Linear-algebraic approach to electron-molecule collisions: Separable exchange approximations

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The linear-algebraic method for electron-molecule collisions developed by Schneider and Collins is generalized to include separable expansions of the exchange kernel. These separable expansions are constructed using bound-state integral programs and spherical-harmonic projections which may be performed by analytic methods. The short-range nature of the exchange operator obviates the need for large basis sets in the separable expansion and allows for a very efficient construction of the required integrals. The method is applied to $e + H_2$ and $e + LiH$ scattering in the static-exchange approximation. Comparison of the separable expansion with more standard numerical techniques for exchange is excellent ($< 1\%$) even for strongly polar systems like LiH.

I. INTRODUCTION

In a recent letter[1] we described a new approach to electron-molecule scattering which reduces the coupled partial-wave Lippmann-Schwinger equations to a set of linear-algebraic equations. The technique has been modified and extended to include R matrix boundary conditions and will be described in detail in a subsequent publication.

The purpose of this note is to describe an alternative way of including exchange interactions in the method which has some advantages over more traditional approaches. The central idea is quite simple and has been used to treat correlation and polarization in electron-atom collision problems.[2] Recently, Rescigno and Orel[3] have proposed a similar technique for electron-molecule scattering using the numerical static Green's function as the unperturbed system. In all of these treatments the exchange operator is represented by a sum of separable terms using a discrete basis of Gaussian or Slater orbitals. By restricting the separable expansion to the exchange kernel, which is of short range, the need for large basis sets is obviated and convergence is rapid even for strongly polar molecules. The essential difference between our use of the separable exchange potential and that of other workers is the manner in which it is included in the scattering equations. As we pointed out in Ref. 1, the most time consuming step in many of the newer approaches to electron-molecule collisions, is the construction of the exchange operator. By utilizing discrete basis set expansions we are able to construct representations of the exchange kernel using standard bound-state integral programs, quickly and independently of the scattering calculation. The linear-algebraic approach discussed previously allows us to incorporate these separable expansions *directly* in configuration space without the need to construct a distorted-wave Green's function or to solve additional inhomogeneous equations. The size of the set of algebraic equations does not increase, and the additional complexity of the exchange interaction over the purely local potential is quite minor. The price paid is the additional work required to calculate the matrix elements of the exchange kernel in a typical bound-state basis plus the transformation from function to configuration space. Since both steps are energy independent, we feel this is a small price to pay for the simplicities introduced in the actual solution of the scattering problem. At a given energy, the time to solve the scattering equations with the separable exchange potential is from three to ten times less than that with an exchange potential determined by numerical quadrature. However, a realistic comparison of computational times must include a contribution from the energy-independent basis set calculations to the time to solve the scattering equation for the separable potential. When this is taken into account, we find that the separable potential technique becomes the more cost-effective method after four or five runs of the scattering code. Far more importantly, the approximation has been shown to give reliable results (~2% or less) with moderate sized basis sets even for strongly polar molecules.

II. THEORY

The form of the separable exchange kernel used in our calculations is

$$K = \sum_{\alpha,\beta} |\alpha\rangle K_{\alpha\beta} \langle\beta| , \tag{1a}$$

where

$$K_{\alpha\beta} = \sum_{i=1}^{N} b_i \left\langle \phi_\alpha \chi_i \left| \frac{1}{r_{12}} \right| \chi_i \phi_\beta \right\rangle . \tag{1b}$$

The set of orbitals (χ_i) and the "occupation numbers" b_i depend on the actual form of the scattering wave function. For a closed-shell system, the χ_i run over all the occupied bound molecular orbitals and $b_i = -1.0$ for all i. In order to transform from the (ϕ_α) representation to configuration space it is necessary to calculate the projection of the L^2 basis functions onto sperhical harmonics. If we define

$$F_{\alpha lm}(r) = \langle Y_{lm} | \phi_\alpha \rangle_\Omega , \tag{2}$$

then

$$K_{lm,l'm'}(r|r') = \sum_{\alpha,\beta} F_{\alpha lm}(r) K_{\alpha\beta} F^*_{\beta l'm'}(r') . \tag{3}$$

The double summation may be reduced to a single sum by transforming the operator from the (ϕ_α) representation to the representation which diagonalizes the $K_{\alpha\beta}$ matrix. This requires one extra energy-independent unitary transformation and results in the expression

$$K_{lm,l'm'}(r|r') = \sum_\lambda G_{\lambda lm}(r) \lambda G_{\lambda l'm'}(r') \tag{4}$$

for the exchange operator. Although this last step is not necessary to use the separable expansion in practical calculations, it does reduce the work needed to extract the scattering information. More importantly, however, there is much to be learned by studying the eigenvalue spectrum of K. In all of the systems we have examined, the eigenvalue spectrum has rapidly proceeded from moderate negative values (a few hartrees) to zero. The number of near zero eigenvalues ($\leq 10^{-4}$) has always been a significant fraction of the total set. Since these eigenvalues always multiply the configuration-space functions, one has a practical tool to study convergence questions. In the calculations we have performed, we have tested the convergence by deleting functions from the summation in Eq. (4). Essentially, no loss of accuracy was observed if all eigenvalues below 10^{-4} were deleted from the summation. In fact, one could often obtain 2–5% accuracy with the lowest four or five eigenvalues. These results are consistent with the short-range nature of the exchange operator and make calculations on even small triatomic molecules practical.

The computational savings one achieves in the scattering calculations using the linear-algebraic method can be seen by considering the integral

$$I(r) = \int G_l^0(r|r') K_{ll'}(r'|r'') \psi_{l'}(r'') dr' dr'' , \tag{5}$$

where $G_l^0(r|r')$ is the free-particle Green's function and $\psi_l(r)$ the unknown scattering wave function. Introducing a quadrature we get

$$I(r) = \sum_i \sum_j G_l^0(r|r_i) K_{ll'}(r_i|r_j) \psi_{l'}(r_j) W_i W_j \tag{6}$$

and

$$I(r_k) = \sum_{i,j} G_l^0(r_k|r_i) K_{ll'}(r_i|r_j) \psi_{l'}(r_j) W_i W_j$$

$$= \sum_j M_{ll'}(r_k|r_j) \psi_{l'}(r_j) W_j , \tag{7a}$$

where

$$M_{ll'}(r_i|r_j) = \sum_k G_l^0(r_i|r_k) K_{ll'}(r_k|r_j) W_k , \tag{7b}$$

and W_i is the quadrature weight. Substituting Eq. (4) into (7b) yields

$$M_{ll'}(r_i|r_j) = \sum_k \sum_\lambda G_l^0(r_i|r_k) G_{\lambda lm}(r_k) \lambda G^*_{\lambda l'm}(r_j) w_k . \tag{7c}$$

Thus the separable form of the exchange operator reduces the formation of the $M_{ll'}(r_i|r_j)$ submatrices from an N^3 to an N^2 problem in the number of radial quadrature points. The calculation can be made even more efficient by using the greater and/or lesser form of the unperturbed Green's function. This enables us to reduce the summation over k in Eq. (7c) to a set of two recursion formulas, each of which is proportional to N. The final process is still proportional to N^2 but the constant in front of the N^2 term is considerably reduced.

The entire formation of the configuration-space representation of the exchange kernel from Eq. (1) rests on the ability to calculate the projections of the molecular orbitals onto the spherical harmonics. These projections may be calculated numerically using Gauss-Legendre quadratures but for certain types of basis sets analytic procedures are available. If the molecular orbitals are expressed as linear combinations of Cartesian Gaussians it is possible to reduce the projections to the calculation of modified spherical Bessel functions. These may be computed very quickly for many l values by using recursion relations. One may then step up to higher angular-momentum quantum numbers using the recursion relationships satisfied by the Legendre functions. The procedure is quite simple and accurate and has been implemented in our computer programs.

TABLE I. Results for $e + H_2$ scattering in the static-exchange approximation ($k^2 = 0.04$ Ry, number of channels = 4, number of exchange terms $l = 2$, and number of points = 30).

No. of terms in separable expansion	Eigenphase sum[a,b]
2	−0.4427 (−0.4398)
4	−0.4392 (−0.4363)
8	−0.4199 (−0.4171)
15	−0.4199 (−0.4171)

[a] The numbers refer to matching the solutions to asymptotic forms at $R = 10.0$ and 20.0 a.u., respectively.
[b] The value from the same program using numerical exchange is −0.4171.

TABLE II. Results for $e + LiH$ scattering in the static-exchange approximation ($k^2 = 1.0$ Ry, number of channels = 8, number of exchange terms $l = 7$, and number of points = 56).

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

[a] The numbers refer to matching the solutions to asymptotic forms at $R = 16.0$ and 64.0 a.u., respectively.
[b] The value from the same program using numerical exchange is 1.8559.

III. CALCULATIONS

The technique described above has been applied to the scattering of electrons from H_2 and LiH. The latter molecule provides a particularly stringent test of the numerical procedure since the older L^2-type approaches had great difficulty with the representation of the strong anisotropic static interaction of this highly polar system. In Tables I and II we present the results of our study as a function of the number of terms kept in the separable expansion for the two molecules mentioned above. For comparison we give the converged eigenphase sums using the same number of channels and exchange l values obtained with the linear-algebraic technique with numerical exchange. The results clearly show that the separable expansion of the exchange kernel is a viable alternative to the older methods. It converges quite rapidly with basis set size and yields results which deviate by less than 1% from the "more exact" treatments.

[1]B. I. Schneider and L. A. Collins, J. Phys. B 14, L101 (1981).
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[3]T. N. Rescigno and A. E. Orel, Phys. Rev. A 23, 1134 (1981).