In: Handbook of Computational Chemistry Research ISBN 978-1-60741-047-8 Editors: C.T. Collett and C.D. Robso, pp. 467-476 © 2010 Nova Science Publishers, Inc.

Chapter 17

ON THE ZERO POINT ENERGY DIFFICULTY OF QUASICLASSICAL TRAJECTORY SIMULATIONS

Song Ling and Robert Q. Topper Department of Chemistry, Medical Technology, and Physics Monmouth University Thomas A. Edison Hall of Science West Long Branch, NJ 07764-1898

Abstract

Following the work of Guo, Thompson, and Sewell (Y.Guo, D.L.Thompson, and T.D. Sewell, J.Chem.Phys. **104**, 576 (1996)) on the zero point energy correction of classical trajectories, we emphasize that the zero-point energy of a molecule is a quantum phenomenon with no classical counterpart, rooted soundly in the position-momentum uncertainty principle. As a consequence certain quantum "ingredients," such as those introduced using Heller's thawed Gaussian wavepacket dynamics (E.J. Heller, J.Chem.Phys. **62**, 1544 (1975)), are probably necessary to avoid the computational difficulties in applying zero-point energy corrections to classical molecular dynamics trajectories which have been described in the literature to date.

1. Introduction

Despite remarkable advances in computing technology and algorithms, the vibrational and rotational motions of medium-sized polyatomic molecules still defy full quantummechanical analysis, and so classical trajectory studies are still widely applied [1, 2]. However, in quantum mechanics the slowest possible motion of each rovibrational mode is not literally "standing still", i.e. it is not a fixed point in the classical phase space. This is the so-called zero point motion, and it leads to the zero-point energy (ZPE) for that mode. Since there are many rovibrational modes in a polyatomic molecule, setting the ZPE of one mode to be zero by resetting the energy scale does not reset the ZPE to be zero for all modes; there is thus no loss of generality in speaking of the ZPE (rather than the zero-point motion) problem for classical trajectory studies.

Even though conventionally the study of classical-quantum correspondence happens at high energies or large quantum numbers for polyatomic molecules, [3], the low energy

states of molecules are of great chemical interest as well. For example, if the ZPEs of several modes of a large molecule are "squeezed out" at the same time, the amount of that energy may be sufficient to break a chemical bond. Another example is the umbrella motion of NH_3 , which is well-described by a double well potential. At low energies the umbrella motion is classically forbidden and is only achievable by quantum mechanical tunneling with a time scale inversely proportional to the energy splitting of the ground states. If an NH_2 functional group is attached to a large polyatomic molecule which functions like a leat bath, the energies of the modes of the bath can flow into the attached $-NH_2$ group and make the umbrella motion more probable than it would be for the isolated NH_3 molecule.

Guo, Thompson, and Sewell (GTS)[4] pointed out that past efforts[5] to modify classical mechanics, either *passively* by abandoning trajectories with a mode energy lower than the ZPE after the trajectories are integrated or *actively* by modifying the equations of motion during the integration to enforce the ZPE condition lead to unphysical results. GTS emphasized that statistics (or probability) must be utilized in the comparison between classical trajectory and quantum studies. It is not the individual classical trajectory but the ensemble average of a swarm of them that should be compared to the quantities like the mode energy calculated by the propagation of a quantum wavefunction.

We note in the GTS paper, after they compared classical ensemble averages with quantum expectation values they concluded: "The search for practical solutions to the ZPE problem should focus upon ways for accounting for interference effects (i.e., semiclassical theories) and perhaps by improving the quasiclassical procedures, under the guidance of quantum mechanics, so as to obtain a better classical-quantum correspondence."[4]

Using the semiclassical Gaussian wavepackets that Heller[6] proposed for other studies to treat a single "stiff" mode while the "soft" modes were still treated classically, Alimi, Garcia-Vela, and Gerber[7] described the melting of some inert gas clusters. However, in their paper the cases studied for the "stiff" mode were one-dimensional. The ZPE issue troubles chemists the most in multi-mode systems, and in such systems there is likely more than one "stiff" mode.

Heller[6] proposed a multi-dimensional semiclassical scheme to integrate the time dependent Schrödinger equation, different from the conventional approach of letting a dimensionless parameter with \hbar in the numerator go to zero. In this paper, Heller used a quadratic Taylor expansion of the potential function about the moving "center" of a Gaussian wavefunction. The resulting wavefunction remains Gaussian with determining parameters governed by a set of equations of motion, i.e., ordinary differential equations (ODE) in time. Interestingly, the time-dependent position and momentum expectation values fall out to follow exactly the classical equations of motion, while the other complex parameters account for interference effects (since the wavepacket corresponds to a swarm of classical trajectories moving in phase space), with a phase factor containing the classical action integral.

Computationally, this becomes an initial value problem of ODE integrations. In addition to integrating the classical equations of motion, the (complex) quantum parameters are also integrated along the way. We present a multi-dimensional Gaussian derivation in Section 2 and study the choice of both classical and quantum initial conditions in Section 3. Also in Section 3 we show that the thawed Gaussian helps avoid the ZPE difficulty by calculating the mode energy quantum mechanically as an expectation value of the propagating wavepacket, and the result contains the classical mode energy in the $\hbar - > 0$ limit.

On tl

2. The

We pres in Cartesian Follow

 $\psi(x_1,...,x_n,$

where it is and \hat{p}_j , i.e., The Han

and the pote the instantan

 $V(x_1,$

The above Schrödinger

Comparing li r and s are le e.g., $\dot{\alpha} \equiv \frac{d\alpha}{dt}$)

2. The Gaussian Wavefunction

We present a derivation for arbitrary dimensional systems of the Gaussian wavepacket in Cartesian coordinates, and then we derive the expression for the mode energy. Follow Heller[6], we write the wavefunction as:

$$\psi(x_1, ..., x_n, t) = \exp\{\frac{i}{\hbar} \sum_{k=1}^n \sum_{j=1}^n \alpha_{jk}(t)(x_j - x_j(t))(x_k - x_k(t)) + \frac{i}{\hbar} \sum_{j=1}^n p_j(t)(x_j - x_j(t)) + \frac{i}{\hbar}\gamma(t)\}$$
(1)

where it is straightforward to show that $x_j(t)$ and $p_j(t)$ are the expectation values of $\hat{x_j}$ and $\hat{p_j}$, i.e., the j^{th} position operator and momentum operator, respectively. The Hamiltonian operator in a general time-independent potential is

$$H = -\frac{\hbar^2}{2} \sum_{j=1}^n \frac{1}{m_j} \frac{\partial^2}{\partial x_j^2} + V(x_1, ..., x_n)$$
(2)

and the potential function is Taylor-expanded up to quadratic about $(x_1(t), ..., x_n(t))$, i.e., the instantaneous "center" of the coordinate space wavefunction. Thus we obtain:

$$V(x_1, ..., x_n) \approx V(x_1(t), ..., x_n(t)) + \sum_{j=1}^n \frac{\partial V}{\partial x_j}|_{x_1(t), ..., x_n(t)} (x_j - x_j(t)) + \frac{1}{2} \sum_{k=1}^n \sum_{j=1}^n \frac{\partial^2 V}{\partial x_j \partial x_k}|_{x_1(t), ..., x_n(t)} (x_j - x_j(t)) (x_k - x_k(t))$$
(3)

The above ψ and the Taylor-expanded V are substituted into the time dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi(x_1, ..., x_n, t)}{\partial t} = H\psi(x_1, ..., x_n, t)$$
(4)

Comparing like coefficients of the powers of $(x_j - x_j(t))^r (x_k - x_k(t))^s$, where the sum of r and s are less than or equal to 2, we get (where we apply the dot convention to denote $\frac{d}{dt}$, e.g., $\dot{\alpha} \equiv \frac{d\alpha}{dt}$)

$$\dot{x}_j(t) = \frac{p_j(t)}{m_j} \tag{5}$$

$$\dot{p}_j(t) = -\frac{\partial V}{\partial x_j}|_{x_1(t),\dots,x_n(t)} \tag{6}$$

$$\dot{\alpha}_{jk}(t) = -2\sum_{l=1}^{n} \frac{\alpha_{jl}(t)\alpha_{kl}(t)}{m_l} - \frac{1}{2}\frac{\partial^2 V}{\partial x_j \partial x_k}|_{x_1(t),\dots,x_n(t)}$$
(7)

$$\dot{\gamma}(t) = \sum_{l=1}^{n} \frac{p_l^2(t)}{2m_l} - V(x_1(t), ..., x_n(t)) + i\hbar \sum_{l=1}^{n} \frac{\alpha_{ll}(t)}{m_l}$$
(8)

PEs of of that motion nbrella meling . If an : like a up and ecule. classier than notion mphaassical semble energy

e ZPE assical nce of

studies Alimi, ver, in 3 issue / more

ne delimenadratic wave-'s govı time. to folccount ijectoral. In adneters ion in tion 3. by calgating

11.1

We note that the complex α matrix is symmetric, i.e., $\alpha_{jk}(t) = \alpha_{kj}(t)$ since $(x_j - x_j(t))(x_k - x_k(t)) = (x_k - x_k(t))(x_j - x_j(t))$. As a consequence, the real and imaginary parts of the α matrix form two real symmetric matrices. We count the number of *real* equations of motion for an *n*-dimensional system as below: *n* equations for the position expectation values $x_j(t)$, *n* equations for the momentum expectation values $p_j(t)$, n(n+1) equations for the $\alpha_{jk}(t)$ matrix elements, and 2 equations for $\gamma(t)$. Therefore the total number of real equations of motion is (n + 1)(n + 2) and increases as n^2 (as opposed to classical *n*-dependence). It must be noted that this behavior may limit the use of the Gaussian wavefunctions in place of classical trajectories for large *n* systems.

Since the time evolution of the position and momentum expectation values are classical as shown above, the choice of the initial positions and momenta can be done by any conventional method applied in classical trajectory studies[1]. When choosing the other initial conditions, the matrix of the imaginary part of $\alpha_{jk}(0)$ must be positive definite to ensure that the Gaussian wavefunction is square integrable throughout the time evolution. Without losing generality, the real part of the $\alpha_{jk}(0)$ matrix elements, $Re[\alpha_{jk}(0)]$, and the real part of $\gamma(0)$, $Re[\gamma(0)]$, can be chosen to be zero. The imaginary part of the diagonal α matrix elements, $Im[\alpha_{ll}(0)]$, can be chosen to mimic the ground state wavefunction of each mode, i.e.,

$$Im[\alpha_{ll}(0)] = \frac{1}{2} \sqrt{m_l} \left\| \frac{\partial^2 V(x_1, ..., x_n)}{\partial x_l^2} \right|_{x_1(0), ..., x_n(0)} \right\|$$
(9)

After the diagonal matrix elements are chosen, the off-diagonal imaginary α matrix elements can thus be selected to satisfy the matrix positive definite condition, reflecting the physical fact that the coupling between different modes are perturbative to the modes, not overtaking the modes. The imaginary part of $\gamma(0)$, $Im[\gamma(0)]$, can be determined by normalizing the initial Gaussian wavefunction. As a special case, if all of the imaginary parts of the off-diagonal elements of the initial $\alpha_{jk}(0)$ matrix are chosen to be zero, (this amounts to saying that at a moment of the wavepacket evolution there is no coupling between different modes so that *at that moment* the wavefunction is a product of the wavefunctions of each mode), the imaginary part of $\gamma(0)$ is

$$Im[\gamma(0)] = \frac{\hbar}{2} \ln\{(\frac{\pi\hbar}{2})^{\frac{n}{2}} \prod_{l=1}^{n} \frac{1}{Im[\alpha_{ll}(0)]}\}$$
(10)

3. Applications to Generalized 2-Dimensional Systems and the Hénon-Heiles Potential

For purposes of discussion, at this juncture we develop and present the equations of motion for two-dimensional systems, with application to a model system widely known as the Hénon-Heiles potential.[8] The extension of these equations to multidimensional systems is straightforward but less illustrative.

The Gaussian wavefunction for a general 2-dimensional system is written as follows:

$$\psi(x, y, t) = \exp\{\frac{i}{\hbar} [\alpha_{xx}(t)(x - x(t))^2 + 2\alpha_{xy}(t)(x - x(t))(y - y(t)) + \alpha_{yy}(t)(y - y(t))^2 + p_x(t)(x - x(t)) + p_y(t)(y - y(t)) + \gamma(t)]\}$$
(11)

On th

Assumin equations of

 $\dot{R}e[lpha_{xx}(t)] =$

İn

 $\dot{R}e[\alpha_{xy}]$

İm

 $\dot{R}e[\alpha_{yy}(t)] =$

İr

 $Re[\gamma(t)]$ =

Assuming the mass factor is scaled so that $m_x = m_y$, the (n + 1)(n + 2) = 12 real equations of motion read:

$$\dot{x}(t) = \frac{p_x(t)}{m} \tag{12}$$

$$\dot{y}(t) = \frac{p_y(t)}{m} \tag{13}$$

$$\dot{p}_x(t) = -\frac{\partial V}{\partial x}|_{x(t),y(t)}$$
(14)

$$\dot{p}_y(t) = -\frac{\partial V}{\partial y}|_{x(t),y(t)}$$
(15)

$$\dot{R}e[\alpha_{xx}(t)] = -\frac{2}{m} \{Re^2[\alpha_{xx}(t)] - Im^2[\alpha_{xx}(t)] + Re^2[\alpha_{xy}(t)] - Im^2[\alpha_{xy}(t)]\} - \frac{1}{2}\frac{\partial^2 V}{\partial x^2}|_{x(t),y(t)}$$
(16)

$$\dot{I}m[\alpha_{xx}(t)] = -\frac{4}{m} \{ Re[\alpha_{xx}(t)]Im[\alpha_{xx}(t)] + Re[\alpha_{xy}(t)]Im[\alpha_{xy}(t)] \}$$
(17)

$$\dot{R}e[\alpha_{xy}(t)] = -\frac{2}{m} \{Re[\alpha_{xx}(t)]Re[\alpha_{xy}(t)] - Im[\alpha_{xx}(t)]Im[\alpha_{xy}(t)] + Re[\alpha_{xy}(t)]Re[\alpha_{yy}(t)] - Im[\alpha_{xy}(t)]Im[\alpha_{yy}(t)]\} - \frac{1}{2}\frac{\partial^2 V}{\partial x \partial y}|_{x(t),y(t)}$$
(18)

$$\dot{I}m[\alpha_{xy}(t)] = -\frac{2}{m} \{ Re[\alpha_{xx}(t)]Im[\alpha_{xy}(t)] + Im[\alpha_{xx}(t)]Re[\alpha_{xy}(t)] \\
+ Re[\alpha_{xy}(t)]Im[\alpha_{yy}(t)] + Im[\alpha_{xy}(t)]Re[\alpha_{yy}(t)] \}$$
(19)

$$\dot{R}e[\alpha_{yy}(t)] = -\frac{2}{m} \{Re^{2}[\alpha_{yy}(t)] - Im^{2}[\alpha_{yy}(t)] + Re^{2}[\alpha_{xy}(t)] - Im^{2}[\alpha_{xy}(t)]\} - \frac{1}{2}\frac{\partial^{2}V}{\partial y^{2}}|_{x(t),y(t)}$$
(20)

$$\dot{I}m[\alpha_{yy}(t)] = -\frac{4}{m} \{ Re[\alpha_{xy}(t)]Im[\alpha_{xy}(t)] + Re[\alpha_{yy}(t)]Im[\alpha_{yy}(t)] \}$$
(21)

$$\dot{R}e[\gamma(t)] = \frac{p_x^2(t) + p_y^2(t)}{2m} - V(x_1(t), ..., x_n(t)) - \frac{\hbar}{m} \{Im[\alpha_{xx}(t) + Im[\alpha_{yy}(t)]\}$$
(22)

$$\dot{I}m[\gamma(t)] = \frac{\hbar}{m} \{ Re[\alpha_{xx}(t)] + Re[\alpha_{yy}(t)] \}$$
(23)

 $(x_j - ginary)$ of *real* osition n+1) e total oposed of the assical

y coninitial ensure /ithout al part matrix mode,

(9)

ix eleng the es, not ormalarts of unts to fferent of each

(10)

1 the

ons of known isional

 $(t))^2 +$

ows:

(11)

lin

The choice of the initial conditions of x(0), y(0), $p_x(0)$, and $p_y(0)$ can be made based on established methods for choosing initial conditions for classical trajectory studies depending on the system of interest [1]. The choice of the initial α 's and γ is as follows: $Re[\alpha_{xx}(0)] = Re[\alpha_{xy}(0)] = Re[\alpha_{yy}(0)] = Re[\gamma(0)] = 0$, and $Im[\alpha_{xx}(0)] = \frac{1}{2}\sqrt{m} \|\frac{\partial^2 V}{\partial x^2}|_{x(0),y(0)}\|$, $Im[\alpha_{yy}(0)] = \frac{1}{2}\sqrt{m} \|\frac{\partial^2 V}{\partial y^2}|_{x(0),y(0)}\|$, and $Im[\alpha_{xy}(0)] = 0.1\sqrt{Im[\alpha_{xx}(0)]Im[\alpha_{yy}(0)]}$ (to choose the coupling strength to be 10% of the average mode strength). The normalization of the initial wavefunction gives $Im[\gamma(0)] = \frac{\hbar}{2} \ln \frac{\pi\hbar}{2\sqrt{Im[\alpha_{xx}(0)]Im[\alpha_{yy}(0)]-Im^2[\alpha_{xy}(0)]}}$, where we notice the determinant of the imaginary part α matrix is under the square root and must be positive as mentioned previously.

Following GTS, the Hamiltonian (symbolically for both classical and quantum operators) of the Hénon-Heiles system [8] is written as:

$$H = \frac{p_x^2}{2} + \frac{p_y^2}{2} + \frac{1}{2}\omega_x^2 x^2 + \frac{1}{2}\omega_y^2 y^2 + x^2 y - \frac{1}{3}y^3$$
(24)

Also following the GTS paper, the classical initial conditions are selected by the random phase method for the uncoupled 2-dimensional harmonic oscillator:

$$q_i(0) = \sqrt{\frac{(2n_i + 1)\hbar}{\omega_i}} \sin \phi_i \tag{25}$$

$$p_i(0) = \sqrt{(2n_i + 1)\hbar\omega_i}\cos\phi_i \tag{26}$$

where i = x and y, ϕ_x and ϕ_y are each chosen randomly between 0 and 2π and the size of \hbar is chosen as an adjustable parameter indicating the deviation from the classical regime. We note that these initial conditions do not correspond to picking up points from the constant energy shell, or the microcanonical ensemble, due to the anharmonic coupling terms. Therefore, generally speaking each classical trajectory has a different total energy to start with (but each energy stays constant over the propagation time).

The classical mode energy is

$$E_i^{cl}(t) = \frac{1}{2}p_i^2(t) + \frac{1}{2}\omega_i^2 q_i^2(t)$$
(27)

where $q_i(t)$ and $p_i(t)$ are the position-momentum expectation values of the Gaussian wavefunction at time t.

The quantum mode energy with the Gaussian wavefunction approximation can be calculated analytically, where we let the state vector propagate in time (this is a general formula, not specific to the Hénon-Heiles system):

$$E_{i}^{qu}(t) = \frac{1}{2} < \psi(t)|\hat{p_{i}^{2}} + \omega_{i}^{2}\hat{q_{i}^{2}}|\psi(t) >$$
(28)

Integrating over the coordinate space Gaussian wavefunction, we obtain for the x mode (replacing x by y will give the y-mode formula):

 $+\frac{1}{I}$ where E $Im[\alpha_{xx}($ and $D_2(1)$ Even t (which non-zero trajector time proj sical traj expectati cal equat stark cor or odd) a Gaussian of the Ga a classica Simi

0

 E_x^q

and its Fo The c

 $C_i^{qu}(t)$

(29)

)

$$E_x^{qu}(t) = E_x^{cl}(t)$$

$$+ \frac{\hbar}{D_1(t)} \{ \frac{1}{2} |\alpha_{xx}(t)|^2 Im[\alpha_{yy}(t)] + \frac{1}{2} |\alpha_{xy}(t)|^2 Im[\alpha_{xx}(t)] - Im[\alpha_{xy}(t)] D_2(t) + \frac{\omega_x^2}{8} Im[\alpha_{yy}(t)] \}$$
(29)

where $E_x^{cl}(t) = \frac{1}{2}p_x^2(t) + \frac{1}{2}\omega_x^2 x^2(t)$ is the classical x-mode energy as in eq. 27, $D_1(t) =$ $Im[\alpha_{xx}(t)]Im[\alpha_{yy}(t)] - Im^2[\alpha_{xy}(t)]$ is the determinant of the imaginary part α matrix, and $D_2(t) = Re[\alpha_{xx}(t)]Re[\alpha_{xy}(t)] + Im[\alpha_{xx}(t)]Im[\alpha_{xy}(t)].$

Even if the expectation values x(t) and p(t) happen to both be equal to zero at some time t (which results in zero classical mode energy), the quantum mode energy $E_{\pi}^{qu}(t)$ is still non-zero. Moreover, the comparison between the Gaussian wavefunction and the classical trajectory with the same initial position-momentum conditions is closer than comparing the time propagation of an unperturbed harmonic oscillator eigenfunction and a swarm of classical trajectories. First of all, the initial Gaussian already has its position and momentum expectation values chosen classically and these expectation values are integrated by classical equations of motion, i.e., their evolution is identical to that of classical trajectories. In stark contrast, the unperturbed quantum eigenfunctions tend to have a parity (either even or odd) and therefore have zero position and momentum expectation values. Secondly, the Gaussian wavefunction contains the classical trajectory as a special case, and when the size of the Gaussian shrinks to a point the position-momentum expectation values will trace out a classical phase space trajectory.

Similarly, the classical coordinate autocorrelation function is defined as

$$C_i^{cl}(t) = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt' q_i(t') q_i(t'+t)$$
(30)

and its Fourier transform gives the power spectrum. The quantum counterpart is defined as

$$\begin{split} C_{i}^{qu}(t) &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(0) |\hat{q}_{i}^{\dagger}(t')\hat{q}_{i}(t'+t)|\psi(0) > \\ &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(0) |\exp(\frac{i}{\hbar} \hat{H}t)\hat{q}_{i}\exp(\frac{i}{\hbar} \hat{H}t)\hat{q}_{i}\exp(-\frac{i}{\hbar} \hat{H}(t+t'))|\psi(0) > \\ &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t') |\hat{q}_{i}\exp(\frac{i}{\hbar} \hat{H}t)\hat{q}_{i}|\psi(t+t') > \\ &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t')|(\hat{q}_{i}-q_{i}(t')+q_{i}(t')) \\ &\exp(\frac{i}{\hbar} \hat{H}t)(\hat{q}_{i}-q_{i}(t+t')+q_{i}(t+t'))\psi(t+t') > \\ &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t')|(\hat{q}_{i}-q_{i}(t')\exp(\frac{i}{\hbar} \hat{H}t)(\hat{q}_{i}-q_{i}(t+t'))|\psi(t+t') > \\ &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t')|(\hat{q}_{i}-q_{i}(t')\exp(\frac{i}{\hbar} \hat{H}t)(\hat{q}_{i}-q_{i}(t+t'))|\psi(t+t') > \\ &= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t')|(\hat{q}_{i}-q_{i}(t')\exp(\frac{i}{\hbar} \hat{H}t)(\hat{q}_{i}-q_{i}(t+t'))|\psi(t+t') > \\ &= C_{i}^{cl}(t) + \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t')|(\hat{q}_{i}-q_{i}(t')\exp(\frac{i}{\hbar} \hat{H}t)(\hat{q}_{i}-q_{i}(t+t'))|\psi(t+t') > \\ &= C_{i}^{cl}(t) + \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt' < \psi(t')|(\hat{q}_{i}-q_{i}(t'))|\psi(t+t') > \\ &= \sum_{i} (\frac{i}{\hbar} \hat{H}t)(\hat{q}_{i}-q_{i}(t+t'))|\psi(t+t') > \end{split}$$

: made jectory 's and = 0,||, and ·e 10% 1 gives nant of

opera-

itioned

(24)

andom

(25)

(26)

size of egime. ie conterms. to start

(27)

wave-

calcurmula,

(28)

mode

We see that the quantum autocorrelation function is a sum of the classical autocorrelation function and a correction term which accounts for quantum interference effects (such as those which give rise to the zero-point energy). Unfortunately, since the time propagator operates on the linear term of the coordinate times the wavefunction, the resolution of the correction term is even beyond Gaussian wavefunction dynamics, and either Hamiltonian matrix diagonalization, Feynman path integration, or the numerical integration of the time dependent Schrödinger equation must be resorted to.

4. Conclusion

Heller's thawed Gaussian wavefunction seems to be able to help avoid the mode ZPE for classical trajectories. Its mode energy can be calculated analytically, as shown in Section 3, and is shown to be a sum of the classical mode energy plus a quantum correction term. Even though the classical mode energy often goes below the mode ZPE, the quantum correction term helps maintain the mode energy to be above the mode ZPE throughout the integration of the wavefunction.

Computationally, the Gaussian wavefunction provides a straightforward extension of integrating the classical equations of motion, i.e., all that is involved in principle is the solution of additional equations of motion to the classical ones. Since the method is based on integrating ordinary differential equations, upon which classical simulations are based, the computational effort of the Gaussian wavepacket need not necessarily be taxing if appropriate algorithms are used. The method formally scales as n^2 , which may prevent its use for very large systems; however, simulations of intermediate-sized systems should be attainable.

Our understanding of the GTS paper is that it is both unnecessary and incorrect to abandon or modify individual trajectories, since the ZPE-violating trajectories are part of the statistics, without which the statistics would be skewed, biased, and untrue. In the results shown in the GTS paper, the unrestricted classical ensemble calculations match the quantum results far better than the other techniques that attempted to correct the ZPE by removing ZPE-violating trajectories (see Fig. 2 and Fig.5 of Ref. 1). The very presence of the ZPE violating trajectories is ostensibly responsible for this behavior. Generally speaking, a swarm of classical trajectories behaves differently from individual ones. In this regard it would seem that quasiclassical trajectory studies of reaction dynamics ought to be based on the statistical properties of a swarm of trajectories, and not solely the individual dissociating or isomerizing trajectories which are part of the statistics contributing to the overall probability distribution. Dissociating or isomerizing trajectories may correspond to a small probability amplitude of the quantum wavefunction in the relevant coordinate (or momentum) space regions. For classical trajectory studies such trajectories should not be abandoned or modified.

The fundamental cause of the classical ZPE difficulty is that the ZPE is a quantum concept with no classical counterpart. It is a consequence of our inability to simultaneously determine the position and momentum of a particle to an arbitrary precision as we may do in classical mechanics (at least in principle). Rather than a fixed point in phase space, when we try to minimize both the position and momentum at the same time, the closest we can get

On the

is a ground s There is a fin low from the and energy. 7 is unlikely. V ZPE difficult There are ets extend to 1 nate space, th scales rather reasons why effects are im does not corr pectation valu which intefer is of quantum Schrödinger (single trajecto scribe the ent: (and higher o position-mor. and $\langle x^2 \rangle$ a part. This h already conta time depende: superposition Gaussian as a wavefunction. weighted sur to consistently tained in a sin

Acknowledg

RQT is gr suggestions.

Reference

[1] J. S. Hu R. E. W *ibid*.

[2] G. H. Pe (1996); I

is a ground state wavefunction with a finite position or momentum probability amplitude. There is a finite uncertainty in both the position and momentum, as if the motion, however low from the classical point of view, persists; thus, we have the so-called zero point motion and energy. To help "fix" such an issue from within the classical realm in a consistent way is unlikely. We believe that some quantum ingredients are needed to address the classical ZPE difficulty.

There are three final points worth emphasizing. One is that thawed Gaussian wavepackets extend to multiple dimensions in a straightforward way, as shown in section 2 (in coordinate space, they are simply multi-coordinate wavefunctions), and the computational effort scales rather modestly with the size of the system. There appears to be no fundamental reasons why they cannot be computationally applied to polyatomic molecules where ZPE effects are important. The second point is that a single time-evolving Gaussian wavepacket does not correspond to a single classical trajectory, even though its position-momenta expectation values trace out that trajectory. Rather, it corresponds to a swarm of trajectories which intefere with one another in the Feynman path-integral sense. The wavepacket itself is of quantum-mechanical nature, as it is an approximate solution to the time dependent Schrödinger equation. The wavefunction is much richer in information content than any single trajectory, requiring more than the position-momentum expectation values to describe the entire statistics. For example, other expectation values, like $\langle p^2 \rangle$ and $\langle x^2 \rangle$ (and higher order "moments") cannot be generated by the single trajectory that carries the position-momentum expectation values; as we saw in Section 3, it is the $\langle p^2 \rangle$ vs. $\langle p \rangle^2$ and $\langle x^2 \rangle$ vs. $\langle x \rangle^2$ difference that helps maintain the mode energy of which ZPE is a part. This helps bring out the last point we want to emphasize: a single thawed Gaussian already contains interference effects by its wave nature (as an approximate solution to the time dependent Schrödinger equation). More explicitly, a Gaussian can be expressed as a superposition of other waves. A well-known example is to express the coordinate space Gaussian as a weighted sum of plane waves, where the "weight" is the momentum space wavefunction. In the present context, a single Gaussian itself can be approximated by a weighted sum of other Gaussians. This illustrates that the interference effects necessary to consistently describe the pheonomenon of zero-point energy avoidance are indeed contained in a single, time-evolving Gaussian wavefunction.

Acknowledgments

RQT is grateful to Edward Kelsey (Monmouth University) for helpful comments and suggestions.

References

- J. S. Hutchinson, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Marcel Dekker, New York, 1996); H. R. Mayne, *ibid.*
- [2] G. H. Peslherbe and W. L. Hase, J. Chem. Phys. 104, 9445 (1996); ibid., 105, 7432 (1996); D. A. McCormack and K. F. Lim, J. Chem. Phys. 106, 572 (1997); A.J. Marks,

orrelas (such agator of the tonian e time

PE for tion 3, . Even rection gration

ion of the sobased based, ; if apent its uld be

rect to part of the reich the PE by ' presnerally In this it to be ividual to the ond to ate (or not be

eously nay do , when can get

J. Chem. Phys. 108, 1438 (1998); U. Mller and G. Stock, J. Chem. Phys. 111, 77 (1999); E. Martinez-Núñez, A. Pea-Gallego, and S. A. Vázquez, J. Chem. Phys. 114, 3546 (2001); E. Martinez-Núñez, J. M. C. Marques, and S. A. Vázquez, J. Chem. Phys. 115, 7872 (2001); H. F. Busnengo, C. Crespos, W. Dong, J. C. Rayez, and A. Salin, J. Chem. Phys. 116, 9005 (2002); P. Fleurat-Lessard, S. Y. Grebenshchikov, R. Schinke, C. Janssen, and D. Krankowsky, J. Chem. Phys. 119, 4700 (2003); R. Schinke and P. Fleurat-Lessard, J. Chem. Phys. 122, 94317 (2005); M. V. Ivanov, H. Zhu, and R. Schinke, J. Chem. Phys. 126, 54304 (2007); J.Espinosa-Garcia, J. Phys. Chem. A 111, 9654 (2007).

- [3] R. L. Liboff, Phys. Today, 37, 26 (1984).
- [4] Y. Guo, D. L. Thompson, and T. D. Sewell, J. Chem. Phys. 104, 576 (1996).
- [5] G. Nyman and J. Davidsson, J. Chem. Phys. 92, 2415 (1990); A. J. C. Varandas and J. M. C. Marques, J. Chem. Phys. 97, 4050 (1992); A. J. C. Varandas, J. Chem. Phys. 99, 1076 (1993); J. M. C. Marques, W. Wang, and A. J. C. Varandas, J. Chem. Soc. Faraday Trans. 90, 2189 (1994); A. J. C. Varandas, Chem. Phys. Lett. 225, 18 (1994); J. M. Bowman, B. Gazdy, and Q. Sun, J. Chem. Phys. 91, 2859 (1989); W. H. Miller, W. L. Hase, and C. L. Darling, J. Chem. Phys. 91, 2863 (1989); G. H. Peslherbe and W. L. Hase, J. Chem. Phys. 100, 1179 (1994); F. E. Budenholzer, M. Y. Chang, and K. C. Huang, J. Phys. Chem. 98, 12501 (1994); A. J. C. Varandas and J. M. C. Marques, J. Chem. Phys. 100, 1908 (1994); M. Ben-Nun and R. D. Levine, J. Chem. Phys 101, 8768 (1994); K. F. Lim and D. A. McCormack, J. Chem. Phys. 102, 1705 (1995); T. D. Sewell and D. L. Thompson, J. D. Gezelter, and W. H. Miller, Chem. Phys. Lett. 193, 512 (1992).

[6] E. J. Heller, J. Chem. Phys. 62, 1544 (1975).

[7] R. Alimi, A. Garcia-Vela, and R. B. Gerber, J. Chem. Phys. 96, 2034 (1992).

[8] M. Hénon and C. Heiles, Astron. J. 69, 73 (1964).

In: Handbe Editors: C.

Chapter 1

FC

The man ideas ferer theoi set to critic matr hype mecl ferer of oi than poin

1. Int

The st of stratosp of this protem, when it is clear tion and tl quantity o explored. simple pho