

Discrete-basis-function approach to electron-molecule scattering

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The authors discuss two discrete-basis-function approaches to the solution of the T -matrix equations for the scattering of electrons by atoms or molecules. Both methods, one of which is based on the Schwinger variational principle, have major advantages over the previously proposed T -matrix methods and do not require large-basis-set expansions. Results are reported for s - and p -wave scattering for helium.

I. INTRODUCTION

There has been increasing interest in adapting the discrete-basis-function expansion techniques of quantum chemistry to the solution of problems in electron-molecule scattering. This has been stimulated by the difficulties encountered in the straightforward extension of the traditional numerical methods developed in electron-atom scattering to molecular problems. Moreover, the discrete basis functions can be very effective in describing the important short-range effects of nonspherical molecular potentials. These approaches include the R -matrix method used by Schneider for H_2 , N_2 , and F_2 ¹⁻³ and the T -matrix method introduced by Rescigno, McCurdy and McKoy^{4,5} and applied to H_2 , N_2 , and CO .⁶⁻⁹ In particular the T -matrix method uses an N -term separable potential of the form

$$V^t = \sum_{\alpha\beta} |\alpha\rangle V_{\alpha\beta} \langle\beta|, \quad (1)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the Cartesian Gaussian functions. While this approach effectively accounts for the coupling of angular momentum by the nonspherical potential without resorting to partial wave expansions and numerical integrations, it results in the loss of point by point stability which numerical methods enjoy. First-order errors in the cross sections arise which are proportional to the difference $V - V^t$, where V is the exact potential and V^t is the $N \times N$ separable approximation [Eq. (1)]. Even with reasonable basis sets these first-order errors are found to be important for nonspherical systems such as N_2 ⁷ and for dipolar systems.⁹ This is very apparent at low momenta. To correct these first-order errors generally involves solving for an approximate wave function which can then be used in conjunction with one of the variational principles to obtain a stable cross section. For example, in the T -matrix approach a Kato-type correction term which requires the evaluation of bound-free and free-free matrix elements of the potential

has been developed.^{5,8} This procedure is obviously more time consuming than the evaluation of the initial L^2 cross section which requires only bound-bound matrix elements.

The purpose of this study is to investigate ways to reduce the errors introduced by the use of this type of separable potential [Eq. (1)] in the solution of the T matrix. This is a particularly simple choice for the separable expansion of a potential and we will see that other more effective choices can be made. We will take advantage of the fact that the bound-free and free-free matrix elements of the potential needed for the new approaches can be evaluated analytically. The proposed methods provide in a single step phase shifts free from first-order errors and include some higher-order corrections which may be important. We present here two new discrete basis function approaches for calculating phase shifts.

II. THEORY

The Lippmann-Schwinger equation for the transition matrix is

$$T = U + UG_0^+T, \quad (2)$$

where U is twice the potential, V , for the effective interaction between the target and the incident electron and G_0^+ is the free-particle Green's function for the outgoing wave boundary condition. To solve this equation Rescigno, McCurdy, and McKoy⁴ assumed a separable approximation for the potential of the form

$$U^t(\vec{r}, \vec{r}') = \sum_{\alpha\beta} |\phi_\alpha(\vec{r})\rangle \langle\phi_\alpha(\vec{r})| U(\vec{r}, \vec{r}') |\phi_\beta(\vec{r}')\rangle \langle\phi_\beta(\vec{r}')|, \quad (3)$$

where $|\phi_\alpha\rangle$ and $|\phi_\beta\rangle$ are Cartesian Gaussian functions of the form

$$\phi_\alpha(\vec{r}) \equiv |\alpha\rangle = N_{lmn} (x - A_x)^l (y - A_y)^m \times (z - A_z)^n e^{-\alpha|\vec{r} - \vec{A}|^2}. \quad (4)$$

The vector \vec{A} locates the basis function center and N_{lmn} is a normalization factor.

A separable potential in the Lippmann-Schwinger equation results in a separable kernel allowing one to solve a finite matrix equation for T ,

$$T^t = U^t + U^t G_0^t T^t, \quad T^t = (1 - U^t G_0^t)^{-1} U^t, \quad (5)$$

by a simple matrix inversion. The on-shell T matrix is obtained by the transformation

$$\langle \vec{k}' | T^t | \vec{k} \rangle = \sum_{\alpha\beta} \langle \vec{k}' | \alpha \rangle \langle \alpha | T^t | \beta \rangle \langle \beta | \vec{k} \rangle. \quad (6)$$

T^t possesses nonvanishing matrix elements only in the L^2 subspace defined by V^t , thus this approximation to the T matrix is the exact solution in this subspace. If one is able to use a sufficiently large set of square-integrable functions to define an adequate subspace, the errors due to the truncation of the potential can be small. Unfortunately, the problem is not one of simply increasing the size of the basis set used in the expansion of Eq. (3), since problems of linear dependence arise if the basis sets become too large. The Kato correction which requires bound-free and free-free matrix elements of the potential essentially corrects for the finiteness of the L^2 subspace.

A. Schwinger method

There are other methods of constructing separable potentials which can be used to obtain separable kernels in the Lippmann-Schwinger equation.¹⁰ One method which has been widely used in nuclear¹¹⁻¹⁸ physics uses a separable potential of the form

$$V^s = \sum_{m,n} V |f_m\rangle [d^{-1}]_{m,n} \langle f_n | V, \quad (7)$$

where $d_{m,n} = \langle f_m | V | f_n \rangle$ and $|f_m\rangle$ is an arbitrary expansion function. Substitution of this expression into the Lippmann-Schwinger equation yields

$$T^s = \sum_{m,n} U |f_m\rangle [(U - UG_0U)^{-1}]_{m,n} \langle f_n | U. \quad (8)$$

This is an exact expression for the T matrix corresponding to the potential V^s . The on-shell representation of T^s is

$$\langle \vec{k}' | T^s | \vec{k} \rangle = \sum_{m,n} \langle \vec{k}' | U | f_m \rangle [(U - UG_0U)^{-1}]_{m,n} \times \langle f_n | U | \vec{k} \rangle. \quad (9)$$

This form for a separable potential is of particular interest because of its relation to the Schwinger variational principle. Adhikari and Sloan¹⁶ have shown that a separable potential of this form in

the Lippmann-Schwinger equation results in an expression for the T matrix which is identical to that obtained from the Schwinger variational expression,

$$\langle \vec{k}' | T | \vec{k} \rangle = \langle \vec{k}' | U | \psi_{\vec{k}}^+ \rangle + \langle \psi_{\vec{k}}^- | U | \vec{k} \rangle - \langle \psi_{\vec{k}}^- | U - UG_0U | \psi_{\vec{k}}^+ \rangle, \quad (10)$$

with the trial wave functions

$$|\psi_{\vec{k}}^+\rangle = \sum_n a_n(\vec{k}) |f_n\rangle, \quad \langle \psi_{\vec{k}}^-| = \sum_n \langle f_n | b_n(\vec{k}). \quad (11)$$

The barrier to the use of this method in atomic and molecular problems has been the evaluation of the term containing G_0 which appears in the denominator. For realistic atomic and molecular potentials this is extremely difficult to evaluate exactly without resorting to numerical integrations. In our application of this method we evaluate this term by inserting a complete set of states on either side of G_0 . We use the same set of Cartesian Gaussian functions which are chosen to expand the potential although this is not a requirement and the denominator can now be readily evaluated. The numerator, which involves bound-free integrals of the potential, can be evaluated exactly (Appendix A). The resulting on-shell T matrix, $T^{s'}$, which is our approximation to T^s is

$$\langle \vec{k}' | T^{s'} | \vec{k} \rangle = \sum_{\alpha\beta} \langle \vec{k}' | U | \alpha \rangle [D^{-1}]_{\alpha\beta} \langle \beta | U | \vec{k} \rangle, \quad (12)$$

where $D_{\alpha\beta} = U_{\alpha\beta} - \sum_{\gamma\delta} U_{\alpha\gamma} G_0 \gamma\delta U_{\delta\beta}$ and α, β, γ , and δ refer to Cartesian Gaussian functions.

To understand the relationship between these two separable potentials, V^t and V^s , it is instructive to use projection operators. We follow closely the work of Ernst, Shakin, and Thaler.¹³ Let p project onto the L^2 subspace. i.e.,

$$p = \sum_{\alpha} |\alpha\rangle \langle \alpha|, \quad (13)$$

and define

$$q = 1 - p. \quad (14)$$

All matrix elements of V^t and V^s between states in this subspace will be identical to the matrix elements of the true potential V :

$$V^t = p V p, \quad p V^t p = p^2 V p^2 = p V p; \quad (15)$$

and

$$V^s = V p (p V p)^{-1} p V, \\ p V^s p = p V p (p V p)^{-1} p V p \\ = p V p. \quad (16)$$

Here the similarity ends. All other matrix ele-

ments of V^t vanish:

$$pV^tq = qV^tp = 0, \quad (17)$$

$$qV^tq = 0, \quad (18)$$

while for V^s ,

$$pV^sq = pVq, \quad qV^sp = qVp, \quad (19)$$

$$qV^sq \neq qVq, \quad (20)$$

only the elements qV^sq are different from those of the true potential. This property of V^s , Eq. (19), is taken advantage of when one evaluates the bound-free integrals in Eq. (9). T^s is the exact solution of the Lippmann-Schwinger equation in the larger Hilbert space, $pHp + pHq + qHp$, while T^t is the exact solution in that subspace, pHp , defined by V^t . Clearly the Kato correction to T^t is an attempt to bring in contributions to T^t from the enlarged Hilbert space.

A useful feature of the Schwinger method is the appearance of the wave function (or the expansion functions, f_m) only in conjunction with the potential. This quantity, $V\psi$, which is often called a form factor, generally has smoother behavior than the wave function itself.¹² Blatt and Jackson¹⁹ utilize this feature in their use of the Schwinger variational principle by using expansion functions which represent the wave function correctly only within the range of the potential. This allows the use of trial functions which do not have the correct asymptotic form which is in the spirit of L^2 methods. This advantage is not present in other variational methods such as the Kohn variational method, which requires that the wave function have the correct asymptotic form

B. Full Green's function method

In our second method we consider the following exact expression for T :

$$T = U + UG^*U, \quad (21)$$

where G^* is the full Green's function for the system for the outgoing wave boundary condition. Insertion of a complete set of states on either side of G^* leads to the equation

$$\tilde{T} = U + \sum_{\alpha\beta} U|\alpha\rangle\langle\alpha|G^*|\beta\rangle\langle\beta|U. \quad (22)$$

The on-shell T matrix is

$$\begin{aligned} \langle \vec{k}' | \tilde{T} | \vec{k} \rangle &= \langle \vec{k}' | U | \vec{k} \rangle \\ &+ \sum_{\alpha\beta} \langle \vec{k}' | U | \alpha \rangle \langle \alpha | G^* | \beta \rangle \langle \beta | U | \vec{k} \rangle, \end{aligned} \quad (23)$$

which involves both bound-free and free-free matrix elements of U , and the Gaussian matrix ele-

ments of G^* . The bound-free and free-free matrix elements of U may be obtained in closed form. We now observe that a matrix of G^* in this basis may be obtained by solving the Lippmann-Schwinger equation for G^* ,

$$G^t = G_0^t + G_0^t U^t G^t, \quad G^t = (1 - U^t G_0^t)^{-1} G_0^t \quad (24)$$

in the L^2 subspace in an identical way to the solution of the Lippmann-Schwinger equation for the T matrix, Eq. (5). The use of the truncated potential, U^t , in the solution of G^* does not introduce any first-order errors in the resulting expression for the T matrix as we will show below.

To compare this approximation for the T matrix [Eq. (22)] with the exact T matrix and with T^s , we write the expressions in terms of the uncorrected $L^2 T$ matrix, T^t , plus various correction terms. The exact T matrix satisfies the equation

$$\begin{aligned} T &= U + UGU \\ &= U + (U^t + \Delta U)(G^t + \Delta G)(U^t + \Delta U) \\ &= U^t + U^t G^t U^t + \Delta U + U^t G^t \Delta U + \Delta U G^t U^t \\ &\quad + \Delta U G^t \Delta U + U^t \Delta G \Delta U + \Delta U \Delta G U^t + \Delta U \Delta G \Delta U, \end{aligned} \quad (25)$$

where $\Delta U = U - U^t$ and $\Delta G = G - G^t$. The first two terms are equivalent to the $L^2 T$ matrix as can be easily seen by applying the operator identity

$$GU = G_0 T \quad (26)$$

and comparing to Eq. (5). The remaining terms can be loosely grouped into first-, second-, and third-order terms where we assume that the errors proportional to ΔU and ΔG are comparable. Now comparing this expression to \tilde{T} of Eq. (22),

$$\begin{aligned} \tilde{T} &= U + UG^t U \\ &= U^t + \Delta U + (U^t + \Delta U)G^t(U^t + \Delta U) \\ &= U^t + U^t G^t U^t + \Delta U + U^t G^t \Delta U \\ &\quad + \Delta U G^t U^t + \Delta U G^t \Delta U, \end{aligned} \quad (27)$$

one sees that \tilde{T} includes all first-order corrections to the uncorrected T^t plus one "second-order" term $\Delta U G^t \Delta U$.

A similar analysis of T^s ,

$$\begin{aligned} T^s &= U(U^t - U^t G_0^t U^t)^{-1} U \\ &= UU^{t-1}(1 + U^t G_0^t + U^t G_0^t + \dots)U \\ &= UU^{t-1}U + UG^t U, \end{aligned} \quad (28)$$

shows that T^s differs from \tilde{T} only in its evaluation of the leading Born term. It therefore includes all first-order terms as well as the second-order term $\Delta U G^t \Delta U$. Furthermore, the use of the separable expansion $UU^{t-1}U$ to approximate the

Born term avoids the need to evaluate free-free integrals of the potential which can be important in molecular applications.

III. RESULTS

To ensure unitarity and to avoid working with complex elements in general we work with the corresponding K -matrix equations,

$$\tilde{K} = U + UG^P U \quad (29)$$

$$K^s = U(U^t - U^t G_0^P U^t)^{-1} U, \quad (30)$$

where G_0^P is the principal-value free-particle Green's function, and G^P satisfies the operator identity

$$G^P = G_0^P + G_0^P U G^P. \quad (31)$$

G^P is not the usual principal-value full Green's function (see Ref. 20) in the sense that it does not define the standing wave boundary conditions for the system. However, its matrix representation in the L^2 subspace may be obtained in the usual way by solving Eq. (31) by matrix inversion.

We tested these two methods for electron-helium scattering in the static-exchange approximation. To set up the static exchange potential we expanded the $1s$ orbital in the basis of $5s$ Gaussians given by Huzinaga.²¹ This same basis with no additional s functions was used to describe the s -wave scattering. Two more basis sets composed of two additional diffuse s functions and five additional s functions were also used to investigate the convergence. Six p_z functions were added to the target to describe the p -wave channel. These basis sets are listed in Table I. We kept the basis sets relatively small so as to assess the utility of the methods for larger systems, where the adequacy of basis sets will be limited by linear dependency problems as well as computational effort.

Tables II and III give a comparison of the K -matrix elements for the uncorrected $L^2 K$ -matrix, K^t , with \tilde{K} and $K^{s'}$ and the accurate static exchange results of a variational calculation by Sin-

failam and Nesbet.²² In the s -wave channel the results for $K^{s'}$ are excellent at all energies. Even the values for these small basis sets are within 5% of the exact values in most cases. The results for \tilde{K} are somewhat poorer although generally within 10% of the exact results. The convergence as the number of basis functions increases is not strictly uniform, which seems characteristic of discrete basis function methods.

The threshold behavior of these K -matrix elements shows remarkable stability as the momentum of the incident electron decreases. The quantity $a_s = K_s/k$ whose limit as k goes to zero defines the scattering length remains almost constant for $K^{s'}$ (1.46) and \tilde{K} (1.31) from $k=0.1$ to $k=0.01$. The L^2 uncorrected K -matrix elements are of uneven quality throughout the energy range and show erratic behavior as the number of basis functions is increased. These results are especially poor at low energies, showing no stability at threshold.

Table III gives p -wave results. These K -matrix elements are very small so they should be a sensitive test of the various methods. Both \tilde{K} and $K^{s'}$ are in very good agreement with the variational results of Ref. 22. In this case \tilde{K} is slightly better than $K^{s'}$. The uncorrected K -matrix elements are in general very poor, with the values at low momenta again showing the worst behavior. The threshold behavior for potentials vanishing faster than $r^{-(2l+3)}$, where l is the angular momentum of the incident electron, has been shown by Blatt and Jackson¹⁹ to be

$$k^{2l+1} \cot \delta_l = -(1/a_l) + O(k^2)$$

or

$$\tan \delta_l \sim -a_l k^3. \quad (32)$$

Our phase shifts ($\delta = \tan^{-1} K$) obey this behavior exactly. The a_1 derived from the K^s -matrix elements remains constant from $k=0.1$ to $k=0.01$ with a value of 0.39. For \tilde{K} a_1 is 0.42 at $k=0.1$ and 0.01. The uncorrected phase shifts show no stability as k approaches zero and in addition are

TABLE I. Basis sets for s - and p -wave scattering of He.

Target functions l m n α	Two		Five		p scattering functions	
	l	α	l	α	l	α
0 0 0 96.729 76	0 0 0	0.135 848	0 0 0	0.135 848	0 0 1	1.5
0 0 0 14.609 4	0 0 0	0.075 471	0 0 0	0.075 471	0 0 1	0.75
0 0 0 3.304 241			0 0 0	0.041 928	0 0 1	0.30
0 0 0 0.873 098			0 0 0	0.023 293	0 0 1	0.12
0 0 0 0.244 528			0 0 0	0.012 940	0 0 1	0.048
					0 0 1	0.01

TABLE II. K -matrix elements for s -wave scattering of helium.

Number of functions	5	7	10	Sinfailam and Nesbet
$k = 0.01$				
K^t	-0.0109	+0.000583	+0.0428	
$K^{s'}$	-0.0130	-0.0135	-0.0146	
\tilde{K}	-0.0110	-0.0120	-0.0131	
$k = 0.1$				
K^t	-0.110	-0.0198	-0.00732	} -0.149
$K^{s'}$	-0.133	-0.142	-0.148	
\tilde{K}	-0.114	-0.128	-0.134	
$k = 0.3$				
K^t	-0.347	-0.350	-0.418	} -0.468
$K^{s'}$	-0.460	-0.461	-0.464	
\tilde{K}	-0.421	-0.433	-0.436	
$k = 0.5$				
K^t	-0.647	-0.854	-0.743	} -0.858
$K^{s'}$	-0.858	-0.825	-0.820	
\tilde{K}	-0.833	-0.808	-0.804	

more than an order of magnitude too high. The difficulty at low momenta stems from the inability of the discrete basis set to adequately represent $|\vec{k}\rangle$ by the expansion

$$|\vec{k}\rangle = \sum_{\alpha} |\alpha\rangle \langle \alpha | \vec{k}\rangle. \quad (33)$$

The small basis set which we have chosen is simply inadequate to do this expansion of free waves, especially at very low energy where the wavelength is long. At low momenta the scattering solution is more sensitive to the mathematical irregularities introduced in V^t by the discrete basis set expansion so it is not surprising that this should be reflected in the on-shell T matrix $\langle \vec{k}' | T | \vec{k}\rangle$. The two new methods both do the transformation of T to its on-shell values exactly, which explains their surprising stability near threshold.

IV. COMPARISON

Previously the L^2 K -matrix elements have been corrected by computing a variational correction of the form

$$\langle \psi^t | U - U^t | \psi^t \rangle, \quad (34)$$

where ψ^t is the scattering wave function associated with the L^2 K matrix

$$\psi^t = |\vec{k}\rangle + G_0 K^t |\vec{k}\rangle. \quad (35)$$

Two methods of computing ψ^t and the Kato correction term have been developed.^{5,8} We have applied both techniques to $e + \text{He}$ scattering in order to compare the resulting K -matrix elements to \tilde{K} and K^s .

The first method which was used in a model potential problem⁵ involves using the L^2 -matrix representation of G_0 in the expression for ψ^t .

TABLE III. K -matrix elements for p -wave scattering of helium.

k	Uncorrected K^t	Schwinger K^s	New \tilde{K}	Sinfailam and Nesbet K^{SN}
0.01	0.80×10^{-4}	0.39×10^{-6}	0.42×10^{-6}	
0.1	0.0385	0.00039	0.00042	0.0006*
0.2	0.0152	0.0031	0.0033	0.0035
0.3	0.0448	0.0100	0.0106	0.0108
0.4	0.0888	0.0222	0.0233	0.0239
0.5	0.0500	0.0400	0.0415	0.0426

* Private communication, R. K. Nesbet.

TABLE IV. Comparison of present K -matrix elements with Kato-corrected K -matrix elements for s -wave scattering.

k	Numerical Kato ^a K^N	Analytic Kato ^b K^{RMM}	Schwinger K^s	New \tilde{K}	Sinfailam and Nesbet K^{SN}
0.01	-0.0449	-0.0353	-0.0146	-0.0131	
0.1	-0.163	-0.144	-0.148	-0.134	-0.149
0.5	-0.860	-0.805	-0.820	-0.804	-0.858

^aKato correction obtained numerically (Ref. 8).

^bKato correction obtained using a basis set approximation to G_0 as described by Rescigno, McCurdy, and McKoy (Ref. 5).

This is then substituted into the Kato formula and the resulting terms evaluated

$$\begin{aligned} \langle \psi_{\text{out}}^t | U - U^t | \psi_{\text{in}}^t \rangle &= \langle \vec{k}_{\text{out}} | U - U^t | \vec{k}_{\text{in}} \rangle \\ &+ \langle \vec{k}_{\text{out}} | T^t G_0^t (U - U^t) | \vec{k}_{\text{in}} \rangle \\ &+ \langle \vec{k}_{\text{out}} | (U - U^t) G_0^t T^t | \vec{k}_{\text{in}} \rangle \\ &= \langle \vec{k}_{\text{out}} | T^t G_0^t (U - U^t) G_0^t T^t | \vec{k}_{\text{in}} \rangle. \end{aligned} \quad (36)$$

This expression contains only first-order correction terms.

Later applications of the T -matrix approach obtain the Kato correction by expanding the potential and the scattering wave function in partial waves and solving for the wave function numerically⁸:

$$\psi_{\vec{k}} = \left(\frac{2}{\pi}\right)^{1/2} \sum_{l'l'm} i^l g_{l'l'm}(k, r) Y_{l'l'm}(\hat{r}) Y_{l'm}^*(\hat{k}), \quad (37)$$

$$(-\nabla^2 - k^2) r g_{l'l'm}(k, r) = r \langle Y_{l'l'm} | K^t | j_l(kr) Y_{l'm}(\hat{r}) \rangle, \quad (38)$$

where $j_l(kr)$ is a spherical Bessel function. This method enforces the correct asymptotic form by solving Eq. (38) numerically, which is equivalent to treating the free-particle Green's function exactly. The bound-free and free-free matrix elements are then obtained by numerical integration. Because of this exact treatment of G_0 we expect to see higher-order differences between this cor-

rected phase shift and \tilde{K} and K^s . However, the numerical method does not contain a higher-order correction of the form $\Delta U G^t \Delta U$. When the difference $U - U^t$ is very small we would expect this method to be slightly more accurate than any of the other methods which all use the matrix representation of G_0 .

We applied these two corrections to s - and p -wave He scattering using the same basis sets used for \tilde{K} and K^s . In general the s -wave results above $k=0.01$ a.u. are all close, suggesting that the higher-order corrections are not very important. At $k=0.5$ a.u. the numerical method appears to be slightly more accurate than the other methods which use an L^2 representation of G_0 . At $k=0.01$ a.u. both Kato-corrected K -matrix elements fail to show the proper threshold behavior shown by the two new methods. The quantity a_s calculated from the numerical Kato phase shifts changes from a fairly accurate value of 1.63 at $k=0.1$ a.u. to 4.49 at $k=0.01$ a.u. The values calculated using the analytic Kato correction, Eq. (36), are 1.44 at $k=0.1$ a.u. and 3.53 at $k=0.01$ a.u.

In the p -wave channel the Kato-corrected K -matrix elements are poor below $k=0.5$ a.u. and again show no stable behavior as the momentum goes to zero. The striking differences in these results suggests that the higher-order terms in-

TABLE V. Comparison of present K -matrix elements with Kato-corrected K -matrix elements for p -wave scattering.

k	Numerical Kato ^a K^N	Analytic Kato ^b K^{RMM}	Schwinger K^s	New \tilde{K}	Sinfailam and Nesbet K^{SN}
0.01	-0.17×10^{-4}	-0.15×10^{-4}	0.39×10^{-6}	0.42×10^{-6}	
0.3	0.0030	0.0053	0.0100	0.0106	0.0108
0.5	0.0400	0.0409	0.0400	0.0415	0.0426

^aKato correction obtained numerically (Ref. 8).

^bKato correction obtained using a basis set approximation to G_0 as described by Rescigno, McCurdy, and McKoy (Ref. 5).

cluded in the \bar{K} and K^s are important. Tables IV and V show some selected numbers for comparison.

V. CONCLUSIONS

The present results are encouraging and suggest that the proposed methods may be effective in their application to the more difficult problem of electron-molecule scattering. They derive these advantages over the previously proposed L^2T -matrix methods^{5,6} by using a superior form of the separable expansion of the scattering potential and by not requiring that the basis set itself be capable of expanding the momentum eigenstates, $|k\rangle$. The methods are also free of numerical integration procedures but do require the evaluation of bound-free and free-free molecular integrals which, however, can be evaluated in closed form. Projection of the free-particle Green's function or full Green's functions onto a basis of Cartesian Gaussian functions is an effective way to evaluate terms which would otherwise require complicated numerical integrations. Applications of these methods to the scattering of electrons by H_2 and CO_2 are underway.

The stability of calculated phase shifts at low energies where polarization effects can be important suggests that the methods should be useful for including such effects. These extensions and their applications to diatomic molecules are in progress.

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APPENDIX: EVALUATION OF BOUND-FREE AND FREE-FREE MATRIX ELEMENTS OF THE POTENTIAL

The success of the two new methods presented in this study depends in large measure on the ability to evaluate the bound-free and free-free matrix elements of the potential exactly. For electron-helium scattering the integrals are fairly simple due to the single-center nature of the problem. However, the extension of the method to larger nonspherical systems requires the evaluation of multicenter integrals for general Cartesian Gaussian basis functions. The direct free-free integrals for general Gaussians are well known.²³ The remaining integrals have been evaluated for s and p Gaussians using straightforward differentiation of the formulas for integrals containing only s functions.⁵ This procedure of differentiation quickly becomes tedious and error-prone as more types of Gaussians are needed. To avoid this difficult differentiation we use the method of Ostlund²⁴ and the recurrence relationships of spherical Bessel functions to generate analytic formulas for all these integrals. We extend his formulas for s Gaussians to formulas for general Cartesian Gaussians. To illustrate the method we will outline the evaluation of the bound-free integrals.

Consider the integral

$$\langle e^{-ik \cdot r_1} \phi_\lambda^C(\vec{r}_1) (1/r_{12}) \phi_\alpha^A(\vec{r}_2) \phi_\beta^B(\vec{r}_2) \rangle, \quad (A1)$$

where \vec{k} is the momentum of the incident electron and ϕ_α^A , ϕ_β^B , and ϕ_λ^C are Cartesian Gaussian functions on centers \vec{R}_A , \vec{R}_B , and \vec{R}_C , respectively:

$$\begin{aligned} \phi_\lambda^C &= N_{lmn} x_{1C}^l y_{1C}^m z_{1C}^n \exp(-\lambda |\vec{r}_1 - \vec{R}_C|^2), \\ \phi_\alpha^A &= N_{l'm'n'} x_{2A}^{l'} y_{2A}^{m'} z_{2A}^{n'} \exp(-\alpha |\vec{r}_2 - \vec{R}_A|^2), \\ \phi_\beta^B &= N_{l''m''n''} x_{2B}^{l''} y_{2B}^{m''} z_{2B}^{n''} \exp(-\beta |\vec{r}_2 - \vec{R}_B|^2), \end{aligned} \quad (A2)$$

where $x_A = (x - R_{Ax})$, etc., and N_{lmn} is the normalization factor. We may combine ϕ_α^A and ϕ_β^B on centers \vec{R}_A and \vec{R}_B into a third Gaussian on center

$$\vec{R}_p = \left(\frac{\alpha A_x + \beta B_x}{\alpha + \beta}, \frac{\alpha A_y + \beta B_y}{\alpha + \beta}, \frac{\alpha A_z + \beta B_z}{\alpha + \beta} \right)$$

by using the general formula

$$\begin{aligned} \phi_{\alpha+\beta}^P(r_2) &= x_A^{l'} y_A^{m'} z_A^{n'} x_B^{l''} y_B^{m''} z_B^{n''} \exp(-\alpha |\vec{r}_2 - \vec{R}_A|^2) \exp(-\beta |\vec{r}_2 - \vec{R}_B|^2) \\ &= \sum_{i'j'k'}^{l'm'n'} \sum_{i''j''k''}^{l''m''n''} C_{i'j'k'}^{l'm'n'} C_{i''j''k''}^{l''m''n''} x_P^{i'+i''} y_P^{j'+j''} z_P^{k'+k''} \exp\left(-\frac{\alpha\beta}{\alpha+\beta} |\vec{R}_B - \vec{R}_A|^2\right) \exp[-(\alpha+\beta) |\vec{r}_2 - \vec{R}_P|^2], \end{aligned} \quad (A3)$$

where

$$C_{i'j'k'}^{l'm'n'} = \binom{l'}{i'} \binom{m'}{j'} \binom{n'}{k'} [- (A_x - P_x)]^{l'-i'} [- (A_y - P_y)]^{m'-j'} [- (A_z - P_z)]^{n'-k'}$$

and

$$C_{i''j''k''}^{l''m''n''} = \binom{l''}{i''} \binom{m''}{j''} \binom{n''}{k''} [-(B_x - P_x)]^{l''-i''} [-(B_y - P_y)]^{m''-j''} [-(B_z - P_z)]^{n''-k''}. \quad (\text{A4})$$

We now express ϕ_λ and $\phi_{\alpha+\beta}$ as their Fourier transforms using

$$x_C^l y_C^m z_C^n \exp[-\lambda(x_C^2 + y_C^2 + z_C^2)] = \frac{\pi^{3/2} i^{l+m+n}}{\lambda^{(l+m+n+3)/2} 2^{l+m+n}} \int e^{+i\vec{k} \cdot \vec{R}} c e^{-k'^2/4\lambda} e^{-i\vec{k}' \cdot \vec{r}_1} H_l\left(\frac{k'_x}{2\sqrt{\lambda}}\right) H_m\left(\frac{k'_y}{2\sqrt{\lambda}}\right) H_n\left(\frac{k'_z}{2\sqrt{\lambda}}\right) d\vec{k}', \quad (\text{A5})$$

where H_l , H_m , and H_n are Hermite polynomials. We also express $(1/r_{12})$ as its Gaussian transform

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{\pi}} \int_0^\infty ds s^{-1/2} e^{-s|\vec{r}_1 - \vec{r}_2|^2}. \quad (\text{A6})$$

The resulting integral can now be easily evaluated over \vec{r}_1 , \vec{r}_2 , s , and \vec{k}'' to give

$$\begin{aligned} I = & N_{lmn} N_{l'm'n'} N_{l''m''n''} \frac{\pi i^{l+m+n}}{\lambda^{(l+m+n+3)/2} 2^{l+m+n+1}} \exp\left(-\frac{\alpha\beta}{\alpha+\beta} |\vec{R}_B - \vec{R}_A|^2\right) \exp(-i\vec{k} \cdot \vec{R}_C) \exp[-k^2/4(\alpha+\beta+\lambda)] \\ & \times \sum_{i'j'k'}^{l'm'n'} \sum_{i''j''k''}^{l''m''n''} C_{i'j'k'}^{l'm'n'} C_{i''j''k''}^{l''m''n''} \frac{i^{i+j+k}}{(\alpha+\beta)^{(i+j+k+3)/2} 2^{i+j+k}} \int \frac{d\vec{X}}{X^2} \exp[-iX \cdot (\vec{R}_P - \vec{R}_C)] \\ & \times \exp\left[-\frac{\alpha+\beta+\lambda}{4\lambda(\alpha+\beta)} \left(\vec{X} - \frac{\alpha+\beta}{\alpha+\beta+\lambda} \vec{k}\right)^2\right] \\ & \times H_l\left(\frac{X_x - k_x}{2\sqrt{\lambda}}\right) H_m\left(\frac{X_y - k_y}{2\sqrt{\lambda}}\right) H_n\left(\frac{X_z - k_z}{2\sqrt{\lambda}}\right) \\ & \times H_i\left(\frac{-X_x}{2\sqrt{\alpha+\beta}}\right) H_j\left(\frac{-X_y}{2\sqrt{\alpha+\beta}}\right) H_k\left(\frac{-X_z}{2\sqrt{\alpha+\beta}}\right), \quad (\text{A7}) \end{aligned}$$

where

$$\vec{X} = \vec{k} + \vec{k}', \quad i = i' + i'', \quad j = j' + j'', \quad k = k' + k''.$$

The remaining integral, J , over \vec{X} can be done by making the change of variable suggested by Ostlund,

$$\vec{A} = [(\alpha+\beta)/(\alpha+\beta+\lambda)] \vec{k}, \quad a^2 = (\alpha+\beta+\lambda)/4\lambda(\alpha+\beta)$$

$$\vec{B} = \vec{R}_P - \vec{R}_C, \quad \vec{C} = \vec{B} + 2ia^2 \vec{A}$$

$$= \vec{R}_P - \vec{R}_C + i\vec{k}/2\lambda, \quad (\text{A8})$$

and expanding the plane wave, $e^{-i\vec{k} \cdot \vec{C}}$

$$e^{-i\vec{k} \cdot \vec{C}} = 4\pi \sum_{LM} (-i)^L j_L(XC) Y_{LM}(\hat{C}) Y_{LM}^*(\hat{X}). \quad (\text{A9})$$

Then

$$\begin{aligned} J = & e^{-a^2 k^2} 4\pi \sum_{LM} (-i)^L \int dX e^{-a^2 X^2} j_L(XC) \int d\hat{X} Y_{LM}^*(\hat{X}) H_l\left(\frac{X_x - k_x}{2\sqrt{\lambda}}\right) H_m\left(\frac{X_y - k_y}{2\sqrt{\lambda}}\right) H_n\left(\frac{X_z - k_z}{2\sqrt{\lambda}}\right) H_i\left(\frac{-X_x}{2\sqrt{\alpha+\beta}}\right) \\ & \times H_j\left(\frac{-X_y}{2\sqrt{\alpha+\beta}}\right) H_k\left(\frac{-X_z}{2\sqrt{\alpha+\beta}}\right) Y_{LM}(\hat{C}). \quad (\text{A10}) \end{aligned}$$

The angular integration can be done analytically. The radial integral over X results in integrals of the form

$$I_L^p = \int dX X^p e^{-a^2 X^2} j_L(XC), \quad (\text{A11})$$

where the values of p and L depend on the types

of Gaussians being considered. These can be obtained for all combinations of Cartesian Gaussian functions by using both differentiation and the recursive properties of the spherical Bessel functions. (See Ref. 25 for details.)

The final expression is

$$\begin{aligned} & \langle e^{-i\vec{k}\cdot\vec{r}_1} \phi_\lambda^C(\vec{r}_1)(1/r_{12}) \phi_\alpha^A(\vec{r}_2) \phi_\beta^B(\vec{r}_2) \rangle \\ &= N_{l'm'n'} N_{l''m''n''} A(\alpha, \beta, \lambda; k) \sum_{i'j'k'}^{l'm'n'} \sum_{i''j''k''}^{l''m''n''} C_{ijk}(l'm'n', l''m''n'') \sum_{LM} (-i)^L f_{LM}(\alpha\beta\lambda, lmn, ijk) Y_{LM}(\hat{C}), \end{aligned} \quad (\text{A12})$$

where

$$A(\alpha, \beta, \lambda; k) = \frac{2\pi^2 i^{l+m+n}}{2^{l+m+n\lambda} (l+m+n+3)^{1/2}} \exp\left(-\frac{\alpha\beta}{\alpha+\beta} |\vec{R}_B - \vec{R}_A|^2\right) \exp(-i\vec{k}\cdot\vec{R}_C) \exp(-k^2/4\lambda), \quad (\text{A13})$$

$$C_{ijk}(l'm'n', l''m''n'') = C_{i'j'k'}^{l'm'n'} C_{i''j''k''}^{l''m''n''} \frac{i^{i+j+k}}{(\alpha+\beta)^{(i+j+k+3)/2} 2^{i+j+k}} \quad (\text{A14})$$

$$\begin{aligned} f_{LM}(\alpha\beta\lambda, lmn, ijk) &= \int dX e^{-a^2 X^2} j_L(XC) \int d\hat{X} Y_{LM}^*(\hat{X}) H_l\left(\frac{X_x - k_x}{2\sqrt{\lambda}}\right) H_m\left(\frac{X_y - k_y}{2\sqrt{\lambda}}\right) H_n\left(\frac{X_z - k_z}{2\sqrt{\lambda}}\right) \\ &\times H_i\left(\frac{-X_x}{2\sqrt{\alpha+\beta}}\right) H_j\left(\frac{-X_y}{2\sqrt{\alpha+\beta}}\right) H_k\left(\frac{-X_z}{2\sqrt{\alpha+\beta}}\right), \end{aligned} \quad (\text{A15})$$

where

$i = i' + i''$, $j = j' + j''$, $k = k' + k''$, $a^2 = \frac{\alpha + \beta + \lambda}{4\lambda(\alpha + \beta)}$ and $C_{ijk}^{l'm'n'}$ is defined by Eq. (A4). We present below analogous formulas for the remaining bound-free and free-free integrals.

A. Nuclear hybrid integral

$$\begin{aligned} & \left\langle e^{-i\vec{k}\cdot\vec{r}} \frac{1}{|\vec{r}-R|} \phi_\lambda^C(\vec{r}) \right\rangle \\ &= N_{l'm'n'} A(\lambda, k) \sum_{LM} (-i)^L f_{LM}(\lambda, k; lmn) Y_{LM}(\hat{C}), \end{aligned} \quad (\text{A16})$$

where

$$\vec{C} = \vec{R} - \vec{R}_C + (i\vec{k}/2\lambda),$$

$$A(\lambda, k) = \frac{16\pi^{7/2} i^{l+m+n}}{(2\pi)^3 \lambda^{(l+m+n+3)/2} 2^{l+m+n}} e^{-i\vec{k}\cdot\vec{R}_C} e^{-k^2/4\lambda}, \quad (\text{A17})$$

$$\begin{aligned} f_{LM}(\lambda, k; lmn) &= \int dX e^{-X^2/4\lambda} j_L(XC) \\ &\times \int d\hat{X} Y_{LM}^*(\hat{X}) H_l\left(\frac{X_x - k_x}{2\sqrt{\lambda}}\right) \\ &\times H_m\left(\frac{X_y - k_y}{2\sqrt{\lambda}}\right) H_n\left(\frac{X_z - k_z}{2\sqrt{\lambda}}\right) \end{aligned} \quad (\text{A18})$$

B. Direct free-free integral

$$\begin{aligned} & \langle e^{-i\vec{k}\cdot\vec{r}_1} \phi_\alpha^A(\vec{r}_2)(1/r_{12}) e^{i\vec{k}\cdot\vec{r}_1} \phi_\beta^B(\vec{r}_2) \rangle \\ &= N_{l'm'n'} N_{l''m''n''} A(\alpha, \beta, q) \sum_{i'j'k'}^{l'm'n'} \sum_{i''j''k''}^{l''m''n''} C_{ijk}(\alpha, \beta, q), \end{aligned} \quad (\text{A19})$$

where

$$\begin{aligned} A(\alpha, \beta, q) &= \frac{4\pi^{5/2}}{q^2} \exp\left(-\frac{\alpha\beta}{\alpha+\beta} |\vec{R}_B - \vec{R}_A|^2\right) \\ &\times \exp(-iq\cdot R_p) \exp[-q^2/4(\alpha+\beta)], \end{aligned} \quad (\text{A20})$$

$$\begin{aligned} C_{ijk}(\alpha, \beta; q) &= C_{i'j'k'}^{l'm'n'} C_{i''j''k''}^{l''m''n''} \frac{i^{i+j+k}}{(\alpha+\beta)^{(i+j+k+3)/2} 2^{i+j+k}} \\ &\times H_i\left(\frac{-q_x}{2\sqrt{\alpha+\beta}}\right) H_j\left(\frac{-q_y}{2\sqrt{\alpha+\beta}}\right) H_k\left(\frac{-q_z}{2\sqrt{\alpha+\beta}}\right), \end{aligned} \quad (\text{A21})$$

$$i = i' + i'', \quad j = j' + j'', \quad k = k' + k'', \quad \vec{q} = \vec{k}' - \vec{k}.$$

C. Exchange free-free integral

$$\begin{aligned} & \langle e^{-i\vec{k}\cdot\vec{r}_1} \phi_\alpha^A(\vec{r}_1)(1/r_{12}) e^{i\vec{k}\cdot\vec{r}_2} \phi_\beta^B(\vec{r}_2) \rangle \\ &= N_{l'm'n'} N_{l''m''n''} \\ &\times A(\alpha, \beta; k, k') \sum_{LM} (-i)^L f_{LM}(\alpha, \beta; k, k') Y_{LM}(\hat{C}), \end{aligned} \quad (\text{A22})$$

where

$$\begin{aligned} A(\alpha, \beta; k, k') &= \frac{2\pi^2}{\alpha^{(l'+m'+n'+3)/2} \beta^{(l''+m''+n''+3)/2}} \left(\frac{i}{2}\right)^{l'+m'+n'+l''+m''+n''} \\ &\times \exp(-i\vec{k}'\cdot\vec{R}_A + i\vec{k}\cdot\vec{R}_B) \exp(-k^2/4\beta - k'^2/4\alpha), \end{aligned} \quad (\text{A23})$$

$$f_{LM}(\alpha, \beta; k, k') = \int dX \exp\left(-\frac{\alpha + \beta}{4\alpha\beta} X^2\right) j_L(XC) \int d\hat{X} Y_{LM}^*(\hat{X}) H_{l'}\left(\frac{X_x - k'_x}{2\sqrt{\alpha}}\right) H_{m'}\left(\frac{X_y - k'_y}{2\sqrt{\alpha}}\right) H_{n'}\left(\frac{X_z - k'_z}{2\sqrt{\alpha}}\right) \\ \times H_{l''}\left(\frac{k_x - X_x}{2\sqrt{\beta}}\right) H_{m''}\left(\frac{k_y - X_y}{2\sqrt{\beta}}\right) H_{n''}\left(\frac{k_z - X_z}{2\sqrt{\beta}}\right), \quad (\text{A24})$$

$$\vec{C} = \vec{R}_B - \vec{R}_A + 2i[(\beta\vec{k}' + \alpha\vec{k})/4\alpha\beta].$$

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