A simple model for correcting the zero point energy problem in classical trajectory simulations of polyatomic molecules

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A simple model is proposed for correcting problems with zero point energy in classical trajectory simulations of dynamical processes in polyatomic molecules. The “problems” referred to are that classical mechanics allows the vibrational energy in a mode to decrease below its quantum zero point value, and since the total energy is conserved classically this can allow too much energy to pool in other modes. The proposed model introduces hard sphere-like terms in action–angle variables that prevent the vibrational energy in any mode from falling below its zero point value. The algorithm which results is quite simple in terms of the cartesian normal modes of the system: if the energy in a mode $k$, say, decreases below its zero point value at time $t$, then at this time the momentum $P_k$ for that mode has its sign changed, and the trajectory continues. This is essentially a time reversal for mode $k$ (only!), and it conserves the total energy of the system. One can think of the model as supplying impulsive “quantum kicks” to a mode whose energy attempts to fall below its zero point value, a kind of “Planck demon” analogous to a Brownian-like random force. The model is illustrated by application to a model of CH overtone relaxation.

I. INTRODUCTION

One of the frustrating shortcomings in using classical mechanics to simulate dynamical processes in polyatomic molecules has to do with a problem involving the zero point energy of vibrational degrees of freedom.

To describe the problem, recall first the simpler situation of an atom–diatom (gas phase) bimolecular reaction,

$$A + BC(v_i = 0) \rightarrow AB(v_f) + C,$$

where it is indicated that the reactant diatom BC is initially in its ground vibrational state. It is well known that a classical trajectory simulation of this process works best if initial conditions for the trajectory are chosen to have the correct zero point vibrational energy in the diatom, with the initial phase of the vibrational motion selected at random (i.e., averaged over), so-called “quasiclassical” initial conditions. Agreement with (the correct) quantum reaction probabilities, or cross sections, would be much worse if the trajectory were begun with no vibrational energy. A problem can arise even for this process if the reaction is endoergic and most of the product is produced in $v_f = 0$. It is possible classically to obtain reactive trajectories with less than the zero point vibrational energy in the product molecule AB, clearly an unphysical result since this permits reaction below the quantum threshold for the reaction! This problem is usually dealt with by performing the classical simulation always in the exoergic direction and then using microscopic reversibility to obtain probabilities or cross sections in the reverse direction.

One thus believes that a classical simulation of a polyatomic molecular system will mimic nature (i.e., quantum mechanics) more closely if trajectories are begun with (at least) zero point vibrational energy in all vibrational degrees of freedom, with the phases of the vibrational motion selected at random (i.e., averaged over). To simulate vibrational relaxation of CH local mode overtones in benzene, for example, it would seem most reasonable to begin trajectories with the appropriate vibrational energy in the CH stretch and zero point vibrational energy in all the other normal modes.

Since the potential energy function for the polyatomic system is in general anharmonic, energy can flow between various degrees of freedom; often, in fact, it is this intramolecular vibrational energy redistribution (IVR) that one is wishing to simulate. The “zero point energy problem” mentioned in the first paragraph is that the energy in some vibrational modes may fall below the (quantum) zero point energy ($\hbar \omega_k$, where $\omega_k$ is the harmonic frequency for mode $k$). This may not at first seem like a serious problem, but in even a medium size polyatomic molecule (e.g., benzene) the zero point energy is a sizeable amount of energy (52.2 kcal/mol in benzene). It is a particularly serious problem if the zero point energy flows out of several modes and “pools” into a specific weak bond. For large molecules it may even happen that the classical mechanics is chaotic at its zero point energy. These are all clearly unphysical effects that arise because classical mechanics cannot prevent the energy in each vibrational mode from dipping below its zero point value.

The purpose of this paper is to describe a model for modifying the classical equations of motion in order to remedy this situation, i.e., to prevent the vibrational energy in each mode from at any time dipping below its zero point value. The algorithm we present affects the classical trajec-
tory only when the vibrational energy of a mode attempts to decrease below its zero point value; otherwise the trajectory is the ordinary classical one. The algorithm conserves the total energy of the polyatomic system, and since it prevents the energy in each mode from decreasing below its zero point value, there can be no unphysical "energy pooling" of the zero point energy from many modes into one bond.

Section II develops the model, first in its simplest version, and then a more general version. The resulting algorithm is actually quite simple: if the energy in any mode \( k \), say, decreases below its zero point value at time \( t \), then at this time the (Cartesian) momentum \( p_k \) has its sign changed, and the trajectory continues; this is essentially a time reversal for mode \( k \) (only!). One can think of the model as supplying impulsive quantum kicks to a mode whose energy is trying to fall below its point value, i.e., a kind of Planck demon analogous to a Brownian-like random force.

An application to CH local mode overtone relaxation is presented and discussed in Sec. III, and Sec. IV concludes.

II. THE MODEL

A. Simple version

The Hamiltonian is assumed to be of standard Cartesian form

\[
H(p, x) = \frac{1}{2} p^2 + V(x),
\]

where \( x \equiv \{x_k\} \) are the mass-weighted Cartesian coordinates of the system. The potential energy function consists of a harmonic part plus an anharmonic coupling,

\[
V(x) = V_0(x) + V_1(x),
\]

where

\[
V_0(x) = \sum_k \frac{1}{2} \omega_k^2 x_k^2.
\]

It is useful to introduce the usual harmonic action-angle variables \( (n_k, \theta_k) \), in terms of which the Cartesian variables are

\[
x_k = \sqrt{(2n_k + 1)\hbar/\omega_k} \cos \theta_k,
\]

\[
p_k = -\sqrt{(2n_k + 1)\hbar/\omega_k} \sin \theta_k.
\]

In terms of the action-angle variables, the Hamiltonian is

\[
H(n, \theta) = H_0(n) + V_1(x(n, \theta)),
\]

where

\[
H_0(n) = \sum_k \hbar \omega_k (n_k + \frac{1}{2}).
\]

The actions \( n_k \) are the classical counterparts to the harmonic quantum numbers, and the angles \( \theta_k \) are the phases of the vibrational motion. The actions \( n_k \) are actually the classical action in units of \( \hbar \), with the added constant \( \frac{1}{2} \) so that integer values of \( n_k \) correspond to the quantum numbers; i.e., \( n_k = (\text{classical action})/\hbar - \frac{1}{2} \).

We seek a modified classical mechanics that maintains

\[
n_k(t) > 0
\]

at all times and for all modes \( k \). This is accomplished by adding to the Hamiltonian hard wall terms \( W(n_k) \), such that

\[
W(n_k) = \begin{cases} 0, & n_k > 0 \\ +\infty, & n_k < 0 \end{cases}
\]

This is analogous to a hard sphere repulsive potential \( V(r) \) that keeps an interparticle distance \( r(t) \) greater than a hard sphere radius \( r_0 \), i.e.,

\[
V(r) = \begin{cases} 0, & r > r_0 \\ +\infty, & r < r_0 \end{cases}
\]

In the hard sphere case it is well known how to deal with the situation: the hard sphere potential (2.7) has no effect unless \( r(t) \) decreases to the value \( r_0 \), at which time one makes the instantaneous change

\[
(r(t) \rightarrow r(t)), \quad (p(t) \rightarrow -p(t)),
\]

i.e., the hard spheres experience an impulsive collision and are reflected. We follow this same course for the hard wall term in the action variable, Eq. (2.6).

Thus the hard wall potentials of Eq. (2.6) have no effect so long as \( n_k(t) > 0 \), but if \( n_k(t) \) dips below zero at some time along the trajectory, one makes the replacement

\[
(n_k(t) \rightarrow -n_k(t)), \quad (q_k(t) \rightarrow -q_k(t)).
\]

Equation (2.9) results from integrating the classical equations of motion with the hard wall potential \( W(n_k) \) over the infinitesimal time increment of the impulsive interaction. By using Eq. (2.3), this can be expressed in terms of the original Cartesian variables as

\[
(x(t) \rightarrow x(t)), \quad (p(t) \rightarrow -p(t)).
\]

Equation (2.10) shows that the modification made to mode \( k \) at time \( t \) is essentially a time reversal for that mode. Only the mode for which \( n_k(t) \) dips below 0 is modified as in Eq. (2.10).

One can verify more directly that Eq. (2.10) will indeed keep \( n_k(t) > 0 \). Hamilton's equations show that

\[
\frac{d}{dt} n_k(t) = -\frac{\partial H(n, \theta)}{\partial q_k} = -\frac{\partial V_1}{\partial q_k} = -\frac{\partial V_1}{\partial x_k} \frac{\partial x_k}{\partial q_k} = -\frac{\partial V_1}{\partial x_k} p_k/\omega_k.
\]

Thus, if \( n_k(t) \) is decreasing through 0 at time \( t_0 \) — i.e., \( n_k(t_0) = 0 \) and \( n_k(t_0) < 0 \) — making the replacement \( p_k \rightarrow -p_k \) will change the sign of \( n_k \) [cf. Eq. (2.11)] so that \( n_k(t_0) > 0 \), and \( n_k(t) \) will then increase and remain above 0.

Since the Hamiltonian (2.1) is Cartesian, it is also clear that the instantaneous modification (2.10) conserves the value of \( H \), i.e., the total energy.

The algorithm may be summarized as follows, all in terms of the original Cartesian variables

1. Start the trajectory in the appropriate manner (e.g., quasiclassical initial conditions).

2. At the end of each time step in the trajectory, insert the Fortran statement

\[
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\]
\[ p_k = p_k \cdot \text{Sign} \left( i\hbar^2 + \frac{i\hbar}{\omega_k} \right) \]
for all \( k \).

(3) Keep on computing!

Equation (2.12) clearly accomplishes the modifications discussed above.

B. More general version

The simple version of the model described in the previous section prevents the zeroth order actions \( \{ n_k \} \) of the fixed-frequency reference Hamiltonian \( H_0 \), Eq. (2.4), from becoming negative. If the dynamics of interest involves motion about a relatively well-defined equilibrium geometry, then this treatment should be adequate. In the more extreme case of a fragmentation process, e.g., unimolecular decomposition, however, it will not be a reasonable description because the physically relevant modes of the system change radically (the frequencies of some vibrations even going to zero as they evolve into rotations). In this section we show how the model of Sec. II A can be generalized by applying it to the zero point energy of the instantaneous normal modes.

Thus, at every time \( t \) along the classical trajectory \( \mathbf{x}(t) \) we determine the energy in the various instantaneous normal modes, and then require that this not be below their respective zero point values. At the arbitrary time \( t \), therefore, the potential is expanded through quadratic terms about the instantaneous position \( x(t) \equiv \mathbf{x}_r \),

\[ V(\mathbf{x}) \approx V(\mathbf{x}_r) + \mathbf{f}(\mathbf{x}_r) \cdot (\mathbf{x} - \mathbf{x}_r) + \frac{1}{2}(\mathbf{x} - \mathbf{x}_r)^T \cdot \mathbf{K}(\mathbf{x}_r) \cdot (\mathbf{x} - \mathbf{x}_r), \]

where

\[ \mathbf{f}(\mathbf{x}) = \frac{\partial V(\mathbf{x})}{\partial \mathbf{x}}, \]

\[ \mathbf{K}(\mathbf{x}) = \frac{\partial^2 V(\mathbf{x})}{\partial \mathbf{x} \partial \mathbf{x}}. \]

If \( \{ \mathbf{L}_k \} \) are the eigenvectors of the force constant matrix \( \mathbf{K}(\mathbf{x}_r) \) and \( \{ \Omega_k^2 \} \) the eigenvalues, then the local normal coordinates \( \mathbf{Q} \) and momenta \( \mathbf{P} \) are related to the original Cartesian variables \( \mathbf{x}, \mathbf{p} \) by

\[ \mathbf{x} - \mathbf{x}_r = \sum_k \mathbf{L}_k \Omega_k = \mathbf{L} \cdot \mathbf{Q}, \]

\[ \mathbf{p} = \mathbf{L} \cdot \mathbf{P}. \]

Within this local quadratic approximation about \( \mathbf{x}_r \), the Hamiltonian is given in terms of the local normal mode coordinate \( \mathbf{Q}, \mathbf{P} \) by

\[ H(\mathbf{Q}, \mathbf{P}) = V(\mathbf{x}_r) + \sum_k \left( \mathbf{P}_k^2 + D_k \mathbf{Q}_k + \frac{i\hbar}{2} \right) \]

\[ = \mathbf{P}_k^2 + \frac{i\hbar}{2} \mathbf{Q}_k \left( \mathbf{Q}_k + (D_k/\Omega_k^2) \right)^2 - (D_k/2\Omega_k^2), \]

so that the zero point energy constraint

\[ \mathbf{P}_k^2 + (D_k/2\Omega_k^2) > \frac{1}{2} \hbar \Omega_k \]

for each mode \( k \). We are actually interested in imposing this constraint at the instantaneous position \( \mathbf{x} = \mathbf{x}_r \), i.e., \( Q = 0 \), so that the constraints we wish to impose are

\[ \mathbf{P}_k^2 + (D_k/2\Omega_k^2) > \frac{1}{2} \hbar \Omega_k \]

for all \( k \). In terms of the original Cartesian coordinates and momenta, this reads

\[ \frac{1}{2}(\mathbf{L}_k^T \cdot \mathbf{p})^2 + \frac{1}{2} \left( \mathbf{L}_k^T \cdot \frac{\partial \mathbf{V}}{\partial \mathbf{x}} \right)^2 / \Omega_k^2 > \frac{1}{2} \hbar \Omega_k. \]

The left-hand side of Eq. (2.17) may be thought of as the instantaneous (i.e., at time \( t \)) energy in the local, harmonic mode \( k \): the first term of Eq. (2.17b) is clearly the kinetic energy in mode \( k \), and the second term is the potential energy which is due to the fact that the position \( \mathbf{x}(t) \) is not at the minimum of the instantaneous harmonic potential. If some of the frequencies \( \Omega_k \) are zero, or imaginary (i.e., mode \( k \) corresponds to moving over a barrier rather than in a well), then one does not apply a zero point energy constraint because there is no quantum zero point energy for such modes. We note also that more rigorously, one should diagonalize the projected force constant matrix,\(^8\) so that the six degrees of freedom corresponding to overall translations and rotations of the polyatomic systems will yield zero frequencies and thus have no zero point energy constraint.

We thus summarize, in terms of the original Cartesian variables, the more general algorithm as follows.

(1) Begin the trajectory in the appropriate manner to describe the process of interest.

(2) After each time step diagonalize the force constant matrix \( \nabla^2 V/\partial \mathbf{x} \cdot \partial \mathbf{Q} \) (more rigorously, the projected force constant matrix) at the current position \( \mathbf{x}(t) \), yielding the eigenvalues \( \{ \Omega_k^2 \} \) and eigenvectors \( \{ \mathbf{L}_k \} \).

(3) For all modes \( k \) for which \( \Omega_k^2 > 0 \), make the replacement

\[ \mathbf{p} \rightarrow \mathbf{p} - 2\mathbf{L}_k \cdot \mathbf{L}_k^T \cdot \mathbf{p}, \]

if

\[ \frac{1}{2}(\mathbf{L}_k^T \cdot \mathbf{p})^2 + \frac{1}{2} \left( \mathbf{L}_k^T \cdot \frac{\partial \mathbf{V}}{\partial \mathbf{x}} \right)^2 / \Omega_k^2 < \frac{1}{2} \hbar \Omega_k. \]

[It is not hard to show that Eq. (2.18a) corresponds to \( P_k \rightarrow -P_k \) for mode \( k \), no change for all other modes.]

To conclude this description of the model, we note that imposition of the zero point energy constraint within a harmonic approximation should not be a serious limitation. This is because the algorithm affects the classical mechanics of a vibrational mode only when it is near its zero point level, and most such degrees of freedom are reasonably well-described harmonically at this low level of excitation.

III. EXAMPLE CALCULATION

To illustrate the above method, calculations of CH overtone relaxation were performed for a collinear \( \text{HC}_4 \) model.
studied previously by Hutchinson et al. This is a particularly interesting system to consider, since it was reported that relaxation of the CH overtone is independent of the zero point energy: i.e., the same result was found with and without zero point energy added. No terms are neglected in the kinetic energy for the HC$_4$ Hamiltonian and the potential energy is a sum of a CH Morse oscillator and CC harmonic oscillators

$$V = D_{CH} \left[ 1 - e^{-\beta_{CH}(r - r_0)} \right]^2 + \sum_{i=2}^{n} f_{CC} (R_i - R_0)^2/2,$$

(3.1)

where $\beta_{CH} = 1.946 \text{ A}^{-1}$, $D_{CH} = 84.101 \text{ kcal/mol}$, $r_0 = 1.079 \text{ Å}$, $f_{CC} = 12.107 \text{ mdyn/Å}$, and $R_0 = 1.531 \text{ Å}$. The harmonic vibrational frequencies are 981.8, 1819.2, 2395.7, and 2886.9 cm$^{-1}$. A modified version of the general chemical dynamics computer program VENUS, which solves Hamilton's classical equations of motion in Cartesian coordinates, was used in the calculations. Representing the HC$_4$ Hamiltonian in Cartesian coordinates is a straightforward procedure.

To generate the initial conditions for the classical trajectory simulation, an approach described previously is used to add zero point energy to each normal mode of the collinear HC$_4$ model. The CH bond is then further extended or compressed until the CH bond energy

$$E_{CH} = \frac{1}{2} \frac{m_H m_C}{m_H + m_C} r^2 + D_{CH} \left[ 1 - e^{-\beta_{CH}(r - r_0)} \right]^2$$

(3.2)

equals the energy for state $|n>$ of a Morse oscillator; i.e., $E(n) = (n + 1)\omega - (n + 1)^2 \omega^2$. Exciting the CH bond alters the energy of the HC$_4$ normal modes, and an initial condition is only accepted if the energy for each normal mode is greater than or equals the zero point energy. Hamilton's equations of motion are integrated with a fourth order Runge Kutta algorithm. [Changing the signs of the normal mode momenta while integrating the trajectories, Eq. (2.12), makes the use of a nonself-starting algorithm such as a predictor-corrector less practical.] After each integration step the normal mode coordinates and momenta are formed by a linear transformation of the Cartesian coordinates and momenta, and the normal mode energies are compared with the zero point energies. If a normal mode energy is less than the zero point value and less than that found for the previous integration step, the sign of the normal mode's momentum is reversed. After this test is performed for each normal mode, the normal mode momenta are transformed to Cartesian momenta and the trajectory is continued. (This prescription corresponds to the "simple version" of the present model, that described in Sec. II A; i.e., the normal modes referred to here are those about the equilibrium geometry and not the instantaneous normal modes involved in the more general version of the model in Sec. II B.)

Calculations were carried out for 100 randomly chosen sets of initial conditions, i.e., 100 different trajectories, so that the average energy in the various degrees of freedom could be determined as a function of time. We first discuss the results for the CH bond itself. Figures 1 and 2 show the energy in the CH bond vs time for the initial state with $n = 2$ and $n = 7$ quanta in the CH stretch, respectively. The upper panel in each figure is the result of the present quasiclassical model with the zero point energy constraint, the middle panel the result of the standard quasiclassical method (i.e., with zero point energy in all the other modes but no dynamical constraints), and the lower panel is the result without zero point energy initially in the other modes. The first observation is that the results in the three panels are different, i.e., it matters how zero point energy is treated and whether or not it is included. The fact that inclusion of zero point energy affects the results is in contrast to the earlier report, but it is consistent with the work of others.

More specifically, on comparing the upper and middle

![Fig. 1. Plot of the average energy in the CH Bond of HC$_4$ vs time for the $n = 2$ overtone. Upper: present quasiclassical trajectory method with zero point energy constraint. Middle: standard quasiclassical trajectory method with zero point energy (but no constraint). Lower: classical trajectory method with no zero point energy initially in the normal modes.](http://jcp.aip.org/jcp/figure?article=2866&volume=91&issue=5&year=1989&figure=1)
panels of Figs. 1 and 2 one sees that the present model (upper panel) leads to less energy in the CH stretch at the final time (t ~ 1 ps). This is presumably due to the fact that none of the other modes are permitted to have energy below their zero point values (see discussion below). We also note in Fig. 2 that the final energy in the CH stretch is about the same with the present constraint model (~ 20–22 kcal/mol) as is the result with no initial zero point energy (lower panel); the CH bond is considerably hotter at t ~ 1 ps (~ 26 kcal/mol) if zero point energy is included initially but not constrained (middle panel). This is consistent with earlier suggestions that it is better to include no zero point energy in modes, rather than to have it present and allow it to flow in an unrestricted fashion.

Next, in Figs. 3 and 4 we consider the energy in the other three (normal) modes as a function of time. Figure 3 shows the results of the standard quasiclassical trajectory method (i.e., initial zero point energy with no constraint) and Fig. 4 the results of the present quasiclassical method with zero point energy constraint. The zero point energies for these three modes are 3.4, 2.6, and 1.4 kcal/mol, and one clearly sees in Fig. 3 that the mode energies for all three modes dip below their zero point values at some times. This violation appears to be most serious for the mode with the middle frequency. In Fig. 4, on the other hand, one sees that the present model prevents energy of each mode from falling below its zero point value.

VI. CONCLUDING REMARKS

The model presented in Sec. II is a plausible one for constraining the classical dynamics so as to avoid the zero point energy problems described in the Introduction. The

FIG. 3. Energies in three of the HCN normal modes vs time for a single trajectory calculated with the standard quasiclassical trajectory method: 981.4 cm⁻¹ mode (—), 1819.2 cm⁻¹ mode (—), and 2395.7 cm⁻¹ mode (—).

FIG. 4. Same as Fig. 3 (including the trajectory initial conditions), except with the present trajectory model which constrains the zero point energy as described in the text.
example treated in Sec. III illustrates how the model can be applied (at least in the simple version), and it also shows that it does matter how zero point energy is treated. It is not possible at present, though, to claim that the results given by this model are better (i.e., more in accord with quantum mechanics) than other approaches. Pursuant to this question it will be useful to apply the model to simpler systems, ones for which accurate quantum calculations can be carried out to provide the right answer. Other applications of interest to us are CH overtone relaxation in benzene as well as to endoergic bimolecular $A + BC$ reactions.

Finally, we note that essentially this same model (at least the simple version of Sec. II A) has been obtained by Bowman et al.\textsuperscript{14} and tested on the Henon-Heiles model of two coupled oscillators.

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