A new accurate (time-independent) method for treating three-dimensional reactive collisions: The application of optical potentials and projection operators

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This work describes a new (time-independent) approach to the study of atom–diatom reactive collisions in three dimensions. The method is based on the idea of converting a reactive multirangement problem into an inelastic single-arrangement problem. This conversion is done by applying optical potentials which are located at all exits of the reagents arrangement. The reactive transition probabilities are calculated applying flux formulas. The method is reminiscent of a previous time-dependent method successfully applied for both collinear and three-dimensional reactive collisions.

I. INTRODUCTION

A new method to treat atom–diatom exchange collisions, employing the time-dependent (TD) wave-packet approach, has recently been introduced.1–3 The method makes use of imaginary negative short-range potentials (as will be explained below) to convert a multirangement channel problem into a (slightly extended) single-arrangement problem. As has been demonstrated for both collinear1 and three-dimensional systems,2,3 this conversion did not affect the final results. In fact, in all cases, whether high- or low-energy processes, whether high- or low-temperature rate constants, whether J = 0 or J ≠ 0 cases and, recently, also for exothermic reactions, the results were found to be identical to those obtained by more established methods.4–15 As will also be demonstrated in this paper, this achievement is not necessarily due to the wave-packet TD approach but is of much more general aspect. The employment of a short-range negative imaginary potential,16,17 substituted at a place where only outgoing waves are encountered, has the important feature of not affecting the wave function in the region before it, and once it passes through it, causes the wave function to decay to zero along a very short distance.16 With these kinds of potentials being available, they can be substituted at exits that lead from the entrance arrangement to any product arrangement.1–3 Moreover, we found it convenient to substitute such a potential at the entrance (reagents) arrangement itself, and by doing this we reduced the numerical effort associated with this channel as well.18

In general, one may substitute these potentials either at exits to some of the products arrangements and then the S matrix elements for the other arrangements can be calculated accurately, or at exits of all arrangements and then the transition probabilities can be obtained employing flux expressions.

So far all of our applications of absorbing (optical) potentials were done within the TD approach.1,2 In the present work we would like to demonstrate their relevance for the time-independent (TID) approach. The advantage of such a TID method is very significant because the numerical treatment will take place in one (the reagents) arrangement channel only. In this way the savings in computer-time consumption and in programming effort is not only due to the reduced number of arrangements but also to the fact that the transformation from reagents to products coordinates (which is done in most current available methods4–15) is avoided.

The method as described so far has one disadvantage, namely, it does not produce the desired S-matrix elements. This is not a limitation as long as one is only interested in integral (even state-to-state) cross sections or rate constants. However, in case differential cross sections are required, this version of our method is not suitable yet.

It should also be pointed out that in our case the inelastic arrangement is somewhat extended (as compared to those of ordinary nonreactive systems), and therefore the usual close-coupling techniques, which are based on the asymptotic vibrational states, are not of practical use. Instead, we decided to follow the numerical procedure used in our wave-packet TD study and utilize the projection operators19–21 and the grid-point approach. In this sense the method becomes reminiscent of some methods employed one or two decades ago to solve the collinear (reactive) system.22–25

In this work we consider the reactive system in its full dimensionality (namely in three dimensions). However, since most of the three-dimensional concepts and relations are known and have appeared recently many times in the published literature,4–15 we shall not always carry out the required algebra in detail. Another fact to be mentioned is that a paper in which the collinear version of this method is described appeared in print.18

The paper is organized in the following way: In Sec. II we give a full description of the theory with emphasis on the three-dimensional aspects of the problem; numerical facts and a few results are presented in Sec. III and conclusions in Sec. IV.
II. THEORY

A. The methodology

1. The Schrödinger equation

We consider two Schrödinger equations.

(a) The first stands for the general case, where the motion of the three interacting particles is described in terms of the full Hamiltonian

\[(E - H) \Psi = 0.\]  

(2.1)

(b) The second stands for the unperturbed case, where the motion of the three interacting particles is described in terms of an unperturbed Hamiltonian \(H_0\):

\[(E - H_0) \Psi_0 = 0.\]  

(2.2)

Accordingly, \(\Psi\) is the full and \(\Psi_0\) is the unperturbed solution.

If \(V(R, r, \gamma)\) is the perturbation potential (\(\gamma\) is the orientation angle defined as \(\gamma = \cos^{-1}(R \tau)\)), then the time relation between \(H\) and \(H_0\) is

\[H = H_0 + V.\]  

(2.3)

In what follows \(V(R, r, \gamma)\) is assumed to fulfill the following condition:

\[\lim_{R \to \infty} V(R, r, \gamma) = 0.\]  

(2.4)

Assuming the unperturbed solution \(\Psi_0\) is known, the full solution \(\Psi\) can be written as

\[\Psi = \Psi_0 + G,\]  

(2.5)

where it can be easily shown that \(G\) fulfills the following inhomogeneous equation:

\[(E - H) G = V \Psi_0.\]  

(2.6)

The next step is to choose the unperturbed potential \(W(R, r, \gamma)\). In the present treatment we assumed \(W(R, r, \gamma)\) to be independent of \(\gamma\) and to be of the following form:

\[W(R, r, \gamma) = W(R, r) = v(R) + w(R),\]  

(2.7)

where \(v(R)\) is the diatomic potential (of the reagent molecule) and \(w(R)\) is a distortion potential which increases as \(R\) decreases so that \(R \Psi_0(R, r)\) is guaranteed to go to zero as \(R \to 0\). In the actual applications \(w(R)\) was chosen to be

\[w(R) = U(R, r = r_0y) = 0,\]  

(2.8a)

where \(U(R, r, \gamma)\) is the full potential and \(r_0\) is the equilibrium distance of the reagent molecule.

Once the unperturbed potential is determined [see Eq. (2.7)] it follows that \(V(R, r, \gamma)\) is given in the following form:

\[V(R, r, \gamma) = U(R, r, \gamma) - W(R, r).\]  

(2.8b)

The above choice of \(W(R, r)\) guarantees elasticity with regard to both the rotational and vibrational motions. Consequently, the solution of Eq. (2.2) can be written (in the fixed-body frame) as

\[\Psi_0(R, r | n_0, J_0 | M) = \frac{1}{Rr} \left(\frac{2j + 1}{4\pi}\right)^{1/2} \phi(r | n_0, J_0)\]

\[\times \sum_{n_0 = -n_0}^{n_0} D'_{n_0, n} (\Lambda) \gamma_{n_0} (\gamma, 0)\]

\[\times \xi (R | n_0, J_0 | M | \Omega, J),\]  

(2.9)

where \(J\) is the total angular momentum, \(M\) and \(\Omega\) are the \(z\) components in the space-fixed and the body-fixed systems of coordinates, respectively, \(\Lambda\) stands for the three Euler angles

\[\Lambda = (\phi, \theta, \delta),\]  

(2.10)

\(D'_{n_0, n} (\Lambda)\) are the coefficients of the irreducible representation of the rotation group, \(\gamma_{n_0, n} (\gamma, 0)\) are the spherical harmonics, \(\phi(r | n_0, J_0)\) are the vibrational eigenfunctions of the Hamiltonian:

\[\left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + v(r) + \frac{J_0 (J_0 + 1)}{r^2} - \epsilon_{n_0} \right] \phi(r | n_0, J_0) = 0,\]  

(2.11)

\[\xi (R | n_0, J_0 | M | \Omega, J)\) are the corresponding translational components of the wave function, and \(\sigma_0\) stands for

\[\sigma_0 = \min (j_{max}).\]  

(2.12)

In the case \(J_0 = 0\), \(\sigma_0\) becomes equal to zero, as does \(\Omega\), so that the summation in Eq. (2.9) reduces to a single term. As for Eq. (2.11), here \(\epsilon_{n_0}\) is the vibrational eigenvalue and \(\mu\) is the reduced mass of the system (here and throughout this paper \(R\) and \(r\) are assumed to be mass scaled):

\[\mu = \left( \frac{m_A m_B m_C}{m_A + m_B + m_C} \right)^{1/2},\]  

(2.6)

where the three masses \(m_A\), \(m_B\), and \(m_C\) refer to the masses of the three interacting atoms. Equation (2.6) can be used without essential difficulties for a nonreactive case, but it is expected that it will be a formidable task when rearrangements are included. We present here an approach which converts the reactive problem into a pseudo-nonreactive one, and as a consequence Eq. (2.6) can be used with relative ease to treat collisions which involve rearrangements.

The conversion of a reactive into a pseudo-nonreactive system is done by applying the short-range negative imaginary absorbing potentials \(V_I (R, r, \gamma)\), which are substituted at the entrances of all products channels. Since these potentials can be made "total" absorbers, they will not affect the wave functions in the interior region as long as they are not substituted too close to the interaction region. In the actual application, the absorbing potentials are added to the total potential and the solution of Eq. (2.6) is carried out with them included in \(H\) (but not in \(H_0\)). The absorbing potentials (as in our previously described TID wave-packet approach\(^{1,2}\)) cause \(G\) and consequently also \(\Psi\) to be zero in regions beyond them, namely in the products regions. Consequently, the products channels become obsolete and the whole reactive system reduces to a pseudo-nonreactive one.

In Fig. 1 is shown the potential-energy surface for a three-dimensional reactive system in terms of the reagents (mass-scaled) coordinates. The absorbing potential is presented as a cylinder in the vicinity of the strong interaction region and is seen to wrap the entrance channel, thus ensuring that \(G\) (and \(\Psi\)) will be zero outside this cylinder. A convenient form for such a potential would be

\[V_I (R, r, \gamma) = \begin{cases} -i V_k \frac{r - r_I}{\Delta r_I}, & r_I < r < r_I + \Delta r_I \quad (2.13) \\ 0, & \text{otherwise}, \end{cases}\]
where $V_{r_e}$ is a real constant. As can be seen, the potential depends neither on $R$ nor on $\gamma$; it is a linear increasing function of $r$ in the region $(r_I, r_I + \Delta r)$ and zero otherwise. Elsewhere, we verified that in order for this potential to be a complete absorber $V_{r_e}$ for a given kinetic energy $E_k$ and a (reduced) mass $\mu$, it must fulfill the two conditions:\footnote{16}{\textit{This completes the presentation of the Schrödinger equation.}}

\begin{equation}
\hbar E^{1/2} / (\Delta r_{r_e} / \sqrt{8\mu}) < V_{r_e} < E^{1/2} / \Delta r_{r_e} / \sqrt{8\mu} / \hbar.
\end{equation}

Further discussion about the flux calculation will be presented in Sec. II E.

\section*{B. Derivation of the explicit equation}

Following the presentation of $\Psi_0$ in Eq. (2.9), the function $G(R, r) | n_o, j_o, M \rangle$ will be written as:

\begin{equation}
G(R, r) | n_o, j_o, M \rangle = \frac{1}{R^r} \sum_{\alpha = -J}^{J} \sum_{\beta = |\alpha|}^{|\alpha|} (2J + 1)^{1/2} \times D_{\alpha \beta}^{(2J + 1)} (A) \psi_{j_o} (\gamma, 0) \times \xi (R, r) | n_o, j_o, M \rangle \langle j, \Omega, J).
\end{equation}

The corresponding Hamiltonian is of the following form:

\begin{align}
H &= -\hbar^2 \left( \frac{1}{R} \frac{\partial^2}{\partial R^2} + \frac{1}{r} \frac{\partial^2}{\partial r^2} \right) + \frac{1}{2\mu} \left( \frac{1}{R^2} + \frac{1}{r^2} \right) J^2 \\
&\quad + \frac{1}{2\mu R^2} (J^2 - J^2) + J_{+} J_{-} - J_{-} J_{+}
\end{align}

where all the angular momenta are operators [here $J_{+}$ ($J_{-}$) and $J_{\pm}$ ($J_{\mp}$) are the raising and lowering operators]. Substituting Eqs. (2.9), (2.18), and (2.19) in Eq. (2.6) and performing all the usual multiplications and integrations yields the following set of differential equations:

\begin{equation}
T_{\alpha \nu}^{(\pm 1)} = -\frac{\hbar^2}{2\mu R^2} \left( [J^2 (J + 1) - \Omega^2 (\Omega + 1)] \right)
\end{equation}

\begin{equation}
U^{(\pm 1)} (R, r, j, f) = 2\pi \int_{-1}^{+1} d(\cos \gamma) y_{\alpha} (\gamma, 0) \times U (R, r, \gamma) y_{\alpha} (\gamma, 0),
\end{equation}

where $P_{re} = \int dS j(r = r_I, \hat{r}, R)$, and $dS = u_d d^3R d^3r \delta (r - r_I)$.
and a similar expression for $V_{\Omega j_{j}}(R,r|j_{j},j_{j})$.

It must be emphasized that when the $U(R,r|j_{j},j_{j}^{'})$ matrix elements are calculated, the negative imaginary absorbing potentials must be included.

In order to shorten the notation, we omit the variables $R$ and $r$ and introduce the following two matrices:

$$H^{'j}(j_{j},j_{j}^{'},\Omega) = \begin{cases} \mathbb{T}^{\Omega_{j_{j}}} + U(\Omega,j_{j},j_{j}^{'},j_{j}^{'},\Omega), & j_{j} = j_{j}^{'}, \Omega = \Omega^{'}, \\ \mathbb{T}^{\Omega_{j_{j}}} + 1, & j_{j} = j_{j}^{'}, \Omega = \Omega^{'}, \\ U(\Omega,j_{j},j_{j}^{'},j_{j}^{'},\Omega), & j_{j} \neq j_{j}^{'}, \Omega = \Omega^{'}, \\ 0, & \text{otherwise}, \end{cases}$$

where $U(\Omega,j_{j}^{'},j_{j}) = U_{0}(R,r|j_{j},j_{j}^{'})$.

Also, we shall make the following abbreviation:

$$V(j_{j},j_{j}^{'},\Omega_{j_{j}}) = V_{0}(R,r|j_{j},j_{j}^{'},\Omega_{j_{j}}),$$

so that Eq. (2.20) becomes

$$\sum_{j_{j}^{'}} [E_{D_{j}} \delta_{\Omega_{j_{j}}} - H^{'j}(j_{j},j_{j}^{'},\Omega)] \zeta(R,r|n_{0},j_{0}M,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'})$$

$$= \delta_{\Omega_{j_{j}}} V(j_{j},j_{j}^{'},\Omega_{j_{j}}) \phi(r|n_{0},j_{0}) \zeta(R,n_{0},j_{0},M,\Omega_{j_{j}}).$$

(2.24)

This concludes the derivation of the equation to be solved for the unknown functions $\zeta(R,r|n_{0},j_{0}M,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'})$.

### C. Evaluation and Discussion

There are several ways to solve equations of the above type. We shall mention two of them and describe one in more detail. However, first we shall make one additional change related to the negative imaginary short-range potentials. So far they were substituted at all exits from the reagents arrangement channel. We found it most convenient to assume such a potential also at the entrance of this channel (at $R = R_{1}$; see Fig. 1). This addition, in fact, converts the scattering problem to a bound-state problem. The reason is that the unknown functions $\zeta(R,r|n_{0},j_{0}M,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'})$ go to zero whenever either $R \rightarrow 0$ or $r \rightarrow 0$, or when both $R$ and $r$ are large (the plateau region), or at the exits of the reagents channel due to the absorbing potentials and now also at the entrance to this channel, again due to an absorbing potential. The fact that the values of the $\zeta$ functions are known at all boundaries, as well as the fact that the equation to be solved is inhomogeneous, has important consequences not only with respect to the method to be applied to solve it but also with respect to the fact that the derived solution is unique, so that for each set of initial conditions the system of coupled equations can be solved separately. In other words, with this method one can generate one single column of the $S$ matrix or the probability $P$ matrix at a time (in this sense the method is reminiscent of a different method suggested about ten years ago by Thomas and of more recent methods applied within the operator formalism). The advantage of such an approach becomes most apparent in case the system of algebraic equations which follows from Eq. (2.24) is so large that it has to be solved iteratively (for a general discussion of this subject, see Ref. 30).

Since the scattering problem is now converted into a boundary value problem, several methods can be used to deal with it. One method is to expand the unknown functions

in an orthogonal (double) basis set and solve for the coefficients; other methods are based on calculating the values of the unknown functions at a given set of grid points. In this work we follow the latter approach.

It is noticed that each of the three functions depends on two variables, $R$ and $r$, and therefore a double grid will be required. However, to employ a double grid for the whole required space configuration will lead to too large a set of algebraic equations and therefore it is suggested to divide the (extended) inelastic channel into two regions: (a) the quasiasymptotic region, located along the interval $[R_{1}, R_{1}]$ and (b) the strong interaction region, located along the interval $[0, R_{1}]$. Consequently, each $\zeta$ function will be written as

$$\zeta(R,r|n_{0},j_{0}M,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'})$$

$$= \chi(R,r|n_{0},j_{0}M,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'})$$

$$+ \sum_{n} \eta(R,n_{0},j_{0}M,n,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'}) \phi(r,n_{j}^{'},r).$$

(2.25)

Presenting the $\zeta$ functions in this way makes the first term responsible for the exchange part, and therefore it is expected to be nonzero only along the strong interaction region, namely for $0 < R < R_{1}$. The second term represents the nonreactive contribution and therefore will extend along the whole channel, i.e., $0 < R < R_{1}$. Since $R_{1}$ is much smaller than $R_{1}$, we have double-grid functions defined along a relatively short interval and several single-grid functions throughout the whole interval. As long as the energy is not too high, $N_{j}$ for each case is expected to be small because it may not exceed the number of open states.

Equation (2.25) will now be substituted in Eq. (2.24), and in order to form the corresponding close-coupling system of equations for the two types of functions, the projection operator approach will be employed.

### D. Introducing the projection operator approach

In what follows, the bra and ket notation is used and consequently to shorten the notation of the independent variables, $R$ and $r$, and some of the quantum numbers are frequently omitted.

Two kinds of projection operators will be introduced:

$$P_{n_{j}} = |\phi_{n_{j}}\rangle \langle \phi_{n_{j}}|$$

(2.26)

and

$$Q_{j} = 1 - \sum_{n_{j} = 1} \langle \phi_{n_{j}}| \phi_{n_{j}}\rangle.$$  

(2.27)

Here $\{\phi_{n_{j}}\}$ are the vibrational eigenfunctions introduced in Eq. (2.11) and $P_{n_{j}}$ are projection operators which operate on $r$ only and satisfy

$$P_{n_{j}}^{2} = \delta_{n_{j}} P_{n_{j}},$$  

(2.28a)

$$P_{n_{j}}^{2} = 0.$$  

(2.28b)

Following these definitions, the partial wave function,

$$|\zeta_{n_{j}}\rangle = |\zeta(R,r|n_{0},j_{0}M,j_{j}^{'},\Omega^{'},j_{j}^{'},\Omega^{'})\rangle,$$

(2.29)

will be written in the following form:

$$|\zeta_{n_{j}}\rangle = Q_{j} |\zeta_{n_{j}}\rangle + \sum_{n_{j} = 1} \langle \phi_{n_{j}}| \phi_{n_{j}}\rangle.$$  

(2.30)
Defining \( |\chi_{n\Omega} \rangle \) as
\[
|\chi_{n\Omega} \rangle = Q_j |\xi_{n\Omega} \rangle ,
\]
using the previously introduced \( |\eta_{n\Omega} \rangle \) translational functions,
\[
|\phi_{n'} \rangle |\eta_{n\Omega} \rangle = P_{n'} |\xi_{n\Omega} \rangle ,
\]
and substituting Eqs. (2.32) and (2.31) in (2.30) yields
\[
|\xi_{n\Omega} \rangle = |\chi_{n\Omega} \rangle + \sum_{n' = 1}^{N_f} |\phi_{n'} \rangle |\eta_{n\Omega} \rangle ,
\]
which is identical to the presentation given in Eq. (2.25). Substituting Eq. (2.33) into Eq. (2.24) and operating on the resulting equation once with \( |\phi_{n'} \rangle |P_{n'} \rangle \) and once with \( Q_j \) yields the following system of equations:
\[
E |\eta_{n\Omega} \rangle = \sum_{n'f} \left( \phi_{n'} |H^f(j,\Omega)' \rangle |\eta_{n\Omega} \rangle \right) 
\times \left( \sum_{n'f} |\phi_{n'} \rangle |\eta_{n'f\Omega} \rangle + |\chi_{n\Omega} \rangle \right) 
= \delta_{nn'} (\phi_{n'} |V(\Omega_0,j,f) |\phi_{n} \rangle |\xi_{n\Omega} \rangle ,
\]
where
\[
t_{\text{int}} = \left\{ \begin{array}{c}
- \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu R^2} \left[ J(J+1) + j(j+1) - 2\Omega^2 \right], \\
T_{\text{int}}^g.
\end{array} \right.
\]
As an example, we shall treat Eq. (2.34a) by considering the following term:
\[
\langle \phi_{n'} |H^f(j,\Omega)' \rangle |\eta_{n'f\Omega} \rangle = (t_{\text{int}}^g + \epsilon_{n'} |\Omega_{n'} \rangle \delta_{nn'} |\xi_{n\Omega} \rangle 
+ [ - v(n,j,n',f) |\delta_{nn'} |\xi_{n\Omega} \rangle 
+ \Omega_0(j,n',f) |\xi_{n\Omega} \rangle ,
\]
(2.35)
where
\[
\Pi_{n \neq \Omega}.
\]
Recalling Eqs. (2.11), (2.28b), and (2.38), as well as the explicit forms of \( T_{\text{int}}^g \), it can be shown that
\[
\langle \phi_{n'} |H^f(j,\Omega)' |\xi_{n\Omega} \rangle = \langle \phi_{n'} |U(\Omega_0,j,f) |\chi_{f\Omega} \rangle .
\]
(2.42)
(2) \( \Omega \neq \Omega' \). Since for this case we have [see Eq. (2.22)]
\[
H^f(j,\Omega)' |\Omega \rangle = T_{\text{int}}^g \delta_{nn'},
\]
it follows from Eq. (2.28b) that
\[
\langle \phi_{n'} |H^f(j,\Omega)' |\chi_{f\Omega} \rangle = 0.
\]
Recalling Eqs. (2.35) through (2.43), we get for Eq. (2.34a) the following expression:
\[
E \eta_{n\Omega} = \sum_{n'f\Omega} \left[ H^f(n,j,n',f,\Omega) |\eta_{n'f\Omega} \rangle \right] + \langle \phi_{n'} |T_{\text{int}}^g |\chi_{f\Omega} \rangle 
+ \langle \phi_{n'} |U(\Omega_0,j,f) |\phi_{n} \rangle |\xi_{n\Omega} \rangle ,
\]
(2.40)
Here, \( \Omega_0(n,j,n',f) \) is a function of \( R \) only.

The second expression in Eq. (2.34a) to be evaluated is
\[
\langle \phi_{n''} |H^f(j,\Omega)' |\chi_{f\Omega} \rangle \quad \text{and we distinguish between two cases}
\]
(1) \( \Omega = \Omega' \). Thus
\[
\langle \phi_{n''} |H^f(j,\Omega)' |\chi_{f\Omega} \rangle = \langle \phi_{n''} |T_{\text{int}}^g |\chi_{f\Omega} \rangle 
+ \langle \phi_{n''} |U(\Omega_0,j,f) |\phi_{n} \rangle |\xi_{n\Omega} \rangle ,
\]
(2.41)
\[
E \chi_{n\Omega} = \sum_{f\Omega} H^f(j,\Omega)' |\chi_{f\Omega} \rangle + \sum_{n'f\Omega} \langle \phi_{n''} |U(\Omega_0,j,f) |\chi_{f\Omega} \rangle 
+ \sum_{n'f\Omega} \langle \phi_{n''} |U(\Omega_0,j,f) |\chi_{f\Omega} \rangle 
+ \sum_{n'f\Omega} \langle \phi_{n''} |U(\Omega_0,j,f) |\phi_{n} \rangle |\xi_{n\Omega} \rangle ,
\]
(2.44)
In applying Eqs. (2.44), it must be remembered that \( \Omega_0 \) also varies between \( \alpha_0 \) and \( - \alpha_0 \), where \( \alpha_0 \) is given in Eq. (2.12).
E. Total and state-to-state reactive transition probability

In order to obtain the total reactive probability, we employ Eq. (2.17'). Substituting Eq. (2.18) in Eq. (2.17'), which is then substituted in Eq. (2.15) and carrying out all analytical integrations yields the following result:

\[
P_{re} = \frac{\hbar}{\mu} \sum_{\alpha, \alpha'} \sum_{J, J'} \int dR \text{Im} \left[ \tilde{\xi}^* (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right] \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right]_{r = r_c}.
\]  

(2.46)

However, recalling Eq. (2.25) and since all \( \wp (r) \eta_{n, j} \) functions become zero as \( r \) becomes large enough yields for \( P_{re} \)

\[
P_{re} = \frac{\hbar}{\mu} \sum_{\alpha, \alpha'} \sum_{J, J'} \int dR \text{Im} \left[ \tilde{\xi}^* (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right] \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right]_{r = r_c}.
\]  

(2.47)

In order to obtain the state-to-state transition probabilities, we must not only reconsider the \( G \) function given in Eq. (2.18), but also distinguish between two arrangement channels \( \lambda \) and \( \nu \), where \( \lambda \) is the initial (reagents) channel and \( \nu \) the final products channel:

\[G_\alpha (R, r, | n_{0, j = 0} J, 0, M | j, \Omega, J) = \frac{1}{R_{a, \alpha}} \sum_{\alpha'} \sum_{J, J'} \sum_{n_{0, j = 0} J, 0, M} \left( \frac{2 J + 1}{4 \pi} \right)^{1/2} D_{\alpha J, \alpha' J'}^\nu (\Lambda_\alpha) \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right)_{r = r_c},
\]  

(2.48)

All calculations are carried out employing \( \lambda \) coordinates, and it is now our aim to determine the flux that passes through the plane \( R_a = R_{a, \alpha} \) into a particular final product state \( (n_{0, j = 0} J, 0, M) \). For this purpose, we shall have to calculate the corresponding \( \xi (R, r, | n_{0, j = 0} J, 0, M | j, \Omega, J) \) functions and then expand them in terms of the \( \nu \)-vibrational basis functions. Before we continue we must make a comment: The following derivation is done for \( R_a \) values large enough so that any contributions due to \( \psi_0 \) [see Eq. (2.25)] are negligibly small. Thus,

\[
\epsilon_\nu (R, r, | n_{0, j = 0} J, 0, M | j, \Omega, J) = \frac{2 J + 1}{4 \pi} \sum_{\alpha, \alpha'} \sum_{J, J'} \sum_{n_{0, j = 0} J, 0, M} \int d\Lambda_\alpha \cos \gamma \frac{R_{a, \alpha}}{R_{a, \alpha}} \times D_{\alpha J, \alpha' J'}^\nu (\Lambda_\alpha) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right) \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right)_{r = r_c}.
\]  

(2.49)

The integration over the three Euler angles \( (\Lambda_\alpha) \) can be carried out analytically because of the following relation:

\[D_{\alpha J, \alpha' J'}^\nu (\Lambda_\alpha) = \sum_{\alpha''} D_{\alpha J, \alpha'' J'}^\nu (\Lambda_\alpha) D_{\alpha'' J, \alpha' J'}^\nu (\Lambda'),
\]  

(2.50)

where

\[d_{\alpha', \alpha''}^J (\Delta_\alpha) = D_{\alpha', \alpha''}^J (0, \Delta_\alpha, 0).
\]  

(2.51)

Here the angle \( \Delta_\alpha \) is defined as

\[\Delta_\alpha = \cos^{-1} (\vec{\Lambda}_\alpha \cdot \vec{R}_a).
\]  

(2.52)

(2.53)

Substituting Eq. (2.50) into Eq. (2.49) and carrying out the integrations over the three Euler angles yields the desired representation:

\[\xi_\nu (R, r, | n_{0, j = 0} J, 0, M | j, \Omega, J) = \sum_{\alpha, \alpha'} \sum_{J, J'} \sum_{n_{0, j = 0} J, 0, M} \int d\gamma \frac{R_{a, \alpha}}{R_{a, \alpha}} \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right) \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right)_{r = r_c}.
\]  

(2.54)

As a final step we must project out the translational components: \( \eta_\nu (R, | n_{0, j = 0} J, 0, M | n_{j, j'}, \Omega, J) \), namely

\[\eta_\nu (R, | n_{0, j = 0} J, 0, M | n_{j, j'}, \Omega, J) = \sum_{\alpha, \alpha'} \sum_{J, J'} \sum_{n_{0, j = 0} J, 0, M} \int d\gamma \frac{R_{a, \alpha}}{R_{a, \alpha}} \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right) \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right)_{r = r_c}.
\]  

(2.55)

Once the \( \eta_\nu \) functions are calculated, the state-to-state transition probabilities are given in the following form:

\[P_{re} (n_{j, j'}, | n_{0, j = 0} J, 0, M | J, M) = \sum_{\alpha, \alpha'} \sum_{J, J'} \sum_{n_{0, j = 0} J, 0, M} \text{Im} \left[ \eta_\nu^* (R, | n_{0, j = 0} J, 0, M | n_{j, j'}, \Omega, J) \right] \times \wp (R, r) \eta_{\alpha, J, 0, J', 0} M | j, \Omega, J \right)_{r = r_c},
\]  

(2.56)

III. NUMERICAL TREATMENT

As an example of the above method, we describe a calculation carried out for the following reaction:

\[H + H_2 (u_1 = 0, J_1 = 0) \rightarrow H_3 (S_\nu, u_\gamma) + H
\]  

(3.1)

in the case of \( J = 0 \) and with the LSTH potential.\(^{32}\) The fact that \( J = 0 \) implies that all \( \Omega \)'s are identically zero and therefore the summations over \( \Omega \) are omitted. The equations to be solved are those given in Eqs. (2.44), and for this purpose a grid of 32 \times 32 points is employed for the two-dimensional \( \chi_\nu (R, r) \) functions defined in the region: \( 0 < R < R_{ii} \); \( 0 < r < r_c \) and a grid of 64 points is employed for the one-dimensional (translational) \( \eta_\nu (R) \) functions defined along the interval \( 0 < R < R_{ii} \). In the actual treatment, \( R_{ii} \) is expected to be much smaller than \( R_1 \). The value of \( R_{ii} \) depends, to a certain extent, on the number of closed vibrational states one includes for each \( j \) in the expression given in Eq. (2.25). The larger this number, the smaller is \( R_{ii} \). Since the \( H_2 \) is a homonuclear molecule, and since we, in fact, solve an inelastic problem, only even (odd) \( j \) values must be included in a single calculation. The calculations were carried out for the energy range \( 0.55 < E < 1.0 \) eV and for this we included six to eight \( \chi_\nu \) functions and approximately 2 or 3 times as many \( \eta_\nu \) functions.

Because all exit channels are blocked by optical potentials [the optical potential in the entrance channel does not affect the unperturbed elastic solution \( \psi_0 (R, r, | n_{0, j = 0} J, 0, M) \)],
which contains the incoming component of the total wave function, the \( \chi(R,r|n_{\Omega J},M|j,\Omega J) \) wave functions are nonzero only in a finite region defined by \( 0 < r < R_1 \), \( 0 < r < r_1 \). This implies that the \( \chi(R,r|n_{\Omega J},M|j,\Omega J) \) functions are nonzero only in the finite region \( 0 < r < R_{11} \), \( 0 < r < r_{11} \) and the \( \eta(R|n_{\Omega J},M|j,\Omega J) \) functions are nonzero along the interval \( 0 < R < R_1 \). The fact that the \( \gamma \) functions are equal to zero at both ends of the \( R \) interval, namely at \( R = 0 \) and \( R = R_{11} \), means that they can be considered as having a periodic behavior in the \( R \) direction, with a periodicity of \( R_{11} \). In the same way, since these functions are equal to zero at \( r = 0 \) and \( r = r_1 + \Delta r_1 \), they can be considered as also having a periodic behavior in the \( r \) direction, with a periodicity of \( (r_1 + \Delta r_1) \). All these facts led us to the idea of employing the fast-Fourier-transform (FFT) method to obtain the second derivatives in an efficient way. According to the FFT, any of the above functions is expanded at each grid point in the following form (see also Ref. 18):

\[
g(x_n) = \sum_{l=-M}^{M} f_l \exp(2\pi ilx_n/\Delta x), \quad n = 1, \ldots, 2M, \tag{3.2}
\]

where \( \Delta x \) is the periodicity of \( g(x) \). Consequently, the second derivative of \( g(x) \) at \( x = x_n \) is

\[
g''(x_n) = -\frac{4\pi^2}{(\Delta x)^2} \sum_l l^2 f_l \exp(2\pi ilx_n/\Delta x). \tag{3.3}
\]

Once the functions corresponding to the one given in Eq. (3.2) are substituted into Eqs. (2.44), one obtains a large set of linear equations to be solved for unknowns that correspond to \( g(x_n) \) in Eq. (3.2). Such a large system of equations (which runs into the thousands and more) can only be solved by employing iterative methods. In our particular case, we employed the iterative conjugate gradient method, which can be found in textbooks (see also Ref. 30).

In Table I we show a few results for reaction (3.1) and compare them with those obtained by a more established method. As can be seen, for all practical purposes the results are identical. The calculations were carried out employing the following parameters: \( V_{in} = 0.5 \text{ eV}, \Delta R_1 = \Delta R_2 = 0.5 \text{ Å}, r_1 = 2.8 \text{ Å}, R_{11} = 2.8 \text{ Å}, \) and \( R_1 = 4.5 \text{ Å} \).

IV. CONCLUSIONS

In this work we described a new method to treat reactive atom–diatom systems. The method is very similar to the one we presented earlier, employing the TD wave-packet approach, except that now the treatment is carried out within a TID framework.

The main idea of these two methods (the present one and the previous TD one) is that it suffices to solve a slightly extended nonreactive scattering process and the correct reactive probabilities are still obtained. This statement may not be correct for all rotational state-to-state integral cross sections, but we found it to be fulfilled for vibrational state-to-state integral cross sections, as has been recently demonstrated within the TD approach (a similar study within TID approach has not been done yet) and for total cross sections, as has been shown to be the case in both the TD and TID approaches.

At this stage it should be mentioned that many attempts were made in the past to achieve this goal. These were, in fact, the different types of transition-state theories, of which the one closest to our approach is the detailed quantum transition-state theory (DQSTST) of Light and Altenberger-Siezke. However, it is important to emphasize that, in contrast to all these approaches, not only is ours "exact" (in the sense that the convergence to the correct results can be attained by moving the position of the optical potentials deeper into the various product channels), but it can be used for any case without restrictions, namely, for reactions with or without a barrier, for endothermic or exothermic reactions, for low-energy or high-energy reactions, and, which is not less important, for any multi-arrangement channel systems (namely, systems with more than three arrangement channels).

Except for the important advantage of treating one arrangement this method belongs to a (small) family of methods which are able to produce one single solution for a given initial state. This may not be a significant advantage when the number of states to be included in close-coupling expansions is small, but it is a most desired feature to have once the number of states runs into the hundreds or the thousands. The reason for this is that in such cases, the algebraic equations to be finally processed can be solved only by iterative methods and iterative solutions must be derived for each initial state separately. Thus, a method that does not have this ability is not expected to have the potential for extension to more complicated systems.

Since the present method possesses the two above-described features, its potential for treating correctly more complicated systems (i.e., systems which contain three heavy atoms or those with more than three arrangements) is rather high. In fact, the limits of its potential are set by the ability of solving the relevant inelastic process, and as long as this can be done for a given system it is expected that the method will be able to also yield the correct reactive integral cross sections. This may not be the case for every kind of state-to-state transition, but it is guaranteed to be the case for total cross sections (and therefore also for rate constants) and for those transitions, such as the vibrational state-to-state transitions, which take place in the strong interaction region and are not affected by the long tail of the potential.

The method as presented here also has several disadvantages. In addition to not being able to produce the correct

<table>
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<th>( E_{in} ) (eV)</th>
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rotational state-to-state cross sections (unless the substitution of optical potentials enters far enough into the products arrangement region), it also is incapable of producing differential cross sections. In order to obtain those, one has to know all the relevant phase shifts, and those can be obtained only once the wave function is given in the appropriate asymptotic region.

So far, we have only presented the method and demonstrated its ability to yield the correct results in a few simple cases. We hope to be able to perform a sensitivity study with respect to the various numerical parameters used in such a calculation. Moreover, we hope to apply it to more interesting cases so that results of chemical interest can be extracted.