Forward−Backward Semiclassical Dynamics without Prefactors

Jiushu Shao

School of Chemical Sciences, University of Illinois, 601 South Goodwin Avenue, Urbana, Illinois 61801

Nancy Makri*

School of Chemical Sciences, University of Illinois, 601 South Goodwin Avenue, Urbana, Illinois 61801, and Theoretical & Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens, Greece 11635

Received: April 30, 1999; In Final Form: June 30, 1999

Using a forward−backward representation of all degrees of freedom in a system, we present a rigorous formulation of semiclassical correlation functions or expectation values where the contribution of the prefactor is compensated for by the semiclassical phase. This procedure eliminates the need for computing the semiclassical prefactor whose determination amounts to evaluating the full stability matrix, resulting in a scheme that scales linearly with the number of degrees of freedom. Numerical calculations show that, while some interference is lost, the scheme is capable of capturing most features important to the vibrational dynamics and spectroscopy of multidimensional systems.

As efforts to tackle the many-body quantum dynamics problem continue, significant attention has been given to semiclassical methods. Time-dependent semiclassical theory[1,2] offers an approximate, yet rigorous alternative to full quantum mechanics. Despite its restriction to trajectories that satisfy Newton's classical equations, the semiclassical propagator has been shown to capture all aspects of quantum dynamical effects semiquantitatively[3,4] (with the possible exception of tunneling[5]) and its accuracy is deemed adequate for application to atomic or molecular systems, even when the underlying classical motion is chaotic.[6,7] The focus of these efforts during the 1990s has been on the further development and the use of convenient representations that avoid the root search problem[3,8,9] as well as techniques for dealing with the sign problem that originates from the rapidly oscillatory semiclassical phase.[10−13] A major step toward a rigorous solution of the latter is the development of forward−backward semiclassical dynamics (FBSD).[14−18] The main idea is to combine the forward and reverse time evolution operators entering ensemble averaged correlation functions into a single propagator which is then evaluated semiclassically. After reaching the desired propagation time, each sampled trajectory continues in the negative time direction. The backward propagation step results in extensive cancellation and the corresponding action is generally small, leading to a smooth integrand that is amenable to Monte Carlo procedures.

Given the dramatic success of FBSD in reducing the severity of the phase cancellation, rigorous semiclassical simulations of truly large systems appear to be hindered mainly by the need to evaluate the prefactor, various forms of which enter all representations of the semiclassical propagator. The prefactor involves elements of the stability matrix, whose evaluation for a system of n degrees of freedom requires the solution of $(2n)^2$ differential equations. As a consequence, the required numerical effort grows rapidly and systems of several tens of atoms appear to remain out of reach. Miller and co-workers have shown[12,13] that by linearizing the actions that appear in the semiclassical representation of correlation functions in the difference of the endpoints of the forward and backward trajectories one arrives at the conventional quasiclassical dynamics method[19,20] where initial conditions are sampled from the Wigner−Weyl transform[21,22] of the initial density. That prescription is appealing because of its simplicity and practical because it does not require the evaluation of a prefactor. The cost of the simplification is the partial loss of interference.[23]

The present Letter presents a rigorous FBSD expression in which the prefactor can be compensated for by the semiclassical phase. The elimination of the prefactor in the present formulation arises naturally from a stationary phase treatment of all integration variables, which results in trajectories whose forward and backward parts differ by an infinitesimal amount. Because of this last feature, the present formulation is similar in spirit to the linearization approximation,[12,13,19,20] although its mathematical form is not related to the latter in any obvious way and it does not involve any other approximations besides the stationary phase method. While rigorous and consistent in its treatment of all degrees of freedom, this formulation also neglects interference between distinct forward and backward trajectories. As in the linearization approximation, the limitations of this scheme need to be examined carefully, and numerical calculations are employed to evaluate the accuracy of the procedure.

Throughout this Letter we focus on correlation functions of the type

$$C(t) = \mathrm{Tr}(\rho(0)Ae^{iHt/\hbar}Be^{-iHt/\hbar}) \tag{1}$$

where $\rho(0)$ is the density operator of the initial ensemble, and A and B are general operators. To keep the presentation simple we use one-dimensional notation, noting that the multidimensional generalization of the theory presented below is straightforward. Miller and co-workers have employed the Weyl

* Author to whom correspondence should be addressed at School of Chemical Sciences, University of Illinois, 601 South Goodwin Avenue, Urbana, IL 61801.

10.1021/jp991433v CCC: $18.00 © 1999 American Chemical Society
Published on Web 09/11/1999

transformation to convert operators to an exponential form.[16,18] Instead, we use here a derivative identity to arrive at an exponential representation. The correlation function is thus written as

$$C(t) = -i\frac{\partial}{\partial\mu}\mathrm{Tr}(\rho(0)Ae^{iHt/\hbar}e^{i\mu B}e^{-iHt/\hbar})|_{\mu=0} \tag{2}$$

The product of three exponential operators in this expression can be interpreted as propagation with the following time-dependent Hamiltonian:[16,18]

$$\tilde{H}(t') \equiv H - \hbar\mu B\delta(t' - t) \tag{3}$$

The classical dynamics generated by this effective Hamiltonian are described by Hamilton's equations,

$$\begin{aligned}\dot{x}(t') &= \frac{\partial\tilde{H}}{\partial p} = \frac{\partial H}{\partial p} - \hbar\mu\frac{\partial B}{\partial p}\delta(t - t'),\\ \dot{p}(t') &= -\frac{\partial\tilde{H}}{\partial x} = -\frac{\partial H}{\partial x} + \hbar\mu\frac{\partial B}{\partial x}\delta(t - t')\end{aligned} \tag{4}$$

According to these, the position and momentum of a trajectory jump at time t by the amounts

$$\delta x = -\hbar\mu\frac{\partial B}{\partial p}, \quad \delta p = -\hbar\mu\frac{\partial B}{\partial x} \tag{5}$$

The action generated by the Hamiltonian of eq 3 also increments discontinuously at the time t by the amount

$$\delta S = \hbar\mu B(t) \tag{6}$$

Application of the semiclassical approximation to the effective Hamiltonian in the coherent state representation brings eq 2 to the form

$$\begin{aligned}C(t) = -i(2\pi\hbar)^{-1}\frac{\partial}{\partial\mu}\int dx_0\int dp_0\, D(x_0,p_0)\exp\left(\frac{i}{\hbar}S(x_0,p_0)\right)\\ \times\langle g(x_0,p_0)|\rho(0)A|g(x_f,p_f)\rangle|_{\mu=0}\end{aligned} \tag{7}$$

Here $|g\rangle$ are coherent states described by the wave functions

$$\langle r|g(r_0,p_0)\rangle = \left(\frac{2\gamma}{\pi}\right)^{1/4}\exp\left(-\gamma(x - x_0)^2 + \frac{i}{\hbar}p_0(x - x_0)\right), \tag{8}$$

S is the action in combined forward and backward time which includes the discontinuous increment of eq 6, and D is the forward−backward Herman−Kluk prefactor which is given by the expression

$$D(x_0,p_0) = 2^{-1/2}\sqrt{\frac{\partial x_f}{\partial x_0} + \frac{\partial p_f}{\partial p_0} - 2i\hbar\gamma\frac{\partial x_f}{\partial p_0} - \frac{1}{2i\hbar\gamma}\frac{\partial p_f}{\partial x_0}} \tag{9}$$

Equation 7 is to be evaluated via the finite difference method. Note that since no momentum jump occurs for $\mu = 0$, the classical trajectories remain continuous at all times in this case, implying $x_f = x_0$, $p_f = p_0$, and $S = 0$. As a consequence, evaluation of the derivative requires a single trajectory propagation at a small value of μ:

$$\begin{aligned}C(t) \approx -\frac{i}{\mu}(2\pi\hbar)^{-1}\int dx_0\int dp_0\Big[D(x_0,p_0)\exp\left(\frac{i}{\hbar}S(x_0,p_0)\right)\\ \times\langle g(x_0,p_0)|\rho(0)A|g(x_f,p_f)\rangle - \langle g(x_0,p_0)|\rho(0)A|g(x_0,p_0)\rangle\Big]\end{aligned} \tag{10}$$

For simplicity of presentation we assume below that the operator B depends only on the position of the probed degree of freedom; in this case only the momentum jumps at time t, while the position of the trajectory remains continuous.

All three factors in the integrand of eq 7 depend on the parameter μ. In the prefactor and coherent state matrix element this dependence enters through the endpoints of the trajectory, which are determined by the momentum increment at the time t. The action, however, depends on μ both through its dependence on the backward trajectory and through the increment given by eq 6. The momentum jump and the action increment are uniquely determined from the Hamiltonian dynamics generated by eq 3. Below, however, we allow them to vary independently, attempting to compensate for the contribution of the prefactor by the other terms.

To this end, we partition the correlation function into a part $c_1(t)$ involving the derivative of the prefactor and a part $c_2(t)$ comprising both other terms:

$$C_1(t) \equiv -i(2\pi\hbar)^{-1}\int dx_0\int dp_0\frac{\partial D}{\partial\mu}\bigg|_{\mu=0}\langle g(x_0,p_0)|\rho_0 A|g(x_0,p_0)\rangle \tag{11a}$$

$$C_2(t) \equiv C(t) - C_1(t) \tag{11b}$$

Since the momentum jump is proportional to the finite difference parameter μ, which is infinitesimal, we proceed to linearize the trajectories as well as the action in δp. The details will be presented in another publication.[24] The result is of the form

$$\begin{aligned}C_1(t) &= \int dx_0\int dp_0 f(x_0,p_0)\frac{\partial p(t)}{\partial\mu},\\ C_2(t) &= -2\int dx_0\int dp_0 f(x_0,p_0)\frac{\partial p(t)}{\partial\mu} + \lambda(t)\end{aligned} \tag{12}$$

where $\partial p(t)/\partial\mu$ is the change of the momentum jump with respect to the parameter μ and the term $\lambda(t)$ arises from the action increment, eq 6. Noting that the ratio of the slopes of these functions is independent of the system, it is clear that one can scale the momentum jump to eliminate the contribution from $C_1(t)$. Since the ratio of the slopes is equal to 2, it follows that $\partial p_{\mathrm{opt}}(t)/\partial\mu = 1/2\hbar B'(t)$ and thus the optimal value of the momentum jump for which the correlation function is given entirely by the second component is

$$\delta p_{\mathrm{opt}} = \frac{1}{2}\hbar\mu B'(t) \tag{13}$$

To summarize, the correlation function is given by the expression

$$\begin{aligned}C(t) = -i(2\pi\hbar)^{-1}\frac{\partial}{\partial\mu}\int dx_0\int dp_0\exp\left(\frac{i}{\hbar}S(x_0,p_0)\right)\\ \times\langle g(x_0,p_0)|\rho(0)A|g(x_f,p_f)\rangle|_{\mu=0}\end{aligned} \tag{14}$$

The trajectories follow the classical equations of motion with the Hamiltonian H up to the time t, at which point the momentum component jumps by the value given in eq 13 for a small value of the finite difference parameter μ. At the same time the action increments by the full amount given by eq 6. Subsequent evolution takes place in the negative time direction and the integrand is evaluated when the time parameter reaches zero once again.

As the momentum jumps in this formulation are infinitesimal, the net forward−backward action is small; in addition, the proximity of the final trajectory values to the initial conditions implies smoothness of the coherent state matrix element. For these reasons Monte Carlo evaluation of the phase space integral

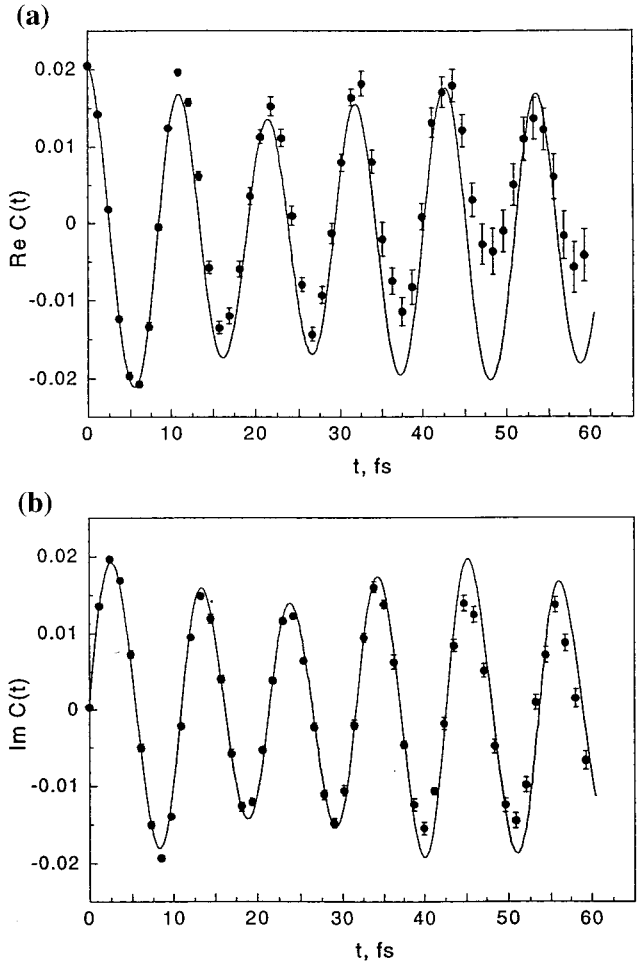

Figure 1. Position correlation function for the three-dimensional model of energy transfer in benzene. Solid line: exact results obtained via the split propagator method. Markers: FBSD without prefactor with 20 000 trajectories for each integration variable. (a) Real part. (b) Imaginary part.

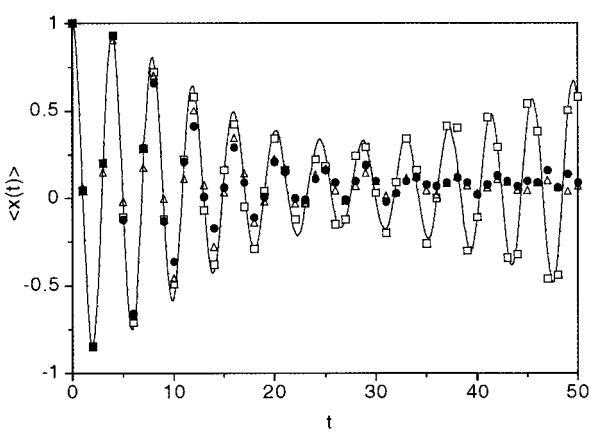

Figure 2. Average position for a one-dimensional quartic oscillator. Solid line: exact results obtained via the split propagator method. Solid circles: FBSD without prefactor. Hollow squares: fully semiclassical propagation. Hollow triangles: linearized (Wigner) approximation.

of eq 14 is well behaved numerically. More importantly from the point of view of the present work, the absence of a prefactor from eq 14 leads to practically linear scaling of the method with the number of degrees of freedom.

It should be noted, however, that the prefactor-free expression obtained in this Letter is not equivalent to the semiclassical expression obtained recently in other works.[16,17] These expressions break up the semiclassical propagation into separate forward and backward components in the space of the system; for example, the result of ref 17 reverts when applied to a one-dimensional system to the full semiclassical expression that employs a double-phase space average,

$$C(t) = (2\pi\hbar)^{-2}\int dx_F \int dp_F \int dx_B \int dp_B\, D_F(x_F,p_F) \times D_B(x_B,p_B)\exp\left(\frac{i}{\hbar}S(x_F,p_F,x_B,p_B)\right) \times \langle g(x_F,p_F)|\rho(0)A|g(x'_B,p'_B)\rangle\langle g(x_B,p_B)|B|g(x'_F,p'_F)\rangle \quad (15)$$

where x'_F,p'_F and x'_{BB},p'_B are the endpoints of *separate* forward and backward trajectories, respectively. By integrating explicitly over the initial condition of the backward trajectory, eq 15 accounts for the interference between distinct classical trajectories of the forward and reverse time propagators. At the same time, evaluation of eq 15 is considerably more demanding, primarily due to the need for integration of the stability matrix.

Equation 14 is still exact for harmonic potentials. This is a consequence of the lack of multiple bounce solutions for linear systems. The neglect of forward−backward interference may result in large error if eq 14 is applied to highly anharmonic Hamiltonians. Sun et al.[23] have found that the linearization approximation of Miller and co-workers, which also neglects similar interference terms, captures the short time, transition-state-like features of thermal rate constants correctly but fails to describe nonclassical aspects of the recrossing dynamics resulting from quantum interference on the time scale of two or more vibrational periods. We expect eq 14 as well to yield reasonably accurate results for correlation functions in multidimensional potentials where relaxation and dissipative effects tend to weaken interference phenomena.

To test the ability of eq 14 to describe the intermediate-time behavior of observables or correlation functions we apply it to three model problems. The first model is motivated from the vibrational spectroscopy and local mode dynamics of benzene. We choose a three-dimensional model of the form

$$V(x_1,x_2,x_3) = D(1 - e^{-ax_1})^2 + \frac{1}{2}m_0\omega_0^2 e^{-cx_1}x_2^2 + \frac{1}{2}m_0\omega_0^2 e^{-2cx_1}x_3^2 \quad (16)$$

where x_1 represents the coordinate of a CH stretch and x_2 the CCH in-plane wag,[25,26] while x_3 is a fictitious mode degenerate with x_2 but coupled to x_1 twice as strongly which is added to provide a challenge to the calculation. Rather than studying the energy flow out of an excited local mode, we calculate here the position correlation function of x_1. The results of the present FBSD scheme, eq 14, with 20 000 Monte Carlo samples per integration variable are shown in Figure 1 and compared to those of a converged fully quantum mechanical calculation using the split operator method.[27] The agreement is quite satisfactory for both the real and the imaginary parts over several oscillation periods.

The next two cases involve the average position of a strongly anharmonic oscillator,

$$H_0 = \frac{1}{2}p^2 + \frac{1}{2}\omega_0^2 x^2 - ax^3 + bx^4 \quad (17)$$

with $\omega_0 = \sqrt{2}$ and $a = b = 0.1$. Figure 2 shows the position expectation value $\langle x(t)\rangle$ with respect to an initially shifted ground

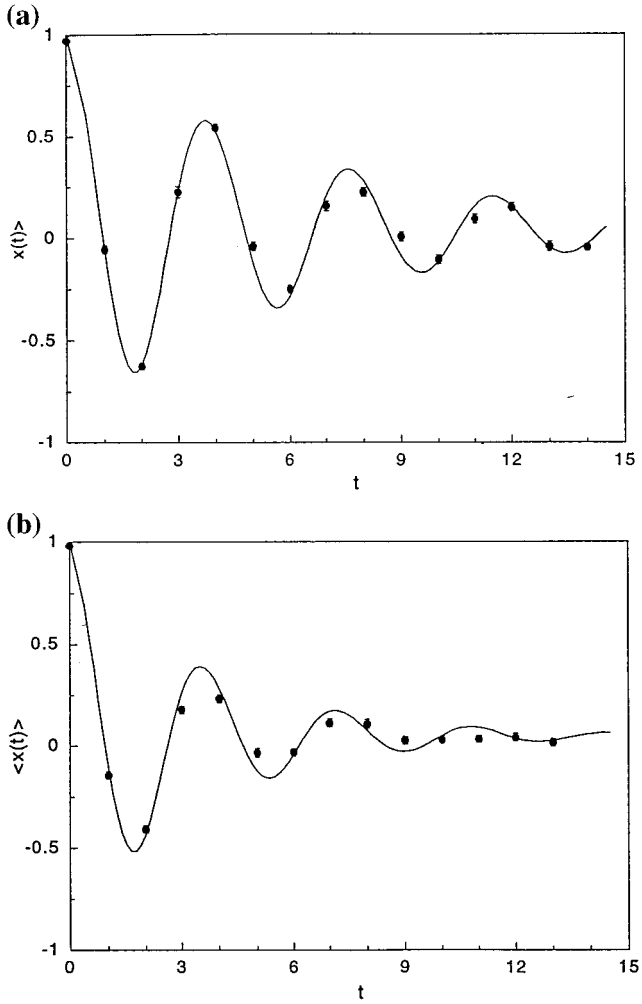

Figure 3. Average position for a quartic oscillator coupled to a bath of 30 harmonic degrees of freedom at zero temperature. The Kondo parameter is (a) $\xi = 0.25$ and (b) $\xi = 0.50$. Markers: FBSD results with 10 000 trajectories for each integration variable. Solid line: exact results obtained via iterative evaluation of the path integral.

state (centered about $x_0 = 1$) as obtained according to eq 14 and compares to exact quantum mechanical results[27] and also to the results of the full semiclassical expression[17] (which in this one-dimensional case is equivalent to eq 15) and those of the Wigner-type linearized approximation.[12,13,19,20] It is seen that the single forward−backward trajectory treatment of eq 14 captures the dynamics semiquantitatively over several vibrational periods, although its accuracy degrades with each successive bounce and leads to faster dephasing compared to the quantum mechanical result. The Wigner expression displays very similar behavior. By contrast, the full semiclassical result leads to a faithful representation of the dynamics over much longer times but at a much higher computational cost.

As a final test, we examine the average position of the same system in the presence of a 30-dimensional harmonic bath,

$$H = H_0 + \sum_{k=1}^{30}\left\{\frac{1}{2}P_k^2 + \frac{1}{2}\omega_k^2\left(Q_k - \frac{c_k x}{\omega_k^2}\right)^2\right\} \qquad (18)$$

whose frequencies and coupling constants are distributed according to an Ohmic spectral density.[28] Although the 30 degrees of freedom of eq 18 cannot provide true dissipation, the observed behavior closely resembles dissipative dynamics over many periods of motion. As seen in Figure 3, the agreement between the results of eq 14 and the exact quantum mechanical evolution obtained via iterative evaluation of the path integral[29] is now nearly quantitative at all times for which the particular bath discretization employed here provides a valid representation of the dissipative dynamics.

In conclusion, the present FBSD scheme represents a rigorous semiclassical treatment of all degrees of freedom in combined forward and backward time where the contribution of the prefactor is compensated for by the semiclassical phase, eliminating the need for evaluation of the stability matrix. As the forward−backward treatment is equivalent to a stationary phase evaluation of the midpoint integral in the full semiclassical expression where each time evolution operator separately is approximated by the Van Vleck expression, some interference features are lost in the present formulation. Yet, the numerical examples presented show that the method is capable of capturing semiquantitatively most aspects of the evolution that are relevant to the vibrational dynamics and spectroscopy of polyatomic systems.

Acknowledgment. This work has been supported by the David and Lucile Packard Foundation through a Packard Fellowship for Science and Engineering. N.M. thanks the Director and the Faculty of the Theoretical and Physical Chemistry Institute for their hospitality during her sabbatical stay.

References and Notes

(1) Van Vleck, J. H. *Proc. Nat. Acad. U. S. Sci.* **1928**, *14*, 178.
(2) Morette, C. *Phys. Rev.* **1952**, *81*, 848.
(3) Miller, W. H. *J. Chem. Phys.* **1970**, *53*, 3578−3587.
(4) Miller, W. H. *Adv. Chem. Phys.* **1974**, *25*, 69.
(5) Kay, K. *J. Chem. Phys.* **1997**, *107*, 2313−2328.
(6) Tomsovic, S.; Heller, E. J. *Phys. Rev. Lett.* **1991**, *67*, 664−667.
(7) Sepulveda, M. A.; Tomsovic, S.; Heller, E. J. *Phys. Rev. Lett.* **1992**, *69*, 402−405.
(8) Herman, M. F.; Kluk, E. *Chem. Phys.* **1984**, *91*, 27−34.
(9) Heller, E. J. *J. Chem. Phys.* **1991**, *94*, 2723.
(10) Walton, A. R.; Manolopoulos, D. E. *Mol. Phys.* **1996**, *84*, 961.
(11) Brewer, M. L.; Hulme, J. S.; Manolopoulos, D. E. *J. Chem. Phys.* **1997**, *106*, 4832−4839.
(12) Wang, H.; Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 9726−9736.
(13) Sun, X.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 7064−7074.
(14) Makri, N.; Thompson, K. *Chem. Phys. Lett.* **1998**, *291*, 101−109.
(15) Thompson, K.; Makri, N. *J. Chem. Phys.* **1999**, *110*, 1343−1353.
(16) Miller, W. H. *Faraday Discuss.* **1998**, *110*, 1−21.
(17) Thompson, K.; Makri, N. *Phys. Rev. E* **1999**, *59*, R4729−R4732.
(18) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 6635−6644.
(19) Heller, E. J. *J. Chem. Phys.* **1976**, *65*, 1289.
(20) Brown, R. C.; Heller, E. J. *J. Chem. Phys.* **1981**, *75*, 186.
(21) Weyl, H. *Z. Phys.* **1927**, *46*, 1.
(22) Wigner, E. J. *Chem. Phys.* **1937**, *5*, 720.
(23) Sun, X.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 4190−4200.
(24) Shao, J.; Makri, N. *J. Phys. Chem.* **1999**, in press.
(25) Sibert, E. L.; Reinhardt, W. P.; Hynes, J. T. *J. Chem. Phys.* **1984**, *81*, 1115.
(26) Makri, N. *Chem. Phys. Lett.* **1989**, *159*, 489−498.
(27) Feit, M. D.; Fleck, J. A. *J. Comput. Phys.* **1982**, *47*, 412.
(28) Caldeira, A. O.; Leggett, A. J. *Physica A* **1983**, *121*, 587−616.
(29) Makri, N.; Makarov, D. E. *J. Chem. Phys.* **1995**, *102*, 4611−4618.