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Generalization of the linear algebraic method to three dimensions

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We present a numerical method for the solution of the Lippmann-Schwinger equation for electron-molecule collisions. By performing a three-dimensional numerical quadrature, this approach avoids both a basis-set representation of the wave function and a partial-wave expansion of the scattering potential. The resulting linear equations, analogous in form to the one-dimensional linear algebraic method, are solved with the direct iteration-variation method. Several numerical examples are presented. The prospect for using this numerical quadrature scheme for electron-polyatomic molecules is discussed.

INTRODUCTION

Low-energy electron-molecule collisions are important in many processes;[1] e.g., modeling planetary atmospheres, gas-discharge lasers, and low-temperature plasma physics. Accurate and reliable methods for obtaining the scattering cross sections are necessary for such modeling efforts. For collisions with linear molecules various theoretical and numerical approaches have been developed including the linear algebraic method,[2] the Schwinger-variational method,[3] and the R-matrix method.[4] In general, these techniques rely on a decomposition of the scattering potential, the continuum wave function, and/or the scattering amplitude into spherical harmonics. However, the extensions of these approaches to nonlinear systems have been slow due to the loss of cylindrical symmetry which substantially increases the difficulty for a numerical solution of the electron-molecule collisional equations.

The study of electron-polyatomic molecule scattering introduces many inherently interesting features absent or substantially reduced in the linear molecule analogs. These include a richer electronic structure and a more dynamical interplay between the electronic and nuclear degrees of freedom. Recently several *ab initio* techniques, e.g., the Schwinger multichannel method[3,5] (SMC) and the complex Kohn method[6] (CKM), have been developed, refined, and applied to a variety of systems, e.g., NH_3,[7] CH_4,[8,9] H_2CO,[10] and H_2O.[11] In both of these variational methods the wave function is expanded in a basis set and matrix elements that contain either the Green's function (SMC) or the Hamiltonian (CKM) are computed. Early applications of the SMC relied on a spectral decomposition of the Green's function using finite, L^2 (Gaussian) basis sets. Due to the slow convergence of this expansion with respect to the Gaussian basis set, this procedure has now been replaced by a three-dimensional, numerical quadrature in momentum space.[8(c)] These results as well as earlier studies[12] for solving the integral scattering equation in momentum space have demonstrated the efficiency of such multidimensional numerical methods in electron-scattering problems.

In order to investigate multidimensional quadrature schemes in coordinate space we have developed a three-dimensional (3D) numerical method for solving the electron-molecule collisional equations. In this procedure the Lippmann-Schwinger integral equation is cast into a set of linear algebraic equations by introduction of a 3D quadrature. The resulting large set of linear equations are then solved by the direct iteration-variation method.[13] This approach is a straightforward generalization of the one-dimensional linear algebraic method,[2] where the angular degrees of freedom are handled analytically through a partial-wave expansion. One advantage of this 3D approach is the ability to avoid a basis-set expansion of the scattering wave function and potential. However, basis-set expansions of the complicated, nonlocal portions of the scattering potential may still be implemented.

Although the primary goal of this work is application to molecular systems, we have first performed scattering calculations with model spherical potentials in order to investigate the feasibility of this 3D numerical method. The first potential chosen is the following attractive exponential potential: $V(r)=-e^{-r}$, where accurate results are available for comparison.[14] Since the Green's function is represented in its 3D form, even this spherical potential requires a full 3D treatment. Therefore these calculations provide meaningful tests for the 3D grid driven linear algebraic method (LAM). In addition to the exponential potential the K matrix for s-wave scattering from the long-range model potential $V(r)=-(1-e^{-r})^2/r^3$ was also calculated. This potential, $V(r) \underset{r\to\infty}{\longrightarrow} -1/r^3$, has an asymptotic behavior characteristic of long-range potentials which can dominate low-energy electron-molecule collisions.[15] Such potentials are quite difficult to represent using L^2 basis sets and thus represent a critical test of our new approach.

In the following sections the method, its implementation, and drawbacks are discussed. Results for the model systems and the potential such direct 3D numerical methods hold are analyzed.

3D LINEAR ALGEBRAIC METHOD

The Schrödinger equation governing potential scattering processes can be replaced with an equivalent integral equation, i.e., the Lippmann-Schwinger equation, given by

$$\phi_{\mathbf{k}}(\mathbf{r})=\phi_{\mathbf{k}}^{0}(\mathbf{r})+\int G^{0}(\mathbf{r}|\mathbf{r}')U(\mathbf{r}')\phi_{\mathbf{k}}(\mathbf{r}')d\mathbf{r}' \ , \tag{1}$$

where $U(\mathbf{r})$ is the scattering potential and for simplicity we restrict the analysis to local potentials. In Eq. (1) k^2 is the kinetic energy of the electron, $\phi_{\mathbf{k}}^{0}(\mathbf{r})$ is the plane-wave solution of the homogeneous equation,

$$\phi_{\mathbf{k}}^{0}(\mathbf{r})=(1/2\pi)^{3/2}e^{i\mathbf{k}\cdot\mathbf{r}} \ , \tag{2}$$

and $G^{0}(\mathbf{r}|\mathbf{r}')$ is the 3D principal-value free-particle Green's function given by

$$G^{0}(\mathbf{r}|\mathbf{r}')=-\frac{\cos(k|\mathbf{r}-\mathbf{r}'|)}{4\pi|\mathbf{r}-\mathbf{r}'|} \ . \tag{3}$$

The solution of Eq. (1) provides the full scattering wave function and amplitude. For many cases of interest, i.e., low-energy electron-molecule collisions, only a small number of angular momentum states contribute to the scattering. We therefore cast Eq. (1) into its partial-wave form,

$$\phi_{klm}(\mathbf{r})=\phi_{klm}^{0}(\mathbf{r})+\int G^{0}(\mathbf{r}|\mathbf{r}')U(\mathbf{r}')\phi_{klm}^{0}(\mathbf{r})d\mathbf{r}' \ , \tag{4}$$

where the homogeneous solution $\phi_{klm}^{0}(\mathbf{r})$ is constructed from a product of a regular spherical Bessel function (j_l) and a spherical harmonic,

$$\phi_{klm}^{0}=j_l(kr)Y_{lm}(\Omega_r) \ . \tag{5}$$

Equation (4) is then solved for the relatively small number of asymptotically important waves. Although in some applications it may be more convenient to treat the full Lippmann-Schwinger equation, we consider here the solution of the partial-wave form, i.e., Eq. (4). However, rather than expanding the wave function, Green's function, and scattering potential in spherical harmonics and then numerically solving the coupled radial equations, we introduce a 3D quadrature directly into the integral equation. This quadrature converts the integral in Eq. (4) to a summation and produces the following set of linear equations:

$$\phi_{klm}(i)=\phi_{klm}^{0}(i)+\sum_{j} G^{0}(i|j)U(j)\phi_{klm}(j)\omega_j \ , \tag{6}$$

where j is a point in coordinate space and ω_j is the jth weight of the quadrature. This weight is a product of the r, θ, and ϕ quadrature weights. The central feature of this approach is that the large number of partial waves necessary to converge the expansion of the scattering potential is circumvented.

At first sight the presence of the on-diagonal $G^{0}(i|i)$ term in Eq. (6) is of some concern since at $j=i$ the denominator of the Green's function approaches 0. In practice, as discussed more thoroughly below, one can simply drop the $j=i$ term from the summation. However, this singularity can be strictly removed by adding and subtracting to Eq. (4) the following function:[16]

$$U(\mathbf{r})\phi_{klm}(\mathbf{r})\int G^{0}(\mathbf{r}|\mathbf{r}')e^{-\alpha|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \ . \tag{7}$$

The integral in Eq. (7) can be done analytically and equals $-(a^2-k^2)/(a^2+k^2)^2$. The introduction of this function into Eq. (4) modifies the on-diagonal terms, removes the singularity, and produces

$$\begin{aligned}\phi_{klm}(i)=\phi_{klm}^{0}(i)-U(i)\phi_{klm}(i)&\left[\frac{\alpha^2-k^2}{(\alpha^2+k^2)^2}\right]\\ &+\sum_{j\,(\neq i)} G^{0}(i|j)\omega_j[U(j)\phi_{klm}(j)\\ &\qquad -U(i)\phi_{klm}(i)e^{-\alpha|i-j|}] \ .\end{aligned} \tag{8}$$

Equation (8) can be written as a set of linear equations,

$$(1+M)\phi=\phi^{0} \ , \tag{9}$$

where the matrix M is given by

$$M_{ii}=U(i)\frac{\alpha^2-k^2}{(\alpha^2+k^2)^2}-U(i)\sum_{j\,(\neq i)} G^{0}(i|j)\omega_j e^{-\alpha|i-j|} \tag{10}$$

and

$$M_{ij}=G^{0}(i|j)\omega_j U(j) \ . \tag{11}$$

Equation (9) is of the same form as the one-dimensional (1D) linear algebraic method and can be solved by standard LU decomposition. However, the size of the vectors ϕ and ϕ^0 and the matrix M is often so large (1000–10000) that LU decomposition becomes prohibitive. Therefore the direct iteration-variation method[13] is used for these large sets of linear equations. The matrix M is not formed or stored, but generated as needed in the iteration process. The details of this technique and the similarities to direct configuration-interaction approaches and the Lanczos method are well documented in the literature.[13] The solutions are the scattering wave function $\phi_{klm}(\mathbf{r})$, from which the K matrix, or other scattering quantities such as the cross sections and angular distributions, can be obtained.

Results obtained from Eq. (8) must be independent of the chosen value of α since the α-dependent terms formally cancel. Incomplete cancellation of the added terms leads to quantities, such as the K matrix, which vary with α and indicate that the numerical quadrature is not converged. Therefore α independence of the solutions to Eq. (8) provides a useful check on the accuracy of the numerical quadratures. It is useful to note that in the limit $\alpha\rightarrow\infty$, $M_{ii}\rightarrow 0$ since

$$\frac{\alpha^2-k^2}{(\alpha^2+k^2)^2}\xrightarrow[\alpha\rightarrow\infty]{}0 \ , \tag{12}$$

and

$$e^{-\alpha|i-j|}\xrightarrow[\alpha\rightarrow\infty]{}0 \quad (j\neq i) \ . \tag{13}$$

This limit in effect allows one to simply remove the $j=i$ term in the summation in Eq. (6).

A few comments are necessary on the spherically symmetric model potentials presently under study. Even when U is spherically symmetric the use of the 3D form of the Green's function in Eq. (3) requires that the quadrature be performed in 3D. In fact, since we are interested in relevant test cases for the 3D linear algebraic method we not not want to invoke any possible simplifications based on the symmetry of these model potentials. For example, the standard approach is to perform a partial-wave expansion of the Green's function,

$$G^0(\mathbf{r}|\mathbf{r}')=-k\sum_l j_l(kr_<)\eta_l(kr_>)Y_{lm}(\Omega_r)Y^*_{lm}(\Omega_{r'}) , \tag{14}$$

where j_l (η_l) is the regular (irregular) spherical Bessel (Neumann) function. Due to the spherical symmetry of the scattering potential the wave function is also spherically symmetric and the angular integrations of Eq. (4) reduce to

$$\sum_{l,m}\int Y^*_{lm}(\Omega_{r'})Y_{00}(\Omega_{r'})d\Omega_{r'}=\delta_{l0}\delta_{m0} , \tag{15}$$

with numerical quadrature required only for the radial coordinate. For spherical and even cylindrically symmetric potentials this procedure is reasonably efficient and results in the standard 1D linear algebraic method.[2] In addition, it is of interest to note that the use of the 3D form of G^0 for spherical potentials implies that a numerical calculation of the δ functions in Eq. (15) is performed.

RESULTS AND DISCUSSION

The first case studied is the numerical evaluation of the following test integral over the Green's function:

$$I=\frac{1}{4\pi}\int\frac{\cos(k|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}e^{-\beta|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' . \tag{16}$$

This integral is independent of $\mathbf{r}$ and can be evaluated analytically, e.g.,

$$I=\frac{\beta^2-k^2}{(\beta^2+k^2)^2} . \tag{17}$$

For example, with $\beta=1$ and $k=0.15$ I equals 0.9349. In Table I the results for performing this integral numerically for $|\mathbf{r}|=0$ and 1 are reported. The radial and θ integrations are performed using a Gauss-Legendre quadrature while Simpson's rule is used for the ϕ integrations. For $\mathbf{r}=0$, where $|\mathbf{r}-\mathbf{r}'|=|\mathbf{r}'|$, the angular integrations are not necessary and a 30 point radial grid gives the analytical results to four figures. Alternately the θ and ϕ quadratures can be explicitly performed, which amounts to a numerical calculation of the angular volume element (4π). The grid used for this calculation is presented in Table I. Again four figure agreement with the analytic value is obtained. The results for $|\mathbf{r}|=1$, using the two grids reported in Table I demonstrate that adequate quadratures are necessary to obtain reliable numerical integration. For example, using a larger number of grid points (7840 versus 2680 points) produces an integration error that is less than 0.1%.

TABLE I. Test integral. The grid is chosen as follows: The radial coordinate is blocked into three regions as indicated in the second column. For each region the number of r, θ, and ϕ quadrature points are indicated in the third column. $k=0.15$, $\beta=1$.

$\|\mathbf{r}\|$	$\|\mathbf{r}'\|$ range	Number of points r'	θ'	ϕ'	I
0	0–2	10	15	15	0.9349
	2–5	10	6	7	
	5–10	10	1	1	
1	0–2	10	15	15	0.8859
	2–5	10	6	7	
	5–10	10	1	1	
1	0–2	30	15	15	0.9344
	2–5	10	10	10	
	5–10	10	3	3	

TABLE II. α dependence of the K matrix for $V(r)=-e^{-r}$.

α value	Number of points[a]	$\tan\delta$
1.0	3267	-1.647
10.0		-1.741
1 000.0		-1.733
1.0	4239	-1.765
10.0		-1.735
1 000.0		-1.728
10 000.0		-1.728
Remove singular term[b]	4239	-1.728
Accurate value[c]		-1.744

[a] The 3267 point grid was chosen as follows: There are three radial segments which span $r=0\rightarrow1.0$, $1.0\rightarrow2.5$, and $2.5\rightarrow5.0$ a.u. Each segment contains 9 radial, 11 θ, and 11 ϕ quadrature points. The 4239 point grid was generated by augmenting the 3267 point grid with a fourth shell containing 12 radial ($5.0\rightarrow15.0$ a.u.), 9 θ, and 9 ϕ quadrature points.

[b] Drop the $j=i$ term in Eq. (8).

[c] Reference 6.

The first potential used in these studies is $V(r)=-e^{-r}$. The s-wave K-matrix results for $k=0.15$ are presented in Table II. Two grids were used and are described in detail in the table. Using the smaller grid (3267 points) the results depend on α at about the 5% level. The K-matrix

TABLE III. K matrix for s-wave scattering from $V(r)=-e^{-r}$.

Energy (Ry)	3D LAM[a]	1D LAM	Accurate value[b]
0.0225	-1.728	-1.736	-1.7449
0.1225	9.4052	9.2503	9.0918
0.3025	2.2343	2.2089	2.2004

[a] Please see footnote b in Table II for a description of the grid.

[b] Reference 6.

TABLE IV. K matrix for s-wave scattering from $V(r)=-(1-e^{-r})^2/r^3$.

Energy (Ry)	3D LAM	Complex Kohn[a]	Kapur-Peierls[a]
0.0225	−0.8033	−0.7891	−0.7967
0.1225	−3.1618	−3.1025	−3.1204
0.3025[b]	1.5604	1.5650	1.5640

[a] Reference 6.

[b] The phase shifts δ are reported rather than the K matrix. For this energy $\delta \approx \pi/2$ and small deviations in δ produce large fluctuations in the K matrix, $K=\tan\delta$.

elements using this grid are in much better agreement with the results reported in Ref. 6 when larger α values are chosen. This deviation of the lower α $(=1)$ solutions is most likely a result of incomplete cancellation of the α-dependent terms in Eq. (8). Indeed this dependence is reduced, to about 2%, by using the larger grid (4240 points) and indicates that the integrations are being performed with high accuracy. Therefore with sufficient grids the calculations become α independent. In order to avoid the error introduced by incomplete cancellation of the α-dependent terms, the following studies were performed in the $\alpha \rightarrow \infty$ limit, i.e., simply drop the $j=i$ term in Eq. (6).

In Table III results for s-wave scattering from the exponential potential for several kinetic energies are reported and compared to the standard 1D linear algebraic method. In the latter case the form of the Green's function is given by Eq. (14) and the angular integrations are performed analytically with the radial integrations done numerically. The radial grids, see footnote b in Table II, are identical in the two calculations. As seen in Table III the differences in the K matrix between the 1D and 3D linear algebraic method are less than 2%, indicating reasonable convergence for the angular integrations. In addition, we compare our calculations to the CKM results and the values reported in Ref. 6 with about a 3.5% difference between these calculations. In fact, it is only for $\varepsilon=0.1225$ that the error is at the 3.5% level.

Finally, since long-range potentials such as Q/r^3 and α_0/r^4 (Q represents the quadrupole moment, α_0 represents the polarizability) play such an important role in low-energy electron scattering, we have investigated scattering from $V(r)=-(1-e^{-r})^2/r^3$. One might expect that both basis-set and numerical methods, which must sample regions of space where the potential is nonnegligible, would have more difficulty treating such long-range potentials. In Table IV the present results for the s-wave K matrix are reported. In these calculations the r variable is truncated at 30 a.u. with a total of 5210 grid points used. The α dependence for the K matrix is approximately equal to 1% for $\varepsilon=0.0225$ and approximately equal to 2% for $\varepsilon=0.1255$. At $\varepsilon=0.3025$ the phase shift δ is nearly $\pi/2$ and therefore small variations in δ cause large deviations in the K matrix, $K=\tan\delta$. For this energy we report the phase shifts which have an α dependence that is less than 1%. Comparisons to both the complex Kohn and Kapur-Peierls results[6] indicate that our results are in good agreement with the earlier studies and in general are adequately converged.

At this point several comments should be made about the viability of applying the 3D linear algebraic method to molecular systems. First, the time-consuming step in these calculations is the evaluation of the special functions, e.g., the square root, cosine, and exponential functions in Eq. (8), which must be performed during each iteration. The solution of the linear equations via the direct iteration-variation method is a small fraction of the total CPU. Therefore the demonstration that calculations using the $\alpha \rightarrow \infty$ limit can be employed is very helpful. In this case evaluation of the exponential terms is not necessary and the total computation time is reduced by nearly a third. In addition preliminary studies indicate that a considerable savings of CPU can be obtained by using interpolation schemes for the Green's function. This would make the 3D approach competitive with other methods. Clearly the use of a grid with as few points as possible is highly desirable. Second, the systems studied here do not contain nuclear centers where the potential has large variations with r. In these regions many points are required for an accurate representation of the potential. No attempts were made in this initial study to optimize the grid. One could construct a multiple origin grid similar to muffin-tin approaches,[17] where each atom is enclosed in a sphere, thereby substantially reducing the total number of grid points. Such an approach has been used by Cohen and Struensee[18] in an entirely different context but would clearly be useful here as well. Overall, the preliminary studies for the 3D linear algebraic method are quite encouraging. The numerical results are of very good accuracy for both short- and long-range potentials. The extension of these studies to molecular systems is currently in progress.

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