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Singular Value Decomposition Solution of the Schrödinger Equation in the Presence of Exchange Terms

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Abstract A new numerical method of solving integro-differential equations appearing in the theory of atomic and nuclear scattering systems has been devised. It is termed Singular Value Decomposition Method (SVD). It consists in expanding the exchange kernel into a number of separable terms by means of the Singular Value Decomposition and then iterating over the remainder. In this paper, we extend our SVD method to the scattering of low energy electron-helium which has been the subject of interest, both theoretically and experimentally. We compare our results with the Moments Method which is widely used. The Moments Method consists of making an expansion of the solution into an especially favorable basis that takes care of the non-exchange part of the Hamiltonian.

Keywords SVD · Integro · Kernel · Non-local

1 Introduction

Taking into account the Pauli Exclusion Principle for identical Fermi particles, requires that the quantum-mechanical wave function be totally antisymmetric. In the Hartree-Fock approximation this leads to an integro-differential form of the Schrödinger equation, whose integral kernel is made up from the exchange terms. For this reason, the solution is not as easily obtained as for the case without exchange terms. In the early investigations [18] the exchange terms were taken into account iteratively, by using Green's functions defined by the local part of the potential. However, the iterations do not always converge. Methods to accelerate the convergence have been introduced, but such methods tend to be cumbersome and unpredictable. An improved iteration procedure that is known as "SVD method" has

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been obtained by means of a separable representation of the integral kernel [5, 6]. We have shown that it is a definite improvement over the conventional iteration techniques. Other methods have been developed which consist in introducing a set of basis functions such as Laguerre polynomials, and expanding both the solution and the target states into this basis [1, 2, 4, 7, 10, 12, 14, 17]. Another such expansion that is widely used and accurate is known as the Moments Method [3, 8, 9, 11, 13, 15, 16] which uses a set of basis functions obtained by applying successively higher powers of the Hamiltonian operator with local potentials on an initial scattering wave function. This method has been very successful in applications to nuclear and atomic physics problems. All of these procedures, however, that depend on having a basis are not easy to implement.

In this paper, we extend our SVD method to the scattering of low energy electron-helium. This scattering reaction has been the subject of continuing interest, both theoretically and experimentally. We compare numerically our method of calculation to the Moments Method. Our SVD method consists in replacing the exchange kernel by a number of fully separable terms, and carrying out iterations only over the remainder. This is possible because, as is well known, the Green's function for a Schrödinger equation with both local and non-local but fully separable potentials can be obtained without much difficulty by adding solution-dependent constants to the Green's function distorted only by the local potential.

2 Electron Scattering from Helium

In atomic units, the Schrödinger equation for a helium atom and one free electron can be written as

$$\left[-\left(\nabla_1^2+\nabla_2^2+\nabla_3^2\right)-\frac{4}{r_1}-\frac{4}{r_2}-\frac{4}{r_3}-\frac{4}{r_{12}}-\frac{4}{r_{13}}-\frac{4}{r_{23}}-E\right]\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3)=0, \tag{1}$$

where

$$r_{ij}=|\vec{r}_i-\vec{r}_j|, \quad i\geq 1, j\leq 3,$$

and where E is the total energy of the scattering system and Ψ is total wave function of the scattering system.

The Pauli exclusion principle requires that the total wave function for the system be antisymmetric in the interchange of any two electrons. Since the target configuration forms a singlet spin state, only one orientation of the scattering electron spin need to be considered. Furthermore, since exchange is explicitly included, the atomic orbitals must be properly paired with the wave function for the scattering electron. From these considerations the total wave function with total angular momentum $L=0$ and total spin $S=1/2$ quantum numbers describing the scattering electron by a helium atom is written as

$$\begin{aligned}\Psi^{L=0,S=1/2}(\vec{r}_1,\vec{r}_2,\vec{r}_3)\approx\frac{1}{\sqrt{3}r_1r_2r_3}&[\Phi(1,2)u(3)S(1,2)\alpha(3)+\Phi(1,3)u(3)S(1,3)\alpha(2)\\&+\Phi(2,3)u(1)S(2,3)\alpha(1)],\end{aligned} \tag{2}$$

where S is the singlet spin function

$$S(i,j)=\frac{1}{\sqrt{2}}\left[\alpha(i)\beta(j)-\alpha(j)\beta(i)\right] \tag{3}$$

α and β are single electron spinors with projections $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ respectively, u is the wave function of the scattering electron and $\Phi^{(n)}(i, j)$ is the wave function of the helium atom. Without loss of generality, we consider the helium atom in its ground state, i.e.,

$$\Phi(i, j) = \psi(i)\psi(j).$$

The radial scattering differential equation for u is obtained by multiplying (1) by $S(1,2)$ $\psi(r_1)\psi(r_2)$ then integrating over the radial coordinates r_1 and r_2 and all angles. The u equation is given as

$$\left[\frac{d^2}{dr^2} + k^2 - V^S(r)\right]u(r) = Y^S(r) = \int dr' K(r, r')u(r') \tag{4}$$

where

$$V^S(r) = \frac{-4}{r} + \int dr' \psi(r') \frac{4}{r_>} \psi(r') \tag{5}$$

and

$$\begin{aligned} Y^S(r) = & -\int dr' \psi(r')u(r') \left(-\frac{d^2}{dr^2} - E - a_1\right)\psi(r) - \left(\int_0^\infty dr' \psi(r')u(r')\right. \\ & \times \left.\int dr' \psi(r') \left(\frac{2}{r_{12}} - \frac{2}{r}\right)\psi(r')\right)\psi(r) \\ & - \left(\int_0^\infty dr' \psi(r')u(r') \left(\frac{2}{r_{12}} - \frac{2}{r}\right)u(r')\psi(r)\right) \\ = & \int_0^\infty dr' K(r, r')u(r') \\ a_1 = & \int\int dr_1 dr_2 \psi(r_2)^2 \left(-\frac{d^2}{dr_1^2} - \frac{d^2}{dr_2^2} - \frac{4}{r_1} - \frac{4}{r_2} + \frac{4}{r_{12}}\right)\psi(r_1)u(r_2) \end{aligned} \tag{6}$$

3 The Separable Content of the Nonlocal Kernel

The singular value decomposition method (SVD) consists of decomposing the kernel $K_l(v', v'')$ into a number of fully separable terms plus a remainder. The method is as follows. First a numerical integration algorithm is chosen which divides the range of integration $[0, r_{max}]$ into a set of N discrete points. Correspondingly the kernel $K_l(r', r'')$ is transformed into a $N \times N$ matrix $K_l(i, j)$, with $i = 1, 2, \dots, N$, and likewise for j. We perform a singular value decomposition on K as follows:

$$K = U\sigma V^T, \tag{7}$$

where the columns of U are the column vectors $\boldsymbol{u}_s$ of length N, and the columns of V are the column vectors $\boldsymbol{v}_s$ of length N, and σ is a $N \times N$ diagonal matrix of the non-negative quantities σ_s, $s = 1, 2, \dots N$, ordered by decreasing size (the largest ones first). The matrices

U and V are each orthogonal,

$$\begin{aligned}\sum_{i=1}^{N} u_{is}u_{ir} &= \delta_{sr} \quad 1 \le s \le N, 1 \le r \le N\\ \sum_{i=1}^{N} v_{is}v_{ir} &= \delta_{sr} \quad 1 \le s \le N, 1 \le r \le N\end{aligned} \tag{8}$$

size (the largest ones first). As a result of the above, a fully separable piece of rank n can be separated out of the matrix K, leaving a residual matrix K^R,

$$K = K^S + K^R \tag{9}$$

by carrying the sum in (8) to an upper limit n which includes only the largest values σ_s.

$$K^S = \sum_{s=1}^{n} \boldsymbol{u}_s \sigma_s \boldsymbol{v}_s^T \equiv \sum_{s=1}^{n} |\boldsymbol{u}_s\rangle\, \sigma_s\, \langle \boldsymbol{v}_s|\,. \tag{10}$$

4 Greens Function for a Separable Potential

In order to obtain the Green's function $G_{V+K^S}(r, r')$, which is distorted by both the local potential V and the fully separable Kernel K^S, we write the solution of (1) symbolically in the form

$$\psi(r) = f(r) + G_V\left(K^S + K^R\right)\psi(r) \tag{11}$$

where the integration over the variables is implicitly assumed. For simplicity, let us assume that only two terms in K^S are responsible for the divergence of the iterative Green's function approach, (11). In order to obtain the overlap integrals $\langle v_i|\psi\rangle$, $i = 1, 2$ we multiply (11) on the left with $\sqrt{\sigma_i}\langle v_i|$ and integrate over all r's, with the result that $\sqrt{\sigma_i}\langle v_i|\psi\rangle = \sqrt{\sigma_i}\langle v_i|f\rangle + \sqrt{\sigma_i}\langle v_i|G_V(K^S + K^R)|\psi\rangle$. Rearranging terms one obtains the following matrix equation for $\sqrt{\sigma_i}\langle v_i|\psi\rangle$

$$M\sqrt{\sigma}\begin{bmatrix}\langle v_1|\psi\rangle\\ \langle v_2|\psi\rangle\end{bmatrix} = \sqrt{\sigma}\begin{bmatrix}\langle v_1|f\rangle\\ \langle v_2|f\rangle\end{bmatrix} + \sqrt{\sigma}\begin{bmatrix}\langle v_1|K^R|\psi\rangle\\ \langle v_2|K^R|\psi\rangle\end{bmatrix}, \tag{12}$$

where

$$M = \begin{pmatrix}1 - G_{11} & -G_{12}\\ -G_{21} & 1 - G_{22}\end{pmatrix}, \qquad \sqrt{\sigma} = \begin{pmatrix}\sqrt{\sigma_1} & 0\\ 0 & \sqrt{\sigma_2}\end{pmatrix}$$

and

$$G_{ss'} = \sqrt{\sigma_s}\langle v_s|G_V|u_{s'}\rangle\sqrt{\sigma_{s'}}, \qquad s = 1, 2.$$

Solving (12) for $[\langle v_1|\psi\rangle, \langle v_2|\psi\rangle]$ and inserting the result into Eq. (11), one obtains

$$\psi = f - G_V\,[u_1\rangle, u_2\rangle]\,\sqrt{\sigma}M^{-1}\sqrt{\sigma}\left\{\left[\langle v_1|f\rangle, \langle v_2|f\rangle\right]^T + \left[\langle v_1|K^R|\psi\rangle, \langle v_2|K^R|\psi\rangle\right]^T\right\}, \tag{13}$$

from which the result for G_{V+K^S} emerges:

$$G_{V+K^S} = G_V\left\{1 - [|u_1\rangle|u_2\rangle]\,\sqrt{\sigma}M^{-1}\sqrt{\sigma}\begin{bmatrix}\langle v_1|\\ \langle v_2|\end{bmatrix}\right\} \tag{14}$$

Table 1 We display the phase shift values in radians for the electron-helium-positron scattering case calculated from the HF theory, δ^{HF} at $ka_0 = 0.2, 0.4, 0.6$, and 1.0 where ka_0 is the continuum wave number. Also displayed are phase shifts calculated using the moments method

ka_0	$\delta^{\mathrm{HF(SVD)}}$	$\delta^{\mathrm{HF(Moments)}}$
0.4	2.559	2.563
0.6	2.298	2.319
0.8	2.085	2.101
1.0	1.902	1.903

Hence, the solution of (11) in terms of G_{V+K^S} is:

$$\psi(r) = G_{V+K^S} f(r) + G_{V+K^S} K^R \psi(r). \tag{15}$$

5 Results and Discussion

The set of coupled integro-differential equations was iterated through a self consistent field procedure. We solved the equation in the presence of only the local potential, and then including the non-local part through Green's function iteration. The iterations converged with up to 5 singular values and at most 10 iterations are required to obtain a convergence of one part in ten thousand. Our phase shift results in the Table below are in perfect agreement with Moments Method results of one single open channel e-Helium scattering.

In conclusion, our method described here improves upon the convergence by separating out of the non-local kernel a fully separable part by means of the Singular Value Decomposition method (SVD). By this means the region of convergence could be extended to a larger domain. Moreover, the SVD method has the advantage that it can be used for non-localities, which are more general than the semi-separable exchange ones. SVD is inherently stable therefore it is likely the method of choice.

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