Reduced equations of motion for semiclassical dynamics in phase space

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(Received 10 November 1986; accepted 8 December 1986)

Time-dependent self-consistent equations for semiclassical dynamics in phase space are developed. The method is based on constructing a Gaussian density matrix, whose equations of motion are obtained by requiring that the first two moments of the coordinates and momenta have the correct time evolution. The method can yield, in principle, the exact values of these moments for all time. The present method can be applied for the time evolution of mixed states in phase space and may, therefore, be particularly useful for molecular dynamics in condensed phases. Raman excitation profiles in anharmonic molecules are calculated and show excellent agreement with exact calculations.

I. INTRODUCTION

The calculation of molecular dynamical processes such as energy transfer, vibrational relaxation, scattering processes, and spectral line shapes requires the development of efficient methods for the numerical solution of the Schrödinger equation for interacting many-body systems. Some of the methods commonly used include wave packet dynamics,1-9 grid methods,10 and the path integral formalism.11-14 We have recently proposed a new type of self-consistent semiclassical reduced equations of motion in phase space,15 which are based on projection operator techniques of nonequilibrium statistical mechanics.16-19 To lowest order, the equations provide a time-dependent self-consistent field approximation (TDSCF),20,21 which can then be systematically improved. The present approach is formulated in terms of the density matrix in Liouville space22,23 and as such 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 line shapes of molecules in solution and on solid surfaces, desorption, vibrational relaxation, etc.). In Sec. II, we develop the general TDSCF equations. In Sec. III, we connect the present procedure to the maximum entropy formalism18,19,24 used in nonequilibrium statistical mechanics. In Sec. IV, we discuss and analyze our results. Finally in Sec. V, we make a specific application to the absorption and the Raman excitation profiles of anharmonic diatomic molecules and present detailed calculations for the first two moments with respect to coordinates and momenta for the Morse oscillator.25 We further make a detailed critical comparison with the Thawed Gaussian procedure.1

II. THE TDSCF REDUCED EQUATIONS OF MOTION

We consider a system characterized by $N$ coordinates $x_j, j = 1,...,N$, their conjugate momenta $p_j = i\hbar \partial / \partial x_j$, and masses $m_j$. Its Hamiltonian is given by

$$H = \sum_{j=1}^{N} p_j^2/2m_j + V(x_1,...,x_N),$$

where $V$ is the interaction potential. Our system is specified by the density matrix $\rho(x,x';t)$ where $x$ is a vector with $N$ components $x_1,...,x_N$. The density matrix evolves in time according to the quantum mechanical Liouville equation

$$\frac{d\rho}{dt} = -i [H,\rho] = -(i/\hbar) [H,\rho].$$

(2)

If the system is in a pure state characterized by a wave function $\psi(x,t)$, then $\rho(x,x';t) = \psi(x,t)\psi^*(x',t)$ and Eq. (2) is identical to the Schrödinger equation. Because the total density matrix $\rho(x,x';t)$ can be quite complicated and contains more information than necessary for the calculation of various physical quantities of interest, we define a reduced density matrix $\sigma(x,x';t)$, constructed as follows.15 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 shall focus on the following set of $6N$ operators:

$$A_{ij} = 1, \quad A_{ij} = x_i, \quad A_{ij} = p_j, \quad A_{ij} = x_j^2, \quad A_{ij} = p_j^2,$$

$$A_{ij} = x_i p_j + p_j x_i, \quad i = 1,...,N.$$  

(3)

The expectation values of these operators will be denoted $\langle a_{ij} \rangle$. They represent the complete set of first and second moments of the coordinates and momenta of each particle, i.e.,

$$a_{ij}(t) = \langle A_{ij} \rangle = \text{Tr} [A_{ij} \rho(x,x';t) ],$$

$$\alpha = 0,...,5, \quad j = 1,...,N.$$  

(4)

$A_{ij}$ is the unit operator and normalization requires its expectation value to be independent of time, $\langle a_{ij} \rangle = 1$. The approximate density matrix $\sigma(x,x';t)$ is taken to be in the form of a product of single particle density matrices:

$$\sigma(x,x';t) = \prod_{j=1}^{N} \phi_j(x_j,x'_j;t),$$

(5)

where $\phi_j$ are taken to be Gaussian:

$$\phi_j(x_j,x'_j;t) = \exp \left[ -b_{ij} - b_{ij} x_j - b_{ij}^* x'_j - b_{ij} x_j x'_j \right].$$

(6)

The time-dependent parameters $b_{ij}$ may be uniquely expressed in terms of $a_{ij}$ by requiring that the expectation values of our operators $A_{ij}$ evaluated using the exact ($\rho$) and the approximate ($\sigma$) density matrix will be the same, i.e.,
For each degree of freedom $j$ we define a $6 \times 6$ matrix with matrix elements:

$$S'_{\alpha \beta}(t) = \left\langle \sigma(t) A_{\alpha} | \sigma(t) A_{\beta} \right\rangle = \text{Tr}[A_{\alpha} \rho(x,x';t) A_{\beta}],$$

$$\alpha, \beta = 0, 1, \ldots, 5$$

and the Liouville-space projection operator

$$P(t) = \sum_{j=1}^{N} \sum_{\alpha = 0}^{5} \left| \sigma(t) A_{\alpha} \right\rangle \left\langle \sigma(t) A_{\alpha} \right|.$$

We further introduce the complementary projection

$$Q(t) = 1 - P(t).$$

We are using here Liouville space notation, whereby an ordinary operator $A$ is written as a ket $|A\rangle$ and the scalar product of two operators $\left\langle A \left| B \right\rangle \right\rangle = \text{Tr}(A^+ B)$ is a scalar product of two operators. $\left\langle A \left| L \right| B \right\rangle = \text{Tr}(A^+ L B)$ is a Liouville space “matrix element.” The properties of the projection operator $P(t)$ have been discussed previously. Using the assumption that at some initial time $t = t_0$, $\rho(t_0) = \sigma(t_0)$, we can derive the following exact reduced equations of motion (REM):

$$\dot{a}_{\alpha j}(t) = -i\left\langle A_{\alpha} | L \right| \sigma(t) \right\rangle + \sum_{\beta} K_{\alpha \beta}(t) a_{\beta j}(t),$$

where we have introduced the $6 \times 6$ matrices

$$W'_{\alpha \beta}(t) = -i\left\langle A_{\alpha} \left| L Q(t) U(t,t_0) \right| \sigma(t_0) A_{\beta} \right\rangle,$$

$$V'_{\alpha \beta}(t) = \left\langle A_{\alpha} \left| U(t,t_0) \sigma(t_0) A_{\beta} \right\rangle,$$

and

$$K'_{\alpha \beta}(t) = \sum_{\gamma} W'_{\alpha \gamma}(t) V'_{\gamma \beta}(t) [V'(t,t_0)]^{-1}.$$  

Equation (10d) can be recast in matrix notation:

$$K'(t,t_0) = W'(t,t_0) \left[ V'(t,t_0) \right]^{-1}.$$  

Here $U(t,t_0)$ is the propagator

$$U(t,t_0) = \exp[-iL(t - t_0)].$$

Equations (10) are $5N$ coupled nonlinear differential equations for $a_{\alpha j}$. In these equations the time derivative of $a_{\alpha j}$ at time $t$ depends on all $a_{\beta j}$ at the same time. Alternatively we may derive REM which are in the form of coupled integral equations. In the new REM the time derivative of $a_{\alpha j}$ at time $t$ depends on the values of all $a_{\beta j}$ at all previous times $t_0 < s < t$. The detailed derivation is given in Appendix A. The resulting equations are

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

where

$$\bar{K}(t,s) = \exp_{+} \left[-i \int_{s}^{t} d\tau Q(\tau) L \right],$$

and $\exp_{+}$ denotes the time ordered exponential. The first term on the right-hand side of both REM [Eqs. (10a) and (11a)] represents a mean field evolution arising if $\rho(t) = \sigma(t)$ for all times, whereas the second term, the fluctuation kernel, arises from the fact that, in general, $\rho(t) \neq \sigma(t)$ for $t > t_0$ and it corrects the time evolution of $\sigma(t)$. It should be noted that both REM [Eqs. (10a) and (11a)] are exact, provided the appropriate kernels $K$ and $\bar{K}$ are evaluated to infinite order using some expansion parameter. In practice, once the kernel is truncated, Eqs. (10) and (11) yield different approximations. The choice of the proper reduction scheme depends on the statistical properties of the system.  

It will be convenient to make a minor change of variables and use the following $5N$ variables $\sigma_{\alpha j}$ instead of the $a_{\alpha j}$:

$$\sigma_{\gamma j} = \left\langle x_j \right|,$$

$$\sigma_{\gamma j} = \left\langle p_j \right|,$$

$$\sigma_{\gamma j} = \left\langle x_j^2 \right| - \left\langle x_j \right|^2,$$

$$\sigma_{\gamma j} = \left\langle p_j^2 \right| - \left\langle p_j \right|^2,$$

$$\sigma_{\gamma j} = \left[ \left\langle x_j p_j \right| + p_j x_j \right| - 2 \left\langle x_j \right| \left\langle p_j \right| \right]/2.$$  

Making use of Eqs. (7), we can express the parameters $b_{\alpha j}$ [Eq. (6)] in terms of the moments of the fields $\sigma_{\alpha j}$, resulting in

$$b_{\gamma j} = \frac{\sigma_{\gamma j}^2 + \sigma_{\gamma j} \log(2\pi \sigma_{\gamma j})}{2 \sigma_{\gamma j}},$$

$$b_{\gamma j} = -\hbar \sigma_{\gamma j} + 2i \left[ \sigma_{\gamma j} \sigma_{\gamma j} - \sigma_{\gamma j} \sigma_{\gamma j} \right],$$

$$b_{\gamma j} = -\hbar^2 + 4 \left[ \sigma_{\gamma j} \sigma_{\gamma j} - \sigma_{\gamma j}^2 - i\hbar \sigma_{\gamma j} \right],$$

$$b_{\gamma j} = \frac{\hbar^2 + 4 \left( \sigma_{\gamma j}^2 - \sigma_{\gamma j} \sigma_{\gamma j} \right)}{4 \hbar^2 \sigma_{\gamma j}}.$$  

The TDSCF equations, which will be developed in this article, are obtained by retaining only the mean field term in Eqs. (10a) or Eqs. (11a), i.e.,

$$\dot{\sigma}_{\gamma j} = -i \left\langle A_{\alpha} | L \right| \sigma(t) \right\rangle.$$  

We have evaluated Eq. (14) explicitly for the Hamiltonian [Eq. (1)]. The final result, recast in terms of the new variables $\sigma_{\alpha j}$ is:

$$\dot{\sigma}_{\gamma j} = \sigma_{\gamma j}/m_j,$$

$$\dot{\sigma}_{\gamma j} = -\left\langle V_j(x) \right|,$$

$$\dot{\sigma}_{\gamma j} = 2 \sigma_{\gamma j}/m_j,$$

$$\dot{\sigma}_{\gamma j} = -2 \left\langle V_j(x) \right| \sigma_{\gamma j},$$

$$\dot{\sigma}_{\gamma j} = \frac{\sigma_{\gamma j}^2}{m_j} - \left\langle V_j(x) \right| \sigma_{\gamma j},$$

where

$$V_j(x) = \frac{\partial V}{\partial x_j},$$

$$V_j(x) = \frac{\partial^2 V}{\partial x_j^2},$$

$$\left\langle V_j(x) \right| = \int dx_v V_j(x) \sigma(x,x';t),$$

$$\sigma(x,x';t) = \prod_{j=1}^{N} \phi_j(x_j,x_j';t).$$
\[\phi_j(x_j,x_j';t) = \frac{1}{\sqrt{2\pi\sigma_y}} \exp \left[ - \frac{(x_j - \sigma_j)^2}{2\sigma_y} \right]. \tag{16e}\]

\(\langle V_{y'}(x) \rangle\) is defined in an analogous way to Eq. (16c) by replacing \(V_j(x)\) with \(V_{y'}(x)\). Equations (15) are the phase space TDSCF equations, and they will be analyzed in the coming sections.

III. RELATION TO THE MAXIMUM ENTROPY FORMALISM

The choice of the form of \(\phi_j\) [Eq. (5)] is crucial in a successful application of the REM. In principle, we can choose any reasonable function depending on six parameters, which can be determined via Eq. (7). Equations (10a) or (11a) will then result in a closed set of equations for these parameters. The particular choice of \(\phi_j\), adopted in this article [Eq. (6)], was motivated by physical considerations and is by no means unique. A powerful, systematic way to construct \(\phi_j\) is provided by the maximum entropy formalism.\(^{15,18,19,24}\) Within this formalism we construct a density matrix \(\sigma(x,x';t)\), which maximizes the entropy subject to the constraints [Eqs. (7)]. For our chosen set of variables [Eq. (3)], the maximum entropy distribution is in the form of Eq. (5), where

\[\phi_j(x_j,x_j';t) = \langle x_j | \phi(t) | x_j' \rangle \tag{17a}\]

with

\[\phi(t) = \exp \left[ \sum_{\alpha=0}^5 \lambda_{\alpha} A_{\alpha} \right], \tag{17b}\]

where \(A_{\alpha}\) are numerical coefficients which may be expressed in terms of \(\sigma_{\alpha}\). We shall now show that our Gaussian choice [Eq. (6)] is identical to the maximum entropy distribution [Eqs. (17)]. This provides an additional physical insight for our choice [Eq. (6)] and connects the present semiclassical procedure with the more general problem of the derivation of reduced equations of motion in nonequilibrium statistical mechanics. To simplify the notation, we shall consider in this section only one degree of freedom. The proof holds, however, for any number \(N\). In the remainder of this section, we shall, therefore, omit the subscript \(j\) and replace Eq. (17) by

\[\sigma(x,x';t) \equiv \langle x | \phi(t) | x' \rangle \tag{18a}\]

with

\[\phi(t) = \exp \left[ \sum_{\alpha=0}^5 \lambda_{\alpha} A_{\alpha} \right]. \tag{18b}\]

We further define the density matrix in the Wigner representation \(\sigma_w\),\(^{27,28}\) i.e.,

\[\sigma_w(q,p;t) \equiv \frac{1}{\pi \hbar} \int_{-\infty}^{\infty} \sigma(q + s, q - s; t) \exp \left[ - \frac{ip s}{\hbar} \right] ds \tag{19a}\]

and the inverse transform

\[\sigma(q + s, q - s; t) = \int_{-\infty}^{\infty} \sigma_w(q,p;t) \exp \left[ \frac{ip s}{\hbar} \right] dp \tag{19b}\]

In Eqs. (19) we have used the substitutions

\[q = \frac{x + x'}{2}, \tag{20a}\]

\[s = \frac{x - x'}{2}. \tag{20b}\]

The Wigner function is normalized as

\[\int \int \sigma_w(q,p,t) dq dp = 1. \tag{21}\]

In Appendix B, we show that the Wigner representation of Eq. (18) assumes the form\(^{29-32}\)

\[\sigma_w(q,p;t) = \frac{1}{\pi} \left[ \alpha \beta - \gamma^2/4 \right]^{1/2} \times \exp \left[ (\delta^2 \beta + \phi^2 \alpha - \gamma \phi)/(4 \alpha \beta - \gamma^2) \right] \times \exp \left[ (\alpha q^2 + \beta p^2 + \gamma pq + \delta + \phi) \right] \tag{22a}\]

with \(\alpha, \beta, \gamma, \delta, \phi\) being real parameters, which may be expressed in terms of \(\lambda_1, \ldots, \lambda_5\). Using Eq. (19b), we then have\(^{29}\)

\[\sigma_{\alpha}(t) = [\langle x p + px \rangle - \langle x \rangle \langle p \rangle]/2 = -\gamma(\gamma^2 - 4 \alpha \beta)^{-1} \tag{23a}\]

or

\[\alpha = \sigma_{\alpha}, \tag{24a}\]

\[\beta = \sigma_{\beta}, \tag{24b}\]

\[\gamma = -\sigma_{\gamma}, \tag{24c}\]

\[\delta = 2 \sigma_{\lambda_2} - \sigma_{\lambda_3}, \tag{24d}\]

\[\phi = 2 \sigma_{\lambda_5} - \sigma_{\lambda_4}, \tag{24e}\]

\[\text{J. Chem. Phys., Vol. 86, No. 6, 15 March 1987}\]
where
\[ c = \frac{1}{2} \left( \gamma^2 - 4\alpha \beta \right) = \frac{1}{2(\sigma^2 - \sigma\sigma_d)}. \]  
(24f)

Equations (22)–(24) result in
\[
\sigma(x, x'; t) = \frac{1}{\sqrt{2\pi} \sigma_3} \exp \left( -\frac{1}{2\sigma_3}(x + x')^2 \right) \times \exp \left[ -\frac{1}{8\sigma_3}(x + x')^2 + \frac{\sigma_1}{2\sigma_3}(x + x') \right.
\]
\[
+ \frac{1}{4\hbar^2 \sigma_3} (x - x')^2 + \frac{i\sigma_5}{2\sigma_3 \hbar} (x^2 - x'^2)
\]
\[
- \frac{i}{\sigma_3 \hbar} (\sigma_1 \sigma_5 - \sigma_2 \sigma_3)(x - x') \]  
(25a)

and
\[
\sigma_\omega(q, p; t) = \frac{1}{2\pi \sqrt{\sigma_3 \sigma_4 - \sigma_5}} \exp \left\{ -\frac{1}{2(\sigma_3 \sigma_4 - \sigma_5)} \left[ \sigma_4(q - \sigma_1)^2 + \sigma_5(p - \sigma_2)^2 - 2\sigma_5(q - \sigma_1)(p - \sigma_2) \right] \right\}. \]  
(25b)

Equation (25a) is identical to Eq. (6). We have thus established the equivalence of our Gaussian choice [Eq. (6)] with the maximum entropy density matrix obtained using the variables \( A_{ij} \) [Eq. (3)].

IV. DISCUSSION

The present TDSCF formulation enjoys several advantages over the existing wave packet propagation schemes.\(^\text{1-7}\) It is a density matrix formulation not restricted to pure states, thus allowing a wider range of problems to be accessible to the method. We have further shown in Sec. III that our Gaussian choice for the reduced density matrix is identical to the maximum entropy distribution. Thus, the TDSCF is intimately connected with the more general problem of deriving reduced equations of motion in nonequilibrium statistical mechanics.\(^\text{15-19,33}\) We shall now analyze the significance of our final equations. We first note that Eqs. (15) may be rewritten as an expansion in the width of the wave packet by expanding the potential around the minimum of the wave packet
\[
\langle V_j(x) \rangle = \sum_{n=0}^\infty 2^n \sigma_5^n /[ (2n)! ] V_j^{(2n+1)}(x), \]  
(26a)

\[
\langle V_\omega(x) \rangle = \sum_{n=0}^\infty 2^n \sigma_5^n /[ (2n)! ] V_\omega^{(2n+2)}(x), \]  
(26b)

with
\[
V_j^{(n)}(x) = \frac{\partial^n V_j}{\partial x^n} \bigg|_{x = x}. \]  
(26c)

The thawed Gaussian (TG) equations\(^\text{3} \) may be obtained from our TDSCF equations [Eqs. (15)] if the following approximations are made: (i) We take only the zeroth order terms in Eqs. (26). Dropping the higher order terms is equivalent to assuming that the density matrix is essentially a delta function and thus highly localized. We then set
\[
\langle V_j(x) \rangle = V_j(\langle x \rangle) \]  
(27a)

and
\[
\langle V_\omega(x) \rangle = V_\omega(\langle x \rangle). \]  
(27b)

(ii) We further assume that initially the system is in a pure state. For a pure state, our density matrix assumes the form
\[
\phi_j(x, x'; t) = \psi(x, t) \psi^*(x', t). \]  
(28)

A necessary and sufficient condition for \( \phi_j \) to represent a pure state is \( b_j = 0 \), i.e.,
\[
\sigma_j^2 = \sigma_\omega \sigma_j - (\hbar/2)^2. \]  
(29)

Thus, for a pure state \( \sigma_j \) is uniquely determined, up to a sign, by \( \sigma_\omega \) and \( \sigma_\omega \). Equations (6), (13), (28), and (29) result in
\[
\psi(x, t) = (2\pi \sigma_3)^{-1/4} \exp \left\{ \frac{1}{4\sigma_3} + \frac{i\sigma_5}{2\hbar \sigma_3} \right\} (x - \sigma_1)^2 + \frac{i\sigma_5}{\hbar} (x - \sigma_1) + \frac{i\gamma}{\hbar}, \]  
(30)

where \( \gamma \) is a time-dependent phase factor. Equations (15) together with the approximations [Eqs. (27) and Eq. (29)] reduce to the thawed Gaussian equations.\(^\text{1} \) When the density matrix represents a mixed state, Eq. (29) is not satisfied. It can be easily verified from Eqs. (15) that the solution of \( \sigma_{ij} \) is
\[
\sigma_j^2(t) = \sigma_j(t) \sigma_\omega(t) + C, \]  
(31)

where \( C \) is a constant determined by the initial conditions. If \( C = -(\hbar/2)^2 \), Eq. (29) will be satisfied for all time. Thus, within the TDSCF, 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 state to evolve into a mixed state. This is a necessary requirement for a reduced description which should show, e.g., how a system relaxes to thermal equilibrium with a thermal bath. For the sake of illustration, let us consider the density matrix for a harmonic system in thermal equilibrium:\(^\text{11,29}\)
\[
\sigma_j(t) = \exp(-\beta H)/Tr \exp(-\beta H) \]  
(32)

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

\[
H(x, p) = \frac{p^2}{2m} + \frac{1}{2} \omega^2 x^2. \]  
(33)

In this case we have \( \sigma_1 = 0, \sigma_2 = 0 \),
\[
\sigma_3 = (\hbar/2m) \coth[1/2 \beta \hbar \omega], \]
\[
\sigma_4 = \frac{1}{2} m \hbar \coth(1/2 \beta \hbar \omega), \sigma_5 = 0, \]  
and we have
\[
\sigma_j(x, x'; t) = \frac{1}{\sqrt{2\pi} \sigma_3} \exp \left\{ -\frac{(x + x')^2}{8\sigma_3} - \frac{\sigma_4(x - x')}{2\hbar^2} \right\} \]  
(34a)

and
\[
\sigma_\omega(q, p; t) = \frac{1}{2\pi \sqrt{\sigma_3 \sigma_4}} \exp \left\{ -\frac{q^2}{2\sigma_3} - \frac{p^2}{2\sigma_4} \right\} \]  
(34b)

The thermal density matrix can be represented by our Gaussian form [Eq. (25a)], but since it corresponds to a mixed

state, it cannot be represented by a single wave function [Eq. (28)]. The present phase space REM, based on Eq. (5), unlike the wave packet approach [Eq. (28)], may therefore be used to describe the relaxation of a system to thermal equilibrium. TDSCF 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.\textsuperscript{1-10,21} They are also extremely useful for a mixed description in which some degrees of freedom are treated quantum mechanically and others are treated classically. The present phase space TDSCF 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 averaging. The "bundle of trajectories" used by Gerber, Ratner, and co-workers\textsuperscript{21} applies naturally within the phase space TDSCF. We further note that Eqs. (15) 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. (2) with the classical Liouville operator. $\rho_j(x_j,p_j;\tau)$ should then be replaced by a phase space distribution function of coordinates and momenta [Eq. (19a)]. Taking this function to be Gaussian in $x_j$ and $p_j$ [Eq. (25b)], we can repeat the derivative step-by-step and obtain Eqs. (15). The TDSCF equations for the moments $\sigma_j, \ldots, \sigma_n$, using Gaussian wave packets, are therefore completely classical. Another advantage of the present formalism compared with other propagation schemes\textsuperscript{1-7} is that Eqs. (15) are the lowest order of a systematic expansion which may be carried out order-by-order. The present equations may be extended by various ways. One possibility is to expand the fluctuation term in Eqs. (10a) or (11a) perturbatively. Note that for harmonic systems the TDSCF equations are exact, provided we take $x_c$ to be the normal modes. This suggests that an expansion of the kernel $K$ or $\bar{K}$ in anharmonicities may be appropriate. We may, for example, go beyond the Hartree approximation implied in the factorization of $\sigma$ into a product of single-particle density matrices [Eq. (5)] and consider a complete set of bilinear operators $x_j x_k$, $p_j p_k$, and $x_j p_k + x_k p_j$. This will result in $2N^2 + 3N$ dynamical variables (instead of the $5N$ used here). Such a choice may, therefore, be useful for few-body problems (small $N$) but is impractical for macroscopic systems due to the large number of variables involved. Such extension of Eqs. (15) is straightforward, requires the use of a multivariable Gaussian distribution for $\sigma$, and was not included here for clarity. Alternatively, we may add more dynamical variables to our chosen set $A_{ij}$ (e.g., $x_j x_i$, $j = 1$) and construct a non-Gaussian density matrix with more parameters. The TDSCF will then provide an improved reduced description of the system.

V. RAMAN EXCITATION PROFILES OF ANHARMONIC MOLECULES

In this section, we apply the TDSCF equations toward the calculation of absorption and Raman line shapes of a diatomic molecule.\textsuperscript{26} Consider a diatomic molecule with two electronic states, a ground state $|g\rangle$ and an excited state $|e\rangle$. Its Hamiltonian is

$$H = |g\rangle H_g |g\rangle + |e\rangle (H_e + H_s) |e\rangle.$$  \[(35a)\]

We assume the ground state potential to be harmonic and the excited state potential to be given by a Morse oscillator. We then have

$$H_g = p^2/2m + 1/2\omega_a^2 x^2,$$  \[(35b)\]

$$H_e = p^2/2m + D[1 - \exp(-a(x - x_0))].$$  \[(35c)\]

We denote the eigenstates of $H_g$ by $|\Psi_n\rangle$:

$$H_g |\Psi_n\rangle = \hbar \omega n (n + 1/2) |\Psi_n\rangle,$$  \[(36a)\]

with

$$\Psi_n(y) = C_n \exp(-y^2/2) H_n(y),$$  \[(36b)\]

where $H_n$ being the Hermite polynomials, and

$$y = \sqrt{\frac{\hbar \omega}{m}} x,$$  \[(36c)\]

$$C_n = \left(\frac{\sqrt{\hbar \omega / \pi m}}{n!}\right)^{1/2}.$$  \[(36d)\]

For the eigenstates of $H_e$, we define the following variables:

$$c = \sqrt{2mD / (\hbar \omega a)},$$  \[(37a)\]

$$z = 2c \exp[-a(x - x_0)],$$  \[(37b)\]

$$N_n = \frac{1}{2^{1/2}} \left[\frac{n!(2c - 2n - 1)!}{\Gamma(2c - n)}\right]^{1/2},$$  \[(37c)\]

$$\omega = \sqrt{\frac{2a^2 D}{m}},$$  \[(37d)\]

$$\lambda x = \hbar \omega a / 2m.$$  \[(37e)\]

The eigenstates of the Morse oscillator are then given by\textsuperscript{34}

$$H_e |\chi_j\rangle = E_j |\chi_j\rangle,$$  \[(38a)\]

with

$$\chi_j(z) = N_j \exp(-z/2) e^{-j + 0.5} L_n^{(3/2 - j + 1)}(z),$$  \[(38b)\]

where $L_n^{(j)}$ is the associated Laguerre polynomial, while the corresponding eigenvalue is given by

$$E_j = \hbar \omega (j + 1/2) - \hbar \omega x, (j + 1/2).$$  \[(38c)\]

Finally, the number of bound states is given by $N_{\text{max}} = \text{Int}(c)$. Invoking the Condon approximation we take the dipole operator to be independent of the nuclear coordinates. The absorption spectrum is then given by\textsuperscript{35}

$$I(\omega_L) = \text{Re} \int_0^\infty G_{\omega_0}(t) \exp(-i \omega_L t - \Gamma t/2) dt.$$  \[(39)\]

The Raman excitation profiles are given by the Kramers-Heisenberg formula

$$Q_{\omega_0}(\omega_L) = \left| \int_0^\infty \langle G_{\omega_0}(t) \exp(-i \omega_L t - \Gamma t/2) dt \right|^2,$$  \[(40)\]

where the Green functions

$$G_{nm}(t) = \langle \psi_n | \exp(-i H t) | \psi_m \rangle = \langle \psi_n | \psi_m(t) \rangle,$$  \[(41)\]

with

$$| \psi_m(t) \rangle = \exp(-i H t) | \psi_m \rangle.$$  \[(42)\]

Here $\Gamma$ is the lifetime of the electronically excited state. $Q_{\omega_0}(\omega_L)$ denotes the intensity of the Raman transition in

FIG. 1. (a) The mean displacement $\sigma_x = \langle x \rangle$ vs time for a Gaussian wave packet propagated on a Morse potential. The Morse oscillator frequency is $\omega = (2D\alpha^2/m)^{1/2} = 1$, $D/\hbar\omega = 5$, and $\hbar\omega/m\alpha = 0.1$. These parameters correspond to an anharmonicity of $\alpha x_x = 0.05$. The coordinate $x$ is given in units of $(\hbar/m\omega)^{1/2}$ and the momentum in units of $(\hbar\omega)^{1/2}$. In these units $x_0 = -0.3$, and the initial conditions corresponding to $|\phi_0 \rangle$ [Eq. (36b)] are given by $\sigma_x(0) = 0$, $\sigma_x(0) = 0$, $\sigma_x(0) = 0.48$, $\sigma_x(0) = 0.53$. (b) The present calculation [Eq. (15)] (SCF), the exact calculation [Eq. (47b)] (E), and the thawed Gaussian [Eq. (46)] (TG) calculation. (b) The dimensionless variance of the displacement $\sigma_x = \langle x^2 \rangle - \langle x \rangle^2$ for the system of Fig. 1(a). (c) The dimensionless mean momentum $\sigma_p = \langle p \rangle$ for the system of Fig. 1(a). (d) The dimensionless variance of the momentum $\sigma_p = \langle p^2 \rangle - \langle p \rangle^2$ for the system of Fig. 1(a).
FIG. 2. (a) The dimensionless mean displacement for the model of Fig. 1 with $x_0 = -0.001$. (b) The dimensionless variance of the displacement $\sigma_x = \langle x^2 \rangle - \langle x \rangle^2$ for the system of Fig. 2(a). (c) The dimensionless mean momentum $\sigma_\pi = \langle \pi \rangle$ for the system of Fig. 2(a). (d) The dimensionless variance of the momentum $\sigma_\pi^2 = \langle \pi^2 \rangle - \langle \pi \rangle^2$ for the system of Fig. 2(a).
which the molecule changes its state from \( |\psi_0\rangle \) to \( |\psi_n\rangle \) as a function of the incident photon frequency \( \omega_L \). We have taken the molecule to be initially in the ground vibrational state \( |\psi_0\rangle \). Since the density matrix contains no information about the phase \( \gamma(t) \) [Eq. (30)], an additional equation is necessary. The equation of motion for the phase factor \( \gamma(t) \) is derived by using the Schrödinger equation

\[
\langle \dot{E}_G \rangle = \langle p^2/2m + V(x) \rangle = i\hbar \langle \psi | \dot{\psi} \rangle.
\]

Thus we get

\[
\gamma = -\frac{\hbar}{4m\sigma_3} + \frac{V_0\sigma_3}{2} + \frac{\sigma_3^2}{2m} - V_0.
\]

With \( V_2 = \langle \partial^2 V/\partial x^2 \rangle \) and \( V_0 = \langle V \rangle \). Our equations may be recast in a form similar to the thawed Gaussian procedure\(^1\) by rewriting our wave packet in terms of the parameters \( x_1, p_1, \alpha_1, \alpha_2, \) and \( \gamma \).
The Raman fundamental $Q_{10}$ for the system of Fig. 5. Notice that the TG plot is magnified by a factor of $5 \times 10^4$. (b) Same as Fig. 6(a), plotted on a logarithmic scale (base 10). The dashed curve is the exact calculation.

Our new parameters are related to the $\sigma_i$ as follows:

$$x_i = \sigma_i, \quad p_i = \sigma_i, \quad \alpha_1 = \frac{\hbar}{4\sigma_3}, \quad \alpha_2 = \frac{\sigma_5}{4\sigma_3}.$$  

We have performed detailed numerical calculations of the time evolution, the Raman excitation profiles, and the absorption line shapes of the model system of Eq. (35). In all calculations the molecule is assumed to be initially in the ground vibrational state of $H_s$, i.e., the state $|\psi_0\rangle$, and it evolves in time according to the excited state Hamiltonian $H_t$. The time evolution of $|\psi_0(t)\rangle$ was calculated using the present self-consistent procedure (SCF) [Eq. (15)]. For comparison, we also solved the evolution using the thawed Gaussian (TG) algorithm [Eqs. (45) and (46)]. In addition, we have solved $|\psi_0(t)\rangle$ exactly. The exact calculations ($E$) were made by expanding the wave function $|\psi_0(t)\rangle$ in the basis set of the eigenstates of $H_s$, resulting in

$$\dot{\psi}(x,t) = \left(\frac{2\alpha_1}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{\alpha_1 + \alpha_2}{\hbar} (x - x_i)^2\right]$$

$$+ \frac{i}{\hbar} p_t (x - x_i) + \frac{i\gamma}{\hbar},$$  

Upon changing variables and performing the necessary approximations [Eqs. (27) and (29)], we finally obtain the TG equations:

$$\dot{x}_i = p_i,$$  

$$\dot{p}_i = -\frac{\partial V}{\partial x_i} \bigg|_{x = x_i}.$$  

We have performed detailed numerical calculations of the time evolution, the Raman excitation profiles, and the absorption line shapes of the model system of Eq. (35). In all calculations the molecule is assumed to be initially in the ground vibrational state of $H_s$, i.e., the state $|\psi_0\rangle$, and it evolves in time according to the excited state Hamiltonian $H_t$. The time evolution of $|\psi_0(t)\rangle$ was calculated using the present self-consistent procedure (SCF) [Eq. (15)]. For comparison, we also solved the evolution using the thawed Gaussian (TG) algorithm [Eqs. (45) and (46)]. In addition, we have solved $|\psi_0(t)\rangle$ exactly. The exact calculations ($E$) were made by expanding the wave function $|\psi_0(t)\rangle$ in the basis set of the eigenstates of $H_s$, resulting in

$$\dot{\alpha} = -\frac{2}{m} \alpha^2 - \frac{1}{2} \frac{\partial^2 V}{\partial x^2} \bigg|_{x = x_i},$$  

$$\dot{\gamma} = \frac{i\hbar\alpha}{m} + \frac{\gamma^2}{2m} - V(x_i).$$
FIG. 8. (a) The first Raman overtone $Q_{20}$ for the system of Fig. 7 with $x_0 = -0.5$. (b) Same as Fig. 8(a), plotted on a logarithmic scale (base 10). The dashed curve is the exact calculation.

FIG. 9. (a) The Raman fundamental $Q_{10}$ for the system of Fig. 5 with $x_0 = -0.5$. Notice that the TG plot is scaled down by a factor of 0.25. (b) Same as Fig. 9(a), plotted on a logarithmic scale (base 10). The dashed curve is the exact calculation.

\[ |\psi_0(t)\rangle = \sum_j |\chi_j\rangle \langle \chi_j | \psi_0\rangle \exp(-iE_j t) \]  \hspace{1cm} (47a)

where $j$ runs over the discrete eigenstates of the Morse oscillator. The Green function matrix elements $G_{\alpha\beta}(t)$ were then calculated making use of the relation

\[ G_{\alpha\beta}(t) = \sum_j (\langle \psi_\alpha | \chi_j \rangle \langle \chi_j | \psi_\beta\rangle \exp(-iE_j t) \) \hspace{1cm} (47b)

The Franck–Condon factors $\langle \psi_\alpha | \chi_j \rangle$ and $\langle \chi_j | \psi_\beta\rangle$ were calculated numerically. In all calculations, we took the ground-state frequency $\omega^* = 1.05$ and the Morse oscillator frequency $\omega = (2Da^2/m)^{1/2} = 1$. We further changed variables to dimensionless units in which the coordinate $x$ is given in units of $(\hbar/m\omega)^{1/2}$, and the momentum $p$ given in units of $(\hbar \omega)^{1/2}$. A lifetime of $\Gamma^{-1} = 0.16$ was assumed. The calculations were done for three values of the dimensionless displacement $x_0 = -0.001$, $-0.5$, and $-1.5$, and for the two values of anharmonicity $\alpha x_0 = 0.01$ and 0.05.

In applying the TDSCF and TG methods, the equations for the parameters were solved numerically using a fifth order Runge–Kutta routine in the IMSL library. Approximately 10^6 time steps were used. A resolution of 0.02 was used in calculating the spectra. Equations (46) were linearized via Heller’s $x-z$ transform prior to numerical solution. Figures 1 display the four moments $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle - \langle x \rangle^2$, and $\langle p^2 \rangle - \langle p \rangle^2$ for $x_0 = -0.5$ and $\alpha x_0 = 0.05$, while Fig. 2 shows these moments for a small displacement $x_0 = -0.001$. The exact calculation $\langle E \rangle$ required about 20 times more computer time than the approximate methods (SCF or TG). It is clear that the SCF procedure yields reasonably accurate results. The second moments calculated in the TG procedure are qualitatively incorrect; they simply increase. Another point to be noted is that in the SCF procedure all four moments are coupled, whereas in the TG procedure the first moments $\langle x \rangle$ and $\langle p \rangle$ are decoupled from the
second moments. A dramatic manifestation of this is shown in Fig. 2, where the displacement $x_0$ is small. A classical particle will essentially remain in its initial position and will not move. A quantum particle will move due to the effect of the second moments. In Figs. 3–6, we display a series of calculations of Raman line shapes for a small displacement $x_0 = -0.001$. Figures 3 and 4 use a small anharmonicity $\omega x_a = 0.01$, whereas Figs. 5 and 6 use $\omega x_a = 0.05$. Calculated are the fundamental $Q_{10}$ and the first overtone $Q_{20}$ Raman profiles. For clarity, each calculation is shown on a linear and a logarithmic scale.

The SCF provides a reasonable approximation near resonance $\omega_L = \omega_{eg}$, as well as for large detunings of $\omega_L$ where it converges to the exact result. The TG procedure, which does not have the correct short time dynamics, does not converge, even at large detunings. This is illustrated very clearly in Fig. 3, in which the TDSCF calculation is in excellent agreement with the exact result, whereas the TG calculation yields a Raman cross section, which is off by four orders of magnitude. The same observation holds also for Figs. 7–11, whereby we repeat these calculations using a larger displacement, $x_0 = -0.5$. We first consider a small anharmonicity $\omega x_a = 0.01$ (Figs. 7 and 8) then a larger anharmonicity $\omega x_a = 0.05$ (Figs. 9 and 10). Figure 11 displays the absorption spectrum of the system of Fig. 9. Finally in Fig. 12, we display the Raman $Q_{10}$ transition for a larger displacement $x_0 = -1.5$ and for the anharmonicity $\omega x_a = 0.01$.

The present calculations demonstrate the usefulness of our TDSCF procedure, even for the simplest case of a single degree of freedom, in a pure state. Applications to mixed states, for which the present approach is extremely powerful, will be made in the future.
\[ \dot{\sigma}(t) = -iP(t)L\sigma(t) - iP(t)L\phi(t), \quad (A5) \]
\[ \dot{\phi}(t) = -iQ(t)L\sigma(t) - iQ(t)L\phi(t). \quad (A6) \]

Equation (A6) may be solved by the standard convolution techniques for inhomogeneous differential equations, resulting in
\[ \phi(t) = V(t)\phi(0) - i \int_0^t \overline{K}(t,\tau) Q(\tau) L \sigma(\tau) d\tau, \quad (A7) \]
where the evolution kernel \( \overline{K}(t,\tau) \) is given by
\[ \overline{K}(t,\tau) = V(t) V^{-1}(\tau) = \exp_+ \left[ -i \int_\tau^t d\tau' Q(\tau') L \right], \quad (A8a) \]
where
\[ \exp_+ \left[ -i \int_\tau^t d\tau' Q(\tau') L \right] \]
\[ = 1 - i \int_\tau^t d\tau' Q(\tau') L \]
\[ + ( -i)^2 \int_\tau^t d\tau_1 \int_\tau^{\tau_1} d\tau_2 Q(\tau_2)L Q(\tau_2)L \]
\[ + \cdots \quad (A8b) \]
and \( V(t) \) is given by
\[ V(t) = \exp_+ \left[ -i \int_0^t Q(\tau)L d\tau \right]. \quad (A9) \]

\( \phi(t) \) may now be substituted into Eq. (A5), yielding the desired REM:
\[ \dot{\sigma}(t) = -iP(t)L\sigma(t) - iP(t)LV(t)\phi(0) \]
\[ - \int P(t)L\overline{K}(t,\tau) Q(\tau)L \sigma(\tau) d\tau. \quad (A10) \]

We apply the condition
\[ \rho(0) = \sigma(0) \quad [i.e., \phi(0) = 0]. \quad (A11) \]

The equations of motion for \( \sigma(t) \) may then be derived by multiplying the left-hand side of Eq. (A10) by \( A \), and taking the trace. This results in Eq. (11).

**APPENDIX B: THE EQUIVALENCE OF EQUATIONS (6) AND (18)**

Starting from the density operator, Eq. (18),
\[ \dot{\sigma}(t) = \exp(\lambda_0 t) \exp[\lambda_1 \hat{x} + \lambda_2 \hat{p} + \lambda_3 \hat{x}^2 + \lambda_4 \hat{p}^2 \]
\[ + \lambda_5 (\hat{L} \hat{p} + \hat{p} \hat{L})]. \quad (B1) \]

We first use the commutator
\[ [\hat{x}, \hat{p}] = -i\hbar \]
\[ (B2) \]

\[ \text{to get } \]
\[ \dot{\sigma}(t) = \exp(\lambda_0 + i\hbar t) \exp[\lambda_1 \hat{x} + \lambda_2 \hat{p} \]
\[ + \lambda_3 \hat{x}^2 + \lambda_4 \hat{p}^2 + 2\lambda_5 \hat{L} \hat{p}] \]
\[ \quad (B3) \]

Now following Eq. (10.27) of Wilcox,30 \( \dot{\sigma}(t) \), in normal ordered form (\( \hat{x} \text{-left, } \hat{p} \text{-right} \))30-32 can be written as
\[ \dot{\sigma}(t) = \sigma_N(t), \quad (B4a) \]
\[ \dot{\sigma}_N(t) = \exp(\lambda_0 + i\hbar \hat{L}_x) \]
\[ \times \{ \exp[A \hat{\beta}^2 + B \hat{\beta} + G \hat{\beta} + D \hat{\beta} + E \hat{\beta} + F] \}. \quad (B4b) \]
Here $\hat{\sigma}_N(t)$ is the normal ordered density operator and

$$\hat{\sigma}_N(t) = \text{e}^{-i H t} \hat{\sigma}_N \text{e}^{i H t},$$

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_i \frac{1}{2}\omega_i x_i^2,$$

where $\hat{\sigma}_N$ is the normal ordered density operator and

$$\hat{\sigma}_N(t) = \text{e}^{-i H t} \hat{\sigma}_N \text{e}^{i H t},$$

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_i \frac{1}{2}\omega_i x_i^2,$$

so that $C = -i\hbar$. Using the properties of normal ordered density operator, as given in Eqs. (10.27) of Wilcox, we have

$$\langle x|\hat{\sigma}(t)|p \rangle = \langle x|\hat{\sigma}_N(t)|p \rangle = \exp(\lambda_0 + i\hbar_3 \sin \lambda_1) \exp[4p^2 + Bx^2 + Gxp + Dp + Ex + FT] \langle x|p \rangle,$$

where $|x\rangle, |p\rangle$ are eigenstates of operators $\hat{x}$ and $\hat{p}$, respectively,

$$\hat{x}|x\rangle = x|x\rangle,$$

$$\hat{p}|p\rangle = p|p\rangle,$$

and

$$\langle x|p \rangle = \frac{1}{\sqrt{2\pi \hbar}} \exp(i px/\hbar).$$

Now, the coordinate representation of the density operator

$$\sigma(x,x';t) = \langle x|\hat{\sigma}(t)|x'\rangle = \int_{-\infty}^{\infty} dp \langle x|\hat{\sigma}(t)|p \rangle \langle p|x'\rangle,$$

or

$$\sigma(x,x';t) = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dp \exp(\lambda_0 + i\hbar_3 \sin \lambda_1) \exp[4p^2 + Bx^2 + Gxp + Dp + Ex] \exp\left[\frac{i}{\hbar} p(x - x')\right],$$

Performing the Gaussian integration in Eq. (B11), results in Eq. (22b). Using the transformation of coordinates

$$q = (x + x')/2,$$

$$s = (x - x')/2,$$

and performing the Gaussian integration,

$$\sigma_{\omega}(q,p;t) = \frac{1}{\pi \hbar} \int_{-\infty}^{\infty} \sigma(q + s, q - s; t) \exp(-2ips/\hbar) ds.$$

we obtain Eq. (22a). Since Eq. (22b) is identical to Eq. (6), we have established the equivalence of Eqs. (18) and (6).

ACKNOWLEDGMENTS

The support of the National Science Foundation, the Office of Naval Research, the U.S. Army Research Office, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.


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