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On exact analytical solutions for the few-particle Schrödinger equation: III. Spatially symmetric S states of two identical particles in the field of a massive third particle

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Abstract. A procedure for solving the few-particle Schrödinger equation exactly is applied to a model system consisting of two identical particles and a massive third particle. The type of interaction potential is not specified except that it should not diverge more rapidly than r^{-2} at the particle positions. Allowable interactions include the Coulomb and the harmonic oscillator potentials. The principles are illustrated by reference to the spatially symmetric states of the system.

The solution has the form of a multipole expansion in spherical polar coordinates. The radial dependence for each multipole component is defined by a power series including logarithmic terms. Explicit expressions are given for the coefficients in the expansion. Provided the equations are solved in an appropriate order, each coefficient is expressed directly in terms of the energy and of parameters associated with the normalisability of the function. The explicit expressions, obtained initially from recurrence relations and from the continuity of the derivative of the wavefunction, are simplified dramatically by the use of appropriate identities. Further simplification is possible for potentials of suitable form. Exact coefficients are obtained for low-order terms in the wavefunction of a two-electron atom.

1. Introduction

The quantum mechanical behaviour of a system of particles interacting via central forces is of fundamental importance. The few-particle Schrödinger equation describes this behaviour for systems where relativistic effects are negligible. There is a vast literature associated with the approximate solution of that equation, one of many reviews being by Hurley (1976). Exact solutions have been found for two-particle systems (such as the hydrogen atom) and for special three-particle systems where the forms of the potentials allow the Schrödinger equation to be separated (see e.g. Kestner and Sinanoglu 1962). Many interesting systems, including those with Coulomb forces, have a non-separable Schrödinger equation. This paper deals with a method of solution applicable to non-separable equations.

The archetypal system contains three particles. If two of these are chosen to be identical we may study the special properties arising from that choice. It is convenient to choose the third particle to be massive compared with the identical particles. This restriction removes one term of modest complexity from the Hamiltonian, but is not essential to the solution procedure. The restricted form translates directly to the case of a two-electron atom, which is of special interest.

Eigenfunctions of two-electron atoms are not analytic in the interparticle separations (Morgan 1978a, b). Power series of these variables cannot be solutions of the Schrödinger equation. Thus, as pointed out by Morgan (1978a), the variationally determined coefficients in power series wavefunctions of the type employed by Kinoshita (1957) and Pekeris (1958) do not converge to well defined limits as the series are lengthened to improve the estimates of the energy. By contrast, coefficients in an analytical expansion would converge in a predictable way. Furthermore, it is possible to determine at least some of the coefficients in an analytical expansion exactly.

Papers by Bartlett (1937), Fock (1954), Newman (1973) and Knirk (1974a, b, c, d) have revealed that two-electron eigenfunctions can be expressed as series with terms involving logarithms of the interparticle distances. The approaches of Newman and Knirk are particularly interesting in that the coefficients in the expansion are numbers related by algebraic recurrence relations. In principle, algebraic expressions for the coefficients could be obtained from the recurrence relations. Tedious but essentially straightforward manipulations are involved. Additional conditions, such as the requirement that the wavefunctions should be normalisable (square-integrable), must be applied to determine the coefficients uniquely.

Davis and Maslen (1982, hereafter called paper II) have described a perturbation treatment of the ground state of helium. They used recurrence relations derived from the perturbation equations to generate numerical values for the coefficients in the wavefunction expansions, and developed a numerical method for estimating the parameters associated with normalisability. We now extend this approach to solve the Schrödinger equation itself, with particular emphasis on obtaining and simplifying algebraic expressions for the coefficients. Exact expressions for the coefficients will permit the normalisability problem to be solved by a potentially exact method described in the following paper (Davis and Maslen 1983, hereafter referred to as IV).

The methods developed here apply to the spatially symmetric S states of any three-particle system with two identical particles and a massive third particle, provided the interparticle potentials are not too singular. When the identical particles are electrons, the relevant states are those with ^{1}S symmetry. Special properties of the Coulomb potential are described later, where the ^{1}S states of two-electron atoms are discussed.

2. The form of the wavefunction

Hyperspherical coordinates (Knirk 1974a) are frequently used in studies of the three-particle problem. Here we prefer spherical polar coordinates for which the radial components of the wavefunction have the important property of asymptotic separability (see IV). Following a centre-of-mass transformation with $m_3 \gg m_1 = m_2$, we take the limit $m_3 \to \infty$. The ^{1}S states may then be described in terms of three coordinates r_1, r_2 and Θ shown in figure 1. With further rescaling of lengths and energies, the Hamiltonian operator in the Schrödinger equation

$$(H - E)\Psi = 0$$

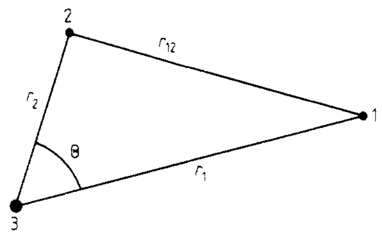

Figure 1. Coordinates for describing the spatially symmetric S states of the identical particles 1 and 2 in the field of a massive particle 3.

may be written as

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+V(r_1,r_2,\Omega),$$

leading to the equation

$$\left[-\tfrac{1}{2}\sum_{\tau=1}^{2}\left(r_\tau^{-2}\frac{\partial}{\partial r_\tau}r_\tau^2\frac{\partial}{\partial r_\tau}+r_\tau^{-2}\frac{\partial}{\partial\Omega}(1-\Omega^2)\frac{\partial}{\partial\Omega}\right)+V(r_1,r_2,\Omega)-E\right]\Psi(r_1,r_2,\Omega)=0 \qquad (1)$$

where $\Omega=\cos\Theta$.

The wavefunction is to be written as a multipole expansion with logarithmic contributions to the radial functions. The logarithmically varying functions may be written in a variety of equivalent forms (see II). Here we write the trial solution as

$$\sum_{l=0}^{\infty}\sum_{ijp}C_{ijlp}P_l(\Omega)r_1^ir_2^j\exp(-\lambda_1r_1)\exp(-\lambda_2r_2)\ln^p r_1 \qquad r_1>r_2 \qquad (2)$$

where $P_l(\Omega)$ is a Legendre polynomial. Logarithmic singularities are avoided by restricting the region of definition of the radial functions. The expression for the $r_1<r_2$ region is obtained by interchanging r_1 and r_2 in equation (2). The resulting spatial wavefunction is symmetric with respect to the interchanging of identical particles. Multiplying by an antisymmetric singlet spin function guarantees the overall antisymmetry of the wavefunction, when the identical particles are electrons.

The exponential factors $\exp(-\lambda_1r_1)$ and $\exp(-\lambda_2r_2)$ are not essential features of the formal solution. Their inclusion has certain computational advantages discussed in IV. Their effect can in any case be simulated by changes in the coefficients C_{ijlp}.

The trial solution (2) can be expressed in a variety of alternative forms. The one chosen provides a convenient structure for the coefficients associated with the normalisability of the wavefunction. Although no systematic attempt has been made to minimise the number of terms in the expansion, or to optimise the rate of convergence of the coefficients, the series truncates in important asymptotic cases. In the perturbation treatment of the helium atom, the convergence of the radial functions is rapid. These properties are described in II.

Convergence of the expansion of Legendre polynomials is rather slow. On the other hand, the results given in IV indicate that this expansion quickly approaches a simple asymptotic form. Assuming that the analytical expression for the asymptotic form can be identified, the remaining l dependence could be expressed as a multiplying series converging rapidly in l.

3. Recurrence relations

Substituting the trial solution (2) into the Schrödinger equation (1) yields recurrence relations

$$
\begin{aligned}
-\{l, i+2\}C_{i+2\,j\,l\,p} - \{l, j+2\}C_{i\,j+2\,l\,p} \\
= \lambda_1(i+2)C_{i+1\,j\,l\,p} + \lambda_2(j+2)C_{i\,j+1\,l\,p} - (p+1)(i+\tfrac{5}{2})C_{i+2\,j\,l\,p+1} \\
+ (p+1)\lambda_1 C_{i+1\,j\,l\,p+1} - \tfrac{1}{2}(p+1)(p+2)C_{i+2\,j\,l\,p+2} \\
- (E + \tfrac{1}{2}\lambda_1^2 + \tfrac{1}{2}\lambda_2^2 - V_{\mathrm{op}})C_{ijlp}
\end{aligned}
\tag{3}
$$

where

$$\{l, m\} = \tfrac{1}{2}[l(l+1) - m(m+1)].$$

In these relations the potential V from the Schrödinger equation is represented by an operator V_{op} which, typically, multiplies the coefficient C_{ijlp} and varies its indices (see equation (25), for example). The use of a different form of logarithmic factor in equation (2) changes the form of the right-hand side, but does not alter the left-hand side of equation (3). The analysis which follows does not depend on the particular form chosen for the logarithmic terms.

4. Explicit expressions

The recurrence relation (3) does not define the energy E and the coefficients C_{ijlp} uniquely. Additional constraints are imposed by the requirement that an eigenfunction must belong to the domain of the Hermitian operator H. These requirements (II) confine non-zero coefficients to the region

$$j \geqslant 0 \qquad \text{and} \qquad k = i + j \geqslant -1 \tag{4}$$

and also lead to the condition

$$-\sum_{i+j=k} (i-j)C_{ijlp} = (p+1)\sum_{i+j=k} C_{i\,j\,l\,p+1} + (\lambda_2 - \lambda_1)\sum_{i+j=k-1} C_{ijlp} \tag{5}$$

which ensures continuity of the derivative of the wavefunction at $r_1 = r_2$.

Formal solution of these equations follows the procedure described by Davis and Maslen (II) in their analysis of the perturbation equations for the ground state of helium. The domain of non-zero coefficients, restricted by hermiticity as in equation (4), is further restricted by the form of the recurrence relation to the region with $j \geqslant l$.

Provided the potential V is not more singular than r_1^{-2} or r_2^{-2} at the nucleus, the right-hand side of the recurrence relation (3) involves coefficients C_{ijlp} with lower $k = i + j$ or higher p than coefficients on the left-hand side. The simultaneous recurrence and derivative continuity equations may then be solved in order of increasing k and decreasing p. Solution of the simultaneous equations yields the set of expressions

$$C_{-l+k\,l\,l\,p} = X^{-1}(k, l, 0)\left[-2\sum_{g=1}^{\infty} g^{-1}(2l+1+g)^{-1}X(k, l, g)R(k, l, g, p) - D(k, l, p)\right] \tag{6a}$$

$$C_{-l+k-1\,l+1\,l\,p}=[1(2l+2)]^{-1}2R(k,l,1,p)$$
$$C_{-l+k-2\,l+2\,l\,p}=[2(2l+3)]^{-1}[2R(k,l,2,p)+(k+1)(2l-k)C_{-l+k\,l\,l\,p}]$$
$$C_{-l+k-3\,l+3\,l\,p}=[3(2l+4)]^{-1}[2R(k,l,3,p)+k(2l-k+1)C_{-l+k-1\,l+1\,l\,p}]$$
$$C_{-l+k-4\,l+4\,l\,p}=[4(2l+5)]^{-1}[2R(k,l,4,p)+(k-1)(2l-k+2)C_{-l+k-2\,l+2\,l\,p}]\text{ etc,} \tag{6}$$

with

$$X(k,l,g)=\sum_{m=0}^{\infty} \times\frac{(-2l+k-4m-2g)(k+1-g,k+1-g-2m)!!\times(2l-k-2+g+2m,2l-k-2+g)!!}{(g+2m,g)!!(2l+1+g+2m,2l+1+g)!!} \tag{7}$$

The notation $(a, b)!!$ for a product string is defined in the appendix. $R(i+j+2, l, j+2-l, p)$ and $D(k, l, p)$ are a shorthand notation for the expressions on the right-hand side of equations (3) and (5) respectively. The related terms in equations (6) and (6a) are obtained by appropriate adjustment of the indices.

Solved in the correct order, equations (6) give the value of an unknown coefficient (on the left) in terms of known coefficients and some undetermined parameters associated with normalisability of the wavefunction (on the right). Within each k, p plane the order for l is irrelevant. For each k, l, p line the order is that of increasing j, following the arrangement of the above equations. Numerical calculations following this procedure are described in IV.

5. The reduced expressions

5.1. *The reduction procedure*

The nature of the solution is clarified if the explicit expressions are simplified. We first consider the functions $X(k, l, g)$ defined in (7). These are independent of the potential terms. Combining neighbouring terms in (7) leads to

$$X(k,l,g)=-(2l+g+1)-(2l-k-2)\sum_{m=1}^{\infty}(-1)^m(2m+g-k-3,g-k-3)!!\times(2l-k-4+g+2m,2l-k-2+g)!!(g,g+2m)!!\times(2l+g+1,2l+g-1+2m)!!. \tag{8}$$

Simplification now proceeds in two stages. The first is to expand products in the denominator by partial fractions (see appendix), obtaining a finite sum resembling a binomial expansion and involving the functions

$$\mathcal{F}_{2n+1}=\sum_{m=n}^{\infty}(-1)^{m-n}(2m+1)^{-1}=(-1)^n\left[\pi/4+\mathop{\mathcal{S}}_{m=n}^{-1}(-1)^m(2m+1)^{-1}\right]$$
$$\mathcal{F}_{2n+2}+\sum_{m=n}^{\infty}(-1)^{m-n}(2m+2)^{-1}=(-1)^n\left[\tfrac{1}{2}\ln 2+\mathop{\mathcal{S}}_{m=n}^{-1}(-1)^m(2m+2)^{-1}\right].$$

The summation $\mathscr{S}_{m=p}^{q-1}$ is interpreted as $\Sigma_{m=p}^{q-1}$ for $p<q$, as $-\Sigma_{m=q}^{p-1}$ for $p>q$ and as zero when $p=q$. Next, identities based on the equation

$$\binom{s}{j}=\binom{s-1}{j}+\binom{s-1}{j-1}$$

are used to reduce the order of the binomial expansion coefficients. This shortens the finite sum, in some cases to a single term.

The procedure that applies when k is odd differs in detail from that used when k is even. In both cases equation (8) is rearranged in the form

$$X(k, l, g)=-(2l+g+1)+\alpha(k, l, g)S(k, l, b), \tag{9}$$

where $b=\frac{1}{2}(g-k)$.

5.2. Reduction for odd k

For odd k

$$\alpha(k, l, g)=(2l-k-2)(g, g-k-3)!!(2l+g+1, 2l-k-2+g)!!$$

and

$$S(k, l, b)=\sum_{n=b}^{\infty}(-1)^{n-b}(2n-1, 2n+k+2)!!(2n+2l-2, 2n+2l+k+1)!!$$

which may be expanded by the partial fractions method to give

$$S(k, l, b)=[(k+1)!!]^{-1}\sum_{p=0}^{(k+1)/2}(-1)^p\binom{\frac{1}{2}(k+1)}{p} \times(2l-3-2p, 2l+k-2p)!!(\mathscr{F}_{2b+2p+1}-\mathscr{F}_{2b+2l+k-2p+1}). \tag{10}$$

We now apply the identities

$$\binom{\frac{1}{2}(k+1)}{j}(2l-3-2j, 2l+k-2j)!!=(2l+k)^{-1}\left\{\left[2\binom{\frac{1}{2}(k-1)}{j-1}+\binom{\frac{1}{2}(k-1)}{j}\right](2l-3-2j, 2l+k-2-2j)!!-\binom{\frac{1}{2}(k-1)}{j-1}\times(2l-1-2j, 2l+k-2j)!!\right\}$$

$$\binom{\frac{1}{2}(k-1)}{j}(2l-5-2j, 2l+k-4-2j)!!=(2l-k-2)^{-1}\left\{\left[2\binom{\frac{1}{2}(k-3)}{j}+\binom{\frac{1}{2}(k-3)}{j-1}\right](2l-3-2j, 2l+k-4-2j)!!-\binom{\frac{1}{2}(k-3)}{j}\times(2l-5-2j, 2l+k-6-2j)!!\right\}$$

and

$$S(k,l,j)+S(k,l,j+1)=(2j-1,2j+k+2)!!(2j+2l-2,2j+2l+k+1)!!$$
$$=[(k+1)!!]^{-1}\sum_{p=0}^{(k+1)/2}(-1)^p\binom{\frac{1}{2}(k+1)}{p}(2l-3-2p,2l+k-2p)!!$$
$$\times[(2j+2p+1)^{-1}-(2j+2l+k-2p+1)^{-1}]$$

in order, obtaining

$$S(k,l,b)=(k+1)^{-1}(2l+k)^{-1}\bigg((2b-1,2b+k)!!(2b+2l-2,2b+2l+k-1)!!$$
$$+\frac{2(2b+1,2b+k)!!(2b+2l-2,2b+2l+k-3)!!-4S(k-4,l,b+1)}{(k-1)(2l-k-2)}\bigg). \tag{11}$$

Equation (11) constitutes a ladder operation for lowering k by 4 and increasing b by 1. Repeated use of this operation enables $S(k,l,b)$ to be related to $S(-1,l,b+\frac{1}{4}(k+1))$ when $\frac{1}{2}(k+1)$ is even and to $S(1,l,b+\frac{1}{4}(k-1))$ when $\frac{1}{2}(k+1)$ is odd. These special cases can be obtained directly from equation (10), leading to:

for k odd and $\frac{1}{2}(k+1)$ even

$$S(k,l,b)=(-4)^{(k+1)/4}[(k+1)!!]^{-1}(2l-k-6,2l+k)!!!!(\mathcal{F}_{2b+(k+3)/2}-\mathcal{F}_{2b+2l+(k+1)/2})$$
$$+\sum_{j=0}^{(k-3)/4}(-4)^j(k-1-4j,k+1)!!(2l-k-6,2l+k)!!!!$$
$$\times(2l+k-4-4j,2l-k-6+4j)!!!!$$
$$\times(2b+2j-1,2b-2j+k)!!(2b+2j+2l-2,2b-2j+2l+k-1)!!$$
$$+2\sum_{j=0}^{(k-3)/4}(-4)^j(k-3-4j,k+1)!!(2l-k-6,2l+k)!!!!$$
$$\times(2l+k-4-4j,2l-k-2+4j)!!!!$$
$$\times(2b+2j+1,2b-2j+k)!!(2b+2j+2l-2,2b-2j+2l+k-3)!! \tag{12}$$

for k odd and $\frac{1}{2}(k+1)$ odd

$$S(k,l,b)=-2(-4)^{(k-1)/4}[(k+1)!!]^{-1}(2l-k-6,2l+k)!!!!$$
$$\times(\mathcal{F}_{2b+(k+5)/2}-\mathcal{F}_{2b+2l+(k-1)/2})$$
$$+\sum_{j=0}^{(k-1)/4}(-4)^j(k-1-4j,k+1)!!(2l-k-6,2l+k)!!!!$$
$$\times(2l+k-4-4j,2l-k-6+4j)!!!!$$
$$\times(2b+2j-1,2b-2j+k)!!(2b+2j+2l-2,2b-2j+2l+k-1)!!$$
$$+2\sum_{j=0}^{(k-5)/4}(-4)^j(k-3-4j,k+1)!!(2l-k-6,2l+k)!!!!$$
$$\times(2l+k-4-4j,2l-k-2+4j)!!!!$$
$$\times(2b+2j+1,2b-2j+k)!!(2b+2j+2l-2,2b-2j+2l+k-3)!!. \tag{13}$$

5.3. Reduction for even k

When k is even we define

$$\alpha(k, l, g) = (2l-k-2)(g, 2l-k-2+g)!!(2l+g+1, g-k-3)!!$$

and

$$S(k, l, b) = \sum_{n=b}^{\infty} (-1)^{n-b}(2n-1, 2n+2l+k+1)!!(2n+2l-2, 2n+k+2)!!$$

which, for $k > 2l$, expands by partial fractions to

$$\begin{aligned} S(k, l, b) = {} & [(k+2l)!!]^{-1} \sum_{p=0}^{k/2+l} (-1)^p \binom{k/2+l}{p} (2l-3-2p, k+1-2p)!! \mathscr{F}_{2b+2p+1} \\ & + [(k+2-2l)!!]^{-1} \sum_{q=0}^{k/2-l+1} (-1)^q \binom{k/2-l+1}{q} \\ & \times (-2l-1-2q, k+1-2q)!! \mathscr{F}_{2b+k+2-2q}. \end{aligned} \qquad (14)$$

Successive use of the identities

$$\begin{aligned} \binom{k/2+l}{j}(2l-3-2j, k+1-2j)!! = {} & \left[(2l-3)\binom{k/2+l-1}{j} \right. \\ & \left. -(k+3)\binom{k/2+l-1}{j-1} \right] (2l-5-2j, k+1-2j)!! \end{aligned}$$

$$\begin{aligned} \binom{k/2+l-1}{j}(2l-7-2j, k-1-2j)!! = {} & \left[(k+1)\binom{k/2+l-2}{j} \right. \\ & \left. -(2l-3)\binom{k/2+l-2}{j-1} \right] (2l-7-2j, k+1-2j)!! \end{aligned}$$

$$\begin{aligned} S(k, l, j) + S(k, l, j+1) = {} & (2j-1, 2l+k+2j+1)!!(2l+2j-2, k+2j+2)!! \\ = {} & [(k+2l)!!]^{-1} \sum_{p=0}^{k/2+l} (-1)^p \binom{k/2+l}{p} \\ & \times (2l-3-2p, k+1-2p)!!(2j+2p+1)^{-1} \\ & + [(k+2-2l)!!]^{-1} \sum_{q=0}^{k/2-l+1} (-1)^q \binom{k/2-l+1}{q} \\ & \times (-2l-1-2q, k+1-2q)!!(k+2+2j-2q)^{-1} \end{aligned}$$

leads to the ladder operation

$$\begin{aligned} S(k, l, b) = {} & (k+2l)^{-1}[(2l-3)(2b-1, 2l+k+2b-1)!! \\ & \times (2l+2b-4, 2b+k+2)!! + (k+6-2l)S(k, l-2, b+1)]. \end{aligned} \qquad (15)$$

The same ladder operation is obtained by a related method when $k < 2l$. The ladder operation relates $S(k, l, b)$ for arbitrary l to the simpler cases $S(k, k/2+2, b-\frac{1}{2}(k/2+2-l))$ when $k/2-l$ is even and $S(k, k/2+1, b-\frac{1}{2}(k/2-l+1))$ when $k/2-l$ is odd and $l \leqslant k/2+1$. These simpler cases may be evaluated from (14) directly. The resulting expressions are inconvenient for computer evaluation because they contain cancelling infinite terms for some values of the arguments. Applying the transformation

$$S(k,l,b)=(-1)^{b-b'}S(k,l,b')+\mathop{\mathscr{S}}_{j=b}^{b'-1}(-1)^{j-b}(2j-1,2j+2l+k+1)!!$$
$$\times(2j+2l-2,2j+k+2)!! \qquad (k \text{ even})$$

with $b'=b+\frac{1}{2}(k/2-l+2)$ when $k/2-l$ is even, and $b'=b+\frac{1}{2}(3k/2-l+3)$ when $k/2-l$ is odd, overcomes this problem. We obtain:

for k even and $k/2-l$ even

$$\begin{aligned}S(k,l,b)=(-1)^{(k/2-l+2)/2}\Bigg[&(2k+4,k+2l)!!!!\\&\times(-2,k-2l+2)!!!!2^{k+2}(0,2k+4)!!\\&\times\left(\mathscr{F}_{2b+1}-\tfrac{1}{2}\sum_{j=0}^{k+1}(k+1-2j)!(2b-1,2b+2k-2j+3)!!\right)\\&+\mathop{\mathscr{S}}_{j=(k/2-l+2)/2}^{-1}(k+2l+4j,k+2l)!!!!\\&\times(k-2l-2-4j,k-2l+2)!!!!(2l+1+4j)\\&\times(2b-2j+k/2-l-1,2b+3k/2+l+3+2j)!!\\&\times(2b+2j+k/2+l,2b-2j+3k/2-l+2!!)\Bigg]\\&+\sum_{j=b}^{b+(k/2-l)/2}(-1)^{j-b}(2j-1,2l+k+2j+1)!!\\&\times(2l+2j-2,k+2j+2)!!\end{aligned} \tag{16}$$

for k even, $k/2-l$ odd and $l\leqslant k/2+1$

$$\begin{aligned}S(k,l,b)=(-1)^{(3k/2-l+3)/2}\Bigg[&(2k+2,k+2l)!!!!(0,k-2l+2)!!!![(k+1)!!]^{-2}\\&\times\Bigg((-1)^{(k+2)/2}\mathscr{F}_{2b+2k+4}+\tfrac{1}{2}(-1)^{k/2}(2b+2k+3)^{-1}\\&+\tfrac{1}{2}\sum_{j=0}^{(k-2)/2}(-1)^{j}(k-1-2j,-1)!!(k-1-2j,-1)!!\\&\times(2b+2j+k+1,2b+3k-2j+3)!!\Bigg)\\&-\sum_{j=0}^{(k/2-l-1)/2}(k+2l+4j,k+2l)!!!!(k-2l-2-4j,k-2l+2)!!!!\\&\times(2l+1+4j)(2b-2j+3k/2-l,2b+2j+5k/2+l+4)!!\\&\times(2b+2j+3k/2+l+1,2b-2j+5k/2-l+3)!!\Bigg]\\&+\sum_{j=b}^{b+(3k/2-l+1)/2}(-1)^{j-b}(2j-1,2l+k+2j+1)!!\\&\times(2l+2j-2,k+2j-2)!!.\end{aligned} \tag{17}$$

The values of $S(k, l, b)$ when $k/2-l$ is odd and $l \geq k/2+3$ are related to those of $S(k, k/2+3, b+\frac{1}{2}(l-k/2-3))$, which may be established from the $l=k/2+1$ form of equation (15) directly. This gives

$$S(k, l, b) = \tfrac{1}{2}(2k+6, k+2l)!!!!(-4, k-2l+2)!!!!(2b+l-\tfrac{1}{2}k-4, 2b+l+\tfrac{3}{2}k+2)!!$$
$$+ \sum_{j=(k/2-l+3)/2}^{-1} (k+2l+4j, k+2l)!!!!$$
$$\times(k-2l-2-4j, k-2l+2)!!!!(2l+1+4j)$$
$$\times(2b-2j-3, 2b+2l+2j+k+1)!!(2b+2l+2j-2, 2b-2j+k)!!. \qquad (18)$$

5.4. *Further simplification*

Further reduction of the expressions for the $X(k, l, g)$ is possible for particular ranges of k and l. In cases where the original expressions for $X(k, l, g)$ (equation (7)) truncate, zeros arise in the numerators of the multipliers $\alpha(k, l, g)$ that cancel with zeros in the denominators of some terms in the expressions for $S(k, l, b)$. Some of the simplified $X(k, l, g)$ expressions are given in § 7.

6. Analytic continuation of the $X(k, l, g)$ expressions

The procedure described above, resulting in different simplified expressions for $X(k, l, g)$ in the various regions of k, l, g space, is valid only when k, l and g are integers. In some (but not all) cases these expressions can be simplified by making use of a connection between $X(k, l, g)$ and the hypergeometric function. To do so we must allow k and l to be non-integral. This does not affect the validity of equation (3) or, consequently, the definition of $X(k, l, g)$, provided factorials are replaced by gamma functions, where necessary.

The restriction of l to integral values in the physical solution arises because the Legendre functions with non-integral l do not belong to the domain of the Hamiltonian (Davis *et al* 1982). The index j must be integral if l is integral (II).

A restriction on k emerges when the lowest value of k for which non-zero coefficients C_{ijlp} occur is considered. Suppose, as is usual when starting the solution (II), that the value of p is such that coefficients with larger p are zero. Then the functions $R(k, l, g, p)$ and $D(k, l, p)$ in the numerator of equation (6*a*) are all zero. A zero value for $C_{-l+k\,l\,l\,p}$, leading to the trivial solution, can be avoided only if $X(k, l, 0)$ vanishes. Equation (21) shows that this occurs when

$$k = 2l+4n \qquad n=0, 1, 2, \ldots$$

and so k (and i) must also be integers. Writing the double factorials in (8) as gamma functions and taking the even g case as an example, we obtain

$$X(k, l, g) = -\frac{(2l+g+1)}{(2l-k-2+g)}[g+(2l-k-2)(-1)^{g/2}(g/2)!I(-1)] \qquad (g \text{ even}) \qquad (19)$$

where

$$I(z)=I(z_{g/2})=\int_0^{z_{g/2}}\dots\int_0^{z_2}\int_0^{z_1}F(l+g/2-k/2-1,g/2-k/2-\tfrac{1}{2};l+g/2+\tfrac{1}{2};z)\,dz_1\,dz_2\dots dz_{g/2}. \tag{20}$$

$F(a, b; c; z)$ is the hypergeometric function (Abramowitz and Stegun 1965).

The $g=0$ case is especially important as $X(k, l, 0)$ appears in the denominator of the expression for $C_{-l+2\,llp}$ (equation (6a)). The vanishing of this denominator causes some of the C_{ijlp} coefficients to be undetermined by the recurrence relations and the derivative continuity conditions. When $g=0$, equation (19) reduces to

$$X(k,l,0)=-(2l+1)F(l-k/2-1,-k/2-\tfrac{1}{2};l+\tfrac{1}{2};-1)=\frac{2^{k/2-l+1}(2l+1)\sin[(k-2l)\pi/4]\Gamma(l+\tfrac{1}{2})\Gamma(k/4-l/2+1)}{\pi^{1/2}\Gamma(k/4+l/2+1)}. \tag{21}$$

Equation (21) unifies the expressions obtained by the method of § 5 and is valid for non-integral values of k and l.

Simplification of (19) when $g>0$ is facilitated by the use of Euler's formula (Erdelyi 1953)

$$F(a,b;c;z)=\frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)}\int_0^1 t^{b-1}(1-t)^{c-b-1}(1-tz)^{-a}\,dt$$

valid for $\mathrm{Re}(c)>\mathrm{Re}(b)>0$. For example, consider the case of $k=2$ and $g=4$. After performing the z integrations in (20),

$$I(-1)=\frac{\Gamma(l+\tfrac{5}{2})}{\Gamma(l)\Gamma(\tfrac{5}{2})}\int_0^1[\tfrac{4}{3}t^{l-3}[(1-t^2)^{3/2}-(1-t)^{3/2}]-2t^{l-2}(1-t)^{3/2}]\,dt \qquad (l>0). \tag{22}$$

The remaining integrals are beta functions (Erdelyi 1953) which may be expressed as gamma functions, giving

$$X(2,l,4)=-\frac{4(2l+5)}{3l}\left(\frac{8\pi^{1/2}\Gamma(l+\tfrac{5}{2})}{2^l(l+1)\Gamma(l/2+\tfrac{1}{2})\Gamma(l/2+\tfrac{1}{2})}-5l-6\right) \qquad (l\geqslant 0). \tag{23}$$

Although the restricted validity of Euler's formula requires l to be greater than zero (22), the expression for $X(2, l, 4)$ has a well defined limit

$$X(2,0,4)=40\ln 2-\tfrac{100}{3}$$

at $l=0$, in agreement with (17). Equation (23) unifies the results of (16), (17) and (18) and is valid for non-integral l. While such a unification can easily be achieved for particular values of k and g, it is difficult to find a simple expression for $I(z)$ valid for general g. The use of (19) and (20) does not necessarily result in expressions for $X(k, l, g)$ more convenient than those of § 5.

7. An example—the two-electron atom

7.1. The potential terms

If particles 1 and 2 in figure 1 are electrons and the massive particle 3 has a positive charge Z, then with suitable scaling of the coordinates the potential term in (1) becomes

$$V(r_1, r_2, \Omega) = -r_1^{-1} - r_2^{-1} + (Zr_{12})^{-1} = -r_1^{-1} - r_2^{-1} + Z^{-1} \sum_{l=0}^{\infty} r_n^l r_{3-n}^{-l-1} P_l(\Omega) \qquad (24)$$

where $n = 1$ if $r_1 < r_2$ and $n = 2$ if $r_1 > r_2$. In the recurrence relation (3) we now have

$$V_{\text{op}} C_{ijlp} = -C_{i+1\,jlp} - C_{i\,j+1\,lp} + Z^{-1} \sum_{\substack{n=-l \\ (n+l \text{ even})}}^{l} \sum_{m=(l+n)/2}^{j} C_{i+m+1\,j-m\,m-n\,p}\, a_l^{m,m-n} \qquad (25)$$

where

$$a_l^{m,m-n} = \frac{(2l+1)(l-n-1)!!(l+n-1)!!(2m+l-n)!!(2m-l-n-1)!!}{(l-n)!!(l+n)!!(2m-l-n)!!(2m+l-n+1)!!}$$

is a Clebsch–Gordan coefficient defined so that

$$P_m(\Omega)P_n(\Omega) = \sum_{l=0}^{\infty} a_l^{m,n} P_l(\Omega).$$

The third term in (25) represents the electron–electron interaction. For a given k, the functions $R(k, l, g, p)$ in (6) are completely specified by (3) and (25), provided the C_{ijlp} coefficients corresponding to lower values of k are known.

The coefficients C_{ijlp} with the given k are specified unless both p and $X(k, l, 0)$ vanish (II), in which case $C_{-l+k\,l\,l\,0}$ is undetermined. An analysis of the coefficients with $k \leqslant 2$ enables the nature of the undetermined coefficients to be clarified.

7.2. The coefficients for $k = -1, 0, 1$

The lowest value of k consistent with (4) is -1. By the argument of § 6, non-zero coefficients do not occur for $k = -1$ since $X(k, l, 0)$ does not vanish for any $l \geqslant 0$. When $k = 0$, $X(k, l, 0)$ vanishes for $l = 0$ only. The coefficients C_{000p} are therefore arbitrary, but to be finite the numerator of (6a) must vanish. This condition requires that $C_{000p} = 0$ for $p \geqslant 1$. C_{0000} is the only non-zero coefficient for $k = 0$, and represents a factor multiplying the complete solution. We choose its value to be $C_{0000} = 1$.

For $k = 1$ the C_{0000} coefficient propagates to all values of l via the electron–electron term in the recurrence relation, which contributes an amount $Z^{-1} C_{0000} a_l^{l,0} = Z^{-1}$ to $R(1, l, 2, 0)$. The functions $R(1, l, g, 0)$ are zero for $g > 2$. The required $X(k, l, g)$ values, obtained from (13), are

$$X(1, l, 0) = -2(2l-1) \qquad X(1, 0, 1) = -1 \qquad X(1, l, 2) = -(2l+3).$$

With these results the non-zero coefficients for $k = 1$ are found to be

$$C_{1000} = \lambda_1 - 1 + \tfrac{1}{2}Z^{-1} \qquad C_{0100} = \lambda_2 - 1 \qquad C_{-1200} = \tfrac{1}{6}Z^{-1}$$

$$C_{-l+1\,l\,l\,0} = -Z^{-1}/[2(2l-1)] \qquad C_{-l-1\,l+2\,l\,0} = Z^{-1}/[2(2l+3)] \qquad \text{for } l \geqslant 1.$$

7.3. $k=2$ coefficients

The electron–electron term in (25) simplifies to the extent that only terms with $g \leq 4$ in (6*a*) are non-zero when $k=2$. For $l=0$ and $l=1$ it is easy to show that the electron–electron expression sums to zero for $g \geq 4$. This simplification removes all terms proportional to Z^{-2} from the electron–electron expression for $l=1$, leaving only Z^{-1} terms. The same conclusion applies when $l \geq 2$. Here Z^{-2} terms, the only contribution for $g \geq 4$, also sum to zero. In this case the electron–electron expression reduces to a sum over ratios of double factorials and can be simplified by the method applied to $X(k, l, g)$ in § 5. For example, the coefficient multiplying Z^{-2} for $g=2$ is

$$-\tfrac{1}{2} \sum_{\substack{n=-l \\ (l+n \text{ even})}}^{l} \frac{(l-n-3)!!(l+n-1)!!}{(l-n)!!(l+n)!!}$$

$$= [(2l)!!]^{-1} \sum_{n=0}^{l} \binom{l}{n} (2n-3)!!(2l-2n-1)!!$$

$$= [(2l)!!]^{-1} \sum_{n=0}^{l} \left[\binom{l-1}{n-1} + \binom{l-1}{n}\right] (2n-3)!!(2l-2n-1)!!$$

$$= (2l-2)[(2l)!!]^{-1} \sum_{n=0}^{l-1} \binom{l-1}{n} (2n-3)!!(2l-2n-3)!!.$$

Continuing in this way, the order of the binomial expansion coefficient can be reduced to 1, when the sum is seen to vanish.

The results of § 5 may be used to show that $X(2, l, 1) = -\frac{2}{3}(5l-1)$ and $X(2, l, 3) = -(2l+4)$, valid for $l \geq 0$. An expression for $X(2, l, 4)$ was derived in § 6 and the result

$$X(2, l, 2) = \tfrac{2}{3}(2l+3)\left(1 - \frac{4\pi^{1/2}\Gamma(l+\frac{3}{2})}{2^l(l+1)\Gamma(l/2+\frac{1}{2})\Gamma(l/2+\frac{1}{2})}\right) \qquad (l \geq 0)$$

can be derived by the same method. Equations (6) produce the following non-zero coefficients for $k=2$:

for $l \geq 0$ and $n \geq 0$

$$C_{-l-2n-2\; l+2n+4\; l\; 0} = \frac{-2Z^{-1}(-1)^n(2l+1)(2l-2)!!!!(2l+2n)!!(2n-1)!!}{(2l)!!!!(2n+4)!!(2l+2n+5)!!\nu}$$

where $\nu = \frac{1}{4}\pi$ when l is odd and $\nu = 1$ when l is even,

$$C_{2000} = \tfrac{1}{6}\{Z^{-1}[\tfrac{1}{2}Z^{-1} + 3(\lambda_1 - 1) + \ln 2] + 3(\lambda_1 - 1)^2 - E - 1\}$$

$$C_{1100} = (\lambda_2 - 1)[\tfrac{1}{2}Z^{-1} + (\lambda_1 - 1)]$$

$$C_{0200} = \tfrac{1}{6}\{Z^{-1}[\tfrac{1}{2}Z^{-1} + \lambda_1 - \ln 2] + 3(\lambda_2 - 1)^2 - E - 1\}$$

$$C_{-1300} = \tfrac{1}{18}Z^{-1}(3\lambda_2 - 2)$$

for $l \geq 2$

$$C_{-l+2\; l\; l\; 0} = \frac{-Z^{-1}}{6l(l-1)}\left(\frac{3l(l-1)\lambda_1 - 4l^2 + l + 1}{2l-1} + \frac{[(-2l-2)!!!!]^2}{(2l-1)!!\nu}\right)$$

$$C_{-l+1\; l+1\; l\; 0} = \tfrac{1}{2}Z^{-1}[1 - (l+1)\lambda_2]/[(l+1)(2l-1)]$$

$$C_{-l\,l+2\,l\,0}=\frac{Z^{-1}}{2l(l+3)}\left(l\lambda_1+1-\frac{[(2l-2)!!!!]^2}{(2l-1)!!\nu}\right)$$

$$C_{-l-1\,l+3\,l\,0}=\frac{Z^{-1}}{6(l+2)}\left(\lambda_2-\frac{2l+1}{l+1}+\frac{(l+3)\lambda_2-1}{(2l+3)}\right).$$

The $l=1$ case is special in that $p=1$ terms appear for the first time. $X(2,1,0)$ is zero, so the numerator in (6*a*) must vanish if C_{1110} is to be finite. This fixes the value of C_{1111} to be $\frac{4}{3}Z^{-1}(\pi^{-1}-\frac{1}{2})$. The other non-zero coefficients for $l=1$ are

$$C_{0210}=\tfrac{1}{4}Z^{-1}(1-2\lambda_2) \qquad C_{-1310}=\tfrac{1}{10}Z^{-1}(\lambda_1+1-4/\pi)$$

$$C_{-2410}=\tfrac{1}{10}Z^{-1}(\lambda_2-\tfrac{17}{18}).$$

7.4. *Undetermined coefficients*

Inspection of the $l=1$ coefficients given above for $k=2$ shows that they are just the $l\to 1$ limits of the corresponding $l\geqslant 2$ coefficients. It may be asked whether C_{1110} is given correctly by the limit as $l\to 1$ of the $l\geqslant 2$ expression for $C_{-l+2\,l\,l\,0}$. This is not so. Whereas the $X(k,l,g)$ are continuous functions of l at $l=1$, the numerator in (6*a*) for $p=0$ and $k=2$ is not. The discontinuity arises in a term proportional to $C_{-l+2\,l\,l\,1}$ in $R(2,l,2,0)$. This coefficient can be written consistently with the value of C_{1111} determined above as

$$C_{-l+2\,l\,l\,1}=[4Z^{-1}(\pi^{-1}-\tfrac{1}{2})/3+(l-1)x]\delta_{l1}$$

where the value of x is arbitrary. δ_{l1} is the Kronecker delta. Equation (6*a*) then gives

$$C_{1110}=Z^{-1}[-\tfrac{1}{2}\lambda_1+16/27\pi^2-8/27\pi+\tfrac{1}{2}Zx].$$

Thus C_{1110} is not completely determined by the recurrence and derivative continuity equations.

Undetermined coefficients arise in this way whenever $X(k,l,0)$ vanishes in (6*a*) for $p=0$. Thus the coefficients $C_{l+4n\,l\,l\,0}$ for $n\geqslant 0$ remain to be determined by the application of additional restrictions on the solution.

7.5. *Relation to the Z^{-1} perturbation expansion*

The two-electron wavefunction generated by this procedure appears naturally as a power series in Z^{-1}. Thus, for a given state, the Z^{-n} component of the wavefunction will be identical to the solution of the nth-order Rayleigh–Schrödinger perturbation equation. After setting $\lambda_1=\lambda_2=1$ and performing some minor manipulation, the Z^{-1} components of the coefficients derived above are seen to be the same as the coefficients in the first-order perturbation solution for the ground state of helium, described in II. Note that the energy term was not shown in the perturbation solution.

There are two major differences between the perturbation approach and the method in this paper. In this treatment all powers of Z^{-1} contributing to a coefficient are obtained simultaneously. Secondly, the treatment applies to the wavefunction of any state with ^{1}S symmetry. State selection is achieved by setting the Z-independent components of the energy and arbitrary coefficients equal to their values in the independent electron problem, where the electron–electron potential is neglected. The use of spherical polar coordinates is particularly helpful in this instance, since the independent electron problem is separable with these coordinates. Its solutions are just products of hydrogen atom wavefunctions.

As an example, the ground state of the two-electron system is selected by choosing $\lambda_1 = \lambda_2 = 1$ and the Z^0 component of the energy to be -1. The Z-independent components of the other arbitrary coefficients (always confined to $l = 0$) should be zero. The Z^0 part of the solution is then represented by a series truncating at $k = 0$, corresponding to the product of 1s wavefunctions of hydrogen.

Having selected a state for consideration, the Z-dependent components of the energy and arbitrary coefficients are determined by the normalisability requirement (see IV). A unique set of values for these parameters will be obtained for each state.

8. Conclusions

A systematic procedure has been developed for obtaining and simplifying exact expressions for coefficients in formal series solutions for the Schrödinger equation describing the spatially symmetric S states of two identical particles in the field of a massive third particle.

Arbitrary coefficients, whose values determine the normalisability of the solution, are rigorously identified for solutions expressed in spherical polar coordinates.

For Coulomb systems, exact expressions for infinitely many coefficients (those with $k = 0$, 1 and 2) are given. The expressions for large values of k are more complicated, but preliminary studies, which have reached an advanced stage for $k = 3$, show that they may be simplified by the methods described here. In particular, we note that the summand in (6*a*) for $k = 3$ mainly involves ratios of factorials. Sums of this type can be simplified by the methods applied successfully to $X(k, l, g)$ and to the electron–electron potential terms.

The techniques developed here, used in conjunction with the treatment of the normalisability problem as described in IV, will assist in the search for exact solutions of the few-particle Schrödinger equation.

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Appendix. String notation

Product strings of even or odd factors are denoted in this paper by $(a, b)!!$, where a and b are both even or both odd integers. Specifically,

$$(a, b)!! = \begin{cases} a(a-2)(a-4)\dots(b+2) & \text{if } a > b \\ 1 & \text{if } a = b \\ [b(b-2)(b-4)\dots(a+2)]^{-1} & \text{if } a < b. \end{cases}$$

For any string we observe that

$$(a, b)!! = [(b, a)!!]^{-1}$$

while for strings of the same parity (even or odd)

$$(a, b)!!(c, d)!! = (a, d)!!(c, b)!!.$$

The definition also applies when a and b are non-integral real numbers and $a-b$ is an even integer. It can be generalised to describe strings whose successive factors differ by an integer other than 2. For example, if $l>0$,

$$(k+2l, k-2l)!!!! = [(k+2l)(k+2l-4)(k+2l-8)\dots(k-2l+4)].$$

When manipulating strings of even integers it is often desirable to cancel zeros where these occur in both the numerator and denominator of an expression. This procedure is justified by regarding the expression as a limit of ratios of non-integral strings.

Care is required when extracting a common factor from the factors in a string. Thus

$$(6, -4)!!(-4, 2)!! = \lim_{x\to 0} (-1)^5 \frac{(-6-x)(-4-x)(-2-x)(-x)(2-x)}{(2+x)(x)(-2+x)}$$

$$= (-1)^4(2, -8)!!(-4, 2)!!$$

so that

$$(6, -4)!! = (-1)^4(2, -8)!!.$$

By examining cases of this type we arrive at the following *ad hoc* rule for extracting a common factor from a string containing zero—do not extract the common factor from zero.

Factorials of integers, including negative integers, may be defined in terms of the string notation. For example, if n is an integer

$$n! = (n, 0)! \qquad (2n)!! = (2n, 0)!! \qquad (2n+1)!! = (2n+1, -1)!!$$

$$(4n)!!!! = (4n, 0)!!!! \qquad (4n+2)!!!! = (4n+2, -2)!!!!.$$

Products of strings in the denominator of an expression may be expanded by partial fractions. For example, if $s \geq 0$,

$$(n-2, n+2s)!! = (2s)^{-1}[(n, n+2s)!! - (n-2, n+2s-2)!!]$$

$$= (2s)^{-1}(2s-2)^{-1}[(n+2, n+2s)!!$$

$$-2(n, n+2s-2)!! + (n-2, n+2s-4)!!]$$

$$= [(2s)!!]^{-1} \sum_{j=0}^{s} (-1)^j \binom{s}{j} (n+2j)^{-1}.$$

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