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Exchange in low-energy electron-molecule scattering: Orthogonalization and free-electron-gas approximations for collisions with polar and nonpolar molecules

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Three approximate treatments of the exchange interaction in low-energy electron-molecule scattering are applied to a variety of collision systems. Static-exchange calculations for e-H_2, e-N_2, e-CO, e-LiH, e-HCl, and e-LiF collisions with scattering energies from 0.01 to 1.0 Ry are discussed, and results obtained using approximate treatments of exchange are compared with those obtained in a corresponding study in which exchange is incorporated exactly via an iterative procedure. The approximate treatments considered are orthogonalized-static, free-electron-gas model potential, and orthogonalized-model-potential procedures. The latter procedure is found to be uniformly superior to other approximate methods for all systems studied, in many cases yielding results indistinguishable from those of the exact static-exchange calculation. Strengths and weaknesses of each method are discussed.

I. INTRODUCTION

In the past several years, there has been increasing activity in the field of electron-molecule collision theory.[1-3] Considerable progress has been made in developing techniques to study the quantum-mechanical problem of the scattering of a "low-energy" electron (i.e., one with incident kinetic energy ≤ 10.0 eV) from "small" diatomic and polyatomic molecules (e.g., H_2, N_2, LiF, CO_2), advances being reported both in formulation of the collision problem and in treatment of the electron-molecule interaction potential.

The interaction potential that appears in the nonrelativistic Schrödinger theory for this collision problem arises from the Coulomb forces between the scattering electron and the target electrons and nuclei. This "static potential" is often augmented by an approximate polarization potential that takes account of second-order effects due to distortion of the molecular charge cloud by the electric field of the scattering electron.

One must also ensure that the electron-molecule wave function is antisymmetric under pairwise electron interchange. This quantum-mechanical requirement produces integral "exchange terms" in the Schrödinger equation for the wave function of the scattering electron. It is essential that this exchange interaction be incorporated in any theory of low-energy electron-molecule scattering,[4] but its inclusion in tractable computational schemes for determining cross sections is very difficult, largely due to its nonlocal character.

With the recent advent of L^2-variational methods[5] and the introduction of new numerical close-coupling procedures,[6-10] it is now possible to treat exchange exactly in a variety of small-molecule collision systems (e.g., e-N_2, e-LiH). These studies provide valuable benchmark results but are at present numerically feasible only for a limited range of systems. This situation, together with a desire to probe the physical nature of exchange in electron collisions, has provoked the investigation of more tractable approximate treatments of this interaction.[11-31]

In developing such treatments, two quite different strategies have been adopted. In *orthogonalization procedures*,[19-23] exchange is taken into account only to the extent of ensuring that each continuum orbital is orthogonal to all bound molecular orbitals (MO's) of the same symmetry. This approach has been implemented for electron collisions with N_2, CO, HCl, HF, CH_4, H_2O, and H_2S. An alternative tactic is to use *model-exchange potentials*.[11-13,16-18,24-31] These potentials are *local* approximations to the exchange terms in the scattering equations which mock, in some average sense, the effects of exchange on the scattering function. Two types of model-exchange potentials have been used in electron scattering calculations: *free-electron gas* (FEG)[11-13,16-18,25-27,29-31] and *semiclassical-exchange*[12,13,24-28] potentials. In electron-molecule scattering studies, use of the latter potentials has been restricted primarily to intermediate-energy collisions.[30] The FEG potentials have been employed in calculations of low-energy electron scattering from CO_2, H_2, N_2, LiF, LiH, and HCl.

It is not possible to evaluate these various approximate treatments of exchange from research reported to date. This situation is partly due to the use of different target wave functions and standards of numerical accuracy in various calculations. Secondly, in many of these studies polarization effects are taken into account. Of course, polarization must be included in theories that are expected to produce results for comparison with experimental data.[1] But this additional interaction can obscure the effects of exchange,[18] which are at issue in the present work. Ideally, an investigation of approximations to exchange effects should be carried out in the static-exchange (SE) approximation, in which polarization is ignored.[11,12] Finally, a systematic evaluation of these approximations requires that well-converged *exact-static-exchange* (ESE) results for a wide variety of systems be used for comparison. Only very recently has such data become available.[9,10]

In the present work, we have investigated three approximate treatments of exchange: the orthogonalized-static method, the FEG model-exchange-potential method, and a combination orthogonalized-model-potential method. These models are described in Sec. II. Static-exchange scattering calculations using these three procedures have been carried out for the e-H_2, e-N_2, e-CO, and e-LiH systems. Results for these systems are presented and discussed, together with earlier calculations[16-18] for e-LiF and e-HCl collisions, in Sec. III. To ensure internal consistency, we use the same static potential and impose the same standards of numerical accuracy as in our earlier exact SE calculations,[9,10] the results of which are used herein for comparison. This investigation of the validity of the aforementioned approximate treatments of exchange for these six systems, which span a wide range of characteristic polar and nonpolar electron-diatomic collision problems, provides the basis for the concluding remarks in Sec. IV. (Unless otherwise indicated, atomic units are used throughout.[32])

II. THEORETICAL TREATMENTS OF EXCHANGE IN ELECTRON-MOLECULE SCATTERING

The electron-molecule collision problem is formulated in single-center coordinates in a body-fixed reference frame. The fixed-nuclei approximation[29,33] is made; i.e., the orientation of the internuclear axis and the internuclear separation are held fixed for the duration of the collision. The electron-molecule system wave function is expanded in the complete set of Born-Oppenheimer electronic wave functions of the target, and the expansion is truncated to include only the ground electronic state. The wave function of the scattering electron is expanded in partial waves (spherical harmonics), leading to body-frame coupled radial equations.[11] In this formulation, channels are designated by quantum numbers representing the orbital angular momentum of the scattering electron (l) and the projection of this angular momentum along the internuclear axis (m).

A discussion of this approach to the collision theory in the context of the general electron-molecule scattering problem can be found in a recent review by Lane.[1] Special concerns attending its application to collisions with polar targets are discussed by Collins and Norcross.[16] In earlier papers, we have presented thorough discussions of the exact-static-exchange (ESE) equations,[11] of an iterative procedure for solving them,[10] and of the theory of the free-electron-gas model potentials.[11] Therefore, in the present paper we shall merely summarize the key points of the theory, giving special attention to the orthogonality constraint. (We shall refer to our earlier model-exchange-potential paper[11] as I and to the iterative exact-static-exchange paper[10] as II.)

When the antisymmetrization requirement mentioned in Sec. I is imposed on the system wave function in the context of the present theoretical formulation, the resulting ESE coupled equations for the radial scattering functions $f_{ll_0}^{\mathrm{ESE}}$ are [I, Eq. (2.15)]

$$\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+k^2\right)f_{ll_0}^{\mathrm{ESE}}(r)$$

$$=2\sum_{l'}\left(V_{ll'}^{(m)}(r)f_{l'l_0}^{\mathrm{ESE}}(r)-\int_0^\infty K_{ll'}^{(m)}(r,r')f_{l'l_0}^{\mathrm{ESE}}(r')\,dr'\right), \qquad (1)$$

where k^2 is the incident kinetic energy of the scattering electron (in Ry), and l_0 denotes the incident channel and labels the linearly-independent solutions of (1). We have suppressed the label m on the scattering function since in the body-frame fixed-nuclei theory there is no coupling of channels with different values of m. Coupling between channels (lm) and $(l'm)$ is provided by $V_{ll'}^{(m)}$, the matrix element of the static potential (averaged over the ground electronic state of the molecule) between spherical harmonics $Y_l^m(\hat{r})$ and $Y_{l'}^m(\hat{r})$, and by the exchange kernel $K_{ll'}^{(m)}(r,r')$, which is calculated from radial expansion coefficients of the bound molecular orbitals (MO's). The integral exchange terms in (1) also depend on the scattering energy, through the presence of the radial scattering functions. [Expressions for these coupling matrix elements are given I, Eq. (2.16)–(2.21).] The coupled integrodifferential equations (1) are also known as the continuum Hartree-Fock equations.[34] By examining the asymptotic ($r\rightarrow\infty$) behavior of the solutions of these equations, one can[1] extract the S matrix and calculate from it collision quantities such as eigenphase sums and various cross sections.

The integrals in the ESE equations (1) are called "two-electron exchange terms." If these equations are to be solved for electron collisions with open-shell molecules, additional terms must be retained.[14,34] These "one-electron exchange terms" contain the bound-orbital energies and overlap integrals of the continuum orbital and the bound MO's. For scattering from closed-shell targets, like the molecules considered in the present study, these terms can be omitted, as in Eq. (1). The resulting continuum orbital, with partial-wave projections $f_{ll_0}^{\mathrm{ESE}}$, *will be rigorously orthogonal* to all bound MO's.[34] No further orthogonality constraints must be imposed.

The iterative procedure we use to solve the ESE equations (1) is described in paper II. Here we wish to emphasize that in these ESE calculations, we enforce orthogonality of the continuum orbital to bound molecular orbitals of the same symmetry as the continuum orbital at each iteration *only* to improve convergence. As illustrated in Table I of paper II for e-H_2 scattering, fewer iterations are required to achieve a high degree of convergence if orthogonality is imposed. However, this constraint is not necessary, since in this procedure no approximations are made to the ESE equations (1).

Orthogonality is no longer guaranteed if one introduces approximations to the exchange terms in Eq. (1). The two strategies for doing so that are examined here adopt fundamentally different points of view.

Our approach is to replace the nonlocal exchange terms in the ESE scattering equations by a local term involving a model-exchange potential.[11] Thus in Eq. (1) we set

$$\int_0^\infty K_{ll'}^{(m)}(r,r') f_{l'l_0}^{\mathrm{ESE}}(r')\,dr' \simeq \langle Y_l^m | V_{\mathrm{FEG}}(\vec{r}) | Y_{l'}^m \rangle f_{l'l_0}^{\mathrm{ESE}}(r)\,, \tag{2}$$

where the matrix element on the right entails integration over the body-frame angular coordinates $\hat{r}$. The principle advantage of this replacement is that it reduces the integrodifferential ESE equations to differential (approximate) SE equations. The assumptions underlying the FEG exchange potential V_{FEG} are discussed in paper I. Several variants of this potential have been investigated[11,12,25-27] since the initial implementation of this approach by Hara[29] (cf. Sec. III A). His HFEGE potential has the form

$$V_{\mathrm{HFEGE}}(\vec{r}) = -\frac{2}{\pi}[3\pi^2\rho(\vec{r})]^{1/3}\left(\frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right), \tag{3}$$

where $\rho(\vec{r})$ is the charge density of the (undistorted) target molecule as calculated from near-Hartree-Fock electronic wave functions.[35] The quantity η is given by

$$\eta(\vec{r}) = \frac{[2(E_{\mathrm{inc}} + I) + k_F^2(\vec{r})]^{1/2}}{k_F(\vec{r})}\,, \tag{4}$$

where $k_F(\vec{r}) = [3\pi^2\rho(\vec{r})]^{1/3}$ is the Fermi momentum

TABLE I. Parameters for close-coupling calculations and molecular data for the molecular targets considered in Sec. III. The parameters are described in the text.

	H_2	N_2	CO	LiH	LiF[e]	HCl
Electronic Wave function[a]	Ref. 40	Ref. 41	Ref. 42	Ref. 43	Ref. 42	Ref. 44
$R_{\mathrm{eq}}(a_0)$	1.402	2.068	2.132	3.015	2.987	2.409
$\mu(ea_0)$[b]	0	0	0.105	2.361	2.59	0.4714
$q(ea_0^2)$[c]	0.48	−0.939	−1.63	−3.377	−4.564	2.83
$I(E_{\mathrm{h}})$	0.564	0.492	0.560	0.302	0.472	0.435
$\lambda_{\max}$	12	20	16	14	36	
$\lambda_{\max}^{\prime\mathrm{el}}$	12	14	14	10	24	17
$l_{\max}(\Sigma)$[d]	6(7)	14(15)	8	7	26	9
$l_{\max}(\Pi)$[d]	6(7)	26(15)	9	6	26	
$r_{\max}(a_0)$	60.0	85.0	52.0	200.0	200.0	64.0

[a] Near-Hartree-Fock wave function for $R = R_{\mathrm{eq}}$ are used in all calculations.

[b] Extracted from the $\lambda = 1$ (dipole) expansion coefficient of the static potential.

[c] Extracted from the $\lambda = 2$ (quadrupole) expansion coefficient of the static potential.

[d] For homonuclear targets, $\Sigma_g(\Sigma_u)$ and $\Pi_g(\Pi_u)$. These numbers are for nonorthogonalized calculations. See Ref. 61.

[e] See Ref. 16.

of the molecule, E_{inc} is the incident energy of the scattering electron (in hartrees), and I is the ionization potential of the target (in hartrees).

Once the replacement (2) has been made in the ESE equations (1), the approximate continuum orbital obtained by solving the resulting SE equations need not be orthogonal to the bound MO's although such *may* be the case. In other words, the ESE scattering function has nodes at particular values of r which are prescribed in part by the aforementioned orthogonality conditions. Unless these conditions are explicitly imposed as constraints on the *approximate* SE scattering function,[14] the nodal structure of this solution may differ from that of the ESE scattering function.

The second type of approximate treatment of exchange in electron scattering is predicated on the argument that the most important effect of the exchange interaction is to constrain the nodal structure of the scattering function through the orthogonality conditions.[19–23] As the first step in developing a method based on this premise, the two-electron exchange terms in (1) are neglected, leaving a purely static interaction potential in the collision equations, viz.,

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2\right) f^S_{ll_0}(r) - 2\sum_{l'} V^{(m)}_{ll'}(r) f^S_{l'l_0}(r) = 0\,. \tag{5}$$

This is the static approximation (S), in which exchange is completely ignored. In the orthogonalized-static (OS) procedure, one solves for solutions of the static equations which also satisfy the orthogonality constraints

$$\sum_l \int_0^\infty \phi_l^{(i)}(r)^* f^{\text{OS}}_{ll_0}(r)\,dr = 0, \quad i = 1, 2, \ldots, n_b, \tag{6}$$

where $\phi_l^{(i)}(r)$ is the lth projection in a spherical-harmonic expansion of the ith bound MO. There will be one such constraint for each of the n_b bound MO's of the same symmetry as the continuum orbital under consideration and for each linearly independent solution vector (labelled by l_0). These constraints are imposed by the method of Lagrange undetermined multipliers,[36,37] in which one solves the inhomogeneous differential equations

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2\right) f^{\text{OS}}_{ll_0}(r) - 2\sum_{l'} V^{(m)}_{ll'}(r) f^{\text{OS}}_{l'l_0}(r) = \sum_{i=1}^{n_b} \phi_l^{(i)}(r)\lambda_{l_0}^{(i)} \tag{7}$$

rather than the static equations (5). In (7) the $\lambda_{l_0}^{(i)}$ are the Lagrange multipliers.

It is important to notice that neither the two-electron exchange terms nor approximations to these terms appear in the OS equations (7). The significance of this observation becomes apparent if one thinks about the collision in terms of the various electron-molecule symmetries that correspond to the irreducible representations of the point group of the molecule. (In the body-frame/fixed-nuclei formulation, the sets of coupled equations that describe scattering in each of these symmetries are independent of one another.) In this context, we see that exchange effects are completely ignored in all symmetries except those for which there happens to be a corresponding bound MO in the electronic configuration of the target molecule. This defect in the OS procedure can be quite important, as in e-N_2 scattering, where a Π_g shape resonance is found[9] in the ESE total integrated cross section at a collision energy of 3.90 eV. Since there is no bound π_g MO in the $X^1\Sigma_g^+$ ground state of N_2, the OS procedure reduces to the static approximation in this symmetry, and the resonance does not appear (see Sec. III B and Fig. 2).

However, this predicament does not arise for most systems to which the OS method has been applied.[20–23] In these calculations, the principal contributions to the cross sections of interest are due to electron-molecule symmetries with corresponding bound MO's, so we can enforce orthogonality. Then the validity of the OS method rests on the extent to which it accurately represents exchange effects in these symmetries. This question can be addressed by comparing ESE and OS results for several systems (see especially the results for e-CO collisions in Sec. III C).

In addition to these comparisons for the FEG and OS methods, we consider in Sec. III a third alternative in which the model-potential and orthogonalization strategies are combined. The possible utility of such an "orthogonalized-model-potential" approach was first suggested by Riley and Truhlar[14] in a study of triplet scattering of electrons by hydrogen atoms.[15] The possibility that such a procedure could improve the accuracy of local model-exchange potentials for electron-molecule scattering was suggested by earlier studies.[17,18] In the present implementation, we begin by making the replacement (2) of the FEG exchange potential in the ESE equations. The resulting approximate SE equations are solved for radial scattering functions which also satisfy the orthogonality constraints (6). This is the OHFEGE method. Conceptually, the imposition of the orthogonality constraints can be thought of as "correcting" the approximate SE collision equations by re-imposing conditions on the continuum orbital that were "lost" when the replacement (2) was made. Of course, if the HFEGE model potential is itself a very good approximation, the orthogonality constraints will have little effect on the results. This appears to be the case in the e-HCl scattering calculations for the Σ symmetry that Collins *et al.* have reported.[18] These results are discussed briefly in Sec. III D.

III. RESULTS AND DISCUSSION

The coupled differential SE equations described in Sec. II were solved using an integral equations algorithm.[38] The details of our application of this algorithm to electron-molecule collisions have been discussed elsewhere.[39]

Several parameters are germain to these calculations; their values are given in Table I for each of the molecules under consideration. The electrostatic interaction potential, averaged over the equilibrium-geometry, near-Hartree-Fock ground-state target wave function, is expanded in Lengendre polynomials[45] of order $\lambda = 0$ through $\lambda = \lambda_{\max}$. Each coefficient in this expansion is the sum of an electronic part and a nuclear part. For all λ such that $\lambda_{\max}^{\mathrm{el}} < \lambda < \lambda_{\max}$, only the nuclear part is retained; it is the dominant contribution to these high-order coefficients.[31,39] From this static potential, which appears in the matrix elements $V_{ll'}^{(m)}(r)$ in Eqs. (1), (5), and (7), we determine the long-range permanent quadrupole ($\lambda = 2$) and, for polar systems, dipole ($\lambda = 1$, moments shown in Table I.

In the expansion of the scattering function in spherical harmonics, which leads to the coupled radial equations in Sec. II, we retain partial waves through order[46] $l_{\max}$. Thus this parameter determines the number of channels N in each close-coupling calculation. In calculations that require orthogonalization, such as those that use the OS or OHFEGE methods, we include Lagrange undetermined multipliers for *all* bound MO's of the same symmetry as the continuum orbital. These bound MO's are also expanded in partial waves; this expansion results in the function $\phi_l^{(i)}(r)$ of Eq. (6). The solution matrix is propagated to $r_{\max}$, where the T matrix is extracted from it.[39]

In determining the values of these parameters, we have required that the results of the approximate SE calculations be globally converged[11] to the same degree of accuracy as the iterative ESE data to which they are compared.[9,10] This ensures that these comparisons actually reveal differences in the various treatments of the physics of exchange rather than vagaries in the numerical process of the different calculations. Convergence criteria for each system are given below. Eigenphase sums and/or cross sections are globally converged to these criteria in the parameters discussed above.

Finally, specification of the HFEGE potential for a particular molecule requires the ionization potential I [see Eq. (4)]. Experimentally determined ionization potentials were used; they are given in Table I.

A. e-H_2 scattering

In our earlier study of FEG potentials for e-H_2 scattering in the Σ_g symmetry,[11] three such potentials were used: (1) the HFEGE of Eqs. (3) and (4); (2) the asymptotically adjusted FEG exchange potential (AAFEGE) of Riley and Truhlar,[13] in which $I = 0$ in Eq. (4); and (3), a "tuned" FEG exchange potential (TFEGE), in which I was treated as an adjustable parameter. In the third model, I is chosen so that the TFEGE and ESE Σ_g eigenphase sums are equal at a scattering energy of 0.04 Ry. The resulting model-exchange potential is used in scattering calculations for energies from 0.01 to 1.0 Ry. Subsequently, Gibson and Morrison[12] extended this work to include all other important e-H_2 symmetries, investigated the semiclassical exchange potential for this system, and explored the effect of including polarization in these calculations.

These studies showed the TFEGE potential to be capable of producing SE cross sections in excellent agreement with the ESE results in the energy range from 0.01 to 1.0 Ry. However, the HFEGE and AAFEGE models generate cross sections that are consistently above (HFEGE) or below (AAFEGE) their ESE counterparts, as shown in Fig. 1. This behavior indicates that for this

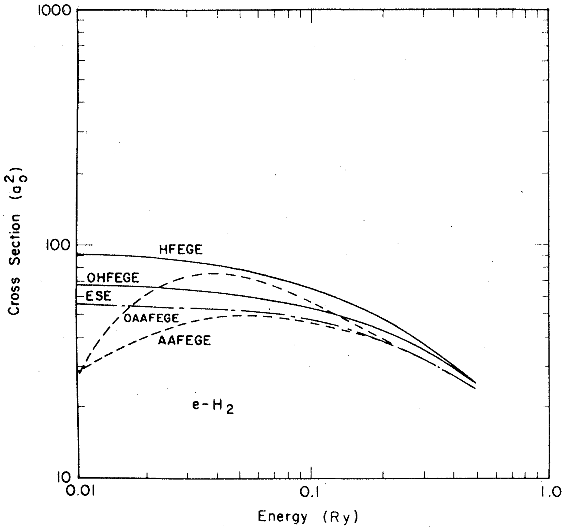

FIG. 1. Static-exchange cross sections for e-H_2 scattering in the Σ_g symmetry from calculations in which exchange is included exactly (ESE curve, from Ref. 10), and where FEG model potentials are used with and without orthogonalization. (The AAFEGE and OAAFEGE results above 0.2 Ry agree with the ESE cross sections to within accuracy of this graph.)

system the HFEGE potential is too weak and the AAFEGE too strong. This is consistent with the observation that changing I from I (HFEGE) = 0.564 E_h to I (TFEGE) = 0.071 E_h deepens the (attractive) exchange potential and improves the results.

Orthogonality was not considered in these earlier papers. In Fig. 1, we show Σ_g cross sections for the OHFEGE and OAAFEGE approximations. These were determined by using the indicated FEG potentials and imposing orthogonality of the Σ_g continuum orbital to the bound $1\sigma_g$ MO of H_2. (Since this is the only bound MO in this problem, orthogonality constraints cannot be imposed in the other electron-molecule symmetries.) The OAAFEGE results in Fig. 1 further support the conclusion of paper I that, although this potential does have the correct asymptotic energy dependence, it is simply too strong in the short-range region, where exchange effects are most important. Evidently, the AAFEGE potential is too strong (for electron-molecule systems studied to date[47]) for orthogonalization to correct its deficiencies. We shall not consider this potential further.

Orthogonalization does improve the results of calculations in which the HFEGE is used. However, the improvement is not as great for the e-H_2 system as for the others discussed below. The remaining difference between the OHFEGE and ESE cross sections in Fig. 1 may be an indication of the inadequacy of the approximation that the two-electron H_2 molecule be treated as a free-electron-gas. This assumption seems less problematical for molecules such as N_2 and CO, which have more electrons.

B. e-N_2 scattering

Shape resonances are common features of low-energy electron-molecule collisions cross sections.[48] Scattering at energies near these resonances is particularly sensitive to the exchange interaction, because the scattering function is concentrated in the short-range region. The Π_g shape resonance is found in the ESE eigenphase sums for e-N_2 collisions[9,49,50] at an energy of 3.90 eV as shown in Fig. 2. Eigenphase sums[52] in the Π_g symmetry calculated with the HFEGE potential are shown by the solid curve in this figure. This model does produce the Π_g resonance, but at too high an energy. The HFEGE resonance is also a bit wider than the ESE width of 1.33 eV.

As mentioned in Sec. II, there is no bound π_g MO in the ground state of N_2. Hence the OS model in the Π_g symmetry reduces to the static approximation [cf., Eq. (5)]. Eigenphase sums in this approximation, labelled S in Fig. 2, do not show a resonance in this energy range.

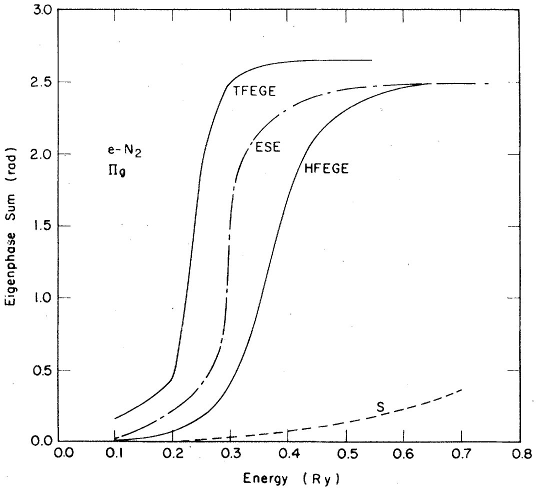

FIG. 2. Eigenphase sums for the Π_g resonant symmetry of the e-N_2 system. The ESE resonance energy is 3.90 eV. For the TFEGE, $I = 0.215\ E_h$ in Eq. (4); for the HFEGE, $I = 0.573\ E_h$ (from Ref. 51). In this symmetry, the OS method reduces to the static approximation (dashed curve). (ESE results are from Ref. 9.).

Except very near the resonance energy, the dominant contributions to the e-N_2 cross sections in the SE approximation come from scattering in the Σ_g, Σ_u, and, to a lesser extent, Π_u symmetries.[11] In order to evaluate the OS, HFEGE, and OHFEGE approximate treatments of exchange, we have compared the sums of the total integrated cross sections[53] in the *nonresonant* symmetries for these three models with the corresponding ESE cross sections. The results, which are graphed in Fig. 3, show the OS and HFEGE cross sections to be too large at low scattering energies. As the energy increases, the HFEGE results come into better agreement with their ESE counterparts, while the OS cross sections remain too large. The OHFEGE model consistently yields cross sections that are in excellent agreement with those of the ESE calculations (see also Ref. 54).

Eigenphase sums in these nonresonant symmetries for selected energies are presented in Table II. These results are all converged to better than 0.05 rad. For each model, we also give the percentage differences between the approximate SE δ_{sum} and the ESE result (from paper II). Notice that the OHFEGE eigenphase sums are within ~1% of δ_{sum} (ESE) except in the Π_u symmetry, which contributes very little to the scattering except at higher energies. The error introduced by using the OS method increases with energy. This is illustrated in Fig. 4, where OS, HFEGE, and OHFEGE Σ_g eigenphase sums are compared with δ_{sum} (ESE), the latter being indicated by crosses.

In an earlier study of e-H_2 scattering,[11] an ex-

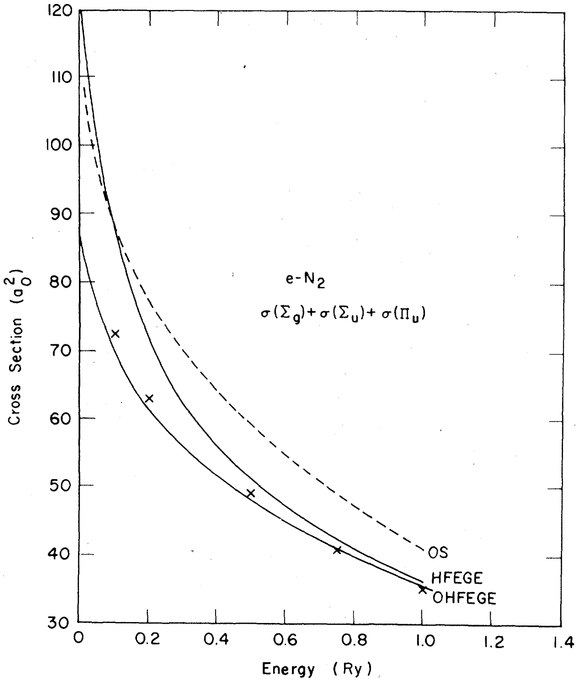

FIG. 3. Total, integrated, static-exchange cross sections for e-N_2 scattering, including Σ_g, Σ_u, and Π_u symmetries. (Note that the resonant Π_g cross section is not included.) ESE results (from Ref. 10) are denoted by crosses.

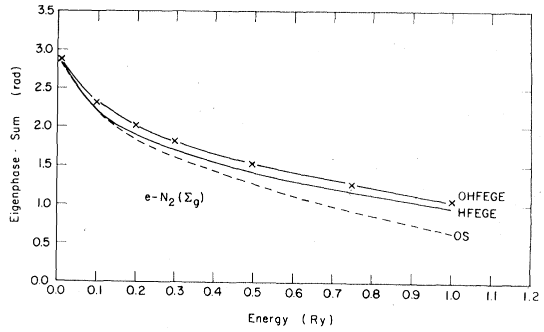

FIG. 4. Static-exchange eigenphase sums for e-N$_2$ scattering in the Σ_g symmetry. The crosses are results of the ESE calculation reported in Ref. 10.

cellent (nonorthogonalized) model potential was generated by "tuning" the FEG form in Eqs. (3) and (4). Specifically, in this "tuned free-electron-gas" exchange (TFEGE) potential I in these equations was treated as an adjustable parameter and chosen to force agreement between δ_{sum} (TFEGE) and δ_{sum} (ESE) in the Σ_g symmetry at *one* energy. We have performed such a tuning for e-N$_2$ in order to examine the sensitivity of the FEG model to I. The results, which are shown in Fig. 5, indicate that by choosing $I = 0.215\ E_{\mathrm{h}}$, the resulting TFEGE $\delta_{\mathrm{sum}}(\Sigma_g)$ at 0.01 Ry can be made to agree with the ESE result[10] at this energy, 2.874 rad. This decrease in I from the experimental value[51] of 0.573 E_{h} strengthens the approximate SE interaction potential over that in the HFEGE model. Consequently the Π_g resonance is shifted to lower energy. Regrettably, as shown in Fig. 2, the TFEGE resonance lies below the ESE energy.

In general, this sort of adjustment of the model-exchange potentials is not a practical procedure, since ESE results will not always be available. For the e-N$_2$ system, the sensitivity of the resonance to I is of particular interest because one cannot orthogonalize in the resonant symmetry.

TABLE II. Selected[a] eigenphase sums (modulo π) for e-N$_2$ scattering in the static-exchange approximation using models of exchange described in Sec. II. Nonresonant symmetries only. See Fig. 2 for resonant (Π_g) eigenphase sums.

Energy (Ry)		OS	HFEGE	OHFEGE	ESE[b]
0.01	Σ_g	2.839	2.826	2.875	2.874
	Σ_u	3.113	3.112	3.115	3.119
	Π_u	−0.0003	−0.0014	−0.0024	
0.10	Σ_g	2.209	2.204	2.322	2.311
	Σ_u	2.904	2.901	2.942	2.937
	Π_u	−0.141	−0.104	−0.090	−0.075
1.50	Σ_g	1.245	1.411	1.519	1.524
	Σ_u	2.198	2.260	2.339	2.316
	Π_u	−0.676	−0.506	−0.487	−0.455
1.00	Σ_g	0.639	0.953	1.031	1.043
	Σ_u	1.698	1.865	1.926	1.908
	Π_u	−1.010	−0.747	−0.737	−0.694

[a] Additional scattering calculations were carried out at $k^2 = 0.20$, 0.30, and 0.75 Ry. See Figs. 3 and 4.
[b] From Ref. 10.

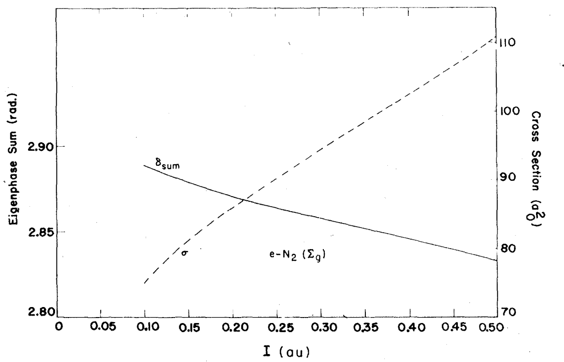

FIG. 5. Sensitivity of the Σ_g eigenphase sum δ_{sum} and integrated cross section σ to the ionization potential, I in the FEG potential of Eq. (4). The scattering energy for these calculations is 0.01 Ry. Agreement with the ESE result (2.874 rad.) at this energy is obtained with $I = 0.215\ E_{\mathrm{h}}$. See also Fig. 2.

C. e-CO collisions

The CO molecule is isoelectronic with N_2, and e-N_2 and e-CO scattering share many common features. For example, a Π shape resonance is found in e-CO collisions.[48] In ESE calculations,[10,55] this resonance occurs at 3.54 eV with a width of 2.07 eV.

However, CO is a polar molecule, with a permanent dipole moment $\mu = 0.267$ Debye (D). This fact has a pronounced effect on the behavior of electrons in collisions with CO targets.[56] A second important difference between N_2 and CO is that the electronic configuration of the latter includes a bound MO in the resonant electron-molecule symmetry (Π). Therefore, the effects of orthogonalization, in the OS and OHFEGE methods, can be studied in the sensitive resonant symmetry.

Eigenphase sums in the Π symmetry are graphed in Fig. 6; selected results are presented in Table III. The HFEGE model does produce a Π-shape resonance, but, like the e-N_2 Π_g HFEGE resonance, it occurs at too large an energy. When the OHFEGE method is used, the resonance is closer to the ESE resonance, but is still about 0.75 eV too high. The OS procedure does not produce a resonance in the Π symmetry in the energy range below 10.0 eV.

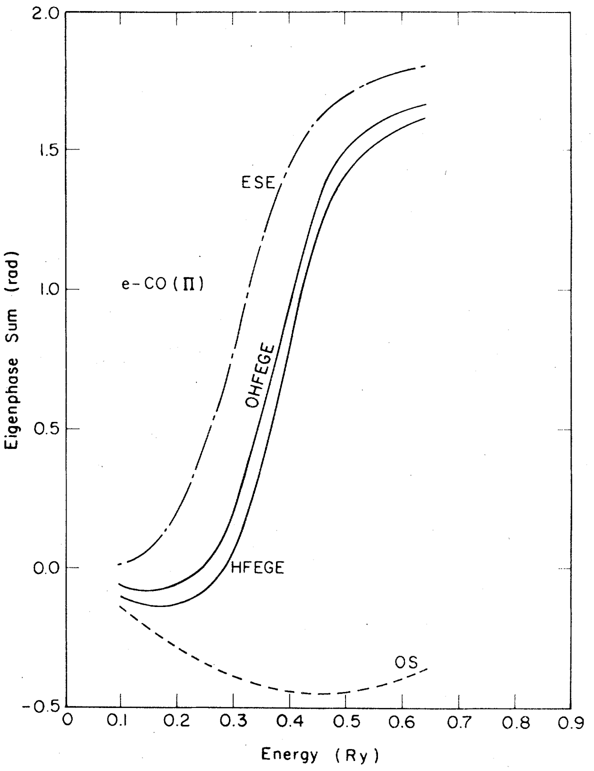

FIG. 6. Static-exchange eigenphase sums for the resonant Π symmetry of e-CO scattering. The ESE results, from Ref. 10, show a resonance at 3.54 eV.

TABLE III. Selected[a] eigenphase sums (modulo π) for e-CO scattering in the static-exchange approximation. The models of exchange used are described in Sec. II.

Energy (Ry)		OS	HFEGE	OHFEGE	ESE[b]
0.10	Σ	1.865	1.560	1.993	
	Π[c]	−0.138	−0.094	−0.060	
0.25	Σ	1.029	0.750	1.259	1.284
	Π	−0.344	−0.075	0.019	
0.49	Σ	0.146	0.004	0.505	0.542
	Π	−0.455	1.382	1.471	
0.64	Σ	−0.268	−0.323	0.157	0.193
	Π	−0.365	1.618	1.660	

[a] Additional scattering calculations were carried out at $k^2 = 0.16$, 0.30, 0.36, and 0.40 Ry. See Figs. 6 and 7.

[b] From Ref. 10.

[c] See Fig. 6 for comparison to ESE results.

To calculate cross sections for comparison with experimental data, one must go beyond the SE approximation and take account of induced polarization effects.[1] In earlier studies[20] of e-CO collisions in which orthogonalization is used to approximate exchange effects, the polarization interaction is included approximately by adding to the static potential a polarization potential of the form

$$V_{\rm pol}(\vec{r}) = \left(-\frac{\alpha_0}{2r^4} - \frac{\alpha_2}{2r^4}P_2(\cos\theta)\right) C(r)\,, \tag{8}$$

where α_0 and α_2 are the spherical and nonspherical polarizabilities of the target molecule and θ is the azimuthal angle of the scattering electron referred to the internuclear axis. This semiempirical form includes a spherical cutoff function, which is usually taken to be of the form $C(r) = 1 - \exp[-(r/r_c)^6]$, where r_c is an adjustable cutoff radius. For example, in his orthogonalized static-exchange-polarization (OSP) calculation of e-CO scattering Chandra[20] used $r_c = 1.605a_0$ to position the Π resonance at the experimentally determined energy of 1.75 eV. This cutoff radius is well within the charge cloud of the molecule.[42] The results of Fig. 6 suggest that the "polarization potential" in this study is actually attempting to include long-range polarization effects *and* mock the attractive short-range effect of exchange. It is by no means clear that a potential of the form of (8) is sufficiently flexible to do all this. Moreover, there is the danger that such strong polarization potentials will completely dominate the exchange effects that the OS procedure does incorporate.[18] This problem may explain the difficulty Gianturco and Thompson[23] found in trying to choose a cutoff radius for an OSP calculation of e-CH_4 scattering.

Of course, the same problem obtains in the e-N_2 system. For example, Chandra and Temkin,[57] in their OSP study using the OS method, used $r_c = 1.592a_0$ to position the Π_g resonance at 2.3 eV. (By way of contrast, using the HFEGE potential in an earlier OSP calculation,[11] we required $r_c = 2.341a_0$.) However, the significance of the e-CO case is that here it *is* possible to orthogonalize. The results of Fig. 6 indicate that this procedure alone is simply an inadequate approximation to the exchange interaction.

The other important e-CO symmetry in the energy range of interest here is the Σ symmetry. The eigenphase sums in Fig. 7 and Table II show that in this case the OS approximation is superior to the HFEGE model. The OHFEGE procedure gives results that agree with the ESE eigenphase sums to within the accuracy of the two calculations.

D. Electron collisions with other polar molecules

CO is somewhat unusual among polar molecules because of its small dipole moment.[58] Electron scattering from LiH ($\mu = 6.0$ D), HCl ($\mu = 1.198$ D), and LiF ($\mu = 6.58$ D) have also been studied using approximate treatments of exchange.[16-18] We shall consider these cases briefly in this section in order to widen the range of systems embraced by the present study.

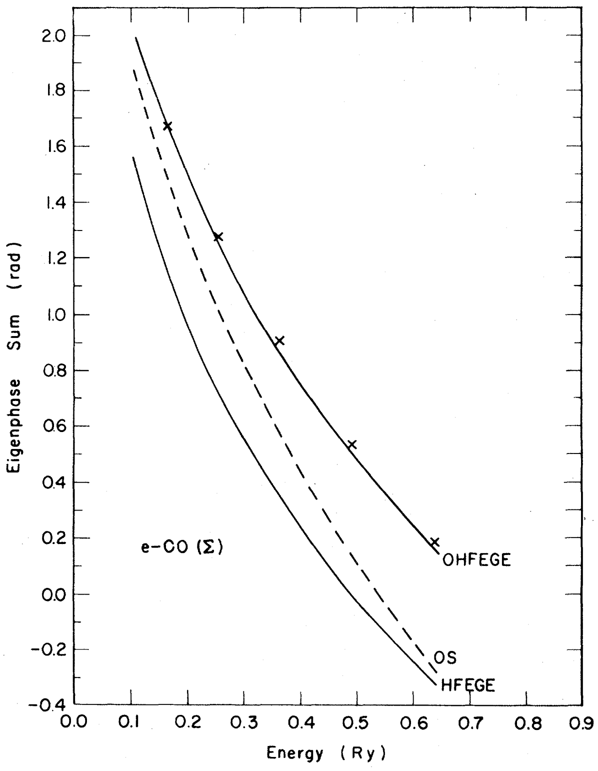

FIG. 7. Eigenphase sums for the Σ symmetry of the e-CO system. The crosses are ESE results from Ref. 10.

The role of exchange in e-LiF scattering has been discussed by Collins and Norcross[16] and Collins *et al.*[17] The latter paper is particularly germane to our concerns here. In it, the authors show that spurious Σ- and Π-shape resonances appear in approximate SE calculations in which the HFEGE potential is used. These resonances disappear when orthogonality conditions are imposed on the HFEGE model.

A similar phenomenon occurs in e-LiH scattering in the Σ symmetry. Eigenphase sums for this symmetry calculated using the S, OS, HFEGE, and OHFEGE models are given in Table IV and compared with δ_{sum} (ESE) in Fig. 8. Collins *et al.*[17] have suggested, as one possible explanation for the appearance of this spurious feature, that the HFEGE potential, when combined with the static contribution, produces an approximate SE potential which is too weak to bind the Σ LiH^- state, leaving it in the continuum and producing a spurious shape resonance. This bogus feature vanishes in the OHFEGE model, which produces results in excellent agreement with those of the ESE calculation. The eigenphase sums determined with the OS model are uniformly too small.

It is interesting to note that the OHFEGE method is more successful for the e-LiH system (Fig. 8) than for e-H_2 (Fig. 1). This may be surprising, since in both cases a FEG approximation is used to represent a target with few electrons. The inadequacy of this approximation for such molecules, which is apparent in the e-H_2 results discussed in Sec. III A, may be obscured in e-LiH

TABLE IV. Selected[a] static-exchange eigenphase sums (modulo π) for e-LiH scattering. The models of exchange used are described in Sec. II.

Energy (Ry)		OS	HFEGE	OHFEGE	ESE[b]
0.01	Σ	4.829	2.378	5.093	5.107
	Π[c]		0.439		0.454
0.10	Σ	3.108	1.817	3.380	3.400
	Π		0.575		0.674
0.25	Σ	2.209	2.067	2.541	2.604
	Π		0.732		0.896
1.00	Σ	0.973	1.488	1.560	1.562
	Π		1.143		1.300

[a] Additional scattering calculations were carried out at $k^2 = 0.04$, 0.16, 0.49, and 0.81 Ry. See Figs. 8 and 9.

[b] From Ref. 10

[c] It is not possible to orthogonalize in the Π symmetry. See Sec. III D.

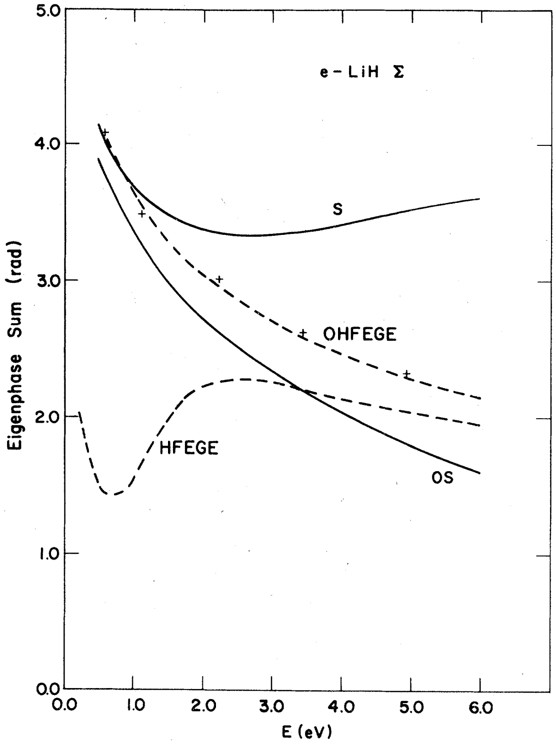

FIG. 8. Static-exchange eigenphase sums for e-LiH scattering in the Σ symmetry. The OS, HFEGE, and OHFEGE results are compared to those of an ESE calculation (+) and of a calculation in which a purely static potential was used (S) (from Ref. 17).

scattering by the strong long-range dipolar (r^{-2}) potential.

We have calculated Π eigenphase sums for e-LiH using the HFEGE model; these results appear in Fig. 9 and Table IV. Since the electronic configuration of the ground state of LiH is $1\sigma^2 2\sigma^2$, it is not possible to orthogonalize in the Π symmetry.

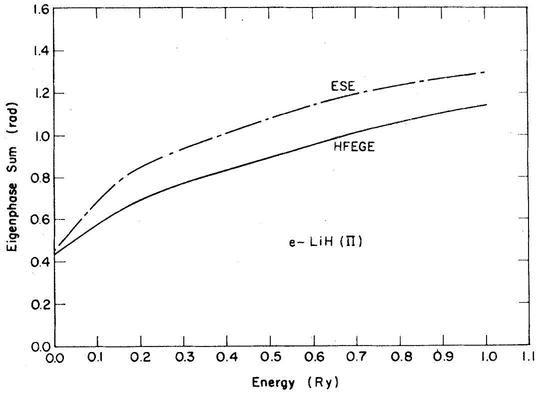

FIG. 9. Eigenphase sums from ESE and HFEGE calculations of e-LiH scattering in the Π symmetry.

An interesting contrast to the polar systems considered thus far is afforded by e-HCl, which has been studied by Collins *et al.*[18] Eigenphase sums in the Σ symmetry for this system are given in Fig. 10. As Fig. 7 showed for e-LiH scattering, this graph illustrates the inability of the OS method to accurately mock exchange effects. In contrast to the other polar systems studied, the e-HCl *nonorthogonalized* HFEGE eigenphase sums are in very good agreement with those determined from the ESE calculations. In this case, then, the model-exchange potential alone seems to be a good approximation to exchange, and, as noted by Collins *et al.*,[11] "imposition of orthogonalization in addition to the local exchange potential leads to a small improvement in the results." (Riley and Truhlar[14] found a similar result for electron-atom collisions.)

IV. CONCLUSIONS

The approximate treatments of exchange that have been introduced thus far are all, to some degree, *ad hoc*. Consequently, systematic studies of their accuracy for a diverse range of electron-molecule systems are needed if an assessment of their relative merits is to be made. Such an assessment can provide the foundation for the application of these methods to more complex systems.

We have considered three approximate ways to handle the exchange interaction: the orthogonalized-static (OS), free-electron-gas (HFEGE), and orthogonalized-free-electron-gas (OHFEGE) methods. The results of the approximate static-

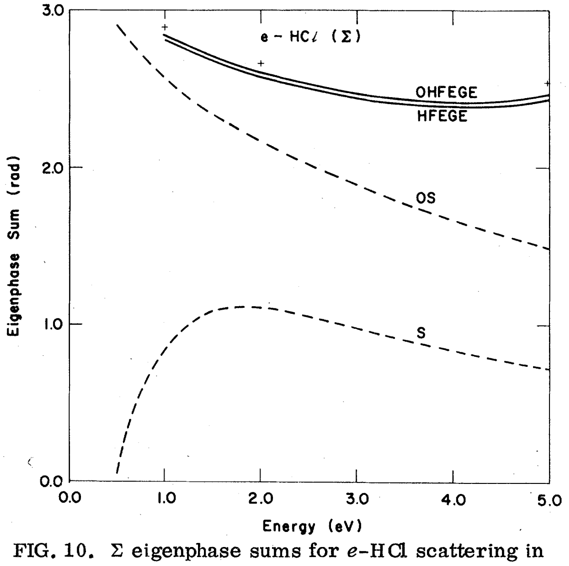

FIG. 10. Σ eigenphase sums for e-HCl scattering in the static (S), ESE(t), and model-exchange approximations (from Ref. 18).

exchange calculations discussed above for e-H_2, e-N_2, e-CO, e-LiH, e-LiF, and e-HCl scattering span a wide variety of "small-diatomic" systems and provide a basis for some conclusions regarding these models.

In comparison with ESE results, we find the OS method to be consistently in error, especially at scattering energies above a few tenths of a Rydberg. In addition to the well-known inability of the OS procedure to incorporate any exchange effects in resonant symmetries for systems such as e-N_2, where there is no bound MO for orthogonalization, this method also fails to produce a resonance in e-CO scattering, where orthogonalization is possible in the resonance Π symmetry. The present results suggest that orthogonalization alone is an insufficient representation of the exchange interaction for electron-molecule collisions.

The HFEGE model potential is more successful, producing resonances in the proper symmetries and generally yielding results in qualitative agreement with those of ESE calculations. In some cases, like the Σ symmetry in e-HCl scattering, the HFEGE results are excellent.

However, in every case studied, the OHFEGE method gave superior results to any other procedure. In most cases, the agreement between the OHFEGE and ESE eigenphase sums is within the numerical accuracy of the calculations (typically ~2%). Examination of δ_{sum} in the various models reveals that orthogonalization acts like a strengthening of the approximate static-HFEGE potential.

There are instances in which even the OHFEGE method is unable to reproduce the ESE results. Thus, in resonant symmetries (e.g., Π for e-CO), which are very sensitive to the short-range part of the electron-molecule interaction, this method does not produce the correct (ESE) resonance energy or width. In some "high-order" nonresonant symmetries (e.g., Π_u for e-N_2), the OHFEGE is inadequate. This may have little effect on low-energy cross sections, which are largely determined by lower-symmetry contributions (cf. Fig. 3). Finally, if it is impossible to orthogonalize in an important resonant (e.g., Π_g in e-N_2) or nonresonant (e.g., Π in e-LiH) symmetry, the OHFEGE method reduces to the HFEGE model potential.

Compared to an exact treatment of exchange, the OHFEGE method is not particularly difficult to implement. (In this regard, we should note that calculation of the HFEGE potential is straightforward and very efficient[59] once the target charge density has been calculated. This quantity is needed anyway for determination of the static potential.) Scattering calculations using the OHFEGE procedure required roughly an *order-of-magnitude* less computer time[60] than our (iterative) ESE calculations. In many cases, fewer channels were required for convergence in the OHFEGE procedure than when the HFEGE potential alone was used.[61]

A logical extension of the present study would be the consideration of the HFEGE and OHFEGE methods for low-energy electron collisions with polyatomic molecules, such as CO_2 and H_2O, for which ESE results are not currently available. Of course, the results of this research in no way preclude the possibility that some *other* approximate treatment of exchange may be superior to those considered here. We hope that this paper will provide a foundation for this line of inquiry.

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[60] The calculations in this paper were carried out at the Los Alamos Scientific Laboratory on their phalanx of CDC 7600 computers.

[61] For example, calculations for the e-LiF system using the static + HFEGE potential required $l_{\max} = 22$, while only $l_{\max} = 10$ was needed when orthogonality conditions were imposed. Similarly, for e-CO, the HFEGE calculations required $l_{\max} = 18$, while the OHFEGE required $l_{\max} = 9$.