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Polarization and Exchange Effects in Low-Energy Electron-H_2 Scattering*

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The scattering formalism of Arthurs and Dalgarno, as generalized by Ardill and Davison, is used to take account of exchange in the scattering of slow electrons by molecular hydrogen. Adiabatic polarization terms are included in the direct potential. Exchange and polarization effects on elastic and 0 → 2 and 1 → 3 rotational excitation of H_2 by electron impact are found to be important for energies less than 10 eV. In the energy ranges where measurements and theory overlap, good agreement is obtained for total and differential cross sections, as well as for 0 → 2 and 1 → 3 rotational excitation cross sections.

I. INTRODUCTION

The importance of electron exchange in the *s*-wave elastic scattering of slow electrons by molecular hydrogen has been shown by Massey and Ridley.[1] However, the role of exchange in the scattering of higher partial waves has, aside from semi-empirical investigations, only recently been considered in the work of Wilkins and Taylor[2] on elastic scattering, and Ardill and Davison[3] on rotational excitation of H_2 by incident *p*-wave electrons. Both these calculations omit long-range polarization terms, which have been found to be especially important for rotational excitation. In this paper, we investigate the effects of polarization and exchange terms on elastic and rotational excitation cross sections for scattering by molecular hydrogen of electrons with energies less than 10 eV.

In an early investigation of electron-molecule scattering, Fisk[4] constructed an empirical scattering potential in such a form as to allow the separation of the scattering equation in spheroidal coordinates. He showed that the observed total cross sections for scattering of electrons by H_2 could be fitted reasonably well. While Massey and Ridley[1] also used spheroidal coordinates, they employed the Hulthen and Kohn variational principles to calculate the cross section for scattering of *s*-wave electrons. They made full allowance for exchange of the incident electron with one of the orbital electrons of the molecule, and concluded that this electron exchange effect is important. Carter, March, and Vincent[5] also found exchange to be important for *s*-wave scattering, although they only included it in an approximate manner. Since the scattering equation is not separable in spheroidal coordinates when more realistic molecular fields are used, these authors employed spherical coordinates and a spherically symmetric potential field. Wilkins and Taylor[2] solved the Hartree-Fock equations for an electron moving in the field of a hydrogen molecule. They included both spherical and nonspherical terms in the potential and obtained very good agreement with experiment for energies greater than 4 eV.

In the above calculations of elastic scattering cross sections, the long-range polarization interaction, which arises from the interaction of the incident electron with the induced dipole moment of the molecule, has been neglected. Hara[6] included the effective polarization interaction by cutting off the correct asymptotic form of the potential at some value of r, determined by fitting the calculated elastic cross sections to low-energy elastic scattering measurements. Further, he included exchange through an approximate attractive potential function, similar to that employed in Slater-Hartree-Fock atomic structure calculations. Hara's calculated differential cross sections are in good agreement with the measurements of Ramsauer and Kollath[7] in the energy range $2.0 < E < 10.0$ eV.

In an early investigation of rotational excitation of molecular hydrogen by electron impact, Gerjuoy and Stein[8] used the Born approximation and assumed that the only significant interaction is that due to the permanent quadrupole moment of H_2. This long-range interaction qualitatively accounts for the large rotational-excitation cross sections inferred from electron swarm experiments for energies < 1.0 eV. Dalgarno and Moffett[9] also used the Born approximation and included quadrupole and polarization terms in the long-range interaction potential. They obtained cross sections which, although larger than those of Gerjuoy and Stein,[8] are smaller than the experimental values. Dalgarno and Henry[10] explicitly calculated the short-range terms and long-range quadrupole contributions to the potentials, but they omitted polarization effects. They used the distorted wave approximation and obtained results similar in magnitude to those given by Gerjuoy and Stein.[8]

The distorted wave approximation was also used by Sampson and Mjolsness,[11] who included the long-range quadrupole and polarization interactions by cutting off the correct asymptotic forms at some value of r specified by variable parameters. They determined the parameters by fitting their elastic cross sections to low-energy momentum-transfer measurements. The resulting potentials were then used in the calculation of rotational excitation cross sections. A similar method was employed by Geltman and Takayanagi,[12] except that, in their case, short-range terms were explicitly included, and the cut-off parameters chosen so that the calculated elastic cross sections were in reasonable agreement with total cross sections at higher energies. In the particular case of $0 \rightarrow 2$ rotational excitation, the distorted wave calculations, which include polarization in a semi-empirical manner, are seen to yield cross sections larger by factors of about 2 and 10 at 0.5 and 5.0 eV, respectively, than the Born approximation results which include only the long-range electron-quadrupole interactions. Thus, it is clear that polarization is important, and that it should be included as accurately as possible in any calculation.

Lane and Geltman[13] pointed out that since all partial waves are not affected by the potential in the same way, adjustment of parameters to fit low-energy measurements can be misleading. In particular, one would not expect p-wave scattering, which is dominant for rotational excitation, to be given correctly since momentum-transfer cross sections at low energies are primarily due to s-wave scattering. When the potential is adjusted to fit total cross-section measurements at higher energies, cross sections for inelastic processes must also be included. Lane and Geltman[13] explicitly included short-range terms in their potential and empirically included quadrupole and polarization terms. Cut-off parameters were adjusted to fit experimental elastic scattering data in the range of energies where the p-wave scattering also makes a large contribution to the elastic scattering. They used a close coupling method, in which they included as many rotational states as necessary for convergence, and investigated effects of exchange by an empirical adjustment of the short-range static field, making it more attractive. Their results for energies below about 1 eV are qualitatively similar to those obtained by Sampson and Mjolsness[11] and Geltman and Takayanagi.[12]

Lane and Henry[14] did not employ any adjustable parameters in their electron-molecule potential, which contained short-range terms and long-range quadrupole and polarization terms. The effective polarization interaction was determined by a variational treatment of the $e + \mathrm{H}_2$ system. The resulting potential was then used in a close coupling calculation in which electron exchange was neglected. Their results are similar to those of Lane and Geltman.[13] Ardill and Davison[3] used an exchange distorted-wave treatment to calculate the dominant p-wave contribution to the $0 \rightarrow 2$ rotational cross section. They explicitly included electron exchange, but ignored the polarization interaction, so their direct potential contained only short-range terms and a long-range quadrupole term. For an energy of 0.5 eV, they found that the inclusion of exchange increases the cross section by 70% over that calculated without exchange. Thus, exchange effects are found to be important for $0 \rightarrow 2$ rotational excitation as well as for elastic scattering of electrons by molecular hydrogen.

The theory discussed in Sec. II is based on the work of Ardill and Davison,[3] who generalized the scattering formalism of Arthurs and Dalgarno[15] to take account of exchange. The direct and exchange interaction potentials, given in Sec. III, are then used in a close coupling calculation. The importance of exchange and polarization effects on elastic scattering and $0 \rightarrow 2$ and $1 \rightarrow 3$ rotational excitation of H_2 by electron impact is discussed in Sec. IV, where total and differential cross sections are compared with experiment. Also, the possibility of rotational resonances is discussed in Sec. IV, and the principal conclusions are summarized in Sec. V.

II. ELECTRON-DIATOMIC MOLECULE SCATTERING THEORY

Let us consider a diatomic molecule in the Born-Oppenheimer approximation. We shall ignore vibrational motion of the nuclei, and thus take the internuclear separation to be fixed. In the case of Σ molecular states, for which the component of electronic angular momentum along the internuclear axis vanishes, the nuclear motion of the molecule may be described by a rigid rotator. The rigid rotator wave functions are the familiar spherical harmonics $Y_{jm_j}(\hat{s})$ which satisfy (we shall use atomic units throughout)

$$[H_R - j(j+1)/2I]\, Y_{jm_j}(\hat{s}) = 0 \ , \tag{1}$$

where H_R is the rotational Hamiltonian of the molecule, I is the moment of inertia of the rigid rotator, $\hat{s}$ denotes the orientation of the internuclear axis, $\vec{j}$ is the rotational angular momentum, and m_j is its component along the z axis, taken along the incident direction.

The total Hamiltonian for the electron-molecule system may be written

$$H = H_R - \tfrac{1}{2}\nabla_r^2 + V(\vec{r}, \hat{s}) , \tag{2}$$

where $-\frac{1}{2}\nabla_r^2$ is the kinetic-energy operator for the projectile electron, $V(\vec{r}, \hat{s})$ is the electron-molecule effective interaction potential, and $\vec{r}$ (or $\vec{r}_3$) denotes the coordinates of the electron.

The angular momentum $\vec{l}$ of the projectile electron is coupled with $\vec{j}$ to form $\vec{J}$, the total angular momentum of the system. The quantum numbers J and $M = m_j + m_l$ represent the magnitude and component along the z axis, respectively, of $\vec{J}$. Thus, convenient angular basis functions are the eigenfunctions of J^2 and J_z given by

$$\mathcal{Y}_{jl}^{JM}(\hat{r}, \hat{s}) = \sum_{m_l m_j} C(jlJ; m_j m_l M)\, Y_{jm_j}(\hat{s})\, Y_{lm_l}(\hat{r}) , \tag{3}$$

where $C(jlJ; m_j m_l M)$ are the Clebsch-Gordan coefficients.

The total wave function must satisfy

$$(H - E_j)\, \Psi_{jl}^{JM}(\vec{r}, \hat{s}) = 0 \tag{4}$$

subject to scattering boundary conditions, where E_j is the total energy of the system, given by

$$E_j = E_0 + E + j(j+1)/2I . \tag{5}$$

Here E_0 is the energy of the ground state of the molecule, and E is the energy of the incident electron. The total wave function, antisymmetric with respect to interchange of electrons, may be expanded in the set of coupled angular basis functions

$$\Psi_{jl}^{JM}(\vec{r}, \hat{s}) = \sum_{j'l'} \sum_{1,2,3} r^{-1} u_{j'l'}^{Jjl}(r)\, \mathcal{Y}_{j'l'}^{JM}(\hat{r}, \hat{s})\, \phi_0(\vec{r}_1, \vec{r}_2; s)\, \chi(1,2;3) , \tag{6}$$

where the inner summation is over cyclic interchanges of electrons, $\chi(1,2;3)$ is the doublet spin function, $\phi_0(\vec{r}_1, \vec{r}_2, s)$ is the wave function for the ground state of the hydrogen molecule, and $u_{j'l'}^{Jjl}(r)$ are the radial functions which describe the motion of the projectile electron, and which may be shown to satisfy the set of coupled equations

$$\left(\frac{d^2}{dr^2} - \frac{l'(l'+1)}{r^2} + k_{j'j}^2 \right) u_{j'l'}^{Jjl}(r) - 2 \sum_{j''l''} \langle j'l'; J | V | j''l''; J \rangle\, u_{j''l''}^{Jjl}(r)$$
$$+ 2 \sum_{j''l''} \int_0^\infty k(j'l', j''l''; J | r_1, r)\, u_{j''l''}^{Jjl}(r_1)\, dr_1 = 0 , \tag{7}$$

where $k_{j'j}$ is the channel wave number given by

$$k_{j'j}^2 = k_{jj}^2 - [j'(j'+1) - j(j+1)]/I . \tag{8}$$

The direct matrix elements which appear in the coupled equations are given by

$$\langle j'l'; J | V | j''l''; J \rangle = \iint \mathcal{Y}_{j'l'}^{JM*}\, V\, \mathcal{Y}_{j''l''}^{JM}\, d\hat{r}\, d\hat{s} . \tag{9}$$

The exchange contributions are contained in the last term on the left-hand side of Eq. (7). If we assume that the wave function for the ground state of the hydrogen molecule is orthogonal to the radial function which describes the motion of the free electron (an assumption which will be shown to be valid in our case), then only one term contributes to the exchange kernel. Thus, we have

$$k(j'l',j''l'';J\,|\,r_1,r)=r_1 r\iiiint \mathcal{Y}_{j'l'}^{JM*}(\hat{r},\hat{s})\phi_0^*(\vec{r}_1,\vec{r}_2,\hat{s})\,r_{13}^{-1}\,\phi_0(\vec{r}_2,\vec{r},\hat{s})\mathcal{Y}_{j''l''}^{JM}(\hat{r}_1,\hat{s})\,d\hat{r}_1\,d\vec{r}_2\,d\hat{r}\,d\hat{s} \tag{10}$$

Since Ardill and Davison[3] did not make use of this orthogonality, they obtained much more complicated expressions for the exchange kernel.

The coupled equations (7) have to be solved subject to the boundary conditions

$$\begin{aligned} &u_{j'l'}^{Jjl}(0)=0,\\ &u_{j'l'}^{Jjl}(r)\underset{r\to\infty}{\sim}\delta_{jj'}\delta_{ll'}\exp[-i(k_{jj}r-\tfrac{1}{2}l\pi)]-\left(\frac{k_{jj}}{k_{j'j}}\right)^{\frac{1}{2}}S^J(jl,j'l')\exp[i(k_{j'j}r-\tfrac{1}{2}l'\pi)]\,, && k_{j'j}^2>0,\\ &\qquad\underset{r\to\infty}{\sim}\exp[-|k_{j'j}|r]\,, && k_{j'j}^2<0. \end{aligned} \tag{11}$$

Thus, the scattering matrix $S^J(jl,j'l')$ is specified, and its elements may be used to obtain the differential cross section for $j\to j'$ transitions averaged over all m_j and summed over m_j'. We obtain

$$\frac{d\sigma}{d\theta}(j\to j'\,|\,\theta)=\frac{\pi(-1)^{j'-j}}{2(2j+1)k_{jj}^2}\sum_{\lambda=0}^{\infty}A_\lambda P_\lambda(\cos\theta), \tag{12}$$

where the A_λ coefficients are defined by Arthurs and Dalgarno,[15] and a factor 2π from integration over azimuthal angle has been included. The expression for the total cross section is

$$\sigma(j\to j')=[\pi/(2j+1)k_{jj}^2]\sum_{J=0}^{\infty}\sum_{l,l'}(2J+1)|T^J(jl,j'l')|^2, \tag{13}$$

where the transmission matrix $T^J(jl,j'l')$ is given by

$$\underline{T}=\underline{1}-\underline{S}, \tag{14}$$

and l and l' take on all values consistent with j, j', and J. The momentum-transfer cross section may be expressed as

$$\sigma_m=[\pi/(2j+1)k_{jj}^2](A_0-\tfrac{1}{3}A_1). \tag{15}$$

Since it is more convenient to deal with real solutions of the coupled equations, we may replace the asymptotic conditions (11) by

$$\begin{aligned} u_{j'l'}^{Jjl}(r)&\underset{r\to\infty}{\sim}\sin(k_{jj}r-\tfrac{1}{2}l\pi)\delta_{jj'}\delta_{ll'}+\cos(k_{j'j}r-\tfrac{1}{2}l'\pi)R^J(jl,j'l'), && k_{j'j}^2>0,\\ &\underset{r\to\infty}{\sim}\exp(-|k_{j'j}|r), && k_{j'j}^2<0, \end{aligned} \tag{16}$$

where the R matrix is related to the S matrix through

$$\underline{S}=(\underline{1}+i\underline{R})(\underline{1}-i\underline{R})^{-1}. \tag{17}$$

III. ELECTRON-H_2 POTENTIALS

The interaction potential for the e-H_2 system may be represented by

$$V(\vec{r},\hat{s})=\sum_\lambda v_\lambda(r)P_\lambda(\hat{r}\cdot\hat{s}). \tag{18}$$

As a result, the direct matrix element in (7) may be reduced to

$$\langle j'l';J|V|j''l'';J\rangle=\sum_\lambda f_\lambda(j'l',j''l'';J)v_\lambda(r), \tag{19}$$

where the f_λ coefficients are given by Arthurs and Dalgarno.[15]

We choose radial potentials of the form

$$v_0(r) = v_W{}^0(r) + v_P{}^0(r), \quad v_2(r) = v_W{}^2(r) + v_Q{}^2(r) + v_P{}^2(r), \quad v_4(r) = v_W{}^4(r), \tag{20}$$

in which the subscripts W, Q, and P refer to Wang (short range), quadrupole, and polarization, respectively. The short-range terms v_W were determined by Lane and Geltman[13] using the Wang ground-state function.[16] Dalgarno and Henry[10] obtained similar values when they used the Hagstrom-Shull function.[17] Thus, we conclude that these terms are rather insensitive to the choice of single-center wave function.

The quadrupole interaction may be represented by

$$v_Q{}^2(r) = -Qr^{-3}\{1 - \exp[-(r/r_0)^6]\}, \tag{21}$$

where Q and r_0 are taken to be 0.49 $ea_0{}^2$ and $1.8a_0$, respectively.[18] This choice for r_0 is consistent with the general behavior of the unperturbed e-H_2 potential as calculated by Dalgarno and Henry.[10]

In the derivation of the scattering equation (7), the molecule is assumed to remain in its ground electronic state. Thus, polarization of the molecule in the field of the free electron is neglected. However, this omission may be rectified by including an effective adiabatic polarization potential. In a previous paper Lane and Henry[14] employed a variational treatment, in which the total energy of the static e-H_2 system is minimized with respect to parameters $c_{\alpha\beta}$ in a trial function of the form

$$\phi_0(\vec{r}_1, \vec{r}_2, \hat{s}) \sum_{\alpha,\beta} c_{\alpha\beta}(x_1 + x_2)^\alpha (z_1 + z_2)^\beta, \tag{22}$$

where ϕ_0 is the ground-state wave function of H_2, and x_1, x_2, z_1, and z_2 are electronic coordinates. They used the Joy and Parr single-center wave function[19] to represent the unperturbed ground-state molecule, and calculated the terms $v_P{}^0(r)$ and $v_P{}^2(r)$, which may be represented analytically by

$$\begin{aligned} v_P{}^0(r) &= -[\alpha_0/2(r^2 + r_1{}^2)^2]\{1 - \exp[-(r/r_a)^3]\} \\ v_P{}^2(r) &= -[\alpha_2/2(r^2 - r_2{}^2)^2]\{1 - \exp[-(r/r_b)^4]\}, \quad && r \geqslant 0.5 \\ &= 0, && r < 0.5. \end{aligned} \tag{23}$$

where α_0 and α_2 are taken to be 5.50 and 1.38 $a_0{}^3$,[18] and r_1, r_2, r_a, and r_b are 1.22, 0.1, 1.7, and 2.0 a_0, respectively. This choice of parameters is consistent with the nonpenetrating scaled (NPS[1]) case of Lane and Henry.[14] In the calculation of the polarization potentials, the predominant polarization effects are assumed to be adiabatic only in the region exterior to the space occupied by the bound electrons, and therefore in the calculation the incident electron is not allowed to penetrate inside the molecular cloud. The potentials are scaled in order to obtain the correct asymptotic behavior. While the unperturbed electron-molecule interaction dominates for $r \leqq 1.6\,a_0$, the polarization potentials are more important for larger values of r.

We follow Ardill and Davison[3] in the evaluation of the exchange kernel (10). The integrals present little difficulty if a single-center wave function is used. We have employed the five-term Huzinaga function,[20] which contrasts with the 38-term Hagstrom-Shull function[17] used by Ardill and Davison.[3] The most important contributions to the exchange term in (7) may be given by

$$\begin{aligned} \delta_{j'j''}\delta_{l'l''}\{&[0.495\,61\,u_{1s}(r) + 0.333\,05\,u_{2s}(r)]\,Y^{l'}(1s, j'l' \mid r) \\ &+ [0.333\,05\,u_{1s}(r) + 0.271\,81\,u_{2s}(r)]\,Y^{l'}(2s, j'l' \mid r)\}/(2l' + 1), \end{aligned} \tag{24}$$

where $u_{1s}(r) = 1.130\,50\,r\,e^{-1.1r} + 20.518\,13\,r^4\,e^{-4.3r}, \quad u_{2s}(r) = 1.431\,08\,r\,e^{-0.8r}$,

and $Y^\lambda(ns, j'l' \mid r) = r^{-\lambda-1}\int_0^r u_{ns}(r_1)\,r_1{}^\lambda\,u_{j'l'}{}^{Jjl}(r_1)\,dr_1 + r^\lambda \int_r^\infty u_{ns}(r_1)\,r_1{}^{-\lambda-1}\,u_{j'l'}{}^{Jjl}(r_1)\,dr_1.$

We find that the exchange terms associated with the remaining terms of the Huzinaga wave function and those for $j'l' \neq j''l''$ are unimportant, and so expressions for these are omitted.

IV. RESULTS

We calculate cross sections for rotational excitation and elastic scattering by solving the set of coupled equations (7) subject to the asymptotic conditions (16). The numerical solution is obtained by using Numerov's method to integrate the equations outwards and inwards, with subsequent matching to obtain a final continuous solution. The asymptotic expansion method of Burke and Schey[21] is used to determine the eigenphase shift from the function $u_{j'l'}^{Jjl}(r)$. A combination of these methods has been outlined by Smith, Henry, and Burke.[22] Since there will be no significant change in results, we will ignore values of $l' > 5$ for energies in the range of interest, thus reducing the total number of channels involved in Eq. (7).

We have included exchange terms in the scattering equation (7) in a manner analogous to that given by Ardill and Davison.[3] However, our methods differ in several respects: (1) We have assumed that the wave function for the ground state of the hydrogen molecule is orthogonal to the radial function which describes the motion of the free electron. This is a valid assumption if the approximate wave functions used to represent the H_2 molecule is good. We have evaluated the nonorthogonality terms for several energies and verified that they are small. Ardill and Davison also omitted these terms since preliminary calculations showed that the dominant contribution to the exchange kernel came from Eq. (10). We have used the simple Huzinaga wave function[20] in our calculation of the exchange terms, whereas Ardill and Davison used the more complicated Hagstrom-Shull function.[17] (2) We have employed the direct potential given by Lane and Henry,[14] which includes both short-range terms and long-range quadrupole and polarization terms, while Ardill and Davison omitted the polarization terms. (3) We have solved the coupled integro-differential equations numerically in the close coupling approximation, whereas they made use of the distorted wave approximation, which ignores the coupling between different energy levels of the rigid rotator.

When we reduce our equations to the case solved by Ardill and Davison,[3] i.e., omit polarization terms in the direct potential and omit the coupling terms, then the $0 \rightarrow 2$ rotational cross sections for a dominant incident p-wave electron agree to within 6%. Thus, we conclude that the Huzinaga wave function gives an adequate representation of the hydrogen molecule, at least for purposes of calculating the exchange terms.

A. Elastic Cross Sections

Figure 1 compares our total cross sections, i.e., the sum of elastic $0 \rightarrow 0$ and rotational $0 \rightarrow 2$ cross sections, with the measured cross sections of Ramsauer and Kollath[7] and Golden, Bandel, and Salerno,[23] given by squares and circles, respectively. Curve A is obtained when both polarization and exchange terms are included, curve B results when polarization terms are retained but exchange terms neglected, and curve C results when exchange terms are included but polarization terms omitted. In all curves, short-range terms and a long-range quadrupole term are included in the direct potential. The dashed curve represents the total cross section for the $j = 1$ level, where all direct and exchange terms have been included in the potentials.

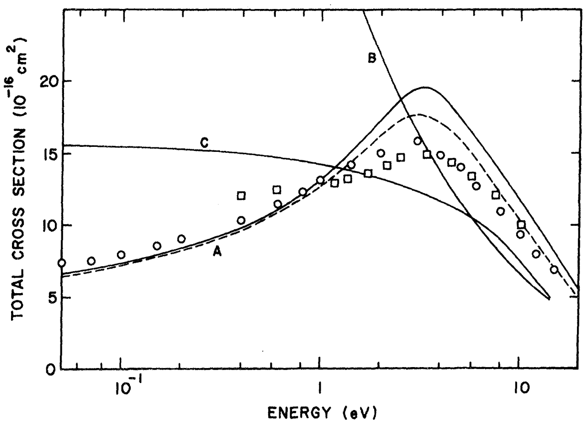

FIG. 1. Total cross sections for scattering of electrons by H_2 as a function of energy. Curve A represents results obtained when polarization and exchange terms are included; solid and dashed curves represent total cross sections for the $j = 0$ and $j = 1$ levels, respectively; curve B results when polarization terms are retained but exchange terms neglected; curve C results when exchange terms are included but polarization terms omitted. Experimental results are given by ○: Golden *et al.* (Ref. 23) and □: Ramsauer and Kollath (Ref. 7).

In Fig. 1, when exchange terms are neglected, total cross sections are much larger than experimental values for energies < 3 eV. Since neglect of exchange means that the short-range part of the potential is not sufficiently attractive, the phase shifts are not close enough to π for low energies, and calculated cross sections are too large. When exchange terms are included but polarization terms omitted, the energy dependence of the calculated cross section does not agree with experiment. In this case, the long-range part of the potential is not attractive enough. When all potential terms are included, there is good agreement between theory and experiment. The maxima in the calculated and observed cross section curves both occur at about the same energy, i.e., $E = 3.5$ eV. An analysis of the partial wave contributions to the elastic cross section shows that the p-wave component also has a maximum at this energy. However, the corresponding eigenphase shift,[21] given in Table I, is not going through $\pi/2$, and so the behavior of the cross section cannot be described as being due to a shape resonance.

TABLE I. Eigen phase shift (p wave) as a function of energy for $J=1$, $j=0$.

k^2(Ry)	Eigen phase shift
0.005	0.009 13
0.01	0.022 80
0.02	0.050 67
0.05	0.147 39
0.10	0.333 94
0.18	0.614 56
0.25	0.792 13
0.325	0.916 20
0.588	1.085 26
1.0	1.118 60

Figure 2 compares our elastic $0\rightarrow 0$ cross sections with those of Massey and Ridley[1] and Wilkins and Taylor.[2] Measured total cross sections of Ramsauer and Kollath[7] and Golden *et al.*[23] are given by squares and circles, respectively. Exchange terms have been included in all calculations. Results of Massey and Ridley[1] are lower than experiment primarily because they included only s-wave scattering. Also, the trial wave function which they used in the Hulthen variational principle is expected to be poor for higher energies. Calculations of Wilkins and Taylor[2] are in very good agreement with experiment for energies >4 eV, but the energy dependence of their cross sections is not correct for lower energies. Our curve results from the proper inclusion of the static field, electron exchange effects, and the effective polarization interaction.

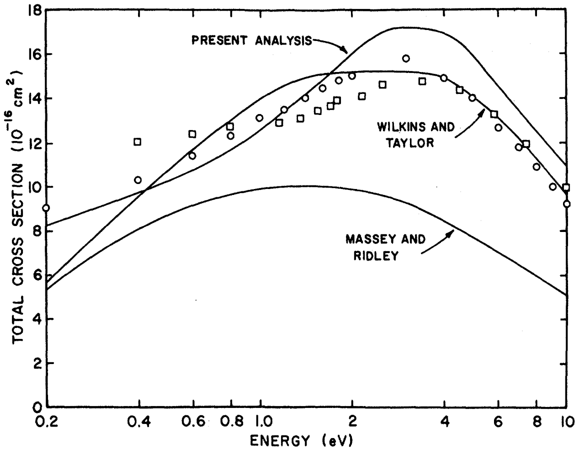

FIG. 2. Total elastic cross sections for scattering of electrons by H_2 as a function of energy, compared with theoretical calculations of Massey and Ridley (Ref. 1) and Wilkins and Taylor (Ref. 2). Circles and squares as in Fig. 1.

Note added in proof: A calculation by J. Tully and R. S. Berry [J. Chem. Phys. (to be published)] in which polarization effects are ignored and a method similar to that of Wilkins and Taylor[2] is used, gives results which are consistent with our curve C, Fig. 1. Their results indicate that polarization effects are important in contrast to the conclusion reached by Wilkins and Taylor.[2]

B. Rotational Excitation Cross Sections

Figure 3 gives the $0\rightarrow 2$ rotational excitation cross section for H_2 as a function of electron impact energy E. Circles and squares denote values deduced from swarm experiments by Engelhardt and Phelps[24] and Crompton *et al.*,[25] respectively, who measured the electron transport coefficients which characterize the motion of electrons as they drift through a gas under the influence of a uniform electric field. Curves A, B, and C have the

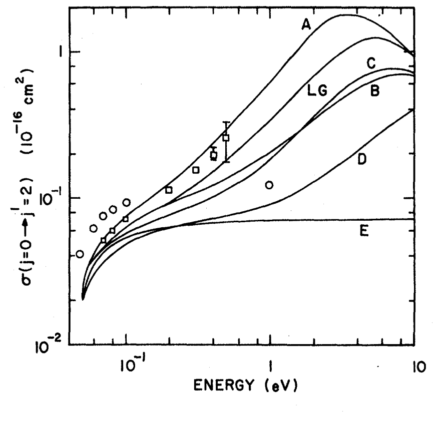

FIG. 3. Rotational excitation cross sections for the $j=0\rightarrow 2$ transition in H_2 by electron impact as a function of energy. Curves A, B, and C as in Fig. 1; curve D represents results obtained when only static field and quadrupole terms are retained; curve E gives Born approximation results of Gerjuoy and Stein (Ref. 8); curve LG – Lane and Geltman (Ref. 13). Experimental results are given by ○: Engelhardt and Phelps (Ref. 24) and □: Crompton *et al.* (Ref. 25).

same meaning as for Fig. 1, with the added fact that curve *B* represents the results of Lane and Henry[14] for their nonpenetrating scaled case. Curve *D* is obtained when both polarization and exchange effects are neglected. This is essentially equivalent to the approach of Dalgarno and Henry,[10] since in the e-H_2 problem, the coupling is found to be weak and the close coupling and distorted wave approximations should give similar results. Cross sections given by curve *E* represent calculations of Gerjuoy and Stein[8] using the quadrupole interaction in the Born approximation. Curve *LG* represents cross sections obtained by Lane and Geltman,[13] who used a semiempirical potential which takes some account of exchange effects by means of an adjusted short-range static field. Their results are smaller than the measurements of Crompton *et al.*[25]

Inclusion of both polarization and exchange terms clearly has a large effect on the 0 → 2 rotational excitation cross section. Their retention results in cross sections which, for energies $E > 0.4$ eV, are larger by factors of 2–3 than those calculated with either polarization terms or exchange terms only. For $E < 0.5$ eV, calculations which include all potential terms are in very good agreement with measurements of Crompton *et al.*[25] These experimental results were determined from electron transport coefficients which are believed to be accurate to ± 1%, and are thus felt to be much more accurate than the results of Engelhardt and Phelps.[24] When our cross sections are used to calculate electron drift velocities and characteristic energies, agreement with measured values of these electron transport coefficients is good to within ± 2%. The error limits on the cross sections of Crompton *et al.* are assigned to be ± 3% from threshold to 0.3 eV, since this is the shift necessary to cause a 1% change in the values of the transport coefficients. Above 0.3 eV, the effect of the 0 → 1 vibrational transition is noticed, and a unique rotational cross section cannot be determined from experiment. Thus, the error limits expand rapidly to ± 10% at 0.4 eV and ± 30% at 0.5 eV.

Results for the 1 → 3 rotational excitation cross section are given in Fig. 4 as a function of electron energy. The circles denote the measurements of Ehrhardt and Linder,[26] who measured differential cross sections by a crossed beam technique from 20° to 120° for elastic and for 1 → 3 rotational scattering of electrons by H_2. They extrapolated their measurements to 180°, integrated over the angular range, then normalized their results to the absolute total cross sections of Golden *et al.*[23] These authors quote an accuracy of about 10%. Curves *A*, *B*, and *C* have the same meaning as for Fig. 1, and curve *LG* has the same meaning as for Fig. 3. Lane and Geltman's results[13, 27] are again somewhat lower than the measured cross sections. It is clear that if either exchange or polarization terms are neglected (curves *B* and *C*), a large discrepancy would exist between theory and experiment. The shape and magnitude of curve *A*, which includes both of these effects, is in fair agreement with experiment. The maximum in our total cross section is 10% larger than that of Golden *et al.*[23] and the maximum in our 1 → 3 excitation cross section is 20% larger than that of Ehrhardt and Linder.[26] If the results of Ehrhardt and Linder were normalized to our total cross sections calculated with exchange and polarization terms, then the discrepancy in magnitude of the 1 → 3 rotational excitation cross sections would be decreased.

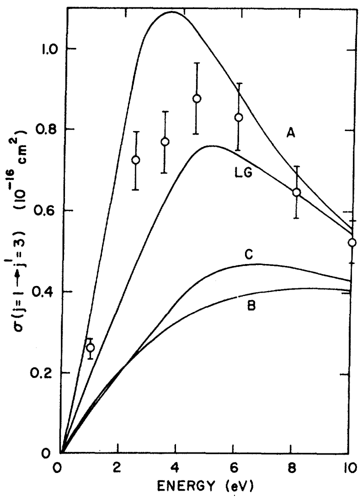

FIG. 4. Rotational excitation cross sections for the $j = 1 \rightarrow 3$ transition in H_2 by electron impact as a function of energy. Curves *A*, *B*, and *C* as in Fig. 1; curve *LG* – Lane and Geltman (Ref. 27). Circles represent experimental points of Ehrhardt and Linder (Ref. 26).

C. Differential Cross Sections

Differential cross sections for elastic scattering of electrons by molecular hydrogen are given as a function of angle in Fig. 5. Theoretical curves are calculated with all terms included in the direct and exchange potentials. Curves *A*, *B*, and *C*

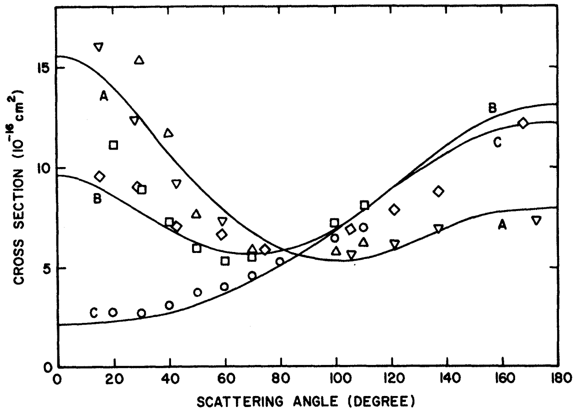

FIG. 5. Differential cross sections for elastic scattering of electrons by H_2 as a function of angle. Curve A: $E=4.42$ eV; curve B: $E=2.45$ eV; curve C: $E=1.0$ eV. Experimental points of Ehrhardt (Ref. 28) are given by △: $E=4.42$ eV; □: $E=2.45$ eV; ○: $E=1.0$ eV, and Ramsauer and Kollath's (Ref. 7) measurements are denoted by ▽ : $E=4.5$ eV; ◇ : $E=2.5$ eV.

represent theoretical results for energies 4.42, 2.45, and 1.0 eV, respectively. Symbols △, □, and ○ denote the measurements of Ehrhardt and Linder[28] at 4.42, 2.45, and 1.0 eV, respectively, and ▽ and ◇ denote the measurements of Ramsauer and Kollath[7] at 4.5 and 2.5 eV. Experimental results of Ramsauer and Kollath are absolute, but those of Ehrhardt and Linder have been normalized to the theoretical curves at 90°. The overall agreement in shape and magnitude is satisfactory. The elastic differential scattering cross section is almost independent of energy at 90° for the energies studied. Furthermore, it becomes more forward peaked as the energy is increased.

Figure 6 denotes differential cross sections for rotational excitation as a function of scattering angle at 4.42 eV. The circles represent relative measurements of Ehrhardt and Linder[26, 28] for the $j=1\rightarrow j'=3$ transition. They state that for $2\rightarrow 4$ and $3\rightarrow 5$ transitions, the differential cross sections have about the same shape and magnitude as those for $1\rightarrow 3$ transitions. Our theoretical curves are in agreement with this observation when we include both exchange and polarization terms in the potentials. Further, we find that the rotational $3\rightarrow 1$ de-excitation cross section is about one-half of the rotational $3\rightarrow 5$ excitation cross section at all angles and energies. The shape of the rotational differential scattering cross section does not change much with energy, and is almost isotropic at low energies.

Momentum-transfer cross sections are given in Fig. 7 as a function of energy. The solid curve represents results of our calculations when all terms are included in the potentials. Differential

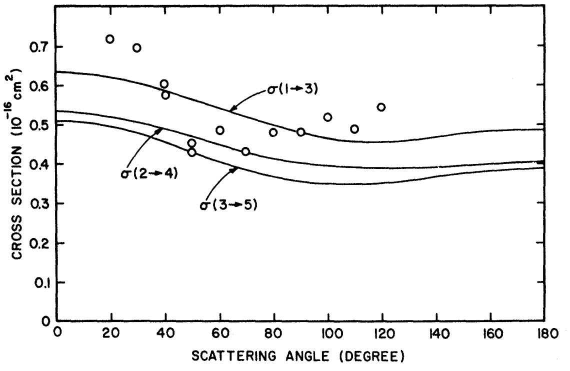

FIG. 6. Differential cross sections for rotational excitation of H_2 by electron impact, as a function of angle at $E=4.42$ eV. Circles represent relative measurements of Ehrhardt (Ref. 28) for the $j=1\rightarrow 3$ transition.

cross sections are calculated from Eq. (12) and the momentum-transfer cross section is obtained by integrating over angle, the integrand being weighted by a $(1-\cos\theta)$ factor. Thus, the probability that an electron is scattered through angles approaching 180° is preferentially weighted. Alternatively, we may calculate the momentum-transfer cross section from Eq. (15). These values for momentum-transfer cross sections are in good agreement with those of Bekefi and Brown,[29] Engelhardt and Phelps,[24] and Crompton *et al.*,[25] which are given by circles, squares, and triangles, respectively. The results of Bekefi and Brown were obtained from measurements of the microwave conductivity of a plasma. Since differential elastic scattering cross sections are

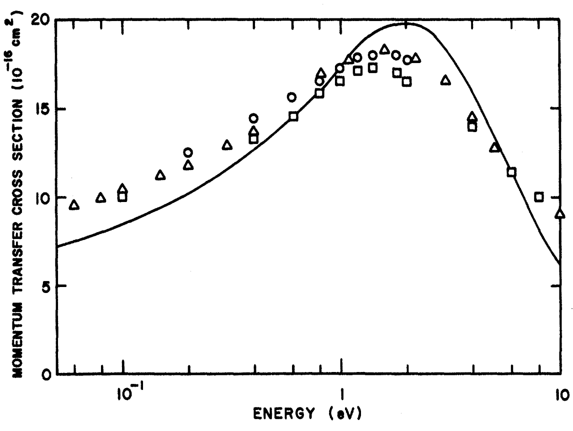

FIG. 7. Momentum-transfer cross section as a function of energy for scattering of electrons by H_2. ○: Bekefi and Brown (Ref. 29); □ : Engelhardt and Phelps (Ref. 14); and △: Crompton *et al.* (Ref. 25).

predominantly forward peaked only at high energies, momentum-transfer cross sections are larger than elastic scattering cross sections for energies less than 3.4 eV.

D. Rotational Resonances

Recent experimental studies on the drift of electrons through gases have indicated that the electron drift velocity depends on the pressure of the gas.[30–33] Electron trapping can efficiently slow down the drift motion of electrons in an electric field, particularly if the densities are high. An electron may be temporarily captured by a gas molecule and, since the resultant negative ion moves much more slowly than the electron, the electron would be delayed. After some time, the short-lived compound state would decompose collisionlessly. If an electron is trapped and released many times when drifting through a gas, it will become increasingly delayed as densities are increased.

Frommhold,[34] assuming the existence of rotational resonances as the mechanism for electron trapping, was able to reproduce the qualitative features of the low-energy experimental data. A semi-empirical study of such resonances in electron-H_2 and electron-D_2 scattering was made by Kouri,[35] who assumed a Morse function for the interaction potential. He was able to choose parameters for the potential so as to give positions of resonances which are in quantitative agreement with those necessary to reproduce experimental data.

We have included the static field, electron exchange effects, and an effective polarization potential for the electron-H_2 interaction. Resonance states have not been found below the $j'=2$ or $j'=3$ rotational levels. Since good agreement was obtained with experimental data on low-energy total cross sections and $0\rightarrow 2$ and $1\rightarrow 3$ rotational excitation cross sections, we are fairly confident that our effective potential is realistic. If it takes a large distortion of our potentials to produce a resonance state, the existence of such a resonance would probably be inconsistent with our other results. However, the possibility of rotational resonances cannot be completely ruled out, since their positions would be expected to be extremely sensitive to values chosen for the parameters, and some change in the potential may be sufficient to trap a bound state at the top of the potential well. For example, for the Morse interaction assumed by Kouri,[35] the curvature parameter $a=1.54847$ leads to a resonance energy in the electron-H_2 system at 0.030 eV, whereas with $a=1.548$, the position of the resonance would change to 0.020 eV.

V. SUMMARY

Electron exchange effects have been explicitly included in the scattering of electrons by molecular hydrogen. They are found to be very important for both elastic and rotational excitation cross sections. When the effects of exchange are properly considered, and realistic polarization and static potentials included, the theoretical cross sections are found to be in good agreement with experiment.

Total cross sections are in very good agreement with experiment[23] for energies $E<1$ eV, and for energies up to 15 eV, good accord is obtained. The $0\rightarrow 2$ rotational excitation cross sections are in excellent agreement with measurements of Crompton *et al.*[25] over the experimental energy range $E<0.5$ eV, and results for $1\rightarrow 3$ rotational excitation cross sections agree well with measurements of Ehrhardt and Linder[26] for $E<10$ eV. Satisfactory agreement is obtained between theory and experiment for both elastic[7] and inelastic[28] differential cross sections, and momentum-transfer cross sections are consistent with experiments of Bekefi and Brown,[29] Engelhardt and Phelps,[24] and Crompton *et al.*[25] A preliminary search for resonance states below the $j'=2$ or $j'=3$ rotational levels has failed to uncover any such states.

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Impact-Parameter Treatment of Hydrogen-Hydrogen Excitation Collisions. I. Two-State Approximation

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The impact-parameter versions of the full two-state and the Born approximations are used to calculate the $n=2$ and 3 single-excitation cross sections describing collisions between two ground-state hydrogen atoms. Effects similar to those encountered by Bates in his distortion calculations of the $2s$ and $2p$ excitations of hydrogen by proton impact are observed. Cross sections for excitation up to the $4s$ state are also provided by using the Born approximation. The percentage polarization of impact radiation emitted is evaluated.

I. INTRODUCTION

Knowledge of inelastic cross sections for collisions between heavy particles is important in interpreting the aurorae, airglow, and the luminosity accompanying a meteor trail. At present there is no direct method available for calculating excitation cross sections over the entire energy range of the colliding particles. However, two approximations, in principle, different and valid in mutually exclusive regions, are useful. The perturbed stationary state (PSS) method[1] describes the formation of a quasimolecule by molecular wave functions that tend to the initial and final states of the colliding atoms at infinite separation; the kinetic energy of relative motion, assumed small, is responsible for the transition. This adiabatic procedure is the continuum analog