

TIME-DEPENDENT SELF-CONSISTENT FIELD APPROXIMATION FOR SEMICLASSICAL DYNAMICS USING GAUSSIAN WAVEPACKETS IN PHASE SPACE

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Gaussian wavepackets in phase space, which are constructed to have the exact first and second moments with respect to the coordinates and momenta, are used to develop self-consistent equations of motion for the semiclassical time evolution of interacting anharmonic systems. The equations apply to pure as well as to mixed states and may, therefore, be particularly useful for molecular dynamics in condensed phases.

1. Introduction

The construction of approximate algorithms for solving the time evolution of interacting quantum systems is one of the major problems in molecular dynamics. Considerable recent activity in this area has focused on the usage of Gaussian wavepackets and their propagation according to the prescription developed by Heller [1–6]. This method is exact for harmonic systems. Its applicability to anharmonic systems has been analyzed by several authors [4–7]. A new type of self-consistent semiclassical reduced equations of motion, which is based on projection operator techniques of non-equilibrium statistical mechanics, was suggested recently [7]. To lowest order the equations provide a time-dependent self-consistent field approximation (TD SCF), which can then be systematically improved. Under certain limits, it reduces to Heller's procedure [1]. It should be noted that the existing Gaussian wavepacket formalism [1–6] treats the time evolution of pure states using the Schrödinger equation. Our approach is capable of handling mixed states as well, since it is based on the density matrix [7,8]. It therefore has a multitude of potential applications to molecular dynamics in condensed phases. In this note, we evaluate explicitly the TD SCF equations of motion using the formalism developed earlier [7,9].

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2. The TD SCF equations in phase space

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

$$H = \sum_j p_j^2/2m_j + V(x_1, x_2, \dots, x_N), \quad (1)$$

where V is the interaction potential. We wish to develop a semiclassical self-consistent procedure for the approximate solution of the Liouville equation

$$d\rho/dt = -iL\rho \equiv (-i/\hbar)[H, \rho]. \quad (2)$$

Here L is the Liouville operator and $\rho(\mathbf{x}, \mathbf{x}', t)$ is the total density matrix where \mathbf{x} is a vector with N components x_1, \dots, x_N . If the system is in a pure state with a wavefunction $\psi(\mathbf{x}, t)$, then $\rho(\mathbf{x}, \mathbf{x}', t) = \psi(\mathbf{x}, t)\psi^*(\mathbf{x}', t)$ and eq. (2) is identical to the Schrödinger equation. Eq. (2) applies, however, to mixed states as well. The self-consistent procedure for solving eq. (2) is obtained in the following steps [7,9]. 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 $5N$ operators:

$$A_{1j} = x_j, \quad A_{2j} = p_j, \quad A_{3j} = x_j^2, \quad A_{4j} = p_j^2,$$

$$A_{5j} = x_j p_j + p_j x_j, \quad j=1, \dots, N. \quad (3)$$

The expectation values of these operators will be

denoted $a_{\alpha j}$,

$$a_{\alpha j}(t) \equiv \langle A_{\alpha j} \rangle \equiv \text{Tr}[A_{\alpha j} \rho(\mathbf{x}, \mathbf{x}', t)],$$

$$\alpha = 1, \dots, 5, \quad j = 1, \dots, N. \quad (4)$$

We next construct an approximate density matrix $\sigma(\mathbf{x}, \mathbf{x}', t)$ chosen to be in the form of a product of single-particle density matrices

$$\sigma(\mathbf{x}, \mathbf{x}', t) \equiv \prod_{j=1}^N \phi_j(x_j, x'_j, t). \quad (5)$$

ϕ_j are taken to be Gaussian

$$\begin{aligned} \phi_j(x_j, x'_j, t) = \exp(-b_{0j} - b_{1j}x_j - b_{1j}^*x'_j \\ - b_{2j}x_j^2 - b_{2j}^*x_j'^2 - b_{3j}x_jx'_j). \end{aligned} \quad (6)$$

The time-dependent parameters $b_{\alpha j}$ may be uniquely expressed in terms of $a_{\alpha j}$ by requiring that the expectation values of our operators $A_{\alpha j}$ evaluated using the exact (ρ) and the approximate (σ) density matrix will be the same, i.e.,

$$\begin{aligned} a_{\alpha j}(t) \equiv \text{Tr}[A_{\alpha j} \rho(\mathbf{x}, \mathbf{x}', t)] \\ = \text{Tr}[A_{\alpha j} \sigma(\mathbf{x}, \mathbf{x}', t)]. \end{aligned} \quad (7)$$

Making use of projection operator techniques [10,11] we can then derive closed equations of motion for $a_{\alpha j}$. The equations are constructed to yield the exact values of $a_{\alpha j}$. $\sigma(\mathbf{x}, \mathbf{x}', t)$ may then provide a reasonable approximation for $\rho(\mathbf{x}, \mathbf{x}', t)$. The detailed derivation of the equations is given elsewhere, resulting in [7,9]

$$\begin{aligned} \dot{a}_{\alpha j} = -i \langle \langle A_{\alpha j} | L | \sigma(t) \rangle \rangle \\ + \int_0^t d\tau K_{\alpha j}(t, \tau, \sigma(\tau)). \end{aligned} \quad (8a)$$

Here the dot represents a derivative with respect to time, i.e. $\dot{a}_{\alpha j} \equiv da_{\alpha j}/dt$, and

$$\begin{aligned} \langle \langle A_{\alpha j} | L | \sigma(t) \rangle \rangle \equiv \text{Tr}[A_{\alpha j} L \sigma(t)] \\ = \text{Tr}[A_{\alpha j} H \sigma(t) - A_{\alpha j} \sigma(t) H]. \end{aligned} \quad (8b)$$

The kernel $K_{\alpha j}$ has an explicit formal expression in terms of projection operators, and it may be evaluated approximately [7,9]. Eqs. (8) are $5N$ equations for the $5N$ quantities $a_{\alpha j}$. The first term in the rhs of

eq. (8a) represents the mean field dynamics. If $\sigma(t) = \rho(t)$ at all times, the second term vanishes identically, and the first term represents the exact evolution. The second term represents the effect of fluctuations (the fact that the actual density matrix $\rho(t)$ is different from $\sigma(t)$). The TD SCF equations, which will be developed here, are obtained by neglecting the second term, i.e. taking

$$\dot{a}_{\alpha j} = -i \langle \langle A_{\alpha j} | L | \sigma(t) \rangle \rangle. \quad (9)$$

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

$$\begin{aligned} \sigma_{1j} &= \langle x_j \rangle, \quad \sigma_{2j} = \langle p_j \rangle, \\ \sigma_{3j} &= \langle x_j^2 \rangle - \langle x_j \rangle^2, \\ \sigma_{4j} &= \langle p_j^2 \rangle - \langle p_j \rangle^2, \\ \sigma_{5j} &= \langle x_j p_j + p_j x_j \rangle - 2 \langle x_j \rangle \langle p_j \rangle. \end{aligned} \quad (10)$$

Making use of eqs. (7), we can express the parameters $b_{\alpha j}$ (eq. (6)) in terms of the moments $\sigma_{\alpha j}$, resulting in [7,9]

$$b_{0j} = [\sigma_{1j}^2 + \sigma_{3j} \log(2\pi\sigma_{3j})]/2\sigma_{3j}, \quad (11a)$$

$$b_{1j} = [-\hbar\sigma_{1j} + i(\sigma_{1j}\sigma_{5j} - 2\sigma_{2j}\sigma_{3j})/2\hbar\sigma_{3j}], \quad (11b)$$

$$b_{2j} = (4\sigma_{3j}\sigma_{4j} + \hbar^2 - \sigma_{3j}^2 - 2i\hbar\sigma_{5j})/8\hbar^2\sigma_{3j}, \quad (11c)$$

$$b_{3j} = (\hbar^2 + \sigma_{5j}^2 - 4\sigma_{3j}\sigma_{4j})/4\hbar^2\sigma_{3j}. \quad (11d)$$

We have evaluated eq. (9) explicitly for the Hamiltonian, eq. (1). The final result, recast in terms of the new variables $\sigma_{\alpha j}$, is [9]

$$\dot{\sigma}_{1j} = \sigma_{2j}/m_j, \quad (12a)$$

$$\dot{\sigma}_{2j} = -\langle V_j(\mathbf{x}) \rangle, \quad (12b)$$

$$\dot{\sigma}_{3j} = \sigma_{5j}/m_j, \quad (12c)$$

$$\dot{\sigma}_{4j} = -\langle V_{jj}(\mathbf{x}) \rangle \sigma_{5j}, \quad (12d)$$

$$\dot{\sigma}_{5j} = (2/m_j)\sigma_{4j} - 2\langle V_{jj}(\mathbf{x}) \rangle \sigma_{3j}, \quad (12e)$$

where

$$V_j(\mathbf{x}) = \partial V / \partial x_j, \quad (13a)$$

$$V_{jj}(\mathbf{x}) = \partial^2 V / \partial x_j^2, \quad (13b)$$

$$\langle V_j(\mathbf{x}) \rangle = \int d\mathbf{x} V_j(\mathbf{x}) \sigma(\mathbf{x}, \mathbf{x}, t), \quad (13c)$$

$$\sigma(\mathbf{x}, \mathbf{x}, t) = \prod_{j=1}^N \phi_j(x_j, x_j, t), \quad (13d)$$

$$\phi_j(x_j, x_j, t) = (2\pi\sigma_{3j})^{-1/2} \times \exp[-(x_j - \sigma_{1j})^2 / 2\sigma_{3j}]. \quad (13e)$$

$\langle V_{jj}(\mathbf{x}) \rangle$ is defined in an analogous way to eq. (13c) by replacing $V_j(\mathbf{x})$ with $V_{jj}(\mathbf{x})$. Eqs. (12) are the phase space TD SCF equations, and they will be analyzed in section 3.

3. Discussion

We shall now discuss the significance of the phase space TD SCF procedure (eqs. (12)):

(1) 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 non-equilibrium statistical mechanics [10–14]. A powerful way to achieve that goal is provided by the maximum entropy formalism [12–14]. Within this formalism we construct a density matrix $\sigma(\mathbf{x}, \mathbf{x}', t)$, 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

$$\phi_j^{\text{ME}}(x_j, x_j', t) = \exp\left(-\lambda_{0j} - \sum_{\alpha=1}^5 \lambda_{\alpha j} A_{\alpha j}\right), \quad (14)$$

where $\lambda_{\alpha j}$ are numerical coefficients which may be expressed in terms of $\sigma_{\alpha j}$. We have shown that our Gaussian choice (eq. (6)) is identical to the maximum entropy distribution ϕ_j^{ME} [9]. 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 non-equilibrium statistical mechanics.

(2) Note that eqs. (12) 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. $\sigma_j(x_j, x_j', t)$ should then be replaced by a phase space distribution function of coordinates and momenta $\bar{\phi}_j(x_j, p_j, t)$. Taking $\bar{\phi}_j$ to be Gaussian in x_j and p_j , we can repeat the present derivation step-by-step and derive eqs. (12). The TD SCF for the moments using Gaussian wavepackets is therefore completely classical.

(3) If $\phi_j(x_j, x_j', t)$ is to represent a pure state, it should be factorized in the form of a product of a function of x_j and a function of x_j' . A necessary and sufficient condition for that is $b_{3j} = 0$, i.e.

$$\sigma_{3j}^2 = 4\sigma_{3j}\sigma_{4j} - \hbar^2. \quad (15)$$

In this case, σ_{5j} (up to a sign) is uniquely determined by σ_{3j} and σ_{4j} and is not independent. The density matrix (eq. (6)) may represent, however, mixed states as well, whenever eq. (15) is not satisfied.

(4) The equations of motion of Heller [1] may be obtained from our TD SCF equations, (eqs. (12)), if the following approximations are made: (i) replacing $\langle V_j(\mathbf{x}) \rangle$ by $V_j(\langle \mathbf{x} \rangle)$ and $\langle V_{jj}(\mathbf{x}) \rangle$ by $V_{jj}(\langle \mathbf{x} \rangle)$; (ii) assuming that initially the system is in a pure state and satisfies eq. (15). If we then make the substitutions $\sigma_{1j} = x_t$, $\sigma_{2j} = p_t$, $\sigma_{3j} = \hbar/4\alpha_t$ and $\sigma_{4j} = \hbar|\alpha_t|^2/\alpha_t$, we obtain Heller's thawed Gaussian (TG) equations for x_t , p_t , and α_t . Here α_t is the imaginary part of α_t . In figs. 1–4 we display the time-dependent moments of a one-dimensional Gaussian wavepacket propagated on a Morse potential,

$$V(x) = D\{1 - \exp[-a(x - x_0)]\}^2. \quad (16)$$

Shown are the exact moments (E) calculated using an expansion in a basis set of the bound eigenstates of the Morse potential, the SCF calculation (eqs. (12)) and Heller's thawed Gaussian (TG) method. It is clear that the TD SCF provides a major improvement over the TG. A similar conclusion is obtained by comparing the Raman spectra of this model system [9].

(5) It can be easily verified from eqs. (12) that the solution of σ_{5j} is

$$\sigma_{5j}^2(t) = 4\sigma_{3j}(t)\sigma_{4j}(t) + \gamma, \quad (17)$$

where γ is a constant determined by the initial conditions. If $\gamma = -\hbar^2$, then eq. (15) will be satisfied at all times. This shows that within the TD SCF if the

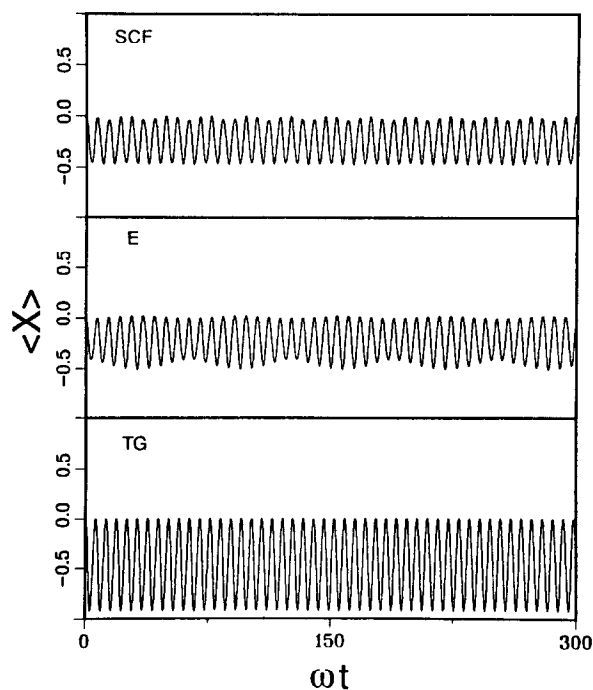


Fig. 1. The mean displacement $\sigma_1 = \langle x \rangle$ versus time for a Gaussian wavepacket propagated on a Morse potential (eq. (16)). The Morse oscillator frequency is $\omega \equiv (2Da^2/m)^{1/2} = 1$, $D/\hbar\omega = 5$ and $\hbar a^2/m\omega = 0.1$. These parameters correspond to an anharmonicity of $\omega x_c = 0.05$. We have calculated the dimensionless coordinate x in units of $(\hbar/m\omega)^{1/2}$ and the dimensionless momentum p in units of $(\hbar\omega m)^{1/2}$. In these units, we took $x_0 = -0.5$, and the initial conditions $\sigma_1(0) = 0$, $\sigma_2(0) = 0$, $\sigma_3(0) = 0.48$, $\sigma_4(0) = 0.53$. $\sigma_5(0)$ is given by eq. (15). Shown is the present calculation (eq. (12)) (SCF), the exact calculation (E) and the thawed Gaussian calculation (TG).

initial density matrices ϕ , represent a pure state, they will represent a pure state at all times. This is no longer the case, however, once the fluctuation terms in eq. (8a) are included. The fluctuation terms allow a pure 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 [8].

(6) TD SCF 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 [2-5, 15-17]. They are also extremely useful

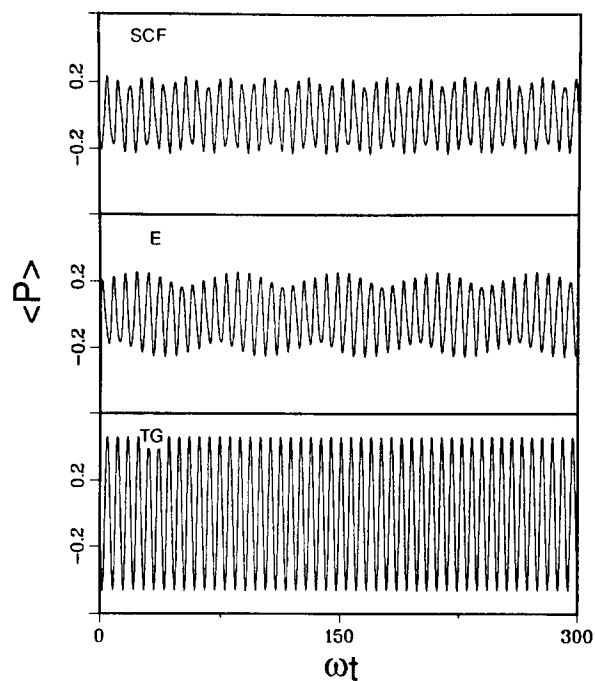


Fig. 2. The dimensionless mean momentum $\sigma_2 = \langle p \rangle$ for the system of fig. 1.

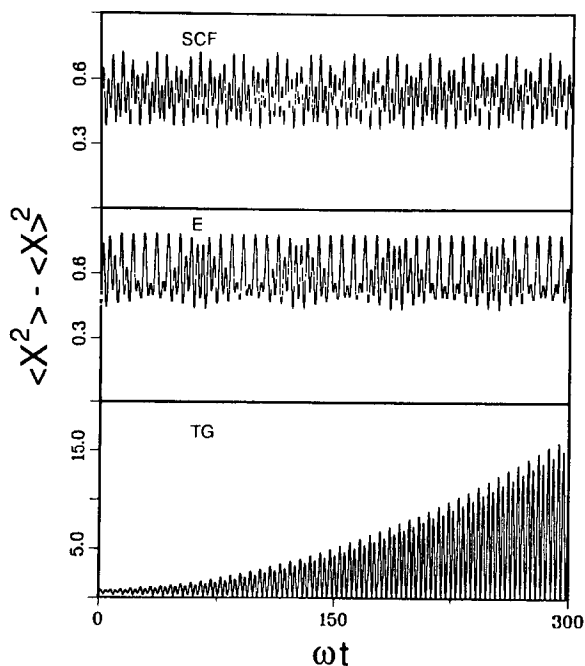


Fig. 3. The dimensionless variance of the displacement $\sigma_3 = \langle x^2 \rangle - \langle x \rangle^2$ for the system of fig. 1.

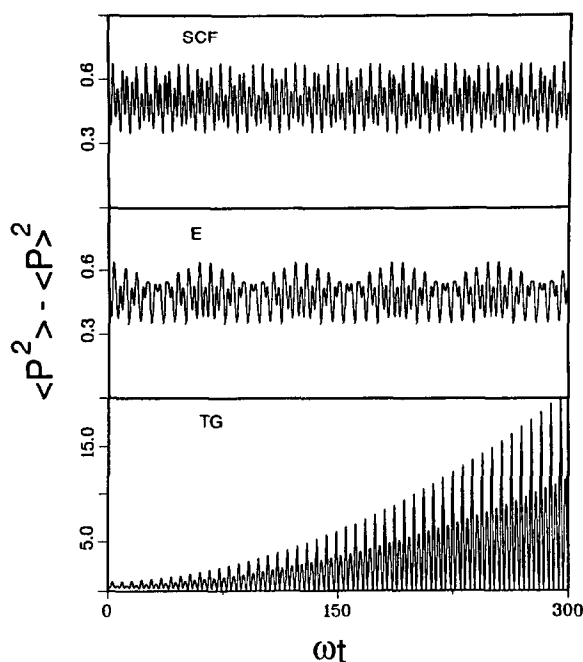


Fig. 4. The dimensionless variance of momentum $\sigma_4 = \langle p^2 \rangle - \langle p \rangle^2$ for the system of fig. 1.

for a mixed description in which some degrees of freedom are treated quantum mechanically and the others are treated classically. The present phase space TD SCF 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 [15] applies naturally within the phase space TD SCF.

(7) The present equations may be extended by various ways [7]. One possibility is to expand the fluctuation term perturbatively. Note that for harmonic systems the TD SCF formulation is exact, provided we take x_j to be the normal modes. This suggests that an expansion of the kernel $K_{\alpha\gamma}$ in anharmonicities may be appropriate. Alternatively, we may add more dynamical variables to our chosen set $A_{\alpha\gamma}$ and construct a more elaborate wavepacket with more parameters. We may, for example, go beyond the Hartree approximation implied in the factorization of σ 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 $p_j x_k + x_k p_j$. 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 because of the large number of variables involved. Such extension of eqs. (12) is straightforward, requiring the use of a multivariable Gaussian distribution for σ , and it was not included here for the sake of clarity. Another possibility is to add higher moments (x_j^3 , p_j^3 , etc.) and to use non-Gaussian wavepackets. The resulting equations will then provide an improved reduced description of the system.

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