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INTEGRAL EQUATION FOR $d\mu$, A PROGRESS REPORT

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NUMERICAL SOLUTION OF THE SCHROEDINGER
INTEGRAL EQUATION FOR dtu , A PROGRESS REPORT*

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Abstract

The Schroedinger Integral Equation is derived for an N-body system, and solutions for required Green's functions are obtained. The initial method of numerical solution has yielded the correct ground states and lower excited states of He (test case) and dtu . Steps are being taken to improve the numerical accuracy.

1. Introduction

The Schroedinger Integral Equation (SIE) is defined here to be an integral equation that is the equivalent to the ordinary, differential Schroedinger Equation [1]. It is derived in Section 3, as a general equation for N-body systems. It is applied in later sections to bound states of 3-body systems (including dtu) with zero angular momentum.

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The numerical method employed solves the SIE as a generalized matrix eigenvalue problem for values of the wave function, ψ , at a finite number of spatial points. Since ψ is determined directly, it is expected to have a fairly uniform accuracy at all points, including the set of points in $d\tau$ where the d - t separation is zero. The wave function there determines both the d - t fusion probability and the α - μ sticking coefficient.

The SIE requires no boundary conditions (they are in the Green's function), and it can be applied for all potential energies, which enter on a purely numerical basis.

2. Coordinates

Derivation and application of the SIE are facilitated by the use of an orthogonal coordinate system for N particles in which no mass factors appear in the kinetic energy operator.

After the center of mass motion has been separated out in the Schroedinger equation, Jacobain coordinates are defined in sets of three, with each coordinate being a cartesian component of a vector. The first vector runs from any one particle to any other, the second from the center of mass of the first two to any third particle, the third from the center of mass of the first three particles to any fourth, etc. The kinetic energy operator in the Schroedinger Equation is then (electron atomic units, where $\hbar = e = m_e = 1$, are used throughout)

$$-\frac{1}{2} \sum_{i=1}^{N-1} \left(\frac{1}{M_i} + \frac{1}{m_i} \right) \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right),$$

where
$$M_i = \sum_{j=0}^{i-1} m_j ,$$

x_1, y_1 , and z_1 are the components of the 1th vector, m_1 is the mass of the particle where the 1th vector ends, and M_0 is the mass of the particle where the first vector begins. A new set of coordinates is then chosen:

$$\xi_1 = c_1 x_1, \quad \xi_2 = c_1 y_1, \quad \xi_3 = c_1 z_1, \quad \xi_4 = c_2 x_2, \quad \xi_5 = c_2 y_2, \text{ etc. ,}$$

where

$$c_i = \left(\frac{1}{M_i} + \frac{1}{m_i} \right)^{-\frac{1}{2}} .$$

The kinetic energy operator is then

$$-\frac{1}{2} \sum_{i=1}^n \frac{\partial^2}{\partial \xi_i^2} \equiv -\frac{1}{2} \nabla_n^2$$

where $n = 3(N-1)$ is the dimensionality of the problem, and ∇_n^2 is the Laplacian in the space of the cartesian ξ coordinates.

In these coordinates the N-body Schoedinger equation is

$$\left(-\frac{1}{2}\nabla_n^2 + V - E\right)\Psi = 0, \quad (1)$$

where the masses now appear in the expression for the potential energy, V .

3. Derivation of the SIE

Equation (1) is written as

$$(\nabla_n^2 - k^2)\Psi[x] = \lambda(V[x] - E - \frac{1}{2}k^2)\Psi[x] \quad (2)$$

and the corresponding Green's function equation is

$$(\nabla_n^2 - k^2)G_k[x, x']_n = \delta[x - x'], \quad (3)$$

where

$$\delta[x - x'] = \prod_{i=1}^n \delta[\xi_i - \xi'_i].$$

The terms involving k^2 add generality, but only $k = 0$ is employed in the applications reported here. The n -component vector $\underline{r}$ runs from the origin in ξ space to the point defined by the ξ_i , or it may be thought of as simply designating the set of ξ_i values.

To obtain the SIE, $\underline{r}$ is replaced by $\underline{r}'$ in Eq. (2) and both sides are multiplied by $G_k[\underline{r}, \underline{r}']_n$, followed by integration over the full n -dimensional space of the primed coordinates. The result is

$$\begin{aligned} & \int G_k[\underline{r}, \underline{r}']_n (\nabla_n^2 - k^2) \psi[\underline{r}'] d\mathbf{r}' \\ &= 2 \int G_k[\underline{r}, \underline{r}']_n (V[\underline{r}'] - E - \frac{1}{2} k^2) \psi[\underline{r}'] d\mathbf{r}', \quad (4) \end{aligned}$$

where $\int d\mathbf{r}' = \prod_{i=1}^n \int_{-\infty}^{\infty} d\xi'_i$.

Integration by parts is performed twice on the part of the left side of Eq. (4) involving ∇_n^2 , resulting, in effect, in the exchange in position of G and ψ there. Equation (3) is then employed with $\underline{r}$ and $\underline{r}'$ interchanged, and the left side of Eq. (4) evaluates to $\psi[\underline{r}]$. These latter steps are valid when $\psi[\underline{r}]$ and $G_k[\underline{r}, \underline{r}']_n \rightarrow 0$ with sufficient strength as $r \rightarrow \infty$

and $G_k[\underline{r}, \underline{r}']_n = G_k[\underline{r}', \underline{r}]$. This last condition is apparent from the results of the following ^{section} where G is determined. The asymptotic conditions are met for any k , at least when ψ is a bound state.

The result for the SIE following from Eq. (4) is

$$\psi[r] = 2 \int G_k[r, r']_n (V[r'] - E - \frac{1}{2} k^2) \psi[r'] d\tau' \quad (5)$$

The coordinates appearing in Eq. (5) can be transformed to any other set, thus the vector r can be thought of as representing any set of coordinates in Eq. (5).

Equations equivalent or similar to Eq. (5) have been employed elsewhere. For instance, Kalos [2] has solved for simple systems, an equation essentially equivalent to Eq. (5), by quantum monte carlo methods. If V is treated as a perturbation, a perturbation expansion for ψ is substituted in Eq. (5), and $k = 1/\sqrt{2E}$, then the Born expansion for scattering problems results.

4. The Green's Function

Solution of Eq. (3) for $G_k[r, r']_n$ is begun by generalizing the standard three-dimensional method for obtaining G to n dimensions. Thus,

$$G_k[r, r']_n = - \int \frac{\phi_s^*[r'] \phi_r[r]}{k^2 + k'^2} d\tau_k \quad (6)$$

where r is defined as before, r is a vector in an n -dimensional space with cartesian components r_i , the integral is over all of r space and

$$\kappa^2 = \sum_{i=1}^n \kappa_i^2 \quad ;$$

and where

$$\phi_{\kappa}[x] = (2\pi)^{-n/2} e^{i\kappa \cdot x}$$

is a solution to

$$(\nabla_n^2 + \kappa^2) \psi_{\kappa}[x] = 0$$

with normalization conditions,

$$\int \phi_{\kappa'}^*[x] \phi_{\kappa}[x] d\tau = \delta[\kappa - \kappa']$$

and

$$\int \phi_{\kappa}^*[x'] \phi_{\kappa}[x] d\tau_{\kappa} = \delta[x - x'] .$$

Eq. (6) is evaluated by the substitution

$$\frac{1}{\kappa^2 + k^2} = \int_0^{\infty} e^{-k^2 u - \kappa_1^2 u - \kappa_2^2 u - \dots - \kappa_n^2 u} du .$$

The integral in Eq. (6) then becomes an integral over u of a product of n uncoupled integrals, each of which is easily evaluated, and the remaining integral is evaluated in terms of a Bessel function, giving

$$G_k[r, r'] = -(2\pi)^{-\frac{n}{2}} \left(\frac{k}{|r-r'|} \right)^{\frac{n}{2}-1} K_{\frac{n}{2}-1}[k|r-r'|], \quad (7)$$

where K is a modified Bessel function of the second kind.

Kalos [2] and Hobson [3] obtained results essentially equivalent to Eq. (7). Hobson's solution involves the fact that

$$\left(\frac{\partial^2}{\partial \rho^2} + \frac{n-1}{\rho} \frac{\partial}{\partial \rho} - k^2 \right) G = 0, \quad \rho \neq 0,$$

where $\rho = |r - r'|$. For n odd, $K_{\frac{n}{2}-1}$ is an exponential times an inverse power series in $|r - r'|$ of finite length; for n even, K is an infinite series. The oddness or evenness of n is opposite to that of the number of particles.

Eq. (7) is not the unique solution to Eq. (3) since any solution to the homogeneous form of Eq. (3) could be added to it. Many, if not all, possible additions would yield unacceptable divergences. It is probably true that Eq. (7) is the solution to Eq. (3) that comes closest to matching the boundary, finiteness, and integrability conditions imposed on ψ .

For $k = 0$, $G_k[r, r']_n$ reduces to simpler form. By taking the limit $k \rightarrow 0$ in Eq. (7) and neglecting additive constants (for $k=0$ they have no effect) one obtains

$$G_0[r, r']_{2m+1} = \frac{1}{2} \left(\prod_{i=0}^{m-1} (i - \frac{1}{2}) \right) \pi^{-m} |r - r'|^{-2m+1},$$

$$G_0[r, r']_2 = \frac{1}{2\pi} \ln |r - r'|, \quad (8)$$

$$G_0[r, r']_{2m+4} = -\frac{m!}{4\pi^{m+2}} |r - r'|^{-2m-2},$$

where m is zero or a positive integer and the product in the first equation is unity for $m=0$. Thus, for $n = 2$, $G_0[r, r']_n$ has the form $C_n/|r - r'|^{n-2}$.

For S states ψ does not depend on the external orientation angles of the N -body system. If the same is true of V , then the integral of G over these angles in Eq. (5) may be performed before solving for ψ . The result is a reduced form of G designated g . These functions may be called radial Green's functions because they depended only on the inter-particle distances. For $N \geq 3$ there are three external angles, and the dimensionality of the problem is reduced by three. When ψ depends on the external angles but V does not, and a dependence of ψ on these angles can be assigned, a similar reduction in dimensionality can be achieved.

For application in the following section (3-particle S states), $G_0[r, r']_6$ from Eq. (8) is integrated over the external angles to give

$$g_0[\xi, \eta, \mu; \xi', \eta', \mu']_3 =$$

$$-\frac{2}{\pi} \left(A^2 + 16\xi\eta\xi'\eta' A (1-\mu\mu') + 64(\xi\eta\xi'\eta')^2 (\mu-\mu')^2 \right)^{-\frac{1}{2}},$$

(9)

where $A = (\xi^2 - \xi'^2 + \eta^2 - \eta'^2)^2 + 4(\xi\eta - \xi'\eta')^2,$

and where, with reference to the coordinates defined in Section 1.,

$$\xi = (\xi_1^2 + \xi_2^2 + \xi_3^2)^{\frac{1}{2}}, \quad \eta = (\xi_4^2 + \xi_5^2 + \xi_6^2)^{\frac{1}{2}},$$

and μ is the cosine of the angle between the two vectors.

The SIE with $k = 0$ for the S states of three particles is therefore

$$\Psi[\xi, \eta, \mu] =$$

$$2 \int_0^\infty \int_{-1}^1 \int_{-1}^1 g_0[\xi, \eta, \mu; \xi', \eta', \mu']_3 (V[\xi', \eta', \mu'] - E) \Psi[\xi', \eta', \mu'] \xi'^2 \eta'^2 d\mu' d\eta' d\xi'. \quad (10)$$

For three particles interacting by coulomb forces only,

$$\begin{aligned}
 V[\xi, \eta, \mu] = & \frac{\sqrt{m_1+m_2} \, e_1 e_2}{\sqrt{\frac{m_1}{m_2} \xi^2 + \frac{m_1}{m_3} \eta^2 - 2 \sqrt{\frac{m_1 m_1}{m_2 m_3}} \xi \eta \mu}} \\
 & + \frac{\sqrt{m_1+m_2} \, e_3 e_1}{\sqrt{\frac{m_2}{m_1} \xi^2 + \frac{m_1}{m_3} \eta^2 + 2 \sqrt{\frac{m_1 m_2}{m_1 m_3}} \xi \eta \mu}} \\
 & + \sqrt{\frac{m_1 m_2}{m_1+m_2}} \frac{e_1 e_2}{\xi} ,
 \end{aligned}$$

where e_i are the electric charges on the particles and $m = m_1 + m_2 + m_3$.

5. Numerical Method

A discrete analogue to Eq. (10) may be obtained by employing center-point integration to implicitly evaluate the integral. The result is

$$\psi_{\underline{i}} = 2 \Delta \xi \Delta \eta \Delta \mu \sum_{\underline{j}} \xi_{\underline{j}}^2 \eta_{\underline{j}}^2 g_{\underline{i}\underline{j}} (V_{\underline{j}} - E) \psi_{\underline{j}} , \quad (11)$$

where $\underline{i}$ and $\underline{j}$ are indices denoting discrete points in ξ - η - μ space.

and $\Delta\xi, \Delta\eta$, and $\Delta\mu$ are the constant interval lengths on the edges of the cell surrounding each point. Implicit in Eq. (11) are upper limits to the values of ψ and η . The larger these limits and the smaller the interval lengths, the more accurate is Eq. (11) as a representation of Eq. (10).

Whenever $j=1$ in the summand of Eq. (11) $g_{ij} = g_{11} = \infty$ (cf. Eq. 9 for $\xi=\xi'$, $\eta = \eta'$, and $\mu = \mu'$), although the integral of g in any region surrounding this singularity is finite. Therefore g_{11} is replaced by its mean value in the cell.

For $\Delta\xi, \Delta\eta$, and $\Delta\mu$ small, that value is

$$\bar{g}[\xi, \eta, \mu] = -(4\pi \Delta\xi \Delta\eta \Delta\mu \xi^2 \eta^2 (1-\mu^2))^{-1} I[x, y, z]$$

where

$$I[x, y, z] = 8xy \sinh^{-1} \frac{z}{\sqrt{x^2+y^2}} + 8yz \sinh^{-1} \frac{x}{\sqrt{y^2+z^2}} + 8zx \sinh^{-1} \frac{y}{\sqrt{z^2+x^2}} \\ - 4x^2 \tan^{-1} \frac{yz}{x\sqrt{x^2+y^2+z^2}} - 4y^2 \tan^{-1} \frac{zx}{y\sqrt{x^2+y^2+z^2}} - 4z^2 \tan^{-1} \frac{xy}{z\sqrt{x^2+y^2+z^2}},$$

where

$$x = \frac{\Delta\xi}{2} \sqrt{(\xi^2 + \eta^2)(1-\mu^2)}, \quad y = \frac{\Delta\eta}{2} \sqrt{(\xi^2 + \eta^2)(1-\mu^2)}, \quad z = \frac{\Delta\mu}{2} \xi \eta.$$

The singularities in V , also integrable, occur only on the edges of the cells.

Accuracy of the implicit integration can be improved, in particular in regions of space near or enclosing the singularities in g and V , by numerically integrating the products of known functions appearing in the integral over a finer mesh within each cell. That process is termed subintegration and is denoted by placing a bar over the products involved. The numerical analogue of the SIE for 3-particle S states is then

$$\psi_{\tilde{j}} = 2 \Delta \xi \Delta \eta \Delta \mu \sum_{\tilde{j}} \left(\overline{\xi_{\tilde{j}}^2 \eta_{\tilde{j}}^2 g_{\tilde{i}\tilde{j}} V_{\tilde{j}}} - E \overline{\xi_{\tilde{j}}^2 \eta_{\tilde{j}}^2 g_{\tilde{i}\tilde{j}}} \right) \psi_{\tilde{j}} \quad (12)$$

With the following definitions,

$$\begin{aligned} A_{\tilde{i}\tilde{j}} &= 2 \Delta \xi \Delta \eta \Delta \mu \overline{\xi_{\tilde{j}}^2 \eta_{\tilde{j}}^2 g_{\tilde{i}\tilde{j}} V_{\tilde{j}}} - \delta_{\tilde{i}\tilde{j}} , \\ B_{\tilde{i}\tilde{j}} &= 2 \Delta \xi \Delta \eta \Delta \mu \overline{\xi_{\tilde{j}}^2 \eta_{\tilde{j}}^2 g_{\tilde{i}\tilde{j}}} , \end{aligned} \quad (13)$$

Eq. (12) becomes

$$\underline{\underline{A}} \underline{\underline{\psi}} = E \underline{\underline{B}} \underline{\underline{\psi}} , \quad (14)$$

where $\underline{\underline{A}}$ and $\underline{\underline{B}}$ are matrices with components given by Eq. (13) and $\underline{\underline{\psi}}$ is a vector with components $\psi_{\tilde{j}}$.

Equation (14) with the definitions given by Eq (13) was solved for the helium atom as a test and for the d^+u mesomolecule. The results are given in the following section. Solution was obtained by a computer routine that obtains all eigenvalues and eigenvectors. Methods will be sought that give only those lowest few of interest. This will permit the use of a larger number of grid points.

There are a number of additional ways to improve accuracy and efficiency of the numerical solution. Implementation has begun on two of them. First, the wave function will be expressed as a product of an approximate ψ and an unknown function. Most of the variation in ψ would be in the approximate form, which will be included in the subintegration. With less variation in the unknown part, the accuracy of the implicit integration will be improved. Second, a variable grid spacing will be employed. This improves accuracy by allowing concentration of the grid points in regions where ψ varies most rapidly.

A planned improvement is a transformation of the radial coordinates so that their infinities occur at finite values of the new coordinates. Coupled with the use of an approximate wave function, this improvement should allow integration to infinity in the radial coordinates.

6. Current Results

As a test case Eq. (14) was applied to the S states of the helium atom. Particle 1 was taken to be the nucleus, particles 2 and 3 were the electrons. Maximum values of ξ and η were those for which ψ was about 0.003 of its maximum value. A $12 \times 12 \times 4$ grid in ξ , η , and μ was employed. Thus ψ varied by an average factor of about 1.7 from point to point in each of these radial directions.

Several solutions corresponding to bound states were obtained, all with the correct symmetry properties. The eigenvalues for the ground state and first two excited states were reasonably accurate. Table 1. shows a comparison of the ground state with the ground state obtained by Kinoshita with a 39-term variational wave function [4]. As given to three figures the variational eigenvalue is essentially exact. The discrepancy in the SIE eigenvalue comes in part from the fact that the eigenvalue has only first order accuracy relative to errors in ψ , in contrast to the variational method where there is second order accuracy. The SIE wave function may be substituted into the variational expression for energy to obtain a second-order-accurate upper bound. The numerical result of this calculation is given in the table, and it is an improvement over the eigenvalue.

A measure of the accuracy of a wave function is the constancy of the local energy, $((-1/2\nabla^2 + V)\psi)/\psi$. The rms relative difference between the values of this quantity and its mean value is given in Table 1. for both the SIE and variational wave functions. Both wave functions have about the same value of the rms relative difference. Thus, at the present time, the SIE wave function for the He ground state is probably about as accurate as the variational result, but the energy is not as accurate.

Preliminary results for $\text{d}\mu$ on a $12 \times 12 \times 6$ grid are encouraging. The wave functions of the ground state and the one excited S state have proper symmetry and show the correct qualitative dependencies on ξ , η , and μ . The ground state wave function accuracy is estimated to be about 5% on the

average. On a scale in which the dtu energy is zero when all three particles are unbound with zero kinetic energy, the ground state energy is 2% below the correct value.

Tests with the SIE applied to one and two dimensional systems indicated, as expected, that accuracy improves without limit as the integration ranges increase and the integration intervals decrease. In all cases to date, as accuracy improves from a poor value, the ground state eigenvalue first oscillates around its correct value and then approaches the correct value from the negative side.

In tests on S states of H with Green's functions for various values of k , $k=0$ gave the best accuracy. An iterative solution of Eq. (11) for the same system gave encouraging results. An approximate ψ was placed in the sum, and the ψ calculated was then used to repeat the process. The solution converged for several iterations, but after many iterations divergences occurred. Whether the divergences were fundamental to the problem or the result of numerical instability is uncertain. This method of solution will be investigated further.

At present, the steps to improve accuracy described in the previous section are being pursued, and others are being investigated.

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Table 1. Results for the SIE applied to He on a 12 x 12 x 4 grid compared to those of Kinoshita [4] using a 39-term variational wave function.

Energies [e^2/a_0]:

	Eigenvalue	Numerical	Relative Energy Variation
		Upper Bound	
Variational	-2.90	—	0.03
SIE	-2.95	-2.87	0.04

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