

SEMICLASSICAL DYNAMICS IN PHASE SPACE;
TIME-DEPENDENT SELF-CONSISTENT FIELD APPROXIMATION

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ABSTRACT. 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. Numerical calculations of Raman excitation profiles, using a Morse oscillator, demonstrate the accuracy of the present equations.

I. Introduction

The development of efficient methods for calculating 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 to represent the time-dependent wavefunction. The propagation is usually made by taking the interaction potential to be locally quadratic[1-6]. This method is exact for harmonic systems. Its applicability to anharmonic systems has been critically analyzed by several authors[4-7]. In this article we develop a new type of self-consistent semiclassical reduced equations of motion, which is based on projection operator techniques of nonequilibrium statistical mechanics in phase space[7,8]. To lowest order the equations provide a time-dependent self-consistent field approximation (TDSCF) which can then be systematically improved. It should be noted that the existing Gaussian wavepacket formalism[1-6] treats the time evolution of pure states using the Schrodinger equation. Our approach is capable of handling mixed states as well, since it is based on the density matrix[7-9]. It therefore has a multitude of potential applications to molecular dynamics in condensed phases. In this article, we evaluate explicitly the TDSCF equations of motion and perform numerical calculations of the time evolution and the Raman lineshapes of a diatomic molecule with a harmonic ground state and an excited state given by a Morse oscillator[8]. The calculations demonstrate

that the present equations are by far superior to the Thawed Gaussian procedure[1].

II. THE TDSCF 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

$$\frac{d\rho}{dt} = -i L\rho \equiv \frac{-i}{\hbar} [H, \rho]. \quad (2)$$

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 $\psi(\mathbf{x})$, then $\rho(\mathbf{x}, \mathbf{x}', t) = \psi(\mathbf{x}, t)\psi^*(\mathbf{x}', t)$ and Eq.(2) is identical to the Schrodinger equation. Equation (2) applies, however, to mixed states as well. The self-consistent procedure for solving Eq.(2) is obtained in the following steps[7,8]. 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:

$$A_{0j} = 1, A_{1j} = x_j, A_{2j} = p_j, A_{3j} = x_j^2, A_{4j} = p_j^2, A_{5j} = x_j p_j + p_j x_j \\ j=1\dots N. \quad (3)$$

The expectation values of these operators will be denoted $a_{\alpha j}$.

$$a_{\alpha j}(t) \equiv \langle A_{\alpha j} \rangle \equiv \text{Tr} [A_{\alpha j} \rho(\mathbf{x}, \mathbf{x}', t)] \quad \alpha=0\dots 5, j=1\dots N. \quad (4)$$

Note that normalization requires that $a_{0j}=1$. 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

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

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.,

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

Making use of projection operator techniques[9,10], we can then derive closed reduced equations of motion (REM) 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[7,8]. For each degree of freedom j we define a 6×6 matrix

$$S_{\alpha\beta}^j(t) = \text{Tr} [A_{\alpha j}^+ \sigma(t) A_{\beta j}] \quad \alpha, \beta = 0, 1, \dots, 5 \quad (8)$$

the time dependent projection operator,

$$P(t) = \sum_{j=1}^N \sum_{\alpha, \beta=0}^5 |\sigma(t) A_{\alpha j}\rangle\rangle [S_{\alpha\beta}^j(t)]^{-1} \langle\langle A_{\beta j} | \quad (9)$$

and 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 $|A\rangle\rangle$ and $\langle\langle A|B\rangle\rangle = \text{Tr}(A^\dagger B)$ is the scalar product of two operators. Using the assumption that at some initial time t_0 $\rho(t_0) = \sigma(t_0)$, we can derive the following exact REM for $a_{\alpha j}(t)$:

$$\dot{a}_{\alpha j}(t) = -i \langle\langle A_{\alpha j} | L | \sigma(t) \rangle\rangle - \int_{t_0}^t ds \langle\langle A_{\alpha j} | L K(t, s) Q(s) L | \sigma(s) \rangle\rangle, \quad (10)$$

where

$$K(t, s) = \exp_+ \left(-i \int_s^t d\tau Q(\tau) L \right) \quad (11)$$

Here the dot represents a derivative with respect to time, i.e.,

$\dot{a}_{\alpha j} \equiv da_{\alpha j}/dt$, \exp_+ denotes the time-ordered exponential, and

$$\begin{aligned} \langle\langle A_{\alpha j} | L | \sigma(t) \rangle\rangle &\equiv \text{Tr} [A_{\alpha j} L \sigma(t)] \\ &= \text{Tr} [A_{\alpha j} H \sigma(t) - A_{\alpha j} \sigma(t) H] \end{aligned} \quad (12)$$

Equations (10) are $5N$ equations for the $5N$ variables $a_{\alpha j}$. It should be noted that Eqs.(10) are exact, provided $K(t, s)$ is evaluated to infinite order. The first term in the r.h.s. of Eq.(10) represents the "mean field". If $\sigma(t) = \rho(t)$ at all times, then 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 TDSCF equations, which will be developed here, are obtained by neglecting the second term, i.e., taking

$$\dot{a}_{\alpha j} = -i \langle \langle A_{\alpha j} | L | \sigma(t) \rangle \rangle \quad (13)$$

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

$$\begin{aligned} \sigma_{1j} &= \langle x_j \rangle; \quad \sigma_{2j} = \langle p_j \rangle \\ \sigma_{3j} &= \langle x_j^2 \rangle - \langle x_j \rangle^2; \quad \sigma_{4j} = \langle p_j^2 \rangle - \langle p_j \rangle^2 \\ \sigma_{5j} &= \langle x_j p_j + p_j x_j \rangle - 2\langle x_j \rangle \langle p_j \rangle \end{aligned} \quad (14)$$

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[8]

$$b_{0j} = \frac{\sigma_{1j}^2 + \sigma_{3j} \log(2\pi \sigma_{3j})}{2 \sigma_{3j}} \quad (15a)$$

$$b_{1j} = \frac{-\hbar \sigma_{1j} + i [\sigma_{1j} \sigma_{5j} - 2\sigma_{2j} \sigma_{3j}]}{2\hbar \sigma_{3j}} \quad (15b)$$

$$b_{2j} = \frac{4\sigma_{3j} \sigma_{4j} + \hbar^2 - \sigma_{5j}^2 - 2i\hbar \sigma_{5j}}{8\hbar^2 \sigma_{3j}} \quad (15c)$$

$$b_{3j} = \frac{\hbar^2 + \sigma_{5j}^2 - 4\sigma_{3j} \sigma_{4j}}{4\hbar^2 \sigma_{3j}} \quad (15d)$$

We have evaluated Eq.(13) explicitly for the Hamiltonian Eq.(1). The final result, recast in terms of the new variables $\sigma_{\alpha j}$, is[8]

$$\dot{\sigma}_{1j} = \sigma_{2j}/m_j \quad (16a)$$

$$\dot{\sigma}_{2j} = -\langle V_j(\mathbf{x}) \rangle \quad (16b)$$

$$\dot{\sigma}_{3j} = \sigma_{5j}/m_j \quad (16c)$$

$$\dot{\sigma}_{4j} = - \langle V_{jj}(\mathbf{x}) \rangle \sigma_{5j} \quad (16d)$$

$$\dot{\sigma}_{5j} = \frac{2}{m_j} \sigma_{4j} - 2 \langle V_{jj}(\mathbf{x}) \rangle \sigma_{3j} \quad (16e)$$

where

$$V_j(\mathbf{x}) = \frac{\partial V}{\partial x_j} \quad (17a)$$

$$V_{jj}(\mathbf{x}) = \frac{\partial^2 V}{\partial x_j^2} \quad (17b)$$

$$\langle V_j(\mathbf{x}) \rangle = \int d\mathbf{x} V_j(\mathbf{x}) \sigma(\mathbf{x}, \mathbf{x}, t) \quad (17c)$$

$$\sigma(\mathbf{x}, \mathbf{x}, t) = \prod_{j=1}^N \phi_j(x_j, x'_j, t) \quad (17d)$$

$$\phi_j(x_j, x'_j, t) = \frac{1}{\sqrt{2\pi} \sigma_{3j}} \exp\left[-\frac{(x_j - \sigma_{1j})^2}{2 \sigma_{3j}}\right] \quad (17e)$$

$\langle V_{jj}(\mathbf{x}) \rangle$ is defined in an analogous way to Eq.(17c) by replacing $V_j(\mathbf{x})$ with $V_{jj}(\mathbf{x})$. Equations (16) are the phase space TDSCF equations, and they will be analyzed in the next section.

III. Discussion

We shall now discuss the significance of the phase space TDSCF procedure, (Eqs.16):

(1) We first note that Eqs.(16) 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. $\phi_j(x_j, x'_j, t)$ 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 TDSCF for the moments using Gaussian wavepackets, is therefore completely classical.

(2) 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. $\sigma_{5j}^2 = 4 \sigma_{3j} \sigma_{4j} - M^2$. 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 the above condition is not satisfied.

(3) The Thawed Gaussian equations of motion[1] may be obtained from our TDSCF equations, (Eqs.(16)), 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. If we then make the substitutions $\sigma_{1j}=x_t$, $\sigma_{2j}=p_t$, $\sigma_{3j}=M/(4\alpha_1)$ and $\sigma_{4j}=M|\alpha_t|^2/\alpha_1$, we obtain the Thawed Gaussian (TG) equations for x_t, p_t , and α_t . Here α_1 is the imaginary part of α_t . Another point to be noted is that in the present TDSCF equation all five moments are coupled, whereas in the TG procedure the first moments $\langle x_j \rangle$ and $\langle p_j \rangle$ obey the classical equations of motion and are decoupled from the second moments.

(4) It can be easily verified from Eqs.(16) that the solution of σ_{5j} is

$$\sigma_{5j}^2(t) = 4 \sigma_{3j}(t) \sigma_{4j}(t) + \gamma, \text{ where } \gamma \text{ is a constant determined}$$

by the initial conditions. If $\gamma=-M^2$, then the system will be in a pure state at all times. This shows that within the TDSCF, if the initial density matrices ϕ_j 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.(10) 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.

(5) 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[2-6,11,12]. They are also extremely useful for a mixed description in which some degrees of freedom are treated quantum mechanically and the 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 averagings. The "bundle of trajectories" used by Gerber, Ratner, and coworkers[11] applies naturally within the phase space TDSCF.

(6) The present equations may be extended by various ways[7,8]. One possibility is to expand the fluctuation term perturbatively. Note that for harmonic systems the TDSCF formulation is exact, provided we take x_j to be the normal modes. This suggests that an expansion of the fluctuation kernel $K(t,s)$ in anharmonicities may be appropriate. Alternatively, we may add more dynamical variables to our chosen set $A_{\alpha j}$ (e.g., x_j^3 , p_j^3 , etc.) and construct a more elaborate wavepacket with more parameters. The TDSCF will then provide an improved reduced description of the system. The methodology of the present approach is analogous to the development of reduced equations of motion in nonequilibrium statistical mechanics[13,14].

IV. Raman Excitation Profiles of Anharmonic Molecules

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

$$H = |g\rangle H_g \langle g| + |e\rangle (\omega_{eg} + H_e) \langle e| \quad (18)$$

with

$$H_g = p^2/2m + m\omega^2 x^2/2 \quad (19a)$$

$$H_e = p^2/2m + D\{1 - \exp(-a(x-x_0))\}^2. \quad (19b)$$

We denote the eigenstates of H_g by $|\psi_n\rangle$

$$H_g |\psi_n\rangle = \hbar\omega^n (n+1/2) |\psi_n\rangle \quad n=0,1,\dots \quad (20)$$

The Raman excitation profiles were calculated within the Condon approximation using the Kramers-Heisenberg formula:

$$Q_{n0}(\omega_L) = |\int G_{n0}(t) \exp[-i(\omega_L - \omega_{eg})t - \Gamma t/2]|^2, \quad (21a)$$

Γ^{-1} being the lifetime of $|e\rangle$. The Green function is

$$G_{nm}(t) = \langle \psi_n | \exp(-i H_e t) | \psi_m \rangle = \langle \psi_n | \psi_m(t) \rangle \quad (21b)$$

and

$$|\psi_m(t)\rangle = \exp(-i H_e t) |\psi_m\rangle. \quad (21c)$$

$Q_{n0}(\omega_L)$ denotes the intensity of the Raman transition in which the molecule changes its state from $|\psi_0\rangle$ to $|\psi_n\rangle$ as a function of the incident photon frequency ω_L . In order to calculate the spectra, the

wavefunction corresponding to the reduced density matrix must be used. Thus, we must specialize our reduced density matrix to a pure state. Setting $\sigma_{s_j}^2 = 4\sigma_{s_j} \sigma_{s_j}^{-1} M^2$, we have

$$\sigma(x, x', t) = \psi(x, t) \psi^*(x', t) \quad (22a)$$

$$\psi(x, t) = (2\pi\sigma_s)^{-1/4} \exp\left\{\left(-\frac{1}{4\sigma_s} + \frac{i\sigma_s}{4\hbar\sigma_s}\right)(x-\sigma_1)^2 + \frac{i\sigma_2}{\hbar}(x-\sigma_1) + \frac{i\gamma}{\hbar}\right\}. \quad (22b)$$

The equation of motion for the phase factor $\gamma(t)$ (which does not appear in the density matrix σ) is derived by demanding that the quantum energy is conserved,

$$\langle E \rangle = \langle \psi | p^2/2m + V(x) | \psi \rangle = i\hbar \langle \dot{\psi} | \psi \rangle \quad (23)$$

We thus get:

$$\dot{\gamma} = \frac{-\hbar}{4m\sigma_s} + \frac{V_2\sigma_s}{2} + \frac{\sigma_2^2}{2m} - V_0. \quad (24)$$

We have performed detailed numerical calculations of the time evolution, and the Raman excitation profiles of the model system of Eq.(18). In all calculations the molecule is assumed to be initially in the ground vibrational state of H_g , i.e., $|\psi_0\rangle$, and it evolves in time according to the excited state Hamiltonian H_e . Each

calculation was performed with both the SCF and TG methods. For comparison, the exact calculations were made by expanding the wavefunction $|\psi(t)\rangle$ in the basis set of the discrete spectrum of the Morse oscillator. 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 $(M/m\omega)^{1/2}$, and the momentum p gives in units of $(\hbar m\omega)^{1/2}$. The calculations were done for two values of the dimensionless displacement $x_0 = -0.5$ and -1.5 , and for the anharmonicity $\omega x_e = \hbar a^2/2m = 0.05$. Figures 1 and 2 display the moments $\langle x^2 \rangle - \langle x \rangle^2$, and $\langle p^2 \rangle - \langle p \rangle^2$ for $x_0 = -0.5$ and $\omega x_e = 0.05$. It is clear that the SCF procedure yields reasonably accurate results. The second moments calculated in the TG procedure monotonically increase and are qualitatively incorrect. In Fig. 3, we display the fundamental Raman profiles Q_1 , using the same parameters of Figs. 1 and 2 and $\Gamma = 0.16$. The calculation is shown also on a logarithmic scale in Fig. 4. The SCF provides a reasonable approximation near the center. In the far wings 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. The same observations hold also for Fig. 5, where we repeat these calculations using a larger displacement, $x_0 = -1.5$.

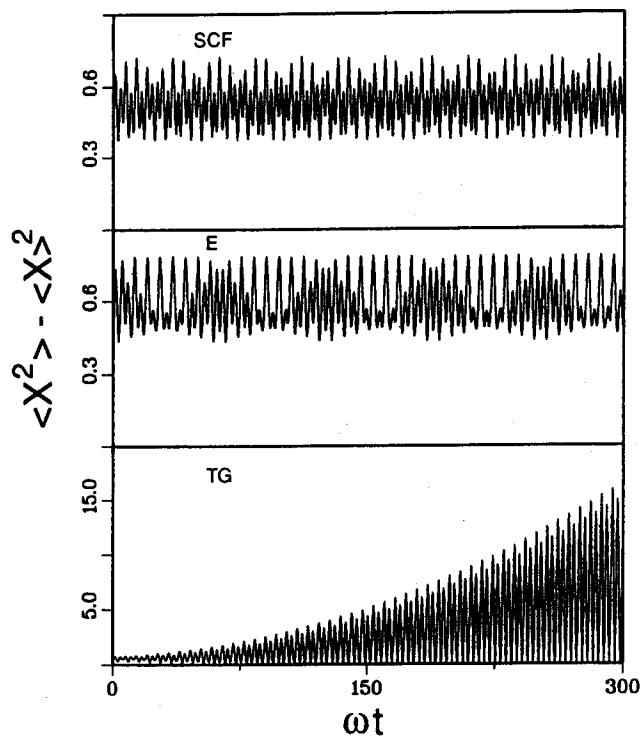


Figure 1

The dimensionless variance of the displacement $\sigma_3 = \langle x^2 \rangle - \langle x \rangle^2$ vs. time for the Gaussian wavepacket propagated on a Morse potential. The Morse oscillator frequency is $\omega \equiv (2Da^2/m)^{.5} = 1$, $D/\hbar\omega = 5$, and $\hbar a^2/m\omega = .01$. These parameters correspond to an anharmonicity of $\omega x_e = .05$. We have calculated the dimensionless coordinate x in units of $(\hbar/m\omega)^{.5}$ and the dimensionless momentum p in units of $(m\omega\hbar)^{.5}$. In these units, we took $x_f = -0.5$, and the initial conditions $\sigma_1(0) = 0$, $\sigma_2(0) = 0$, $\sigma_3(0) = 0.48$, $\sigma_4(0) = 0.53$. Since this is a pure state, $\sigma_5(0)$ is uniquely determined by $\sigma_3(0)$ and $\sigma_4(0)$. Shown is the present calculation (Eq.(16)) (SCF), the exact calculation (E), and the Thawed Gaussian calculation (TG).

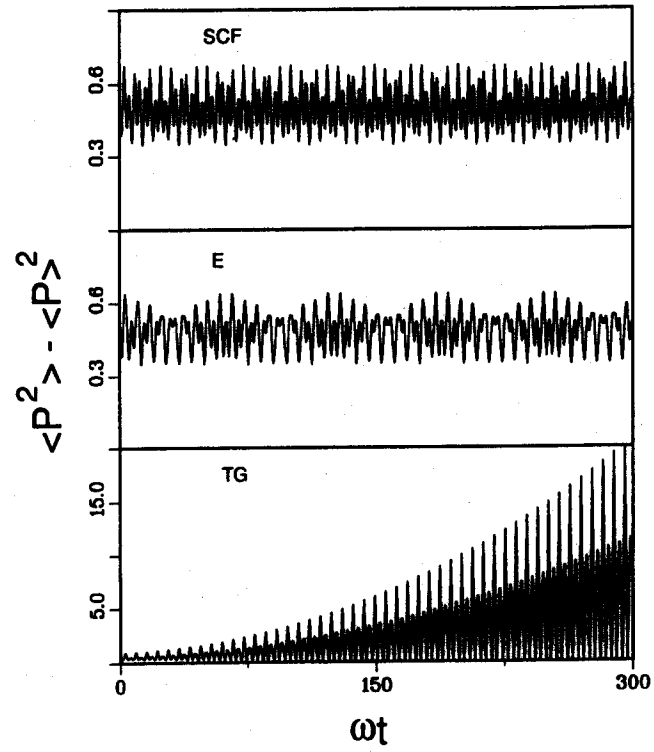


Figure 2

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

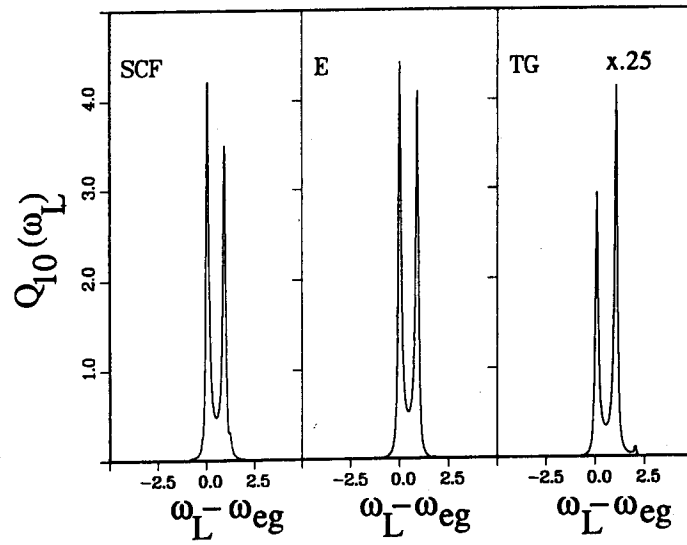


FIGURE 3

The fundamental Raman excitation profile Q_{10} for the system of Fig. 1. Note that we had to multiply the calculated TG profile by 0.25 in order to put it on the same scale of the E and SCF calculations.

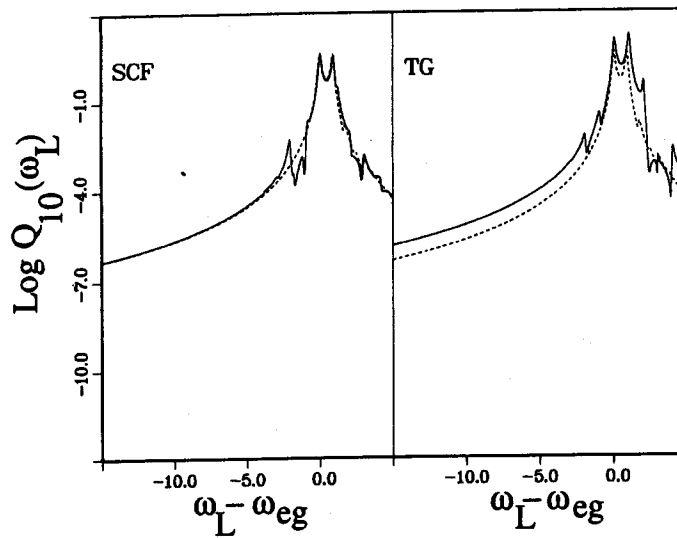


FIGURE 4

Same as Fig. 3, shown on a logarithmic scale base (10). The dashed line is the exact calculation.

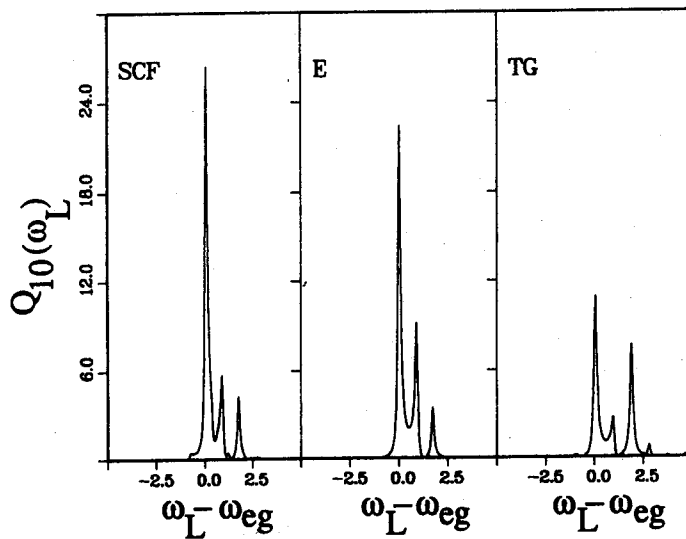


Figure 5

The fundamental Raman excitation profile Q_{10} for a dimensionless displacement $x_0 = -1.5$. Other parameters same as in Fig. 3.

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