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Coordinate systems and analytic expansions for three-body atomic wavefunctions: III. Derivative continuity via solutions to Laplace's equation

J E Gottschalk and E N Maslen

Department of Physics, University of Western Australia, Nedlands 6009, Western Australia, Australia

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Abstract. Terms in a few-particle wavefunction, written as an expansion of homogeneous functions, are derived by a method which resembles standard techniques for solving differential equations in one variable. The addition of solutions to the homogeneous equation, i.e. Laplace's equation, converts a particular solution to a physically acceptable form consistent with the boundary conditions. Some earlier workers had derived expansions which, although satisfying the differential equation, were not consistent with those boundary conditions. A study of these inconsistencies assisted the development of this simpler method for obtaining the terms in the wavefunction in their reduced form. The power of the method is demonstrated by its application to *nsms* ^{3}S and *npmp* ^{1}S helium wavefunctions up to and including terms of fourth order in the hyper-radius.

1. Introduction

An expansion containing logarithmic functions which formally solves the Schrödinger equation for a system of three particles with Coulombic potentials was proposed by Bartlett (1937) and Fock (1954, 1958). Fock's derivation involved the use of hyperspherical coordinates (r, α, θ) defined by

$$r = (r_1^2 + r_2^2)^{1/2} \qquad \tan(\alpha/2) = r_2/r_1 \qquad \cos\theta = \boldsymbol{r}_1 \cdot \boldsymbol{r}_2/(r_1 r_2).$$

The wavefunction, expanded about $r = 0$, is

$$\Psi(r, \alpha, \theta) = \sum_{k=0}^{\infty} r^k \sum_{p=0}^{[k/2]} \Psi_{kp}(\alpha, \theta)(\ln r)^p. \tag{1}$$

Leray (1982a, b, 1983, 1984) and Morgan (1986) have shown the necessity of this expansion. The hyperspherical expansion (1) has been generalised to a system of N particles and states of any symmetry, and applies to a wide class of potentials (Ermolaev 1958, Demkov and Ermolaev 1959, Tulub 1969, Tulub *et al* 1971). For any energy there is an infinite set of Fock expansions, convergent for r finite. The physical boundary conditions must be applied to select the physically acceptable solution from that infinite set.

The coefficients Ψ_{kp} of (1) are determined by substituting the expansion into the Schrödinger equation, producing a set of coupled partial differential equations. These are solved in order of increasing k and decreasing p. A common method of solution involves expanding $\Psi_{kp}(\alpha, \theta)$ as a series of hyperspherical harmonics (HH). This produces simple algebraic recurrence equations for the expansion coefficients (Ermolaev 1961, David 1975, Feagin *et al* 1985), but it generates the wavefunction in the form of infinite series of HH. It is more desirable to determine the Ψ_{kp} in their reduced (closed) form.

Techniques for obtaining some Ψ_{kp} in closed form are established by Abbott and Maslen (1987, hereafter referred to as I). These apply straightforwardly to terms with the highest value of p for a given k, such as Ψ_{10}, Ψ_{21}, Ψ_{31} and Ψ_{42}. The resulting functions are polynomials in r_1, r_2 and r_{12}. For the term Ψ_{20}, compaction of the hyperspherical expansion for $nsms\,{}^1$S states described in I yields an expansion in spherical polar coordinates (r_1, r_2, θ). Clearly it is more efficient to commence with an expansion in spherical polar coordinates than with hyperspherical coordinates (Pluvinage 1982). Compaction of the spherical polar coordinate expansion is more straightforward. It yields Ψ_{20} in terms of polynomial, rational, logarithmic and inverse trigonometric functions of r_1, r_2 and r_{12} in addition to four Lobachevskiy's functions (Pluvinage 1985, Gottschalk *et al* 1987, hereafter referred to as II). For $nsms\,{}^3$S states Ψ_{40} is comparable in complexity to the $nsms\,{}^1$S Ψ_{20} term (Pluvinage 1982). The spherical polar coordinate expansion has been partly compacted (Gottschalk 1986) using the method for Ψ_{20} reported in II. The results indicate that the fully reduced expression will have a similar form.

Although this technique may be extended to doubly excited states the procedure is still lengthy. The extension to higher k may be unnecessarily complicated. In this paper previous formal solutions including both Laurent series and spherical polar expansions are studied. Although these series without logarithmic terms cannot represent the physical solution (Bartlett 1937) they may nevertheless satisfy the Schrödinger equation. The boundary conditions required for physical solutions not satisfied initially are accommodated by adding logarithmic solutions to Laplace's equation. The complete solution is achieved more directly, providing an efficient method for obtaining the Fock coefficients in closed form. Because the major part of the wavefunction is generated by the kinetic energy operator, rather than the potential, the method should also apply to non-Coulombic potentials, as well as to other atoms and molecules.

2. Solutions of the Schrödinger equation

It is emphasised that, as with any physical problem, solving the differential equation does not describe atomic and molecular systems completely. The physically acceptable solution is chosen from the infinite ensemble of solutions by applying the physical boundary conditions. For the non-relativistic approximation these boundary conditions have been determined by Kato (1951, 1957). The relevant conditions are (i) the wavefunction Ψ is finite and continuous everywhere, (ii) the first derivatives are continuous everywhere except at the cusps (particle coalescences) and (iii) Ψ and its gradient must be square integrable.

Initially a system of three particles interacting via the Coulomb interaction is studied as an archetypal case. The requirements for satisfying the boundary conditions are given in a later section. For convenience one of the particles is chosen to be infinitely massive while the others (particles 1 and 2) have finite and equal masses. The length r_i is the distance from the origin to particle i and θ is the angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Atomic units are used throughout.

The Schrödinger equation for this system is

$$(-\tfrac{1}{2}\Delta + V)\Psi = E\Psi \tag{2}$$

where $\Delta \equiv \nabla_1^2 + \nabla_2^2$. The potential V is specified incompletely at this stage, but it is assumed to be not too singular. The exact requirements become apparent later. To solve (2) the eigenfunction is expanded as

$$\Psi = \sum_{k=k'}^{\infty} \boldsymbol{\Psi}_k \tag{3}$$

where $\boldsymbol{\Psi}_k$ are homogeneous functions of degree k in the hyper-radius r. Since Ψ is finite at the origin $k' \geq 0$; k' is also even (I). The bold notation denotes a homogeneous function and is consistent with that in I and II. A homogeneous function of degree λ, $\boldsymbol{H}_\lambda(\boldsymbol{r})$, can be written as

$$\boldsymbol{H}_\lambda(\boldsymbol{r}) = r^\lambda H_\lambda(\boldsymbol{u})$$

where r is the hyper-radius, $\boldsymbol{r}$ is an n-dimensional vector and $\boldsymbol{u}$ is the corresponding unit vector. Initially the $\boldsymbol{\Psi}_k$ are represented as series of powers of the independent coordinates, but this is easily generalised, since logarithmic functions are homogeneous of degree 0. As shown in § 4 it is helpful to include components with logarithmic character in the initial form of $\boldsymbol{\Psi}_k$. Substituting (3) into (2) gives

$$\Delta\boldsymbol{\Psi}_k = 2\boldsymbol{V}\boldsymbol{\Psi}_{k-1} - 2E\boldsymbol{\Psi}_{k-2} \qquad k \geq k'+2 \tag{4}$$

to be solved in order of increasing k. The Fock recurrence relations are now obtained by setting

$$\boldsymbol{\Psi}_k = r^k \sum_{p=0}^{\infty} \Psi_{kp}(\alpha, \theta)(\ln r)^p. \tag{5}$$

The expansions studied in this section are for $nsms$ ^{1}S ($k'=0$) unless stated otherwise. For these states Bartlett (1937) gave the first two terms:

$$\boldsymbol{\Psi}_0 = 1 \qquad \boldsymbol{\Psi}_1 = -Z(r_1 + r_2) + r_{12}/2$$

where

$$\boldsymbol{V} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}.$$

2.1. Earlier calculations

In some cases solutions to the Schrödinger equation have been derived using polynomial expansions which do not satisfy the boundary conditions. The first formal solution of $\boldsymbol{\Psi}_2$, due to Pluvinage (1950), was expressed in the coordinates

$$\rho_{12} = \tfrac{1}{2}r_{12} \qquad \sigma = \tfrac{1}{2}(2r^2 - r_{12}^2)^{1/2} \qquad \gamma = \cos\delta.$$

σ has a useful geometrical interpretation, 2σ being the length of the trapezium formed by $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ (figure 1).

Pluvinage simplified the equation for $\boldsymbol{\Psi}_2$ by setting

$$\boldsymbol{\Psi}_2 = Z^2 r_1 r_2 - Z(r_1 + r_2)\rho_{12} - \tfrac{1}{3}(2E - 4Z^2 - 1)\rho_{12}^2 + a_{21}\boldsymbol{Y}_{21} + \boldsymbol{\chi}_2(\sigma, \rho_{12}, \gamma). \tag{6}$$

Note that there are errors in Pluvinage's equation (4). Substituting this into (4) gives

$$\Delta\boldsymbol{\chi}_2 = Z\left(\frac{\rho_{12} + \sigma\gamma}{r_1} + \frac{\rho_{12} - \sigma\gamma}{r_2}\right) = Z(\cos\theta_1 + \cos\theta_2) \tag{7}$$

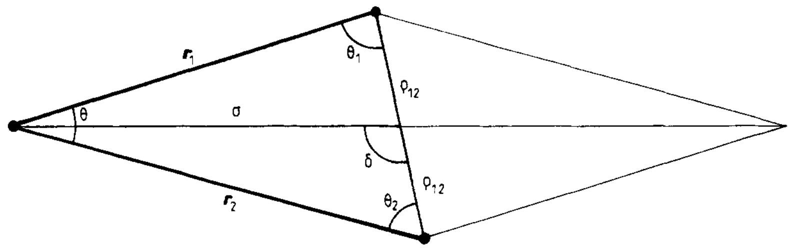

Figure 1. Interparticle coordinates showing the trapezium formed by r_1 and r_2.

which may be compared to equation (82) of I. Equation (7) was solved by expanding both sides into a series of Legendre polynomials $P_n(\gamma)$ and the dimensionless ratio $(\rho_{12}/\sigma)^i$ where $i, n \geqslant 0$ and $\rho_{12} \leqslant \sigma$. Pluvinage summed this series to yield the result, valid for all ρ_{12}, σ and γ,

$$\chi_2 = -\frac{Z}{6}\left[(r_1+r_2)r_{12} - 2r_{12}(2r^2 - r_{12}^2)^{1/2} + \boldsymbol{Y}_{21}\ln\left(\frac{r_1+r_2+r_{12}}{r_1+r_2-r_{12}}\right)\right.$$
$$\left. -\tfrac{1}{2}\boldsymbol{Y}_{20}\ln\left(\frac{(r_1+r_{12}-r_2)(1-\gamma)}{(r_2+r_{12}-r_1)(1+\gamma)}\right)\right]. \tag{8}$$

This function solves the Schrödinger equation for all space except the singular points of χ_2. Throughout this paper $\boldsymbol{Y}_{kl}$ denote the unnormalised hyperspherical harmonics (I). The ones used here are listed in table 1. Noting that

$$\frac{1-\gamma}{1+\gamma} = \frac{r_{12}(2r^2 - r_{12}^2)^{1/2} - r_1^2 + r_2^2}{r_{12}(2r^2 - r_{12}^2)^{1/2} + r_1^2 - r_2^2}$$

it has since been found that the terms in Pluvinage's solution are included in the physical solution (II), but with different multipliers. Pluvinage noted that his $\boldsymbol{\Psi}_2$ had logarithmic singularities at $r_1 \pm r_{12} = r_2$ and $r_1 + r_2 = r_{12}$. Because of the failure to satisfy the boundary condition that atomic and molecular wavefunctions are finite (Kato 1957) (6) and (8) cannot describe the physical solution. Pluvinage noted that the singularity cannot be removed by adding a well behaved solution to Laplace's equation, $\Delta h = 0$.

Table 1. Separable finite series solutions to Laplace's equation. N_{kl} is the normalisation constant for $\boldsymbol{Y}_{kl}$.

k	l	$\pi^3 N_{kl}^2$	Unnormalised $\boldsymbol{Y}_{kl}(r_1, r_2, r_{12})$	Relation to $\boldsymbol{Q}^{\mathrm{I}}_{kl}(r_1, r_2, r_{12})$
0	0	1	1	$\boldsymbol{Q}^{\mathrm{I}}_{00}$
2	0	1	$2(r_1^2 - r_2^2)$	$2\boldsymbol{Q}^{\mathrm{I}}_{20}$
2	1	4	$r^2 - r_{12}^2$	$2\boldsymbol{Q}^{\mathrm{I}}_{21}$
4	0	1	$3r^4 - 16r_1^2r_2^2$	$3\boldsymbol{Q}^{\mathrm{I}}_{40}$
4	1	$\frac{3}{2}$	$4(r_1^2 - r_2^2)(r^2 - r_{12}^2)$	$8\boldsymbol{Q}^{\mathrm{I}}_{41}$
4	2	8	$\frac{3}{2}(r^2 - r_{12}^2)^2 - 2r_1^2r_2^2$	$4\boldsymbol{Q}^{\mathrm{I}}_{42}$

k	l	$\boldsymbol{Q}^{\mathrm{II}}_{kl}(\alpha, \theta)$	$\boldsymbol{Q}^{\mathrm{II}}_{kl}(r_1, r_2, r_{12})$
0	0	$2\cos\alpha/\sin\alpha$	$(r_1^2 - r_2^2)/r_1r_2$
2	0	$2\cos(2\alpha)/\sin\alpha$	$(r^4 - 8r_1^2r_2^2)/r_1r_2$
2	1	$4\cos\theta\cos\alpha(1 + 2\sin^2\alpha)/\sin^2\alpha$	$(r^2 - r_{12}^2)(r_1^2 - r_2^2)(r^4 + 8r_1^2r_2^2)/2r_1^3r_2^3$

However, the singularity can be removed when one relaxes the restriction that the solution is well behaved everywhere. The solutions required are derived in § 3.

Kinoshita (1957) studied the series

$$\sum_{lmn=0}^{\infty} C_{lmn} s^l p^m q^n \tag{9}$$

where $s = r_1 + r_2$, $p = r_{12}/s$, $q = (r_2 - r_1)/r_{12}$. Note that since only s has the dimension of length, one has the correspondence with the Fock equation, identifying l with k. Substituting this expansion into the Schrödinger equation yields a recurrence equation for the coefficients C_{lmn}. Scherr (1979) studied this more closely, achieving a partial summation of the expansion (9). He established the result that $C_{lmn} = 0$ for $n > m$. For $l = 2$ Scherr examined

$$\boldsymbol{\Psi}_2 = \boldsymbol{\Psi}_{2,\mathrm{odd}} + \boldsymbol{\Psi}_{2,\mathrm{even}}$$

where

$$\boldsymbol{\Psi}_{2,\mathrm{odd}} = s^2 \sum_{\mu\nu} C_{22\mu+12\nu} p^{2\mu+1} q^{2\nu}$$

and

$$\boldsymbol{\Psi}_{2,\mathrm{even}} = s^2 \sum_{\mu\nu} C_{22\mu 2\nu} p^{2\mu} q^{2\nu}.$$

For symmetric states q occurs only to even powers. Scherr obtained

$$\boldsymbol{\Psi}_{2,\mathrm{odd}} = \tfrac{1}{3} Z s^2 \left[\tfrac{1}{4}(2p^2 - 1 - p^2 q^2) \ln\left(\frac{1+p}{1-p}\right) + pu - 2p - pq \ln\left(\frac{1+r}{1-r}\right) \right]$$

where $u^2 = 1 - p^2 + p^2 q^2$, $r = q(1-\lambda)/(u+\lambda)$ and $\lambda^2 = 1 - p^2$. Transforming to interparticle coordinates yields

$$\begin{aligned}\boldsymbol{\Psi}_{2,\mathrm{odd}} = & -\tfrac{1}{6} Z Y_{21} \ln\left(\frac{r_1 + r_2 + r_{12}}{r_1 + r_2 - r_{12}}\right) + \tfrac{1}{3} Z r_{12} (2r^2 - r_{12}^2)^{1/2} - \tfrac{2}{3} r_{12} Z (r_1 + r_2) \\ & + \tfrac{1}{6} Z Y_{20} \ln\left(\frac{r_{12}(2r^2 - r_{12}^2)^{1/2} - r_1^2 + r_2^2 + (s^2 - r_{12}^2)^{1/2}(r_{12} + r_1 - r_2)}{r_{12}(2r^2 - r_{12}^2)^{1/2} + r_1^2 - r_2^2 + (s^2 - r_{12}^2)^{1/2}(r_{12} - r_1 + r_2)}\right). \end{aligned} \tag{10}$$

Scherr noted that this contains logarithmic singularities, which he concluded must cancel with an equivalent singularity in $\boldsymbol{\Psi}_{2,\mathrm{even}}$, but did not derive a compact expression for this term.

Hylleraas (1956, 1960, reproduced in Hylleraas 1968) solved the equation for $\boldsymbol{\Psi}_2$ (4) using an expansion in the spherical polar coordinates (r_1, r_2, θ) which, unlike the work of Pluvinage (1950) and Kinoshita (1957), contained logarithmic terms explicitly. Unlike Fock's $\ln r$, the terms used by Hylleraas were not introduced to satisfy the boundary conditions and are not necessary to solve the equations. They were obtained by an integration procedure (Hylleraas 1956).

Hylleraas (1960) set

$$\boldsymbol{\Psi}_2 = \boldsymbol{P}_2 - \tfrac{1}{24} Z \boldsymbol{\Phi}_2$$

where $\boldsymbol{P}_2$ is a homogeneous polynomial of degree 2 in r_1, r_2 and r_{12} and, from (4),

$$\Delta \boldsymbol{\Phi}_2 = 6 r_{12}(1/r_1 + 1/r_2) + 12(r_1 + r_2)/r_{12}.$$

This was solved by expanding both sides as a series in

$$r_1^i r_2^j P_l(\cos\theta).$$

The expansion of r_{12} is region dependent. After summing the series for $\boldsymbol{\Phi}_2$ a region-dependent expression, valid for $r_1 > r_2$,

$$\boldsymbol{\Psi}_2 = \boldsymbol{P}_2 + \tfrac{1}{3}Zr_1r_2 - \tfrac{2}{3}Z(r_1+r_2)r_{12} + \alpha\boldsymbol{Y}_{20} + \beta\boldsymbol{Y}_{21} - \tfrac{1}{3}Z\boldsymbol{Y}_{21}\ln(r_1+r_2+r_{12}) + \tfrac{1}{6}Z\boldsymbol{Y}_{20}\ln(r_1-r_2+r_{12}) \tag{11}$$

was obtained. The corresponding expression valid for $r_1 < r_2$ is derived from this by interchanging r_1 and r_2. The presence of the artificial boundary between the domains of validity of the two expansions requires an examination of the continuity of Ψ and its derivatives. The wavefunction should be continuous everywhere, with first derivatives continuous except at the cusps. Although Hylleraas's solution (11) is continuous it has a discontinuous derivative at $r_1 = r_2$. It is also singular at $r_1 - r_2 \pm r_{12} = 0$.

2.2. Power series solutions for spherical polar coordinates

Work involving power series with no explicit logarithmic terms is described by Pluvinage (1950), Kinoshita (1957) and Scherr (1979). This shows that series solutions for the Schrödinger equation in spherical polar coordinates may be found to second order in r at least. Solutions that are series of

$$r_1^i r_2^j P_l(\cos\theta) \tag{12}$$

have been examined by Newman (1973) and Davis and Maslen (1982). These studies correspond to the $nsms$ ^{1}S states of helium in that the expressions have non-zero $\boldsymbol{\Psi}_0$.

In a more detailed examination of expansions using (12) by Gottschalk and Maslen (1985), states of arbitrary symmetry and general potentials are considered. To ensure a normalisable expansion at the origin using (12) it is necessary to use a region-dependent expression

$$\Psi = \begin{cases} \sum\limits_{ijl} C_{ijl} r_1^i r_2^j P_l(\cos\theta) & r_1 > r_2 \\ \sum\limits_{ijl} C'_{ijl} r_1^j r_2^i P_l(\cos\theta) & r_1 < r_2. \end{cases} \tag{13}$$

To satisfy the boundary conditions at the origin $l \geqslant 0$, $j \geqslant l$ and $k = i+j \geqslant 0$ in both series. This is equivalent to the hyperspherical expansion

$$\Psi = \sum_{k=0}^{\infty} r^k \Psi_k(\alpha, \theta) \tag{14}$$

(Fock's expansion (1) with $p = 0$). It is the process of expanding $r = (r_1^2 + r_2^2)^{1/2}$ using the binomial theorem which differentiates between the regions $r_1 > r_2$ and $r_1 < r_2$. Symmetric or antisymmetric functions may be produced by requiring that

$$C_{ijl} = \pm C'_{ijl}.$$

Straightforward substitution of (13) into the Schrödinger equation leads to recurrence equations for C_{ijl} and C'_{ijl}. These can be solved in order of increasing $k = i+j$, yielding

$$C_{k-l-2n-1\,l+2n+1\,l} = \frac{(-1)^n\Gamma(n+l-k/2+\frac{1}{2})\Gamma(n-k/2)}{\Gamma(n+\frac{3}{2})2\Gamma(n+l+2)} \sum_{t=0}^{n} \frac{(-1)^t\Gamma(t+\frac{1}{2})\Gamma(t+l+1)}{\Gamma(t+l-k/2+\frac{1}{2})\Gamma(t-k/2)} \times R(k, l, 2t+1) \qquad n \geqslant 0 \tag{15a}$$

and

$$C_{k-l-2n\,l+2n\,l}=\frac{(-\frac{1}{2}-k/2)_n(l-k/2)_n(-1)^n}{(l+\frac{3}{2})_n n!}C_{k-lll}-\frac{(-1)^n\Gamma(n-\frac{1}{2}-k/2)\Gamma(n+l-k/2)}{2\Gamma(n+\frac{3}{2}+l)n!}$$

$$\times\sum_{t=0}^{n-1}\frac{(-1)^t\Gamma(t+1)\Gamma(t+l+\frac{3}{2})}{\Gamma(t+l-k/2+1)\Gamma(t-k/2+\frac{1}{2})}R(k,l,2t+2)\qquad n\geqslant 1\qquad(15b)$$

where

$$(a)_b\equiv\frac{\Gamma(a+b)}{\Gamma(a)}$$

is the Pochhammer symbol and

$$R(k,l,g)=(V_{\mathrm{op}}-E)C_{k-l-g\,l+g-2\,l}.$$

$V_{\mathrm{op}}C_{ijl}$ represents the effect of the potential operator acting on the expansion (13). The only restriction on V is that it is less singular than r_1^{-2} or r_2^{-2} at the origin.

These equations do not specify the coefficients C_{k-lll}. The significance of this, shown in the next section, is that C_{k-lll} multiplies a solution to Laplace's equation. Although equations (15) may be used to construct a series solution to the Schrödinger equation, the resulting function and its derivatives will, in general, be discontinuous. Continuity can be satisfied in part by using equations (14)-(16) in Gottschalk and Maslen (1985) (see also II, equations (A3) and (A4)). However, for $k=2l+2n$, $n=0,1,2,\ldots$, this cannot be achieved for the general asymmetric series, indicating the breakdown of the validity of a power series (13) representing the physical solution. Ensuring continuity of the function and its first derivative for $r_1=r_2$ also precludes infinities elsewhere in the wavefunction (although this is not rigorously proven here). Note that the eigenfunctions have discontinuous derivatives (cusps) at the Coulomb singular points but, as these are not regions or lines of discontinuity, the procedure is justified.

2.3. *Expansions in hyperspherical coordinates*

The failure of expansion (13) is not obvious in the hyperspherical approach. As much work in the field is based on hyperspherical coordinates it is worth examining this matter in some detail. The argument used here, given originally by Bartlett (1937), shows that the helium ground state cannot be represented by series of positive powers of the hyper-radius. This is also shown by Morgan (1978) in dismissing the Kinoshita expansion (9).

Substitution of (14) into the Schrödinger equation (2) yields

$$[\Lambda^2-k(k+4)]\Psi_k=-2V\Psi_{k-1}+2E\Psi_{k-2}$$

where Λ^2 is the generalised angular momentum operator (I) and, in this case,

$$V=-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}.$$

From the evaluation of Ψ_0 and Ψ_1 the second-order terms are determined by

$$[\Lambda^2-12]\Psi_2=-2V\Psi_1+2E\Psi_0.\qquad(16)$$

This is solved by expansion of Ψ_k into hyperspherical harmonics $Y_{kl}(\alpha, \theta)$ using their orthogonality when inverting the resulting equations for the expansion coefficients (I). As the harmonics Y_{20} and Y_{21} satisfy

$$[\Lambda^2 - 12] Y_{2l} = 0$$

it is necessary for the right-hand side of (16) to be orthogonal to Y_{20} and Y_{21} for this procedure. Bartlett (1937) showed numerically this was not the case, and hence the physical solution requires logarithmic terms. The integrals required for the analysis have been evaluated analytically in I and by Ermolaev (1961).

It is possible to solve (16) by another procedure. Pluvinage (1982) solved the equation

$$[\Lambda^2 - 12] f = 8 Y_{21} \tag{17}$$

using the solutions to the homogeneous equation and the method of variation of parameters to give, in hyperspherical coordinates,

$$f = -\frac{\cos\theta}{4\sin\alpha} + \frac{\alpha\cos\alpha(1+2\sin^2\alpha)\cos\theta}{4\sin^2\alpha}. \tag{18}$$

Further details are given in appendix 1. Note that if orthogonality was applied to (17) one would conclude that no well behaved solution exists. The derivative of solution (18) is clearly singular at $\alpha = \pi/2$ and, to be rigorous, solves (17) in the region with $\alpha = 0$ excluded, and so no contradiction arises.

A distinction must be made here between these two approaches. The first method, i.e. the true hyperspherical technique, requires the orthogonality property of the HH and chooses the physical solution readily. This is due to the property of the harmonics which are, by definition, finite, continuous and infinitely differentiable. The variation of parameters method, applied above, uses hyperspherical coordinates but does not use orthogonality of the HH. Although this is able to solve equations which the true hyperspherical method cannot, it introduces functions with non-physical behaviour.

It is well known that the orthogonality method selects the physical solution, automatically rejecting singular solutions such as (18). As shown in § 4, however, the compact form of the wavefunction is derived far more readily via the singular solutions to (4) with which singular solutions to Laplace's equation are combined in amounts such that the divergences cancel. Because expressions can be generated in a near to reduced form the method is more convenient than the hyperspherical approach. The technique is hinted at by Pluvinage (1982) who solved the Fock recurrence relations (I) via region-dependent expansions similar to (13). By satisfying the boundary conditions with the addition of functions such as (18) to the particular solutions, he obtained expressions for helium *nsms* ^{1}S and *nsms* ^{3}S states in the simplest form available at that time.

3. Solutions of Laplace's equation

The method described below differs from that of Pluvinage (1982) in that logarithmic solutions to Laplace's equation are also considered.

3.1. *Separable series solutions*

Homogeneous S-state solutions, of degree k, to

$$\Delta \boldsymbol{Q}_k = 0 \tag{19}$$

are sought. Initially separable solutions of the class

$$\boldsymbol{Q}_{kl} = r^k Q_{kl}(\alpha, \theta) = r^k A_{kl}(\alpha)\Theta_l(\theta)$$

where l is a degeneracy label, are examined. Substitution into (19) yields

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + l(l+1)\right)\Theta_l(\theta) = 0 \tag{20}$$

and

$$\left(\frac{\partial^2}{\partial\alpha^2} + 2\cot\alpha\frac{\partial}{\partial\alpha} - \frac{l(l+1)}{\sin^2\alpha} + \tfrac{1}{4}k(k+4)\right)A_{kl}(\alpha) = 0. \tag{21}$$

Equation (20) is a standard differential equation, its solutions being Legendre polynomials of the first and second kinds:

$$\Theta_l(\theta) = \begin{cases} P_l(\cos\theta) \\ Q_l(\cos\theta) \end{cases} \tag{22}$$

(Abramowitz and Stegun 1972, ch 8). Only integral l and $l \geqslant 0$ are of interest here.

Substituting

$$x = \cos\alpha \qquad A_{kl} = (1-x^2)^{l/2} B_{kl}$$

transforms (21) to

$$\left[(1-x^2)\frac{\partial^2}{\partial x^2} - x(2l+3)\frac{\partial}{\partial x} + \left(\frac{k}{2} - l\right)\left(\frac{k}{2} + l + 2\right)\right]B_{kl}(x) = 0. \tag{23}$$

This can be expressed in hypergeometric form, setting $z = (1 \pm x)/2$, to give

$$\left[z(1-z)\frac{\partial^2}{\partial z^2} + [l + \tfrac{3}{2} - z(2l+3)]\frac{\partial}{\partial z} + \left(\frac{k}{2} - l\right)\left(\frac{k}{2} + l + 2\right)\right]B_{kl}(z) = 0.$$

The two linearly independent solutions are

$$B_{kl}(x) = {}_2F_1\left[\begin{matrix} l - k/2, l + k/2 + 2 \\ l + \frac{3}{2} \end{matrix}; \frac{1 \pm x}{2}\right] \tag{24a}$$

and

$$B_{kl}(x) = {}_2F_1\left[\begin{matrix} -k/2 - \frac{1}{2}, k/2 + \frac{3}{2} \\ \frac{1}{2} - l \end{matrix}; \frac{1 \pm x}{2}\right]\left(\frac{1 \pm x}{2}\right)^{-1/2-l}. \tag{24b}$$

Note that there are no logarithmic solutions to (23) (Rainville 1960, p 54). For even k and $l - k/2 \geqslant 0$ the first solution (24a) is proportional to a Gegenbauer polynomial (Rainville 1960, p 279)

$$\frac{\Gamma(k/2 - l + 1)\Gamma(2l+2)}{\Gamma(k/2 + l + 2)} C^{l+1}_{k/2-l}(\mp x).$$

Since $(1+x)/2 = r_1^2/r^2$ and $(1-x)/2 = r_2^2/r^2$ the A_{kl} can be written

$$A_{kl} = \begin{cases} {}_2F_1\left[\begin{matrix} l-k/2, l+k/2+2 \\ l+\frac{3}{2} \end{matrix}; \; r_i^2/r^2\right]\left(\dfrac{r_1 r_2}{r^2}\right)^l \\ {}_2F_1\left[\begin{matrix} k/2-l+1, -k/2-l-1 \\ \frac{1}{2}-l \end{matrix}; \; r_i^2/r^2\right]\left(\dfrac{r^2}{r_1 r_2}\right)^{l+1} \end{cases}$$

where Euler's transform (Abramowitz and Stegun 1972, equation 15.3.3) was applied to (24*b*), and a factor of 2^l is discarded for convenience. It is useful to express these in the coordinates from II, via equation (17) of that paper. Restricting attention to $r_1 > r_2$ and $i = 2$ gives

$$A_{kl} = \begin{cases} {}_2F_1\left[\begin{matrix} l/2-k/4, l/2+k/4+1 \\ l+\frac{3}{2} \end{matrix}; \; y^2\right]\left(\dfrac{y}{2}\right)^l & (25a) \\ {}_2F_1\left[\begin{matrix} k/4-l/2+\frac{1}{2}, -k/4-l/2-\frac{1}{2} \\ \frac{1}{2}-l \end{matrix}; \; y^2\right]\left(\dfrac{2}{y}\right)^{l+1} & (25b) \end{cases}$$

where $y = 2r_1r_2/r^2 = \sin\alpha$. Noting that $\cos\alpha = (r_1^2 - r_2^2)/r^2$, another useful (antisymmetric) form for these functions, obtained with the assistance of Euler's transform, is

$$A_{kl} = \begin{cases} {}_2F_1\left[\begin{matrix} l/2+k/4+\frac{3}{2}, l/2-k/4+\frac{1}{2} \\ l+\frac{3}{2} \end{matrix}; \; y^2\right]\left(\dfrac{y}{2}\right)^l \cos\alpha & (26a) \\ {}_2F_1\left[\begin{matrix} -k/4-l/2, k/4-l/2+1 \\ \frac{1}{2}-l \end{matrix}; \; y^2\right]\left(\dfrac{2}{y}\right)^{l+1} \cos\alpha. & (26b) \end{cases}$$

Expression (25) may also be transformed to (Abramowitz and Stegun 1972, equation 15.3.23)

$$A_{kl} = \begin{cases} {}_2F_1\left[\begin{matrix} l-k/2, -\frac{1}{2}-k/2 \\ l+\frac{3}{2} \end{matrix}; \; -\rho^2\right]\left(\dfrac{r_>}{r}\right)^k \rho^l & (27a) \\ {}_2F_1\left[\begin{matrix} -k/2-l-1, -\frac{1}{2}-k/2 \\ \frac{1}{2}-l \end{matrix}; \; -\rho^2\right]\left(\dfrac{r_>}{r}\right)^k \rho^{-l-1} & (27b) \end{cases}$$

where $\rho = r_</r_>$ and $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. Setting $i = 1$ or $r_1 < r_2$ yields the same functions, so (25)-(27) represent the full set of solutions. When k is even and $l > k/2$, (27*a*) is an infinite series. The second series (27*b*) is always finite. The HH $Y_{kl}(\alpha, \theta)$ are reproduced, to within a numerical factor, using (25*a*) or (26*a*) and $P_l(\cos\theta)$. Some examples of these $\boldsymbol{Q}_{kl}$ are given in table 1. $\boldsymbol{Q}^{\mathrm{I}}$ represents solutions A_{kl} of the first kind (25*a*) and $\boldsymbol{Q}^{\mathrm{II}}$ represents (25*b*), both combined with $P_l(\cos\theta)$. From (15), (22) and (27*a*) it is seen that the contribution due to C_{k-lll} in (13) is

$$\sum_{l=0}^{\infty} C_{k-lll} Q^{\mathrm{I}}_{kl}. \tag{28}$$

That is, C_{k-lll} multiplies a solution to Laplace's equation.

3.2. Separable logarithmic solutions

Simple logarithmic solutions to Laplace's equation can be generated assuming an expansion of the form

$$\boldsymbol{\Phi}_k = r^k \sum_{p=0}^{m} \phi_{kp}(\alpha, \theta)(\ln r)^p$$

where m is arbitrary. Substituting this into Laplace's equation (19) gives equations for ϕ_{kp} similar to the Fock recurrence relation,

$$[\Lambda^2 - k(k+4)]\phi_{kp} = 2(k+2)(p+1)\phi_{kp+1} + (p+1)(p+2)\phi_{kp+2}. \tag{29}$$

Although the limitation to finite m is not immediately obvious, this is necessary to solve (29) in order of decreasing p. For the purpose of this analysis there is in any case no point in choosing m larger than $[k/2]$. As an example, suppose $m=1$, $k=2$. Putting $p=1$ in (29) gives

$$[\Lambda^2 - 12]\phi_{21} = 0.$$

If the solutions Y_{2l}, $l=0$, 1 are chosen, putting $p=0$ gives

$$[\Lambda^2 - 12]\phi_{20} = 8\,Y_{2l}.$$

This was solved previously ((17), (18)) for $l=1$. The solution for $l=0$ (appendix 1) yields

$$\boldsymbol{\Phi}_{21} = \begin{cases} \boldsymbol{Y}_{20} \ln r + \frac{1}{4}\boldsymbol{Q}_{20}^{11} \sin^{-1} y \\ \boldsymbol{Y}_{21} \ln r + \frac{1}{16}\boldsymbol{Q}_{21}^{11} \sin^{-1} y - \dfrac{r^4}{8r_1 r_2} \cos\theta. \end{cases}$$

Note that these are well behaved as $r_1 \to 0$ and $r_2 \to 0$.

In general however the solutions to Laplace's equation described so far are not sufficient to help solve the equations (4), since the solutions required cannot be expressed as finite sums of separable functions of r, α and θ. Presumably these could be described as infinite series of separable solutions, but the objective in this paper is to avoid such expressions when solving few-body equations.

3.3. *Non-separable logarithmic solutions*

As is evident when comparing Pluvinage's, Scherr's and Hylleraas's expressions ((6), (10) and (11)) with the physically acceptable wavefunction (equation (42) of II), the latter must be composed largely of non-separable solutions to Laplace's equation. It is easy to find three homogeneous solutions of degree zero, namely

$$s_1(r_1, r_2, r_{12}) = \ln[r_{12}(2r^2 - r_{12}^2)^{1/2} + r_1^2 - r_2^2]$$

and

$$\begin{aligned} s_2(r_1, r_2, r_{12}) = \alpha \ln\left(\frac{1+\Omega}{1-\Omega}\right) &- \beta\{\ln[r_{12}(2r^2 - r_{12}^2)^{1/2} + r_1^2 - r_2^2] \\ &- \ln[r_{12}(2r^2 - r_{12}^2)^{1/2} - r_1^2 + r_2^2]\} \\ &+ 2\left[L\left(\frac{\alpha-\beta}{2}\right) - L\left(\frac{\alpha+\beta}{2}\right) + L\left(\frac{\pi-\alpha+\beta}{2}\right) - L\left(\frac{\pi-\alpha-\beta}{2}\right)\right] \end{aligned}$$

where $\alpha = \sin^{-1} y$, $\beta = \sin^{-1}(y\Omega)$, in addition to the simple

$$Q_0(\Omega) = \tfrac{1}{2}\ln\left(\frac{1+\Omega}{1-\Omega}\right)$$

where $\Omega = \cos\theta$ at this stage. The region in which s_1 and s_2 satisfy

$$\Delta s = 0 \tag{30}$$

requires careful study. s_1 solves Laplace's equation as long as both s_1 and its first derivatives are not singular, i.e. at $(r_1, r_2, r_{12}) = (0, 0, 0)$. Hence symmetric and antisymmetric solutions may be constructed as

$$s_1^{\pm} = s_1(r_1, r_2, r_{12}) \pm s_1(r_2, r_1, r_{12}). \tag{31}$$

However, s_2 has the property

$$\Delta s_2(r_1, r_2, r_{12}) \begin{cases} = 0 & r_1 > r_2 \\ \neq 0 & r_1 < r_2. \end{cases}$$

Thus the symmetric or antisymmetric solutions, valid everywhere except at the singular points, are

$$s_2^{\pm} = \begin{cases} s_2(r_1, r_2, r_{12}) & r_1 > r_2 \\ \pm s_2(r_2, r_1, r_{12}) & r_1 < r_2. \end{cases} \tag{32}$$

An infinite number of solutions to Laplace's equation can be produced from s_1 and s_2. This can be achieved by multiplying these functions by the harmonics $\boldsymbol{Y}_{kl}$ or by $\boldsymbol{Q}_{kl}$, producing a homogeneous solution of degree k. The notation $s_i^{[k,l]}$ is used to denote a solution to Laplace's equation based on multiplying s_i by $\boldsymbol{Y}_{kl}$. To be consistent

$$s_i^{[0,0]} = s_i.$$

Note that functions based on $\boldsymbol{Q}_{kl}$ do not seem to be required.

The following solutions of degree two of (30), valid for $r_1 > r_2$, are found by inspection from equation (42) of II:

$$s_1^{[2,0]}(r_1, r_2, r_{12}) = \boldsymbol{Y}_{20} s_1(r_1, r_2, r_{12}) - 2r_{12}(2r^2 - r_{12}^2)^{1/2} \tag{33a}$$

$$s_1^{[2,1]}(r_1, r_2, r_{12}) = \boldsymbol{Y}_{21} s_1(r_1, r_2, r_{12}) \tag{33b}$$

$$s_2^{[2,0]}(r_1, r_2, r_{12}) = \boldsymbol{Y}_{20} s_2(r_1, r_2, r_{12}) + 8\boldsymbol{Y}_{21} \ln r + 4r_{12} \sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2} \tag{33c}$$

$$s_2^{[2,1]}(r_1, r_2, r_{12}) = \boldsymbol{Y}_{21} s_2(r_1, r_2, r_{12}) + 2\boldsymbol{Y}_{20} \ln r - 4r_1 r_2 \sin^{-1} y. \tag{33d}$$

Symmetric solutions valid in the whole space except for specified singular points are constructed from these using (31) or (32).

In order to obtain solutions to equations (4) in closed form, a systematic method of producing the necessary solutions to Laplace's equation is desirable. The authors are not aware of any general method which enables the desired solutions to be selected from the uncountably infinite ensemble of solutions. However it is possible, through careful study of the equations (4), to derive the additional set of solutions with the required properties. Hopefully this will facilitate the systematic selection of the desired functions without the need of solution by expansion.

Once archetypal solutions have been found it is easy to extend these to the infinite set of similar functions. It is convenient to define the homogeneous polynomial of degree k with coefficients a,

$$\boldsymbol{P}_k^a = \sum_{i=0}^{k} \sum_{j=0}^{k-i} a_{ijk-i-j} r_1^i r_2^j r_{12}^{k-i-j}.$$

To generate solutions to (30) of degree 4 based on s_1 and s_2 the functions

$$s_1^{[4,l]}(r_1, r_2, r_{12}) = \boldsymbol{Y}_{4l} s_1(r_1, r_2, r_{12}) + (2r^2 - r_{12}^2)^{1/2} \boldsymbol{P}_3^a + \boldsymbol{P}_4^b \tag{34a}$$

Table 2. Non-separable solutions to Laplace's equation, $r_1 > r_2$.

i	k	l	$s_i^{[k,l]}$
1	4	0	$\boldsymbol{Y}_{40}s_1(r_1, r_2, r_{12}) - 2\boldsymbol{Y}_{20}r_{12}(2r^2 - r_{12}^2)^{1/2} + \frac{8}{3}r_1^2r_2^2$
1	4	1	$\boldsymbol{Y}_{41}s_1(r_1, r_2, r_{12}) - 4\boldsymbol{Y}_{21}r_{12}(2r^2 - r_{12}^2)^{1/2}$
1	4	2	$\boldsymbol{Y}_{42}s_1(r_1, r_2, r_{12}) - \frac{1}{4}\boldsymbol{Y}_{20}r_{12}(2r^2 - r_{12}^2)^{1/2} + \frac{4}{3}r_1^2r_2^2$
2	4	0	$\boldsymbol{Y}_{40}s_2(r_1, r_2, r_{12}) + 4\boldsymbol{Y}_{41}\ln r + 4r_{12}\boldsymbol{Y}_{20}\sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2}$
2	4	1	$\boldsymbol{Y}_{41}s_2(r_1, r_2, r_{12}) + 8r_{12}\boldsymbol{Y}_{21}\sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2} - 8r_1r_2\boldsymbol{Y}_{20}\sin^{-1}y$ $+ \frac{8}{3}\boldsymbol{Y}_{40}\ln r + \frac{32}{3}\boldsymbol{Y}_{42}\ln r - \frac{16}{3}r_1^2r_2^2$
2	4	2	$\boldsymbol{Y}_{42}s_2(r_1, r_2, r_{12}) + 2\boldsymbol{Y}_{41}\ln r - 6r_1r_2\boldsymbol{Y}_{21}\sin^{-1}y + \frac{1}{2}r_{12}\boldsymbol{Y}_{20}\sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2}$

and

$$s_2^{[4,l]}(r_1, r_2, r_{12}) = \boldsymbol{Y}_{4l}s_2(r_1, r_2, r_{12}) + \sin^{-1} y\boldsymbol{P}_4^a + \sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2}\boldsymbol{P}_3^b + \ln r\boldsymbol{P}_4^c + \boldsymbol{P}_4^d \qquad (34b)$$

with $l = 0$, 1 or 2, are proposed. The form of these functions was suggested by (33). The coefficients in the polynomials may be determined simply by requiring (34*a*) or (34*b*) to solve Laplace's equation. Functions obtained in this way are listed in table 2. Although other solutions can be generated using other $\boldsymbol{Q}_{kl}$ in place of the $\boldsymbol{Y}_{kl}$ in (34), these are not listed here.

4. Boundary conditions

The physically acceptable solutions are to be determined from a particular solution to equation (4) and the relevant solutions to Laplace's equation. This requires the use of the homogeneous functions $\boldsymbol{\Psi}_k$, specified by the differential equation (4), to satisfy the boundary conditions of continuity and finiteness of the eigenfunctions for finite values of the independent coordinates. The method is exactly analogous to a well known technique for solving ordinary differential equations. Having found a particular solution the boundary conditions specify the amount of the homogeneous solutions which must be added to eliminate the singularities. The objective of producing closed form solutions is hindered if it is necessary to manipulate series solutions to the equations. A large set of equations can be solved while still avoiding expansions, as shown below.

It is well known (Fock 1954, 1958) that, for even k, $\boldsymbol{\Psi}_k$ contains $(k/2+1)$ coefficients, denoted a_{kl}, which for bound states are determined by ensuring the wavefunction is normalisable at $r \to \infty$. The notation in I requires extension for this work. While in $\boldsymbol{\Psi}_k$ the coefficient a_{kl} multiplies the harmonic $\boldsymbol{Y}_{kl}$, the physically acceptable propagation of a_{kl} in $\boldsymbol{\Psi}_\kappa$ is denoted by $\boldsymbol{\Psi}_\kappa^{[k,l]}$. These are solutions of

$$\Delta\boldsymbol{\Psi}_\kappa^{[k,l]} = 2V\boldsymbol{\Psi}_{\kappa-1}^{[k,l]} - 2E\boldsymbol{\Psi}_{\kappa-2}^{[k,l]}. \qquad (35)$$

To be consistent

$$\boldsymbol{\Psi}_k^{[k,l]} = \boldsymbol{Y}_{kl}$$

and

$$\boldsymbol{\Psi}_\kappa^{[k,l]} = 0 \qquad \kappa < k.$$

These functions are further subdivided into particular and complementary solutions of (35)

$$\boldsymbol{\Psi}_\kappa^{[k,l]} = {}^{\mathrm{P}}\boldsymbol{\Psi}_\kappa^{[k,l]} + {}^{\mathrm{c}}\boldsymbol{\Psi}_\kappa^{[k,l]}.$$

The complete contribution of the coefficient a_{kl} to the wavefunction is

$$a_{kl} \sum_{\kappa=k}^{\infty} \boldsymbol{\Psi}_\kappa^{[k,l]}$$

and the total wavefunction is the sum

$$\Psi = \sum_{k=k',2}^{\infty} \sum_{l=0}^{k/2} a_{kl} \sum_{\kappa=k}^{\infty} \boldsymbol{\Psi}_\kappa^{[k,l]}. \tag{36}$$

Particular eigenstates are chosen by setting certain a_{kl} to zero. For example

$$\begin{array}{lll} k'=0 & a_{00}\neq 0 & \rightarrow nsms\ {}^1\mathrm{S} \\ k'=2 & a_{00}=a_{21}=0,\ a_{20}\neq 0 & \rightarrow nsms\ {}^3\mathrm{S} \\ k'=2 & a_{00}=a_{20}=0,\ a_{21}\neq 0 & \rightarrow npmp\ {}^1\mathrm{S}. \end{array}$$

as explained in I. Comparison with the series of homogeneous functions of degree k (3)

$$\Psi = \sum_{k=k'}^{\infty} \boldsymbol{\Psi}_k$$

implies that

$$\boldsymbol{\Psi}_k = \sum_{\kappa=0,2}^{2[k/2]} \sum_{l=0}^{\kappa/2} a_{\kappa l} \boldsymbol{\Psi}_k^{[\kappa,l]}.$$

Using the functions and procedures described in this paper, finding the contribution of a_{kl} to $\boldsymbol{\Psi}_{k+2}$ in closed form is straightforward. The use of these methods is demonstrated by their application to the $nsms\ {}^1\mathrm{S}$ states to second order, and to the $nsms\ {}^3\mathrm{S}$ and $npmp\ {}^1\mathrm{S}$ states to fourth order. These were tabulated to first and third order respectively in I.

An infinite number of particular solutions for the multivariable equation exist, as indicated in § 2. The approach here is to commence with the simplest particular solution available, which is then modified by adding appropriate amounts of solutions to the homogeneous equation, as given by Hylleraas (1960) (11). In keeping with the approach in I and II a more general potential is chosen, namely

$$V = \frac{\mu_1}{r_1} + \frac{\mu_2}{r_2} + \frac{\mu_{12}}{r_{12}}.$$

A particular solution for $nsms\ {}^1\mathrm{S}$ may be found by proposing

$${}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]} = \boldsymbol{P}_2^a \ln(r_1+r_2+r_{12}) + \boldsymbol{P}_2^b \ln(r_1-r_2+r_{12}) + \boldsymbol{P}_2^c \qquad r_1 > r_2.$$

Substitution into (35) determines the coefficients. The calculation is reduced by noting that the logarithmic terms do not appear in $\boldsymbol{\Psi}_1$. Using (A2.1) $\boldsymbol{P}_2^a$ and $\boldsymbol{P}_2^b$ must both satisfy

$$\Delta \boldsymbol{P}_2 = 0.$$

To ensure that Ψ is finite at the origin these polynomials must be linear combinations of solid harmonics,

$$b_0 \boldsymbol{Y}_{20} + b_1 \boldsymbol{Y}_{21}.$$

Particular solutions for other states, found in the same way, are

$$\begin{aligned}
{}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]} = & -\tfrac{1}{6}\mu_{12} \ln(r_1 + r_2 + r_{12})(\mu_{\mathrm{A}} \boldsymbol{Y}_{20} - 2\mu_{\mathrm{S}} \boldsymbol{Y}_{21}) - \tfrac{1}{6}\mu_{12} \ln(r_1 - r_2 + r_{12})(\mu_{\mathrm{S}} \boldsymbol{Y}_{20} - 2\mu_{\mathrm{A}} \boldsymbol{Y}_{21}) \\
& - \tfrac{1}{6}Er^2 + \tfrac{1}{3}\mu_2 r_1 r_2(3\mu_1 - \mu_{12}) + \tfrac{1}{12}r_{12}^2(2\mu_1^2 + 2\mu_2^2 + \mu_{12}^2) \\
& + \tfrac{2}{3}\mu_{12} r_{12}(\mu_1 r_1 + \mu_2 r_2) + a_{20} \boldsymbol{Y}_{20} + a_{21} \boldsymbol{Y}_{21}
\end{aligned}$$

$$\begin{aligned}
{}^{\mathrm{P}}\boldsymbol{\Psi}_4^{[2,0]} = & -\tfrac{1}{90}\mu_{12} \ln(r_1 + r_2 + r_{12})(10\mu_{\mathrm{A}} \boldsymbol{Y}_{40} - 21\mu_{\mathrm{S}} \boldsymbol{Y}_{41} + 40\mu_{\mathrm{A}} \boldsymbol{Y}_{42}) \\
& - \tfrac{1}{90}\mu_{12} \ln(r_1 - r_2 + r_{12})(10\mu_{\mathrm{S}} \boldsymbol{Y}_{40} - 21\mu_{\mathrm{A}} \boldsymbol{Y}_{41} + 40\mu_{\mathrm{S}} \boldsymbol{Y}_{42}) \\
& - \tfrac{1}{5}Er_{12}^2(r_1^2 - r_2^2) + \tfrac{1}{15}\mu_{12} r_{12}(\mu_1 r_1^3 - \mu_2 r_2^3) + \tfrac{2}{3}\mu_{12} r_{12}^3(\mu_1 r_1 - \mu_2 r_2) \\
& - \tfrac{1}{9}r_1^2 r_2^2(\mu_1^2 - \mu_2^2) + \tfrac{1}{60}r_{12}^2(r_1^2 - r_2^2)(10\mu_1^2 + 10\mu_2^2 + 3\mu_{12}^2) - \tfrac{4}{9}\mu_{12}\mu_1 r_1^2 r_2^2 \\
& + \tfrac{4}{3}\mu_1 \mu_2 r_1 r_2(r_1^2 - r_2^2) - \tfrac{2}{15}\mu_{12}\mu_2 r_1 r_2(12r_1^2 - 5r_{12}^2 - 2r_2^2) \\
& - \tfrac{29}{15}\mu_{12} r_{12} r_1 r_2(\mu_1 r_2 - \mu_2 r_1) \\
& + a_{40} \boldsymbol{Y}_{40} + a_{41} \boldsymbol{Y}_{41} + a_{42} \boldsymbol{Y}_{42}
\end{aligned}$$

and

$$\begin{aligned}
{}^{\mathrm{P}}\boldsymbol{\Psi}_4^{[2,1]} = & \tfrac{1}{180}\mu_{12} \ln(r_1 + r_2 + r_{12})(10\mu_{\mathrm{S}} \boldsymbol{Y}_{40} - 21\mu_{\mathrm{A}} \boldsymbol{Y}_{41} + 40\mu_{\mathrm{S}} \boldsymbol{Y}_{42}) \\
& + \tfrac{1}{180}\mu_{12} \ln(r_1 - r_2 + r_{12})(10\mu_{\mathrm{A}} \boldsymbol{Y}_{40} - 21\mu_{\mathrm{S}} \boldsymbol{Y}_{41} + 40\mu_{\mathrm{A}} \boldsymbol{Y}_{42}) \\
& + \tfrac{1}{30}E(3r^2 r_{12}^2 - 16r_1^2 r_2^2) - \tfrac{1}{24}(\mu_1^2 + \mu_2^2)(3r^2 r_{12}^2 - 10r_1^2 r_2^2) + \tfrac{3}{80}r_{12}^4(\mu_1^2 + \mu_2^2) \\
& - \tfrac{1}{24}\mu_{12}^2(r^2 r_{12}^2 - 6r_1^2 r_2^2) + \tfrac{3}{10}\mu_{12} r_{12}(\mu_1 r_1^3 + \mu_2 r_2^3) - \tfrac{1}{2}\mu_{12} r_{12}^3(\mu_1 r_1 + \mu_2 r_2) \\
& + \tfrac{2}{9}\mu_{12}\mu_1 r_1^2 r_2^2 + \tfrac{1}{4}\mu_1 \mu_2 r_1 r_2(r^2 - r_{12}^2) - \tfrac{1}{15}\mu_{12}\mu_2 r_1 r_2(12r_1^2 - 5r_{12}^2 - 2r_2^2) \\
& + \tfrac{29}{30}\mu_{12} r_{12} r_1 r_2(\mu_1 r_2 + \mu_2 r_1) + a_{40} \boldsymbol{Y}_{40} + a_{41} \boldsymbol{Y}_{41} + a_{42} \boldsymbol{Y}_{42}.
\end{aligned}$$

These are valid for $r_1 > r_2$. The expressions valid for $r_1 < r_2$ are obtained by interchanging r_1 with r_2, μ_1 with μ_2 and a_{ij} with a'_{ij} (Gottschalk and Maslen 1985). For the ^{3}S state the expression for $r_1 < r_2$ is also multiplied by -1.

The non-physical behaviour of these functions is now examined. Consider the function ${}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]}$. It is easily verified that

$$\left.\frac{\partial {}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]}}{\partial r_1}\right|_{r_1 \to r_2^+} - \left.\frac{\partial {}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]}}{\partial r_1}\right|_{r_1 \to r_2^-}$$

$$= 2r_2(2a_{20} + 2a'_{20} + a_{21} - a'_{21}) + \tfrac{1}{3}\mu_{12} r_2(\mu_1 - \mu_2) - \tfrac{4}{3}\mu_{12}\mu_2 r_2 \ln r_{12} \tag{37a}$$

and

$$\begin{aligned}
{}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]}(r_1 \to r_2^+) - {}^{\mathrm{P}}\boldsymbol{\Psi}_2^{[0,0]}(r_1 \to r_2^-) \\
= -(a_{21} - a'_{21})(r_{12}^2 - 2r_2^2) + \tfrac{1}{3}\mu_{12} r_2^2(\mu_1 - \mu_2) \\
- \tfrac{1}{3}\mu_{12}(\mu_1 - \mu_2)(r_{12}^2 - 2r_2^2) \ln r_{12}.
\end{aligned} \tag{37b}$$

The logarithmic singularities are removed by subtracting the homogeneous solutions with equivalent behaviour. Note that Pluvinage's (1950) power series solution contains such logarithmic singularities. In general the complementary expressions (equation (33), table 2) do not have the correct behaviour. Linear combinations of these functions are required. When examining the behaviour of the complementary solutions at $r_1 = r_2$

it must be remembered that $\sin^{-1} y$ has discontinuous derivatives with respect to r_1 and r_2. The following equality is helpful in avoiding errors:

$$\sin^{-1} y = 2\tan^{-1}\rho.$$

The $\ln r_{12}$ terms in (37) are eliminated completely using the complementary solutions listed in (33). Cancellation of the remaining polynomial terms relates a'_{20} to a_{20} and a'_{21} to a_{21}. The wavefunction is still not in the form of (36), however, due to the presence of a_{ij} multiplying $\boldsymbol{Y}_{ij}$ for $r_1 > r_2$ and a'_{ij} multiplying $\boldsymbol{Y}_{ij}$ with r_1 interchanged with r_2 for $r_1 < r_2$. To obtain the required form (36) it is necessary that $a_{ij} = \pm a'_{ij}$, depending on the symmetry of the wavefunction and $\boldsymbol{Y}_{ij}$. This is easily achieved using the relation between a_{ij} and a'_{ij} to add the required amount of HH. The physically acceptable $\boldsymbol{\Psi}_2^{[0,0]}$ is now completely determined apart from terms proportional to a_{20} and a_{21}. Evaluation of these coefficients would require knowledge of the asymptotic form of the wavefunction. The behaviour of the reduced function for various values of r_1, r_2 and r_{12} was examined in II.

Since determination of $\boldsymbol{\Psi}_4^{[2,0]}$ and $\boldsymbol{\Psi}_4^{[2,1]}$ follows that for $\boldsymbol{\Psi}_2^{[0,0]}$ only the results are presented. These have not been derived previously.

$nsms$ ^{1}S: $\Psi = a_{00}(\boldsymbol{Y}_{00} + \boldsymbol{\Psi}_1^{[0,0]} + \boldsymbol{\Psi}_2^{[0,0]}) + a_{20}\boldsymbol{Y}_{20} + a_{21}\boldsymbol{Y}_{21} + \mathrm{O}(r^3)$

$$\boldsymbol{\Psi}_1^{[0,0]} = \mu_1 r_1 + \mu_2 r_2 + \tfrac{1}{2}\mu_{12} r_{12}$$

$$\begin{aligned}\boldsymbol{\Psi}_2^{[0,0]} = {} & -\tfrac{1}{6}\mu_{12}\ln(r_1+r_2+r_{12})(\mu_A \boldsymbol{Y}_{20} - 2\mu_S \boldsymbol{Y}_{21}) + \tfrac{1}{6}\mu_{12}\ln(r_1-r_2+r_{12})(2\mu_A\boldsymbol{Y}_{21} - \mu_S\boldsymbol{Y}_{20}) \\ & -\tfrac{1}{12}\mu_{12}\left(s_1 - \frac{1}{\pi}s_2\right)(2\mu_A\boldsymbol{Y}_{21} - \mu_S\boldsymbol{Y}_{20}) + \frac{1}{3\pi}\mu_{12}\ln r(\mu_A\boldsymbol{Y}_{20} - 2\mu_S\boldsymbol{Y}_{21}) \\ & -\frac{2}{3\pi}\mu_{12}\mu_A r_1 r_2 \sin^{-1} y - \frac{1}{3\pi}\mu_{12}\mu_S r_{12}\sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2} \\ & -\tfrac{1}{6}\mu_{12}\mu_S r_{12}(2r^2 - r_{12}^2)^{1/2} - \tfrac{1}{6}Er^2 + \tfrac{1}{12}r_{12}^2(2\mu_1^2 + \mu_{12}^2 + 2\mu_2^2) \\ & +\tfrac{2}{3}\mu_{12}r_{12}(\mu_1 r_1 + \mu_2 r_2) + \tfrac{1}{3}\mu_2 r_1 r_2(3\mu_1 - \mu_{12})\end{aligned}$$

$nsms$ ^{3}S: $\Psi = a_{20}(\boldsymbol{Y}_{20} + \boldsymbol{\Psi}_3^{[2,0]} + \boldsymbol{\Psi}_4^{[2,0]}) + a_{40}\boldsymbol{Y}_{40} + a_{41}\boldsymbol{Y}_{41} + a_{42}\boldsymbol{Y}_{42} + \mathrm{O}(r^5)$

$$\boldsymbol{\Psi}_3^{[2,0]} = \tfrac{2}{3}\mu_1 r_1(2r_1^2 - 3r_2^2) + \tfrac{2}{3}\mu_2 r_2(3r_1^2 - 2r_2^2) + \tfrac{1}{2}\mu_{12}r_{12}(r_1^2 - r_2^2)$$

$$\begin{aligned}\boldsymbol{\Psi}_4^{[2,0]} = {} & -\tfrac{1}{90}\mu_{12}\ln(r_1+r_2+r_{12})(10\mu_A\boldsymbol{Y}_{40} - 21\mu_S\boldsymbol{Y}_{41} + 40\mu_A\boldsymbol{Y}_{42}) \\ & -\tfrac{1}{90}\mu_{12}\ln(r_1-r_2+r_{12})(10\mu_S\boldsymbol{Y}_{40} - 21\mu_A\boldsymbol{Y}_{41} + 40\mu_S\boldsymbol{Y}_{42}) \\ & +\tfrac{1}{180}\mu_{12}\left(s_1 - \frac{1}{\pi}s_2\right)(10\mu_S\boldsymbol{Y}_{40} - 21\mu_A\boldsymbol{Y}_{41} + 40\mu_S\boldsymbol{Y}_{42}) \\ & +\frac{2}{45\pi}\mu_{12}\ln r(7\mu_A\boldsymbol{Y}_{40} - 15\mu_S\boldsymbol{Y}_{41} + 28\mu_A\boldsymbol{Y}_{42}) \\ & -\frac{2}{15\pi}\mu_{12}r_1 r_2\sin^{-1} y(7\mu_A\boldsymbol{Y}_{20} - 10\mu_S\boldsymbol{Y}_{21}) \\ & -\frac{1}{15\pi}\mu_{12}r_{12}\sin^{-1}(y\Omega)(2r^2 - r_{12}^2)^{1/2}(5\mu_S\boldsymbol{Y}_{20} - 14\mu_A\boldsymbol{Y}_{21}) \\ & -\tfrac{1}{30}\mu_{12}r_{12}(2r^2 - r_{12}^2)^{1/2}(5\mu_S\boldsymbol{Y}_{20} - 14\mu_A\boldsymbol{Y}_{21}) - \tfrac{1}{5}Er_{12}^2(r_1^2 - r_2^2) \\ & +\tfrac{1}{60}r_{12}^2(r_1^2 - r_2^2)(10\mu_1^2 + 3\mu_{12}^2 + 10\mu_2^2) - \frac{28}{45\pi}\mu_{12}\mu_A r_1^2 r_2^2 - \tfrac{1}{9}r_1^2 r_2^2(\mu_1^2 - \mu_2^2) \\ & +\tfrac{2}{3}\mu_{12}r_{12}^3(\mu_1 r_1 - \mu_2 r_2) - \tfrac{4}{9}\mu_{12}\mu_A r_1^2 r_2^2 - \tfrac{2}{15}\mu_{12}\mu_2 r_1 r_2(12r_1^2 - 5r_{12}^2 - 2r_2^2) \\ & -\tfrac{29}{15}\mu_{12}r_{12}r_1 r_2(\mu_1 r_2 - \mu_2 r_1) + \tfrac{1}{15}\mu_{12}r_{12}(\mu_1 r_1^3 - \mu_2 r_2^3) + \tfrac{4}{3}\mu_1\mu_2 r_1 r_2(r_1^2 - r_2^2)\end{aligned}$$

$$npmp\ ^1\mathrm{S}\colon\ \Psi = a_{21}(Y_{21}+\Psi_3^{[2,1]}+\Psi_4^{[2,1]})+a_{40}Y_{40}+a_{41}Y_{41}+a_{42}Y_{42}+\mathrm{O}(r^5)$$

$$\Psi_3^{[2,1]}=\tfrac{1}{2}(\mu_1 r_1+\mu_2 r_2)(r^2-r_{12}^2)+\tfrac{1}{12}\mu_{12}r_{12}(6r^2-5r_{12}^2)$$

$$\begin{aligned}\Psi_4^{[2,1]}=&\tfrac{1}{180}\mu_{12}\ln(r_1+r_2+r_{12})(10\mu_{\mathrm{S}}Y_{40}-21\mu_{\mathrm{A}}Y_{41}+40\mu_{\mathrm{S}}Y_{42})\\&+\tfrac{1}{180}\mu_{12}\ln(r_1-r_2+r_{12})(10\mu_{\mathrm{A}}Y_{40}-21\mu_{\mathrm{S}}Y_{41}+40\mu_{\mathrm{A}}Y_{42})\\&-\tfrac{1}{360}\mu_{12}\left(s_1-\frac{1}{\pi}s_2\right)(10\mu_{\mathrm{A}}Y_{40}-21\mu_{\mathrm{S}}Y_{41}+40\mu_{\mathrm{A}}Y_{42})\\&-\frac{1}{45\pi}\mu_{12}\ln r(7\mu_{\mathrm{S}}Y_{40}-15\mu_{\mathrm{A}}Y_{41}+28\mu_{\mathrm{S}}Y_{42})\\&+\frac{1}{15\pi}\mu_{12}r_1r_2\sin^{-1}y(7\mu_{\mathrm{S}}Y_{20}-10\mu_{\mathrm{A}}Y_{21})\\&+\frac{1}{30\pi}\mu_{12}r_{12}\sin^{-1}(y\Omega)(2r^2-r_{12}^2)^{1/2}(5\mu_{\mathrm{A}}Y_{20}-14\mu_{\mathrm{S}}Y_{21})\\&+\tfrac{1}{60}\mu_{12}r_{12}(2r^2-r_{12}^2)^{1/2}(5\mu_{\mathrm{A}}Y_{20}-14\mu_{\mathrm{S}}Y_{21})+\tfrac{1}{30}E(3r^2r_{12}^2-16r_1^2r_2^2)\\&-\tfrac{1}{24}\mu_{12}^2(r^2r_{12}^2-6r_1^2r_2^2)+\tfrac{3}{80}r_{12}^4(\mu_1^2+\mu_2^2)+\frac{14}{45\pi}\mu_{12}\mu_{\mathrm{S}}r_1^2r_2^2\\&+\tfrac{3}{10}\mu_{12}r_{12}(\mu_1r_1^3+\mu_2r_2^3)-\tfrac{1}{2}\mu_{12}r_{12}^3(\mu_1r_1+\mu_2r_2)+\tfrac{2}{9}\mu_{12}\mu_{\mathrm{S}}r_1^2r_2^2\\&-\tfrac{1}{15}\mu_{12}\mu_2r_1r_2(12r_1^2-5r_{12}^2-2r_2^2)+\tfrac{29}{30}\mu_{12}r_{12}r_1r_2(\mu_1r_2+\mu_2r_1)\\&-\tfrac{1}{24}(3r^2r_{12}^2-10r_1^2r_2^2)(\mu_1^2+\mu_2^2)+\tfrac{1}{4}\mu_1\mu_2r_1r_2(r^2-r_{12}^2).\end{aligned}$$

Pluvinage's (1950) (8) and Scherr's (1979) (10) expressions can be related to $\Psi_2^{[0,0]}$ by adding solutions to Laplace's equation. These are obtained by subtracting their functions from the physical solution.

5. Extension to higher orders

It is expected that the procedure for finding $\Psi_{k+2}^{[k,l]}$ in closed form described in § 4 will extend to the higher-order components of the wavefunction, $\Psi_\kappa^{[k,l]}$ where $\kappa > k+2$. Information helpful to this extension can be obtained by examining the spherical polar representation outlined in § 2.2. The complete formulation in these coordinates is given by Gottschalk and Maslen (1985) and is based on the expansion

$$\Psi=\begin{cases}\sum_{ijlp} C_{ijlp}r_1^ir_2^j(\ln r_1)^pP_l(\cos\theta)/p! & r_1>r_2\\ \sum_{ijlp} C'_{ijlp}r_1^jr_2^i(\ln r_2)^pP_l(\cos\theta)/p! & r_1<r_2\end{cases}\tag{38}$$

where $p,\ l\geq 0$, $j\geq l$ and $k=i+j\geq 0$. The $p!$ factor achieves a mild simplification of the recurrence equations. This expression for the wavefunction is related to $\Psi_\kappa^{[k,l]}$ in (36). The expansions and equations determining the coefficients C_{ijlp} and C'_{ijlp} of Ψ also apply to $\Psi_\kappa^{[k,l]}$. The equations for C_{ijlp} and C'_{ijlp} are similar to those in § 2.2 for C_{ijl} and C'_{ijl} to the extent that there is no need to reproduce them here.

Consider first $\Psi_\kappa^{[k,l]}$ for odd κ and $\kappa \geqslant k+3$. The recurrence equations for C_{ijlp} and C'_{ijlp}, obtained by substituting (38) into equation (35), specify all the coefficients apart from C_{k-ll0} and C'_{k-ll0}. These are determined by the continuity and derivative continuity requirement. As already noted in (28), each multiplies a separable series solution to Laplace's equation. This indicates that once a particular solution of (35), ${}^{\mathrm{p}}\Psi_\kappa^{[k,l]}$, has been found, the complementary solution ${}^{\mathrm{c}}\Psi_\kappa^{[k,l]}$ required to satisfy the boundary conditions can, if necessary, be expanded as a sum of the separable series solutions to Laplace's equation.

For $\Psi_\kappa^{[k,l]}$ with even κ and $\kappa \geqslant k+2$, application of the boundary conditions requires more complex solutions to Laplace's equation. An additional logarithmic term is needed. That is, if the highest power of $\ln r$ in $\Psi_{\kappa-1}^{[k,l]}$ is p then $\Psi_\kappa^{[k,l]}$ requires $(\ln r)^{p+1}$. This is well known and the required complementary functions ${}^{\mathrm{c}}\Psi_\kappa^{[k,l]}$ were derived in closed form in § 4 for $\kappa = k+2$. If a systematic method for producing the non-separable logarithmic functions in reduced form is not available, solution by expansion will be necessary. Note, however, that the work completed so far suggests that compact expressions will exist in the cases of interest. Pluvinage (1985) used the independent coordinates

$$r = (r_1^2 + r_2^2)^{1/2} \qquad \xi = \tfrac{1}{2}(\alpha - \beta) \qquad \eta = \tfrac{1}{2}(\pi - \alpha - \beta)$$

where r and α were given previously (1), and $\beta = \sin^{-1}(y\Omega)$. He wrote $\Psi_2^{[0,0]}$ in terms of trigonometric functions of (r, ξ, η), logs of these trigonometric functions and integrals of these logarithms. The latter corresponds to Lobachevskiy's function. This is reasonable since differentiation of each produces the preceding class of function. Lobachevskiy's function is expressible in terms of the Clausen function, $\mathrm{Cl}_2(x)$, or the dilogarithm, $\mathrm{Li}_2(x)$ (Lewin 1958)

$$L(\pi/2 \pm x) = (\pi/2 \pm x)\ln 2 \pm \tfrac{1}{2}\mathrm{Cl}_2(2x)$$

and

$$\mathrm{Im}[\mathrm{Li}_2(\mathrm{e}^{\mathrm{i}\theta})] = \mathrm{Cl}_2(\theta).$$

It is thus reasonable to expect to encounter solutions to Laplace's equation related to the polylogarithm,

$$\mathrm{Li}_n(z) = \int_0^z \frac{\mathrm{Li}_{n-1}(z)}{z}\,\mathrm{d}z \qquad |z| \leqslant 1.$$

6. Conclusions

Wavefunctions can be written as infinite series containing homogeneous functions Ψ_k of degree k in the hyper-radius r, the remaining coordinates (hyperangles) being denoted here by Ω, not to be confused with $\Omega = \cos\theta$ used above. Substituting the expansion into the Schrödinger equation gives a set of coupled differential equations for the Ψ_k. As $k \geqslant 0$ these may be solved in order of increasing k. The physically acceptable solutions are extracted by applying the appropriate boundary conditions. This procedure is applicable to a wide range of potentials and an arbitrary number of particles. It is a generalisation of the method developed by Fock who determined the form of the wavefunctions near $r=0$ and expanded the homogeneous functions Ψ_k into $\Psi_{kp}(\Omega)$

$$\Psi_k = r^k \sum_{p=0}^{k} \Psi_{kp}(\Omega)\ln^p r.$$

The common hyperspherical approach, proposed by Fock (1954, 1958), involves expanding both sides of the resulting differential equations into hyperspherical harmonics (HH), followed by the use of orthogonality to invert the equation. The properties of the HH ensure that the solution is valid for all finite r and does not contain any singularities. A major disadvantage of this method is the difficulty of reducing the series solution to its compact form. The method presented here reduces these difficulties by avoiding the Fock expansion and HH. It is found that some particular solutions for Ψ_k are simple functions. These solutions, although singular and with discontinuous derivatives, are sought deliberately because of their simple form. As in the case for ordinary differential equations, the physically acceptable solutions are then formed by adding solutions to the homogeneous equation to the particular solution. The homogeneous equation is Laplace's equation and the solutions required are logarithmic and not necessarily valid in all space.

In the examples quoted, expansions are avoided. This may not be possible in all cases because of the complexity of the inhomogeneous term. In such instances expansions which introduce discontinuities naturally, such as spherical polar coordinate expansions, are preferable to hyperspherical expansions because of the simpler form of the resulting series.

To elucidate this procedure the three-particle Schrödinger equation with Coulombic potentials, of which helium is a special case, is examined. The closed form for $nsms$ ^{1}S states to second order is rederived and expansions are avoided. The result is consistent with earlier derivations in I and II, based on expansions in hypersphericals and spherical polars, respectively. It is obtained far more efficiently by the new method. The $nsms$ ^{3}S and $npmp$ ^{1}S states are determined in compact form to fourth order in r for the first time. The process can be extended straightforwardly to other doubly excited states using the results listed.

Even if the required solutions to Laplace's equation must be found by expansion, resumming the resulting wavefunction (in, say, spherical polar coordinates) will be much simpler than the use of HH expansions for the complete problem. The homogeneous functions Ψ_k naturally decompose into solutions to Laplace's equation plus additional components due to the potential. As both parts are singular the HH expansions necessarily mix the two. The decomposition necessary to sum the series in HH is far more difficult than solution by the present method.

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Appendix 1. Solution of $[\Lambda^2 - k(k+4)]F = Y_{kl}$

Equations such as

$$[\Lambda^2 - k(k+4)]F(\alpha, \theta) = Y_{kl}(\alpha, \theta) \tag{A1.1}$$

where $F(\alpha, \theta) = f(\alpha)P_l(\Omega)$ and $\Omega = \cos\theta$, arise in some cases. These are not solvable by the method of expanding $f(\alpha)P_l(\cos\theta)$ into HH, using their orthogonality to find the expansion coefficients. The difficulty is that Y_{kl}, an eigenfunction of the differential operator on the left-hand side of (A1.1), also appears on the right. This may be solved by the method of variation of parameters as discussed below.

From equation (11) in I

$$\Lambda^2(\alpha, \theta) = -4(\sin\alpha)^{-2}\left(\frac{\partial}{\partial\alpha}\sin^2\alpha\frac{\partial}{\partial\alpha} + (\sin\theta)^{-1}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right).$$

Noting that

$$(\sin\theta)^{-1}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} = \frac{\partial}{\partial\Omega}(1-\Omega^2)\frac{\partial}{\partial\Omega}$$

and

$$\frac{\partial}{\partial\Omega}(1-\Omega^2)\frac{\partial}{\partial\Omega}P_l(\Omega) = -l(l+1)P_l(\Omega)$$

it is found that

$$\Lambda^2 f(\alpha)P_l(\Omega) = -4(\sin\alpha)^{-2}\left(\frac{\partial}{\partial\alpha}\sin^2\alpha\frac{\partial}{\partial\alpha} - l(l+1)\right)f(\alpha)P_l(\Omega). \qquad \text{(A1.2)}$$

Orthogonality of the Legendre polynomials is used to reduce equation (A1.1) to an ordinary differential equation,

$$-\left[4(\sin\alpha)^{-2}\left(\frac{\partial}{\partial\alpha}\sin^2\alpha\,\frac{\partial}{\partial\alpha} - l(l+1)\right) + k(k+4)\right]f(\alpha) = I(\alpha) \qquad \text{(A1.3)}$$

where $I(\alpha)$ can be obtained from table 1 and either (25a) or (26a), depending on the symmetry of Y_{kl}. Solutions to the homogeneous equation are given by (25a) and (25b), and (A1.3) is solved by the method of variation of parameters (Boyce and DiPrima 1977, p 121).

As an example consider $k=2$ and $l=0$, where

$$I(\alpha) = 2\cos\alpha$$

and the two independent homogeneous solutions are

$$y_1 = \cos\alpha \qquad y_2 = 2\cos(2\alpha)/\sin\alpha. \qquad \text{(A1.4)}$$

In this case the Wronskian is $-(8\sin^2\alpha)^{-1}$ and a particular solution to (A1.3) is

$$f(\alpha) = \frac{\alpha\cos(2\alpha)}{16\sin\alpha}. \qquad \text{(A1.5)}$$

The corresponding solution to (A1.1) is

$$F(\alpha, \theta) = \tfrac{1}{32}\alpha Q_{20}^{11}(\alpha, \theta).$$

The case of $k=2$ and $l=1$ has already been calculated by Pluvinage (1982) (18) with the solution of (A1.1) being

$$F(\alpha, \theta) = \tfrac{1}{128}\alpha Q_{21}^{11}(\alpha, \theta) - \frac{\cos\theta}{32\sin\alpha}.$$

The result (A1.5) is implied in the work of Fock (1954, 1958). It can be shown that a suitable linear combination of f and y_2 (A1.4) yields the (generalised) Green function for the differential equation (A1.1). Fock gave these Green functions for $k \geq 0$. The appearance of these is not surprising. The connection of Green functions to the method of variation of parameters is discussed by Whitten and McCormick (1975).

Appendix 2. Action of the Laplacian

As only S states are considered the Laplacian reduces to

$$\Delta = r_1^{-2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + r_2^{-2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + 2r_{12}^{-2}\frac{\partial}{\partial r_{12}} r_{12}^2 \frac{\partial}{\partial r_{12}}$$
$$+ 2\cos\theta_1 \frac{\partial^2}{\partial r_1 \partial r_{12}} + 2\cos\theta_2 \frac{\partial^2}{\partial r_2 \partial r_{12}}$$

with

$$\cos\theta_1 = \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1 r_{12}} \qquad \cos\theta_2 = \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2 r_{12}}.$$

For the differential equations considered the Laplacian usually acts on products of functions. The action of the Laplacian can be derived from that for each term separately. The calculations are simplified and insight gained by use of the equation

$$\Delta fg = f\Delta g + g\Delta f + 2\frac{\partial f}{\partial r_1}\frac{\partial g}{\partial r_1} + 2\frac{\partial f}{\partial r_2}\frac{\partial g}{\partial r_2} + 4\frac{\partial f}{\partial r_{12}}\frac{\partial g}{\partial r_{12}}$$
$$+ 2\cos\theta_1\left(\frac{\partial f}{\partial r_1}\frac{\partial g}{\partial r_{12}} + \frac{\partial f}{\partial r_{12}}\frac{\partial g}{\partial r_1}\right) + 2\cos\theta_2\left(\frac{\partial f}{\partial r_2}\frac{\partial g}{\partial r_{12}} + \frac{\partial f}{\partial r_{12}}\frac{\partial g}{\partial r_2}\right). \qquad \text{(A2.1)}$$

Consider, for example,

$$\Delta(fg + h) = e.$$

If Δf, Δh, e and $\partial g/\partial r_i$ do not contain g, then from (A2.1) f must satisfy Laplace's equation,

$$\Delta f = 0.$$

Usually this implies that f is a finite series solution, i.e. $\boldsymbol{Q}^{\mathrm{I}}$ or $\boldsymbol{Q}^{\mathrm{II}}$ from table 1. Invoking this reduces the calculations. It also explains why the HH multiply special functions for many terms in $\boldsymbol{\Psi}_k$. The $\boldsymbol{Q}^{\mathrm{II}}$ option can often be ignored as these are singular as r_1 or $r_2 \to 0$. However they may be present if multiplied by appropriate functions. For example

$$\boldsymbol{Q}_{20}^{\mathrm{II}} \sin^{-1} y$$

is well behaved at the origin.

The action of the Laplacian on some of the more complicated functions is listed to assist the verification and extension of the formulae in this paper. All are valid for $r_1 > r_2$:

$$f_1 = \sin^{-1} y \ln\left(\frac{1+\Omega}{1-\Omega}\right) \qquad \Delta f_1 = 4\ln\left(\frac{1+\Omega}{1-\Omega}\right)\frac{(r_1^2 - r_2^2)}{r^2 r_1 r_2}$$

$$f_2=\sin^{-1}(y\Omega)s_1(r_1, r_2, r_{12}) \qquad \Delta f_2=-8[s_1(r_1, r_2, r_{12})+1]\frac{(r^2-r_{12}^2)}{r^2r_{12}(2r^2-r_{12}^2)^{1/2}}$$

$$f_3=L\left(\frac{\alpha-\beta}{2}\right)-L\left(\frac{\alpha+\beta}{2}\right)+L\left(\frac{\pi-\alpha+\beta}{2}\right)-L\left(\frac{\pi-\alpha-\beta}{2}\right)$$

$$\Delta f_3=-2\ln\left(\frac{1+\Omega}{1-\Omega}\right)\frac{(r_1^2-r_2^2)}{r^2r_1r_2}-4[s_1(r_1, r_2, r_{12})-s_1(r_2, r_1, r_{12})]\frac{(r^2-r_{12}^2)}{r^2r_{12}(2r^2-r_{12}^2)^{1/2}}$$

$$f_4=\boldsymbol{Y}_{40}s_1(r_1, r_2, r_{12}) \qquad \Delta f_4=\frac{64r^2(r_1^2-r_2^2)}{r_{12}(2r^2-r_{12}^2)^{1/2}}-16r^2$$

$$f_5=\boldsymbol{Y}_{41}s_1(r_1, r_2, r_{12}) \qquad \Delta f_5=\frac{32r^2(r^2-r_{12}^2)}{r_{12}(2r^2-r_{12}^2)^{1/2}}$$

$$f_6=\boldsymbol{Y}_{42}s_1(r_1, r_2, r_{12}) \qquad \Delta f_6=\frac{8r^2(r_1^2-r_2^2)}{r_{12}(2r^2-r_{12}^2)^{1/2}}-8r^2$$

$$f_7=\boldsymbol{Y}_{40}s_2(r_1, r_2, r_{12}) \qquad \Delta f_7=-128\sin^{-1}(y\Omega)\frac{r^2(r_1^2-r_2^2)}{r_{12}(2r^2-r_{12}^2)^{1/2}}$$

$$f_8=\boldsymbol{Y}_{41}s_2(r_1, r_2, r_{12}) \qquad \Delta f_8=32\sin^{-1}y\frac{r^2(r_1^2-r_2^2)}{r_1r_2}-64\sin^{-1}(y\Omega)\frac{r^2(r^2-r_{12}^2)}{r_{12}(2r^2-r_{12}^2)^{1/2}}$$

$$f_9=\boldsymbol{Y}_{42}s_2(r_1, r_2, r_{12}) \qquad \Delta f_9=24\sin^{-1}y\frac{r^2(r^2-r_{12}^2)}{r_1r_2}-16\sin^{-1}(y\Omega)\frac{r^2(r_1^2-r_2^2)}{r_{12}(2r^2-r_{12}^2)^{1/2}}.$$

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