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EFFECTIVE POTENTIALS FOR INTERMEDIATE-ENERGY ELECTRON

SCATTERING: TESTING THEORETICAL MODELS

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I. INTRODUCTION

Electron scattering by molecules is important from a fundamental point of view as well as for many applications to practical concerns. An electron is the most elementary possible probe of a target. An electron scattering experiment can yield both structural and spectral information. From the chemist's point of view the spectral information obtainable this way is often invaluable because the selection rules of photon spectroscopy are inoperative. In particular, at impact energies up to about 100 eV, many optically forbidden transitions appear very strongly in electron impact spectroscopy.^{1,2} The energy range from 10-100 eV is thus a very important one for chemistry, and it is often called the intermediate energy range for electron scattering.³ Data on electron scattering cross sections at energies below 100 eV are also required for understanding electron mobilities, discharges, flames, radiation chemistry and radiation biology, electron-impact laser initiation, magnetohydrodynamic power generators and other devices containing plasmas, the atmosphere of the planets (especially the upper atmosphere of the earth), the interstellar medium, and stars (including the sun).^{4,5}

The present article is concerned with modelling the effective interaction potential between a scattering electron and a molecule for collision energies of about 100 eV or less. This is the first step in the effective-potential approach to calculating the transition probabilities and scattering cross sections. The effective potential is much more complicated for low and intermediate energy than for the very high energies used for electron diffraction

studies. Electron diffraction studies are typically carried out at 10-50 keV, and they can be analyzed to yield not only geometries but also (unperturbed) molecular electronic densities.⁶ At these very high energies the scattering electron comes and goes so rapidly that the target does not have time to respond appreciably. Thus the electrostatic potential, which is the interaction energy of a point charge with the unperturbed target, plays a very direct role in these experiments. At low and intermediate energy, however, target response cannot be neglected. Another complication at these energies is that exchange of the scattering electron and the target electrons cannot be neglected. Electrons are always indistinguishable but a large difference in kinetic energy renders them effectively classically distinguishable. According to the virial theorem, the kinetic energy of a target electron is about equal to its ionization potential. Thus if the kinetic energy of the scattering electron is not too much longer than this, electron exchange is very important.

For purposes of computation, it is convenient to break up the effective potential for electron-molecule scattering into the electrostatic potential, an exchange potential, and the rest. For electron scattering, the electrostatic potential is usually called the static potential, and the sum of the static and exchange potentials is called the static-exchange potential. The third part is the difference between the true effective potential and the static-exchange potential; it is called the polarization potential because it would be zero if the charge distribution of the target were not polarized (*i.e.*, perturbed) by the scattering electron. In practice the polarization potential is not obtained by subtraction. There are two reasons. First, the calculation of the true effective potential is equivalent to the complete solution of the scattering problem but even electron-hydrogen atom scattering cannot be solved exactly. Second, the exchange potential and the true effective potential are nonlocal. Whereas a local potential acting on a wave function can be written $V(\vec{r})\psi(\vec{r})$, a nonlocal potential takes the form $\int d\vec{r}' V(\vec{r}, \vec{r}')\psi(\vec{r}')$. In general a nonlocal potential can be written as a potential that depends on the position and local momentum; the connection to the previous statement is that the probability amplitude for momentum involves an integral over the coordinate-representation wave function. The local momentum can be approximated semiclassically, however, in terms of the asymptotic kinetic energy and the local effective potential. Such an approach allows one to approximate the effective potential as a function of position and asymptotic kinetic energy of the scattering electron. Such a potential will be said to be energy-dependent but local in the coordinate representation; examples will be given below.

Having obtained the effective potential one must perform scattering calculations to obtain cross sections. The target has three kinds of degrees of freedom. Its electronic degrees of

freedom are included by means of the effective potential; vibrational and rotational degrees of freedom must be included explicitly in the scattering calculation. The effective collision time (time during which the scattering electron is in strong interaction with the target) is hard to define precisely but a working value for intermediate-energy scattering is on the order of the time required for a 50 eV electron to move $10 a_0$. This requires 3×10^{-16} s, which is comparable to the time constant for bound orbital motion of the valence electrons. The similarity of these time scales is one reason why electronic charge polarization of the target is hard to estimate at intermediate energy; with respect to the collisional perturbation, the electronic coordinates of the target change neither completely suddenly nor completely adiabatically during the collision. The vibrational and rotational time scales are much longer though, about 10^{-14} s and 10^{-12} s, respectively, for N_2 . Thus we can treat the target as a rigid asymmetric potential during the scattering event, and obtain transition matrix elements by a coupled-channels calculation in a target-fixed frame of reference where the scattering electron has a definite molecule-frame symmetry, *e.g.*, Σ_g or Π_g . One can of course also use a laboratory-fixed frame of reference and sometimes this is more convenient. For high orbital angular momentum of the scattering electron and polar targets it is necessary to average the charge-dipole interactions over target rotational motion to get finite cross sections; this is done most conveniently in the laboratory-frame coordinates. In this chapter the initial state of the target is always the ground state. To perform vibrational averaging we simply average over a set of calculations at various internuclear distances; the effect is small. The same set of calculations can also be used to calculate vibrationally inelastic cross sections by the vibrational sudden approximation. The various rotational transitions are not usually resolved experimentally so we define rotationally summed cross sections by summing over all possible final rotational states for a given final vibrational level and electronic state. Integral cross sections may be obtained either by summing the partial cross sections for various symmetries of the scattering electron or by integrating the differential cross sections over scattering angle. Further details of the scattering calculations are given in the original papers.

In the rest of this chapter we will discuss the three components (static, exchange and polarization) of the effective potential one at a time. We will compare various calculations to each other, and we discuss how the calculated cross sections compare to experimental results.

All equations in this chapter are in hartree atomic units, which are discussed in the preface of this book.

II. STATIC POTENTIAL

The classical coulombic interaction between the incident electron at a given position and the unperturbed target charge distribution is the static potential, which is the unifying element in all the chapters in this book. In the rest of the present chapter we follow the usual conventions of the electron scattering literature and call it the static potential rather than the electrostatic potential. In this chapter we define it for the probe charge being negative, which differs from the convention followed in most of the other chapters in this book.

Any of the methods used to calculate the static potential for other applications, as discussed for example by Politzer and Daiker⁷ or used by the other authors in this book, could also be applied for applications to electron scattering. In fact, however, some special methods have been developed in the electron scattering context. One difference between the electron scattering calculations and other classes of applications is that for electron scattering one often uses a single-center expansion of the static potential, *i.e.*, it is expressed in spherical polar coordinates with the origin at the center of mass of the molecule. For example, consider a linear molecule with fixed internuclear distances and its internuclear axis along the unit vector \hat{R} , and let \vec{r} (with magnitude r and direction \hat{r}) be a vector from the center of mass of the molecule to the electron. Then we can write the static potential as

$$V^S(\vec{r}, \hat{R}) = \sum_{\lambda} V_{\lambda}^S(r) P_{\lambda}(\cos \chi) \quad (1)$$

where $\cos \chi = \vec{r} \cdot \hat{R}$. Notice that equation (1) can be and is used at all r , not just at large r where it becomes a multipole series. One way to evaluate $V_{\lambda}^S(r)$ is to expand the molecular electronic density $\rho(\vec{r}, \hat{R})$ around the molecular center of mass

$$\rho(\vec{r}, \hat{R}) = \sum_{\lambda} a_{\lambda}(r) P_{\lambda}(\hat{r} \cdot \hat{R}) \quad (2)$$

and calculate the $V_{\lambda}(r)$ from the $a_{\lambda}(r)$.⁸⁻¹⁰ Another approach, the one we usually use, is to evaluate $V^S(\vec{r}, \hat{R})$ as a one-electron property of the (unreexpanded) molecular charge distribution by standard quantum chemical techniques for a set of χ values at a given r , then to solve for the $V_{\lambda}^S(r)$ by solving linear equations (when results are available for only a few evenly spaced χ) or by Gaussian integration (when results can be generated at the nodes of a Gauss-Legendre grid in $\cos \chi$). To generate the $V_{\lambda}(r)$ for scattering calculations by the Gaussian integration method, we have used 20-32 χ values for N_2 ,

20 for C_2H_2 and 32 for symmetric CO_2 . In these cases one uses symmetry and all the points are located in the $(0, \pi/2)$ interval. For CO and asymmetrically stretched CO_2 , the points are spread over $(0, \pi)$, and we used 48 χ values for these calculations. These numbers of χ values are large enough to converge $V_\lambda(r)$ even for $\lambda > 30$. The above considerations are easily extended to nonrigid molecules, for which V^S , V_λ^S and a_λ all depend on internuclear distance R for a diatomic or on all the vibrational coordinates for a triatomic or larger. For nonlinear molecules one can expand in spherical harmonics about the center of mass or one can use a symmetry-adapted expansion basis.¹¹

Since the electrostatic potential must be calculated at many points (r, χ) for each set of internuclear distances used for scattering calculations, its computation can be time-consuming. For this reason, and because we wish to develop methods well suited to polyatomic molecules, we have explored the validity of semiempirical molecular orbital theory for this quantity. We have studied N_2 and CO at their equilibrium geometries in the most detail. Table 1 compares three *ab initio* calculations of $V_0(r)$ to two calculations employing semiempirical molecular orbital theory. The calculations denoted by numbers in brackets are *ab initio* matrix Hartree-Fock calculations, and the numbers in the brackets are the number of contracted-basis-functions subshells of each symmetry at each nucleus. The calculation denoted [432] is for an extended basis set including two d subshells at each nucleus. These results

Table 1. Spherical average of $V^S(\vec{r})$ for N_2^a

(a_0)	$V_0^S(r)$ (eV)				
	[432]	[53]	[21]	INDO/1s	INDOXI/1s
0.0	-51	-57	-66	-64	-48
1.0	-88	-90	-95	-91	-83
1.6	-22	-23	-25	-21	-19
2.0	-8.3	-8.5	-9.4	-7.2	-6.2
2.2	-5.0	-5.1	-5.8	-4.0	-3.5

^a $R = 2.068 a_0$. Reference 12.

are very accurate and serve as a standard. The [53] basis is better than "double-zeta" quality but has no d functions, and the [21] basis is a minimum basis set of atomic SCF functions (a "minimum basis set" for C, N or O consists of two s subshells and one p subshell at each nucleus). The INDO/1s calculation is a semiempirical molecular orbital calculation by the intermediate-neglect-of-differential-overlap valence-shell SCF method of Pople and coworkers (INDO),¹³ but augmented after the SCF stage to explicitly include atomic 1s orbitals in the charge density. The result may be considered an approximate minimum-basis-set matrix Hartree-Fock calculation. The INDOXI/1s result is similar except that the intra-atomic 2s-2p element of the INDO density matrix is neglected in calculating the static potential; this exclusion was originally suggested¹² as a way to make the static-potential calculation more consistent with the INDO approximations made in the SCF calculations. The main point illustrated by Table 1 is that, at least at small r, there is no advantage in *ab initio* calculations over the semi-empirical ones unless one uses an extended basis set including d functions in the former.

Table 2 includes two additional methods and shows some values for $V_2^S(r)$ and $V_4^S(r)$ as well as $V_0^S(r)$. For $\lambda > 0$, $V_\lambda^S(r=0)$ is zero and $V_\lambda^S(r)$ is strongly peaked at $r = \frac{1}{2}R_e$, where R_e is the N_2 bond distance (2.068 a_0); see, *e.g.*, Figure 1. At large r, the $V_\lambda(r)$ for $\lambda > 0$ are dominated by the permanent multipole moments of the target. *E.g.*,

$$V_2(r) \underset{r \rightarrow \infty}{\sim} -\theta/r^3 = -Q/(2r^3) \quad (3)$$

where θ and Q are two ways to define the quadrupole moment. The multipole expansion is valid when the scattering electron is far from the target so that the electron-electron and electron-nucleus interactions largely cancel. *E.g.*, Table 3 gives the electronic and nuclear contributions to the quadrupole moment θ , as calculated from two *ab initio* electronic wave functions: the Cade-Sales-Wahl (CSW) wave function with a basis set near the Hartree-Fock limit and another, the [53] wave function, with a better-than-double-zeta basis set. Although the electronic contributions differ by only 5%, the net quadrupole moments differ by a factor of 1.9. This illustrates that a quantity involving extensive cancellation like the quadrupole moment is hard to calculate accurately; thus neither INDO/1s nor INDOXI/1s is expected to lead to an accurate value. As a result, Table 2 shows that these methods do not yield accurate $V_2^S(r)$ at large r although they do yield reasonably accurate $V_2^S(r)$ and $V_4^S(r)$ at small r. In the INDOX/1s method,^{15,16} we multiply the 2s-2p intra-atomic density matrix element, neglected in INDOXI/1s, by a constant X and determine X to make the quadrupole moment come out right. This yields $X = 0.19$, and Table 2 shows that it yields

Table 2. Legendre components of the static potential for N_2
for $r = 0.8, 1.6, 2.2$ and $4.0 a_0^a$

λ	$V_\lambda^S(r)$ (eV)				
	[432] ^b	INDO/1s ^b	INDOXI/1s ^b	INDOX/1s ^c	SSA ^d
0	-74 ^e	-80	-70	-72	-72
	-22	-21	-19	-19	-20
	-5.0	-4.0	-3.5	-3.6	-4.4
	-0.03	-0.01	-0.01	-0.01	-0.03
2	-149	-146	-148	-148	-146
	-47	-40	-46	-45	-46
	-8.2	-2.6	-7.4	-6.4	-8.5
	0.31	1.15	0.15	0.34	-0.05
4	-99	-99	-100	-99	-99
	-26	-25	-27	-27	-27
	-2.6	-1.9	-3.2	-2.9	-3.7
	0.13	0.17	0.05	0.07	0.01

^a $R = 2.068 a_0$.

^bReference 12.

^cReference 16.

^dReference 18.

^eTop value is for $r = 0.8 a_0$; successive values are for $r = 1.6, 2.2$ and $4.0 a_0$, respectively.

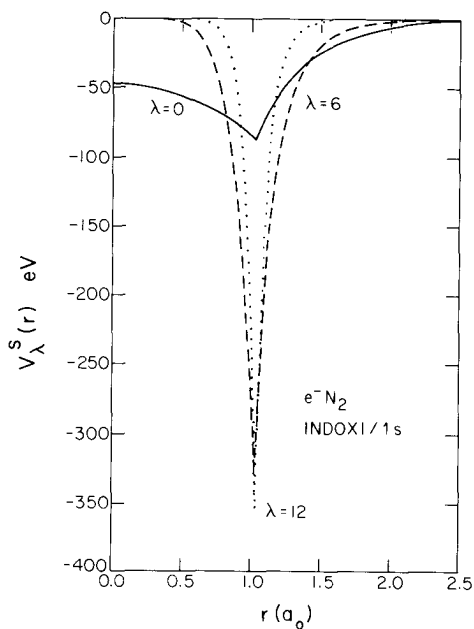


Figure 1. Some Legendre components of the static potential for N_2 at $R = 2.068 a_0$ as calculated by the INDOXI/1s method (references 12, 77 and 78). The spherical average ($\lambda = 0$) and the $\lambda = 6$ components are solid and dashed curves, respectively; the $\lambda = 12$ component is a dotted curve.

Table 3. Contributions to the N_2 quadrupole moment (in atomic units) as calculated from two *ab initio* wave functions^a

<u>Wave function</u>	<u>Electronic</u>	<u>Nuclear</u>	<u>Total</u>
CSW ^b	-15.9160	14.9682	-0.9478
[53] ^c	-16.7581	14.9682	-1.7899

^a $R = 2.068 a_0$.

^bCade, Sales, Wahl (reference 14).

^cReference 12.

a reasonably accurate static potential, although $V_0^S(r)$ does decrease too rapidly at large r . That problem can be traced to the use of Slater's values for the exponential parameters in the INDO orbital basis.¹³ One way to incorporate the more accurate orbital tails is to use a minimum basis set with optimized exponential parameters.¹⁷ The SSA method in Table 2 is in this spirit but even simpler. It stands for sum of scaled atoms and it corresponds to a sum of two scaled atomic static potentials.¹⁸ A distribution of spherical densities centered at the atoms has no permanent multipole moments so $V_\lambda^S(r)$ calculated this way decreases too rapidly at large r for $\lambda > 0$, but Table 2 shows that the small- r static potentials obtained by this method are of useful accuracy.

To converge the scattering calculations one must use very high values of λ , *e.g.*, for N_2 , $\lambda \geq 28$ is necessary, with the precise upper limit depending on the incident energy and the symmetry of the scattering-electron wave function.^{20,21} For $\lambda > 14$, however, the electron-electron contribution is negligible compared to the electron-nuclear contribution, which may be obtained analytically.^{12,20} Furthermore, it causes negligible error in the scattering results if the $\lambda = 6-14$ contributions are evaluated by the INDO/ls method, as long as the 0-4 contributions are evaluated accurately.²¹ These considerations are illustrated by Figure 1 which shows that the higher- λ components of $V^S(r)$ for N_2 are well localized near $r = R/2$, where $R/2$ is the distance of a nucleus from the center of mass.

Thus the simpler methods of calculating the static potential give realistic values for $\lambda \leq 4$ and are entirely adequate for $\lambda > 4$. Table 4 illustrates how much the quantitative errors in the static potential effect the partial cross sections. In this table, calculations are shown for two different ways of calculating the effective potential. In both cases it is the sum of a static, an exchange, and a polarization part; the exchange part is calculated by the semiclassical exchange approximation discussed below; and the polarization part is the semiempirical polarization potential of Morrison and Collins.²⁰ For both sets of 13.6 eV calculations, 15 coupled channels were retained in the scattering calculations for each symmetry, and for all 30 eV calculations 24 coupled channels were retained. Thus the only difference between the two sets of calculations is in the source of the electronic density for calculation of the static and exchange potentials: for one set it is obtained from the accurate wave function of Cade, Sales and Wahl;^{14,20} for the other it is obtained by the INDO/ls method.^{12,21} Thus the table is a test of how the scattering results are affected by the errors in the INDO/ls density. At an impact energy of 13.6 eV, roughly on the borderline between low and intermediate energy, there is a large error in the INDO/ls partial cross section for Π_g symmetry, which is resonant at low

Table 4. Partial cross sections for electronically elastic scattering of rigid N_2 by electrons in the static-exchange-plus-polarization approximation^a at two impact energies with two different target wave functions

Symmetry	$\sigma^{MP} (a_0^2)^b$			
	13.6 eV ^c		30 eV ^d	
	CSW	INDO/1s	CSW	INDO/1s
Σ_g	12.0	12.6	6.2	6.3
Π_g	1.4	8.4	3.1	5.5
Δ_g	9.4	9.8	6.4	6.8
Φ_g	0.1	0.1	0.4	0.4
Σ_u	8.6	11.7	6.9	10.4
Π_u	6.2	8.2	11.7	11.3
Δ_u	1.3	0.8	3.0	2.2
Φ_u	0.8	1.2	1.3	1.6
SUM	39.8	52.8	39.0	44.6

^aAll calculations use semiclassical exchange and the Morrison-Collins (reference 20) polarization potential. R is $2.068 a_0$.

^bVibrationally, electronically elastic cross section summed over final rotational states.

^cReference 21.

^dReference 22.

energy, and there are 30-50% errors for Σ_u , Π_u , Δ_u and ϕ_u . As a result the INDO/1s integral cross section, summed through $M = 4$, is too large by 33%.²¹ At 30 eV the errors in the Π_g and Π_u partial cross sections are much smaller and the integral cross sections, summed through $M = 4$, is overestimated by only 14%.²² This is an acceptable error, especially considering the uncertainties in the polarization potential and the considerable gain in simplicity obtained by using the INDO/1s method. These results give us confidence that reliable calculations could be performed using the INDO/1s method for large polyatomics where more accurate *ab initio* calculations would be prohibitively difficult or expensive.

In conclusion the above comparisons show that one can obtain the qualitative features of the static potential from very simple models of the molecular charge distribution. Basically the static potential is a set of screened coulomb potentials centered at the atoms, and it can be obtained realistically for small r if the screening orbitals have a realistic size. Similar accuracy was obtained for CO as for N_2 , with the region of good quantitative accuracy being $r \lesssim 2.3 a_0$ in both cases.¹⁹ At large r there is extensive cancellation, and accurate multipole moments must be used if the weak long-range anisotropic tails on the potential are to be realistic. The scattering results at low energy, especially for resonant symmetries, are very sensitive to the quantitative accuracy of the potential; but the simple methods of calculating the scattering potential can give good accuracy for the scattering results at intermediate energy.

III. EXCHANGE POTENTIAL

The Hartree-Fock exchange potential is a direct consequence of antisymmetrizing the wave function and asking for the variationally best orbitals. The equations for the variationally best orbitals contain and thereby define the Hartree-Fock exchange potential. Because this is a nonlocal potential it greatly increases the expense of solving the coupled-channels scattering equations, and until recently the Hartree-Fock exchange potential was not included properly in any electron-molecule scattering calculations for targets larger than H_2 . Nevertheless exchange interactions are very important at low and intermediate energy. Thus there is great interest in approximate exchange potentials that are local and hence easier to use.

The most popular exchange potential for bound-state electronic structure calculations on molecules and solids is the free-electron-gas exchange (FEGE) approximation, which has its origin in Thomas-Fermi-Dirac theory. The FEGE exchange potential is

$$V^{\text{FEGE}}(\vec{r}) = -\frac{2}{\pi} K_{\text{F}}^{\text{F}}(\eta) \quad (4)$$

where

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \quad (5)$$

$$\eta = K/K_{\text{F}}(\vec{r}) \quad (6)$$

K is the local momentum of the electron under consideration and K_{F} is the Fermi momentum

$$K_{\text{F}}(\vec{r}) = [3\pi^2\rho(\vec{r})]^{1/3} \quad (7)$$

Slater²³ derived an average exchange potential for a bound system by averaging $F(\eta)$ over the Fermi sphere. This yields equation (4) with $F(\eta)$ replaced by $3/4$, and the resulting potential is proportional to $[\rho(\vec{r})]^{1/3}$. Gaspar²⁴ and Kohn and Sham²⁵ gave alternate derivations in which $F(\eta)$ is replaced by its value at the surface of the Fermi sphere. This gives the same form as used by Slater with $3/4$ replaced by $1/2$. For bound-state calculations this constant is often replaced by a variable parameter, called $\frac{3}{4}\alpha$.²⁶ Although the $\rho^{1/3}$ potential has been used for scattering calculations, it is really inappropriate for that purpose because the scattering electron is not an average electron in the Fermi sea. Rather it has a particular higher energy exceeding that at the surface of the Fermi sphere by the ionization potential I plus the scattering kinetic energy $\frac{1}{2}k^2$. This was first pointed out by Hara²⁷ who suggested determining K in equation (6) by

$$K^2(\vec{r}) = K_{\text{F}}^2(\vec{r}) + 2I + k^2 \quad (8)$$

Other procedures have also been suggested^{20,28-31} for determining $K^2(\vec{r})$, but equation (8) has been the most widely used. Equations (4) - (8) define the Hara free-electron-gas exchange (HFEGE) potential. It clearly has a complicated dependence on $\rho(\vec{r})$.

Local exchange potentials can also be derived by expanding the Hartree-Fock exchange kernel.^{28,32,33} Here we review the derivation of reference 28. Consider the nonlocal exchange operator \hat{V}_{ijj}^{E} defined by

$$\hat{V}_{ijj}^{\text{E}} f_j(\vec{r}_1) = M_{ij}(\vec{r}_1) \phi_j(\vec{r}_1) \quad (9)$$

where $f_j(\vec{r}_1)$ is a scattering wave function, $\phi_j(\vec{r}_1)$ is a bound orbital,

$$M_{ij}(\vec{r}_1) = \left\langle \phi_i(\vec{r}_2) \left| \frac{1}{r_{12}} \right| f_j(\vec{r}_2) \right\rangle \quad (10)$$

and the Dirac notation is used for an integral over \vec{r}_2 . Assume

$$M_{ij}(\vec{r}) \cong A_{ij}(\vec{r}) f_j(\vec{r}) \quad (11)$$

where $A_{ij}(\vec{r}_1)$ is slowly varying so that

$$\nabla^2 M_{ij}(\vec{r}) \cong A_{ij}(\vec{r}) \nabla^2 f_j(\vec{r}) \quad (12)$$

This is a semiclassical approximation equivalent to assuming that the scattering electron has a small deBroglie wavelength on the atomic scale. This approximation and the identity

$$\nabla^2 M_{ij}(\vec{r}) = -4\pi \phi_i(\vec{r}) f_j(\vec{r}) \quad (13)$$

yield a functional relationship of the form

$$\hat{V}^E \cong V^E \left[\kappa_j^2(\vec{r}_1), \rho(\vec{r}_1) \right] \quad (14)$$

where κ_j^2 is the local momentum defined by

$$\left[\nabla_1^2 + \kappa_j^2(\vec{r}_1) \right] f_j(\vec{r}_1) = 0 \quad (15)$$

and $\rho(\vec{r}_1)$ is the electron density $|\phi_i(\vec{r}_1)|^2$. By assuming that V^E is local, we can express $\kappa_j^2(\vec{r}_1)$ as a function of the impact energy E , the static potential $V^S(\vec{r}_1)$, and the local exchange potential $V^E(\vec{r}_1)$. Then equation (14) becomes a quadratic equation for $V^E(\vec{r}_1)$ which can be solved to yield what we call the semiclassical exchange (SCE) potential.²⁸ For closed-shell targets it becomes the following attractive potential²⁸

$$V^{\text{SCE}}(\vec{r}) = \frac{1}{2} \left[E - V^S(\vec{r}) \right] - \frac{1}{2} \left\{ \left[E - V^S(\vec{r}) \right]^2 + 4\pi\rho(\vec{r}) \right\} \quad (16)$$

By using Thomas-Fermi theory we can express the semiclassical exchange potential for electron-rare gas scattering in the low-energy limit in terms of $\rho(\vec{r})$ alone. Although we do not do this for actual

calculations, it makes for an interesting comparison with the familiar $\rho^{1/3}$ potential. We obtain²⁸

$$v^{\text{SCE}}(\vec{r}) \underset{\substack{E \rightarrow 0 \\ r \rightarrow 0}}{\sim} - \frac{2\pi}{(3\pi^2)^{2/3}} [\rho(\vec{r})]^{1/3} \quad (17)$$

$$v^{\text{SCE}}(\vec{r}) \underset{\substack{E \rightarrow 0 \\ r \rightarrow \infty}}{\sim} - [\pi\rho(\vec{r})]^{1/2} \quad (18)$$

We can find the high-energy limit without using any Thomas-Fermi relations.²⁸

$$v^{\text{SCE}}(\vec{r}) \underset{E \rightarrow \infty}{\sim} = \frac{\pi\rho(\vec{r})}{E - V^{\text{S}}(\vec{r})} \quad (19)$$

The limit in equation (18) is called the high-energy exchange (HEE) approximation;²⁸ the HFEGE potential also tends to this limit. Thus the two quite different methods lead to the same high energy limit, and we expect in general that they become more similar and more reliable as the impact energy increases. At even higher energies where the denominator of equation (19) may be replaced by E , the high-energy approximation becomes equivalent to the Fourier transform of the high-energy limit of the exchange scattering amplitude derived by Bonham³⁴ and Ochkur.³⁵

Table 5 gives some examples²⁸ of scattering phase shifts for electron-He and electron-Ar scattering calculated in the static-exchange approximation. In these calculations, exchange is treated by the Hartree-Fock nonlocal kernel^{36,37} and by the three different local exchange potentials. For the cases shown, and for many other cases for electron-atom scattering,^{28,30} the SCE potential is the most accurate of the local approximations, but the HFEGE potential and sometimes even the HEE potential also give useful accuracy. There have now been several extensive tests of these and other local exchange potentials against accurate exchange for electron-atom scattering;^{28,30,38-40} the general conclusion from this work is that local approximations are capable of representing the exchange effect with good absolute accuracy at intermediate and high energy and sometimes even at low energy. Our attitude, however, is that nonlocal exchange should generally be used for accurate nonempirical calculations at impact energies below about 10 eV.

Table 5. Phase shifts for electron-He and electron-Ar scattering calculated in the static-exchange approximation with various approximations to exchange

ℓ^a	E (eV)	n_ℓ (rad)				
		<u>XE</u> ^b	<u>Hartree-Fock exchange</u> ^c	<u>HFEGE</u> ^d	<u>SCE</u> ^d	<u>HEE</u> ^d
He						
0	16.46	1.36	1.80	1.69	1.77	1.84
	54.42	1.08	1.28	1.24	1.26	1.27
1	16.46	0.07	0.21	0.14	0.22	0.27
	54.42	0.20	0.33	0.27	0.32	0.33
Ar						
0	21.26	7.10	7.46	7.47	7.46	7.50
	54.42	6.42	6.72	6.69	6.66	6.68
1	21.26	0.51	1.39	1.17	1.32	1.47
	54.42	1.50	1.84	1.87	1.84	1.86

^aOrbital angular momentum of scattering electron.

^bNo exchange. Reference 28.

^cExact exchange. References 36 and 37.

^dLocal exchange. Reference 28.

One advantage of the semiclassical exchange approximation and the high-energy approximation, as compared to free-electron-gas methods, is that they can be applied to the nondiagonal exchange operators \hat{V}_{ijk}^E that occur in calculations of electronically inelastic scattering.^{28,39,40} This is illustrated in Table 6, which shows partial cross sections for excitation of the 2s state of H.³⁹ The standard for comparison is a 2-state calculation (in a bound-state context, this would generally be called a 2-configuration calculation) with nonlocal exchange.⁴¹ Again the local exchange approximations are reasonably accurate, although the errors for electronically inelastic scattering are somewhat larger than those for electronically elastic scattering.

Local exchange potentials have also been tested against calculations^{20,42-44} employing nonlocal exchange kernels for electron-molecule scattering, in particular for electronically elastic scattering by H₂^{20,45,46} and N₂.²² An example²² of the results is given in Table 7. This table shows that the HFEGE potential yields results very similar to Hartree-Fock treatment of exchange even at an energy as low as 13.6 eV, with the biggest difference occurring for Δ_g symmetry. The SCE potential does almost as well or better for most symmetries but does very poorly for the Π_g symmetry. As already mentioned, the Π_g scattering has a resonance at low energy, and this resonance causes a great sensitivity to approximations

Table 6. Partial cross sections for the 1s-2s excitation of H by electrons as calculated by 2-state close coupling with various approximations to exchange at an impact energy of 54.4 eV for the triplet spin coupling

ℓ	$\sigma_{1s-2s} (a_0^2)$			
	<u>XE^a</u>	<u>Hartree-Fock exchange^b</u>	<u>SCE^c</u>	<u>HEE^c</u>
0	0.049	0.021	0.026	0.026
1	0.125	0.068	0.081	0.031
2	0.102	0.086	0.089	0.089

^aNo exchange; reference 39.

^bNon-local exchange; reference 41.

^cLocal exchange; reference 39.

Table 7. Partial cross sections for electronically elastic scattering of electrons by N_2 in the static-exchange approximation^a at 13.6 eV impact energy with various approximations to exchange

Symmetry	$\sigma^{MP} (a_0^2)^b$		
	Hartree-Fock exchange ^c	SCE ^d	HFEGE ^d
Σ_g	11	13	12
Π_g	10	4	9
Δ_g	3.2	2.5	1.5
Σ_u	12	9	11
Π_u	12	10	12
Δ_u	0.1	0.15	0.1
SUM	48	38	46

^aAll calculations use the CSW wave function (reference 14) for the target.

^bVibrationally, electronically elastic cross section summed over final rotational states.

^cReference 44.

^dReference 21.

even at 13.6 eV. A detailed study²² of the low-energy scattering shows that the SCE is too attractive at low energy for N_2 and apparently predicts the resonance to be a bound state. As the energy is raised the HFEGE and SCE approximations are expected to become more accurate and to agree better with one another. The accuracy cannot be verified directly because there are no calculations including Hartree-Fock exchange for energies greater than 13.6 eV,* but the increasing similarity of the two approximate

*Later in this chapter we discuss the comparison of calculations to experiment for energies greater than 13.6 eV, but this tests the whole static-exchange-plus-polarization potential, not just the exchange approximation.

treatments of exchange is demonstrated by the differential cross sections^{47,48} in Table 8. The differential cross sections in this table are for 30 eV impact energy and are summed over all final rotational states. The rotationally summed differential cross sections computed with the SCE and HFEGE potentials agree very well over the whole angular range, with the largest difference being 14% for forward scattering ($\theta = 0^\circ$). The rotationally summed integral cross sections computed from the differential cross sections in Table 8 are $39 a_0^2$ for the SCE potential and $42 a_0^2$ for the HFEGE potential, differing by 7%. All state-to-state rotationally inelastic differential cross sections agree within 13% or better, and all state-to-state rotationally inelastic integral cross sections agree to 10% or better.

Table 8. Differential cross sections as functions of scattering angle for electronically elastic scattering of electrons by rigid-rotor N_2 in the static-exchange-plus-polarization approximation^a at 30 eV impact energy with two different approximations to exchange.

θ (deg)	$d\sigma/d\Omega$ (a_0^2/sr) ^b	
	SCE ^c	HFEGE ^d
0	37	42
30	8.5	9.5
60	1.7	1.8
90	0.50	0.53
120	1.5	1.5
150	4.3	4.3
180	6.9	7.0

^aAll calculations use the INDOX/1s wave function (reference 16) for the target and the INDOX/AAP (reference 16) polarization potential.

^bVibrationally, electronically elastic cross section summed over final rotational states.

^cReference 47.

^dReference 47 and 48.

The electron-atom tests also showed that the SCE potential sometimes becomes too attractive at low energy.^{28,30,38} The HFEGE potential works better at low energy, but free-electron-gas exchange potentials have the incorrect functional form near the origin, where they are too attractive.³⁰ Yau *et al.*⁴⁹ have suggested a new potential, the joined semiclassical-Hara exchange (JSHE) potential, which is formed by joining the SCE potential in the inner region with the HFEGE potential in the outer region at their point of intersection. Since the local kinetic energy is larger in the inner region, this corresponds to using the SCE potential at high local kinetic energy, where the semiclassical expansion of the nonlocal exchange kernel is most valid. However, it is doubtful that the JSHE potential will lead to overall improvement since the HFEGE potential is not attractive enough at large r .^{22,28} Also the JSHE potential is always less attractive than both the SCE and HFEGE potentials, but the HFEGE potential itself is often insufficiently attractive at both low and intermediate energy, and the SCE potential is often insufficiently attractive at intermediate energy.²⁸ The problem with the HFEGE potential at large r can be corrected by using the asymptotically adjusted free-electron-gas exchange (AAFEGE) potential, but the AAFEGE potential is even more attractive than the too attractive HFEGE potential at small r .²⁸ Morrison and Collins⁵⁰ found that the AAFEGE potential is too strong for electron-H₂ scattering at $E < 3$ eV, but that it is quite accurate already at $E = 5$ eV. For electron-atom scattering, the AAFEGE potential is more accurate than the HFEGE potential for high enough ℓ .²⁸ The HFEGE potential is insufficiently attractive at high ℓ for electron-atom scattering²⁸ and at high M for electron-molecule scattering.²²

Another procedure that has been suggested is "tuning" the free electron gas potentials to predict a resonance energy position at low energy where the scattering results are very sensitive to exchange.²⁰ This might be useful for studies over a limited energy range, but the "tuned potentials" might well be less accurate than the untuned ones at intermediate energy.

Even by conservative standards it is already clear that the SCE potential is quite reliable for impact energies greater than about 30 eV, but in some cases one or more of the local exchange potentials is quite accurate down to much lower energy. Further work will be required to delineate the accuracy that can be expected from the various local approximations for different targets, orbital angular momenta and symmetries, and impact energies.

There is another promising method for conveniently including the exchange effect in scattering calculations. Instead of including the nonlocal operators from the beginning, one determines radial wave functions for the scattering electron either by

neglecting exchange or by a local approximation. Then these radial wave functions are used to define a trial wave function which is antisymmetrized and inserted into a variational functional. This leads to exchange integrals but not to the more complicated situation, integrodifferential equations, which obtains if the antisymmetrization step is performed before determining the radial wave functions. This idea has now been applied successfully to a sequence of increasingly more complicated cases.⁵¹

IV. POLARIZATION POTENTIAL

Next we consider the inclusion of charge polarization effects. The rigorous way to include these in an effective potential is the exact-optical-potential method, in which the optical potential is defined so that the electronically elastic scattering amplitude is exact.⁵²⁻⁵⁴ The exact optical potential is energy-dependent, non-local, and too hard to calculate; thus we shall be satisfied with approximations. In particular we shall examine energy-dependent, local approximations obtained by adding another term to the static-exchange potentials already considered. In principle the new term should be complex, *i.e.*, have a nonzero imaginary part. The real part represents the effect of virtual charge polarization and is called the polarization potential. The imaginary part accounts for electronically inelastic scattering, *i.e.*, loss of flux from channels corresponding to the initial electronic state, and is called the absorption potential. The imaginary part of the optical potential is thus rigorously zero at energies below the first electronic-excitation threshold but not at intermediate energy. Recently several groups have applied complex, local optical-potential models to electron-atom scattering at intermediate energy.^{32,33,55-59} There has also been some use of complex, nonlocal optical-potential models for intermediate-energy electron-atom scattering.⁶⁰⁻⁶² At Minnesota, we have applied optical-potential models to intermediate-energy electron-molecule scattering. In this work, which is discussed next, we have neglected the imaginary part of the optical potential. At the end of this section we will discuss an approach, called the matrix effective potential (MEP) model,^{63,64} in which the imaginary part is included implicitly by treating the optical potential as a 2×2 real matrix.

As an important part of our program to develop more accurate models of the polarization potential, we⁶⁵⁻⁷⁰ have been calculating *ab initio* adiabatic polarization potentials for both electron-atom and electron-molecule scattering. In the adiabatic approximation,^{53,54,71-76} the scattering electron is assumed distinguishable from the bound electrons, and the target is assumed to respond completely to the scattering electron as if it were a fixed perturbing charge. Thus the position of the scattering electron is treated as

a slowly varying parameter in the target Hamiltonian. In this approximation the scattering electron is treated on the same footing that a nucleus is treated in the electronically adiabatic separation of electronic and internuclear motion. To include polarization of the target's charge distribution by the adiabatic approximation, we fix the position of the scattering electron at \vec{r} and recalculate the wave function for the target in the presence of this fixed perturbing charge. The difference between the energy calculated this way and the energy of an isolated target system is the sum $v^{\text{SPa}}(\vec{r})$ of the static and adiabatic polarization potentials. Subtracting the static potential $v^{\text{S}}(\vec{r})$ or adding the exchange potential $v^{\text{E}}(\vec{r})$ yields the adiabatic polarization potential $v^{\text{Pa}}(\vec{r})$ or the static-exchange-plus-adiabatic-polarization potential $v^{\text{SEPa}}(\vec{r})$, respectively.

As discussed elsewhere,^{68,70} to calculate accurate adiabatic polarization potentials it is necessary to use extended basis sets including both bond-polarization functions and diffuse functions. The latter are necessary to represent the perturbation caused by the scattering electron. The resulting adiabatic polarization potential generally dominates the static potential for a wide range of electron-molecule relative positions, especially at large distances of approach. For example, for approach of a scattering electron to N_2 along the perpendicular bond-bisector, $|v^{\text{Pa}}(\vec{r})|$ exceeds $|v^{\text{S}}(\vec{r})|$ from about $r = 2 a_0$ to $r = 10 a_0$, and for the same direction of approach of a scattering electron to Li_2 , $|v^{\text{Pa}}(\vec{r})|$ exceeds $|v^{\text{S}}(\vec{r})|$ for all r less than about $17 a_0$. These and some other cases are summarized in Table 9. The conclusion to be drawn is that polarization effects, at least as calculated with the adiabatic approximation, are often dominant over some range from medium r to a large enough r that the interaction is negligible or almost negligible. Furthermore, for large electron-target separations and intermediate-energy incident electrons, the perturbation is small enough and the scattering electron is moving slow enough that the adiabatic approximation might give realistic results. The large- r interactions dominate the large-impact-parameter, small-scattering-angle collisions and so we expect small-angle electronically elastic scattering to be dominated by polarization effects at intermediate impact energies. The small- r region is harder to treat. The interaction of the scattering electron with the nuclei is strong; this interaction is fully included in the static potential; thus the static potential dominates near the nuclei. In the middle region where the static potential and polarization potential are comparable and are both large, the polarization potential cannot be neglected but it cannot be calculated with the adiabatic approximation (both because the interaction is larger and also because the large static potential speeds up the scattering electron). We⁷⁷ have performed tests of the sensitivity of differential cross sections to the small- r polarization potential. In particular we examined the electronically elastic scattering by rigid N_2 and

Table 9. Range of distances over which $|v^{Pa}(\vec{r})|$ exceeds $|v^S(\vec{r})|$ for collinear ($\chi = 0^\circ$) and perpendicular-bisector ($\chi = 90^\circ$) approach of an electron to various targets

<u>Target</u>	<u>χ (deg)</u>	<u>Δr (a_0)</u>
H_2^a	0	2.2 - 7
	90	0.9 - 11
Li_2^b	90	0.0 - 17
N_2^c	0	2.5 - 7
	90	2.0 - 10

^aInterpolated from reference 66.

^bInterpolated from reference 67.

^cInterpolated from reference 68.

summed the cross sections over all final rotational states. This yields what we call the electronically, vibrationally elastic, rotationally summed cross section or, for short, the rotationally summed cross section. For 30 eV incident electrons, the greatest sensitivity of the rotationally summed differential cross section to the small- r effective potential was found for scattering angles θ near 85° , *i.e.*, for approximately sideways scattering. In the example showing the greatest sensitivity, changing the polarization potential such that the maximum magnitude of its spherical average increased from 4 eV to 18 eV changed the rotationally summed differential cross section at 85° by a factor of 1.8.

Figure 2 compares three calculated differential cross sections^{47,69,78} for electron scattering by rigid N_2 at 30 eV to experimental results.^{79,80} All the differential cross sections in this figure are for electronically, vibrationally elastic scattering but are summed over final rotational states. One calculation is in the static-exchange approximation, *i.e.*, polarization is neglected. In this calculation the differential cross section for $\theta < 30^\circ$ is seriously underestimated. This means that the large- r effective potential, which controls the scattering at small scattering angles, is seriously underestimated when polarization is neglected. For another calculation in Figure 2, the polarization

potential is the *ab initio* extended-basis-set adiabatic one.^{68,69} The spherical average of this polarization potential for N₂ has a well depth of 13 eV. The figure shows that the differential cross section for $\theta = 60^\circ - 100^\circ$ is overestimated by a factor of about 1.4 - 2.2. The model studies⁷⁷ mentioned in the previous paragraph show that this overestimate corresponds to too much attraction in the small-*r* effective potential. Figure 2 also shows a curve that is in good agreement with the experimental results for both near-forward and near-sideways scattering. For this curve polarization is treated in the INDOX/AAP model.¹⁶ The first step in this model is to calculate the polarization by the adiabatic method using the INDOX molecular orbital formalism with X adjusted to the static potential. Since the INDOX formalism is a minimum-basis-set method, it seriously underestimates the adiabatic polarization potential; thus the well depth of the spherical average of the INDOX polarization potential for N₂ is only 3 eV. The next step is to expand the polarization potential

$$V_\lambda^P(\vec{r}, \hat{R}) = \sum_{\lambda=0}^P \max_{\lambda} V_\lambda^P(r) P_\lambda(\hat{r} \cdot \hat{R}) \quad (20)$$

Notice that

$$V_\lambda(r) \underset{r \rightarrow \infty}{\sim} - \frac{\alpha_\lambda}{2r^4} \quad \lambda = 0, 2 \quad (21)$$

and

$$r^4 V_\lambda(r) \underset{r \rightarrow \infty}{\sim} 0 \quad \lambda \neq 0, 2 \quad (22)$$

where α_0 is the spherical average of the static (*i.e.*, zero-frequency) electric dipole polarizability, α_2 is its anisotropy, and all odd- λ terms vanish at all *r* for homonuclear diatoms. As discussed above on the theoretical grounds of the size of the perturbation and also on the empirical grounds of the comparison to experiment of the differential cross section calculated from the adiabatic model, we expect that the adiabatic approximation is realistic at large *r* but that it overestimates the effective potential at small *r*. Thus we decided to create a hybrid potential composed of the INDOX one at small *r* and the accurate adiabatic one at large *r*. Although the INDOX method seriously underestimates V_0^{Pa} and α_0 , it is systematically more accurate for α_2 . Thus we defined the INDOX/AAP polarization potential so that it is given by the INDOX polarization potential for $\lambda = 0$ at small *r* and for $\lambda > 0$ at all *r* but equals the accurate asymptotic adiabatic polarization

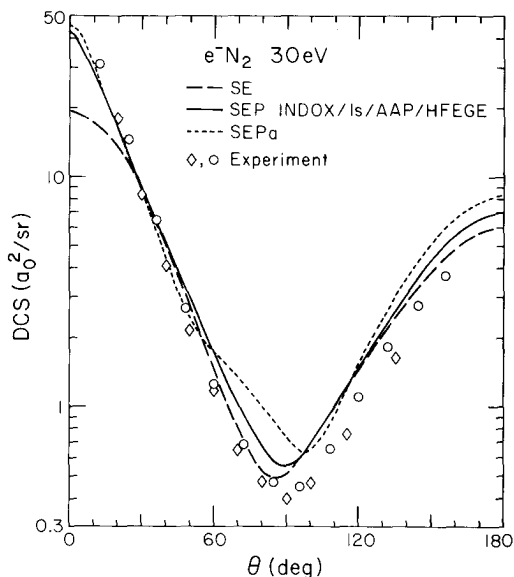


Figure 2. Rotationally summed differential cross sections for electronically elastic scattering of electrons by rigid N_2 at 30 eV impact energy. The curve labelled SE is a static-exchange result for the INDOX/1s static potential and density and the semiclassical exchange approximation. This calculation is from Onda and Truhlar (reference 78). The curve labelled SEP INDOX/1s/AAP/HFEGE is a static-exchange-plus-polarization result for the INDOX/1s static potential and perturbed density, the Hara free-electron-gas exchange approximation, and the INDOX/AAP model for the polarization potential. This is potential ix of Onda and Truhlar (references 47 and 81), and the differential cross section is an unpublished calculation of Onda and Truhlar based on rotational-orbital basis set XX/2-6 of Onda and Truhlar (references 48 and 81). Less well-converged calculations of the differential cross section for this potential were published in Truhlar *et al.* (reference 69) and Onda and Truhlar (reference 47). The curve labelled SEPa is a static-exchange-plus-adiabatic-polarization result in which the accurate static potential of Rumble and Truhlar (reference 21), based on the Cade-Sales-Wahl wave function, and the accurate adiabatic polarization potential of Eades *et al.* (reference 68) are substituted for the static and polarization parts of the $\lambda = 0$ and $\lambda = 2$ terms in potential ix. The differential cross section is based on that in Truhlar *et al.* (reference 69), where the potential is called potential x. Since J_{\max} for that calculation is only 20, the

Figure 2 (continued)

differential cross section is not converged for $\theta < 5^\circ$, and the results are corrected for that in the present figure (the correction is about 7% at 0°). The experimental results are shown as symbols. The diamonds are from the experimental results of Srivastava *et al.* (reference 79), as re-analyzed by Onda and Truhlar (reference 48). The circles are the experimental results of Shyn and Carignan (reference 80).

potential for $\lambda = 0$ for large r . Details of the joining are given elsewhere.¹⁶ The physical motivation behind the choice of a minimum-basis-set polarization potential for small r is that when the scattering electron gets speeded up by the strongly attractive static potential at small r , the target does not have time to polarize into the full Hilbert space. Rather it gets polarized only into "nearby" regions of Hilbert space. Although this motivates reducing the variational freedom for the small- r polarization potential, it does not justify the precise choice of the INDOX formalism. That choice, however, can be and has been tested empirically by applications to several molecules,^{16,48,69,81-84} such as in Figure 2. Figure 2 shows that the INDOX/AAP model provides a reasonable treatment of charge polarization effects for N_2 at 30 eV.

A very commonly used form for the polarization potential is

$$V^P(\vec{r}, \hat{R}) = \left[-\frac{\alpha_0}{2r^4} - \frac{\alpha_2}{2r^4} P_2(\cos \chi) \right] f(\vec{r}, \hat{R}, r_c) \quad (23)$$

where $f(\vec{r}, \hat{R}, r_c)$ is a cutoff function containing a cutoff parameter r_c . This model has its historical roots in the Bates-Massey polarization potential for electron-atom scattering. Bates and Massey⁸⁵ suggested that one need not know the form of the polarization potential at small r because polarization effects are relatively unimportant there. Thus for the electron-0 scattering, they used

$$V^P(r) = - \sum_{n\ell} \frac{\alpha_{n\ell}}{2(r_{n\ell}^2 + r^2)^2} \quad (24)$$

where $\alpha_{n\ell}$ is the contribution to the atomic static electric dipole polarizability from the $(n\ell)$ subshell and $r_{n\ell}$ is the subshell radius. This procedure can now be better justified since it is known more rigorously^{71,72,86} that the true polarization potential for electron-atom scattering at energies below the first electronically inelastic threshold has the asymptotic form

$$V^P(r) \underset{r \rightarrow \infty}{\sim} - \frac{\alpha}{2r^4} \quad (25)$$

where

$$\alpha = \sum_{n\ell} \alpha_{n\ell} \quad (26)$$

The result of equation (25) can also be obtained with the adiabatic approximation, either variationally or by second order perturbation theory; thus the adiabatic approximation is rigorously valid at large r at energies below the first electronically inelastic threshold. We have argued above that the adiabatic approximation is reasonable at large r even at intermediate energies. We have also shown that the form of the polarization potential is important at small r for intermediate-energy electron-molecule scattering,^{45,77} and several other studies (see, *e.g.*, references 5, 20 and 87 and references therein) have shown that the low-energy electron-molecule scattering processes, especially low-energy shape resonances, are also sensitive to the small- r polarization potential. Nevertheless the most popular model for the cutoff function has been to simplify $f(\vec{r}, \hat{R}, r_c)$ to^{5,20-22,65,87-89}

$$f(r, r_c) = 1 - \exp[-(r/r_c)^6] \quad (27)$$

This model assumes that the cutoff function is spherically symmetric and that V^P vanishes at the center of the molecule. Neither of these assumptions is strictly justifiable. Notice that the cutoff function in equation (23) must serve a dual role. It must account for deviations of the adiabatic polarization potential from its asymptotic form, and it must account for deviations of the true (nonadiabatic) polarization potential from the adiabatic one. It might be easier to model the polarization potential as follows^{65,69,76}

$$V^P(\vec{r}, \hat{R}) = V^{Pa}(\vec{r}, \hat{R})g(\vec{r}, \hat{R}, \text{parameters}) \quad (28)$$

where V^P is the true polarization potential, V^{Pa} is the adiabatic one, and g is a nonadiabaticity function. In this case one would expect g to depend primarily on the local kinetic energy and on the magnitude of V^{Pa} . At small r the local kinetic energy is dominated by the speedup caused by the static potential and depends only secondarily on the incident kinetic energy.⁸⁹ Thus one approach to calculating g at small r is to neglect the dependence on the incident energy and to model g as the ratio of the polarization potential calculated adiabatically with restricted variational freedom to the full adiabatic polarization potential. This leads us back to the

INDOX/AAP kind of model. This discussion illustrates one advantage of this kind of model over the combination of equations (23) and (27), namely, the INDOX/AAP model uses a physical model to avoid more explicit assumptions about the dependence of $V^P(r, \chi)$ on r and χ at small r . This difference becomes even more important for the calculation of vibrational-excitation cross sections, where the dependence of V^P on internuclear distances is required.^{48,81,84} Equations (23) and (27) require extra assumptions, *e.g.*, that r_c is independent of internuclear distances, whereas the INDOX/AAP model can, if desired, be applied to additional geometries with no additional assumptions and no new parametrization. Alternatively, the parameter X may be readjusted at each new molecular geometry.⁸⁴

Another approach^{64,90} to the nonadiabaticity function g in equation (28) may be based on an extrapolation of the leading non-adiabatic correction at low energy and large r . The static electric dipole polarizability of an S-state atom may be calculated by second order perturbation theory as⁹¹

$$\alpha = \sum_{n \neq 1}^{\infty} \frac{2 |\mu_{n1}|^2}{\omega_n} \quad (29)$$

where the sum is over excited P states and it includes an integral over the continuum, μ_{n1} is a dipole transition matrix element from the ground state, and ω_n is an excitation energy. In the average energy approximation ($\omega_n \cong \omega$ for all important n), this becomes

$$\alpha \cong \frac{2S}{\omega} \quad (30)$$

where

$$S = \sum_n |\mu_{n1}|^2 \quad (31)$$

Using the same average energy approximation, the dipole part of the polarization potential has the form^{92,93}

$$V^P(\text{di})(r) \underset{r \rightarrow \infty}{\sim} - \frac{S}{\omega r^4} + \frac{3S}{\omega^2 r^6} + \frac{6Sv^2}{\omega^3 r^6} \quad (32)$$

where v is the incident speed, which equals k in atomic units. The third term is the leading nonadiabatic correction and the first term is the leading term [compare equations (25) and (30)] in the adiabatic polarization potential. Comparing these two terms shows that

$$V^P(r) \underset{r \rightarrow \infty}{\sim} V^{Pa}(r) \left(1 + \frac{6v^2}{\omega r^2} \right) \quad (33)$$

The relation in equation (33) is an approximation based only on the leading adiabatic and leading nonadiabatic term at large r ; it ignores for example the r^{-6} quadrupole-polarizability term in $V^{Pa}(r)$. Nevertheless we made the ansatz that equation (33) can be used to obtain an effective (nonadiabatic) polarization potential from the adiabatic one at all r at low and intermediate energy. The theory has been tested so far only for electronically elastic electron-He scattering.⁶⁴ The results are quite encouraging; see, *e.g.*, Table 10 where phase shifts calculated this way are called SE/EDPP (static-exchange plus energy-dependent polarization potential). These phase shifts are compared to static-exchange (SE) ones, for which polarization is neglected, to static-exchange-plus-adiabatic-polarization (SEPa) ones, and to accurate⁹⁴ ones. (The MEP method, for which results are also given in this table, will be discussed below.) The exchange potential used for the SE, SE/EDPP, SEPa and MEP calculations on electron-He is the semiclassical exchange potential. A comparison to accurate calculations or to experiment tests both the exchange and polarization potentials. However, semiclassical exchange is accurate enough for He at the energies considered here that we can discuss the results as if they are a test of the polarization potential alone. The results are not very sensitive to the parameter ω ; for Table 10 we set it equal to

Table 10. Calculated phase shifts for electron-He scattering at two impact energies

ℓ	E (eV)	η (rad)				
		SE ^a	SEPa ^a	SE/EDPP ^a	MEP ^a	Accurate ^b
0	19	1.70	1.97	1.73	2.13	1.80
	100	1.05	1.24	1.05	1.15 ± 0.11i	
1	19	0.24	0.45	0.29	0.44	0.32
	100	0.34	0.51	0.34	0.45 ± 0.11i	
2	19	0.03	0.09	0.05	0.08	0.06
	100	0.11	0.22	0.12	0.19 ± 0.06i	

^aReference 64 (semiclassical exchange).

^bReference 94.

30 eV, which is 1.22 times higher than the ionization potential.⁶⁴ A larger positive phase shift corresponds to a more attractive potential; thus Table 10 shows that the EDPP does reduce the attractiveness of the adiabatic polarization potential by about the right amount at 19 eV impact energy. The differential cross section at 19 eV as calculated by the SE/EDPP model is in excellent agreement with experiment.⁹⁵ Unfortunately Table 10 shows that the SE/EDPP model predicts results very close to the SE ones for s, p and d waves at 100 eV impact energy. The effect of polarization is greater for the higher partial waves in the SE/EDPP model and as a consequence the differential cross section at 0° scattering angle is increased from 1.0 a₀²/sr in the SE model to 1.5 a₀²/sr in the SE/EDPP one. However, the experimental value⁹⁶ is 3.1 a₀³/sr. Thus the non-adiabaticity function in this model decreases too rapidly with increasing energy for He. The model could be applied to any molecule for which an adiabatic polarization potential is available, and it would be interesting to do so.

We conclude this section with a brief discussion of the matrix effective potential (MEP) method. This is a dynamic method for including polarization effects in electron scattering calculations. One way to include charge polarization effects in electron scattering calculations is by a close coupling expansion^{97,98} of the scattering wave function, where the radial wave functions f_j(r) are determined either by numerical integration or by some alternative method like R matrix theory or an algebraic variational calculation.^{3,5,87,99-103} For example, for electron-atom scattering we may write

$$\Psi(\vec{r}, \vec{x}) = \sum_{j=1}^N \psi_j(\vec{x}) \frac{1}{r} f_j(r) \psi_{\ell_j m_j}(\hat{r}) \quad (34)$$

to illustrate the idea, although in practice one would generally work in a total angular momentum representation and antisymmetrize. In equation (34) the $\psi_j(\vec{x})$ are target eigenstates⁹⁷⁻¹⁰⁰ or pseudo-states¹⁰¹ and the close coupling equations are

$$\left[-\frac{d^2}{dr^2} + \frac{\ell_i(\ell_i + 1)}{r^2} - k_i^2 \right] f_i(r) = -2 \sum_{j=1}^N V_{ij}^S(r) f_j(r) \quad (35)$$

$$i = 1, 2, \dots, N$$

To include the effect of antisymmetrization we replace the $N \times N$ matrix V_{ij}^S by V_{ij}^{SE} , as discussed in section III; then the equation for $f_i(r)$ becomes

$$\left[-\frac{d^2}{dr^2} + \frac{l_1(l_1 + 1)}{r^2} - k_1^2 \right] f_1(r) = -2 \sum_{j=1}^N V_{ij}^{SE}(r) f_j(r) \quad (36)$$

To obtain accurate results one must converge the calculations with respect to increasing N . In the optical potential approach we seek to replace the right side of equation (36) with a single term: $-2V_{11}^{SEP}(r)f_1(r)$. In the matrix optical potential method (also called the generalized potential method),^{3,104-108} we replace the N coupled equations (36) by a small set of M coupled equations ($M < N$) and we modify all the potential terms, *i.e.*, replace all the V_{ij}^{SE} by W_{ij}^{SEP} . The W_{ij}^{SEP} should be chosen so that the solution to the M coupled equations yields transition amplitudes among the M retained states equivalent to those that would be obtained from equation (36) with large N . If $M = 1$, the matrix optical potential reduces to the original optical potential that we have been discussing in this chapter. In the matrix effective potential method of references 63 and 64, we replace the N coupled equations by a smaller number, generally two, we retain $V_{11}^{SE}(r)$ unmodified, and we try to choose the other elements of the potential matrix so that the elastic scattering in the first channel is approximately equivalent to what would be calculated from equation (36) with large N . Thus the second channel does not represent any one eigenstate or pseudostate of the target; it is a pseudochannel but it does not represent a pseudostate, *i.e.*, there is in general no single r -independent state of the target whose inclusion would accomplish what we try to accomplish with one or a few pseudochannels.

In our work^{63,64} we used second order perturbation theory and the adiabatic polarization potential to obtain the matrix effective potential. In second order perturbation theory the adiabatic polarization potential is given by^{53,54,86,99}

$$V^{Pa}(r) = \sum_{j \neq 1}^N \frac{|V_{1j}(r)|}{\omega_j} \quad (37)$$

where ω_j is the excitation energy, *i.e.*,

$$k_j^2 = k_1^2 - 2\omega_j \quad (38)$$

We determine $V_{12}(r)$ such that a single term on the right side of equation (37) yields the full (and assumed known) adiabatic polarization potential. Thus the matrix effective potential is

$$\vec{V}(r) = \begin{pmatrix} V_{11}^{SE}(r) & [V^{Pa}(r)\omega]^{1/2} \\ [V^{Pa}(r)\omega]^{1/2} & V_{22}^{SE}(r) \end{pmatrix}$$

where ω is some average excitation energy (which we set equal to the ionization potential for our applications). We call this the MEP method. For simplicity we set $V_{22}^{SE}(r)$ equal to $V_{11}^{SE}(r)$.

Table 10 shows that the MEP model predicts phase shifts that are too large at 19 eV, *i.e.*, the effective potential is too attractive at low energy. Thus the forward peak in the MEP differential cross section is about 15% too large at 19 eV.⁶⁴ The differential cross section calculated by this MEP model becomes more accurate at high energy.⁶⁴

An interesting aspect of the MEP model is that the pseudo-channel can have outgoing flux if $E > \omega$. Thus it is not necessary to use complex potentials to mimic the loss of flux from the first electronic channel. Since the pseudochannel is supposed to mimic the total effect of all excited electronic states, the flux associated with it should be compared to the whole electronically inelastic cross section. Table 11 compares this inelastic cross section and the total (elastic plus inelastic) cross section to

Table 11. Inelastic and total cross sections for electron-He scattering

E (eV)	σ_{inel} (a_0^2)			σ_{tot} (a_0^2)		
	NLEP ^a	MEP ^b	Experiment ^c	NLEP ^a	MEP ^b	Experiment ^c
30	1.00	0.99	0.82	8.59	9.96	8.80
50	1.82	2.13	1.53	6.35	7.65	6.47
100	1.10	2.47	1.89	3.15	4.93	4.07
200	0.46	1.98	1.65	1.38	3.05	2.63
400	--	1.37	1.16	--	1.85	1.61

^aReference 62.

^bReferences 63 and 64.

^cReference 109.

experiment.^{64,109} The agreement is very good, especially considering that the calculation involves no adjustable parameters. As a standard of comparison, Table 11 also shows the prediction of the recent effective potential formalism of Scott and Taylor.⁶² Their effective potential, which is derived from the many-body Green's function formalism of Schneider *et al.*,⁶² is nonlocal, complex and energy-dependent. In contrast the matrix effective potential is local in the coordinate representation, real and independent of energy. The table shows that the matrix effective potential accounts more realistically for the energy dependence of the loss of flux from the electronically elastic channel. The MEP model can be applied to any system for which the adiabatic polarization potential is known; it would be interesting to apply it to molecules.

Two promising *ab initio* methods for including charge polarization effects are R matrix theory including electronic pseudostates¹¹⁰ and the T matrix method including an optical potential obtained by diagrammatic perturbation theory.¹¹¹ So far these methods have only been applied at low energy where only one electronic channel is open.^{110,111}

V. FURTHER TESTS AGAINST EXPERIMENT

We have already mentioned some comparisons of our calculated cross sections to experimental ones for He and N₂. In this section we briefly summarize some other comparisons.

For most atoms and molecules, the static potential near the nuclei is so strong that scattering calculations using plane wave scattering states do not give very useful results at intermediate energies.^{81,112,113} For H₂ the nuclear charge is small and plane wave approximations are more useful. We have applied the Born approximation (first order perturbation theory with plane wave scattering states and a static interaction potential) and the polarized Born approximation (plane wave scattering states and a static-plus-polarization interaction potential) to electron-H₂ scattering at 7-912 eV to calculate elastic scattering, rotational excitation, and vibrational excitation cross sections.^{89,114-117} For these calculations the static potential was a sum of scaled atomic potentials plus quadrupole terms, the exchange potential was obtained from the Rudge modification of the Bonham-Ochkur expression, and the polarization potential was an analytic fit to the nonadiabatic model of Lane and Henry.¹¹⁸ The results for the rotationally summed vibrationally elastic and rotationally summed vibrationally inelastic cross sections were found to be in generally good agreement with experiment for all scattering angles (θ) at the lowest energies and for scattering angles less than about 90°

at 30-100 eV. At even higher energies the plane wave approximation begins to break down at even lower scattering angles.

When the plane wave approximation breaks down we must include distortion of the scattering states caused by their interaction with the effective potential. Possible ways to do this are by the Glauber approximation¹¹⁹ and the multiple scattering method.¹²⁰ More complete treatments of the scattering by an anisotropic potential lead to coupled-channels equations. If rotation of the molecule is neglected during the collisional event, which is an excellent approximation for intermediate-energy electron-molecule scattering, this leads to the fixed-nuclei coupled-channels formalism in which various values of ℓ (the orbital angular momentum quantum number of the relative motion) are coupled together, but molecule-frame symmetries, like M (the component of $\vec{\ell}$ along the molecular axis for a linear molecule) are conserved.^{5,11,87} The problem is block diagonal in the conserved symmetries. This formalism was used for the calculations already presented in Tables 4 and 7. To calculate $j \rightarrow j'$ cross sections (where j is now the rotational quantum number) we can make a transformation of the molecule-frame results to a new representation,^{5,87} or we can include rotational motion in the calculation all along. The latter procedure leads to rotational close coupling.^{5,87,121} Rotational close coupling calculations are coupled-channels calculations for the radial wave functions for the scattering electron in a representation where the angular wave functions are combinations of $Y_{\ell m_\ell}(\hat{r})$ and $Y_{j m_j}(\hat{R})$. Here the components m_ℓ and m_j are defined along a laboratory-frame axis, and the linear-combination basis functions correspond to definite values of the total angular momentum quantum number J . Since J is conserved, the problem is block diagonal in J . The usual procedure is to limit the basis set to a maximum rotational quantum number j_{\max} and a maximum total angular momentum quantum number J_{\max} and then to include for all (J, j) pairs all the ℓ values allowed by parity conservation and the triangle inequality, $|J - j| \leq \ell \leq J + j$. Another scheme for picking the ℓ values for given (J, j) pairs has also been proposed¹⁶ and has been shown to lead to convergence with few basis functions, *i.e.*, fewer coupled channels.^{16,48} In either scheme a converged calculation for a system with a highly anisotropic interaction potential requires a high value of j_{\max} . The rotational close coupling method was used for the calculations already discussed in Table 8 and Figure 2.

H_2 is the only molecule for which nonresonant rotational excitation has been experimentally resolved from pure elastic scattering.^{122,123} The ratio of rotational excitation to pure elastic scattering was found to increase by one order of magnitude as θ was increased from 20° to 120° at 10 eV and by two orders of magnitude when θ was increased from 10° to 135° at 40 eV. To compare with these calculations we performed rotational close coupling

calculations for a static-exchange-plus-polarization approximation.⁴⁵ The static potential was a sum of scaled atomic potentials plus a quadrupole term (as used for the Born calculations), the exchange potential was the semiclassical exchange potential, and three different polarization potentials were tried. The various polarization potentials were all obtained by applying various cutoff functions to the accurate adiabatic asymptotic form, *i.e.*, by using equation (23). The effect of the variations of polarization potential on the calculated cross sections was small. With no empirical parameters, good agreement with experiment was obtained for the angle dependences and magnitudes of the differential cross sections for both pure elastic scattering and rotational excitation except for elastic scattering for $\theta \lesssim 30^\circ$, where the theoretical differential cross section is too large; at 40 eV and 10° the discrepancy is about a factor of $2\frac{1}{2}$.

For H_2 we included only rotational states up to $j = 3$ in the rotational close coupling expansion. This effectively truncates the Legendre expansion of the potential at $\lambda_{\max} = 6$. This is apparently sufficient for qualitatively correct results for H_2 , which is not very anisotropic. For N_2 we performed a series of rotational-vibrational close coupling calculations with $j_{\max} = 2$ for impact energies of 5, 10 and 30-70 eV.¹²⁴⁻¹²⁶ This effectively truncates the potential at $\lambda_{\max} = 4$. For $E \geq 30$ eV this gave poor agreement with the experimental rotationally summed, vibrationally elastic differential cross sections for $\theta > 30^\circ$. The large-angle scattering is controlled by the short-range part of the effective potential. This comparison to experiment indicates that the e^-N_2 interaction potential is too anisotropic at short range for a $j_{\max} = 2$ truncation of the angular basis set of the scattering calculation to yield to a correct dependence of the differential cross section on scattering angle for $\theta > 40^\circ$. These calculations did, however, predict the magnitude of the vibrationally inelastic integral cross sections within a factor of 2.3 at all seven energies examined. Note, however, that the energy range 10-30 eV was not included in this series of tests. This energy range will be discussed again below.

Based on the experience summarized above and in sections I-III, we see that to obtain qualitatively accurate differential cross sections for general molecules at intermediate energy, one requires a certain minimum description of the scattering event. This consists of using an effective potential containing static, exchange and nonadiabatic polarization interactions and treating the scattering by this potential with many coupled channels to handle the high anisotropy. Onda, Thirumalai and I have recently implemented this approach by performing converged or nearly converged rotational close coupling calculations with nonadiabatic SEP potentials for N_2 ,^{16,47,48,69,77,78,81} CO,⁸² C₂H₂,⁸³ and

CO_2 .^{15,69,84} In parallel work Rumble and I^{21,22,127,128} have studied intermediate-energy electron- N_2 scattering by converged molecule-frame coupled channels calculations, again including all three interactions (static, exchange and polarization) in the effective potential. Some of the calculations for vibrationally elastic scattering by N_2 were summarized in section III. We also performed calculations of the vibrationally inelastic cross sections for N_2 at 5, 10, 20, 25, 30, 35 and 50 eV.^{48,81,128} One set of calculations^{48,81} used the INDOX/1s wave function to compute the charge density for the static and exchange potentials and used the INDOX/AAP polarization potential. The other¹²⁸ used *ab initio* charge densities and a semiempirical polarization potential based on equations (23) and (27). The following discussion refers to the former set of calculations since the latter ones are only partially analyzed at this time. The results of the former set at 10 eV are in excellent agreement with experiment.^{81,126} In fact they agree better than the calculation of Chandra and Temkin¹²⁹ for which the polarization potential contains a parameter adjusted to the low-energy Π_g resonance (this symmetry still dominates vibrational excitation at 10 eV). It is probable, however, that the difference of our calculated cross section from theirs is caused by our better treatment of exchange or our better convergence of the coupled-channels expansion than by the difference in polarization potentials. Our static potential differs from theirs too.

At 20-35 eV our calculated vibrational excitation cross sections exhibit a resonance,^{48,69} as do the experimental cross sections.^{112,125,130} Since this resonance can be predicted by a scattering calculation involving only the effective potential in a single electronic state, it must be classified as a single-particle resonance, popularly called a shape resonance. Our calculations predict that the $0 \rightarrow 6$ rotational excitation will also exhibit this shape resonance.⁴⁸ The shape resonance is characterized by $J = \ell = 3$ in our laboratory-frame calculations and by Σ_u symmetry in molecule-frame calculations. For the vibrational excitation case, cross sections exhibiting the intermediate-energy shape resonance have also been calculated by Dehmer *et al.*^{120,131} They used a muffin-tin effective potential in which polarization is entirely neglected inside in the muffins and the effective potential is assumed constant in the inter-muffin regions.¹²⁰ These muffin-tin approximations affect the shape of the effective potential and the magnitudes of the calculated partial cross sections in important quantitative ways.¹²⁷ To the extent though that the strong static-exchange potentials near the nuclei dominate certain aspects of the scattering, the muffin-tin method provides a useful semiquantitative way to survey the qualitative features of the scattering cross sections. Its success in explaining this intermediate-energy shape resonance in N_2 shows that the static-exchange potential near the nuclei does indeed sometimes dominate the scattering. In such

cases the muffin-tin method is especially useful as a survey tool because the calculations are much less expensive than the coupled-channels calculations required for a converged treatment of a non-muffin-tin effective potential like ours.

Our calculated integral cross section for vibrational excitation of N_2 at 50 eV exceeds the experimental one by a factor of 2.3.⁸¹ Both the calculated⁸¹ and the experimental¹²⁵ vibrational-excitation differential cross sections are flat to within a factor of two for scattering angles 20° to 135° . The reason for the discrepancy in the magnitudes is unknown.

CO and C_2H_2 are interesting cases for comparison with N_2 since the three molecules are isoelectronic. The rotationally summed differential cross section calculated for CO at 10 eV⁸² is very similar to the one calculated for N_2 , in agreement with the experimental finding¹³² that these cross sections are similar. The rotationally summed cross sections for 10 eV scattering by C_2H_2 ,⁸³ however, is much larger than for N_2 . In fact the calculated rotationally summed integral cross section for C_2H_2 at 10 eV is $96 a_0^2$, as compared to calculated⁸¹ and experimental^{95,133} values of $53 a_0^2$ for N_2 at 10 eV. There is no experimental data available yet for C_2H_2 , although Newell and coworkers¹³⁴ have promised to present some soon. Apparently the cross section is larger for C_2H_2 than for CO or N_2 because of the much greater spatial extent of the tetra-atomic; this is a static potential effect. It is also clear that the spatial-extent factor in C_2H_2 has a larger effect than asymmetry factor does in CO.

Figure 3 compares our calculated cross sections for CO_2 and CO. In this case the theoretical cross sections^{82,84} differ more than the experimental ones^{132,135,136} do. The difference is caused by the calculations overestimating the differential cross section for CO_2 . The magnitude of the CO_2 cross section at 10 eV appears to be very sensitive to details of effective potential,¹³⁷ and Figure 3 presents a challenge for us to improve our effective potential models. As discussed in section II, however, we expect our models to be more accurate as we proceed from 10 eV, the bottom of the intermediate-energy region, up to higher energies. The angle dependence of the CO_2 cross section in Figure 3 provides an interesting test of theory because the experimental angle dependence is independent of any possible errors in putting the experiment on an absolute scale. The theoretical and experimental angle dependence agree very well for $\theta = 15^\circ$ - 70° . The angle dependence of an earlier CO_2 calculation^{15,69} at 20 eV agreed well with an unnormalized experiment¹³⁸ for $\theta = 15^\circ$ - 60° .

This chapter has emphasized electronically elastic scattering. As discussed in the first paragraph, though, electronically inelastic

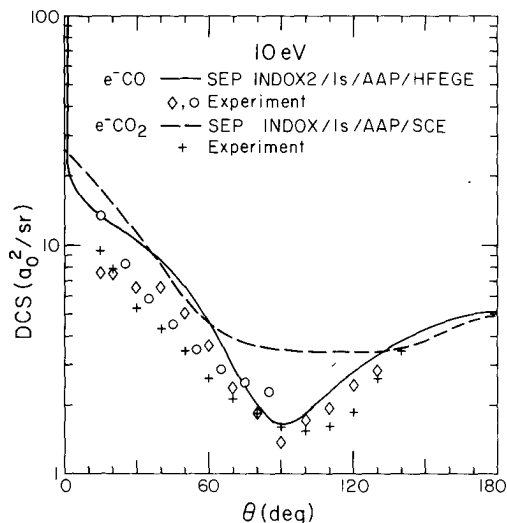


Figure 3. Rotationally summed differential cross sections for electronically elastic scattering of electrons by rigid CO and CO₂ at 10 eV impact energy. The curves for both molecules are static-exchange-plus-polarization results using the INDOX/1s static potential and perturbed density and the INDOX/AAP model for the polarization potential. The CO results are for Hara free-electron-gas exchange and the CO₂ results are for semiclassical exchange. The CO results are from Onda and Truhlar (reference 82) and the CO₂ results are from Thirumalai *et al.* (reference 84). The diamonds and +'s are respectively the experimental results of Tanaka *et al.* (reference 132) for CO and the experimental results of Register *et al.* (reference 135) for CO₂. The circles are the experimental results of the JPL group (reference 136) for CO. The last-named measurements yield only relative values; they were normalized to the calculation of reference 82 at 15° for this figure.

scattering in the intermediate-energy region is very important. The potentials we have discussed so far are diagonal matrix elements in the electronic quantum numbers of the target. To treat electronically inelastic scattering we require transition potentials. These are off-diagonal matrix elements in the electronic quantum numbers of the target, and, just like the diagonal potentials, they can be decomposed into static, exchange and polarization parts.³ The simplest way to extend the present treatment to electronically inelastic scattering is to treat the target asymmetry by the same coupled-channels methods based on diagonal effective potentials, thus yielding electronically elastic coupled-channels trial functions for both the initial and final states of an electronically inelastic collision. The coupling of these states can then be treated to first order in the transition potential, *i.e.*, by the distorted-wave Born approximation^{55,59} (usually called DWBA in nuclear physics and DWA in molecular physics). The whole calculation just outlined is a coupled-channels approximation for rotational and relative orbital motions and a distorted wave approximation only for electronic motions. Calculations involving this approach are just now starting to appear in the literature for intermediate-energy electron-molecule scattering.¹³⁹⁻¹⁴¹ So far, however, both diagonal and off-diagonal polarization effects have been neglected in these calculations. To go beyond a DWBA treatment of electronic motions, one can use electronic close coupling, which has been applied to electronically inelastic electron-molecule scattering by Lane and Lin and their coworkers.^{142,143} In these cases, as in the distorted wave calculations mentioned above, polarization effects were neglected in both the diagonal potentials and transition potentials. As one increases the number of electronic states explicitly retained in the wave function expansion, the polarization contributions to the matrix optical potential become smaller, and in the limit they disappear. However, in the applications to electron-molecule scattering that have been made so far, only two electronic states were retained in each calculation. There are several methods for treating electronically inelastic scattering that have so far not been applied to electron-molecule scattering. Two particularly promising approaches are R matrix theory^{87,110,144} including electronically excited open channels and various versions of algebraic variational methods.^{3,102,103,145-149} The further development of off-diagonal effective potentials and techniques for using them to calculate electronically inelastic electron-molecule scattering cross sections at intermediate energies are research problems that we hope will show more progress in the near future.

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*There are several misprints in this chapter: Page 151: $r \cdot R$ and $r_c =$ should be $\hat{r} \cdot \hat{R}$ and $r_c = \infty$, respectively. Page 155: $\theta > 30^\circ$ eV should be $\theta > 30^\circ$ at 30 eV. Page 159: v_{ad}^P should be v_4^{adP} . Page 162: F. A. Van-Catledge is misspelled. Page vi: add K. Onda, University of Minnesota, to list of participants.

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