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# *Electron Scattering*

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## **1. Introduction**

This chapter discusses some approximate methods for the calculation of electron scattering cross sections of molecules.

There has been much progress in the development of computational methods for electron scattering over the last five or so years. Entirely new methods have been developed, old methods have been improved, and both have been applied more systematically than previously. Some of the approaches which have been made to the calculation of electron scattering cross sections will be discussed in this chapter, and special emphasis will be placed on those aspects of the approximations which naturally link up with the approximation methods used for bound-state calculations which are discussed in the rest of this treatise. Representative but not exhaustive references will be given. We will treat the electronic part of the wave function, but the rotational and vibrational motions involved in electron-molecule scattering will not be discussed in detail. While many aspects of the approximate theories used for the electronic part of the bound-state problems are useful for electron scattering, some more specialized techniques and approximations are also useful.

In theoretical chemistry, more attention is directed to electron-molecule scattering than to electron-atom scattering. Thus we will emphasize methods which have been shown to be useful for electron-molecule scattering or which show promise of future usefulness for electron-molecule scattering calculations. It would be particularly appropriate if the methods discussed here were all illustrated by applications to electron-molecule scattering. However, some

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of the techniques which show the most promise for future electron-molecule scattering calculations have so far only been applied to electron-atom scattering or have been applied in a much more definitive fashion to electron-atom scattering. Thus in many cases the best illustrations must be taken from electron-atom scattering. Of course electron-molecule scattering involves treating both the electronic part and the internuclear part and the latter has no analog in electron-atom scattering.

In a few cases involving electron scattering by hydrogen and helium atoms essentially exact cross sections have been computed. But most electron scattering calculations contain approximations of uncertain validity. Nevertheless, it is often possible to judge the general reliability of various approximation schemes for various accuracy requirements, targets, types of information about scattering processes, and energy ranges. A method which is successful for one application will often not be satisfactory for another and *vice versa*. Thus an understanding of the uses of electron scattering cross sections and of the characteristics of the different energy ranges is a necessary prerequisite for understanding the usefulness of the various approximation schemes.

A few of the more important applications of electron scattering cross sections are electron-impact spectroscopy, radiation chemistry, aeronomy and other studies involving atmospheres of the earth and other planets, astrophysics, the study of the sun's corona, electron-drift experiments and gaseous electronics, the study of laboratory discharges and plasmas, fusion, and lasers. Laboratory measurements on electron impact processes have been thoroughly reviewed by Massey *et al.*<sup>(1,2)</sup> and Christophorou.<sup>(3)</sup>

Several textbooks and monographs with an appreciable emphasis on the theory of electron scattering are available<sup>(4-11)</sup> and should be consulted for an introduction to the field.

Both for classifying the physical processes occurring and for sorting the appropriate computational procedures it is useful to distinguish five ranges of impact energy (very low, low, intermediate, high, and very high).

The low-energy region is characterized by  $T_i < U_i$ , where  $T_i$  is the initial translational energy of the scattering electron and  $U_i$  is the ionization energy of the interacting target electrons. In this energy range the scattering electron and the target electrons are best treated on an equivalent basis since they have roughly equivalent energies. Thus the procedure for calculating the total wave function may resemble a bound-state calculation for the composite system of target plus scattering electron more than at higher energies, where the scattering electron may be usefully treated on a nonequivalent basis due to its higher energy. When  $T_i = 1$  eV the de Broglie wavelength is 12.3 Å. This is very large (larger than the dimensions of the target for most targets of interest in this chapter) and indicates the need of a quantum mechanical treatment and that classical mechanical concepts should be used with utmost caution if at all. In the

low-energy region, elastic and inelastic scattering occur and, provided too many channels are not open, variational minimum principles may be used to perform accurate calculations. (Since these principles require explicit inclusion of all open channels in the trial scattering wave function, they are not of practical value at higher energies.) At this low energy it is the usual practice to expand the total scattering wave function in terms of eigenfunctions of the total angular momentum. Although this is more complicated for electron-molecule scattering than electron-atom scattering, it still provides enough simplifications that it is often worth attempting even if further approximations are required. Less than ten angular momenta need to be treated by full calculations using low-energy methods. If angular momenta above the lowest few values are needed at all (e.g., to adequately include large-impact-parameter collisions to converge the differential cross section at small scattering angles), they can usually be treated by perturbation theory or other high-energy approximations. For the lower angular momenta the close coupling method and the matrix close coupling (also called algebraic close coupling) method are often used; in the language of bound-state calculations, these are continuum configuration interaction methods. Resonances (temporary negative ions for electron-neutral scattering or temporary electron attachment for electron-ion scattering) are often important at low energies, particularly shape resonances at initial or final translational energies up to a few eV and Feshbach resonances near thresholds.\* Since a resonance may be visualized as an electron temporarily bound to some state of the target, bound-state calculational procedures can sometimes be used almost without modification for the description of resonances.

At very low energies, e.g., thermal energies, additional simplifications occur. For very low energies all scattering is elastic. The de Broglie wavelength at  $T_i = 0.026$  eV is  $76 \text{ \AA}$ . When the de Broglie wavelength is much greater than the dimensions of the target, all elastic scattering occurs only in the component at the wave function corresponding to zero orbital angular momentum of the scattering electron, i.e., in the  $s$  wave, and the  $s$  wave is sensitive only to the spherically symmetric part of the interaction potential. This yields an isotropic differential cross section. In the limit of zero translational energy, the scattering information is all contained in the scattering length† and at very low energies

\*"Shape resonances" are resonances which can be described reasonably correctly by a model involving scattering of the electron by an effective potential due to its interaction with the target in some unperturbed or perturbed state. "Feshbach resonances" require a target-excitation mechanism for their description. They involve temporary binding of the scattering electron to some excited state of the target when the electron is incident on the target in some lower energy state.

†The "scattering length" is the limit as the incident momentum tends to zero of the  $s$ -wave phase shift divided by the momentum in atomic units. Generalizations of the scattering length definition to higher partial waves are not needed in this chapter.

the effective range formalism<sup>(12)</sup> may be used to express the deviation from the zero-energy limit. (This formalism, which is not discussed in this chapter, is also useful at higher energies for high orbital angular momentum of the scattering electron.) An upper bound on the scattering length may be obtained by an extension of the upper bound theorem used for bound-state energies.<sup>(13)</sup>

The intermediate-energy region is roughly characterized by  $U_i < T_i < 15U_i$ . The precise location of the intermediate energy range thus depends on the target and the process considered, but it may often be considered as about 10–150 eV. The de Broglie wavelength of an electron varies from 3.9 Å at 10 eV to 1.0 Å at 150 eV. In this energy region elastic and inelastic scattering and ionization may occur and many channels are open. Thus the variational minimum principles which are useful in the low-energy region are not useful here. There are some resonances, but most scattering is nonresonant. The optical electric dipole selection rules that hold in the high-energy limit are not in effect here and this is the region useful for electron-impact spectroscopy.<sup>(14,15)</sup> The plane-wave perturbation theories, which become accurate at higher energies where the interaction potential is small compared to the initial kinetic energy, are not yet accurate because the incident electron is not well described by a plane wave unless its initial energy is higher and because target charge polarization effects are hard to treat by perturbation theory at intermediate energy. The intermediate-energy region is the most difficult region to treat and is the subject of much current interest. Most of this work involves modifying the low-energy or high-energy methods so that they will be more appropriate for this energy region.

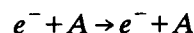
In the high-energy region corresponding to  $U_i < T_i \ll \text{few keV}$ , the de Broglie wavelength of an electron varies from about 1.0 to 0.3 Å. Thus classical pictures are more appropriate than at lower energies. The usual theory is perturbation theory with a plane wave (or a Coulomb wave) for the zeroth-order free wave and no interaction potential (or a pure Coulombic interaction) in the zeroth-order Hamiltonian. The perturbation series is the well-known Born series (explained in introductory texts) and its modifications. The first term in the series is the first Born approximation. It consists of an integral over the unperturbed initial and final target wave functions, the initial and final plane waves, and the interaction potential. Thus intermediate target states (which are necessary to represent target charge polarization) and distortion of the scattering electron's wave function by the interaction are neglected in the zeroth-order wave function. Contrary to popular assumption, there is no proof that the high-energy limit of the differential cross section is correctly given by the first Born approximation and there is some evidence that it is not.<sup>(16)</sup> In many respects the angular momentum  $l$  of the scattering electron plays a role similar to the energy. Just as the high- $l$  components of the low-energy scattering wave function can often be treated using high-energy methods, the low- $l$  components (e.g., the  $s$  wave) of the high-energy scattering wave

function should be treated for many purposes using low-energy methods. This is necessary because these low- $l$  components are not prevented by the centrifugal potential from penetrating into regions where the interaction potential is not negligible with respect to even high initial kinetic energies. But the high-energy scattering is often treated without making a partial wave decomposition of the wave function into its components with various  $l$  or total angular momenta so the requirement for a more accurate treatment at low  $l$  is often ignored.

The very-high-energy region includes energies above a few keV. The usual energy for electron diffraction experiments is 40 keV, where the de Broglie wavelength of an electron is 0.06 Å. Some special techniques have been developed for this energy region.<sup>(2,11)</sup> For example, the atoms of a molecule may sometimes be considered to scatter independently. Some high-resolution spectroscopy may be done in this energy region,<sup>(17)</sup> although selection rules identical to the optical ones are valid to a good approximation.

The nuclei may be treated as point charges at energies as high as 3 MeV.<sup>(18)</sup> When electrons with energies of 15 MeV and higher collide with an atom, a significant contribution to the scattering is made by electrons that have penetrated the nucleus.<sup>(18,19)</sup> Such energies are out of the range considered in this chapter.

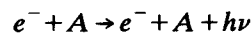
This chapter is concerned with the  $(1e, 1e)$  scattering process where an electron scatters from a gas-phase target  $A$



(where  $A$  need not be neutral). In this collision process, the state of  $A$  may remain the same (elastic scattering) or it may change (inelastic scattering). The  $(1e, 2e)$  and  $(1e, \text{many } e)$  electron-impact ionization processes are closely related but are more complicated due to the presence of three or more bodies in the final state. The  $(0e, 1e)$  photoionization process



is easier to treat than the  $(1e, 1e)$  scattering process, but because it involves a free electron in the final state it provides an interesting link between bound states and scattering states. Recently there has been much progress in treating photoionization using bound-state techniques.<sup>(20,21)</sup> These treatments can profitably be compared to earlier treatments using scattering techniques<sup>(22,23)</sup> but photoionization will not be discussed much more in this chapter. Another interesting electron scattering problem not treated here is free-free radiation<sup>(24)</sup>:



For electron scattering the center of mass may be assumed to coincide with the center of mass of the nuclei and in the center-of-mass system (barycentric

system) the wave function for electron scattering by an  $N$ -electron target depends on relative nuclear coordinates  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{\nu-1}$  (for a molecule with  $\nu$  nuclei), on the coordinates  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N+1}$  of the electrons with respect to the center-of-mass of the nuclei, and on spin coordinates. The electronic part of the wave function can be expanded in a set of basis functions which depend on electronic coordinates and spins (and thus are determined by the Schrödinger equation with nuclear kinetic energy terms omitted) and depend parametrically on relative nuclear coordinates and spins. This is the fixed-nuclei formalism and it is analogous to the electronically adiabatic separation of electronic and nuclear motion which is usually made for treating bound states.\* In this chapter we will not explicitly indicate the parametric dependence of the electronic wave function and the electronic basis functions on the nuclear coordinates and nuclear spins.

The fixed-nuclei approach offers important simplifications in general but not at large distances  $r$  of the scattering electron from the target (greater than about 10 bohrs),<sup>(28)</sup> especially for polar molecules,<sup>(29)</sup> because of the long-range nature of their interactions with electrons, and for very low energies ( $T_i \leq 0.1$  eV). The breakdown of the fixed-nuclei approach in these cases (large  $r$  and low  $T_i$ ) is similar to its breakdown in Rydberg bound states, where the molecular framework may be pictured as rotating appreciably during an orbit of the distant and slowly moving electron. For these cases, it is more appropriate to use the laboratory-frame approach in which the electron is considered to be interacting with the molecule in a given rotational-vibrational state. Scattering calculations have been performed using both formalisms. Procedures necessary for interrelating them and for using the fixed-nuclei approach at small  $r$  and the laboratory-frame approach at large  $r$  have also been developed.<sup>(28,30)</sup> In this chapter we use the fixed-nuclei approach for consistency with the rest of the volume.

## 2. Explicit Inclusion of Electronic Excitations

### 2.1. Expansions Including Free Waves

#### 2.1.1. Coupled Equations

First we consider methods based on expanding the electronic wave function in a suitable set of functions, including products of target eigenstates and continuum functions (free waves) for the scattering electron. These free

\*For bound states this is usually called the Born-Oppenheimer adiabatic approximation<sup>(25)</sup> and for electron scattering it is sometimes called the adiabatic or the adiabatic-nuclei approximation.<sup>(26)</sup> The former nomenclature is sometimes used in electron scattering but it should not be confused with the Born-Oppenheimer exchange approximation for electron scattering<sup>(27)</sup> or the adiabatic polarization assumption of electron scattering (see Section 4).

waves are included in order to satisfy scattering boundary conditions, and the variational methods of scattering theory are applicable to trial functions which satisfy scattering boundary conditions [scattering boundary conditions are defined by Eqs. (1) and (8)–(11) below]. Some methods formulated entirely in terms of square-integrable basis functions are considered in Section 2.2.

Variational principles are not used for electron-impact ionization since the correct boundary conditions are not completely known, due to the presence of two free electrons in the final state.<sup>(31)</sup> Further, the correct wave function for any electron collision at energies above the target's ionization potential must include some terms corresponding to such two-free-electron final states. Nevertheless, these terms are usually neglected except when electron-impact ionization is the quantity of interest, and ionization cross sections are usually calculated using perturbation theory with no attempt at a complete expansion of the final state wave function.<sup>(32)</sup>

The most general possible trial function for electron scattering by an  $N$ -electron target which satisfies correct scattering boundary conditions (neglecting ionization channels) may be written

$$\psi^p(x_1, x_2, \dots, x_{N+1}) = \hat{O} \left[ \sum_{i=1}^P X_{ip}(r_{N+1}) f_i(x_1, x_2, \dots, x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) + \sum_{m=1}^M c_{mp} W_m(x_1, x_2, \dots, x_{N+1}) \right] \quad (1)$$

where  $\hat{O}$  is a permutation operator (which may be the antisymmetrizer or a partial antisymmetrizer) acting on the  $\{x_i\}_{i=1}^{N+1}$ ;  $x_i$  is the set of coordinates  $(\mathbf{r}_i, \sigma_i)$  or equivalently  $(r_i, \hat{\mathbf{r}}_i, \sigma_i)$ ;  $\mathbf{r}_i$  is the spatial coordinate of electron  $i$ ;  $r_i$  is the distance  $|\mathbf{r}_i|$  from the center of mass to electron  $i$ ;  $\hat{\mathbf{r}}_i$  is the unit vector from the center of mass to electron  $i$ ;  $\sigma_i$  is the spin coordinate of electron  $i$ ;  $p$  and  $i$  are sets of channel indices, where  $p$  designates a particular choice of boundary conditions and  $i$  designates an arbitrary channel;  $P$  and  $M$  are constants representing the numbers of terms retained in each sum in the trial function;  $W_m$  is a square-integrable basis function;  $f_i$  is

$$\Phi_i(x_1, x_2, \dots, x_N) Y_{lm}(\hat{\mathbf{r}}_{N+1}) \chi_{m_l}(\sigma_{N+1})$$

or a linear combination of such products involving degenerate  $\Phi_i$ , where  $\Phi_i$  is an eigenfunction of the channel Hamiltonian  $H_i$  defined in terms of the total Hamiltonian  $H$  by

$$H_i(x_1, x_2, \dots, x_N) = \lim_{r_{N+1} \rightarrow \infty} [H(x_1, x_2, \dots, x_{N+1}) - T(\mathbf{r}_{N+1})] \quad (2)$$

where  $T$  is the kinetic energy of the scattering electron defined by

$$T(\mathbf{r}_{N+1}) = p_{N+1}^2 / 2m \quad (3)$$

and

$$H_i(x_1, x_2, \dots, x_N)\Phi_i(x_1, x_2, \dots, x_N) = E_i\Phi_i(x_1, x_2, \dots, x_N) \quad (4)$$

$$T(\mathbf{r}_{N+1})X_{lp}(r_{N+1})Y_{lm_i}(\hat{\mathbf{r}}_{N+1}) \xrightarrow{r_{N+1} \rightarrow \infty} \frac{\hbar^2 k_i^2}{2m} X_{lp}(r_{N+1})Y_{lm_i}(\hat{\mathbf{r}}_{N+1}) \quad (5)$$

where the total energy is

$$E = E_i + \frac{\hbar^2 k_i^2}{2m} \quad (6)$$

$$= E_i + T_i \quad (7)$$

and  $Y_{lm_i}$  is a spherical harmonic;  $\chi_{m_i}$  is a spin wave function;  $X_{lp}$  is the channel radial function, which is square-integrable if  $k_i$  is imaginary and may be assumed to satisfy the following scattering boundary condition for the  $N_{op}$  open channels,  $i = 1, 2, \dots, N_{op}$ , for which  $k_i$  is real:

$$X_{lp}(r) \sim Y_{lp}(r; \tau) \quad (8)$$

$$Y_{lp}(r; \tau) = \alpha_{0lp}(\tau)A_{l0}(r; \tau) + \alpha_{1lp}(\tau)A_{l1}(r; \tau) \quad (9)$$

$$A_{lp}(r; \tau) \sim r^{-1} a_0^{-1/2} \sin(\Theta_i + \frac{1}{2}\beta\pi + \tau) \quad (10)$$

$$\Theta_i = k_i r - \frac{1}{2}l\pi + Zk_i^{-1} \ln 2k_i r + \arg \Gamma(l_i + 1 - iZk_i^{-1}) \quad (11)$$

Here  $\alpha_{0lp}$  and  $\alpha_{1lp}$  are coefficients for channel  $i$  depending on the particular choice  $p$  of boundary condition;  $\tau$  is an arbitrary phase angle;  $a_0$  is the unit of length, which is taken as the bohr;  $Z$  is the net charge of the target—the sum of the nuclear charges of the atoms minus the number of bound electrons, i.e.,

$$Z = z_1 + z_2 + \dots + z_v - N \quad (12)$$

and  $\Gamma$  is the gamma function.

Notice that the first sum in Eq. (1) consists of terms representing a scattering electron, represented by  $X_{lp}$  and the  $\mathbf{r}_{N+1}$ -dependent and  $\sigma_{N+1}$ -dependent parts of  $F_i$ , moving in the field of one or more target eigenstates  $\Phi_i$ . The dummy index  $i$  labels the channels and, for the particular choice of boundary conditions  $\alpha_{0lp} = \delta_{lp}$ ,  $p$  denotes the initial channel (the initial channel was designated  $i$  in Section 1). In general, a particular choice of boundary conditions singles out one channel, here called  $p$ , for special treatment. The second sum in Eq. (1) consists of terms which represent the  $(N+1)$ -electron system without necessarily singling out the scattering electron for nonequivalent treatment. Thus mathematically this sum is used to obtain a more complete expansion of the total wave function. Physically it may be used to represent compound states of the scattering electron plus target or to include correlation of scattering and target electrons.



Illustrative examples of the form (1) for scattering wave functions are given in detail for various atoms elsewhere.<sup>(33-35)\*</sup> A general formulation for electron scattering by atoms or ions with any number of incomplete subshells is given by Smith and Morgan.<sup>(38)</sup> It should be noted that terms with square-integrable  $X_{ip}$  may be moved from the first sum to the second sum in (1) without changing the total wave function but involving a change in  $P$ , which is therefore not a well-defined quantity for a given trial wave function. Where such terms are placed is a matter of convenience. We will place them in the second sum.

The scattering cross sections may be expressed<sup>(39,40)</sup> in terms of the asymptotic form of the wave function  $\psi^P$  (by using Green's theorem it is possible to write the asymptotic form of the wave function in terms of an integral over the wave function). To calculate cross sections it is convenient to define three  $N_{op} \times N_{op}$  matrices which are independent of  $\tau$  and the particular choice of scattering boundary conditions on the wave function. The reactance matrix  $\mathbf{R}$  is defined by

$$\mathbf{R} = \mathbf{V}^{1/2}[(\sin \tau)\alpha_0 + (\cos \tau)\alpha_1][(\cos \tau)\alpha_0 - (\sin \tau)\alpha_1]^{-1}\mathbf{V}^{-1/2} \quad (13)$$

where  $\mathbf{V}$  is the diagonal velocity matrix, i.e.,

$$V_{ij} = (\hbar k_i/m)\delta_{ij} \quad (14)$$

and

$$(\alpha_\beta)_{ij} = \alpha_{\beta ij}, \quad \beta = 0, 1 \quad (15)$$

Although  $\alpha_0$  and  $\alpha_1$  depend on the particular choice of boundary condition,  $\mathbf{R}$  as defined above is independent of this choice.

Then the scattering matrix  $\mathbf{S}$  is related to the reactance matrix and the diagonal unit matrix  $\mathbf{I}$  by

$$\mathbf{S} = (\mathbf{I} - i\mathbf{R})^{-1}(\mathbf{I} + i\mathbf{R}) \quad (16)$$

and the transition matrix  $\mathbf{T}$  is defined by

$$\mathbf{T} = \mathbf{S} - \mathbf{I} \quad (17)$$

Note that some authors use slightly different definitions of  $\mathbf{T}$ .

We can illustrate the use of these matrices by a simple example: the scattering of an electron with initial momentum  $\hbar k_p$  off a target with spherically symmetric eigenstates  $n = 1, 2, \dots$ . For the partial wave with relative orbital angular momentum  $\hbar l$ , the scattering amplitude for scattering angle  $\theta$  and a  $p \rightarrow n$  transition is

$$f_{np}^l = \frac{-1}{2i(k_n k_p)}(2l+1)T_{np}^l P_l(\cos \theta) \quad (18)$$

where  $P_l$  is a Legendre polynomial. The total scattering amplitude is a sum over  $l$  which converges because the scattering amplitude becomes small for high  $l$

\*The work of Smith *et al.*<sup>(34)</sup> contains an error which was later corrected.<sup>(36,37)</sup>

(the classical argument for this is that the impact parameter is  $l/k_p$  and scattering is small or zero if this exceeds the range of the potential). For more general collision processes the scattering amplitude may still be expressed in terms of  $T$  matrix elements but it involves a multiple-index sum over  $T$  matrix elements corresponding to degenerate processes. Further, complicated angular momentum coupling coefficients, which are not needed in this chapter, occur instead of the simple factor  $(2l+1)$ . In general the integral cross section  $Q_{ij}$  for the electron-impact excitation of the  $i \rightarrow j$  transition (or for elastic scattering when  $i = j$ ) is related to the differential cross section  $I_{ij}(\Omega)$  and the scattering amplitude  $f_{ij}(\Omega)$  corresponding to scattering solid angle  $\Omega$  by

$$Q_{ij} = \int I_{ij}(\Omega) d\Omega \quad (19a)$$

$$I_{ij}(\Omega) = (k_j/k_i) |f_{ij}(\Omega)|^2 \quad (19b)$$

Performing the absolute square in Eq. (19b), we can express the integral and differential cross sections in terms of weighted sums of products of transition matrix elements. The weights include the angular momentum coupling coefficients. The complete formulas are given elsewhere<sup>(10,39-42)</sup> but they are not given here because we shall not need to define all the angular momentum coupling coefficients which these expressions contain. It is important to use consistent phase conventions for  $Y_{lm}$  and the angular momentum coupling coefficients in calculating these quantities.<sup>(42-44)</sup> We shall generally deal with the reactance matrix, from which  $T$  and  $f_{ij}(\Omega)$  may be calculated, rather than with  $T$  and  $f_{ij}(\Omega)$ , because  $R$  is real while the latter two quantities are complex.

When the exact reactance matrix cannot be obtained, one must resort to variational methods, to perturbation theory, or to other approximation schemes. In variational methods a variationally correct expression\* for the reactance matrix can be written in terms of the reactance matrix obtained from the asymptotic form of a trial function plus an integral over the trial function. For example, we introduce a matrix  $L$  with elements

$$L_{ij} = \langle \psi^i | H - E | \psi^j \rangle \quad (20)$$

and consider variations of the functions  $\psi^i$  and  $\psi^j$  with constant  $\tau$  and constant  $\alpha_0 = I$ . In other words,  $\psi^i$  and  $\psi^j$  are represented by Eq. (1) with the second sum and  $X_p$  variable (except for  $\tau$  and  $\alpha_0$ ). The Kohn variational principle<sup>(45-47)</sup> is†

$$\delta(\alpha_1 - 2\alpha_0 \hbar^{-1} \mathbf{V}^{-1} \mathbf{L}) = 0 \quad (21)$$

for small variations of the trial function about the exact wave function. Since

\*A variationally correct expression for a scattering parameter in terms of trial scattering wave functions yields an approximate value for the scattering parameter which depends quadratically (not linearly) on the errors in the trial functions.

†Strictly speaking, this is the Kohn variational principle only when  $\tau$  is zero. We have considered a generalization to simplify the following discussion.

$\alpha_0$ ,  $\tau$ , and the velocity matrix are known constants in a given application of Eq. (21), Eq. (13) can be used and often is used to rewrite Eq. (21) in terms of  $\mathbf{R}$  instead of  $\alpha_1$ . Our treatment in terms of  $\alpha_1$  at fixed  $\alpha_0$  will simplify our subsequent discussion. Thus, given trial functions with asymptotic forms specified by  $\alpha_0 = \mathbf{I}$  and  $\alpha_1 = \alpha_1^0$ , an expression for the  $N_{op} \times N_{op}$  coefficient matrix  $\alpha_1$  which is stationary for small variations (with constant  $\tau$  and  $\alpha_0 = \mathbf{I}$ ) of the trial function about the exact wave function is

$$\alpha_1^K = \alpha_1^0 - 2a_0\hbar^{-1}\mathbf{V}^{-1}\mathbf{L} \quad (22)$$

Use of this variationally correct expression and Eq. (13) provides a prescription for calculating cross sections from any appropriate scattering wave functions.

The Kohn variational principle is even more valuable in providing a means for optimizing trial wave functions of given functional form with variable coefficients. The standard variational derivation shows that if the condition (21) is satisfied for all possible small variations of the set of functions  $\{\psi^p\}_{p=1}^{N_{op}}$  consistent with constant  $\tau$  and  $\alpha_0 = \mathbf{I}$ , then these functions must be exact solutions of the Schrödinger equation. In practice we impose certain restrictions on the set of functions, such as finite  $P$  and  $M$  in Eq. (1) and particular choices of the  $\{W_m\}_{m=1}^M$ . Nevertheless, using the usual variational procedure, the "optimum" set of functions  $\{\psi^p\}_{p=1}^{N_{op}}$  consistent with these restrictions may be determined by requiring (21) to be satisfied for all small variations consistent with these restrictions. As usual, the resulting equations for the unknown functions and coefficients in the trial function are the same as would be obtained by requiring that the projection of  $(H-E)\psi^p$  have no overlap with the function space spanned by the known or predetermined functions in the trial function. In this respect the derivation and resulting equations are very similar to the derivation of multiconfiguration Hartree-Fock equations for bound-state problems. For example, one may require the variational functional  $\alpha_1^K$  to be stationary with respect to point-by-point variation of the functions  $X_{ip}$ . If  $\hat{O} = 1$ , this yields a set of coupled differential equations for the  $X_{ip}$  which are called the close coupling equations without exchange.\* If  $\hat{O}$  is an operator which makes the total wave function antisymmetric to permutation of any two electrons, point-by-point variation of the  $X_{ip}$  yields a set of coupled integrodifferential equations for the  $X_{ip}$  which are called the close coupling equations.† The actual form of these equations is displayed in the next subsection [see Eq. (50)]. When  $M > 0$  and the coefficients  $c_{mp}$  are also varied,

\*This refers to exchange of the scattering electron with the bound electrons. Of course it is still possible to include exchange effects in the  $\Phi_i$  functions in this formalism.

†An approach halfway between the close coupling methods with and without exchange is the post-symmetrization method.<sup>(48)</sup> In this case the trial function is optimized with  $\hat{O} = 1$  but then a variational correction is calculated with  $\hat{O}$  as an antisymmetrizer. This approach is similar in spirit to the Musher-Silbey<sup>(49)</sup> method for bound-state calculations.

these equations are coupled to algebraic equations for the  $c_{mp}$  and the whole set of coupled equations are generally called the correlation method equations if the  $W_m$  are thought to represent electron correlation<sup>(33,50,51)</sup> but they are still called the close coupling equations if the  $W_m$  are merely added to allow the  $X_{ip}$  to be constrained orthogonal to the bound orbitals.<sup>(34,35)</sup> The close coupling method and the correlation method are scattering analogs of the multiconfiguration Hartree-Fock equations<sup>(52)</sup> with numerical radial functions for bound-state problems. In fact they have sometimes been called the continuum Hartree-Fock method.

Numerical radial functions are often used for bound states of atoms and for electron-atom scattering but are less useful for molecular problems because the expansion about the molecular center of mass strongly couples terms with widely different orbital angular momenta. This problem can be alleviated for diatomic molecules by using an expansion in prolate spheroidal coordinates and such an approach has been used both for bound states<sup>(53)</sup> and for electron scattering<sup>(54)</sup> for diatomic molecules. This approach is more complicated, however, and is not useful for general polyatomic molecules. The alternative usually adopted for bound-state calculations on molecules is an expansion in nuclear-centered exponential-type or Gaussian-type functions,<sup>(55)</sup> in Gaussian lobe functions, or in floating Gaussian-type orbitals.<sup>(56)</sup> This leads to an algebraic problem, i.e., a matrix equation for the coefficients. The resulting methods are the matrix Hartree-Fock method<sup>(57)\*</sup> and the matrix multiconfiguration Hartree-Fock method.<sup>(58)†</sup> The matrix elements may be evaluated *ab initio*<sup>(59)</sup> or approximated by techniques such as neglect-of-differential-overlap (NDO)<sup>(60)</sup> or the  $X\alpha$ <sup>(61)</sup> method. These approximation techniques may be parametrized against *ab initio* calculations or against experiments. The scattering analogs of these matrix methods are the matrix variational methods of scattering theory.<sup>(46,47)</sup> These are also called algebraic variational methods.

In matrix variational methods the  $X_{ip}$  are expanded in terms of square-integrable functions with variable coefficients  $c_{ap}^i$  and non-square-integrable functions with constant coefficients  $\alpha_{1ip}$ , i.e.,

$$X_{ip}(r_{N+1}) = Y_{ip}(r_{N+1}) + \sum_{a=1}^{n_i} c_{ap}^i \eta_a^i(r_{N+1}) \quad (23)$$

where  $Y_{ip}$  is defined by Eqs. (9)–(11) and the variational functional  $\alpha_1^K$  is required to be stationary with respect to variations of the  $c_{ap}^i$ ,  $\alpha_{1ip}$ , and  $c_{mp}$  at fixed  $\tau$  and  $\alpha_{0ip}$ . This yields a matrix equation which must be satisfied by the vectors of varied coefficients. Examples of the types of equations which must

\*This is also called the Hartree-Fock-Roothaan method.

†This is also called the multiconfiguration self-consistent-field method.

actually be solved are given later in this section [see, e.g., Eq. (38) and the discussion following Eq. (41)]. Before working out these details, it will be valuable to consider a few general features of such matrix variational methods. The matrix elements in the matrix equation are integrals involving  $(H - E)$  and pairs of terms in the expansion of the wave function. They may be reduced to one-electron and two-electron integrals using standard methods.<sup>(46)</sup> But, in addition to the usual integrals involving square-integrable functions which occur in bound-state problems, there are integrals involving up to two non-square-integrable one-electron functions.

Matrix variational methods have been successfully applied to *ab initio* electron-atom scattering calculations in the last few years using not only the Kohn variational method described above but also more refined algebraic techniques (see below) which have important advantages in actual calculations. Extensions to electron-molecule scattering are just beginning. Semiempirical methods of evaluating most of the integrals occurring in these methods have not yet been developed or extensively tested but it is possible that such semiempirical methods will eventually prove to be just as successful (or unsuccessful) for scattering problems as for bound-state problems. Some approximation methods for calculating the static potentials and exchange potentials occurring in these integrals have been developed and tested, however, and are discussed in Section 2.1.2.

In using the variational principle (21) it sometimes happens that the variational correction (22) is very large even for a trial function which appears to be fairly accurate at nearby energies or with one less or one more term. In such cases the results are often inaccurate. This problem is not due to an inaccurate representation of the physics in the trial function but is most easily understood in terms of accidental near-singularities of some of the matrices involved in the calculation. This is a defect of the Kohn variational method first discussed in detail by Schwartz.<sup>(62)</sup> Schwartz was nevertheless able to obtain accurate results by varying a nonlinear parameter in his trial function so that the accidental near-singularities were removed. This is an undesirable computational inconvenience. Saraph *et al.*<sup>(63)</sup> suggested the problem could be alleviated by choosing the phase angle  $\tau$  based on the results of a calculation with  $P = 1$  and  $M = 0$ . Nesbet<sup>(64)</sup> made a more complete analysis of this defect of the variational method and suggested it could be alleviated by choosing  $\tau$  as either zero or  $\pi/2$  based on certain ratios of matrix elements. This is called the anomaly-free method. This analysis has been reviewed elsewhere<sup>(46,47)</sup> (along with other methods designed to eliminate anomalies and other aspects of algebraic variational methods). The anomaly-free method is not completely free of anomalies.<sup>(47,65)</sup> Subsequent attempts to improve the method led to the optimized anomaly-free and optimized minimum-norm methods.<sup>(65)</sup> Experience has shown that none of these methods is completely satisfactory.<sup>(66-68)</sup> Nevertheless the problem is well enough understood that spurious results due

to the singularities of the matrices involved should never be mistaken for accurate ones.\*

Malik and Rudge have suggested another procedure for eliminating anomalies by varying nonlinear parameters in the trial function.<sup>(70)</sup> This is not very efficient for computations. It has also been suggested that in each case several of these methods plus the closely related minimum-norm method<sup>(46,47)</sup> be applied and the results not be accepted as more accurate than the bounds which can be placed around the results of three or more variational methods.<sup>(47,67)</sup> This is not too difficult for cases where most of the computer time is spent on the evaluation of elements of  $(H-E)$  and relatively little is spent on the algebraic problem. For large molecules and intermediate energies, however, where a large number of basis functions are required and approximation methods may be used for the integrals, the algebraic problem may become very time-consuming. Then the size of the algebraic problem may be profitably reduced using contracted basis functions.<sup>(71)</sup> However, additional computational simplifications are still desirable. Recently, we have shown<sup>(68)</sup> that the variational least squares (VLS) method<sup>(72)</sup> is very successful at avoiding anomalies, it provides results which are continuous functions of energy and any nonlinear parameters in the trial functions, and does not require comparing the results of alternative computational schemes. We recommend this method or the least squares variational method discussed below it for routine production runs and it is described here as an example of the basis function approach to scattering. It should be noted that the same basic one-electron and two-electron integrals occur in all the variationally corrected methods since they involve the calculation of  $L$  in the last step.

The VLS method may be motivated by noting that the anomalies in the Kohn method are due to a certain matrix of  $(H-E)$  becoming singular. The minimum-norm method and the VLS methods deal with matrices of  $(H-E)^2$  in an attempt to avoid such singularities. In fact the VLS method is analogous to the Kohn method but with  $(H-E)^2$  replacing  $(H-E)$ . However, to avoid having to calculate the complicated integrals involving  $H^2$ , the minimum-norm and VLS methods effectively use an approximate resolution of the identity, equivalent to applying the closure property to an incomplete basis set.

It is most convenient to set all  $n_i = 0$  on the right-hand side of Eq. (23) and include these square-integrable terms in the second sum of Eq. (1). Recalling the meaning of  $P$  and  $M$  from the two paragraphs following Eq. (12), we see that  $P$  in this case is equal to  $N_{op}$  and is the number of target eigenstates, all open, included in the first sum in Eq. (1), and  $M$  is the number of square-integrable terms in the trial wave function. The VLS method is derived by

\*Shimamura,<sup>(69)</sup> however, has shown that the problem of anomalies is far more general than an analysis in terms of singular matrices would suggest and anomalous resonances occur even in trial functions which are not of the linear-combination type. The author is grateful to Dr. Shimamura for valuable correspondence concerning Refs. 47 and 69.

considering the matrix

$$\mathbf{U} = \begin{bmatrix} \mathbf{U}^{00} & \mathbf{U}^{01} & \mathbf{U}^{0W} \\ \mathbf{U}^{10} & \mathbf{U}^{11} & \mathbf{U}^{1W} \\ \mathbf{U}^{W0} & \mathbf{U}^{W1} & \mathbf{U}^{WW} \end{bmatrix} \quad (24)$$

where

$$U_{ij}^{\alpha\beta} = \langle A_{i\alpha} f_i | H - E | \hat{O} A_{j\beta} f_j \rangle, \quad \alpha = 0, 1; \beta = 0, 1; i = 1, 2, \dots, P; j = 1, 2, \dots, P \quad (25)$$

$$U_{mj}^{W\beta} = U_{jm}^{\beta W} = \langle W_m | H - E | \hat{O} A_{j\beta} f_j \rangle, \quad \beta = 0, 1; j = 1, 2, \dots, P; m = 1, 2, \dots, M \quad (26)$$

$$U_{nm}^{WW} = \langle W_n | H - E | \hat{O} W_m \rangle, \quad n = 1, 2, \dots, M; m = 1, 2, \dots, M \quad (27)$$

Therefore  $\mathbf{U}$  is a square matrix of order  $2P + M$ . If we define

$$\mathbf{Z} = \begin{bmatrix} \alpha_0 \\ \alpha_1 \\ \mathbf{c} \end{bmatrix} \quad (28)$$

where  $(\mathbf{c})_{mp} = c_{mp}$  and  $\mathbf{Z}$  is a rectangular  $(2P + M) \times P$  matrix, then if  $\psi^p$  of Eq. (1) were exact, it would satisfy

$$(H - E)\psi^p = 0 \quad (29)$$

and therefore it would satisfy the set of equations

$$\int dx_1 dx_2 \dots dx_{N+1} A_{i\alpha}(r_{N+1}) f_i(x_1, x_2, \dots, x_N, \hat{\mathbf{r}}_{N+1}, \sigma) (H - E) \times \psi^p(x_1, x_2, \dots, x_{N+1}) = 0, \quad i = 1, 2, \dots, P; \alpha = 0, 1 \quad (30)$$

$$\int dx_1 dx_2 \dots dx_{N+1} W_n(x_1, x_2, \dots, x_{N+1}) (H - E) \psi_p(x_1, x_2, \dots, x_{N+1}) = 0 \quad n = 1, 2, \dots, M \quad (31)$$

which, together for all  $p = 1, 2, \dots, P$ , are equivalent to the matrix equation

$$\mathbf{UZ} = 0 \quad (32)$$

In general for approximate trial functions, (32) does not hold and it is not possible to make it hold by varying the parameters  $\alpha_{1p}$  and  $c_{mp}$  with constant  $\tau$  and

$$\alpha_0 = \mathbf{I} \quad (33)$$

It is possible to make this equation hold by considering point-by-point variation of the radial functions, but as discussed above, this is not always practical. In the variational least squares method we therefore define a matrix  $\mathbf{D}$  of dimension  $(2P + M) \times P$  as follows:

$$\mathbf{D} = \mathbf{UZ} \quad (34)$$

and attempt to minimize its norm at constant  $\tau$  and  $\alpha_0 = \mathbf{I}$ . To do this we require the  $P \times P$  matrix  $\mathbf{D}^\dagger \mathbf{D}$  be stationary through first order in small variations, which yields

$$\mathbf{U}^\dagger \mathbf{U} \mathbf{Z} = 0 \quad (35)$$

Since  $\alpha_0 = \mathbf{I}$ , Eq. (35) represents  $P$  sets of  $(2P + M)$  inhomogeneous equations, which may be written in partitioned form as

$$\begin{bmatrix} (\mathbf{U}^\dagger \mathbf{U})^{01} & (\mathbf{U}^\dagger \mathbf{U})^{0w} \\ (\mathbf{U}^\dagger \mathbf{U})^{11} & (\mathbf{U}^\dagger \mathbf{U})^{10} \\ (\mathbf{U}^\dagger \mathbf{U})^{w1} & (\mathbf{U}^\dagger \mathbf{U})^{ww} \end{bmatrix} \mathbf{a} = - \begin{bmatrix} (\mathbf{U}^\dagger \mathbf{U})^{00} \\ (\mathbf{U}^\dagger \mathbf{U})^{10} \\ (\mathbf{U}^\dagger \mathbf{U})^{w0} \end{bmatrix} \quad (36)$$

where

$$\mathbf{a} = \begin{pmatrix} \alpha_1 \\ \mathbf{c} \end{pmatrix} \quad (37)$$

Since the unknown vector  $\mathbf{a}$  contains only  $(P + M)$  linear variational coefficients for each of the  $P$  initial states, only a subset  $(P + M)$  of these equations can be satisfied simultaneously for each initial state. Wladawsky suggested that the following  $P$  sets of  $(P + M)$  equations be satisfied exactly:

$$\begin{bmatrix} (\mathbf{U}^\dagger \mathbf{U})^{11} & (\mathbf{U}^\dagger \mathbf{U})^{1w} \\ (\mathbf{U}^\dagger \mathbf{U})^{w1} & (\mathbf{U}^\dagger \mathbf{U})^{ww} \end{bmatrix} \mathbf{a} = \begin{bmatrix} (\mathbf{U}^\dagger \mathbf{U})^{10} \\ (\mathbf{U}^\dagger \mathbf{U})^{w0} \end{bmatrix} \quad (38)$$

Equation (38) may be solved; it yields for  $\alpha_1$

$$\alpha_1 = -(\mathbf{Q}^{11})^{-1} \mathbf{Q}^{10} \quad (39)$$

where for convenience in representing the mathematical solution we have defined

$$\mathbf{Q}^{1\beta} = (\mathbf{U}^\dagger \mathbf{U})^{1\beta} - (\mathbf{U}^\dagger \mathbf{U})^{1w} [(\mathbf{U}^\dagger \mathbf{U})^{ww}]^{-1} (\mathbf{U}^\dagger \mathbf{U})^{w\beta}, \quad \beta = 0, 1 \quad (40)$$

[The only justification for selecting a subset of equations as Wladawsky did is that it yields useful results. This aspect of the derivation is discussed again in the paragraph before Eq. (43) and in the section containing Eqs. (43)–(49).]

Then the asymptotic form of the optimized trial function yields the following approximation to the reactance matrix [by using Eq. (13) with  $\alpha_0 = \mathbf{I}$ ]:

$$\mathbf{R}_{\text{VLS}} = \mathbf{V}^{1/2} [(\sin \tau) - (\cos \tau)(\mathbf{Q}^{11})^{-1} \mathbf{Q}^{10}] [(\cos \tau) + (\sin \tau)(\mathbf{Q}^{11})^{-1} \mathbf{Q}^{10}] \mathbf{V}^{-1/2} \quad (41)$$

This is the zeroth-order variational least squares reactance matrix. Equations (39)–(41) are identical in form to the Kohn variational method except that in the Kohn method  $\mathbf{U}^\dagger \mathbf{U}$  is replaced by  $\mathbf{U}$  and  $\mathbf{R}_{\text{VLS}}$  is replaced by the Kohn zeroth-order reactance matrix  $\mathbf{R}_K$ . In either method, once the trial function has



been optimized one should substitute it into (22) to obtain an improved estimate of the asymptotic form of the wave function since  $L$  is not zero. In fact

$$L = Z^{\dagger}UZ \quad (42)$$

From the improved  $\alpha_1$  one can compute an improved reactance matrix using (13).

Once the asymptotic form of the wave function is improved variationally, the coefficients may be redetermined by solving a subset of  $M$  of the equations (38) for the vector  $\mathbf{c}$  in terms of the improved vector  $\alpha_1$ . This was recommended by Matese and Oberoi,<sup>(23)</sup> although it has not been justified variationally. Unless one does this, one does not have an approximate wave function whose asymptotic form corresponds to the variationally improved reactance matrix. The asymptotic form of the optimized trial function corresponds to the zeroth-order reactance matrix. For applications which use the whole wave function, e.g., photoionization, it may be preferable to use a wave function corrected by the procedure of Matese and Oberoi.

It has been demonstrated that the wave function in the VLS method generally corresponds to a smaller value of  $L$  than that obtained by several other variational methods.<sup>(68)</sup> Recalling the definition of  $L$  [Eq. (42)] and the discussion preceding Eq. (32); we see that this means that the wave function in the VLS method satisfies the Schrödinger equation "better" than the wave function obtained in several other variational methods. Further, the zeroth-order reactance matrix is generally more accurate than the zeroth-order reactance matrix of other methods to which it has been compared.<sup>(68)</sup> Finally, the zeroth-order VLS method is free, for all values of  $\tau$ , of the anomalies which plague most of the other variational methods discussed above.<sup>(72)</sup>

It has been suggested that rather than satisfying the last two rows of Eq. (36), as in Eq. (38), one might satisfy, for example, the first and third rows.<sup>(68)</sup> Schmid and co-workers have developed a similar but even more general method called the least-squares variational method.<sup>(73-75)</sup> They point out that if  $\psi^P$  of Eq. (1) were exact, it would satisfy (29) and therefore, in particular, it would satisfy Eq. (30) with  $\alpha = 1$ , Eq. (31), and

$$\int dx_1 dx_2 \cdots dx_{N+1} \omega_{\rho}(x_1, x_2, \dots, x_{N+1}) \times (H - E)\psi^P(x_1, x_2, \dots, x_{N+1}) = 0 \quad \rho = 1, 2, \dots, C \quad (43)$$

where the  $\omega_{\rho}$  are square-integrable or non-square-integrable functions of longer range than the set  $\{W_m\}$  and each  $\omega_{\rho}$  contains a weight factor whose value can be freely specified. Equation (30) with  $\alpha = 1$  and Eqs. (31) and (43) can be written

$$A\mathbf{a} = \mathbf{b} \quad (44)$$

where

$$\mathbf{A} = \begin{bmatrix} \mathbf{U}^{\omega 1} & \mathbf{U}^{\omega W} \\ \mathbf{U}^{11} & \mathbf{U}^{1W} \\ \mathbf{U}^{W1} & \mathbf{U}^{WW} \end{bmatrix} \quad (45)$$

$$\mathbf{b} = \begin{bmatrix} \mathbf{U}^{\omega\omega} \\ \mathbf{U}^{1\omega} \\ \mathbf{U}^{W\omega} \end{bmatrix} \quad (46)$$

and  $\mathbf{U}^{\omega 1}$ ,  $\mathbf{U}^{\omega W}$ ,  $\mathbf{U}^{\omega\omega}$ ,  $\mathbf{U}^{1\omega}$ , and  $\mathbf{U}^{W\omega}$  are defined analogously to Eqs. (25)–(27); for example,

$$U_{\rho i}^{\omega 1} = \langle \omega_{\rho} | H - E | \hat{O} A_{i1} f_i \rangle \quad (47)$$

so that  $\mathbf{A}$  and  $\mathbf{b}$  are rectangular matrices of dimensions  $(C+P+M) \times (P+M)$  and  $(C+P+M) \times P$ , respectively. For a given trial function with constant  $\tau$  and  $\alpha_0 = \mathbf{I}$ , the  $(C+P+M)$  equations (44) are incompatible. So we impose the condition that the norm of  $(\mathbf{A}\mathbf{a} - \mathbf{b})$  be minimum, which leads to

$$\mathbf{A}^{\dagger} \mathbf{A} \mathbf{a} = \mathbf{A}^{\dagger} \mathbf{b} \quad (48)$$

This is the least-squares variational method for optimizing a trial function. The optimized trial function may then be substituted into the Kohn variational expression (22) to obtain a variationally improved reactance matrix.

It is clear that if

$$w_i(x_1, x_2, \dots, x_{N+1}) = w_i A_{i0}(r_{N+1}) f_i(x_1, x_2, \dots, x_N, \hat{r}_{N+1}, \sigma_{N+1}) \quad i = 1, 2, \dots, P \quad (49)$$

where  $w_i$  are the weight factors and if the weight factors are all set equal to unity and  $C = P$ , that the least-squares variational method of Schmid and co-workers reduces to the VLS method of Wladawsky.

Schmid and co-workers<sup>(73,74)</sup> have used the least-squares variational method for potential scattering and nuclear scattering problems. They obtained accurate results which are insensitive to the choice of weight factors and are free of anomalies.

When all the open-channel radial functions are allowed to vary point-by-point, and the exact target wave functions for open channels are known, the variational principles may become minimum principles for certain scattering parameters.<sup>(76)</sup> In the matrix variational methods, these minimum principles do not hold, but a quasiminimum principle can be very useful.<sup>(77)</sup> If the integrals are approximated, however, the quasiminimum principle does not hold. When the exact target wave functions are not known, a subsidiary minimum principle may be useful.<sup>(78)</sup>

Unfortunately space does not allow a fuller discussion of these points here,

but the reader should be aware that these aspects of the calculations are a current research area.

The best illustrations of accurate calculations using the matrix variational methods are the electron-atom calculations of Nesbet and co-workers, who used the optimized anomaly-free variational method.<sup>(50)</sup> In some cases they also used a semiempirical net correlation energy parameter.

When the many-electron Hamiltonian is substituted into Eqs. (25)–(27), (30), (31), (43), and (47), these integrals reduce to products of one-electron and two-electron integrals.<sup>(46)</sup> Methods have been developed for performing these integrals using nuclear-centered exponential-type basis functions and various non-square-integrable functions for electron-atom scattering.<sup>(79)</sup> For molecules it is easier to evaluate the integrals if Gaussian-type basis functions are used for the square-integrable basis functions<sup>(80)</sup> or if integral approximations such as mentioned before Eq. (23) are used. The most difficult integrals to evaluate are those containing free waves and another approach to simplifying the integrals is to extract scattering information from an expansion of the wave function which involves only square-integrable ( $L^2$ ) basis functions. These methods are considered in Section 2.2. Chung and Ajmera<sup>(81)</sup> developed a procedure for carrying out calculations by the Kohn variational method in which free waves are used in the expansion but the most difficult integrals (those involving two free waves) are not evaluated. This will simplify the calculation, but in large calculations the computer time is often dominated by the much larger numbers of easier integrals.

### 2.1.2 Approximations to Potential Terms

The close coupling equations for the radial functions, in the case where the second term in (1) is omitted, may be written

$$\left[ \frac{-d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} - k_i^2 \right] F_{ip}(r) + 2 \sum_j [V_{ij}(r)F_{jp}(r) + \int dr' K_{ij}(r, r')F_{jp}(r')] = 0 \quad (50)$$

where the direct radial potentials are given by

$$V_{ij}(r) = \int d\mathbf{r} \hat{V}_{ij}(\mathbf{r}) \quad (51)$$

in terms of the direct potentials defined in the following way:

$$\hat{V}_{ij}(\mathbf{r}_{N+1}) = \int dx_1 dx_2 \dots dx_N d\sigma_{N+1} f_i^*(x_1, x_2, \dots, x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) V_{\text{int}} \times f_j(x_1, x_2, \dots, x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \quad (52)$$

$$V_{\text{int}} = H(x_1, x_2, \dots, x_{N+1}) - H_i(x_1, x_2, \dots, x_N) - T(\mathbf{r}_{N+1}) \quad (53)$$

and the exchange potential terms are

$$\int dr' K_{ij}(r, r') F_{ip}(r') = \int d\hat{r} d\hat{r}' \hat{K}_{ij}(\mathbf{r}, \mathbf{r}') F_{ip}(r') Y_{lmj}(\hat{r}') \quad (54)$$

with kernels

$$\begin{aligned} \hat{K}_{ij}(\mathbf{r}_{N+1}, \mathbf{r}_N) = -N \int dx_1 dx_2 \cdots dx_{N-1} d\sigma_N d\sigma_{N-1} f_i^*(x_1, x_2, \dots, x_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \\ \times [H(x_1, x_2, \dots, x_{N+1}) - E] \Phi_j(x_1, x_2, \dots, x_{N-1}, X_{N+1}) \chi_{mj}(\sigma_N) \end{aligned} \quad (55)$$

The physical meaning of the omission of the second term in (1) is that the scattering electron is represented by a single orbital in every term in Eq. (1); some workers would say that "the scattering electron is not explicitly correlated." Then the equations for the radial function parts  $F_{op}$  of the scattering electron orbitals assume the form (50). The interpretation of Eq. (50) is familiar because it has the same form as the multiconfiguration Hartree-Fock equation for bound-state radial functions. The difference is that the scattering electron is unbound so at least one and maybe all of the radial functions  $F_{ip}$  are non-square-integrable. Then the diagonal potential terms contain the nuclear attraction, electronic screening, and exchange effects, while the nondiagonal terms are responsible for coupling of channels, i.e., inelastic effects, by both nonexchange and exchange mechanisms. Because the equations in the form (50) are closely analogous to the equations for bound states and because the approximations we will consider are closely analogous to those used for bound states, Eq. (50) provides a good basis for discussion of the potential terms. However, the same potentials occur, albeit in a more complicated algebraic framework, even if the second term in (1) is included and they occur as parts of the matrix elements in  $U$  when the radial functions are expanded in a basis set in the matrix variational methods. Note that Eqs. (51) and (54) are functions of  $r$ . The  $r$ -independent integrals discussed in the previous subsection [see, e.g., Eqs. (24)–(27)] involve matrix elements of these potentials with the basis functions of  $r$ . Next we consider the approximate evaluation of these potentials by methods similar to those used for approximate calculations on bound states.

For most atomic calculations  $\Phi_i$  and  $\Phi_j$  are built up using a basis set of orthonormal one-electron orbitals  $P_{klk}(r) Y_{lmk}(\hat{r})$ . Then it is convenient for simplifying the exchange potential to constrain the free orbitals  $F_{ip}(r) Y_{lmi}(\hat{r})$  to be orthogonal to the members of this set.\* This constraint is enforced by the use of Lagrange multipliers  $\mu_{ik}$  and adds terms like  $\delta_{ik} \mu_{ik} P_{klk}(r)$  to Eq. (50).<sup>(35)†</sup> Similar orthogonality constraints are useful for electron-molecule scattering.

\*This need not be a constraint on the total wave function if appropriate square-integrable terms are added in the second sum of Eq. (1). Inclusion of such terms adds additional terms to Eq. (50).

†An alternative to this orthogonalization procedure is discussed by Smith *et al.*<sup>(36)</sup> Orthogonalization is usually not employed for electron scattering by the hydrogen atom.<sup>(50,68,71)</sup>

When  $i = j$ ,  $V_{ij}(\mathbf{r}_{N+1})$  with  $f_i$  replaced by  $\Phi_i$  is called the static potential (for electron scattering). Its negative, the static potential for positron or proton scattering, has been called the electrostatic potential. One can envisage a whole series of approximations to the static potential corresponding to a given electronic state of a given atom or molecule. However, since it is a one-electron property of the target charge distribution, one expects the Hartree-Fock approximation to be fairly accurate<sup>(82)</sup> and we need only consider a sequence of approximations to the *ab initio* Hartree-Fock static potential. Accurate static potentials for atoms may be easily determined.<sup>(83)</sup> To obtain accurate *ab initio* one-electron properties for molecules, one must use an extended basis set including polarization functions. In a few cases<sup>(84-87)</sup> such accurate calculations have been carried out for ground states and have been used as standards for testing more approximate calculations.<sup>(85,86,88-90)</sup> At small  $r$ , the static potential is dominated by the attractive interactions of the scattering electron with the screened nuclei. At large  $r$  the static potential is dominated by the interaction of the electron with the multipole moments of the target. Thus it is necessary to use approximations which yield accurate charge densities near the nuclei and accurate multipole moments, respectively, to obtain these two features of the potential correctly.

There has been much interest in the electrostatic potential as an approximation of the interaction energy of certain electrophilic reagents with organic molecules. In this context the general shape of the electrostatic potential energy surface has been mapped for many molecules and the errors introduced in such surfaces by the approximation methods of quantum chemistry have been studied. This work has been reviewed by Scrocco and Tomasi.<sup>(91)</sup>

A particularly interesting study of CNDO/2 and INDO approximation methods for evaluating such potentials is included in two articles by Giessner-Prettre and Pullman.<sup>(92)</sup> They distinguish four levels of approximation, which are most easily discussed in reverse order from their numbering:

(iv) The coefficients of the NDO wave function are interpreted as coefficients of orthogonalized atomic orbitals (OAOs) obtained from the NDO method's minimum basis set of exponential-type functions by Löwdin's method.<sup>(93)</sup> From these coefficients one may obtain by a transformation the deorthogonalized coefficients, i.e., the coefficients of the original nonorthogonal exponential-type functions. From these the static potential is calculated correctly. In this case differential overlap cannot be neglected during the calculation of the static potential because it is the OAOs rather than the AOs which are assumed to have zero differential overlap. This calculation differs from an *ab initio* calculation only in that the core electrons are frozen into the nuclei and the density matrix of the target is obtained by a calculation using approximate integrals. The latter is a simplification of  $\Phi_i$  rather than of the step by which  $V_{ii}$  is obtained from  $\Phi_i$ .

(iii) In this case the coefficients of the NDO wave function are interpreted as coefficients of the nonorthogonal atomic orbitals. Then the static wave function is computed using the NDO method's density matrix with the basic assumption of neglect of differential overlap of basis functions on different centers.

(ii) Approximation (ii) is like approximation (iii) except for two differences: (a) intraatomic differential overlap is also neglected (this is called the XI approximation) and (b) the entire valence charge distribution on a given center is treated as if the charge were in the valence  $s$  orbital (this is called the  $V_{ss}$  approximation).

(i) Approximation (i) is like approximation (ii) but the interactions of the target electron with the external charge are approximated using the formula used in the NDO method for repulsion integrals between  $s$  orbitals (the sign must be switched if the external charge is positive).

They did not study the XI approximation independently of the  $V_{ss}$  approximation. They found that deorthogonalization [approximation (iv)] yields the best results but that the  $V_{ss}$  method [approximation (ii)] yields results of useful accuracy very inexpensively. However, some caution is warranted in using these conclusions because the *ab initio* results to which they make comparisons are computed with limited basis sets which do not include polarization functions.

We have compared calculations of the static potential for the ground state of  $N_2$  at its equilibrium internuclear separation using three *ab initio* calculations to INDO [approximation (iii)] and INDO XI calculations<sup>(86)</sup> and to a calculation using a sum of modified atomic densities.<sup>(89)</sup> The latter calculation is called Massey's method; for this calculation the atomic density is divided into a contribution from core electrons and a contribution from valence electrons and the latter is contracted uniformly in an attempt to account for one of the effects of bond formation. Van-Catledge<sup>(94)</sup> has also computed the INDO- $V_{ss}$  result [approximation (ii)] for comparison with these results. Finally, we have performed calculations (INDO/1s and INDO XI/1s) in which the NDO calculation is modified by pulling the core electrons out of the nucleus and adding the sum of atomic core densities to the NDO valence electronic charge distributions.<sup>(86)</sup> These calculations are compared in Tables 1-3. In these tables the [432] and [53] calculations are extended-basis *ab initio* calculations, where the former includes polarization functions. The [21] calculation is a minimum-basis-set calculation using a basis set of accurate Hartree-Fock atomic orbitals.

Some of the methods are also compared in Fig. 1.<sup>(94)\*</sup>

Massey's method is fairly accurate at small  $r$ . It is easy to incorporate accurate atomic densities in this method, whereas the basis set of exponential-type functions used in the NDO methods does not yield an accurate atomic

\*The author is grateful to Prof. F. A. Van-Catledge for supplying these isopotential maps.

Table 1. Static Potential in Hartrees for Electron-N<sub>2</sub> Scattering for Collinear Approach as a Function of Distance in Bohrs from Electron to Center of N<sub>2</sub>

$r, a_0$	$V,^a h$									
	<i>Ab initio</i>									
	[432]	[53]	[21]	IA	INDO	INDO/1s	INDO XI	INDO XI/1s	INDO-V <sub>st</sub>	
0	-1.882	-2.806	-2.439	-1.943	-1.761	-1.761	-1.761	-1.761	-1.761	-1.919
0.6	-7.076	-7.195	-7.510	-6.974	-6.804	-6.858	-6.845	-6.899	-6.899	-3.161
1.2	-2.813(1)	-2.813(1)	-2.831(1)	-2.793(1)	-2.521(1)	-2.795(1)	-2.519(1)	-2.793(1)	-2.793(1)	-4.236
1.8	-2.195	-2.139	-2.191	-2.197	-1.885	-1.885	-2.110	-2.110	-2.110	-1.667
2.4	-3.207(-1)	-2.747(-1)	-2.773(-1)	-3.769(-1)	-9.235(-2)	-9.235(-2)	-2.816(-1)	-2.816(-1)	-2.816(-1)	-4.478(-1)
3.0	-2.648(-1)	1.758(-3)	6.250(-3)	-7.450(-2)	9.309(-2)	9.309(-2)	-2.191(-2)	-2.191(-2)	-2.191(-2)	-9.428(-2)
3.6	1.510(-2)	<sup>b</sup>	3.662(-2)	-1.603(-2)	7.512(-2)	7.512(-2)	7.630(-3)	7.630(-3)	7.630(-3)	-1.699(-2)
4.2	1.566(-2)	2.592(-2)	2.990(-2)	-3.639(-3)	4.891(-2)	4.891(-2)	7.379(-3)	7.379(-3)	7.379(-3)	-2.756(-3)

<sup>a</sup>Numbers in parentheses are powers of ten by which the entries should be multiplied.

<sup>b</sup>Not calculated.

Table 2. Static Potential in Hartrees for Electron- $N_2$  Scattering for Approach at  $45^\circ$  Angle to Bond Axis as Function of Distance in Bohrs from Electron to Center of  $N_2$

$r, a_0$	Ab initio					$V,^a h$	
	[432]	[53]	[21]	IA	INDO, INDO/1s		INDO XI, INDO XI/1s
0	-1.882	-2.086	-2.439	-1.943	-1.761	-1.761	-1.919
0.6	-2.661	-2.803	-3.084	-2.600	-2.945 <sup>b</sup>	-2.483 <sup>b</sup>	-2.040
1.2	-1.805	-1.850	-1.993	-1.651	-1.800	-1.603	-1.428
1.8	-5.523(-1)	-5.489(-1)	-6.092(-1)	-4.712(-1)	-4.603(-1)	-4.257(-1)	-5.434(-1)
2.4	-1.362(-1)	-1.240(-1)	-1.494(-1)	-1.115(-1)	-7.180(-2)	-8.120(-2)	-1.414(-1)
3.0	-3.099(-2)	-2.179(-2)	-3.234(-2)	-2.600(-2)	5.236(-4)	-1.286(-2)	-2.929(-2)
3.6	-6.017(-3)	<sup>c</sup>	-4.608(-3)	-6.166(-3)	8.927(-3)	-1.380(-3)	-5.235(-3)
4.2	-3.06(-4)	2.963(-3)	1.432(-3)	-1.491(-3)	7.643(-3)	3.265(-4)	-8.452(-4)

<sup>a</sup>Numbers in parentheses are powers of ten by which the entries should be multiplied.

<sup>b</sup>The INDO/1s and INDO XI/1s static potentials are the same (to four significant figures) as the INDO and INDO XI ones, respectively, for all entries in this table except  $r = 0.6a_0$ , where the results including 1s orbitals are more negative by 0.001.

<sup>c</sup>Not calculated.



Table 3. Static Potential in Hartrees for Electron- $N_2$  Scattering for Perpendicular Approach as Function of Distance in Bohrs from Electron to Center of  $N_2$

$r, a_0$	$V, h$							
	[432]	[53]	[21]	IA	INDO <sup>a</sup>	INDO XI <sup>b</sup>	INDO-V <sub>st</sub> <sup>b</sup>	
0.0	-1.882	-2.087	-2.439	-1.943	-1.761	-1.761	-1.919	
0.6	-1.210	-1.374	-1.616	-1.215	-1.534	-1.063	-1.337	
1.2	-4.417(-)	-5.391(-1)	-6.338(-1)	-4.108(-1)	-5.924(-1)	-3.185(-1)	-5.187(-)	
1.8	-1.352(-1)	-1.880(-1)	-2.155(-1)	-1.112(-1)	-2.143(-1)	-7.211(-2)	-1.389(-1)	
2.4	-4.388(-2)	-7.187(-2)	-7.848(-2)	-2.828(-2)	-9.257(-2)	-1.739(-2)	-2.950(-2)	
3.0	-1.724(-2)	-3.260(-2)	-3.374(-2)	-7.098(-3)	-4.886(-2)	-6.260(-3)	-5.383(-3)	
3.6	-8.526(-3)	-1.755(-2)	-1.755(-2)	-1.785(-3)	-2.940(-2)	-3.411(-3)	-8.839(-4)	
4.2	-5.160(-3)	-1.082(-2)	-1.078(-2)	-4.516(-4)	-1.914(-2)	-2.251(-3)	-1.344(-4)	

<sup>a</sup>Numbers in parentheses are powers of ten by which the entries should be multiplied.

<sup>b</sup>The contribution from the  $1s$  orbitals does not affect the first four significant figures of the static potential at  $90^\circ$ .

<sup>c</sup>Not calculated.

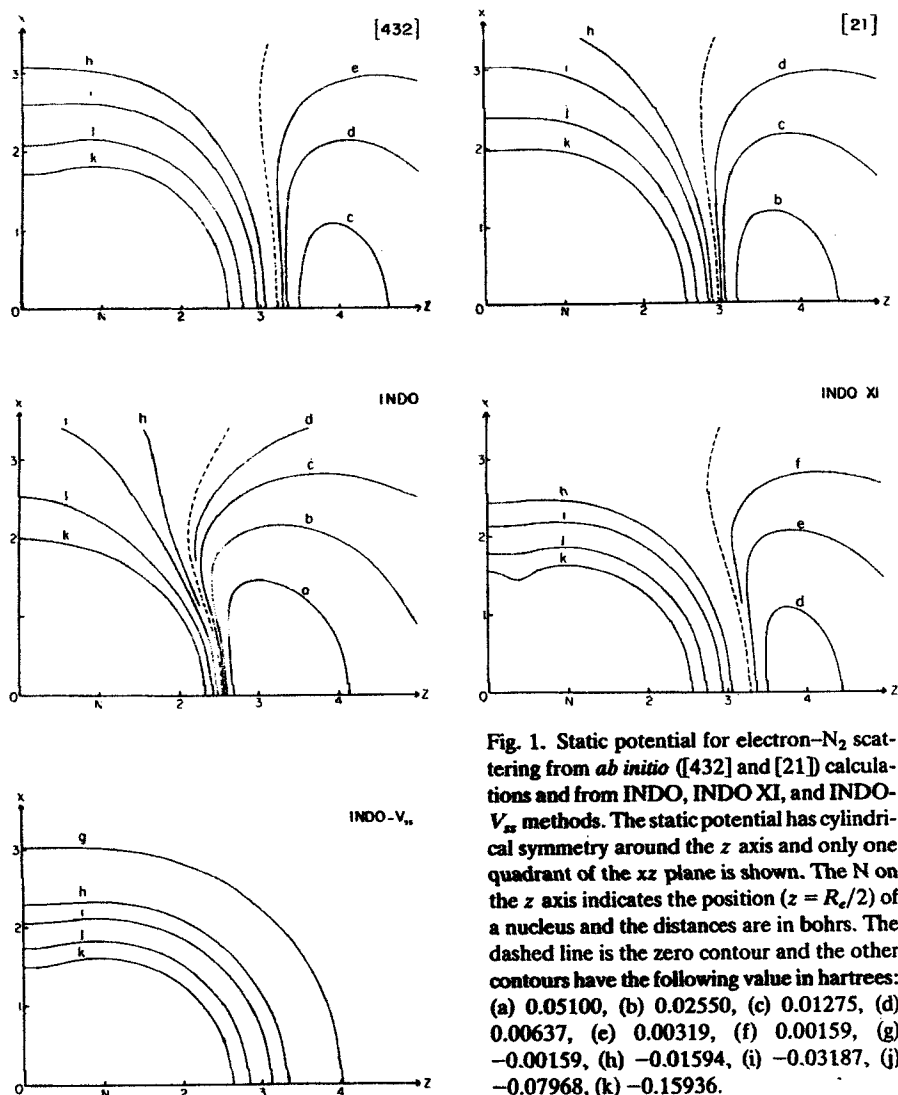


Fig. 1. Static potential for electron- $N_2$  scattering from *ab initio* ([432] and [21]) calculations and from INDO, INDO XI, and INDO- $V_{ee}$  methods. The static potential has cylindrical symmetry around the  $z$  axis and only one quadrant of the  $xz$  plane is shown. The N on the  $z$  axis indicates the position ( $z = R_e/2$ ) of a nucleus and the distances are in bohrs. The dashed line is the zero contour and the other contours have the following value in hartrees: (a) 0.05100, (b) 0.02550, (c) 0.01275, (d) 0.00637, (e) 0.00319, (f) 0.00159, (g) -0.00159, (h) -0.01594, (i) -0.03187, (j) -0.07968, (k) -0.15936.

density, although it is accurate enough for many purposes. (The NDO methods were not originally parametrized with the goal of obtaining accurate charge distributions through all space. A version using different basis functions and reparametrized with this goal would be valuable.)

The [21] and INDO static potentials show positive regions behind the nitrogen nucleus which are closer to the nucleus and more repulsive at the maximum than the positive region in the [432] potential. This is consistent with density difference maps for  $N_2$ , which show that minimum-basis set<sup>(95,96)</sup> and INDO<sup>(96)</sup> charge densities show too much buildup of electron charge in the lone-pair region and not enough between the nuclei. Wherever the NDO

calculations agree with the [432] results better than the [21] results do, it is due to a cancellation of effects which cannot be expected in general.

Massey's method and the  $V_{es}$  approximation predict that all the multipole moments of the target are zero and the static potential is everywhere negative. Thus while these methods have some applicability at small  $r$ , they are bad at large  $r$ .

Overall the INDO XI/1s approximation yields a static potential in best overall agreement with the *ab initio* results at small  $r$ . The contribution from the 1s orbitals is important only near the nuclei but provides significant improvement there.<sup>(86)</sup> The INDO XI/1s calculation is economical enough that the small- $r$  part of the static potential can be calculated inexpensively at the many geometries necessary for a complete scattering calculation.

At large  $r$  the static potential is dominated by the electron's interaction with the lowest order nonnegligible electric multipole moment of the target. Dipole moments are predicted fairly accurately by NDO wave functions (CO, partly because the dipole moment is small, is a well-known exception<sup>(90)</sup>).

Some progress has been made in the semiempirical calculation of quadrupole moments.<sup>(97)</sup> However, quadrupole moments arise from large cancellation of electronic and nuclear contributions and are very sensitive to approximations. For scattering calculations the quadrupole moment is generally required as a function of internuclear distance and it seems unlikely that semiempirical methods can yield the necessary accuracy<sup>(98)</sup> as a function of internuclear distance. Information on multipole moments available from any source is often incorporated directly into electron scattering calculations without requiring consistency with the quadrupole moment which would be obtained from the wave function or static potential used for the rest of the calculation.\*

Green and co-workers have developed an "independent-particle model" for electron-atom potentials and have used this to generate potentials for electron-N<sub>2</sub> scattering.<sup>(100)</sup> However, they made an arbitrary change in the potential in the regions of the nuclear singularities to effect a numerical simplification in their calculations.

An even simpler approximation scheme has been used for electron scattering by Itikawa.<sup>(101)</sup> He has represented molecules as a system of point charges placed on the atoms in such a way as to give the correct value of the dipole moment. Of course such a model does not give an accurate potential at small  $r$ .

It has sometimes been the practice to further approximate the static potential by expanding it in spherical harmonics about the molecular center of mass,

$$V_H(\mathbf{r}) = \sum_L \sum_{M^L} V_{HLM^L}(r) Y_{LM^L}(\hat{\mathbf{r}}) \quad (56)$$

\*See, for example, the work of Itikawa and Takayanagi.<sup>(99)</sup>

This expansion is rapidly convergent at large  $r$ , where it is a multipole-moment expansion, but it is very slowly convergent near the nuclei due to the strong singularities there.<sup>(102,103)</sup>

Semiempirical molecular orbital (SEMO) calculations can be used to economically map the electronic excitation energies as functions of molecular geometries.<sup>(104)</sup> While these calculations may often be inaccurate, they are still useful for interpreting electron-impact spectra. But there are indications that the excited-state charge distributions obtained by SEMO calculations are sometimes less accurate than the excited-state energetics or the ground-state charge distributions.<sup>(105)</sup> Thus it may be more difficult to approximate excited-state static potentials than ground-state ones in some cases.

When  $i \neq j$ , the integral of Eq. (52) is a transition potential. If states  $i$  and  $j$  may be connected by an electric dipole-allowed transition, then  $V_{ij}(\mathbf{r}_{N+1})$  is proportional to the transition dipole moment divided by  $r_{N+1}^2$  in the large- $r_{N+1}$  limit. Because of its long range, this asymptotic part of the transition potential is very important. The difficulties of calculating transition dipole moments, or equivalently optical oscillator strengths, using approximate wave functions are well known for both atoms<sup>(106)</sup> and molecules.<sup>(107)</sup>

When  $i = j$ , the nonlocal potential of Eq. (54) is the diagonal radial exchange potential. There has been much work on the approximation of this exchange potential for bound-state calculations. The use of the Slater exchange potential and its modified version, the  $X\alpha$  method, has been particularly successful.<sup>(61,108)</sup> In this case the exchange potential is approximated by the local potential

$$W_X(\mathbf{r}) = \alpha_X W_S(\mathbf{r}) \quad (57)$$

where  $\alpha_X$  is a parameter and  $W_S(\mathbf{r})$  is the Slater exchange potential,

$$W_S(\mathbf{r}) = -3e^2 K_F / (2\pi) \quad (58)$$

where  $\hbar K_F$  is the Fermi momentum,

$$K_F = (3\pi^2)^{1/3} / r_S \quad (59)$$

and  $r_S$  is the electron gas parameter

$$r_S = \rho^{-1/3} \quad (60)$$

where  $\rho$  is the electron density. Kohn and Sham<sup>(109a)</sup> and Gaspar<sup>(109b)</sup> have derived the value  $2/3$  for  $\alpha_X$ , although values a little larger than this are often used. Although such  $\rho^{1/3}$ -type potentials have been applied to electron scattering problems several times, the derivation from the free-electron-gas model is not applicable to the scattering problem. The Slater potential is averaged over the electrons of an atom and the Kohn-Sham potential is for the exchange interaction of an electron at the Fermi level. But the scattering electron has an energy above the Fermi level. This was originally pointed out by Hara<sup>(110)</sup> and

Mittleman and Watson.<sup>(111)</sup> Hara suggested that correct application of the free-electron-gas model to scattering problems leads to the following approximation to the exchange potential when  $i = j$  and  $\Phi_i(x_1, x_2, \dots, x_N)$  is a closed-shell wave function with doubly occupied spatial orbitals. The exchange potential is to be given by the free-electron-gas approximation

$$W_{\text{Hara}}(\mathbf{r}) = -2e^2 K_{\text{F}}(\mathbf{r}) F(\eta) / \pi \quad (61)$$

where

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \quad (62)$$

$$\eta = K(\mathbf{r}) / K_{\text{F}}(\mathbf{r}) \quad (63)$$

and  $\hbar^2 K^2(\mathbf{r}) / 2m$  is an approximation to the local kinetic energy of the scattering electron. Further, Hara suggested the latter be approximated using

$$K^2(\mathbf{r}) = [2m(T_i + U_i) / \hbar^2] + K_{\text{F}}^2(\mathbf{r}) \quad (64)$$

which has an obvious physical justification at small  $r$ . But Eq. (64) clearly has the wrong limit at large  $r$  since it implies the local kinetic energy there is  $T_i + U_i$  instead of  $T_i$ . Mittleman and Watson derived Eqs. (61)–(63) with  $K^2(\mathbf{r})$  given by  $2mT_i$  as a high-energy approximation to the exchange potential in the Thomas–Fermi approximation. Riley and Truhlar<sup>(112)</sup> have suggested that the deficiency of Eq. (64) be corrected by setting  $U_i = 0$  and have called the resulting approximation the asymptotically adjusted free-electron-gas exchange potential (AAFEGE potential). As  $T_i$  tends to zero, the AAFEGE potential tends to the Kohn–Sham potential as expected since the AAFEGE model treats a zero-energy scattering electron as if it is at the Fermi level. But at high energy

$$W_{\text{AAFEGE}}(\mathbf{r}) \underset{\text{high } T_i}{\cong} -\pi e^2 \hbar^2 \rho(\mathbf{r}) / m T_i \quad (65)$$

which is proportional to the first rather than the one-third power of the density. The right-hand side of Eq. (65) was also derived as the high-energy limit by Mittleman and Watson and clearly illustrates the well-known fact that exchange is less important at higher  $T_i$ .

Riley and Truhlar<sup>(112)</sup> have also derived an approximation to the exchange potential which treats the scattering electron semiclassically. For the case when  $i = j$  and  $\Phi_i(x_1, x_2, \dots, x_N)$  is a closed-shell wave function with doubly occupied spatial orbitals, the resulting potential is

$$W_{\text{SCE}}(\mathbf{r}) = \frac{1}{2}[T_i - V_{ii}(\mathbf{r})] - \frac{1}{2}\{[T_i - V_{ii}(\mathbf{r})]^2 + \alpha^2\}^{1/2} \quad (66)$$

$$\alpha^2 = (4\pi e^2 \hbar^2 / m) \rho(\mathbf{r}) \quad (67)$$

This potential is called the semiclassical exchange (SCE) potential. It has the same high-energy limit as the AAFEGE and Hara exchange potentials.

**Table 4. Phase Shifts in Radians for Electron Scattering in the Static-Exchange Approximation with and without the Nonlocal Exchange Potential and with Three Other Exchange Approximations<sup>a</sup>**

Target	<i>l</i>	No exchange	Nonlocal exchange	Hara exchange	AAFEGE	SCE
He	0	2.65	2.99	2.96	3.03	3.01
	1	0.00009	0.0004	0.0002	0.002	0.002
Ar	0	9.15	9.3	9.25	9.68	9.37
	1	3.15	6.3	6.28	6.29	6.28

<sup>a</sup>The initial translational energy  $T_i$  is equal to 0.14 eV;  $l$  is the orbital angular momentum of the scattering electron.

**Table 5. Phase Shifts in Radians for Electron Scattering in the Static-Exchange Approximation with and without the Nonlocal Exchange Potential and with Three Other Exchange Approximations<sup>a</sup>**

Target	<i>l</i>	No exchange	Nonlocal exchange	Hara exchange	AAFEGE	SCE
He	0	1.761	2.436	2.304	2.442	2.422
	1	0.010	0.042	0.023	0.068	0.076
	2	0.0003	0.001	0.001	0.002	0.003
Ar	0	8.200	8.647	8.561	8.746	8.658
	1	3.882	6.001	5.909	6.042	5.938
	2	0.010	0.045	0.024	0.061	0.061

<sup>a</sup>The initial translational energy  $T_i$  is equal to 3.40 eV;  $l$  is the orbital angular momentum of the scattering electron.

Although these potentials (Hara, AAFEGE, and SCE) are local in coordinate space, they are not, strictly speaking, local potentials since they depend parametrically on the asymptotic translational energy of the scattering electron. However, they are as easy to use as local potentials. These approximations have been tested against the Hartree-Fock nonlocal exchange potential for electron scattering from ground-state helium and argon.<sup>(112)</sup> The resulting phase shifts are given in Tables 4-6.

The tables show that these approximate exchange potentials are accurate enough to be useful for many applications. They are more accurate for Ar than for He, as expected theoretically, since they are more appropriate for high-density than for low-density regions. Since they are as easy to calculate and use as direct potentials, they should be very useful for electron-molecule scattering where exchange has previously proved to be more difficult to include.

An interesting feature of the results of Table 4 is that the approximate exchange potentials are good enough that the zero-energy limit of the phase shift\* satisfies Swann's generalization<sup>(113)</sup> of Levinson's theorem,<sup>(114)</sup> viz., the

\*The phase shift is ordinarily defined only modulo  $\pi$ . For the present discussion it must be put on an absolute basis by requiring it to be a continuous function of  $T_i$  which tends to zero as  $T_i \rightarrow \infty$ .

phase shift for orbital angular momentum  $l$  tends to  $(n_{bl} + n_{pl})\pi$ , where  $n_{pl}$  is the number of orbitals of symmetry  $l$  from which the scattering electron is excluded by the Pauli exclusion principle. Thus for He,  $n_{p0} = 1$  and  $n_{p1} = 0$ , while for Ar,  $n_{p0} = 3$  and  $n_{p1} = 2$ . In all cases the number of bound states  $n_{bl}$  is zero.

An alternative method of including exchange in electron scattering from closed-shell systems has been suggested and applied by Burke, Chandra, and Gianturco,<sup>(87,115-118)</sup> based on a treatment of electron-hydrogen atom scattering in the triplet state by Lippmann and Schey.<sup>(119)</sup> These workers force the scattering electron's wave function for appropriate symmetries to be orthogonal to the  $n_p$  orbitals from which the scattering electron is excluded by the Pauli principle. This ensures at least  $n_p$  nodes in the inner region of the wave function so that Swann's theorem may be satisfied. They found good agreement for N<sub>2</sub> with an earlier calculation<sup>(120)</sup> using the nonlocal exchange potential. It is clear, however, that the orthogonality requirement cannot give the whole effect of exchange; e.g., it gives no exchange effect for  $l = 1$  for He. Also, Burke *et al.* encountered convergence difficulties using the orthogonalization procedure for CO.<sup>(103)</sup>

The semiclassical exchange approximation is not restricted to closed-shell targets. It has also been pointed out that the semiclassical exchange approximation can also be applied to terms with  $i \neq j$  and that its high-energy limit should be a particularly easy-to-use approximation for such terms.<sup>(112)</sup> Yet for  $i = j$  the high-energy limit has been shown to be remarkably accurate in the intermediate- and high-energy regions.

In the discussion of the use of INDO approximation we distinguished approximations in the bound-state wave functions  $\Phi_i$  from approximations to the integrals involving such functions which occur in scattering theory. The general effect of inaccuracies in  $\Phi_i$  functions on the results of scattering calculations requires more study. The reader should carefully distinguish in this regard the  $\Phi_i$  functions corresponding to open channels, which are input to the

Table 6. Phase Shifts in Radians for Electron Scattering in the Static-Exchange Approximation with and without the Nonlocal Exchange Potential and with Three Other Exchange Approximations<sup>a</sup>

Target	$l$	No exchange	Nonlocal exchange	Hara exchange	AAFEGE	SCE
He	0	1.076	1.279	1.236	1.262	1.257
	1	0.196	0.327	0.274	0.297	0.315
	2	0.044	0.074	0.064	0.072	0.076
Ar	0	6.417	6.722	6.692	6.716	6.664
	1	4.215	4.548	4.544	4.570	4.500
	2	1.498	1.837	1.873	1.916	1.840

<sup>a</sup>The initial translational energy  $T_i$  is equal to 54.40 eV;  $l$  is the orbital angular momentum of the scattering electron.

scattering calculations and cannot be reoptimized during it,<sup>(47)</sup> from the  $\Phi_i$  corresponding to closed channels and the  $W_n$ . These latter functions are essentially arbitrary and are chosen specifically to enhance convergence of the scattering wave function (see Section 4).

Only for electron-hydrogen atom scattering can the exact  $\Phi_i$  functions be used. The problem of using approximate  $\Phi_i$  functions in multichannel calculations has recently been studied by several workers.<sup>(13,74,78,121)</sup> An earlier study was carried out by Delves.<sup>(122)</sup>

## 2.2. $L^2$ Expansions

Many methods have now been developed for extracting scattering information from a calculation using square-integrable ( $L^2$ ) basis functions. These methods are most closely related to methods used for bound-state calculations on molecules and thus it can be expected that bound-state *computer programs* and *approximation methods* will be adapted for such scattering calculations.

Square-integrable approximations to resonances have been used for both atoms and molecules for many years.<sup>(123)</sup> Many *ab initio* calculations have been carried out for resonances in electron scattering by atoms and  $H_2$ . Semiempirical calculations have been performed for resonances in electron scattering from  $N_2$ ,<sup>(124)</sup>  $CO_2$ ,<sup>(125)</sup> and  $H_2O$ <sup>(126)</sup> and used to discuss vibrational excitation and dissociative attachment.

Recently the use of square-integrable approximations has been extended to also include the treatment of nonresonant scattering. Such methods hold great promise for electron-molecule scattering calculations; so far, however, most of the calculations which have been performed have been *ab initio* electron-atom scattering calculations. A few *ab initio* electron-molecule calculations have been performed and references are given in Section 3.1.

Several different methods have been used for  $L^2$  scattering calculations. In one approach (for example, that used in derivative matrix theory\*) the wave function is obtained in an  $L^2$  basis in a finite volume enclosing the target. The size of the volume is arbitrary, except that it should be large enough so that the solution of the Schrödinger equation in the external region is simple. The scattering information is obtained by matching the wave functions of the internal and external regions on the surface of the volume. A reexpansion technique may be used so that all the integrals except overlap integrals may still be evaluated over all space (not just the interior region) as is done in bound-state calculations and computer programs. In another approach<sup>(129)</sup> (Jacobi matrix theory) a particular complete  $L^2$  basis set  $\{\phi_n\}_{n=0}^{\infty}$  is chosen for

\*This is also called *R* matrix theory or, to avoid confusion with the reactance matrix, *NR* matrix theory. It has recently been reviewed by Burke and Robb.<sup>(127)</sup> Some alternative techniques have been described by Schneider.<sup>(128)</sup>



which a zeroth-order Hamiltonian (for neutral targets,  $H - V_{\text{int}}$ ) can be solved exactly. Then the remaining part of  $H$  (for neutrals,  $V_{\text{int}}$ ) is approximated by an  $N \times N$  matrix representation in the set  $\{\phi_n\}_{n=0}^{N-1}$  and the Schrödinger equation with this approximation is solved in this basis. In another approach<sup>(130)</sup> the transition matrix or Fredholm determinant is calculated for complex energies or coordinates, where the wave function is square-integrable and only  $L^2$  basis functions are needed, and continued (extrapolated) to the real axis to obtain physical scattering information. Other approaches to  $L^2$  scattering, the  $T$  matrix projection methods, are discussed elsewhere.<sup>(21,131)</sup> In these methods, overlap integrals involving regular free waves are required.

### 3. Neglect of Electronic Excitation Except for Final State

#### 3.1. Strong-Coupling, Static-Exchange, and Distorted-Wave Approximations

At high energies, virtually excited states do not play an important role, inelastic cross sections become small, and the close coupling equations may be terminated at two states for inelastic collisions and at one state for elastic collisions. The former is called the strong-coupling approximation and the latter is called the static-exchange approximation.

The strong-coupling approximation is useful over a wider energy range for cases where two states are much more strongly coupled to each other than to all other states, e.g., for the resonance transition in alkali scattering.<sup>(132)</sup> But the strong-coupling approximation may be useful at intermediate energies for other optically allowed transitions, too.<sup>(133)</sup>

The static-exchange approximation is not expected to be valid at low energies, but it has recently been used for electron-molecule scattering at low energies for testing electron-molecule scattering formulations involving single-center numerical radial functions,<sup>(120)</sup> the Kohn variational method with nonsquare-integrable basis functions and nuclear-centered Gaussian basis functions,<sup>(80)</sup> and  $L^2$  methods using Gaussian basis functions.<sup>(134,135)</sup>

Various versions of the distorted-wave approximation for excitation collisions have been derived from the strong-coupling approximation,<sup>(6,136)</sup> from the two-potential formalism,<sup>(137,138)</sup> from the exact formula for the transition amplitude,<sup>(16)</sup> and from many-body perturbation theory.<sup>(21,139)</sup> They have recently been tested for several problems.<sup>(16,136,137,140)</sup>

#### 3.2. High-Energy Approximations

At energies high enough that electronic states other than the initial and final ones may be neglected, many other simplifications of the static-exchange

and strong-coupling approximations may often be made. These approximations generally treat the scattering electron on quite a different basis than the bound electrons and these approximation methods may bear little resemblance to the approximation schemes used for bound states and discussed elsewhere in this volume. Some of them have recently been reviewed elsewhere.<sup>(141-144)</sup>

From the point of view of the target (rather than the electron-target system), however, these high-energy approximation schemes often take the form of a transition matrix element involving the initial and final states of the target and a one-electron operator.<sup>(27)</sup> For example, the first Born approximation<sup>(141,143,145,146)</sup> for the  $i \rightarrow f$  transition involves the operator  $\exp[i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}_1]$ . Thus these high-energy theories require accurate charge densities for elastic scattering and accurate transition densities for inelastic scattering and may be evaluated using any approximations for the target states which give accurate values of these quantities.<sup>(147,148)</sup>

#### 4. Inclusion of Effect of Omitted Electronic States by Approximate Polarization Potentials

At intermediate and low energies many electronic states must be included in the expansion of the electron scattering wave function. Static-exchange and strong-coupling calculations are generally inadequate and expansions in target eigenstates converge slowly. For this reason it has become popular to use target pseudostates<sup>(51,67,149)</sup> or perturbed first-order functions<sup>(150)\*</sup> for the expansion of wave functions. For elastic scattering a calculation involving one polarized orbital is often surprisingly accurate.<sup>(151,152)</sup> Perturbed first-order functions have also been used in a modified distorted-wave formalism.<sup>(153)</sup>

Alternatively, the omitted states may be included implicitly by using modified potentials. The dipole polarization of the target makes a long-range contribution to such potentials which is very important and for this reason the difference between the modified potential matrix and the potential matrix occurring in the truncated close coupling equations is often called the polarization potential matrix.

Following Volkin,<sup>(154)</sup> "by a generalized potential we refer to a simplified Hamiltonian which will yield a scattering solution having the same asymptotic behavior in a certain group of channels as that which the scattering state of the full Hamiltonian, with the corresponding boundary conditions, has in these channels."† Such a generalized potential must be complex if some of the

\*The perturbation is the interaction of the target with the incident electron or a multipole component of this interaction. Such a perturbed first-order function may be called a polarized orbital,<sup>(151)</sup> although this term has also been used to describe the free wave associated with the perturbed first-order function.

†These potentials are also called equivalent potentials<sup>(155,156)</sup> or generalized optical potentials.<sup>(157)</sup>

channels that are not explicitly included are open; the imaginary part accounts for loss of flux to these channels. Exact formal theories for such generalized potentials are well known<sup>(154-156,158)</sup> and are most easily written using the Feshbach projection operators.

The diagonal elements of such potentials have been well studied and approximations to them have been heavily used.\* In practice, diagonal elements of the polarization potential are usually represented as real potentials of the form (letting  $r_{N+1} = r$ )

$$V_{\text{pol}}(\mathbf{r}) = -\frac{e^2 \alpha(\hat{\mathbf{r}})}{2r^4} f(r) \quad (68)$$

where  $\alpha(\hat{\mathbf{r}})$  is the static dipole polarizability of the target as a function of its orientation in space and  $f(r)$  is function which at small  $r$  cuts off the strong, unphysical singularity of the  $r^{-4}$  factor. The dipole term dominates because at large  $r$  the leading term in the perturbation of the target there is

$$H_1 = r^{-2} \sum_{i=1}^N r_i P_1(\cos \delta_i) \quad (69)$$

where  $\delta_i$  is the angle between  $\mathbf{r}$  and  $\mathbf{r}_i$ . The static polarizability is used in (68) because it may be shown that the adiabatic polarization approximation, in which the target response is calculated for a fixed position of the scattering electron and the polarization potential is the interaction of the scattering electron with the perturbed target, is correct in the large- $r$  limit for energies below the first inelastic threshold.<sup>(160)</sup> But the adiabatic polarization approximation overestimates the response near the nucleus at small  $r$  where the scattering electron's velocity is large and exchange effects become inseparable from polarization effects. For atomic targets, the polarized-orbital polarization potential, in which the perturbation is taken to be equal to that given in Eq. (69) for all  $r > r_i$  and to be zero for  $r < r_i$  and the perturbed wave function is also zero for  $r < r_i$ , appears to give reasonable, and sometimes even remarkably accurate, results for electron-atom scattering.<sup>(151,159)</sup> For molecules, however, this approximation may be less valid since the nuclei are not at the origin.<sup>(161)</sup> The correct form of  $f(r)$  for molecules is not known, although a polarized-orbital-type polarization potential has been obtained by Lane and Henry<sup>(162)</sup> for  $\text{H}_2$ .†

For molecules,  $\alpha(\hat{\mathbf{r}})$ ,  $V_{\text{pol}}(\hat{\mathbf{r}})$ , and  $f(\hat{\mathbf{r}})$  should also depend on the nuclear coordinates. But very little is known quantitatively about the dependence of  $\alpha(\hat{\mathbf{r}})$  on internuclear distances and the dependence of  $f(\hat{\mathbf{r}})$  on internuclear distances has always been neglected.

There have been only a few attempts to include the imaginary part of the diagonal polarization potential, but both empirical and *ab initio* approaches have been taken.<sup>(144,164)</sup>

\*A review and extensive references are given elsewhere.<sup>(151,159)</sup>

†See also the calculation by Hara.<sup>(163)</sup>

Nondiagonal elements of the polarization potential have likewise received very little attention,<sup>(144,157,159,165)</sup> although there are many studies of the effect of intermediate electronic states on electron scattering processes and these studies (some of which even use the Feshbach formalism<sup>(33)</sup>) could provide a basis for parametrizing generalized potentials.

Huo has developed a closely related conceptual potential called the effective potential.<sup>(166)</sup> While a generalized potential is determined so that the scattering calculated for it in a truncated close coupling approximation is exact, the effective potential of Huo is defined such that the nonexchange scattering calculated for it in the first Born approximation is exact.

Generalized potentials have been considered in a variety of approximations to the scattering; for example, the Born approximation,<sup>(159)</sup> the eikonal approximation,<sup>(167)</sup> the static-exchange approximation,<sup>(168)</sup> and coupled channels approaches.

The Feshbach projection-operator approach has recently been applied to the analysis of semiempirical approximation schemes for molecular bound states,<sup>(105)</sup> and this work might provide some ideas about how to extend such schemes to electron scattering problems.

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