PHYSICAL REVIEW A VOLUME 24, NUMBER 5 NOVEMBER 1981

Linear-algebraic approach to electron-molecule collisions: General formulation

L. A. Collins and B. I. Schneider

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 8 June 1981)

We present a linear-algebraic approach to electron-molecule collisions based on an integral equations form with either logarithmic or asymptotic boundary conditions. The introduction of exchange effects does not alter the basic form or order of the linear-algebraic equations for a local potential. In addition to the standard procedure of directly evaluating the exchange integrals by numerical quadrature, we also incorporate exchange effects through a separable-potential approximation. Efficient schemes are developed for reducing the number of points and channels that must be included. The method is applied at the static-exchange level to a number of molecular systems including H_2, N_2, LiH, and CO_2.

I. INTRODUCTION

Over the past ten years a number of methods[1-11] have been advanced for treating electron collisions with molecular targets. The problem is complicated by a strongly anisotropic electrostatic potential arising mainly from the nuclear singularities and by a nonlocal, energy-dependent exchange interaction. Both close-coupling[1-7] and L^2 (Refs. 8–11) approaches have been developed to address these complications. Although these methods have proved successful in calculating static-exchange cross sections for a number of small molecular systems, difficulties with the procedures still arise. In the close-coupling (CC) approach, the scattering wave function is expanded in terms of a set of target and angular functions, which are usually referred to a single center. Within this expansion, the Schrödinger equation can be reduced to a set of coupled, radial integro-differential equations. Each component (channel) of the solution is labeled by a target state and the angular momentum l of the incident electron. These coupled equations have been solved by inward-outward propagation[1-4,6] and boundary-value, linear-algebraic[5,7] schemes. The principal difficulty with this approach rests with the large number of terms that must be included in the expansion in order to accurately represent the scattering solution near the nuclei. Thus, very high partial waves (large l), which make a negligible contribution to the scattering results, must be included in the expansion. In addition, their inclusion greatly increases the size of the system of equations that must be solved. The exchange contribution can be represented by reasonably small expansions as it depends on the diffuse electronic charge density and not on the nuclear potential. However, its nonlocal character does further complicate the solution of the coupled equations either by increasing the order of the set of equations[2-4] that must be solved over the static case or by forcing an iterative prescription[1] on the solution. In the L^2 approach, coordinate space is usually divided into two regions according to the strength of the interactions. The scattering solutions are determined separately in each region and then matched at the boundary to obtain the scattering quantities. In the outer region where the potential is local and weak, the scattering solution is usually determined by a close-coupling propagation scheme. On the other hand, the system in the inner region, where the nuclear static and exchange interactions are important, is treated much as a bound, negative molecular ion. The scattering solution is expanded in a discrete basis, and standard bound-state methods employed. The number of terms needed to represent the solution near the nuclei can be greatly reduced by introducing nuclear-centered basis functions. However, an accurate representation of the low partial waves, which display distinct continuum behavior, still requires a large number of basis functions. Exchange also introduces complications, but usually not to the same extent as in the CC methods since the direct (static) and exchange contributions are treated on much more equal footing in standard bound-state integral packages.

These difficulties have prompted a renewed search for techniques to handle the electron-molecule collision problem. One quite successful investigation has been mounted by McKoy and coworkers[11] using the Schwinger variational principle. This variational principle is based on the integral equation form of the scattering equations and seems to yield more accurate results for a given discrete basis than, for example, the Kohn method. Since the procedure is independent of the norm of the scattering wave function, any type of basis function may be used. This flexibility eliminates one of the principal drawbacks of a purely L^2 approach—namely, having to represent highly oscillatory functions in terms of a discrete basis. The method as actually implemented is more an iteration-variation scheme. The Schwinger variational principle is employed to generate an initial K matrix from a discrete basis-set expansion, which in turn is used in the Lippmann-Schwinger equation to generate a new trial wave function. The procedure is iterated until a converged K matrix is produced.

In the method[7] described in this paper, we have taken a different approach. We begin with the coupled integrodifferential equations within the single-center expansion and close-coupling approximation. We convert this set of equations to a set of coupled integral equations. This set of equations is in turn transformed to a set of linear-algebraic equations by approximating these integrals by discrete numerical quadratures. The procedure is similar to one developed by Seaton[12] for electron-atom collisions and Crees and Moores[5] for electron-molecule scattering except that it is based on an integral rather than a differential equations formulation. This system of linear equations, whose solution is the scattering wave function, can be solved by standard linear equations packages. Exchange terms present no formal difficulty in that a suitable rearrangement of the quadratures produces a set of linear equations identical in form to the local potential case. The exchange interaction does introduce some additional integrals that must be performed. The linear-algebraic (LA) method has excellent numerical stability and has the further advantage of being ideally suited to the new vector machines. Thus, the linear-algebraic approach overcomes two of the aforementioned difficulties. The channel wave functions are determined by a direct, numerical integration of the scattering equations. The quadrature meshes can be adjusted to conform to the physical form of the individual channel functions. Therefore, the method is not constrained to a single type of basis to represent all scattering solutions. In addition, the nonlocal exchange effects can be straightforwardly incorporated into the scheme without changing the basic form of the linear-algebraic equations.

By using the single-center expansion, we seem to have retained the difficulty of having to represent the scattering solution near the nuclei by a large number of terms. This complication is largely circumvented by the ability to select mesh sizes independently for each channel. In this case, the order of the linear-algebraic equations, which determines the practicality of the method, is equal to the sum over channels of the number of points per channel. To represent the low-partial-wave solutions, which usually oscillate throughout the short-range region, we typically need from 50 to 60 points in the mesh. Clearly, for a 20 channel problem, which required this number of points in each channel, the order of the resulting linear-algebraic equations would lead to an intractable problem, even on a large vector machine. However, the solutions for high partial waves are concentrated around the nuclei, and far fewer points (typically 15 to 20) are needed to represent these channel wave functions than those for the lower partial waves. Thus, adding large numbers of high-l channels does not drastically increase the order of the linear-algebraic equations, and single-center expansions prove tractable under this approach.

In this paper we describe in general the linear-algebraic approach. In Sec. II we develop the basic formulation. The general form taken by the linear-algebraic equations subject to asymptotic and R-matrix boundary conditions is described in Sec. II B. Section II C is devoted to a detailed treatment of the exchange interaction. We develop schemes to evaluate the exchange term by direct and separable-potential techniques. In Sec. III we turn our attention to various techniques for solving the coupled linear-algebraic equations. The results of calculations for the method for a number of representative molecular systems are presented in Sec. IV. In addition, we present a study of the separable-potential technique for e-LiH collisions. We close the section with an investigation of electron-CO_2 collisions in the static-exchange approximation. Finally, we summarize our findings in Sec. V.

II. FORMULATION

In this section we develop the basic linear-algebraic (LA) formalism for treating electron-molecule collisions. Since we are interested in the exact treatment of the short-range exchange interaction, we perform all calculations in the body frame (BF) within the fixed-nuclei (FN) approximation.[13] Efficient procedures for converting the resulting BF K-matrix elements to laboratory-frame cross sections are discussed elsewhere.[14] In addition, we restrict our derivation to the static-exchange (SE) approximation for closed-shell molecular targets. This simplification is made for pedagogical reasons and is in no way a restriction on the LA method. For example, for electronic excitation, the matrix elements and Green's function will change, but the basic techniques, presented in this and the following section, for solving a coupled set of LA equations still apply. In subsection A, we present a brief derivation of the BF, FN coupled radial differential equations in the SE approximation in terms of a general nonlocal potential. We then proceed in subsection B to derive two integral equations solutions to this set of coupled equations in terms of asymptotic (K-matrix) or R-matrix boundary conditions. These coupled integral equations are solved by a linear-algebraic method. In subsection C, we specifically treat the nonlocal exchange interactions. Again we proceed along two lines of attack. In the first, more traditional approach, we construct an exact numerical solution for the exchange term. In a second approach, we approximate the exchange term by a separable potential. This second approach considerably simplifies the scattering equations with little loss in accuracy. We reserve for Sec. III a discussion of the methods for solving the LA equations.

A. The static-exchange equations

In the BF within the fixed-nuclei and static-exchange approximations, the Schrödinger equation for electron-molecule collisions has the following form[15]:

$$[\vec{\nabla}^2 - 2V_{\rm st}(\vec{r}) - 2V_{\rm ex}(\vec{r}) + k^2]F(\vec{r}) = 0\,, \tag{1}$$

where $F(\vec{r})$ is the continuum wave function at position $\vec{r}$ from the origin (usually the center of mass of the molecule) and k^2 is the energy of the incident electron in rydbergs. The kinetic energy of the electron is given by $\vec{\nabla}^2$, the static potential by $V_{\rm st}$, and the nonlocal exchange interaction by $V_{\rm ex}F$. For a closed-shell molecular target, the second and third terms have the following simple form:

$$V_{\rm st}(\vec{r}) = -\sum_\alpha \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} + 2\sum_{i=1}^{N} \int |\phi^i(\vec{r}\,')^2|\,|\vec{r} - \vec{r}\,'|^{-1} d\vec{r}\,' \tag{2a}$$

and

$$V_{\rm ex}(\vec{r})F(\vec{r}) = \int K(\vec{r}, \vec{r}\,')F(\vec{r}\,')d\vec{r}\,' \tag{2b}$$

with

$$K(\vec{r}, \vec{r}\,') = -\sum_{i=1}^{N} \phi^i(\vec{r})\,|\vec{r} - \vec{r}\,'|^{-1}\phi^i(\vec{r}\,')\,. \tag{2c}$$

In Eqs. (2), the nuclear charge (position) is given by $Z_\alpha(\vec{R}_\alpha)$, the spatial component of the ith molecular orbital by $\phi^i(\vec{r})$, and the number of occupied molecular orbitals by N.

We now convert Eq. (2) to a set of coupled radial differential equations. To accomplish this, we make a single-center expansion of the bound and continuum orbitals about the origin as

$$\begin{gathered} \phi(\vec{r}) = \sum_{l_i} r^{-1}\phi^i_{l_i m_i}(r) Y_{l_i m_i}(\hat{r})\,, \\ F(\vec{r}) = \sum_{l} r^{-1} f_{lm}(r) Y_{lm}(\hat{r})\,, \end{gathered} \tag{3}$$

where $Y_{lm}(\hat{r})$ is a spherical harmonic and $m(m_i)$ gives the symmetry of the continuum (bound) orbital. In addition, we expand the $|r - r'|^{-1}$ term and the static potential $V_{\rm st}(\vec{r})$ in Legendre series as

$$\begin{gathered} |\vec{r} - \vec{r}\,'|^{-1} = \sum_\lambda \frac{r_<^\lambda}{r_>^{\lambda+1}} P_\lambda(\cos\theta) \\ \text{and} \\ V_{\rm st}(\vec{r}) = \sum_\lambda v_\lambda^{\rm st}(r) P_\lambda(\cos\theta_r)\,, \end{gathered} \tag{4}$$

where θ is the angle between $\vec{r}$ and $\vec{r}\,'$, θ_r is the angle between $\vec{r}$ and the internuclear axis, and $r_{\gtrless} = {}^{\max}_{\min}\{r, r'\}$. Substituting Eqs. (3) and (4) into Eqs. (1) and (2) and integrating over the angular variables, we obtain the coupled radial static-exchange equations of the form

$$L_l f_{ll_0}(r) = \sum_{l'} \int V_{ll'}(r\,|\,r') f_{l'l_0}(r')dr'\,, \tag{5}$$

where

$$L_l \equiv \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2 \tag{6a}$$

and

$$V_{ll'}(r\,|\,r') \equiv 2V^{\rm st}_{ll'}(r)\delta(r - r') - 2K_{ll'}(r\,|\,r')\,, \tag{6b}$$

with

$$V^{\rm st}_{ll'}(r) = \left(\frac{2l'+1}{2l+1}\right)^{1/2} \sum_{\lambda=0}^{\infty} v_\lambda^{\rm st}(r) C(l'\lambda l\,|\,m0) C(l'\lambda l\,|\,00) \tag{7a}$$

and

$$K_{ll'}(r\,|\,r') = \sum_{i=1}^{N} \sum_{l''l'''\lambda} g_\lambda(ll'l''l'''\,|\,mm_i)\phi_{l''m_i}(r) \times \phi^i_{l'''m_i}(r') r_<^\lambda / r_>^{\lambda+1}\,. \tag{7b}$$

The term g_λ is a product of four vector-coupling coefficients,[15] the channel label l gives the orbital angular momentum of the scattering electron, and l_0 designates a particular linearly independent solution. We, of course, invoke the close-coupling approximation by which the expansions in Eq. (3) are limited to a finite number of terms and the order of the coupled differential equations in (5) is equal to the number of channels (terms) retained in the expansion of the continuum orbital.

B. Linear-algebraic solutions

We choose to base the linear-algebraic approach on the integral rather than on the differential equation formulation. For various propagation schemes, we have found the integral equation to be the most stable. Preliminary results[7] seem to indicate the same advantage in the LA approach since we have been able to use much higher-order quadrature schemes in the integral LA solutions than have been employed in the differential approach.[5] In order to make the conversion, we must choose a set of boundary conditions. We have developed two equivalent approaches in this regard. The first uses the standard asymptotic boundary conditions and solves for the wave function. The second approach imposes logarithmic boundary conditions at a point (usually just outside the exchange region) and solves for the R matrix.

1. Asymptotic or K-matrix boundary conditions

We convert Eq. (5) to an integral equation by using the free-particle Green's function. The continuum wave function is represented over all radial coordinates. The resulting integral equations have the form

$$f_{ll_0}(r)=G_l^1(r)\delta_{ll_0}+\sum_{l'}\int G_l^0(r|r')\int V_{ll'}(r'|r'')\times f_{l'l_0}(r'')dr''dr' , \tag{8a}$$

where $G_l^0(r|r')$ is given by

$$G_l^0(r|r')=-\begin{cases}G_l^1(r)G_l^2(r') , & r<r'\\ G_l^1(r')G_l^2(r) , & r>r'\end{cases} \tag{8b}$$

and where $G_l^1(r)=\hat{j}_l(kr)$ and $G_l^1(r')=(1/k)\hat{n}_l(kr)$, with $\hat{j}_l(\hat{n}_l)$ the Ricatti-Bessel (Neumann) function of order l.

We now proceed to solve Eq. (8) by converting it to a set of linear-algebraic equations. We begin the procedure by introducing a quadrature for the integrals as

$$f_{ll_0}(r)=G_l^1(r)\delta_{ll_0}+\sum_{l'}\sum_{\alpha\beta}G_l^0(r|r_\alpha)V_{ll'}(r_\alpha|r_\beta)f_{l'l_0}(r_\beta)\omega_\alpha\omega_\beta , \tag{9}$$

where r_α, ω_α is a set of points and weights for the given quadrature. We observe that a separate quadrature can be introduced for *each* scattering channel. This flexibility is extremely important and will be discussed in more detail in Sec. III A. We now impose a mesh on the remaining radial variable and rearrange the resulting equations to obtain

$$\sum_{l'\beta}(\delta_{\gamma\beta}\delta_{ll'}-M_{l\gamma,l'\beta})f_{l'l_0}(r_\beta)=G_l^1(r_\gamma)\delta_{ll_0} , \tag{10a}$$

where

$$M_{l\gamma,l'\beta}\equiv\sum_\alpha G_l^0(r_\gamma|r_\alpha)V_{ll'}(r_\alpha|r_\beta)\omega_\alpha\omega_\beta . \tag{10b}$$

We can write this in a more specific form by substituting Eq. (6b) into Eq. (10b) to obtain

$$M_{l\gamma,l'\beta}=2G_l^0(r_\gamma|r_\beta)V_{ll'}^{\mathrm{st}}(r_\beta)\omega_\beta-2W_{ll'}(r_\gamma|r_\beta)\omega_\beta , \tag{10c}$$

where

$$W_{ll'}(r_\gamma|r_\beta)\equiv\sum_\alpha G_l^0(r_\gamma|r_\alpha)K_{ll'}(r_\alpha|r_\beta)\omega_\alpha . \tag{10d}$$

In order to make the form of these equations more transparent, we represent them in matrix form. We assume that the expansion of the continuum wave function is truncated at N_c channels and that there are N_p points in the quadratures. We define three "supermatrices": $\underline{M}$, $\underline{f}$, and $\underline{g}$. The $\underline{M}$ matrix consists of N_c^2 blocks of $N_p\times N_p$ elements each and is of order $N_{cp}=N_c\times N_p$. The form taken by the M matrix is

$$\underline{M}\equiv\begin{bmatrix}\underline{M}_{11}\cdots\underline{M}_{1N_c}\\ \cdot\qquad\cdot\\ \cdot\qquad\cdot\\ \cdot\qquad\cdot\\ \underline{M}_{N_c1}\cdots\underline{M}_{N_cN_c}\end{bmatrix} , \tag{11}$$

where

$$(\underline{M}_{ll'})_{\gamma\beta}\equiv\delta_{ll'}\delta_{\gamma\beta}-M_{l\gamma,l'\beta} .$$

The $\underline{f}$ matrix is defined by

$$\underline{f}\equiv\begin{bmatrix}f_{11}(r_1)\cdots f_{1N_c}(r_1)\\ \cdot\qquad\\ \cdot\qquad\cdot\\ \cdot\qquad\\ f_{11}(r_{N_p})\qquad\cdot\\ f_{21}(r_1)\qquad\cdot\\ \cdot\qquad\\ \cdot\qquad\\ \cdot\qquad\\ f_{N_c1}(r_{N_p})\cdots f_{N_cN_c}(r_{N_p})\end{bmatrix} \tag{12}$$

and the $\underline{g}$ matrix by

$$\underline{g} \equiv \begin{bmatrix} G_1^1(r_1)\cdots & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ G_1^1(N_p) & 0 \\ 0 & G_{N_c}^1(r_1) \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ 0 & \cdots G_{N_c}^1(r_{N_p}) \end{bmatrix} . \tag{13}$$

The size of the $\underline{M}$, $\underline{f}$, and $\underline{g}$ matrices are, respectively, $N_{cp}\times N_{cp}$, $N_{cp}\times N_c$, and $N_{cp}\times N_c$. Equation (10) can then be written in compact matrix form as

$$\underline{M}\,\underline{f} = \underline{g} . \tag{14}$$

This equation can be solved by standard linear-algebraic techniques. Since the correct asymptotic boundary conditions were included in the Green's function, the K matrix can be directly calculated from the expression

$$f_{ll_0}(r_{N_p}) = \hat{j}_l(kr_{N_p}) + K_{ll_0}\hat{n}_l(kr_{N_p}) . \tag{15}$$

2. *R-matrix boundary conditions*

In the previous section, we derived a set of linear-algebraic equations whose solution was the continuum wave function $\underline{f}$ over all space. The practicality of the LA approach depends on the order of $\underline{M}$ not becoming too large (typically 1000 for modern vector machines). For strongly polar molecules, we need the wave function out to several hundred bohr in order to extract an accurate K matrix. Since at least five mesh points are usually required for a de Broglie wavelength, the range required by the polar problem would clearly lead to LA equations of a prohibitive order. A better strategy is to employ the LA approach to determine a solution in the region occupied by most of the charge cloud of the molecule, where the static and exchange interactions are strong, and then to extend this solution into the asymptotic region by an efficient propagation scheme for local potentials such as the R-matrix propagator.[16] As we shall demonstrate in subsection C, the LA approach is especially suited for handling strong and nonlocal potentials. It does not have any clear advantage in speed over the R-matrix propagator in the region of a weak local potential and has the disadvantage of requiring far more storage.

We now seek a solution to Eq. (5) subject to logarithmic boundary conditions at $r=a$:

$$\left.\frac{d}{dr} f_{ll_0} f_{ll_0}^{-1}\right|_a = b , \tag{16}$$

where for convenience we choose $b=0$. The most straightforward procedure for introducing this restriction is to subtract the Bloch operator[17]

$$\delta_{l'l}\,\delta(r-a)\frac{\partial}{\partial r}$$

from both sides of Eq. (5) to obtain

$$\hat{L}_l f_{ll_0} = 2\sum_{l'} \int V_{ll'}(r\,|\,r')dr' - \delta(r-a)\frac{\partial}{\partial r} f_{ll_0}(r) , \tag{17}$$

where

$$\hat{L}_l = L_l - \delta(r-a)\frac{\partial}{\partial r} .$$

The Bloch operator guarantees that the solution of Eq. (17) will have the boundary conditions of Eq. (16). We now convert Eq. (17) to an integral equation form

$$f_{ll_0}(r) = \sum_{l'} \int_0^\infty \hat{G}_l(r\,|\,r') \int \Big(V_{ll'}(r'\,|\,r'') f_{l'l_0}(r'') - \delta(r-a)\frac{\partial}{\partial r} f_{ll_0}(r') \Big) dr'dr'' , \tag{18}$$

where $\hat{G}_l(r\,|\,r')$ is given by Eq. (8b) with $G_l^2(r)$ replaced by $(1/k)[\hat{n}_l(kr)+C_l\hat{j}_l(kr)]$ with $C_l = -\hat{n}_l(ka)'/\hat{n}_l(ka)$. This replacement forces the correct boundary condition at $r=a$ on the Green's function. We solve Eq. (18) by constructing an alternative solution $g_{l'\bar{l}}(r\,|\,a)$ defined by

$$f_{ll_0}(r) = \sum_{\bar{l}} g_{l\bar{l}}(r\,|\,a) \left.\frac{\partial f_{\bar{l}l_0}}{\partial r}\right|_a , \tag{19a}$$

such that it solves

$$g_{l\bar{l}}(r\,|\,a) = \sum_{l'} \int_0^a \Big(\hat{G}_l(r\,|\,r') \int V_{ll'}(r'\,|\,r'') \times g_{l'\bar{l}}(r''\,|\,a) dr'dr'' \Big) - \hat{G}_l(r\,|\,a)\delta_{l\bar{l}} . \tag{19b}$$

By directly substituting Eq. (19a) into Eq. (18) and by using Eq. (19b), we can demonstrate that if $g_{l\bar{l}}$ is a solution of Eq. (19b) then f_{ll_0} constructed from (19a) is a solution of Eq. (18). We note one other important feature that at $r=a$, $g_{l\bar{l}}(a\,|\,a)$ is just the R matrix.

We now convert Eq. (19b) into a system of linear-algebraic equations. We proceed as we did in the previous section and obtain the following result:

$$\sum_{l'\beta}(\delta_{\gamma\beta}\delta_{ll'}-\bar{M}_{l\gamma,l'\beta})g_{l'\bar{l}}(r_\beta)=\hat{G}_l(r_\gamma|a)\delta_{l\bar{l}} \tag{20a}$$

with

$$\bar{M}_{l\gamma,l'\beta}\equiv\sum_{\alpha}\hat{G}_l(r_\gamma|r_\alpha)V_{ll'}(r_\alpha|r_\beta)\omega_\alpha\omega_\beta\,. \tag{20b}$$

These equations can also be converted to matrix form, and the solution $\underline{g}$ can be obtained over the range $(0,a)$. At $r=a$, this function is just the R matrix. Knowing the R matrix at a point and the form of the local static potential over all space, we can use the R-matrix propagation method[16] to extend the R matrix into the asymptotic region.

C. Exchange

The nonlocal character of the exchange interaction greatly complicates the solution of the coupled radial equations. Fortunately, the interaction is of short range and can be handled with the methods of Sec. II B 2. In this section, we develop two approaches to calculating the exchange terms that appear in the linear-algebraic equations. Our first approach is a direct numerical evaluation of the exchange integrals that appear in Eqs. (5)–(7b). This procedure is similar to that used in other noniterative[2-4,6] and iterative[1] close-coupling schemes. In the second approach, we construct a separable-potential representation for the kernel [Eq. (2c)] by expanding it in an orthonormal basis. This construction greatly facilitates the calculation of the exchange integrals that appear in the scattering equations.

We spend a great amount of time in this section describing methods for the more efficient evaluation of the exchange term. The reason for this preoccupation becomes clearer by examining the amount of time spent in each part of the code. On conventional computers, we spend about half the time on evaluating $W_{ll'}$, and the other half solving the LA equations. The construction of the static potential takes a negligible amount of time compared with exchange. This even division alone would make a study of means to more efficiently evaluate $W_{ll'}$ profitable. On vector machines such as the CRAY-1, even greater differences in timings between solution and evaluation can arise since the linear-algebraic step yields better to a vector treatment than the evaluation of $W_{ll'}$. In fact, we find representative times of 1 second for solving a system of linear equations of order 600 on the CRAY-1. In this case, the direct exchange evaluation can be four to six times slower. The separable-potential form restores somewhat the balance.

1. Direct evaluation

We construct an explicit form of the exchange contribution $W_{ll'}$ in Eq. (10c) by substituting Eq. (7b) into Eq. (10d). We split the g_λ term and explicitly display the sum over projections of the symmetry of the bound orbitals m_i. The term which results has the form[4,15]

$$W_{ll'}(r_\gamma|r_\beta)=\sum_{i=1}^{N}\sum_{\mu=-|m_i|}^{|m_i|}\sum_{l'''\lambda}\phi^i_{l'''m_i}(r_\beta)\times C_a^{l'''\mu}(l'\lambda|m\mu-m)\times Y^\lambda_{l\,-\mu}(r_\gamma|r_\beta) \tag{21a}$$

with

$$Y^\lambda_{l\mu}(r_\gamma|r_\beta)\equiv\sum_{l''}C_a^{l''\mu}(l\lambda|-mm+\mu)\,y_\lambda^{l''l}(r_\gamma|r_\beta) \tag{21b}$$

and

$$y_\lambda^{l''l}(r_\gamma|r_\beta)=\sum_{\alpha}\omega_\alpha\phi^i_{l''m_i}(r_\alpha)\frac{r_<^\lambda}{r_>^{\lambda+1}}G_l^0(r_\gamma|r_\alpha)\,. \tag{21c}$$

Since the evaluation of the y_λ integrals forms the most costly step in the construction of the $W_{ll'}$ terms, we employ the above formulation, suggested by Raseev,[4,18] which minimizes the number of evaluations of these integrals. In addition to reducing the number of evaluations, we have also developed efficient schemes for evaluating the y_λ integrals. We divide the y_λ integrals into four regions of coordinate space according to the greater- or lesser-than constraints on the Green's function and $r_{\lessgtr}$ terms. This quadrapartite division is made clearer by representing the integrals in the following form:

$$y_\lambda^{l''l}(r_\gamma|r_\beta)=r_\beta^{-\lambda-1}\Gamma_\lambda(r_\gamma|r_\beta)+r_\beta^\lambda\Gamma'_\lambda(r_\gamma|r_\beta)\,, \tag{22a}$$

with

$$\Gamma_\lambda(r_\gamma|r_\beta)=\begin{cases}-G_l^2(r_\gamma)\gamma_\lambda^1(r_\gamma)-G_l^1(r_\gamma)[\gamma_\lambda^2(r_\gamma)-\gamma_\lambda^2(r_\beta)]\,, & \gamma<\beta\\ -G_l^2(r_\gamma)\gamma_\lambda^1(r_\beta)\,, & \gamma\geqslant\beta\end{cases} \tag{22b}$$

$$\Gamma'_\lambda(r_\gamma|r_\beta)=\begin{cases}-G_l^1(r_\gamma)\bar{\gamma}_\lambda^2(r_\beta)\,, & \gamma<\beta\\ -G_l^2(r_\gamma)[\bar{\gamma}_\lambda^1(r_\gamma)-\bar{\gamma}_\lambda^1(r_\beta)]-G_l^1(r_\gamma)\bar{\gamma}_\lambda^2(r_\gamma)\,, & \gamma\geqslant\beta\end{cases} \tag{22c}$$

and

$$\gamma^1_\lambda(r_\gamma) = \sum_{\alpha=1}^{\gamma} G^1_l(r_\alpha)\phi_{l'''m_l}(r_\alpha)r^\lambda_\alpha\omega_\alpha ,$$

$$\gamma^2_\lambda(r_\gamma) = \sum_{\alpha=\gamma}^{N_p} G^2_l(r_\alpha)\phi_{l'''m_l}(r_\alpha)r^\lambda_\alpha\omega_\alpha . \tag{22d}$$

The $\bar{\gamma}_\lambda$ terms have the same form as Eqs. (22d) with r^λ_α replaced by $r_\alpha^{-\lambda-1}$. The γ^1_λ terms are evaluated by upwards recursion while the γ^2_λ terms are determined by downwards recursion. We have found this dual recursion scheme to give the most accurate values for the γ terms. The Γ and $W_{ll'}$ terms can then be constructed from a table of the γ_λ values.

2. *Separable exchange potential*

The exchange interaction is complicated not so much from being nonlocal, but from being nonseparable.[19,20] This complication is introduced by the $|\vec{r}-\vec{r}\,'|^{-1}$ term in Eq. (2c) which links the $\vec{r}$ and $\vec{r}\,'$ variables of the bound functions. In a previous report,[19] we introduced the separable potential in a vector-space formulation. In this section, we derive its form in coordinate space to remain consistent with the previous sections.

We can construct a separable form of the exchange kernel by expanding in terms of an orthonormal basis $\{x^i(\vec{r})\}$. Making this expansion on both radial variables in Eq. (2c), we obtain

$$K(\vec{r},\vec{r}\,') = \sum_{jk} X^j(\vec{r})K_{jk}X^k(\vec{r}\,')^* , \tag{23a}$$

such that

$$K_{jk} = \iint X^j(\vec{r})^*K(\vec{r},\vec{r}\,')X^k(\vec{r}\,')d\vec{r}\,d\vec{r}\,' . \tag{23b}$$

We remove the angular dependence in Eq. (23a) by expanding the basis functions in spherical harmonics as

$$X^i(\vec{r}) = \sum_l X^i_{lm}(r)Y_{lm}(\hat{r}) . \tag{23c}$$

Substituting Eq. (23c) into (23a) and integrating over the angular variables, we obtain

$$K_{ll'}(r\,|\,r') = \sum_{kj} X^j_{lm}(r)K_{jk}X^k_{l'm}(r')^* . \tag{24}$$

Before proceeding with the construction of the exchange term, we introduce an additional simplification. We note that one of the sums in Eq. (24) can be eliminated if we replace the matrix $\underline{K}_{jk} \equiv K_{jk}$ by its diagonal form. We introduce a unitary transformation $\underline{U}$ and a new basis $\{\bar{X}^i\}$ such that

$$\underline{U}^\dagger\underline{K}\,\underline{U} = \underline{\Lambda}$$

and

$$\bar{X}^\lambda(\vec{r}) = \sum_j U_{j\lambda}X^j(\vec{r}) , \tag{25}$$

where $(\underline{\Lambda})_{\lambda k} = \Lambda_\lambda\delta_{\lambda k}$. Substituting Eq. (25) in Eq. (24), we obtain

$$K_{ll'}(r\,|\,r') = \sum_\lambda \bar{X}^\lambda_{lm}(r)\Lambda_\lambda\bar{X}^\lambda_{l'm}(r') . \tag{26}$$

The expansion of the exchange kernel in Eq. (26) is *independent of energy* and need only be determined once for a given molecular system. By comparing Eqs. (26) and (7b), we see that the number of sums that must be performed at each energy has been reduced from four to one. This reduction is not as dramatic as it might seem. The summations in Eq. (7b) extend only over the occupied molecular orbitals. The expansions of the bound molecular orbitals can usually be truncated at a few terms since the exchange interaction depends on the diffuse electronic change density and not on the strongly singular nuclear potential. On the other hand, no such restriction applies to the expansion in Eq. (26), which forms an approximate representation of K that improves as more basis functions are added. Thus, the separable form of the kernel will be more efficient to evaluate provided that the number of basis functions needed to give an accurate representation is smaller than the total number of terms that appear in the sums in Eq. (7b).

We now investigate the form taken by the exchange term in the LA equations when the separable form of the kernel is used. To this end, we substitute Eq. (26) into Eq. (10d) to obtain

$$W_{ll'}(r_\gamma\,|\,r_\beta) = \sum_\lambda \bar{X}^\lambda_{l'm}(r_\beta)\bar{Y}_{\lambda l}(r_\gamma) , \tag{27a}$$

where

$$\bar{Y}_{\lambda l}(r_\gamma) \equiv \sum_\alpha G^0_l(r_\gamma\,|\,r_\alpha)\bar{X}^\lambda_{lm}\Lambda_\lambda\omega_\alpha . \tag{27b}$$

Comparing Eqs. (21) and (25), we find that the exchange term in the separable form is considerably simpler. Explicitly, the integral in Eq. (27b) has only one radial label while that in the direct evaluation [Eq. (21b)] has two. This means that the evaluation of the $Y_{\lambda l}$ integral has been reduced in order of the radial variables from N_p^2

to N_p. Thus, not only does the separable prescription place part of the calculation into an energy-independent step but also reduces the amount of computation at each energy by considerably simplifying the radial integrals.

III. METHODS OF SOLUTION

In the previous section we developed the formalism for representing the scattering equations in linear-algebraic form. In this section, we concentrate on the various methods used to solve the LA equations. The first subsection is devoted to a discussion of the various quadrature schemes employed. In particular, we display the merits of choosing different meshes and ranges for the various collisional channels. The main advantage of this choice is the reduction in order of the M matrix and therefore the reduction of time spent in the linear-systems solution. In subsection B, we consider techniques for handling very large matrices that cannot be stored in small-core memory. The partitioning of the supermatrices is so far the most efficient means of accommodating such matrices. In the final section, we describe an optical potential, based on the partitioning scheme, for including the effects of channels with high angular momentum.

A. Quadrature schemes

The critical constraint on the efficacy of the LA approach is the size of the M matrix [Eq. (10) or (20)]. As indicated before, the order of this matrix is the product of the number of channels N_c and the number of quadrature points per channel N_p. Since we invoke the single-center expansion, we have very little control on the number of channels. Thus, we concentrate on means of minimizing the number of quadrature points. We achieve this result by two procedures: (1) use of high-order quadrature schemes and (2) use of variable number and range of points in each channel.

1. Choice of quadrature

The type and order of the quadrature selected is highly dependent on the functional form of the solution. This form, in turn, is determined by the effective "potential" $V_{ll'}$. Since in all practical calculations we use the R-matrix formulation of Eq. (20), we are only concerned in the LA method with the solution from $r=0$ to $r=a$, where a is a point beyond which the exchange contribution is negligible and the static potential has reached multipolar form. For a homonuclear molecule, we can divide this region into four subdivisions according to the strength of the potential. The subregions have the following bounds: (1) $0 \leqslant r_1 \leqslant r_N - \epsilon$ (where r_N is the position of the nucleus and $\epsilon \sim 0.2-0.5a_0$), (2) $r_N - \epsilon \leqslant r_2 \leqslant r_N + \epsilon$, (3) $r_N + \epsilon \leqslant r_3 < 2r_N$, (4) $2r_N \leqslant r_4 \leqslant a$. For a heteronuclear molecule, we must add a region between the two nuclei. In region 1, the potential is nearly constant and consists of a strong mixture of exchange and v_0-static components, while in region 2, the static potential becomes very strong (deep) due to the nuclear singularity. The static and exchange potentials contribute about equally in region 3 with the static potential being considerably weaker than in region 2. Finally, in region 4, the exchange potential is dying rapidly, and the static potential is tending to a weaker, multipolar form. We select a quadrature scheme and apply it to each of these regions. We vary the number of points in each region according to the strength of the potential. Thus, we place the largest number of points in region 2 and the second largest in region 3. A smaller number of points suffices to represent the two other regions.

We have found that high-order quadrature schemes, such as the Gauss-Legendre quadrature,[21] work best since they give the highest degree of accuracy for the smallest investment of points. In region 2, for example, we have applied Gauss-Legendre quadratures of 20 to 30 points. This points to one of the major advantages of an integral-equations linear-algebraic approach—that high-order quadrature schemes, which are notoriously unstable in propagation methods, are quite effective in such boundary-value problems. We have experimented with other quadrature schemes such as the trapezoidal[21] and Simpson's.[21] In region 2, these schemes allow a small reduction in the number of points over the Gaussian scheme due to their slightly greater density in the region of the singularity. However, over the entire region from $r=0$ to $r=a$, the Gaussian scheme requires from two to four times fewer points than either of these schemes. Thus, the Gauss-Legendre quadrature is generally applied to all four subregions.

In order to illustrate some of these points, we consider e-N_2 collisions in the Σ_g symmetry at 0.1 Ry. The calculations are performed at the static-exchange (SE) level. The expansion of the continuum wave function is truncated at eight terms ($l_m = 14$) in the scattering equations (20) and at two terms ($l_m^{ex} = 2$) within the exchange term. All six bound molecular orbitals are represented by a two-term expansion ($n_{1-6}^{ex} = 2$) in the exchange term and are constructed from the Cade, Sales, and Wahl[22] (CSW) SCF Hartree-Fock wave function. Since we are interested in the choice of meshes within the inner region ($r < a$), we match at $10a_0$.

TABLE I. (a) Gauss-Legendre quadrature meshes. (b) Eigenphase sums as a function of number of mesh points for the same mesh in all channels for SE e-N$_2$ Σ_g collisions at 0.1 Ry.[b] (c) Eigenphase sums as a function of mesh size for SE e-N$_2$ Σ_g collisions at 0.1 Ry.[c]

(a)

Subregion[a] r_i r_f	No. of points in (r_i, r_f) mesh number							
	1	2	3	4	5	6	7	8
0.0–0.7	5	5	5	10	10			5
0.7–1.5	10	15	15	20	25	15	15	10
1.5–2.5	5	5	10	10	10		3	10
2.5–10.0	5	5	5	10	10		2	5
Total no.	25	30	35	50	55	15	20	30

(b)

Mesh no.	Total pts.	O_m	δ_{sum} (rad)
1	25	200	−0.7034
2	30	240	−0.7893
3	35	280	−0.7938
4	50	400	−0.8132
5	55	440	−0.8145

(c)

Case	Mesh[d]	No. channels/mesh	O_m	δ_{sum} (rad)
1	3	8	280	−0.7938
2	3	6	240	−0.7938
	6	2		
3	3	4	200	−0.7940
	6	4		
4	3	2	160	−0.8918
	6	6		
5	3	2	170	−0.7930
	7	2		
	6	4		

[a] (r_i, r_f) gives the initial and final radial points of the subregion in bohr. $r_N = 1.034\ a_0$.

[b] $l_m = 14$, $\lambda_m = 28$, $l_m^{\text{ex}} = 2$, $\eta_{1-6}^{\text{ex}} = 2$, $r_m = 10.\ a_0$, CSW N$_2$ wave function.

[c] See Table I(a) for description of scattering parameters.

[d] First mesh listed corresponds to lowest partial waves. For example, in case 2, channels with $l = 0$ to 10 use mesh 3, while channels with $l = 12$ use mesh 6.

In Table I(a) we present the various meshes employed in this and the following section, while in Table I(b) we study the sensitivity of the eigenphase sum to the choice of mesh. We employ the same mesh in all eight channels. We take as our standard for comparison the results for mesh 5. More elaborate calculations employing different divisions of the inner region, different point distributions, and different choices of quadratures in the various channels yielded, in each case, eigenphase sums within better than 1% of the result for mesh 5. We can draw several important conclusions from a perusal of this table. We first note that our basic prescription for assigning point densities to the subregions, discussed above, is indeed valid. We note a significant improvement in going from mesh 1 to 2 due to the increase in the number of points around the nucleus (region 2). A slight improvement is obtained with mesh 3 which places an additional number of points in region 3. Finally, by further increasing the density of points around the nucleus, we obtain still more accurate results. Second, we observe that an accuracy on the order of 5% can be obtained with a fairly small number of mesh points (e.g., mesh 3). To push the accuracy further requires a much larger concentration of points, especially near the nucleus. Since the order of the M matrix (O_m) sets a practical computational limit on the LA approach, we are always searching for techniques that reduce O_m. If we are content with an accuracy of 5%, we can reduce the order of $\underline{M}$ by almost a factor of 2. This, in turn, reduces the storage by a factor of 4. Since the linear-systems routines on most computers (matrix operations on vector machines do not follow such simple scaling rules) involve operations that go as O_m^3 or higher, considerable savings are also realized in the execution step.

2. Channel quadratures

As pointed out in Sec. II B, a different set of weights and points can be introduced into each channel. This can be more graphically illustrated by attaching a channel label to the quadrature index in Eq. (20) to give

$$\sum_{l'\beta_{l'}} (\delta_{\gamma_l \beta_{l'}} \delta_{ll'} - \overline{M}_{l\gamma_l, l'\beta_{l'}}) g_{l'\bar{l}}(r_{\beta_{l'}}) = \hat{G}_l(r_{\gamma_l}|a)\delta_{l\bar{l}} \,. \tag{28}$$

The order of the $\overline{M}$ matrix is given by

$$O_m = \sum_{i=1}^{n} (N_c^i \times N_p^i) \,, \tag{29}$$

where N_c^i is the number of channels with mesh i, N_p^i is the number of points in the ith mesh, and n is the number of distinct quadrature meshes. The advantage of this formulation is at once made apparent by investigating the behavior of channels associated with large values of the orbital angular momentum (i.e., high-l values). For homonuclear targets, these high partial waves make a negligible contribution to the cross section. Although for polar targets the contribution to the cross section from K-matrix elements involving high angular momenta cannot be neglected, these elements can be accurately calculated by more approximate methods such as Born I and unitarized Born.[14] Thus, for either case, the effect of the high partial waves is simply computational; they are needed in the single-center expansion to properly represent the solution in the strong-coupling regime near the nuclei. For the high-l channels, we can concentrate the points in region 2 near the nuclei and eliminate or drastically reduce the number of points in the other three regions. If the number of points in region 2 does not substantially increase over the value used for the low-partial waves, then the order of $\underline{M}$ can be significantly reduced.

In order to further investigate these claims, we consider the collision problem of the previous subsection. In Fig. 1 we present the channel wave functions $f_{l1}(r_B)$ as a function of the radial variable for electron-N_2 collisions in the Σ_g symmetry at 0.1 Ry. The solutions for low values of l (≤ 2) are fairly spread out over the inner region ($r \leq a$); as l increases, the wave functions become progressively more confined to the region around the nitrogen nucleus. This pattern supports the strategy mentioned above for selecting channel meshes—namely, for the low partial waves spread the points over the inner region and for the high partial waves concentrate the points around the nucleus. If the number of points in each channel is the same, we gain accuracy by a more intelligent placement of points for the upper channels, but we do not reduce the order of $\underline{M}$. However, we find that not only can the range of points in the upper channels be reduced but also the *number* of points.

In Table I(c) we illustrate some of the above points for e-N_2 Σ_g collisions. We use case 1 as a standard. In going from case 2 to 4, we progressively place more of the upper channels on the smaller mesh. By case 3, we have split the channel space evenly between the two meshes. We observe no loss of accuracy in the eigenphase sum, while we have reduced the order by 30%. Case 4 is misleading. The third and fourth partial waves do contribute to the eigenphase sum. By better representing these channels in regions 3 and 4, we are able to improve the solution with only a slight increase in order (compare cases 5 and 4). The calculation of electron-CO_2 cross sections in the Σ_g symmetry, in which 30 or more channels are needed for convergence, is only tractable within the LA approach due to this ability to choose smaller mesh sizes for the upper channels.

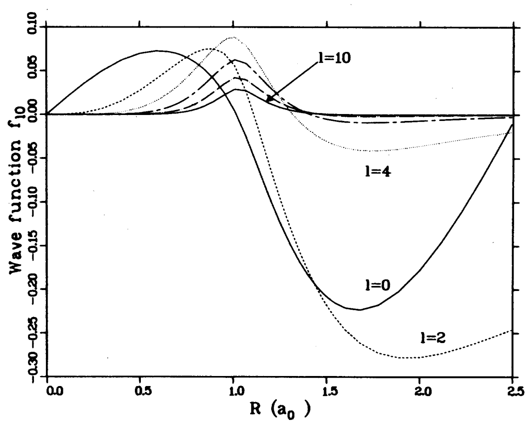

FIG. 1. Channel wave functions f_{l1} as a function of radius for the first linearly independent solution for e-N_2 Σ_g scattering at 0.1 Ry.

In Sec. II A we have described techniques for reducing the number of quadrature points and therefore the order of the LA equations. We briefly review our findings. First, we employ high-order quadrature schemes which give a high degree of accuracy for a small number of points. Second, we divide the inner scattering region ($r \leq a$) into subregions and choose the density of points in each region to correspond to the strength of the effective potential. Third, we reduce the number of points in the high-partial-wave channels by concentrating them entirely near the nucleus.

B. Partitions

Even the most judicious application of the procedures of the previous sections will not ineluctably lead to matrices which can be accommodated within small-core memory. Therefore, we must investigate schemes for treating these very large matrices. We have found that partitioning schemes, much along the lines of the Feshbach decompositions,[23] are usually adequate to solve this problem. We return now to the matrix form of solution in Eq. (14). As an illustration of this technique, we consider only a single partitioning, although the method can be readily generalized.

In order to demonstrate the partitioning technique more fully, we consider a particular example. We assume that there are N_c channels and, for simplicity, that there are N_p points per channel. In this case, the M matrix in Eq. (14) has an order $O_m = N_c \times N_p$, and the matrices $\underline{f}$ and $\underline{g}$ are $O_m \times N_c$ in size. Each column of $\underline{f}(\underline{g})$ corresponds to a separate linearly independent solution. We now divide channel space into two parts, say P and Q, with P space consisting of N_c' channels and Q space with $N_c'' = N_c - N_c'$ channels. We define two new orders $O_d = N_c' \times N_p$ and $O_a = N_c'' \times N_p$. With this dicotomy, we can write Eq. (14) as

$$\begin{pmatrix} \underline{M}_{PP} & \underline{M}_{PQ} \\ \underline{M}_{QP} & \underline{M}_{QQ} \end{pmatrix} \begin{pmatrix} \underline{f}_P \\ \underline{f}_Q \end{pmatrix} = \begin{pmatrix} \underline{g}_P \\ \underline{g}_Q \end{pmatrix} , \tag{30}$$

where $\underline{M}_{PP}$, $\underline{M}_{PQ}$, $\underline{M}_{QP}$, and $\underline{M}_{QQ}$ are $O_d \times O_d$, $O_d \times O_a$, $O_a \times O_d$, and $O_a \times O_a$ matrices, respectively. The $\underline{f}_P(\underline{g}_P)$ matrices are of size $O_d \times N_c$ while the $\underline{f}_Q(\underline{g}_Q)$ matrices are $O_a \times N_c$. We may then solve for $\underline{f}_P$ and $\underline{f}_Q$ by a simple 2×2 linear-equations scheme as

$$(\underline{M}_{PP} - \underline{M}_{PQ}\underline{M}_{QQ}^{-1}\underline{M}_{QP})\underline{f}_P = \underline{g}_P - \underline{M}_{PQ}\underline{M}_{QQ}^{-1}g_Q , \tag{31a}$$

$$\underline{f}_Q = \underline{M}_{QQ}^{-1}(\underline{g}_Q - \underline{M}_{QP}\underline{f}_P) , \tag{31b}$$

where M_{ij}^{-1} represents the inverse of matrix M_{ij}. It is important to note that *no* approximation has been introduced in going from Eq. (14) to Eq. (31)—the solutions of the two equations will be exactly the same. What is gained by the form of Eq. (31) is storage. If we assume that $O_d \geq O_a$, then all we need for the principal storage of Eq. (31) at any one time is two $O_d \times O_d$ matrices. In other words, Eq. (31a) can be solved quite independently of Eq. (31b). To solve Eq. (14) we must store a $O_m \times O_m$ matrix. We can see the savings in core more readily by taking a particular example. We choose the following parameters: $N_c = 10$, $N_p = 50$, $N_c' = 5$. Then, we have $O_m = 500$, $O_{d(a)} = 250$. Thus to solve Eq. (14) we must have O_m^2 or 250-K positions in memory, while to solve Eq. (31a) we need only $2\times O_d$ or 125-K positions—in other words, half the core. Efficient techniques for solving large equations based on an N-partition scheme are currently under development.

C. Optical potential for high-*l* channels

In Sec. III A, we investigated schemes for reducing the number of quadrature points as a means of reducing the order of the LA equations since we had little control over the number of channels in the close-coupling expansions. However, there are techniques for attacking the channel problem. We could use a prolate spheroidal rather than a spherical coordinate system. In fact, Crees and Moores[5] in their LA calculations on N_2 demonstrated that such a transformation reduced the number of channels by two. Unfortunately, prolate spheroidal systems are limited to diatomics or linear polyatomics. Several authors[24] have considered expansions in terms of adiabatic bases, much as is done in heavy particle scattering. These approaches appear to lead to a reduction in channels, but it is unclear whether the number of points must be accordingly increased. Thus, such techniques may be more suited to propagation schemes rather than an LA approach. The form of Eq. (31) provides another possible approach. We showed in the previous section that the solutions for the upper channels are not needed to construct the cross section. In other words, if we let Q space contain all channels whose asymptotic solution makes a negligible contribution to the scattering information, we no longer need to solve for f_Q in (31b). In addition, we may be able to make an approximation to M_{QQ} in Eq. (31a). Such a tact leads to an optical potential formulation.

We consider this idea by investigating Eq. (31a). As a first approximation we consider the block-diagonal form of $\underline{M}_{QQ}$. This leads to a great simplification since the inverse of a block-diagonal matrix is the inverse of *each* block. Thus, rather than storing a matrix of the order M_{QQ}, we need at any one time in the computation to store only one block $(N_P \times N_P)$ of $\underline{M}_{QQ}$. Physically this approximation is equivalent to replacing the upper-channel wave functions by their distorted waves. We make no approximation to $\underline{M}_{PQ}$ and $\underline{M}_{QP}$ so that all forward and backward coupling of the high partial waves to the lower ones in P space is retained. Only the coupling *between* the partial waves in Q space is neglected. We may then view $\underline{M}_{PQ}$ $\underline{M}_{QQ}^{-1}$ $\underline{M}_{QP}$ as an approximate optical potential. We have found for e-N_2 scattering that from three to four channels associated with high partial waves can be added by this technique with a loss of accuracy of less than five percent.

IV. RESULTS AND DISCUSSION

We divide this section into three parts. In the first subsection, we compare the results of the LA approach with those of other methods for several molecular systems. The second subsection is reserved for a comparison of the direct and separable-potential approaches to the evaluation of the exchange term. Finally, in the third subsection, we present static-exchange results of electron-CO_2 collisions.

A. Comparison with other methods

We compare the results of static-exchange calculations with the linear-algebraic method with those of other techniques for several molecular systems. In Table II, we present representative results from electron collisions with H_2, N_2, and LiH in the LA and iterative close-coupling[1] (ICC) methods. We observe excellent agreement in all cases. For the LA method, the calculations were performed with the direct exchange procedure (Sec. II C 1) with 30, 50, and 55 points in each channel for H_2, N_2, and LiH, respectively. In the SE case, a calculation at a given energy in the LA approach takes a time equivalent to about two iterations in

TABLE II. Comparison of the linear-algebraic and iterative close-coupling techniques in the static-exchange approximation.

Molecule	Symmetry	k^2	l_m	l_m^{ex}	η^{ex}	r_m	δ_{sum} (rad) LA	 ICC
H_2	Σ_g	0.04	6	2	2	20.0	−0.4224	−0.4229
		0.49					−1.2752	−1.2747
N_2	Σ_g	0.10	14	2	2	10.0	−0.8132	−0.7912
		0.50	10	2	2	10.0	1.5495	1.5732
	Σ_u	0.30	15	3	2	85.0	2.5873	2.584
	Π_g	0.24	10	4	2	10.0	1.3744	1.2382
LiH	Σ	0.20	5	2	3	16.0	−0.3254	−0.3103
		1.00	7	2	3	100.0	1.5470	1.5620
			7	7	8	16.0	1.8344	
	Π	0.25	6	3	3	100.0	0.9090	0.8961

the ICC method. In practical terms, this implies that the LA method is faster by a factor of 2 or more over the ICC technique. Even larger differences of time are observed when the separable-potential prescription is introduced in the LA approach.

We also find excellent agreement for these same three molecular systems with the noniterative close-coupling (NCC) method[5] and various variational schemes such as the Schwinger (SV) (Ref. 11) and Kohn (KV).[6] For example, for e-LiH Σ scattering at 1.0 Ry, the LA, SV,[25] and NCC (Ref. 26) give, respectively, 1.83, 1.82, and 1.74 for the eigenphase sum. The slightly lower result of the NCC method can be traced to a lower-order expansion in the exchange term.

B. Separable exchange: LiH

In a recent paper,[19] we developed in more detail the separable-exchange technique and applied it to e-H_2 and -LiH scattering. We also made comparisons with a similar method developed by Rescigno and Orel.[20] For completeness, we present a brief description of our findings in this section.

We choose to illustrate the separable-potential method on e-LiH collisions. In Table III, we study the behavior of the eigenphase sum as a function of the number of terms included in the separable expansion [Eq. (26)]. We observe that from 10 to 20 terms seem sufficient to produce an accurate representation of the exchange terms $W_{ll'}$. In fact, a ten-term expansion guarantees an accuracy of better than 10%. The computation time for the construction of the M matrix is considerably reduced in the separable approach over the direct method of section II C 1. For the LiH case of Table III, the separable approach was three times faster in the collision step, due entirely to the more efficient construction of the exchange contribution to $\underline{M}$. However, to gain a more realistic comparison between the two approaches, we must include the time spent in calculating the energy-independent expansion of the exchange kernel. Even with this addition, the separable method breaks even with the direct after about three energies. Thus, when cross sections at a large number ($\geqslant 3$) of energies are sought, the separable technique is preferable. Another advantage of the separable approach is the straightforward analysis of its convergence properties in λ. The diagonalization of the exchange kernel K in Eqs. (25) and (26) produces an eigenvalue spectrum. We find that this spectrum contains a significant number of very small values. The contribution of the eigenfunctions associated with these small eigenvalues to the representation of the exchange term is also small. Thus, we can use the eigenvalue spectrum to determine the minimum set of basis functions needed to represent $W_{ll'}$ to a particular accuracy. This approach also lends itself quite readily to

TABLE III. Eigenphase sum as a function of number of terms included in the expansion of the separable potential for SE e-LiH Σ collisions at 1.0 Ry.[a]

No. of terms in separable expansion	Eigenphase sum[b,c]
5	1.3786 (1.3652)
10	1.7089 (1.6944)
20	1.8573 (1.8424)
45	1.8578 (1.8429)

[a] Collision parameters: $l_m=7$, $\lambda_m=14$, no. of points in quadrature = 56.

[b] The numbers refer to matching the solutions to asymptotic forms at $R=16.0$ and 64.0 a.u., respectively.

[c] The value from the same program using numerical exchange is 1.8559.

the inclusion of other effects such as excited electronic channels and polarization through a separable-optical-potential formulation. We reserve for a later paper a description of this procedure.

C. Electron-CO_2 collisions: static exchange

The collision of electrons with CO_2 is one of the largest cases that has been handled by a single-center, close-coupling formulation.[27] In this calculation, the exchange and polarization terms were approximated by model potentials while the static contribution was treated exactly. In order to obtain accurate Σ_g elastic cross sections, 30 terms (channels) had to be included in the single-center expansion of the continuum wave function or over twice as many channels as are needed in N_2 and LiH calculations. Thus, the CO_2 system should prove a formidable test for the LA approach and should provide a demonstration of its practicality in treating large molecular systems. In addition, it provides a case for which exact static-exchange results are not available.

TABLE IV. Eigenphase sums as a function of energy for e-CO_2 collisions in the static-exchange approximation.

k^2	δ_{sum}(rad) Σ_g	Σ_u	Π_g	Π_u
0.036 75	−0.3263	−0.1556	−0.0370	
0.0735	−0.4548	−0.3461	−0.0577	
0.1472	−0.6264	−0.5786	−0.1039	−0.1082
0.2205	−0.7605	−0.7762	−0.1561	−0.1834
0.2940	−0.8788	−0.9467	−0.2117	−0.1973
0.4410	−1.1025	−1.2244	−0.3266	1.9960
0.5880	−1.2536	−1.4404	−0.4338	2.2406
0.7350	−1.3244	−1.6115	−0.5280	
l_m	58	19	20	23
l_m^{ex}	6	7	6	13
n_{1-9}^{ex}	4	4	4	7
r_m	100	100	100	100

We have performed e-CO_2 calculations in the Σ_g, Σ_u, Π_g, and Π_u symmetries using the near Hartree-Fock-SCFMO Σ_g^+ ground-state wave function of McLean and Yoshmine[28] at the equilibrium separation of 2.1944 a_0 between the C and O atoms. In all calculations, we represented the exchange term through the direct method described in Sec. IIC1. As the Σ_g symmetry presents the greatest challenge to convergence, we begin by describing our calculations for this symmetry. We found, much as in the earlier model study,[27] that 30 channels ($l_m = 58$) were needed to converge the scattering orbital. With this choice, we judge from extrapolation that the Σ_g eigenphase sum is converged to 10%. Such a large number of channels presents a difficulty to the LA approach for CO_2 since the number of points in the lower channels must be large to cover both the regions around the C and O nuclei and to span the remaining inner region ($r \leq 8\ a_0$). In fact, if 60 points were necessary in each channel, then the order of the M matrix would by 1800—far outside the storage of present machines. However, the technique devised in Sec. IIIA2 of introducing a different mesh in each channel comes to our aid. We find no loss of accuracy in the eigenphase sum or K-matrix elements by making the following channel/mesh assignments: (1) first six channels with 60 points, second two channels with 37 points, (2) all remaining channels with 26 points. The first mesh has points spread throughout the inner region with a concentration near the nuclei, while the second mesh has a greater concentration near nuclei and a small number of points in regions 3 and 4 in order to communicate scattering information to the boundary. Finally, mesh 3 has all its points concentrated on the O nucleus. This choice yields an M matrix of order 934 or almost half the order of the one first considered. The exchange contribution is, of course, represented by a much smaller expansion of the bound and continuum orbitals. We found that a choice of $l_m^{\mathrm{ex}} = 6$ and $n^{\mathrm{ex}} = 4$ (for all nine bound orbitals) guaranteed an exchange term converged to better than 5%. A typical Σ_g calculation for one energy on the CRAY-1 computer took around 35 seconds. This time can be reduced by going to the separable exchange form. For the Σ_u and Π_g symmetries, far fewer channels were needed for convergence, and the LA calculations were performed with the same mesh for all channels. In Table IV we present a summary of SE eigenphase sums for all four symmetries for e-CO_2 collisions, while in Fig. 2 we present the integrated cross section as

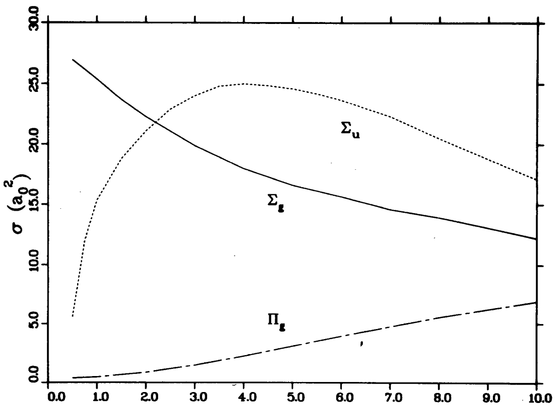

FIG. 2. Integrated cross sections as a function of energy for Σ_g, Σ_u, and Π_g symmetries for e-CO_2 collisions.

a function of energy for the nonresonant symmetries.

The resonant Π_u symmetry formed another test of the LA method. In this case, the number of channels needed to converge the scattering solution was not as great as in the Σ_g symmetry [14 ($l_m = 27$) as compared with 30]. However, near the center of the resonance, more terms are needed to represent the exchange term due to the greater concentration of the resonant, scattering wave function in the short-range region. We find that a choice of $l_m^{\mathrm{ex}} = 13$ and $n_{1-9}^{\mathrm{ex}} = 7$ guarantees convergence of the eigenphase sum to only about 10% at resonant center (~5.4 eV). However, slightly away from this point the convergence significantly improves. For the parameters, $l_m = 23$, $l_m^{\mathrm{ex}} = 13$, and $n_{1-9}^{\mathrm{ex}} = 7$, we obtain a width ($\Gamma$) of 0.68 eV and a position (E_r) of 5.4 eV. While the phase sum near E_r is in error by 10%, the position is probably given to a greater accuracy since it also depends on values of δ_{sum} away from E_r. In our earlier letter,[7] we reported a width of 2 eV and a position of 8 eV. The difference arises from errors in the calculation of the γ^2 and $\bar{\gamma}^2$ terms [Eq. (22d)]. In the original program, these terms were evaluated by upwards recursion. This scheme introduces large errors for resonant symmetries. Evaluating these integrals by downwards recursion completely eliminates these errors. For nonresonant symmetries we found very little difference in the two recursion schemes. The experimentally determined position of the resonance lies near 3.8 eV. Thus, the remaining shift in position is due to polarization terms.

We thus observe that even a case as CO_2, involving a large number of channels and points, can be efficiently handled by the linear-algebraic approach.

V. SUMMARY

We have presented a detailed development of a linear-algebraic (LA) approach to electron-molecule collisions. The set of integrodifferential equations, which arise from making the fixed-nuclei approximation in the body-frame and the close-coupling approximation on the single-center expansion of the bound and continuum orbitals, are transformed to a set of coupled integral equations. We prefer this integral representation for its stability and flexibility. This set of coupled integral equations is, in turn, converted to a set of linear-algebraic equations of the form

$$\underline{M}\underline{f} = \underline{g}$$

by introducing a quadrature on the integrals. These supermatrices are labeled by both the channels and mesh points. The M matrix contains the representation of the scattering "potential," and $\underline{f}$ contains the continuum solution. Equations of this form can be solved by standard linear-systems packages and are well suited to vector machines.

We have developed two formulations for the integral equations based on the choice of boundary conditions. In the first case, we choose asymptotic boundary conditions and solve for the continuum wave function over all space. This approach leads to prohibitively large systems of equations for electron-polar molecule collisions since the solution must be obtained out to very large radii in order to extract an accurate K matrix. An alternative approach is to impose logarithmic boundary conditions at a given radius (say a). The LA approach has clear advantages over propagation schemes in the treatment of nonlocal potentials like exchange and in the inclusion of channels with high partial waves. This distinction disappears for a weak, local potential such as is found in the region beyond the charge cloud of the molecule. Thus, the best strategy is to employ a different method of solution in the inner and outer regions. In the inner region ($r < a$), where the static and exchange interactions are strong, we employ the LA approach to solve for the R matrix rather than the wave function. A propagation scheme such as the R-matrix propagator is then used to extend the solution from $r = a$ into the asymptotic region.

The nonlocal character of the exchange interaction complicates the solution of the electron-molecule collisional problems. We have devised two methods for handling the exchange interaction within the LA approach. The introduction of exchange by either method does not alter the basic form or order of the linear-algebraic equations for a local potential; only the time to compute the matrix $\underline{M}$ is increased. In our first approach, we directly evaluate the exchange integrals by numerical quadratures. Efficient ordering and recursion schemes have been developed to reduce the number of evaluations of these integrals and the time spent in each evaluation. In our second approach, we expand the exchange kernel in separable form in terms of a discrete basis set. This procedure, which is independent of the collisional energy, leads to an expression for the kernel which greatly simplifies the form of the exchange integrals in the scattering formulation. For scattering calculations, the two forms break even in computational time after about three energies, with the separable form being the faster thereafter.

We have also devised a variety of techniques for efficiently solving the LA equations. The practicality of the LA approach rests with the order of the LA equations not becoming too large. The order depends both on the number of channels and the number of mesh points employed. The number of points can be kept at a minimum by three procedures: (1) by using high-order quadrature schemes such as Gauss-Legendre, (2) by judiciously selecting the density of points to correlate with the strength of the interaction potential, and (3) by selecting a different mesh for each channel or group of channels. For the channels associated with high partial waves, only a few points need be concentrated near the nuclei since their wave functions are confined to this region. On the other hand, for low partial waves which are highly oscillatory, the points must be spread throughout the inner region. This ability to reduce the number of points associated with high partial waves makes the LA approach tractable for large molecular systems since the introduction of channels with large values of l does not drastically increase the order of the LA equations. We have also developed partitioning schemes for treating large matrices that will not fit in small-core memory as well as approximate, optical potential techniques for reducing the large number of channels that arise from the single-center expansion.

Finally, we have applied the linear-algebraic approach with both forms of the exchange interaction to a variety of molecular systems (H_2, N_2, LiH) and obtained excellent agreement with other methods. In addition, we have demonstrated the practicality of the method by applying it to the CO_2 system.

ACKNOWLEDGMENTS

This project was performed under the auspices of the U. S. Department of Energy through the Theoretical Division of the Los Alamos National Laboratory.

---

[1] L. A. Collins, W. D. Robb, and M. A. Morrison, Phys. Rev. A 21, 488 (1980).

[2] E. R. Smith and R. J. W. Henry, Phys. Rev. A 7, 1585 (1973).

[3] B. D. Buckley and P. G. Burke, J. Phys. B 10, 725 (1977).

[4] G. Raseev, A. Guisti-Suzor, and H. Lefebvre-Brian J. Phys. B 11, 2735 (1978).

[5] M. A. Crees and D. L. Moores, J. Phys. B 8, L195 (1975).

[6] L. A. Collins and W. D. Robb, J. Phys. B 13, 1637 (1980).

[7] B. I. Schneider and L. A. Collins, J. Phys. B 14, L101 (1981).

[8] B. I. Schneider and P. J. Hay, Phys. Rev. A 13, 2049 (1976); M. A. Morrison and B. I. Schneider, *ibid.* 16, 1003 (1977); B. I. Schneider, M. LeDourneuf, and Vo Ky Lan, Phys. Rev. Lett. 43, 1926 (1979); S. Chung and C. C. Lin, Phys. Rev. A 17, 1874 (1978).

[9] T. N. Rescigno, C. W. McCurdy, and V. McKoy, Phys. Rev. A 11, 825 (1975); A. W. Fliflet, D. A. Levin, M. Ma, and V. McKoy, *ibid.* 17, 160 (1978).

[10] H. Takagi and H. Nakamura, J. Phys. B 11, L675 (1978).

[11] D. K. Watson and V. McKoy, Phys. Rev. A 20, 1474 (1979); R. R. Lucchese, D. K. Watson, and V. McKoy, *ibid.* 22, 421 (1980).

[12] M. J. Seaton, J. Phys. B 7, 1817 (1974).

[13] A. Temkin and K. V. Vasavada, Phys. Rev. 160, 109 (1967).

[14] L. A. Collins and D. W. Norcross, Phys. Rev. A 18, 467 (1978); N. T. Padial, D. W. Norcross, and L. A. Collins, J. Phys. B (in press); J. Seigal, J. L. Dehmer, and D. Dill, J. Phys. B 13, L215 (1980).

[15] M. A. Morrison and L. A. Collins, Phys. Rev. A 17, 918 (1978).

[16] J. C. Light and R. B. Walker, J. Chem. Phys. 65, 4272 (1976).

[17] C. Bloch, Nucl. Phys. 4, 503 (1967); B. I. Schneider, Chem. Phys. Lett. 31, 237 (1975).

[18] G. Raseev, Comput. Phys. Commun. 20, 275 (1980).

[19] B. I. Schneider and L. A. Collins, Phys. Rev. A (in press).

[20] T. N. Rescigno and A. E. Orel, Phys. Rev. A 23, 1134 (1981); Phys. Rev. A (in press).

[21] *Handbook of Mathematical Functions*, edited by Abramowitz and A. Stegun (U. S. GPO, Washington, 1968).

[22] P. E. Cade, K. O. Sales, and A. C. Wahl, J. Chem. Phys. 44, 1973 (1966).

[23] H. Feshbach, Ann. Phys. (N. Y.) 5, 357 (1958); W. R. Garrett, Phys. Rev. A 11, 1297 (1975).

[24] N. A. Mullaney and D. G. Truhlar, Chem. Phys. Lett. 58, 512 (1978); Vo Ky Lan, M. LeDourneuf, and J. M. Launay, Electron-Atom and Molecule Collisions (Plenum, New York, in press).

[25] R. R. Luccahese and V. McKoy, Phys. Rev. A (in press).

[26] G. Raseev, J. Phys. B (in press).

[27] M. A. Morrison, N. F. Lane, and L. A. Collins, Phys. Rev. A 15, 2186 (1977).

[28] A. D. McLean and M. Yoshmine, IBM J. Res. Dev. 12, 206 (1968).