Evaluation of thermal rate constants in the eigenbasis of a Hamiltonian with an optical potential

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Miller and co-workers [J. Chem. Phys. 61, 1823 (1974); ibid., 79, 4889 (1983)] have derived an exact quantum mechanical expression for reactive thermal rate constants in terms of the time integral of a flux autocorrelation function. The evaluation of this integral in a finite basis poses the problem that spurious oscillations in the correlation function due to recurrences can occur at long times, corrupting the result. To obviate this difficulty, we add to the Hamiltonian an optical potential in the asymptotic region, and evaluate eigenvalues and eigenvectors using the technique of successive truncation. These operations allow a diagonal (although nonorthogonal) representation of the propagator in which the eigenvalues are exponentially decaying functions of time, which damp the components of the propagated vectors before the spurious reflection back into the interaction region. In this manner, the infinite time limit of the integral may be evaluated properly. Furthermore, the results of a single diagonalization may be used to compute the thermal rate constant over a range of temperatures.

1. INTRODUCTION

Over two decades, Miller and co-workers have derived a quantum mechanically exact expression for the thermal rate constant for a chemical reaction and expressed it in terms of a flux autocorrelation function. This latter result is

\[ k(T) = \lim_{t \to \infty} \frac{1}{Q} \int_0^\infty dt \sum_{m \neq n} \sin \left( \frac{\hbar}{2} (E_m - E_n) \right) / (E_m - E_n) \left( m \left| F_g \right| n \right)^2. \]

The difficulty with this procedure is that the norm-conserving nature of the time evolution (which in this case may be thought of as the time evolution of flux or thermal flux eigenvectors) forces flux directed out of the interaction region to be reflected back toward the interaction region from the end of the finite basis after a finite time; therefore, the expression in Eq. (4) oscillates, and the infinite time limit cannot be taken. Instead, the upper limit of the integral in Eq. (1) must be replaced by a finite time after which the correlation function has decayed to zero; thus, there is a residual time dependence in the evaluation of the thermal rate constant in a finite basis which does not exist for the exact expression. This complication also implies a constraint on the basis; both the size (i.e., the number of basis functions) and the range must be large enough to allow the correlation function to decay to zero before reflected probability amplitude returns to the interaction region. Such a constraint may be expected to become particularly troublesome if the reacting species can form a complex which would extend the decay time of the autocorrelation function.

These problems are held in common by all time-dependent treatments of unbounded motion of quantum systems; a basis or grid of finite range cannot support the exact dynamics indefinitely. Sooner or later, the propagated wave packet must reflect from the nonphysical boundaries of the grid or basis and interfere with itself. One successful way of circumventing this difficulty which has gained considerable popularity in the past few years is to add to the Hamiltonian a negative imaginary (optical) potential localized outside the interaction region. When
TABLE I. DVR and successive truncation parameters, and physical constants.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_\rho$</td>
<td>Number of $\rho$ DVR points</td>
</tr>
<tr>
<td>$n_\chi$</td>
<td>Number of $\chi$ DVR points</td>
</tr>
<tr>
<td>$\rho_{\text{min}}$, $\rho_{\text{max}}$</td>
<td>Minimum and maximum values for $\rho$ DVR points</td>
</tr>
<tr>
<td>$E^{1}<em>{\text{ID}}$, $N^{1}</em>{\text{ID}}$</td>
<td>Energy cutoff defining first truncation, the total number of 1D eigenvectors kept after the first truncation</td>
</tr>
<tr>
<td>$E^{2}<em>{\text{ID}}$, $N^{2}</em>{\text{ID}}$</td>
<td>Energy cutoff defining second truncation, the total number of 2D eigenvectors kept after the second truncation</td>
</tr>
</tbody>
</table>

*These parameters are not set by the user but are rather determined by the preceding ones.

chosen correctly, this optical potential serves to absorb the outgoing components of the wave packet so that they do not reflect. We apply this strategy to the evolution of the thermal flux operator. Most studies of time-dependent propagations using optical potentials have focused on some variant of short-time propagators; in this study, we diagonalize the Hamiltonian plus the optical potential. This technique allows us to evaluate the rate constant in a manner similar to Eq. (4). Now, however, the eigenvectors are nonorthogonal, and the eigenvalues have a negative imaginary part, which results in the exponential damping of the terms in the sum in Eq. (4). This result permits us to take the infinite time limit in Eq. (1). In addition, it will be shown that the addition of an optical potential does not necessarily lead to a substantial increase in the computational requirements, and that very accurate results can be obtained with a simple linear optical potential.

In Sec. II, we will briefly discuss the techniques employed to diagonalize the complex Hamiltonian. In Sec. III, we will discuss the construction of the flux and thermal flux operators in the discrete variable representation (DVR). In Sec. IV, we give results for collinear H+H$, and in Sec. V we conclude with a brief discussion.

II. METHOD

The Hamiltonian with a negative imaginary potential is first constructed in a direct product discrete variable representation (DVR) and then diagonalized using the technique of successive diagonalization/truncation. Since these techniques have been discussed and reviewed repeatedly in the past several years, we refer the reader to Refs. 9 and 10 for the necessary background. We summarize the parameters and constants which are required for the calculation in Table I.

For the collinear H+H$, our DVR is the direct product of DVR’s based on Tschebychev functions of the second kind (sine functions) in the hyperspherical (Delves) coordinates $\chi$ and $\rho$. These coordinates are by now well known, so we define them only briefly. The transformation from mass-scaled Jacobi to hyperspherical coordinates are given by

\[ \chi = \tan^{-1} \left( \frac{r}{R} \right), \]

\[ \rho = \sqrt{R^2 + r^2}. \]

The range of $\chi$ extends from 0 to a mass-dependent angle $\chi_{\text{max}}$; for a system with three identical atoms, this angle is just $\pi/3$. The $\rho$ points are distributed on the range ($\rho_{\text{min}}$,$\rho_{\text{max}}$). In all calculations, $\rho_{\text{min}}$ is chosen to be 2 bohr. All distances in this study are mass scaled, so the reduced mass is always $\mu = (m_1 m_2 m_3)/(m_1 + m_2 + m_3)^{1/2}$.

The wave functions are factorized as follows:

\[ \Psi(\rho,\chi) = \frac{1}{\sqrt{\rho}} \psi(\rho,\chi), \]

and $\psi$ is expanded in the finite basis. With this factorization, the volume element for integration is $d\rho \, d\chi$, and the Hamiltonian is

\[ H = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{4\rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \chi^2} \right) + V(\rho,\chi). \]

The potential $V$ in this study is the potential energy surface of Liu, Seibahn, Truhlar, and Horowitz (LSTH). Our optical potential is linear and takes one of two forms

\[ V_{\text{opt}} = -i V_0 (\rho - \rho_0) \Theta(\rho - \rho_0) \Theta \left( \chi - \frac{\pi}{6} \right), \]

\[ -i V_0 (\rho_0 - \rho) \Theta(\rho_0 - \rho) \Theta \left( \frac{\pi}{6} - \chi \right), \]

where $\Theta(x)$ is the Heaviside step function. In Eq. (8a), the optical potential is a linear function of $R_{\alpha\beta}$, where $\alpha = 1,2$ labels the arrangement channel. The step functions in $\chi$ impose the restriction that the optical potential in one arrangement channel is not felt by a particle localized in the other. Equation (8b) is a linear function of $\rho$ alone. The parameters $R_0$ and $\rho_0$ indicate the inner boundary of the optical potential. The outer boundary is identical (for fixed basis); it is simply the surface $\rho = \rho_{\text{max}}$ which bounds the basis. Throughout the paper, we will refer to the “range” of either form of the optical potential as the distance from the inner to the outer boundary measured along the line $\chi = 0$; thus, the ranges of the potentials in Eqs. (8a) and (8b) are $\rho_{\text{max}} - R_0$ and $\rho_{\text{max}} - \rho_0$, respectively. The choice of slope parameters $V_0$ will be dealt with in the next section. Schematic representations of these optical potentials are given in Fig. 1.

In a slight departure from the usual procedure of successive diagonalization/truncation, the optical potential, although diagonal in the DVR, is added to the Hamiltonian after the full real Hamiltonian has been diagonalized. There are two reasons for this modification. First, the Hamiltonian plus the optical potential is not a Hermitian matrix; in a real basis it is complex symmetric. Since four real multiplications are required to evaluate one product of two complex numbers, the time required to diagonalize a
FIG. 1. Schematic of the optical potentials represented in Eq. (8). The outer arc represents the outer boundary of the basis. The inner (dashed) arc is the inner boundary the potential in Eq. (gb). The two straight lines form the inner boundary for the potential in Eq. (8a). Axes are mass scaled distances in \( a_0 \).

A complex symmetric matrix is expected to be four times that required to diagonalize a real one, so we prefer to do this once rather than at every step in the truncation procedure. Furthermore, truncation of the full (real) Hamiltonian eigenbasis yields a smaller representation for the Hamiltonian plus the optical potential than the full basis, reducing the required amount of work substantially. The second reason is that the operator which we evolve in time is the thermal flux operator. Since this operator is expressible in terms of functions of finite range, it can be conveniently expressed in terms of the eigenvectors of the real Hamiltonian (see below).

We will denote the real Hamiltonian as \( H \) and the Hamiltonian plus the optical potential as \( \tilde{H} \). The eigenvectors of \( H \) will be denoted by kets \( |n\rangle \),

\[
|m\rangle = C_{mn} |n\rangle = \sum |\tilde{n}\rangle \langle \tilde{n}|m\rangle,
\]

while the eigenvectors of \( \tilde{H} \) will also be denoted with a tilde,

\[
|\tilde{m}\rangle = \langle \tilde{m}| |\tilde{n}\rangle = \langle \tilde{n}|m\rangle = (\epsilon_n - i\Gamma_n) \delta_{mn}.
\]

The bar over the \( \tilde{m} \) in the bra vector indicates an element of the set of vectors biorthogonal to the \( |\tilde{m}\rangle \)'s (which do not form an orthogonal set). These vectors are themselves the left eigenvectors of \( \tilde{H} \), or the right eigenvectors of \( H \). Because \( \tilde{H} \) is complex symmetric, the matrix which diagonalizes this Hamiltonian—whose matrix elements are given by \( C_{mn} = \langle m|\tilde{n}\rangle \)—is complex orthogonal, \( C^T C = 1 \). Therefore, the coordinate representation of \( |\tilde{m}\rangle \) is just the complex conjugate of the coordinate representation of \( |\tilde{n}\rangle \).

If a wave packet begins inside the basis, has negligible overlap with the optical potential, and eventually leaves this region, we may represent its dynamics in the basis determined above. Let

\[
|\psi(0)\rangle = \sum c_n |\tilde{n}\rangle = \sum |\tilde{n}\rangle \langle \tilde{n}|\psi(0)\rangle,
\]

where the \( |\tilde{n}\rangle \)'s and \( |\tilde{m}\rangle \)'s have already been defined. Then

\[
|\psi(t)\rangle = \sum |\tilde{n}\rangle \langle \tilde{n}|\psi(0)\rangle e^{-(i\epsilon_n t + i\Gamma_n t)/\hbar}.
\]

III. THE FLUX AND THERMAL FLUX OPERATORS

The operator for flux through a multidimensional configuration space surface \( f \) separating reactants from products is\(^6\)

\[
F = \frac{1}{2\mu} (p \delta(p') + \delta(p') p),
\]

where \( p \) is the multidimensional momentum vector and \( n \) is the unit normal to the surface, \( n = \nabla f / |\nabla f| \). We use the same surface as Park and Light:\(^4\) \( f = R - (\sqrt{3}/2)r \), where \( R \) and \( r \) are the mass-weighted Jacobi coordinates for the collinear problem. In hyperspherical coordinates, this surface is \( f = p \sin(\chi - (\pi/6)) \). Using the transformation equations \( R = p \cos(\chi) \) and \( r = p \sin(\chi) \) and the fact that at \( p = 0 \) all wave functions are zero, we can write the flux operator in Eq. (13) as

\[
F = \frac{\hbar}{2\mu \rho^2} \left[ \delta(\chi - \pi) \frac{\partial}{\partial \chi} + \frac{\partial}{\partial \chi} \delta(\chi - \pi) \right].
\]

This expression has only functional dependence on \( \rho \) and so is diagonal in the \( \rho \) part of the DVR. For each \( \rho \) point, the form of the \( \chi \) dependence of the flux operator is that of a 1D flux operator.\(^14\) The fact that the 1D flux operator has rank 2 has been noted by Park and Light,\(^4\) proven by Miller,\(^16\) and used by Seideman and Miller.\(^17\) Thus, the total number of linearly independent vectors defining the flux operator for collinear \( \text{H}+\text{H}_2 \) is \( 2 \times n_p \). The two linearly independent vectors which define the 1D flux matrix are the basis representations of the Dirac delta function and its derivative, i.e.,

\[
|m\rangle = \frac{\hbar}{2\mu i} \left( \phi_m^* \frac{\partial}{\partial \chi} - \phi_m \frac{\partial}{\partial \chi} \phi_m^* \right)|\chi = \pi/6\rangle
\]

\[
= -\frac{\hbar}{2\mu i} \left( \langle m|\delta\rangle \langle \delta'|n\rangle - \langle m|\delta\rangle \langle \delta'|n\rangle \right),
\]

where \( \langle m|\delta\rangle \) and \( \langle m|\delta'\rangle \) are the projections of the Dirac delta function and its derivative, respectively, onto the \( m \)th basis function. We will label the vectors which define the flux operator \( |\alpha\delta\rangle = |\rho_\alpha\rangle \otimes |\delta\rangle \) and \( |\alpha\delta'\rangle = |\rho_\alpha\rangle \otimes |\delta'\rangle \), where \( |\rho_\alpha\rangle \) is the \( \alpha \)th DVR vector in \( \rho \) and \( |\delta\rangle \) and \( |\delta'\rangle \) are the vectors representing the Dirac delta function and its derivative in \( \chi \).

From the foregoing discussion, we see that the thermal flux operator may be written as...
where

\[ \beta_\alpha = e^{-\left(b/4\right)H} \alpha \delta_\chi_\alpha \]  

and

\[ \beta_\alpha' = e^{-\left(b/4\right)H} \alpha \delta_\chi_\alpha'. \]  

Because the eigenvectors of \( H \) are \( L^2 \), they can be represented accurately in a basis of finite range which we choose to be the basis of Hamiltonian eigenvectors which result from the diagonalization in the previous section (before the addition of the optical potential). Its matrix elements are then computed by

\[ F_{mn} = \frac{1}{2 \mu i} \sum_\alpha e^{-\left(b/4\right)(E_n + E_m)} \left( \langle m | \alpha \delta_\chi_\alpha \langle \alpha \delta_\chi_\alpha | n \rangle \right. \\
\left. - \langle m | \alpha \delta_\chi_\alpha' \langle \alpha \delta_\chi_\alpha' | n \rangle \right). \]  

We now address the question of choice of slope of the optical potential. By imposing upon the wave function in the optical potential region the conditions that less than 1% of the plane wave should be reflected from the inner boundary of the optical potential and that 99% of the wave should be absorbed by the optical potential, Child\(^1\) has derived a pair of inequalities for the slope of a linear optical potential given a 1D plane wave with energy \( E \). His result is\(^9\)

\[ \begin{align*}
V_{\text{min}} &< V_0 < V_{\text{max}}, \\
V_{\text{min}} &= \frac{20 \hbar}{(8m)^{1/2}} \frac{E^{1/2}}{\Delta R^2}, \\
V_{\text{max}} &= \frac{1}{10} \frac{(8m)^{1/2}}{\hbar} E^{1/2},
\end{align*} \]  

where \( \Delta R \) is the range over which the optical potential is nonzero and \( m \) is the asymptotic channel reduced mass, \( \mu \) in our case.

Child's studies were performed for a wave function of fixed momentum, i.e., a plane wave. Since a wave packet is spread over many momenta, the range and slope of the optical potential must be chosen in such a way that all the momentum components are efficiently absorbed. In order to form the matrix elements of the thermal flux operator, we must compute matrix elements of the form \( \langle n | \beta_\alpha \rangle \) and \( \langle n | \beta_\alpha' \rangle \). We take as the energy which dominates the calculation the energy corresponding to the eigenvector which results in the maximum value of \( \langle n | \beta_\alpha \rangle^2 + | \langle n | \beta_\alpha' \rangle^2 \) for any \( \alpha \). The asymptotic kinetic energy \( F \) is estimated by subtracting the zero point vibrational energy of \( H_2 \) from this eigenvalue. The range \( \Delta R \) is as defined in the previous section for the two optical potentials, Eqs. (8a) and (8b). With this data, the minimum and maximum values of \( V_0 \) [the upper and lower limits of the inequalities in Eq. (18)] are computed, and \( V_0 \) is chosen as the geometric mean. As will be seen shortly, a single value of \( V_0 \) may give accurate results over a range of temperatures.

Finally, we transform the thermal flux operator into the eigenbasis of \( H \). We can then calculate the flux autocorrelation function using the partition of unity \( I = \sum_n |\tilde{n}\rangle \langle \tilde{n}| \);

\[ C_{ff}(t) = -\sum_{mn} \langle \tilde{m} | e^{-\left(i/T\right)H} F e^{-\left(i/T\right)\tilde{H}} | \tilde{n} \rangle \langle \tilde{n} | F_{\tilde{m}} | \tilde{m} \rangle, \]  

\[ = \sum_{mn} e^{\left(i/T\right)(\epsilon_n - \epsilon_m)} e^{-\left(i/T\right)(\Gamma_n + \Gamma_m)} \langle \tilde{m} | F_{\tilde{m}} | \tilde{n} \rangle \langle \tilde{n} | F_{\tilde{m}} | \tilde{m} \rangle. \]  

This expression may be simplified by noting that \( F = iG \), where \( G \) is some real operator. Then

\[ \langle \tilde{m} | F_{\tilde{m}} | \tilde{n} \rangle = (\langle \tilde{n} | F_{\tilde{m}} | \tilde{m} \rangle)^*, \]  

\[ = -i \langle \tilde{n} | G | \tilde{m} \rangle, \]  

\[ = -\langle \tilde{n} | F_{\tilde{m}} | \tilde{m} \rangle \]  

so that Eq. (19) becomes

\[ C_{ff}(t) = -\sum_{mn} e^{\left(i/T\right)(\epsilon_n - \epsilon_m)} e^{-\left(i/T\right)(\Gamma_n + \Gamma_m)} \langle \tilde{m} | F_{\tilde{m}} | \tilde{n} \rangle \langle \tilde{n} | F_{\tilde{m}} | \tilde{m} \rangle^2. \]  

Note that this expression is manifestly real, as it should be; each term in the sum is added to its complex conjugate. At last, we integrate this expression from zero to infinity, giving

\[ k(T)Q = \sum_{mn} \frac{\hbar}{(i \epsilon_n - \epsilon_m) - (\Gamma_n + \Gamma_m)} \langle \tilde{m} | F_{\tilde{m}} | \tilde{n} \rangle \langle \tilde{n} | F_{\tilde{m}} | \tilde{m} \rangle^2. \]  

Note that in Eqs. (21) and (22), unlike Eq. (4), the \( m = n \) term appears in the summation. This condition occurs because the eigenfunctions of \( H \) are complex. If they were viewed as the initial condition for an ordinary propagation, they would transport momentum across the flux surface, and so the mean value of the flux (and thermal flux) operator in these states is nonzero.

**IV. RESULTS**

The results in this section are for the thermal rate constant for the collinear \( \text{H} + \text{H}_2 \) reaction. For purposes of comparison, we give the exact rate constants in the second column of Table II and rate constants computed with the optical potential in Eq. (8a) in the third, together with the values of the parameters in Table I; these values are sufficient to converge the results but probably larger than necessary. The exact results were calculated in a real DVR basis (the conventional way, as discussed in the introduction). We note in passing that the value of \( E_{\text{cut}} \) required to converge the rate constants—3.26 eV—is considerably higher than that required to converge the eigenvalues up to the reaction barrier height to four significant figures; in fact, \( E_{\text{cut}}^{1D} = 2.2 \) eV will converge the eigenvalues to four
TABLE II. Exact values for \( k(T) \). The third column contains \( k(T) \) as computed with the optical potential in Eq. (8a) with \( \rho_{\text{max}} = 7.5 a_0 \) and \( R_0 = 5.5 a_0 \). The slopes \( V_0 \) which accompany \( k_{\text{op}} \) are given in eV/\( a_0 \). All rate constants are in cm/molecule/s. \( \rho_{\text{min}} = 2 a_0 \) for all calculations.

<table>
<thead>
<tr>
<th>( T(K) )</th>
<th>( k_{\text{ex}}(T) )</th>
<th>( k_{\text{op}}(T), V_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>4.8 ( a_0 )</td>
<td>4.82, 0.167</td>
</tr>
<tr>
<td>500</td>
<td>225 ( a_0 )</td>
<td>225, 0.217</td>
</tr>
<tr>
<td>1000</td>
<td>66.8 ( a_0 )</td>
<td>66.6(3), 0.333</td>
</tr>
<tr>
<td>1500</td>
<td>2.2(4) ( a_0 )</td>
<td>2.2(1), 0.333</td>
</tr>
<tr>
<td>2000</td>
<td>4.2(4) ( a_0 )</td>
<td>4.1(6), 0.333</td>
</tr>
<tr>
<td>2400</td>
<td>5.8(4) ( a_0 )</td>
<td>5.9(1), 0.333</td>
</tr>
</tbody>
</table>

*The integration time for all calculations was 6.46 ps.

TABLE III. Percent error in \( k(T) \) for different \( \rho_{\text{max}} \). The optical potential \( a_0 \) is given by Eq. (8a). Table III(a) and III(b) are identical to their counterparts in Table IV (a) and IV (b). All distances are in \( a_0 \) for all calculations.

<table>
<thead>
<tr>
<th>( \rho_{\text{max}} )</th>
<th>( k(300 \text{ K}) )</th>
<th>( k(500 \text{ K}) )</th>
<th>( k(1000 \text{ K}) )</th>
<th>( k(2000 \text{ K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>7.5</td>
<td>0.2</td>
<td>0.4</td>
<td>-0.3</td>
</tr>
<tr>
<td>6.5</td>
<td>-0.2</td>
<td>-0.2</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>5.5</td>
<td>-8.5</td>
<td>-3.6</td>
<td>-5.6</td>
<td>-3.3</td>
</tr>
<tr>
<td>5.0</td>
<td>-38.4</td>
<td>-44.8</td>
<td>-34.3</td>
<td>-34.3</td>
</tr>
</tbody>
</table>

*The optical potential slopes \( V_0 \) in eV/\( a_0 \) for the 7.5, 6.5, 5.5, and 5.0 calculations, respectively, are given in the footnotes below.

V. DISCUSSION

For large \( \rho_{\text{max}} \), the shorter-range optical potential from Eq. (8b) actually performs slightly better than either the long- or short-range potential of Eq. (8a); however, the relative performance of the \( \rho \)-dependent optical potential degrades rapidly as \( \rho_{\text{max}} \) is decreased. The reason for the discrepancy is probably that we determine the ranges of the optical potentials solely by their extents along the line \( \chi \) the slightest pretense to accuracy. The errors for large \( \rho_{\text{max}} \) are perceptible even on the log scale, particularly for the lower temperatures. On each curve in both Figs. 2 and 3, the center cross corresponds to the \( V_0 \) for that temperature; the left and right crosses represent \( V_{\text{min}} \) and \( V_{\text{max}} \), respectively, as computed from Eq. (18).

TABLE IV. Percent error in \( k(T) \) for different \( \rho_{\text{max}} \). The optical potential \( a_0 \) is given by Eq. (8b) with \( \rho_0 = \rho_{\text{max}} = 2.0 a_0 \) in part (a) of the table and \( \rho_0 = \rho_{\text{max}} = 1.5 a_0 \) in part (b). All distances are in \( a_0 \) for all rate constants are in cm/molecule/s.

<table>
<thead>
<tr>
<th>( \rho_{\text{max}} )</th>
<th>( k(300 \text{ K}) )</th>
<th>( k(500 \text{ K}) )</th>
<th>( k(1000 \text{ K}) )</th>
<th>( k(2000 \text{ K}) )</th>
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<td>5.5</td>
<td>-8.5</td>
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<td>-3.3</td>
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<tr>
<td>5.0</td>
<td>-38.4</td>
<td>-44.8</td>
<td>-34.3</td>
<td>-34.3</td>
</tr>
</tbody>
</table>

The optical potential slopes \( V_0 \) in eV/\( a_0 \) for the 7.5, 6.5, 5.5, and 5.0 calculations, respectively, are given in the footnotes below.

The slope \( V_0 \) is the geometric mean of these two numbers anyway.
Along the edges denote the exact rate constants.

The short horizontal bars along the edges denote the exact rate constants.

The units of $k(T)$ are cm/molecule/s; those of $V_o$ are eV/$a_o$. The short horizontal bars along the edges denote the exact rate constants.

When $\rho_{\text{max}}$ is large, the effects of the two optical potentials are roughly the same (for fixed range) since any vibrational wave functions will be zero in the regions where they differ appreciably. However, when $\rho_{\text{max}}$ is decreased (again keeping the range fixed for both forms), the $\rho$-dependent optical potential encroaches more rapidly on the interaction region, thereby interfering with the dynamics of the thermal flux eigenvectors which determine the rate. By the time $\rho_{\text{max}}$ is $5\ a_0$, the most accurate rate constant calculated with the $\rho$-dependent optical potential of either range—the short range calculation of $k(2000\ K)$—differs from the exact result by 12%, comparable to the 16% error in the least accurate result—$k(300\ K)$—for the short-range $R$-dependent optical potential.

In all cases, the degradation of the accuracy of the rate constant as $\rho_{\text{max}}$ is decreased is the more pronounced the lower the temperature. This effect is simply a reflection of the more extensively delocalized nature of the low-temperature thermal eigenvectors.\footnote{Inspection of Fig. 2 suggests that $V_{\text{min}}$ and $V_{\text{max}}$ serve as rather conservative estimates of the limits of the range of slopes which will give an accurate result. Indeed, in some of the calculations, it turned out that the $V_{\text{min}} > V_{\text{max}}$ yet their geometric mean gave a reasonable answer, at least for optical potential (8a) [see Tables III(b) and IV(b)]. We include Fig. 3 in order to show that when the basis range becomes small enough that the rate constant depends sensitively on the slope of the optical potential, the scheme used here for determining $V_o$ [Eq. (18)] gives optimal, or nearly optimal, estimates of the rate constant. Another very important result of this study which is apparent from both Figs. 2 and 3 is that the $V_o$'s for the low-temperature fall within ranges of $V_o$ for which the error in the higher-temperature rate constant is small. This observation means that once an optical potential for the determination of a lower-temperature rate constant has been found, it will work for higher-temperature rate constants as well; thus the diagonalization of $\mathbf{H}$ need only be done once for a range of temperatures. Both Figs. 2 and 3 suggest that the low-temperature rate constants deteriorate more drastically as $V_o$ is increased. This result may be rationalized by the observation that the low-temperature thermal flux eigenvectors are more strongly confined to low energies, and so are more susceptible to scattering from the discontinuity in derivatives of the linear optical potentials at their inner boundaries.}

We now make a few comments concerning the efficiency of this technique. We note that if we can reduce the range of the basis, we can reduce the size as well. The result for $k_{\text{opt}}(2000\ K)$ in Table II can be converged to three significant figures on range $\rho \in (2\ a_0, 7.5\ a_0)$ using 24 points in $\rho$, 24 in $\chi$, and with an $E_{\text{cut}}$ of 3.26 eV and an $E_{\text{cut}}^{2D}$ of 2.7 eV. The resulting truncated basis sizes were $N_{1D} = 264$ and $N_{2D} = 107$. By comparison, the same degree of convergence for $k(2000\ K)$ when $\rho_{\text{max}} = 5.5\ a_0$ and using the short-range potential in Eq. (8a) can be achieved with 20 $\rho$ points, 20 $\chi$ points, and with $E_{\text{cut}}^{2D}$ of 2.7 eV and an $E_{\text{cut}}^{2D}$ of 2.7 eV. In this case, $N_{1D} = 159$ and $N_{2D} = 57$, a decrease of nearly a factor of 2. The total CPU time required by the second calculation for diagonalization is roughly a factor of 8 less than the time required by the first, although their accuracies are comparable. The actual decrease in computational effort (if any) will of course depend on the temperature and the desired degree of accuracy in the rate constant. For the case of H+H₂, a further reduction in basis size by a factor of 2—and the total CPU time required for diagonalization by a factor of 4—can be achieved by symmetry adapting the basis in $\chi$. Whitnell and Light have given the details of how to symmetry adapt a DVR\footnote{20} and the $C_{2v}$ symmetry of the H+H₂ reaction, and some of its isotopomers has been exploited by Park and Light.\footnote{7}}
We did not examine the value of other functional forms for the optical potentials, as suggested by Vibók and Balint-Kurti\textsuperscript{21} and by Seideman and Miller.\textsuperscript{17} Their studies suggest that an even greater savings may be obtained by using such a more general optical potential than the linear forms used here.

The recent study of the microcanonical rate constant by Seideman and Miller\textsuperscript{17} is very closely related to the study presented here. In their formalism, this rate constant is given by

\begin{equation}
N(E) = R \left( \text{Tr} [ G^* (E) - FGFG] \right),
\end{equation}

where $R$ denotes the real part. The exact Green's operator $G^+(E) = (E - \hat{H} + i\epsilon)^{-1}$ is replaced by $\left( E - \hat{H} \right)^{-1}$. The authors accomplish the evaluation of the Greens operator by direct matrix inversion. We note, however, that $\left( E - \hat{H} \right)^{-1}$ has the same eigenvectors as $\hat{H}$. By transforming the flux operator into the eigenbasis of $\hat{H}$, the matrix inversion required in Eq. (23) becomes simple multiplication by the eigenvalues $\left( E - \epsilon_n \pm i\tau_n \right)^{-1}$ [the operator $G^*$ is equal to $\left( E - \hat{H} \right)^{-1}$], allowing the rapid computation of the microcanonical rate constant at several energies from the result of a single complex diagonalization. Thus, the techniques described in this paper may be fruitfully applied to the microcanonical rate constant formalism as well.

In summary, we have diagonalized a Hamiltonian with an optical potential using the technique of successive diagonalization/truncation, and shown that this artifice can be used to reduce both the range and the basis size required to compute the thermal rate constant. Furthermore, the upper limit of integration of the flux autocorrelation function can be taken to infinity, thus eliminating the residual time dependence in the thermal rate constant formalism caused by the finite basis. It is likely that in cases where the reacting species form a complex so that the flux autocorrelation function decays slowly, such a technique will be not only convenient but necessary.

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16. W. H. Miller (private communication).
19. This expression is not quite the same as that reported by Child; the discrepancy is due to the fact that Child's $V_{ij}$ is equal to $V_{ij} R$.