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Separable approximation for exchange interactions in electron-molecule scattering

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We have formulated and applied a separable approximation for treating the nonlocal exchange interactions that arise in electron-molecule collision problems. A separable representation of the exchange terms in the electron-molecule interaction potential is obtained by projection onto a finite set of Cartesian Gaussian functions and is combined with a single-center expansion of the direct potential terms that accurately treats the long-range, multipolar forces. An integral-equation method is used to obtain a solution of the set of coupled equations obtained in a body-frame formulation of the collision problem. The method is illustrated by application to low-energy e^--H_2 and e^--LiH scattering in the static-exchange approximation.

I. INTRODUCTION

The development of discrete-basis-set approaches based on multicentered expansions has played a key role in recent years in the *ab initio* calculation of cross sections for low-energy, electron-molecule scattering.[1] Nevertheless, there are aspects of the electron-molecule collision problem, namely, the long-range nature of the interaction potential, that are difficult to treat solely with finite-basis-set expansions. In a recent paper[2] (hereafter referred to as I), we proposed a modification of the usual separable expansion[3] in which the long-range, direct components of the interaction potential are treated exactly and the short-range, nonlocal components are projected onto a finite basis set. The technique was illustrated for the simple case of single-channel, potential scattering and was found to converge quite rapidly.

We have generalized the approach outlined in I to the case of low-energy, electron-molecule scattering. The present formalism is based upon a single-center, body-frame treatment of the collision problem,[4] and our initial studies have been confined to the static-exchange approximation. The exchange component of the interaction potential is first projected onto a finite set of symmetry-adapted, Cartesian Gaussian basis functions. The motivation for such a construction is that the electron-exchange potential, though strong and, in general, highly aspherical, does not extend beyond the charge density of the target molecule and consequently should be well represented in a small basis of short-ranged functions. Indeed, we have found that accurate results can be obtained with the present approach by employing the same basis set to represent the exchange potential that is used to expand the occupied molecular orbitals. This contrasts markedly with earlier T-matrix[5,6] and R-matrix[7] work where large expansion sets were needed to assure adequate convergence.

In the present work, the entire electron-molecule interaction potential is subjected to a single-center expansion; the resulting set of coupled equations must be solved numerically. In the approach we followed in I, a two-potential formalism[8] was used to express the K matrix in terms of matrix elements of the reference Green's function for the static potential, which required two numerical integrations of the reference Schrödinger equation for both regular and irregular solutions. We have avoided the latter construction in the present work by employing an integral-equation method of solution. The method of solution used here is essentially that of Sams and Kouri,[9] generalized to the case of multichannel scattering with a separable potential of rank >1.[10] Although the integral-equations method has been used by others in studying electron-molecule collision problems,[11] its combination with a separable representation of the exchange interaction is a new development and leads to a highly efficient numerical technique that avoids the need for *iterative* methods of solution[12] or the inversion of large matrices.[13]

In Sec. II of this paper, we outline the approximation scheme we have developed and the integral-equation method of solution. Section III presents the results of a numerical application of the method to electron-H_2 and electron-LiH scattering in the static-exchange approximation. Section IV contains a brief discussion and suggestions for future work.

II. THEORY

We restrict ourselves to a discussion of electron-molecule scattering in the static-exchange approximation for which the interaction potential can be written (for closed-shell molecules):

$$\tfrac{1}{2}U(\vec{r},\vec{r}\,')=\left(-\sum_i \frac{Z_i}{|\vec{R}_i-\vec{r}|}+2J(\vec{r})\right)\delta(\vec{r}-\vec{r}\,')-K(\vec{r},\vec{r}\,')$$
$$\equiv\tfrac{1}{2}U_{\mathrm{dir}}(\vec{r})\delta(\vec{r}-\vec{r}\,')+U_{\mathrm{ex}}(\vec{r},\vec{r}\,'), \quad (1)$$

where J and K are the usual Coulomb and exchange operators and the sum runs over all the nuclei in the target molecule. As in I, we use a separable approximation for the exchange potential,

$$K(\vec{r},\vec{r}\,')=\sum_\alpha \chi_\alpha(\vec{r})\gamma_\alpha\chi_\alpha(\vec{r}\,'), \quad (2)$$

where, for convenience, we have chosen an orthonormal basis of Gaussian functions $\{\chi_\alpha\}$ that gives a diagonal representation of the exchange potential with eigenvalues $\{\gamma_\alpha\}$. Carrying out a single-center expansion of the potential gives the following set of coupled equations for the radial components of the scattering wavefunction:

$$\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+k^2\right)\phi_{ll_0}(r)=\sum_{l'}\left(U_{ll'}(r)\phi_{l'l_0}(r)+\sum_\alpha \chi_\alpha^l(r)\gamma_\alpha\int_0^\infty \chi_\alpha^{l'}(r')\phi_{l'l_0}(r')dr'\right), \quad (3)$$

where the functions $U_{ll'}(r)$ are matrix elements of the direct potential

$$U_{ll'}(r)=\int Y_l^{m*}(\hat{r})U_{\mathrm{dir}}(\vec{r})Y_{l'}^m(\hat{r})d\hat{r}, \quad (4)$$

and $\chi_\alpha^l(r)$ is the radial function obtained by projecting a Gaussian basis function onto a spherical harmonic,

$$\chi_\alpha^l(r)=r\int d\hat{r}\,\chi_\alpha(\vec{r})Y_l^m(\hat{r}). \quad (5)$$

The radial functions χ_α^l can be evaluated in closed form.[6(a)] We have assumed a linear molecule and, hence, dropped the implicit dependence of the wave function on the quantum number m.

The set of coupled equations (3) is first written in integral form:

$$\phi_{ll_0}(r)=\delta_{ll_0}j_l(kr)+\sum_{l'}\int_0^r g_l(r,r')U_{ll'}(r')\phi_{l'l_0}(r')dr'+\sum_{l'\alpha}\gamma_\alpha\int_0^r g_l(r,r')\chi_\alpha^l(r')dr'\int_0^\infty \chi_\alpha^{l'}(r'')\phi_{l'l_0}(r'')dr''. \quad (6)$$

Note that we are using the *regular* Green's function[14] which vanishes for $r'>r$ and is defined by

$$g_l(r,r')=\frac{1}{k}[n_l(kr)j_l(kr')-j_l(kr)n_l(kr')], \quad (7)$$

where j_l and n_l are Riccati-Bessel functions. We then express the solution as a linear combination of homogeneous and inhomogeneous terms,[9,10]

$$\phi_{ll_0}(r)=\phi_{ll_0}^0(r)+\sum_\alpha \phi_l^\alpha(r)c_{l_0}^\alpha, \quad (8)$$

which satisfy the following set of Volterra equations:

$$\phi_{ll_0}^0(r)=\delta_{ll_0}j_l(kr)+\sum_{l'}\int_0^r g_l(r,r')U_{ll'}(r')\phi_{l'l_0}^0(r')dr', \quad (9a)$$

$$\phi_l^\alpha(r)=\gamma_\alpha\int_0^r g_l(r,r')\chi_\alpha^l(r')dr'+\sum_{l'}\int_0^r g_l(r,r')U_{ll'}(r')\phi_{l'}^\alpha(r')dr'. \quad (9b)$$

It is simple to show that the constants c_l^α are determined by the set of linear-algebraic equations,

$$\sum_\beta A_{\alpha\beta}c_{l_0}^\beta=B_{\alpha l_0}, \quad (10)$$

where

$$A_{\alpha\beta}=\delta_{\alpha\beta}-\sum_{l'}\int_0^\infty \chi_\alpha^l(r)\phi_{l'}^\beta(r)dr, \quad (11)$$

and

$$B_{\alpha l_0}=\sum_{l'}\int_0^\infty \chi_\alpha^{l'}(r)\phi_{l'l_0}^0(r)dr. \quad (12)$$

Newton[10] has pointed out the need for careful counting of the dimensions of the matrices involved in treating an N-channel problem with an M-term separable potential. It is important to note here that the potential eigenvalues $\{\gamma_\alpha\}$ of Eq. (2) are independent of l. Thus, the dimensionality of the square matrix A which has to be inverted to obtain the coefficients $c_{l_0}^\alpha$ is equal to the number of separable terms employed in Eq. (2), and is independent of the number of angular-momentum terms used in the single-center expansion.

The basic numerical techniques used in solving a set of coupled Volterra integral equations have been discussed by a number of different investigators[9,11,15,16] and only a brief summary is given here. It is convenient to write the homogeneous solution $\phi_{ll_0}^0$ [Eq. (9a)] as

$$\phi_{ll_0}^0(r)=j_l(kr)Q_{ll_0}(r)+n_l(kr)P_{ll_0}(r), \quad (13)$$

where the auxiliary matrices P and Q are defined as

$$P_{ll_0}(r)=\frac{1}{k}\sum_{l'}\int_0^r j_l(kr')U_{ll'}(r')\phi_{l'l_0}^0(r')dr', \quad (14)$$

$$Q_{ll_0}(r)=\delta_{ll_0}-\frac{1}{k}\sum_{l'}\int_0^r n_l(kr')U_{ll'}(r')\phi^0_{l'l_0}(r')dr'. \tag{15}$$

If the integrals in Eqs. (14) and (15) are now replaced by numerical quadratures, the solution matrix can be propagated *noniteratively* to large r values, since the kernel vanishes at the upper limit of integration, giving

$$\phi^0_{ll_0}(r_j)=j_l(kr_j)Q_{ll_0}(r_{j-1})+n_l(kr_j)P_{ll_0}(r_{j-1}). \tag{16}$$

The same procedure is used to develop numerical solutions to the inhomogeneous equations(9b), which are written as

$$\phi^\alpha_l(r)=j_l(kr)Q^\alpha_l(r)+n_l(kr)P^\alpha_l(r), \tag{17}$$

where,

$$P^\alpha_l(r)=\frac{1}{k}\left(\gamma_\alpha\int_0^r j_l(kr')\chi^l_\alpha(r')dr' +\sum_{l'}\int_0^r j_l(kr')U_{ll'}(r')\phi^\alpha_{l'}(r')dr'\right), \tag{18}$$

$$Q^\alpha_l(r)=\frac{1}{k}\left(\gamma_\alpha\int_0^r n_l(kr')\chi^l_\alpha(r')dr' +\sum_{l'}\int_0^r n_l(kr')U_{ll'}(r')\phi^\alpha_{l'}(r')dr'\right). \tag{19}$$

Introduction of a quadrature mesh into Eqs. (18) and (19) again leads to a noniterative propagation scheme for outward integration of the equations. In the work reported here, trapezoidal quadratures were used. It is also worth noting that numerical values for the A and B matrices, which are required for the solution of Eq. (10), are developed stepwise as the wave functions are propagated outwardly.

The reactance matrix $\underline{K}$ is obtained from a *physical* solution of the coupled equations [Eq. (3)] specified by the asymptotic normalization

$$\phi^{\text{phys}}_{ll_0}(r)\to j_l(kr)\delta_{ll_0}-K_{ll_0}n_l(kr). \tag{20}$$

Comparing this with the asymptotic behavior of the *regular* solution we have developed, we see that the K matrix can be obtained from the latter as

$$\underline{K}=-\underline{V}\cdot\underline{W}^{-1}, \tag{21}$$

where

$$V_{ll'}=P_{ll'}(\infty)+\sum_\alpha P^\alpha_l(\infty)c^\alpha_{l'} \tag{22}$$

and

$$W_{ll'}=Q_{ll'}(\infty)+\sum_\alpha Q^\alpha_l(\infty)c^\alpha_{l'}. \tag{23}$$

Thus, the K matrix is determined from the values of the auxiliary P and Q matrices at the final point in the integration mesh and the inhomogeneous " mixing" coefficients $c^\alpha_{l'}$. It is, in fact, unnecessary to store the solution matrices $\phi^0(r)$ and $\phi^\alpha(r)$ in order to evaluate the $\underline{K}$ matrix.

There is an additional point about the solution of the inhomogeneous equations worth mentioning. These were formulated with a set of orthonormal functions that diagonalize the exchange potential. In actual practice, it is easier to solve the inhomogeneous equations [Eqs. (17)–(19)] with the χ^l_α replaced by a primitive set of Gaussians, which avoids the need for an orthogonal transformation at every step in the integration. A single linear transformation is performed at the end of the integration to obtain P^α_l and Q^α_l at the final mesh point.

III. NUMERICAL EXAMPLES

We have applied the separable-exchange technique to electron-H_2 and electron-LiH scattering in the static-exchange approximation. Both these systems have been studied previously in some detail and it was therefore not our intention to provide an extensive set of collision parameters. These examples were chosen to get some feeling for the accuracy and timings achievable with the approach outlined above.

For the e^-+H_2 calculations, we used a $[5s/2p]$ set of Gaussian functions to solve the self-consistent-field (SCF) equations for the occupied $1\sigma_g$ orbital. The basis-set parameters are identical to those given in Ref. 17. Two sets of scattering calculations are reported here for the $^2\Sigma^+_g$ and $^2\Sigma^+_u$ symmetries. In one set, the same $[5s/2p]$ basis was used to form the separable representation of the exchange potential. We also performed calculations with an unoptimized $[7s/6p]$ valence basis set. The $^2\Sigma^+_g$ and $^2\Sigma^+_u$ K-matrix elements and eigenphase sums are given in Table I for scattering energies of 0.01, 0.25, and 1 Ry.

Detailed comparison with numerical results obtained by other methods are often difficult because of small differences in the target orbitals being used, the number of single-center terms retained in the expansions, and the quadrature meshes used for integration. Individual K-matrix elements can be quite sensitive to these details. Therefore, we have also performed " exact" static-exchange calculations for comparison—that is, numerical solutions of the single-center coupled equations using the same SCF orbitals, l expansions, and quadrature grids. These were obtained using the iterative Schwinger variational technique of Lucchese, Watson, and McKoy.[18] The results shown in Table I for $^2\Sigma^+_g$ ($^2\Sigma^+_u$) were obtained by retaining terms up to $l=6(7)$ in both the occupied $1\sigma_g$ and the scattering orbitals. Nuclear terms up to $\lambda=2l$ were retained in the expansion of the static potential. Piecewise trapezoidal meshes extending out to 90 a.u. were used in the computations. In spite

TABLE I. K-matrix elements and eigenphase sums for $^2\Sigma^+$ symmetry in H_2. See text for description of calculations.

k^2 (Ry)	SCF basis	[7*s*/6*p*] basis[a]	"Exact"
		$^2\Sigma_g^+$	
		K_{00}	
0.01	−0.211	−0.216	−0.217
0.25	−1.490	−1.551	−1.551
1.00	8.051	7.984	7.945
		K_{02}	
0.01	0.348(−2)	0.350(−2)	0.349(−2)
0.25	0.120(−1)	0.131(−1)	0.134(−1)
1.00	0.121	0.121	0.120
		K_{22}	
0.01	0.209(−2)	0.208(−2)	0.208(−2)
0.25	0.148(−1)	0.181(−1)	0.164(−1)
1.00	0.876(−1)	0.919(−1)	0.914(−1)
		Eigenphase sum	
0.01	−0.205	−0.210	−0.211
0.25	−0.961	−0.976	−0.977
1.00	1.542	1.545	1.545
		$^2\Sigma_u^+$	
		K_{11}	
0.01	0.126(−1)	0.124(−1)	0.122(−1)
0.25	0.423	0.411	0.410
1.00	1.353	1.340	1.336
		K_{13}	
0.01	0.109(−2)	0.109(−2)	0.109(−2)
0.25	0.653(−2)	0.743(−2)	0.693(−2)
1.00	0.291(−1)	0.314(−1)	0.302(−1)
		K_{33}	
0.01	0.936(−3)	0.936(−3)	0.937(−3)
0.25	0.518(−2)	0.567(−2)	0.526(−2)
1.00	0.180(−1)	0.193(−1)	0.191(−1)
		Eigenphase Sum	
0.01	0.140(−1)	0.138(−1)	0.136(−1)
0.25	0.408	0.398	0.398
1.00	0.958	0.954	0.953

[a] The orbital exponents of the *s* functions are 3.0, 2.0, 1.0, 0.5, 0.25, 0.125, and 0.06. The *p* exponents are the same, except that the 0.06 functions were deleted.

of the fact that the quadratures used represented something of an overkill ($N \approx 900$), the computational times are quite modest. The calculations with the [7*s*/6*p*] basis required about 1.5 sec per energy on a Cray 1 computer. The results obtained with the separable-exchange approximation are in good agreement with the "exact" numerical results and are evidently insensitive to the basis sets used in the expansion.

For the $e^- +$LiH calculations we used a [5*s*4*p*3*d*/3*s*4*p*] set of contracted Gaussian functions to construct the target SCF wave function. The exponents and contraction coefficients are the same as those used in our earlier Schwinger calculation on LiH and are given in Ref. 19. The results reported here were obtained by retaining terms up to $l = 10$ in the expansion of the occupied orbitals and scattering wave function and nuclear terms up to $\lambda = 20$ in the expansion of the static potential. A set of calculations was performed using the same SCF basis as the expansion basis for constructing the separable representation of the exchange potential. A second set of calculations was carried out using an uncontracted [9*s*6*p*4*d*/5*s*5*p*] basis. The $^2\Sigma$ eigenphase sums for both sets are shown in Table II, along with converged results obtained from an iterative Schwinger[18] calculation with the same target basis and expansion parameters. The uncontracted basis

TABLE II. K-matrix elements and eigenphase sums for $^2\Sigma^+$ symmetry in LiH. See text for description of calculations.

K^2 (Ry)	SCF basis	[9*s*6*p*4*d*/5*s*5*p*] basis[a]	"Exact"
		K_{00}	
0.25	0.903	0.916	0.914
1.00	−0.189	−0.188	−0.188
		K_{01}	
0.25	−0.281	−0.252	−0.248
1.00	0.105	0.163	0.165
		K_{11}	
0.25	−4.451	−4.200	−4.299
1.00	1.651	1.511	1.517
		K_{02}	
0.25	0.284	0.309	0.310
1.00	0.220	0.189	0.190
		K_{12}	
0.25	−2.741	−2.587	−2.638
1.00	0.684(−1)	0.114	0.111
		K_{22}	
0.25	−1.022	−0.939	−0.969
1.00	1.185	1.160	1.163
		Eigenphase sum[b]	
0.25	−0.388	−0.387	−0.396
1.00	1.914	1.859	1.857

[a] The orbital exponents are as follows: Li*s*: 22.0, 6.0, 3.0, 1.5, 0.8, 0.4, 0.15, 0.07, 0.03; Lip_z: 1.5, 0.8, 0.4, 0.15, 0.07, 0.03; Lid_{zz}: 1.0, 0.5, 0.1, 0.05; H*s* and Hp_z: 2.0, 1.0, 0.5, 0.25, 0.1.

[b] Terms up to $\lambda = 6$ were retained in computing the eigenphase sums.

does slightly better than the SCF basis in this case, giving results that lie within 1–3% of the Schwinger results.

IV. DISCUSSION

We have formulated a separable approximation for treating exchange interactions in electron-molecule scattering and presented some illustrative results for the $e^- + H_2$ and $e^- + LiH$ systems in the static-exchange approximation. The preliminary indications are that accurate results can be obtained with small basis sets. The integral-equations approach we have outlined has the advantage of offering a computationally rapid, noniterative propagation technique that does not require the storage or inversion of large matrices. It also avoids construction of the static Green's function, in contrast to the approach we previously employed in I. The essential point of the development, however, is that the separable approximation offers a simple and accurate means for treating the exchange effects which had previously represented the most time-consuming aspect of numerical approaches to electron-molecule scattering. The separable expansion of exchange terms may prove useful in other numerical approaches to electron-molecule scattering, such as the numerical Schwinger variational technique of McKoy and co-workers[18] and the linear-algebraic approach recently proposed by Schneider and Collins.[20] The techniques outlined here for electron-molecule scattering in the static-exchange approximation should also prove useful for extensions to multichannel calculations and electronic excitation.

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