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A remedy for zero-point energy problems in classical trajectories: A combined semiclassical/classical molecular dynamics algorithm

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A new method is proposed for dealing with difficulties in molecular dynamics (MD) simulations caused by nonpreservation of zero-point energies (ZPE) in classical dynamics. Specifically addressed is a difficulty, for molecules held in weakly bound clusters, of energy flow from the initial ZPE of stiff molecular vibrations into soft cluster modes, causing unphysical dissociation or melting of the cluster. The remedy proposed is a classicallike MD algorithm, which treats the stiff modes by semiclassical Gaussian wave packets and the soft modes by classical dynamics, using the time-dependent self-consistent field (TDSCF) approach to couple the classical and the semiclassical modes. The resulting algorithm is very similar in form to classical MD, is computationally simple, stable, and appears free of unphysical effects. The method is illustrated by test applications to models of the clusters I_2He and $(HBr)_2$ in the ground states, which dissociate at the expense of their ZPE classically, but remain stable in the new method.

INTRODUCTION

Classical trajectory simulations provide a computationally powerful approach to the dynamics of many-atom systems, but have the disadvantage of not describing quantum effects such as tunneling, interferences, or zero-point energy (ZPE). The importance of omitting each of these quantum effects depends on the system. There is, in particular, extensive evidence that lack of preservation of zero-point energies in classical dynamics can be a source of serious difficulties in simulations of various realistic systems. Classical trajectory simulations of several unimolecular[1,2] and bimolecular[3–6] reactions were, for instance, shown to give unreasonable results as a consequence of not obeying the "ZPE requirement" according to which, quantum mechanically, each internal molecular mode must contain an amount of energy at least equal to the ZPE. Some atom–diatomic reactions were found when treated by classical trajectories to result in a large fraction of the products having a vibrational energy much lower than the ZPE.[7] Several *ad hoc* solutions for such unphysical behavior were proposed.[8] Similarly, a recent study of photolysis of HI in low-temperature solid Xe has shown that classical molecular dynamics simulations lead to a final energy for the H photoproduct in the lattice that is much lower than the ZPE value.[9] A particularly important difficulty arises in cases where the large ZPE from stiff vibrational modes is transferred to other, soft modes, leading to dramatic, but unphysical effects. A very simple example is found for a van der Waals cluster in which a vibrationally stiff diatomic molecule is bound loosely to rare-gas atoms. In a classical calculation in which one initially gives the stiff oscillator an energy equal to the quantum ZPE, part of the energy will ultimately flow to the weak bonds leading to dissociation of the cluster. Another interesting example is in the case of large molecules, such as proteins, in which ZPE given initially to stiff local stretching modes such as CH vibrations is transferred to softer vibrations and causes unphysical conformational changes. Not putting ZPE in stiff modes to prevent this problem may result in incorrect description of various system properties, since the effective coupling among vibrational modes is changed.

There have been several attempts to deal with this problem. One suggestion is the so-called reduced dimensionality approximation,[10–12] which is based on an adiabatic treatment of the relevant modes. It is not clear to what extent this approximation of classical dynamics should be suitable for large polyatomic systems. Recently, two groups[13,14] have independently proposed a simple correction of the molecular dynamics (MD) algorithm which prevent the violation of the ZPE constraint. This method requires, however, an *ad hoc* procedure which perturbs discontinuously and suddenly the classical equations of motion and which can lead to instabilities.

The purpose of the present paper is to present a new method for dealing with the ZPE problem described above. The new method is computationally easy and stable and has the advantage that it leads to equations that are very similar to those of classical MD, so the same integrators can be used (and essentially the same computational effort is involved). At the same time, the method eliminates the ZPE problem not by imposing arbitrary constraints on classical dynamics, but by introducing the appropriate quantum effect through a semiclassical approximation. The method appears thus to have conceptual as well as computational advantages.

The contents of the paper are as follows: Sec. II describes the method. In Sec. III, we present two applications of the new scheme, one for a case of a diatomic molecule weakly bound to an atom, the other for a van der Waals cluster of two diatomic molecules. Brief conclusions are given in Sec. IV.

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II. METHOD

The method is based on treating the vibrationally stiff mode, which has a high ZPE, by a semiclassical Gaussian wave packet, and the soft, large amplitude modes of the system by classical trajectories. There can certainly be cases in which a vibrational mode that is not the stiffest loses its initial ZPE to the soft modes and then the scheme should be modified to treat this vibration semiclassically. In a recent study of photodissociation of HI in solid Xe,[9] classical MD calculations resulting in the H photofragment having final kinetic energies much lower than the ZPE and this was corrected by a hybrid method that treated the light atom by time-dependent quantum wave packets and the heavy atoms by classical trajectories.[9] The method proposed here is similar, but further simplified by using a semiclassical wave packet to describe the quantum mode. Since semiclassical wave functions yield the ZPE effect, the additional approximation seems reasonable and the gain in simplicity is substantial. To couple the classical and the quantum mechanical degrees of freedom, we use the mixed quantum/classical time-dependent self-consistent field (Q/C-TDSCF) method.[9,15-19] The validity of this approximation was tested numerically against exact quantum calculations for certain processes such as photodissociation[19] and we shall later discuss its validity in the present context.

While the approach is quite general, we consider here for simplicity a system of two modes $\{r,R\}$. The Hamiltonian operator is

$$\hat{H}=\hat{T}+\hat{V}=\frac{\hat{p}_r^2}{2\mu_r}+\frac{\hat{p}_R^2}{2\mu_R}+\hat{V}(r,R), \tag{1}$$

where $\hat{p}_r$ and $\hat{p}_R$ are the momenta associated with the modes r, R, respectively, and μ_r, μ_R are the corresponding masses. Suppose that physical considerations justify treating the R mode in the classical approximation, while for the r mode a quantum description must be retained. In the Q/C-TDSCF approach, the R mode is described by classical trajectories. Let $R(t)$ be a trajectory in time of the R mode (we discuss below the determination of such trajectories). In the Q/C-TDSCF, this trajectory is taken to define a time-dependent potential function

$$V_2(r,t)\equiv\hat{V}[r,R(t)], \tag{2}$$

which governs the r motion. $\hat{V}[r,R(t)]$ is the full potential function of the system as in Eq. (1), with R replaced by the trajectory value $R(t)$ at time t. The r dynamics is described by a wave packet satisfying the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi(r,t)}{\partial t}=\left[-\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2}+V_2(r,t)\right]\psi(r,t). \tag{3}$$

The potential that governs the classical motion in Q/C-TDSCF is the mean potential obtained by averaging the full potential over the r state

$$V_1(R,t)\equiv\langle\psi(r,t)|\hat{V}(r,R)|\psi(r,t)\rangle_r. \tag{4}$$

The trajectory $R(t)$ is obtained by solving Newton's equation of motion

$$\dot{P}_R=-\frac{\partial V_1(R,t)}{\partial R},\quad P_R=\mu_R\dot{R}. \tag{5}$$

In the Q/C-TDSCF, the trajectory $R(t)$ and the wave packet $\psi(r,t)$ are calculated self-consistently, using Eqs. (2)–(5).[18,19] The initial conditions required are the values $R(0)$, $P_R(0)$, and the wave function $\psi(r,0)$ at some initial time point $t=0$. If the initial state of the system is described by several classical initial values, e.g., $R^{(\alpha)}(0)$ and $P_R^{(\alpha)}(0)$ for $\alpha=1,\dots,N$, then for each classical initial values $R^{(\alpha)}(0)$ and $P_R^{(\alpha)}(0)$ are calculated from the Q/C-TDSCF trajectory $R^{(\alpha)}(t)$, $P_R^{(\alpha)}(t)$, and a wavepacket $\psi_\alpha(r,t)$. Any observable property is then calculated as an average from this ensemble of N hybrid quantum/classical states.

In the present problem, we assume that the Q/C-TDSCF can be further simplified by approximating the quantum wave packet $\psi(r,t)$ by a semiclassical Heller-type Gaussian wave packet.[20,21] In the situation considered here, the quantum mode is essentially expected to be carrying out zero-point motions, in which case a near-harmonic description of the potential governing that mode should be suitable for most systems and the Gaussian wave packet approximation should be valid.[20] Quite obviously, a Gaussian wave packet has the essential physical properties for describing the zero point effect. The Gaussian wave packets have the form[20,21]

$$G(r,t)=\exp\left\{\frac{i}{\hbar}\left[\alpha_t(r-r_t)^2+p_t(r-r_t)+\gamma_t\right]\right\}, \tag{6}$$

where the parameters r_t and p_t, which represent, respectively, the position of the center of the wave packet and its momentum, are real-valued and the parameters α_t and γ_t are complex valued. Using Heller's equations for the time propagation of the parameters γ_t, p_t, α_t, and γ_t,[15] we have

$$\dot{r}_t=p_t/\mu_r,\quad \dot{p}_t=-\frac{\partial V_2(r_t,t)}{\partial r_t}, \tag{7}$$

$$\dot{\alpha}_t+\frac{2\alpha_t^2}{\mu_r}=-\frac{1}{2}\frac{\partial^2V(r_t,t)}{\partial r_t^2}, \tag{8}$$

$$\dot{\gamma}_t=p_t\dot{r}_t+\frac{i\hbar\alpha_t}{\mu_r}-\frac{p_t^2}{2\mu_r}-V_2(r_t,t), \tag{9}$$

where $V_2(r,t)$ in Eqs. (7)–(9) is defined as in Eq. (2). Somewhat modified equations for the parameters have been proposed by Metiu *et al.*[22] and by other authors. In particular, Eq. (7) can be replaced by

$$\dot{p}_t=-\frac{\partial}{\partial r_t}\{\langle G(r,t)|V[r,R(t)]|G(r,t)\rangle_r/\langle G|G\rangle_r\}. \tag{10}$$

We tested both Eqs. (7) and (10) in our calculations and the results were very similar. In summary, the working equations in the hybrid semiclassical/classical scheme are given by Eqs. (5) and (7) for $R(t)$ and $P_R(t)$ and for r_t and p_t, respectively, supplemented by Eqs. (8) and (9) for α_t and γ_t. As for the potentials, $V_2(r,t)$ is given by Eq. (2) and $V_1(R,t)$ in the Gaussian scheme is

$$V_1(R,t)=\langle G(r,t)|\hat{V}(r,R)|G(r,t)\rangle_r. \tag{11}$$

The equations for $R(t)$, $P_R(t)$, r_t, and p_t are essentially of the same form as the Newton equations. The equations for α_t and γ_t are of the same type and the whole scheme can be handled essentially by existing molecular dynamics algorithms and with similar efficiency. The main additional effort is to need to calculate a Gaussian integral over the potential [Eq. (11)], but this is computationally very simple. The scheme is less demanding than treating the full system by Heller's equations,[20] since the latter inquire a matrix of coefficients for the exponent of the multidimensional Gaussian. At the same time, the use of nonfrozen Heller wave packets as done here is important in cases where the local frequency of the potential changes appreciably over the pertinent region of the potential surface. We note that extension of the formulation to many (classical) degrees of freedom is quite straightforward and the application involves essentially the same level of effort as the usual classical molecular dynamics calculations. A system of one semiclassical plus N classical modes includes, of course, only two additional dynamical equations compared with classical MD for the same system, the equations for α_t and γ_t, which becomes negligible in relative importance when the number of classical modes N is large. It may be interesting to note that when the potential is quadratic in r over the width of the Gaussian, $\bar{V}_1(R,t)$ reduces to the local potential at the center of the Gaussian (the potential experienced in classical dynamics) plus the local zero point energy. While this offers a simple interpretation of the methods, the applications we shall present involve, however, fairly anharmonic potentials.

III. APPLICATIONS

Test calculations will now be presented for two simple model systems to verify that the method proposed does indeed overcome the ZPE problem of classical dynamics in cases of a stiff vibration coupled to soft modes that can develop large amplitude motions. The calculations will also examine whether the method proposed causes other unphysical effects and whether it involves undesirable numerical features, such as instabilities.

A. The collinear diatomic molecule–atom cluster

The atoms were taken to have the masses of the $I_2 \cdots He$ system atoms. We denote by r the I_2 bond distance and by R the He to center of mass of I_2 distance. The potential is then written

$$V(r,R) = V_1(r) + V_2(r,R), \qquad (12)$$

with

$$V_1(r) = \epsilon_1 (e^{-2\beta_1(r-r_m)} - 2e^{-\beta_1(r-r_m)}), \qquad (13)$$

TABLE I. Parameters of the potentials used in the paper (see the text for details).

	V_1	V_2	V_a	V_b	V_c
ϵ (cm^{-1})	4839.6	14.0	31 606.5	7.6	139.5
β (Å^{-1})	1.77	5.00	1.81	2.12	6.00
r_m (Å)	3.01	4.00	1.41	2.96	4.00

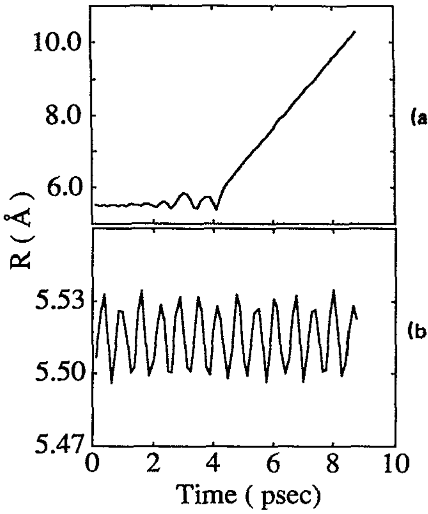

FIG. 1. Time evolution of the van der Waals mode R (a) classically and (b) semiclassically for the model $I_2 \cdots He$ system.

$$\begin{aligned} V_2(r,R) = {} & \epsilon_2\{\exp[-2\beta_2(R-1/2r-r_m)] \\ & -2\exp[-\beta_2(R-1/2r-r_m)]\} \\ & +\epsilon_2\{\exp[-2\beta_2(R+1/2r-r_m)] \\ & -2\exp[-\beta_2(R+1/2r-r_m)]\}. \end{aligned} \qquad (14)$$

We chose for convenience potential parameters for which violation of ZPE in the classical case occurs on a short time scale. The system parameters (except for the masses) do not correspond to real $I_2 \cdots He$. They are summarized in Table I.

First classical trajectories were run with an initial energy of 1354 cm^{-1} in the molecular bond, which corresponds to the ZPE. In Fig. 1(a), we show the time evolution of the van der Waals mode R. After about 2 ps of stability, the bond enters into high vibrations which finally lead to the dissociation of the cluster at $t = 4$ ps. Figure 2(a) describes the evo-

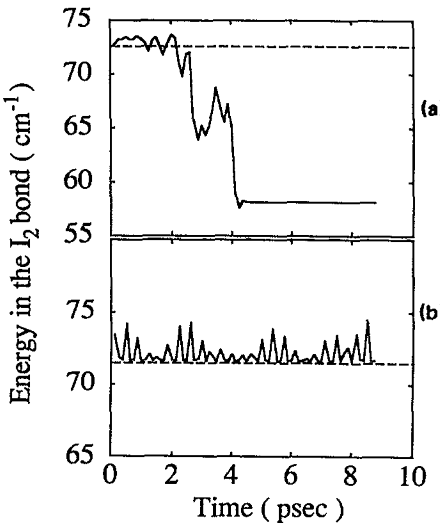

FIG. 2. Time evolution of the internal energy of the I_2 mode (a) classically and (b) semiclassically for the model $I_2 \cdots He$ system.

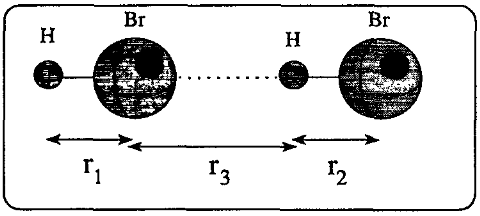

FIG. 3. Coordinate system for the model $(HBr)_2$ system.

lution of the internal energy of the I_2 mode during the same amount of time. After some relative stability, energy is suddenly transferred between 2 and 4 ps from the chemical bond to the van der Waals bond, resulting in a final value *below* the ZPE limit. This is of course an unphysical process which would not have occurred in an exact quantum mechanical treatment.

We now turn to the semiclassical description of the system. An initially normalized wave packet is prepared for the I_2 mode, with a wide α_0 consistent with the ZPE of the bond. The system is propagated within the same amount of time as the classical calculation, using the same integrator (Adams–Moulton) to solve Eqs. (7)–(10). Figures 1(b) and 2(b) show the time evolution of R and the internal energy of I_2, respectively. In contrast to the classical results, we see that (i) the van der Waals bond keeps showing stable oscillation of the vibrating complex and (ii) the energy stays constantly *above* the initial zero-point value, proving that no forbidden process occurs in the system.

B. A cluster of two diatomic molecules

The previous section has shown the successful application of the semiclassical method to a single mode system. Hence, we turn now to a more complex model system where two vibrational modes are susceptible to relax below the ZPE and contribute to artificial dissociation. A collinear version of the HBr dimer was chosen for this purpose. This is shown, together with the coordinate choice in Fig. 3.

The potential is given by

$$V(r_1,r_2,r_3) = V_a(r_1) + V_a(r_2) + V_a(r_3) + V_b(r_1 + r_3) + V_c(r_2 + r_3) + V_a(r_1 + r_2 + r_3), \tag{15}$$

where V_a, V_b, and V_c are Morse potentials with parameters summarized in Table I. Again we stress that except for the masses, this is merely a model system and does not represent real $(HBr)_2$.

As in the first case, we first let the system evolve completely classically with both r_1 and r_2 modes chosen initially at the ZPE limit. Figure 4(a) shows the time evolution of r_3. After less than 1 ps, the complex undergoes one single collision and dissociates. We have computed the energy of the two stiff modes during the process and the result is shown in Fig. 5(a). The initial straight line lies on the ZPE. After the collision (and also during it), the ZPE is violated seriously by *both modes* r_1 and r_2. Again this is the forbidden relaxation which has led to the dissociation of the cluster.

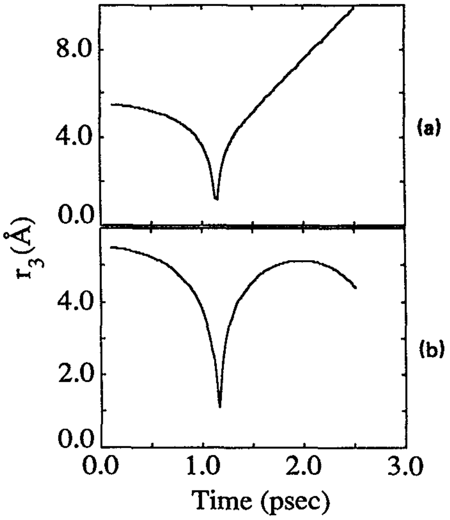

FIG. 4. Same as Fig. 1 for the model $(HBr)_2$ system.

The semiclassical method is now applied to each of the stiff modes, starting with two Gaussian wave packets with an initial width compatible with the ZPE values. The system is then propagated using the same initial conditions as the classical simulation. Figure 4(b) shows that the r_3 mode stays bonded after the collision has occurred and from Fig. 5(b), we see that both energies in r_1 and r_2 remain above the allowed ZPE limit. The system has behaved correctly by constraining itself naturally not to "violate" the ZPE conservation principle.

Both in the first and in the second examples, the total energy of the systems was conserved to good accuracy. Finally, in none of the calculations did there appear any numerical instability over the entire time scale studied.

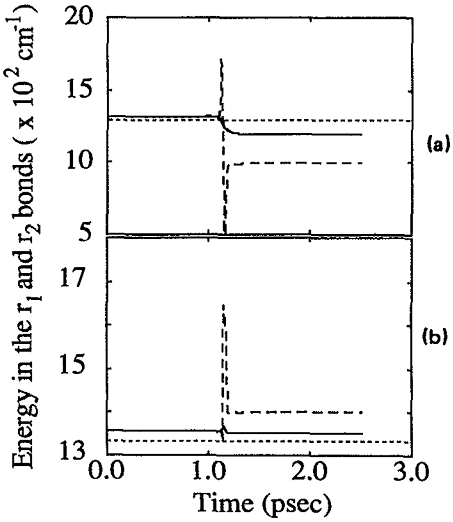

FIG. 5. Same as Fig. 2 for the model $(HBr)_2$ system. The plain line and the dashed line are modes r_1 and r_2, respectively.

IV. CONCLUSIONS

This paper was motivated by unphysical behavior in classical trajectory simulations of systems in which one or several high frequency vibrational modes are coupled to soft modes, which may undergo large amplitude motions when receiving energy. The undesirable behavior in classical dynamics addressed in this study is the flow of "zero point energy" initially put in the high frequency modes, into the low frequency vibrations, resulting in unphysical behavior such as dissociation. The new method proposed here treats the high frequency vibrations semiclassically, the soft modes classically, and the resulting scheme leads to equations similar in form and in computational complexity to the algorithms of classical molecular dynamics. Two test cases were studied numerically and showed that the method proposed does indeed preserve the ZPE of the high frequency modes and eliminates the unphysical behavior of classical trajectory calculations. It appears that the method conserves total energy, although some fluctuations of single-mode energies do indeed occur as they should, since the modes of the system are coupled. Propagation in line of the proposed equations showed numerical stability over the entire time range studied. The method does seem to offer a valid physical description of the type of the system studied.

Extension of the method to systems of many degrees of freedom seems quite straightforward. This should have useful applications to systems such as impurity molecules in soft, low-temperature crystals, weakly bound molecular clusters, and flexible polyatomic molecules that have some stiff vibrational modes and low barriers for conformational changes. The new method appears an attractive tool for simulation of such systems at low temperatures. For this purpose, it is desirable to develop a standard molecular dynamics package based on the present method, i.e., on semiclassical treatment of all stiff modes susceptible to lose their ZPE in the usual classical treatment. Such a project is in progress. At the same time, it should be stressed that the present method solves only a particular class of ZPE problems and there are certainly ZPE problems to which it does not apply. A case in point is when a system has many coupled vibrational modes of comparable frequencies that contribute all to the ZPE problem. Extensions of the method for such cases are currently being pursued.

ACKNOWLEDGMENTS

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