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POLARIZATION POTENTIALS FOR ELECTRON SCATTERING

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Charge polarization effects (due to polarization of the target charge distribution by the incident electron) are important for low and intermediate-energy electron scattering (these energy ranges corresponds to roughly $E < IP$ and $IP < E < 10 IP$, where E is the impact energy and IP is the target ionization potential). There are two approaches to the inclusion of such polarization effects in electron scattering. In the many-body approach, the scattering wavefunction for the whole system (incident electron plus target) is represented explicitly by basis functions or products of basis functions and numerically determined radial functions. Algebraic variational methods² and R matrix³ methods are some particularly powerful variants of this approach. In this approach charge polarization effects enter by configuration mixing. Because of this and because polarization effects are of long range, basis sets are required to be large and the scattering wavefunction must be represented over a big region. To avoid the associated computational problems, most electron-molecule scattering calculations using basis functions have been restricted to the single-configuration level, i.e., the static-exchange approximation, in which polarization effects are neglected.⁴ The second approach to including polarization effects is the use of effective potentials, also called optical potentials or model potentials. In this approach, electronically elastic scattering is reduced from a many-body configuration-mixing problem to single-particle scattering from an effective potential. It is too difficult to calculate the exact optical potential for electron-molecule scattering, so one must use approximations.

One model in use is to assume that the effective potential is the sum of a static potential, an exchange potential, and a polarization potential. The static potential may be calculated straightforwardly from accurate⁵⁻⁸ or simple^{6,9,10} target wavefunctions. The exchange potential may be taken as the nonlocal continuum-Hartree-Fock exchange potential¹¹⁻¹⁷ or as a local (but energy-dependent) approximate exchange potential.^{8,17-22} These are now well tested against non-local exchange;^{17,20,22-29} they lead to great computational simplifications yet they have been shown to be capable of good accuracy at intermediate energy and even, in some fortuitous cases or with tuning,¹⁷ at low energy. Their success at intermediate energy makes an effective potential approach particularly appealing in that energy range. The biggest source of difficulty is the treatment of charge polarization. In this report we discuss our recent work on the polarization potential for electronically and vibrationally elastic electron-molecule scattering.

For electron scattering by linear molecules, it has been popular to use the following semiempirical functional form to represent the polarization potential $V^P(\vec{r}, \vec{R})$:^{8,16,17,19,20,30-34}

$$V^P(\vec{r}, \vec{R}) \left[-\frac{\alpha_0(R)}{2r^4} - \frac{\alpha_2(R)}{2r^4} P_2(\hat{r} \cdot \hat{R}) \right] C(r) \quad (1)$$

where

$$C(r) = \left[1 - \exp\left(-\frac{r}{r_c}\right)^n \right] \quad (2)$$

\vec{r} is a vector from the center of mass of molecule to the scattering electron, n is an integer (whose value is 6 for all cases discussed in this paper), and r_c is a parameter whose value is determined semiempirically. We have assumed a diatomic target so that \vec{R} is the internuclear vector of the molecule and $\alpha_0(R)$ and $\alpha_2(R)$ are the isotropic and anisotropic components of the static electric dipole polarizability tensor for internuclear distance R . The main justification for this polarization potential is that the terms in brackets in equation (1) are known to provide the correct large- r form of the exact optical potential for E less than the lowest electronic excitation threshold,^{35,36} but eventually at small r these terms blow up so it must overestimate the exact optical potential. But there are several difficulties with this form of the polarization potential: (i) There is no justification for $C(r) \leq 1$; in fact the bracketed part of equation (1) probably underestimates the exact optical potential at medium r where the quadrupole polarizability should be included. (ii) There is no justification for $C(r)$ being independent of E ; in fact nonadiabatic effects (the inability of the target electrons to respond adiabatically to the scattering electron at \vec{r} due to the fact that $d\vec{r}/dt$ is not infinitesimal in a scattering event) decrease the target

response at high E . So $C(r)$ should be a decreasing function of E at least at some r and at high E . (iii) There is no justification for $C(r)$ being independent of R and $r \cdot R$. These assumptions are made for simplicity. (iv) There is no justification for neglecting other terms in the expansion

$$V^F(\vec{r}, \vec{R}) = \sum_{\lambda=0}^{\infty} V_{\lambda}^P(r, R) P_{\lambda}(\hat{r} \cdot \hat{R}) \quad (3)$$

at small r , although these other terms do decrease more rapidly than r^{-4} at large r . Despite these difficulties, equations (1) and (2) do seem to represent the dominant physical effect of the scattering electron's interaction with the induced dipole, and these equations have been used successfully by various workers at low energy. One can argue that $C(r)$ need not be too sensitive to E at low energy and small r because nonadiabatic effects should be a function mainly of the local kinetic energy which can be approximated (to zero order in the polarization potential) as

$$T_{loc}(\vec{r}, \vec{R}) = E - V^{SE}(\vec{r}, \vec{R}) \quad (4)$$

where $V^{SE}(\vec{r}, \vec{R})$ is a local (possibly energy-dependent) approximation of the static-exchange potential. At small r , $V^{SE}(r, R)$ has a large negative value, so $T_{loc}(r, R)$ is not too sensitive to E at small r at low E . Intermediate energy calculations have now been performed^{37,38} which partly test whether this argument can be extended to cover the intermediate-energy range by using r_C values determined empirically at low energy. Some of the results³⁷ are shown in Figure 1.

The quantity shown in Figure 1 is the electronically and vibrationally elastic differential cross section, i.e., the sum of the differential cross section for elastic scattering and rotational excitation. We plot this quantity so we can compare to the experimental results,³⁹⁻⁴³ for which rotational excitation is not resolved. The calculated results in Figure 1 are converged close coupling calculations for given approximations to the effective potential. The convergence tests are detailed elsewhere.³⁷ For Figure 1 we used the INDOXI/1s approximation⁶ for the static potential and the electronic density, the semiclassical exchange approximation,²⁴ and the semiempirical polarization potential of equations (1) and (2). The parameter r_C is given the value of $(2.308 a_0)$ determined by Buckley and Burke,¹⁶ who used a more accurate static potential and wavefunction and nonlocal exchange and semiempirically adjusted r_C to the resonance at 2.4 eV. For comparison, Figure 1 also shows the results obtained with $r_C = \infty$, i.e., no polarization potential. (The effect of a more attractive polarization potential will be considered below.) If the experimental uncertainty is estimated as the difference between the various experimental results shown,

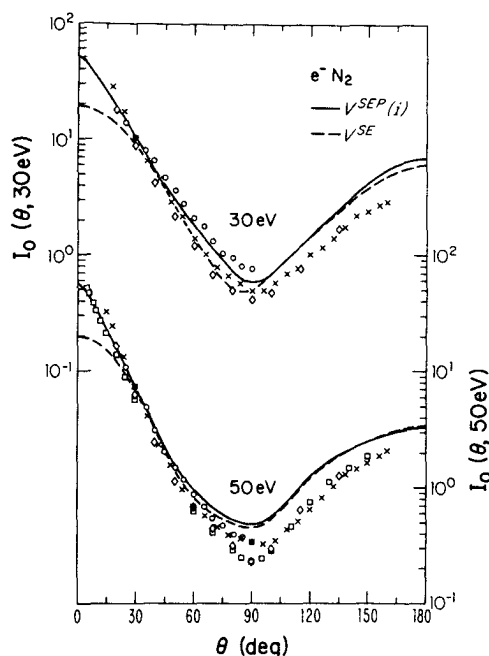


Fig. 1. The vibrationally elastic differential cross section for electron- N_2 at impact energies of 30 and 50 eV. The calculations (from reference 37) involved scattering basis set number IX and are for a fixed internuclear distance ($R=R_0$). For the calculations represented by the dashed line we used the INDOXI/1s method for the static potential and target density and the semiclassical exchange approximation. For the calculations represented by the solid line we also added the Buckley-Burke semiempirical polarization potential. This static-exchange-polarization potential will be called potential *i*. The various symbols represent the various experimental results. \diamond represents the experimental results of Srivastava, Chutjian and Trajmar (reference 42) which were obtained as ratios to the differential cross sections for He. They have been placed on an absolute scale for this figure by using the preliminary results of Register, Trajmar, and Srivastava (Trajmar, private communication) for He. \square represents the absolute measurements of DuBois and Rudd (reference 43). X and O, respectively, represent the relative measurements of Shyn, Stolarski, and Carignan (reference 40) and Finn and Doering (reference 41), normalized to the results of potential *i* at 30° and 30 eV. The measurements of Kuchitsu and Kambara are not included since their measurement was primarily designed for higher energies and their results at 50 eV may be less accurate than their higher-energy ones (Kuchitsu, private communication).

then both choices of r_c agree with experiment within experimental uncertainty for $\theta \geq 30^\circ$ eV although agreement is worse near 90° at 50 eV. However, polarization is clearly necessary at small θ ; neglecting it severely underestimates the differential cross section there. We have obtained a similar level of accuracy for electron scattering by CO_2 at 20 eV³⁸ using a polarization potential of the form of equations (1) and (2) with the value of r_c determined by Morrison, Lane, and Collins,⁸ who used the Hara free-electron-gas approximation for exchange and adjusted r_c to the resonance at 3.8 eV.

Despite the empirical success of equations (1) and (2) and their usefulness for qualitatively correct calculations of the cross sections, the difficulties with their theoretical foundation are unsatisfactory, and we require a theoretically more justified model to further our understanding of the physics, to increase our predictive capability, and to treat vibrational excitation and resolved rotational excitation more reliably.

We suggest a different model for the polarization potential which does not have difficulties (i) to (iv) detailed above. In this model⁴⁴

$$V^P(\vec{r}, \vec{R}) = V^{\text{adP}}(\vec{r}, \vec{R}) g[E, V^{\text{SE}}(\vec{r}, \vec{R})] \quad (5)$$

where $V^{\text{adP}}(\vec{r}, \vec{R})$ is the adiabatic polarization potential and $g[E, V^{\text{SE}}(\vec{r}, \vec{R})]$ is a nonadiabaticity function. The dual role of the function $C(r)$ in equation (1) is accomplished by two separate functions in equation (5). The adiabatic polarization potential has the asymptotic form

$$V^{\text{adP}}(\vec{r}, \vec{R}) \xrightarrow{r \rightarrow \infty} -\frac{\alpha_0(R)}{2r^4} - \frac{\alpha_2(R)}{2r^4} P_2(\hat{r} \cdot \hat{R}) \quad (6)$$

but it includes effects of higher multipoles at middle-range r and the breakdown of the multipole expansion at small r . When expanded in Legendre polynomials

$$V^{\text{adP}}(\vec{r}, \vec{R}) = \sum_{\lambda=0}^{\infty} V_{\lambda}^{\text{adP}}(r, R) P_{\lambda}(\hat{r} \cdot \hat{R}) \quad (7)$$

it includes nonzero contributions from all λ except odd λ for homonuclear molecules for which odd λ terms in $V^P(\vec{r}, \vec{R})$ are also zero. The nonadiabaticity function g can mimic the energy dependence of $V^P(\vec{r}, \vec{R})$ in a realistic way, and the product in equation (5) should be able to mimic the dependence of $V^P(\vec{r}, \vec{R})$ on R and $r \cdot R$ in a realistic way.

The first step in creating a model potential of the form of equation (5) is the calculation of realistic adiabatic polarization potentials for electron-molecule scattering. The adiabatic polarization potential can be calculated analytically for electron-hydrogen atom scattering⁴⁵ but otherwise requires a numerical calculation. The only results available for molecules for a long time were for H₂.⁴⁶⁻⁴⁷ We have now made calculations emphasizing the small-r range for H₂,⁴⁸ N₂,^{44,48,49} and CO.⁴⁴ and Morrison and Hay⁵⁰ have made a preliminary report of calculations for N₂ and CO₂ emphasizing $r \geq 5 a_0$. These calculations are all self-consistent-field (SCF) single-configuration molecular orbital (SCF MO) calculations. The SCF MO's, n-electron wavefunction Ψ_0 , and total electronic energy E_0 are calculated for the usual fixed nuclei electronic Hamiltonian $H_0(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_A, \vec{R}_B)$ for an n-electron target with nuclei of charges Z_A and Z_B at \vec{R}_A and \vec{R}_B . Then the test-charge-added Hamiltonian is defined by

$$H(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_A, \vec{R}_B, \vec{r}) = H_0(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_A, \vec{R}_B) + \sum_{i=1}^n \frac{e^2}{|\vec{r}_i - \vec{r}|} - \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \frac{Z_B}{|\vec{R}_B - \vec{r}|} \quad (8)$$

and new SCF MO's, a new n-electron wavefunction $\psi_{\vec{r}}$, and n-electron energy $E_{\vec{r}}$ are calculated. The static potential $V^S(\vec{r}, \vec{R})$ and polarization potential are then found from

$$\begin{aligned} V^S(\vec{r}, \vec{R}) &= \langle \Psi_0 | H | \Psi_0 \rangle - \langle \Psi_0 | H_0 | \Psi_0 \rangle \\ &= \langle \Psi_0 | H | \Psi_0 \rangle - E_0 \end{aligned} \quad (9)$$

$$\begin{aligned} V^P(\vec{r}, \vec{R}) &= \langle \psi_{\vec{r}} | H | \psi_{\vec{r}} \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \\ &= E_{\vec{r}} - \langle \Psi_0 | H | \Psi_0 \rangle \\ &= E_{\vec{r}} - E_0 - V^S(\vec{r}, \vec{R}) \end{aligned} \quad (10)$$

The SCF MO calculations in our group have been carried out at three different levels of accuracy: the INDO and INDOXI semiempirical molecular orbital schemes employing a minimum basis set of Slater-type functions have been applied to N₂ and CO and ab initio calculations employing extended basis sets of Gaussian-type functions have been carried out for H₂ and N₂. For the calculations discussed here R equals R_e.

Our ab initio calculations for H₂ used a Gaussian basis set with 6 s functions and 4 p functions on each nucleus. The s-function exponential parameters are those of Huzinaga's 5 s set⁵¹ plus 0.03, and the exponential parameters of the p functions are the four smallest in the s set. The two tightest s functions on each nucleus are contracted; all other functions are uncontracted. The

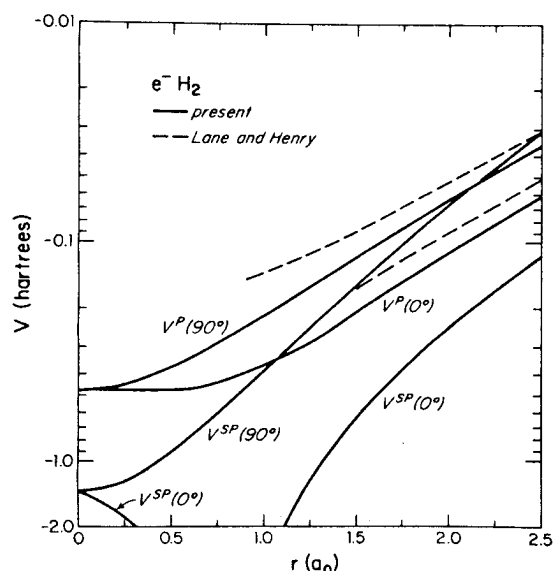


Fig. 2. Adiabatic polarization potentials and static-plus-adiabatic-polarization potentials for collinear (0°) and perpendicular-bisector (90°) approaches of electrons to H_2 . V^P is the polarization potential and V^{SP} is the sum of the static and polarization potentials. The solid lines are present results and the dashed lines are the adiabatic polarization potentials of Lane and Henry.

polarization potentials for collinear and perpendicular-bisector approaches of the electron to H_2 are given in Figure 2 where they are compared to the results of Lane and Henry (Lane and Henry did not publish their adiabatic polarization potentials at small r). Considering the large differences in computational approach, the agreement in the overlapping region is good.

The *ab initio* calculations for N_2 use 9 s functions and 5 sets of p functions centered on each N with exponential parameters ξ from Huzinaga,⁵¹ contracted to a [53] set by Dunning's rules,⁵² and augmented by 4 s functions, 3 p sets, and 1 sd set. The additional s functions consist of bond-centered functions with $\xi = 1.13$ and 0.27 and nuclear-centered functions with $\xi = 0.065$. The additional p sets are all bond-centered and have exponents 0.68 , 0.19 , and 0.0515 . The sd set consists of 6 bond-centered functions [$x^2, y^2, z^2, xy, xz,$ and yz times $\exp(-r^2)$] with $\xi = 0.11$. The parameters 1.13 and 0.68 are from Vladimiroff⁵³ and are chosen to represent the bond region in the unperturbed target. The parameters 0.065 and 0.0515 are chosen from the smallest parts of s and p ξ 's in the Huzinaga basis by extending the sequence as a geometric series. The ξ 's 0.27 and 0.19 are then chosen as geometric means of the larger and smaller ones. The 0.11 value for

the sd set is chosen as Werner and Meyer's polarizability optimized value for an N-centered function in NH_3 .⁵⁴ We have found⁴⁸ by performing calculations at larger r that bond-centered functions are very useful for polarizability calculations.

The basis sets for the INDO/1s and INDOXI/1s calculations involved 2 s functions and 1 p set on each nucleus, with exponential parameters determined by Slater's rules.⁵⁵ This is the standard choice for INDO calculations.^{56,57}

The three calculations of the adiabatic polarization potential and the static-plus-adiabatic-polarization potential for collinear and perpendicular-bisector approach of an electron to N_2 are shown in Figure 3. The INDO and INDOXI methods underestimate the spherical average of the polarization potential but show a qualitatively correct anisotropy. Further, the INDO and INDOXI methods lead to an adiabatic polarization potential that is too weak near $r = 0$ but the error in the static potential partly compensates for this in the INDO approximation.

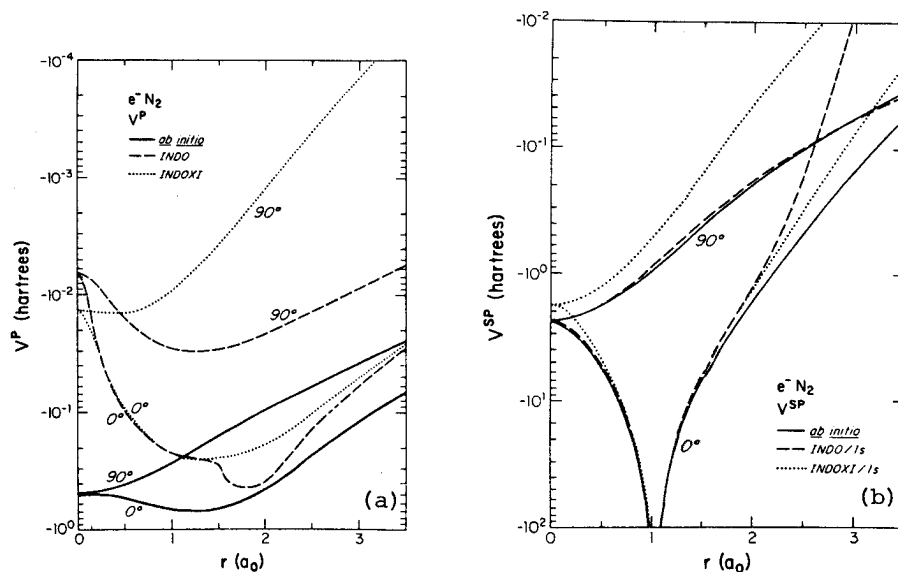


Fig. 3. Adiabatic polarization potentials (a) and static-plus-adiabatic polarization potentials (b) for collinear (0°) and perpendicular-bisector (90°) approaches of electrons to N_2 . The solid line is the *ab initio* result, the long-dashed line is the INDO/1s result, and the dotted line is the INDOXI/1s result.

INDO calculations for other angles of approach of the electron to N_2 show that terms in equation (7) with $\lambda > 2$ are not completely negligible. For example, the INDO method yields $V^{\text{adP}}(r = 1.2a_0) = -0.094$ hartrees and $V_4^{\text{adP}}(r = 2.0a_0) = -0.024$ hartrees. Two additional ab initio calculations at the latter distance show an effect of the same order of magnitude for terms with $\lambda > 2$. Another interesting qualitative feature of the results is the size of $V_1^{\text{adP}}(r)$ for CO. In the INDO approximation the magnitude of this term exceeds 0.2 hartrees for r in the range 0.8 to 1.3 a_0 . In previous effective potential calculations, terms in $V^{\text{P}}(r)$ with $\lambda \neq 0, 2$ have almost always been ignored (see, however, reference 20).

It is interesting to write

$$V_0^{\text{adP}}(r) = -f_0(r) \lim_{r \rightarrow \infty} (2r^4)V_0^{\text{adP}}(r) \quad (11)$$

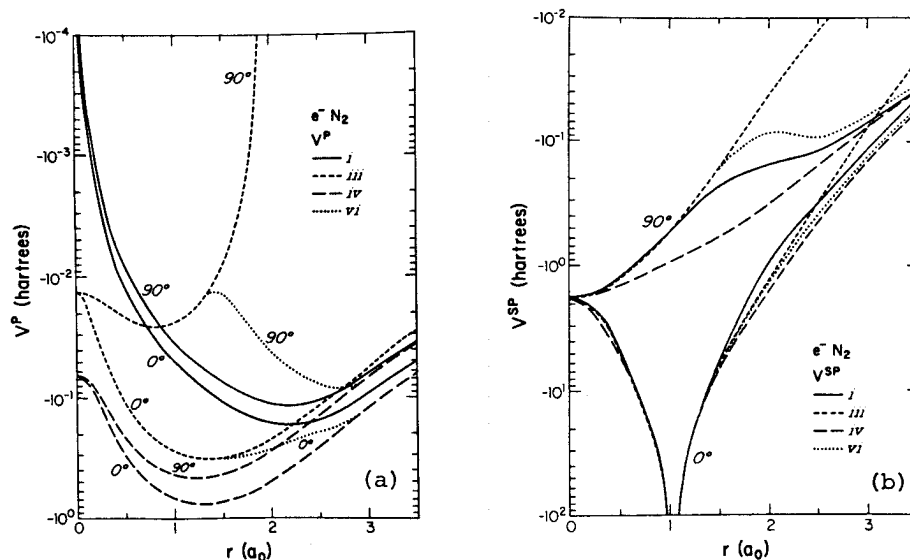
and

$$V_2^{\text{adP}}(r) = -f_2(r) \lim_{r \rightarrow \infty} (2r^4)V_2^{\text{adP}}(r) \quad (12)$$

thereby defining $f_0(r)$ and $f_2(r)$. If this is done, one finds that $f_0(r) \neq f_2(r)$ and that both $f_0(r)$ and $f_2(r)$ may exceed unity. This supports criticisms (i) and (iii) of the usual model.

To test the sensitivity of the vibrationally elastic differential cross section to the form of the polarization potential we repeated the electron- N_2 scattering calculations at 30 eV with several different static-exchange-polarization potentials.⁴⁹ The polarization and static-plus-polarization parts of three of these are shown in Figure 4 for the collinear and perpendicular-bisector geometries, where they are compared to the potentials used for the calculations in Figure 1. The corresponding vibrationally elastic differential cross sections are shown in Figure 5. Potential i is the potential used for Figure 1 and is repeated in Figures 4 and 5 for reference. Potential iii is the INDOXI/1s static-exchange potential plus the $\lambda = 0$ and $\lambda = 2$ components of the INDOXI adiabatic polarization potential, with $V_0^{\text{P}}(r)$ and $V_2^{\text{P}}(r)$ modified for r greater than 5.9 a_0 and 5.0 a_0 , respectively, to have accurate asymptotic forms. Thus the static-exchange parts of potentials i and iii differ only due to the small effect of the polarization potential on the exchange potential. The scattering predicted by the two potentials is very similar except for $\theta < 30^\circ$ where potential iii underestimates the scattering. This is attributable to the fact that the INDOXI method underestimates α_0 by a factor of 5.98. Although potential iii is adjusted for $r > 5.9 a_0$ it is still not attractive enough at medium r and so it underestimates the forward scattering just as complete neglect of polarization does. Potential vi is the same as potential

iii except that $V_0^P(r)$ is deeper in the range $1.25 a_0$ to $5.9 a_0$. The INDOXI calculation of $V_0^{\text{adp}}(r)$ exhibits a minimum at $r = 1.25 a_0$, where it equals $-\alpha_0/[2(2.6 a_0)^4]$ for the accurate α_0 . So we arbitrarily replaced $V_0^{\text{adp}}(\text{INDOXI})(r)$ in the range $1.25 - 2.6 a_0$ by $V_0^{\text{adp}}(\text{INDOXI})(r = 1.25 a_0)$ and in the range $2.6 - 5.9 a_0$ by $-\alpha_0/(2r^4)$ with the accurate α_0 . This modification increases the forward scattering sufficiently to yield good agreement with experiment, as was obtained with the semiempirical potential i. Thus we have achieved good agreement with experiment without any semiempirical parameters by using a simple model in which $V_0^P(r)$ and $V_2^P(r)$ are set equal to $V_0^{\text{adp}}(r)$ and $V_2^{\text{adp}}(r)$ as calculated by the INDOXI method except that $V_0^{\text{adp}}(r)$ is joined smoothly from its minimum to an accurate asymptotic form. Potential vii (for which the results are not shown in Figure 5) is the same as potential vi except the $V_\lambda^P(r)$ for $\lambda > 2$ are set equal to the INDOXI adiabatic calculated values without modification. This produces very little effect on the scattering. Thus although these higher-order anisotropies of $V^{\text{adp}}(r)$ are not always small, they seem to have only a small effect on the vibrationally elastic differential cross section.



Figs. 4(a) and (b) Adiabatic polarization potentials (a) and static-plus-adiabatic polarization potentials (b) for collinear (0°) and perpendicular-bisector (90°) approaches of electrons to N_2 . The solid line is for potential i, the short-dashed line is for potential iii, the long-dashed line is for potential iv, and the dotted line is for potential vi.

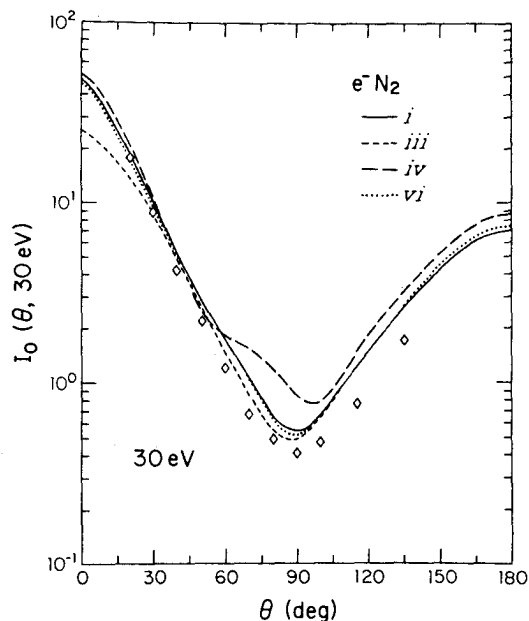


Fig. 5. Vibrationally elastic differential cross section for electron scattering by N_2 . The calculations (reference 49) involved scattering basis set number XIII and are for a fixed internuclear distance ($R = R_e$). The solid, short-dashed, long-dashed, and dotted curves correspond to potentials i, iii, iv, and vi as in Figure 4. \diamond represents the same experimental results as it represents in Figure 1. At large angles the short-dashed curve (iii) merges with the solid one (i).

Finally we consider the effect of making the polarization potential stronger. Potential iv is like potential iii except that $V_0^P(r) = 4.80 V_0^{P(\text{INDOXI})}(r)$ for $r < 5.9 a_0$ where the correction factor is $[-\alpha_0/(2r^4)]/V_0^{P(\text{INDOXI})}(r)$ evaluated at $5.9 a_0$ for the accurate α_0 . For both potentials $V_0^P(r)$ is joined smoothly to the accurate large- r limit for $r > 5.9 a_0$. Comparison of Figures 3 and 4 shows that potentials iii and iv generally bracket the ab initio adiabatic polarization potential. Figure 5 shows that this larger polarization potential seriously overestimates the sideways scattering. Thus the vibrationally elastic differential cross section is sensitive to making the polarization potential stronger. The error could

be corrected by including a nonadiabaticity function. In fact, the spherical average of the adiabatic polarization potential (either the *ab initio* one or the modified ones iv or vi, all of which, when spherically averaged, tend to the same asymptotic form) shows relatively good agreement with the semiempirical polarization potential for r greater than about $3 a_0$ but it becomes deeper at small r where nonadiabaticity effects may be large due to the deep static potential. Thus the adiabatic polarization potentials already provide a rough explanation of the shape of the semiempirical polarization potentials. But the semiempirical ones involve the spherical cutoff function $C(r)$ which artificially constrains their angle dependence. The nonadiabaticity argument may also explain why the energy-independent potential of reference 1 is less accurate for sideways scattering at 50 eV than 30 eV (see Figure 1); this may be because nonadiabaticity decreases the true effective potential more at 50 eV than 30 eV.

We hope that the use of adiabatic polarization potentials and reasonable nonadiabaticity functions will lead to more realistic effective potentials. Of course the potential in equation (5) does have limitations. First, the exact optical potential is complex (has a nonzero imaginary part) at energies above the first electronic excitation threshold. It requires an additional model to estimate the imaginary part of the effective potential. Second, an accurate estimate of the nonadiabaticity function requires a dynamical calculation. For example, Kaldor and Klonover⁵⁹ have estimated the optical potential by using many-body perturbation theory in a scattering calculation. This leads to a nonlocal approximation to the optical potential. (The exact optical potential is also nonlocal, and the energy dependence in the nonadiabaticity function is an attempt to include this aspect.) In contrast to the SCF approach to the adiabatic polarization potential discussed here, the approach taken by Kaldor and Klonover requires third order terms to include the full polarizability.⁵⁹ Since their calculation of an approximate optical potential is part of a basis-set scattering calculation, it provides a suitable link between effective potential methods and the basis-set configuration-mixing approaches mentioned in the first paragraph.

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