis-

placed between the two potential surfaces. We thus take the following Hamiltonians:

$$H_a = P^2/2m + \tfrac{1}{2} m\omega^2 Q^2 \ , \quad (52a)$$

and

$$H_b = P^2/2m + \tfrac{1}{2} m\omega^2(Q^2 + 2QQ_0) \ , \quad (52b)$$

so that

$$\lambda_0 U \equiv H_b - H_a = m\omega^2 Q_0 Q \ . \quad (53)$$

Here H_a and H_b describe an harmonic oscillator with coordinate Q, momentum P, and frequency ω, whose equilibrium position is displaced by an amount Q_0 between the two surfaces. For the sake of convenience we shall introduce the dimensionless coordinate displacement

$$\alpha \equiv \sqrt{(m\omega/\hbar)} \, Q_0 \ . \quad (54)$$

The *exact* quantum mechanical line shape for this model Hamiltonian is given by[24]

$$I(\Delta) = \mathrm{Re} \int_0^\infty d\tau \exp[-i\Delta\tau - \gamma\tau - g(\tau)] \ , \quad (55)$$

where

$$\gamma = \tfrac{1}{2}(\gamma_a + \gamma_b) \ , \quad (56)$$

$$\langle U_a(0) U_a(\tau) \rangle_Q$$

$$= \frac{\hbar^2 \omega^2 \alpha^2}{2} \left[(\bar{n} + 1) \exp(i\omega\tau) + \bar{n} \exp(-i\omega\tau) \right] \ , \quad (57)$$

and

$$g_Q(\tau) = \frac{1}{\hbar^2} \int_0^\tau d\tau_1 (\tau - \tau_1) \langle U_a(0) U_a(\tau) \rangle_Q$$

$$= \frac{\alpha^2}{2} \{ (\bar{n} + 1)[\exp(i\omega\tau) - 1 - i\omega\tau]$$

$$+ \bar{n}[\exp(-i\omega\tau) - 1 + i\omega\tau] \} \ . \quad (58)$$

The subscript Q denotes that this is the exact quantum correlation function. Here $\bar{n}$ is the mean occupation number of the oscillator at temperature T, i.e.,

$$\bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1} \ , \quad (59a)$$

and the mean energy of the oscillator is

$$\langle E \rangle = \hbar\omega(\bar{n} + \tfrac{1}{2}) \ . \quad (59b)$$

Note that for this model the expansion of Eq. (35) to second order in λ is the *exact* solution of the line shape. Upon substitution of Eq. (58) in (55) and performing the integration we finally get[25]

$$I_Q(\Delta) = \exp[-\alpha^2(\bar{n} + \tfrac{1}{2})] \sum_{N=-\infty}^\infty \exp\left[\frac{N\hbar\omega}{2kT}\right]$$

$$\times I_N[\alpha^2 \sqrt{\bar{n}(\bar{n}+1)}] \frac{\gamma}{(\Delta - N\omega)^2 + \gamma^2} \ , \quad (60)$$

where $I_N(Z)$ is the modified Bessel function.[26] Using our classical approach of Sec. II and Eq. (51) we have

$$\langle U_a(0) U_a(\tau) \rangle_c = (m\omega^2 Q_0)^2 \langle Q(0) Q(\tau) \rangle_c \ , \quad (61)$$

where for our Hamiltonian (52):

$$Q(\tau) = \sqrt{(2E/m\omega^2)} \cos(\omega\tau + \phi) \quad (62)$$

and

$$\langle Q(0)Q(\tau)\rangle_c = \frac{2E}{m\omega^2}\frac{1}{2\pi}\int_0^{2\pi} d\phi \cos\phi \cos(\omega\tau+\phi) \ . \quad (63)$$

Upon performing the integration in Eq. (63) and substituting in Eq. (61) we finally get

$$\langle U_a(0)U_a(\tau)\rangle_c = \hbar^2\omega^2\alpha^2(\bar{n}+\tfrac{1}{2})\cos\omega\tau \ , \quad (64)$$

so that

$$g_c(\tau) \equiv \frac{1}{\hbar^2}\int_0^\tau d\tau_1(\tau-\tau_1)\langle U_a(0)U_a(\tau_1)\rangle_c$$

$$= \alpha^2(\bar{n}+\tfrac{1}{2})(\cos\omega\tau-1) \ . \quad (65)$$

Equation (65) when substituted in Eq. (55) results in

$$I_c(\Delta) = \exp[-\alpha^2(\bar{n}+\tfrac{1}{2})]$$

$$\times \sum_{N=-\infty}^\infty I_N[\alpha^2(\bar{n}+\tfrac{1}{2})]\frac{\gamma}{(\Delta-N\omega)^2+\gamma^2} \ . \quad (66)$$

Upon comparing Eqs. (60) and (66) we may evaluate the validity and usefulness of the latter. The following points should be made at this stage:

(1) The present Hamiltonian [Eqs. (52)] is particularly simple so that the expansion of $M^{(2)}$ [Eq. (35)] to second order in λ is the *exact* solution of the problem. Moreover, in this case all three expansions [Eqs. (35), (41), and (46)] are identical.

(2) Both spectra Eqs. (60) and (66) consist of a progression of equally spaced lines at frequencies $\Delta = N\omega$. The classical spectrum [Eq. (66)] is symmetric, i.e.,

$$I_c(\Delta) = I_c(-\Delta) \quad (67a)$$

[we note that $I_N(Z) = I_{-N}(Z)$].[26] The exact quantum spectrum, on the other hand, satisfies in this case the relation

$$I_Q(-\Delta) = \exp(-\hbar\Delta/kT)I_Q(\Delta) \ . \quad (67b)$$

Equation (67b) should not be confused with the more fundamental fluctuation–dissipation relation[22] which states that the imaginary part of any linear-response function $\chi''(\omega)$ satisfies

$$\chi''(-\omega) = \exp(-\hbar\omega/kT)\chi''(\omega) \ . \quad (67c)$$

Equation (67c) is a basic relation which holds regardless of the nature of the system. In contrast to Eq. (67c), there is not in general any simple relation between $I(\Delta)$ and $I(-\Delta)$, where $\Delta \equiv \omega - \omega_{ba}$. This arises since different Franck–Condon factors contribute for positive and negative Δ. Equation (67b) is a *pure coincidence* which holds for the simple case when V_a and V_b are displaced harmonic potentials. Otherwise it does not hold. In fact, even if we take V_a and V_b to be harmonic but with different frequencies Eq. (67b) no longer holds. This is unfortunate since Eq. (67c) is often used to get better classical approximations for response functions.[22] In our case of electronic spectra $\omega_{ba} \gg kT$ under ordinary

conditions so that $\chi''(-\omega) \to 0$ and Eq. (67c) is not useful.

(3) At high temperatures $kT \gg N\hbar\omega$ for the relevant values of N, we may replace $\bar{n}$ and $\bar{n}+1$ in I_Q by $\bar{n}+\tfrac{1}{2}$ and $I_Q(\Delta) \to I_c(\Delta)$. This behavior is expected for any classical theory according to the correspondence principle.

(4) As $T \to 0$ and for $\alpha < 1$ we have

$$\bar{n} = \exp(-\hbar\omega/kT) \quad (68a)$$

and[26]

$$I_N(Z) \sim (\tfrac{1}{2}Z)^N/N! \ , \quad Z \to 0 \ , \quad N > 0 \ . \quad (68b)$$

Upon substitution of Eqs. (68) in Eqs. (60) and (66) we get

$$I_Q(\Delta) = \exp(-\tfrac{1}{2}\alpha^2)\sum_{N=0}^\infty \frac{(\tfrac{1}{2}\alpha^2)^N}{N!}\frac{\gamma}{(\Delta-N\omega)^2+\gamma^2} \ , \quad (69a)$$

and

$$I_c(\Delta) = \exp(-\tfrac{1}{2}\alpha^2)\sum_{N=-\infty}^\infty \frac{(\tfrac{1}{4}\alpha^2)^N}{N!}\frac{\gamma}{(\Delta-N\omega)^2+\gamma^2} \ . \quad (69b)$$

This is the case when the classical approximation is the worst and $I_c(\Delta)$ differs substantially from $I_Q(\Delta)$.

(5) The present Hamiltonian Eqs. (52) may be easily generalized to more dimensions where we have s displaced harmonic oscillators. In this case Eq. (55) still holds but with the straightforward generalization

$$\langle U_a(0)U_a(\tau)\rangle_Q = \sum_{\nu=1}^s \frac{\hbar^2\omega_\nu^2\alpha_\nu^2}{2}[(\bar{n}_\nu+1)\exp(i\omega_\nu\tau)$$

$$+ \bar{n}_\nu\exp(-i\omega_\nu\tau)] \ , \quad (70a)$$

$$\langle U_a(0)U_a(\tau)\rangle_c = \sum_{\nu=1}^s \hbar^2\omega_\nu^2\alpha_\nu^2(\bar{n}_\nu+\tfrac{1}{2})\cos\omega_\nu\tau \ . \quad (70b)$$

The line shape will consist in this case of all possible combinations and overtones of the various frequencies ω_s instead of the single progression of Eqs. (60) and (66).

IV. THE CALCULATION OF TWO-PHOTON PROCESSES—FLUORESCENCE AND RAMAN SPECTRA

In Sec. II we have treated the problem of ordinary absorption spectra (single-photon processes) and our starting point was the two-time dipole correlation function. For higher order processes involving more photons we need consider higher order correlation functions of the dipole operator. In general, when considering multiphoton processes with n photons we need a $2n$-time correlation function of the dipole operator. (The amplitude for the process is of nth order in μ and the cross section is $2n$th order.[18]) A fluorescence (Raman) photon scattering process is a two-photon process whereby a photon ω_1 is being absorbed and a photon ω_2 is being scattered. Its cross section (up to a proportionality constant) is given in terms of the four-time dipole correlation function $M^{(4)}(t_1, t_2, t_3)$,[27-29] i.e.,

$$I(\Delta_1, \Delta_2) = \text{Re}\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3[\chi^{(4)}(\tau_1+\tau_2+\tau_3, \tau_2+\tau_3, \tau_3) + \chi^{(4)}(\tau_2+\tau_3, \tau_1+\tau_2+\tau_3, \tau_3) + \chi^{(4)}(\tau_3, \tau_1+\tau_2+\tau_3, \tau_2+\tau_3)] \ ,$$

$$(71)$$

where

$$\chi^{(4)}(t_1, t_2, t_3) = \exp[-i\Delta_2(t_1 - t_2) - i\Delta_1 t_3$$
$$-\tfrac{1}{2}\gamma_a t_3 - \tfrac{1}{2}\gamma_b(t_1 + t_2 - t_3)$$
$$-\tfrac{1}{2}\gamma_c |t_1 - t_2|\,]\cdot M^{(4)}(t_1, t_2, t_3) , \quad (72)$$

and

$$M^{(4)}(t_1, t_2, t_3) \equiv \langle \mu_{ab}(0)\mu_{ba}(t_1)\mu_{ab}(t_2)\mu_{ba}(t_3)\rangle . \quad (73)$$

Here Δ_1 and Δ_2 are the detunings of the incident and scattered photons, i.e.,

$$\Delta_1 = \omega_1 - \omega_{ba} , \quad (74a)$$

$$\Delta_2 = \omega_2 - \omega_{ba} . \quad (74b)$$

Also,

$$\mu_{ba}(\tau) = \exp(iH_b\tau)|b\rangle\langle a| \exp(-iH_a\tau) , \quad (75a)$$

and

$$\mu_{ab}(\tau) = \exp(iH_a\tau)|a\rangle\langle b| \exp(-iH_b\tau) . \quad (75b)$$

The evaluation of the fluorescence spectrum thus reduces to the evaluation of the four-time dipole correlation function $M^{(4)}$ [Eq. (73)] which may be alternatively written in the form

$$M^{(4)}(t_1, t_2, t_3) = \mathrm{Tr}\,\{\exp(iH_b t_1)\exp[iH_a(t_2 - t_1)]$$
$$\times \exp[iH_b(t_3 - t_2)]\exp(-iH_a t_3)\rho_0\} . \quad (76)$$

Equation (72) may be derived[29] using the tetradic scattering formalism in Liouville space.[30,31] The first two terms in Eq. (72) correspond to incoherent scattering whereas the third corresponds to a coherent scattering process. The evaluation of Eq. (76) proceeds along the same lines developed for the two-time correlation function. We have to choose a zero-order Hamiltonian H_c and expand each exponential appearing in Eq. (76) around it using Eqs. (23) and (24). We shall first choose H_a as our zero-order Hamiltonian. To that end we expand the $\exp(iH_b)$ factors appearing in Eq. (76) using Eq. (24) and obtain

$$M^{(4)}(t_1, t_2, t_3) = \Big\langle \exp_-\Big[i\lambda \int_0^{t_1} d\tau U_a(\tau)\Big]$$
$$\times \exp_-\Big[i\lambda \int_{t_2}^{t_3} d\tau U_a(\tau)\Big]\Big\rangle . \quad (77)$$

Alternatively we may expand around H_b. This is done by expanding the $\exp(iH_a\tau)$ factors in Eq. (76) using Eq. (23), resulting in

$$M^{(4)}(t_1, t_2, t_3) = \Big\langle \exp_+\Big[-i\lambda \int_{t_2}^{t_1} d\tau U_b(\tau)\Big]$$
$$\times \exp_+\Big[-i\lambda \int_0^{t_3} d\tau U_b(\tau)\Big]\Big\rangle , \quad (78)$$

where $U_a(\tau)$, $U_b(\tau)$ are given by Eqs. (34) and (40). The expansions (77) or (78) are obviously not the only choices. We may, for example, also expand Eq. (76) around H_s, but the number of terms appearing in this case will be larger which makes it less convenient. Equations (77) or (78) are our starting points for the further expansions. Using the ansatz

$$M^{(4)}(t_1, t_2, t_3) = \exp[i\lambda k_a^{(1)} + (i\lambda)^2 k_a^{(2)} + \cdots] \quad (79)$$

and comparing with Eq. (77) we get

$$k_a^{(1)} = \langle U_a\rangle(t_1 + t_3) . \quad (80)$$

As before [Eqs. (37)] we may choose $\langle U_a\rangle = 0$ (without loss of generality) so that

$$k_a^{(1)} = 0 , \quad (81a)$$

and

$$k_a^{(2)} = \int_0^{t_1} d\tau' \int_0^{\tau'} d\tau'' \langle U_a(\tau'')U_a(\tau')\rangle$$
$$+ \int_{t_2}^{t_3} d\tau' \int_{t_2}^{\tau'} d\tau'' \langle U_a(\tau'')U_a(\tau')\rangle$$
$$+ \int_0^{t_1} d\tau' \int_{t_2}^{t_3} d\tau'' \langle U_a(\tau')U_a(\tau'')\rangle. \quad (81b)$$

Similarly, we may use the alternative form [Eq. (78)] to get the following expansion for $M^{(4)}$:

$$M^{(4)}(t_1, t_2, t_3) = \exp[i\lambda k_b^{(1)} + (i\lambda)^2 k_b^{(2)} + \cdots] , \quad (82)$$

where

$$k_b^{(1)} = -\int_{t_2}^{t_1} d\tau \langle U_b(\tau)\rangle - \int_0^{t_3} d\tau \langle U_b(\tau)\rangle , \quad (83a)$$

$$k_b^{(2)} = \int_{t_2}^{t_1} d\tau' \int_{t_2}^{\tau'} d\tau'' \langle U_b(\tau')U_b(\tau'')\rangle$$
$$+ \int_0^{t_3} d\tau' \int_0^{\tau'} d\tau'' \langle U_b(\tau')U_b(\tau'')\rangle$$
$$+ \int_{t_2}^{t_1} d\tau' \int_0^{t_3} d\tau'' \langle U_b(\tau')U_b(\tau'')\rangle - \tfrac{1}{2}[k_b^{(1)}]^2 . \quad (83b)$$

The same intramolecular correlation functions ϕ_a^n that entered the calculation of $M^{(2)}$ in Sec. II will now enter in the evaluation of $M^{(4)}$ and their semiclassical analog is the same as discussed in the previous section. We have thus obtained a classical approximation for the fluorescence spectra of polyatomic molecules.

Making use of the translational invariance of $\langle U_a(\tau'')U_a(\tau')\rangle$ we may rearrange $k_a^{(2)}$ in the form

$$k_a^{(2)} = g(t_1) + g(t_3) - g(t_2) + g(t_3 - t_2) - g(t_3 - t_1) + g(t_2 - t_1) , \quad (84)$$

where

$$g(\tau) \equiv \int_0^\tau d\tau_1(\tau - \tau_1)\langle U_a(0)U_a(\tau)\rangle . \quad (85)$$

Using the model Hamiltonian introduced in Sec. III we then have the exact solution of $M^{(4)}(t_1, t_2, t_3)$[27-29]:

$$M^{(4)}(t_1, t_2, t_3) = \exp[-g(t_1) - g(t_3) + g(t_2) - g(t_3 - t_2)$$
$$+ g(t_3 - t_1) - g(t_2 - t_1)] , \quad (86)$$

where quantum mechanically we have

$$g_Q(\tau) = \sum_{\nu=1}^s \frac{\hbar^2\alpha_\nu^2}{2}\{(\bar{n}_\nu + 1)[\exp(i\omega_\nu\tau) - 1 - i\omega_\nu\tau]$$
$$+ \bar{n}_\nu[\exp(-i\omega_\nu\tau) - 1 + i\omega_\nu\tau]\} \quad (87a)$$

or classically

$$g_c(\tau) = \sum_{\nu=1}^s \hbar^2\alpha_\nu^2(\bar{n}_\nu + \tfrac{1}{2})(\cos \omega_\nu\tau - 1) . \quad (87b)$$

V. SUMMARY

In this paper we have considered the problem of the semiclassical evaluation of molecular electronic spectra either in absorption or in fluorescence. We have shown how techniques, originally developed for collisional broadening of spectral lines[32] may be used for the treatment of intramolecular line broadening. Our main results may be summarized as follows:

(1) The molecular information relevant for the evaluation of the electronic spectra was put in the form of a hierarchy of intramolecular correlation functions ϕ^n [Eq. (48)] or ϕ_α^n [Eq. (50)] which have well defined classical analogs.

(2) We have shown that the classical $(\hbar \to 0)$ limit of the quantum mechanical spectrum is not unique. In fact, we were able to write the exact quantum spectrum in several equivalent forms which yielded a different limit when we set $\hbar \to 0$. This arises since in this case the electronic degrees of freedom are treated quantum mechanically (a two-level system) and the classical limit is taken for the nuclear motions only. Therefore, the classical limit still contains some quantum character which depends on the way we perform the limit $\hbar \to 0$. We have shown how the spectra in the classical limit are obtained by running classical trajectories and performing ensemble averages using a zero-order Hamiltonian H_c whose free choice is a reflection of the nonuniqueness of the classical limit. We should note however that when $V_b - V_a$ is sufficiently small then the semiclassical spectra will not depend heavily on the choice of H_c and the three choices made in Sec. II (i.e., $H_c = H_a$, $H_c = H_b$, and $H_c = (H_a + H_b)/2$) will yield practically identical results for $I(\Delta)$.

(3) The present formalism may be used to study systematically the interrelation between the quantum mechanical and the classical calculations of molecular spectra. In particular, the question of quantum vs classical stochasticity may be directly attacked using this approach.

(4) The evaluation of cross sections for n photon processes $(n > 2)$ is a straightforward generalization of our present equations. In general, for an n photon process we need $M^{(2n)}(\tau_1, \tau_2, \ldots, \tau_{2n})$ ($M^{(2)}$ and $M^{(4)}$ considered here are special cases of one and two photon processes respectively).[18] Any $M^{(2n)}$ may be expanded in a similar way we did for $M^{(4)}$ in terms of the same quantities ϕ^n [Eq. (48)]. The classical evaluation of the latter proceeds then along the lines developed in the present work.

Note added in proof: The expansions presented in Sec. II [Eqs. (37), (42), or (47)] enable us to go beyond the semiclassical limit using the Wigner representation.[20] If we truncate the expansions to lowest order in $\hbar$ [Eq. (51)], we may do it on Eq. (29) directly resulting in $M^{(2)}(\tau) = \langle D(0) D(\tau) \exp[i\lambda \int_0^\tau d\tau_1 U(\tau_1)] \rangle$, where the time evolution of $U(\tau)$ is made using the arbitrarily chosen Hamiltonian H_c [Eq. (25)]. The last expression may be used to calculate $M^{(2)}(\tau)$ directly without performing any λ expansion.[32] This demonstrates clearly how the semiclassical limit of $M^{(2)}(\tau)$ is not unique and depends on the choice of H_c. In the extreme classical limit we ignore the kinetic energy in the Hamiltonian altogether and Eq. (18) gives $M^{(2)}(\tau) = \langle D(0) D(0) \exp(iU \cdot \tau) \rangle$. No dynamics is required for the evaluation of $M^{(2)}(\tau)$ in this case.

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