Semiclassical calculation of cumulative reaction probabilities

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It is shown how the rigorous quantum mechanical expression for the cumulative reaction probability (CRP) obtained by Seideman and Miller [J. Chem. Phys. 96, 4412; 97, 2499 (1992)], \(N(E)=4 \text{tr}[\hat{\epsilon}_r \cdot \hat{G}^* (E) \cdot \hat{\epsilon}_p \cdot \hat{G}(E)]\), which has been the basis for quantum calculations of the CRP for simple chemical reactions, can also be utilized with a semiclassical approximation for the Green’s function, 
\[
\hat{G}(E) = (E + i\varepsilon - \hat{H})^{-1} = (i\hbar)^{-1} \int_0^\infty dt e^{iE t/\hbar} e^{-i(\hat{H} - i\varepsilon)/\hbar}.
\]
Specifically, a modified Filinov transformation of an initial value representation of the semiclassical propagator has been used to approximate the Green’s function. Numerical application of this trajectory-based semiclassical approximation to a simple one-dimensional (barrier transmission) test problem shows the approach to be an accurate description of the reaction probability, even some ways into the tunneling regime. © 1996 American Institute of Physics, [S0021-9606(96)01701-4]

I. INTRODUCTION

There has been considerable progress over the last few years in the development of rigorous quantum mechanical methods to compute the cumulative reaction probability (CRP) for simple chemical reactions.\(^1\)\(^-\)\(^8\) The CRP, \(N(E)\), is defined in terms of the \(S\)-matrix elements connecting asymptotic reactant and product quantum states \(|\phi_r\rangle\) and \(|\phi_p\rangle\), respectively,
\[
N(E) = \sum_{n_r, n_p} |S_{n_r, n_p}(E)|^2 ,
\]
where \(E\) is the total energy of the molecular system. The microcanonical rate constant, most often of interest for unimolecular reactions, is given in terms of the CRP by
\[
k(E) = [2\pi \hbar \rho(T)]^{-1} N(E),
\]
where \(\rho(T)\) is the density of reactant states per unit energy, and the canonical (or thermal) rate constant, usually the quantity of interest for bimolecular reactions, is given by the Boltzmann average of the CRP,
\[
k(T) = [2\pi \hbar Q_r(T)]^{-1} \int_{-\infty}^\infty dE e^{-\beta E} N(E),
\]
where \(\beta = (kT)^{-1}\) and \(Q_r\) is the reactant partition function per unit volume.

The “progress” alluded to in being able to calculate \(N(E)\) is that ways have been developed that avoid having to use Eq. (1.1), i.e., that avoid having to solve the reactive scattering problem at the complete “state-to-state” level; they allow one to compute \(N(E)\) “directly,” yet still “correctly,” i.e., without inherent approximation. The basic equation that has been used is\(^9\)
\[
N(E) = \frac{1}{2}(2\pi \hbar)^2 \text{tr} [\delta(E - \hat{H}) \hat{F} \delta(E - \hat{H}) \hat{F}],
\]
where \(\hat{F}\) is a flux operator (defined with respect to a dividing surface that separates reactants and products), and \(\hat{H}\) is the total Hamiltonian for the molecular system. Seideman et al.\(^{1(a),1(b)}\) were able to cast this in the following form which is more useful for practical calculations,
\[
N(E) = 4 \text{tr}[\hat{\epsilon}_r \cdot \hat{G}^* (E) \cdot \hat{\epsilon}_p \cdot \hat{G}(E)],
\]
where \(\hat{G}\) is the Green’s function for the total Hamiltonian,
\[
\hat{G}(E) = (E + i\varepsilon - \hat{H})^{-1},
\]
\(\varepsilon\) being an absorbing potential\(^{1,11}\) that enforces outgoing wave boundary conditions. The absorbing potential function \(\varepsilon(q)\) is typically chosen to be essentially zero in the interaction region where the relevant dynamics for determining the reactive flux occurs and is “turned on” in the reactant and product exit valleys of the potential surface; \(\varepsilon_r(q)\) is the part of \(\varepsilon(q)\) in the reactant region and \(\varepsilon_p(q)\) is the part of \(\varepsilon(q)\) in the product region. The absorbing potential allows one to evaluate the Green’s function Eq. (1.6) by forming an \(L^2\) matrix representation of \((E + i\varepsilon - \hat{H})\) and then inverting this matrix to evaluate the trace in Eq. (1.5).

Even with these advances, however, rigorous quantum calculations are still feasible only for relatively simple chemical reactions. The largest molecular system studied to date using these approaches is \(\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}\) for total angular momentum \(J = 0\), a six degree-of-freedom system.\(^{12}\) The fundamental limitation in these rigorous quantum approaches is that the number of basis functions (or grid points in a discrete variable representation\(^{13}\)) grows exponentially with the number of degrees of freedom for the system, and the linear algebra calculation necessary to obtain the Green’s function grows in difficulty more than linearly with the number of basis functions.

One is thus clearly interested in approximate approaches that have the potential for treating far more complex systems, but which are also of useful reliability. To this end, we present herein a semiclassical, classical trajectory-based approach for evaluating the CRP. The general approach is described in Sec. II, and results of its application to a simple test problem is presented in Sec. III to illustrate the capabilities of the semiclassical approximation. The results are in good overall agreement with the accurate quantum result for

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this example, even an interesting way into the tunneling regime, suggesting that the semiclassical approximation should be quite useful for determining thermal rate constants.

II. SEMICLASSICAL APPROXIMATION FOR THE CRP

The semiclassical approach is in principle quite straightforward: We use Eq. (1.5) with a semiclassical approximation for the Green’s function. (A similar kind of semiclassical approximation for the Green’s function has also been used to obtain the S-matrix itself.) For a generic Cartesian Hamiltonian with \( d \) degrees of freedom, the primitive, or Van Vleck\(^ {15,16} \) approximation for the Green’s function has also been used to approximate the Green’s function.

The sum in Eq. (2.1) is over all values of the initial momentum \( \mathbf{p}_1 \) that satisfy the boundary condition

\[
\mathbf{x}(\mathbf{x}_1, \mathbf{p}_1, t) = \mathbf{x}_2.
\]

The absorbing potential factor \( e^{-\epsilon_r t/\hbar} \) is the only non-standard feature in Eq. (2.1). Fortunately, it is much simpler to deal with the absorbing potential semiclassically than it is quantum mechanically: it cannot cause any unwanted reflections in the above semiclassical expression because we have implicitly made an infinitesimal approximation for it. Thus it does not affect the dynamics and only causes absorption; see also the discussion by Seideman et al.\(^ {10(b)} \)

The key feature to making a semiclassical approach practical is to avoid having to deal explicitly with the double ended boundary conditions in Eq. (2.3).\(^ {17-21} \) (The initial condition, \( \mathbf{x}(\mathbf{x}_1, \mathbf{p}_1, 0) = \mathbf{x}_1 \) is obviously easy to deal with.) One way to do this is to write Eq. (1.5) as

\[
N(E) = 4 \text{ tr} \left[ \epsilon_r^{1/2} \hat{G}(E) \cdot \epsilon_p^{1/2} \cdot \epsilon_r^{1/2} \hat{G}^*(E) \cdot \epsilon_r^{1/2} \right], \tag{2.4}
\]

and to evaluate the trace in a coordinate representation, while inserting a basis set representation of the identity operator,

\[
1 = \sum_n \langle \chi_n |, \tag{2.5}
\]

between the two factors of \( \epsilon_r^{1/2} \). This gives

\[
N(E) = 4 \sum_n \int d\mathbf{x}_1 \epsilon_r(\mathbf{x}_1) \left| \langle \chi_n | \epsilon_p^{1/2} \hat{G}(E) | \mathbf{x}_1 \rangle \right|^2, \tag{2.6}
\]

and by using the initial value representation (IVR) trick,\(^ {17(d)} \)

the matrix element of the Green’s function is given by,

\[
\langle \chi_n | \epsilon_p^{1/2} \hat{G}(E) | \mathbf{x}_1 \rangle
\]

\[
= \frac{1}{i\hbar} \int_0^\infty dt \int d\mathbf{p}_1 \left[ \frac{\partial x_i}{\partial p_1} \right] / (2\pi i\hbar)^{1/2} \chi_n(\mathbf{x}_1) \times e_p(\mathbf{x}_1)^{1/2} \exp \left[ i \hbar \left[ E t + S(\mathbf{x}_1, \mathbf{p}_1, t) + i\epsilon_j \right] \right] \times \exp(-i\pi \nu/2). \tag{2.7}
\]

Because of the factor \( \epsilon_p^{1/2} \) in the integrand of Eq. (2.7), the basis \( \{ \chi_n(\mathbf{x}) \} \) only has to span the product absorbing region.

We have used Eq. (2.6) with Eq. (2.7) and found it to work quite well using several different choices for the \( \{ \chi_n \} \) basis, such as Legendre polynomials and sinc functions.

Subsequently, however, we have utilized the following approach which we feel is more systematic and has advantages for multidimensional implementations. It is based on a standard coordinate space representation of Eq. (1.5),

\[
N(E) = 4 \int d\mathbf{x}_1 \int d\mathbf{x}_2 \epsilon_r(\mathbf{x}_1) \epsilon_p(\mathbf{x}_2) \left| \langle \mathbf{x}_2 | \hat{G}(E) | \mathbf{x}_1 \rangle \right|^2, \tag{2.8}
\]

and we initially planned to use the following IVR for the Green’s function;\(^ {20(b)} \)

\[
\langle \mathbf{x}_2 | \hat{G}(E) | \mathbf{x}_1 \rangle^\text{IVR}
\]

\[
= \frac{1}{i\hbar(2\pi\hbar)^{1/2}} \int d\mathbf{p}_1 \int_0^\infty dt \sqrt{\frac{\partial p_i}{\partial \mathbf{p}_1}} \times \exp \left[ i \hbar \left[ E t + S(\mathbf{x}_1, \mathbf{p}_1, t) - \mathbf{p}_1(\mathbf{x}_1 - \mathbf{x}_2) + i\epsilon_j \right] \right] ; \tag{2.9}
\]

this comes about by making the primitive semiclassical approximation in a momentum representation and then Fourier transforming this to obtain \( \langle \mathbf{x}_2 | \hat{G}(E) | \mathbf{x}_1 \rangle \). We found, however, that the direct use of Eq. (2.9) gave quite unstable and erratic results (vide infra). Excellent results are obtained, though, if Eq. (2.9) is subjected to a modified Filinov transformation (MFT) of the type used by Makri and Miller;\(^ {22} \) this replaces Eq. (2.9) by

\[
\langle \mathbf{x}_2 | \hat{G}(E) | \mathbf{x}_1 \rangle^\text{MFT}
\]

\[
= \frac{1}{i\hbar(2\pi\hbar)^{1/2}} \int d\mathbf{p}_1 \int_0^\infty dt \left[ \frac{\partial \mathbf{p}_i}{\partial \mathbf{p}_1} - i\hbar A \frac{\partial x_i}{\partial \mathbf{p}_1} \right] \times \exp \left[ -\frac{A}{2} (\mathbf{x}_2 - \mathbf{x}_1)^2 \right] \exp \left[ i \hbar \left[ E t + S(\mathbf{x}_1, \mathbf{p}_1, t) - \mathbf{p}_1(\mathbf{x}_1 - \mathbf{x}_2) + i\epsilon_j \right] \right] \times \exp(-i\pi \nu/2). \tag{2.10}
\]

In the limit \( A \to 0 \), the IVR of Eq. (2.9) is regained, and as \( A \to \infty \) one sees that

\[
e^{-A/2(\mathbf{x}_2 - \mathbf{x}_1)^2} \left[ \frac{A}{2\pi} \right]^{1/2} \delta(\mathbf{x}_2 - \mathbf{x}_1). \tag{2.11}
\]
and it is not hard to show that Eq. (2.10) then reverts to the original primitive semiclassical result for \( G \), Eq. (2.1) [with the boundary condition, Eq. (2.3)]. Equation (2.10) is also closely related to the “cellular dynamics” approach of Heller and co-workers\(^{19} \) and to some of the IVRs used by Herman et al.\(^{18} \) and by Kay.\(^{21} \)

The final expression used to generate the results discussed in the next section is thus

\[
N(E) = \frac{4}{(2\pi\hbar)^2} \int dx_1 \int dx_2 \, \epsilon_\phi(x_1) \epsilon_\phi(x_2) \times \frac{\partial}{\partial p_1} \left. \frac{\partial}{\partial p_1} \right|_{x_1} \left[ E \right. + S(x_1, p_1, t) - \left. p_1(x_1 - x_2) + i \epsilon_\phi \right] \times \exp \left[ -\frac{A}{2} (x_2 - x_1)^2 \right]. \tag{2.12}
\]

Regarding practical aspects of the calculation, we note that for given values of the initial conditions \((x_1, p_1)\), the time integral in Eq. (2.12) is evaluated along the trajectory while one is computing it; i.e., one does not need to store all the time dependent quantities and then do the integral over \( t \). Doing the \( t \) integral thus entails essentially no extra effort in the calculation. (One continues the integral over \( t \) until the absorption factor \( e^{-\epsilon_\phi / \hbar} \) damps the integrand effectively to zero.) Also due to the structure of Eq. (2.12), one can do the calculation for many different values of the integration variable \( x_1 \)—and also for many different values of energy \( E \)—all from the same set of initial conditions \((x_1, p_1)\), i.e., from the same set of trajectories. The most crucial numerical aspect of the calculation is the integral of initial momenta \( p_1 \), because the integrand has positive and negative contributions (while the integrals over \( x_1 \) and \( x_2 \) involve positive definite quantities). The Filinov damping factor, \( \exp[-A(x_2 - x_1)^2/2] \), greatly improves this aspect of the calculation and is the principal reason why the modified Filinov representation of the Green’s function is preferable to the IVR of Eq. (2.9).

Finally, note that in Eq. (2.12) we have included no Maslov phase factor related to the square root of the Jacobian determinant \( D \),

\[
D(x_1, p_1; t) = \left. \frac{\partial}{\partial p_1} \frac{\partial}{\partial p_1} \right|_{x_1} \left[ E \right. + S(x_1, p_1, t) - \left. p_1(x_1 - x_2) + i \epsilon_\phi \right]. \tag{2.13}
\]

This is because in this “hybrid representation” \( D(t) \) will in general never vanish for any value of \( t \) (because \( \partial p_1 / \partial p_1 \) and \( \partial x_1 / \partial p_1 \) are each real). It is easy to see that the initial value \((t = 0) \) of \( D(t) \) is unity (since \( x_1 = x_1 + p_1 t / m, \ p_1 = p_1 \)) and to obtain the correct phase of \( D(t)^{1/2} \) for all later \( t \) one simply follows the complex value of \( D(t) \) along the trajectory, adding the necessary phase \( e^{i \pi} \) anytime the branch line, \( D(t) = 0 \) a negative real number, is crossed so that \( D(t)^{1/2} \) is a continuous function of \( t \).

### III. RESULTS AND DISCUSSION

As a first test of the semiclassical approach described above we have computed the transmission probability through the Eckart potential barrier,

\[
V(x) = V_0 \text{sech}^2(x) \tag{3.1}
\]

with a barrier \( V_0 = 0.425 \text{ eV} \) and the mass \( m = 1060 \text{ a.u.} \) chosen, as before,\(^{1(10)} \) to correspond approximately to the \( \text{H} + \text{H}_2 \text{–H}_2 + \text{H} \) reaction. For the absorbing potential we have used

\[
\epsilon_\phi(x) = h(-x_0 - x) \lambda \left[ \frac{x + x_0}{x_{\text{max}} - x_0} \right]^4 \tag{3.2}
\]

\[
\epsilon_p(x) = h(x - x_0) \lambda \left[ \frac{x - x_0}{x_{\text{max}} - x_0} \right]^4 \tag{3.3}
\]

\[
\epsilon(x) = \epsilon_\phi(x) + \epsilon_p(x) \tag{3.4}
\]

where \( h(x) \) is the Heaviside step function, \( x_0 \) is where the absorbing strip starts, \( x_{\text{max}} \) is where the absorbing strip ends, and \( \lambda \) determines the strength of the absorbing potential. As discussed above, there is no concern about reflection caused by the absorbing potential, as there is in the fully quantum mechanical case,\(^{1} \) so they could be turned on as rapidly (as a function of \( x \)) as desired; we turn them on quickly enough to minimize the length of the trajectory, but not so sharply as to make the integrals difficult. We have also added a cut-off factor to the integral over \( p_1 \),

\[
f_{\text{cut}}(p_1) = [1 + \exp((p_1 - p_{\text{cut}})/\eta)]^{-1} \tag{3.5}
\]

to eliminate the very high energy contribution that is highly oscillatory and makes no contribution to the integral, and finally we have transformed to the new integration variable \( \tilde{p}_1 \),

\[
p_1 = p_{\text{top}} + \tilde{p}_1^2 \tag{3.6}
\]

where

\[
p_{\text{top}} = \sqrt{2m(V_0 - V(x_1))} \tag{3.7}
\]

\( p_{\text{top}} \) is the initial momentum that leads to the “orbiting” trajectory, and changing from integral variable \( p_1 \) to \( \tilde{p}_1 \) eliminates the singularity in the integrand related to it. For all of the results shown below, we have used the following parameters unless otherwise specified: \( x_0 = 3.5 \text{ a.u.}, \ x_{\text{max}} = 5.5 \text{ a.u.} \), and \( \lambda = 2.5 \text{ eV} \) for the absorbing potential parameters; \( \Delta x_1 = \Delta x_2 = 0.25 \text{ a.u.} \) for integration (via the trapezoidal rule) over \( x_1 \) and \( x_2 \); and \( P_{\text{cut}} = 13.0 \text{ a.u.}, \ \eta = 0.50, \ p_{\text{max}} = 16.0 \text{ a.u.} \), and \( \Delta \tilde{p}_1 = 0.02 \) are the parameters for the \( p_1 \) integral (also done via the trapezoidal rule).

The first important feature to show is the extent to which the Filinov “smoothing” transformation simplifies the integral over \( p_1 \) (actually over \( \tilde{p}_1 \)). For the values \( x_1 = -4.75 \text{ a.u.} \) and \( x_2 = 4.25 \text{ a.u.} \), Fig. 1 shows the real part of the integral of Eq. (2.10) for several values of the parameter \( \Delta (0, 1.0, \) and 10.0) and two values of the energy \( E \), one below the barrier (\( E = 0.3 \text{ eV} \)) and one above the barrier (\( E = 0.6 \text{ eV} \)). One clearly sees the effect of the Filinov smoothing \((A > 0)\) on damping the oscillatory nature of the integral. One also

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sees the stationary phase region of the integral for the case above the barrier, $E=0.6$ eV, near the value of $\tilde{p}_1 \approx 1.0$. There is no stationary phase region for the energy below the barrier, $E=0.3$ eV, and this is of course why the transmission probability is small in this case (i.e., in the tunneling regime).

Figure 2 shows the results obtained for $N(E)$ for several values of $A$. We do not obtain satisfactory results for $A=0$, but for a wide range of $A>0$ we obtain quite stable results that are relatively insensitive to the particular value of this smoothing parameter. This is precisely the behavior one wishes to see.

It is significant that the results in Fig. 2 are accurate for some ways into the “classically forbidden” tunneling regime, in this case for energies as much as 0.1 eV or so below the barrier, down to a transmission probability of $\approx 10^{-3}$.

This is achieved without “heroic” efforts in evaluating the $p_1$ integral: the results in Fig. 2 have been obtained with 9 values each of $x_1$ and $x_2$ for the integrals over these variables, and 161 values for the $p_1$ integral. We actually obtain good results with significantly fewer points in the $p_1$ integral. With $\Delta \tilde{p}_1 = 0.06$, for example, one needs only 54 points for the $p_1$ integral.

IV. CONCLUDING REMARKS

With regard to the application of this approach to systems with many degrees of freedom, it is clear that one can utilize Monte Carlo methods to carry out the integrals over $x_1$ and $x_2$ in Eq. (2.12); this is straightforward because their integrands are positive definite. The integral over $p_1$ is the most challenging aspect of the calculation. The Filinov smoothing transformation definitely helps matters, but the integral is still the bottleneck to the approach. The “classical dynamics” algorithm of Heller and co-workers has similarities to the Filinov result, and it may also make useful contributions in the present application. This is clearly the aspect of the calculation that needs the most attention and further development.

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