Ab initio optical potentials applied to low-energy e-H$_2$ and e-N$_2$ collisions in the linear-algebraic approach

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We propose a method for constructing an effective optical potential through which correlation effects can be introduced into the electron-molecule scattering formulation. The optical potential is based on a nonperturbative, Feshbach projection-operator procedure and is evaluated on an L^2 basis. The optical potential is incorporated into the scattering equations by means of a separable expansion, and the resulting scattering equations are solved by a linear-algebraic method based on the integral-equation formulation. We report the results of scattering calculations, which include polarization effects, for low-energy e-H$_2$ and e-N$_2$ collisions. The agreement with other theoretical and with experimental results is quite good.

I. INTRODUCTION

The interactions that characterize elastic, low-energy electron-molecule collisions are traditionally divided into three categories: (1) static, (2) exchange, and (3) polarization (or correlation). The static potential, which is simply the average of the electrostatic electron-molecule interactions over the ground state of the target molecule, has been an integral part of all scattering calculations since the earliest endeavors some 50 years ago.[1] Despite its strength, the static potential alone is not sufficient to give an accurate representation of low-energy scattering.[2] This shortcoming can be overcome by introducing exchange effects, which arise from the constraint that the total system wave function be antisymmetric with respect to electron-pair interchanges. This constraint introduces into the scattering equations nonlocal terms involving integrals of the continuum and undistorted bound orbitals. The nonlocal nature of exchange greatly complicates the solution of the scattering equations and necessitates the introduction of special numerical techniques, not required for handling the local static potentials, in order to treat the exchange exactly. Although the exact treatments of exchange were first performed almost 15 years ago,[3] we have only recently been able to extend this treatment routinely to small and intermediate-sized molecules. The methods for the exact treatment of exchange are quite diverse and include noniterative[4-7] and iterative[8] close coupling, R-matrix,[9] T-matrix,[10] and Kohn[11] and Schwinger[12] variational methods.

The past few years have also witnessed a complementary development[13] in the area of modeling the exchange effects so that an accurate, local model exchange potential can now be constructed for rather large molecular systems. Thus, a wide variety of molecular systems can now be treated at the static-exchange (SE) level. Despite the better representation of the scattering process provided by the SE formulation, the picture remains incomplete without some consideration of polarization effects.

Polarization effects must be included to complete the description of the scattering process in order to obtain better agreement with the experiments[6,13,14] and to better specify resonant widths and positions.[5(a),6,13,14] These polarization or correlation effects arise from the response or distortion of the target electronic system to the incident electron and, as such, require consideration of the interaction of electronic configurations other than the ground state.[15] This multiconfigurational nature of polarization implies that even with the most sophisticated modern computers and numerical methods, the effect can only be handled in an approximate fashion.

Before proceeding with a description of our own method, we briefly review some of the more common treatments of polarization. Our enumeration is by no means exhaustive, and the interested reader is referred to several recent reviews[16] for a more comprehensive exposition. One of the simplest and most popular forms employed to model these correlation effects is the cutoff, asymptotic polarization potential.[6,13,17] The asymptotic expression depends only on the polarizabilities of the molecule and exhibits an inverse quartic dependence (r^{-4}) on the radial coordinate of the electron. At small distances, this expression is scaled by a radial function which forces the potential to zero at the molecular center.

This radial scaling is usually effectuated by a single parameter or cutoff radius which is selected on the basis of some physical property of the system (e.g., molecular size) or in order to place some prominent feature in the scattering (e.g., a resonance) at its experimentally determined position. The short-range adiabatic and nonadiabatic or dynamic effects are mocked by the departure of this model potential from its pure asymptotic form and are thus represented by the choice of the cutoff radius. This simplicity provides the chief advantage of this prescription; it also characterizes the major drawback—that the form is not flexible enough to describe the complicated nature of the polarization interaction. A somewhat better approximation can be obtained by calculating the effective adiabatic polarization potential.[18] This procedure accounts for the distortion of the target molecule by the field of an electron fixed at a given position in space. This procedure does not provide a very good representation of the polarization effects once the electron penetrates the molecular charge cloud. At this juncture, the strong short-range potential accelerates the electron from its asymptotic velocity. Thus, dynamic effects must be included to properly represent the interaction in this region. A popular procedure for reducing the constraints imposed by the adiabatic technique at short range is to "cut off" the interaction between the bound and continuum electrons once the scattering electron is within the charge cloud.[19,20] This truncation procedure provides an approximate representation of the nonadiabatic effects and is the basis of the polarized-orbital method.[21] In addition, other models, designed to correct the adiabatic potential and based on semiclassical arguments, have been developed.[22] The problem with all of these nonpenetrating approaches is the difficulty in systematically assessing the accuracy of this representation of the nonadiabatic terms. A rather different approach has been taken by Klonover and Kaldor,[23] who introduce polarization effects into the elastic-scattering equations through an optical potential. The optical potential which contains all virtual excitation of the target system is evaluated on an L^2 basis through perturbation theory. The perturbative approach allows for the systematic improvement of the potential; however, to date, only second-order corrections have been determined. While this procedure appears to work quite well for e-H_2 scattering, it remains to be seen whether second-order effects are sufficient to describe the polarization for larger molecular systems. In addition, the size of the basis set may become prohibitive for more extended molecules. We should note that the close-coupling method also provides an approximate representation of the polariza-

tion effects through the inclusion of energetically closed electronic states in the wave-function expansion.[15] This expansion can sometimes converge quite slowly,[4(d),5(b),15] thus making the evaluation of the polarization contributions rather time consuming. One procedure for greatly reducing the number of closed states that must be retained in the close-coupling (CC) expansion is to introduce pseudostates. In this case a few basis functions are selected to mock the effects of the infinite CC sum. There are a variety of methods for determining these states; one involves forcing them to correctly produce the polarizability of the molecule. This approach has been particularly successful when combined with the R-matrix method.[24]

In the remainder of the paper, we describe a new approach for introducing polarization effects in electron-molecule collisional calculations. We base the approach on the optical-potential formulation.[25] The optical potential is extracted directly from bound-state self-consistent-field (SCF) and configuration-interaction (CI) calculations with no resort to perturbative expansions[4(b)] and is incorporated into a linear-algebraic method[4] through a sum of separable terms in much the same manner as the exchange terms.[4(a),4(c)] The linear-algebraic approach has been shown to be quite effective and efficient in handling the nonlocal terms that arise in static-exchange (SE) potential calculations.[4] A preliminary report on the optical-potential method which includes an application to low-energy e-H_2 scattering appears elswhere.[4(b)] The present calculations incorporate several improvements over this earlier endeavor. First, we have made a more systematic study of the adequacy of our basis sets and discovered that at very low energies (<1 eV) more diffuse basis functions are required. Second, a more realistic attempt is made to represent the polarization effects by employing pseudostates based on a coupled Hartree-Fock method.[24] This procedure allows us to incorporate the full static polarizability of the molecule with minimal computational effort.

In Secs. II and III we develop the theoretical and computational techniques required to describe the optical potential and collisional physics. The final section is devoted to a discussion of the results for e-H_2 and e-N_2 scattering and to a comparison with calculations and experiments.

II. THEORY

The Schrödinger equation for an electron incident on an N-electron molecule can be written as

$$\left[H_T + T_e + V_{en} + \sum_{i=1}^{N} g_{ie} - E \right] |\psi\rangle = 0 , \qquad (1a)$$

where H_T represents the Hamiltonian of the molecule

$$T_e = -\tfrac{1}{2}\nabla_e^2 , \tag{1b}$$

$$V_{en} = -\sum_\alpha \frac{Z_\alpha}{|\vec{r}_e - \vec{r}_\alpha|} , \tag{1c}$$

$$g_{ie} = \frac{1}{|\vec{r}_i - \vec{r}_e|} , \tag{1d}$$

where $\vec{r}_e$ ($\vec{r}_i$) is the position vector of the incident (target) electron and Z_α ($\vec{r}_\alpha$) the charge (position) of nucleus α. We now divide configuration space into two regions bounded by a sphere of radius $r = a$. In the internal region it is necessary to treat electron exchange and correlation between the incident and target particles to full accuracy. Outside the R-matrix sphere the incident electron is subject to simple electrostatic forces which are purely local in character. Since the scattered electron is essentially distinguishable from the target electrons in the outer region, the dynamical problem can be reduced to the solution of a set of coupled differential equations for $r \geq a$. The coupling terms are the long-range direct and transition moments of the target wave functions retained in the expansion of the scattering wave function.

In order to solve the Schrödinger equation in the internal region we add and subtract an operator of the form

$$L_b = \tfrac{1}{2}\sum_c |\phi_c\rangle\delta(r-a)\left[\frac{\partial}{\partial r} - b\right]\langle\phi_c| \tag{2}$$

to Eq. (1a). This operator, first introduced by Bloch,[26] has the effect when added to the Hamiltonian of converting our internal Schrödinger equation to Hermitian form. The wave functions $|\phi_c\rangle$ are the channel wave functions of the molecule and the operator L_b provides the link between the internal and external wave function. Consequently, we arrive at the equation

$$\left[H_T + T_e + V_{en} + \sum_{i=1}^N g_{ie} + L_b - E\right]|\psi\rangle = L_b|\psi\rangle \tag{3}$$

for the wave function inside the R-matrix sphere. To simplify the notation in what follows we define the operator

$$K = H_T + T_e + V_{en} + \sum_{i=1}^N g_{ie} + L_b \tag{4}$$

and rewrite Eq. (3) as

$$(K - E)|\psi\rangle = L_b|\psi\rangle . \tag{5}$$

The scattering wave function is now expanded as

$$\psi = \sum_{c=1}^m \mathscr{A}[\phi_c(1, \ldots, N)F_c(N+1)]$$

$$+ \sum_q C_q \psi_q(1, \ldots, N+1) , \tag{6}$$

where $\phi_c(1, \ldots, N)$ is the antisymmetrized channel wave function, $F_c(r)$ is the wave function for the scattered electron, and the symbol $\mathscr{A}$ represents the antisymmetrization operator. The additional set of functions $\psi_q(1, \ldots, N+1)$ is needed to ensure that the wave function is expanded in a complete set. The details of how the ϕ_c and ψ_q are constructed will be presented in Sec. III. Here it is only important to recognize that the expansion implies a division of Hilbert space into two components. We may therefore define two projection operators P and Q having the properties[25]

$$P + Q = I , \tag{7a}$$

$$P\chi = \sum_{c=1}^m \mathscr{A}[\phi_c(1, \ldots, N)\chi_c(N+1)] , \tag{7b}$$

$$Q\chi = \sum_q d_q \psi_q(1, \ldots, N+1) , \tag{7c}$$

where $|\chi\rangle$ is an arbitrary $(N+1)$-electron wave function. In addition, we require that the $\psi_q(1, \ldots, N+1)$ satisfy the condition

$$L_b|\psi_q\rangle = 0 . \tag{7d}$$

Thus all asymptotically important information about the scattered electron is contained in the P-space part of the wave function. We may derive an equation for the P-space component of the wave function by projecting Eq. (5) onto P:

$$(K_{PP} - E)P|\psi\rangle + K_{PQ}Q|\psi\rangle = L_b P|\psi\rangle . \tag{8a}$$

Using

$$(K_{QQ} - E)Q|\psi\rangle + K_{QP}P|\psi\rangle = 0 , \tag{8b}$$

$$Q|\psi\rangle = (E - K_{QQ})^{-1}K_{QP}P|\psi\rangle , \tag{8c}$$

we finally arrive at the desired result

$$(K_{PP} - E)P|\psi\rangle + K_{PQ}(E - K_{QQ})^{-1}K_{QP}P|\psi\rangle$$

$$= L_b P|\psi\rangle . \tag{9}$$

The second term on the left-hand side of Eq. (9) is the optical potential. It is a highly nonlocal, energy-dependent potential which accounts for the coupling of the P- and Q-space components of the wave function. However, in contrast to more standard treatments it is a Hermitian operator. This arises because Eq. (8) is defined using R-matrix boundary conditions within a sphere of radius $r \leq a$. An important consequence of this property is that it is

possible to use all of the powerful techniques developed for bound-state problems in finding suitable representations for this operator. This will be discussed in more detail in Sec. III. Equation (9) may be reduced to a set of coupled one-particle equations by multiplying by $\phi_c(1, \ldots, N)$ and integrating over the target coordinates. The derivation of these equations, while tedious, is quite straightforward and may be found in Ref. 27. Here we only state the results

$$(h_e - E_c)\,|\,F_c\,\rangle + \sum_{c'} U_{cc'}\,|\,F_{c'}\,\rangle$$

$$= L_b\,|\,F_c\,\rangle + \sum_c \lambda_q\,|\,\gamma_{cq}\,\rangle \ , \qquad (10a)$$

$$h_e = -\frac{1}{2}\frac{d^2}{dr^2} + \delta(r-a)\left[\frac{d}{dr}-b\right] \ , \qquad (10b)$$

$$L_b = \delta(r-a)\left[\frac{d}{dr}-b\right] \ , \qquad (10c)$$

$$|\,\gamma_{cq}\,\rangle = \langle\,\phi_c\,|\,\psi_q\,\rangle_{1,\ldots,N} \ , \qquad (10d)$$

where E_c are the channel energies and $U_{cc'}$ is taken to be the full electron-electron interaction potential including both local and nonlocal parts. The second term on the right-hand side contains the Lagrange multiplies λ_q needed to enforce orthogonality of the channel functions F_c to any bound-state orbitals used to construct the $\psi_q(1, \ldots, N+1)$. The radial parts of these bound-state orbitals are the γ_{cq} of Eq. (10d). The Lagrange multipliers are determined by enforcing the orthogonality at the end of the calculation. This condition is necessary to maintain the many-electron orthogonality of the P- and Q-space components of the total wave function. In actual calculations the number of these terms is quite limited, and they present no real computational problem.

Following our usual procedure, we now convert Eq. (10) to integral form

$$F_c(r) + \sum_{c'} \int G_c(r\,|\,r')U_{cc'}(r',r'',E)F_{c'}(r'')\,dr'\,dr'' = G_c(r\,|\,a)\left[\left[\frac{d}{dr}-b\right]F_c\right]_a$$

$$+ \sum_q \lambda_q \int G_c(r\,|\,r')\gamma_{cq}(r')\,dr' \ , \qquad (11)$$

where $G_c(r\,|\,r')$ is the unperturbed Green's function. The coupled equations (11) are the fundamental working equations of our approach. By introducing a suitable quadrature for the integrals, they may be converted to a set of linear-algebraic equations which may then be solved by standard techniques.[4]

III. COMPUTATIONAL AND NUMERICAL DETAILS

The solution of Eq. (11) requires a number of steps. In this section we shall consider these in some detail.

As is the case with any bound-state calculation, it is necessary to choose a one-particle basis set which is efficient for representing the many-particle wave functions of the problem. This question of appropriate basis sets is more difficult in the scattering problem for several reasons. First, low-energy scattering processes are dominated by exchange and polarization effects which require basis sets not needed for bound-state calculations. Second, if we are to find efficient techniques to represent the optical potential, it will be necessary to project parts of $U_{cc'}(r,r',E)$ onto a finite basis set. Although the type of basis function required for this projection has certain features in common with the usual

bound-state functions, it is often important to include more diffuse functions to better span the space of the channel functions. In order to accomplish these objectives we begin by choosing a primitive basis which includes the usual bound-state basis, augmented by more diffuse functions to represent the optical potential. Additional primitive functions are added to represent the polarization effects if they are not already present in the basis. The choice of these functions depends on what type of induced moment needs to be represented. If, for example, the target state was of Σ_g symmetry and the induced dipole was important to the problem it would be necessary to include moderately diffuse functions which gave good representation of the Σ_u and Π_u pseudostates of the molecule. By examining the orbital structure of the target it is straightforward to decide which symmetries would need to be included in the primitive basis. Having chosen an appropriate primitive set one performs a few SCF-type calculations to contract this basis to a physically meaningful form. Ground-state occupied orbitals are obtained from standard SCF or generalized—valence-bond (GVB) calculations[28] on the target. If electronic excitation is being considered, appropriate excited-state orbitals are constructed using the improved—virtual-orbital (IVO) procedure.[28] The

one-particle pseudostate orbitals are obtained using the coupled Hartree-Fock method.[29] In this approach the SCF equations are solved in the presence of an electric field. The field may be inserted into the SCF equations directly or by adding an additional nuclear charge placed at large distances from the molecule.[18] The coupled Hartree-Fock method is known to be useful for the calculation of the static polarizabilities of atoms and molecules, and it is this that makes it an excellent zeroth-order description of the pseudostates for low-energy electron scattering. Having chosen the one-particle basis set, the many-electron target and pseudostates $\phi_c(1, \ldots, N)$ and $\psi_q(1, \ldots, N+1)$ are constructed by diagonalizing the appropriate Hamiltonian in antisymmetrized products of the occupied, IVO, and pseudostate orbitals. The remaining part of the one-particle basis, which is needed for a complete description of the scattered electron, is excluded from this diagonalization. This is necessary in order to maintain the orthogonality of the many-particle wave functions. Thus we have the relations

$$\int \phi_c(1, \ldots, N)^* \phi_{c'}(1, \ldots, N) d\vec{r}_1 \cdots d\vec{r}_N = \delta_{cc'} \ ,$$

$$(12a)$$

$$\int \psi_q^*(1, \ldots, N+1)\psi_{q'}(1, \ldots, N+1)d\vec{r} \cdots d\vec{r}_{N+1}$$

$$= \delta_{qq'} \ , \qquad (12b)$$

$$\int \phi_c^*(1, \ldots, N)F_{c'}(1)d\vec{r}_1 = 0 \ , \qquad (12c)$$

$$\int \psi_q(1, \ldots, N+1)F_c(1)d\vec{r}_1 = 0 \ , \qquad (12d)$$

to ensure the orthonomality. The presence of the Lagrange multipliers in Eq. (11) is a consequence of the condition (12d) placed on F_c and it necessary to determine the λ_q so that the condition is satisfied.

A simple example, $^1\Sigma_g$ scattering in $e + H_2^+$, should clarify these points. In the SE approximation the wave function would be written as

$$\psi = \mathscr{A}(1\sigma_g F) + C\mathscr{A}(1\sigma_g^2) \ , \qquad (13a)$$

where

$$P|\Psi\rangle = \mathscr{A}(1\sigma_g F) \ , \qquad (13b)$$

$$Q|\Psi\rangle = \mathscr{A}(1\sigma_g^2) \ . \qquad (13c)$$

The effect of the single Q-space configuration would be folded into scattering calculation using the optical potential. In order to ensure the orthogonality of the scattering orbital F to the $1\sigma_g$ target function, a single nonzero Lagrange multiplier would appear on the right-hand side of Eq. (10a). This multiplier would be determined at the end of the calculation by enforcing the orthogonality condition on F. Since the $1\sigma_g^2$ configuration appears in the optical poten-

tial there is no loss of generality in requiring this orthogonality. The generalization of these ideas to a many-dimensional Q space is quite straightforward and adds little complexity to the above argument.

Perhaps the most difficult part of the scattering calculation involves the construction of the interaction potential $U_{cc'}(\vec{r},\vec{r}',E)$. Our approach is to divide this interaction into two parts

$$U_{cc'}(\vec{r},\vec{r}',E) = U_{cc'}^{(1)}(\vec{r},\vec{r}')\delta(\vec{r}-\vec{r}')$$

$$+ U_{cc'}^{(2)}(\vec{r},\vec{r}',E) \qquad (14)$$

and to use different methods for each of the parts. The calculation of the local energy-independent static potential may be accomplished by generalizing methods already developed for the SE problem.[4] To be more precise we have

$$U_{cc'}(\vec{r}_e) = \int \phi_c^*(\vec{r}_1, \ldots, \vec{r}_N) \left[V_{en} + \sum_{i=1}^{N} g_{ie} \right]$$

$$\times \phi_{c'}(\vec{r}_1, \ldots, \vec{r}_N)d\vec{r}_1 \cdots d\vec{r}_N$$

$$= V_{en}\delta_{cc'} + \int \rho_{cc'}(\vec{r}) \frac{1}{|\vec{r}-\vec{r}_e|} d\vec{r} \ , \qquad (15)$$

where $\rho_{cc'}(\vec{r})$ represents the transition density matrix. The transition density matrix may be extracted from bound-state CI codes.[28] These programs, which are used routinely to compute one-electron molecular properties and natural orbitals, provide a decomposition of $\rho_{cc'}(\vec{r})$ into the one-particle components of the basis. Thus we start with

$$\rho_{cc'}(\vec{r}) = \sum_{\alpha,\beta} \psi_\alpha(\vec{r})\gamma_{\alpha\beta}^{cc'}\psi_\beta(\vec{r}) \ , \qquad (16)$$

where $\gamma_{\alpha\beta}^{cc'}$ are the structure factors from the CI codes. It is a straightforward procedure to decompose the product of the two molecular orbitals into spherical harmonics. First, using codes already developed for the SE calculation,[4] we perform a Y_{Jm} decomposition of the individual orbitals. Then using Clebsch-Gordon algebra these are combined to give

$$\rho_{cc'}(\vec{r}) = \sum_{Jm} \rho_{cc'}^{Jm}(r)Y_{Jm}(\Omega) \qquad (17)$$

[with Ω being the solid angle (θ,ϕ)], which when inserted into (15) provides a single-center decomposition of the interaction potential.

The techniques used to treat the nonlocal energy-dependent potential $U_{cc'}^{(2)}(\vec{r},\vec{r}',E)$ are quite different. While it would certainly be possible to follow procedures similar to those used for the local interaction, the size of the Q space would make these

prohibitively expensive. Fortunately, the generally shorter-range character of this potential allows us to employ separable expansions of the form

$$U_{cc'}^{(2)}(\vec{r},\vec{r}',E)=\sum_\lambda \gamma_{c\lambda}^E(\vec{r})\lambda(E)\gamma_{c'\lambda}^E(\vec{r}') \tag{18}$$

with high efficiency. To accomplish this, we replace the P-space projector by

$$P=\sum_{c,a}|\,\mathscr{A}[\phi_c(1,\ldots,N)\mathscr{X}_a(N+1)]\rangle$$

$$\times\langle\mathscr{A}[\phi_c(1,\ldots,N)\mathscr{X}_a(N+1)]|\,, \tag{19}$$

where the $\mathscr{X}_a$ are sets of square integrable functions, orthogonal to all the orbitals used to construct the target states. Proceedings in this fashion we may use standard bound-state CI codes to construct a matrix representation of the Hamiltonian. By employing the partitioning techniques outlined earlier,

the Hamiltonian matrix may be transformed into the optical potential. This potential is then transformed to a diagonal representation

$$U^{(2)}=\sum_\lambda|\,\phi_\lambda^E(1,\ldots,N+1)\rangle$$

$$\times\lambda(E)\langle\phi_\lambda^E(1,\ldots,N+1)|\,, \tag{20}$$

where $\phi_\lambda(1,\ldots,N+1)$ and $\lambda(E)$ are the eigenfunctions and eigenvalues which diagonalize the optical potential. By projecting $U^{(2)}$ onto the channel functions $\phi_c(1,\ldots,N)$ we obtain Eq. (18) with

$$\gamma_{c\lambda}^E(r_{N+1})=\int\phi_c^*(1,\ldots,N)\phi_\lambda^E(1,\ldots,N+1)$$

$$\times d\vec{r}_1\cdots d\vec{r}_N\,. \tag{21}$$

When we insert the above developments into Eq. (11) we obtain

$$F_c(r)+\sum_{c'}\int G_c(r,r')U_{cc'}^{(1)}(r')F_{c'}(r')dr'+\sum_{c',\lambda}\int G_c(r\,|\,r')\gamma_{c\lambda}^E(r')\lambda(E)\gamma_{c'\lambda}^E(r'')F_{c'}(r'')dr'dr''$$

$$=G_c(r\,|\,a)\left[\left[\frac{\partial}{\partial r}-b\right]F_c\right]_a+\sum_q\int\lambda_q G_c(r\,|\,r')\gamma_{cq}(r')dr'\,, \tag{22a}$$

where c now refers to the complete channel index. We now define the functions

$$\mathscr{X}_{c\lambda}^E(r)=\int G_c(r\,|\,r')\gamma_{c\lambda}^E(r')dr'\,, \tag{22b}$$

$$\mathscr{X}_{cq}(r)=\int G_c(r\,|\,r')\gamma_{cq}(r')dr'\,, \tag{22c}$$

to get

$$F_c(r)+\sum_{c'}G_c(r\,|\,r')U_{cc'}^{(1)}(r')F_{c'}(r')dr'+\sum_{c'\lambda}\lambda(E)\mathscr{X}_{c\lambda}^E(r)\int\gamma_{c'\lambda}^E(r')F_{c'}(r')dr'$$

$$=G_c(r\,|\,a)\left[\left[\frac{\partial}{\partial r}-b\right]F_c\right]_a+\sum_q\lambda_q\mathscr{X}_{cq}(r)\,. \tag{23a}$$

An important point to be noticed about Eq. (23a) is the clean separation of the variables r and r' in the optical-potential term. This separation, which is a direct consequence of the use of matrix methods to form $U_{cc'}^2(\vec{r},\vec{r}',E)$, leads to important simplifications in the solution of Eq. (23a) by the linear-algebraic method (see also, Rescigno and Orel[30]). The approach we use depends on whether there are nonzero Lagrange multipliers in Eq. (23a). If there is no need to impose any orthogonality constraints on the channel functions it is quite straightforward to incorporate the effects of the optical potential directly into the definition of the matrix to be inverted. Another approach, which works for the both zero and nonzero Lagrange multipliers, is to define the

following homogeneous and particular solutions:

$$\sum_{c'}\int M_{cc'}(r\,|\,r')F_{c'\bar{c}}^a(r')=G_c(r\,|\,a)\delta_{c\bar{c}}\,, \tag{23b}$$

$$\sum_{c'}\int M_{cc'}(r\,|\,r')F_{c'\lambda}(r')=\mathscr{X}_{c\lambda}^E(r)\,, \tag{23c}$$

$$\sum_{c'}\int M_{cc'}(r\,|\,r')F_{c'q}(r')=\mathscr{X}_{cq}(r)\,, \tag{23d}$$

where

$$M_{cc'}(r\,|\,r')=\delta_{cc'}\delta(r-r')+G_c(r\,|\,r')U_{cc'}^{(1)}(r')\,. \tag{23e}$$

The solution for F_c can then be written as (b equal to zero)

$$F_c(r) = \sum_{c'} F_{cc'}^a(r) \frac{\partial F_{c'}}{\partial r}\bigg|_a + \sum_q \lambda_q F_{cq}(r)$$

$$- \sum_{\lambda c'} \lambda(E) F_{c\lambda}(r) A_{\lambda c'} , \tag{24a}$$

where

$$A_{\lambda c} = \int \gamma_{c\lambda}^E(r) F_c(r) dr . \tag{24b}$$

Let us define the following two vectors:

$$X_q = \lambda_q , \tag{25a}$$

$$X_\lambda = -\sum_{c'} A_{\lambda c'} , \tag{25b}$$

and rewrite Eq. (24a) as

$$F_c(r) = \sum_{c'} F_{cc'}^a(r) \frac{\partial F_{c'}}{\partial r}\bigg|_a + \sum_q X_q F_{cq}(r)$$

$$+ \sum_\lambda X_\lambda F_{c\lambda}(r) \lambda(E) . \tag{26}$$

The unknown vector components may be determined by solving the following set of algebraic equations:

$$\sum_{c'} b_{\lambda c'} \frac{\partial F_{c'}}{\partial r}\bigg|_a + \sum_q T_{\lambda q} X_q + \sum_{\lambda'} T_{\lambda\lambda'} X_{\lambda'} = 0 , \tag{27a}$$

$$\sum_{c'} b_{qc'} \frac{\partial F_{c'}}{\partial r}\bigg|_a + \sum_{q'} T_{qq'} X_q + \sum_\lambda T_{q\lambda} X_\lambda = 0 , \tag{27b}$$

where

$$b_{\lambda c'} = \sum_c \langle \gamma_{c\lambda}^E | F_{cc'}^a \rangle , \tag{28a}$$

$$b_{qc'} = \sum_c \langle \gamma_{cq} | F_{cc'}^a \rangle , \tag{28b}$$

$$T_{\lambda\lambda'} = \sum_c \langle \gamma_{c\lambda} | F_{c\lambda'}^E \rangle \lambda'(E) - \delta_{\lambda\lambda'} , \tag{28c}$$

$$T_{\lambda q} = \sum_c \langle \gamma_{c\lambda}^E | F_{cq} \rangle , \tag{28d}$$

$$T_{q\lambda} = \sum_c \langle \gamma_{cq} | F_{c\lambda} \rangle \lambda(E) , \tag{28e}$$

$$T_{qq'} = \sum_c \langle \gamma_{cq} | F_{cq'} \rangle . \tag{28f}$$

Equation (27b) is the condition for orthogonality of the channel functions to the orbitals used to construct the Q-space wave functions. The solutions of Eqs. (27) may be written as

$$X_\alpha = -\sum_{\beta,c} T_{\alpha\beta}^{-1} b_{\beta c} \frac{\partial F_c}{\partial r}\bigg|_a \tag{29a}$$

$$= \sum_c U_{ac} \frac{\partial F_c}{\partial r}\bigg|_a , \tag{29b}$$

where α can be either λ or q, and c labels the various linearly independent scattering solutions. Substituting Eqs. (29) into (26) and setting $r = a$ we obtain

$$F_c(a) = \sum_c R_{cc'} \frac{\partial F_{c'}}{\partial r}\bigg|_a , \tag{30a}$$

where

$$R_{cc'} = F_{cc'}^a(a) + \sum_q F_{cq}(a) U_{qc'}$$

$$+ \sum_\lambda F_{c\lambda}(a) U_{\lambda c'} \lambda(E) . \tag{30b}$$

This expression for the R matrix on the surface can be used as an initial condition for propagating the solution into the asymptotic region. Since all of the interaction outside the R-matrix surface is governed by local potentials, well-established techniques, such as the R-matrix propagation method of Light and Walker,[31] may be used for this last step. After propagating $R_{cc'}$ into the asymptotic region, a simple matching of logarithmic derivations gives the scattering information from which it possible to construct all of the cross sections.

TABLE I. Exponential coefficients of Gaussian-type orbitals for $e + H_2$ scattering and computed polarizabilities.

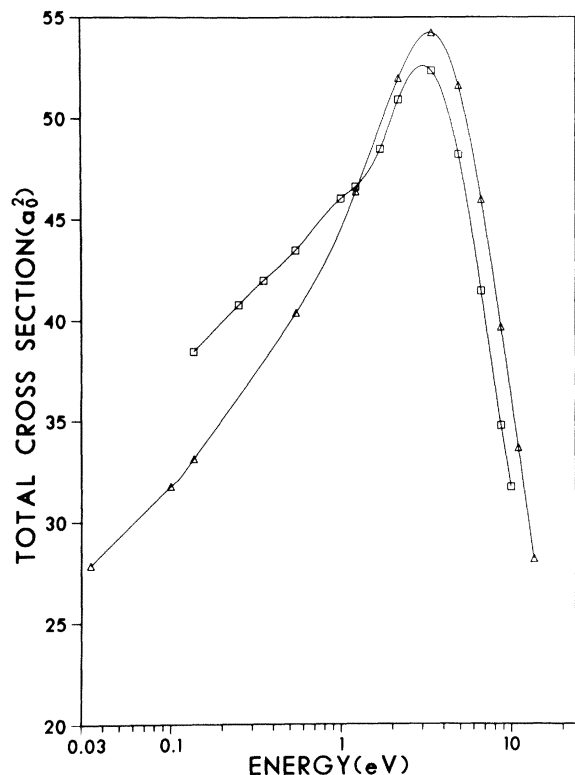| SCF space		Polarization space		Scattering space (All functions at midpoint)		Polarizability
s-type	P_x,P_y,P_z type	s-type	P_x,P_y,P_z type	s-type	P_x,P_y,P_z type	
48.4479	1.5	0.0725	0.25	0.018	0.0156	$\alpha_{||} = 6.39$
7.28346	0.5	0.03625	0.125	0.009	0.0078	$\alpha_\perp = 4.54$
1.65139			0.0625	0.0045	0.0039	
0.462447			0.0312			
0.1458850						

FIG. 1. Comparison of theoretical total cross sections for e-H_2 scattering obtaining with the effective optical-potential method. Curves are as follows: $\square$ represents the basis set of Ref. 4(b) and $\triangle$ represents the basis set of the present paper.

FIG. 2. Comparison of theoretical total cross section for e-H_2 scattering as a function of energy. Curves are as follows: (1) $\triangle$ represents the effective optical potential; (2) $\circ$ represents the generalized polarized orbital [Ref. 20(b)]; and (3) $\square$ represents the perturbative optical potential (Ref. 23).

IV. RESULTS

A. $e + H_2$

The scattering of electrons from H_2 has been extensively studied both theoretically and experimentally for many years. However, it has only been recently that full *ab initio* treatments which include both exchange and polarization have become available.[20,23,24] In order to give the theoretical developments presented in the previous section some concreteness, we list in Table I the atomic basis set used in our calculations. These orbitals have been divided into SCF, polarization, and scattering functions to give the reader some insight into how we represent the various physical effects mathematically. The computed perpendicular and parallel polarizabilities which result from the finite field SCF calculations also appear in the table. The CI calculation used to construct the optical potential contained 350 spin eigenfunctions. It was obtained by generating all
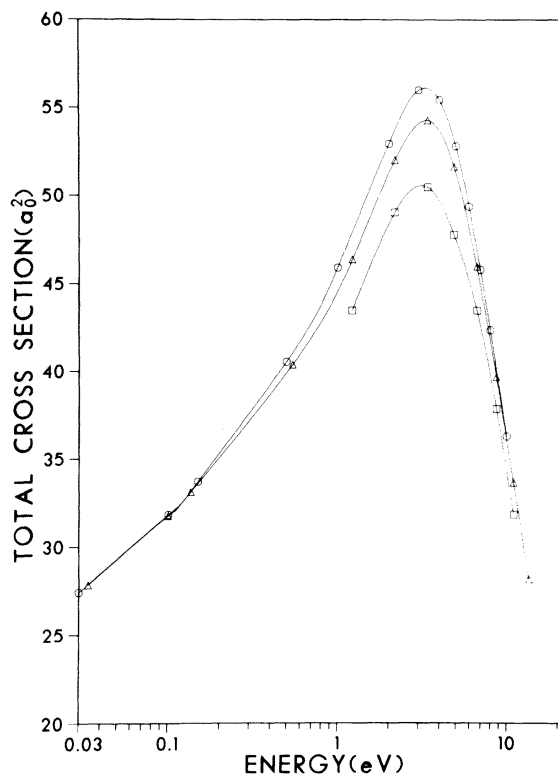
double excitations from the SE configurations containing no more than one electron in the molecular orbitals built from the scattering functions in Table I. In Fig. 1 we present the results of our current calculation compared with that of Ref. 4(b). The calculation contains contributions from $^2\Sigma_g$, $^2\Sigma_u$, $^2\Pi_u$, and $^2\Pi_g$ symmetries. The additional contribution due to higher M_L values has been estimated from other SE calculations and is completely unimportant except at the highest energies of the present paper. Even at these higher energies the contribution of these waves is much less than 5% of the total cross section. It is easily seen that the essential features of the cross section are the same in both calculations. However, there are noticeable differences in the two results below 1 eV. While both calculations decrease in magnitude, the rate of decrease is much more rapid with the current basis set. It is also interesting to point out that the size of the CI expansion used to construct the optical potential is actually smaller than that of Ref. 4(b). The essential differences in the two calculations were use of the coupled
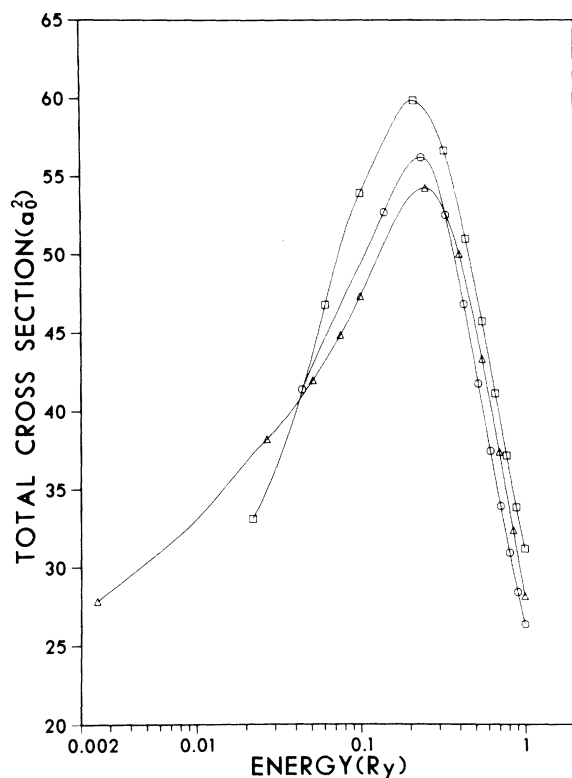
FIG. 3. Comparison of theoretical and experimental total cross sections for e-H_2 scattering. Curves are as follows: (1) $\triangle$ represents the effective optical potential; (2) $\bigcirc$ represents the experiment by Golden et al. (Ref. 31); (3) $\square$ represents the experiment by Dalba et al. (Ref. 32).

FIG. 4. Comparison of theoretical and experimental total cross sections for e-H_2 scattering. Curves are as follows; (1) $\triangle$ represents the effective optical potential (2) $\bigcirc$ represents the experiment by Firch (Ref. 34).

Hartree-Fock (HF) method to construct accurate pseudo-orbitals and a slightly more diffuse basis set for the scattered electron. In Fig. 2 we show the results of our calculation compared with that of Gibson and Morrison[20(b)] and Klonover and Kaldor.[23] All of the calculations were performed with $l=0,2,4,6$ partial waves and exchange was included in each channel. The box radius was $10a_0$ and the R matrix was propagated to $50a_0$. Our present calculations are practically indistinguishable from those of Gibson and Morrison[20(b)] at very low energy and are within a few percent at higher energies. Both calculations are larger in magnitude than that of Klonover and Kaldor and agree better with the experimental data of Golden, Bandel, and Salerno.[32] In Fig. 3 we compare our calculation with the older experimental data of Golden et al. and the recent data of Dalba et al.[33] On the basis of all of theoretical and experimental data available to us we would have to conclude that there is better agreement between the theory and the experiments of Golden
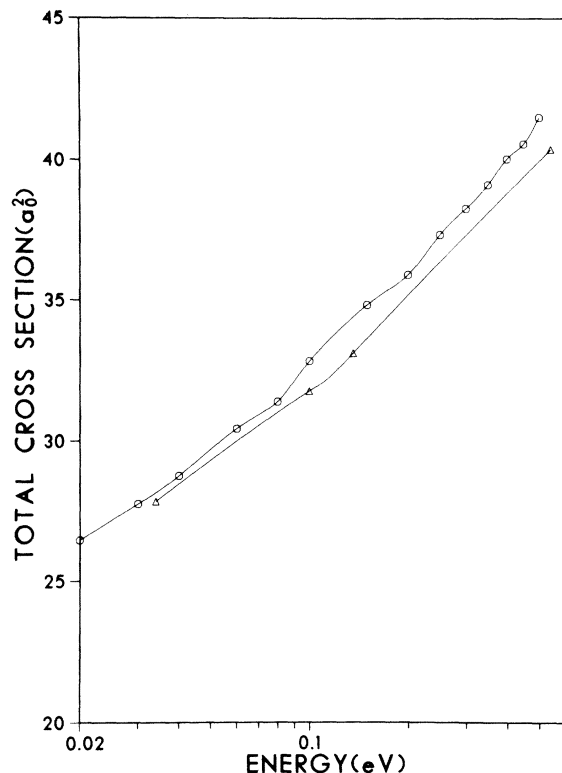
et al. than those of Dalba et al. In Fig. 4 we present a comparison of our theoretical calculations with the very low-energy experiments of Firch.[34] The agreement is excellent.

B. $e + N_2$

In order to demonstrate the power of our optical-potential approach in more complicated problems, we have examined low-energy $e + N_2$ scattering. The object of this calculation was not to perform an exhaustive study of $e + N_2$ collisions but to demonstrate how an *ab intitio* treatment of target polarization of the $^2\Sigma_g^+$ channel brings experimental and

TABLE II. Exponential coefficients of Gaussian-type orbitals used to expand scattering functions for $e + N_2$ scattering.

	All functions at midpoint				
s-type	0.02,	0.006,	0.002,	0.0007	
d type	0.05,	0.017,	0.005,	0.0019,	0.0006

TABLE III. A comparison of low-energy SE, effective optical potential (POL), and experimental (Kennerly) $e + N_2$ cross sections.[a]

k^2 (Ry)	δ^b (SE)	δ (POL)	σ^c (SE)	σ (POL)	σ (Expt)
0.02	−0.3392	−0.2330	72.28	33.45	31.10
0.1	−0.7429	−0.5749	60.57	40.50	38.09
0.2	−0.9984	−0.7691	48.72	36.73	
0.3	−1.1732	−0.9036	41.95	35.24	

[a]The box radius was taken to be $10a_0$ and b was zero.
[b]δ is phase shift in radians.
[c]All cross sections σ are in bohr^2.

theoretical results into better agreement. The atomic basis set consisted of a $9s\,5p\,1d/5s\,3p\,1d$ augmented by additional s, p, and d Gaussians to describe the polarization and scattering electron. The polarization functions were chosen as those used by Morrison and Hay[18] in their study of the polarizability of N_2. The occupied and polarization molecular orbitals were obtained in the same fashion as the $e + H_2$ study by performing SCF calculations in the absence and presence of an additional, distant nuclear charge. The polarizability obtained in this calculation was in perfect agreement with the results of Ref. 18. The additional molecular orbitals which are needed to describe the scattering electron were all of σ_g symmetry and were obtained by Schmidt orthogonalizing the remaining s and d atomic orbitals shown in Table II to the occupied plus polarization functions. In the final $^2\Sigma_g$ CI calculation no excitation of the $1\sigma_g$ and $1\sigma_u$ molecular orbitals was considered and they were transformed away by including their effects in the core potential. The final set of molecular orbitals consisted of only 40 functions. The CI calculation used to construct the optical potential was of the POLCI or first-order type.[28] The reference space consisted of the 18 SE configurations. All double excitations of these 18 references were included which obeyed the restriction that no

more than one electron be present in the virtual or scattering molecular orbitals. The partitioning of the orbital space into valence and virtual functions was done by including all molecular orbitals from the SCF and finite field calculations in the valence space. This partitioning assures us that all important polarization effects will be included in the CI. The final calculation contained 18 configurations in P space and 729 configurations in Q space. The most time-consuming part of the scattering calculation consists of the construction of the optical potential from the Hamiltonian matrix elements. This step takes about 10 sec of computer time on the CRAY I computer. The actual scattering calculation which included $l = 0$ to 14 channels took only 4 sec of computer (central-processing-unit) time. The results of the calculation are shown in Table III. The dramatic reduction of the total cross section due to polarization is similar to that observed in $e + H_2$ collisions. The agreement between theory and the recent experiments of Kennerly[35] is quite good considering that we have not considered the effects of nuclear motion on the cross section. The success of our approach has now been clearly demonstrated in three separate systems. An extension to inelastic scattering is underway and results should be available soon.

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