Accurate quantum thermal rate constants for the three-dimensional \( \text{H} + \text{H}_2 \) reaction\(^a\)

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The rate constants for the three-dimensional \( \text{H} + \text{H}_2 \) reaction on the Liu–Siegbahn–Truhlar–Horowitz (LSTH) surface are calculated using Pack–Parker hyperspherical (APH) coordinates and a \( C_{3v} \) symmetry adapted direct product discrete variable representation (DVR). The \( C_{3v} \) symmetry decomposition and the parity decoupling on the basis are performed for the internal coordinate \( \chi \). The symmetry decomposition results in a block diagonal representation of the flux and Hamiltonian operators. The multisurface flux is introduced to represent the multichannel reactive flux. The eigenvalues and eigenvectors of the \( J = 0 \) internal Hamiltonian are obtained by sequential diagonalization and truncation. The individual symmetry blocks of the flux operator are propagated by the corresponding blocks of the Hamiltonian, and the \( J = 0 \) rate constant \( k^J(T) \) is obtained as a sum of the rate constants calculated for each block. \( k^J(T) \) is compared with the exact \( k^J(T) \) obtained from thermal averaging of the \( J = 0 \) reaction probabilities; the errors are within 5%–20% up to \( T = 1500 \text{ K} \). The sequential diagonalization–truncation method reduces the size of the Hamiltonian greatly, but the resulting Hamiltonian matrix still describes the time evolution very accurately.

For the \( J \neq 0 \) rate constant calculations, the truncated internal Hamiltonian eigenvector basis is used to construct reduced \( \langle JK \rangle \) blocks of the Hamiltonian. The individual \( \langle JK \rangle \) blocks are diagonalized neglecting Coriolis coupling and treating the off-diagonal \( K_j \pm 2 \) couplings by second order perturbation theory. The full wave function is parity decoupled. The rate constant is obtained as a sum over \( J \) of \( (2J + 1)k^J(T) \). The time evolution of the flux for \( J \neq 0 \) is again very accurately described to give a well converged rate constant.

I. INTRODUCTION

A theoretical and quantitative description of chemical reactions can be made by determining the reaction dynamics, i.e., by solving the motion of the nuclei on the Born–Oppenheimer potential energy surface. The traditional approach to the dynamics is via classical mechanics which describes the trajectories of nuclei by numerically integrating the classical equations of motion. However, at the molecular level the description of the dynamics frequently requires quantum mechanics because of unique quantum effects such as tunneling, resonances, etc.

The quantum approach provides the microscopic dynamical information by solving the Schrödinger equation with proper boundary conditions. The main effort in the quantum theory of reaction dynamics has been focused on solving the scattering via the time independent Schrödinger equation. Although less widely applied, the time-dependent wave packet propagation method has also been applied to a variety of dynamical problems.\(^1\)–\(^6\)

The time-independent approach is the most direct approach to state specific dynamical information. However, for the determination of the thermal rate constant, it may not be the most economical in terms of computational efficiency for the following reasons: (1) the full exact quantum calculations must be repeated at a large number of energies and up to a large total angular momentum to get the accurate thermal averages, (2) in the course of summing over final states and the thermal averaging, enormous amounts of state specific information may be completely buried. Due to the rapid growth with energy of the number of open vibration–rotation states at thermally accessible collision energies, the calculation of rate constants via exact quantum state-to-state calculations may not be feasible even for quite simple reactions. Thus, the development of an economical way of determining the rate constant directly and accurately is required (or at least is very desirable).

The traditional (approximate) way of evaluating the rate constant directly is the well known transition state theory (TST).\(^7\) However, TST is inherently approximate because it does not account for recrossings of the system over the transition state dividing surface. Numerous refinements and modifications have been tried to count the barrier recrossings.\(^8\) In variational state theory\(^9\) the effects of recrossing are minimized by locating the transition state surface variationally to minimize the calculated rate. In addition quantum tunneling is treated in an ad hoc fashion in most applications of TST, although there are widely used tunneling correction schemes.\(^9\) Several workers have tried to develop a quantum version of the TST\(^9\) as a zero time approximation to the exact dynamics. However, even the quantum TST does not treat recrossings exactly. Overall, however, variational TST is currently the most accurate general approach to thermal reaction rate calculations.\(^9\)

Miller\(^{10,11}\) and Yamamoto\(^{12}\) separately derived formally exact expressions for the rate constant as a time integral of

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the flux–flux autocorrelation function. This approach is exact in the limit that the dynamics are extended to }t \to \infty\text{. In this approach, the thermally averaged rate constant is determined by time-dependent dynamics while in the time-independent approaches, the rate constants (including state specific dynamical information) are obtained by averaging over the scattering energy, formally over } E \text{ from } 0 \to \infty\text{. The difference between the exact time-dependent approach and the quantum TST is that in the exact approach the projection of the flux onto the positive momentum state is performed for } t \text{ on } (0, \infty)\text{ while in the quantum TST the projection is carried out at } t = 0 \text{ only. This is why the exact method counts the flux recrossing while the quantum TST does not.}

Since the flux–flux autocorrelation is evaluated via time-dependent quantum mechanics, the feasibility of this method depends on the accurate and efficient evaluation of the flux, the Hamiltonian, and the time evolution operator, \( \exp\{-i \mathbf{H} t / \hbar\}\). It is easily understood that this exact approach is especially appropriate for short time collision processes. Several studies have been done to determine rate constants using this method for one-dimensional model problems,\textsuperscript{13} collinear reactions of \( \mathsf{H} + \mathsf{H}_2\),\textsuperscript{14} approximate \( J = 0 \) three-dimensional\textsuperscript{15} \( \mathsf{H} + \mathsf{H}_2\) reactions, and for surface diffusion of gases.\textsuperscript{16} Most of these studies yielded very promising results. In this work, the flux–flux autocorrelation technique is applied to the calculated thermal rate constants of the three-dimensional \( \mathsf{H} + \mathsf{H}_2\) reaction. We use an LSTH potential energy surface\textsuperscript{17,18} and employ Pack–Parker hyperspherical (APH) coordinates.\textsuperscript{19,20} The numerical implementation is performed using the powerful and efficient algorithms, of the direct product discrete variable representation (DVR)\textsuperscript{21} for the basis representation and the sequential diagonalization truncation\textsuperscript{22} for the diagonalization of the Hamiltonian. The \( \mathsf{H} + \mathsf{H}_2\) reaction is the best system for the initial application of the direct rate constant formalism for several reasons. First, the \( \mathsf{H} + \mathsf{H}_2\) reaction is the most extensively investigated system theoretically and has been studied experimentally. As a result the accurate LSTH potential energy surface for theoretical studies, and experimental results are available rendering a comparison between theory and experiment possible. Very recently, a number of accurate quantum calculations have been done on this system for selected energies and angular momenta by Haug et al., Zhang and Miller, Webster and Light, and Schatz.\textsuperscript{23} Second, the \( \mathsf{H} + \mathsf{H}_2\) reaction is known to be a short-time dynamical process with a collinear transition state, thus simplifying the application of theoretical approaches. Third, the \( \mathsf{H} + \mathsf{H}_2\) reaction is the simplest chemical reaction possible, and thus could be the testing ground for measuring the accuracy and efficiency of the direct rate constant formalism. The results have implications for its possible applications to more complex systems.

The composition of this paper is as follows. In Sec. II, a brief review of the flux–flux autocorrelation approach to the reaction rate constant and definitions of the flux are given including the derivation of the coordinate specific expression of the flux. In Sec. III, details of the application to the three-dimensional \( \mathsf{H} + \mathsf{H}_2\) reaction are described, and in Sec. IV, the results and discussion as well as the comparison with other works are provided. Section V contains the conclusions of this work.

II. THEORY

A. Flux–flux autocorrelation function

The exact quantum mechanical thermal rate constant \( k(T) \) is given as a time integral of the flux–flux autocorrelation function \( C_f(t) \) according to Miller et al.\textsuperscript{11} and Yamamoto\textsuperscript{12} as,

\[
k(T) = Q_R^{-1} \int_0^\infty C_f(t) dt, \tag{2.1}
\]

where \( Q_R \) is the partition function of the reactants.

The flux–flux autocorrelation function \( C_f(t) \) is defined as the quantum mechanical flux correlation function;

\[
C_f(t) = tr \{ \mathbf{F}(t) \mathbf{F}(0) \}. \tag{2.2}
\]

The flux \( \mathbf{F}(t) \) is evaluated at time \( t = t_c \) on a coordinate surface dividing reactants and products. The complex time \( t_c \) is \( t_c = t - [i \hbar \beta / 2] \), where \( \beta = 1 / kT \). The Heisenberg representation of the flux operator \( \mathbf{F}(t_c) \) is explicitly written in terms of a complex time evolution operator \( \exp\{i \mathbf{H} t_c / \hbar\} \) as,

\[
\mathbf{F}(t_c) = \exp\{ -i \mathbf{H} t_c / \hbar\} \mathbf{F}(0) \exp\{i \mathbf{H} t_c / \hbar\}, \tag{2.3}
\]

where \( \mathbf{H} \) is the time-independent Hamiltonian of the system.

The flux operator at \( t = 0 \) is defined by

\[
\mathbf{F}(0) = \frac{\hbar}{2\mu} \left\{ \mathbf{s} \cdot \nabla \mathbf{s} \cdot \mathbf{p} + \mathbf{p} \cdot \nabla \mathbf{s} \right\}, \tag{2.4}
\]

where \( \mu \) is the reduced mass of the system, \( \mathbf{p} \) is the momentum operator, and \( s = s(q) \) is the equation of a surface separating reactants and products at which the flux is measured. The derivative \( \nabla s \) is the derivative normal to the surface \( s \).

The rate constant so defined is independent of the choice of the surface at which the flux is measured in this direct rate constant formalism since it is determined by the exact time-dependent dynamics. This makes it possible to express the rate constant in terms of the flux in the derivation. In other words, the \( S \) matrix is related to the flux only when the flux is measured in asymptotic regions or over long times. When the rate constant is approximated in a local time-dependent fashion as in the TST [by the instantaneous treatment \( t = 0 \) of the time-dependent dynamics at a surface], then the approximate rate constant depends on the surface chosen at which to measure the flux. Therefore, the best choice of the surface has been pursued for such approximate calculations. However, for the exact rate constant calculations, the “flux measuring” or transition state surface is usually chosen for convenience. Because of the symmetry for \( \mathsf{H}_2 \), the transition state surface which divides the reactants and products at the barrier maximum is optimal for both approximate and exact calculations.

The flux–flux autocorrelation function \( C_f(t) \), in the Hamiltonian eigenvector representation of an \( \mathcal{L}^2 \) basis,\textsuperscript{1} is

\[
C_f(t) = \sum_{ij} \exp\{ -\beta (E_i + E_j) t / \hbar\} \langle i | \mathbf{F} j \rangle^2, \tag{2.5}
\]
Since in a finite $L^2$ basis the exact time evolution cannot be represented for $t \to \infty$ for an unbound system, we may evaluate Eq. (2.1) at a time $\tau$ which is sufficiently large for the integrand $C_r(t)$ to approach zero, and sufficiently small such that the basis has represented the time evolution of $C_r(t)$ accurately. For a sufficiently large and distributed basis, such a time should exist. For direct reactions it may be quite small.

The rate constant $k(T)$ is then given by

$$k(T)Q_0 = \sum_{ij} \exp\left[ -\beta(E_i + E_j)/2 \right] \times \frac{\sin\left[ (E_i - E_j)(\tau/4\pi) \right]}{E_i - E_j} \left| (\ell | \mathbf{F}_J) \right|^2,$$  

(2.6)

where $E_i$ is the $i$th eigenvalue of the Hamiltonian. Because the flux operator is antisymmetric, the flux from a state to itself is identically zero. Because of symmetry properties, this also holds for degenerate states related by symmetry, and no terms in Eq. (2.6) become singular.

The feasibility of implementation of this formally exact approach to rate constants depends on the accuracy and the efficiency of evaluation of the time evolution of the flux. Especially when a reaction proceeds via long lived collision complexes, this formalism will require new efficient methods for the time evolution of a “flux” wave packet.

**B. Flux**

The flux operator defined as in Eq. (2.4) represents the surface normal component of the local velocity at $s = 0$ and is Hermitian. Due to its physical nature, the flux operator is a singular operator whose largest eigenvalues go to infinity and the corresponding eigenvectors are localized as the representation becomes exact.

The coordinate specific formula for the flux can be derived by expressing the gradient $\nabla$ in the contravariant basis vectors as,

$$\nabla = \sum_i \frac{\partial}{\partial q^i} \hat{\mathbf{e}}^i$$  

(2.7)

where $\hat{\mathbf{e}}^i$ is the $i$th unit vector. Then $\nabla \cdot \mathbf{p}$ is represented as

$$\nabla \cdot \mathbf{p} = \frac{\hbar}{i} \nabla \cdot \mathbf{v}$$

$$= \frac{\hbar}{i} \sum_{ij} \frac{\partial s}{\partial q^j} \hat{\mathbf{e}}^i \cdot \frac{\partial}{\partial q^j} \hat{\mathbf{e}}^i$$

$$= \frac{\hbar}{i} \sum_{ij} g^i_{ij} \frac{\partial s}{\partial q^j} \frac{\partial}{\partial q^i},$$  

(2.8)

where $g^i_{ij}$ is the $ij$th component of the contravariant metric tensor. The metric tensor for a specific coordinate system is obtained from its relation to Cartesian coordinates. The flux in a specific coordinate system is then

$$F = \frac{\hbar}{2\mu} \sum_{ij} \delta(s) \frac{\partial s}{\partial q^j} \frac{\partial}{\partial q^i} \delta(s).$$

(2.9)

Since the surface is a function of the coordinates, a simple and symmetric form of the surface in terms of the coordinates will lead to a simple and convenient expression for the flux operator. The conventional transition state surface belongs to this category because it divides the reactants and products in a symmetrical fashion. However, there is no simple way of choosing the best surface. Since the asymptotic chemical channels can be defined as functions of internal coordinates only, the flux measuring surface can also be defined in these internal coordinates only. If a surface can be found which divides reactants and products symmetrically and provides the rapid decay of the flux–flux autocorrelation function in a finite period of time, then it is a good surface.

In reactions with multiple chemical arrangement channels, the introduction of a multisurface flux operator is needed because the flux from one arrangement to all other arrangements should be considered. The application to a multichannel reaction is carried out below in the rate constant calculations of the three-dimensional $H + H_2$ reaction.

**III. NUMERICAL IMPLEMENTATION**

The thermal rate constant calculation for $J = 0, k^0(T)$, is performed employing the Pack–Parker hyperspherical coordinate system (APH coordinates), 19,20 The $J = 0$ Hamiltonian or internal Hamiltonian ($H_{\text{int}}$) and the flux are represented in terms of a $C_2v$ symmetry adapted direct product DVR basis. Symmetry decomposition of the DVR basis is performed for one internal coordinate $\chi$. The eigenvalues and eigenvectors are evaluated by the sequential diagonalization–truncation procedure and the flux is successively transformed by the truncated eigenvectors of the internal Hamiltonian to the Hamiltonian eigenvector basis for the time evolution. By the symmetry decomposition of the basis in the $\chi$ coordinate, the Hamiltonian and the flux are block diagonal. A specific symmetry block of the flux is propagated by the corresponding block of the Hamiltonian. Then the overall flux–flux autocorrelation function and the rate constant are evaluated as sums of the individual symmetry block results. The truncated eigenvectors of the internal Hamiltonian (i.e., $J = 0$) are used as the basis for the $J \neq 0$ rate constant calculations.

For $J \neq 0$ rate constants, the individual $(J|k_J)$ blocks of the Hamiltonian in the basis of $J = 0$ eigenvectors are diagonalized. The full wave function is parity decoupled. $K_J \pm 2$ couplings (between $K_J$ and $K_J' = K_J \pm 2$) are handled by the second order perturbation theory and the Coriolis interaction is neglected. The perturbation result is compared with the exact treatment of the $K_J \pm 2$ couplings.

Both in $J = 0$ and $J \neq 0$ rate constant calculations, the indistinguishability of the component nuclei is considered.

**A. Hamiltonian and flux**

In the APH coordinates, the Hamiltonian is written as

$$H = H_{\text{int}} + \frac{\hbar}{2} \left[ J^2 + \left( C - \frac{\hbar}{2} \right) J_s^2 \right]$$

$$+ \frac{A - B}{2} (J^2_+ + J^2_-) - \mathbf{J} \cos \theta \frac{\partial}{\partial \chi_i},$$

(3.1)

where $H_{\text{int}}$ is the $J = 0$ Hamiltonian given as

$$H_{\text{int}} = \left[ \frac{\hbar^2}{2\mu} \frac{\partial}{\partial \theta} \sin^2 \theta \frac{\partial}{\partial \phi} + \frac{\hbar^2}{2\mu \rho^2} \frac{\partial^2}{\partial \rho^2} \right]$$

$$+ \left( \frac{4}{\sin 2\theta} \frac{\partial}{\partial \theta} \sin 2\theta \frac{\partial}{\partial \phi} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \chi^2} \right) + V(\rho, \theta, \chi_i),$$

(3.2)
where \( \rho, \theta, \text{ and } \chi_i \) are three internal hyperspherical coordinates with the volume element \((1/16)\rho^2 d\rho \sin \theta d\theta d\chi_i\). The range of each coordinate is \(0 < \rho < \infty\), \(0 < \theta < \pi/2\) and \(0 < \chi_i < 2\pi\), respectively. The three coefficients for the external rotations are functions of \( \rho \) and \( \theta \):

\[
A(\rho, \theta) = \frac{1}{\mu \rho^2 (1 + \sin \theta)},
\]

\[
B(\rho, \theta) = \frac{1}{2 \mu \rho^2 \sin^2 \theta},
\]

\[
C(\rho, \theta) = \frac{1}{\mu \rho^2 (1 - \sin \theta)}.
\]

The three principal moments of inertia are

\[
I_x = \mu \rho^2 (1 + \sin \theta),
\]

\[
I_y = \mu \rho^2,
\]

and

\[
I_z = \mu \rho^2 (1 - \sin \theta).
\]

After wave function factorization by \( \rho^{5/2} \) the internal Hamiltonian becomes:

\[
H_{\text{int}} = \frac{-\hbar^2}{2\mu} \left[ \frac{\partial^2}{\partial \rho^2} + \frac{4}{\rho^2 \sin 2\theta} \frac{\partial}{\partial \theta} \sin 2\theta \frac{\partial}{\partial \theta} + \frac{1}{\rho^2 \sin^2 \theta} \frac{\partial^2}{\partial \chi_i^2} \right] + V(\rho, \theta, \chi_i) + \frac{15 \hbar^2}{8 \mu \rho^2}.
\]

The flux in APH coordinates is obtained using the coordinate specific expression of Eq. (2.8). The equation of the surface \( s \) through which the flux is measured is formally a function of all six coordinates including three Euler angles.

The potential energy surface is highly symmetric in \( \chi_i \) as is given in Fig. 1 which shows the \( \text{H} + \text{H}_2 \) potential energy contours at \( \rho = 5.0 \, a_p \) as a function of \( \chi_i \) and \( \theta \) for \( 0 < \chi_i < \pi \). The minimum energy path (MEP) crosses \( \chi_i = \pi/6 \) perpendicularly, which divides the reactants and the products symmetrically. Therefore, constant \( \chi_i = (\pi/6) \) is a possible transition state at \( \rho = 5.0 \, a_p \) for this reaction channel. Figure 1 shows that the same potential for \( 0 < \chi_i < \pi/3 \) is repeated representing the different channels for the symmetric \( \text{H} + \text{H}_2 \) system. There are six reaction channels which are all equivalent for \( \text{H} + \text{H}_2 \) reactions, two channels for each arrangement \( \alpha, \beta, \text{ and } \gamma \), respectively (due to the range of \( \chi_i \)). All six flux measuring surfaces are located between these channels. The equations of these surfaces are then

\[
\chi' = \frac{\pi}{6} + (j - 1) \frac{\pi}{3}, \quad j = 1, \ldots, 6.
\]

These surfaces provide the correct geometries of the transition states and are the best surfaces for our flux operator. Given these surfaces, the flux operator can be written as

\[
F = \frac{\hbar}{2 \mu} \sum_{i=1}^{6} \left[ \delta(\chi - \chi') \frac{\partial}{\partial \chi} + \frac{\partial}{\partial \chi} \delta(\chi - \chi') \right]
\]

\[
= \frac{\hbar}{2 \mu \rho^2 \sin^2 \theta} \sum_{i=1}^{6} \left[ \delta(\chi - \chi') \frac{\partial}{\partial \chi} + \frac{\partial}{\partial \chi} \delta(\chi - \chi') \right],
\]

where \( g^{\chi} \) is the \( \chi \)-component of the metric tensor. The flux given in Eq. (3.11) is the total flux of the system between all three different arrangements as shown in Fig. 2. The total flux can be represented as a sum of channel-to-channel fluxes as

\[
F = F^{\alpha\beta} + F^{\beta\gamma} + F^{\gamma\alpha}.
\]

However, the flux which contributes to the reactions is the flux from one channel to the other two channels. This might be called the reactive flux. The reactive flux from channel \( \alpha \), \( F^{\alpha} \) is a sum of the two channel-to-channel fluxes as

\[
F^{\alpha} = F^{\alpha\beta} + F^{\alpha\gamma}.
\]

In Fig. 3, \( F^{\alpha\beta} \) and \( F^{\alpha\gamma} \) are illustrated. The designations of the three channels on the potential energy surface provides an easy identifications of the surfaces between the corresponding channels. If \( \alpha, \beta \), and \( \gamma \) are designated as \( 0 < \chi < \pi/6 \), \( \pi/6 < \chi < \pi/2 \), and \( \pi/2 < \chi < 5\pi/6 \), respectively, then surfaces between \( \alpha - \beta, \beta - \gamma \), and \( \gamma - \alpha \) will be \( \chi = \pi/6, \pi/2, \text{ and } 5\pi/6 \). Since \( \chi \) extends to \( 2\pi \), the corresponding surfaces for \( \chi \) between \( \pi \) and \( 2\pi \) will be \( \chi = 7\pi/6 \) \( (\alpha - \beta) \), \( \chi = 3\pi/2 \) \( (\beta - \gamma) \), and \( 11\pi/6 \) \( (\gamma - \alpha) \). The detailed expressions of the channel-to-channel fluxes are

![FIG. 2. Three individual channel-to-channel fluxes.](image)

![FIG. 3. Reactive flux from channel \( \alpha \) represented as a sum of two channel-to-channel fluxes.](image)
\[
F^{\alpha - \beta} = \frac{\hbar}{2\mu^0 \sin^2 \theta} \left[ \delta \left( \frac{\chi - \pi}{6} \right) \frac{\partial}{\partial \chi} + \frac{\partial}{\partial \chi} \delta \left( \frac{\chi - \pi}{6} \right) \right] \\
+ \left[ \delta \left( \frac{\chi - 7\pi}{6} \right) \frac{\partial}{\partial \chi} + \frac{\partial}{\partial \chi} \delta \left( \frac{\chi - 7\pi}{6} \right) \right],
\]
\[ (3.14) \]

Since \( F^{\alpha - \gamma} \) has opposite directionality to \( F^{\alpha - \alpha} \) and thus decreases with increasing \( \chi \), Eq. (3.15) has a negative sign. Constructing the reactive flux \( F^{\alpha} \) from two channel-to-channel fluxes makes \( F^{\alpha} \) symmetric with respect to \( \chi = \pi/2 \) and thus allows \( C_{2v} \) spatial symmetry decomposition.

**B. Basis representation**

The internal Hamiltonian, \( H_{\text{int}} \) [Eq. (3.2)], and the flux are evaluated using the direct product finite basis representation (FBFR) basis and then transformed to the DVR for implementation of the sequential diagonalization truncation. For one internal coordinate \( \chi \), \( C_{2v} \) symmetry adapted bases \( 27 \) are used since the internal Hamiltonian and the flux are symmetric in \( C_{2v} \) representation. Although the internal Hamiltonian can be evaluated easily with symmetry \( D_{3h} \) for this particular reaction, the reactive flux cannot. Therefore, the \( C_{2v} \) group is the highest symmetry group to be used simultaneously for both operators.

The FBFR bases chosen for coordinate \( \rho \) are the Chebyshev polynomials of the first kind \( T_n(\cos \xi) \) and the angular variable \( \xi \) is obtained by the simple manipulation from \( \rho \) as
\[
\xi = \frac{\rho - \rho_{\text{min}}}{\rho_{\text{max}} - \rho_{\text{min}}} \pi ,
\]
\[ (3.16) \]
where \( \rho_{\text{min}} \leq \rho \leq \rho_{\text{max}} \) is the range required for the description of motion along \( \rho \) and is determined in the numerical implementation. Equation (3.16) gives the correct range for \( T_n(\cos \xi) \) as \( 0 \leq \xi \leq \pi \). Since the motion along \( \rho \) is unbounded and the Chebyshev polynomial basis provides an evenly spaced quadrature in the DVR, it is the most appropriate translational basis. The Chebyshev polynomial \( T_n(\cos \xi) \)
\[
T_n(\cos \xi) = \cos n\xi.
\]
\[ (3.17) \]
An unusual feature of the APH coordinate system is that parity operators act on the internal coordinate \( \chi \). For the coordinate \( \chi \), \( C_{2v} \) symmetry adapted trigonometric bases (with parity) are chosen as
\[
\cos 2n\chi, \quad A_1, \quad \text{even}; \\
\sin(2n + 1)\chi, \quad A_2, \quad \text{odd}; \\
\sin 2n\chi, \quad B_1, \quad \text{even}; \\
\cos(2n + 1)\chi, \quad B_2, \quad \text{odd}.
\]
These bases have inversion symmetry in \( \chi \) according to the parity shown. For example, Eq. (3.18) shows the inversion operator on the triatomic plane \( I_{0(2)} \) applied to the \( \cos 2n\chi \) basis
\[
I_{0(2)} \cos 2n\chi = \cos 2n(\chi + \pi) = (-1)^p \cos 2n\chi,
\]
\[ (3.18) \]

<table>
<thead>
<tr>
<th>TABLE I. Symmetric and antisymmetric spin functions for ( H + H_2 ) system in ( C_{2v} ) symmetry group.</th>
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<tr>
<td><strong>Symmetric spin functions</strong></td>
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<tr>
<td>( \alpha(1)\alpha(2)\alpha(3)^a )</td>
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<td>( \beta(1)\beta(2)\beta(3)^b )</td>
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<td>( \beta(1)\alpha(2)\beta(3)^b )</td>
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<td>( \beta(1)\beta(3)\alpha(2)^b )</td>
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*a and \( \beta \) represent the two nuclear spin states of \( I = 1/2 \).

*b The number in the parentheses labels the nucleus and the nucleus 2 is assumed to be on the \( C_2 \) rotation axis.

where \( \rho \) is the parity index, in this case \( \rho = 0 \). The parity decoupling of these bases is used to represent the parity decoupled full wave functions.

For the coordinate \( \theta \) the Legendre polynomials \( P_j(\cos 2\theta) \) are used as bases. Since the range of \( \theta \) is between \( 0 \) and \( \pi/2 \) the argument of the Legendre polynomial should be \( 2\theta \) to satisfy the correct range of the polynomial angles which lies between \( 0 \) and \( \pi \).

Using the basis above, the Hamiltonian and flux are decomposed by \( C_{2v} \) symmetry, as well as by the parity, and thus, the flux−−flux autocorrelation function is obtained as a sum of individual symmetry block results with corresponding parity. However, since the \( H + H_2 \) system is composed of identical nuclei with nuclear spin \( I = 1/2 \), the nuclear spin must be considered in the evaluation of the rate constant, due to the indistinguishability of the constituent atoms in the reaction. Since the nuclei of the \( H + H_2 \) system are fermions, the allowed wave functions must be antisymmetric with respect to the permutation of any two nuclei.

The application of the \( C_{2v} \) symmetry group to the eight possible nuclear spin functions results in six totally symmetric and two antisymmetric species with respect to \( C_2 \) rotation which belong to the \( A \) and \( B \) representations of the \( C_{2v} \) group respectively. The symmetric and the antisymmetric spin functions are given in Table I. As a result, the nuclear spin weights for the spatial wave functions are two for the \( A \) representation and 6 for the \( B \) representation spatial wave functions and these nuclear spin weight factors are multiplied to the specific symmetry block flux−flux autocorrelation functions to evaluate the overall flux−flux autocorrelation functions.

**C. J=0 case**

1. **Diagonalization of the Hamiltonian**

Once the bases are determined for each coordinate, the Hamiltonian and the flux are evaluated in the direct product representations. All these bases lead to simple diagonal representations for the kinetic energy operators for each coordinate which are easily evaluated. The DVR transformation matrices and the quadratures for each coordinate are obtained by diagonalizing the coordinate matrices in the corresponding FBFR basis. The coordinates chosen for these angular variables are \( \cos \xi \) for \( \xi(\rho) \), \( \cos 2\chi \) for \( \chi \) and \( \cos 2\theta \) for \( \theta \).
The DVR representations of the Hamiltonian and the flux are obtained as

$$
H^\text{DVR} = T^\text{DVR} H^\text{FBR} T^\text{DVR},
$$

(3.19)

$$
F^\text{DVR} = T^\text{DVR} F^\text{FBR} T^\text{DVR}.
$$

(3.20)

The symmetry decomposition and the direct product properties are maintained through the DVR–FBR transformation. In other words, no coupling between the different symmetry bases or between the different coordinate bases are introduced as a result of the DVR–FBR transformation. Therefore, the DVR–FBR transformation is performed independently for each coordinate. For coordinate $\chi$ each symmetry block DVR–FBR transformation matrix is evaluated by diagonalizing the coordinate matrix within the corresponding symmetry block basis.

Transformed by the DVR–FBR transformation matrix the Hamiltonian and the flux in the DVR are written as

$$
H^\text{DVR} = K_p^\text{DVR} \otimes I_0 \otimes I_x + f_p^\text{DVR} \otimes (K^\text{DVR} \otimes I_x
+ g^\text{DVR} \otimes K^\text{DVR}) + V^\text{DVR} + V^\text{DVR},
$$

(3.21)

where

$$
f^\text{DVR} = \frac{1}{\rho^2} \delta_{ii},
$$

(3.22)

and

$$
g^\text{DVR} = \frac{1}{\sin \theta} \delta_{ii},
$$

(3.23)

where $i$, $i'$ index the $\rho$ points and $j$, $j'$ index the $\theta$ points.

The individual kinetic energy matrices are

$$
K_p^\text{DVR} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial \rho^2} \right)_{ii},
$$

(3.24)

and similarly, using the DVR transformations for the $\theta$ basis and the $\chi$ basis, we can evaluate the appropriate kinetic energy terms in the Hamiltonian in the full DVR:

$$
K_\theta^\text{DVR} = -\frac{\hbar^2}{2\mu} \left( \frac{16}{\sin 2 \theta} \frac{\partial}{\partial (2 \theta)} \frac{\partial}{\partial (2 \theta)} \right)_{ii},
$$

(3.25)

and

$$
K_{\chi, kk}^\text{DVR} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial \chi^2} \right)_{kk}.
$$

(3.26)

The effective potential comes from the wave function factorization

$$
V^\text{DVR}_{eff, ii'} = \frac{15 \hbar^2}{8 \mu \rho^2} \delta_{ii'}
$$

(3.27)

and the potential energy is

$$
V^\text{DVR}_{ii', kk} = V(\rho_i, \theta_i, \chi_k) \delta_{ii'} \delta_{kk}.
$$

(3.28)

having independent indices $i$ for $\rho$, $j$ for $\theta$, and $k$ for $\chi$. Here $\rho$ is a function of $\xi$. The DVR representations of the function operators are diagonal while DVR representations of the differential operators contain the coupling. Therefore, $f_p^\text{DVR}$, $g^\text{DVR}$, and $V^\text{DVR}$ are evaluated directly in the DVR at the corresponding quadrature points. The evaluations of the FBR representations of these operators and the subsequent transformations to the DVR are unnecessary.

To obtain the eigenvalues and eigenvectors of the Hamiltonian, $H^\text{DVR}$ should be diagonalized. The direct diagonalization of $H^\text{DVR}$ requires tremendous computational effort proportional to $N^3 \rho N^3 \theta N^3 \chi$ where $N_\rho$, $N_\theta$, and $N_\chi$ are the numbers of basis points for each coordinate. Since $H^\text{DVR}$ is very sparse due to its direct product representation and only a relatively few accurate eigenvalues are needed ( ~100), a sequential diagonalization–truncation technique can be applied to reduce its dimension. The details of the sequential diagonalization–truncation method are given in Ref. 22.

2. $J=0$ rate constant, $k^0(T)$

As mentioned in Sec. III B, the $J=0$ flux–flux autocorrelation function is obtained as a nuclear spin weighted sum given by

$$
C^0_\text{J}(t) = 2C^0A_\text{J}(t) + 6C^0B_\text{J}(t).
$$

(3.29)

Correspondingly the $J=0$ rate constant $k^0(T)$ is obtained as

$$
k^0(T) = \frac{1}{Q_R} \int_0^\infty C^0_\text{J}(t) dt = 2k^0A_\text{J}(T) + 6k^0B_\text{J}(T),
$$

(3.30)

where $Q_R$ is given as

$$
Q_R = Q_{tr} Q_{vr} Q_{rot},
$$

(3.31)

$$
Q_{tr} = 2Q_{tr}^\text{dist},
$$

(3.32)

$$
Q_{rot} = 3 \sum_{j, \text{even}} (2j + 1) \exp \left\{ -\frac{i(j+1)B}{kT} \right\}
+ \sum_{j, \text{odd}} (2j + 1) \exp \left\{ -\frac{i(j+1)B}{kT} \right\}.
$$

(3.33)

The $Q_{tr}^\text{dist}$ is the translational partition function for the distinguishable particles and $B$ is the rotational constant. [The weight factors in Eq. (3.29) and the definition of $Q_R$ are compatible.]

D. $J \neq 0$ case

1. Parity decoupling

The parity of wave function of the system is decoupled according to the parity decoupling in the APH coordinates to give

$$
\Psi^M_n = \sum_{J, M_J} \Phi^M_n(\rho, \theta, \chi) D_{J M_J}^M(\alpha_\theta \beta_\theta \gamma_\theta),
$$

(3.34)

where $J$ is the total angular momentum of the system, $M_J$ and $K_J$ are the $z$ component of the total angular momentum along the $SF$ and $BFQ$ coordinates, respectively, and $\rho$ and $\theta$ represent the parity and the state. The full wave function $\Psi^M_n$ of each parity is obtained as a sum of $\Psi^M_n$ over $M_J$ and $J$ as

$$
\Psi^M_n = \sum_{J, M_J = -J}^J \Psi^M_n.
$$

(3.35)

$\Phi^M_n(\rho, \theta, \chi)$ is the internal wave function obtained by solving the Schrödinger equation for the internal Hamiltonian and $D_{J M_J}^M(\alpha_\theta \beta_\theta \gamma_\theta)$ is the normalized definite parity Wigner D function representing the coordinate rotation from $SF$ frame to $BFQ$ frame. For $K_J = 0$, only one parity (either even or odd) Wigner function is not vanishing depending on $J$ (for even $J$, the even parity $D$ function re-
mains, and for odd J, the odd parity D function). Therefore, the \(D_{KJ'MJ'}^{P} \) are decoupled by parity as \(J+1\) even parity D function's and odd parity D function's for even J, and the reverse for odd J. Once the parity is decoupled, \(K_{J'} \) ranges from 0 to \(J\) for one parity, and from \(1\) to \(2J\) for the other.

In the calculations of \(J \neq 0\) flux–flux autocorrelation functions and rate constants, the truncated eigenvectors of

\[
\langle \Phi_{0}^{(m)} D_{KJ'MJ'}^{P} | H | \Phi_{0}^{(m)} D_{KJ'MJ'}^{P} \rangle \\
= \delta_{m} \delta_{J',J} \frac{A + B}{2} | \Phi_{0}^{(m)} \rangle \langle \Phi_{0}^{(m)} | \\
+ \Lambda_{\pm} \frac{\delta_{m} J}{\Lambda_{\pm} \frac{\delta_{m} J}{2} | \Phi_{0}^{(m)} \rangle} \langle \Phi_{0}^{(m)} | \\
+ \Lambda_{\pm} \frac{\delta_{m} J}{\Lambda_{\pm} \frac{\delta_{m} J}{2} | \Phi_{0}^{(m)} \rangle} \langle \Phi_{0}^{(m)} | \\
= \frac{\cos \theta \partial}{\partial \chi} | \Phi_{0}^{(m)} \rangle,
\]

(3.36)

where \(A, B, \) and \(C\) are functions of \(\rho\) and \(\theta\) and are given by Eqs. (3.3)–(3.5), respectively. The fourth term on the right-hand side of Eq. (3.36) is from the \(K_{J'} \pm 2\) couplings, and the fifth term represents the Coriolis interaction (coupling between the external rotation and the internal motion along \(\chi\)). \(\Lambda_{\pm} \) are functions of \(J\) and \(K_{J'}\) and are given by

\[
\Lambda_{\pm} (J, K_{J'}) = \left[ \Lambda_{+} (J, K_{J'}) \Lambda_{+} (J, K_{J'} + 1) \delta_{K_{J'}, J_{k}+2} \right.
\]

\[
+ \Lambda_{-} (J, K_{J'}) \Lambda_{-} (J, K_{J'} - 1) \delta_{K_{J'}, J_{k}-2} \right] \times \left[ (1 + \delta_{K_{J} K_{J'}}) \right]^{-1/2}
\]

and

\[
\Lambda_{\pm} = \left[ \Lambda_{+} (J, K_{J'}) \delta_{K_{J'}, J_{k}+1} \right. - \Lambda_{-} (J, K_{J'}) (1 + \delta_{K_{J} K_{J'}}) \right]^{-1/2},
\]

(3.37)

(3.38)

where \(\Lambda_{\pm} (J, K_{J'})\) are given as

\[
\Lambda_{\pm} (J, K_{J'}) = \left[ (J \mp K_{J'}) \right]^{1/2}.
\]

(3.39)

No couplings arise between the different parity states due to the orthogonality of the D functions as

\[
\langle D_{KJ'MJ'}^{P} | D_{KJ'MJ'}^{P} \rangle = \delta_{K_{J}, K_{J}'} \delta_{M_{J}, M_{J}'} \delta_{P_{J}, P_{J}'}.
\]

(3.40)

Therefore, the matrix representation of \(H\) in Eq. (3.36) is diagonal in parity and the diagonal parity block itself has \(K_{J'}\) subblocks. The diagonal blocks in \(K_{J'}\) are composed of representations of the internal Hamiltonian, \(J^{3}\) and \(J^{3}_{\pm}\), and is diagonal in the \(K_{J'} \pm 2\) coupling states. The first subdiagonal blocks are due to the Coriolis interactions and the second subdiagonal blocks are due to the \(K_{J'} \pm 2\) couplings. The individual \(K_{J'}\) block is composed of the diagonal symmetry blocks (\(A_{1}\) and \(B_{1}\) blocks or \(A_{2}\) and \(B_{2}\) blocks depending on the parity). The Coriolis interaction, however, couples the different symmetry blocks in \(\chi\) due to the derivative \(\partial / \partial \chi\) so that diagonal symmetry blocks are vanishing in Coriolis blocks (\(K_{J'} \pm 1\) couplings). Therefore, the interaction could not be handled properly by considering symmetry decomposition for the internal coordinate only. Instead, overall symmetry decomposition should be considered (not only for the internal bases but the Wigner D functions as well).

In this work the Coriolis interaction is neglected and the \(K_{J'} \pm 2\) couplings are included in second order perturbation. As will be mentioned in the next section, this leads to the block diagonal representation of \(H\) and saves enormous computational effort. To measure the accuracy of the perturbation treatment of the \(K_{J'} \pm 2\), the eigenvalues obtained from the diagonalization of the exact treatment of the \(K_{J'} \pm 2\) couplings for \(J = 2\) and \(J = 3\) are compared with the perturbation result.

Although either the \(A\) and \(B\) blocks or the \(A_{2}\) and \(B_{2}\) blocks of the eigenvectors of \(H_{int}\) are required to expand \(\psi_{J_{k} MN}^{(m)}\), only one parity block of these eigenvectors is needed because the different parity block results are identical to each other in zero order, i.e., omitting \(K_{J'} \pm 2\) coupling as well as Coriolis coupling. Therefore, only one parity block (either even or odd) calculation for the \(J \neq 0\) problem is performed using the corresponding parity block eigenvectors of \(H_{int}\) as a basis.

2. Perturbation treatment of \(K_{J'} \pm 2\) coupling

Each parity block is composed of the Coriolis blocks and the \(K_{J'} \pm 2\) coupling blocks as well as the diagonal blocks. As will be shown, since the magnitude of the \(K_{J'} \pm 2\) coupling is very small compared with \(J^{3}\) or \(J^{3}_{\pm}\) which are diagonal in \(K_{J'} \pm 2\) coupling can be handled by perturbation theory. The treatment of the \(K_{J'} \pm 2\) coupling by perturbation theory and neglecting the Coriolis interaction yields a block diagonal representation of the Hamiltonian with the size of each \(K_{J'}\) block only \(2N_{3D}^{'},\) where \(N_{3D}^{'},\) is the number of the truncated \(J = 0\) eigenvectors for a given symmetry block.

The orders of magnitudes for the coefficients of \(J^{3}, J^{3}_{\pm}\), and \(J^{3}_{\pm} + J^{3}_{\pm}\) evaluated in the eigenvector representation of \(H_{int}\) are

\[
C_{J'} > C_{J_{\pm}} > C_{K_{J'} \pm 2},
\]

(3.41)

where \(C_{J_{\pm}}, C_{J_{\pm}}\), and \(C_{K_{J'} \pm 2}\) are denoted as

\[
C_{J_{\pm}} = C - \frac{A + B}{2},
\]

(3.42)

\[
C_{J_{\pm}} = \frac{A + B}{2},
\]

(3.43)

and

\[
C_{K_{J'} \pm 2} = \frac{A - B}{4}.
\]

(3.44)
The $\Lambda_{\pm 2}$ in Eq. (3.37) due to $K_f \pm 2$ couplings has a maximum of $(J + 1/2)^2$ and thus the magnitudes of $J(J+1)$, $K_f^2$, and $\Lambda_{\pm 2}$ are comparable. This result provides the grounds for treating the $K_f \pm 2$ coupling by perturbation theory.

To handle the $K_f \pm 2$ couplings, we split the Hamiltonian into the unperturbed Hamiltonian $H_0$ and the perturbation term $H'$, neglecting the Coriolis interaction completely. Rewriting the Hamiltonian of Eq. (3.1) with $H_0$ and $H'$ gives

$$H = H_0 + H', \quad (3.45)$$

where $H_0$ is given by

$$H_0 = H_{\text{int}} + C_{J_f} J^2 + C_{J_f} J_z^2, \quad (3.46)$$

and

$$H' = C_{K_f \pm 2} (J^2_+ + J^2_-). \quad (3.47)$$

The matrix representation of $H_0$ in the truncated basis of eigenvectors of $H_{\text{int}}$ contains only diagonal blocks in $K_f$; that is

$$H_0 = E_{\text{int}} + \frac{J(J+1)\hbar^2}{2} C_{J_f} + K_f^2 E_{C_{J_f}}, \quad (3.48)$$

where $C_{J_f}$ and $E_{C_{J_f}}$ are coefficient matrices evaluated in the truncated basis of eigenvectors of $H_{\text{int}}$ and $E_{\text{int}}$ is a diagonal matrix composed of the eigenvalues of $H_{\text{int}}$. Since $H_0$ is block diagonal, the diagonalization is carried out for each ($J K_f$) block separately. Therefore, the CPU time required to diagonalize all the $J + 1$ blocks is proportional to $2(J + 1)(N_{\text{sub}})^3$.

Through the diagonalization of the individual $K_f$ blocks of $H_0$, the $J^2$ and $J^2_z$ operators are handled in an exact manner. The eigenvectors of $H_0$ will be used as a basis for the evaluation of the $K_f \pm 2$ couplings by perturbation theory. The time evolution of the flux will be represented using this basis and the eigenvalues of $H_0$ corrected for the $K_f \pm 2$ couplings by perturbation theory. Since the $K_f \pm 2$ couplings are off-diagonal blocks in $K_f$, the first order correction vanishes. The eigenvalues corrected to second order are

$$E_n^{J K_f} = E_n^{0 J K_f} + \sum_{m K_f} \frac{|\langle n | K_f | \Lambda_{\pm 2} \rangle|^2 | m | K_f | J_f \rangle|^2}{E_n^{0 J K_f} - E_m^{0 J K_f}}, \quad (3.49)$$

where $E_n^{J K_f}$ is the corrected $n$th eigenvalue of the $K_f$ block while $E_n^{0 J K_f}$ and $E_m^{0 J K_f}$ are the $n$th and $m$th unperturbed eigenvalues for the $K_f$ and $J_f$ blocks, respectively. The corresponding eigenvectors are denoted $|n | K_f \rangle$ and $|m | K_f \rangle$, respectively. The above expression is valid for all the symmetry blocks and thus the calculation is repeated for all the symmetry blocks allowed by the parity. Since $\Lambda_{\pm 2}$ is non-vanishing only for $K_f = K_f' \pm 2$, the couplings arise only between these blocks. $C_{K_f \pm 2}$ is evaluated in the eigenvector basis of $H_0$. Note that since $K_f \neq K_f'$, the sum in Eq. (3.49) includes the terms in which $m$ is equal to $n$.

Except for the $K_f = 0$ block, both parity blocks contain the same subblocks corresponding to $K_f$ ranging from 1 to $J$. Each $K_f$ block is represented by those eigenvectors of $H_{\text{int}}$ belonging either to the $A_1$ and $B_1$ representations or the $A_2$ and $B_2$ representations, depending on the parity. As was pointed out previously, however, the eigenvectors of $H_{\text{int}}$ belonging to these two pairs of representations give equivalent results. Therefore, the eigenvalues of $H_0$ are equivalent in either subbasis. Nevertheless, some corrected eigenvalues of one parity block [Eq. (3.49)] are different from those of the other parity block since one has $J + 1$ $K_f$ subblocks while the other has $J$ $K_f$ subblocks, depending on parity; thus the $K_f \pm 2$ couplings for $K_f = 2$ are different in the two parity blocks. This difference in the corrected eigenvalues is small compared to the corrections themselves, however, and since the corrections themselves are small (which is why we can treat them as perturbations), we will treat the differences between the corrections in the different parity blocks as negligible.

3. $J \neq 0$ rate constant, $k^J(T)$

The flux-flux autocorrelations function of an even parity $K_f$ block, $C_f^J(t) | J K_f \rangle$, is obtained considering nuclear spins as discussed in Sec. III B

$$C_f^{J K_f}(t) = 2 C_f^{J K_f^A}(t) + 6 C_f^{J K_f^B}(t). \quad (3.50)$$

The corresponding odd parity $K_f$ block flux-flux autocorrelation function is

$$C_f^{J K_f}(t) = 2 C_f^{J K_f^A}(t) + 6 C_f^{J K_f^B}(t), \quad (3.51)$$

where $C_f^{J K_f^A}(t)$ is $(J K_f A_f)$ subblock flux-flux autocorrelation function. The flux-flux autocorrelation function for a given $(J K_f)$ block is then expressed as a sum of the two parity block flux-flux autocorrelation functions:

$$C_f^{J K_f}(t) = C_f^{J K_f^A}(t) + C_f^{J K_f^B}(t). \quad (3.52)$$

Then the flux-flux autocorrelation function for a given $J$ becomes

$$C_f^{J}(t) = \sum_{K_f=0}^{J} C_f^{J K_f}(t). \quad (3.53)$$

Note the $K_f = 0$ flux-flux autocorrelation function, $C_f^{J}(t)$, is even or odd parity only as $J$ is even or odd.

Accordingly, the $J$ specific rate constant $k^J(T)$ is

$$k^J(T) = \sum_{K_f=0}^{J} k^{J K_f}(T), \quad (3.54)$$

where $k^{J K_f}(T)$ is the rate constant evaluated for the $(J K_f)$ block:

$$k^{J K_f}(T) = Q^{-1} \int_0^\infty C_f^{J K_f}(t) dt. \quad (3.55)$$

E. Overall thermal rate constant $k(T)$

Once the $J$ rate constant $k^J(T)$ is evaluated, the overall thermal rate constant $k(T)$ is easily obtained as

$$k(T) = \sum_{J=0}^{J_{\text{max}}} (2J + 1) k^J(T) \quad (3.56)$$

Formally the sum in Eq. (3.56) extends to the infinity, but it is only performed up to $J_{\text{max}}$, the largest $J$ required for convergence. $J_{\text{max}}$, of course, depends on the temperature. $J_{\text{max}}$ can be estimated from the following approximate ratio of
\[ k(T) \text{ to } k^0(T) \text{ obtained by the assumption of the same transition state for both } J = 0 \text{ and } J \neq 0 \text{ reactions,} \]
\[ \frac{k(T)}{k^0(T)} \approx \sum_{j=0}^{\infty} (2J + 1) \exp \left[ -\frac{BJ(J + 1)}{2\mu c} \right]. \quad (3.57) \]
The comparison of the infinite sum with finite partial sums provides an estimate of \( J_{\text{max}} \) required for convergence at given \( T \). Here \( \mu c^2 \) is the moment of inertia of the (linear) transition state of the \( H + H_2 \) reaction.

**IV. RESULTS AND DISCUSSION**

**A. \( J = 0 \) case**

The following are checked to guarantee convergence of the result as well as efficiency of the sequential diagonalization-truncation technique: (1) 

- the order of the sequential diagonalization;
- the convergence of the eigenvalues of \( H_{\text{int}} \) with respect to the range of \( \rho \); and
- the convergence of the eigenvalues of \( H_{\text{int}} \) with respect to the sizes of the bases in \( \chi, \theta, \) and \( \rho \); and

(4) the convergence in terms of the basis truncation parameters, \( E_{\text{cut}}^1, E_{\text{cut}}^2, \) and \( E_{\text{cut}}^3 \).

**1. Order of the sequential diagonalization**

Since \( H_{\text{int}} \) is a function of \( \rho, \theta, \) and \( \chi \), the diagonalizations can be performed in six different orders. If the basis sizes for each coordinate are sufficiently large and the diagonalizations of the lower dimensional component of \( H_{\text{int}} \) are done without truncations, the eigenvalues of \( H_{\text{int}} \) obtained are equivalent and the efficiency of computation is the same regardless of the order in which the diagonalizations are performed. Since without the truncations this procedure is not computationally practical, the order of diagonalization may affect the convergence of the results as well as the efficiency. In the sequential diagonalization, as in the adiabatic treatment, the lower dimensional components of \( H_{\text{int}} \) which will be diagonalized first are parametrized by other coordinates (namely the DVR quadrature points). Generally, the coordinate along which the motion is the most strongly coupled is diagonalized first and the coordinate along which the motion is the most nearly adiabatic is diagonalized last; therefore, the order of diagonalizations depends on the system concerned.

Since, as is shown in Fig. 1, the motion along the MEP is expected to be coupled strongly, either the \( \theta \) or \( \chi \) component of \( H_{\text{int}} \) might be diagonalized first and the \( \rho \) component will be diagonalized last. Comparing the potential energy along \( \chi \) at constant \( \theta \) and the potential energy along \( \theta \) at constant \( \chi \) for a given value of \( \rho \) provides an idea of which coordinate should be diagonalized first. The potential energy along \( \chi \) is less smooth than along \( \theta \), and the first diagonalization should be done for the coordinate \( \chi \). The basis size required to describe motion along each coordinate may also be used to determine the order of diagonalization. The coordinate for which the largest basis is required should be diagonalized first to reduce the number of diagonalizations for higher dimensional components of \( H_{\text{int}} \). Since the flux has local momentum in \( \chi \) alone, the eigenvectors may be expected to spread along \( \chi \) rapidly so that a large basis may be required along \( \chi \) to represent accurately the flux eigenvectors over the entire time evolution. Thus, \( \chi \) requires the largest basis and should therefore be diagonalized first, \( \theta \) second, and \( \rho \) last. The order is not really crucial, however.

**2. Range of \( \rho \)**

The range of \( \rho \) in which the motion is described should be determined to permit time evolution of the flux wave packet not only in the interaction region but into the asymptotic region as well. The range of \( \rho \) is determined by checking how accurately the eigenvalues of the one-dimensional component in \( \rho \), \( (\hat{\mathbf{p}}^2/(2\mu))^2/(\hat{\mathbf{p}}^2 + V(\rho, \theta, \chi) + V_{\text{eff}}) \), of \( H_{\text{int}} \) represent the asymptotic eigenvalues of the system. In this way, adequate values of \( \rho_{\text{min}} \) and \( \rho_{\text{max}} \) are determined to be 2.5 and 7.0 \( a_0 \) respectively. A value of 7.0 \( a_0 \) is equivalent to a value of \( S_1 \) (the scaled scattering Jacobi coordinate) of 6.88 \( a_0 \) and a value of \( s_1 \) (the scaled diatomic distance) of 1.30 \( a_0 \), which is the equilibrium bond length of \( H_2 \). The collisional dynamics of \( H + H_2 \) are known to be a short-time process; thus, the \( \rho_{\text{max}} \) of 7.0 \( a_0 \) is sufficient to enter the asymptotic region.

**3. Basis sizes for the internal coordinates**

Since the \( \chi \) component \( H_{\text{int}} \) is diagonalized first, the convergence of its eigenvalues at given \( \theta \) and \( \rho \) with respect to the basis size is checked. A value of 36 for \( N_{\rho} \) was found to be sufficient throughout the region defined by \( 2.5 < \rho < 7.0 \) and \( 0 < \theta < \pi/2 \).

\( N_{\rho} \) is required to be 24 or greater using the optimal \( N_{\rho} \) ( = 36) mentioned above and an estimated \( E_{\text{cut}}^{1D} \) ( = 2.0 eV) for the truncation of the one-dimensional eigenvectors by checking the convergence of the two-dimensional eigenvalues. Finally, the basis size \( N_{\rho} \) for \( \rho \) is determined by evaluating the three-dimensional eigenvalues of \( H_{\text{int}} \) using the previously determined values of \( N_{\chi} \) and \( N_{\theta} \) and the estimated \( E_{\text{cut}}^{1D} \) and \( E_{\text{cut}}^{2D} \), the latter being the energy cutoff for the second truncation. Because the dynamics in \( \rho \) are quite adiabatic, we might expect that \( N_{\rho} \) will be the smallest of the three basis sizes. Using \( E_{\text{cut}}^{1D} = 2.0 \) and \( E_{\text{cut}}^{2D} = 1.0 \) eV, the convergence with \( N_{\rho} = 16 \) was deemed adequate from the Table II and was used for the optimal basis size. With \( N_{\chi}, N_{\theta}, \) and \( N_{\rho} \) determined to be 36, 24, and 16, respectively, the three-dimensional eigenvalue calculation is repeated increasing \( E_{\text{cut}}^{1D} \) and \( E_{\text{cut}}^{2D} \) until the desired degree of convergence is obtained for eigenvalues up to 0.8 eV and above.

**4. Truncations of one- and two-dimensional eigenvectors**

The total number of direct product basis vectors used, \( N \), is \( N = N_{\chi} N_{\theta} N_{\rho} = 13 \) 824. The diagonalization of a matrix of this dimension is not practically possible for us. Since not all the eigenvalues from this matrix are required from a practical point of view, the sequential truncation of bases of lower dimensional eigenvectors is useful for increasing the efficiency without losing the desired accuracy. As mentioned, if \( N_{\rho} \) is 22, the truncation is performed by keeping only eigenvectors whose eigenvalues are less than a predetermined energy cut. These operations generate a sequence of
TABLE II. Convergence of three-dimensional eigenvalues of $A_4$ symmetry block up to 0.8 eV in terms of $N'_{x}$.

<table>
<thead>
<tr>
<th>$N'_{x}$</th>
<th>$N'_{x} = 12^b$</th>
<th>$N'_{x} = 14^b$</th>
<th>$N'_{x} = 16^b$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.5397(0)</td>
<td>0.5397(0)</td>
</tr>
<tr>
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<td>0.5397(0)</td>
<td>0.5397(0)</td>
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<tr>
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<td>0.5514(0)</td>
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<td>0.7790(0)</td>
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<tr>
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<td>0.7973(0)</td>
<td>0.7973(0)</td>
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<td>0.5011(0)</td>
<td>0.5012(0)</td>
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<td>0.5012(0)</td>
<td>0.5013(0)</td>
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<tr>
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<td>0.5028(0)</td>
<td>0.5029(0)</td>
<td></td>
</tr>
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<td>0.5346(0)</td>
<td>0.5347(0)</td>
<td></td>
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<tr>
<td>0.5350(0)</td>
<td>0.5349(0)</td>
<td>0.5353(0)</td>
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</tr>
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</table>

*The number of $\theta$ and $\gamma$ bases are $N_{\theta} = 24$ and $N_{\gamma} = 36$, and the energy cuts are $E_{\text{cut}}^{1}\text{D} = 2.0$ eV and $E_{\text{cut}}^{2}\text{D} = 1.0$ eV.

*The number of three-dimensional eigenvectors $N_{\text{3D}}$ are 220.

$N_{\text{3D}} = 257$.

$N_{\text{3D}} = 292$.

Units is eV.

*The number in parentheses is the power of 10.

rectangular transformation matrices which transform the Hamiltonian from a very large, very sparse matrix (in the primitive direct product DVR basis) to a comparatively small, full matrix (in the final basis).

To determine how high the eigenvalues of $H_{\text{int}}$ should be obtained accurately to produce an accurate thermal rate constant, the thermally weighted overlap $S_{\text{i}}$ between the flux and a given eigenvector of the internal Hamiltonian is evaluated and summed over final states:

$$S_{\text{i}} = \sum_{\text{f}} \exp \left[ -\frac{\beta}{2} (E_{\text{f}} + E_{\text{i}}) \right] \left| \langle i|\text{F}|f\rangle \right|^2. \quad (4.1)$$

Here $E_{\text{f}}$ and $\left| i\right>$ are $\text{i}$th eigenvalue and eigenvector of the internal Hamiltonian. In Fig. 4, $S_{\text{i}}$ is plotted vs $E_{\text{i}}$ for two different temperatures and many states $i$. As is shown in the figure, the most significant contributions come from the eigenvectors of the internal Hamiltonian near 0.65 eV. This is near the energy of the classical reaction barrier height ($E_{\text{b}}$) plus the bending zero point energy of the three-dimensional system. The range of $E_{\text{i}}$ for large overlap depends on the temperature as shown in Fig. 4. For example, at $T = 300$ K the range of $E_{\text{i}}$ giving large overlap is 0.4–0.85 eV while at $T = 1500$ K it is 0.65–1.2 eV.

**5. Thermal rate constant $k(T)$**

From parity considerations for the $J = 0$ wave function, only the even parity internal wave function is allowed $\left[ \Phi_{\text{0e}}^{\text{even}} (\rho,\theta,\chi) \right]$ of Eq. (3.34) and leads to only $A_4$ and $B_1$ symmetry block calculations for the $J = 0$ thermal rate constant. With the parameters above, the dimensions of the truncated two-dimensional eigenvector bases for the $A_4$ and $B_1$ blocks are 494 and 470, respectively. Since not all three-dimensional eigenvectors contribute to the reaction, further truncation of the basis to $N'_{\text{3D}}$ (in which the time evolution is performed) is made by defining $E_{\text{cut}}^{2\text{D}} = 1.2$ eV. The numbers of eigenvalues and eigenvectors remaining in the truncated representations, $N'_{\text{3D}}$, are 190 for the $A_4$ block and 179 for the $B_1$ block. In Table IV, the first 30 eigenvalues from both symmetry

**FIG. 4. Plot of the thermally weighted overlap of the flux with the $i$th eigenvectors of the internal Hamiltonian $S_{\text{i}}$ vs $i$th eigenvalue $E_{\text{i}}$.**

To get the three-dimensional eigenvalues in this range accurately, we may reasonably estimate $E_{\text{cut}}^{1\text{D}}$ and $E_{\text{cut}}^{2\text{D}}$ to be 2.0 and 1.2 eV, respectively. The convergence obtained by varying $E_{\text{cut}}^{1\text{D}}$ and $E_{\text{cut}}^{2\text{D}}$ about these values is checked. The results are given in Table III which shows that eigenvalues less than 0.8 eV vary only in the third or fourth significant figures for all cases. We have chosen $E_{\text{cut}}^{1\text{D}} = 2.0$ eV and $E_{\text{cut}}^{2\text{D}} = 1.35$ eV for the rate constant calculations. As a result of the truncations, the size of the Hamiltonian is reduced from $N = 13 824$ to $N_{\text{3D}} \approx 500$. This reduction clearly shows how efficient the sequential truncation method is.
TABLE III. Convergence of three-dimensional eigenvalues of $A_i$ symmetry block up to 0.8 eV in terms of two-dimensional energy cut $E_{\text{cut}}^{2D}$.  

\[
\begin{array}{cccc}
1.0^a & 1.2^a & 1.35^a \\
0.2778(0) & 0.5398(0) & 0.2778(0) & 0.5398(0) \\
0.2778(0) & 0.5398(0) & 0.2778(0) & 0.5398(0) \\
0.2925(0) & 0.5433(0) & 0.2925(0) & 0.5433(0) \\
0.3234(0) & 0.5515(0) & 0.3234(0) & 0.5515(0) \\
0.3234(0) & 0.5528(0) & 0.3234(0) & 0.5528(0) \\
0.3243(0) & 0.5768(0) & 0.3243(0) & 0.5768(0) \\
0.3243(0) & 0.5785(0) & 0.3243(0) & 0.5785(0) \\
0.3383(0) & 0.5907(0) & 0.3383(0) & 0.5907(0) \\
0.3691(0) & 0.5907(0) & 0.3691(0) & 0.5907(0) \\
0.3700(0) & 0.6112(0) & 0.3700(0) & 0.6112(0) \\
0.3700(0) & 0.6113(0) & 0.3700(0) & 0.6113(0) \\
0.3853(0) & 0.6148(0) & 0.3853(0) & 0.6148(0) \\
0.3854(0) & 0.6162(0) & 0.3854(0) & 0.6162(0) \\
0.3991(0) & 0.6213(0) & 0.3991(0) & 0.6213(0) \\
0.4167(0) & 0.6430(0) & 0.4167(0) & 0.6430(0) \\
0.4284(0) & 0.6511(0) & 0.4284(0) & 0.6511(0) \\
0.4284(0) & 0.6835(0) & 0.4284(0) & 0.6835(0) \\
0.4309(0) & 0.6920(0) & 0.4309(0) & 0.6920(0) \\
0.4310(0) & 0.6937(0) & 0.4310(0) & 0.6937(0) \\
0.4564(0) & 0.7097(0) & 0.4564(0) & 0.7097(0) \\
0.4565(0) & 0.7125(0) & 0.4565(0) & 0.7125(0) \\
0.4690(0) & 0.7331(0) & 0.4690(0) & 0.7331(0) \\
0.4772(0) & 0.7476(0) & 0.4772(0) & 0.7476(0) \\
0.4772(0) & 0.7791(0) & 0.4772(0) & 0.7791(0) \\
0.4786(0) & 0.7977(0) & 0.4786(0) & 0.7977(0) \\
0.5012(0) & 0.5009(0) & 0.5012(0) & 0.5009(0) \\
0.5013(0) & 0.5010(0) & 0.5013(0) & 0.5010(0) \\
0.5029(0) & 0.5024(0) & 0.5029(0) & 0.5024(0) \\
0.5347(0) & 0.5343(0) & 0.5347(0) & 0.5343(0) \\
0.5353(0) & 0.5347(0) & 0.5353(0) & 0.5347(0) \\
\end{array}
\]

* $N_{\text{e}} = 16$, $N_{\text{p}} = 24$, $N_{\text{v}} = 36$, and $E_{\text{cut}}^{2D} = 2.0$ eV.

** Value of $E_{\text{cut}}^{2D}$ with unit eV and $N_{\text{e}} = 292$.

\[
\begin{array}{cc}
\text{Symmetry block} & A_i^b \\
0.2778(0) & 0.2778(0) & 0.2925(0) \\
0.3234(0) & 0.3234(0) & 0.3242(0) \\
0.3699(0) & 0.3699(0) & 0.3691(0) \\
0.3853(0) & 0.3859(0) & 0.4167(0) \\
0.4284(0) & 0.4284(0) & 0.4308(0) \\
0.4687(0) & 0.4671(0) & 0.4771(0) \\
0.5024(0) & 0.5008(0) & 0.5009(0) \\
0.5347(0) & 0.5343(0) & 0.5345(0) \\
\end{array}
\]

\[
\begin{array}{cc}
\text{Symmetry block} & B_i^c \\
0.2775(0) & 0.2922(0) & 0.2932(0)^d \\
0.3232(0) & 0.3239(0) & 0.3379(0)^* \\
0.3380(0) & 0.3687(0) & 0.3695(0) \\
0.3697(0) & 0.3852(0) & 0.3988(0) \\
0.3989(0) & 0.4162(0) & 0.4164(0) \\
0.4287(0) & 0.4307(0) & 0.4562(0) \\
0.4687(0) & 0.4688(0) & 0.4768(0) \\
0.4782(0) & 0.4784(0) & 0.5009(0) \\
0.5031(0) & 0.5043(0) & 0.5344(0) \\
0.5392(0) & 0.5427(0) & 0.5439(0) \\
\end{array}
\]

* $N_{\text{p}} = 16$, $N_{\text{d}} = 24$, $N_{\text{v}} = 36$, $E_{\text{cut}}^{1D} = 2.0$ eV, and $E_{\text{cut}}^{2D} = 1.35$ eV.

** $N_{\text{Id}} = 494$.

\[
\begin{array}{cc}
\text{Unit is eV.} \\
N_{\text{Id}} = 470. \\
\text{The number in parentheses is the power of 10.} \\
\end{array}
\]

Note that this result demonstrates numerical accuracy since we use $C_{2p}$ symmetry, not $D_{3h}$.

Figure 5 shows the flux–flux autocorrelation functions obtained by the time evolution in the truncated three-dimensional eigenvector representation of $H_{\text{int}}$ determined with the parameters above for $T = 300$, 700, and 1500 K. For all three temperatures, the flux–flux autocorrelation functions are well converged in 25 fs. This indicates that the basis sizes $N_{\text{F}}$, $N_{\text{p}}$, and $N_{\text{v}}$, and the energy cuts $E_{\text{cut}}^{1D}$, $E_{\text{cut}}^{2D}$, and $E_{\text{cut}}^{3D}$ are sufficient to provide converged rate constants. In spite of the severe (but highly desirable) reduction in the dimension of the Hamiltonian, the time evolution is still described sufficiently accurately that virtually no artificial reflection (from the “edges” of the basis) is observed even after 35 fs. This observation lends support to the adequacy of our primitive direct product basis size.

FIG. 5. $J = 0$ flux–flux autocorrelation functions.

In Table V, the J = 0 rate constants for T = 200–1500 K are given and compared with the rate constants obtained by thermal averaging of the reactive probabilities calculated by R-matrix propagation. The discrepancies between these results are in the range of 1%–20%. For most of the temperatures, the differences are within 5%. The T = 300 K result, which shows the largest percentage discrepancy, has an accuracy comparable to Miller’s work. The J = 0 rate constant is the most important to the overall rate constant at low temperatures.

**B. J ≠ 0 case**

In order to calculate the full thermal rate constant K^J^0^((T))^ must be calculated to high enough J such that the sum over J is converged. Although we outlined our approach earlier, we give here more details of the calculations for J ≠ 0.

**1. Eigenvalues corrected by second order perturbation**

The second order perturbation corrections (for K^J^±^2^ coupling) differ slightly depending on the parity of the full wave function. For a given J, the K^J^ = 0 block has only even or odd parity, depending on whether J is even or odd, respectively. The K^J^ ≠ 0 blocks, on the other hand, appear in both parity blocks. The coupling between K^J^ = 0 and K^J^ = 2 appears only in the parity block containing K^J^ = 0. Apart from these differences, the K^J^ ± 2 couplings in both parity blocks are equivalent.

Table VI shows the first 20 corrected eigenvalues of Eq. (3.49) for each K^J^ of both A_3 and B_3 symmetries. These are the results of the second order perturbation corrections to the eigenvalues of H_0 due to the K^J^ ± 2 couplings. Comparing Table VI with Table IV, we can see that the triple degeneracy is still maintained and that the whole eigenvalue spectrum of H_0 is shifted by the energy of the external angular momentum J. Comparisons of the K^J^ = 0 eigenvalues with the eigenvalues of H_0 and with the K^J^ ≠ 0 eigenvalues show that the J^2^ contribution to the upward shift is far greater than that of J^3^ itself, i.e., the shift with K^J^ is greater than that with J, K^J^ = 0. From Table VI, it can be expected that the K^J^ = 0 block rate constant K^J^0^((T))^ will dominate the J rate constant K^J^((T))^.

To determine the accuracy of the eigenvalues evaluated by the second order perturbation, diagonalization of the exact representation of the Hamiltonian, neglecting only the Coriolis interaction, is performed for J = 2 and J = 3. The first 60 eigenvalues agree to four significant figures with the values in Table VI (computed by perturbation theory). The same result holds for the full diagonalization (K^J^ = 0.2) for the odd parity J = 3 blocks compared to the second order perturbation results. We believe, therefore, that this approximation is of sufficient accuracy to yield accurate rate constants (to at least two significant figures).

**2. Individual J rate constant K^J^((T))^**

For a given J is evaluated from the time evolution of the flux in the eigenvector representation of H_0 of Eq. (3.48). These eigenvectors are in turn extracted by diagonalizing H_0 in the truncated basis of eigenvectors of H_0 which were used to evaluate the J = 0 rate constant. The difference between the two parity blocks with K^J^ ≠ 0 are the K^J^ ± 2 coupling between K^J^ = 0 and K^J^ = 2. However, the contribution of this coupling to the eigenvalues of the K^J^ blocks is very small, and we can neglect this difference and can perform the calculations using only the A_3 and B_3 (even parity) blocks or the A_2 and B_2 (odd parity) blocks of H_0.
vector basis, not both blocks. Following the procedures given in Sec. III D, $k^J(T)$ as given in Eq. (3.54) is obtained. In the calculation of the perturbation correction, only the $A_1$ and $B_1$ blocks of the truncated eigenvector basis are used. Therefore, the dimension of $H_{\text{int}}$ for each $K_J$ block is the same as the dimension of the truncated basis of eigenvectors of $H_{\text{int}}$.

The Table VII, the individual rates, $k^{JK_J}(T)$, for $J = 2$ are provided for comparison. This table shows the dominance of $k^{K_J}(T)$ to $k^2(T)$. At high temperatures, the fractional contribution of $k^{K_J}(T)$ to $k^2(T)$ is reduced.

According to the approximate estimate of $J_{\text{max}}$ mentioned in Sec. III E, $J_{\text{max}}$ required to obtain the overall rate constant with the accuracy of 95% or greater up to 1500 K is $J_{\text{max}} = 18$. At higher temperatures a larger $J_{\text{max}}$ is required for the same accuracy.

The $k^J(T)$ calculations were performed for $J = 1−6$ and for even $J$ up to $J = 24$ because $k(T)$ is expected to converge by $J = 24$ even at $T = 1500$ K. The odd $J$ rate constants for $J = 7−23$ were obtained by cubic spline interpolations. In Fig. 6, the flux−flux autocorrelation functions for $J = 16$ are plotted for $T = 300$ K. Note that even at $J = 16$, the flux−flux autocorrelation function is well converged in time. This point can be understood because the total angular momentum only contributes a shift in the eigenvalue spectrum without significantly affecting the time evolution of the flux so that the dynamics can still be accurately described by the bases used for the $J = 0$ problem.

### Table VII. ($JK_J$) block rate constant $k^{JK_J}(T)$ for $J = 2$ at $T = 300$−1500 K.

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$k^{20}(T)$</th>
<th>$k^{21}(T)$</th>
<th>$k^{22}(T)$</th>
</tr>
</thead>
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<tr>
<td>300</td>
<td>9.00 (−18)</td>
<td>1.36 (−19)</td>
<td>2.75 (−21)$^b$</td>
</tr>
<tr>
<td>500</td>
<td>8.04 (−16)</td>
<td>4.79 (−17)</td>
<td>3.63 (−18)$^c$</td>
</tr>
<tr>
<td>700</td>
<td>5.39 (−15)</td>
<td>6.32 (−16)</td>
<td>9.48 (−17)</td>
</tr>
<tr>
<td>900</td>
<td>4.17 (−14)</td>
<td>2.53 (−15)</td>
<td>5.56 (−16)</td>
</tr>
<tr>
<td>1100</td>
<td>2.69 (−14)</td>
<td>5.85 (−15)</td>
<td>1.62 (−15)</td>
</tr>
<tr>
<td>1300</td>
<td>3.95 (−14)</td>
<td>1.01 (−14)</td>
<td>3.25 (−15)</td>
</tr>
<tr>
<td>1500</td>
<td>5.09 (−14)</td>
<td>1.49 (−14)</td>
<td>5.19 (−15)</td>
</tr>
</tbody>
</table>

$^a$ $J = 2$ and $K_J = 2$ block rate constant.
$^b$ Unit is cm$^2$/molecule/s.
$^c$ The number in parentheses is the power of 10.

### Table VIII. $J$ thermal rate constant $k^J(T)$, for $J = 1−24$ at $T = 300$−1500 K.

<table>
<thead>
<tr>
<th>$J$</th>
<th>$T = 300$</th>
<th>500</th>
<th>700</th>
<th>900</th>
<th>1100</th>
<th>1300</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.17 (−17)</td>
<td>9.48 (−16)</td>
<td>6.08 (−15)</td>
<td>1.62 (−14)</td>
<td>2.92 (−14)</td>
<td>4.25 (−14)</td>
<td>5.46 (−14)$^a$</td>
</tr>
<tr>
<td>1</td>
<td>1.09 (−17)</td>
<td>9.51 (−16)</td>
<td>6.53 (−15)</td>
<td>1.84 (−14)</td>
<td>3.46 (−14)</td>
<td>5.24 (−14)</td>
<td>6.95 (−14)$^b$</td>
</tr>
<tr>
<td>2</td>
<td>9.14 (−18)</td>
<td>8.55 (−16)</td>
<td>6.12 (−15)</td>
<td>1.78 (−14)</td>
<td>3.45 (−14)</td>
<td>5.34 (−14)</td>
<td>7.21 (−14)</td>
</tr>
<tr>
<td>3</td>
<td>7.03 (−18)</td>
<td>4.27 (−16)</td>
<td>5.43 (−14)</td>
<td>1.63 (−14)</td>
<td>3.23 (−14)</td>
<td>5.08 (−14)</td>
<td>6.98 (−14)</td>
</tr>
<tr>
<td>4</td>
<td>4.96 (−16)</td>
<td>5.81 (−15)</td>
<td>4.62 (−15)</td>
<td>1.44 (−14)</td>
<td>2.91 (−14)</td>
<td>4.67 (−14)</td>
<td>6.51 (−14)</td>
</tr>
<tr>
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<td>4.41 (−15)</td>
<td>3.78 (−15)</td>
<td>1.23 (−14)</td>
<td>2.55 (−14)</td>
<td>4.18 (−14)</td>
<td>5.92 (−14)</td>
</tr>
<tr>
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<td>3.18 (−16)</td>
<td>2.97 (−15)</td>
<td>1.01 (−14)</td>
<td>2.17 (−14)</td>
<td>3.63 (−14)</td>
<td>5.23 (−14)</td>
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<td>2.26 (−15)</td>
<td>0.86 (−15)</td>
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<td>3.14 (−14)</td>
<td>4.58 (−14)</td>
</tr>
<tr>
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<td>1.40 (−16)</td>
<td>1.63 (−15)</td>
<td>0.83 (−15)</td>
<td>1.47 (−14)</td>
<td>2.61 (−14)</td>
<td>3.92 (−14)</td>
</tr>
<tr>
<td>9</td>
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<td>8.67 (−17)</td>
<td>1.16 (−15)</td>
<td>0.47 (−15)</td>
<td>1.18 (−14)</td>
<td>2.16 (−14)</td>
<td>3.31 (−14)</td>
</tr>
<tr>
<td>10</td>
<td>1.07 (−19)</td>
<td>4.99 (−17)</td>
<td>7.65 (−16)</td>
<td>3.48 (−15)</td>
<td>9.04 (−15)</td>
<td>1.73 (−14)</td>
<td>2.75 (−14)</td>
</tr>
<tr>
<td>11</td>
<td>3.84 (−20)</td>
<td>2.73 (−17)</td>
<td>5.10 (−15)</td>
<td>2.37 (−15)</td>
<td>6.75 (−15)</td>
<td>1.37 (−14)</td>
<td>2.24 (−14)</td>
</tr>
<tr>
<td>12</td>
<td>1.57 (−20)</td>
<td>1.45 (−17)</td>
<td>3.10 (−16)</td>
<td>1.07 (−15)</td>
<td>5.03 (−15)</td>
<td>1.06 (−14)</td>
<td>1.80 (−14)</td>
</tr>
<tr>
<td>13</td>
<td>7.28 (−18)</td>
<td>1.83 (−16)</td>
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<td>6.4 (−16)</td>
<td>1.6 (−15)</td>
<td></td>
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<td>7.1 (−16)</td>
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<td>3.1 (−16)</td>
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</table>

$^a$ Unit is cm$^2$/molecule/s.
$^b$ The number in parentheses is the power of 10.
$^c$ For odd $J$ rate constants between $J = 7−23$ are obtained by cubic spline fit of the even $J$ results of $J = 0−24$.  

Table VIII provides $k^J(T)$ for $J = 1–24$ and Fig. 7 shows a plot of $[k^J(T)/k^0(T)]$ as a function of $J$ for $T = 300, 700,$ and 1500 K. In Fig. 7, the largest $k^J(T)$ shifts from $J = 0$ to higher $J$ with increasing temperature.

In Fig. 8, the degeneracy multiplied ratio $(2J + 1) [k^J(T)/k^0(T)]$ is plotted vs $J$ for several temperatures to show which total angular momentum makes the most significant contribution to $k(T)$ at each temperature. Due to the factor of $2J + 1$, the largest contribution does not necessarily correspond to the largest $k^J(T)$. A shift in the maximum with increasing temperature is observed, as expected.

C. Overall thermal rate constant $k(T)$

Since all the individual $k^J(T)$ for $J$ up to $J = 24$ have been evaluated, the overall rate constant may be obtained by a sum over $J$ of $(2J + 1)k^J(T)$, and the converged $k(T)$ are given in Table IX, where they are compared with the result of other works. These results of Colton and Schatz and of Truhlar et al. are claimed to be the most accurate rate constants on the LSTH surface reported so far. The experimental thermal rate constants of $H + H_2$ are reported in the range of $T = 299$–549 K. Comparison with experiments is made by interpolation of our work to the experimental temperatures shown in Table 11. As is shown, the agreement seems to be quite good.

Since no exact quantum mechanical close coupling calculations have been completed for large $J$ for the $H + H_2$ reaction on the LSTH surface, the most accurate thermal rate constants reported are from the coupled state scattering calculations of Colton and Schatz mentioned previously. Their calculation neglects the couplings between the different $K_f$ states while our calculation treats the $K_f = 2$ couplings by perturbation theory, neglecting only $K_f = 1$ (Coriolis) couplings; therefore, our results might be expected to be more accurate.

V. CONCLUSIONS

In this work, the powerful algorithms, i.e., the DVR and the sequential diagonalization truncation are applied to the thermal rate constant calculation of the three-dimensional $H + H_2$ reaction. The approach appears to be both efficient and accurate. The accuracy and efficiency of the direct rate constant formalism via flux–flux autocorrelation function are also established. Since this calculation includes the couplings between the different projection states by second order perturbation theory and full close coupling calculations have not been performed for all $J$, this work currently seems to provide the most accurate theoretical rate constants available. Now that these techniques have been successfully applied to the three dimensional $H + H_2$ reaction, the direct rate constant calculation formalism and the efficient algorithms can be extended to more complex atom–diatom reactions ($F + H_2$, $O + H_2$, and etc.) to determine their rate constants accurately as well.
TABLE IX. Comparison of converged thermal rate constant \( k(T) \) of this work with other results and the experiment.

<table>
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<tr>
<th>T,K</th>
<th>( k(T)^a )</th>
<th>( k(T)_{CSWm}^b )</th>
<th>( k(T)_{ICVT/LAG}^c )</th>
<th>( k(T)_{exp}^d )</th>
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<td>2.3(−16)</td>
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<td>327(^a)</td>
<td>7.49(−16)</td>
<td>4.4(−16)</td>
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<td>9.8(−16),8.3(−16)</td>
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<tr>
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<td>549(^b)</td>
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<td>4.4(−14)</td>
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<tr>
<td>1500</td>
<td>8.27(−12)</td>
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\(^a\) This work.
\(^b\) Distinguishable atom result from Ref. 29.
\(^c\) Distinguishable atom result from Ref. 30.
\(^d\) From Refs. 12 and 14.
\(^e\) Unit is cm\(^3\)/molecule/s.
\(^f\) The number in parentheses is the power of 10.
\(^g\) Obtained from the log\(k(T)\) vs 1/T plot for \(T = 300\)–700 K.
\(^h\) Obtained from the log\(k(T)\) vs 1/T plot for \(T = 700\)–1500 K.


