Some New Classical and Semiclassical Models for Describing Tunneling Processes with Real-Valued Classical Trajectories†

Jianhua Xing, Eduardo A. Coronado, and William H. Miller*

Department of Chemistry and Kenneth S. Pitzer Center for Theoretical Chemistry, University of California at Berkeley, and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

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A model for describing barrier tunneling (or other classically forbidden processes) using purely real-valued classical trajectories is presented. The basic idea is to introduce an auxiliary degree of freedom that allows for fluctuations in the potential-energy surface for the original classical degrees of freedom. The model can be applied purely classically or better semiclassically (e.g., via the initial value representation). Numerical results for 1D barrier tunneling are presented to illustrate the model.

I. Introduction

It has been well-appreciated for a long time that the correct semiclassical description of tunneling (or, more generally, "classically forbidden") processes requires classical trajectories that explore complex-valued regions of phase space.[1−6] For example, in the 1-*d* WKB approximation for barrier tunneling, the momentum of the particle is imaginary when it is inside the barrier. Recent work by Kay[7] and Heller and co-workers[8,9] reemphasizes this fact. For practical reasons, however, for example, if one wishes to use classical molecular dynamics to treat systems with many degrees of freedom, one would like to have at least an approximate way of describing tunneling-like phenomena that utilizes only real-valued classical trajectories, within either a fully classical or a semiclassical approach. Several examples of such approaches exist; for example, a model used by Miller and co-workers[10,11] (which is patterned after Tully and Preston's surface-hopping models for treating electronically nonadiabatic processes[12]) is a fairly primitive way of describing tunneling processes with only real-valued trajectories, but it has found some utility.[13−19] Within the semiclassical (SC) initial value representation (IVR), it has also been shown that purely real-valued classical trajectories can describe tunneling processes to a very useful extent.[20−22] (The very reason the IVR was first introduced,[23] in fact, was to be able to describe classically forbidden vibrationally inelastic scattering with real-valued trajectories.)

The purpose of this paper is to present another family of models for describing tunneling (or any classically forbidden) processes with real-valued classical trajectories; it can be implemented at a fully classical level, as described in section II, or much more accurately using the SC−IVR version of semiclassical theory, as described in section III. Some numerical tests are presented and discussed in section IV.

II. The Model

We illustrate the model by application in this paper to one-dimensional barrier transmission, but one can easily imagine how models of this type could be applied more generally. The Hamiltonian of the system we consider is thus of the form

$$\hat{H} = \hat{P}^2/(2M) + V(\hat{R}) \tag{2.1}$$

where $V(R)$ is a potential barrier in one-dimension, $-\infty < R < \infty$.

The model we propose was motivated by the McCurdy−Meyer−Miller model[24−31] for describing the electronic degrees of freedom (in electronically nonadiabatic processes) by auxiliary classical variables, but it can be stated more generally and independently of that work. Specifically, we introduce an auxiliary degree of freedom, a harmonic oscillator of unit frequency and mass, with coordinate and momentum operators $\hat{x}$ and $\hat{p}$; if the oscillator is in quantum state n, then because

$$\frac{1}{2}(\hat{p}^2 + \hat{x}^2)|\phi_n\rangle = \left(n + \frac{1}{2}\right)|\phi_n\rangle \tag{2.2}$$

where we use units such that $\hbar = 1$ and $|\phi_n\rangle$ is the usual eigenstate of the harmonic oscillator, one has the identity

$$\frac{1}{2}(\hat{p}^2 + \hat{x}^2 + 1 - 2n)|\phi_n\rangle = |\phi_n\rangle \tag{2.3}$$

The Hamiltonian $\hat{H}(\hat{P}, \hat{R}, \hat{p}, \hat{x})$ in the expanded, 2D space is now defined by

$$\hat{H}(\hat{P}, \hat{R}, \hat{p}, \hat{x}) = \hat{P}^2/(2M) + \alpha V(\hat{R}) + (1 - \alpha)\frac{1}{2}(\hat{p}^2 + \hat{x}^2 + 1 - 2n)V(\hat{R}) \tag{2.4}$$

where α is an arbitrary parameter which in principle can take any value. We think of eq 2.4 as the Hamiltonian for a multichannel scattering problem, with R being the scattering (or translational) coordinate and x the coordinate for the bound degree of freedom. It is clear that an exact wave function for eq 2.4 is

$$\Psi(R, x) = \phi_n(x)\psi(R) \tag{2.5}$$

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* To whom correspondence should be addressed.

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and with this choice the quantum mechanics resulting from the Hamiltonian 2.4 is identical to that of the original 1D Hamiltonian 2.1, because

$$\frac{1}{2}(\hat{p}^2 + \hat{x}^2 + 1 - 2n)V(\hat{R})|\phi_n\rangle|\psi\rangle = V(\hat{R})|\phi_n\rangle|\psi\rangle \quad (2.6)$$

Another way to look at eq 2.4 is to rewrite it in the following way:

$$\hat{H}(\hat{P}, \hat{R}, \hat{p}, \hat{x}) = \hat{P}^2/(2M) + V(\hat{R}) + \left[\frac{1}{2}(1-\alpha)(\hat{p}^2 + \hat{x}^2 + 1 - 2n) + (\alpha - 1)\right]V(\hat{R}) \quad (2.7)$$

the last term in the above expression is zero when operating on the wave function defined by eq 2.5 and, therefore, may be thought of as a pseudo "quantum" potential.

The classical (or semiclassical) model is now obtained by treating the 2D system classically; i.e., Hamiltonian 2.4 is taken to be a classical Hamiltonian. For definiteness (and also simplicity of application, below), we choose the state n of the auxiliary degree of freedom to be its ground state, $n = 0$, so that the classical Hamiltonian of the 2D system becomes

$$H(P, R, p, x) = P^2/(2M) + \frac{1}{2}[(1-\alpha)(p^2 + x^2) + 1 + \alpha]V(R) \quad (2.8)$$

To see the effect of the auxiliary degree of freedom at the classical level, we compute the transmission probability using the "classical Wigner" model, i.e., a classical trajectory calculation with initial conditions chosen from the appropriate Wigner distribution function. The Wigner distribution for the ground state of the oscillator degree of freedom is

$$\rho_w(x_0, p_0) = e^{-2\epsilon_0}/\pi \quad (2.9)$$

where $\epsilon_0 = {}^1/_2(p_0{}^2 + x_0{}^2)$ and the translational degree of freedom is taken to be a pure momentum state. Because ${}^1/_2(p^2 + x^2)$ is a constant of the motion (classically as well as quantum mechanically), a classical particle will be transmitted via the Hamiltonian 2.8 if and only if the initial translational energy E is greater than $[(1 - \alpha)\epsilon_0 + {}^1/_2(1 + \alpha)]V_b$, where V_b is the barrier height of $V(R)$, i.e., the auxiliary degree of freedom causes fluctuations in the barrier height. Averaging over the Wigner distribution of the auxiliary degree of freedom thus gives the transmission probability as

$$P(E) = \int_0^\infty d\epsilon_0\, 2e^{-2\epsilon_0} h\left\{E - \left[(1-\alpha)\epsilon_0 + \frac{1}{2}(1+\alpha)\right]V_b\right\} \quad (2.10)$$

where $h\{\}$ is the Heaviside function

$$h\{\xi\} = \begin{cases} 1 & \text{if } \xi > 0 \\ 0 & \text{if } \xi < 0 \end{cases}$$

and we have used the fact that

$$\int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dp_0\{\ \} = 2\pi\int_0^\infty d\epsilon_0\{\ \} \quad (2.11)$$

evaluating the integral over ϵ_0 gives the final (classical) result

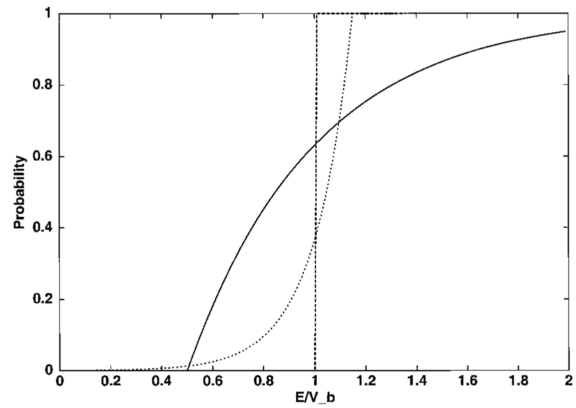

Figure 1. Transmission probability given by the classical treatment of the 2D system, eq 2.12, for $\alpha = 0$ (solid line), $\alpha = 1$ (short-dashed line), and $\alpha = 1.3$ (long-dashed line).

$$P(E) = \left\{1 - \exp\left[\frac{-2\left(E - \frac{1}{2}(1+\alpha)V_b\right)}{(1-\alpha)V_b}\right]\right\} \times h\left\{E - \frac{1}{2}(1+\alpha)V_b\right\}, \quad \text{if } \alpha < 1$$

$$= h\left[E - \frac{1}{2}(1+\alpha)V_b\right] + \exp\left[\frac{-2\left(E - \frac{1}{2}(1+\alpha)V_b\right)}{(1-\alpha)V_b}\right] \times h\left[\frac{1}{2}(1+\alpha)V_b - E\right], \quad \text{for } \alpha > 1 \quad (2.12)$$

If the parameter α is chosen to be 1, then (as is clear from eq 2.8) the auxiliary degree of freedom has no effect and eq 2.10 reduces to

$$P_{\alpha=1}(E) = h(E - V_b) \quad (2.13)$$

the classical transmission probability for the original 1D barrier Hamiltonian 2.1. However, for the choice $\alpha \neq 1$, one sees (cf. Figure 1) that eq 2.12 gives a result that qualitatively mimics the effects of tunneling. As noted above, this comes about because the classical distribution of energy in the auxiliary degree of freedom generates a distribution of barrier heights and, thus, some probability of being transmitted at energies below the 1D barrier height V_b (and reflected at energies above the barrier).

So, we have the situation that if the 2D system (with Hamiltonian 2.8) were treated fully quantum mechanically the transmission probability would be the correct quantum value, independent of the parameter α. Treated classically, the transmission probability is not independent of α and, in fact for $\alpha \neq 1$, gives a finite transmission probability for $E < V_b$ (and also a finite reflection probability for $E > V_b$).

In the next section, we treat this 2D system, eq 2.8, semiclassically, via the initial value representation.

III. The Semiclassical Initial Value Representation

The SC−IVR approach provides an approximate way for adding quantum effects to classical dynamics.[2,7,23,29,32−68] It should thus give a transmission probability for the 2D system (defined by Hamiltonian 2.8) in better agreement with the correct quantum mechanical result than does the classical treatment (eq 2.12) and, thus, which also depends less on the parameter α (because the quantum result is completely independent of α). We briefly summarize the SC−IVR approach below.

The coherent state or Herman–Kluk (HK) IVR expresses the time evolution operator as (with $\hbar = 1$)

$$e^{-i\hat{H}t} = \left(\frac{1}{2\pi}\right)^N \int_{-\infty}^{\infty} d\mathbf{p}_0 \int_{-\infty}^{\infty} d\mathbf{q}_0 \, |\mathbf{p}_t, \mathbf{q}_t; \gamma\rangle C_t(\mathbf{p}_0, \mathbf{q}_0) \exp(iS_t(\mathbf{p}_0, \mathbf{q}_0))\langle \mathbf{p}_0, \mathbf{q}_0; \gamma| \quad (3.1)$$

where N is the total number of degrees of freedom, and $|\mathbf{p}, \mathbf{q}; \gamma\rangle$ is a coherent state, the wave function for which is

$$\langle \mathbf{q}'|\mathbf{p}, \mathbf{q}; \gamma\rangle = \prod_{j=1}^{N} \left(\frac{\gamma_j}{\pi}\right)^{1/4} \exp\left[-\frac{\gamma_j}{2}(q_j' - q_j)^2 + \frac{i}{\hbar} p_j (q_j' - q_j)\right] \quad (3.2)$$

Here, $(\mathbf{p}_t, \mathbf{q}_t)$ are the coordinates and momenta at time t that result from the initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$ and S_t is the classical phase along this trajectory

$$S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t (\mathbf{p}\cdot\dot{\mathbf{q}} - \mathrm{H}) \, dt \quad (3.3)$$

and C_t is the HK prefactor which involves the various monodromy matrices

$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\left|\frac{1}{2}\left(\frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} + \gamma^{-1}\cdot\frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0}\cdot\gamma - i\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}\cdot\gamma + i\gamma^{-1}\cdot\frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0}\right)\right|} \quad (3.4)$$

For the present application, the coordinates and momenta include both the translational degree of freedom, (R, P), and the auxiliary degree of freedom, (x, p), i.e., $\mathbf{q} = (R, x)$ and $\mathbf{p} = (R, p)$.

The transmission probability can be expressed as the long time limit of a time correlation function

$$P = \lim_{t\to\infty} C_{AB}(t) \quad (3.5)$$

where

$$C_{AB}(t) = tr[\hat{A}e^{i\hat{H}t}\hat{B}e^{-i\hat{H}t}] \quad (3.6)$$

with operator $\hat{A}$ and $\hat{B}$ given by

$$\hat{A} = |\Psi_0\rangle\langle\Psi_0| \quad (3.7)$$

$$\hat{B} = |\phi_0\rangle\langle\phi_0|h(\hat{R}) \quad (3.8)$$

The initial state $|\Psi_0\rangle$ is

$$|\Psi_0\rangle = |\phi_0\rangle|P_i, R_i, \gamma_i\rangle \quad (3.9)$$

i.e., the ground state of the auxiliary degree of freedom and a coherent state for translation. For this particular case, the correlation function can also be expressed as

$$C_{AB}(t) = \int_0^{\infty} dR \, |\langle R|\langle\phi_0|e^{-i\hat{H}t}|\Psi_0\rangle|^2 \quad (3.10)$$

If the linearized SC approximation (LSC)[63,69] is applied to the IVR expression for the correlation function, then one obtains the classical Wigner approximation

$$C_{AB}(t) \approx \left(\frac{1}{2\pi}\right)^N \int d\mathbf{q}_0 \, d\mathbf{p}_0 \, A_w(\mathbf{q}_0, \mathbf{p}_0) B_w(\mathbf{q}_t, \mathbf{p}_t) \quad (3.11)$$

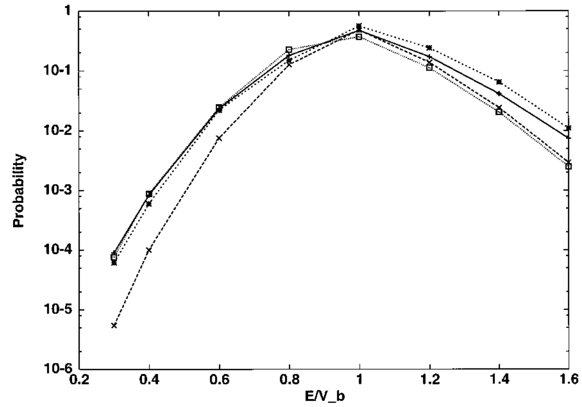

Figure 2. Transmission (for $E/V_b < 1$) and reflection (for $E/V_b \geq 1$) probabilities for the 1D Eckhart barrier as a function of E/V_b. The values of α in eq 2.8 are 0 (short-dashed line), 1 (long-dashed line), and 1.3 (dotted line). The solid line gives the correct quantum results. See the text for details.

where A_w and B_w are the Wigner functions corresponding to these operators, for example

$$A_w(\mathbf{q}, \mathbf{p}) = \int d\Delta\mathbf{q} \, e^{-i\mathbf{p}^T\cdot\Delta\mathbf{q}}\langle \mathbf{q} + \Delta\mathbf{q}/2|\hat{A}|\mathbf{q} - \Delta\mathbf{q}/2\rangle \quad (3.12)$$

IV. Numerical Tests

The test system is chosen to be an Eckart potential[70]

$$V(R) = V_b \, \mathrm{sech}^2(R/a) \quad (4.1)$$

with parameters that correspond approximately to the $H + H_2$ reaction: $V_b = 0.425$ ev, $M = 1060$ au, and $a = 0.734$ au. The initial center position for the translational coherent state is $R_i = -6.0$, with the coherent state parameter $\gamma_R = 0.5$; for the auxiliary degree of freedom, $\gamma_x = 1$, and these same values for γ are also used for the coherent states in the SC propagator, eq 3.1. The translational coherent state is chosen rather broad in coordinate space so as to be fairly sharp in momentum space. Results are shown below as a function of the energy $E = P_i^2/(2M)$ corresponding to the center of the translational coherent state. The quantum results were calculated by the split-operator algorithm[71] for this same initial state.

Figure 2 shows the results of the SC–IVR calculation (the transmission probability is shown for $E < V_b$ and the reflection probability for $E > V_b$) for several values of the parameter α, $\alpha = 0, 1, 1.3$, compared to the correct quantum values. $\alpha = 1$ corresponds to not having the auxiliary degree of freedom (cf. eq 2.4), and one sees that including it, i.e., $\alpha = 0$ or 1.3, gives better agreement with the quantum results. In particular, $\alpha = 0$ shows a very significant improvement and suggests itself as perhaps the "universal" choice. $\alpha = 1.3$ gives very good results in the low energy tunneling region but less good results for over-barrier reflection.

For comparison, Figure 3 shows the results of the linearized SC approximation, i.e., the classical Wigner model; this is the same as the classical result discussed in section I except here averaged over the distribution of initial energy in the translational coherent state. One sees that there is much greater dependence on the α parameter than for the SC–IVR results in Figure 2 and, thus, less good agreement with the correct quantum values.

To focus more explicitly on the α-dependence of the SC–IVR results, Figure 4 shows the transmission probability as a function of α for one particular energy, $E = 0.4 \, V_b$, fairly far

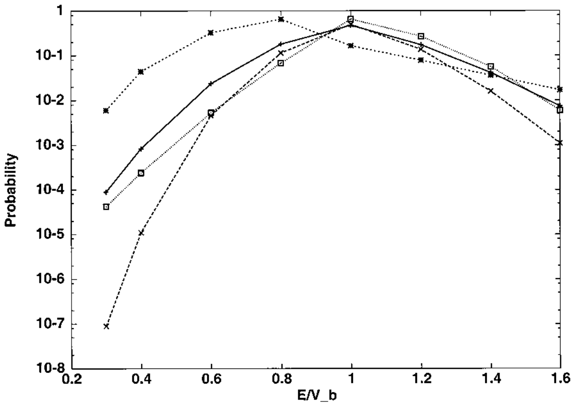

Figure 3. Transmission (for $E/V_b < 1$) and reflection (for $E/V_b \geq 1$) probabilities for the 1D Eckart barrier as a function of E/V_b, given by the linearized SC (or classical Wigner) approximation, eq 3.12, for $\alpha = 0$ (short-dashed line), $\alpha = 1$ (long-dashed line), and $\alpha = 1.3$ (dotted line). For comparison, the correct quantum results are also shown (solid line).

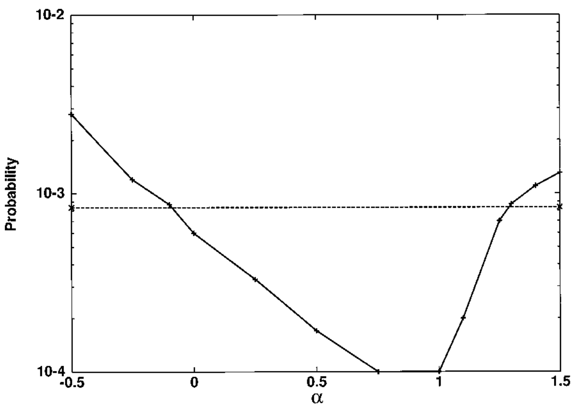

Figure 4. Transmission probabilities as a function of α in eq 2.8, for $E/V_b = 0.4$. Also shown is the correct quantum result (dashed line), which is independent of α.

into the tunneling region, for which the quantum transmission probability is 8×10^{-4}. To understand these results, as well as those in Figure 2, one may notice that the range the barrier can fluctuate is dependent on the value of α. For $\alpha < 1$, the whole potential varies from $(1 + \alpha)V/2$ to ∞. This sets a lower limit on the tunneling energy. For a given tunneling energy, α should be large enough so the barrier fluctuation range covers it. For $\alpha > 1$ the whole potential varies from $-\infty$ to $(1 + \alpha)V/2$. Although there is no lower limit on the range the barrier can fluctuate, the weight of each barrier height is affected by the value of α. Therefore, in Figure 4, the tunneling probability increases when α is away from 1, because more trajectories can pass through the barrier. The semiclassical formulas discussed in this work are derived from the corresponding quantum formulas with the stationary-phase assumption. If the stationary-phase assumption is valid, one would expect the tunneling probability becomes independent of α once the value of α is sufficiently different from 1. For $\alpha > 1$, one does see the tunneling probability first increases quickly with α, then slows down. For $\alpha < 1$, Hamiltonian 2.8 overemphasizes the tunneling trajectories, as can bee seen from the classical results shown in Figures 1 and 3. The final tunneling probability is due to mutual cancellation of contributions from these trajectories, which may result in large statistical errors. Therefore, choices of $\alpha > 1$ may have certain practical advantages.

Theoretically, the models discussed in the paper can be understood in the following way:

For the bare Hamiltonian 2.1, when the limit $\hbar \to 0$ is taken, only trajectories obeying classical mechanics survive. To give an accurate and unambiguous description of nonclassical tunnelling and over-barrier reflection phenomena, one needs to resort to complex-valued trajectories. In the well-known "instanton" theory,[72] for example, the tunneling path is generated by allowing the system to move along an inverted potential, which is accomplished by using imaginary time and momentum.

For the models discussed in this work, one expands the Hilbert space by adding some fictitious degrees of freedom. The role of this fictitious degree of freedom is to multiply the original bare potential by a varying factor. Therefore, the physical subsystem "feels" not only the original potential but a whole ensemble of potentials with varying barrier height: some are higher than the physical potential, some are lower, and even inverted−"instanton"-like trajectories. In a quite different approach,[73−75] Takatsuka and co-workers noticed that including only the instanton trajectories is not sufficient to describe tunneling in certain systems. Furthermore, the over-barrier reflection effect and the tunneling effect are described on the same foot in the present approach, which cannot be easily achieved by other semiclassical tunneling theories.

V. Concluding Remarks

In this paper, we have discussed a class of semiclassical models for describing tunneling with real-valued trajectories. Although adding a fictitious degree of freedom is merely a mathematical trick, the underlying physics is to include classical trajectories that are "off the energy shell" of the original bare Hamiltonian into the semiclassical calculation, an effect which has been shown to be essential for describing tunneling with real-valued classical trajectories.

There are several questions remaining open:

The form of the Hamiltonian with one extra degree of freedom is clearly not unique. One may choose different values of α in eq 2.8. One may couple the fictitious degree of freedom to the momentum term instead of the potential term of the bare Hamiltonian 2.1. The question is how sensitive the tunneling probability depends on the Hamilton form and what is the best choice. The tunneling probabilities reported in this paper are averaged over the energy distribution of the initial wave packet. In the work of Grossman and Heller,[8] the tunneling probabilities for definite energy states were calculated from a correlation function. Primitive calculations with this correlation type calculation show that the calculated semiclassical tunneling probabilities with the expanded Hamiltonian eq 2.8 reproduce the analytic quantum results[76] down to a certain energy. Below this critical energy, the results begin to deteriorate. The location of the critical energy varies with the value of α. This supports the idea that it is crucial that the range of fluctuations in the barrier of Hamiltonian 2.8 covers the tunneling energy under study. Further study along this line would be useful.

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References and Notes

(1) Mclaughlin, D. W. *J. Math. Phys.* **1972**, *13*, 1099.
(2) Miller, W. H.; George, T. F. *J. Chem. Phys.* **1972**, *56*, 5668.
(3) George, T. F.; Miller, W. H. *J. Chem. Phys.* **1972**, *56*, 5722.
(4) George, T. F.; Miller, W. H. *J. Chem. Phys.* **1972**, *57*, 2458.
(5) Miller, W. H. *Adv. Chem. Phys.* **1974**, *25*, 69.
(6) Marcus, R. A.; Coltrin, M. E. *J. Chem. Phys.* **1977**, *67*, 2609.
(7) Kay, K. G. *J. Chem. Phys.* **1997**, *103*, 2313.
(8) Grossmann, F.; Heller, E. J. *Chem. Phys. Lett.* **1995**, *241*, 45.
(9) Heller, E. J. *J. Phys. Chem. A* **1999**, *103*, 10433.
(10) Makri, N.; Miller, W. H. *J. Chem. Phys.* **1989**, *91*, 4026.
(11) Keshavamurthy, S.; Miller, W. H. *Chem. Phys. Lett.* **1993**, *205*, 96.
(12) Tully, J. C.; Preston, R. J. *J. Chem. Phys.* **1971**, *55*, 562.
(13) Sewell, T. D.; Guo, Y.; Thompson, D. L. *J. Chem. Phys.* **1995**, *103*, 8557.
(14) Guo, Y.; Qin, Y.; Sorescu, D. C.; Thompson, D. L. *J. Chem. Phys.* **1996**, *104*, 4041.
(15) Guo, Y.; Thompson, D. L. *J. Chem. Phys.* **1995**, *105*, 1070.
(16) Guo, Y.; Thompson, D. L. *J. Chem. Phys.* **1996**, *105*, 7480.
(17) Guo, Y.; Li, S.; Thompson, D. L. *J. Chem. Phys.* **1997**, *107*, 2853.
(18) Guo, Y.; Wilson, A. K.; Chabalowski, C. F.; Thompson, D. L. *J. Chem. Phys.* **1998**, *109*, 9258.
(19) Guo, Y.; Sewell, T. D.; Thompson, D. L. *J. Phys. Chem. A* **1998**, *102*, 5040.
(20) Keshavamurthy, S.; Miller, W. H. *Chem. Phys. Lett.* **1994**, *218*, 189.
(21) Das, R.; Keshavamurthy, S. *Chem. Phys. Lett.* **2000**, *326*, 544.
(22) Spath, B.; Miller, W. H. *J. Chem. Phys.* **1996**, *104*, 95.
(23) Miller, W. H. *J. Chem. Phys.* **1970**, *53*, 3578.
(24) Miller, W. H.; McCurdy, C. W. *J. Chem. Phys.* **1978**, *69*, 5163.
(25) Miller, W. H.; McCurdy, C. W. *J. Chem. Phys.* **1979**, *70*, 3177.
(26) Meyer, H. D.; Miller, W. H. *J. Chem. Phys.* **1979**, *70*, 3214.
(27) Meyer, H. D.; Miller, W. H. *J. Chem. Phys.* **1979**, *71*, 2156.
(28) Meyer, H. D.; Miller, W. H. *J. Chem. Phys.* **1980**, *72*, 2272.
(29) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1997**, *106*, 6346.
(30) Thoss, M.; Stock, G. *Phys. Rev. A* **1999**, *59*, 64.
(31) Coronado, E. A.; Xing, J.; Miller, W. H. Manuscript in preparation.
(32) Miller, W. H. *J. Chem. Phys.* **1991**, *95*, 9428.
(33) Kay, K. G. *J. Chem. Phys.* **1989**, *91*, 107.
(34) Kay, K. G. *J. Chem. Phys.* **1994**, *100*, 4377.
(35) Kay, K. G. *J. Chem. Phys.* **1994**, *100*, 4432.
(36) Kay, K. G. *J. Chem. Phys.* **1994**, *101*, 2250.
(37) Elran, Y.; Kay, K. G. *J. Chem. Phys.* **1999**, *110*, 3653.
(38) Elran, Y.; Kay, K. G. *J. Chem. Phys.* **1999**, *110*, 8912.
(39) Walton, A. R.; Manolopoulos, D. E. *Mol. Phys.* **1996**, *874*, 961.
(40) Brewer, M. L.; Hulme, J. S.; Manolopoulos, D. E. *J. Chem. Phys.* **1997**, *106*, 4832.
(41) Heller, E. J. *J. Chem. Phys.* **1991**, *94*, 2723.
(42) Heller, E. J. *J. Chem. Phys.* **1991**, *95*, 9431.
(43) Heller, E. J. *J. Chem. Phys.* **1991**, *94*, 2723.
(44) Sepulveda, M. A.; Heller, E. J. *J. Chem. Phys.* **1994**, *101*, 8004.
(45) Maitra, N. T.; Heller, E. J. *Phys. Rev. Lett.* **1997**, *78*, 3035.
(46) Herman, M. F.; Kluk, E. *J. Chem. Phys.* **1984**, *81*, 27.
(47) Herman, M. F. *Chem. Phys. Lett.* **1997**, *275*, 445.
(48) Guerin, B. E.; Herman, M. F. *Chem. Phys. Lett.* **1998**, *286*, 361.
(49) Herman, M. F.; Coker, D. F. *J. Chem. Phys.* **1999**, *110*, 1801.
(50) Garashchuk, S.; Tannor, D. J. *Chem. Phys. Lett.* **1996**, *262*, 477.
(51) Garashchuk, S.; Grossmann, F.; Tannor, D. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 781.
(52) Shalashilin, D. V.; Jackson, B. *Chem. Phys. Lett.* **1998**, *291*, 143.
(53) Shalashilin, D. V.; Jackson, B. *Chem. Phys. Lett.* **2000**, *328*, 305.
(54) Provost, D.; Brumer, P. *Phys. Rev. Lett.* **1995**, *74*, 250.
(55) Campolieti, G.; Brumer, P. *J. Chem. Phys.* **1992**, *96*, 5969.
(56) Campolieti, G.; Brumer, P. *Phys. Rev. A* **1994**, *50*, 1997.
(57) McQuarrie, B. R.; Brumer, B. *Chem. Phys. Lett.* **2000**, *319*, 27.
(58) Batista, V. S.; Zanni, M. T.; Greenblatt, B. J.; Neumark, D. M.; Miller, W. H. *J. Chem. Phys.* **1999**, *1108*, 3736.
(59) Coronado, E. A.; Batista, V. S.; Miller, W. H. *J. Chem. Phys.* **2000**, *112*, 5566.
(60) Guallar, V.; Batista, V. S.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 9922.
(61) Skinner, D. E.; Miller, W. H. *Chem. Phys. Lett.* **1999**, *300*, 20.
(62) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 8870.
(63) Sun, X.; Wang, H. B.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 7064.
(64) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 6635.
(65) Thoss, M.; Miller, W. H.; Stock, G. *J. Chem. Phys.* **2000**, *112*, 10282.
(66) Wang, H. B.; Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 9726.
(67) Wang, H.; Song, X.; Chandler, D.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 4828.
(68) Wang, H.; Thoss, M.; Miller, W. H. *J. Chem. Phys.* **2000**, *112*, 47.
(69) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 9726.
(70) Eckart, C. *Phys. Rev.* **1930**, *35*, 1303.
(71) Feit, M. D.; Fleck, J. A., Jr. *J. Chem. Phys.* **1983**, *301*, 1983.
(72) Miller, W. H. *J. Chem. Phys.* **1975**, *62*, 1899.
(73) Takatsuka, K.; Ushiyama, H. *Phys. Rev. A* **1995**, *51*, 4353.
(74) Ushiyama, H.; Takatsuka, K. *J. Chem. Phys.* **1997**, *106*, 7023.
(75) Takatsuka, K.; Ushiyama, H.; Inoue-Ushiyama, A. *Phys. Rep.* **1999**, *322*, 347.
(76) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics: Non-Relativistic Theory*; Pergamon: Oxford, U.K., 1965; p 79.