Theoretical Studies of $H + H_2$: Rotationally Inelastic Scattering

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Rotationally inelastic $H + H_2$ scattering, without rearrangement, was studied quantum mechanically in three dimensions. A close-coupling technique was employed with a basis set consisting of unperturbed molecular functions. The resulting coupled differential equations were solved numerically by a technique recently developed by Gordon. The Porter–Karpplus semi-empirical potential surface was used to represent the $H_2$ system. Cross sections were calculated for relative kinetic energies of 0.05 to 0.50 eV. Various approximations were investigated and their effect on the inelastic cross sections were computed; they include variation of the number of terms in the expansion of the exact wavefunction, exclusion of high-order asymmetry contributions to the potential surface, treating the $H_2$ target as a rigid rotor fixed at some specified internuclear distance, and modifying the long-range behavior of the Porter–Karpplus surface. Differential cross sections in the helicity representation were also computed for various energies.

1. INTRODUCTION

The inelastic scattering of an atom by a diatomic molecule is the prototype for most gas phase relaxation phenomena and considerable theoretical work has been done in an effort to understand this process. Recent theoretical studies of rotationally inelastic scattering have used weak coupling approximations (distorted wave Born) and various unitarized distorted wave Born approaches as well as close-coupling techniques. In addition, several approximations that decouple the various channels in a multichannel problem have been investigated by Levine and co-workers. Much effort has been devoted also to developing improved numerical techniques for solving the sets of coupled integral or differential equations arising from a rigorous approach to the multichannel scattering problem. While the close-coupled techniques are capable, in principle, of giving exact results, computational problems have limited previous calculations to a few coupled channels, so that an examination of the convergence of the solutions has not been possible.

In the present study, we examine the $H + H_2$ non-reactive rotationally inelastic scattering problem with the close-coupled method. We employ the Porter–Karpplus potential to describe the interaction of the three-atom system. To solve the sets of coupled differential equations, we use the procedure developed by Gordon. Our purpose in undertaking this problem was a twofold. First, since $H + H_2$ is a simple system with widely spaced rotational levels, it can serve as an excellent testing ground for the close-coupled technique. Moreover, although laboratory measurements of inelastic scattering are not available, the values of the rotational cross sections are of some astrophysical interest. Second, the scattering wavefunctions obtained in the solution of the rotational problem serve as the starting point for a close-coupled calculation of the $H + H_2$ reactive scattering, which will be described subsequently.

In the course of the calculation a number of significant features of the inelastic scattering became clear. These include the dependence of the cross section on various orders of asymmetry in the potential surface, the effect of approximations commonly used to simplify the evaluation of the potential, and the effect of an attractive, long-range van der Waals potential. Also, we were able to test several approximations frequently made in studies of inelastic scattering and observe their effect on the cross sections. The conclusions drawn from these results should provide valuable insight for inelastic scattering calculations of other systems. Since the inelastic scattering problem is considerably easier to study theoretically than reactive scattering, the present calculation also serves as a test of related approximations in the reactive scattering problem. While there is obviously no direct correlation between inelastic and reactive scattering, the fact that the solutions obtained for the former are employed as the basis for the latter is indicative of the connection between the two.

Earlier treatments of the rotational inelastic scattering of $H$, $H_2$ include the distorted wave calculations of Dalgarno, Henry, and Roberts and of Tang, and the coupled equation treatment by Allison and Dalgarno and of Hayes, Wells, and Kouri. Dalgarno and co-workers constructed a two-term potential based on the earlier work of Mason and Hirschfelder joined to the long-range van der Waals interaction. Tang began with the Porter–Karpplus surface but used a different method from the present one to reduce the surface to simpler form. Hayes, Wells, and Kouri used the potential presented by Tang. As we show below, highly significant differences in the rotational scattering result from this variation in choice of potential.

The present work is restricted to rotational excitation from the ground vibrational-rotational state of para-$H_2$ ($v_a=0$, $J_a=0$). The relative kinetic energies are never allowed to exceed 0.50 eV. At this energy the $v_a=0$, $J_a=6$ rotational level is the highest state energetically allowed, and the $v_a=1$, $J_a=0$ level is rather far removed. All expansions in molecular eigenfunctions of the target $H_2$ were restricted to the ground vibrational level. The importance of this re-
striction for the energies considered is discussed further below.

In Sec. 2 we derive the close-coupled differential equations following Arthurs and Dalgarno. Section 3 briefly restates some of the properties of the Porter-Karpplus potential surface. Section 4 discusses some of the modifications of the computational method developed by Gordon which were found to be useful in the current work. Section 5 discusses the effects of various approximations on the total cross section and Sec. 6 presents differential cross sections in the helicity representation.

2. DERIVATION OF CLOSE-COUPLING EQUATIONS

The complete Schrödinger equation for the system is

\[ (H - E)\psi_a(r, \mathbf{R}) = 0, \]

where \( r, \mathbf{R} \) denote the internuclear vector and the channel vector (Fig. 1), and \( a \) represents a complete set of quantum numbers that specify the state of the system before the collision occurs; that is, the index \( a \) designates the initial unperturbed state of the target. In the asymptotic region, corresponding to "times" long after the collision, \( \psi_a(r, \mathbf{R}) \) has the form of a spherically scattered beam of atoms and unperturbed molecules in a distribution of internal states plus the unscattered portion of the incident beam. In the coordinates \( r, \mathbf{R} \) the kinetic energy part of the Hamiltonian \( H \) is separable and we have

\[ \left[ -\frac{\hbar^2}{2\mu_{12}} \nabla_r^2 - \frac{\hbar^2}{2\mu_{12,3}} \nabla_{\mathbf{R}}^2 \right] \psi_a(r, \mathbf{R}) + V(r, \mathbf{R}) - E \psi_a(r, \mathbf{R}) = 0, \]

where

\[ \mu_{12} = m_1 m_2 / (m_1 + m_2), \]

\[ \mu_{12,3} = m_3 (m_1 + m_2) / (m_1 + m_3 + m_3), \]

with \( m_k \) the mass of the \( k \)th particle, the function \( V(r, \mathbf{R}) \) the complete potential for the interaction between the three particles, and \( E \) the total energy of the system.

To describe completely a three-particle system in its center-of-mass frame, six coordinates are needed. One may choose three coordinates to specify the size and shape of the triangle formed by the particles and three Euler angles to specify the orientation of this triangle in space. Figure 1 shows one possible choice for the three internal coordinates and is the one used here. It is assumed, as is usually the case, that no external fields are present which would define a preferred direction in space. Thus, the potential function for the system depends only upon the internal coordinates \( r, \mathbf{R}, \gamma \). Furthermore, the total angular momentum of the system \( J \) and its projection \( M_J \) along any space-fixed axis are conserved throughout the collision. The computational labor is greatly reduced if the equations to be solved are written in the coupled representation in which \( J \) and \( M_J \) are good quantum numbers. These equations can be derived following Arthurs and Dalgarno. Their derivation is limited to the case of a structureless, spinless projectile incident upon a rigid diatomic target possessing internal angular momentum. In the present treatment the vibrational motion of the target is included via unperturbed Morse oscillator wavefunctions. When matrix elements of the potential over these oscillator wavefunctions are computed, equations formally the same as those of the atom-rigid rotor scattering problem are obtained. For completeness, we include vibrational quantum numbers in the formulation, although the actual calculations are restricted to the ground vibrational state.

The function \( \psi_a(r, \mathbf{R}) \) is expanded in the coupled representation as

\[ \psi_{J_1 J_2 J_3}^{JM_J}(r, \mathbf{R}) = \sum_{J_0 J_0 J_0} (rR)^{-l_0} \psi_{J_0 J_0 J_0}(r) \times Y_{J_0 J_0 J_0}^{JM_J}(\hat{r}, \hat{R}) | \psi_{J_0 J_0 J_0}(r) \times Y_{J_0 J_0 J_0}^{JM_J}(\hat{r}, \hat{R}) \mathbf{L}, \]

where \( J, M_J \) are the total angular momentum of the three-particle system and its projection along any space-fixed axis, \( j_0 J_0 \) are the vibrational, rotational quantum numbers of the unperturbed target, and \( l_0 \) is the orbital angular momentum of the incident projectile; \( \hat{r}, \hat{R} \) are unit vectors in the direction of \( r, \mathbf{R} \) as defined in Fig. 1. The function \( Y_{J_0 J_0 J_0}^{JM_J}(\hat{r}, \hat{R}) \) describes the coupling of the orbital angular momentum of the projectile with the internal angular momentum of the target and is defined by

\[ Y_{J_0 J_0 J_0}^{JM_J}(\hat{r}, \hat{R}) = \sum_{m_0 m_0 m_0'} \langle J_0 m_0 m_0' | J_0 J_0 J_0 \rangle \times Y_{J_0 m_0'}^{JM_J}(\hat{r}) Y_{J_0 m_0'}^{JM_J}(\hat{R}). \]

Here \( Y_{JM}(\hat{r}) \) are spherical harmonics and

\[ \langle J_0 m_0 m_0' | J_0 J_0 J_0 \rangle \]

are Clebsch–Gordan coefficients in the conventions of Rose. The function \( u_{J_0 J_0}(r) \) is the radial eigenfunction for the isolated target in vibrational-rotational state \( j_0, J_0 \), while the function \( f_{J_0 J_0 J_0}^{JM_J}(\mathbf{R}) \) of the channel coordinate \( R \) is to be determined by integrating the coupled equations. The summation in...
Eq. (3) is formally infinite, but in practice it must be truncated at some finite value of the parameters indicated by $N$. The minimum $N$ needed for adequate convergence must be investigated for each problem.

Substituting Eq. (3) into Eq. (2) and following standard procedures, we obtain

$$\left(\frac{d^2}{dR^2} - \frac{l_a(l_a+1)}{R^2} + k_{r,\ell_a}^2\right)f_{r,\ell_a,\ell_{j_a}}(R)$$

$$+ \frac{1}{\pi k_{r,\ell_a}^2} \sum_{\ell_{j_a}} V_{r,\ell_a,\ell_{j_a},\ell_{j_a}}(R) f_{r,\ell_a,\ell_{j_a},\ell_{j_a},\ell_{j_a}}(R) = 0,$$

where

$$k_{r,\ell_a}^2 = (2\mu_{12,3}/R^2) (E - e_{r,\ell_a})$$

with $e_{r,\ell_a}$ the isolated molecule energy in state $\nu_r J_a$, and

$$V_{r,\ell_a,\ell_{j_a},\ell_{j_a},\ell_{j_a}}(R) = -(2\mu_{12,3}/R^2) \left(-\frac{1}{2}\right)^{\frac{1}{2}} J_a J_{\ell_a}$$

$$\times \left[\sum_{l_{j_a}} \left| J_a \right| \left| J_{\ell_a} \right| \left| l_{j_a} \right| \left| l_{\ell_a} \right| \left| J \right| \left| J_a \right| \left| J_{\ell_a} \right| \right]$$

$$\times \int_0^\infty u_{r,\ell_a}(r) V_{\lambda}(r, R) u_{r,\ell_a}(r) dr.$$}

The $\lambda$ are given by

$$V(r, R, \gamma) = V_{\text{int}}(r, R, \gamma) + V_{\text{mol}}(r)$$

$$= \sum_{\ell_j=0}^\infty V_{\lambda}(r, R) P_{\lambda}(\cos \gamma) + V_{\text{mol}}(r),$$

where $V_{\text{mol}}(r)$ is the isolated molecule potential and the $P_{\lambda}(\cos \gamma)$ are Legendre polynomials. The

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

are the standard 3- and 6- symbols, respectively. We use the notation of Brink and Satchler, who use the phase conventions of Rose. The summations over $\lambda$ and over $J_a$, $l_{\ell_a}$ in Eqs. (4) and (6) are restricted to the values satisfying the triangular inequalities for the 3- and 6- symbols.

In Eq. (4), $\nu_r J_a$ describe the initial state of the system, $\nu_r J_a$ describe the final state of the system, and $\nu_r J_a$ define a complete set of intermediate states used to represent the coupling.

When the target is a homonuclear molecule, the potential $V(r, R, \gamma)$ is symmetric about $\gamma = \pi/2$ plane. Hence, only even $\lambda$ occur in the expansion of the potential in Eq. (7). Since

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = 0$$

unless $j_1 + j_2 + j_3$ is even, we have that $J_a + J_b$ must be even. By the same token, $l_a + l_b$ must be even. We thus find that for inelastic scattering both the molecular parity $(-1)^j_a$ and the total parity, which we define to be $(-1)^{j_a + l_a + l_b}$, are conserved. If $J_a = 0$ then $l_a = J$ and only positive total parity contributes to the scattering. If $J_a = 2, 4 \cdots$ both positive and negative total parities are present in the initial channel, but there is no coupling between them; a corresponding result holds for $J_a = 1, 3, 5 \cdots$. For either case, Eq. (4) partially decouples into two independent sets of equations, one set for each total parity. These can be solved independently and the resulting amplitudes combined to produce the observable cross section. All of the calculations to be described for the nonreactive $H + H_2$ scattering were done for the positive molecular parity and positive total parity only. Hence, only the results for $J_a = 0$ correspond to physically observable cross sections and only the results for this case are discussed below. Implicit in the above discussion, which separates odd and even rotational states, is the assumption that the coupling between them is negligible. For nonreactive collisions, the coupling is produced by spin dependent forces, which have been shown to result in very small cross sections. In reactive scattering, changes in molecular parity make a significant contribution; this effect is considered in a subsequent paper.

For a given $\nu_r, J_a, l_a$ it is useful to rewrite Eq. (4) in matrix notation:

$$\left[\frac{d^2}{dR^2} + d(R) \right] f_{\nu_r, J_a, \ell_a} + V'(R) f_{\nu_r, J_a, \ell_a} = 0$$

where $V'$ is the matrix whose elements are given by Eq. (6), $I$ is the unit matrix, $d(R)$ is the diagonal matrix whose elements are

$$k_{r,\ell_a}^2 - \left[l_a(l_a+1)/R^2\right]$$

and $f_{\nu_r, J_a, \ell_a} = \left[J_a J_a J_a \right]$ is the column vector (labeled by $\nu_r J_a$) obtained by allowing $\nu_r J_a$ to range over the $N$-allowed values. The $N$-coupled second-order differential Eqs. (4) have $2N$ linearly independent solution vectors; $N$ of these, the regular solutions, may be chosen to vanish at $R = 0$, the other $N$ diverge at the origin. It is convenient to write the $N$ regular, linearly independent $f_{\nu_r, J_a, \ell_a}$ solution vectors in a matrix whose rows are labeled by the $N$ possible values of $\nu_r J_a$ and whose columns are labeled by the same $N$ values of $\nu_r J_a$. Thus, we obtain the matrix analog of the vector Eq. (8); i.e.,

$$\left[\frac{d^2}{dR^2} + d(R) \right] \phi'(R) + V'(R) \phi'(R) = 0,$$

with the boundary conditions at the origin that $\phi'(0) = 0$.

For a given collision energy, it may not be possible to excite all the internal states of the target included in Eq. (3). If this is the case, the matrix
$\mathbf{f}(R)$ is conveniently written in block form, where we arrange the internal states in Eq. (3) in order of increasing energy; we represent $\mathbf{f}(R)$ as

$$
\mathbf{f}(R) = \begin{pmatrix}
\mathbf{I} \\
\vdots \\
\mathbf{II}
\end{pmatrix}.
$$

(11)

The projectile is taken to have positive kinetic energy $(E-E_{p,s})$ for all states in Block I. Since the columns of $\mathbf{f}$ correspond to specified initial states while the rows correspond to specified final states, Block I represents physical scattering states in both the initial and final channels. For this block we, therefore, impose the asymptotic boundary conditions

$$
f^R(R) \sim k^{1/2}R\mathbf{j}_i(kR) - k^{1/2}R\mathbf{\eta}_i(kR)R^2 \quad \text{(Block I)},
$$

(12)

where $k^{1/2} \mathbf{j}_i(kR), \mathbf{\eta}_i(kR)$ are diagonal matrices with elements $k_{v_{r,s}}^{1/2}$, and the regular and the irregular spherical Bessel functions $j_{v_{r,s}}(kR)$, $\eta_{v_{r,s}}(kR)$, respectively. The matrix $R^2$ is the real, symmetric reactance matrix from which the scattering matrix $S'$ is determined by the formula

$$
S' = (1+iR^2)(1-iR^2)^{-1}.
$$

(13)

If the energy of the collision is sufficiently high and one is concerned only with low excitations, Block I could constitute all of $\mathbf{f}$.

Block II includes the states in which the projectile has an initial positive kinetic energy, but not enough energy to excite the specified state of the target and still escape to infinity. The boundary conditions imposed are

$$
f^R(R) \sim 0 \quad \text{(Block II)},
$$

(14)

These "virtual excitations" are an essential feature of the scattering in the case of resonances, but may be relatively important even in the case of a direct "impulsive" excitation of the target. The effect of these closed channels is examined in the current calculation (see Sec. 5).

Block III corresponds to the states in which the incident particle has negative kinetic energy and, hence, has no direct interpretation as a physical scattering state. Block III is included so that the set of coupled differential Eqs. (10) can be solved as an initial value problem instead of as a boundary value problem.

To be specific, we assume that $f^R(0) = 0$ and that $(d/dR)f^R(0)$ is a matrix corresponding to any convenient linearly independent set (a diagonal matrix was used in the present work). Equation (10) is integrated to an $R$ value sufficiently large such that $f^R(R) \approx 0$. In general, the boundary conditions [Eqs. (12) and (14)] are not satisfied since we have made an incorrect choice of initial derivatives. However, if $f^R(R)$ is a regular solution of Eq. (10), then so is the linear combination of functions given by $f^R(R)\mathbf{c}$ for any constant matrix $\mathbf{c}$. This freedom allows us to take linear combinations of the columns in Block III with the columns in Blocks I and II to insure that the boundary condition [Eq. (14)] is satisfied. For large $R$, the elements in Block II contain an exponentially increasing part plus an exponentially decreasing part. The corresponding components in Block III have similar behavior. We can choose the matrix $\mathbf{c}$ such that the exponentially increasing components in Block II cancel. However, the matrix product $f^R(R)\mathbf{c}$ involves all the rows of $f^R$ in both Blocks I and II. Thus, choosing $\mathbf{c}$ to ensure the proper behavior in Block II also changes the behavior of Block I. This is the computational mechanism whereby the closed channels of Block II effect the $S'$ matrix, which is solely determined by Block I. The elements of Block III can have any numerically convenient behavior at $R \to \infty$ as long as the above conditions can be satisfied. As formulated by Gordon, transformations of the functions are used to preserve linear independence in the solution vectors when propagating through a classically forbidden region. These transformations suppress the growing components of closed channels within each interval and, thereby, make the functions in asymptotically closed channels approach zero. Thus, the boundary condition [Eq. (14)] is automatically satisfied.

Equation (12) is satisfied by constructing another matrix $\mathbf{c}'$ which operates only on Block I. If

$$
f^R(R) \sim k^{1/2}R\mathbf{j}_i(kR)X - k^{1/2}R\mathbf{\eta}_i(kR)Y,
$$

(15)

then

$$
\mathbf{c}' = X^{-1} \quad \text{and} \quad R^2 = YX^{-1}.
$$

From the $S$ matrix of Eq. (13) we obtain the scattering amplitude and the differential cross section in the helicity representation as

$$
\sigma_{\ell_sJ,\ell_tJ,\ell_rJ,\ell_tJ,\ell_rJ,\ell_rJ}(\theta) = \left| F_{\ell_sJ,\ell_tJ,\ell_rJ,\ell_tJ,\ell_rJ,\ell_rJ}(\theta) \right|^2,
$$

$$
F_{\ell_sJ,\ell_tJ,\ell_rJ,\ell_tJ,\ell_rJ,\ell_rJ}(\theta) = \frac{(-1)^{\ell_s+\ell_t}}{2ik_a} \sum_{J_aJ_a} \left( \frac{J}{2J_a+1} \right) d_{\ell_s,\ell_t,\ell_r,\ell_t,\ell_r,\ell_r}(\theta) \sum_{l_a, l_e} \left( \begin{array}{c}
J_c & J & l_e & (S_{aJ,J_aJ_a,J_eJ_e}) - \delta_{\ell_s,\ell_t} \delta_{\ell_r,\ell_t} \\
\ell_s & \ell_t & l_e & 0
\end{array} \right)
$$

(16)

where $d_{\ell_s,\ell_t,\ell_r,\ell_t,\ell_r,\ell_r}(\theta)$ is the Wigner rotation matrix in the convention of Rose.
The total cross section, summed over final $m$ values, averaged over initial $m$ values, and integrated over all angles is

$$
\sigma_{v_J \rightarrow v_f J_f}^{\text{total}} = \sum_{J=0}^{\infty} \sigma_{v_J \rightarrow v_f J_f}^{J} ,
$$

where the partial total cross sections for each $J$, $\sigma_{J}$, are given by

$$
\sigma_{v_J \rightarrow v_f J_f}^{J} = \pi (2J+1)/[(2J+1)k_s^2]\sum_{l_{\alpha \epsilon}} |S_{v_J l_{\alpha \epsilon}, v_f l_{\alpha \epsilon}}^{J} - \delta_{v_J l_{\alpha \epsilon}}^{J} \delta_{v_f l_{\alpha \epsilon}}^{J} \delta_{J_f \epsilon}|^2 .
$$

The numerical method used in solving the coupled equations is discussed in Sec. 4.

### 3. POTENTIAL SURFACE

The Porter–Karplus (PK) semi-empirical formula was used for the potential energy in the present study. The advantage of this surface is that it appears to be a reasonable approximation to the true potential near the saddlepoint region (which is crucial for a meaningful study of reactive scattering) expressed in a relatively simple analytic form.

The PK surface uses a Morse curve with a specific choice of parameters for the potential of an isolated $H_2$ molecule. For a calculation to be internally consistent one must use this potential and the energy levels associated with it, rather than a more accurate model, to describe the vibration-rotation energy levels of the $H_2$ diatomic. Table I contains the low-lying vibration-rotation levels of $H_2$ both from the Morse curve of the PK surface, and from the more detailed results of Waech and Bernstein. The Morse curve is seen to provide a reasonably accurate description for $H_2$.

<table>
<thead>
<tr>
<th>$v, J$</th>
<th>Morse</th>
<th>Waech, Bernstein$^{37}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0*</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0, 1</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>0, 2</td>
<td>0.045</td>
<td>0.044</td>
</tr>
<tr>
<td>0, 3</td>
<td>0.088</td>
<td>0.087</td>
</tr>
<tr>
<td>0, 4</td>
<td>0.146</td>
<td>0.145</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.218</td>
<td>0.216</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.302</td>
<td>0.299</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.399</td>
<td>0.395</td>
</tr>
<tr>
<td>0, 8</td>
<td>0.507</td>
<td>0.502</td>
</tr>
<tr>
<td>1, 0</td>
<td>0.522</td>
<td>0.516</td>
</tr>
<tr>
<td>1, 1</td>
<td>0.536</td>
<td>0.530</td>
</tr>
<tr>
<td>1, 2</td>
<td>0.564</td>
<td>0.558</td>
</tr>
<tr>
<td>1, 3</td>
<td>0.606</td>
<td>0.599</td>
</tr>
</tbody>
</table>

$V(\text{Morse}) = 4.7466 \text{ eV} \exp[-(R-R_0)]$

$$
\alpha = 1.04435 \text{ a.u.}
$$

$$
R_0 = 1.40083 \text{ a.u.}
$$

*The energy zero for each spectrum is taken to be its own (0, 0) state; the WB (0, 0) state is 0.003 eV lower than the Morse curve (0, 0) state.

![Fig. 2. Components $V_3(r, R)$ of the Porter–Karplus surface averaged over the $v=0$, $J=0$ state of $H_2$ [see Eq. (6)].](image-url)

The PK surface was expanded in a series of Legendre polynomials according to Eq. (7). In order to fit the surface to an accuracy of $10^{-6}$ eV, even $\lambda$ values up to and including $\lambda = 12$ were used. Fig. 2 shows the $V_3(r, R)$ integrated over $r$ with the $v=0$, $J=0$ Morse potential wavefunctions for $H_2$. As expected, the higher order nonspherical terms ($\lambda > 2$) contribute over only a very limited region. The repulsive spherically symmetric term $V_0$ acts as an “effective shield” for all the other components of the potential. Thus, $V_0$ and $V_2$ are expected to dominate the scattering.

### 4. NUMERICAL METHOD

The coupled differential equations [Eqs. (10)] were solved by the numerical technique developed by
Gordon. The essence of this method in the one-channel case is to approximate the exact potential \( V(R) \) by a sum of terms \( U(R) \), each of which has a simple (and usually linear) functional form that provides a satisfactory fit to \( V(R) \) over a small range of \( R \). The entire range of \( R \) from the origin to the asymptotic region is broken up into intervals and a different approximate \( U(R) \) is used in each interval. Analytic solutions for each \( U(R) \) are constructed and are joined smoothly at the left side of a given interval with the functions generated at the right side of the preceding interval. First-order perturbation theory is used to estimate how much the solutions for \( U(R) \) evaluated at the right side of the interval differ from the exact solutions for \( V(R) \). This perturbation result serves to correct slightly the approximate solutions and to estimate the size of the next step to be taken (see below). One thus proceeds step by step into the asymptotic region where an \( R \) matrix can be obtained [Eq. (12)] and an \( S \) matrix can be constructed according to Eq. (13) of Sec. 2.

For the coupled channel case of interest here, we transform the problem so as to be able to solve uncoupled differential equations to obtain the solutions. Following Gordon, we construct a unitary matrix \( T_i \) at the center of the \( i \)th interval \((R = \bar{R}_i)\) to diagonalize the exact potential matrix; that is,

\[
T_i^* V(\bar{R}_i) T_i = v(\bar{R}_i) \quad \text{(a diagonal matrix).} \quad (19)
\]

This is formally equivalent to taking linear combinations of the basis functions of Eq. (10) to diagonalize \( V(R) \); that is, we effectively transform the wavefunction expansion from the "free" basis [defined in terms of the unperturbed molecular functions, Eq. (3)] to a new or "local" basis which diagonalizes \( V(R_i) \) at the center of the \( i \)th interval. The interval must, of course, be sufficiently small that \( v(R) \) remains nearly diagonal when \( R \) lies anywhere within the interval.

Since the transformation matrices \( T_i \) are independent of the energy of the collision, they need not be recomputed when an \( S \) matrix is calculated for a different energy at the same total \( J \). Thus, for each total \( J \), an initial calculation is done at one of the energies of interest. Perturbation corrections are computed, a set of satisfactory step sizes is determined, and the \( T_i \) transformation matrices are evaluated and saved on magnetic tape. Subsequent collisions at the same total \( J \) but different energies are done using the same step sizes and \( T_i \), matrices, simply shifting the diagonal elements of \( v(R) \) by the correct amount. These perturbation corrections are neglected in these calculations, since their chief purpose is to determine the step size (which must be sufficiently small that the perturbation corrections are also small).

The steps were adjusted to keep \( \max_{ij} |\Delta \psi_{ij}| + a_i^{-1} |\Delta \psi_{ij}'| \) less than 0.005, where \( \Delta \psi_{ij}, \Delta \psi_{ij}' \) are the first-order perturbation corrections to the \( i, j \) wavefunction and derivative component, respectively, and \( a_i \) represents an estimate of the magnitude of a typical derivative for a normalized wavefunction component in channel \( i \). One could, alternatively, require that the maximum error in any wavefunction component not exceed some specified fraction (say, 1%) of that particular component. If a step happens to fall very close to a node for one of the components in the wavefunction, however, one would need a very small next step to insure 1% accuracy in this component. In other words, for a wavefunction component of \( 10^{-4} \) coupled to other components of order 1.0, extremely small steps are needed to insure that errors no larger than \( 10^{-4} \) are introduced. This could result in a drastic increase in the number of steps taken. The larger components of the wavefunction would then be much more accurate than is really necessary and the considerable increase in computational effort was felt not to be justified. To check the effect of the neglect of the perturbation corrections, calculations were done with and without them at the same energy with the same steps. A comparison of the two \( S \) matrices gives an estimate of the importance of the perturbation corrections and, hence, of the error in the entire calculation. Using this criterion, the estimated error in the calculations to be described below is 2%–5% in the magnitude of the \( S \) matrix and 5%–10% in the phase. As Eqs. (17) and (18) demonstrate, this leads to approximately 2%–5% errors in the total inelastic cross section. The effect of an error in the phases on the inelastic differential cross sections is considered in Sec. 5.

One point of practical interest should be mentioned. The first two terms that enter in the computation of

![Fig. 3. Potential \( V(R) \) on two propagation intervals. The midpoints of the intervals (•) and the end points (x) are indicated. Line A is the true tangent at the midpoint of the \( i \)th interval while line B is the approximation used here for the derivative of the potential at \( \bar{R}_i \).]
the perturbation corrections [Eqs. (2.18), (2.19) of Ref. 15] are the off-diagonal elements of the derivative of the potential at the center of the $i$th interval, $V'(R_i)$, and the entire second derivative matrix $V''(R_i)$, which are also transformed to the local basis. However, the matrix that diagonalizes $V(R_i)$ will not in general diagonalize these derivative matrices. Since the evaluation of $V(R)$ is quite time consuming for the PK surface, $V'(R_i)$ was estimated by

$$V'(R_i) \approx \left[ V(R_i) - V(R_{i-1}) \right] / [R_i - R_{i-1}], \quad (20)$$

which is line B in Fig. 3; the true derivative is shown as line A in the figure. Use of Eq. (20) allows us to employ the known potential matrices for determining the derivative. If line A is, in fact, known, $V''(R_i)$ may also be estimated. To obtain an expression for $V''(R_i)$, we write the Taylor series expansion of $V(R)$ about $R_i$ as

$$V(R) \approx V(R_i) + V'(R_i)(R - R_i)$$

$$+ \frac{1}{2} V''(R_i)(R - R_i)^2 + \cdots. \quad (21)$$

With $R = R_{i-1}$, we can solve for $V''(R_i)$ to obtain

$$V''(R_i) \approx 2 \left[ V(R_{i-1}) - V(R_i) - V'(R_i) \right] / (R_{i-1} - R_i)^2$$

$$\approx 2\delta V / (R_{i-1} - R_i)^2 \quad (22)$$

where $\delta V$ is positive for the case represented in Fig. 3, negative if line A passes above line B at $R_{i-1}$. If Eq. (20) is used for $V'(R_i)$, the estimate of the contribution $\delta V$ is zero and the entire first-order correction comes from the off-diagonal terms of the first derivative matrix. This approximation is consistent with the choice of sufficiently small steps that the deviations of the exact potential from linearity can be neglected.

The origin for the integration was chosen at 1.4 a.u. where the potential is very large compared to the kinetic energy of the incoming H atom (which never exceeded 0.50 eV) and the wavefunction is very small. To a good approximation, the wavefunction can be set equal to zero inside this point. Another reason for starting the integration at 1.4 a.u. is that the PK potential surface becomes invalid (predicting a very large attraction) at separations smaller than about 1.2 a.u.\textsuperscript{18}

For the 16-channel problem to be discussed below, the initial collision for a given $J$ takes about 9 min on an IBM 7094 while subsequent collisions with the same $J$ but different energies take from 0.5 to 2 min, depending on the size of the $R^J$ matrix (from 4 to 16 open channels) that must be manipulated in the final step to find the $S^J$ matrix. Typically, 40–50 steps were needed to propagate from 1.4 a.u. out to the asymptotic region at 11–12 a.u.

Figure 4 shows a typical component of a wavefunction matrix obtained in the present calculation. We have plotted the $J_a = 2$, $J_a = 2$ component of the total $J = 0$ wavefunction matrix at an energy of 0.50 eV above the $\text{H}_2$ ground state. The basis set used for this particular collision included only the 0 and 2 rotational states for the ground vibrational state. The
wavefunction is expressed in terms of the free basis satisfying the boundary conditions given by Eq. (15) of Sec. 2; that is, it approaches some linear combination of regular and irregular spherical Bessel functions. The points marked on the figure indicate the end points of the intervals the program selected using the perturbation correction as the criterion for choosing the steps. Within each step we have plotted the wavefunction by evaluating the proper linear combination of the Airy functions $Ai(R)$, $Bi(R)$ generated by the program. As $R$ increases and $V(R)$ changes more slowly, the steps become larger, encompassing more and more oscillations in the wavefunction. This clearly demonstrates the advantage achieved by the method in approximating the potential rather than attempting to follow accurately the oscillations in the wavefunction itself.

<table>
<thead>
<tr>
<th>$J_e$</th>
<th>$E$ (eV)</th>
<th>2</th>
<th>4</th>
<th>6</th>
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<tr>
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<td>2.79 x 10^{-3}</td>
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<td>...</td>
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<tr>
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<td>0.400</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>1.13 x 10^{-3}</td>
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</table>

The angular integration to obtain $V_A(r, R)$ and the radial integration in Eq. (6) were both done by Gauss-Legendre integration (requiring 12 to 16 points for each integral). These integrations were the most time-consuming part of the calculation. Since Gordon's method requires relatively few potential evaluations (40 to 50 in the present case), we were able to do the integrations as written, with no additional approximations. As mentioned above, these potential evaluations are independent of the collision energy and need be done only once for each total $J$.

5. RESULTS AND DISCUSSION

A detailed solution to the inelastic scattering problem from a realistic potential surface can provide a useful standard by which to evaluate various approximations both to the potential surface and to the computation of cross sections from that surface. The total cross-section results for excitations from the ground rotational state as a function of incident energy are given in Table II. In what follows we consider the convergence of the cross section as more terms are included in the expansion of the wavefunction [Eq. (3)], the restriction of the potential to two terms ($V_0$, $V_2$) in Eq. (7), and approximations to the evaluation of the integral over molecular vibration, and the addition of an $R^{-4}$ attractive van der Waals term to the PK surface. Comparisons are made also with the results for $H+H_2$ rotationally inelastic scattering obtained from other potential surfaces. Differential cross sections are presented for various energies and an estimate of how they are affected by numerical error in the phases of the $S_J$ matrices is given.
A. Convergence

Figure 5 shows (for a kinetic energy of 0.50 eV) the partial total cross sections defined by Eq. (18) plotted as a function of $J$ for the $0 \rightarrow 2$ excitation as more rotational functions are added to the basis, Eq. (3); "JMAX" is the maximum rotational state of the target included in the basis set. Since we do not include excited vibrational levels in the present work, all reference to vibrational quantum numbers is omitted in subsequent discussions. The relative kinetic energy of 0.50 eV is the largest value used and should maximize the effect of the uppermost rotational levels. From Table I we see that the $0 \rightarrow 8$ excitation is barely closed at this energy. For a given set of target states, all values of orbital angular momentum consistent with the given total $J$ and giving positive total parity were included. For JMAX = 2, 4,

Fig. 6. Partial cross sections for the $0 \rightarrow 2$ rotational excitation at $E=0.25$ eV using the full Porter-Karplus surface (—) compared to the results obtained using only the $V_6$ and $V_8$ terms (--- x ---).

Fig. 7. Partial cross sections for the $0 \rightarrow 4$ rotational excitation at $E=0.5$ eV using the full Porter-Karplus surface (—) compared to the results obtained using only the $V_6$ and $V_8$ terms (--- x ---).
6, 8 this leads to 4, 9, 16, 25 coupled equations, respectively. As is clear from Fig. 5, including only the 0, 2 molecular J values seriously overestimates the 0→2 cross section at 0.5 eV. This suggests that the inelastic scattering which could result in 0→4 or 0→6 excitations, if these states were included in the basis set, tends to go instead into the 0→2 excitation. Including the Jα=4 target state leads to a considerable improvement. In fact, the cross sections for JMAX=4, JMAX=6, and JMAX=8 are indistinguishable to within the error of the calculation. Although the 0→6 process is energetically possible at 0.50 eV, we conclude that negligible flux goes into that channel. This is confirmed by the total cross sections given in Table II. (The slight decrease in the 0→6 cross section from 0.35 to 0.40 eV is not significant. With the present technique, very small S matrix elements tend to be relatively less accurate than larger ones; this is discussed in more detail below.) Unless otherwise stated, all the calculations described below were done using JMAX=6.

B. Truncation of Potential Surface at Vα(R)

A commonly used approximation is to truncate the interaction potential after a small number of terms. For each choice of JMAX, the largest value of λ that can contribute is equal to 2 JMAX. However, in many cases, a potential including only V0 and V2 is constructed. To test this approximation for H, H2, the 0→2 partial cross sections at an intermediate energy (0.25 eV) are plotted in Fig. 6 for scattering from the full PK surface and from the V0+V2 portion. The effect of Vα=2 is seen to be small. This is not surprising from the values of Vα, λ>2 in the accessible scattering region—i.e., for R values that are not excluded by the V0 term at the energies considered here (E≤0.5 eV).

A more stringent test of this approximation is to study the 0→4 excitation, which is first order in the neglected V4 term and second order in V2. The results of this comparison are shown in Fig. 7 at an energy of 0.50 eV. Again the V0+V2 terms provide a highly satisfactory approximation for scattering from this surface. However, it must be remembered that the surfaces for the interaction of other atoms and molecules may have significantly larger contributions from the higher harmonics, so that consideration of the form of the potential in each specific case is required.

C. Approximate Construction of Two-Body Potential

The evaluation of the double integral over the PK surface to determine Vα(R) is very time consuming. Since we do not have the potential directly in terms of Vα, there is no way to avoid projecting out Vα by means of the angular integral over the Legendre polynomials. However, the full radial integral in Eq. (6) can be avoided by fixing the diatomic molecule

\[ \int_{r}^{\infty} [u_{\alpha,\lambda}(r)] \mathcal{P} V_{\alpha}(r, R) dr. \]

(b) Comparison of two-body potentials. The upper curve (---) is V5(ρ, R), where ρ is the equilibrium internuclear distance, the lower curve (-----) is

\[ \int_{r}^{\infty} [u_{\alpha,\lambda}(r)] \mathcal{P} V_{5}(r, R) dr. \]
at some appropriate internuclear distance \( r_0 \). Two possible choices for \( r_0 \) that have been suggested are the equilibrium internuclear separation and an effective radius determined from the experimental moment of inertia. These two distances differ only slightly for \( \text{H}_2 \) being 1.40 and 1.41 a.u., respectively.\(^2\)

Figures 8(a) and 8(b) show the fully integrated \( V_0(r, \bar{R}) \), \( V_2(r, \bar{R}) \) (using ground state Morse oscillator wavefunctions) and \( \bar{V}_0(r_0, \bar{R}) \), \( \bar{V}_2(r_0, \bar{R}) \), where \( r_0 \) is the equilibrium internuclear distance. As established above (Sec. 5.b), we are justified in looking at these terms alone to explain features in the scattering cross section. Since the fully integrated \( \bar{V}_2(r, \bar{R}) \) has a much deeper well (i.e., generates a larger asymmetry), one would expect a larger inelastic cross section. With \( r_0=1.41 \) a.u., a \( \bar{V}_2(r_0, \bar{R}) \) curve with a minimum near \(-0.1 \) eV is obtained, still significantly less deep a well than the \(-0.165 \) eV minimum in the fully inte-

![Graph](image1)

**Fig. 9.** Partial cross sections for the \( 0\rightarrow2 \) rotational excitation at \( E=0.25 \) eV for the fully integrated Porter-Karplus surface (---) compared to the rigid rotor approximation (-----).

![Graph](image2)

**Fig. 10.** Comparison of two-body potentials. The term \( V_2(R) \) from the Porter-Karplus surface (---) and from Dalgarno, Henry, and Roberts (-----).

![Graph](image3)

**Fig. 11.** Comparison of two-body potentials. The term \( V_2(R) \) from Porter-Karplus surface (□) and from Dalgarno, Henry, and Roberts (+).
Fig. 12. Partial cross sections for the 0→2 excitation at $E=0.25$ eV from the Porter-Karplus surface (—) compared to the results for the Porter-Karplus surface connected to an attractive long range $R^{-4}$ potential (-----x-----).

Fig. 13. Partial cross sections for the 0→2 excitation at $E=0.1$ eV from the Porter-Karplus surface (—) compared to the results for the Porter-Karplus surface connected to an attractive long range $R^{-4}$ potential (-----x-----).

grated $V_2(r, R)$. It is not until the $H_2$ target is stretched to 1.48 a.u. that $V_2(r_0, R)$ gives a reasonable approximation to the fully integrated $V_2(r, R)$. Thus, lacking a simple criterion for selecting the best fixed internuclear distance, one is forced to perform the full radial integral to determine a satisfactory potential.

The conclusion drawn from the comparison of potentials is confirmed by calculation of the cross sections. Fig. 9 shows the partial cross sections for the target fixed at its equilibrium internuclear separation and for the full radial integral. Clearly, the $V_2(r_0, R)$ approximation leads to rather poor results.

The sensitivity of the inelastic scattering to the procedure used for constructing the two-body potential (see also the comparison with the results of Tang, Sec. 5.E) indicates that the inclusion of excited vibrational states may be of importance for accurate calculations. Even though the excited vibrational states represent closed channels (see Table I), the distortion of the effective internuclear distance due to their presence might yield a significantly altered interaction potential and consequently change the scattering cross section. An analysis of this effect is beyond the scope of the present work.

**D. van der Waals Potential**

The PK surface, while providing a reasonable description of $H+H_2$ near the saddlepoint region, decays
to zero exponentially with large $R$ and does not have a long-range van der Waals ($-C_6/R^6$) behavior. Although there are accurate values for the $H$, $H_2$ van der Waals coefficient $C_6$, there is no unique procedure for joining the correct $R^{-6}$ long-range interaction with the potential surface computed at smaller distances. In the present study, which provides a basis for a reactive scattering calculation, we are chiefly interested in the energies above 0.20 eV. One expects that at these energies, the effect of the van der Waals potential will be negligible. To test this point, we modify the PK surface by joining it\textsuperscript{90} at large $R$ to the Dalgarno, Henry, and Roberts\textsuperscript{3} $H$, $H_2$ potential (DHR), which consists of a $V_6$ and $V_2$ term only, and has the required $R^{-6}$ dependence for large $R$.

The DHR potential is given by

\begin{equation}
V_0(eV) = 511.088 \exp(-1.9R) - 251.546/R^6,
\end{equation}

\begin{equation}
V_2(eV) = 346.664 \exp(-2.0R) - 27.8767/R^6,
\end{equation}

with $R$ in atomic units. Figures 10 and 11 compare the $V_2$ and $V_2$ terms from the Porter-Karplus surface with those of Eq. (23). The $V_0$ curves cross at $R = 4.6$ a.u. To the scale of Fig. 11, the PK $V_2$ and the DHR $V_2$ are indistinguishable from zero for $R$ larger than 7.0 a.u. Detailed numerical results show that in this region the PK $V_2$ is slightly positive while the DHR $V_2$ is slightly negative. They cross at about 7.0 a.u. and, for $R > 7.0$ a.u., both curves lie within ±0.0001 eV of each other; for $R < 7.0$ a.u. the two curves are drastically different, as is evident from the figure.

The modified surface obtained by joining the DHR potential to the PK potential at the points of intersection of $V_0$ and $V_2$ has three regions:

I. $R \geq 7.0$ a.u.
\begin{align*}
V_\lambda(\lambda > 2) &= 0, \\
V_0, V_2 &\text{ are given by Eq. (23).}
\end{align*}

II. $4.6$ (a.u.) $\leq R \leq 7.0$ (a.u.)
\begin{align*}
V_0 &\text{ is given by Eq. (23).} \\
V_\lambda(\lambda > 0) &\text{ are obtained from the PK surface.}
\end{align*}

III. $R \leq 4.6$ (a.u.)
\begin{align*}
V_\lambda &\text{ (all} \lambda \text{) from PK surface.}
\end{align*}

The resulting surface has cusps at the connection points, but these cusps do not affect the scattering. The steps are rather coarse in the region where the crossing occurs and, as mentioned in Sec. 4, the derivative of the potential is approximated by linear cords without introducing significant errors.

Figures 12 and 13 compare the partial cross sections obtained at 0.1 and 0.25 eV from the hybrid potential defined above with those from the unmodified PK surface. There is very little effect on the cross section at the higher energy but a significant increase in the cross section at the low energy. Since the $V_2$ term is virtually unchanged, the observed differences are due to the changes in $V_0$. For rotationally inelastic scattering, the spherical potential $V_0$ affects are due to the changes in $V_0$. For inelastic scattering, the spherically symmetric potential $V_0$ affects the cross section only insofar as it shields the higher order asymmetric terms. As Fig. 10 shows, the change in $V_0$ involves only energies below 0.05 eV.
Thus, for high incident energies, the modified $V_\theta$ provides only slightly different shielding than the unmodified $V_\theta$ and the cross sections are expected to be unaltered. For low incident energies, the modified $V_\theta$ is significantly less repulsive, allowing the incident particle better access to regions of large $V_2$; hence, the inelastic cross section increases. This result should be contrasted with that of Tang and Karplus\textsuperscript{50} where the effect of a similarly modified $V_\theta$ on elastic scattering was studied. Since $V_\theta$ dominates the elastic scattering, the shorter range of the modified $V_\theta$ yields a smaller cross section than that obtained from the unmodified potential.

E. Comparison with Related Results

Figure 14 compares total 0→2 rotationally inelastic cross sections from the DHR potential (as computed by Allison and Dalgarno\textsuperscript{55} using the close-coupled method including only the 0, 2 molecular rotational states) with the cross sections from the unmodified PK surface (including the 0, 2, 4, 6 molecular rotational states). Including only the 0, 2 molecular rotational states tends to increase the cross sections from the PK surface, as discussed above, but they still remain considerably below the Allison–Dalgarno results. Since the $V_\theta$ term of DHR does not shield the $V_2$ term as well as in the PK surface (Figs. 2, 10, 11), the somewhat larger cross section is quite reasonable.

Tang\textsuperscript{4} has used a form for the $V_\theta$ and $V_2$ terms for H+H\textsubscript{2} based on the Tang and Karplus results\textsuperscript{50} to compute rotationally inelastic cross sections by the distorted wave method. Hayes, Wells, and Kouri\textsuperscript{9} have done close-coupled calculations with the same potential and find good agreement with Tang's results. Tang's potential, like the van der Waal's corrected potential of Sec. 5.D, was chosen to provide the correct $R$ dependence for large $R$, yet approximate the PK values at smaller $R$. The $V_2$ term used by Tang has a positive region at large $R$ values, and a negative well at smaller $R$ values. This leads to total 0→2 inelastic cross sections approximately one-tenth of those observed by Allison and Dalgarno\textsuperscript{10} or in the present study. Tang attributes this to an effective cancellation of the positive part of $V_2$ with the negative portion, which results in a net decrease in the over-all $V_2$ experienced by the incident H atom. These differences again emphasize the importance of treating correctly the molecular distortion during the collision (see Sec. 5.C).

F. Differential Cross Sections

Figure 15 shows the differential cross section in the helicity representation for various final $m$ values at an energy of 0.40 eV obtained with the unmodified PK surface; the molecular rotational states 0, 2, 4, and 6 were included.

The rather considerable oscillations seen in the cross section suggested that some attempt should be made to ascertain their validity. To do this, we examine the magnitude (squared) and the phase, respectively, of the complex $S$ matrix that was used in Eq. (16).
to generate the cross sections of Fig. 15. They are shown in Figs. 16 and 17, respectively. For the $0\rightarrow2$ excitation considered here, the orbital angular momentum in the initial channel $l_0$ is equal to the total angular momentum $J$ of the system. In the final channel, the orbital angular momentum $l_e$ can have, in general, three possible values, $l_e=J$, $J\pm2$; for $J=0,1$ some of these $l_e$ values are forbidden by triangle inequalities implicit in the 3-$j$ symbols of Eq. (12).

The wiggles in the phases starting around $J=19$ in Fig. 17 are an indication of the numerical errors associated with the computational procedure. In the present calculation, which is designed to give a greater
relative accuracy for large components of the wavefunction than for small (see Sec. 4), it is the large $J$ values which are expected to be most inaccurate. As a test on just how these errors in the phases of $S$ affected the differential cross sections, the phases were artificially smoothed and the differential cross sections recomputed. For large $J$, where the phases are small, we expect the distorted wave Born approximation (DWBA) to be valid. The DWBA determines the phases of the inelastic $S$ matrix from the phase shifts obtained by solving the scattering from the spherically symmetric portion of the potential.¹ Using the JWKB expression for these phase shifts, $\eta'$, and assuming that the $V_\theta$ potential is a simple exponential (which the PK surface approaches for large $R$), we are led to approximate $\eta'$ by powers of $J$ times an exponential. Writing

\[
\frac{\eta'}{2\pi} = (a_1 + a_2 J) \exp(-\alpha J), \quad 0 \leq J \leq 30,
\]

\[
= 0, \quad 30 < J \quad (24)
\]

we find that a good fit is obtained with the coefficients

\[
a = 0.060666,
\]

\[
a_1 = -5.15531,
\]

\[
a_2 = 0.177284.
\]

This was used to generate the $L_\theta = J+2$ branch. The other two branches of the phases were generated simply by displacing this curve one unit along $J$.

The differential cross sections summed over final $m$ values with and without smoothing are compared in Fig. 18. The cross sections become somewhat smoother using the artificial phases. A few of the tiny maxima disappear, and some of the relative heights of the peaks change. Over-all, however, the differential cross section remains nearly the same when the spurious wiggles in the phases are removed. The only exception to this is that the sharp forward peak in the cross section [see Fig. (15)] decreases to less than half its value when the smoothed phases are used; i.e., $\sigma(0) = 1.556 \text{ } \text{Å}^2/\text{s}$ for the computed phases as compared with $\sigma(0) = 0.757 \text{ } \text{Å}^2/\text{s}$ for the smoothed phases. Since the forward scattering is extremely sensitive to the large $J$ behavior of the $S$ matrix, the major contribution comes from precisely the region where the numerical errors are greatest (see Sec. 4 and above). Hence, we are forced to conclude that no definite statement can be made about the existence of the sharp forward peak in Fig. 15; that is, its magnitude could be varied significantly by changes in the $S$ matrix well within numerical accuracy of the computation.

Figure 19 shows the $0\rightarrow2$ differential cross sections at various energies; the peak at $\theta = 0$ has been omitted. The oscillations in the differential cross section are seen to be quite regular functions of the energy. The maxima present at $0.10 \text{ } \text{eV}$ persist in approximately the same position as the energy is increased to $0.40 \text{ } \text{eV}$. For higher energies, additional maxima are seen to appear near the forward direction and move toward
larger angles as the energy increases. As indicated by the comparison in Fig. 18, the small maxima near the backward direction at 0.40 eV are probably spurious.

The two curves at 0.14 and 0.15 eV bracket the $0\rightarrow 4$ threshold which occurs at 0.146 eV. The cross section is seen to change in a regular manner quite consistent with a small increase in energy. In some one-dimensional calculations, a new channel opening up has a noticeable effect on scattering into lower channels. We observe here what has been generally known for three-dimensional collisions and collisions involving many partial waves; i.e., that the threshold for a higher channel has no appreciable effect on scattering into lower channels.

The present differential cross section should be compared with the close-coupled results of Allison and Dalgarano, and the distorted wave Born results of Tang. We observe many more oscillations than are apparent in the Allison and Dalgarano results. Tang, however, also finds drastic oscillations in the differential cross section, but unlike the present calculation finds strong scattering in the forward hemisphere. As yet, there is no satisfactory correlation between these differences and the potentials used.

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5 M. von Seegern and J. P. Toennies (to be published).