

CHAPTER XII

REDUCED EQUATIONS OF MOTION FOR MOLECULAR LINESHAPES AND SEMICLASSICAL DYNAMICS IN LIOUVILLE SPACE

SHAUL MUKAMEL* and YI JING YAN

*Department of Chemistry, University of Rochester, Rochester, New York,
14627*

CONTENTS

- I. Introduction
- II. Time Evolution in Liouville Space
- III. Reduced Equations of Motion for Molecular Electronic Spectroscopy
- IV. Semiclassical Calculation of the Density Matrix and the Time-Dependent Self-Consistent Field (Hartree) Approximation
- V. Discussion
- VI. Absorption and Raman Excitation Profiles of Anharmonic Molecules
- Appendix: The Generating Function in the Coordinate Representation
- References

Reduced equations of motion (REM) for semiclassical dynamics in Liouville space, which may be used in the calculation of intramolecular and intermolecular dynamics, correlation functions, and electronic lineshapes, are developed. The method is based on constructing a Gaussian propagator whose equations of motion are obtained by requiring that the first two moments of the coordinates and momenta have the exact time evolution. The present method can be applied for the time evolution of mixed states in phase space and may therefore be particularly useful for molecular processes in condensed phases. The absorption lineshapes and Raman excitation profiles of model anharmonic molecules at finite temperatures are calculated as a demonstration.

*Camille and Henry Dreyfus Teacher-Scholar.

I. INTRODUCTION

Much of the current effort in semiclassical molecular dynamics is focused on the development of efficient methods for the numerical solution of the Schrödinger equation for interacting many-body systems [1–18]. The calculation of molecular dynamical processes such as energy transfer, vibrational relaxation, scattering processes, and spectral lineshapes [19, 20] depends crucially on the development of suitable approximate methods for propagating the molecular wavefunction. Some of the methods commonly used include the path integral formalism [4–8] grid methods [9] and wavepacket dynamics [12–18]. Performing dynamical calculations in Liouville space [21] using the density matrix (instead of the wavefunction) offers a major theoretical challenge. The connection between classical and quantum mechanics is much more transparent in phase space, particularly if we make use of the Wigner representation [22–24], which allows for a systematic expansion of the dynamics in powers of \hbar . However, this formal elegance carries a price tag. The dimensionality of phase space is twice that of the configuration space. When the wavefunction can be represented by n coefficients corresponding to some basis set, the density matrix will require n^2 such coefficients. This often poses a significant difficulty. On the other hand, the development of a *reduced description* of molecular processes in which we follow explicitly only a few chosen degrees of freedom can only be achieved using the density matrix [20, 21] since an ensemble-averaged wavefunction (unlike the density matrix) has no physical significance. The future of molecular dynamics in large polyatomic molecules and in condensed phases depends, therefore, on the extension of the semiclassical methods to the evolution of the density matrix in Liouville space. We have recently proposed a new type of self-consistent semiclassical REM in Liouville space [25–27] based on projection operator techniques of nonequilibrium statistical mechanics [28–31]. To lowest order, the equations provide a time-dependent mean field approximation [32, 33], which can be systematically improved. Since this approach is formulated in terms of the density matrix in Liouville space [21, 34], it can be applied to pure states as well as to mixed states. In that respect, it should be particularly useful for molecular dynamics in condensed phases (spectral lineshapes of molecules in solution and on solid surfaces, desorption, vibrational relaxation, etc.). In this chapter we review this Liouville space propagation scheme and discuss possible applications to vibrational dynamics of anharmonic molecules and to electronic spectroscopy; absorption and Raman and fluorescence spectroscopy of isolated and solvated polyatomic molecules.

In Section II, we consider the dynamics in Liouville space and define the propagators relevant for a general time evolution and for the calculation of correlation functions. In Section III, we consider a molecule with two

electronic states and develop a semiclassical propagator for the calculation of electronic absorption. This is done using projection operators in Liouville space. In Section IV, we consider the evolution of the density matrix on a single potential surface. This is a special case of the formalism developed in Section III. The time-dependent self-consistent field (TDSCF) (Hartree) approximation is developed and analyzed. In Section V, we discuss and summarize our results, and in Section VI, we present numerical calculations of absorption lineshapes and Raman excitation profiles of model anharmonic systems obtained using the present Liouville space propagation scheme.

II. TIME EVOLUTION IN LIOUVILLE SPACE

We consider a quantum system characterized by N coordinates x_j , $j = 1, \dots, N$, their conjugate momenta $\hat{p}_j = -i\hbar \partial/\partial x_j$, and masses m_j . Its Hamiltonian is

$$H = \frac{1}{2} \sum_{j,k} \Omega_{jk} \hat{p}_j \hat{p}_k + V(x_1, x_2, \dots, x_N), \quad (1)$$

where V is the interaction potential and Ω_{jk} is a mass matrix. For Cartesian coordinates we have $\Omega_{jk} = 1/m_j \delta_{jk}$. We shall hereafter introduce a vector notation and define the N -dimensional vectors $\underline{\mathbf{x}}$ and $\underline{\hat{\mathbf{p}}}$ with components x_j and \hat{p}_j , respectively, and the $N \times N$ matrix $\underline{\Omega}$ with matrix elements Ω_{jk} . A matrix is represented by a boldface letter, whereas a vector is represented by a boldface letter with an underbar. Equation 1 then assumes the form

$$H = \frac{1}{2} \underline{\hat{\mathbf{p}}}^T \underline{\Omega} \underline{\hat{\mathbf{p}}} + V(\underline{\mathbf{x}}). \quad (2)$$

Here $\underline{\hat{\mathbf{p}}}^T$ is the transpose of $\underline{\hat{\mathbf{p}}}$. Our goal is to develop a semiclassical self-consistent procedure for the approximate solution of the Liouville equation

$$\frac{d\rho}{dt} = -iL\rho \equiv -\frac{i}{\hbar} [H, \rho]. \quad (3a)$$

Here L is the Liouville operator, and $\rho(\mathbf{x}, \mathbf{x}'; t)$ is the system density matrix. We further define the density matrix in the Wigner representation ρ_w [22–24]:

$$\rho_w(\underline{\mathbf{q}}, \underline{\mathbf{p}}; t) \equiv \frac{1}{(\pi\hbar)^N} \int_{-\infty}^{\infty} \rho(\underline{\mathbf{q}} + \underline{\mathbf{s}}, \underline{\mathbf{q}} - \underline{\mathbf{s}}; t) \exp\left(-\frac{2i\underline{\mathbf{p}}\underline{\mathbf{s}}}{\hbar}\right) d\underline{\mathbf{s}}. \quad (3b)$$

The inverse transform of Eq. 3b is

$$\rho(\underline{\mathbf{q}} + \underline{\mathbf{s}}, \underline{\mathbf{q}} - \underline{\mathbf{s}}; t) = \int_{-\infty}^{\infty} \rho_w(\underline{\mathbf{q}}, \underline{\mathbf{p}}; t) \exp\left(\frac{2i\underline{\mathbf{p}}\underline{\mathbf{s}}}{\hbar}\right) d\underline{\mathbf{p}}. \quad (3c)$$

In Eqs. 3 we have used the substitutions

$$\underline{\mathbf{q}} = \frac{1}{2}(\underline{\mathbf{x}} + \underline{\mathbf{x}'}), \quad (4a)$$

$$\underline{\mathbf{s}} = \frac{1}{2}(\underline{\mathbf{x}} - \underline{\mathbf{x}'}). \quad (4b)$$

The density matrix is normalized as

$$\iint d\underline{\mathbf{x}} d\underline{\mathbf{x}'} \rho(\underline{\mathbf{x}}, \underline{\mathbf{x}'}; t) = \iint \rho_w(\underline{\mathbf{q}}, \underline{\mathbf{p}}; t) d\underline{\mathbf{q}} d\underline{\mathbf{p}} = 1. \quad (5)$$

The equation of motion for the density matrix in the Wigner representation is

$$\frac{d\rho_w}{dt} = -iL_w\rho_w, \quad (6a)$$

where the Liouville operator in the Wigner representation is

$$iL_w\rho_w = \frac{2}{\hbar} H_c \sin \left[\frac{\hbar}{2} \left(\overrightarrow{\partial}_{\underline{\mathbf{p}}} \overrightarrow{\partial}_{\underline{\mathbf{q}}} - \overleftarrow{\partial}_{\underline{\mathbf{q}}} \overleftarrow{\partial}_{\underline{\mathbf{p}}} \right) \right] \rho_w. \quad (6b)$$

Here H_c is the classical Hamiltonian, and the arrows indicate the direction of operation of the derivative. Note that when Eq. 6 is expanded in powers of \hbar , the leading (zero-order) term is the classical Liouville equation.

The simplest dynamical problem we may be interested in, is the calculation of the expectation value of some dynamical operator A :

$$\langle A(t) \rangle = \text{Tr} [A\rho(t)]. \quad (7)$$

Equation 7 can be written in the coordinate representation

$$\langle A(t) \rangle = \iint d\underline{\mathbf{x}} d\underline{\mathbf{x}'} A(\underline{\mathbf{x}'}, \underline{\mathbf{x}}) \rho(\underline{\mathbf{x}}, \underline{\mathbf{x}'}; t) \quad (8a)$$

or in the Wigner phase space representation

$$\langle A(t) \rangle = \iint d\underline{\mathbf{p}} d\underline{\mathbf{q}} A_w(\underline{\mathbf{p}}, \underline{\mathbf{q}}) \rho_w(\underline{\mathbf{p}}, \underline{\mathbf{q}}; t). \quad (8b)$$

Since Eqs. 8a and 8b simply correspond to different representations, we shall introduce hereafter a unified notation and recast them in the form

$$\langle A(t) \rangle = \int d\underline{\Gamma} A(\underline{\Gamma}) \rho(\underline{\Gamma}; t). \quad (9)$$

Equation 9 should be understood as follows: We either express A and ρ in the coordinate representation, and then $d\Gamma = d\underline{x} d\underline{x}'$, or A and ρ are given in the Wigner representation, and then $d\Gamma = d\underline{p} d\underline{q}$. The evaluation of $\langle A(t) \rangle$ then reduces to solving the Liouville equation (Eq. 3a or 6) for $\rho(\Gamma; t)$ and then performing the integration (Eq. 9).

Correlation functions constitute another type of dynamical quantities whose calculation is of considerable interest. Experimental (e.g., spectroscopic) observables can usually be expressed in terms of appropriate correlation functions, and their calculation is a key step in the interpretation of these experiments. Given two dynamical operators A and B and the equilibrium density matrix of the system ρ_{eq} , we define the two time correlation function [35]

$$\langle A(t)B(0) \rangle \equiv \text{Tr}[A \exp(-iHt/\hbar)B\rho_{\text{eq}} \exp(iHt/\hbar)], \quad (10a)$$

or making use of the Liouville operator,

$$\langle A(t)B(0) \rangle \equiv \text{Tr}[A \exp(-iLt)B\rho_{\text{eq}}], \quad (10b)$$

with

$$\rho_{\text{eq}} = \frac{\exp(-H/kT)}{\text{Tr} \exp(-H/kT)}. \quad (11)$$

Equation 10 can be rewritten in the form

$$\langle A(t)B(0) \rangle = \int d\Gamma A(\Gamma)\bar{\rho}(\Gamma; t), \quad (12a)$$

where $\bar{\rho}(\Gamma; t)$ is given by

$$\bar{\rho}(\Gamma; t) = \exp(-iLt)B\rho_{\text{eq}}. \quad (12b)$$

Here $\bar{\rho}(\Gamma; t)$ can be obtained from the solution of the Liouville equation (Eq. 3 or 6) with the initial condition

$$\bar{\rho}(\Gamma; 0) = B\rho_{\text{eq}}. \quad (13)$$

Note that $\bar{\rho}$, which satisfies the Liouville equation (Eq. 3a) with the initial condition Eq. 13, is not the density matrix of the system. It should be rather interpreted as a *generating function* that allows the calculation of any two time correlation function using Eqs. 12. In the next section, we shall develop a

semiclassical procedure for solving the Liouville equation and calculating $\rho(\underline{\Gamma}; t)$ or $\bar{\rho}(\underline{\Gamma}; t)$.

III. REDUCED EQUATIONS OF MOTION FOR MOLECULAR ELECTRONIC SPECTROSCOPY

We shall now develop a semiclassical procedure for the efficient calculation of molecular electronic spectra. We consider a polyatomic molecule with N vibrational degrees of freedom and two electronic states: a ground state $|g\rangle$ and an electronically excited state $|e\rangle$. The molecular Hamiltonian is given by [20]

$$H = |g\rangle H_g \langle g| + |e\rangle (\omega_{eg} + H_e) \langle e|, \quad (14)$$

where

$$H_g = \frac{1}{2} \underline{\mathbf{p}}^T \underline{\Omega} \underline{\mathbf{p}} + V_g(\underline{\mathbf{x}}). \quad (15b)$$

$$H_e = \frac{1}{2} \underline{\mathbf{p}}^T \underline{\Omega} \underline{\mathbf{p}} + V_e(\underline{\mathbf{x}}). \quad (15b)$$

Here V_g and V_e are the adiabatic potentials for the ground and the excited states, respectively, and ω_{eg} is the electronic energy gap between their minima. The absorption lineshape is given by

$$I(\omega_L) = \int dt \exp [i(\omega_L - \omega_{eg})t] \langle \mu(t) \mu(0) \rangle, \quad (16)$$

where ω_L is the photon frequency, $\mu(\underline{\mathbf{x}})$ is the dipole operator, and the dipole correlation function is given by

$$\langle \mu(t) \mu(0) \rangle = \text{Tr} [\mu \exp(-iH_e t/\hbar) \mu \rho_{eq} \exp(iH_g t/\hbar)] \quad (17)$$

with

$$\rho_{eq} = \frac{\exp(-H_g/kT)}{\text{Tr} \exp(-H_g/kT)}. \quad (18)$$

Equation 17 can be rewritten in the form

$$\langle \mu(t) \mu(0) \rangle = \int d\underline{\Gamma} \mu(\underline{\Gamma}) \tilde{\rho}(\underline{\Gamma}; t), \quad (19)$$

where $\tilde{\rho}(\underline{\Gamma}; t)$ satisfies the equation

$$\frac{d\tilde{\rho}}{dt} = -\frac{i}{\hbar} [H_e \tilde{\rho} - \tilde{\rho} H_g] \quad (20a)$$

with the initial condition

$$\tilde{\rho}(\underline{\Gamma}; 0) = \mu \rho_{\text{eq}}. \quad (20b)$$

We note that $\tilde{\rho}(\underline{\Gamma}; t)$ [similar to $\bar{\rho}(\underline{\Gamma}; t)$] is not a density matrix but rather a generating function for electronic spectra. The solution of the Liouville equation (Eq. 20) has been the subject of numerous studies in the context of spectral line broadening [20, 21, 36–38]. It bears some resemblance to the dynamics of nonadiabatic transitions (curve crossing) [39]. The ordinary time evolution in Liouville space considered in Section II, is a special case of the present formulation constructed for electronic spectroscopy, since Eq. 20a reduces to Eq. 3a when we set $H_e = H_g$. In this section, we shall develop reduced equations of motion (REM) toward the approximate semiclassical solution of Eq. 20a.

Our REM will be derived as follows. We start with a set of dynamical operators whose expectation values are believed to be relevant for the dynamics. In the present reduced description, we choose to consider the following operators: x_j , \hat{p}_j , $x_j x_k$, $\hat{p}_j \hat{p}_k$, and $\hat{p}_j x_k$, $j, k = 1, 2, \dots, N$. These $M = 2N^2 + 3N$ operators constitute the complete set of linear and bilinear products of x_j and \hat{p}_j . Let us denote these operators by A_α , $\alpha = 1, \dots, M$. We shall further introduce the “expectation values” σ_α of these operators with respect to the generating function $\tilde{\rho}(\underline{\Gamma}; t)$, that is,

$$\sigma_\alpha(t) = \langle A_\alpha \rangle = \int d\underline{\Gamma} A_\alpha(\underline{\Gamma}) \tilde{\rho}(\underline{\Gamma}; t) / \int d\underline{\Gamma} \tilde{\rho}(\underline{\Gamma}; t), \quad \alpha = 1, 2, \dots, M. \quad (21a)$$

Note that $\tilde{\rho}(\underline{\Gamma}; t)$ is not a density matrix; therefore, the σ_α are not really expectation values. They are, however, M parameters characterizing $\tilde{\rho}(\underline{\Gamma}; t)$, and they represent the complete set of first and second “moments” of the coordinates and momenta. It should further be noted that the trace of $\tilde{\rho}(\underline{\Gamma}; t)$ is not conserved when $H_e \neq H_g$, and its variation with time carries a valuable dynamical information. We shall therefore introduce another operator $A_0 = 1$, the unit operator, and define

$$\sigma_0(t) = \int d\underline{\Gamma} A_0 \tilde{\rho}(\underline{\Gamma}; t). \quad (21b)$$

To simplify the notation, we shall rearrange our operators in a matrix form. To that end, we introduce the following quantities:

$$A_0 = 1,$$

$$\underline{A}_1 = \underline{\mathbf{x}},$$

$$\begin{aligned}
\mathbf{A}_2 &= \hat{\mathbf{p}}, \\
\mathbf{A}_3 &= (\underline{\mathbf{x}} - \underline{\mathbf{x}}^0) \cdot (\underline{\mathbf{x}} - \underline{\mathbf{x}}^0)^T, \\
\mathbf{A}_4 &= (\hat{\mathbf{p}} - \underline{\mathbf{p}}^0) \cdot (\hat{\mathbf{p}} - \underline{\mathbf{p}}^0)^T, \\
\mathbf{A}_5 &= (\underline{\mathbf{x}} - \underline{\mathbf{x}}^0) \cdot (\hat{\mathbf{p}} - \underline{\mathbf{p}}^0)^T - \frac{1}{2}i\hbar\mathbf{I},
\end{aligned} \tag{22a}$$

with

$$\begin{aligned}
\underline{\mathbf{x}}^0 &= \int d\underline{\Gamma} \underline{\mathbf{x}} \tilde{\rho}(\underline{\Gamma}; t) / \int d\underline{\Gamma} \tilde{\rho}(\underline{\Gamma}; t), \\
\underline{\mathbf{p}}^0 &= \int d\underline{\Gamma} \hat{\mathbf{p}} \tilde{\rho}(\underline{\Gamma}; t) / \int d\underline{\Gamma} \tilde{\rho}(\underline{\Gamma}; t).
\end{aligned} \tag{22b}$$

Here A_0 is a number representing the unit operator in phase space; \mathbf{A}_1 and \mathbf{A}_2 are N -component vectors each containing N operators; whereas \mathbf{A}_3 , \mathbf{A}_4 , and \mathbf{A}_5 are $N \times N$ matrices each containing N^2 operators. The matrix \mathbf{I} is the unit matrix. Since \mathbf{A}_3 and \mathbf{A}_4 are symmetric matrices, Eqs. 22 contain altogether $M + 1$ distinct operators, where $M = 2N^2 + 3N$. Similarly, we shall rearrange σ_x in a matrix form analogous to A_x . Here σ_0 will be a number; σ_1 and σ_2 will be N -component vectors; and σ_3 , σ_4 , and σ_5 are $N \times N$ matrices. We have thus identified $M + 1$ relevant dynamical variables (Eq. 22) and $M + 1$ parameters σ_x related to the expectation values of these operators. The REM will now be derived by introducing a reduced propagator $\sigma(\underline{\Gamma}; t)$:

$$\sigma(\underline{\Gamma}; t) \simeq \tilde{\rho}(\underline{\Gamma}; t). \tag{23}$$

We shall choose the following form for $\sigma(\underline{\mathbf{p}}, \underline{\mathbf{q}}; t)$ in the Wigner representation:

$$\begin{aligned}
\sigma(\underline{\mathbf{p}}, \underline{\mathbf{q}}; t) &= \frac{\sigma_0(t)}{(2\pi)^N [\det \mathbf{W}(t)]^{1/2}} \\
&\times \exp \left\{ -\frac{1}{2} [\underline{\mathbf{q}}^T - \sigma_1^T(t), \underline{\mathbf{p}}^T - \sigma_2^T(t)] \mathbf{W}^{-1}(t) \begin{bmatrix} \underline{\mathbf{q}} - \sigma_1(t) \\ \underline{\mathbf{p}} - \sigma_2(t) \end{bmatrix} \right\}
\end{aligned} \tag{24}$$

with

$$\mathbf{W}(t) = \begin{bmatrix} \sigma_3(t) & \sigma_5(t) \\ \sigma_5^T(t) & \sigma_4(t) \end{bmatrix}. \tag{25}$$

Here $\det \mathbf{W}(t)$ denotes the determinant of the $\mathbf{W}(t)$ matrix, and \mathbf{A}^T denotes the transpose of \mathbf{A} .

Equation 24 implies that $\sigma(\underline{\Gamma}; t)$ is Gaussian at all times. If initially $\sigma(\underline{\Gamma}; 0)$ or $\tilde{\rho}(\underline{\Gamma}; 0)$ (Eq. 20b) is not a Gaussian, we can always represent it as a

superposition of Gaussians. In the Appendix we give $\sigma(\underline{x}, \underline{x}'; t)$ in the coordinate representation. Equation 24 depends on $M + 1$ time-dependent parameters, which consist of a number σ_0 , two N -dimensional vectors $\underline{\sigma}_1$ and $\underline{\sigma}_2$, and three $N \times N$ matrices $\underline{\sigma}_3$, $\underline{\sigma}_4$ and $\underline{\sigma}_5$. These time-dependent parameters may be uniquely determined by requiring the expectation values of our operators A_α (Eqs. 22) evaluated using the exact ($\tilde{\rho}$) and the approximate (σ) propagators to be the same:

$$\sigma_0(t) = \int d\underline{\Gamma} \tilde{\rho}(\underline{\Gamma}; t) = \int d\underline{\Gamma} \sigma(\underline{\Gamma}; t), \tag{26a}$$

$$\begin{aligned} \sigma_\alpha(t) &= \int d\underline{\Gamma} A_\alpha(\underline{\Gamma}) \tilde{\rho}(\underline{\Gamma}; t) \bigg/ \int d\underline{\Gamma} \tilde{\rho}(\underline{\Gamma}; t) \\ &= \int d\underline{\Gamma} A_\alpha(\underline{\Gamma}) \sigma(\underline{\Gamma}; t) \bigg/ \int d\underline{\Gamma} \sigma(\underline{\Gamma}; t), \quad \alpha = 1, 2, \dots, M. \end{aligned} \tag{26b}$$

We further define the ‘‘overlap’’ $(M + 1) \times (M + 1)$ matrix with matrix elements

$$S_{\alpha\beta}(t) = \langle\langle A_\alpha | \sigma(\underline{\Gamma}; t) A_\beta \rangle\rangle \equiv \text{Tr} [A_\alpha^\dagger \sigma(\underline{\Gamma}; t) A_\beta], \quad \alpha, \beta = 0, \dots, M, \tag{27a}$$

and introduce the Liouville space projection operator

$$P(t) = \sum_{\alpha, \beta=0}^M |\sigma(t) A_\alpha\rangle\rangle [S(t)]_{\alpha\beta}^{-1} \langle\langle A_\beta | \tag{27b}$$

and the complementary projection

$$Q(t) = 1 - P(t). \tag{27c}$$

We are using Liouville space notation [21, 34], whereby an ordinary operator A is represented by a ket $|A\rangle\rangle$ and the scalar product of two operators is defined by $\langle\langle A|B\rangle\rangle \equiv \text{Tr} (A^\dagger B)$. Here $\langle\langle A|L|B\rangle\rangle \equiv \text{Tr} (A^\dagger LB)$ is a Liouville space ‘‘matrix element.’’ The properties of the projection operator $P(t)$ have been discussed previously [25–27]. In order to simplify the notation, we introduce the auxiliary quantities $\tilde{\sigma}_\alpha$, $\alpha = 0, 1, \dots, M$, defined by

$$\tilde{\sigma}_0 = \sigma_0, \tag{28a}$$

$$\tilde{\sigma}_\alpha = \sigma_\alpha \sigma_0. \tag{28b}$$

We further introduce the generalized Liouville operator \tilde{L} by its action on an

arbitrary dynamical variable A :

$$\tilde{L}A \equiv \frac{1}{\hbar}(H_e A - A H_g). \quad (29)$$

Using the assumption that at some initial time t_0 , $\tilde{\rho}(\underline{\Gamma}; t_0) = \sigma(\underline{\Gamma}; t_0)$, we have derived the following exact REM for $\tilde{\sigma}_\alpha$:

$$\dot{\tilde{\sigma}}_\alpha(t) = -i \langle\langle A_\alpha | \tilde{L} | \sigma(t) \rangle\rangle - \int_{t_0}^t ds \langle\langle A_\alpha | \tilde{L} K(t, s) Q(s) \tilde{L} | \sigma(s) \rangle\rangle, \quad (30a)$$

$\alpha = 0, \dots, M,$

where

$$K(t, s) = \exp_+ \left[-i \int_s^t d\tau Q(\tau) \tilde{L} \right], \quad (30b)$$

and \exp_+ denotes the time-ordered exponential

$$\begin{aligned} \exp_+ \left[-i \int_s^t d\tau Q(\tau) \tilde{L} \right] &\equiv 1 - i \int_s^t d\tau Q(\tau) \tilde{L} \\ &+ (-i)^2 \int_s^t d\tau_1 \int_s^{\tau_1} d\tau_2 Q(\tau_1) \tilde{L} Q(\tau_2) \tilde{L} + \dots \end{aligned} \quad (30c)$$

The first term on the right side of the REM Eq. 30a represents the mean field evolution which is exact if $\tilde{\rho}(\underline{\Gamma}; t) = \sigma(\underline{\Gamma}; t)$ for all times, whereas the second term, the fluctuation kernel, arises from the fact that, in general, $\tilde{\rho}(\underline{\Gamma}; t) \neq \sigma(\underline{\Gamma}; t)$ for $t > t_0$, and it corrects the time evolution of $\sigma(\underline{\Gamma}; t)$. In this REM the time derivative of $\tilde{\sigma}_\alpha$ at time t depends on the values of $\tilde{\sigma}_\beta$ at all previous times $t_0 < s < t$. The derivation of the REM (Eqs. 30) is given elsewhere [25–27].

The mean field approximation is obtained by retaining only the first term on the right side of Eq. 30a;

$$\dot{\tilde{\sigma}}_\alpha(t) = -i \text{Tr} [A_\alpha^\dagger \tilde{L} \sigma(\underline{\Gamma}; t)]. \quad (31)$$

We have evaluated Eq. 31 explicitly and obtained a closed set of equations of motion for $\tilde{\sigma}_\alpha$, $\alpha = 0, 1, \dots, M$. The REM for σ_α may then be obtained making use of Eqs. 28. Using the matrix notation introduced in Eq. 22, the REM assume the form [27]

$$\dot{\sigma}_0(t) = -\frac{i}{\hbar} U_0 \sigma_0(t),$$

$$\begin{aligned}
 \dot{\underline{\sigma}}_1(t) &= \underline{\Omega}\underline{\sigma}_2 - \frac{i}{\hbar}\underline{\sigma}_3\underline{U}_1, \\
 \dot{\underline{\sigma}}_2(t) &= -\underline{V}_1 - \frac{i}{\hbar}\underline{\sigma}_5^T\underline{U}_1, \\
 \dot{\underline{\sigma}}_3(t) &= \underline{\sigma}_5\underline{\Omega} + \underline{\Omega}\underline{\sigma}_5^T - \frac{i}{\hbar}\underline{\sigma}_3\underline{U}_2\underline{\sigma}_3, \\
 \dot{\underline{\sigma}}_4(t) &= -\underline{V}_2\underline{\sigma}_5 - \underline{\sigma}_5^T\underline{V}_2 - \frac{i}{\hbar}(\underline{\sigma}_5^T\underline{U}_2\underline{\sigma}_5 - \frac{1}{4}\hbar^2\underline{U}_2), \\
 \dot{\underline{\sigma}}_5(t) &= -\underline{\sigma}_3\underline{V}_2 + \underline{\Omega}\underline{\sigma}_4 - \frac{i}{\hbar}\underline{\sigma}_3\underline{U}_2\underline{\sigma}_5,
 \end{aligned} \tag{32}$$

where

$$V = \frac{1}{2}(V_g + V_e), \tag{33a}$$

$$\underline{V}_1 = \left\langle \frac{\partial V}{\partial \underline{x}} \right\rangle, \tag{33b}$$

$$\underline{V}_2 = \left\langle \frac{\partial^2 V}{\partial \underline{x} \cdot \partial \underline{x}^T} \right\rangle, \tag{33c}$$

and

$$U = V_e - V_g, \tag{34a}$$

$$U_0 = \langle U \rangle, \tag{34b}$$

$$\underline{U}_1 = \left\langle \frac{\partial U}{\partial \underline{x}} \right\rangle, \tag{34c}$$

$$\underline{U}_2 = \left\langle \frac{\partial^2 U}{\partial \underline{x} \cdot \partial \underline{x}^T} \right\rangle. \tag{34d}$$

The angular brackets denote

$$\langle R \rangle = \int d\underline{\Gamma} R(\underline{\Gamma}) \sigma(\underline{\Gamma}; t) / \int d\underline{\Gamma} \sigma(\underline{\Gamma}; t). \tag{35}$$

Here $\sigma(\underline{\Gamma}; t)$ may be used for the calculation of Raman excitation profiles as well. Consider a Raman process in which the molecule starts at the vibronic state $|a\rangle$ and ends in the vibronic state $|c\rangle$ (both belonging to the ground-state manifold) by absorbing an ω_L photon and emitting an ω_S photon such that $\omega_L - \omega_S = \omega_{ca}$. The Raman excitation profile is the intensity of this Raman

transition versus the incident frequency ω_L . It is given by [21, 26, 27]

$$Q_{ca}(\omega_L) = \left| \int_0^\infty dt \exp [i(\omega_L - \omega_{cg})t] G_{ca}(t) \right|^2, \quad (36a)$$

with

$$G_{ca}(t) = \text{Tr} [D_f \exp(-iH_e t/\hbar) D_i \exp(iH_g t/\hbar)]. \quad (36b)$$

Here

$$D_i = \mu |a\rangle \langle a|, \quad (36c)$$

and

$$D_f = |a\rangle \langle c| \mu, \quad (36d)$$

Equation 36b can be written as

$$G_{ca}(t) = \int d\underline{\Gamma} D_f(\underline{\Gamma}) \tilde{\rho}(\underline{\Gamma}; t), \quad (37a)$$

where $\tilde{\rho}(\underline{\Gamma}; t)$ satisfies Eq. 20a with the initial condition

$$\tilde{\rho}(\underline{\Gamma}; 0) = D_i. \quad (37b)$$

Further applications of the present REM (Eqs. 32) can be made to fluorescence spectroscopy and to nonlinear optical lineshapes, such as four-wave mixing [21, 27].

IV. SEMICLASSICAL CALCULATION OF THE DENSITY MATRIX AND THE TIME-DEPENDENT SELF-CONSISTENT FIELD (HARTREE) APPROXIMATION

In Section III, we developed REM suitable for the calculation of molecular electronic lineshapes. In that case $\tilde{\rho}(\underline{\Gamma}; t)$ is not a density matrix. It obeys Eq. 20a, in which H_e acts on $\tilde{\rho}$ from the left, and H_g acts from the right. The diagonal elements $\tilde{\rho}(\underline{\mathbf{x}}, \underline{\mathbf{x}}; t)$ are complex, and its normalization $\sigma_0(t)$ (Eq. 26a) changes with time. We shall now return to the ordinary Liouville space evolution as introduced in Section II and consider the time evolution of the density matrix. Equation 3a is a special case of Eq. 20a obtained by taking $H_e = H_g$. Equation 24 thus provides an approximate solution for the density matrix (Eq. 3b). By setting $U \equiv H_e - H_g = 0$, the REM (Eqs. 32) assume the form

$$\dot{\underline{\sigma}}_1 = \underline{\Omega} \underline{\sigma}_2,$$

$$\begin{aligned}
 \dot{\underline{\sigma}}_2 &= -\underline{V}_1, \\
 \dot{\underline{\sigma}}_3 &= \underline{\sigma}_5 \underline{\Omega} + \underline{\Omega} \underline{\sigma}_5^T, \\
 \dot{\underline{\sigma}}_4 &= -\underline{V}_2 \underline{\sigma}_5 - \underline{\sigma}_5^T \underline{V}_2, \\
 \dot{\underline{\sigma}}_5 &= -\underline{\sigma}_3 \underline{V}_2 + \underline{\Omega} \underline{\sigma}_4.
 \end{aligned} \tag{38}$$

Since the normalization of the density matrix is conserved [$\sigma_0(t) = 1$], we omit σ_0 and do not consider it in this section as a dynamical variable. These equations provide a general semiclassical mean field theory for molecular dynamics. They focus on the complete set of $M = 2N^2 + 3N$ linear and bilinear products of the coordinates and momenta. Such a choice may be useful for few-body problems (small N) but is impractical for macroscopic systems due to the large number of variables involved. A simplified and commonly used procedure is the TDSCF, or Hartree, approximation. In this case we consider only $5N$ expectation values corresponding to \underline{A}_1 and \underline{A}_2 (denoted σ_{1j} and σ_{2j} , respectively, $j = 1, \dots, N$) and the diagonal elements of \underline{A}_3 , \underline{A}_4 , and \underline{A}_5 (denoted σ_{3j} , σ_{4j} , and σ_{5j} , respectively, $j = 1, \dots, N$). We thus consider only single-particle operators and do not consider explicitly correlations among particles.

Similarly, the approximate density matrix $\sigma(\underline{\Gamma}; t)$ is taken to be in the form of a product of single-particle density matrices

$$\sigma(\underline{\Gamma}; t) = \prod_{j=1}^N \sigma_j(\Gamma_j; t), \tag{39}$$

where in the Wigner (phase space) representation,

$$\begin{aligned}
 \sigma_j(q_j, p_j; t) &= \frac{1}{2\pi \sqrt{\sigma_{3j}\sigma_{4j} - \sigma_{5j}^2}} \\
 &\times \exp \left\{ -\frac{1}{2(\sigma_{3j}\sigma_{4j} - \sigma_{5j}^2)} [\sigma_{4j}(q_j - \sigma_{1j})^2 + \sigma_{3j}(p_j - \sigma_{2j})^2 \right. \\
 &\quad \left. - 2\sigma_{5j}(q_j - \sigma_{1j})(p_j - \sigma_{2j})] \right\},
 \end{aligned} \tag{40a}$$

and in the coordinate representation,

$$\begin{aligned}
 \sigma_j(x_j, x'_j; t) &= \frac{1}{\sqrt{2\pi\sigma_{3j}}} \exp \left(-\frac{\sigma_{1j}^2}{2\sigma_{3j}} \right) \\
 &\times \exp \left\{ -\frac{1}{2\sigma_{3j}} \left[\frac{1}{4}(x_j + x'_j)^2 + \frac{1}{\hbar^2}(\sigma_{3j}\sigma_{4j} - \sigma_{5j}^2)(x_j - x'_j)^2 \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\sigma_{5j}}{i\hbar}(x_j + x')(x_j - x') - \sigma_{ij}(x_j + x') \\
& - \frac{2}{i\hbar}(\sigma_{1j}\sigma_{5j} - \sigma_{2j}\sigma_{3j})(x_j - x') \Big] \Big\}. \quad (40b)
\end{aligned}$$

In this case Eqs. 38 reduce to the form [26]

$$\dot{\sigma}_{1j} = \sigma_{2j}/m_j, \quad (41a)$$

$$\dot{\sigma}_{2j} = -\langle V_j(\underline{\mathbf{x}}) \rangle, \quad (41b)$$

$$\dot{\sigma}_{3j} = 2\sigma_{5j}/m_j, \quad (41c)$$

$$\dot{\sigma}_{4j} = -\langle V_{jj}(\underline{\mathbf{x}}) \rangle \sigma_{5j}, \quad (41d)$$

$$\dot{\sigma}_{5j} = -\langle V_{jj}(\underline{\mathbf{x}}) \rangle \sigma_{3j} + \sigma_{4j}/m_j, \quad (41e)$$

where

$$V_j(\underline{\mathbf{x}}) = \frac{\partial V}{\partial x_j}, \quad (42a)$$

$$V_{jj}(\underline{\mathbf{x}}) = \frac{\partial^2 V}{\partial x_j^2}. \quad (42b)$$

The angular brackets here denote

$$\langle R(\underline{\mathbf{x}}) \rangle = \int d\underline{\mathbf{x}} R(\underline{\mathbf{x}}) \sigma(\underline{\mathbf{x}}, \underline{\mathbf{x}}; t), \quad (42c)$$

where

$$\sigma(\underline{\mathbf{x}}, \underline{\mathbf{x}}; t) = \prod_{j=1}^N \frac{1}{\sqrt{2\pi\sigma_{3j}}} \exp \left[-\frac{(x_j - \sigma_{1j})^2}{2\sigma_{3j}} \right]. \quad (43)$$

Equations 41 constitute the Liouville space TDSCF equations. They provide a cruder approximation for the dynamics than the complete mean field equations 38 since they do not follow explicitly the correlations among particles. Their main advantage over the complete mean field equations 38 is that the number of dynamical variables is $\sim N$ for the TDSCF instead of $\sim N^2$ for the complete mean field equations. This makes the TDSCF particularly useful for large-scale molecular dynamics computations involving many particles. Moreover, in many problems of chemical interest we need to develop a *mixed description* in which some degrees of freedom are treated quantum mechanically and others are treated classically. An example would be the

vibrational relaxation of large polyatomic molecules in a solvent [27, 40, 41]. The high-frequency molecular vibrations are quantum mechanical, whereas the solvent degrees of freedom may be treated classically. The TDSCF allows such a mixed description to be developed systematically since all it takes is to keep only the first moments (σ_1 and σ_2) for the classical degrees of freedom and set the other variables (σ_3 , σ_4 , and σ_5) to zero. At the same time, we may retain all five moments for the other degrees of freedom.

V. DISCUSSION

We shall now analyze the significance of our semiclassical procedure. We first note that Eqs. 38 do not contain \hbar . This suggests that they are completely classical. Indeed, the present procedure may be repeated for classical mechanics by replacing L in Eq. 3a with the classical Liouville operator obtained by expanding Eq. 6b to zero order in \hbar :

$$-iL\rho = H_c \left[\frac{\overline{\partial}}{\partial \underline{\mathbf{q}}} \frac{\overline{\partial}}{\partial \underline{\mathbf{p}}} - \frac{\overline{\partial}}{\partial \underline{\mathbf{p}}} \frac{\overline{\partial}}{\partial \underline{\mathbf{q}}} \right] \rho = \sum_j \left(\frac{\partial H_c}{\partial q_j} \frac{\partial}{\partial p_j} - \frac{\partial H_c}{\partial p_j} \frac{\partial}{\partial q_j} \right) \rho(\underline{\mathbf{p}}, \underline{\mathbf{q}}; t). \quad (44)$$

We can then repeat the present derivation step-by-step and obtain Eqs. 38 or 41. *The mean field equations for the moments $\sigma_1, \dots, \sigma_5$ obtained by using a Gaussian propagator are therefore completely classical.* A major advantage of the present formalism compared with other propagation schemes [12–18] is that Eqs. 38 and 32 are the lowest order of a systematic expansion that may be carried out order by order. The problem of constructing an approximate density matrix for a complicated system using the expectation values of a few dynamical variables is common to many areas of nonequilibrium statistical mechanics [28–31]. A powerful way to achieve that goal is provided by the maximum-entropy formalism [25, 26, 30, 31, 42]. Within this formalism we construct a density matrix $\sigma(\underline{\Gamma}; t)$ that maximizes the entropy subject to the constraints (Eqs. 26). For our chosen set of variables (Eqs. 22), the maximum-entropy distribution is given by [25, 26, 30, 31, 42]

$$\sigma(\underline{\Gamma}; t) = \exp \left(- \sum_{\alpha=0}^M \lambda_{\alpha} A_{\alpha} \right), \quad (45)$$

where λ_{α} is a numerical coefficient that may be expressed in terms of σ_{α} . We have shown [26] that our Gaussian choice (Eq. 24) is identical to the maximum-entropy distribution (Eq. 45). This provides an additional physical insight for our choice (Eq. 24) and connects the present semiclassical procedure with the more general problem of the derivation of REM in nonequilibrium statistical mechanisms. The present equations may be ex-

tended by various ways. One possibility is to expand the fluctuation kernel K in Eq. 30a perturbatively. Note that for harmonic systems the mean field equations 32 or 38 are exact. This suggests that an expansion of the kernel K in anharmonicities may be appropriate. Alternatively, we may add more dynamical variables to our chosen set (e.g., x_j^3 and p_j^3) and construct a more elaborate density matrix with more parameters. A natural choice will be to expand the propagator as a Gaussian times a truncated set of Hermite polynomials in p_j and q_j . This will provide an improved reduced description of the system. Once this is done, true quantum propagation effects will enter into the description. We shall now compare our TDSCF equations with the thawed Gaussian (TG) procedure [12], which is widely used in molecular dynamics. We first note that Eqs. 41 may be written as an expansion in the width of the density matrix by expanding the potential around the maximum of the density matrix:

$$\langle V_j(\underline{\mathbf{x}}) \rangle = \sum_{n=0}^{\infty} [2^n \sigma_3^{2n} / (2n)!!] V_j^{(2n+1)}(\langle \underline{\mathbf{x}} \rangle), \quad (46a)$$

$$\langle V_{jj}(\underline{\mathbf{x}}) \rangle = \sum_{n=0}^{\infty} [2^n \sigma_3^{2n} / (2n)!!] V_j^{(2n+2)}(\langle \underline{\mathbf{x}} \rangle), \quad (46b)$$

with

$$V_j^{(n)}(\langle \underline{\mathbf{x}} \rangle) \equiv \left. \frac{\partial^n V}{\partial x_j^n} \right|_{\underline{\mathbf{x}} = \langle \underline{\mathbf{x}} \rangle}. \quad (46c)$$

The TG equations may be obtained from our TDSCF equations (Eqs. 41) if the following approximations are made: (i) We take only the zero-order terms in Eqs. 46. Dropping the higher order terms is equivalent to assuming that the density matrix is highly localized and may be approximated by a delta function. We then set

$$\langle V_j(\underline{\mathbf{x}}) \rangle = V_j(\langle \underline{\mathbf{x}} \rangle), \quad (47a)$$

and

$$\langle V_{jj}(\underline{\mathbf{x}}) \rangle = V_{jj}(\langle \underline{\mathbf{x}} \rangle). \quad (47b)$$

(ii) We further assume that initially the system is in a pure state with a wavefunction $\Psi(\underline{\mathbf{x}}, t)$. For a pure state, our density matrix assumes the form

$$\sigma_j(x_j, x'_j; t) = \psi_j(x_j, t) \psi_j^*(x'_j, t). \quad (48)$$

A necessary and sufficient condition for σ_j (Eq. 40) to represent a pure state is

$$\sigma_{5j}^2 = \sigma_{3j} \sigma_{4j} - (\hbar/2)^2. \quad (49)$$

Thus, for a pure state σ_{5j} is uniquely determined, up to a sign, by σ_{3j} and σ_{4j} . Equations 40, 48, and 49 then result in

$$\psi(x_j, t) = (2\pi\sigma_{3j})^{-1/4} \exp \left\{ \left(-\frac{1}{4\sigma_{3j}} + \frac{i\sigma_{5j}}{2\hbar\sigma_{3j}} \right) (x_j - \sigma_{1j})^2 + \frac{i\sigma_{2j}}{\hbar} (x_j - \sigma_{1j}) + \frac{i\gamma_j}{\hbar} \right\}. \quad (50)$$

If we then make the substitutions $\sigma_{1j} = x_t$, $\sigma_{2j} = p_t$, $\sigma_{3j} = \hbar(4\alpha_1)$, and $\sigma_{4j} = \hbar|\alpha_t|^2/\alpha_1$, we obtain the TG equations for x_t , p_t , and α_t [12]. Here α_1 is the imaginary part of α_t and γ is a time-dependent phase factor. We note that the phase information of γ is carried in our REM (Eqs. 32) by the variable σ_0 . It should be reiterated that our analysis shows that the mean field equations (Eqs. 38) (and in particular the TG procedure) represent purely classical dynamics. The second-moment bilinear variables (σ_3 , σ_4 , and σ_5) merely reflect the uncertainty in the initial conditions, but their equations of motion are purely classical since no \hbar appears in Eqs. 38. The appearance of \hbar in Eq. 50 and in the equations of motion of x_t , p_t , and α_t [12] may lead to the conclusion that the propagation is quantum or at least semiclassical. Our analysis shows clearly that this is not the case. Only when the propagator is extended beyond the Gaussian form will true quantum propagation effects enter. The REM for $\tilde{\rho}$ (Eqs. 32), unlike Eqs. 38, contain \hbar . The appearance of \hbar in Eqs. 32 merely reflects the quantum nature of the electronic two-level system. The nuclear dynamics described by these equations is, however, purely classical, as is evident from our present analysis.

When the density matrix represents a mixed state, Eq. 49 is not satisfied. It can be easily verified from Eqs. 41 that the solution of σ_{5j} is

$$\sigma_{5j}^2(t) = \sigma_{3j}(t)\sigma_{4j}(t) + C, \quad (51)$$

where C is a constant determined by the initial conditions. If $C = -(\hbar/2)^2$, Eq. 49 will be satisfied for all time. Thus, within the mean field approximation (Eq. 29), if the initial single-particle density matrix represents a pure state, it will represent a pure state for all times. Once the fluctuation kernel is included, however, this is no longer the case. Therefore, the fluctuation kernel allows a single-particle pure state to evolve into a mixed state. This is a necessary requirement for a *reduced description*, which should show, for example, how a system relaxes to thermal equilibrium with a thermal bath. For the sake of illustration, let us consider the density matrix for a one-dimensional harmonic system in thermal equilibrium (4):

$$\rho_{\text{eq}} = \exp(-\beta H) / \text{Tr} \exp(-\beta H), \quad (52)$$

with $\beta = (kT)^{-1}$, and the Hamiltonian is

$$H(x, \hat{p}) = \hat{p}^2/2m + \frac{1}{2}m\omega^2 x^2. \quad (53)$$

In this case we have $\sigma_1 = 0$, $\sigma_2 = 0$, $\sigma_3 = (\hbar/2m\omega) \coth(\frac{1}{2}\beta\hbar\omega)$, $\sigma_4 = \frac{1}{2}m\omega\hbar \coth(\frac{1}{2}\beta\hbar\omega)$, and $\sigma_5 = 0$, and we get

$$\rho_{\text{eq}}(x, x') = \frac{1}{\sqrt{2\pi\sigma_3}} \exp\left[-\frac{(x+x')^2}{8\sigma_3} - \frac{\sigma_4(x-x')^2}{2\hbar^2}\right], \quad (54a)$$

and in the Wigner representation,

$$\rho_{\text{eq}}(q, p) = \frac{1}{2\pi\sqrt{\sigma_3\sigma_4}} \exp\left[-\frac{q^2}{2\sigma_3} - \frac{p^2}{2\sigma_4}\right]. \quad (54b)$$

The thermal density matrix (Eq. 54) can be represented by our Gaussian form (Eq. 24), but since it corresponds to a mixed state, it cannot be represented by a single wavefunction (Eq. 48). The present phase space REM, based on Eq. 24, may therefore be used to describe the relaxation of a system to thermal equilibrium. Time-dependent self-consistent field equations using pure states were shown to provide useful approximations for a variety of molecular dynamical problems, including molecular scattering, electronic spectra, the dissociation of clusters, and thermal desorption from surfaces [5–18]. The present Liouville space approach enjoys all these advantages. In addition, it is particularly suitable for dynamics in condensed phases since it may eliminate the necessity of performing tedious thermal averagings. Further applications to fluorescence and four-wave mixing [21, 43] and to solvation dynamics in molecular rate processes [44] are given elsewhere.

Finally, it should be pointed out that the Winger representation is one of several possible prescriptions for converting functions of operators to ordinary functions of parameters. The various representations differ by the choice of time ordering and by the choice of the parameters [45–48]. Although the various representations are all formally exact, they may yield different results when approximations are made. The present formulation may be extended to apply to these alternative representations.

VI. ABSORPTION AND RAMAN EXCITATION PROFILES OF ANHARMONIC MOLECULES

We have applied the present REM (Eqs. 32) toward the calculation of absorption lineshapes and Raman excitation profiles in anharmonic molecules. The absorption spectra were calculated for a two-mode system. We have

used two different potentials for the electronically excited state. The first is a Morse potential:

$$V_e(x, x_2) = D_1[1 - \exp(-a_1x_1)]^2 + D_2[1 - \exp(-a_2x_2)]^2. \quad (55a)$$

For this potential the harmonic frequencies (obtained by expanding V_e to quadratic order in x_1 and x_2) are

$$\omega'_j = [2a_j^2 D_j / m_j]^{1/2}, \quad j = 1, 2, \quad (55b)$$

and the anharmonicity parameters [49] are

$$\omega'_j x_e = \frac{a_j}{\sqrt{8m_j D_j}}. \quad (55c)$$

The second model we used for the excited state was a Henon-Heiles potential [50] with cubic anharmonicities:

$$V_e(x, x_2) = \frac{1}{2}(m_1 \omega_1'^2 x_1^2) + \frac{1}{2}(m_2 \omega_2'^2 x_2^2) + \lambda_1(x_1^2 x_2 - \frac{1}{3}x_1^3) + \lambda_2(x_1 x_2^2 - \frac{1}{3}x_2^3). \quad (56a)$$

For this model the anharmonicity parameters are

$$\omega'_j x_e = (\hbar m_j^3 \omega_j'^5)^{-1/2} \lambda_j, \quad j = 1, 2. \quad (56b)$$

The ground-state potential was taken to be harmonic,

$$V_g(x_1, x_2) = \frac{1}{2}(\underline{\mathbf{x}} - \underline{\bar{\Delta}})^T \underline{\mathbf{g}}(\underline{\mathbf{x}} - \underline{\bar{\Delta}}), \quad (57a)$$

with

$$\underline{\mathbf{g}} = \underline{\Omega}^{-1/2} \underline{\mathbf{S}}^T \underline{\omega}''^2 \underline{\mathbf{S}} \underline{\Omega}^{-1/2}, \quad (57b)$$

where $\underline{\Omega}$ and $\underline{\omega}''$ are diagonal 2×2 matrices with diagonal elements $1/m_j$ and ω_j'' , respectively, $j = 1, 2$, and $\underline{\mathbf{S}}$ represents a Dushinsky rotation matrix [51],

$$\underline{\mathbf{S}} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix}, \quad (58a)$$

with

$$\underline{\mathbf{S}} \underline{\mathbf{S}}^T = \underline{\mathbf{1}}. \quad (58b)$$

$\bar{\Delta}_i$ represent the linear displacement of the equilibrium position of mode j

between the ground and the excited states. We further introduce the dimensionless displacement

$$\Delta_j = (m_j \omega_j / \hbar)^{1/2} \bar{\Delta}_j. \quad (59)$$

The following parameters were used in our calculations: $\hbar = 1$, $m_1 = m_2 = 1$, $\sin \theta = 0.25$, and $\omega''_1 = 1000 \text{ cm}^{-1}$, $\omega'_1 = 910 \text{ cm}^{-1}$, $\Delta_1 = 1$, $\omega''_2 = 300 \text{ cm}^{-1}$, $\omega'_2 = 260 \text{ cm}^{-1}$, and $\Delta_2 = 1.414$. The system is taken to be initially in thermal equilibrium with temperature T within the ground electronic state. The initial conditions $\sigma_\alpha(0)$ for Eq. 32 are therefore

$$\begin{aligned} \sigma_0(0) &= 1, \\ \sigma_1(0) &= \bar{\Delta}, \\ \sigma_2(0) &= \mathbf{0}, \\ \sigma_3(0) &= \frac{\hbar}{2} \mathbf{\Omega}^{1/2} \mathbf{S}^{-1} (\mathbf{1} + 2\bar{n}) \omega''^{-1} \mathbf{S} \mathbf{\Omega}^{1/2}, \end{aligned}$$

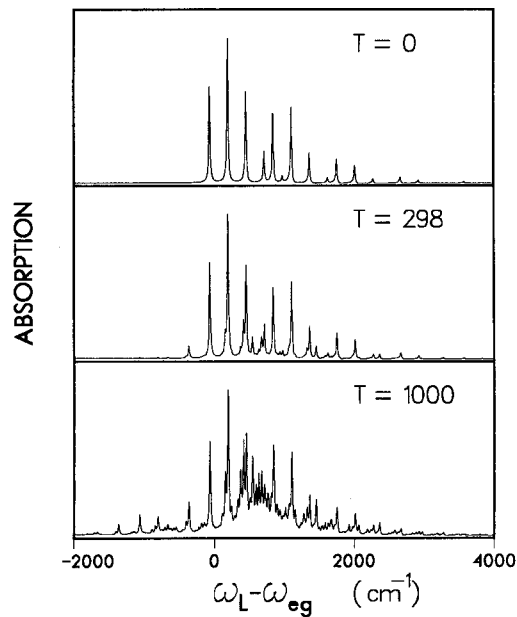


Figure 1. The absorption spectrum of a two-mode harmonic system (Eqs. 57 and 56a with $\lambda_1 = \lambda_2 = 0$) at three temperatures as indicated.

$$\sigma_4(0) = \frac{\hbar}{2} \mathbf{\Omega}^{-1/2} \mathbf{S}^{-1} (\mathbf{1} + 2\bar{n}) \boldsymbol{\omega}'' \mathbf{S} \mathbf{\Omega}^{-1/2},$$

$$\sigma_5(0) = \mathbf{0}, \quad (60)$$

with

$$\bar{n} = [\exp(\beta \hbar \boldsymbol{\omega}'') - \mathbf{1}]^{-1}, \quad (61a)$$

$$\beta = \frac{1}{kT}. \quad (61b)$$

Figure 1 displays the absorption spectrum in the harmonic limit (Eq. 56a) with $\lambda_1 = \lambda_2 = 0$ at three temperatures. Equations 32 were solved with the initial condition (Eqs. 60), and the absorption spectrum was then calculated using Eq. 16 and a standard fast Fourier transform routine. We have further invoked the Condon approximation and set $\mu(\mathbf{x}) = 1$. 8192 points were used in the calculation with a resolution of 5 cm^{-1} . The high-temperature calculations require computation time comparable to the zero-temperature calculation.

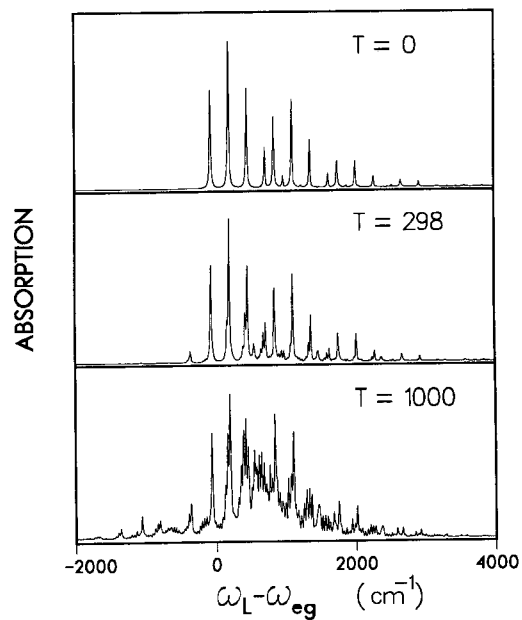


Figure 2. The absorption spectrum of a two-mode system whose ground state is harmonic (Eq. 57) and the excited state is given by a Morse potential (Eq. 55). The anharmonicity parameters are $\omega'_1 x_e = \omega'_2 x_e = 10^{-4}$.

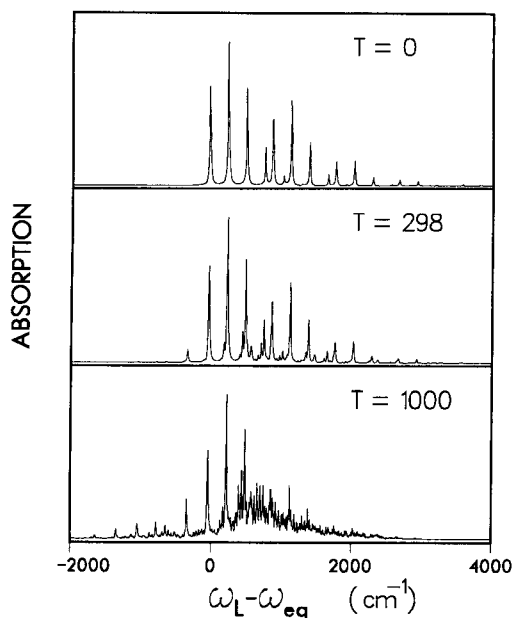


Figure 3. The absorption spectrum of a two-mode system whose ground state is harmonic (Eq. 57) and excited state is given by the cubic potential (Eq. 56). The anharmonicity parameters are $\omega'_1 x_e = \omega'_2 x_e = 0.005$.

This is the main advantage of the present approach compared with calculations using pure states in which the thermal averaging is done at the end and the computation time increases considerably with temperature. Figure 2 displays the absorption spectrum for the Morse potential (Eq. 55) for three temperatures calculated in the same way. The excited-state anharmonicity is $\omega'_1 x_e = \omega'_2 x_e = 10^{-4}$. Figure 3 repeats this calculation for the cubic anharmonic potential (Eq. 56a) with anharmonicity $\omega'_1 x_e = \omega'_2 x_e = 0.005$. A smoothing of the Fourier transform was needed in these calculations. We have also calculated the Raman excitation profiles (Eq. 36) for a single mode whose ground state is harmonic and the excited state is a Morse potential. Figure 4 shows the fundamental 0–1 Raman excitation profile for the single-mode system at $T = 0$ K. We have used $\omega'' = 1050 \text{ cm}^{-1}$, $\omega' = 1000 \text{ cm}^{-1}$, $\omega' x_e = 0.001$, and $\Delta = 1.5$ and a spectral resolution of 20 cm^{-1} . For comparison we show also the exact excitation profile obtained using a sum over states. Figure 5 displays the same calculation on a logarithmic scale (base 10). The good agreement demonstrates the capabilities of the present REM, which should be particularly useful for large systems with many degrees of freedom.

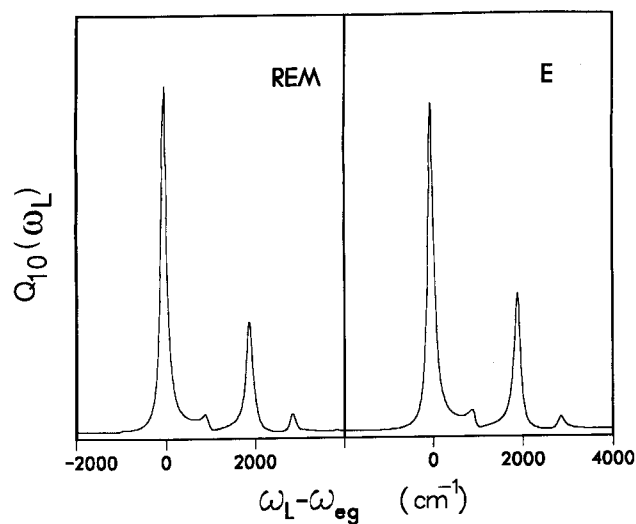


Figure 4. Raman excitation profile (Eq. 36) for a single-mode system with a harmonic ground state and an excited-state Morse potential (Eq. 55 with one mode). Shown is the Raman fundamental 0-1 versus the incident frequency [26]: REM, using the present equations (Eqs. 32); E, exact calculation made by a sum over states.

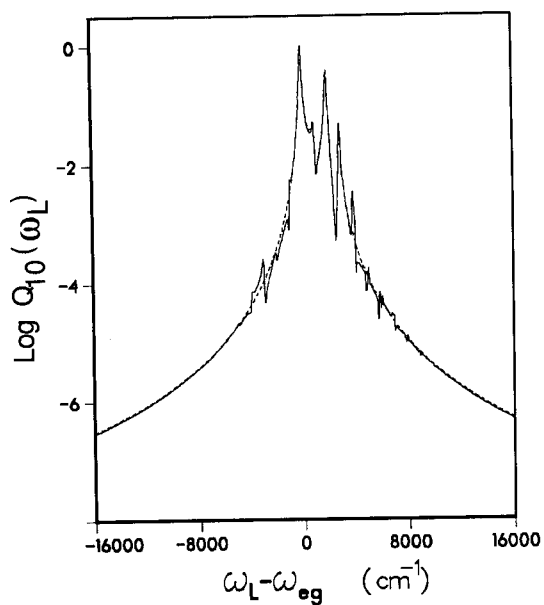


Figure 5. Same as Figure 4 plotted on logarithmic state (base 10). The solid curve is our calculation using the REM and the dashed curve is the exact calculation [26].

**APPENDIX: THE GENERATING FUNCTION IN THE
COORDINATE REPRESENTATION**

Equation 24 may be transformed to the coordinate representation using Eq. 3c. We then get

$$\sigma(\underline{x}, \underline{x}'; t) = C \exp[-\underline{\eta}^T \underline{x} - \underline{\delta}^T \underline{x}' - \underline{x}^T \underline{\alpha} \underline{x} - \underline{x}'^T \underline{\beta} \underline{x}' - 2\underline{x}^T \underline{\gamma} \underline{x}'],$$

where

$$C = \sigma_0 (2\pi)^{-N/2} [\det \sigma_3]^{-1/2} \exp[-\frac{1}{2} \underline{\sigma}_1^T \sigma_3^{-1} \underline{\sigma}_1],$$

$$\underline{\eta} = \frac{1}{i\hbar} (\underline{\sigma}_2 - \sigma_5^T \sigma_3^{-1} \underline{\sigma}_1) - \frac{1}{2} \sigma_3^{-1} \underline{\sigma}_1,$$

$$\underline{\delta} = -\frac{1}{i\hbar} (\underline{\sigma}_2 - \sigma_5^T \sigma_3^{-1} \underline{\sigma}_1) - \frac{1}{2} \sigma_3^{-1} \underline{\sigma}_1,$$

$$\underline{\alpha} = \frac{1}{2\hbar^2} [\sigma_4 - (\sigma_5^T + \frac{1}{2}i\hbar \mathbf{I}) \sigma_3^{-1} (\sigma_5 + \frac{1}{2}i\hbar \mathbf{I})],$$

$$\underline{\beta} = \frac{1}{2\hbar^2} [\sigma_4 - (\sigma_5^T - \frac{1}{2}i\hbar \mathbf{I}) \sigma_3^{-1} (\sigma_5 - \frac{1}{2}i\hbar \mathbf{I})],$$

$$\underline{\gamma} = -\frac{1}{2\hbar^2} [\sigma_4 - (\sigma_5^T + \frac{1}{2}i\hbar \mathbf{I}) \sigma_3^{-1} (\sigma_5 - \frac{1}{2}i\hbar \mathbf{I})].$$

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