Direct iteration-variation method for scattering problems

Barry I. Schneider and Lee A. Collins
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 16 December 1985)

We propose a direct iterative-variational scheme to solve the large sets of coupled integro-differential equations that arise in a variety of atomic and molecular scattering problems. The method, which is similar to direct configuration-interaction schemes of quantum chemistry, is applied within the linear algebraic (LA) prescription and involves the construction of an orthonormal basis from successive applications of the general LA matrix, labeled by channels and mesh points, to an initial guess for the solution vector. The solution vector is expanded in this basis, and the linear coefficients determined by a variational scheme. Since the basis is orthonormal, the procedure is guaranteed to converge within n iterations, where n is the order of the matrix. For all cases treated, the convergence is much more rapid. In addition, since a direct method is employed, only the potential, Green's function, and solution vector need be stored. This formulation drastically reduces the central storage requirements of the LA method as well as improves the solution times since the integrals involved can be constructed from recursion relations. We apply the method to elastic scattering of electrons by N_2 and LiH as well as inelastic collisions from H_2^+.

I. INTRODUCTION

During the past five years we have developed an approach to electron-molecule scattering based on the conversion of the coupled integro-differential equations to a set of linear algebraic equations which can be solved by standard "matrix inversion" methods.[1-4] The theory has the advantage of numerical stability, the possibility of using high-order Gauss quadratures, and the ability to utilize the vector architecture of the newer computers, such as the Cray and Cyber 205. In all of the applications the matrix has been formed and stored in central memory or placed on disk. When the matrix has become too large for the available memory, a partitioning into smaller submatrices has enabled the solution of the algebraic equations to be performed by direct $\underline{L}$-$\underline{U}$ factorization using a generalization of Gaussian elimination to matrix subblocks. Although these approaches are quite general, they have the disadvantage of having to form and alter the matrix many times during the forward elimination procedure. This is particularly tedious when the matrix cannot be stored in central memory and must be read and written to disk numerous times in the course of the forward solution. In addition, the amount of work to be performed is proportional to the size of the matrix to the third power (n^3). All of these factors prompted us to explore other approaches which are less demanding of memory and CPU operations.

The approach we have developed has much in common with the Lanczos[5,6] and direct configuration interaction methods[7-10] which have been so successful in quantum chemistry and are related to other iterative-variational schemes.[11-13] The idea is quite simple: iterative formation of a vector space to expand the solution of the equation. The convergence of the method depends on the technique used to generate the iterates. However, for a matrix of order n, we are guaranteed that the iteration will converge to the correct solution after at most n iterations, provided we can maintain numerical linear independence of the iterates. In order for the method to be practical, convergence must be more rapid since the number of multiplications will exceed that of the direct $\underline{L}$-$\underline{U}$ factorization if too many iterations are required. The coefficients of the basis vectors are determined by substituting the expansion into the original equation and projecting onto the vectors. This is equivalent to a least-squares solution using the iterates as the linear variational functions. The method works quite well and, while specifically applied to several cases of electron scattering from molecules, should be of value to many other areas of atomic and molecular physics. In the next section, we discuss the basic principles behind the technique and derive the most important equations and algorithims. We follow this by a section on applications of the method to electron scattering from N_2, LiH, and H_2^+.

II. GENERAL FORMULATION

A. Linear algebraic equations

Many of the formalisms describing the scattering of an electron by an atom or molecule reduce to a set of coupled, radial second-order integro-differential equations of the form

$$L_\alpha \psi_{\alpha\alpha_0}(R) = \sum_{\beta=1}^{n_c} \int_0^\infty W_{\alpha\beta}(R \mid R')\psi_{\beta\alpha_0}(R')dR' , \quad (1)$$

where

$$L_\alpha = \frac{d^2}{dR^2} - l_\alpha(l_\alpha+1)R^{-2} + k_\alpha^2 \quad (2a)$$

and

$$W_{\alpha\beta}(R \mid R') = V_{\alpha\beta}(R)\delta(R-R') + K_{\alpha\beta}(R \mid R') . \quad (2b)$$

The solution $\psi_{\alpha\alpha_0}(R)$ represents the radial scattering wave function in a given channel α for a particular linearly independent solution α_0. In deriving Eq. (1), we have invoked the close-coupling approximation by which the expansion is truncated at a finite number of channels n_c. The orbital angular momentum (energy) of the scattered electron in channel α is given by l_α (k_α^2). We have deliberately left the definition of the channel index α general so as to encompass many different scattering cases. For example, for electronic excitation in molecules, the index would contain a reference to the target-state quantum numbers as well as to the orbital angular momentum and symmetry of the associated scattering function. We have divided the "potential" W into a local and nonlocal part. The local term usually represents the static or direct coupling, while the nonlocal part may contain contributions from exchange and polarization-correlation effects.

The standard prescription we have employed in the past[1-4] to solve Eq. (1) is to convert it to a set of coupled integral equations of the form

$$\psi_{\alpha\alpha_0}(R)=\psi_\alpha^0(R)\delta_{\alpha\alpha_0}+\sum_{\beta=1}^{n_c}+\int_0^\infty G_\alpha^0(R\mid R')\int_0^\infty W_{\alpha\beta}(R'\mid R'')\psi_{\beta\alpha_0}(R'')dR'\,dR'' . \tag{3}$$

where

$$L_\alpha\psi_\alpha^0(R)=0 , \tag{4a}$$

$$\psi_\alpha^0(0)=0 , \tag{4b}$$

$$L_\alpha G_\alpha^0(R\mid R')=\delta(R-R') . \tag{4c}$$

In this formulation, G_α^0 is the free-particle Green's function and is given as a product of a regular (Bessel) and irregular (Neumann) function for the open channels. In some cases, we have found that the generalized R matrix $g_{\alpha\beta}(R\mid a)$, given by

$$\psi_{\alpha\alpha_0}(R)=\sum_\beta g_{\alpha\beta}(R\mid a)\left.\frac{\partial\psi_{\beta\alpha_0}}{\partial R}\right|_{R=a}$$

is more appropriate. This function satisfies an integral equation of the same form as Eq. (3) and yields the standard R matrix at $R=a$.

We transform Eq. (3) to a set of linear algebraic (LA) equations by introducing a discrete quadrature of n_p points for the integrals and functions. With some slight rearrangement, we obtain the following set of LA equations:[1,3]

$$\sum_{\beta,j}M_{\alpha i,\beta j}\psi_{\beta\alpha_0}(j)=\psi_\alpha^0(i)\delta_{\alpha\alpha_0} , \tag{5}$$

where

$$M_{\alpha i,\beta j}=\delta_{ij}\delta_{\alpha\beta}-W_{\alpha i,\beta j} , \tag{6}$$

$$W_{\alpha i,\beta j}=G_\alpha^0(i\mid j)V_{\alpha\beta}(j)w_j+\sum_{k=1}^{n_p}G_\alpha^0(i\mid k)K_{\alpha\beta}(k\mid j)w_k w_j ,$$

and w_i is a quadrature weight. The order ($N_0=n_c n_p$) of the LA equations is the product of the number of radial mesh points (n_p) and the number of channels (n_c). We generally choose a Gauss-Legendre quadrature since this insures an economy of points with a high degree of accuracy. Other schemes, such as the trapezoidal and Simpson's-rule[3] schemes, have also been explored as well as various Newton-Cotes prescriptions.[14]

We may express Eq. (5) in a compact matrix form as

$$\underline{M}\boldsymbol{\psi}=\boldsymbol{\psi}^0 , \tag{7}$$

where $\underline{M}$ is a matrix of order $N_0=n_c n_p$ and $\boldsymbol{\psi}$ ($\boldsymbol{\psi}^0$) is a vector of length N_0 elements. In other words, we define

$$(\boldsymbol{\psi})_{i\alpha_0}=\psi_{\alpha\alpha_0}(j) ,$$

where

$$i=(\alpha-1)n_p+j .$$

For this treatment, we have assumed that the number of radial mesh points n_p is the same for each channel. As we have shown, this restriction can be relaxed to allow a different mesh for each scattering channel. In fact, for converging single-center expansions about the molecular nuclei such a scheme is necessary in order to reduce the LA equations to a manageable size. The following iterative-variational prescriptions are amenable to this more general treatment; however, for pedagogical reasons, we shall employ a single radial mesh.

In the past, we have solved Eq. (7) by standard $\underline{L}$-$\underline{U}$ factorization techniques. Since such prescriptions can take full advantage of the vector architecture of the new generation of computers, we have witnessed large savings of times, sometimes as much as a factor of 15 over the scalar mode. Such gains in efficiency have made the LA approach viable for a large class of scattering problems. Despite these advantages, we have found several drawbacks to the current approach. First, in order to take the fullest advantage of the $\underline{L}$-$\underline{U}$ prescription, we must keep the full matrix $\underline{M}$ in central memory. Since typical electron-molecule scattering problems at the static-exchange level require $\underline{M}$ to be of the order of 500 to several thousand, the storage requirements can tax even the largest computers. We have circumvented this problem to some extent by employing partitioning schemes[1,3] for $\underline{M}$. While effective in reducing the requirements for central memory, these procedures rely on regular or solid-state disks, which reduce the efficiency of the $\underline{L}$-$\underline{U}$ factorization. In addition, for matrices of such large orders, the solution times are not insignificant. Therefore, prescriptions that reduce the memory requirements as well as improve the solution time are most desirable.

B. Iterative-variational schemes

The problems mentioned in the previous section can be largely overcome by invoking various iterative-variational

schemes. These prescriptions are at the heart of the direct configuration interaction (CI) methods of quantum chemistry, although they have their antecedents in the Lanczos[5,6] and conjugate-gradient methods.[15] We divide this section into two parts. In the first part, we consider the solution of a general set of LA equations given by Eq. (7). While this derivation will illustrate the basic concepts behind the iterative-variational prescription, it does not present the most efficient formulation for a scattering problem. The formulation in the first part requires a matrix-vector multiplication and thus does not relieve the large storage requirements discussed earlier. In the second part, we show how the equation can be recast in order to reduce the storage to the Green's function, the potential, and the solution array. This reformulation not only reduces the needed memory but also makes a great gain in computational time.

1. General matrix

We seek to solve the following LA system represented by the matrix equation

$$\underline{M}\mathbf{X}=\mathbf{b} , \tag{8}$$

where $\underline{M}$ is a matrix of order N_0 and $\mathbf{X}$ ($\mathbf{b}$) is a vector with N_0 elements. The vector $\mathbf{X}$ represents a single solution $\{\psi_{\alpha\alpha_0}(i) \mid \alpha=1,\ldots,n_c;\ i=1,\ldots,n_p\}$. We must solve Eq. (8) n_c times to generate the complete set of linearly independent solutions. We propose to effect the solution to Eq. (8) through an iterative-variational prescription. We generate a set of m ($\leq N_0$) orthonormal (linearly independent) vectors $\{\boldsymbol{\alpha}_i \mid i=1,\ldots,m\}$ by successive applications of the matrix $\underline{M}$ to an initial guess for the solution vector $\mathbf{X}$. The orthonormality of the vectors are guaranteed by employing the Gram-Schmidt technique. At a particular iteration m for a given set of vectors $\{\boldsymbol{\alpha}_i \mid i=1,\ldots,m\}$, we expand the solution in terms of a linear combination of the generated basis. We then invoke a variational prescription to determine the unknown linear expansion coefficients. The procedure is repeated until successive solutions agree to within a given tolerance. Owing to the fact that the basis we construct is orthonormal, we are guaranteed a solution in N_0 iterations since the generated vectors will completely span the space. For practical applications we obtain convergence in far fewer than N_0 iterations. This is a distinct advantage of the method over other iterative prescriptions such as the Gauss-Seidel, which has no guaranteed convergence limit.

We first present a description of the iterative and variational parts separately and then demonstrate how they can be combined into an effective method. We start the iterative procedure with an initial guess

$$\boldsymbol{\beta}_1=\mathbf{g} . \tag{9}$$

We may choose $\mathbf{g}$ to be any reasonable representation of the final solution. However, the better the initial guess the faster the convergence. In electron scattering problems, we typically begin with the Born solution although other guesses based on simple model potentials may prove more efficacious. We then generate a normalized vector $\boldsymbol{\alpha}_1$ by

$$\boldsymbol{\alpha}_1=\boldsymbol{\beta}_1/O_1 ,$$

where $O_i=(\boldsymbol{\alpha}_i \mid \boldsymbol{\alpha}_i)^{1/2}$. We have used the (|) notation to represent a scalar product,

$$(\boldsymbol{\alpha}_i \mid \boldsymbol{\beta}_j)=\sum_{k=1}^{n} \alpha_{ki}\beta_{kj} ,$$

where k is a sum over the elements of vectors $\boldsymbol{\alpha}_i$ and $\boldsymbol{\beta}_i$. We now construct a new vector by applying the matrix to $\boldsymbol{\alpha}_1$ as

$$\boldsymbol{\beta}_2=\underline{M}\boldsymbol{\alpha}_1 .$$

We generate a normalized vector orthogonal to $\boldsymbol{\alpha}_1$ by invoking the Gram-Schmidt scheme

$$\boldsymbol{\alpha}_2'=\boldsymbol{\beta}_2-(\boldsymbol{\alpha}_1 \mid \boldsymbol{\beta}_2)\boldsymbol{\alpha}_1 ,$$

$$\boldsymbol{\alpha}_2=\boldsymbol{\alpha}_2'/O_2 .$$

This process is repeated until convergence is reached. For a general iteration m, we have

$$\begin{aligned}\boldsymbol{\beta}_m&=\underline{M}\boldsymbol{\alpha}_{m-1} ,\\ \boldsymbol{\alpha}_m'&=\boldsymbol{\beta}_m-\sum_{j=1}^{m-1}(\boldsymbol{\alpha}_j \mid \boldsymbol{\beta}_m)\boldsymbol{\alpha}_j ,\\ \boldsymbol{\alpha}_m&=\boldsymbol{\alpha}_m'/O_m .\end{aligned} \tag{10}$$

This procedure produces a set of linearly independent, orthonormal vectors $\{\boldsymbol{\alpha}_i \mid i=1,\ldots,m\}$ such that

$$(\boldsymbol{\alpha}_i \mid \boldsymbol{\beta}_j)=\delta_{ij} \quad \text{for } i,j\leq m .$$

At a given iteration m, we perform a variational calculation in order to determine the best form of the vector solution in terms of the basis described in the previous paragraph. We consider a trial solution of the form

$$\mathbf{X}_m^t=\sum_{i=1}^{m} a_i\boldsymbol{\alpha}_i . \tag{11}$$

We seek to vary the linear coefficients a_i so as to obtain the "best" representation in terms of the basis. Several prescriptions are available to perform this task; all lead to the same result. The simplest scheme is based on the Galerkin approach, which considers the following expression:

$$F=\langle \mathbf{X}_m^t \mid M \mid \mathbf{X}_m^t\rangle-\langle \mathbf{X}_m^t \mid \mathbf{b}\rangle . \tag{12}$$

If $\mathbf{X}_m^t$ were a solution to Eq. (8), then F would be zero. Following the Galerkin scheme, we substitute Eq. (11) into Eq. (12) and demand that

$$F=\sum_i a_i \sum_j a_j(\boldsymbol{\alpha}_i \mid M \mid \boldsymbol{\alpha}_j)-\sum_i a_i(\boldsymbol{\alpha}_i \mid \mathbf{b})=0 . \tag{13}$$

A necessary and sufficient condition for this equation to be satisfied for all of the linearly independent coefficients a_i is

$$\sum_{j=1}^{m} A_{ij}a_j=b_i \quad \text{for all } i , \tag{14}$$

where $A_{ij}=(\alpha_i \mid M \mid \alpha_j)=(\alpha_i \mid \beta_{j+1})$ and $b_i=(\alpha_i \mid \mathbf{b})$. Thus, the linear coefficients a_j that solve Eq. (14) will guarantee that Eq. (13) is satisfied. A similar set of LA equations can be derived from a least-squares formulation. In this case, we can show that Eq. (14) guarantees a minimum in the square of the error $\epsilon=\underline{M}\mathbf{X}_m^t-\mathbf{b}$. We note that Eq. (14) is of the order of the *number of iterations,* not of the original system of LA equations. We solve Eq. (14) for the linear coefficients by standard techniques.

At any iteration m, we therefore have a set of orthonormal vectors $\{\alpha_i \mid i=1,\ldots,m\}$ generated by the iterative process described above, and a set of linear coefficients $\{a_i \mid i=1,\ldots,m\}$ of the expansion of the solution vector in terms of the iterative basis. From these two sets, we construct the solution vector $\mathbf{X}_m$ by Eq. (11) and in turn calculate the error vector $\epsilon_m=\underline{M}\mathbf{X}_m^t-\mathbf{b}$. If this error vector is within some tolerance, we terminate the procedure and declare $\mathbf{X}_m$ the solution; if not, we perform another iteration. Rather than using the error vector as a criterion, we usually employ a measure of the relative error given by the ratio of the maximum value of ϵ to the maximum value of $\mathbf{X}_m$. One last important point is in order. The standard $\underline{L}$-$\underline{U}$ factorization prescription requires N_0^3 operations while the iterative-variational scheme needs only mN_0^2, where m is the number of iterations. As long as $m \ll N_0$, the new procedure requires far less computational time than the $\underline{L}$-$\underline{U}$ scheme. For matrices of the order of 500—1000 associated with scattering problems, we typically find m to be between 10 and 20, thus providing a substantial savings in computational time.

As pointed out before, this prescription illustrates the main features of the iterative-variational approach. However, since a matrix-vector multiplication is needed at each iteration and since such an operation is most efficient when the full matrix can be stored in central memory, the procedure does not lend itself straightforwardly to very large systems. In addition, more efficient procedures for manipulating the matrix can be devised as will be seen in the next section.

2. *Direct form*

We now return to Eq. (5) in a slightly modified form where we explicitly depict the wave function as

$$\psi_{\alpha\alpha_0}(i)=\psi^0_{\alpha\alpha_0}(i)\delta_{\alpha\alpha_0}+\sum_{\beta,j} W_{\alpha\beta}(i \mid j)\psi_{\beta\alpha_0}(j) . \tag{15}$$

The iterative-variational prescription proceeds much as in the previous section except that the iterates are generated from $\underline{W}$ rather than the full matrix $\underline{M}$ as

$$\chi^n_{\alpha\alpha_0}(i)=\sum_{\beta,j} W_{\alpha\beta}(i \mid j)\hat{\chi}^{n-1}_{\beta\alpha_0}(j) , \tag{16}$$

where the caret denotes a normalized vector

$$\sum_{\beta,j} \hat{\chi}^{n}_{\beta\alpha_0}(j)\hat{\chi}^{n'}_{\beta\alpha_0}(j)w_j=\delta_{nn'} . \tag{17}$$

Equation (18) can be written in supermatrix form as

$$\chi^n=\underline{W}\hat{\chi}^{n-1} , \tag{18}$$

where χ^n ($\hat{\chi}^{n-1}$) is a vector of length $N_0=n_c n_p$, and $\underline{W}$ is a matrix of order N_0. Thus, just as described in the previous section, the iterates may be generated by a matrix-vector multiplication. The number of storage locations and multiplications to accomplish this is proportional to N_0^2. The iterates are used to construct an orthonormal basis $\{\hat{\chi}^n \mid n=1,\ldots,m\}$ in which the solution vector is expanded [Eq. (11)]. The linear coefficients of this expansion are then determined by a variational prescription [Eq. (13)]. We recall that we must repeat the full iterative procedure for each linearly independent solution α_0. At this juncture we appear to have reconstructed the method of the previous section in a slightly different form.

Provided the number of iterates can be kept smaller than N_0, the method can be quite powerful. In actual applications, the matrix must be stored in central memory or read from disk in reasonably large blocks to vectorize Eq. (16) efficiently. When the matrix must be read from disk many times the input-output operations can be large and dominate the calculation. In the direct CI methods, which have been developed to extract eigenvalues and eigenvectors of very large (10^6) matrices, the matrix is not stored but calculated as needed for each iteration. An interesting question arises as to whether a similar approach can be used in the scattering problem. For purposes of this demonstration, we consider single-channel ($n_c=1$) scattering. If we specialize the kernel to

$$W(i \mid j)=G^0(i \mid j)V(j)w_j , \tag{19a}$$

where

$$G^0(i \mid j)=R(i)I(j), \quad i<j \tag{19b}$$

$$=R(j)I(i), \quad i>j \tag{19c}$$

and $R(I)$ is the regular (irregular) solution to the free-particle Hamiltonian, we may write Eq. (16) as

$$\chi^n(i)=I(i)\sum_{j(\le i)} R(j)w_j V(j)\hat{\chi}^{n-1}(j) + R(i)\sum_{j(>i)} I(j)w_j V(j)\hat{\chi}^{n-1}(j) . \tag{20}$$

We define two partial sums as

$$A_i=\sum_{j\le i} R(j)w_j V(j)\hat{\chi}^{n-1}(j) , \tag{21a}$$

$$B_i=\sum_{j(>i)} I(j)w_j V(j)\hat{\chi}^{n-1}(j) . \tag{21b}$$

These sums may be computed by recursion as

$$A_i=A_{i-1}+R(i)w_i V(i)\hat{\chi}^{n-1}(i) , \tag{22a}$$

$$B_i=B_{i-1}+I(i)w_i V(i)\hat{\chi}^{n-1}(i) . \tag{22b}$$

We must use the recursion relation downward in Eq. (22b) since the irregular solution grows quite large at small radial distances. The similarity of Eqs. (22) to the fundamental approach used in the noniterative integral equation methods developed much earlier[16–20] is striking. However, the noniterative methods only contain forward summations. This corresponds to a solution of the integral equa-

tions with different boundary conditions than those of the scattering problem. Since the irregular solution of the unperturbed problem and the unknown wave function appear in these summations, we cannot use recursion in the backward direction and must numerically stabilize the outward integration process by performing $\underline{L}$-$\underline{U}$ decomposition of the solution matrix. This corresponds to a reselection of the initial conditions of the integration. Unfortunately, the stabilization process is an n_c^3 procedure, where n_c is the number of coupled channels. In our iteration-variation approach, the backward recurrence may be performed directly since a known vector appears under the summation sign. Thus each iteration of our process is equivalent to the noniterative integral equation method *without* stabilization. This is quite efficient and in addition does not require the matrix to be formed and stored. Only the unperturbed regular and irregular solutions, the potential matrix, the iterates, and the small set of matrix equations are stored in central memory. Thus the entire process can be formulated within the central memory, and input-output times are drastically reduced. Unfortunately, the recursion process does not readily yield to vector optimization, and the gain in speed on the Cray or Cyber 205 is not comparable to the matrix multiplication. However, the gain obtained for the small number of iterations ($m \ll N_0$) more than compensates for this drawback.

Before turning to some specific examples, we offer a few further remarks. Since in the multichannel version of Eq. (22) the partial sums contain channel labels, we must be a little more careful with the recursion. As long as the integration mesh is the same for every channel there is no difficulty. If the mesh is not the same, we must place one or more conditional (IF) statements in the recursion loop. Since this slows down the calculation, the authors would caution others of this approach without a thorough investigation of their particular problem.

C. Born series

Before leaving this section, we remark on the relationship between the Born series over a finite radial range and the iterative-variational scheme proposed in Sec. II B 2. The Born series is also constructed by successive substitutions of approximate solutions into the general integral equation form (3). Since we consider a finite range for the potential, we shall employ Eq. (15) rather than (3) in order to demonstrate the procedure. In addition, we have employed a discrete quadrature for the integral. The zeroth-order Born approximation is just the plane-wave solution $\psi^0_{\alpha\alpha_0}$, and the first-order correction is found by substituting the free-wave solution for the exact solution in Eq. (15):

$$\psi^{\mathrm{I}}_{\alpha_0}=\psi^0_{\alpha_0}+\underline{W}^0\psi^0_{\alpha_0}\,, \tag{23a}$$

where ψ_{α_0} is a vector of order N_0 labeled by a specific linearly independent solution α_0. The second correction is formed by reintroducing ψ^{I} into Eq. (15) as

$$\psi^{\mathrm{II}}_{\alpha_0}=\psi^0_{\alpha_0}+\underline{W}\psi^{\mathrm{I}}_{\alpha_0}\,, \tag{23b}$$

or

$$\psi^{\mathrm{II}}_{\alpha_0}=\psi^0_{\alpha_0}+\underline{W}\psi^0_{\alpha_0}+\underline{W}\underline{W}\psi^0_{\alpha_0}\,. \tag{23c}$$

We note that the higher-order corrections in the Born series can be constructed from successive applications of the matrix $\underline{W}$ to the initial guess $\psi^0_{\alpha_0}$ just as in the iterative-variational scheme. The application of the orthonormality condition and the variational prescription does not alter this basic formulation—only the relative weights given to the successive iterates. However, we shall demonstrate in the next section that the plane-wave solution is a rather poor starting point for the iterative-variational scheme.

III. RESULTS AND DISCUSSION

In this section, we demonstrate the efficacy of the iterative-variational approach for a wide class of electron-molecule collision problems. We consider elastic scattering from both homonuclear and polar systems as well as inelastic excitation in $H_2{}^+$. We consider scattering only from the direct or static potential; however, the formalism can be easily generalized to incorporate nonlocal terms. While confining our attention to electron-molecule scattering, we wish to emphasize the applicability of this technique to many other scattering cases including electronic and atomic collisions.

A. N_2

We treat $^2\Sigma_g$ elastic scattering of electrons from the nitrogen molecule N_2 in the static approximation within the LA iterative-variational scheme. We use a single-center expansion of ten channels ($n_c=10$), which includes angular momentum up to $l=18$, and a mesh of 50 points ($n_p=50$). We distribute these points according to a Gauss-Legendre quadrature as follows: ten from $R=0.0a_0$ to $0.7a_0$, 20 from $0.7a_0$ to $1.5a_0$, 10 from $1.5a_0$ to $2.5a_0$, and 10 from $2.5a_0$ to $10.0a_0$ (10, 20, 10, 10; 0.0–0.7, 0.7–1.5, 1.5–2.5, 2.5–10.0). We utilize the near-Hartree-Fock target wave function of Cade, Sales, and Wahl[21] and include in the determination of the static potential all allowed values of l.

In Figs. 1–3, we present the dependence of several channel wave functions $g^i_{ll_0}(R)$ on the radial distance R for several iterations for the first linearly independent solution $l_0=0$ at $k^2=0.1$ Ry. We consider the first ($l=0$), second ($l=2$), and fifth ($l=8$) channels and also display the first (– – –), second (○), fourth (–·–·–), fifth (△), sixth (×), and final converged (——) iterations. We shall for clarity maintain this labeling of the iterates throughout this and the next section. We note that in all three cases the initial guess of the plane-wave solution $\psi^0_{ll_0}$ is rather poor. The method slowly corrects for this deficiency in the next few iterations and then suddenly makes a large departure on the third substitution. After this large correction, the procedure then approaches the converged result fairly smoothly. The interesting and important point to observe is that, even though the initial guess is poor, the method is self-corrective and eventually

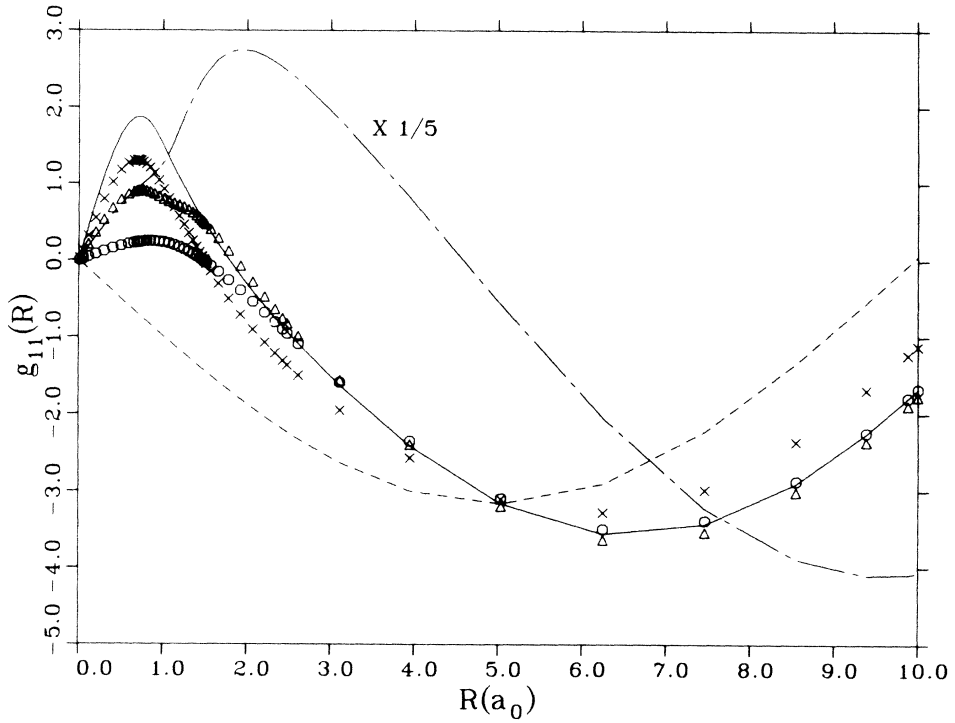

FIG. 1. Radial solution as a function of iteration for e-N_2 $^2\Sigma_g$ scattering at $k^2=0.1$ Ry in the static approximation for lowest channel ($l=0$) for the first linearly independent solution. Nomenclature for iterates: 1 (— — —), 2 (○), 4 (—·—·—), 5 (△), 6 (×), and 15 converged result (——).

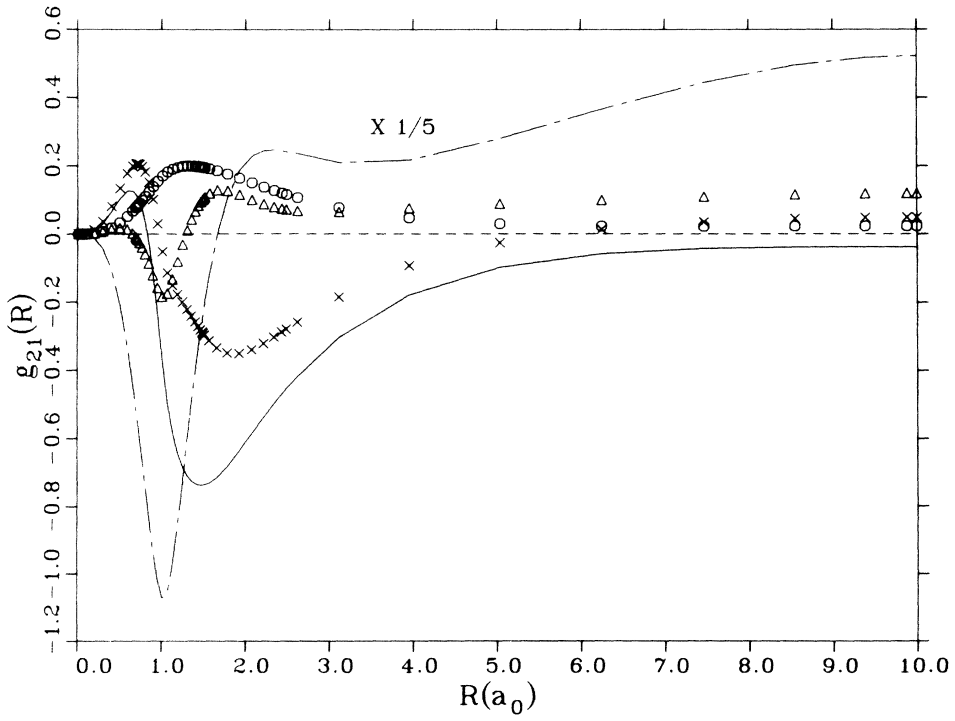

FIG. 2. Same as Fig. 1 except for the second channel ($l=2$).

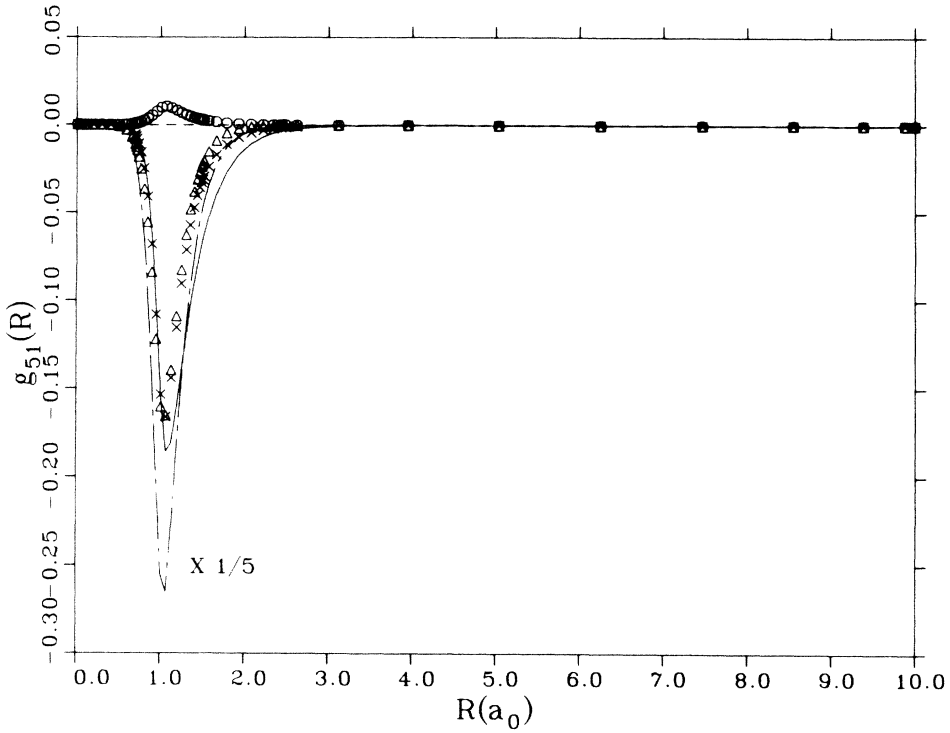

FIG. 3. Same as Fig. 1 except for the fifth channel ($l=8$).

adjusts and converges to the correct result. We present a summary of the convergence as a function of iteration in Table I. We have found similar trends for N_2 for energies from $k^2=0.01$ to 1.0 Ry with convergence occurring in about the same number of iterations.

B. LiH

We further demonstrate the iterative-variational technique by treating electron scattering from the strongly polar system LiH ($D=6.0$ debye) in the static approximation. We have performed the calculations with the following parameters: $n_c=6$, $n_p=55$, mesh (15, 20, 10, 10; 0.0–0.5, 0.5–2.5, 2.5–10.0, 10.0–15.0), and a Gauss-Legendre quadrature in each region. We employed the target LiH wave function of Cade and Huo[22] and treated the $^2\Sigma$ scattering symmetry. The labeling scheme for the iterates is the same as for N_2 except that the crosses represent the seventh rather than the sixth iteration. We list in Table II a summary of the convergence pattern.

In Figs. 4–6, we present several channel solutions $[g^i_{l_0}(R)]$ as a function of the radial variable R for various iterations i for the first linearly independent solution ($l_0=0$) at a scattering energy of 0.10 Ry. We note again that the initial plane-wave guess is rather poor, in fact being in error by over an order of magnitude for the first channel ($l=0$). Since the outer radial region is dominated by dipole coupling while the inner part is influenced by the nuclear singularities at $R=0.38a_0$ and $2.64a_0$, the iterative solutions must adjust to both regimes. We note

TABLE I. Convergence trend for static $^2\Sigma_g$ e-N_2 scattering at $k^2=0.10$ Ry and a tolerance in the maximum error of 10^{-10}.

Independent solution (l_0)	Number of iterations
0	16
2	16
4	14
6	13
8	11
10	9
12	5
14	3
16	3
18	3

TABLE II. Convergence trend for static $^2\Sigma$ e-LiH scattering at $k^2=0.10$ Ry and a tolerance of 10^{-10}.

Independent solution (l_0)	Number of iterations
0	18
1	18
2	17
3	17
4	17
5	17

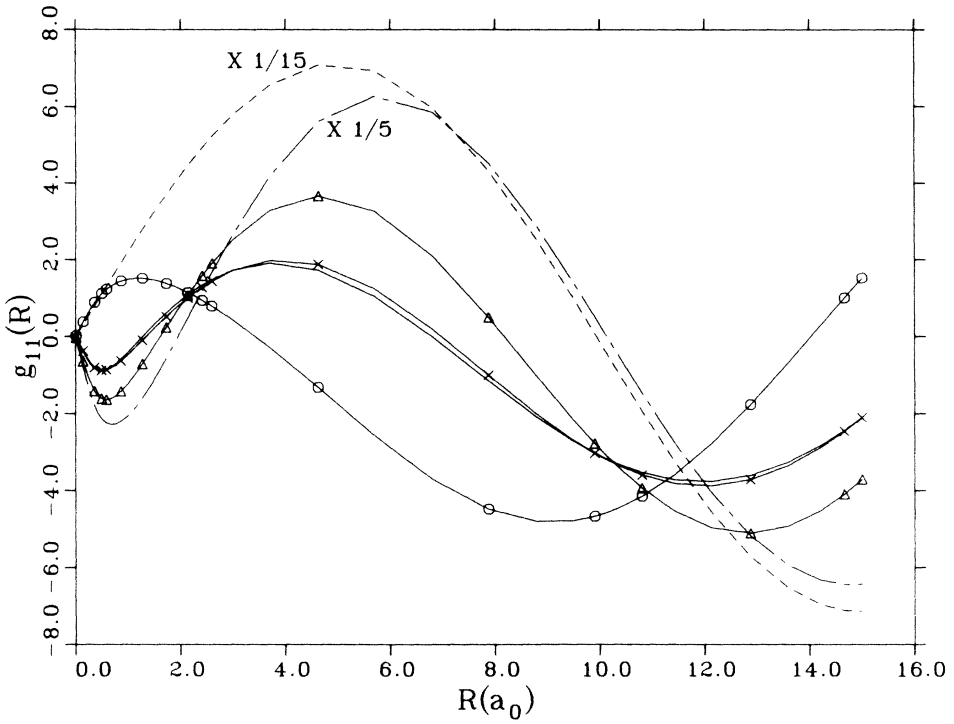

FIG. 4. Radial solution as a function of iteration for e-LiH $^2\Sigma$ scattering at $k^2=0.1$ Ry in the static approximation for the lowest channel ($l=0$) and first linearly independent solution. Nomenclature for iterates: 1 (— — —), 2 (○), 4 (—·—·—), 5 (△), 7 (×), and 17 converged result (——).

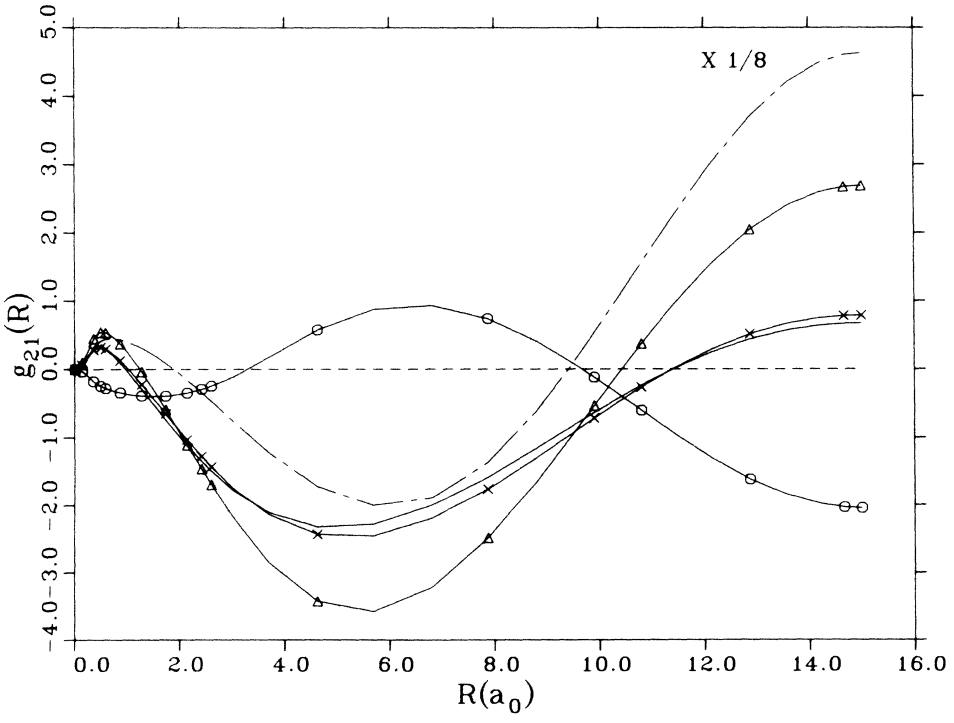

FIG. 5. Same as Fig. 4 except for the second channel ($l=1$).

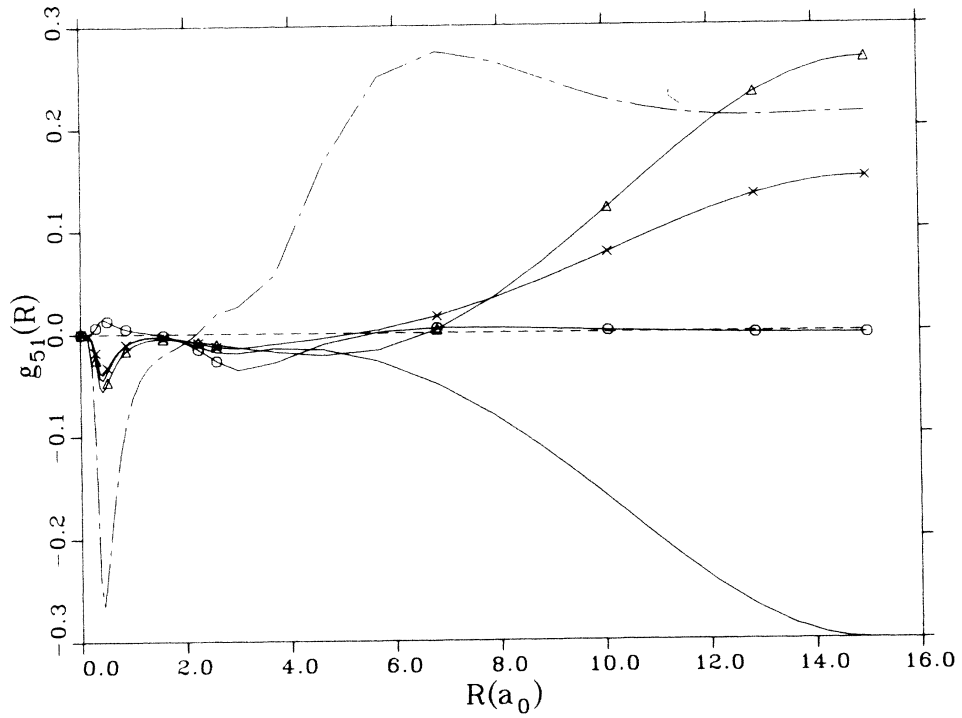

FIG. 6. Same as Fig. 4 except for the fifth channel ($l=4$).

that the convergence in the inner, nuclear-dominated region is faster. Once a good result is obtained in this zone, the solution then systematically improves in the outer, dipole region. We once again observe the versatility of the procedure to compensate for a poor initial guess and home in on a solution, which has very different radial behavior in two rather distinct coupling regimes. Such trends also hold at other energies and other symmetries for this system.

In order to provide a more dramatic illustration of the ability of our approach to obtain the correct solution given a poor initial guess, we have plotted some three-dimensional color graphs of the electron density in Figs. 7 and 8. The plots, which were done for the first and second linearly independent solutions, show how the solution to the scattering equation changes with iteration number for an energy of 0.10 Ry. The figures were made using the program camera developed by M. Prueitt of Los Alamos National Laboratory. In each of the frames of the figures, the size of the box enclosing the electron density is the same. This was done to give the viewer a sense of the scale over which the wave function is changing with iteration. It is quite apparent that some violent changes occur in the initial phases of the iteration before the solution settles down to its converged value. This behavior has been seen in other systems such as N_2 and at other energies. In all of the cases studied, it was possible to obtain highly accurate solutions provided enough iterations were used.

C. H_2^+

In this section, we apply the iterative-variational method to inelastic scattering of electrons by H_2^+. We invoke a two-state $(1\sigma_g, 1\sigma_u)$ close-coupling formulation with three partial waves in each state ($n_c=6$) and consider only direct or static coupling. We use a mesh of 50 points ($n_p=50$) distributed over four subregions (10, 20, 10, 15; 0.0—0.5, 0.5—1.5, 1.5—3.0, 3.0—10.0). In Tables III and IV, we present selected R-matrix elements as a function of the independent solution (IS) and the iteration (IT) for 0.9 and 2.0 Ry, respectively. The channels are labeled by the state (s) and the orbital angular momentum (l_s) of the incident electron. The state labels are $s=1$ (2) for $1\sigma_g$ ($1\sigma_u$). The R matrix is defined by the following convention:

$$f_{\alpha\alpha_0}(\alpha)=\sum \mathscr{R}_{\alpha\alpha'}\frac{\partial f_{\alpha'\alpha_0}}{\partial R}\bigg|_{R=a},$$

where a is the matching radius and α is given by (s,l_s). For the H_2^+ calculations, we have selected a to be $10a_0$. The R matrix is in turn related to the reactance matrix (K) and to the cross section.

We notice that the R-matrix elements displayed in Tables III and IV exhibit similar behavior as a function of iteration as the wave functions for elastic scattering. At an early iteration, we observe a large jump in $\mathscr{R}$ followed by a smooth convergence to the correct result. These

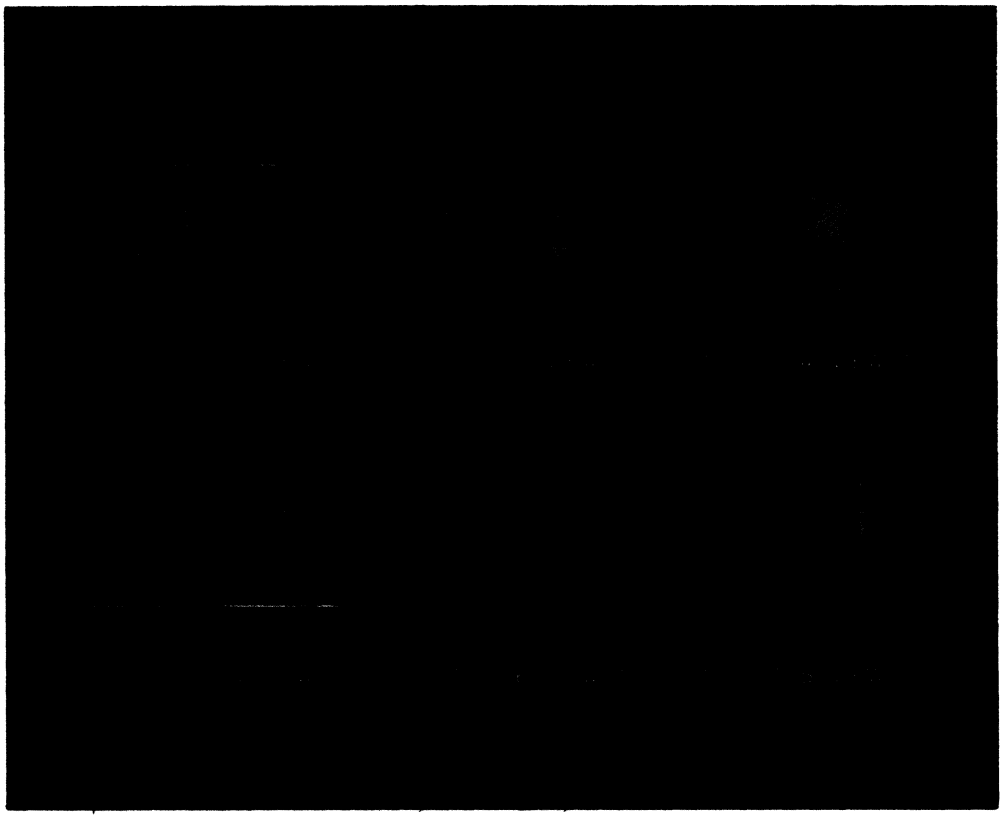

FIG. 7. First linearly independent solution for e + LiH $^2\Sigma$ scattering at an energy of 0.1 Ry as a function of the number of iterates.

FIG. 8. Same as Fig. 7 for second linearly independent solution.

TABLE III. R-matrix elements as a function of iteration (IT) and independent solution (IS) for e-H_2^+ $^1\Sigma_g$ scattering in the 2CC ($1\sigma_g, 1\sigma_u$) approximation for an energy of 0.9 Ry. Channels are designated by (s,l_s), where s labels the electronic state and l_s the orbital angular momentum within s. Numbers in parentheses give powers of 10 [$(-1)=10^{-1}$].

		Channel labels (s,l_s)			
IS	IT-1	(1,0)	(1,2)	(2,1)	(2,5)
1	0	3.757(−1)	0.000(0)	0.000(0)	0.000(0)
	1	−2.077(−2)	3.897(−1)	1.662(−1)	9.474(−7)
	2	5.427(−2)	−1.005(−1)	−1.213(−2)	6.578(−6)
	3	1.192(−1)	8.348(−2)	−5.374(−2)	−4.418(−6)
	4	1.023(−1)	−6.072(−2)	−7.284(−2)	1.314(−5)
	5	1.041(−1)	−5.997(−2)	−7.625(−2)	8.678(−6)
	8	1.050(−1)	−6.049(−2)	−7.582(−2)	−1.196(−5)
	12	1.050(−1)	−6.049(−2)	−7.584(−2)	−1.228(−5)
4	0	0.000(0)	0.000(0)	−1.253(0)	0.000(0)
	1	2.664(−1)	7.509(−1)	4.227(−1)	1.873(−4)
	2	−9.138(−2)	6.252(−1)	8.625(−1)	5.731(−4)
	3	−7.790(−2)	5.190(−1)	9.876(−1)	5.228(−4)
	6	−7.558(−2)	5.336(−1)	9.650(−1)	6.883(−4)
	12	−7.584(−2)	5.339(−1)	9.652(−1)	6.955(−4)

cases for H_2^+ once again demonstrate the power of the iterative-variational approach to recover properly from a poor initial guess and the probable enhancement to convergence afforded by a better first solution.

IV. SUMMARY

We have developed a direct iterative-variational prescription for solving large sets of linear algebraic equations associated with a wide variety of scattering problems. The method has several advantages over the standard $\underline{L}$-$\underline{U}$ factorization procedure. First, the method requires mN_0 operations, where m is the number of iterations, as opposed to N_0^3 for the $\underline{L}$-$\underline{U}$ factorization. Since m is much less than N_0, the method yields substantial savings in computational time for large matrices. Second, only a small number of arrays need be stored at any time,

TABLE IV. R-matrix elements as a function of iteration and independent solution for e-H_2^+ $^1\Sigma_g$ scattering at 2.0 Ry in the 2CC approximation. Nomenclature as in Table III. Numbers in parentheses give powers of 10 [$(-1)=10^{-1}$].

		(s,l_s)			
IS	IT-1				
1	0	1.352(0)	0.000(0)	0.000(0)	0.000(0)
	1	5.389(−1)	−4.091(−1)	−1.478(−1)	−6.004(−6)
	2	5.633(−1)	−4.577(−2)	4.466(−2)	2.651(−4)
	3	6.413(−1)	−7.891(−2)	9.565(−2)	4.782(−5)
	4	6.658(−1)	−7.436(−2)	9.331(−2)	2.288(−4)
	6	6.645(−1)	−7.737(−2)	8.360(−2)	1.742(−5)
	8	6.647(−1)	−7.705(−2)	8.366(−2)	6.312(−5)
	12	6.647(−1)	−7.705(−2)	8.366(−2)	6.402(−5)
4	0	0.000(0)	0.000(0)	−1.202(0)	0.00(0)
	1	1.916(−1)	−1.744(−1)	−3.009(−1)	9.155(−4)
	2	1.173(−2)	−2.289(−1)	−1.475(−1)	1.203(−3)
	3	6.870(−2)	−1.899(−1)	−1.105(−1)	1.727(−3)
	4	8.116(−2)	−1.827(−1)	−1.177(−1)	2.441(−3)
	6	8.359(−2)	−1.853(−1)	−1.157(−1)	2.437(−3)
	8	8.366(−2)	−1.854(−1)	−1.159(−1)	2.361(−3)
	12	8.366(−2)	−1.854(−1)	−1.159(−1)	2.360(−3)

thus drastically reducing the central memory requirements. The efficacy of the method has been demonstrated for several types of electron-molecule collisions.

ACKNOWLEDGMENTS

We wish to acknowledge useful conversations and suggestions by Dr. A. L. Merts and Dr. P. W. Saxe. We especially wish to thank Dr. Merts for his suggestions regarding the variational prescriptions and the relationship of the method to the Born series. We also wish to thank Dr. Saxe for his recommendations relating to the direct methods. This work was performed under the auspices of the U.S. Department of Energy through the Theoretical Division of the Los Alamos National Laboratory.

[1]B. I. Schneider and L. A. Collins, Phys. Rev. A **24**, 1264 (1981).
[2]B. I. Schneider and L. A. Collins, Phys. Rev. A **27**, 2847 (1983).
[3]L. A. Collins and B. I. Schneider, Phys. Rev. A **24**, 2387 (1981).
[4]L. A. Collins and B. I. Schneider, J. Phys. B **17**, L235 (1984).
[5]C. Lanczos, J. Res. Nat. Bur. Stand. **45**, 255 (1950).
[6]C. Lanczos, J. Res. Nat. Bur. Stand. **49**, 33 (1952).
[7]B. Roos, Chem. Phys. Lett. **15**, 153 (1972).
[8]P. E. M. Siegbahn, J. Chem. Phys. **70**, 5391 (1979).
[9]B. Liu and M. Yoshimine, J. Chem. Phys. **74**, 612 (1981).
[10]H. Lischka, R. Shepard, F. B. Brown, and I. Shavitt, Int. J. Quantum Chem. Symp. **15**, 91 (1981).
[11]H. E. Saraph and M. J. Seaton, Proc. Phys. Soc. London **80**, 1057 (1962).
[12]V. B. Sheorey, Proc. Phys. Soc. London **92**, 531 (1967).
[13]J. P. Coleman, J. Phys. B **9**, 1079 (1976).
[14]D. H. Oza and J. Callaway, Phys. Rev. A **32**, 2534 (1985).
[15]D. K. Fadeev and V. N. Fadeeva, *Computational Methods of Linear Algebra* (Freeman, London, 1963).
[16]W. N. Sams and D. J. Kouri, J. Chem. Phys. **51**, 4809 (1969).
[17]W. N. Sams and D. J. Kouri, J. Chem. Phys. **51**, 4815 (1969).
[18]M. A. Morrison, N. F. Lane, and L. A. Collins, Phys. Rev. A **15**, 2186 (1977).
[19]T. N. Rescigno and A. E. Orel, Phys. Rev. A **24**, 1267 (1981).
[20]N. T. Padial and D. W. Norcross (unpublished).
[21]P. E. Cade, K. D. Sales, and A. C. Wahl, J. Chem. Phys. **44**, 1973 (1966).
[22]P. E. Cade and W. M. Huo, J. Chem. Phys. **47**, 614 (1967).

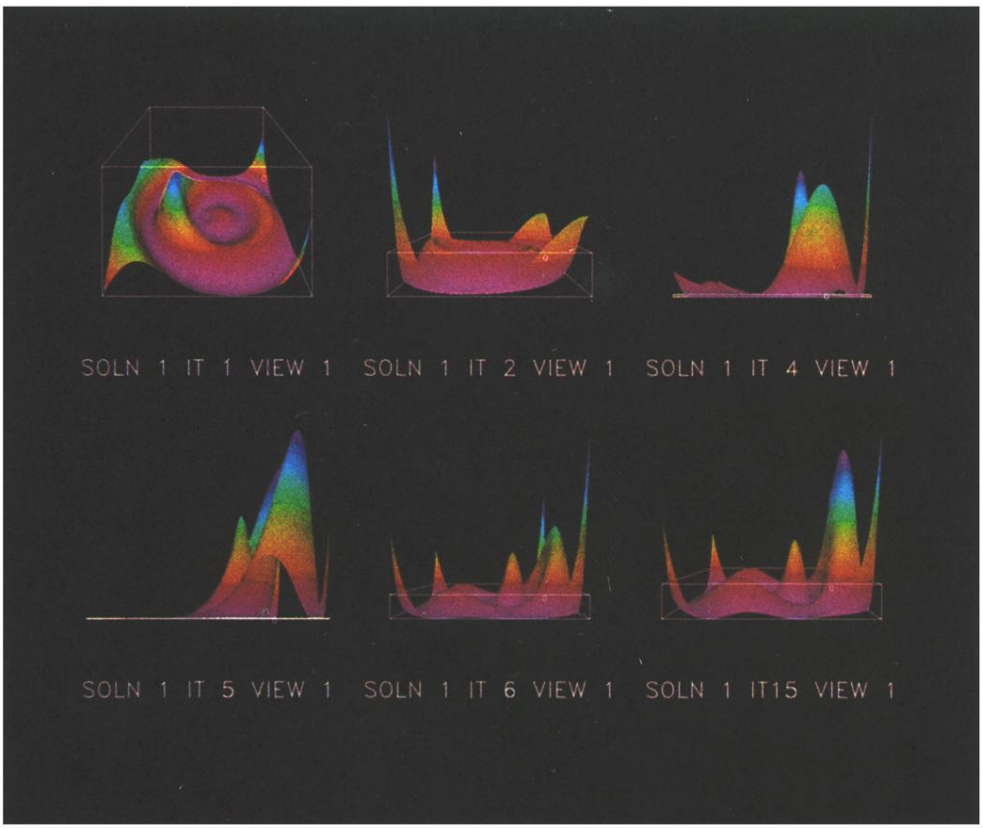

FIG. 7. First linearly independent solution for e + LiH $^2\Sigma$ scattering at an energy of 0.1 Ry as a function of the number of iterates.

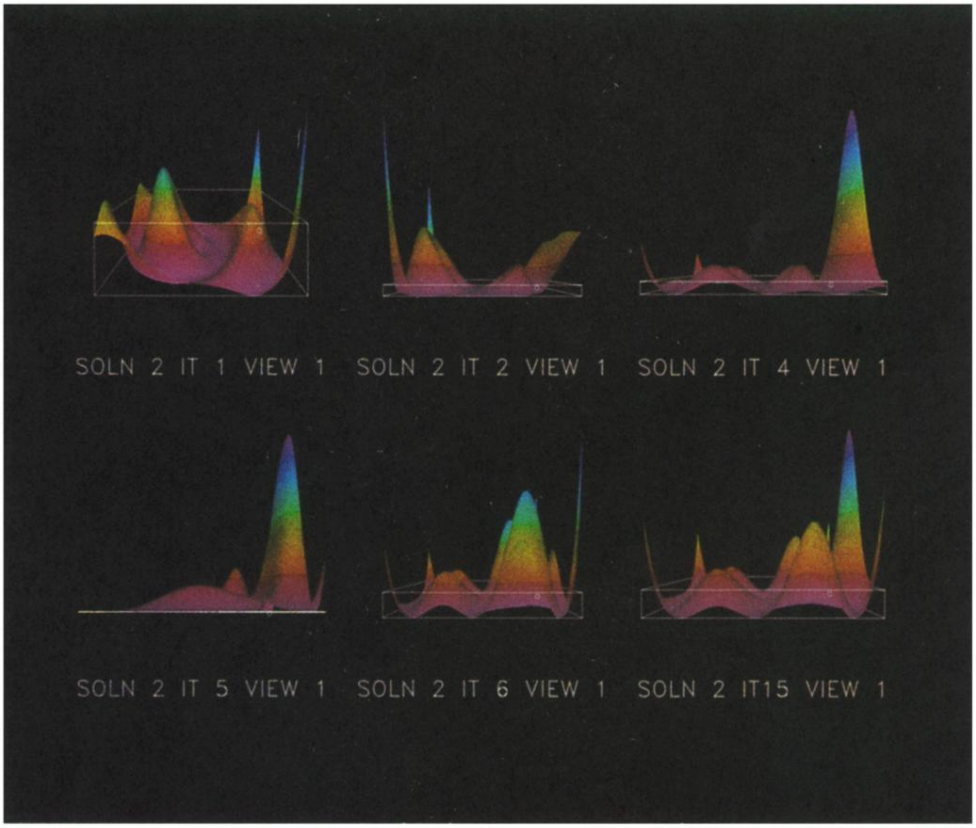

FIG. 8. Same as Fig. 7 for second linearly independent solution.