A three dimensional quantum mechanical theory to treat tetra-atom reactions: State-to-state cross sections for the H$_2$+OH→H$_2$O+H process

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A quantum mechanical approach to treat diatom–diatom exchange processes of the type $AB+CD→ABC+D$ is presented. The approach is based on three types of wave functions $\varphi_{0\alpha}$, $\psi_{0\beta}$, and $\chi$, where the first two are (asymptotic) elastic distorted wave functions for the two arrangement channels $\nu$ and $\lambda$, and $\chi$ is a short range (square integrable) wave function describing the system in the close interaction region. The functions $\varphi_{0\alpha}$ and $\psi_{0\beta}$ are presented within the $j_2$ approximation, and to calculate $\chi$, a perturbative-type Schrödinger equation which contains negative imaginary potentials (to form absorbing boundary conditions) is solved. The variationally stable solution is obtained employing Gaussians and local adiabatic basis sets. The actual calculation of $\chi$ is done employing the quasibreathing sphere model, where the relevant angular coordinates are selected randomly (about 50 sets like that were used) employing a Monte Carlo approach. With this approach, most detailed state-to-state cross sections were calculated for the reaction $\text{H}_2(n_1=0, j_1=0)+\text{OH}(n_2=0, j_2=0)→\text{H}_2\text{O}(v,fu,K\Omega_K)+\text{H}$, where $(v,fu)$ are the usual vibrational-bending states of the water molecule, and $K$ and $\Omega_K$ are, respectively, the overall rotational quantum number and the corresponding magnetic component. The results were compared with those due to other treatments and with experiment.

I. INTRODUCTION

In the present work, we consider the diatom–diatom reaction

$$\text{H}_2+\text{OH→H}_2\text{O+H} \quad (I)$$

with the aim of calculating quantum mechanical (QM) three dimensional (3D) state-to-state reactive cross sections. Numerous experimental$^{12}$ and numerical studies$^{34}$ of this reaction and the reverse one

$$\text{H}_2\text{O+H→H}_2+\text{OH} \quad (II)$$

as well as their isotopic analogs were studied in the last years. The first experiments on the effect of translational energy on the cross section of reaction (I) were carried out by Wolfrum and co-workers.$^{1(0)}$ Similar studies, on reaction (II), were done by Kessler and Kleinermann.$^{1(0)}$ The first studies of reaction (II) with excited H$_2$O (and D$_2$O) were done by Crim and co-workers$^{1(0)1(1)}$ as well as by Zare and co-workers. Recently, the first study of the differential cross section for the OH+D$_2$ reaction was reported by Alagia et al.$^{1(m)}$

The most relevant experimental studies to our present results are those of Koppe et al.$^{2(a)}$ who measured the integral cross sections for reaction (I) at two energies. The higher energy is close to the energy value for which our calculations were carried out. Recently, Jacobs et al.$^{2(b)}$ performed similar experiments for reaction (II).

Numerical studies of processes (I) and (II) have employed quasiclassical trajectories (QCT),$^{3(a),3(b),3(e),3(f),3(i)}$ variational transition state,$^{3(e)}$ semiclassical,$^{3(c)}$ and quantum mechanical (QM) treatments.$^{3(g),3(h),3(j),4(a),4(b)}$ Most of these studies were carried out on a potential energy surface calculated by Walch and Dunning$^{5(a)}$ and fitted by Schatz and Elgersma.$^{5(a),5(c)}$ Whereas the QCT calculations are done essentially without approximations, the QM ones employ (sometimes even drastic) approximations to reduce the number of internal degrees of freedom.

We have so far carried out two such studies.$^4$ In the first, we treated reaction (II) assuming all four atoms to be aligned$^4(a)$ (this is considered to be a study of a collinear system), and in the second, we treated reaction (I) in 3D and calculated state-to-state reactive cross sections for the processes$^4(b)$

$$\text{H}_2(j_1=0,n_1)+\text{O}\text{X}(j_2=0,n_2)→\text{HOX}(v,fu'|K=0)+\text{H}, \quad \text{X=H.D} \quad (I')$$

Here $v, j, u'$, and $K$ are, respectively the asymmetric, bending, symmetric, and (overall) rotational quantum numbers. In the present publication, this study is extended to values of $K \neq 0$ and so we were also able to calculate integral cross sections. In the previous publication,$^4(b)$ we also presented the theory that finally led to the calculated state-to-state cross section. However, in order to make the presentation as comprehensive as possible, we limited ourselves to the case of $K = 0$, and in this way, simplified significantly the notation. In the present publication, the theory is given for the general case. As before, it is based on the application of negative imaginary potentials (NIPs),$^6,7$ which create absorbing boundary conditions. The employment of NIPs help in two ways (1) it enables the decoupling of all arrangement channels from the one under consideration (in this way, a reactive system is essentially treated like an inelastic nonreactive system) and (2) it enables the conversion of a scattering problem into a bound system problem, and in this way permits the application of square integrable basis sets.$^8$

The theoretical approach is based on the derivation of three wave functions: (a) two asymptotic ones—$\psi_{0\alpha}$ for the reagents and $\psi_{0\beta}$ for the products—where both are assumed
to describe elastic collision processes and (b) a short range wave function which is responsible for the processes in the strong interaction region.

The approximations that will be made are as follows: the two (elastic) asymptotic functions will be treated within the \( j_z \) (coupled states) approximation in particular, see Ref. 10(d). The short range function \( \chi \) will be derived employing the quasibreathing-sphere (QBS) approximation.

The breathing-sphere-potential follows from the ordinary potential by treating the three reagent Jacobi angles as parameters rather than variables which are randomly selected by the Monte Carlo method. The calculations are repeated many times, each time for a different set of three angles. The final outcome follows from an averaging procedure, as will be discussed in the next section. Whereas the \( j_z \) approximation is known to be a reliable approximation [see Refs. 10(a)–10(c) for inelastic triatom systems, Ref. 10(d) for an inelastic diatom–diatom system, and Ref. 7(c) for triatom reactive systems], the QBS approximation could be questionable, but since it is applied only to a short range function (and not for the whole wave function), that makes it much more justifiable.

The publication is arranged in the following way: the theory for the general process \( A + B \rightarrow C + D \) is described in detail in Sec. II, numerical information concerning the calculation of the state-to-state cross sections for reaction (I) is presented in the Sec. III, results are given in Sec. IV, and conclusions are made in Sec. V.

II. THEORY

The relevant Schrödinger equation to be considered is:

\[
(E-H)\chi_{\lambda} = V_{\lambda}\phi_{\lambda},
\]

where \( E \) is the total energy, \( \phi_{\lambda} \) is the unperturbed part of the total wave function [henceforth \( \lambda \) designates the atom–triatom arrangement channel (AC)], \( V_{\lambda} \) is the relevant perturbation potential, \( H \) is the full Hamiltonian (which contains the relevant NIPS) defined in the \( \nu \) AC (henceforth \( \nu \) designates the diatom–diatom AC), and \( \chi_{\lambda} \) is the function which stands for the perturbed part of the overall wave function \( \Psi_{\lambda} \). Thus

\[
\chi_{\lambda} = \Psi_{\lambda} - \phi_{\lambda}. \tag{2}
\]

The aim of the numerical treatment is to obtain the state-to-state \( S \) matrix element:

\[
S(\nu \rightarrow \lambda) = \langle \psi_{\lambda}|V_{\nu}|\psi_{\nu}\rangle = \langle \psi_{\nu}|V_{\nu}|(\chi_{\lambda} + \psi_{\lambda})\rangle, \tag{3}
\]

where \( \psi_{\nu} \) is the \( \nu \) unperturbed wave function and \( V_{\nu} \) is the relative perturbation potential in this AC.

To obtain \( S(\nu \rightarrow \lambda) \), it is necessary to perform the following steps:

A. Derivation of the unperturbed wave functions \( \psi_{\nu\alpha} \): \( \alpha = \lambda, \nu \)

To derive \( \psi_{\nu\alpha} \), \( \alpha = \lambda, \nu \), we consider the unperturbed Hamiltonian \( H_{0\alpha} \) and the relevant Schrödinger equation (SE)

\[
(E-H_{0\alpha})\psi_{\nu\alpha} = 0, \quad \alpha = \lambda, \nu. \tag{4}
\]

\( H_{0\alpha} \) is written in the form

\[
H_{0\alpha} = -\frac{\hbar^2}{2\mu_{i}} \frac{\partial^2}{\partial r_i^2} + W_{\alpha}, \quad \alpha = \lambda, \nu, \tag{5}
\]

where \( T_{\alpha} \) is the kinetic energy and \( W_{\alpha} \) is the unperturbed potential. Since different clusters are encountered in the two ACs, we discuss each equation (and solution) separately.

1. The reagents equation (\( \alpha = \nu \))

Here two diatoms are encountered and consequently \( T_{\nu} \) takes the form

\[
T_{\nu} = -\frac{\hbar^2}{2\mu_{i}} \left( \frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial r_j^2} \right) + \frac{\hbar^2}{2\mu_{i}} \frac{\partial^2}{\partial r_i^2} + \frac{\hbar^2}{2\mu_{i}} \frac{\partial^2}{\partial r_j^2} + \frac{\hbar^2}{2\mu_{i}} \frac{\partial^2}{\partial R_{\nu}^2} \left[ j_{1}(j_{1}+1) + j_{2}(j_{2}+1) + \frac{I_{\nu}^2}{2\mu_{i} R_{\nu}^2} \right], \tag{6}
\]

where \( \mu_{i}, r_{i}, j_{i}; i = 1,2 \) are the reduced masses, the vibrational coordinates, and the internal rotational quantum numbers, respectively, of the two diatomics; \( \mu_{i} \) is the \( \nu \)th reduced mass; \( R_{\nu} \) is the \( \nu \)th translational coordinate; and \( I_{\nu} \) is the orbital angular momentum operator. If \( J_{\nu} \) is defined as

\[
J_{\nu} = j_{1} + j_{2}, \tag{7}
\]

and if \( J \) is the total angular momentum (operator) of the system, then \( I_{\nu} \) is written as

\[
I_{\nu} = J - J_{\nu}. \tag{8}
\]

Henceforth, we shall employ the body-fixed (BF) framework, in which the \( z \) axis is assumed to be along \( R_{\nu} \). Next, we introduce the \( j_z \) approximation and consequently the representation of \( I_{\nu}^2 \) is

\[
I_{\nu}^2 = \hbar^2 \left[ (J(J+1) - 2\Omega_{\nu}^2) + J_{\nu}^2 \right], \tag{9}
\]

where \( \Omega_{\nu} \) is the projection of both \( J \) and \( J_{\nu} \) along \( R_{\nu} \). In what follows, \( J_{\nu}^2 \) will be presented as

\[
J_{\nu}^2 = \hbar^2 J_{\nu}(J_{\nu}+1), \tag{10}
\]

where \( J_{\nu} \) is an integer assumed to be in the range \( |j_{1}-j_{2}| \leq J_{\nu} \leq j_{1}+j_{2} \). Also it can be seen that

\[
\Omega_{\nu} = m_{1} + m_{2}. \tag{11}
\]

As for \( W_{\nu} \), it is assumed to be of the form

\[
W_{\nu}(r_{1}r_{2}R_{\nu}Y_{1}Y_{2}S) = v_{1}(r_{1}) + v_{2}(r_{2}) + w_{\nu}(R_{\nu}), \tag{12}
\]

where \( v_{i}(r_{i}), i = 1,2 \) are the asymptotic vibrational potentials of the two diatoms; \( w_{\nu}(R_{\nu}) \) is the \( \nu \)th distortion potential (assumed to increase once \( R_{\nu} \) is small enough and decreases); \( \gamma_{i}, i = 1,2 \) are two Jacobi angles defined as

\[
\gamma_{i} = \cos^{-1}(R_{\nu}/r_{i}), \quad i = 1 \text{ and } 2, \tag{13}
\]

and \( \delta \) is the angle between the \( (R_{\nu}, r_{1}) \) and \( (R_{\nu}, r_{2}) \) planes. The potential \( w_{\nu}(R_{\nu}) \) is usually taken as

\[
w_{\nu}(R_{\nu}) = U(r_{1}r_{2}R_{\nu}Y_{1}Y_{2}S_{0}), \tag{14}
\]

where \( U \) is the full potential expressed in terms of the \( \nu \) th coordinates; \( r_{1}, r_{2}, i = 1,2 \) are diatomic asymptotic equilibrium distances and \( \gamma_{0}, i = 1,2 \) and \( \delta_{0} \) are three fixed angles to be discussed later.

Since the \( W_{\nu} \) potential is separable in terms of all variables, the solution of Eq. (4) can be written
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**FIG. 1.** The Jacobi coordinates of the four atom system. (a) Reagent (diatom-diatom) coordinates; (b) product (atom-triatom) coordinates.

\[ Y(R,\eta,\theta) = c^{(j_1,j_2,m,m_1,m_2)}(R,\eta,\theta) \]

Here $J_\alpha$ fulfills the two inequalities $|j_1-j_2|=j_1+j_2$. $\phi_{0v}(r_1|t_1)$, $i=1,2$ are the $i$th vibrational eigenfunctions; $y(\gamma_1,\gamma_2,|j_1,m_1)$ are the respective spherical harmonics; $\zeta_{0v}(R_1|t_1,t_2,J_\eta,J_\Omega_v)$ is the corresponding translational function; $C(j_1,j_2,m_1,m_2|J_\eta,J_\Omega_v)$ are the Clebsch-Gordan coefficients; $\delta_\eta$ and $\delta_\Omega$ stand for the two quantum numbers $(n_j,|j_1,j_2)$, where $n_j$ and $j_1$ are vibrational and rotational quantum numbers. As for $\delta_\Omega$, $i=1,2$, the final result will depend only on $\delta_\eta=\delta_\Omega[\text{the Jacobi coordinates for the two interacting diatoms are shown in Fig 1(a)}]$

The translational equation for $\zeta_{0v}(R_1|t_1,t_2,J_\eta,J_\Omega_v)$ is given in the form

\[ \frac{-\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R_{1\eta}^2} + w(R_{1\eta}) + \frac{\hbar^2}{2\mu_2} \frac{J(J+1)+J_\eta(J_\eta+1)-2\Omega_\eta^2}{R_{1\eta}^2} - \frac{\hbar^2}{2\mu_3} k(t_1t_2) \zeta_{0v}(R_1|t_1,t_2,J_\eta,J_\Omega_v) = 0, \]

where

\[ k(t_1t_2) = \left[ \frac{2\mu_3}{\hbar^2} \left[ E - e_1(t_1) - e_2(t_2) \right] \right]^{1/2} \]

and $e_i(t_i)$, $i=1,2$ are eigenvalues of the two diatomics.

**2. The products equation** ($\alpha=\lambda$)

In the case of $\alpha=\lambda$, one encounters an atom and a triatom and consequently $T_\lambda$ becomes

\[ T_\lambda = -\frac{\hbar^2}{2mr} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial \rho_\lambda^2} + \frac{\hbar^2}{2\mu_3} \frac{\partial^2}{\partial R_\lambda^2} + \frac{1}{2\mu_2} \frac{\partial^2}{\partial \rho_\lambda^2} \frac{\hbar^2}{2mr^2} \]

where $\Omega_\lambda$ is the projection of $K$ and $J$ along \( \hat{r} \). Next $R_\lambda$ is considered to be the BF z axis for the triatom system and consequently the representation of $(K-j)^2$ is

\[ (K-j)^2 = h^2 [K(K+1)-2\Omega_\lambda^2] + j^2, \]

where $\Omega_\lambda$ is the projection of both $K$ and $J$ along $\hat{r}$. As for $W_\lambda$, it is assumed to be of the form

\[ W_\lambda(rp_\lambda,\theta) = v(rp\theta) + w_\lambda(R_\lambda) \]

where $v(rp\theta)$ is the potential of the isolated triatom and $w_\lambda(R_\lambda)$ is the $\lambda$th distortion potential which is assumed to increase once $R_\lambda$ is small enough and decreases. If $\theta$ is the spherical angle defined as

\[ \theta = \cos^{-1} (\hat{r} \cdot \hat{\rho}), \]

then $w_\lambda(R_\lambda)$ is assumed to be

\[ w_\lambda(R_\lambda) = U(R_\lambda p_\rho\rho_\sigma \sigma_\rho \beta_\sigma), \]

where $U$ again is the full potential, this time expressed in
FIG. 2. Bend–vibrational–rotational eigenstates as calculated for the H$_2$O molecule. Results are for $\Omega = 0$.

terms of $\lambda$ coordinates; and $r_e$, $\rho_e$, and $\theta_e$ are the equilibrium coordinates for the triatom. $\beta$ and $\gamma$ are two spherical coordinates relating $\rho$ to $R_\lambda$, in particular, $\gamma$ is the angle between $R_\lambda$ and $\rho$, namely,
\[
\gamma = \cos^{-1}(\hat{R}_\lambda \cdot \hat{\rho}).
\] (25)

$\beta$ and $\gamma$ are fixed angular values which serve as parameters and the final results are not expected to be dependent on them (the same as for $r_e$, $\rho_e$, and $\theta_e$). The Jacobi coordinates for the interacting atom–triatom system are shown in Fig. 1(b).

Since the potential $W_\lambda$ is separable, the solution of Eq. (4) for $\alpha = \lambda$ takes the form
\[
\psi_{\lambda}(r \rho \theta \gamma | v\tilde{y}u' K \Omega v' \Omega) = \frac{1}{r \rho \lambda} \phi_\lambda(r \rho \theta | v\tilde{y}u' K \Omega \lambda) \zeta_\lambda(R_\lambda | v\tilde{y}u' K \Omega v' \Omega) \chi_{\lambda}(\gamma),
\] (26)

where $\phi_\lambda(r \rho \theta | v\tilde{y}u' K \Omega \lambda)$ and $\zeta_\lambda(R_\lambda | v\tilde{y}u' K \Omega v' \Omega)$ are the eigenfunctions of the equation
\[
\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2 \mu} \frac{\partial^2}{\partial \rho^2} + \frac{j^2}{2} \left( \frac{1}{mr^2} + \frac{1}{\mu \rho^2} \right)
\right. \\
+ \frac{\hbar^2 [K(K+1) - 2\Omega_\lambda^2]}{2 \mu \rho^2} + v(r \rho \theta) - e(v \tilde{y}u' K \Omega v' K \Omega)
\left. \right\} \phi_\lambda(r \rho \theta | v\tilde{y}u' K \Omega \lambda) = 0
\] (27)
and $\zeta_\lambda(R_\lambda | v\tilde{y}u' K \Omega v' \Omega)$ are solutions of the equation
\[
\left\{ -\frac{\hbar^2}{2 \mu} \frac{\partial^2}{\rho \partial R_\lambda^2} + w_\lambda(R_\lambda) + \frac{\hbar^2}{2 \mu} \frac{j(j+1)}{R_\lambda} \frac{K(K+1)}{2 \Omega_\lambda^2} R_\lambda^2
\right. \\
+ \frac{\hbar^2}{2 \mu} k^2(v \tilde{y}u' K \Omega v' K \Omega) \right\} \zeta_\lambda(R_\lambda | v\tilde{y}u' K \Omega v' \Omega) = 0.
\] (28)

Here $e(v \tilde{y}u' K \Omega v')$ are eigenvalues of Eq. (27) (see Fig. 2) and $k(v \tilde{y}u' K \Omega v')$ are given in the form
\[
k(v \tilde{y}u' K \Omega v') = \left( \frac{2 \mu_k}{R_\lambda^2} [E - e(v \tilde{y}u' K \Omega v')] \right)^{1/2}.
\] (29)

B. The derivation of the perturbed function $\chi_\lambda$

The function $\chi_\lambda$ is derived by solving Eq. (1) in $v$ AC (the AC of the two interacting diatomics). For this sake, $v$ AC is enlarged significantly by extending the range of the reactants’ vibrational coordinate(s) into the corresponding reactive AC(s). In our particular case, only one reactive bond is encountered, namely, the H$_2$ bond; consequently, as will be seen, the calculations are carried out for an extended range of the H$_2$ vibrational coordinate $r_1$, i.e., $0.4 \leq r_1 \leq 3.2$ Å.

The Hamiltonian $H_\lambda$ in Eq. (1) will be written in the form
\[
H_\lambda = \tilde{T}_v + \tilde{U}(R_r, r_1 r_2) + V_\lambda(R_r, r_1 r_2),
\] (30)
where $\tilde{T}_v$ is the kinetic energy operator takes the form
\[
\tilde{T}_v = \frac{\hbar^2}{2 \mu_r} \frac{\partial^2}{\partial r_1} r_1^2 + \frac{\hbar^2}{2 \mu_r} \frac{\partial^2}{\partial r_2} r_2^2 + \frac{\hbar^2}{2 \mu_r} \frac{\partial^2}{\partial R_v} R_v \\
+ \frac{\hbar^2}{2} j_1(j_1+1) \left( \frac{1}{\mu_r} + \frac{1}{\mu_r} \right) + \frac{\hbar^2}{2} j_2(j_2+1) \\
- \left( \frac{1}{2 \mu_r^2} \right) + \frac{\hbar^2}{2 \mu_r^2} [J(j+1) - 2 \Omega_\lambda^2].
\] (31)

$\tilde{U}(R_r, r_1 r_2)$ is the QBS potential which follows from $U(R_r, r_1 r_2, \gamma_1 \gamma_2 \delta)$ by treating the three angles ($\gamma_1 \gamma_2 \delta$) as parameters and not as variables.

$\tilde{U}(R_r, r_1 r_2) = U(R_r, r_1 r_2 | \gamma_1 = \gamma_1, \gamma_2 = \gamma_2, \delta = \delta_0),
\] (32)
and $V_\lambda(R_r, r_1 r_2)$ is the required NIP which is made up of several terms. They number $M+1$ at most, with $M$ being the number of reactive bonds. In our case, in $v$ AC, two bonds (the H$_2$ and the OH bonds) are encountered, and of these, only the H$_2$ bond is reactive (for energies below breakup). Consequently, two negative imaginary terms are to be added to the real Hamiltonian—a vibrational term $iv_r$ and the translational term $iv_{IR}$. Thus
\[
\tilde{V}_\lambda(R_r, r_1 r_2) = -i[v_r(r_1) + v_{IR}(R)].
\] (33)

The potentials are assumed to be the Baer–Neuhauser (BN) linear ramp potentials$^5$
\[
\tilde{V}_{\lambda}(x) = \begin{cases}
\frac{x-x_L}{\Delta x}, & x_L \leq x \leq x_L + \Delta x_L, \\
0, & \text{otherwise}.
\end{cases}
\] (34)

Here $x_L$ is a point in the asymptotic region, $\Delta x_L$ is the range along which $V_{\lambda} \neq 0$, and $V_{\lambda}$ is the height of the potential. The two parameters $\Delta x_L$ and $V_{\lambda}$ are determined according to the BN inequalities.$^5$

Returning to Eqs. (1) [and (3)], it is noticed that $V_{\lambda}$ (and $V_{\nu}$) must still be presented explicitly. In both cases $V_{\lambda}$, $V_{\lambda}$, and $V_{\nu}$ are defined as
where \( W_v \) and \( W_k \) are given in Eqs. (12) and (19), respectively.

We continue to describe the derivation of \( \chi_\lambda \). Since the whole treatment is to be carried out in \( \nu \) AC for a given set of three Jacobi angles \( (\gamma_1, \gamma_2, \gamma_3) \), we shall omit the index \( \nu \) and any references to these angles.

Adding the two NIPS to the real potential \( U \) converts the scattering problem into a bound system problem and, consequently, \( \chi_\lambda \) can be expanded in terms of square integrable \( L^2 \) functions. The ones we chose are localized functions for the translational components and adiabatic basis sets related to the two vibrational coordinates. Thus

\[
\chi_\lambda(R_1R_2|j_1j_2\Omega\nu|v\hat{j}v'K\Omega_k\Omega_k) = (R_1R_2)^{-1} \sum_{q} a^j(j_1j_2\Omega\nu|v\hat{j}v'K\Omega_k\Omega_k\nu)g(R|q)f(r_1r_2|j_1j_2\nu|q't') \]

where

\[
g(R|q) = \left( \frac{\alpha}{\sigma^2 \pi} \right)^{1/2} \exp \left[ -\frac{\alpha^2}{2} \left( \frac{R - R_q}{\sigma} \right)^2 \right].
\]

Here \( \sigma \) is the translational step size.

As for \( f(r_1r_2|j_1j_2\nu|q't') \), it is an eigenfunction of the equation

\[
-\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} + U(r_1r_2R=\hat{R}) + \frac{\hbar^2}{2} \left[ \frac{j_1(j_1+1)}{\mu_1r_1^2} + \frac{j_2(j_2+1)}{\mu_2r_2^2} \right] - \epsilon(t_1j_1|\hat{R})f(r_1r_2|j_1j_2\nu|q't') = 0.
\]

Substitution of Eqs. (26) and (36) in Eq. (1), multiplying it by \( g(R'q')f(r_1r_2|j_1j_2\nu|q't') \), and integrating over \( R, r_1, \) and \( r_2 \), we obtain the following algebraic matrix equation:

\[
(A - iT)\alpha = \gamma,
\]

where

\[
A_{q'q} = (g(R|q)f(r_1r_2|j_1j_2\nu|q't'))
\]

and

\[
B_{q'q} = (g(R|q)f(r_1r_2|j_1j_2\nu|q't'))\delta(R|q')f(r_1r_2|j_1j_2\nu|q't').
\]

Once Eq. (40) is solved, we substitute Eqs. (15), (26), and (36) in Eq. (3) to obtain the following \( S \) matrix element:

\[
S^J(\nu|\lambda) = S^J(t_1t_2J_\nu\Omega\nu|v\hat{j}v'K\Omega_K\Omega_k),
\]

which is then used to calculate the relevant state-to-state cross sections

\[
\sigma(t_1t_2|v\hat{j}v'K) = \pi \sum_{J_\nu} \sum_{J_\eta} \sum_{n_\kappa} \sum_{n_\eta} |S^J(t_1t_2J_\nu\Omega\nu|v\hat{j}v'K\Omega_K\Omega_k)|^2,
\]

where \( k(t_1t_2) \) is given in Eq. (18) and the summation over \( J_\nu \) is in the range \( |J_1 - J_2| \leq J_\nu \leq J_1 + J_2 \). Summing \( \sigma(n_1j_1n_2j_2|v\hat{j}v'K) \) over \( K \) yields \( \sigma(n_1j_1n_2j_2|v\hat{j}v') \) and summing it over \( (v\hat{j}v') \) will yield \( \sigma(n_1j_1n_2j_2|K) \).

These two cross sections in addition to the total cross section (all of them calculated at \( E = 0.3 \) eV) will be discussed in the next section.

### III. NUMERICAL DETAILS

In this work were calculated reactive cross sections given in Eq. (43) which stand for the following reaction:

\[
H_2(n_1j_1) + OH(n_2j_2) \rightarrow H_2O(v\hat{j}v'K\Omega_K) + H.
\]
TABLE I. Reactive cross sections (in atomic units) for the process H,(v,=0, j,=0) + OH(v2=0, j2=0) → HO(j=K)+H as calculated for E,=0.3 eV.

| K
| (000) | (010) | (020) | (030) | (040) | (001) | (011) | (021) | Total* |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0   | 0.058  | 0.038  | 0.032  | 0.028  | 0.006  | 0.020  | 0.008  | 0.006  | 0.002  |
| 1   | 0.122  | 0.083  | 0.048  | 0.024  | 0.007  | 0.034  | 0.017  | 0.007  | 0.005  |
| 2   | 0.138  | 0.083  | 0.020  | 0.016  | 0.018  | 0.010  | 0.004  | 0.006  | 0.001  |
| 3   | 0.140  | 0.069  | 0.035  | 0.019  | 0.005  | 0.022  | 0.008  | 0.003  | 0.002  |
| 4   | 0.114  | 0.071  | 0.029  | 0.016  | 0.004  | 0.015  | 0.005  | 0.002  | 0.003  |
| 5   | 0.079  | 0.063  | 0.022  | 0.010  | 0.001  | 0.010  | 0.004  | ...    | 0.200  |
| 6   | 0.054  | 0.056  | 0.017  | 0.009  | ...    | 0.005  | 0.001  | ...    | 0.153  |
| Total | 0.705  | 0.463  | 0.203  | 0.122  | 0.041  | 0.116  | 0.047  | 0.024  | 0.013  |
| Corrected | 1.003  | 0.658  | 0.398  | 0.174  | 0.058  | 0.165  | 0.067  | 0.034  | 0.019  |

*The numbers in this column are usually larger than the sum of the numbers in the corresponding row. The differences are due to round off errors.

of which the largest one was excluded altogether as it was found, after a careful study, that no reactions originated from there. We found that a large fraction of the reactions came from configurations, where the three atoms H-H-O are almost collinear and the fourth (H) atom oscillates on the right-hand side of the oxygen atom in the range (0°-45°).

To solve Eq. (1) (for a given ψK), the R, translational axis was divided by 30-35 equidistant grid points. To each point was attached one Gaussian which stands for a translational basis function and a set of adiabatic doubly vibrational basis functions [see Eq. (39)]. The number of these functions varies from one grid point to the other and is determined by two given energy values [see also the discussion in Ref. 6(c)]. The first energy value determines the number of adiabatic states in the strong interaction region and the other in the outside region where usually only a small number of states is needed and therefore is much lower (even lower than the total energy).

The R, axis was also divided into two large intervals—the one along which the NIP is defined (this interval is located in the asymptotic part of R,.) and the other where the NIP is identically zero. In the present treatment, the whole range of R, is (1.0-4.5 Å) and the one along which the NIP is different from zero is (R, (R,+ΔR,))=(3.8-4.5 Å). The height V,R of the NIP is 0.6 eV.

The last subject is related to the size of the A, matrix defined as [see Eq. (40)]

\[ A_i = A_{i'} - iB \]

We found out that in order to ensure convergence, the number of states that are required to expand the χ formation is about 600. Consequently, we had to construct a matrix of 600×600 and a system of 600 complex equations had to be solved for each value of J (and, of course, for each value K, ΩK and Ω, and each set of angles (γ1γ2δ)). This is in addition to the construction of the inhomogeneous columns (the Z matrix) and the calculation of the various overlaps.

IV. RESULTS AND DISCUSSION

The aim in the present publication is to obtain total cross sections within the approximations presented here. It turned out that in order to achieve this goal, we had to let our workstation run several months. Consequently, we can report on results for one single energy namely E,=0.3 eV and for one single initial state H2(ν,=0, j,=0)+OH(ν2=0, j2=0).

In what follows, all notations of the form a(ijk...) will designate state-to-state cross sections with the final state (ijkl...).

A. Bend–vibrational–rotational final state distribution

Three dimensional cross sections \( σ(ν'j'ν'K) \) are given in Table I for K values between zero and six. In addition to these are presented \( σ(K) \) and \( σ(ν'j') \), which were obtained following a summation over \( (ν'j') \) and \( K \), respectively. Normalized cross sections, namely, \( σ(ν'j'ν'K)/σ(ν'j'ν'K=0) \) are shown in Fig. 3 for four K values, i.e., \( K=0, 2, 4, \) and 6. The main conclusion to be drawn is that our treatment indicates that the higher the bend or the vibrational state, the less populated it becomes. However, it is also noticed that this outcome is caused mainly by the low K values, and as K increases, the relative population of the higher bend states increases as well. There are indications
that this tendency continues to higher $K$ states, but we encountered uncertainties in obtaining results for high $K$ states. The problem in the higher $K$ values is, to a certain extent, presented in Table II, where we give the more detailed cross sections, namely, $\sigma(v_jv'K)$ for $K = 4$, and as is noticed, these numbers are relatively small and they become much smaller for $K$ values larger than six. The reason is not only because $\sigma(K)$ decreases as a function of $K$, but also because the number of $\Omega_K$'s increases as well, and so the relative contribution of each single $\sigma(v_jv'K\Omega_K)$ to $\sigma(v_jv'K)$ (or to less detailed cross sections) becomes smaller and smaller. We arbitrarily decided to stop at $K = 6$.

B. Rotational and total cross sections

Rotational state distribution is presented in Fig. 4. As is noticed, the curve is smooth, peaks at $K = 2$, and from there on gradually decreases to zero. Such a (low energy) functional dependence was also encountered in triatom systems that were recently studied.

In order to obtain the total cross sections $\sigma_{\text{tot}}$, we need to be able to extrapolate $\sigma(K)$ to $K$ values larger than six. This is done in the following way:

Presenting $R(K) = \frac{\sigma(K)}{\sigma(K, \Omega_K = 0)}$ for $0 \leq K \leq 6$ and as can be seen all calculated values except for $K = 0$ are distributed nicely along the straight line. This line is extrapolated to the value of $K = 9$ for which is obtained the value of $R(K=9) = 5.80$. In order to obtain $\sigma(K)$, we calculated $\sigma(K=9, \Omega_K = 0)$ which was found to be 0.0134 a.u. Knowing both $\sigma(K=9, \Omega_K = 0)$ and $R(K)$ yields for $\sigma(K=9)$ the value of 0.078 a.u., which is reason-

![Fig. 3. Normalized bend-vibrational distributions as calculated for various rotational states (namely, $\sigma(v_jv'K)$). Each distribution is normalized separately.](image)

![Fig. 4. The overall final rotational state distribution $\sigma(K)$.](image)

<p>| Table II. Reactive cross sections (in atomic units) for the process $H_2(\sigma_1 = 0, j_1 = 0) + \text{OH}(\sigma_2 = 0, j_2 = 0) \rightarrow H_2O(v_jv'K = 4\Omega_K) + H$ as calculated for $E_r = 0.3$ eV. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>$\Omega_K(v_jv')$</th>
<th>(000)</th>
<th>(010)</th>
<th>(020)</th>
<th>(030)</th>
<th>(040)</th>
<th>(001)</th>
<th>(011)</th>
<th>(100)</th>
<th>(110)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.023</td>
<td>0.024</td>
<td>0.014</td>
<td>0.006</td>
<td>0.002</td>
<td>0.006</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
<td>0.078</td>
</tr>
<tr>
<td>1</td>
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<td>0.018</td>
<td>0.007</td>
<td>0.002</td>
<td>0.001</td>
<td>0.004</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.033</td>
</tr>
<tr>
<td>-1</td>
<td>0.016</td>
<td>0.010</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
<td>...</td>
<td>0.001</td>
<td>0.034</td>
</tr>
<tr>
<td>2</td>
<td>0.018</td>
<td>0.009</td>
<td>0.003</td>
<td>0.001</td>
<td>...</td>
<td>0.002</td>
<td>0.001</td>
<td>...</td>
<td>0.001</td>
<td>0.034</td>
</tr>
<tr>
<td>-2</td>
<td>0.010</td>
<td>0.002</td>
<td>0.001</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>3</td>
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<td>0.003</td>
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<td>0.001</td>
<td>...</td>
<td>...</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>0.006</td>
<td>0.002</td>
<td>0.001</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.007</td>
<td>0.002</td>
<td>...</td>
<td>0.005</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>0.003</td>
<td>0.001</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.114</td>
<td>0.071</td>
<td>0.029</td>
<td>0.016</td>
<td>0.004</td>
<td>0.015</td>
<td>0.005</td>
<td>0.002</td>
<td>0.003</td>
<td>0.269</td>
</tr>
</tbody>
</table>
ably close to the extrapolated value of Fig. 5. Assuming that $\sigma(K)$ for $K \geq 2$ can be presented in the form

$$\sigma(K) = A e^{-\alpha(K-2)}, \quad K \geq 2,$$

it was found that $\alpha \approx 0.297$. Once $\alpha$ is known, we are in the position to estimate $\sigma_{\text{tot}}$,

$$\sigma_{\text{tot}} = \sum_{K=0}^{6} \sigma(K) + \sigma(K=6) \sum_{j=1}^{\infty} e^{-\alpha j}.$$  \hspace{1cm} (47)

The first term is equal to 1.814 a.u. (see Table I), whereas the second term is found to yield the value of 0.644 a.u. Thus altogether is obtained

$$\sigma_{\text{tot}}(E_v=0.3 \text{ Å}) = 2.458 \text{ a.u.}$$  \hspace{1cm} (48)

It is important to mention that about 75% of the total cross section was calculated directly and only 25% of it is estimated by extrapolation.

C. The bend–vibrational cross sections

In Table I are given two types of $\sigma(uju')$'s. The first is just the sum over the seven $K$ values and the second is the one normalized in such a way to give the correct (estimated) total cross section. The values of $\sigma(uju')$ for the various $(uju')$ states are presented in Fig. 7. Here again we see what was already discussed before, namely, the relative large populations of the lower bend states, in particular, $(000)$.

D. Comparison with other numerical results

Reaction (I) was studied by several groups, but the possibilities to compare results are very limited. The two main reasons are (1) that we have integral state-to-state and total cross sections for one energy value only and one single initial state (the other groups have done, in this respect, more extensive calculations) and (2) so far we are the only group to carry out a detailed quantum mechanical study of the rotational distribution. Thus we have to limit ourselves to the comparison given in Table III, where in addition to our results are shown QCT,$^{(a)}$ quantum-classical reaction path (QCRP),$^{(d)}$ and approximate QM$^{(g)}$ cross sections. In Table III are presented final $(uju')$ distributions as calculated for $E_v=0.3$ eV. The following can be said:

1. There is a significant difference between the QCT and all QM results; the QCT treatment is found to yield a much more homogeneous distribution than the QM ones.
2. Our distribution seems to be similar to Billing's QCRP$^{(d)}$ distribution.
3. Our results seem to differ rather significantly from those of Clary$^{(g)}$ in particular, regarding the vibrational excitation. It could be that freezing the OH bond (and some of the angles) as is done in Clary's treatments is responsible for the unusual large vibrational excitation.
4. The fact that relatively large vibrational excitations are encountered in the QCT treatment could be due to the
TABLE III. Reactive cross sections (in atomic units) for the process
H$_2$(n$_1$=0, j$_1$=0) + OH(n$_2$=0, j$_2$=0) → H$_2$O(v', j') + H. A comparison between various results as calculated for $E_r$=0.3 eV.

<table>
<thead>
<tr>
<th>v'j'</th>
<th>QCT</th>
<th>QCRM</th>
<th>QM</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>(000)</td>
<td>0.47±0.09</td>
<td>1.00</td>
<td>0.46</td>
<td>1.00</td>
</tr>
<tr>
<td>(010)</td>
<td>0.44±0.07</td>
<td>0.68</td>
<td>1.20</td>
<td>0.66</td>
</tr>
<tr>
<td>(020)</td>
<td>0.49±0.08</td>
<td>0.25</td>
<td>0.51</td>
<td>0.29</td>
</tr>
<tr>
<td>(030)</td>
<td>0.16±0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.17</td>
</tr>
<tr>
<td>(040)</td>
<td>0.17±0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>(001)</td>
<td>0.57±0.09</td>
<td>0.00</td>
<td>0.68</td>
<td>0.17</td>
</tr>
<tr>
<td>(100)</td>
<td>0.29±0.07</td>
<td>0.04</td>
<td>0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>(011)</td>
<td>0.36±0.07</td>
<td>0.00</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>(110)</td>
<td>0.24±0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>3.70±0.20</td>
<td>2.36</td>
<td>2.95</td>
<td>2.46</td>
</tr>
</tbody>
</table>

*These calculations were done for $E_r$=0.24 eV.
†Calculations carried out with a frozen OH bond and $\Omega_j=0$.
‡Quasiclassical trajectory calculation [Ref. 3(a)].
§Quantum-classical reaction path model calculation [Ref. 3(d)].
‖Approximate quantum mechanical calculation [Ref. 3(g)].

V. CONCLUSIONS

In this work, we treated, quantum mechanically, a tetraatomic reactive system in its full dimensionality and calculated detailed state-to-state exchange cross sections for the processes given in I. To achieve this, the relevant S matrix elements given in Eq. (3) had to be calculated. In what follows, we summarize the theoretical background emphasizing the approximations introduced.

We distinguish among three different treatments:

1. The derivation of $\psi_{0v}$ which is the unperturbed (asymptotic) wave function of the reagents—the two diatomics. The function $\psi_{0v}$ describes an elastic scattering process.

2. The derivation of $\psi_{0x}$ which is the unperturbed (asymptotic) wave function of the products—the atom and the triatom. Like $\psi_{0v}$, the function $\psi_{0x}$ describes an elastic scattering process.

3. The derivation of $\chi_x$ which is the perturbed part of the total wave function calculated in the enlarged reagents’ (or products’) AC.

The two functions $\psi_{0x}$ and $\psi_{0v}$ are treated in their full dimensionality (which also means keeping all relevant quantum numbers), namely, the functions are described employing all six internal coordinates. However, to reduce the computational efforts, we did not use the Arthurs–Dalgarno representation, but the one within the $j_z$ approximation. The $\chi_x$ function is also expressed in terms of all six coordinates, but is treated within the breathing sphere approximation. Here the three angles $(\chi_x)$ are considered as parameters of the potential rather than variables, and consequently for each separate calculation, the potential becomes isotropic. It is important to emphasize that the breathing sphere approximation, as employed here, is different from similar approximations used in the past (for instance, within the infinite order sudden approximation). The difference is in the fact that here this approximation is applied to the internal short-range part of the wave function only and not to the entire wave function. S-matrix elements were obtained for different randomly selected sets of $(\gamma_1\gamma_2\delta)$ angles. Final cross sections are calculated by averaging over these angles.

In general, breathing sphere type models may not always be fully reliable, but it is hard to believe that at this stage tetraatomic systems can be handled quantum mechanically without doing any freezing at all. Thus, within the two other existing approaches, the approximations done are much more severe. Clary [3(a)] freezes the OH bond and in this way misses, for instance, resonance effects in case of H$_2$O and one or two additional angles (the freezing is done for the whole process). Moreover, following his publications, it seems that a summation is not always carried out with respect to $\Omega_f$ and $\Omega_f$. Also, the elements of the rotation matrix $d_{ij}^n\Omega_x(\Delta)$ which play a dominant role in any theory and numerical treatments of state-to-state exchange processes seemed not to be included. The theoretical approach of Wang and Bowman [3(f)] is even more approximate. It is essentially based on deriving the reactive $P$ matrix elements for one single frozen configuration (the dynamical calculations follow an adiabatic
treatment carried out with respect to two angles which in our notation are \( \gamma_1 \) and \( \gamma_2 \) and is then extended to three dimensions employing a \( J \) shifting procedure.

The numerical treatment was carried out for one energy, i.e., \( E_u = 0.3 \) eV only, but still very interesting results were obtained. In particular, our treatment is the first to yield the detailed final vibrational–bend–rotational distribution for a given energy and, in particular, the final rotational distribution. It is important to emphasize that our cross sections follow for summations over all relevant quantum numbers, namely, \( J, a, \) and \( Q, \) and when necessary (for total cross section) also over \((uv')K\). In this respect, as in various other aspects, the present treatment is to date the most complete quantum mechanical treatment of a tetra-atom reactive process.

Note Added to Proof. We would like to thank the referee for calling our attention to Ref. 16. In this publication are considered for the first time rotational distributions for the \( \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} + \text{H} \) system. For the energy value \( E_u = 0.3 \) eV, Schatz and Elgersma obtained a rotational distribution along the range \((0–15)\) which is similar to ours, but is in general narrower and much hotter (it peaks at \( K = 6 \), whereas our peaks at \( K = 2 \)).

ACKNOWLEDGMENT

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