PHYSICAL REVIEW A VOLUME 29, NUMBER 5 MAY 1984

Ab initio nonadiabatic polarization potentials for electron-molecule scattering: The e-H_2 system

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(Received 18 July 1983)

We have calculated an *ab initio* nonadiabatic polarization potential for the e-H_2 system using a procedure that is based on the variational method. The importance of various multipole contributions to this potential has been investigated and the dipole approximation found to be accurate for this system. When used in scattering calculations with accurate representations of the static and exchange components of the interaction potential, the new polarization potential is found to yield total integrated e-H_2 cross sections that are in very good agreement with results of recent measurements and of optical-potential calculations.

I. INTRODUCTION

A detailed theoretical investigation of low-energy ($\lesssim 10$ eV) electron-molecule collisions requires an accurate representation of the full projectile-target interaction potential,[1] which consists primarily of static, exchange, and polarization contributions. The dominant short-range static potential can be efficiently generated at the near-Hartree-Fock level of accuracy from the target electronic wave function.[2,3] It is now possible to include exchange effects in an essentially exact fashion[4-7] for reasonably simple systems or to accurately approximate these effects by the use of a model exchange potential.[8,9] This situation has led to considerable recent interest in finding a reliable method for incorporating induced polarization effects.[11-24]

The origin of these effects can be understood in terms of a semiclassical picture. The induced polarization interaction arises from the distortion of the target charge distribution by the time-varying electric field of the projectile. The energy of the distorted molecule is lower than that of the unpolarized target, which leads to an additional attractive term in the potential energy. For homonuclear diatomic molecules, this additional term has the simple asymptotic ($r_e \to \infty$) form

$$V_{\text{pol}}(\vec{r}_e) \sim -\frac{\alpha_0}{2r_e^4} - \frac{\alpha_2 P_2(\cos\theta_e)}{2r_e^4}, \tag{1}$$

where $\vec{r}_e$ is the coordinate of the scattering electron and α_0 and α_2 are the spherical and nonspherical polarizabilities, respectively. However, obtaining an accurate local representation of $V_{\text{pol}}(\vec{r}_e)$ for smaller values of r_e is a difficult theoretical problem.

The principal difficulty in trying to accurately calculate the polarization potential arises from the dynamic (nonadiabatic) aspects of this interaction. In the *adiabatic approximation*[10,11,25,26] to $V_{\text{pol}}(\vec{r}_e)$, the molecular charge density is allowed to relax in the electric field of a scattering electron fixed at $\vec{r}_e$. However, once the target orbitals can no longer immediately readjust to the instantaneous position of the projectile, nonadiabatic effects become important and must somehow be taken into account.[27-35]

In the past, polarization effects have often been represented by a semiempirical approximation based on the known asymptotic form of the potential[1] in Eq. (1), viz.,

$$V_{\text{pol}}(\vec{r}_e) = C(r_e)\left[-\frac{\alpha_0}{2r_e^4} - \frac{\alpha_2 P_2(\cos\theta_e)}{2r_e^4}\right], \tag{2}$$

where the spherical cutoff function $C(r_e)$ is usually written as

$$C(r_e) = 1 - \exp[-(r_e/r_c)^6] . \tag{3}$$

This form approximates nonadiabatic effects by smoothly cutting off the polarization interaction for $r_e \lesssim r_c$. The cutoff radius r_c is an adjustable parameter which can be "tuned"[36] to bring calculated cross sections into agreement with some experimentally determined feature of the scattering (e.g., a shape resonance).[37]

Some of the inaccuracies associated with this treatment have been demonstrated by Morrison and Hay[10] and by Truhlar *et al.*[11] These studies used molecular structure codes to calculate accurate *ab initio* (though fully adiabatic) polarization potentials; for intermediate values of $r_e (r_e > r_c)$, the semiempirical form (2) was found to provide an inadequate representation of the adiabatic polarization potential.

Rigorously, induced polarization effects are a manifestation of virtual electronic excitation of the target.[25] Thus, in an eigenfunction expansion formulation,[1] inclusion of all energetically closed channels provides a complete description of polarization. Within this quantum-mechanical context two different approaches to the problem of dealing with nonadiabatic effects have been introduced. The first strategy attempts to correct the *adiabatic* polarization potential. Usually, nonadiabatic contributions are included by calculating a correction term directly[20] or by modifying the scattering-bound electron interaction[31] in such a way that nonadiabatic behavior will be incorporated in an otherwise adiabatic treatment. Such a modification was used by Lane and Henry[32] and by Hara[33] to generate approximate nonadiabatic polarization potentials for use in low-energy e-H_2 scattering calculations.[38,39] However, in order to obtain the correct asymptotic behavior, Eq. (1), both of the resulting potentials had to be scaled. This scaling introduced some uncertainty[1] into $V_{\text{pol}}(\vec{r}_e)$ for small and intermediate values of r_e. Recently, this strategy has been used by Jain and Thompson[40] to produce cross sections for e-CH_4 and e-H_2O collisions.

In the second approach, closed channels are included in a more direct fashion.[27,28] This is usually accomplished via a *pseudostate expansion*[41] or by defining a suitable *optical potential.*[16] Low-energy e-H_2 scattering results have been reported by Schneider[12] and by Klonover and Kaldor[13] in which nonadiabatic polarization effects were included at various levels of approximation. In these studies, Schneider utilized a pseudostate approach and Klonover and Kaldor incorporated an optical potential calculated to second order in a diagrammatic perturbation series. More recently Takatsuka and McKoy[14] as well as Berman and Kaldor[15] have developed schemes for extending the Schwinger-variational method[5] beyond the static-exchange approximation; electron-molecule scattering calculations utilizing these methods are underway. Schneider and Collins[16] have reported e-H_2 scattering results in which an approximation to the optical potential is used to represent nonadiabatic polarization in the linear-algebraic method.[7] Subsequently,[17] these authors performed more complete calculations on the e-H_2 system and produced e-N_2 results. For intermediate collision energies ($10\ \text{eV} < E < 100\ \text{eV}$), Truhlar and co-workers[42] have investigated several methods for including polarization effects.

As part of a long-term theoretical study of near-threshold e-H_2 scattering, we have calculated a new *ab initio* (parameter-free) polarization potential for this system.[18] The theoretical treatment of polarization in the present work, which is sketched in Sec. II, is formally similar to that of Lane and Henry[32] and of Hara,[33] in that it is based on the variational method and incorporates nonadiabatic effects approximately via a method that derives from the polarized-orbital theory of Temkin.[31] However, we have based our calculations on a modified molecular-structure code and have used a sufficiently flexible basis set that it was not necessary to scale the polarization potential in order to obtain quantitatively correct asymptotic behavior. The resulting potential is therefore free of the ambiguity that plagued earlier studies. We have also avoided the additional approximations of perturbation theory, which was used by Hara.[33]

In Sec. III we describe the numerical procedures that we used to calculate the polarization potentials that are presented in Sec. IV. In the latter section, the importance of various multipole contributions to this potential is discussed and cross sections from new scattering calculations are examined. Our conclusions are given in Sec. V. Unless otherwise stated, atomic units[43] are used throughout.

II. THEORY

A. Variational determination of the adiabatic polarization potential

The polarization potential is defined as the change in the total energy of the electron-molecule system due to distortion of the probability density of the target electrons. In the present formulation, this quantity is determined as the difference between two energy-optimized variational functionals of an adiabatic electron-molecule Hamiltonian (with the scattering electron fixed in space), the two functionals corresponding to polarized and unpolarized target electronic wave functions, respectively. Nonadiabatic effects are incorporated approximately by modifying certain integrals[31] that appear when a basis set is used to evaluate these functionals (see Sec. III).

In these molecular-structure calculations, a body-fixed reference frame is used,[1,33] with the origin at the center of mass of the molecule and the z axis coincident with the internuclear axis. The spatial coordinates of the molecular electrons, nuclei, and scattering electron in this reference frame will be denoted by $\vec{r}_m$, $\vec{R}_\alpha$, and $\vec{r}_e$, respectively. (Since the present application is to a closed-shell target, we need not explicitly deal with spin coordinates.[1]) The Born-Oppenheimer separation of electronic and nuclear motion is implemented for both the unpolarized and polarized target states; in the present study we are concerned solely with the ground states, which will be connoted by a zero subscript.

Within this theoretical context, the adiabatic Hamiltonian, which describes the system with the scattering electron fixed at $\vec{r}_e$, is simply

$$\hat{\mathscr{H}}^A(\vec{r}_m;\vec{r}_e,R)=\hat{\mathscr{H}}_m^{(e)}(\vec{r}_m;R)+V_{em}(\vec{r}_m;\vec{r}_e,R)\ , \tag{4}$$

where $\hat{\mathscr{H}}_m^{(e)}$ is the electronic Hamiltonian of the molecule and V_{em} is the electron-molecule interaction potential energy. This term arises from electrostatic (Coulomb) interactions and is the sum of electron-electron terms, $V_{em}^{(e)}$, and electron-nuclei terms, $V_{em}^{(n)}$, viz.,

$$V_{em}(\vec{r}_m;\vec{r}_e,R)=\sum_{i=1}^{N_e}\frac{1}{|\vec{r}_e-\vec{r}_i|}-\sum_{\alpha=1}^{N_n}\frac{Z_\alpha}{|\vec{r}_e-\vec{R}_\alpha|}\ . \tag{5}$$

In (5), N_e and N_n are the numbers of electrons and nuclei in the target; R is the internuclear separation, which is held fixed throughout the determination of the polarization potential,[44] and Z_α is the charge of the nucleus at position $\vec{R}_\alpha$.

To calculate the polarization potential we require the average energy of the *polarized* wave function of the target $\psi_0^{(p)}(\vec{r}_m;\vec{r}_e,R)$, i.e.,

$$E_0^{(p)}(\vec{r}_e,R)=\langle\psi_0^{(p)}(\vec{r}_m;\vec{r}_e,R)\,|\,\hat{\mathscr{H}}^A\,|\,\psi_0^{(p)}(\vec{r}_m;\vec{r}_e,R)\rangle\ . \tag{6}$$

This quantity is lower than the corresponding quantity in the "frozen-core approximation," in which no distortion of the target electronic wave function is allowed. The energy of the electron-molecule system in this approximation is

$$E_0(\vec{r}_e,R)=\langle\psi_0(\vec{r}_m;R)\,|\,\hat{\mathscr{H}}^A\,|\,\psi_0(\vec{r}_m;R)\rangle\ , \tag{7}$$

where $\psi_0(\vec{r}_m;R)$ is the electronic wave function of the undistorted target. The difference between these quantities is the adiabatic polarization potential

$$V_{\text{pol}}^A(\vec{r}_e,R)=E_0^{(p)}(\vec{r}_e,R)-E_0(\vec{r}_e,R)\ . \tag{8}$$

A useful alternative form for this potential can be obtained by noting that $E_0(\vec{r}_e,R)$ is just the sum of the Born-Oppenheimer electronic energy of the target

$$\mathscr{E}_0^{(e)}(R)=\langle \psi_0(\vec{r}_m;R)\,|\,\hat{\mathscr{H}}_m^{(e)}\,|\,\psi_0(\vec{r}_m;R)\rangle \ , \tag{9}$$

and the static electron-molecule interaction potential[3] $V_{st}(\vec{r}_e,R)$, viz.,

$$V_{\rm pol}^{A}(\vec{r}_e,R)=E_0^{(p)}(\vec{r}_e,R)-\mathscr{E}_0^{(e)}(R) -\langle \psi_0(\vec{r}_m;R)\,|\,V_{em}\,|\,\psi_0(\vec{r}_m;R)\rangle \ . \tag{10}$$

To see how nonadiabatic corrections are introduced in this theory, it is necessary to look briefly at the detailed structure of the variational functionals $E_0^{(p)}$ and E_0. These quantities are energy optimized using restricted-Hartree-Fock theory.[45] Thus, the polarized and unpolarized wave functions, $\psi_0^{(p)}$ and ψ_0, are represented by single Slater determinants of spin orbitals. For H_2, the spatial parts of these spin orbitals will be denoted by $\varphi_{1\sigma_g}(\vec{r})$ (for the neutral wave function) and $\varphi_1^{(p)}(\vec{r};\vec{r}_e)$ (for the polarized wave function).

Each of these molecular orbitals is variationally determined as an approximate eigenfunction of the appropriate Fock operator. Thus, $\varphi_{1\sigma_g}(\vec{r})$ is an approximate eigenfunction of the Hartree-Fock Hamiltonian[46]

$$\hat{\mathscr{H}}_{\rm HF}=\hat{\mathscr{H}}_0+\hat{J} \ , \tag{11}$$

where $\hat{\mathscr{H}}_0$ is the one-electron Hamiltonian

$$\hat{\mathscr{H}}_0=-\tfrac{1}{2}\nabla^2-\sum_{\alpha=1}^{2}\frac{1}{|\vec{r}-\vec{R}_\alpha|} \tag{12}$$

and $\hat{J}$ is the Coulomb operator

$$\hat{J}\varphi_{1\sigma_g}(\vec{r})=\left\langle \varphi_{1\sigma_g}(\vec{r}\,')\left|\frac{1}{|\vec{r}-\vec{r}\,'|}\right|\varphi_{1\sigma_g}(\vec{r}\,')\right\rangle \varphi_{1\sigma_g}(\vec{r}) \ . \tag{13}$$

In terms of the molecular orbital $\varphi_{1\sigma_g}(\vec{r})$, the quantities required to evaluate the frozen-core energy $E_0(\vec{r}_e,R)$ of (7) are

$$\mathscr{E}_0^{(e)}(R)=2\langle \varphi_{1\sigma_g}\,|\,\hat{\mathscr{H}}_0\,|\,\varphi_{1\sigma_g}\rangle+\langle \varphi_{1\sigma_g}\,|\,\hat{J}\,|\,\varphi_{1\sigma_g}\rangle+\frac{1}{R} \ , \tag{14}$$

where for convenience we have included the potential energy of nuclear repulsion with the Born-Oppenheimer electronic energy and

$$V_{st}(\vec{r}_e,R)=V_{em}^{(n)}(\vec{r}_e,R)+2\left\langle \varphi_{1\sigma_g}\left|\frac{1}{|\vec{r}_e-\vec{r}|}\right|\varphi_{1\sigma_g}\right\rangle \ . \tag{15}$$

The second term in (15) will assume considerable importance once a basis set is introduced, as will its counterpart for the polarized energy $E_0^{(p)}$.

The latter functional is constructed from the polarized orbital $\varphi_1^{(p)}(\vec{r};\vec{r}_e)$, which is an approximate eigenfunction of the adiabatic electron-molecule Hartree-Fock Hamiltonian

$$\hat{\mathscr{H}}_{\rm HF}^{A}=\hat{\mathscr{H}}_0+\frac{1}{|\vec{r}-\vec{r}_e|}+\hat{J} \ . \tag{16}$$

The resulting system energy (6) becomes

$$E_0^{(p)}(\vec{r}_e,R)=2\left\langle \varphi_1^{(p)}\left|\left[\hat{\mathscr{H}}_0+\frac{1}{|\vec{r}-\vec{r}_e|}\right]\right|\varphi_1^{(p)}\right\rangle +\langle \varphi_1^{(p)}\,|\,\hat{J}\,|\,\varphi_1^{(p)}\rangle+V_{em}^{(n)}(\vec{r}_e,R)+\frac{1}{R} \ . \tag{17}$$

In the analytic Hartree-Fock theory,[45] the variational functionals E_0 and $E_0^{(p)}$ are evaluated by expanding the molecular orbitals in a basis set, $\{\eta_i(\vec{r}), i=1,2,\ldots,M\}$. In the present theory, both the polarized and unpolarized orbitals are expanded in the same basis set, which, in the present application, consists of nucleus-centered Cartesian Gaussians $\eta_i(\vec{r})$ (see Sec. III); for example,

$$\varphi_1^{(p)}(\vec{r};\vec{r}_e,R)=\sum_{i=1}^{M}\eta_i(\vec{r})c_i^{(p)}(\vec{r}_e,R) \ , \tag{18}$$

where the linear variational parameters $c_i^{(p)}(\vec{r}_e,R)$ are chosen to minimize

$$E_0^{(p)}(\vec{r}_e,R)=2\sum_{s,t}c_s^{(p)*}c_t^{(p)}\left[\langle \eta_s\,|\,\hat{\mathscr{H}}_0\,|\,\eta_t\rangle+\left\langle \eta_s\left|\frac{1}{|\vec{r}-\vec{r}_e|}\right|\eta_t\right\rangle\right] +V_{em}^{(n)}(\vec{r}_e,R)+\frac{1}{R}+J_{1,1}^{(p)}(\vec{r}_e,R) \tag{19}$$

for fixed $\vec{r}_e$ and R. The last term in (19) is just the matrix element of $\hat{J}$ with respect to $\varphi_1^{(p)}$ evaluated with the expansion (18). A similar expansion is made for $\varphi_{1\sigma_g}(\vec{r})$—with the important exception that the variational parameters $\{c_i(R)\}$ do not depend on $\vec{r}_e$—and is used to minimize the "frozen-core" system energy

$$E_0(\vec{r}_e,R)=2\sum_{s,t}c_s^{*}c_t\left[\langle \eta_s\,|\,\hat{\mathscr{H}}_0\,|\,\eta_t\rangle+\left\langle \eta_s\left|\frac{1}{|\vec{r}-\vec{r}_e|}\right|\eta_t\right\rangle\right] +V_{em}^{(n)}(\vec{r}_e,R)+\frac{1}{R}+J_{1\sigma_g,1\sigma_g}(R) \ . \tag{20}$$

B. Nonpenetrating approximation

Adiabatic electron-molecule polarization potentials have been studied by Truhlar and co-workers[11] and by Morrison and Hay.[10] These potentials represent an improvement over the semiempirical adiabatic form (2) since they accurately represent the effects of polarization in the important "intermediate" range of r_e values [large enough that the adiabatic approximation is still viable (a few times the mean radius of the molecular electron cloud) yet smaller than asymptotic values, where the polarization potential has settled down to its long-range form (1)]. This region may be quite large (as in the e-CO_2 system[10]) and may exert a significant influence on the collision (e.g., at all but near-threshold scattering energies), and the deviation in this region of the adiabatic-potential V_{pol}^{A} from the long-range form (1) may be quite substantial.

Nevertheless, these adiabatic potentials, like their counterparts for electron-atom systems,[25–28] are much too strong near the target. This overestimation of the true effects of polarization arises from the breakdown of the adiabatic approximation that occurs when the "local velocity" of the scattering electron becomes comparable to that of the molecular electrons; even for low-energy collisions this will occur as the electron nears the nuclei. The quantum-mechanical theory behind this semiclassical picture of nonadiabatic polarization has been investigated for electron-atom collisions[30] and shown to lead to an (approximate) r_e^{-6} term that weakens the adiabatic potential for nonasymptotic values of r_e. An additional difficulty with the adiabatic theory of Sec. II A arises for values of r_e within the target charge cloud, because formally the scattering electron is indistinguishable from the molecular electrons. (This fact leads to nonlocal exchange-polarization terms[47] in the scattering equations; these terms are not incorporated in the theory of this study.)

A variety of strategies have been proposed to deal with nonadiabatic effects; many of these have been implemented for electron-atom scattering.[29–31] The procedure we have chosen originated in the polarized-orbital theory of electron-atom scattering by Temkin;[31] it has been successfully used to study a variety of electron-atom systems.[31,48] In this "nonpenetrating approximation," the Coulomb interaction between the scattering and molecular electrons is "turned off" whenever the former is within the target charge cloud.

This modification entails altering the matrix elements $\langle \eta_s | (1/|\vec{r}-\vec{r}_e|) | \eta_t \rangle$ that occur in Eqs. (19) and (20). Specifically, the standard multipole expansion of $1/|\vec{r}-\vec{r}_e|$,

$$\frac{1}{|\vec{r}-\vec{r}_e|}=\sum_{\lambda=0}^{\infty}\frac{\zeta_<^{\lambda}}{\zeta_>^{\lambda+1}}P_\lambda(\cos\Theta)\ , \tag{21}$$

where Θ is the angle between $\vec{r}$ and $\vec{r}_e$ and $\zeta_<$ ($\zeta_>$) is the maximum (minimum) of r_e and r, is cut off whenever r, the variable of integration in these matrix elements, is larger than r_e. Letting $\delta(r<r_e)$ denote a step function that is 0 for $r>r_e$ and 1 for $r<r_e$, we can write the nonpenetrating matrix element as

$$\left\langle \eta_s \left| \frac{1}{|\vec{r}-\vec{r}_e|} \right| \eta_t \right\rangle = \sum_{\lambda=0}^{\infty} \left\langle \eta_s \left| \frac{\zeta_<^{\lambda}}{\zeta_>^{\lambda+1}}\delta(r<r_e)P_\lambda(\cos\Theta) \right| \eta_t \right\rangle . \tag{22}$$

To complete the evaluation of this matrix element, we merely express $P_\lambda(\cos\Theta)$ in terms of spherical harmonics of $\hat{r}$ and $\hat{r}_e$, expand the basis functions as, for example,

$$\eta_s(\vec{r})=\frac{1}{r}\sum_{l,m}a_{lm}^{(s)}(r)Y_l^m(\hat{r})\ , \tag{23}$$

and use the integral formula for three spherical harmonics[49] to obtain

$$\begin{aligned}\left\langle \eta_s \left| \frac{1}{\vec{r}-\vec{r}_e|} \right| \eta_t \right\rangle = {}& \sum_{\lambda}\sum_{l,m}\sum_{l',m'}(-1)^{m'}\left[\frac{4\pi(2l+1)(2l'+1)}{2\lambda+1}\right]^{1/2} Y_\lambda^{m'-m}(\hat{r}_e)\\ &\otimes \begin{bmatrix} \lambda & l & l' \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \lambda & l & l' \\ m-m' & -m & m' \end{bmatrix} \frac{1}{r_e^{\lambda+1}}\int_0^{r_e}[a_{lm}^{(s)}(r)]^{*}a_{l'm'}^{(t)}(r)r^{\lambda}dr\ .\end{aligned} \tag{24}$$

The expansion coefficients in (23) can be evaluated analytically using properties of Cartesian Gaussians.[50] The radial integrals in (24) are evaluated numerically.

The monopole term ($\lambda=0$) in (22) and (24), if retained, gives rise to a polarization potential that is far too strong at small and intermediate radial distances (see Figs. 1 and 2). Outside the target charge cloud this term, $+2/r_e$, is exactly canceled in the polarized and unpolarized energies (19) and (17) by the $-2/r_e$ monopole term in the expansion of the electron-nucleus potential energy. The fact that this cancellation does not obtain for $r_e<(\frac{1}{2}R,r_1,r_2)$ leads to an unphysical discontinuity in the polarization potential. Consequently, we drop the monopole term from (24) leaving the sum over λ to run from 1 to ∞.

A further approximation that has been widely used is the *dipole approximation*[35,51] in which all terms in the sum over λ in (22) and (24) are omitted except $\lambda=1$. This approximation will be examined in the results of Sec. IV.

C. Scattering theory

In order to assess the accuracy of our approximate polarization potential we have calculated cross sections for low-energy e-H_2 scattering. To facilitate comparison with results from a variety of other theoretical studies, we chose to evaluate total integrated cross sections (summed over final rotational-state quantum number) in the *rigid-rotator approximation* with the internuclear separation of H_2 fixed at its equilibrium value $1.4a_0$.

Within the rigid-rotator approximation the fixed-nuclei formulation was used in a body-fixed reference frame.[1,44] Single-center coordinates were used for the particles in the

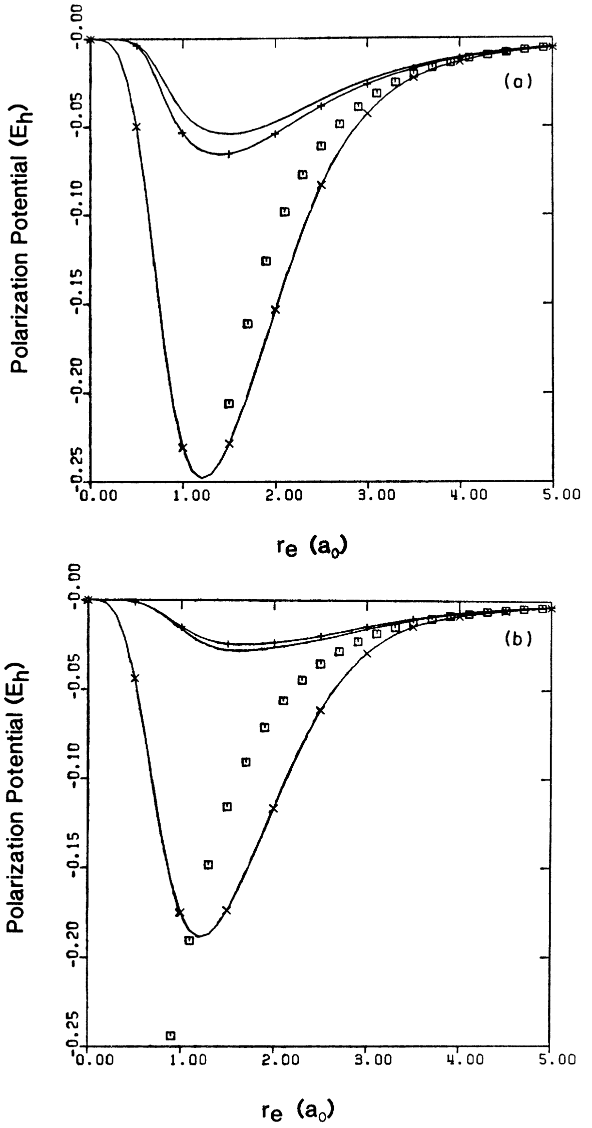

FIG. 1. Polarization potentials for the e-H_2 system for an external electron *fixed* at position r_e on (a), the $\hat{z}$ axis ($\theta_e = 0$) or on (b), the $\hat{x}$ axis ($\theta_e = \pi/2$). In addition to a fully adiabatic potential (squares), three nonpenetrating nonadiabatic potentials are shown: potential A (crosses) contains all multipoles in Eq. (24) required for convergence, potential D (pluses) *excludes* the monopole term from potential A, and potential B (solid curve) is the dipole approximation, i.e., only $\lambda = 1$ is retained in Eq. (22).

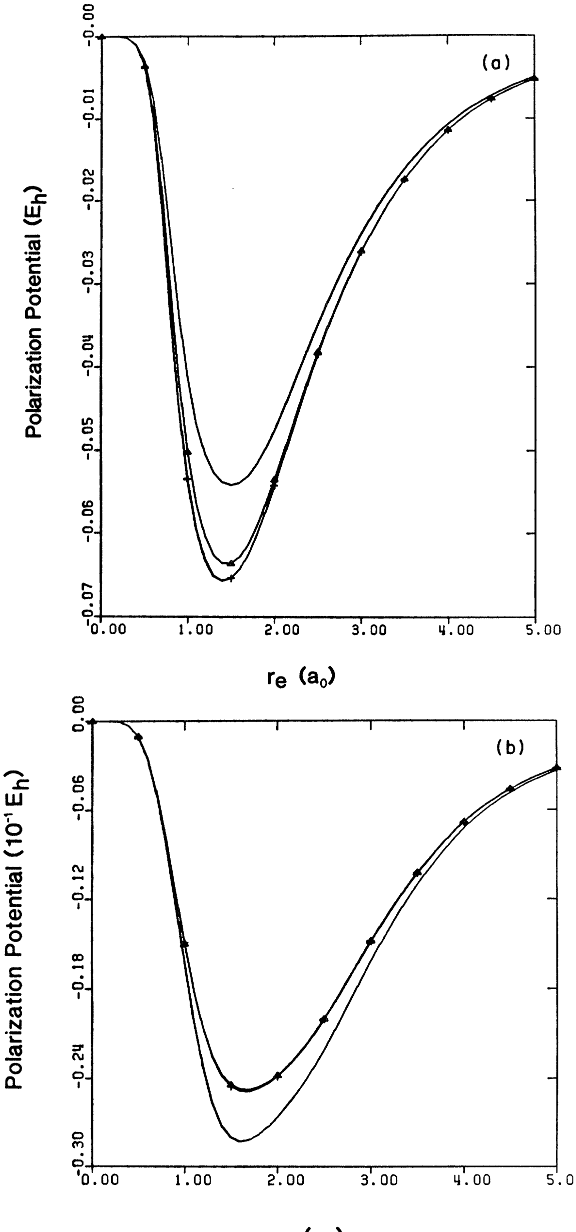

FIG. 2. Nonpenetrating polarization potentials for the e-H_2 system for an external electron *fixed* at position r_e on (a), the $\hat{z}$ axis ($\theta_e = 0$) or on (b), the $\hat{x}$ axis ($\theta_e = \pi/2$). All potentials exclude the monopole term in Eq. (22); potentials B (solid curve), C (triangles), and D (pluses) correspond to $\lambda_{\max} = 1$, 3, and 23, respectively.

system and coupled radial differential scattering equations obtained via a partial-wave expansion in an angular basis of spherical harmonics. We do not allow for real or virtual electronic excitation and therefore consider scattering from the ground state of H_2. This formulation has been widely discussed and reviewed elsewhere.[1,52]

III. COMPUTATIONAL PROCEDURES

A. Basis set

The first step in determining a polarization potential for the e-H_2 system is the choice of an appropriate set of basis functions for calculation of the electronic wave functions of the undistorted and distorted ground states of the target. We start with a [$5s2p/3s2p$] set of contracted, nucleus-centered Cartesian Gaussian basis functions; the exponents and contraction coefficients for this basis are taken from the work of Huzinaga.[53] To introduce sufficient flexibility in the basis to accommodate the polarization distortion of H_2, we include additional diffuse s- and p-type functions. These functions make important contri-

TABLE I. Exponents and contraction coefficients for the nucleus-centered $[6s3p/4s3p]$ Gaussian basis set for H_2.

Type of function	Exponent	Contraction coefficient
s	33.644 400	0.025 374
s	5.057 960	0.189 683
s	1.146 800	0.852 93
s	0.321 144	1.0
s	0.101 309	1.0
s	0.030 000	1.0
p[a]	1.114 200	1.0
p[a]	0.259 200	1.0
p[a]	0.060 000	1.0

[a] Each p-type function represents a set consisting of p_x, p_y, and p_z Gaussians.

TABLE II. Calculated values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ (in a_0^3) for various values of r_e and R. The values of $\alpha_{\perp}$ are listed in parentheses below the corresponding values of $\alpha_{\parallel}$. The column labeled CI contains the configuration-interaction results of Rychlewski (Ref. 56).

	$r_e(a_0)$				
$R(a_0)$	10.0	15.0	20.0	30.0	CI
1.2	5.266	5.212	5.189	5.171	5.152
	(3.851)	(3.865)	(3.867)	(3.867)	(3.947)
1.4	6.635	6.558	6.525	6.499	6.387
	(4.512)	(4.534)	(4.539)	(4.541)	(4.579)
1.8	10.172	10.022	9.957	9.906	9.332
	(5.955)	(6.002)	(6.014)	(6.020)	(5.879)

butions to the polarizability of the target. We have found that for the e-H_2 system a single set of these diffuse functions is sufficient to determine accurate polarizabilities. The exponents and contraction coefficients for the resulting augmented $[6s3p/4s3p]$ basis are given in Table I.

One indicator of the quality of a basis set is the electronic energy of the (isolated) target $\mathscr{E}_0^{(e)}$ of Eq. (9). At the equilibrium internuclear separation, $R=1.4a_0$, the basis of Table I gives an electronic energy of $-1.132\,95E_h$. The Hartree-Fock limit of this energy as calculated by Kolos and Roothan[54] is $-1.133\,63E_h$ and the accurate configuration-interaction (CI) value of Kolos and Wolneiwicz[55] is $-1.174\,47E_h$.

A better indicator of the suitability of a given basis for the calculation of polarization potentials is the polarizability tensor of the target. For a diatomic molecule this quantity is fully specified by the parallel and perpendicular polarizabilities, $\alpha_{\parallel}$ and $\alpha_{\perp}$. In the present computational scheme these quantities are easily calculated once the variational coefficients of the *isolated* molecule have been determined. If these coefficients are used to initialize a self-consistent-field (SCF) calculation[45] for the electron-molecule system, the first iterate of the SCF energy is just the unpolarized-system energy E_0 of Eq. (20) and the final iterate is $E_0^{(p)}$ of Eq. (17), from which the polarization potential and thence the polarizabilities can easily be calculated [cf. Eq. (10)]. Specifically, by positioning the (fixed) scattering electron on the $\hat{x}$ or $\hat{z}$ axes at a distance far from the target (e.g., $r_e \simeq 10.0a_0$), we can calculate "asymptotic" polarization potentials for these special cases. From these potentials the polarizabilities can then be determined as

$$\alpha_{\parallel}=-2V_{\mathrm{pol}}^{A}(z_e,R)z_e^4\ , \tag{25}$$

$$\alpha_{\perp}=-2V_{\mathrm{pol}}^{A}(x_e,R)x_e^4\ . \tag{26}$$

Table II contains the polarizabilities for our $[6s3p/4s3p]$ basis for various values of r_e and R; for comparison the CI values of Rychlewski[56] are also shown. Owing to the nonuniformity of the electric field established by the scattering electron, the calculated polarizabilities will, in general, depend on r_e. However, this field becomes more nearly uniform the farther from the target the scattering electron is located. Hence as r_e increases, the polarizabilities approach their true asymptotic values. For H_2 this occurs by $r_e=10.0a_0$.

B. Polarization potential

Nonadiabatic polarization potentials for e-H_2 scattering were calculated using programs based on the POLYATOM package of computer codes.[57] This package carries out SCF (linear-variational) molecular-structure calculations using basis sets consisting of nucleus-centered Cartesian Gaussians. The modifications required to introduce nonadiabatic effects via the nonpenetrating approximation discussed in Sec. II B entailed altering the subroutines that calculate the electron-electron interaction matrix elements $\langle \eta_s \,|\, (1/|\vec{r}-\vec{r}_e|) \,|\, \eta_t \rangle$ for scattering-electron—bound-electron pairs.[58] The original POLYATOM integral routines for these matrix elements were replaced by ones that evaluate these integrals in the approximation defined by Eq. (22) and given in detail by Eq. (24). The necessary numerical integration over the radial electron coordinate in this equation was performed using a fixed-step-size trapezoidal quadrature scheme. Operationally, once the internuclear separation R is chosen, polarization potentials are calculated as the difference between the converged SCF electronic energies for the polarized and unpolarized systems, both of which are determined with the modified elements in the Hamiltonian matrix. The resulting nonadiabatic polarization potential will be denoted $V_{\mathrm{pol}}^{\mathrm{NP}}(\vec{r}_e,R)$.

To evaluate the coupling matrix elements that appear in the scattering equations that must be solved in order to determine cross sections (in the single-center formalism of Sec. II C), we require the projections of $V_{\mathrm{pol}}^{NP}(\vec{r}_e,R)$ on the set of Legendre polynomials.[3] These quantities

$$v_{\lambda}^{(\mathrm{pol})}(r_e,R)=\frac{2\lambda+1}{2}\int_0^{\pi} V_{\mathrm{pol}}^{\mathrm{NP}}(\vec{r}_e,R)P_{\lambda}(\cos\theta_e)\,d(\cos\theta_e) \tag{27}$$

are easily calculated (by Gaussian quadrature) for a given radial coordinate r_e from the values of $V_{\mathrm{pol}}^{\mathrm{NP}}(\vec{r}_e,R)$ over a mesh of angles θ_e. Since the evaluation of the polarization potential is rather time consuming, it is desirable to use the smallest number of angles and radial values possible.

If the polarization potential is sufficiently weakly nonspherical that a two-term expansion affords a good representation, i.e., if

$$V^{\mathrm{NP}}_{\mathrm{pol}}(\vec{r}_e,R) \simeq v_0^{(\mathrm{pol})}(r_e,R)+v_2^{(\mathrm{pol})}(r_e,R)P_2(\cos\theta_e) \qquad (28)$$

to a good approximation, then the required expansion coefficients $v_\lambda^{(\mathrm{pol})}(r_e,R)$ can be determined from values of $V^{\mathrm{NP}}_{\mathrm{pol}}(\vec{r}_e,R)$ at only two angles, $\theta_e=0$ and $\pi/2$, viz.,

$$v_0^{(\mathrm{pol})}(r_e,R)=\tfrac{1}{3}[2V^{\mathrm{NP}}_{\mathrm{pol}}(x_e,R)+V^{\mathrm{NP}}_{\mathrm{pol}}(z_e,R)]\ , \qquad (29\mathrm{a})$$

$$v_2^{(\mathrm{pol})}(r_e,R)=\tfrac{2}{3}[V^{\mathrm{NP}}_{\mathrm{pol}}(z_e,R)-V^{\mathrm{NP}}_{\mathrm{pol}}(x_e,R)]\ . \qquad (29\mathrm{b})$$

To test the validity of the two-term approximation (28) for the *e*-H_2 system, we used it to evaluate $V^{\mathrm{NP}}_{\mathrm{pol}}(\vec{r}_e,R)$ at $\theta_e=\pi/4$ (for various values of r_e) and compared the results with those obtained via a direct calculation for this angle using the procedure described above. For the full potential this comparison shows that the two-term approximation produces values that are accurate to within 5% for $r_e \le 1.0a_0$ and to within 2% for $r_e \ge 1.5a_0$. (Lane and Henry[32] reported similar agreement with the two-term expansion for their scaled nonpenetration polarization potential.) However, in the dipole approximation the two-term approximation produces potentials that agree with the exact values to better than 0.2% for all values of r_e. Earlier studies[10] of adiabatic polarization potentials for more nonspherical systems (e.g., *e*-N_2 and *e*-CO_2) suggest that a Legendre expansion of a local nonadiabatic polarization potential for such systems will probably require more than two terms. Hence determination of the coefficients $v_\lambda^{(\mathrm{pol})}(r_e,R)$ for these systems will necessitate evaluating $V^{\mathrm{NP}}_{\mathrm{pol}}(\vec{r}_e,R)$ at more than two angles.

The polarization potentials (and their Legendre projections) vary smoothly with r_e, and a good representation of this variation (from 0 to $10.0a_0$) can be obtained with only about 20 values of the radial coordinate. However, in scattering calculations the necessarily dense integration mesh requires values of this potential at far more values of r_e. To obtain these additional values, the values of $V^{\mathrm{NP}}_{\mathrm{pol}}(\vec{r}_e,R)$ at $\theta_e=0$ and $\pi/2$ were fit using a cubic-spline interpolation scheme.[59] From the interpolated values the Legendre projections were determined using Eq. (27).

The discussion above pertains only to $r_e \le 10.0a_0$. At greater distances from the target the polarization potential has settled down to its asymptotic form and can be evaluated via Eq. (1) with the polarizabilities of Table II.

C. Scattering calculations

The acid test of a polarization potential is the cross sections it yields in scattering calculations. In the present study these calculations were carried out (within the theoretical context summarized in Sec. II C) using an integral-equations algorithm[60] that has been discussed in detail elsewhere.[61]

The static component of the electron-H_2 interaction potential was evaluated using standard computer programs[2,3] from a near-Hartree-Fock $X\,^1\Sigma_g^+$ wave function that was determined by Feldt *et al.*[62,63] This wave function was also used in the determination of the exchange terms in the Schrödinger equation. As will be discussed in Sec. IV, exchange effects were incorporated in two ways in different parts of the present study. In some of the calculations a tuned free-electron-gas model exchange potential[8,9] was used to provide an approximate local representation of exchange. In this potential the value $I=2.27$ eV was used for the tuning parameter.

The static and model-exchange components are expanded in a Legendre series for use in calculating coupling matrix elements. The maximum order Legendre polynomial that was retained in this expansion was $\lambda=8$.

Body-frame, fixed-nuclei scattering calculations were performed for six electron-molecule symmetries: Σ_g, Σ_u, Π_u, Π_g, Δ_g, and Δ_u. In the first four of these symmetries five partial waves were sufficient to converge the cross sections to better than 1.0%. In the latter two symmetries only three partial waves were required. Numerical integration of the scattering equations was carried out to radial values from $65.0a_0$ to $250a_0$, depending on the scattering energy. (Lower energies require larger matching radii.)

IV. RESULTS AND DISCUSSION

In this section we shall present and discuss our nonadiabatic polarization potentials. Four such potentials have been investigated; they differ in the number of multipoles retained in the expansion (22). For convenience, these four potentials are described in Table III. In order to assess their utility we shall examine low-energy ($0.02\ \mathrm{eV} \le E \le 10.0$ eV) electron-H_2 scattering results; cross sections will be compared with those obtained in recent theoretical studies in which polarization was treated more rigorously than in the present calculations.

In Figs. 1(a) and 1(b) we show various polarization potentials (see Table III) for $\theta_e=0$ and $\pi/2$, respectively. Comparison of the adiabatic curve in each of these figures with the nonadiabatic curves illustrates the importance of nonadiabatic effects for $r_e \lesssim 5.0a_0$. Among the latter, the most striking feature is the pronounced difference between the curves for potential *A*, which include all multipole contributions required to achieve convergence, and those for potentials *B* and *C*, which do not include the monopole ($\lambda=0$) term. Clearly, retention of this term gives rise to an extremely strong potential; indeed, for $1.2a_0 \lesssim r_e \lesssim 5.0a_0$, potential *A* is stronger than the fully adiabatic potential. This unphysical feature of potential *A* supports the contention that retaining the monopole term is inconsistent with the theoretical formulation of polarization

TABLE III. Multipole contributions retained in polarization potentials used in the scattering calculations of Sec. IV [see Eq. (22)].

Potential	Multipoles	Remarks
A	0–32	Converges cross sections
B	1	Dipole approximation
C	1–3	
D	1–24	

described in Sec. II.

To examine the importance of higher multipoles ($\lambda > 1$) in the nonpenetrating potentials we show potentials *B*, *C*, and *D* (cf. Table III) on an expanded scale in Fig. 2. For the *e*-H_2 system the nonpenetrating polarization potential converges rapidly in λ and is reasonably well represented in the dipole approximation. Of course it is the convergence of cross sections (not of the polarization potential itself) that is of critical concern. We therefore turn to an examination of total integrated cross sections, which were calculated according to the theory of Sec. II C and the computational procedures of Sec. III C.

The sensitivity of these cross sections to the number of multipoles retained in the expansion of Eq. (22) is examined at selected scattering energies in Table IV. The interaction potential used to generate these results included static, model-exchange, and various nonpenetrating polarization contributions. The dipole-only potential (potential *B* in Table III) appears to provide a very good approximation, yielding cross sections in excellent agreement with fully converged results. Considering the savings in computer time that obtains from retaining only the dipole contribution, the formal questions that pertain to the treatment of nonadiabatic effects we are using, and the other approximations inherent in the scattering theory of Sec. II C (e.g., neglect of bound-bound correlation, use of the rigid-rotator approximation), we decided to use the dipole-only nonpenetrating polarization potential in the remainder of this study.

Cross sections obtained with the nonadiabatic potential that includes the monopole term (potential *A*), which are not shown in Table IV, are radically different from those given and do not agree with measured values. This observation is similar to the findings of Weatherford *et al.*[51] who used a nonpenetrating polarization potential (retaining the monopole contribution) to evaluate cross sections for vibrational excitation of H_2.

As described in the Introduction a few other theoretical studies of nonadiabatic polarization potentials for the *e*-H_2 system have been reported. In light of the approximate nature of the nonpenetrating procedure used in the present work, comparison with results from these studies is especially important. In all of them the exact nonlocal exchange kernel was included; this treatment of exchange is more accurate than the model potential used in the calculations discussed thus far. To increase the consistency in the comparisons with other work, we have carried out additional body-frame, fixed-nuclei scattering calculations in which exchange is treated exactly. The iterative static-exchange method of Collins *et al.*[6] was implemented using the static potential described above and the dipole-only nonpenetrating polarization potential. In order to converge the total cross sections over the energy range of interest, six electron-molecule symmetries were included (see Sec. III C).

In Fig. 3 total integrated cross sections for scattering energies below 0.5 eV are shown along with the optical-potential results of Schneider and Collins,[17] the variational results of Henry and Lane,[38] and the measured absolute cross sections of Ferch *et al.*[64] Comparison of cross sections calculated in the rigid-rotator approximation and experimental data is only roughly indicative of the quality of the potential used, since the rigid-rotator cross sections are smaller than those obtained when vibration is taken into account. A more meaningful comparison with experiment awaits the inclusion of the vibrational motion of the nuclei.[65] The study of Henry and Lane,[38] although theoretically quite similar to the present work, used a less-flexible basis to represent the polarized molecular orbitals of the target. This gave rise to a poorer representation of the static interaction and the need for scaling of the polarization potential—factors which are probably responsible for the differences seen in Fig. 3.

Because of the formal rigor of the optical-potential

TABLE IV. Study of sensitivity of total integrated cross sections for *e*-H_2 (at $R = 1.4a_0$) to multipoles retained in the nonadiabatic polarization potential [Eq. (22)]. Exchange is incorporated in the interaction potential used to determine these cross sections via a tuned free-electron-gas model exchange potential with $I = 2.27$ eV (see Ref. 8).

E(Ry)	Cross sections (a_0^2)		
	$\lambda=1$	$\lambda=1-3$	$\lambda=1-24$
0.01	33.282	33.057	32.939
0.09	52.023	52.354	52.365
0.20	59.409	60.186	60.330
0.36	53.423	54.039	54.172
0.64	38.547	38.988	39.073
1.00	26.488	26.903	26.960

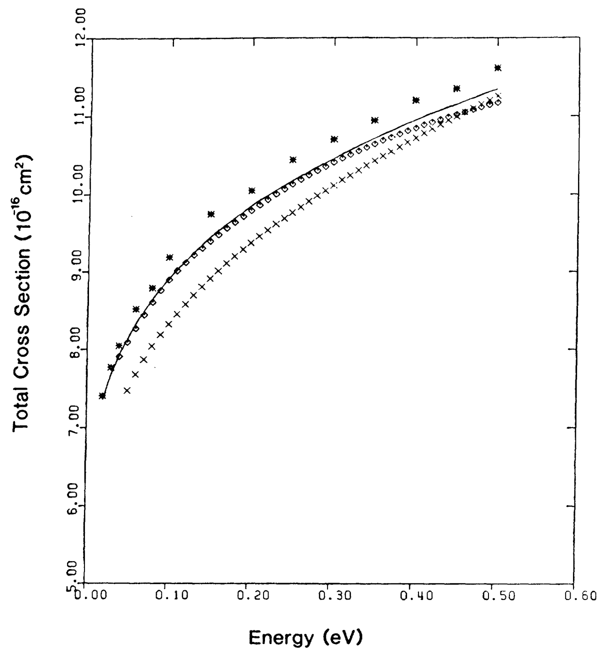

FIG. 3. Total integrated *e*-H_2 cross sections for scattering energies below 0.6 eV. In addition to rigid-rotor theoretical results from the present study (solid curve)—using exact exchange and the dipole-only nonpenetrating polarization potential—and from the work of Henry and Lane (Ref. 38) (crosses) and of Schneider and Collins (Ref. 17) (diamonds), we show the experimental results of Ferch *et al.* (Ref. 64) (stars).

theory, comparison of our results and those of Schneider and Collins[17] is of particular interest. The agreement between the two cross sections is seen in Fig. 3 to be excellent for $E \lesssim 0.5$ eV. Above this energy the two theories yield similar results, as shown in Fig. 4(a). We note that the total cross sections of Schneider and Collins[17] include only the Σ_g, Σ_u, and Π_u electron-molecule symmetries, while our results include additional contributions from the Π_g, Δ_g, and Δ_u symmetries. However, as the three-symmetry curve in Fig. 4(a) indicates, the mild disparity between the two theoretical results is not due to this effect, which is small over the energy range studied.

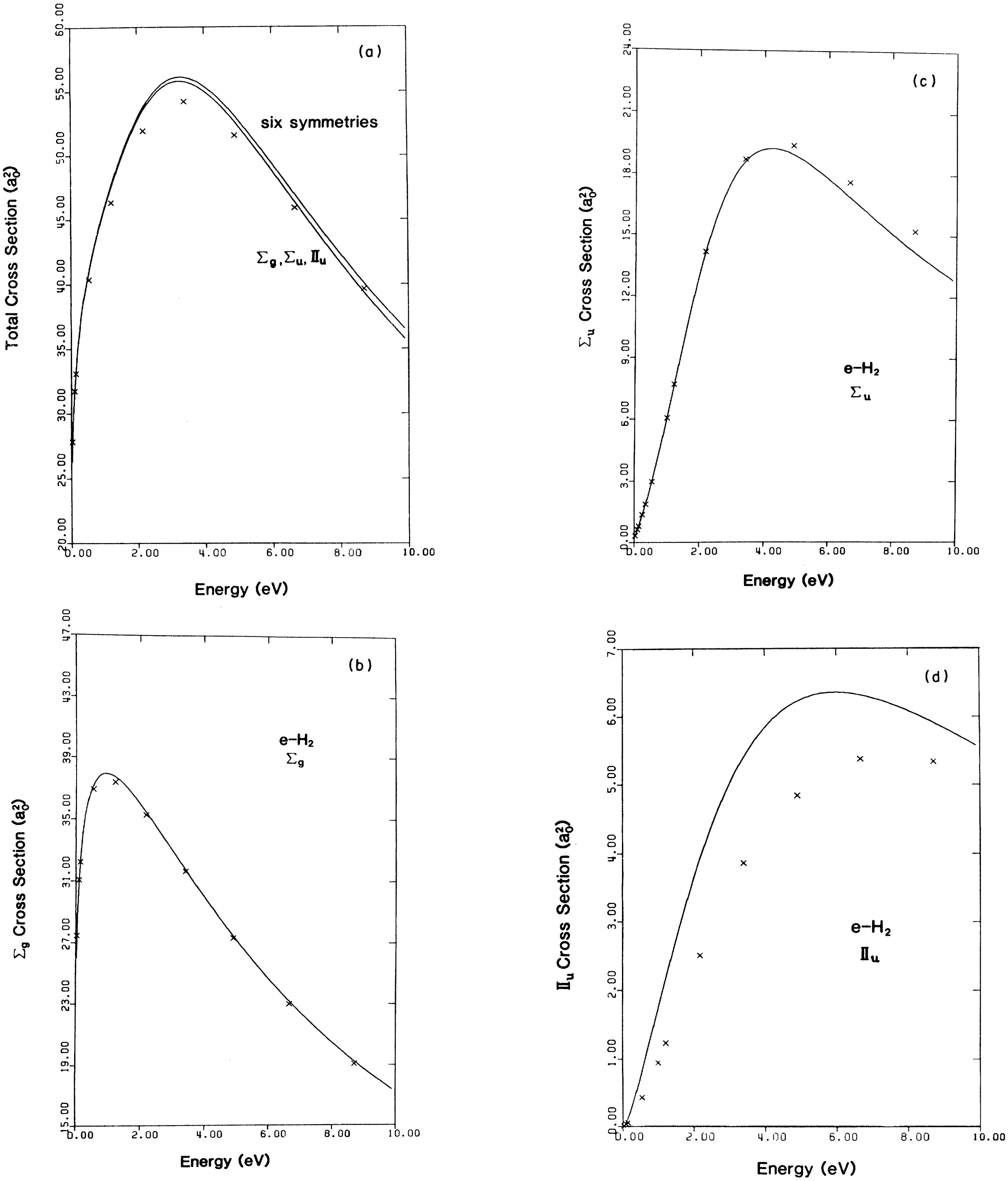

FIG. 4. Detailed comparison of e-H_2 (a) total integrated cross sections and (b)—(d) partial cross sections from the present study (solid curves) and from the optical-potential calculations of Schneider and Collins (Ref. 17) (crosses). All cross sections were determined within the rigid-rotor approximation with $R = 1.4a_0$. The results of Schneider and Collins include only the Σ_g, Σ_u, and Π_u symmetries.

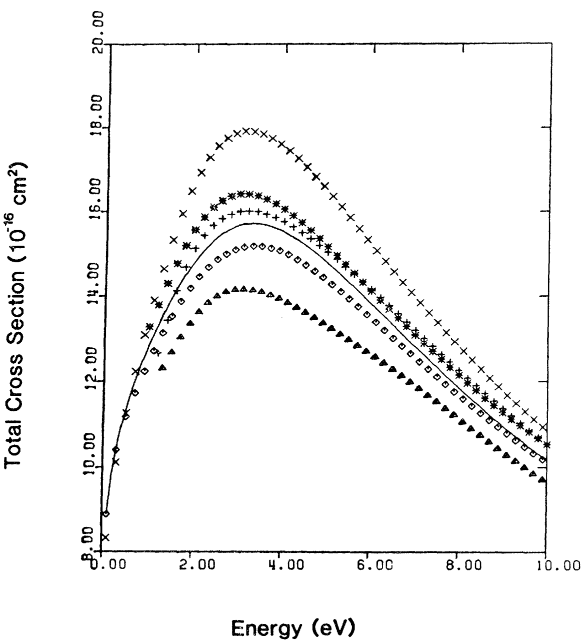

FIG. 5. Summary of total integrated cross sections for e-H_2 scattering. Theoretical results (at $R = 1.4a_0$) are taken from the present study (solid curve), the work of Henry and Lane (Ref. 38) (crosses), Hara (Ref. 33) (pluses), Schneider and Collins (Ref. 17) (diamonds), and Klonover and Kaldor (Ref. 13) (triangles). Experimental results of Jones *et al.* (Ref. 66) are also shown (stars).

Further insight into the nonpenetrating and optical potentials can be gained by comparing cross sections in individual symmetries. To this end Figs. 4(b)—4(d) show the Σ_g, Σ_u, and Π_u partial cross sections for energies from 0 to 10.0 eV. In Fig. 4(a) it is seen that the cross sections disagree most seriously at energies near the 3 eV "enhancement" in the total cross section. Figs. 4(b)—4(d) reveal that this disagreement is due to the Σ_u symmetry, which dominates the total cross section in this energy region. The increasing disparity seen in the Σ_u and Π_u cross sections, which are dominated by partial waves with $l > 1$, suggests that optical and nonpenetrating polarization potentials differ most in the intermediate-r_e range. Nevertheless, the overall quality of the approximate nonpenetrating potential, as indicated by the comparisons of Figs. 4, is very encouraging.

To put these results in perspective, we summarize total integrated cross sections from a variety of theoretical studies (and the recent experimental measurements of Jones *et al.*[66]) in Fig. 5. All of the *theoretical* results shown in this figure were calculated within the rigid-rotator approximation.

V. SUMMARY AND CONCLUSIONS

In this paper we have described a procedure for generating an approximate *ab initio* polarization potential for use in low-energy electron-molecule scattering calculations and application of the method to the e-H_2 system. In this theory the polarization potential is calculated via the linear-variational method, with nonadiabatic effects incorporated using a nonpenetrating approximation originally introduced by Temkin.[31] To explore the accuracy of the resulting polarization potential, scattering calculations (in the body-frame, fixed-nuclei formulation with the rigid-rotator approximation) have been carried out for scattering energies from 0.02 to 10.0 eV. Total integrated cross sections from these calculations are in very good agreement with the recent optical-potential results of Schneider and Collins[17] and in reasonable agreement with recent measured cross sections. This agreement is particularly striking at very low collision energies ($E \lesssim 0.5$ eV). In contrast to the optical potential used by Schneider and Collins,[17] the present nonpenetrating polarization potential is energy independent. The comparison between the results of the two studies suggests that the energy dependence of the e-H_2 polarization potential may not be particularly important for low-energy collisions.

The importance of various multipole contributions to the polarization potential has also been investigated in the present study. Retaining the monopole term is somewhat inconsistent with the nonpenetrating approximation and leads to an unphysically attractive potential. However, potentials that do not include this term converge rapidly with λ and are well represented by neglecting all but the dipole ($\lambda = 1$) term.

The nonpenetrating treatment of polarization, if implemented with a sufficiently flexible basis to accommodate distortions of the target, requires no scaling and entails no adjustable parameters. Internal consistency within a scattering calculation can be ensured by using the same near-Hartree-Fock electronic target wave function to evaluate all three components of the interaction potential.

The method described in this paper has been used in extensive calculations of cross sections for nuclear excitations in low-energy e-H_2 collisions.[65] In these calculations the nonpenetrating theory of Sec. II was used to evaluate polarization potentials for nonequilibrium internuclear separations. These potentials were used to determine vibrational-excitation cross sections. We are currently generalizing our computer programs to implement this theory for other electron-molecule systems.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. P. Jeffrey Hay of the Los Alamos Scientific Laboratory for generously sharing his expertise regarding the POLYATOM computer programs, to Dr. Robert Jones of Indiana University for sending us his experimental results prior to their publication, and to Dr. L. A. Collins and Dr. B. I. Schneider for supplying results of their optical potential calculations prior to publication. Finally, we would like to thank Dr. Collins for his careful reading of this manuscript prior to publication. This work was supported in part by a grant from the U. S. Department of Energy, Office of Basic Energy Sciences. One of the authors (M.A.M.) would also like to acknowledge the support of the Research Corporation.

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[1] N. F. Lane, Rev. Mod. Phys. 52, 29 (1980).

[2] M. A. Morrison, Comput. Phys. Commun. 21, 63 (1980).

[3] L. A. Collins, D. W. Norcross, and G. B. Schmid, Comput. Phys. Commun. 21, 79 (1980).

[4] M. A. Morrison and B. I. Schneider, Phys. Rev. A 16, 1003 (1977).

[5] D. K. Watson and V. McKoy, Phys. Rev. A 20, 1474 (1979); R. R. Lucchese, D. K. Watson, and V. McKoy, *ibid.* 22, 421 (1980).

[6] L. A. Collins, W. D. Robb, and M. A. Morrison, Phys. Rev. A 21, 488 (1980).

[7] A. E. Orel and T. N. Rescigno, Phys. Rev. A 24, 1267 (1981); L. A. Collins and B. I. Schneider, *ibid.* 24, 2387 (1981).

[8] M. A. Morrison and L. A. Collins, Phys. Rev. A 17, 918 (1978); T. L. Gibson and M. A. Morrison, J. Phys. B 14, 717 (1981) and references therein.

[9] W. F. Weitzel, T. L. Gibson, and M. A. Morrison, Comput. Phys. Commun. 30, 151 (1983).

[10] M. A. Morrison and P. J. Hay, Phys. Rev. A 20, 740 (1979) and references therein.

[11] D. G. Truhlar, D. A. Dixon, and R. A. Eades, J. Phys. B 12, 1913 (1979); D. A. Dixon, R. E. Eades, and D. G. Truhlar, *ibid.* 12, 2741 (1979); R. A. Eades, D. G. Truhlar, and D. A. Dixon, Phys. Rev. A 20, 867 (1979); R. A. Eades, D. A. Dixon, and D. G. Truhlar, J. Phys. B 15, 2265 (1982).

[12] B. I. Schneider, Chem. Phys. Lett. 51, 578 (1977).

[13] A. Klonover and U. Kaldor, J. Phys. B 11, 1623 (1978).

[14] K. Takatsuka and V. McKoy, Phys. Rev. A 24, 2473 (1981).

[15] M. Berman and V. Kaldor, J. Phys. B 14, 3993 (1981).

[16] B. I. Schneider and L. A. Collins, J. Phys. B 15, L335 (1982).

[17] B. I. Schneider and L. A. Collins, Phys. Rev. A 28, 166 (1983); this study differs from that in Ref. 16 in that it uses a different basis set for the optical potential and includes more symmetries in the scattering calculations.

[18] T. L. Gibson and M. A. Morrison, J. Phys. B 15, L221 (1982). This letter, which is a preliminary report of this research, contains an analytic form for reproducing our nonpenetrating dipole polarization potential at the equilibrium internuclear separation $R=1.4a_0$.

[19] M. Basu, P. S. Mazumdar, and A. S. Ghosh, Phys. Rev. A 26, 3000 (1982).

[20] K. Onda and D. G. Truhlar, Phys. Rev. A 22, 86 (1980).

[21] S. M. Valone, D. Thirumalai, and D. G. Truhlar, Int. J. Quantum Chem. Symp. 15, 341 (1981).

[22] I. E. McCarthy, B. C. Saha, and A. T. Stelbovics, J. Phys. B 14, 2871 (1981).

[23] J. K. O'Connell and N. F. Lane, Phys. Rev. A 27, 1893 (1983).

[24] K. Onda and A. Temkin, Phys. Rev. A 28, 621 (1983).

[25] L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. R. Soc. London, Ser. A 254, 259 (1960).

[26] D. R. Bates and H. S. W. Massey, Philos. Trans. R. Soc. London, Ser. A 239, 269 (1943); M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 1115 (1958); J. W. Cooper and J. B. Martin, *ibid.* 126, 1482 (1962).

[27] P. G. Burke, C. J. Noble, and S. Salvini, J. Phys. B 16, L113 (1983).

[28] L. A. Collins and B. I. Schneider, Phys. Rev. A 27, 101 (1983).

[29] C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. 165, 53 (1968).

[30] J. Callaway, R. W. LaBahn, R. T. Pu, and W. M. Duxler, Phys. Rev. 168, 12 (1968); Y. C. Jean and D. W. Schrader, Phys. Rev. A 18, 2030 (1978).

[31] A. Temkin, Phys. Rev. 107, 1004 (1957); A. Temkin and J. C. Lamkin, *ibid.* 121, 788 (1961).

[32] N. F. Lane and R. J. W. Henry, Phys. Rev. 173, 183 (1968).

[33] S. Hara, J. Phys. Soc. Jpn. 27, 1262 (1969).

[34] A. Dalgarno, G. W. F. Drake, and G. A. Victor, Phys. Rev. 176, 194 (1968).

[35] P. G. Burke and A. J. Taylor, Proc. Phys. Soc. London 88, 549 (1966); A. Hibbert, M. LeDourneuf, and Vo Ky Lan, J. Phys. B 10, 1015 (1977).

[36] M. A. Morrison, N. F. Lane, and L. A. Collins, Phys. Rev. A 15, 2186 (1977).

[37] See N. T. Padial, D. W. Norcross, and L. A. Collins, Phys. Rev. A 27, 141 (1983) for an alternative way to choose the cutoff radius.

[38] R. J. W. Henry and N. F. Lane, Phys. Rev. 183, 221 (1969).

[39] S. Hara, J. Phys. Soc. Jpn. 27, 1009 (1969).

[40] A. Jain and D. G. Thompson, J. Phys. B 15, L631 (1982).

[41] B. H. Bransden and M. R. C. McDowell, Phys. Rep. 30, 207 (1977); P. W. Coulter, Phys. Rev. A 22, 372 (1980); S. Geltman, in *Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, 1971,* edited by T. R. Groves and F. J. De Heer (North-Holland, Amsterdam, 1972), p. 216.

[42] See D. G. Truhlar, in *Chemical Applications of Atomic and Molecular Electrostatic Potentials,* edited by P. Politzer and D. G. Truhlar (Plenum, New York, 1981), p. 123.

[43] In atomic units $\hbar=m_e=a_0=e=1$. The unit of energy is $\hbar^2/m_e a_0^2=1$ Hartree$=1E_h=2$ Ry$=27.212$ eV. The unit of distance is the first Bohr radius $(a_0)=1$ Bohr$=0.52918\times10^{-10}$ m.

[44] Compare P. G. Burke and A.-L. SinFaiLam, J. Phys. B 3, 641 (1970).

[45] Compare H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results* (Addison-Wesley, Reading, Mass., 1972).

[46] Since the ground state of H_2 has only one occupied orbital, the operator $\hat{\mathscr{H}}_0+2\hat{J}-\hat{K}=\hat{\mathscr{H}}_0+J$.

[47] Compare T. Scott and M. R. C. McDowell, J. Phys. B 10, 1059 (1977).

[48] Compare the review by R. J. Drachman and A. Temkin, in *Case Studies in Atomic Physics II,* edited by E. W. McDaniel (North-Holland, Amsterdam, 1972) and W. M. Duxler, R. T. Poe, and R. W. LaBahn, Phys. Rev. A 4, 1935 (1971). For applications to electron-molecule problems, see A. Temkin and K. V. Vasavada, Phys. Rev. 160, 109 (1967) and S. Hara, J. Phys. Soc. Jpn. 22, 710 (1967).

[49] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[50] I. Shavitt, in *Methods in Computational Physics,* edited by B. Adler, S. Fernbach, and M. Rotenberg, Vol. 2 (Academic, New York, 1963).

[51] C. A. Weatherford, R. J. W. Henry, and M. C. Bruels, Proc. Indian Natl. Sci. Acad. Part A 39, 437 (1973).

[52] For a qualitative introduction to these terms, see M. A. Morrison, Aust. J. Phys. 36, 239 (1983).

[53] S. Huzinga, J. Chem. Phys. 42, 1293 (1965).

[54] W. Kolos and C. C. J. Roothan, Rev. Mod. Phys. 32, 219 (1960).

[55] W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).

[56] J. Rychlewski, Rev. Mod. Phys. 41, 833 (1980).

[57] J. M. Moskowitz and L. C. Snyder, in *Methods of Electronic*

Structure Theory, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 387.

[58] For details, see T. L. Gibson, Ph.D. thesis, University of Oklahoma, 1982 (unpublished).

[59] Compare C. deBoor, *A Practical Guide to Splines* (Springer, New York, 1978).

[60] W. N. Sams and D. J. Kouri, J. Chem. Phys. 51, 4809 (1969).

[61] M. A. Morrison, in *Electron-Molecule and Photon-Molecule Collisions,* edited by T. N. Rescigno, V. McKoy, and B. I. Schneider (Plenum, New York, 1979), p. 15.

[62] A. N. Feldt and M. A. Morrison, J. Phys. B 15, 301 (1982).

[63] M. A. Morrison, A. N. Feldt, and D. Austin, Phys. Rev. A (to be published).

[64] J. Ferch, W. Raith, and K. Schröder, J. Phys. B 13, 1481 (1980).

[65] A. N. Feldt, T. L. Gibson, and M. A. Morrison, Bull. Am. Phys. Soc. 28, 811 (1983).

[66] R. Jones (private communication).