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Ab initio adiabatic polarization potentials for low-energy electron-molecule and positron-molecule collisions: The e-N_2 and e-CO_2 systems

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Most theoretical calculations of cross sections for low-energy electron- and positron-molecule collisions include the important induced-polarization effects in the interaction potential by means of a semiempirical adiabatic approximation based on the known asymptotic form of the potential. In order to examine the validity of the assumptions implicit in this procedure, *ab initio* adiabatic polarization potentials have been calculated at the self-consistent-field level of accuracy for the e-N_2 and e-CO_2 systems. The resulting potentials deviate from the asymptotic form for intermediate electron positions outside the molecular charge cloud. In addition, the angular dependence of the potentials differs from that assumed in the semiempirical form.

I. INTRODUCTION

Long-range electron-molecule interactions[1] play an important role in the theory of electron-molecule collisions at low impact energies (below a few electron volts).[2,3] For polar molecules with sufficiently large permanent dipole moments, the qualitative behavior of the cross section with energy is largely determined by the electron-dipole potential energy.[4] For electron collisions with nonpolar molecules, both the permanent-quadrupole and induced-dipole interactions are known to be important. Indeed, for certain types of low-energy excitation processes (e.g., $j=0 \rightarrow j'=2$ rotational excitation) these long-range interactions are the dominant ones.[3,5] Similarly, long-range interactions must be accurately incorporated into theories of low-energy positron-molecule scattering.[6] For these collisions, the short-range electrostatic interaction potential is repulsive and exchange effects involving the scattering particle are absent. Hence significant distortion of the scattering wave function of the positron takes place in the region well outside the molecular charge cloud, where the polarization and quadrupole terms dominate the interaction potential.

The electron-quadrupole interaction[7] arises from the permanent quadrupole moment of the target molecule; it contributes a term $(-q/r_e^3)P_2(\cos\theta_e)$ to the interaction potential energy for an electron at position r_e, θ_e in the region far from the target. In contrast, the *induced* polarization interaction[7-12] is a second-order effect. Roughly speaking, this interaction arises from the distortion of the molecular charge distribution by the electric field of the scattering electron. The energy of the perturbed molecule is lower than that of the undistorted molecule, giving rise to an additional attractive term in the potential energy. Asymptotically, the additional term has the simple analytic form

$$V_{\text{pol}}(\vec{r}_e) \underset{r_e\to\infty}{\longrightarrow} -\alpha_0/2r_e^4 - (\alpha_2/2r_e^4)P_2(\cos\theta_e)\,, \tag{1}$$

where α_0 and α_2 are the spherical and nonspherical (anisotropic) polarizabilities of the molecule, respectively. For smaller values of r_e, the polarization potential deviates from the simple form (1) and, in general, depends on the velocity of the scattering electron as well as its position.[13] The accurate determination of the induced polarization potential for electron-molecule scattering in this region of space poses a considerable theoretical challenge.

Such second-order polarization effects have long been known to be important in low-energy electron-atom collisions and have been the focus of considerable attention.[14-25] Most calculations of electron-atom scattering make the *adiabatic approximation*[16] for the scattering electron.[26-28] In procedures based on this approximation, $V_{\text{pol}}(\vec{r}_e)$ is calculated by fixing the electron at position $\vec{r}_e$ and calculating the energy lowering due to the distortion of the target wave function. The molecule is not permitted to respond *dynamically* to the scattering electron, and the perturbed molecular wave function depends parametrically on the coordinates $\vec{r}_e$, not on the electron velocity.

Alternatively, induced polarization effects can be described by virtual electronic excitations,[16] i.e., by including closed channels in an eigenfunction expansion of the electron-molecule system wave function. Adopting this approach, Castillejo *et al.*[16] showed that for e-H scattering at impact energies below the inelastic threshold the adiabatic theory is valid as $r_e \rightarrow \infty$. However, it is not correct for small r_e, as Martin *et al.*[15] demonstrated for the e-H system by showing that the theory overestimates the effects of the perturbation. Several investigators have tried to rectify this defect in the adiabatic approximation for the electron-atom problem.[13,21,22,29] For example, in Temkin's polarized-orbital method,[30] nonadiabatic effects are partly taken into account in an approximate way by cutting off appropriate terms in the electron-atom potential energy whenever the scattering electron is within the charge cloud of the molecule. This method has also been applied to low-energy e-H_2^+ collisions.[9] Still another approach to the problem of including the effects of polarization is through the use of pseudostates.[24]

On the whole, much less attention has been given to the determination of accurate polarization potentials for low-energy electron-molecule collisions. A few studies of adiabatic polarization potentials for e-H_2 collisions have been reported[8-12,31,32] and the resulting potentials used successfully in scattering calculation. In addition, Truhlar and Van-Catledge[33] have recently reported a calculation of approximate polarization potentials[34,35] for e-N_2 scattering using the intermediate neglect of diatomic overlap (INDO/1s) method.

In their studies of e-H_2 scattering, Lane and Henry[10] calculated an *ab initio* nonadiabatic polarization potential and fit it to a reasonably simple analytic form, which they subsequently used in scattering calculations[5] (see also Refs. 31 and 32). For more anisotropic targets, accurate polarization potentials have not been available, and less precise treatments of polarization are implemented. The standard stratagem[5,36-41] is to add to the electrostatic interaction potential energy a "semiemperical" adiabatic form (AF) for the polarization potential. This term is given by Eq. (1) modified by a spherical cutoff function, viz.,

$$V_{\mathrm{pol}}^{\mathrm{AF}}(\vec{r}_e) = [-\alpha_0/2r_e^4 - (\alpha_2/2r_e^4)P_2(\cos\theta_e)]C(r_e)\,, \tag{2}$$

where $C(r_e)$ is most commonly taken to have the form

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

The "cutoff radius" r_c and exponent p are chosen in such a way that $C(r_e)$ effectively removes the polarization potential inside the charge cloud of the target. The cutoff radius r_c can be determined by "tuning" the potential[39,40] so that the calculated cross sections reproduce some well-established experimental feature of the scattering (e.g., a resonance). In a sense, this cutoff procedure is a (very crude) attempt to account for nonadiabatic effects.

This procedure is predicated on two assumptions: (i) that the *adiabatic approximation* is valid; and (ii) that the adiabatic polarization potential can accurately be represented by the form given in Eq. (1) for all values of the electron position r_e from the asymptotic region to the near vicinity of the target, where it is removed by the cutoff function. Because of the importance of the polarization interaction and the very wide usage of the semiempirical form (2), it is necessary to examine the validity of these assumptions. In particular, while these assumptions appear to be reasonable for the e-H_2 system,[10,32] they should be studied for systems involving more anisotropic interactions, in which the character of the induced distortions is quite different from that of the nearly spherical H_2 molecule.

In the present paper, we study the validity of the *second* assumption [i.e., the use of Eq. (1) to represent the adiabatic polarization potential beyond the "cutoff radius"] for the highly anisotropic e-CO_2 system and for e-N_2 interactions. We include the latter case because of its widespread interest in current theoretical research in electron-molecule collisions.[40-46] Polarization is known to be important for low-energy collisions in both systems,[39,47] and all scattering calculations[35] reported to data that take into account polarization effects in this way use a semiempirical adiabatic form like Eq. (2).

In order to address this question, we have calculated *ab initio* adiabatic polarization potentials at the self-consistent-field (SCF) level of accuracy for the e-N_2 and e-CO_2 systems. The approach used entails solution of the Hartree-Fock equations for the molecule in the presence of the *fixed* external electron; it is described in Sec. II. The calculated potential energy functions are presented and discussed in relation to Eq. (2) in Sec. III. Unless otherwise stated, atomic units are used throughout.

II. THEORY AND PROCEDURES

A. Calculation of polarization potentials

We shall treat the molecule as a rigid body with its nuclear configuration frozen at the equilibrium geometry.[42] Our calculations are performed in a body-fixed reference frame with the z coordinate axis coincident with the internuclear axis.[3] To implement the *adiabatic approximation*, we fix the position of the scattering electron at $\vec{r}_e$ and solve the (nonrelativistic) Hartree-Fock equation for the N-electron molecule in the presence of the external electron. Thus, for the stationary state labelled by quantum numbers n, we minimize the variational energy

$$E_n(\vec{r}_e) = \langle \Psi_n(1, 2, \ldots, N; \vec{r}_e) | H | \Psi_n(1, 2, \ldots, N; \vec{r}_e) \rangle \tag{4}$$

using a SCF procedure. The Hamiltonian is $\mathcal{H} = \mathcal{H}^0 + V_{\mathrm{em}}$, where $\mathcal{H}^0$ is the usual Hartree-Fock Hamiltonian for the *isolated* molecule[48] and V_{em} is the potential energy due to the Coulomb interaction of the molecule with the scattering electron at $\vec{r}_e$, i.e.,

$$V_{\mathrm{em}} = -\sum_{\alpha} \frac{Z_\alpha}{|\vec{r}_e - \vec{R}_\alpha|} + \sum_{i=1}^{N} \frac{1}{|\vec{r}_e - \vec{r}_i|} . \tag{5}$$

In Eq. (5), the first sum runs over the nuclei of charge Z_α at positions $\vec{R}_\alpha$, and the second sum runs over the molecular electrons at positions $\vec{r}_i$.

The polarization potential energy at $\vec{r}_e$ is defined to be the energy lowering due to the distortion of the molecule. It can be calculated from the ground-state ($n=0$) variationally determined energy of Eq. (4) as

$$V_{\mathrm{pol}}^{\mathrm{SCF}}(\vec{r}_e) = E_0(\vec{r}_e) - E_0^0 - \langle \Psi_0^0 | V_{\mathrm{em}} | \Psi_0^0 \rangle , \tag{6}$$

where E_0^0 and $\Psi_0^0 = \Psi_0^0(1, 2, \ldots, N)$ are the Hartree-Fock ground-state energy and wave function *of the isolated molecule*. The term $\langle \Psi_0^0 | V_{\mathrm{em}} | \Psi_0^0 \rangle$ in Eq. (6) is the electrostatic electron-molecule interaction potential energy (5) averaged over the ground-state target wave function, i.e., it is the *first-order* correction[49] to the zeroth-order energy E_0^0.

The Hartree-Fock equations for E_0, Ψ_0 and for E_0^0 and Ψ_0^0 are solved self-consistently for the unperturbed and perturbed ground-state energies, respectively. The **POLYATOM** computer programs are used in these calculations; details of the computational procedures implemented in these programs are available elsewhere.[50] We use basis sets of nucleus-centered contracted Gaussian functions to describe the undistorted target. These sets are described in Sec. II B below. Then the external electron is introduced as an additional (negative) nuclear center; no basis functions are centered on the electron. In the structure calculation for the perturbed molecule, the aforementioned Gaussian basis set is appropriately augmented with uncontracted functions chosen to allow for the distortion of the target in response to the external field.[51] We then calculate the adiabatic polarization potential from Eq. (6).

Once $V_{\mathrm{pol}}^{\mathrm{SCF}}$ has been computed for a sufficient range of values of r_e and θ_e it can be expanded in Legendre polynomials, viz.,

$$V_{\mathrm{pol}}^{\mathrm{SCF}}(r_e, \theta_e) = \sum_{\lambda=0}^{\infty}{}' v_\lambda^{\mathrm{SCF}}(r_e) P_\lambda(\cos\theta_e) , \tag{7}$$

where the prime denotes that only even-λ terms are present for N_2 and CO_2. In practice, of course, this expansion is truncated at some $\lambda_{\max}$. In the asymptotic limit, the semiempirical adiabatic form (2) for the polarization potential corresponds to $\lambda_{\max}=2$ and $v_\lambda^{\mathrm{AF}}(r) = -\alpha_\lambda/2r^4$ for $\lambda=0$ and 2. Thus we can conveniently study the suitability of the semiempirical form as a representation of the polarization potential by examining the deviation of v_λ^{SCF} from the form v_λ^{AF} for $\lambda=0$ and 2 and by considering the magnitude of higher-λ terms in Eq. (7).

In practice, to obtain the expansion coefficients v_λ^{SCF} at a particular value of r_e, we need only calculate $V_{\mathrm{pol}}^{\mathrm{SCF}}(r_e, \theta_e)$ at a few angles; the number of angles is determined by $\lambda_{\max}$. We can use an N-point Gauss-Legendre quadrature[52] to fit Eq. (8) in order to determine the desired coefficients $v_\lambda^{\mathrm{SCF}}(r_e)$ at a specified r_e; viz.,

$$v_\lambda^{\mathrm{SCF}}(r_e) = \frac{2\lambda+1}{2} \sum_{i=1}^{N} [V_{\mathrm{pol}}^{\mathrm{SCF}}(r_e, \theta_e^{(i)}) P_\lambda(\cos\theta_e^{(i)})] W_i , \tag{8}$$

where $x_i = \cos\theta_e^{(i)}$ are the quadrature points and W_i the corresponding weights.

Because of the computer time involved in the calculation of $V_{\mathrm{pol}}^{\mathrm{SCF}}$, it is desirable to use a small number of electron angles $\theta_e^{(i)}$ in (8). In this variable, the integrand $V_{\mathrm{pol}}^{\mathrm{SCF}} P_\lambda$ is a polynomial of order $\leqslant 2\lambda_{\max}$. Since an N-point quadrature of an integral is exact for an integrand which is a polynomial of degree less than or equal to $2N-1$, we can implement the expansion of Eq. (7) *exactly* using $N = \lambda_{\max}+1$ values of the integrand. Since the molecules of interest here belong to the point group $D_{\infty h}$, we need only consider angles in the interval $[0, \pi/2]$. This reduces the number of distinct values of $V_{\mathrm{pol}}^{\mathrm{SCF}}$ that must be calculated[53] at at each r_e to $\frac{1}{2}\lambda_{\max}+1$. From the resulting expansion coefficients, it is a simple matter to calculate $V_{\mathrm{pol}}^{\mathrm{SCF}}$ for any desired angle θ_e from Eq. (8).

B. Description of the calculations

All calculations were carried out at the equilibrium nuclear geometry. For N_2, the experimental equilibrium internuclear separation[54] is $2.068 a_0$. For CO_2, the equilibrium nuclear geometry[54] is linear and symmetric ($D_{\infty h}$), with an oxygen-carbon separation of $2.1944 a_0$. The orbital occupancies of the ground electronic states of these molecules are

$$N_2(X\,^1\Sigma_g^+):\ 1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 3\sigma_g^2\, 1\pi_u^4 ,$$

$$CO_2(X\,^1\Sigma_g^+):\ 1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 3\sigma_g^2\, 3\sigma_u^2\, 4\sigma_g^2\, 1\pi_u^4\, 1\pi_g^4 .$$

To generate a basis set for calculation of the e-N_2 polarization potential, we begin with a $(9s5p/5s3p)$ contracted basis set that is augmented by a

d-symmetry polarization function with exponent[55] $\zeta(d) = 0.98$. The contracted functions were constructed from the primitive Gaussian basis sets of Huzinaga[56] using contraction coefficients recommended by Dunning.[57] This basis set was further augmented by the addition of one uncontracted Gaussian on each nuclear center of s-, p-, and d-symmetry with exponents $\zeta(s) = 0.06$, $\zeta(p) = 0.05$, and $\zeta(d) = 0.16$. Thus we use a $(10s6p2d/6s4p2d)$ basis. In this basis set, our calculated Hartree-Fock energy of N_2 is −108.974 19 Hartree as compared to the near-Hartree-Fock result of −108.9928 Hartree of Cade *et al.*[58] and the exact Hartree-Fock energy −108.9939 Hartree of Christiansen and McCullough.[59] We obtain a quadrupole moment $q = -0.897ea_0^2$, while Cade *et al.* report $q = -0.939ea_0^2$ and Christiansen and McCullough give $q = -0.940ea_0^2$.

The construction of a basis set for the e-CO_2 calculations proceeds along similar lines. We begin with a $(9s5p/3s2p)$ contracted basis as described by Dunning and Hay[60] together with one polarization d-function[55] on each center, with exponents $\zeta(d) = 0.75$ on the carbon atom and $\zeta(d) = 0.85$ on the oxygen atoms. To supplement this basis set, additional s, p, and d functions on each nucleus are added to the original bases with the following exponents:

$$\text{C:}\ \ \zeta(s) = 0.05,\ \ \zeta(p) = 0.04,\ \ \zeta(d) = 0.11\,,$$

$$\text{O:}\ \ \zeta(s) = 0.09,\ \ \zeta(p) = 0.07,\ \ \zeta(d) = 0.21\,.$$

In the final $(10s6p2d/4s3p2d)$ basis, we calculate a Hartree-Fock energy for the ground state of CO_2 of −187.683 04 Hartree and quadrupole moment $q = -3.837ea_0^2$. The corresponding near-Hartree-Fock results of McLean and Yoshimine[61] are −187.7073 Hartree and $q = -3.860ea_0^2$.

The spherical and nonspherical static polarizabilities, α_0 and α_2 in Eq. (2), have been calculated independently in these basis sets by Morrison and Hay.[51] For reasons of internal consistency in the comparisons of Sec. III, we use their results at equilibrium,

$$N_2\!:\ \ \alpha_0 = 11.43a_0^3 \ \text{ and } \ \alpha_2 = 3.36a_0^3\,,$$

$$CO_2\!:\ \ \alpha_0 = 15.76a_0^3 \ \text{ and } \ \alpha_2 = 8.06a_0^3$$

in calculating the polarization potentials from the semiempirical form (2).

If the polarization potentials, as determined by Eq. (6), are small, then the perturbed energy E_0 and the quantity $E_0^0 + \langle\Psi_0^0|V_{\text{em}}|\Psi_0^0\rangle$ will be very nearly equal, and care must be taken to ensure that the Hartree-Fock energies are sufficiently accurate to allow the determination of a reasonable number of significant figures in $V_{\text{pol}}^{\text{SCF}}$. Typically, to calculate polarization potentials accurate to five significant figures, we require energies accurate to seven-to-nine decimal places, depending on the location of the external electron.

III. RESULTS AND DISCUSSION

In this section we shall compare the e-N_2 and e-CO_2 adiabatic (SCF) polarization potentials, calculated using the *ab initio* procedure of Sec. II, with the corresponding semiempirical adiabatic potentials based on the asymptotic form (1) (AF). In these comparisons, our emphasis will be on values of r_e beyond the region of the charge cloud of the molecule. For smaller values of r_e the nonadiabatic correction terms are quite important. Moreover, the electrostatic contribution to this potential energy begins to dominate the total potential in the vicinity of the nuclear singularities. We note that for r_e beyond the charge cloud, $C(r_e) \simeq 1$ in Eq. (2).

Using Table I, we can compare SCF and AF polarization potentials for the e-CO_2 system for the external electron located at various positions on the z or x axis. These results correspond to parallel ($\theta_e = 0$) and perpendicular ($\theta_e = 90°$) distortions of the molecular charge cloud, respectively.[62] The two forms for $V_{\text{pol}}(\vec{r}_e)$ agree quite closely at large values of r_e. However, discrepancies appear as we decrease r_e, reflecting a breakdown in the validity of the form (2).

The nature of this breakdown is more clearly illustrated by considering V_{pol} as a function of θ_e at several fixed values of r_e. SCF and AF polarization potentials are compared in this fashion at selected values of r_e for the e-CO_2 system in

TABLE I. Comparison of e-CO_2 polarization potentials calculated from SCF theory [Eq. (6)] and from AF of Eq. (2) for (a) $\theta_e = 0$ and (b) $\theta_e = \pi/2$. Note that for $r_e \gtrsim 5.0a_0$, $C(r_e) = 1.0$. The numbers shown are $10^5 V_{\text{pol}}(\vec{r}_e)$ in hartrees.

	(a)	
$z_e(a_0)$	SCF	AF
15.0	−26.21	−23.53
20.0	−7.93	−7.44
25.0	−3.19	−3.05
30.0	−1.52	−1.47
	(b)	
$x_e(a_0)$	SCF	AF
5.0	−766.19	−938.40
10.0	−55.73	−58.65
15.0	−11.32	−11.59
20.0	−3.62	−3.67
25.0	−1.49	−1.501
30.0	−0.72	−0.72

Figs. 1–4 and for the e-N$_2$ system in Figs. 5 and 6. In the former case, agreement between the two forms is good for $r_e \gtrsim 20.0a_0$. However, for smaller values of r_e significant deviations of the accurate SCF potential from the asymptotic form are evident. Typically, $V_{\text{pol}}^{\text{SCF}}$ is more attractive (i.e., deeper) than $V_{\text{pol}}^{\text{AF}}$ for angles $\theta_e \lesssim 65°$ but less attractive for larger angles. This effect, which becomes more pronounced as r_e is decreased, is principally due to the influence of a $P_4(\cos\theta_e)$ angular dependence in $V_{\text{pol}}^{\text{SCF}}$. Analogous behavior is evident in the e-N$_2$ potentials of Figs. 5 and 6, although it is considerably less pronounced at "intermediate" values of r_e (between 10.0 and $20.0a_0$).

The deviations of $V_{\text{pol}}^{\text{SCF}}$ from $V_{\text{pol}}^{\text{AF}}$ are not exclusively due to the presence in the former of higher-order angular dependence. A second cause is revealed by an examination of the expansion coefficients v_λ^{SCF} of Eq. (8). We have expanded the *ab initio* polarization potentials at each r_e in a Legendre series,[53] including polynomials $P_\lambda(\cos\theta_e)$ for $\lambda \leq 6$, using the procedure described at the end of Sec. II A. The resulting coefficients are given for the e-CO$_2$ system in Table II and for e-N$_2$ in Table III. In Tables II and III v_0^{SCF} and v_2^{SCF} are compared to their asymptotic limits $v_\lambda^{\text{AF}}(r_e) = -\alpha_\lambda/2r_e^4$ for $\lambda = 0$ and 2.

These results show that as r_e is decreased, higher multipoles v_4^{SCF} and v_6^{SCF} contribute to $V_{\text{pol}}^{\text{SCF}}$. In addition, v_0^{SCF} and v_2^{SCF} deviate increasingly from their simple asymptotic forms. The contrast is most pronounced for $\lambda = 2$. A further numerical fit of these results to a power series in inverse powers of r_e demonstrates that this change is principally due to an r_e^{-6} dependence in $v_2^{\text{SCF}}(r_e)$. This behavior reflects the importance of higher-order induced effects, such as the induced quadrupole interaction, and may signal the breakdown of

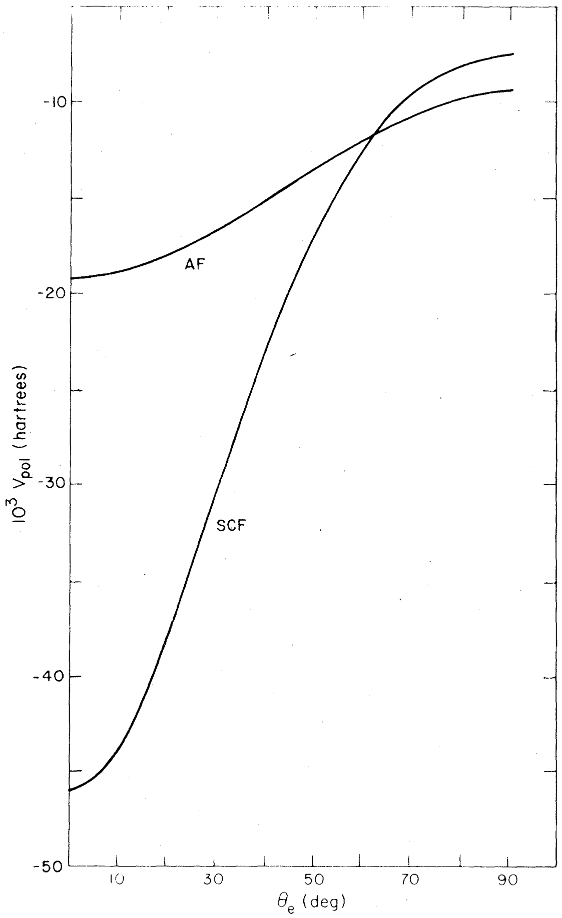

FIG. 1. *Ab initio* polarization potentials (SCF) and semiempirical potentials (AF) for fixed values of r_e, the radial coordinate of the scattering electron with respect to the center-of-mass of the target. Potentials for e-CO$_2$ scattering at $r_e = 5.0a_0$. All potential energies are in atomic units.

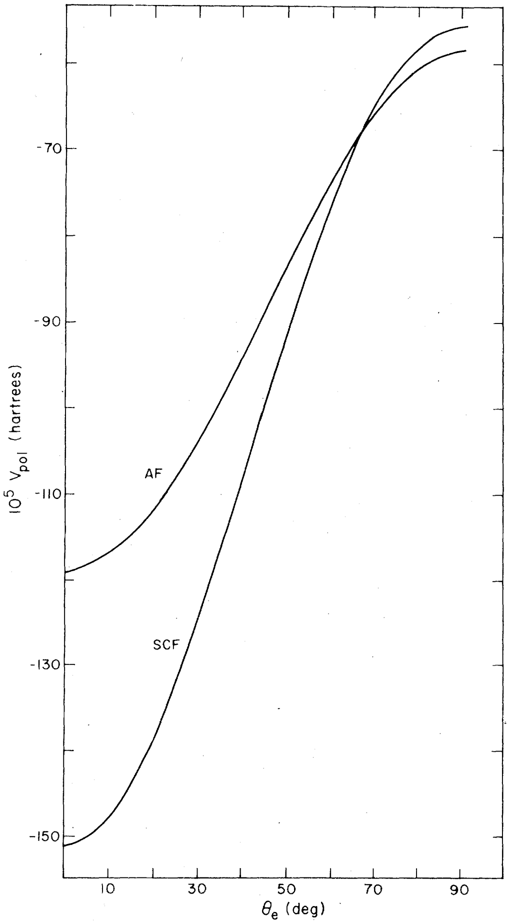

FIG. 2. Same as Fig. 1: e-CO$_2$ at $r_e = 10.0a_0$.

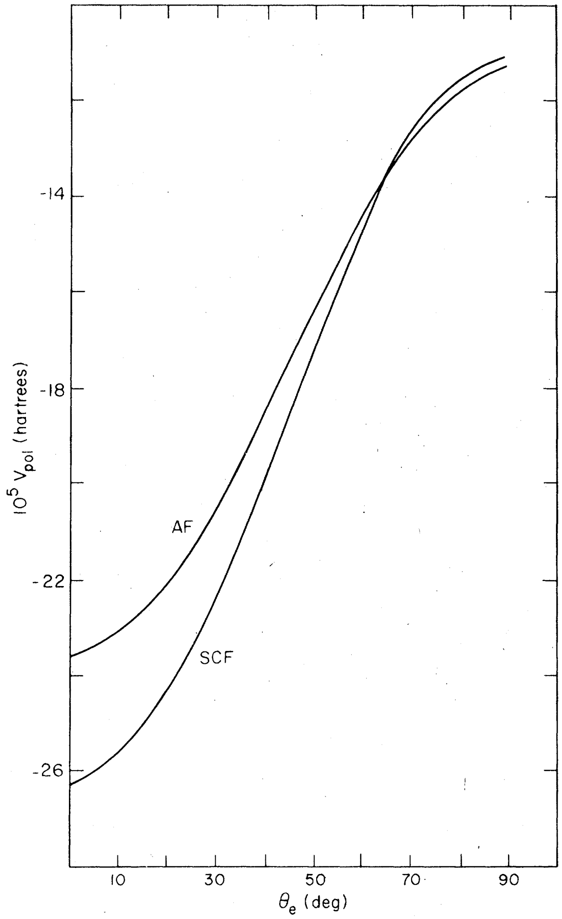

FIG. 3. Same as Fig. 1: e-CO_2 at $r_e = 15.0a_0$.

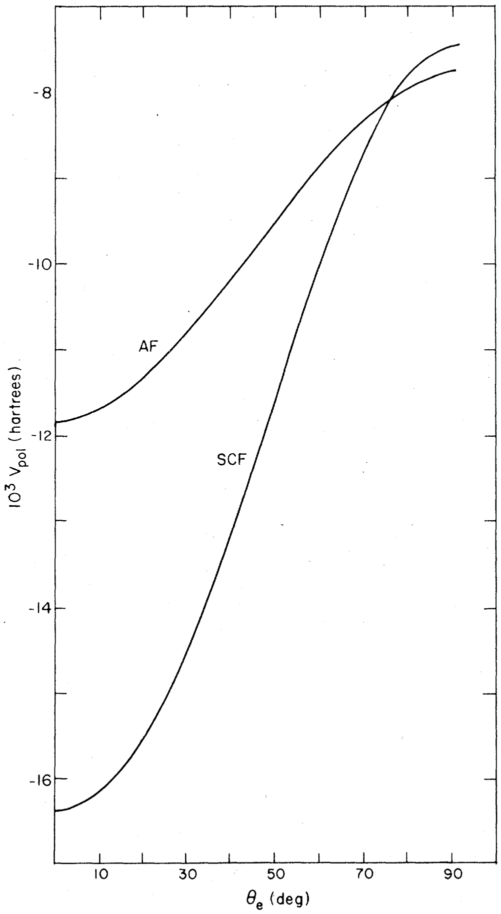

FIG. 5. Same as Fig. 1 for e-N_2: $r_e = 5.0a_0$.

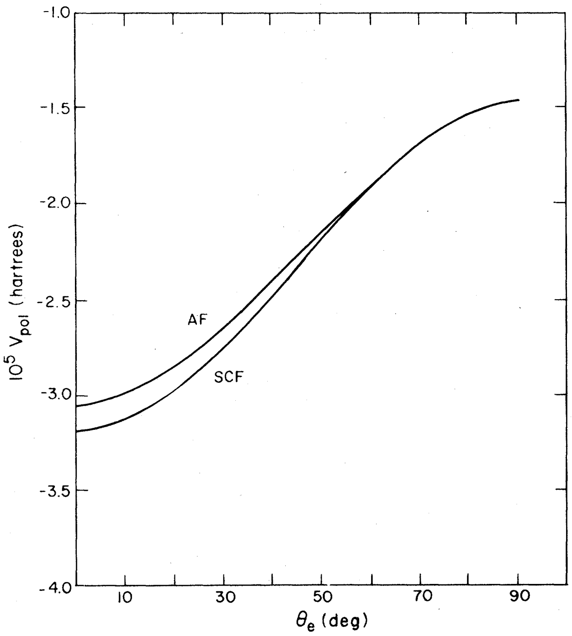

FIG. 4. Same as Fig. 1: e-CO_2 at $r_e = 25.0a_0$.

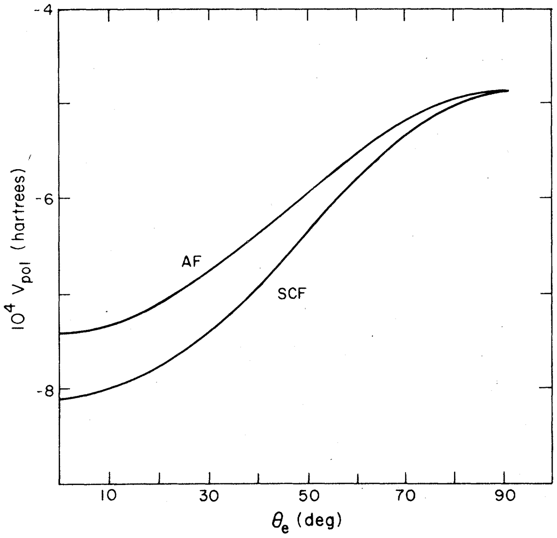

FIG. 6. Same as Fig. 1 for e-N_2: $r_e = 10.0a_0$.

TABLE II. Expansion coefficients of SCF polarization potentials for e-CO_2 [cf. Eq. (8)] in hartrees for $\lambda = 0$, 2, 4, and 6. Values of r_e are in atomic units (a_0). For $\lambda = 0$ and $\lambda = 2$, the corresponding AF coefficients $-\alpha_\lambda/2r^4$ are shown in parentheses with polarizabilities α_0 and α_2 as given in the text ($1.0^{-2} = 1.0\times10^{-2}$).

λ \ r_e	5.0	6.0	7.0	8.0	9.0	10.0	15.0	25.0
0	-1.657^{-2} (-1.261^{-2})	-7.512^{-3} (-6.080^{-3})	-3.849^{-3} (-3.282^{-3})	-2.175^{-3} (-1.924^{-3})	-1.323^{-3} (-1.201^{-3})	-8.524^{-4} (-7.880^{-4})	-1.612^{-4} (-1.557^{-4})	-2.044^{-5} (-2.017^{-5})
2	-2.216^{-2} (-6.448^{-3})	-8.406^{-3} (-3.110^{-3})	-3.698^{-3} (-1.678^{-3})	-1.858^{-3} (-9.839^{-4})	-1.034^{-3} (-6.142^{-4})	-6.219^{-4} (-4.030^{-4})	-9.818^{-5} (-7.960^{-5})	-1.121^{-5} (-1.032^{-5})
4	-6.456^{-3}	-1.775^{-3}	-5.604^{-4}	-2.071^{-4}	-8.798^{-5}	-4.168^{-5}	-2.81^{-6}	-1.99^{-7}
6	-8.130^{-4}	-1.391^{-4}	-2.151^{-5}	-1.91^{-6}	...	...	...	...

the multipole expansion.

From the present results, we conclude that the semiempirical asymptotic form of Eq. (2) is a good approximation to the adiabatic polarization potential for the e-N_2 system for $r_e \gtrsim 8.0a_0$. For e-CO_2, it is an *adequate* representation of $V_{\rm pol}^{\rm SCF}(r_e)$ for $r_e \gtrsim 20.0a_0$. This case is to be contrasted with the e-H_2 system, for which Lane and Henry found[10] that the asymptotic form is good to 5% for $r_e \gtrsim 2.5a_0$ and to 3% for $r_e \gtrsim 5.0a_0$. It appears that in charged-particle interactions with more complex and anisotropic targets than H_2, there may be a substantial range of radial values where the asymptotic form does not accurately represent the true *adiabatic* polarization potential. Such is the case for the e-CO_2 and e-N_2 systems.

Fortunately the differences between $v_\lambda^{\rm SCF}$ and $v_\lambda^{\rm AF}$ are least pronounced for $\lambda = 0$. Often it is precisely this spherical term that is more important in low-energy electron collisions.[2] However, some collision processes emphasize higher-order terms for example, the coupling due to $v_2(r)$ is important to $j = 0 \rightarrow j' = 2$ rotational excitation of H_2 and N_2 at low impact energies.[5]

IV. CONCLUSIONS

In this paper, we have presented the results of *ab initio* SCF calculations of adiabatic polarization

TABLE III. Same as Table II for e-N_2.

λ \ r_e	2.0	3.0	4.0	5.0	6.0	7.0
0	-2.275^{-1} (-3.572^{-1})	-7.244^{-2} (-7.056^{-2})	-2.597^{-2} (-2.232^{-2})	-1.064^{-2} (-9.114^{-3})	-4.984^{-3} (-4.410^{-3})	-2.619^{-3} (-2.380^{-3})
2	-2.661^{-1} (-1.050^{-1})	-6.223^{-2} (-2.074^{-2})	-1.771^{-2} (-6.563^{-3})	-6.134^{-3} (-2.688^{-3})	-2.478^{-3} (-1.296^{-3})	-1.160^{-3} (-6.997^{-4})
4	-2.506^{-2}	2.501^{-3}	9.116^{-4}	2.944^{-4}	1.386^{-4}	6.983^{-5}
6	-4.590^{-4}	2.750^{-3}	4.722^{-4}	8.500^{-5}	2.374^{-5}	8.22^{-6}

λ \ r_e	8.0	9.0	10.0	15.0	25.0
0	-1.505^{-3} (-1.395^{-3})	-9.260^{-4} (-8.711^{-4})	-6.009^{-4} (-5.715^{-4})	-1.155^{-4} (-1.129^{-4})	-1.472^{-5} (-1.463^{-5})
2	-6.127^{-4} (-4.102^{-4})	-3.544^{-4} (-2.561^{-4})	-2.196^{-4} (-1.680^{-4})	-3.755^{-5} (-3.318^{-5})	-4.563^{-6} (-4.301^{-6})
4	3.612^{-5}	1.940^{-5}	1.083^{-5}	1.11^{-6}	...
6	3.29^{-6}	1.39^{-6}	...	...	...

potentials for the e-N_2 and e-CO_2 systems. For "intermediate" values of the radial coordinate of the scattering electron, the SCF potentials differ significantly from the simple two-term semiempirical form usually used in low-energy scattering calculations. We find (1) deviations of the $\lambda = 0$ and $\lambda = 2$ expansion coefficients for $V_{\text{pol}}^{\text{SCF}}$ from the asymptotic forms $-\alpha_\lambda / 2r_e^4$, and (2) the presence of non-negligible coefficients v_λ^{SCF} for $\lambda > 4$.

In preliminary scattering calculations using these SCF potentials, we found that the results at low impact energies are *extremely* sensitive to the cutoff function $C(r_e)$ in Eq. (2). (This sensitivity is to be expected in light of the very large cross sections at these energies and the strength of the interaction potential.) For certain cases, we were unable to implement the usual form for $C(r_e)$, Eq. (3), or a variety of other *spherical* cutoff functions so as to obtain reasonable cross sections. The principle source of the difficulty is that $V_{\text{pol}}^{\text{SCF}}$ is very strongly attractive, much more so for intermediate values of r_e than is $V_{\text{pol}}^{\text{AF}}$. This fact places great demands on the simple cutoff function, which is crudely mocking the effect of the diabatic correction terms (and, perhaps, is also correcting for our approximate treatment of exchange). Of course, the "true" polarization potential, which includes nonadiabatic effects, is likely considerably weaker than $V_{\text{pol}}^{\text{SCF}}$; this is the case for the e-He system.[13,21,22]

In the present study, we have calculated an accurate adiabatic polarization potential. This potential is only part of the more complicated complete polarization interaction, which must include dynamic terms. Our examination of the adiabatic potential, alone and in scattering calculations, suggests that the success of the semiempirical form in low-energy electron-molecule collision theory may be somewhat fortuitous. Apparently, the cutoff function (2) corrects the adiabatic potential so as to account crudely for the absence of the dynamic contribution.

It is possible that use of a more flexible (perhaps nonspherical) multiparameter cutoff function would mitigate this problem.[31] However, the insight afforded by the present study into the nature of adiabatic polarization potentials for low-energy electron-molecule collisions strongly suggests that at least for complex ashperical targets the dynamic correction terms should be considered. Our future investigations will pursue this suggestion.

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