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[7] The ± 20% agreement level for these shift measurements is reasonable when compared to the maximum uncertainty of ±15 in width measurements (see the "Error Analysis" section).

Polarization Potential in Low-Energy Electron-H_2 Scattering[*]

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An adiabatic polarization potential appropriate to low-energy electron-H_2 scattering has been calculated by a variational approach. The total energy of the static electron-H_2 system is minimized with respect to the parameters $C_{\alpha\beta}$ in a trial function of the form

$$\psi_0(1,2)\sum_{\alpha,\beta} C_{\alpha\beta}(x_1+x_2)^{\alpha}(z_1+z_2)^{\beta},$$

where $\psi_0(1,2)$ is Joy and Parr's one-center ground-state function. The subscripts 1 and 2 refer to the molecular electrons. The polarization potential is found to be well represented by $v_p{}^0(r)+v_p{}^2(r)P_2(\cos\theta)$, where θ specifies the position vector of the static electron with respect to the internuclear axis. The radial functions $v_p{}^0(r)$ and $v_p{}^2(r)$ have been determined over a wide range in r. The polarization potentials are used in a calculation of rotational-excitation cross sections. Comparisons are made with results of other investigations.

I. INTRODUCTION

In electron-atom scattering, distortion of the target atom by the incident electron is very important. For sufficiently large electron energies, this distortion process is highly nonadiabatic and results in excitation of the target atom. In the case of electron energies below the threshold for excitation, the atom may be thought of as being "polarized" by the electron, which then moves in a potential field modified by the effects of this polarization. When the velocity of the incident electron is small, compared to that of the bound atomic electrons; the adiabatic approximation may be invoked. It is then appropriate to define an adiabatic polarization potential $V_p(r)$ which has the asymptotic behavior

$$V_p(r)\underset{r\to\infty}{\sim} -\alpha/2r^4, \tag{1}$$

where α is the electric polarizability of the atom. The simplest method for approximating the effects of polarization is to construct some analytic form for the potential[1–3] which has asymptotic behavior (1). Often, the potential is adjusted so as to yield cross sections consistent with experiment. However, such an approach is not very satisfactory. A better technique for the treatment of polarization effects in electron-atom collisions, is Temkin's method of polarized orbitals.[4] This method, which employs first-order perturbation theory to obtain the atomic orbitals in the field of the scattered electron, has been successfully used for various atomic systems.[4–10]

In electron collisions with diatomic molecules, much of what we have said still holds true. Because of the non-spherical character of diatomic molecules, however, the polarizability is not spherically symmetric. Thus the asymptotic form for the adiabatic polarization potential becomes[11]

$$V_p(\vec{r})\underset{r\to\infty}{\sim} -\alpha_0/2r^4-(\alpha_2/2r^4)P_2(\hat{r}\cdot\hat{R}), \tag{2}$$

where $\alpha_0=(\alpha_z+2\alpha_x)/3$,

and $\alpha_2=2(\alpha_z-\alpha_x)/3$.

Here α_z and α_x are the respective polarizabilities (in units of $a_0{}^3$), parallel and perpendicular to the internuclear axis $\hat{R}$. Polarization effects in electron-molecule collisions are particularly interesting, since rotational and even vibrational excitation of the molecule is possible at relatively low energies, where the adiabatic approximation might still be expected to be good. Thus, we can investigate, within the adiabatic framework, the effects of polarization on inelastic scattering. As in the case of atoms, it has previously been the practice to construct an analytic polarization potential with asymptotic form (2). The parameters of this potential can be adjusted so that calculated elastic cross sections agree with either low-energy momentum-transfer measurements,[12] or total cross sections observed at higher energies.[13] However, since all partial waves are not affected by the potential in the same way, comparison with the low-energy measurements can be misleading. For example, p-wave scattering, which is dominant for rotational excitation, may not be given correctly, since the momentum-transfer cross section at low energies is 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.

Recently, the method of polarized orbitals has been applied, by Temkin and Vasavada,[14] to elastic scattering of electrons from H_2^+ molecules. Up to the present time, however, there have been, to our knowledge, no such treatments for other molecules. In the present work, we have employed the variational principle to obtain an adiabatic polarization potential for general use in electron-H_2 scattering. This method is given in Sec. II, and the resulting potentials are discussed in Sec. III. Cross sections for the $j = 0 \rightarrow 2$ rotational excitation of H_2 by electron impact have been calculated using these potentials and are given in Sec. IV for energies less than 20 eV.

II. METHOD

Consider an isolated hydrogen molecule in its ground electronic state, described in the Born-Oppenheimer approximation by a wave function $\psi_0(1, 2) = \psi_0(\vec{r}_1, \vec{r}_2; R)$, where $\vec{r}_1$ and $\vec{r}_2$ indicate center-of-mass coordinates of the bound electrons, and where R denotes the internuclear separation. In the polarization problem, we shall only be concerned with the electronic state of the molecule. The orientation of the nuclear axis is given by $\hat{R}$. For an isolated molecule, we have

$$H_0\psi_0 = (T_0 + V_0)\psi_0 = E_0\psi_0 , \tag{3}$$

where H_0 is the full electronic Hamiltonian, T_0 and V_0 the respective kinetic- and potential-energy contributions, and E_0 the ground-state electronic energy.

We now wish to investigate the wave function and energy of a hydrogen molecule in the field of a third electron situated at $\vec{r}_3$ with respect to the center of mass of the molecule. In the adiabatic approximation, we consider this extra electron to be fixed. Thus, the Hamiltonian for the molecule becomes

$$H = H_0 + V = T_0 + V_0 + V , \tag{4}$$

with
$$V = \frac{1}{r_{13}} + \frac{1}{r_{23}} - \frac{1}{r_{3a}} - \frac{1}{r_{3b}} , \tag{5}$$

where
$$r_{3a} = |\vec{r}_3 + \vec{R}/2| , \quad r_{3b} = |\vec{r}_3 - \vec{R}/2| , \tag{6}$$

(atomic units will be used throughout).
We choose to represent the polarized molecule by a trial wave function of the form

$$\psi(1, 2; 3) = \psi_0(1, 2) \sum_{\alpha=0}^{\alpha_m} \sum_{\beta=0}^{\beta_m} C_{\alpha\beta}(3) x^{\alpha} z^{\beta} , \tag{7}$$

where $x = x_1 + x_2$, $z = z_1 + z_2$, and where the coefficients $C_{\alpha\beta}$, to be determined variationally, will in general depend on $\vec{r}_3$. The indices α and β take on integral values between 0 and α_m, β_m, respectively. From the stationary property of the average energy

$$E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle , \tag{8}$$

we obtain the secular equation

$$\sum_{\alpha, \beta} (H_{\alpha\beta, \alpha'\beta'} - E S_{\alpha\beta, \alpha'\beta'}) C_{\alpha'\beta'} = 0 , \tag{9}$$

where $H_{\alpha\beta, \alpha'\beta'} = \langle \psi_0 | x^{\alpha} z^{\beta} H x^{\alpha'} z^{\beta'} | \psi_0 \rangle$, (10)

and $S_{\alpha\beta, \alpha'\beta'} = \langle \psi_0 | x^{\alpha+\alpha'} z^{\beta+\beta'} | \psi_0 \rangle$.

We may rewrite the secular equation in matrix form as

$$(\underline{H} - E\underline{S})\, \underline{C} = \underline{0} . \tag{11}$$

Thus, once the matrix elements of $\underline{H}$ and $\underline{S}$ are determined, we can find the minimum eigenvalue E_m by a diagonalization of $\underline{S}^{-1}\underline{H}$. This eigenvalue represents an upper limit to the energy of the polarized molecule. The coefficients $\underline{C}_m$, which define the polarized wave function, are then easily determined. We can, if necessary, repeat this procedure for all positions $\vec{r}_3$ of the perturbing electron, and in so doing obtain solutions E_m and $\underline{C}_m$ as functions of $\vec{r}_3$. Since $E_m(\vec{r}_3)$ now represents the total energy of the molecule in the field of an electron at $\vec{r}_3$, we may define a polarization energy by subtracting the unperturbed energy. Thus, we define

$$V_P(\vec{r}_3) = E_m(\vec{r}_3) - E_0 - \langle \psi_0 | V | \psi_0 \rangle , \tag{12}$$

where the last term represents the average interaction energy between the electron and the unperturbed molecule. Because V_P is small in comparison with E, we perform most of the above subtraction algebraically at an early stage in the calculation, rather than numerically at the end.

Let us consider the evaluation of $H_{\alpha\beta, \alpha'\beta'}$; we have

$$\begin{aligned} H_{\alpha\beta, \alpha'\beta'} &= \langle \psi_0 x^{\alpha+\alpha'} z^{\beta+\beta'} | E_0 + V | \psi_0 \rangle \\ &+ \langle \psi_0 | x^{\alpha} z^{\beta} \mathcal{T}_0 x^{\alpha'} z^{\beta'} | \psi_0 \rangle , \end{aligned} \tag{13}$$

where $\mathcal{T}_0$ is defined by

$$\begin{aligned} \mathcal{T}_0 x^{\alpha} z^{\beta} \psi_0 &= \sum_{i=1}^{2} \left[-\tfrac{1}{2} \psi_0 (\nabla_i^2 x^{\alpha} z^{\beta}) - (\nabla_i x^{\alpha} z^{\beta}) \cdot (\nabla_i \psi_0) \right] \\ &= -\psi_0 \left[\alpha(\alpha-1) x^{\alpha-2} z^{\beta} + \beta(\beta-1) x^{\alpha} z^{\beta-2} \right] \\ &- \sum_{i=1}^{2} \left[\alpha x^{\alpha-1} z^{\beta} \frac{\partial \psi_0}{\partial x_i} + \beta x^{\alpha} z^{\beta-1} \frac{\partial \psi_0}{\partial z_i} \right] . \end{aligned} \tag{14}$$

After some manipulation we obtain

$$\begin{aligned} H_{\alpha\beta, \alpha'\beta'} &= \langle \psi_0 | x^{\alpha+\alpha'} z^{\beta+\beta'} (E_0 + V) | \psi_0 \rangle \\ &+ \alpha\alpha' \langle \psi_0 | x^{\alpha+\alpha'-2} z^{\beta+\beta'} | \psi_0 \rangle \\ &+ \beta\beta' \langle \psi_0 | x^{\alpha+\alpha'} z^{\beta+\beta'-2} | \psi_0 \rangle \end{aligned} \tag{15}$$

The interaction potential V may be divided into electron-electron and electron-nucleus parts, viz.,

$$V = V_e + V_n , \tag{16}$$

where $V_e = r_{13}^{-1} + r_{23}^{-1}$ and $V_n = -r_{3a}^{-1} - r_{3b}^{-1}$ Since E_0 and V_n are independent of $\vec{r}_1$ and $\vec{r}_2$ and, hence, unaffected by the variational procedure, we may subtract these terms from the Hamiltonian, i.e., we may subtract $\underline{S}(E_0 + V_n)$ from $\underline{H}$. For large values of $\vec{r}_3$, we may also subtract $2/r_3$ from $\underline{H}$, for reasons which will become clear below. We write V_e as

$$V_e = V_1 + V_2 ,$$

where, for $i = 1, 2$,

$$V_i = \sum_{\lambda=0}^{\infty} \Big[r_i^{\lambda} r_3^{-\lambda-1} \theta(r_3 - r_i) + r_3^{\lambda} r_i^{-\lambda-1} \times \theta(r_i - r_3) \frac{4\pi}{(2\lambda+1)} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}^{*}(\hat{r}_3)\, Y_{\lambda\mu}(\hat{r}_i) \Big] , \tag{17}$$

with
$$\theta(x) = 0, \quad x < 0$$
$$= 1, \quad x \geqslant 0 .$$

We notice that for $r_3 > r_i$ ($i = 1, 2$), the $\lambda = 0$ term dominates, so that $V_e \sim 2r_3^{-1}$ as $r \to \infty$. Similarly $V_n \sim -2r_3^{-1}$ as $r \to \infty$. These Coulomb terms, if not cancelled properly, could lead to inaccuracies in the calculation of the small polarization effects. Therefore, we choose to subtract them at this stage by simply ignoring, for large r_3, the first term in V_e for $\lambda = 0$ and, simultaneously, the corresponding term in V_n.

We have carried out two sets of calculations of the polarization potential $V_P(r_3)$ which differ in the form of the potential V_e. In one case, which we label P, V_e is exactly as given in Eq. (17). In the other, labelled NP, V_e is obtained by ignoring the term in Eq. (17) which corresponds to $r_3 < r_1$ or $r_3 < r_2$. Thus in case NP, we assume that the predominant polarization effects occur exterior to the space occupied by the bound electrons, and we speak of "penetrating" P and "non-penetrating" NP polarization potentials. This is an attempt to take partial account of the nonadiabatic aspects of the problem,[15] and the omission of this term is suggested by the polarized-orbital method.[4] We shall be interested in comparing potentials, and the resulting electron-molecule cross sections, corresponding to these two cases.

The evaluation of the matrix elements $H_{\alpha\beta,\,\alpha'\beta'}$ is straightforward. All elements involve expectation values of terms like $x^{\gamma_x} z^{\gamma_z} V$ and, hence, $x_1^a x_2^b z_1^c z_2^d V$. Using standard expressions for powers of x_1 and z_1 in terms of spherical harmonics (see the Appendix), we may write

$$\langle \psi_0 | x^{\gamma_x} z^{\gamma_z} V | \psi_0 \rangle = \sum_{\rho_x} C(\gamma_x, \rho_x) \sum_{\rho_z} C(\gamma_z, \rho_z) \times \langle \psi_0 | g_1(\gamma - \rho) g_2(\rho)\, V \,|\, \psi_0 \rangle , \tag{18}$$

where $C(\gamma, \rho) = \gamma\,!\,/\rho\,!\,(\gamma - \rho)\,!$, ρ_x and ρ_z take on integral values between 0 and γ_x and γ_z, respectively, and

$$g_i(k) = (-1)^{k_x} (2\pi/3)^{\frac{1}{2}k_x} \sum_{\tau_i} (-1)^{\tau_i} C(k_x, \tau_i) \times A_{k_x - \tau_i} A_{\tau_i} \sum_{\alpha_i} a(k_z, \alpha_i) f_i(k_x, k_z; \alpha_i, \tau_i) . \tag{19}$$

In this expression k_x and k_z take on respective values $\gamma_x - \rho_x$ and $\gamma_z - \rho_z$ for $k = \gamma - \rho$, and ρ_x and ρ_z for $k = \rho$. The parameters τ_i take on integral values between 0 and k_x, and the α_i take on even integral values from 0 to k_z (k_z even) or odd integral values from 1 to k_z (k_z odd). The coefficients A_β and $a(k, \alpha)$ are defined in the appendix and the functions f_i are given by

$$f_i(k_x, k_z; \alpha_i, \tau_i) = r_i^{(k_x + k_z)} Y_{\alpha_i 0}(\hat{r}_i) \times Y_{k_x - \tau_i,\, k_x - \tau_i}(\hat{r}_i) Y_{\tau_i,\, -\tau_i}(\hat{r}_i) , \tag{20}$$

where we recall that $i = 1$ or 2. Thus the problem of determining matrix elements $H_{\alpha\beta,\,\alpha'\beta'}$ reduces to that of calculating average values of one-electron operators using the ground state molecular function ψ_0. If ψ_0 is written as the sum of products of one-electron Slater orbitals, then the matrix elements of $\underline{H}$ involve only one-electron integrals of the form

$$\int \phi_i^{*}(1) x_1^{a} z_1^{b} V_1 \phi_j(1) d\vec{r}_1 . \tag{21}$$

The elements of $\underline{S}$ are of similar form, with V_1 replaced by unity.

In the calculation of the polarization potential, our procedure is to: (1) choose values of r_3 and θ_3 for the coordinates of the external electron (we take $\phi_3 = 0$), (2) decide on the number of terms to be included in the trial wave function of Eq. (7), i.e., the values of α_m and β_m, (3) evaluate all matrix elements and construct $\underline{H}$ and $\underline{S}$, and (4) diagonalize $\underline{S}^{-1}\underline{H}$. The lowest eigenvalue $E_e(\vec{r}_3)$ is representative of the energy of the electron-H$_2$ system relative to that of the unperturbed molecule. We recall that E_0 and V_n were removed from E_m at an early stage of the calculation. Thus, from Eq. (12), we have for the polarization potential,

$$V_P(\vec{r}_3) = E_e(\vec{r}_3) - \langle \psi_0 | V_e | \psi_0 \rangle , \tag{22}$$

where E_e is related to E_m of Eq. (12) by

$$E_e(\vec{r}_3) = E_m(\vec{r}_3) - E_0 - V_n(\vec{r}_3) . \tag{23}$$

III. POLARIZATION POTENTIAL FOR H$_2$

We have chosen to represent the unperturbed ground state of H$_2$ by the one-center 7-term wave function of Joy and Parr.[16] This wave function gives dissociation energy $D = 4.32$ eV and quadrupole moment $Q = 0.60 e a_0^2$, as compared to the more accurate values of Kolos and Wolniewicz,[17] $D = 4.7443$ eV and $Q = 0.490 e a_0^2$. The Joy-Parr function may be written

$$\psi_0 = \sum_{i=1}^{7} c_i \Phi_i(1, 2) , \tag{24}$$

where

$$\Phi_i(1,2)=[2(1+B_i{}^2)]^{-\frac{1}{2}}$$
$$\times[\phi_i(1)\chi_i(2)+\chi_i(1)\phi_i(2)], \quad (25)$$

with $B_i=\langle\Phi_i|\Phi_i\rangle$,

and where each ϕ_i and χ_i is a one-electron Slater orbital of the form

$$\phi=Ar^{n-1}\exp(-\zeta r)Y_{lm}(\hat{r}), \quad (26)$$

with $A = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}$

The coefficients c_i and the n, l, m, and ζ appropriate for each orbital in the 7-term function may be found in the article by Joy and Parr.[16] The integrals (21), for the elements of $\underline{H}$ and $\underline{S}$, may be evaluated in terms of incomplete Γ functions (because n is nonintegral in the orbitals), and integrals over several spherical harmonics (see the Appendix). Since many basic integrals are involved, all calculations are performed by computer.

In Figs. 1 and 2 results for $V_P{}^z(r)$ and $V_P{}^x(r)$, respectively, are presented. The superscripts z and x refer to the respective values $\theta=0$ and $\theta=\pi/2$ for the orientation of the stationary electron with respect to the internuclear axis. For the "penetrating" P and "non-penetrating" NP cases designated in Figs. 1 and 2, the polarization potentials $V_P{}^z$ $(V_P{}^x)$ are obtained over a range of r values by including terms in the trial function (7) consistent with $\alpha_m=0$ and $\beta_m=1$ to 4 ($\beta_m=0$, $\alpha_m=1$ to 4). Since the convergence of $V_P{}^z$ $(V_P{}^x)$ is found to be within 5% in the case P for $r \gtrsim 1.5a_0$, and in case NP for all r, it is unnecessary to include more terms in the trial function (7).

In order to consider the effects of allowing for distortion of the wave function perpendicular to the direction of the stationary electron, the calculations of $V_P{}^z(V_P{}^x)$ are repeated for the NP case with x^2 (z^2) terms also included in the trial function (7) for $\theta=0$ $(\pi/2)$. The resulting polarization potentials are labelled NP^1 in Figs. 1 and 2. The effect of the perpendicular distortion is to further lower the polarization potential. We do not expect the addition of higher-order terms such as x^4 $(\theta=0)$ or z^4 $(\theta=\pi/2)$ to have an appreciable effect. We find, for example, that the NP polarization potentials for $\theta=0$ differ by less than 6% for the two choices of the trial wave function (7) given by $\alpha_m=0$, $\beta_m=2$ and $\alpha_m=0$, $\beta_m=4$; a similar result is found for $\theta=\pi/2$.

The polarization potentials may be represented to within 5% for $r\gtrsim 2.5a_0$, by the expressions

$$V_P{}^z \simeq -[\langle\psi_0|zV|\psi_0\rangle]^2_{\sim} - \alpha'_z - \alpha'_z/2r^4 \;,\; r\to\infty;$$

$$V_P{}^x \simeq -[\langle\psi_0|xV|\psi_0\rangle]^2{}_{\sim} - \alpha'_z - \alpha'_x/2r^4 \;,\; r\to\infty; \quad (27)$$

where $\alpha_z{}'$ and $\alpha_x{}'$ are approximations to the respective polarizabilities, parallel and perpendicular to the internuclear axis of the molecule. Using Joy and Parr's one-center wave function, we obtain

$$\alpha_z{}' = 2[\langle\psi_0|z^2|\psi_0\rangle]^2 = 5.667a_0{}^3,$$
$$\text{and} \quad \alpha_x{}' = 2[\langle\psi_0|x^2|\psi_0\rangle]^2 = 4.486a_0{}^3, \quad (28)$$

These may be compared to the accurate values[17] $\alpha_z=6.38049a_0{}^3$ and $\alpha_x=4.57769a_0{}^3$. Our calculations show that the pure asymptotic forms of Eqs.

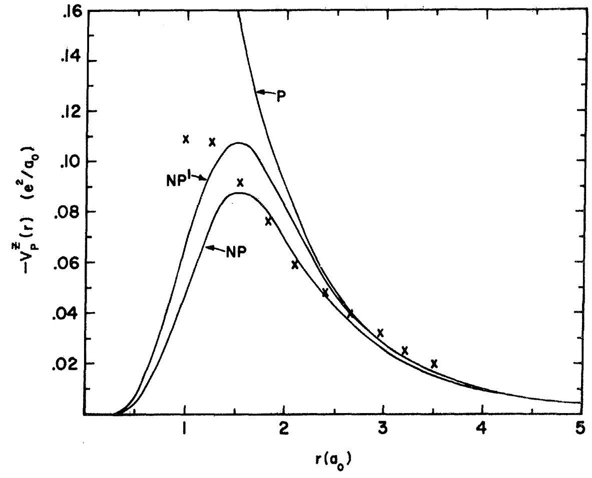

FIG. 1. The polarization potential for $\theta=0$. *Minus* $V_P{}^z(r)$ is plotted versus r for: cases P "penetrating" and NP "nonpenetrating" using a trial function containing only powers of z, and NP^1 "nonpenetrating" using a trial function containing powers of x^2 and z. The points designated by x are those of Adamov, Objedkov, and Evarestov (Ref. 19).

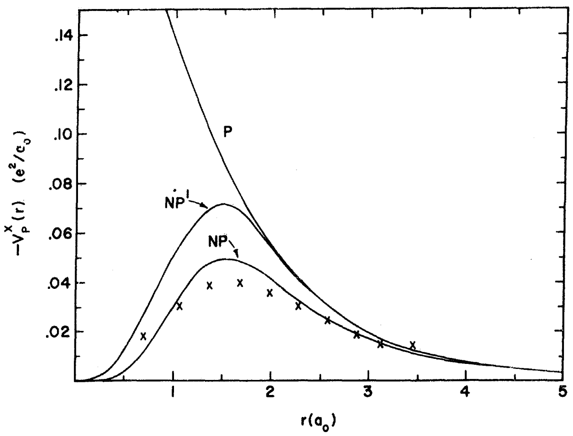

FIG. 2. The polarization potential for $\theta=\pi/2$. *Minus* $V_P{}^x(r)$ is plotted versus r for the cases: P "penetrating" and NP "nonpenetrating" using a trial function containing only powers of x, and NP^1 "non-penetrating" using a trial function containing powers of z^2 and x. The points designated by x are those of Adamov, Objedkov, and Evarestov (Ref. 19).

(27) differ from the calculated polarization potentials by less than 3% for $r > 5a_0$. We note that the choice of trial wave function in Eq. (7) does not lead to appreciable improvement in the polarizabilities. Rather, this particular type of variational function determines polarization potentials which are asymptotically consistent with the approximate polarizabilities of Eqs. (28). Thus, we may scale the potentials in order to obtain the correct asymptotic behavior. Victor *et al.*[18] have shown, in a study of the optical properties of H_2, that terms in the trial function of the form $r_i^n z$ ($r_i^n x$) for $\theta = 0$ ($\pi/2$) are very important to the polarizabilities, yielding values which are in fact somewhat too large and require downward scaling. We do not include these terms in $r_i^n z$ and $r_i^n x$, but rather include nonlinear terms in z and x, which are found to be very important for smaller values of r.

The crosses in Figs. 1 and 2 denote the results of Adamov *et al.*,[19] who represented the polarized molecule by a trial wave function of the form

$$\psi(1,2;3) = \psi_0(1,2) + g(1,2;3),$$

where Weinbaum's function[20] was used for $\psi_0(1,2)$, and first-order perturbation theory was employed to obtain the perturbed part g of the orbital wave function. To first order, the polarization potential may be given by

$$V_p = \langle \psi_0 | V | g \rangle .$$

Adamov *et al.* further assumed that the predominant polarization effects occur exterior to the space occupied by the bound electrons, so their approximation is similar to our NP case. For the polarizabilities they obtained $\alpha_z = 6.5a_0^3$ and $\alpha_x = 4.9a_0^3$.

In low-energy electron-molecule collisions, the long-range part of the polarization potential is particularly important and must be represented as accurately as possible. A comparison of accurate polarizabilities with those appropriate to the Joy and Parr function,[16] suggests that for large values of r, the magnitudes of our potentials V_P^z and V_P^x are too small by factors of 0.82 and 0.93, respectively. Therefore, we would like to adjust our potentials so that they yield accurate polarizabilities. In order to obtain an indication of how the potentials vary with improvement in ψ_0, we repeat calculations of V_P^z and V_P^x for several functions ψ_0. These functions are obtained by ignoring certain orbitals in the Joy and Parr wave function; in the most severe case we ignore the d_0, f_0, and g_0 orbitals. As the wave function is improved, we find that V_P^z and V_P^x, for a wide range of r values, change by approximately the same factors as the respective polarizabilities in the approximation of Eq. (28). Thus, an approximate adjustment of our entire polarization potential may be obtained by scaling V_P^z and V_P^x by factors 1.22 and 1.08, respectively.

In attempting to decide which of the polarization potentials considered might be most representative, we rely to some extent on the polarized-orbital method[4] for electron-atom collisions. An important aspect of this method is the exclusion of the scattered electron from the vicinity of the nucleus, where the adiabatic approximation is invalid because there the electron velocity is not small.[15] Thus, we may expect the potential corresponding to case NP^1 to be superior to that of case P. In addition, we should expect that, for low-energy electrons, where the asymptotic part of the potential is most important, the NPS^1 case (*i.e.*, the case where the NP^1 potential is scaled, so as to have the correct asymptotic behavior) would be the best choice. For larger energies, where short-range features become increasingly important, the simple scaling is probably incorrect.

We find that the angular dependence of $V_P(\vec{r})$ can be well represented by

$$V_p(\vec{r}) = v_p{}^0(r) + v_p{}^2(r) P_2(\cos\theta), \qquad (29)$$

where
$$v_p{}^0(r) = [V_p{}^z(r) + 2V_p{}^x(r)]/3, \qquad (30)$$

and
$$v_p{}^2(r) = 2[V_p{}^z(r) - V_p{}^x(r)]/3. \qquad (31)$$

We checked the above relation by comparing predicted values of $V_P(\vec{r})$ at $\theta = \pi/4$ with a direct calculation at this angle. The agreement is within 5% for $r < 1.5a_0$, and within 1% for $r \gtrsim 1.5a_0$.

We present curves for $v_P{}^0$ and $v_P{}^2$ in Figs. 3 and 4, respectively. The scaled (unscaled) potentials in cases P and NP are denoted by PS (P) and NPS (NP). The curves labelled NP^1 refer to the polarization potentials for the non-penetrating case, where distortion of the trial function is permitted in a direction perpendicular to that of the fixed electron. This extra flexibility in the trial

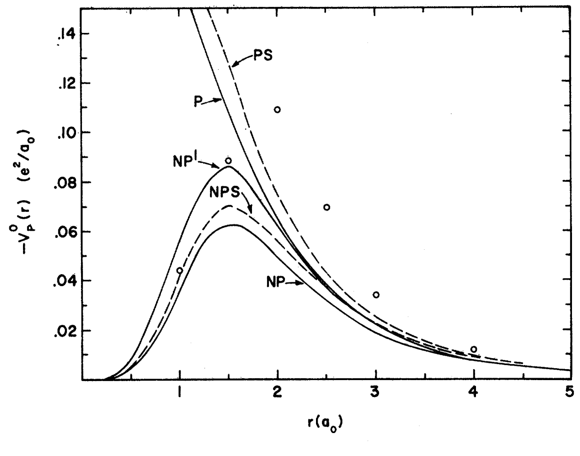

FIG. 3. The spherical part of the polarization potential. *Minus* $V_p{}^0(r)$ is plotted versus r for the cases: P "penetrating" and NP "nonpenetrating" calculated from $V_p{}^z$ and $V_p{}^x$ illustrated in Figs. 1 and 2, NP^1 "nonpenetrating" calculated from the corresponding NP^1 results for $V_p{}^z$ and $V_p{}^x$. The PS and NPS curves result from scaling $V_p{}^z$ and $V_p{}^x$ using accurate polarizabilities. The open circles correspond to the semiempirical potential of Lane and Geltman (Ref. 21).

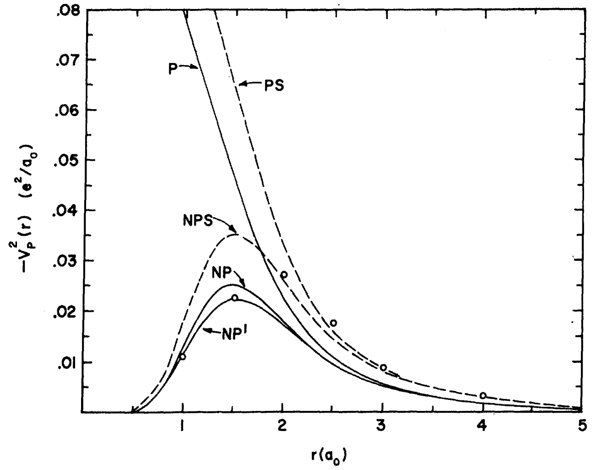

FIG. 4. The anisotropic part of the polarization potential. *Minus* $V_p^2(r)$ is plotted versus r for the cases: P "penetrating" and NP "nonpenetrating" calculated from V_p^z and V_p^x illustrated in Figs. 1 and 2, NP^1 "nonpenetrating" calculated from the corresponding NP^1 results for V_p^z and V_p^x. The PS and NPS curves result from scaling V_p^z and V_p^x using accurate polarizabilities. The open circles correspond to the semiempirical potential of Lane and Geltman (Ref. 21).

function results in a significant lowering of the average polarization potential v_P^0. The anisotropic potential shows a much smaller effect. The circles represent the semiempirical polarization potentials used by Lane and Geltman.[21] They adjusted parameters in their polarization potential so that the calculated total cross sections were in agreement with the measurements of Golden *et al.*[22] at energies above a few electron volts.

IV. ROTATIONAL EXCITATION OF H_2

A meaningful comparison of the various polarization potentials discussed in the previous section can best be made through an illustration of scattering cross sections associated with these potentials. Thus, we have calculated cross sections for the 0→2 rotational excitation of H_2 by electron impact. The method of calculation is based on the formalism of Arthurs and Dalgarno[23] and is described in detail by Lane and Geltman.[21] We solve the set of coupled differential equations (ignoring exchange) and obtain the S-matrix and rotational-excitation cross sections.

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

$$V(\vec{r},\vec{R})=\sum_{\mu} v_{\mu}(r)P_{\mu}(\hat{r}\cdot\hat{R}). \tag{32}$$

We choose the radial potentials given by

$$v_0(r)=v_w^0(r)+v_P^0(r),$$
$$v_2(r)=v_w^2(r)+v_Q^2(r)+v_P^2(r), \tag{33}$$

and $v_4(r)=v_w^4(r)$,

where the short-range terms v_w were determined by Lane and Geltman using the Wang ground-state function.[24] These short-range potential terms are found to be insensitive to the choice of wave function. The quadrupole interaction is represented by

$$v_Q^2(r)=-Qr^{-3}\left[1-e^{-(r/r_0)^6}\right], \tag{34}$$

where Q and r_0 are taken to be $0.49ea_0^2$ and $1.8a_0$, respectively.[17] This choice for r_0 is consistent with the general behavior of the unperturbed electron-molecule potential, corresponding to the Joy and Parr wave function.[16] For the terms v_P, we use the scaled and unscaled polarization potentials, for cases P and NP^1 discussed above. The $\mu=2$ term in Eq. (32) is the dominant anisotropic part of the interaction, and is almost entirely responsible for rotational transitions between levels j and $j\pm2$. The $\mu=0$ term provides most of the average potential field seen by the scattered electrons during the collision. It is important to realize that the unperturbed electron-molecule interaction is much larger than the polarization potential for $r\lesssim1.6a_0$ for $v_0(r)$ or $r\lesssim1.8a_0$ for $v_2(r)$. Thus, the polarization potential is more important for large values of r, where we are most confident of its determination. As an example, the effect of scaling V_P^z and V_P^x in order to ensure their proper asymptotic behavior is never greater than 15% for $v_0(r)$ or 12% for $v_2(r)$.

The rotational-excitation cross sections for the $j=0\to j'=2$ transition in electron collisions with H_2 are given in Fig. 5 for the four choices of the polarization potential discussed above. We also

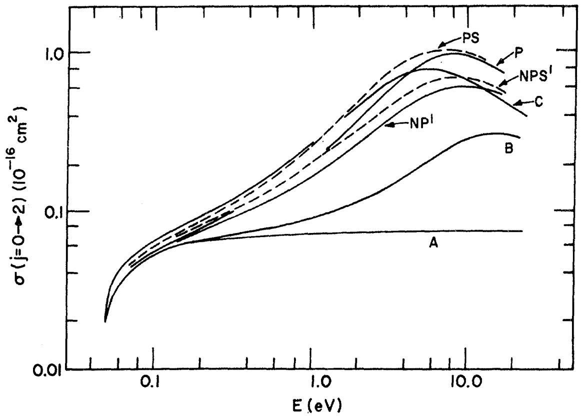

FIG. 5. Rotational-excitation cross sections for the $j=0\to2$ transition in H_2 by electron impact. Curve (A) represents the result of including only the pure quadrupole interaction and employing the Born approximation (Ref. 25). The other curves correspond to including all short-range and quadrupole interactions in the same way; they differ only in the polarization potential. Curves are given for (B) $V_p(r)=0$, (C) the semiempirical potential of Lane and Geltman (Ref. 21), and potentials of cases P, PS, NP^1, and NPS^1.

give, for comparison, cross sections calculated with the following potentials: (A) the quadrupole interaction only (in the Born approximation),[25] (B) the quadrupole and full short-range interactions as described above, but with no polarization included, and (C) the quadrupole, short-range, and semiempirical polarization interactions, used by Lane and Geltman.[21] From Fig. 5, we see that at very low energies the quadrupole interaction is dominant. However, polarization effects become quite important even for energies less than 0.1 eV, and continue to be important throughout the energy range considered here.

In comparing the results obtained with different interaction potentials, we note that, except for energies just above threshold, i.e., $E \leqslant 0.05$ eV, the dominant contribution to the cross sections results from incident and outgoing p-waves. Thus, at low energies, only the asymptotic behavior of the interaction potential is important. Also, rotational excitation arises from the anisotropic part of the potential, i.e., $v_2(r)$. For this radial term, we recall that the potentials considered in the present investigation, differ only in the polarization contribution $v_P{}^2(r)$. From Fig. 4, we see that the same asymptotic behavior is shared by cases P and NP^1 (or PS and NPS^1), and the low-energy cross sections in Fig. 5 reflect this property. At smaller values of r, however, case P (NP) more closely resembles PS (NPS^1), than it does NP^1 (P). These changes in relative behavior of the polarization potentials from large to small values of r are also reflected in the behavior of the cross sections for increasing energies.

Lane and Geltman[21] adjusted their parameterized polarization potential so as to yield satisfactory total cross sections for energies above a few eV, where the p-wave contribution is important. Thus, some averaged effect of exchange was probably included in their potential. The rotational-excitation cross sections corresponding to this semiempirical polarization potential appear to be consistent with recent momentum transfer measurements of Golden *et al.*[22] and McIntosh,[26] for energies around 0.1 eV. Exchange has also been neglected in the present calculation; however, no semiempirical adjustment of the potentials has been made. So, while we expect our polarization potential NPS^1 to be more representative of the system, at least for large values of r, the resulting cross sections may not be better than those of Lane and Geltman.

We find that total cross sections, corresponding to the NPS^1 potential, are 20 to 30% smaller than the experimental values[22] for electron energies above a few eV. This difference is probably due to our neglect of exchange effects. Preliminary results of Ardill and Davison[27] indicate that, at 0.5 eV, inclusion of exchange increases the 0-2 rotational-excitation cross section by about 70% over that calculated without exchange. However, they did not include any polarization effects in their calculation, and since polarization also increases the cross section, the addition of exchange to the present calculations might be expected to increase our results by somewhat less than 70%.

In order to improve upon these theoretical cross sections, it will be necessary to include exchange effects as well as the polarization effects which we have discussed.

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APPENDIX

(a) Parameters $a(k\alpha)$

A convenient representation of $(\cos\theta)^k$ in terms of of spherical harmonics is given by[28]

$$(\cos\theta)^k = \sum_{\alpha=\alpha_0}^{k} a(k,\alpha)\ Y_{\alpha,0}\ (\theta,\phi)$$

where $\alpha_0 = 0$ (k even) or 1 (k odd) and where $k-\alpha$ remains even. The coefficients are given as

$$a(k,0) = \sqrt{4\pi}/(k+1)\ ,\ a(k,1) = 2\ \sqrt{3\pi}/(k+2)\ ,$$

and for $\alpha \geqslant 2$

$$a(k,\alpha) = \frac{2(2\alpha+1)\ \ k(k-1)\cdots(k-\alpha+2)}{(k+\alpha+1)\ (k+\alpha-1)\cdots(k-\alpha+3)}\ \left(\frac{\pi}{2\alpha+1}\right)^{\frac{1}{2}}$$

(b) Parameters A_β

An expression for $(\sin\theta\ \cos\phi)^k$ is readily obtained in terms of spherical harmonics as

$$\begin{aligned}(\sin\theta\ \cos\phi)^k &= (-1)^k\ (2\pi/3)^{k/2}\ [\,Y_{1,1}(\theta,\phi) - Y_{1,-1}(\theta,\phi)\,]^k \\ &= (-1)^k\ (2\pi/3)^{k/2} \sum_{\tau=0}^{k} C(k,\tau)\ (-1)^\tau\,[Y_{1,1}(\theta,\phi)]^{k-\tau}\ [Y_{1,-1}(\theta,\phi)\,]^\tau .\end{aligned}$$

Now, recalling that

$$[\Theta_{1,\pm1}\ (\theta)\,]^\beta = (\mp1)^\beta\ (3/4)^{\beta/2}\ \sin^\beta\theta\ ,$$

and[28]

$$\sin{}^\beta\theta = \frac{2^\beta\beta\,!}{(2\beta)\,!}\ (-1)^\beta P_\beta{}^\beta\,(\cos\ \theta)\ ,$$

we may write

$$[Y_{1,\pm1}\ (\theta,\phi)\,]^\beta = A_\beta Y_{\beta,\pm\beta}\ (\theta,\phi)\ ,$$

where

$$A_\beta = [4\pi\ (3/2\pi)^\beta\ (2\beta+1)\,!\,]^{\frac{1}{2}}\beta\,!$$

(c) Integrals of Products of Spherical Harmonics

The integration of products of several spherical harmonics is easily accomplished by expanding pairs[29]

$$Y_{l_1 m_1}(\theta,\phi)Y_{l_2 m_2}(\theta,\phi) = \sum_L D(l_1,l_2,L;m_1,m_2)Y_{L,m_1+m_2}(\theta,\phi),$$

where L takes on all values such that $|l_1-l_2| \leq L \leq l_1+l_2$ and l_1+l_2+L is even. The coefficients may be given in terms of Clebsch-Gordon coefficients as

$$D(l_1,l_2,L;m_1,m_2)=\left[(2l_1+1)(2l_2+1)/4\pi(2L+1)\right]^{1/2} \times C(l_1,l_2,L;m_1,m_2)C(l_1,l_2,L;0,0).$$

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Variational Bounds in Positron-Atom Scattering

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We have previously applied Dalgarno and Lynn's complete first-order adiabatic correlation function to the problem of low-energy elastic positron scattering by hydrogen and helium atoms. This approach is now extended to yield rigorous lower bounds on the scattering phase shifts in the case of hydrogen and "quasibounds" for helium. In addition, the positron annihilation rate in helium is re-evaluated, and lower values are now found, with the enhancement factor over the Dirac rate varying between 1.5 and 1.8. Some comparisons are made between the present method and other recent work.

I. INTRODUCTION

In two recent papers,[1,2] the problem of low-energy elastic scattering of positrons from simple atoms (hydrogen and helium) has been treated in a modified adiabatic approximation. The method consisted in assuming that the optical potential[3] is well represented by the position-dependent second-order energy shift in the ground state of the target atom due to the electric field of the positron.[4]