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Exchange in low-energy electron-molecule scattering: Free-electron-gas model exchange potentials and applications to e-H_2 and e-N_2 collisions

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Calculations of cross sections for elastic e-N_2 collisions have been performed for impact energies from 0.01 to 1.0 Ry using model exchange potentials based on a free-electron-gas approximation in order to evaluate the utility of such local potentials in low-energy electron-molecule scattering. A body-frame fixed-nuclei formulation of the collision problem is used which treats the molecule as rigid and does not allow for electronic or vibrational excitation. Coupled integro-differential scattering equations which incorporate exchange rigorously are derived and the simplification of the nonlocal exchange potential to an approximate energy-dependent local potential is described. An initial study of e-H_2 collisions is reported in which results obtained with various model exchange potentials are compared to those of exact static-exchange calculations. Cross sections for the e-N_2 system obtained using the model exchange potentials (with and without polarization) are reported and compared with measured cross sections and the results of other theoretical studies. For both systems, good agreement with more rigorous treatments of the exchange can be obtained.

I. INTRODUCTION

The behavior of cross sections for low-energy electron-molecule collisions is principally determined by three types of interactions[1]: (i) a static interaction, which arises from the electrostatic Coulomb forces between the scattering electron and the constituent particles of the target molecule; (ii) an exchange interaction, which reflects the requirement that the electron-molecule system wave function must be antisymmetric under pairwise electron interchange; and (iii) a long-range induced polarization interaction, which is due to the distortion of the target by the external electric field of the scattering electron. Of the three resulting contributions to the electron-molecule interaction potential energy, the first, the static term, can be calculated to any desired degree of accuracy from *ab initio* molecular wave functions for many-electron targets.[2] The third type of interaction, polarization, has been rigorously studied to date only in the context of e-H_2 scattering.[3,4] For other systems, a semiempirical adiabatic polarization potential[5] based on a simple asymptotic form is commonly employed.[6-20]

The importance of the effects of the remaining interaction, electron exchange, on the scattering of low-energy electrons by homonuclear molecular targets has been well known since the work of Massey and Ridley[11] in 1956. In a static-exchange calculation based on the variational method of elastic e-H_2 cross sections these authors showed that for electron impact energies below 15-eV exchange increases the s_σ phase shift, making it approach π more rapidly as energy decreases and therefore substantially lowering the cross section. Subsequently, Carter *et al.*[12] reached the same conclusion for e-H_2 collisions, although their treatment of exchange and their model, spherically symmetric potential field were highly approximate. Recent studies have also demonstrated the importance of exchange effects in electron collisions with strongly polar molecules.[21,22]

In the last decade, several approaches to the problem of treating exchange in low-energy electron-molecule collisions have been developed. Ardill and Davidson[23] introduced exchange into the laboratory frame, close-coupling formalism of Arthurs and Dalgarno,[24] leading to a set of coupled integro-differential equations. In the context of a distorted wave solution of these equations of e-H_2 cross sections, these authors noted the importance of exchange to the $j=0 \to j'=2$ rotational excitation cross section.

The first exact treatment of low-energy e-H_2 scattering was the close coupling calculation of Henry and Lane,[7] who not only solved the relevant set of coupled integro-differential equations to obtain static-exchange cross sections, but also included a highly accurate polarization potential,[3] obtaining results in very good agreement with experiment.[13] Analogous calculations on the e-H_2 system were performed by Hara[14]; again, good agreement with experiment was obtained when exchange and polarization were taken into account.

The coupled scattering equations including exchange for electron scattering from a general many-electron linear target were formulated in the body frame by Burke and Sinfailam,[15] who performed calculations for low-energy e-N_2 scattering. Unfortunately, these authors used a static potential which was far from converged,[9,16,17] thereby inaccurately representing the electron-molecule system and producing unconverged cross sections. Recently, Buckley and Burke[17] have repeated the study of Burke and Sinfailam, bringing the cross sections closer to true convergence. Finally, the application of the static-exchange close-coupling formulation to electron collisions with nonlinear targets (H_2O) has been discussed by Burke *et al.*,[18] but to date no calculations have been reported.

An approximate approach to the problem which avoids solving *integro-differential* equations was originally developed by Burke and Chandra.[9] This entails enforcing orthogonality of the scattering orbital to all molecular orbitals of the same symmetry by introducing Lagrange multipliers. One then solves a set of coupled *inhomogeneous differential* equations, a considerably less arduous task than solving the full scattering equations. The initial application of this procedure,[9] to e-N_2 collisions, suffered from the fact that this system possesses a $^2\pi_g$ shape (potential) resonance[19,20,25] at an electron energy of about 2.4 eV. This feature should appear in the static-exchange cross section (at a somewhat higher energy), but there is no core π_g molecular orbital in the ground-state orbital occupancy of N_2 to which the scattering orbital can be orthogonalized. Hence, Burke and Chandra required an unrealistically strong polarization potential to compensate for the lack of exchange in this symmetry. However, the procedure has subsequently been applied to the other systems,[26-28] notably e-CO collisions,[26] with some success.

Other approaches to the treatment of exchange include accurate solution of the two-dimensional Schrödinger equation for the e-H_2 system[29,30] (a procedure which is not tractable at present for scattering from targets with many more than two electrons), and a variety of L^2 variational approaches.[31-38] These methods view the collision problem from an entirely different perspective than do the more traditional approaches discussed above. Briefly, they treat the electron-molecule system in the region of configuration space near the target as if it were a negative ion, using standard procedures and codes of molecular-structure theory. In the region far from the target, where exchange is unimportant, the remaining interactions usually take on a simple analytic form, and, for comparatively simple targets such as H_2 and N_2, the scattering equations uncouple and the solution of the dynamical problem is easily effected. Details and applications of these procedures are discussed in the relevant papers; they include the R-matrix method,[32,33] the T-matrix expansion technique,[34,35] and a pseudo-bound-state[36] and related low-l spoiling[37,38] procedure. Although these procedures are new and less well tested, they show considerable promise for solving problems in electron-molecule scattering in the static-exchange approximation for small molecular targets. To date, no L^2-variational calculations of electron-molecule scattering including polarization have been reported.

The problems attendant upon including exchange in an eigenfunction expansion formulation of electron-molecule scattering theory (see Sec. II) are exacerbated as the number of nuclei and electrons in the target molecule and its internuclear separations increase. Thus as attention turns to collisions with polyatomic targets (and "large" diatomics), the possibility of modeling at least the exchange part of the electron-molecule interaction becomes increasingly appealing. In addition to simplifying enormously the numerical problems involved in the solution of the appropriate scattering equations, model potentials might usefully illuminate the sometimes elusive physical nature of the exchange interaction in electron-molecule collisions.

An early crude attempt to determine the sensitivity of various cross sections to exchange effects in a close-coupling calculation was that of Lane and Geltman,[6] who, as part of a study of low-energy e-H_2 collisions, augmented the static electron-molecule potential energy with an exponential short-range attractive term, the parameters of which were adjusted to optimize agreement with available measured low-energy elastic cross sections. More recently, a number of studies have been reported on the use of model exchange potentials for electron-atom scattering[39-43] and intermediate-energy ($E > 10.0$ eV) electron-molecule scattering.[44] For the lower-energy electrons of concern here, the first application of such an approach to electron-molecule collisions was that of Hara,[45] who used a spherical electron-molecule interaction potential including a free-electron-gas exchange potential term in a study of low-energy e-H_2 collisions.

In a recent study of low-energy e-CO_2 scattering,[46-48] we used a free-electron-gas model potential together with an *ab initio* static potential and a semiempirical polarization potential to calculate total integrated, momentum-transfer, total differential, and rotational excitation[49] cross sections for electrons with energies from

0.07 to 10.0 eV. The resultant theoretical cross sections were found to be in reasonably good agreement with the measured results,[50] especially at the lower energies, where the unusually steep rise in the cross section as the scattering energy decreases below 1.0 eV was reproduced. Considering the admittedly crude nature of our treatment of exchange in this study, the quality of the results was somewhat surprising and suggested further study of these comparatively simple model exchange potentials. Unfortunately, CO_2 is a highly anisotropic molecule. This fact makes it an impractical (and expensive) choice as the target in any reasonably extensive study of model potentials. Moreover, to date there have been no other theoretical studies of e-CO_2 collisions; in particular, it has not been possible to calculate accurate static-exchange cross sections like those of Henry and Lane[7] for e-H_2 collisions. For these reasons, we have selected the e-N_2 system as the primary focus of this and future studies of exchange in electron-molecule scattering.

The nitrogen molecule is, in some regards, an "ideal" homonuclear diatomic target for such studies: it is sufficiently aspherical (compared to, say, H_2) that the resultant anisotropy of the interaction potential energy introduces considerable partial-wave coupling, and yet it is not *so* aspherical or possessed of so many electrons that extensive scattering calculations become prohibitive. Thus, low-energy e-N_2 collisions have been the subject of studies using close coupling,[15-17] R matrix,[33] highly approximate Born[51] and distorted wave,[52] low-l spoiling,[37] T matrix,[35] and other methods.[9,53]

In the present paper, we report a study of the use of free-electron-gas exchange potentials in low-energy e-H_2 and e-N_2 scattering. In Sec. II we summarize briefly the body-frame formulation of the electron-molecule scattering problem with exchange rigorously included by fully antisymmetrizing the system wave function. The theoretical foundation for and derivation of a free-electron-gas (FEG) exchange potential appropriate to electron-molecule collisions are presented in Sec. III. In Sec. IV we summarize briefly the calculational procedures used to solve the collision problem and present results for e-H_2 collisions which suggest certain important features of the form of a desirable FEG potential. The e-H_2 calculations were performed in order to compare the results calculated using various FEG exchange potentials with those of analogous full static-exchange (SE) calculations. The results for e-N_2 scattering appear in Sec. V and suggest conclusions regarding the use of such potentials in electron-atom and electron-molecule collision calculations. Finally, in Sec. VI we discuss limitations and future directions of this research. Unless otherwise stated, atomic units are used throughout.

II. THEORY: BODY-FRAME STATIC-EXCHANGE EQUATIONS

In this section we shall briefly discuss the derivation of the coupled integro-differential scattering equations for electron collisions with an N-electron closed-shell molecule which obtain when exchange is treated rigorously, i.e., when the electron-molecule system wave function is made fully antisymmetric under pairwise electron interchange. These equations were solved numerically in the "exact static exchange" (ESE), calculations of e-H_2 scattering to be reported in Sec. IV. In this discussion we shall also establish notation and provide a framework for our treatment of approximate exchange potentials in the sequel.

The desired scattering equations can be derived directly from the variational principle[15] or, equivalently, from an eigenfunction expansion.[23,54] We choose the latter approach. The necessary algebraic manipulations are similar whether the derivation is carried out in a space-fixed laboratory reference frame[7,23] or a body-fixed reference frame. Therefore we shall omit the details of the derivation. Our notation is similar to that of Burke and Sinfailam,[15] although our approach is somewhat different and the equations will be presented in a form more suitable for the present discussion.

A. Scattering equations

We shall consider a linear molecule in a body-fixed reference frame, i.e., the $\hat{z}$ coordinate axis lies along the molecular internuclear axis $\hat{R}$. We make the Born-Oppenheimer approximation for the target molecular wave function.[55] We also make the *fixed-nuclei approximation*[45,56] freezing the orientation in space of the target ($\hat{R}$) for the duration of the collision. (The validity and consequences of these assumptions for low-energy electron-molecule collisions have been discussed elsewhere.[17,47,48])

Within this theoretical framework, the Schrödinger equation for the electron-molecule system can be written

$$(\mathcal{H} - E_\gamma)\psi_\gamma(\tau, \vec{r}, \sigma, R_{\text{nuc}}) = 0 , \tag{2.1}$$

where τ collectively denotes the spatial and spin coordinates of the target molecular electrons, $\vec{r}$ and σ denote the spatial and spin coordinates of the scattering electron, and R_{nuc} denotes the nuclear coordinate(s). The total energy of the system is E_γ. The subscript γ represents the set of quantum numbers required to uniquely specify a state of the system. Thus γ includes the molecular electronic state quantum numbers n_γ, the vibrational state quantum number v_γ, and the quantum numbers l_γ and m_γ corresponding to the asymptotic orbital angular momentum of the scattering electron and its $\hat{z}$ projection. [The molecular electronic state quantum numbers n_γ designate[57] symmetry under vertical reflection (±), symmetry under inversion (g, u), the projection on $\hat{R}$ of the total electronic angular momentum of the molecule (Λ), and the total electronic spin (S).]

The electron-molecule Hamiltonian in Eq. (2.1) is

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{\text{mol}}(\tau, R_{\text{nuc}}) + T_e(\vec{r}) \\ &\quad + V_{\text{int}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{r}_{N+1}, R_{\text{nuc}}), \qquad (2.2)\end{aligned}$$

where $\mathcal{H}_{\text{mol}}$ is the nonrelativistic Hamiltonian of the isolated molecular target, T_e is the kinetic energy operator for the scattering electron, and V_{int} is the electron-molecule interaction potential energy,

$$\begin{aligned}&V_{\text{int}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{r}_{N+1}, R_{\text{nuc}}) \\ &\quad = -\sum_{\alpha=1}^{N_{\text{nuc}}} \frac{Z_\alpha}{|\vec{r}_{N+1} - \vec{R}_\alpha|} + \sum_{i=1}^{N} \frac{1}{|\vec{r}_{N+1} - \vec{r}_i|}. \qquad (2.3)\end{aligned}$$

In Eq. (2.3), the first sum runs over the N_{nuc} nuclei, of charge Z_α located at positions R_α. The second sum runs over the N bound molecular electrons, located at positions $\vec{r}_i$. The total energy of the system, appearing in Eq. (2.1) is

$$E_\gamma = \tfrac{1}{2} k_\gamma^2 + \epsilon_{(nv)_\gamma}, \qquad (2.4)$$

where $\epsilon_{(nv)_\gamma}$ is the energy of the target molecule in state $(nv)_\gamma$ and $(\frac{1}{2})k_\gamma^2$ is the energy of the scattering electron for the system in state γ.

In the eigenfunction expansion approach to the scattering formalism, the normalized system wave function is expanded as

$$\begin{aligned}&\psi_\gamma(\tau, \vec{r}, \sigma, R_{\text{nuc}}) \\ &\quad = \frac{1}{(N+1)^{1/2}} \sum_{(nv)_{\gamma'}} \sum_{i=1}^{N+1} (-1)^{N+1-i} X_{(nv)_{\gamma'}}(\bar{i}, R_{\text{nuc}}) \\ &\qquad \times \mathcal{Y}^{(\gamma)}_{(nv)_{\gamma'}}(i). \qquad (2.5)\end{aligned}$$

In this expression $X_{(nv)_{\gamma'}}(\bar{i}, R_{\text{nuc}})$ is the target molecular wave function. The overbar on the argument i denotes the omission of $\vec{r}_i, \sigma_i$ from the $N+1$ possible space-spin coordinates, i.e.,

$$X(\bar{i}, R_{\text{nuc}}) \equiv X(1, 2, \ldots, i-1, i+1, \ldots, N+1, R_{\text{nuc}}).$$

The spin orbital of the scattering electron is $\mathcal{Y}^{(\gamma)}_{(nv)_{\gamma'}}(i)$. The superscript (γ) on the scattering orbital reminds us of the initial state of the electron-molecule system, $(nvlm)_\gamma$. The corresponding spin function will be designated $\xi^\gamma_{\gamma'}$, such that

$$\mathcal{Y}^{(\gamma)}_{(nv)_{\gamma'}}(i) = \mathcal{Y}^{(\gamma)}_{(nv)_{\gamma'}}(\vec{r}_i)\, \xi^\gamma_{\gamma'}(\sigma_i). \qquad (2.6)$$

The sum over $(nv)_\gamma$ runs over all target electronic and vibrational states. The wave function of Eq. (2.5) satisfies the Pauli exclusion principle provided the molecular wave function $X_{(nv)_{\gamma'}}$ does so.

We shall treat the molecule as rigid, freezing the internuclear separation at its equilibrium value for the duration of the collision. Thus we do not allow for vibrational excitation in the present treatment.[53,54] Moreover, we shall retain only the ground electronic state in the expansion of the system wave function, Eq. (2.5), thereby eliminating the possibility of direct (or virtual) electronic excitation. With these approximations the sum over γ' in Eq. (2.5) is no longer present and the molecular target function $X_{(nv)_\gamma}(\tau, R_{\text{nuc}})$ can be replaced by the electronic wave function for the ground state of the target, which in the Born-Oppenheimer[55] approximation depends parametrically on the nuclear coordinates R_{nuc}. This antisymmetrized electronic wave function, which we shall denote $\Phi_{n_\gamma}(\tau)$, can be written in the orbital approximation in terms of singly occupied spin orbitals $\phi_i(\vec{r}_j, \sigma_j)$ as

$$\Phi_{n_\gamma}(\tau) = \frac{1}{\sqrt{N!}} \sum_{\alpha\beta\cdots\pi} \epsilon_{\alpha\beta\cdots\pi}\, \phi_\alpha(1)\phi_\beta(2)\cdots\phi_\pi(N), \qquad (2.7)$$

where $\epsilon_{\alpha\beta\cdots\pi}$ is the Levi-Civita density[58] labeled with N subscripts corresponding to the N spin-orbitals, and where each sum over α, β, γ, etc, runs from 1 to N.

In order to obtain equations for the scattering function $\mathcal{Y}^{(\gamma)}(\vec{r}_i)$, we substitute the expansion, Eq. (2.7), into the Schrödinger equation, Eq. (2.1), then multiply this equation by $[\Phi_{n_\gamma}(\overline{N+1})\xi^{\gamma''}(\sigma_{N+1})]^*$ and integrate over the space and spin coordinates of the N molecular electrons τ, and the spin coordinate of the $N+1$ electron σ_{N+1}. The resulting integral can be simplified by noting[15] that for closed-shell targets, the Pauli exclusion principle forbids the scattering electron from occupying a target orbital of the same symmetry. This leads to the useful orthogonality relation

$$\langle \Phi_{n_\gamma}(\bar{i}) | \mathcal{Y}^{(\gamma)}(j) \rangle_j = 0, \quad 1 \leqslant j \leqslant N+1, \qquad (2.8)$$

where the integral of the matrix element is performed over the coordinates $\vec{r}_j, \sigma_j$.

Carrying out the indicated manipulations, we obtain the following integro-differential scattering equation for electron scattering from a closed-shell N-electron molecule

$$[-\tfrac{1}{2}\nabla^2_{N+1}+V_{\mathrm{st}}(\vec{\mathrm{r}}_{N+1})+V^{(\gamma)}_{\mathrm{ex}}(\vec{\mathrm{r}}_{N+1})-\tfrac{1}{2}k^2]\,\mathcal{Y}^{(\gamma)}(\vec{\mathrm{r}}_{N+1})=0\,, \tag{2.9}$$

where k^2 is the scattering energy (in rydbergs). The static potential energy, V_{st} in Eq. (2.9) is due to the electrostatic (Coulomb) interactions and is equal to the matrix element of the instantaneous potential, V_{int} of Eq. (2.3), with respect to the ground electronic state wave function of the molecule, i.e.,

$$V_{\mathrm{st}}(\vec{\mathrm{r}}_{N+1})=\langle\Phi_{n_\gamma}(\tau)|V_{\mathrm{int}}(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2,\ldots,\vec{\mathrm{r}}_N,\vec{\mathrm{r}}_{N+1},R_\alpha)\times|\Phi_{n_\gamma}(\tau)\rangle\,. \tag{2.10}$$

By substituting for the electronic wave function Φ_{n_γ} its expansion in spin orbitals, Eq. (2.7), we can write the static potential in terms of the $N_{\mathrm{occ}}(=\tfrac{1}{2}N)$ corresponding doubly occupied *spatial* orbitals $\phi_i(\vec{\mathrm{r}}_i)$ as

$$V_{\mathrm{st}}(\vec{\mathrm{r}}_{N+1})=-\sum_\alpha\frac{Z_\alpha}{|\vec{\mathrm{r}}_{N+1}-\vec{R}_\alpha|}+2\sum_{j=1}^{N_{\mathrm{occ}}}\int\phi_j^*(\vec{\mathrm{r}}_1)\,\frac{1}{r_{1,N+1}}\times\phi_j(\vec{\mathrm{r}}_1)\,d\vec{\mathrm{r}}_1\,. \tag{2.11}$$

Similarly, in Eq. (2.9) the *nonlocal* energy-dependent Hartree-Fock exchange operator $V^{(\gamma)}_{\mathrm{ex}}$ is given (in terms of its effect on the scattering function $\mathcal{Y}^{(\gamma)}$) by

$$V^{(\gamma)}_{\mathrm{ex}}(\vec{\mathrm{r}}_{N+1})\ \mathcal{Y}^{(\gamma)}(N+1)=-N\left\langle\Phi_{n_\gamma}(\overline{N+1})\xi^\gamma(\sigma_{N+1})\left|\frac{1}{r_{N,N+1}}\right|\Phi_{n_\gamma}(\bar{N})\mathcal{Y}^{(\gamma)}(N)\right\rangle\,. \tag{2.12}$$

Introducing the spatial molecular and scattering orbital, we have

$$V^{(\gamma)}_{\mathrm{ex}}(\vec{\mathrm{r}}_{N+1})\ \mathcal{Y}^{(\gamma)}(N+1)=-\sum_{j=1}^{N_{\mathrm{occ}}}\phi_j(\vec{\mathrm{r}}_{N+1})\int\phi_j^*(\vec{\mathrm{r}}_1)\,\frac{1}{r_{1,N+1}}\,\mathcal{Y}^{(\gamma)}(\vec{\mathrm{r}}_1)\,d\vec{\mathrm{r}}_1\,. \tag{2.13}$$

It is evident from Eq. (2.13) that exchange is a short-range attractive interaction.[70(a)] In order to deal numerically with Eq. (2.9), we must reduce it to a set of *radial* coupled equations.

B. Reduction to radial equations

In a single-center spherical coordinate system, with all coordinates referred to the origin at the center of mass of the molecule, we can expand the spatial scattering orbital in the complete set of spherical harmonics, e.g.,

$$\mathcal{Y}^{(\gamma)}(\vec{\mathrm{r}})=\frac{1}{r}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}f_l^{(m)}(r)Y_l^m(\hat{r})\,, \tag{2.14}$$

with $f_l^{(m)}(r)$ the radial scattering function. In practice, the summation over l runs from 0 to some l_{max}. This expansion is substituted into Eq. (2.9), the result multiplied by $Y_{l'}^{m'}(\hat{r}_{N+1})^*$ and integrated over $d\hat{r}_{N+1}$ to obtain the coupled radial scattering equations

$$\left(\frac{d^2}{dr^2_{N+1}}-\frac{l(l+1)}{r^2_{N+1}}+k^2\right)f^{(m)}_{ll_0}(r_{N+1})=2\sum_{l'}\left(V^{(m)}_{ll'}(r_{N+1})f^{(m)}_{l'l_0}(r_{N+1})-\int dr_1K^{(m)}(ll'|r_1r_{N+1})f^{(m)}_{l'l_0}(r_1)\right)\,. \tag{2.15}$$

where the additional subscript l_0 denotes the initial asymptotic angular momentum of the scattering electron. We note that owing to the neglect of the rotational Hamiltonian in our body-frame fixed-nuclei formulation, these equations are not coupled in m. The static matrix element in Eq. (2.15) is

$$V^{(m)}_{ll'}(r_{N+1})=\langle lm|V_{\mathrm{st}}(\vec{\mathrm{r}}_{N+1})|l'm\rangle\,, \tag{2.16}$$

where $V_{\mathrm{st}}(r_{N+1})$ is the averaged electrostatic potential energy of Eq. (2.11). By expanding V_{st} in Legendre polynomials, viz.,

$$V_{\mathrm{st}}(\vec{\mathrm{r}}_{N+1})=\sum_{\lambda=0}^{\infty}v^{\mathrm{st}}_\lambda(r_{N+1})P_\lambda(\cos\theta_{N+1})\,, \tag{2.17}$$

and carrying out the indicated integral over $d\hat{r}_{N+1}$, we reduce this matrix element to

$$V^{(m)}_{ll'}(r_{N+1})=\left(\frac{2l'+1}{2l+1}\right)^{1/2}\sum_{\lambda=0}^{\infty}v^{\mathrm{st}}_\lambda(r_{N+1})C(l'\lambda l;m0)\times C(l'\lambda l;00)\,, \tag{2.18}$$

where $C(l_1l_2l_3;m_2m_2)$ is the usual Clebsch-Gordan coefficient.[59] In practice, the sum over λ in Eqs. (2.17) and (2.18) is finite. (For electron collisions with homonuclear targets, only even-λ terms contribute to this summation.) In our earlier treatment of e-CO_2 scattering[46-48] and the present e-N_2 study, we found that the static potential energy, Eq. (2.17), could be converged efficiently by including far more nuclear contributions than electronic contributions. Thus we write each expansion coefficient $v^{\mathrm{st}}_\lambda(r)$ as

$$v^{\mathrm{st}}_\lambda(r)=v^{\mathrm{el}}_\lambda(r)+v^{\mathrm{nuc}}_\lambda(r)\,, \tag{2.19}$$

where $v^{\mathrm{el}}_\lambda(r)$ depends on the electronic wave function, but $v_\lambda^{\text{nuc}}(r)$ is given by a very simple analytic form; see Eq. (2.11). In the sum over λ in Eqs. (2.17) and (2.18), we include nuclear terms up to some $\lambda_{\max}^{\text{nuc}}$ and electronic terms up to smaller $\lambda_{\max}^{\text{el}}$. The values of these limits are determined by our convergence criteria (see Sec. V).

The second term in Eq. (2.15), the "exchange term," contains the *exchange kernel* $K^{(m)}(ll'|r_1 r_{N+1})$. An expression for the exchange kernel can be obtained by expanding the spatial molecular orbitals in spherical harmonics, viz.,

$$\phi_i(\vec{r}) = \frac{1}{r} \sum_{\mu=0}^{\infty} \mathcal{U}_\mu^{(m_i)}(r) Y_\mu^{(m_i)}(\hat{r}) , \qquad (2.20)$$

where m_i is the azimuthal quantum number of the orbital angular momentum of the ith electron and $\mathcal{U}_\mu^{(m_i)}$ the radial expansion coefficient corresponding to the μth partial wave. With these definitions, the exchange kernel is given by

$$K^{(m)}(ll'|r_1 r_{N+1}) = \sum_{i=1}^{N_{\text{occ}}} \sum_{l''l'''\lambda} \mathcal{U}_{l''}^{(i)}(r_{N+1}) \mathcal{U}_{l'''}^{(i)}(r_1) \times g_\lambda(ll'l''l''';m,m_i) \frac{r_<^\lambda}{r_>^{\lambda+1}} , \qquad (2.21)$$

where $r_< = \min(r_1, r_{N+1})$, etc. The factor g_λ is given by

$$g_\lambda(ll'l''l''';m,m_i) = \left(\frac{(2l+1)(2l'+1)}{(2l''+1)(2l'''+1)}\right)^{1/2} \times C(l\lambda l''; -m, m-m_i) C(l\lambda l''; 00) \times C(l'\lambda l'''; m, m_i - m) C(l'\lambda l'''; 00) .$$

For the case in which the target molecule has only σ and π bound orbitals, these equations reduce to those of Burke and Sinfailam.

C. Discussion

Equations (2.9) and (2.15) reveal why fully converged ESE calculations for molecules with several electrons—and hence several molecular orbitals—tend to be quite arduous. Suppose we consider only a single initial partial wave, say, $l=0$. If we couple only one other partial wave l' in the exchange term sum in Eq. (2.15), the summation over l'', l''', and λ in Eq. (2.21) introduces a large number of terms. (Of course, the number of terms is finite, since the summations are restricted[60] by the properties of the Clebsch-Gordon coefficients appearing in g_λ.) A commonly used method for numerically solving sets of coupled integro-differential equations[61] involves transforming the equations to a larger set of coupled differential equations.[62-64] Each new exchange kernel in the exchange term sum gives rise to an additional equation to be solved. Even in a calculation of e-H_2 scattering, where only one molecule orbital is involved and the partial-wave coupling is minimal, the exchange terms rapidly proliferate [see Sec. IV B].

An alternate procedure, in which coupled integrodifferential equations are reduced to coupled algebraic equations,[65,66] does not suffer from this problem. However, the matrices which must be manipulated are typically of dimensionality equal to the number of continuum channels times the number of integration points. For a strongly r-dependent potential (e.g., the electron-molecule static potential), the number of integration points may be so large that computation times are comparable or greater than with other methods.

For larger systems such as e-N_2, not all allowed exchange terms that arise from the summations in Eqs. (2.14) and (2.17) need be included,[17] since, crudely speaking, the scattering electron "exchanges" principally with the outermost molecular orbitals. Moreover, the dominant contributions to the exchange kernel are due to low-order partial waves. Nevertheless, at present N_2 would appear to be the largest target for which such calculations are currently feasible, and there still appears to be difficultes in fully converging e-N_2 cross sections for very low-impact energies (see Sec. IV B).

III. THEORY: FREE-ELECTRON-GAS EXCHANGE POTENTIALS FOR ELECTRON-MOLECULE COLLISIONS

In 1951, Slater[67] suggested that the Hartree-Fock equation for the bound-state wave function of a system could be transformed into much more easily solvable form by the introduction of an average exchange potential[68] based on a free-electron-gas (FEG) approximation for the electrons of the system.[69,70(b)] Since then, the use of such an exchange potential has become widespread in the study of bound states of atoms, molecules, and solids, leading most recently to the $X\alpha$ method.[71]

The basic idea behind the Slater average FEG potential can be applied to collision problems, in which we seek a local exchange potential which mocks the effect of exchange on the scattering electron. However, since this electron has a well-defined momentum, the use of an *average* exchange potential is inappropriate. This point was made by Hara.[45] More recently, such potentials have been used in the study of intermediate-energy (10–40 eV) electron-molecule collisions by Truhlar and co-workers,[44] and of low-energy e-CO_2 scattering.[47]

The most systematic studies of the use of various approximate local exchange potentials have been those of Riley and Truhlar[39,40] for e-He, e-Ar, and e-H and of Bransden *et al.*[41] for e-H, e-He$^+$, and e-He. In such cases, of course, the interaction potential is spherically symmetric. The former authors have introduced a semiclassical exchange potential (not based on an FEG approximation) which appears to be quite successful in treating electron-atom collisions for impact energies above a few tens of eV, and can be extended to collisions with open-shell targets. This model potential is quite similar to that of Furness and McCarthy.[43] However, considerable care is required in generalizing conclusions drawn in the context of electron-atom problems to electron-molecule systems (see Sec. VI).

In this section, we shall briefly derive the local FEG exchange potentials to be used in the calculations of Secs. IV and V and suggest how this treatment differs from the standard analysis for bound-state problems. Further, we shall indicate certain features of the resulting potentials which will be useful in interpreting the results of this study.

Making the FEG approximation for a bound system (e.g., a molecule) amounts to treating all the electrons as noninteracting fermions[69] occupying a volume V. Thus, exchange explicitly is taken into account only to the extent of requiring that the system wave function satisfy the Pauli exclusion principle. All the electrons move in an identical potential field, and there are no mutual forces between them. To implement this approximation, the spatial orbitals of the bound electrons are replaced by plane waves. Thus, using the notation established in Sec. II, we set

$$\phi_i(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}_i\cdot\vec{r}} \quad (i = 1, 2, \ldots, N_{\text{occ}}), \tag{3.1}$$

where $\vec{k}_i$ is the wave vector of the ith electron, which occupies the ith spatial orbital.

In the collision problem, we must also contend with the scattering electron. If we assume initially that the distortion of the wave function of the scattering electron is negligible *insofar as exchange is concerned,* we can make the Born approximation for the scattering function in Eq. (2.13), viz.,

$$\mathcal{Y}^{(\gamma)}(\vec{r}) = c e^{i\vec{k}\cdot\vec{r}}, \tag{3.2}$$

where $\vec{k}$ is the wave number of the scattering electron and c is an arbitrary normalizaton constant. Note that $|\vec{k}| = (2E_{\text{inc}})^{1/2}$, where E_{inc} is the scattering energy in atomic units.

In order to implement these ideas, we begin with the body-frame Hartree-Fock scattering equation, Eq. (2.9), with the corresponding exchange potential given by Eqs. (2.13). In order to transform $V_{\text{ex}}^{(\gamma)}$ to a local FEG exchange potential, we first multiply and divide Eq. (2.13) by $\mathcal{Y}^{(\gamma)}(\vec{r}_1)^*\mathcal{Y}^{(\gamma)}(\vec{r}_1)$, thereby obtaining

$$\begin{aligned} V_{\text{ex}}^{(\gamma)}(\vec{r}_1)\, \mathcal{Y}^{(\gamma)}(\vec{r}_1) &= -\sum_{j=1}^{N_{\text{occ}}} \int \frac{\mathcal{Y}^{(\gamma)}(\vec{r}_1)^*\phi_j(\vec{r}_2)^*\phi_j(\vec{r}_1)\mathcal{Y}^{(\gamma)}(\vec{r}_2)}{\mathcal{Y}^{(\gamma)}(\vec{r}_1)\mathcal{Y}^{(\gamma)}(\vec{r}_1)^*} \\ &\quad \times \frac{1}{r_{12}}\, d\vec{r}_2 \mathcal{Y}^{(\gamma)}(\vec{r}_1). \end{aligned} \tag{3.3}$$

Because of the presence of the bound orbital $\phi_j(\vec{r}_2)$ in the integrand of Eq. (3.3), this integral will be over the finite range of the volume occupied by the molecule, just as in the bound-state problem.[70] We now wish to approximate $V_{\text{ex}}^{(\gamma)}\mathcal{Y}^{(\gamma)}$ by the product of a local exchange potential $V_{\text{FEG}}^{(\gamma)}$ times the scattering wave function $\mathcal{Y}^{(\gamma)}$. We substitute our plane wave and Born approximation, Eqs. (3.1) and (3.2) into Eq. (3.3), obtaining

$$\begin{aligned} V_{\text{FEG}}^{(\gamma)}(\vec{r}_1) &= -\frac{1}{V}\sum_{j=1}^{N_{\text{occ}}} \int_V \exp[i(\vec{k}-\vec{k}_j)\cdot(\vec{r}_2-\vec{r}_1)] \\ &\quad \times \frac{1}{r_{12}}\, d\vec{r}_2 . \end{aligned} \tag{3.4}$$

[Note that the arbitrary constant in Eq. (3.2) is no longer present.] We can carry out the integral over V and then the sum over j, keeping in mind that the $\vec{k}_j$ represents the wave vector of the jth bound electron, obtaining[70]

$$V_{\text{FEG}}^{(\gamma)}(\vec{r}_1) = -(2/\pi)k_F F(\eta), \tag{3.5}$$

where k_F is the Fermi momentum (the radius of the Fermi sphere in momentum space). The function $F(\eta)$ is defined by

$$F(\eta) \equiv \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left|\frac{1+\eta}{1-\eta}\right|, \tag{3.6}$$

with

$$\eta \equiv k/k_F . \tag{3.7}$$

The Fermi momentum is related to the density of the bound-target electrons, $\rho = N/V$, by

$$k_F = [3\pi^2(N/V)]^{1/3} = (3\pi^2\rho)^{1/3} . \tag{3.8}$$

It is worth noting that Eqs. (3.5)–(3.8) have the same form as those obtained by carrying through an analogous derivation of a FEG exchange potential for an electron in a bound system.[69] However, in the bound-state problem, we have $\eta = k_i/k_F$, with $\vec{k}_i$ the wave vector of the *bound* electron in question, rather than Eq. (3.7).

The above form for $V_{\text{FEG}}^{(\gamma)}$ follows directly from making the FEG approximation for the bound electrons and the Born approximation for the scattering electrons. However, some simple modifications can be made which should make this model potential more reasonable. First, the charge density of the target molecule, which appears in the definition, Eq. (3.8), of the Fermi momentum, is certainly not independent of $\vec{r}_1$. This observation suggests replacing ρ with the true $\vec{r}$-dependent charge density $\rho(\vec{r})$, thereby making the Fermi momentum η, and therefore $F(\eta)$, $\vec{r}$ dependent, viz.,

$$k_F(\vec{r}) = [3\pi^2\rho(\vec{r})]^{1/3} . \tag{3.9}$$

Second, we can replace k in the definition of η with a more realistic quantity. We assumed in making the Born approximation of Eq. (3.2) that the wave function of the scattering electron was undistorted by the collision. A more realistic treatment, although still highly approximate, would be to replace k by a local $\vec{r}$-dependent momentum for the scattering electron $\kappa(\vec{r})$.

If we let V denote the potential field in which the electron moves, then by conservation of energy

$$\tfrac{1}{2}\kappa^2(\vec{r}) + V(\vec{r}) = E_{\text{inc}} . \tag{3.10}$$

Now, the Fermi electron, the bound electron with momentum k_F, moves in a potential field, say V'. Its energy is just the ionization potential of the target I. We therefore have approximately

$$\tfrac{1}{2}k_F^2(\vec{r}) + V'(\vec{r}) = -I . \tag{3.11}$$

If we now *assume* that the scattering electron and the outermost bound electron move in the *same* potential field,[45] i.e., $V(\vec{r}) = V'(\vec{r})$, we can define the local momentum $\kappa(\vec{r})$ by

$$\kappa^2(\vec{r}) = 2(E_{\text{inc}} + I) + k_F^2(\vec{r}), \tag{3.12}$$

and replace η of Eq. (3.7) by

$$\eta \equiv \kappa(\vec{r})/k_F(\vec{r}) . \tag{3.13}$$

Thus Eqs. (3.5), (3.6), (3.9), (3.12), and (3.13) define the FEG exchange potential which was used in our treatment of e-CO_2 collisions and in the present study. This form is called the Hara free-electron-gas exchange (HFEGE) potential since Hara[45] used a similar exchange potential in studying low-energy e-H_2 scattering.

An alternate FEG exchange potential has been suggested by Riley and Truhlar.[39] These authors argue that in the limit $r \to \infty$, the local momentum of the scattering electron, $\kappa(\vec{r})$ of Eq. (3.12) reduces not to the correct value, $k = (2E_{\text{inc}})^{1/2}$, but to $[2(E_{\text{inc}} + I)]^{1/2}$ and that a more reasonable way to define $\kappa(\vec{r})$ might be to set $I = 0$ in Eq. (3.12). The resulting form is called the asymptotically adjusted FEG exchange (AAFEGE) potential. Riley and Truhlar found that for e-He and e-Ar collisions use of the AAFEGE potential produced phase shifts for high-order partial waves at low energies that were in better agreement with exact static-exchange results than those obtained with the HFEGE potential. However, for e-Ar scattering, the HFEGE phase shifts for *low-order* partial waves at very low-impact energies were better than the AAFEGE results; the AAFEGE potential apparently being too strong for $k < 0.5a_0^{-1}$. Bransden *et al.*,[41] in their study of e-He collisions for impact energies greater than 3.0 eV, also found that phase shifts obtained with the AAFEGE potential are in good agreement with the results of their exact static-exchange calculations.

IV. CALCULATIONAL PROCEDURE AND RESULTS FOR e-H_2 COLLISIONS

In this section we summarize the procedure used to solve the scattering problem when the local FEG exchange potential of Sec. III is implemented. The theoretical framework and computational details have been explicated elsewhere[48] and will not be repeated here. We shall also discuss the results of a study of FEG exchange potentials for e-H_2 collisions, which includes detailed comparisons of several model exchange potentials with exact static-exchange (ESE) results calculated with the same target wave functions, parameters, and convergence criteria.

A. Calculational procedure

We recall that the problem is formulated in the body frame, making the fixed-nucleus approximation and treating the molecule as rigid, with the internuclear separation fixed at its equilibrium value[72] ($1.402a_0$ for H_2, $2.068a_0$ for N_2). The coupled scattering equations are converted to integral equations,[73] and solved by numerical quadrature.[48]

In the present calculations (and our earlier e-CO_2 studies[47]) considerable care is taken in treating the partial-wave expansion of the scattering function [Eq. (2.14)] and the expansion of the electron-molecule interaction potential energy in Legendre polynomials [Eq. (2.17)] to ensure convergence to some preselected criteria. Since there has been some discussion of this problem in the recent literature,[16,17,66] we would like to clarify several points. The usual procedure for testing convergence is to fix the number of expansion terms in the potential energy $V_{\text{st}}(\vec{r}_{N+1})$ at some $\lambda_{\max}$ [cf. Eq. (2.19)] and then increment the number of partial waves in the expansion of the scattering function [cf. Eq. (2.14)] until successive cross sections are converged to, say, $M\%$, i.e.,

$$\left|\frac{\sigma(N)-\sigma(N-1)}{\sigma(N)}\right| < \frac{M}{100}\,, \tag{4.1}$$

where N is the maximum number of partial waves included in the calculation of the cross section σ. This procedure establishes a "local convergence." However, it can be misleading, for in certain systems (e.g., e-CO_2, e-N_2) convergence may be very gradual, so that $\sigma(N)$ is really quite far from true "global convergence" to within $M\%$. In fact, one must consider comparisons between cross sections calculated in widely differing basis sets to establish global convergence, e.g.,

$$\left|\frac{\sigma(N)-\sigma(N-K)}{\sigma(N)}\right| < \frac{M}{100}\,, \tag{4.2}$$

where the larger K and smaller M employed, the more stringent is the resulting criteria. (The importance of achieving global convergence is illustrated in a recent study of static e-N_2 collisions by the present authors.[16])

Global convergence can be accurately and efficiently achieved by carrying out successive calculations of σ starting with $l_{\max}=\lambda_{\max}$ (for some reasonable $\lambda_{\max}$) and then incrementing $\lambda_{\max}$ and $l_{\max}$ simultaneously. This procedure quickly gets one into the region of these parameters where convergence is at hand and facilitates efficient determination of the optimum values of $l_{\max}$ and $\lambda_{\max}$ for convergence. (It is possible using the conventional procedure of fixing $\lambda_{\max}$ and converging in $l_{\max}$ to miss the global convergence in $\lambda_{\max}$ if extreme caution is not exercised.)

Finally, it is worth noting that the value of $l_{\max}$ (or $\lambda_{\max}$) required for global convergence varies with the scattering energy, sometimes quite strongly. Therefore using the same expansion parameters over a wide range of energies can lead to cross sections with widely differing convergence properties. Of course, this is a problem only if the parameters chosen are too small for certain scattering energies under consideration.

These are not insignificant considerations, even if one is carrying out exact static-exchange calculations, where the considerable effort involved to achieve highly accurate results necessitates an appreciation of the internal accuracy of the calculation. In model studies such as the present one, it is essential to realistically assess the accuracy of the numerical solution of the scattering equations in order to be able to meaningfully evaluate the strengths and weaknesses of the models being used.

Returning to our treatment of the scattering problem, we use a model electron-molecule interaction potential energy, calculating the static potential, Eq. (2.11), from the *ab initio* Hartree-Fock charge density of the ground state of the target, including the FEG exchange potential described in Sec. III, and using a semiempirical polarization potential of the form

$$V_{\text{pol}}(\vec{r}) = \left(-\frac{\alpha_0}{2r^4} - \frac{\alpha_2}{2r^4}P_2(\cos\theta)\right)C(r)\,, \tag{4.3}$$

where α_0 and α_2 are the spherical and nonspherical polarizabilities of the target and $C(r)$ is an exponential cutoff function,

$$C(r) = 1 - e^{-(r/r_c)^6}\,. \tag{4.4}$$

The single parameter r_c, the cutoff radius, is determined by adjusting the theoretical cross sections to some well-established feature (e.g., the 2.4 eV π_g resonance[19,20,25] in e-N_2 collisions).

B. Results for e-H_2 collisions

The e-H_2 system, which has been the subject of very extensive scrutiny since the early days of electron-molecule collision research,[1,3,6-8] was chosen for our initial study for two reasons, both related to its comparative simplicity.[92] For this system the coupled radial integro-differential scattering equations, Eq. (2.15), simplify considerably, since H_2 is a nearly spherical two-electron molecule with only one spatial molecular orbital (σ_g). The solution of the scattering problem therefore does not entail coping with the numerical problems attendant upon studying larger systems.[48] It is relatively simple to determine cross sections globally converged to better than 1% for this system in the exact static-exchange calculations and in those using FEG model potentials.

A computer code written by Sinfailam,[63] which solves the SE scattering equation, Eq. (2.15), using a technique first devised by Marriot,[62] was used in these calculations. This procedure involves converting the set of coupled integro-differential equations to a larger set of coupled differential equations. The resulting coupled equations are solved by inward-outward numerical integration. Since each exchange kernel, corresponding to indices $(ll'l''l'''\lambda, m_1 m_i)$ in Eqs. (2.15) and (2.21), gives rise to an additional differential equation, very large sets of equations obtain even for systems as "small" as e-N_2, although the situation is somewhat ameliorated by the fact that some of these exchange terms can be neglected.

For e-H_2 scattering, we used the Hartree-Fock target wave function of Fraga and Ransil[74] corresponding to an internuclear separation of $1.402a_0$ This function yields a quadrupole moment of $0.48ea_0^2$; compared to the experimental value[75] of

TABLE I. Cross sections (in a_0^2) and eigenphase sums (in rad) for low-energy e-H_2 collisions at scattering energies from 0.01 to 0.36 Ry in the Σ_g symmetry. The S results were determined in the static approximation (neglecting exchange). The ESE results were obtained by solving the exact static-exchange equations (2.14) using the code of Sinfailam (Ref. 63). Three free-electron-gas exchange potentials were used as described in the text (Secs. II and IV A). All results are globally converged to better than 1%. The eigenphase sums appear in parentheses.

E (Ry)	S	ESE	HFEGE	AAFEGE	TFEGE
0.01	493.4	56.7	92.5	28.8	57.0
	(−0.677)	(−0.211)	(−0.274)	(−0.151)	(−0.214)
0.04	247.3	53.3	82.0	41.4	54.3
	(−1.088)	(−0.419)	(−0.532)	(−0.367)	(−0.425)
0.09	132.4	48.1	68.4	43.1	49.7
	(−1.334)	(−0.618)	(−0.767)	(−0.580)	(−0.631)
0.16	78.3	42.0	54.8	40.3	43.7
	(−1.503)	(−0.806)	(−0.975)	(−0.781)	(−0.827)
0.36	33.7	29.5	33.1	29.7	30.5
	(−1.735)	(−1.136)	(−1.312)	(−1.136)	(−1.172)

$0.474 \pm 0.034 e a_0^2$ and the highly accurate theoretical value of $0.484 e a_0^2$ determined by Wolniewicz.[76] Expansion terms for $\lambda = 0$, 2, and 4 were included in the static potential [Eq. (2.17)], partial waves for $l = 0$, 2, and 4 in the expansion of the continuum orbital [Eq. (2.14)], and two terms, $\mu = 0$ and 2, in the partial-wave expansion of the bound σ_g molecular orbital [Eq. (2.20)] in the exchange kernel. These choices resulted in a set of 20 coupled differential equations. The K matrix was extracted[77] at $r = 10 a_0$ and cross sections calculated. We neglected polarization effects, since our purpose here is to focus on the effects of exchange on the scattering. Only results for Σ_g symmetry,[78] which dominates at low energies where the scattering is essentially pure s wave,[6] will be presented here. The code was checked by comparing at selected energies against the total cross sections of Henry and Lane[7] and those of Tully and Berry.[29] Our exact static-exchange (ESE) cross sections for several values of the scattering energy from 0.01 to 0.36 Ry are shown in Table I together with the Σ_g eigenphase sums.[79]

Also shown in Table I are cross sections and eigenphases sums obtained using the local HFEGE and AAFEGE potentials. In the HFEGE calculations, we used the experimentally determined value of $I = 1.128$ Ry for the ionization potential of H_2. For comparison, results obtained in the static approximation (S), in which the exchange potential is set equal to zero, are presented. Although including either the HFEGE or the AAFEGE potential gives cross sections closer to the exact static-exchange values than those obtained in the static approximation, neither model potential would appear to be appropriate for the e-H_2 system for low impact energies. (Of course, the effects of exchange disappear as the scattering energy is increased, and all the models, including the static, tend to produce the same cross sections.) The AAFEGE potential is clearly too strong and appears to be especially poor at very low-scattering energies. The HFEGE, on the

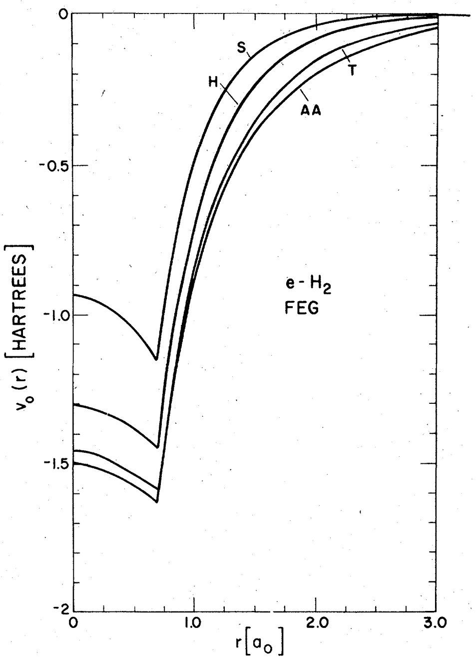

FIG. 1. Spherical components $v_0(r)$ of the static potential energy S and three static-exchange potential energies using FEG exchange potentials for e-H_2 collisions. The HFEGE, AAFEGE, and TFEGE potentials shown here were calculated at $k^2 = 0.09$ Ry using $I(H) = 0.564$ a.u., $I(AA) = 0.0$, and $I(T) = 0.071$ a.u.

other hand, is too weak. To illustrate, we show in Fig. 1 the $\lambda = 0$ expansion term of the HFEGE, AAFEGE, and static-potential energies. The exchange potentials in this figure were calculated at $k^2 = 0.09$ Ry.

To see if we could compensate for this deficiency, we tried "tuning" the FEG exchange potential in the following manner. Selecting a scattering energy of $k^2 = 0.04$ Ry, we treated I in Eq. (3.12) as a parameter, adjusting it until the FEG calculation reproduced the exact static-exchange cross section at that energy. Cross sections and eigenphase sums are shown in Fig. 2 as functions of the parameter I. We note the nearly linear character of both curves for values of I greater than about 0.2 a.u. Matching to the exact static-exchange cross section at $k^2 = 0.04$ Ry, we determined $I = 0.071$ a.u. We call the resulting optimized model exchange potential the tuned FEG exchange (RFEGE) potential. This potential energy, the $\lambda = 0$ coefficient of which is shown in Fig. 1, is intermediate in strength between the HFEGE and the AAFEGE potential energies.

Using the (TFEGE) potential with $I = 0.071$ a.u., we calculated cross sections and eigenphase sums for e-H_2 scattering at several energies, obtaining the results shown in Table I. In Fig. 3 we compare the cross sections for all three model calculations against the exact static-exchange results (open circles) for scattering energies from 0.01 to 1.0 Ry. The TFEGE potential appears to be a very accurate representation of the exchange potential, since the TFEGE results are in excellent agreement with the exact values over the whole energy range studied. It is important to note that the TFEGE potential preserves the form of the FEG exchange potential derived in Sec. III and that the "tuning" required to obtain I in the TFEGE was performed at only *one* energy. Moreover, a small (but nonzero) value of I is required, at least in e-H_2 scattering, to produce a realistic model exchange potential.

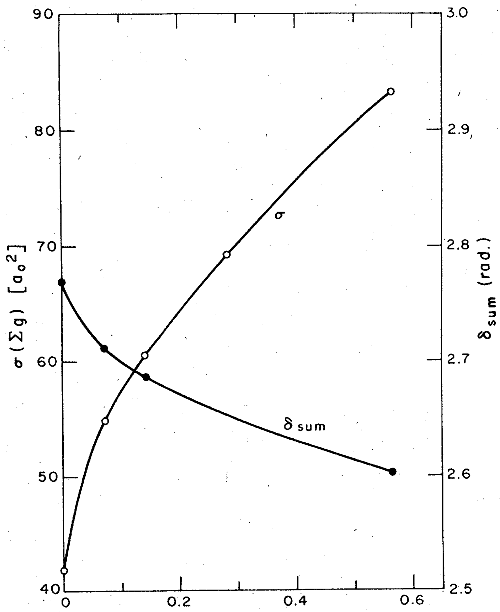

FIG. 2. Cross sections and eigenphase sums for e-H_2 scattering in the Σ_g symmetry at $k^2 = 0.04$ Ry as a function of the parameter I in the TFEGE [cf. Eq. (3.12)]. The calculated model static-exchange results are shown as open circles (cross sections) or solid dots (eigenphase sums). The exact static-exchange cross section $\sigma(\Sigma_g) = 53.3 a_0^2$ was most accurately reproduced by $I = 0.071$ a.u.

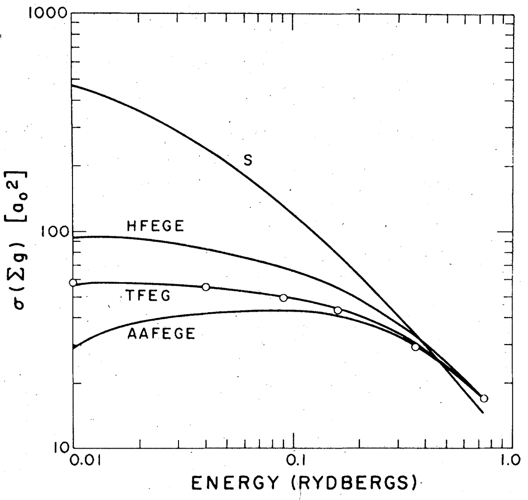

FIG. 3. Cross sections for e-H_2 scattering in the static approximation S and three model exchange calculations (solid curves). The open circles are converged exact static-exchange cross sections obtained by solving Eq. (2.15). The three FEG exchange potentials were recalculated at each scattering energy using $I(H) = 0.564$ a.u., $I(A) = 0.0$ a.u., and $I(T) = 0.071$ a.u. See also Table I.

Finally, it is worth pointing out that the sort of precise tuning and comparison of various models which were carried out on this system require constant application of a fairly stringent convergence criterion in both the exact static-exchange and model-exchange calculations.

V. RESULTS FOR e-N_2 COLLISIONS

We now turn to the e-N_2 system. We have calculated converged results for total integrated, momentum transfer, and differential cross sections for this system for impact energies from 0.01 to 1.0 Ry using the HFEGE and AAFEGE potentials. We have also included induced polarization effects in these calculations. In this section, we shall present and discuss these results and compare them with measured cross sections and selected results of other theoretical treatments e-N_2 collisions.

The nitrogen molecule possesses 14 electrons. In the ground electronic state, its orbital occupancy is

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

This gives seven doubly occupied spatial molecular orbitals, counting $\pi_u(x)$ and $\pi_u(y)$ separately. The equilibrium internuclear separation[72] of N_2, $2.068a_0$, is considerably larger than that of H_2. Thus the electron-molecule interaction potential for the e-N_2 system is much more aspherical, and many more expansion coefficients in the static potential energy and correspondingly more partial waves in the expansion of the scattering orbital are required to achieve a reasonable degree of convergence in the calculated cross sections.[16]

For these reasons, we were unable to carry out exact static-exchange coupled-channel calculations for e-N_2 scattering at the same level of convergence as was employed in of our model studies.

In a preliminary convergence study (in the static approximation) we were unable to obtain reliable cross sections using the Sinfailam code for $\lambda_{\max} > 14$ and $l_{\max} > 13$. Beyond these limits, the program produces nonsymmetric T matrices and erroneous cross sections. This appears to be due to a numerical problem inherent in the procedure implemented in the program. The most nearly convergent available exact static-exchange cross sections for e-N_2 scattering are those of Buckley and Burke, to which we do compare in this section (see Fig. 8). Unfortunately, these authors provide no convergence details and do not state their convergence criterion. [Their calculations used $\lambda_{\max} = 14$ and $l_{\max} = 12$ (g), 13(u).] Moreover, they published cross sections only for calculations in which polarization was included, not for the static-exchange case.[80]

The analytic Hartree-Fock SCF $N_2\,X\,^1\Sigma_g^+$ wave function of Cade *et al.*[81] at $R = 2.068a_0$ was used to calculate the static potential energy, Eq. (2.10), using a procedure described elsewhere.[48] The basis set used by these authors consists of an extended basis of Slater-type orbitals augmented by selected $3d$ and $4f$ polarization Slater functions with the orbital exponents in all the basis functions optimized by repeated SCF calculations to produce a near-Hartree-Fock wave function. The Hartree-Fock energy corresponding to this wave function is -108.9928 hartree; the calculated quadrupole moment is $q = -0.95ea_0^2$. (We should note that in the calculation of Burke and co-workers which we shall discuss below an equilibrium geometry wave function determined by Nesbet,[82] was used. The Hartree-Fock energy for this function is -108.9714 hartree and the quadrupole moment $q = -0.89ea_0^2$. Comparative studies at a few scattering energies suggest that the difference in the electron charge cloud which describes the target resulting from using the wave function of Cade *et al.*, rather than that of Nesbet may produce 10%–15% variation in the e-N_2 cross sections, the greatest discrepancy occuring at the lower scattering energies. Nevertheless, the convergence behavior of the problem appears to be independent of the choice of wave function.) The experimental value of the quadrupole moment[83] of N_2 is $q(\text{expt}) = -1.04 \pm 0.2ea_0^2$. In calculating the HFEGE potential, the experimentally determined value of the ionization potential,[84] $I = 1.146$ Ry, was used.

The same convergence criteria were applied to the present calculations as were used in our previous study of e-N_2 scattering in the static approximation.[16] The trends in the convergence of the cross sections and eigenphase sums for the SE and SEP cases closely paralleled those for the static case. The conditions of local and global convergence are best explicated in the Tables in Ref. 16. In the expansion of the static potential energy [cf. Eqs. (2.17) and (2.19)] we include electronic terms up to $\lambda_{\max}^{\text{el}} = 14$ and nuclear terms up to $\lambda_{\max}^{\text{nuc}} = 28$. Expansion coefficients of the FEG exchange potentials up to $\lambda = 14$ were included. In the model static-exchange calculations, partial waves up to $l_{\max} = 26(\Sigma_g, \Pi_g)$ and $l_{\max} = 25(\Sigma_u, \Pi_u)$ were included for $r < 3.0a_0$ in the expansion (2.14) of the scattering orbital. For $r > 3.0a_0$, all partial waves in this expansion with $l \geq 8$ were truncated from the solution matrix, thereby considerably reducing the dimensionality of the wave-function matrix being propagated. The coupled differential scattering equations were integrated outward to $r_{\max} = 65a_0$ in the calculations in which polarization was neglected and to $r_{\max} = 85a_0$ in those with polarization. By these values of r, the potential energy is weak enough (of the order of 10^{-6} a.u.) that the phase shifts are stable in $r_{\max}$. In order to ensure linear independence in the wave-function matrix, the solutions were stabilized[85] every three mesh points for $r < 3.0a_0$. The quadrupole moment of $q = -0.95ea_0^2$ obtained from the $X\,^1\Sigma_g^+ N_2$ wave function of Cade *et al.*,[81] was used in the long-range quadrupole term of the $\lambda = 2$ expansion coefficent of the static potential energy, i.e.,

$$v_2(r) \underset{r\to\infty}{\sim} -q/r^3 .$$

With the parameters described above, the resulting cross sections are globally converged to better than 3% in all symmetries reported. In e-N_2 scattering, as in e-CO_2 collisions, adding the HFEGE potential to the static term does not markedly alter the convergence properties of the calculations.

A. Static-model-exchange results

We shall first consider cross sections calculated in a static-exchange (SE) approximation, in which induced polarization effects are ignored, using the HFEGE and AAFEGE model exchange potentials. The $\lambda = 0$ expansion coefficients of the electron-molecule interaction potential at $k^2 = 0.1$ Ry for these two SE potential energies are compared with the static contribution to $v_0(r)$ in Fig. 4 (solid curves). Also shown for comparison is the static $v_2(r)$ coefficient (dotted curve).

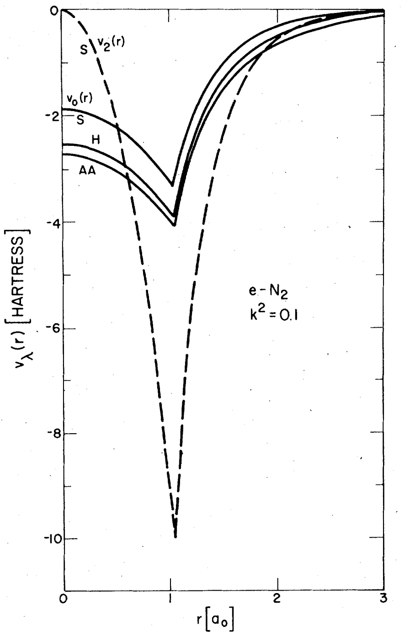

FIG. 4. Spherical components $v_0(r)$ of the static potential energy S and static-exchange potential energies using the HFEGE and AAFEGE potentials for e-N_2 collisions (solid curves). The FEG exchange potentials were calculated with $k^2 = 0.1$ Ry, $I(H) = 1.146$ Ry, and $I(AA) = 0.0$. Also shown for comparison (dashed curve) is the $\lambda = 2$ expansion coefficient of the static potential energy [cf., Eq. (2.17)]. [When the $\lambda = 2$ components of the HFEGE and AAFEGE potentials are added to $v_2^{st}(r)$ the resulting curve does not differ sufficiently from $v_2^{st}(r)$ to be included in this figure.]

In Figs. 5(a) and 5(b) and in Table II are shown partial integrated SE e-N_2 sections for Σ_g, Σ_u, Π_g, and Π_u symmetries for scattering energies from 0.01 to 1.0 Ry. Clearly, the results obtained

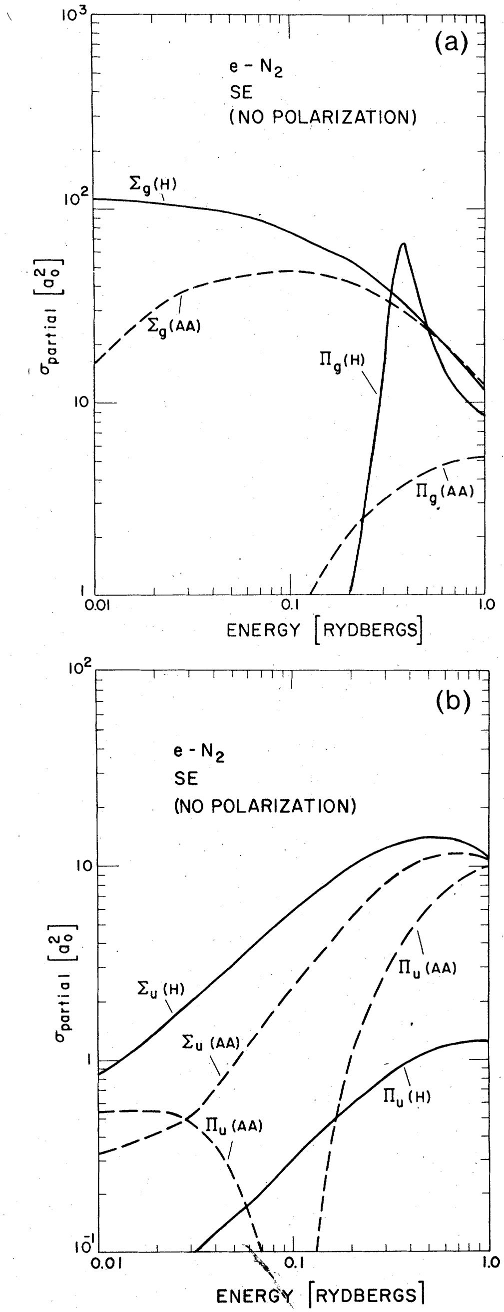

FIG. 5. Partial cross sections an Σ_g, Π_g (a), and Σ_u, Π_u (b) symmetries for e-N_2 scattering using model static-exchange potentials (no polarization). The HFEGE and AAFEGE potentials were calculated at each scattering energy using $I(H) = 1.146$ Ry and $I(AA) = 0.0$, respectively.

TABLE II. Partial integrated cross sections (in a_0^2) for e-N_2 scattering at selected impact energies E for the SE-HFEGE model.

E (Ry)	Σ_g	Π_g	Σ_u	Π_u
0.01	112.441	0.020	0.858	0.060
0.04	98.190	0.015	2.531	0.279
0.10	76.821	0.019	5.983	2.132
0.20	54.195	0.845	10.179	5.572
0.30	40.400	13.886	12.530	8.157
0.40	31.374	61.563	13.663	9.905
0.50	25.158	26.435	14.039	11.037
0.70	17.425	12.373	13.584	12.144
1.00	11.527	8.584	11.786	12.373

using the AAFEGE are radically different in all symmetries from those obtained using the HFEGE. The Π_g resonance, which does not appear at all in the AAFEGE calculations in this energy range,[86] peaks at about 5.42 eV in the HFEGE calculations. In these latter calculations, we verify that it is essentially a d-wave resonance. It is interesting to note that this energy is very near the resonance energy of 5.41 eV obtained by Morrison and Schneider[33] in their *ab initio* study of e-N_2 scattering using the R-matrix method, which, though formally quite different from the theory of Sec. II A, does treat exchange rigorously. This resonance is also seen in the results of Buckley and Burke at an energy of 5.44 eV. The results of Fig. 5 suggest that for the e-N_2 system, the AAFEGE potential is much too strong and the unoccupied $1\pi_g$ orbital of N_2 may be bound in the resulting interaction potential.

B. Static-model-exchange-polarization results

The induced polarization of the target molecule by the electric field of the scattering electron has long been known to have a considerable effect on cross sections for low-energy electron-molecule scattering.[3,6,7] In order to facilitate a meaningful assessment of the usefulness of the FEG exchange potentials under consideration, to enable comparison with measured cross sections and results of other theoretical calculations, and to further study the effects of the AAFEGE potential in this problem, a series of calculations were performed using the semiempirical adiabatic polarization potential described in Sec. IV A [Eqs. (4.3) and (4.4)] with[87] $\alpha_0 = 11.89 a_0^3$ and $\alpha_2 = 4.19 a_0^3$. Results of these model static-exchange polarization calculations will be labeled SEP.

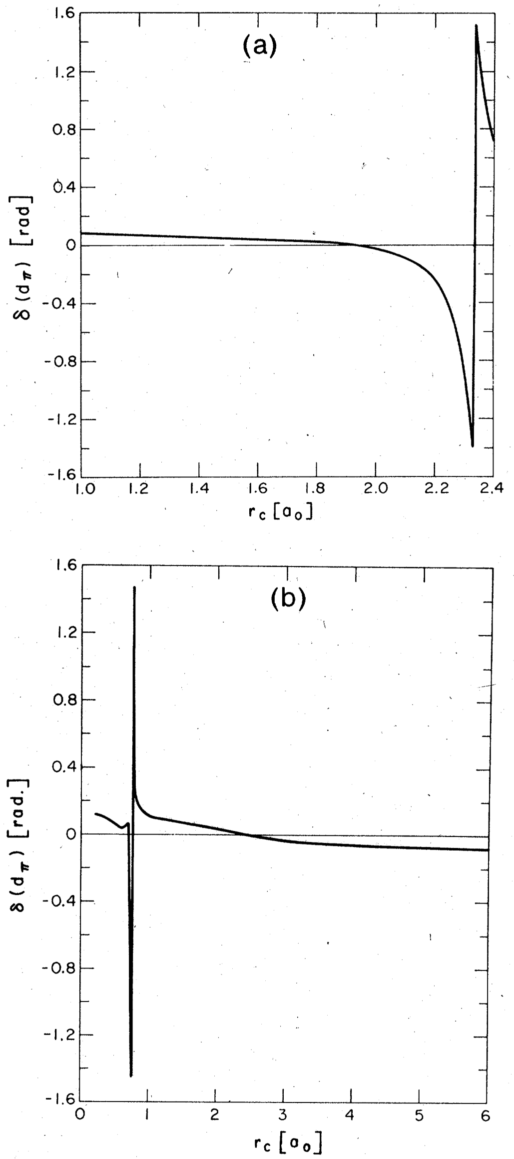

FIG. 6. Resonance tuning in e-N_2 collisions. The d_π eigenphase are shown as a function of the cutoff radius r_c in Eq. (4.4) at a scattering energy of 2.39 eV for model static-exchange-polarization calculations using the HFEGE (a) and AAFEGE (b) potentials. The optimum values of the parameter r_c as determined by these calculations are $r_c(H) = 2.341 a_0$ and $r_c(AA) = 0.753 a_0$.

In order to determine the cutoff radius r_c in Eq. (4.4), we varied this parameter, calculating Π_g cross sections and eigenphases for each choice of r_c until a value was found for which the d_π wave Π_g resonance peaked at the experimentally determined energy of 2.39 eV. In Figs. 6(a) and 6(b), the d_π eigenphase are shown as functions of r_c (modulo π) for the HFEGE and AAFEGE studies, respectively. This analysis produced cutoff radii of $2.341 a_0$ for the HFEGE model system and $0.753 a_0$ for the AAFEGE case. The former value

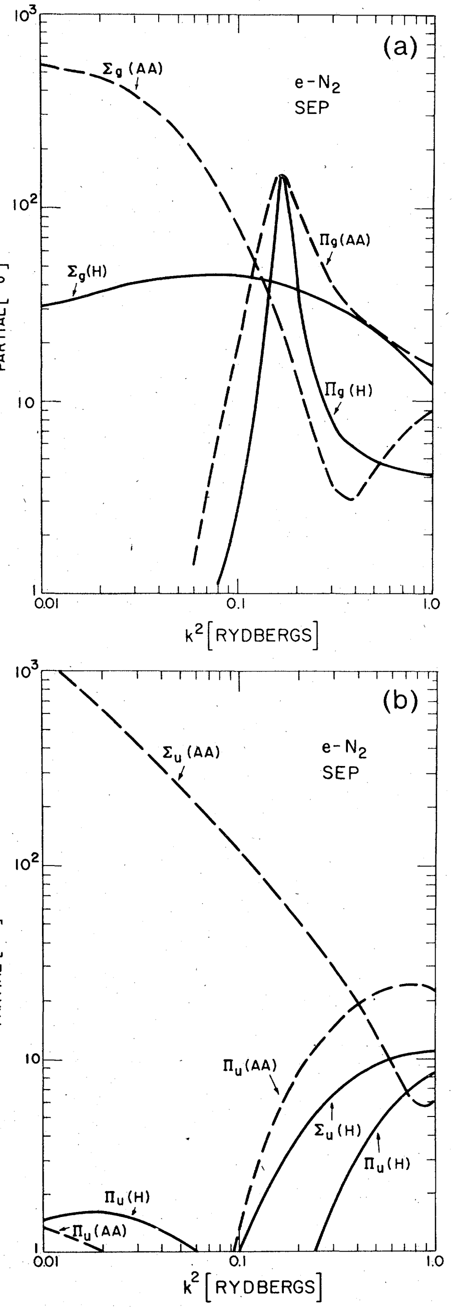

FIG. 7. Partial cross sections in Σ_g, Π_g (a) and Σ_u, Π_u (b) symmetries for e-N_2 scattering in model static-exchange-polarization calculations using the HFEGE and AAFEGE potentials. The potential and convergence criteria used in these calculations are described in the text (Sec. IV B).

lies well outside the principal concentration of electronic charge of the molecule[81] and far from the nuclear centers and therefore seems physically quite reasonable. We note that in their static-exchange calculations, which treat the polarization part of the interaction potential in the same way, Buckley and Burke determined a cutoff radius $r_c = 2.308\,a_0$. However, the cutoff radius of $0.753\,a_0$, which was required to position a Π_g resonance at 2.39 eV in the AAFEGE model system, is physically unreasonable. This value is well within the molecular-charge cloud and the nuclei; it will give rise to a *very* strong attractive polarization potential in this region.

In order to verify that $0.753\,a_0$ is indeed the appropriate cutoff radius for the AAFEGE model system, tuning calculations were carried out for values of r_c from $0.2\,a_0$ to $6.0\,a_0$, by which point polarization ceases to be an effective part of the electron-molecule interaction potential and the eigenphases approach their static-model exchange counterparts calculated without polarization (Sec. V A). A very fine mesh was used in varying r_c, $0.01\,a_0$ for most of the range of values studied, $0.001\,a_0$ from $0.74\,a_0$ to $0.80\,a_0$. No hint of another resonance was seen, and we must conclude that $0.753\,a_0$ is the correct cutoff radius for this model.

Partial cross sections for scattering in Σ_g, Π_g, Σ_u, and Π_u symmetries are shown in Figs. 7(a) and 7(b) for the HFEGE and the AAFEGE calculations. There is virtually no similarily between the two sets of results, with the possible exception of those for the Π_g symmetry, where we forced the cross sections to behave similarly near 2.4 eV, and for the Π_u symmetry. In any case, the lowest-order partial wave contributing to the scattering in Π_g or Π_u symmetries is $l = 1$, which does not "feel" the full effect of the short-range interaction potential because of the presence of the repulsive centrifugal barrier $l\,(l+1)/r^2$ in the effective potential energy [cf. Eq. (2.15)].

These results reinforce the conjecture propounded in Sec. IV A that for low-energy e-N_2 collisions, the AAFEGE potential is too strong, so much so that it binds the unoccupied $1\pi_g$ N_2 orbital, which *should* give rise to the Π_g resonance in the SE calculations. Therefore, in order to induce such a resonance in the SEP calculation, we require a polarization potential strong enough to pull the $2\pi_g$ unoccupied orbital near to zero energy. It is certainly true that the local momemtum $\kappa(\vec{r})$ in the HFEGE potential approaches $[2(E_{\rm inc}+I)]^{1/2}$ as $r \to \infty$ rather than $(2E_{\rm inc})^{1/2}$. However, the effect of this is felt in the factor $F(\eta)$ in Eq. (3.5). Since this multiplies $k_F(\vec{r})$, which vanishes as $r \to \infty$, this apparent asymptotic inconsistency in the HFEGE potential appears not to affect the scattering at low impact energies. Although we did not tune the FEG potential in this case, the quality of the results suggests that this procedure is not necessary for this system. At

TABLE III. Partial and total integrated cross sections (in a_0^2) for e-N_2 scattering at selected impact energies E. The SEP-HFEGE model electron-molecule interaction potential was used as described in the text (Sec. IV B) with $I = 1.146$ Ry and $r_c = 2.341 a_0$. See also Fig. 8.

E (Ry)	Σ_g	Π_g	Δ_g	Σ_u	Π_u	Δ_u	σ_{tot}
0.01	28.072	0.015	0.147	0.021	1.473	0.066	29.733
0.02	34.074	0.039	0.209	0.018	1.610	0.009	35.959
0.04	39.394	0.144	0.318	0.077	1.275	0.016	41.226
0.06	41.359	0.387	0.427	0.252	0.804	0.024	43.253
0.08	41.887	0.944	0.539	0.539	0.423	0.032	44.364
0.10	41.674	2.307	0.654	0.913	0.176	0.040	45.766
0.16	39.192	77.165	1.053	2.037	0.114	0.066	119.898
0.18	38.129	131.698	1.200	2.804	0.252	0.076	174.158
0.20	37.031	56.218	1.355	3.299	0.440	0.086	98.429
0.30	31.704	9.561	2.231	5.558	1.756	0.142	50.952
0.40	27.146	6.240	3.219	7.300	3.187	0.211	47.303
0.50	23.396	5.261	4.224	8.540	4.473	0.294	46.189
0.60	20.326	4.832	5.151	9.378	5.567	0.303	45.648
0.70	17.808	4.603	5.932	9.918	6.485	0.507	45.254
0.80	15.734	4.464	6.537	10.249	7.259	0.636	44.880
0.90	14.020	4.374	6.962	10.448	7.921	0.778	45.504
1.00	12.598	4.312	7.227	10.581	8.496	0.931	44.144

this point in our study, the AAFEGE potential was abandoned.

There remains to evaluate the results obtained using the HFEGE potential, a representative sample of which are presented in Table III. Total integrated cross sections calculated in the SEP approximation with $r_c = 2.341 a_0$ using the HFEGE potential are shown as solid dots in Fig. 8, where they are compared with the measured cross sections of Golden[19] which were determined using a modified Ramsauer apparatus, and the theoretical results of Burke and Buckley and of Burke and Chandra. Partial cross sections for Σ_g, Σ_u, Π_g, Π_u, Δ_g, and Δ_u symmetries were included in our SEP-HFEGE calculations, the contribution to the cross sections of higher symmetries being negligible in the energy range under consideration. Notice that for impact energies below about 8 eV, the major contribution to the total cross section comes from the Σ_g partial cross section.

All of the theoretical cross sections are much too large for energies near the 2.4 eV Π_g resonance owing to the neglect of vibrational motion of the nuclei in the calculations. (This problem has been studied by Chandra and Temkin.[53]) The width of the resonance in the SEP-HFEGE model is about 0.48 eV. The very close agreement of our results with those of Burke and Chandra is especially interesting since they used a completely different procedure of including exchange effects, namely, the orthogonalization procedure mentioned in Sec. I. Our SEP-HFEGE momentum-transfer cross sections calculated with (SEP) and without (SE) polarization are shown in Fig. 9, where they are compared with the measured results of Englehardt *et al.*,[88] obtained from analysis of swarm data. The inclusion of polarization brings the theoretical low-energy momentum-

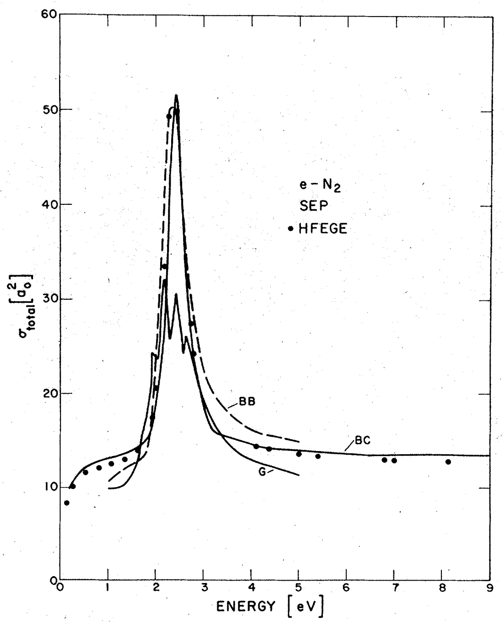

FIG. 8 Total integrated cross sections for e-N_2 collisions. The converged SEP results using the HFEGE potential are shown as solid dots. Cross sections for Σ_g, Σ_u, Π_g, Π_u, Δ_g, and Δ_u symmetries were included in σ_{tot}. Also shown are the measured cross sections of golden (Ref. 19) and the theoretical curves of Burke and Buckley (dashed curve) (Ref. 17) and Burke and Chandra (Ref. 9).

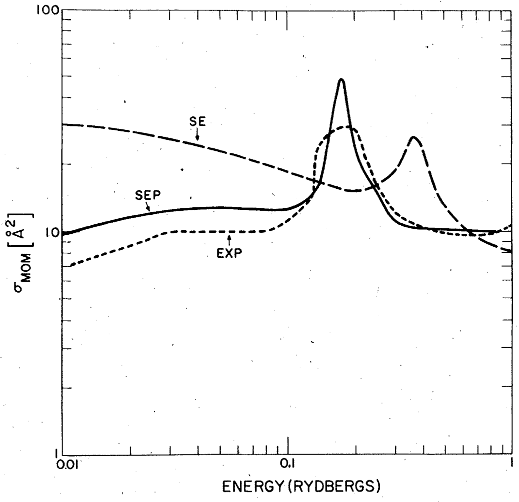

FIG. 9. Momentum-transfer cross sections for e-N_2 scattering. Results of model static-exchange (SE—dashed curve) and static-exchange polarization (SEP—solid curve) calculations are shown. In these calculations the HFEGE potential was used as described in the text and T-matrix elements for Σ_g, Σ_u, Π_g, Π_u, Δ_g, and Δ_u symmetries were included. The dotted curve shows the experimental results of Englehardt *et al.* (Ref. 88).

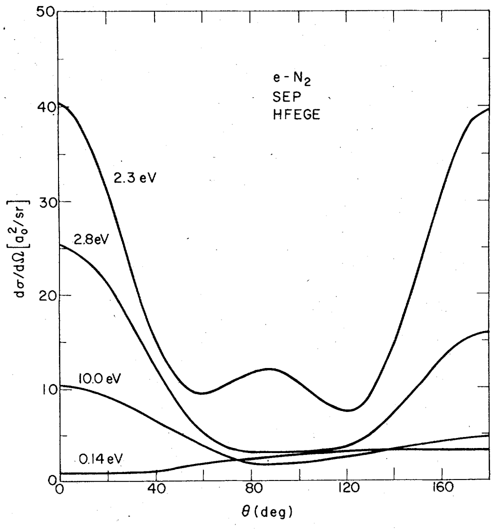

FIG. 10. Differential cross sections for e-N_2 scattering at selected energies calculated with a model SEP potential. The HFEGE potential was used as described in the text, and T-matrix elements corresponding to Σ_g, Σ_u, Π_g, Π_u, Δ_g, and Δ_u symmetries were included in the calculation of $d\sigma/d\Omega$. The polarization cutoff radius used was $r_c = 2.341 a_0$.

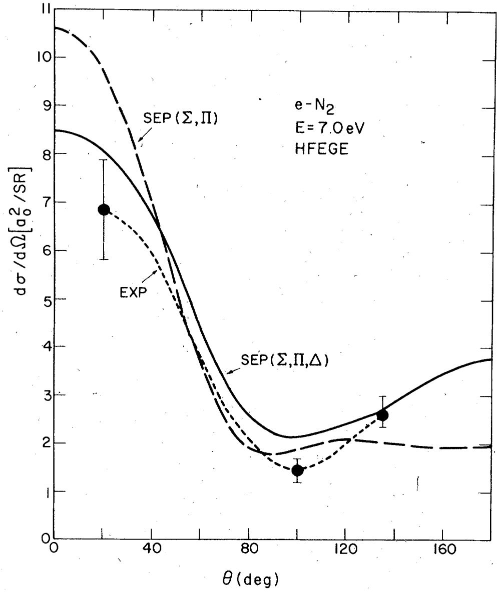

FIG. 11. Theoretical differential cross sections for e-N_2 scattering at an impact energy of 7.0 eV in the SEP-HFEGE model. The solid curve shows results calculating using Σ_g, Σ_u, Π_g, Π_u, Δ_g, Δ_g, and Δ_u symmetries, the dashed curve those with Σ and Π symmetries only. The experimental results (dotted curve) are the absolute cross sections Srivastava *et al.* (Ref. 89). Similar agreement between theory and experiment were obtained at 5.0 and 10.0 eV (Ref. 91).

transfer cross sections into much better qualitative agreement with experimental results.

Differential cross sections are a notoriously sensitive test of the validity of any model-scattering calculation as well as a very difficult quantity to measure for low-energy collisions. In Fig. 10, we illustrate the general behavior of $d\sigma/d\Omega$ for e-N_2 scattering at several representative energies for the SEP-HFEGE model. We note the d-wave character [$P_2(\cos\theta)$] of $d\sigma/d\Omega$ at 2.3 eV, in the vicinity of the Π_g resonance.

Recently, Srivastava *et al.*[89] reported absolute values of the differential cross sections for electron impact energies from 5.0 to 75.0 eV and for an angular range from 20 to 135°. These results were obtained in a crossed-beam experiment in which the ratio of the differential cross section for e-N_2 scattering to that for e-He scattering was measured at each impact energy. The results for e-N_2 scattering were determined by multiplying this ratio by the absolute e-He cross sections of McConkey and Preston.[90] We have compared our SEP-HFEGE results with the experimental differential cross sections at impact energies of 5.0, 7.0, and 10.0 eV. The results at 7.0 eV are illustrative of all these comparisons and are shown in Fig. 11 (solid curve). The error bars on the experimental (dotted) curve in this figure are taken from the paper by Srivastava *et al.* Agreement of theory and experiment is quite reasonable except at angles below about 45°, where the theoretical differential cross section rises above the experimental result. It is interesting to note the effect of the inclusion of T-matrix elements corresponding to Δ symmetry in these calculations; the dashed curve in Fig. 11 was calculated with only Σ and Π symmetries and compares much less favorably with experiment. It also contains a spurious bump at $\theta \simeq 120°$. (For scattering energies below about 2.0 eV, however, the Δ-symmetry contributions are negligible.) The theoretical total- and momentum-transfer cross sections[91] at 7.0 eV are $\sigma_{\text{tot}} = 11.596$ Å^2 and $\sigma_{\text{mom}} = 7.965$ Å^2. The corresponding measured results are $\sigma_{\text{tot}} = 11.0 \pm 2.0$ Å^2 and $\sigma_{\text{mom}} = 8.8 \pm 1.8$ Å^2.

We have also calculated rotational-excitation cross sections for e-N_2 collisions in the SEP-HFEGE model. The results agree with those obtained in other theoretical studies[9,17] about as well as our total cross sections (cf. Fig. 8).

The results of this section indicate that the HFEGE potential is quite appropriate for e-N_2 collisions, producing results comparable to those of rigorous static-exchange methods.

VI. CONCLUSIONS

In this paper, we have summarized the derivation of the body-frame static-exchange equations for electron-molecule scattering, Eqs. (2.9), and their radial counterparts, Eq. (2.15), and shown how the exact treatment of exchange is modified by making a free-electron-gas approximation for the target and the Born approximation for the scattering electron. Making some reasonable modifications to the resulting approximate exchange potential leads to the HFEGE potential, defined in Eqs. (3.5)–(13). Using this potential in calculating cross sections for e-N_2 collisions yields results in good agreement with those of other theoretical treatments and (off resonance) with experimental cross sections. For e-H_2 collisions, the agreement between model static-exchange and exact static-exchange cross sections was considerably improved by "tuning" the FEG exchange potential. This procedure appears not to be necessary for collisions with many-electron molecules. The FEG model is based on a statistical treatment of the molecular electrons and therefore probably gives a better representation of exchange effects for systems with large numbers of electrons.

The present successful applications of the free-electron-gas exchange potential derived in Sec. III to e-H_2 and e-N_2 scattering, taken together with an earlier analogous treatment of e-CO_2 scattering[48] and the work of others on electron-atom collisions,[39-41] augers well for the use of such model potentials in low-energy electron-molecule collision studies. Although certainly highly approximate, such exchange potentials appear to reliably mock the effects of exchange on the scattering event. In particular, the HFEGE potential seems most appropriate for such problems, particularly if the target molecule has many electrons.

It is precisely in the treatment of low-energy electron collisions with many-electron molecules that some form of approximate *local* treatment of exchange is desirable, since the computer time required for an exact solution of the problem rapidly becomes prohibitive as the number of electrons is increased. In contrast, aside from the calculation of the FEG exchange potential, the solution of the scattering problem in the SEP-HFEGE model requires no more computer time than does the solution of the problem in the static approximation, since the convergence behavior (and other numerical features) of the solution are not markedly affected by inclusion of the HFEGE potential.

It is clear from the form of the FEG exchange potential, that in this approximation, exchange is treated as an attractive interaction [cf. Figs. 1 and 4]. In deriving the coupled integro-differential scattering equation (2.15), we implicitly imposed a constraint on the continuum function in using the orthogonality of the scattering orbital to bound molecular orbitals of the same symmetry [cf., Eq. (2.8)]. Therefore, for closed-shell systems, the orbitals one obtains by solving Eqs. (2.15) exactly *are* appropriately orthogonal, and no further orthogonalization need be enforced. However, we do not know at present to what extent replacing the Hartree-Fock exchange potential by an approximate exchange potential affects this conclusion. It may be that our results would be improved by explicitly orthogonalizing in addition to using the model potential. Riley and Truhlar[40] have studied this question in the context of electron collisions with open-shell atoms (e-H).

Hopefully, the use of FEG or other model exchange potentials in conjunction with procedures for solving the collision problem like the one used in these studies will facilitate theoretical examination of a large number of electron-molecule systems that have heretofore been numerically intractable. Moreover, such model potentials may prove illuminating in understanding the physical nature of the quantum-mechanical exchange interaction in electron-molecule collisions.

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