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Coordinate systems and analytic expansions for three-body atomic wavefunctions: I. Partial summation for the Fock expansion in hyperspherical coordinates

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Abstract. A survey of analytic techniques for solving the two-electron atomic Schrödinger equation is presented. The hyperspherical formalism is introduced and specialised to the case of two electrons and zero total angular momentum. Following Fock, the Schrödinger equation is then converted to an infinite set of coupled second-order differential equations by proposing an expansion including logarithmic functions of the interparticle coordinates. The equivalence of the techniques of Pluvinage and Hylleraas to the Fock expansion is demonstrated and the method for solution is illustrated. The extension to states of arbitrary angular momentum and excited states is indicated. Methods for simplifying the recurrence relation generated by the Fock expansion are used to determine the highest power logarithmic terms to sixth order. Finally, the wavefunction for S states is given to second order as a singly infinite sum of Legendre polynomials.

1. Introduction

It is commonly believed that helium, the second simplest of atoms, does not permit exact solution of its Schrödinger equation (SE). This belief reflects earlier difficulties in solving the SE analytically due to non-separability. However, this pessimism is not justified. Although Bartlett *et al* (1935) showed that the ^{1}S-state helium wavefunction could not be expanded into an analytic series of the interparticle coordinates, Bartlett (1937) demonstrated the existence of a formal expansion including logarithmic functions of the interparticle coordinates. Fock (1954, 1958), after introducing hyperspherical coordinates

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

proposed that, in the neighbourhood of $r = 0$, the exact eigenfunctions have the Fock expansion (FE)

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

Fock then substituted (2) into the SE obtaining a recurrence relation, involving differential operators, for the angular functions Ψ_{kp} and obtained solutions for $k = 0$ and 1 in agreement with those of Bartlett (1937). He constructed hyperspherical harmonics

(HH) which form a complete orthonormal set suitable for expanding Ψ_{kp} and demonstrated the appropriate order for solving the recurrence relation. The Ψ_{kp} are not determined completely by the recurrence relation: the remaining degrees of freedom are removed by imposing the physical boundary conditions. Fock also determined Green functions necessary for expressing the coupled system of differential equations in an equivalent integral form.

Macek (1967) proved that for $r<(-8E)^{-1/2}$, where E is the energy, the FE is square integrable over α and θ. Leray (1982a, b, 1983, 1984) sketched a proof of the necessity and sufficiency of the FE by extending Fuchs' theorem. Recently Morgan (1986) has rigorously proved that, for any value (even complex) of E, the SE has infinitely many solutions, each possessing a FE convergent for all finite r.

Ermolaev (1958) and Demkov and Ermolaev (1959) studied the extension of the FE to an arbitrary system of charged particles and to states of any symmetry. Ermolaev (1961) and David (1975) extended the work of Fock obtaining Ψ_{20} by expansion into HH. Algebraically summing the series produced by their technique is difficult. Some results are given in § 5 of this paper. A table of the known Fock coefficients is given by Abbott (1986).

Variational work using conventional expansions containing exponential and polynomial functions of the interparticle distances have been studied since the classic work of Hylleraas (1929). However, as Bartlett *et al* (1935) showed, these analytic expansions cannot satisfy the SE. Variational studies incorporating $\ln(r_1+r_2)$, which is closely related to $\ln r$, have been presented by Hylleraas and Midtdal (1956, 1958), Frankowski and Pekeris (1966), Frankowski (1967) and recently by Freund *et al* (1984). Variational expansions using the exact form of the FE (2) have been presented by Ermolaev and Sochilin (1964, 1968) and Sochilin (1969). The results of Hylleraas and Midtdal were inconclusive but all later works show a dramatic improvement in the convergence of the energy (and other operator expectation values), with respect to the number of variational parameters, upon the inclusion of the logarithmic terms.

The incorporation of the FE in perturbational work has been discussed by Ermolaev (1968) for helium and by Tulub (1969) and Tulub *et al* (1971) for the van der Waals' interaction of two hydrogen atoms.

An alternative technique to the FE is the conversion of the SE into an infinite set of coupled second-order differential equations, using matrix methods to solve a truncated set of these equations (Bartlett 1937, Macek 1968, Knirk 1974a, Fano 1976, Haftel and Mandelzweig 1983, Feagin *et al* 1985). Knirk (1974b) and Klar (1985b) demonstrated the equivalence of the (non-truncated) matrix techniques to the FE. However, the above analyses usually incorporate the adiabatic approximation and, as one solves only a truncated set of these equations, the results are no longer exact. In this paper we focus on exact solutions, so variational, perturbational and matrix techniques are not considered. It is emphasised that approximating, at any stage of the calculation, prevents algebraic simplifications that occur only with exact wavefunctions. This paper and the succeeding one demonstrate that with persistence, and utilising complementary approaches, many of the algebraic hurdles may be resolved. The outlook for simple closed form helium wavefunctions is more favourable than is generally believed.

This paper is organised as follows. In § 2, hyperspherical coordinates for treating the N-electron atom are introduced, with particular emphasis on the case $N=2$. The HH associated with the generalised angular momentum operator, which is the quadratic Casimir operator for SO(n), where $n=3N$, are introduced. The properties of scalar

HH for $N=2$ are summarised. A plausibility argument for the FE is presented in § 3 and its relationship to techniques of Pluvinage (1950) and Hylleraas (1956, 1958, 1960) is demonstrated. (The complete works of Hylleraas are collected in Hylleraas (1968).) In § 4, tools for solving the FE are summarised. Applications are described in § 5. The reduction and the general structure of the wavefunction is examined in Gottschalk *et al* (1987, to be referred to hereafter as II).

2. Coordinate systems for two-electron atoms

After removing the motion of the centre of mass, six coordinates are required for two-electron atoms. These may be decomposed into three external coordinates, describing the orientation of the triangle formed by the nucleus and the two electrons, and three internal coordinates, specifying the size and shape of this triangle. This decomposition is examined in more detail in II.

For S states only the three internal coordinates are required. Several factors should be considered when choosing these coordinates. Different systems may be more favourable for particular aspects of the analysis. For example, interparticle coordinates r_1, r_2, r_{12} (IC) are intuitively obvious and the asymptotic forms as r_1 or $r_2 \to \infty$ are simply expressed in this system (Morgan 1977). Spherical polar coordinates r_1, r_2, θ (SPC) allow simple expansions in terms of Legendre polynomials. Elliptic coordinates $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$ (EC) display the symmetry of the wavefunction and hyperspherical coordinates (HC), defined below, are mathematically expedient for displaying general properties of the solution. The interplay between different solutions and the advantages of working with more than one coordinate system are stressed.

2.1. Hyperspherical coordinates

The partitioning of $\boldsymbol{r}$ into a hyperradius r defined by

$$r=\left(\sum_{i=1}^{N} r_i^2\right)^{1/2}$$

and a set of $n-1$ hyperangles collectively denoted by Ω is general for all hyperspherical systems. As shown using tensor methods by Granzow (1963), the Laplacian becomes

$$\Delta_n=\frac{1}{r^{n-1}}\frac{\partial}{\partial r}r^{n-1}\frac{\partial}{\partial r}-\frac{\Lambda_n^2(\Omega)}{r^2} \qquad (3)$$

where Λ_n^2 is the quadratic Casimir operator for SO(n), termed the generalised or grand angular momentum operator (GAM), and depends only on Ω. Expanding the first term of (3), the Laplacian is seen to be homogeneous of degree -2 in r. We now summarise the general properties of HC. The n-dimensional volume element is

$$\mathrm{d}V_n=\prod_{i=1}^{n}\mathrm{d}x_i\equiv \mathrm{d}r\,\mathrm{d}S=r^{n-1}\,\mathrm{d}r\,\mathrm{d}\Omega$$

where $\mathrm{d}S$ is the element of surface area. The volume of an n-dimensional sphere is

$$V_n=\frac{\pi^{n/2}}{\Gamma(n/2+1)}r^n$$

and also

$$\int \mathrm{d}\Omega = \frac{2\pi^{n/2}}{\Gamma(n/2)}. \tag{4}$$

Now consider a harmonic homogeneous polynomial $\boldsymbol{H}_\lambda(\boldsymbol{r})$ of degree λ. Homogeneity implies

$$\boldsymbol{H}_\lambda(\boldsymbol{r}) = r^\lambda H_\lambda(\boldsymbol{u}) \equiv r^\lambda Y_\lambda(\Omega) \tag{5}$$

where $\boldsymbol{u}$ is an n-dimensional unit vector and there exists a one-to-one correspondence between $\boldsymbol{u}$ and Ω. The $\boldsymbol{H}_\lambda(\boldsymbol{r})$ are called the solid harmonics: throughout this paper, upper case bold symbols denote a solid function and light symbols denote the associated spherical function related, in general, by (5).

Applying the Laplacian (3) to $\boldsymbol{H}_\lambda(\boldsymbol{r})$ and using equation (5) and harmonicity yields

$$\Lambda_n^2(\Omega)\, Y_\lambda(\Omega) = \lambda(\lambda + n - 2)\, Y_\lambda(\Omega). \tag{6}$$

The eigenfunctions $Y_\lambda(\Omega)$ of GAM are the HH. Equations (3) and (6) generalise the familiar SO(3) results. It is emphasised that Λ_n^2 is a (partial) differential operator and the HH are selected from all possible eigenfunctions of (6) by requiring them to be finite, single-valued and continuous over Ω.

Scalar or S-state HH satisfy the additional requirement of having zero total angular momentum, $L = 0$, and are invariant with respect to spatial rotations. The total (ordinary) angular momentum is specified by

$$\boldsymbol{L}^2 Y_\lambda^L(\Omega) = L(L+1)\, Y_\lambda^L(\Omega). \tag{7}$$

HH for $L > 0$ are constructed either by (i) standard Clebsch-Gordan coupling procedures (Zickendraht 1965) or (ii) by directly solving (6) with the constraint (7), where the external coordinates are chosen to be the Eulerian angles: here (Edmonds 1960)

$$\boldsymbol{L}^2 = \frac{-1}{\sin\beta}\frac{\partial}{\partial\beta}\sin\beta\frac{\partial}{\partial\beta} - \frac{1}{\sin^2\beta}\left(\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\gamma^2} - 2\cos\beta\frac{\partial^2}{\partial\alpha\,\partial\gamma}\right) \tag{8}$$

and the eigenfunctions associated with (8) are the rotation matrices, $D^L{}_{MK}(\alpha, \beta, \gamma)$. The GAM for (ii) is given explicitly by Smith (1962), Zickendraht (1965), Tkachenko (1978), Klar and Klar (1980) and Johnson (1983).

Using the Green theorem in n dimensions (Gradshteyn and Ryzhik 1980)

$$\int_{V_n} (f\Delta_n g - g\Delta_n f)\,\mathrm{d}V_n = \int_{\partial V_n} \left(f\frac{\partial g}{\partial n} - g\frac{\partial f}{\partial n}\right)\mathrm{d}S.$$

Choosing V_n to be the unit sphere, $\partial V_n \equiv \Omega$, $\mathrm{d}S \equiv \mathrm{d}\Omega$ and realising that normal derivatives become radial derivatives,

$$(\lambda - \lambda') \int Y_\lambda(\Omega)\, Y_{\lambda'}(\Omega)\,\mathrm{d}\Omega = 0. \tag{9}$$

Hence the HH are orthogonal and may be constructed to be orthonormal. For each λ, there exists a set of degenerate HH distinguished by the label $[\nu]$. Using (9) one may show that

$$\sum_{\lambda[\nu]} Y_{\lambda[\nu]}(\Omega)\, Y_{\lambda[\nu]}(\Omega') = \delta(\Omega - \Omega')$$

and hence the HH are complete.

2.2. $N = 2$ hyperspherical coordinates

To make the preceding discussion more concrete we consider helium ($N = 2$). Introducing the hyperangle $\alpha \in [0, \pi]$ (not to be confused with the Eulerian angle) by

$$r_1 = r\cos(\alpha/2) \qquad r_2 = r\sin(\alpha/2) \qquad r_{12} = r(1 - \sin\alpha\cos\theta)^{1/2} \tag{10}$$

one obtains the set of HC studied by White and Stillinger (1970) and Klar (1985a). The Laplacian is

$$\Delta_6 = \frac{1}{r^5}\frac{\partial}{\partial r} r^5 \frac{\partial}{\partial r} - \frac{1}{r^2}\Lambda_6^2(\alpha, \theta)$$

where

$$\Lambda_6^2(\alpha, \theta) = \frac{-4}{\sin^2\alpha}\left(\frac{\partial}{\partial\alpha}\sin^2\alpha\frac{\partial}{\partial\alpha} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right). \tag{11}$$

The HH associated with (11) are

$$Y_{kl}(\alpha, \theta) = N_{kl}\sin^l\alpha\, C_{k/2-l}^{(l+1)}(\cos\alpha) P_l(\cos\theta) \qquad k = 0, 2, 4, \ldots, \infty;\ l = 0, 1, 2, \ldots, k/2 \tag{12}$$

where the $C_n^{(\nu)}(x)$ and $P_l(x)$ are, respectively, Gegenbauer and Legendre polynomials (Abramowitz and Stegun 1972). The appropriate volume element is

$$\mathrm{d}V_6 = r^5\,\mathrm{d}r\,\mathrm{d}\Omega \qquad \mathrm{d}\Omega = \pi^2\sin^2\alpha\,\mathrm{d}\alpha\,\sin\theta\,\mathrm{d}\theta \qquad r \in [0, \infty),\ \alpha \in [0, \pi],\ \theta \in [0, \pi] \tag{13}$$

where the π^2 ensures that $\int \mathrm{d}\Omega = \pi^3$, in agreement with (4). The normalisation constant N_{kl} is

$$N_{kl} = 2^l l!\left(\frac{(2l+1)(k+2)(k/2-l)!}{2\pi^3(k/2+l+1)!}\right)^{1/2} \tag{14}$$

so that

$$\int Y_{kl}(\alpha, \theta)\, Y_{k'l'}(\alpha, \theta)\,\mathrm{d}\Omega = \delta_{kk'}\delta_{ll'}. \tag{15}$$

Equation (10) may be unified by writing

$$r_n = rc_n(1 - x_n)^{1/2} \tag{16}$$

where

$$x_n = \cos\alpha\cos\alpha_n + \sin\alpha\sin\alpha_n\cos\theta\cos\theta_n \tag{17}$$

and

n	α_n	θ_n	c_n
1	π	—	$2^{-1/2}$
2	0	—	$2^{-1/2}$
12	$\pi/2$	0	1

(18)

Following Abbott and Maslen (1984) and Klar (1985a) the addition theorem may be written

$$\sum_{l=0}^{k/2} Y_{kl}(\alpha, \theta) Y_{kl}(\alpha', \theta') = \frac{k+2}{2\pi^3} C^{(1)}_{k/2}(\cos \gamma) \tag{19}$$

where

$$\cos \gamma = \cos \alpha \cos \alpha' + \sin \alpha \sin \alpha' \cos \theta \cos \theta'.$$

Interchanging particles 1 and 2 is equivalent to replacing α by $\pi - \alpha$. From the symmetry of the Gegenbauer polynomial

$$Y_{kl}(\pi - \alpha, \theta) = (-1)^{k/2-l} Y_{kl}(\alpha, \theta). \tag{20}$$

Any suitable function of r, α, θ may be expanded into HH since they form a complete set:

$$f(r, \alpha, \theta) = \sum_{k=0}^{\infty} \sum_{l=0}^{k/2} f_{kl}(r) Y_{kl}(\alpha, \theta).$$

The eigenvalues of Λ^2 are given by (6):

$$\Lambda^2(\alpha, \theta) Y_{kl}(\alpha, \theta) = k(k+4) Y_{kl}(\alpha, \theta) \tag{21}$$

with degeneracy $k/2+1$. The unnormalised HH and the associated solid harmonics given by (12) and (14) are listed in table 1.

Table 1. Normalisation constants, unnormalised hyperspherical harmonics and the associated solid harmonics.

k l	$\pi^3 N_{kl}^2$	$Y_{kl}(\alpha, \theta)$	$\mathcal{Y}_{kl}(r_1, r_2, r_{12})$
0 0	1	1	1
2 0	1	$2 \cos \alpha$	$2(r_1^2 - r_2^2)$
2 1	4	$\sin \alpha \cos \theta$	$r^2 - r_{12}^2$
4 0	1	$4 \cos^2 \alpha - 1$	$3r^4 - 16 r_1^2 r_2^2$
4 1	$\frac{3}{2}$	$4 \cos \alpha \sin \alpha \cos \theta$	$4(r_1^2 - r_2^2)(r^2 - r_{12}^2)$
4 2	8	$\frac{1}{2} \sin^2 \alpha\, (3 \cos^2 \theta - 1)$	$\frac{3}{2}(r^2 - r_{12}^2)^2 - 2r_1^2 r_2^2$
6 0	1	$4 \cos \alpha\, (2 \cos^2 \alpha - 1)$	$4(r_1^2 - r_2^2)(r^4 - 8 r_1^2 r_2^2)$
6 1	$\frac{4}{5}$	$2 \sin \alpha \cos \theta\, (6 \cos^2 \alpha - 1)$	$2(r^2 - r_{12}^2)(5r^4 - 24 r_1^2 r_2^2)$
6 2	$\frac{16}{9}$	$3 \cos \alpha \sin^2 \alpha (3 \cos^2 \theta - 1)$	$3(r_1^2 - r_2^2)[3(r^2 - r_{12}^2)^2 - 4 r_1^2 r_2^2]$
6 3	$\frac{64}{5}$	$\frac{1}{2} \sin^3 \alpha \cos \theta\, (5 \cos^2 \theta - 3)$	$\frac{1}{2}(r^2 - r_{12}^2)[5(r^2 - r_{12}^2)^2 - 12 r_1^2 r_2^2]$
8 0	1	$16 \cos^4 \alpha - 12 \cos^2 \alpha + 1$	$5r^8 - 80 r^4 r_1^2 r_2^2 + 256 r_1^4 r_2^4$
8 1	$\frac{1}{2}$	$4 \cos \alpha \sin \alpha \cos \theta\, (8 \cos^2 \alpha - 3)$	$4(r_1^2 - r_2^2)(r^2 - r_{12}^2)(5r^4 - 32 r_1^2 r_2^2)$
8 2	$\frac{40}{63}$	$\frac{3}{2} \sin^2 \alpha\, (8 \cos^2 \alpha - 1)(3 \cos^2 \theta - 1)$	$\frac{3}{2}(7r^4 - 32 r_1^2 r_2^2)[3(r^2 - r_{12}^2)^2 - 4 r_1^2 r_2^2]$
8 3	2	$4 \cos \alpha \sin^3 \alpha \cos \theta\, (5 \cos^2 \theta - 3)$	$4(r_1^2 - r_2^2)(r^2 - r_{12}^2)[5(r^2 - r_{12}^2)^2 - 12 r_1^2 r_2^2]$
8 4	$\frac{128}{7}$	$\frac{1}{8} \sin^4 \alpha\, (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$	$\frac{1}{8}[35(r^2 - r_{12}^2)^4 - 120 r_1^2 r_2^2 (r^2 - r_{12}^2)^2 + 48 r_1^4 r_2^4]$

For future reference we state the combination theorem for the HH defined by equation (12). Following Judd (1975) we write

$$Y_{kl}(\alpha,\theta)\,Y_{k'l'}(\alpha,\theta)=\sum_{k''l''}\begin{bmatrix}k & k' & k''\\ l & l' & l''\end{bmatrix}Y_{k''l''}(\alpha,\theta) \tag{22}$$

with

$$\begin{bmatrix}k & k' & k''\\ l & l' & l''\end{bmatrix}=\left(\frac{(2l+1)(2l'+1)(2l''+1)(k+2)(k'+2)(k''+2)}{8\pi^3}\right)^{1/2}(-1)^{(l+l'+l'')/2}$$
$$\times\begin{pmatrix}l & l' & l''\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}k/4 & k/4 & l\\ k'/4 & k'/4 & l'\\ k''/4 & k''/4 & l''\end{Bmatrix}. \tag{23}$$

The [: : :] may be termed a 3-k coefficient (Shibuya and Wulfman 1965, Del Aguila 1980, Mukhtarova and Éfros 1983, Wen and Avery 1985), in analogy with the 3-j coefficient (: : :) and the 9-j coefficient {: : :}. The 3-k coefficient is invariant under permutation of its columns. Both (k, k', k'') and (l, l', l'') obey triangular conditions and, further, both $l+l'+l''$ and $(k+k'+k'')/2$ are even. Equations (22) and (23) simplify the expression for the matrix element of the Coulomb potential used by Feagin *et al* (1985).

2.3. Fock hyperspherical coordinates

Let us contrast the treatment above with that of Fock (1954, 1958). Following Hylleraas (1928, 1929) and Gronwall (1932, 1937), Fock commenced with the internal coordinates r_1, r_2, θ and defined the new variables

$$x=2r_1r_2\sin\theta\cos\phi \qquad y=2r_1r_2\sin\theta\sin\phi \qquad z=2r_1r_2\cos\theta \qquad u=r_1^2-r_2^2 \tag{24}$$

where ϕ is introduced as a device for transforming from $\mathbb{R}^3\to\mathbb{R}^4$. (For a similar example of such use of a non-bijective transformation see Kibler and Negadi (1984).) Fock introduced ϕ so that the correspondence to his classic paper on hydrogen in momentum space (Fock 1935) was transparent. Setting

$$R=(x^2+y^2+z^2+u^2)^{1/2}=r_1^2+r_2^2=r^2 \tag{25}$$

equation (24) becomes

$$x=R\sin\alpha\sin\theta\cos\phi \qquad y=R\sin\alpha\sin\theta\sin\phi$$
$$z=R\sin\alpha\cos\theta \qquad u=R\cos\alpha \tag{26}$$

where

$$\sin\alpha=2r_1r_2/r^2 \qquad \cos\alpha=(r_1^2-r_2^2)/r^2. \tag{27}$$

Equations (1), (10) and (27) are consistent and (26) applies to SPC in four dimensions (Vilenkin 1967). Hence

$$\mathrm{d}V_4=\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}u\equiv R^3\,\mathrm{d}R\,\sin^2\alpha\,\mathrm{d}\alpha\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$R\in[0,\infty) \qquad \alpha\in[0,\pi] \qquad \theta\in[0,\pi] \qquad \phi\in[0,2\pi]$$

and $\int \mathrm{d}\Omega=2\pi^2$ in agreement with (4) for $n=4$. By standard techniques (3) becomes

$$\Delta_4=\frac{1}{R^3}\frac{\partial}{\partial R}R^3\frac{\partial}{\partial R}-\frac{1}{R^2}\Lambda_4^2(\alpha,\theta,\phi)$$

where

$$\Lambda_4^2(\alpha, \theta, \phi) = \frac{-1}{\sin^2 \alpha}\left(\frac{\partial}{\partial \alpha}\sin^2 \alpha \frac{\partial}{\partial \alpha} - l^2(\theta, \phi)\right) \tag{28}$$

and $l^2(\theta, \phi)$ is the standard angular momentum operator. Since ϕ is not physically relevant it is seen, by comparing equations (11) and (28) and using (3) and (25), that

$$4\Lambda_4^2(\alpha, \theta, \phi) \equiv \Lambda_6^2(\alpha, \theta) \qquad 4R\Delta_4 \equiv \Delta_6.$$

This result is given by Ermolaev (1958), who points out that the scalar HH in six dimensions are equivalent to the four-dimensional HH†. Equivalently, the explicit expressions for Λ_6^2 and Λ_4^2 agree (up to a numerical factor) on disregarding derivatives with respect to the (unphysical) angle ϕ.

These results illustrate the relationship between the Fock HC, which are restricted to three-particle S states, to HC that treat general N and L.

3. Conversion of the Schrödinger equation to an infinite set of coupled second-order differential equations

In order to solve the SE for $N \geqslant 2$ it is often converted to an infinite set of coupled second-order differential equations. Since we do not adopt a truncated matrix approach, the results are still essentially exact. A brief discussion of the solution of this system of equations is given in § 3.4. One may also convert the SE to a homogenous integral equation in $3N-3$ variables by means of an appropriate Green function (Bartlett 1937, Fock 1954, 1958, Bellman and Adomain 1985). This approach is not considered in this paper.

3.1. Schrödinger equation

In atomic units, the SE for N particles, in the field of an infinitely massive nucleus, is

$$(-\tfrac{1}{2}\Delta + V)\Psi = E\Psi. \tag{29}$$

Restricting attention to $N=2$, the Coulomb potential for a system of nucleus charge Z, and charges Z_1 and Z_2 is

$$V = \frac{\mu_1}{r_1} + \frac{\mu_2}{r_2} + \frac{\mu_{12}}{r_{12}} \qquad \mu_1 = ZZ_1 \qquad \mu_2 = ZZ_2 \qquad \mu_{12} = Z_1 Z_2. \tag{30}$$

We are especially interested in the cases $Z_1 = Z_2 = -1$, corresponding to the helium isoelectronic sequence (HIS), and in $\mu_{12} = 0$ which corresponds to the case of independent electrons.

3.2. $\mu_{12} = 0$: S-state product wavefunctions

With $\mu_{12} = 0$ the SE (29) is separable and the solutions are simply product hydrogenic wavefunctions. Unnormalised hydrogenic wavefunctions may be written

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

† We thank a referee for drawing our attention to this paper.

where

$$R_{nl}(r) = \rho^l \, e^{-\rho/2} \, {}_1F_1\left[\begin{matrix} l+1-n \\ 2l+2 \end{matrix}; \rho\right] \qquad \rho = \frac{-2\mu r}{n}. \tag{31}$$

Y_{lm} are the spherical harmonics (Normand 1980) and ${}_1F_1$ is the confluent hypergeometric function (Abramowitz and Stegun 1972).

For $\mu_1 = \mu_2$ the potential becomes symmetric and Ψ has definite parity. States of total orbital angular momentum L and spin S are formed by the standard coupling procedure

$$\Psi^{LMS}_{n_1l_1n_2l_2}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{m_1m_2} C^{l_1l_2L}_{m_1m_2M}[\Psi_{n_1l_1m_1}(\boldsymbol{r}_1)\Psi_{n_2l_2m_2}(\boldsymbol{r}_2) + (-1)^S \Psi_{n_1l_1m_1}(\boldsymbol{r}_2)\Psi_{n_2l_2m_2}(\boldsymbol{r}_1)]$$

labelled according to the conventional spectroscopic notation ${}^{2S+1}L$. For S states, $L = M = 0$, requiring $l_1 = l_2 = l$ and $m_1 = -m_2 = -m$. The sum over angular variables becomes the standard addition theorem:

$$\sum_{m=-l}^{l} Y^*_{lm}(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) = \frac{2l+1}{4\pi} P_l(\cos\theta).$$

Thus product wavefunction for S states may be written

$$\Psi^{00S}_{n_1ln_2l}(\boldsymbol{r}_1, \boldsymbol{r}_2) \propto [R_{n_1l}(r_1)R_{n_2l}(r_2) + (-1)^S R_{n_1l}(r_2)R_{n_2l}(r_1)]P_l(\cos\theta). \tag{32}$$

Expanding (32) using (31), one obtains the wavefunction to lowest order in the variables r_1, r_2 and r_{12} (Gottschalk and Maslen 1985). The extension to general L, M is straightforward using the results of Nikitin and Ostrovsky (1985). From table 2 it is clear that, for the lowest order of each independent-particle wavefunction, there exists a corresponding S-state HH tabulated by k and l, as in table 1. This correspondence is important in relation to the excited states and arbitrary coefficients, discussed in §§ 3.3 and 3.5.

3.3. *Generalised power series expansion*

After the SE for hydrogen had been solved by the method of Frobenius, it was natural to attempt a similar treatment for helium. However, Bartlett *et al* (1935) demonstrated that a power series solution did not exist in that case. Pluvinage (1950) and Hylleraas (1956, 1958, 1960) considered the generalised power series expansion

$$\Psi = \sum_{k=k'}^{\infty} \boldsymbol{\Psi}_k. \tag{33}$$

Table 2. Lowest order of S-state independent-particle wavefunctions and the corresponding hyperspherical harmonics.

State	Wavefunction to lowest order	k	l
n_1sn_2s ^{1}S	r^0	0	0
n_1sn_2s ^{3}S	$r_1^2 - r_2^2$	2	0
n_1pn_2p ^{1}S	$r^2 - r_{12}^2$	2	1
n_1pn_2p ^{3}S	$(r_1^2 - r_2^2)(r^2 - r_{12}^2)$	4	1
n_1dn_2d ^{1}S	$3(r^2 - r_{12}^2)^2 - 4r_1^2r_2^2$	4	2
n_1dn_2d ^{3}S	$(r_1^2 - r_2^2)[3(r^2 - r_{12}^2)^2 - 4r_1^2r_2^2]$	6	2
n_1fn_2f ^{1}S	$(r^2 - r_{12}^2)[5(r^2 - r_{12}^2)^2 - 12r_1^2r_2^2]$	6	3

Note that n_1, $n_2 > l$ and that $n_1 \neq n_2$ for ^{3}S states.

where each Ψ_k is homogenous of degree k in the radial variable r. All Ψ_k $(k<k')$ are identically zero, where k' is presently unspecified. Since the Laplacian is homogenous of degree -2 and the Coulomb potential of degree -1, substitution of (33) into (29) shows that the SE is formally equivalent to the infinite set of second-order (partial) differential equations:

$$\Delta\Psi_{k'}=0 \tag{34}$$

$$\Delta\Psi_{k'+1}=2V\Psi_{k'} \tag{35}$$

$$\Delta\Psi_k=2V\Psi_{k-1}-2E\Psi_{k-2}=I_{k-2} \qquad (k\geqslant k'+2) \tag{36}$$

where I_{k-2} is the inhomogenous term of equation (36) and is of degree $k-2$.

The analysis leading to equation (6) indicates that the general solution to (34) for S states is simply the solid harmonic of degree k' tabulated in table 1. Note that only harmonics of even degree k' can arise.

The choice of a particular k' leads to an excited S state as specified by table 2. For instance, commencing with $\Psi_2=r_1^2-r_2^2$ $(k'=2)$ corresponds to the n_1s n_2s ^{3}S states (Hylleraas 1958, Pluvinage 1982). We are particularly interested in the case $k'=0$, the ground state n_1sn_2s ^{1}S, where $\Psi_0=1$. Equation (35) is easily solved. It may be verified that

$$\Psi_1=\mu_1r_1+\mu_2r_2+\tfrac{1}{2}\mu_{12}r_{12} \tag{37}$$

satisfies (35). Equation (36) thus becomes

$$\Delta\Psi_2=2\left[\mu_1^2+\mu_2^2+\frac{\mu_{12}^2}{2}+\frac{\mu_1\mu_2r^2}{r_1r_2}-E+\mu_1\mu_{12}\left(\frac{r_1}{r_{12}}+\frac{r_{12}}{2r_1}\right)+\mu_2\mu_{12}\left(\frac{r_2}{r_{12}}+\frac{r_{12}}{2r_2}\right)\right]=I_0. \tag{38}$$

We solve (38) formally by expanding both Ψ_2 and I_0 into HH. Hence

$$\Psi_2=\sum_{nl}R_{nl}^{[2]}(r)Y_{nl}(\alpha,\theta) \tag{39}$$

and

$$I_0=\sum_{nl}I_{nl}^{[0]}Y_{nl}(\alpha,\theta) \tag{40}$$

where the HH are defined by (12). Applying the Laplacian given by equations (11) and (21), using (38) and assuming suitable convergence of (39) so that we can differentiate term by term, we see that

$$L_nR_{nl}^{[2]}(r)=I_{nl}^{[0]} \tag{41}$$

where

$$L_n=\left(\frac{\partial^2}{\partial r^2}+\frac{5}{r}\frac{\partial}{\partial r}-\frac{n(n+4)}{r^2}\right). \tag{42}$$

Following White and Stillinger (1971), the general solution to (41) can be written down immediately by using the identity

$$L_nr^k\ln^p r=r^{k-2}[(k-n)(k+n+4)\ln^p r+2p(k+2)\ln^{p-1} r+p(p-1)\ln^{p-2} r]. \tag{43}$$

Hence

$$R_{nl}^{[2]}(r)=\frac{-I_{nl}^{[0]}r^2}{(n-2)(n+6)} \qquad n\neq 2$$

$$R_{2l}^{[2]}(r)=\tfrac{1}{8}I_{2l}^{[0]}r^2\ln r+A_{2l}r^2 \tag{44}$$

where A_{2l} ($l=0, 1$) is arbitrary and multiplies the physical solution to the homogeneous equation (41). $\boldsymbol{R}_{nl}^{[2]}(r)$ is homogenous of degree 2 which implies that $\boldsymbol{\Psi}_2$ is likewise, as required for the expansion (33): ln r arises since the roots of the indicial equation associated with (41) differ by an integer (Boyce and DiPrima 1969). Moreover, ln r may be considered to be formally homogeneous of degree 0 since its derivative with respect to r is homogeneous of degree -1 (Leray 1984). Since all the $\boldsymbol{R}_{nl}^{[2]}$ are determined, so is $\boldsymbol{\Psi}_2$. However, the determination of the $I_{nl}^{[0]}$ in equation (40) is not completely trivial and the summation of the series (39) in its present form is algebraically difficult. Both problems are examined in later sections.

We now examine equation (36) for $k=3$. Using (44) and the fact that V is homogeneous of degree -1 and contains HH of all orders, we can write formally

$$\Delta\boldsymbol{\Psi}_3 = \boldsymbol{I}_1 = r\sum_{p=0}^{1} \ln^p r \sum_{nl} I_{nlp}^{[1]} Y_{nl}(\alpha, \theta) \tag{45}$$

where the $I_{nlp}^{[1]}$ are obtained by expanding $\boldsymbol{I}_1$ analogously to (40). Expanding $\boldsymbol{\Psi}_3$ similarly to (39) one obtains

$$L_n\boldsymbol{R}_{nl}^{[3]} = rI_{nl0}^{[1]} + r\ln rI_{nl1}^{[1]}.$$

The solution is

$$\boldsymbol{R}_{nl}^{[3]}(r) = \frac{-r^3(I_{nl0}^{[1]} + I_{nl1}^{[1]}\ln r)}{(n-3)(n+7)} - \frac{10I_{nl1}^{[1]}r^3}{(n-3)^2(n+7)^2}.$$

Finally we examine $k=4$. Using (36) we see that

$$\Delta\boldsymbol{\Psi}_4 = r^2\sum_{p=0}^{1} \ln^p r \sum_{nl} I_{nlp}^{[2]} Y_{nl}(\alpha, \theta).$$

Hence

$$L_n\boldsymbol{R}_{nl}^{[4]} = r^2I_{nl0}^{[2]} + r^2\ln rI_{nl1}^{[2]}.$$

The solution is

$$\boldsymbol{R}_{nl}^{[4]}(r) = \frac{-r^4(I_{nl0}^{[2]} + I_{nl1}^{[2]}\ln r)}{(n-4)(n+8)} - \frac{12r^4I_{nl1}^{[2]}}{(n-4)^2(n+8)^2} \qquad n\neq 4$$

$$\boldsymbol{R}_{4l}^{[4]}(r) = -\tfrac{1}{12}r^4\ln rI_{4l0}^{[2]} - \tfrac{1}{144}r^4\ln rI_{4l1}^{[2]} + \tfrac{1}{24}r^4\ln^2 rI_{4l1}^{[2]} + A_{4l}r^4$$

where A_{4l}($l=0, 1, 2$) is again arbitrary. The pattern is now clear: for each even k a new power ln r of the form r^k (ln $r)^{k/2}$ is required. Associated with this is the appearance of $k/2+1$ arbitrary coefficients A_{kl} ($l=0, 1, \ldots, k/2$). For odd k, no new powers of ln r or arbitrary coefficients appear. In general we can write

$$\boldsymbol{\Psi}_k = \sum_{nl} \boldsymbol{R}_{nl}^{[k]}(r) Y_{nl}(\alpha, \theta) \tag{46}$$

where

$$\boldsymbol{R}_{nl}^{[k]} = r^k \sum_{p=0}^{[k/2]} C_{knlp}\ln^p r. \tag{47}$$

Combining equations (33), (46) and (47) yields

$$\Psi = \sum_{k=0}^{\infty} r^k \sum_{p=0}^{[k/2]} \sum_{nl} C_{knlp}\ln^p rY_{nl}(\alpha, \theta).$$

By identifying

$$\Psi_{kp}(\alpha, \theta) = \sum_{nl} C_{knlp} Y_{nl}(\alpha, \theta) \tag{48}$$

we obtain

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

Comparison with equation (2) shows that we have recovered the FE. Hence the methods of Fock, Pluvinage and Hylleraas are formally equivalent. The Ψ_{kp} are given by (48) and, for each k, the method for constructing the C_{knlp} is as above. For example, from (44)

$$C_{2nl0} = \frac{-I_{nl}^{[0]}}{(n-2)(n+6)} \qquad n \neq 2$$

$$C_{22l0} = A_{2l}$$

$$C_{2nl1} = 0 \qquad n \neq 2$$

$$C_{22l1} = \tfrac{1}{8} I_{2l}^{[0]}.$$

3.4. Comments on the Pluvinage–Hylleraas expansion

We label any generalised power series expansion of the form (33) as the Pluvinage–Hylleraas expansion (PHE). Note that the FE (2) explicitly includes powers of $\ln r$ in the expansion about the singular point $r = 0$, whereas the PHE (33) contains $\ln r$ implicitly, since $\ln r$ may be considered formally homogeneous of degree zero.

Although the derivation of the PHE in § 3.3 is not rigorous, the FE (2) has been shown to be equivalent to the generalisation of Fuchs' theorem required when examining the N-electron SE by Leray (1982a, b, 1983, 1984) and Morgan (1986). Furthermore the solutions by either technique can be shown to be identical for each k. One infers that § 3.3 can be made rigorous.

The extension to any excited state is obvious: the choice of the particular solution to equation (34), i.e. the value of k', determines the state. Note that the PHE only requires slight modification for states of total angular momentum $L > 0$, since L_n does not depend on L.

The treatment of § 3.3 hides the difficult task of computing the I_{nlp}. From (36) we see that I_k contains $V\Psi_{k+1}$. Expanding the potential (30) into HH

$$V = \frac{V(\alpha, \theta)}{r} = \frac{1}{r} \sum_{nl} V_{nl} Y_{nl}(\alpha, \theta) \tag{49}$$

and remembering equations (22), (23), (46) and (47) we see that

$$V\Psi_{k+1} = r^k \sum_{p=0}^{[(k+1)/2]} \ln^p r \sum_{nl} \left(\sum_{n'l'} \sum_{n''l''} C_{k+1n'l'p} V_{n''l''} \begin{bmatrix} n & n' & n'' \\ l & l' & l'' \end{bmatrix} \right) Y_{nl}(\alpha, \theta). \tag{50}$$

The $I_{nlp}^{[k]}$ may be computed from (50). For an example of numerical work using this technique see Feagin *et al* (1985). In analytic work one avoids such calculations because of infinite series of 3-k coefficients in the parenthesis of (50). Techniques for avoiding this difficulty are presented in § 4.2.

It is important to realise that the system of equations (34)-(36) may be solved using any set of internal coordinates. In § 3.3, the coordinates r, α, θ and the associated Laplacian were utilised and the structure of the logarithmic terms emerged in a straightforward fashion. This illustrates the comment made in § 2, that HC are mathematically expedient for studying general properties of these systems. However, the SPC r_1, r_2, θ are a more practical set of coordinates because they generate simplified expressions more directly. The SPC Laplacian is given in II and the $\boldsymbol{\Psi}_k$ are expanded as

$$\boldsymbol{\Psi}_k = \sum_{l=0}^{\infty} \boldsymbol{R}_l^k(r_1, r_2) P_l(\cos\theta) \tag{51}$$

instead of (46). Note that the expansion (51) helps circumvent difficulties associated with equation (50). The relationship between expansions in HC and SPC is made explicit by comparing equations (46) and (51), using (12), yielding

$$\boldsymbol{R}_l^k(r_1, r_2) = \sin^l\alpha \sum_{n=0}^{\infty} N_{nl} C_{n/2-l}^{(l+1)}(\cos\alpha) \boldsymbol{R}_{nl}^{[k]}(r). \tag{52}$$

This connection is examined in § 5.4. Results in the appendix indicate how (52) may be summed for certain $\boldsymbol{R}_{nl}^{[k]}(r)$. To simplify expressions obtained in HC one must be able to sum equation (52) for general $\boldsymbol{R}_{nl}^{[k]}(r)$. This is difficult and may be avoided by working in SPC, as shown in II.

3.5. Arbitrary coefficients

In § 3.3 there arose coefficients A_{kl} that were not determined by the homogeneous differential equation. This general feature of differential equations also arises when solving, for example, the Laplace equation in N dimensions. In equations (34)-(36), for each even k, the homogeneous equation is just Laplace's equation, the solutions being the solid harmonics given in table 1. Note that the arbitrary coefficients are not connected explicitly to the potential. These arbitrary coefficients must be determined by imposing boundary conditions. In the case of the SE this corresponds to restricting the correct asymptotic form (Fock 1954, 1958, Ermolaev 1958, 1961, Demkov and Ermolaev 1959, Morgan 1977) as $r \to \infty$, or more practically as r_1 or $r_2 \to \infty$. This ensures the normalisability of the wavefunction (Davis and Maslen 1982, 1983). This should be compared with hydrogen ($N = 1$): requiring the physical asymptotic form truncates the power series ensuring normalisability and simultaneously quantises the energy.

Section 3.2 demonstrates the connection between separable wavefunctions to lowest order and the solid harmonics. One can see there that the ^{1}S state, for example, consists in part of a superposition of all allowed ^{1}S separable wavefunctions weighted so that the total wavefunction is normalisable. Note however that logarithmic functions, reflecting the behaviour at the triple coalescence, are not apparent in this approach.

3.6. Recurrence relation for the Fock expansion

To solve for the Ψ_{kp} it is usual to convert the FE to a differential recurrence relation. By substituting (2) into the SE (29) and using equations (42), (43) and (49) one obtains the Fock recurrence relation (FRR)

$$[\Lambda^2 - k(k+4)]\Psi_{kp} = 2(k+2)(p+1)\Psi_{kp+1} + (p+1)(p+2)\Psi_{kp+2} - 2V\Psi_{k-1p} + 2E\Psi_{k-2p}. \tag{53}$$

This set of coupled equations is solved in order of increasing k and decreasing p, since $\Psi_{kp} \equiv 0$ for $k<0$ or $p>[k/2]$.

In previous treatments (Ermolaev 1961, David 1975, Pluvinage 1982) the potential (30) was made symmetric by choosing $\mu_1 = \mu_2 = -Z$. For a symmetric potential the wavefunction must be either symmetric or antisymmetric. In what follows the treatment of the symmetric and antisymmetric states is unified. By using the general potential (30) we may examine states of arbitrary symmetry: states with specific symmetry properties can be projected out from the final result by specifying μ_1, μ_2 and μ_{12} and deleting the symmetric or antisymmetric parts as necessary.

4. Techniques for solving the Fock expansion

Techniques for reducing the complexity of terms arising in the FE are given below. These methods were initially demonstrated by Ermolaev (1961) and Pluvinage (1982) but are extended here. Applications are described in § 5.

4.1. Expansion into hyperspherical harmonics

Consider the general function

$$C(\alpha, \theta) = \sum_{nl} C_{nl} Y_{nl}(\alpha, \theta). \tag{54}$$

Multiplying both sides by $Y_{n'l'}$ and integrating using (15) one obtains

$$C_{nl} = \int C(\alpha, \theta) Y_{nl}(\alpha, \theta). \tag{55}$$

We require, in particular, the expansion of

$$\left(\frac{r_1}{r}\right)^i \left(\frac{r_2}{r}\right)^j \left(\frac{r_{12}}{r}\right)^m$$

with i, j and m integers. Following Roberts (1965), it can be shown that

$$\int_0^\pi \left(\frac{r_{12}}{r}\right)^m P_l(\cos\theta) \sin\theta \, d\theta = \frac{2(-m/2)_l}{(3/2)_l} \left(\frac{r_>}{r}\right)^m \rho^l {}_2F_1\left[\begin{matrix} l-m/2, -m/2-\frac{1}{2} \\ l+\frac{3}{2} \end{matrix}; \rho^2\right] \tag{56}$$

where $r_> = \max\{r_1, r_2\}$, $r_< = \min\{r_1, r_2\}$, $\rho = r_</r_>$,

$$(a)_n = \prod_{i=1}^{n} (a+i-1)$$

is the Pochhammer symbol and the ${}_2F_1$ is a Gaussian hypergeometric function. In the notation of Slater (1966, p 41) the generalised hypergeometric series (GHS) is written

$${}_pF_q\left[\begin{matrix}(a) \\ (b)\end{matrix}; z\right] = \sum_{n=0}^{\infty} \frac{((a)_p)_n}{((b)_q)_n} \frac{z^n}{n!}$$

where

$$((a)_p)_n = \prod_{i=1}^{p} (a_i)_n.$$

From equation (10), $r_1 > r_2$ corresponds to $\alpha \in [0, \pi/2)$ and $r_1 < r_2$ to $\alpha \in (\pi/2, \pi]$. Due to this region dependence we examine first the integral for $r_1 > r_2$. From equations (13) and (55) we evaluate

$$C_{nl}^{ijm} = N_{nl}\pi^2 \int_0^\pi \sin^2\alpha\, d\alpha \int_0^\pi \sin\theta\, d\theta \left(\frac{r_1}{r}\right)^i \left(\frac{r_2}{r}\right)^j \left(\frac{r_{12}}{r}\right)^m Y_{nl}(\alpha, \theta).$$

Using (56) and writing the Gegenbauer polynomial appearing in Y_{nl} as a hypergeometric series, one obtains

$$C_{nl}^{ijm} = 2^{l+2} \frac{(n+2)(1)_l(-m/2)_l}{\pi(3/2)_l(1/2)_l} \sum_{p=0}^{n/2-l} \frac{(l-n/2)_p(n/2+l+2)_p}{(1)_p(l+3/2)_p} \times \sum_{q=0}^{q_{\max}} \frac{(l-m/2)_q(-m/2-1/2)_q}{(1)_q(l+3/2)_q} B_{1/2}(\alpha, \beta)$$

where the incomplete beta function is defined by (Abramowitz and Stegun 1972, p 263)

$$\int_0^1 (1-x)^{\alpha-1}(1+x)^{\beta-1}\, dx = 2^{\alpha+\beta-1} B_{1/2}(\alpha, \beta) = \frac{2^{\beta-1}}{\alpha}\, {}_2F_1\left[\begin{matrix}\alpha, 1-\beta \\ \alpha+1\end{matrix}; \tfrac{1}{2}\right]$$

and

$$\alpha = l+p+q+\frac{j+3}{2} \qquad \beta = \frac{m+i+3}{2} - q \qquad q_{\max} = \begin{cases} (m/2)-l & m \text{ even} \\ (m+1)/2 & m \text{ odd} \end{cases}$$

From the symmetry property (20) of the HH one finally obtains

$$T_{nl}^{ijm} = N_{nl} \int \left(\frac{r_1}{r}\right)^i \left(\frac{r_2}{r}\right)^j \left(\frac{r_{12}}{r}\right)^m Y_{nl}(\alpha, \theta)\, d\Omega = [C_{nl}^{ijm} + (-1)^{n/2-l} C_{nl}^{jim}]. \tag{57}$$

The T_{nl}^{ijm} required in § 5 are given in table 3.

The Coulomb potential (30) may be expanded as HH by setting i, j and $m = -1$ in turn in (57). A more direct method exists when any two of i, j, m are zero. Using equations (16)-(19) and following Abbott and Maslen (1984) one obtains

$$\left(\frac{r_p}{r}\right)^\nu = c_p^\nu 2^{\nu/2+2} \pi^{5/2} \frac{\Gamma(\nu/2+\frac{3}{2})}{\Gamma(\nu/2+3)} \sum_{nl} \left(\frac{(-\nu/2)_{n/2}}{(\nu/2+3)_{n/2}} Y_{nl}(\alpha_p, \theta_p)\right) Y_{nl}(\alpha, \theta) \tag{58}$$

where $p = 1, 2, 12$ and $Y_{nl}(\alpha_p, \theta_p)$ follows from equations (12) and (18). Equations (57) and (58) are consistent.

4.2. *Polynomials of degree k in elliptic coordinates*

For each k, terms in $\boldsymbol{\Psi}_k$ are polynomials in the variables r_1, r_2 and r_{12}. For example, $\boldsymbol{\Psi}_1$ given by (37) can be determined simply by assuming a polynomial of degree 1 in r_1, r_2 and r_{12} and solving for the coefficients. This idea is trivially generalised to all k. It is important to note that attempting to solve (35), which led to $\boldsymbol{\Psi}_1$, by expansion into HH is compartively difficult (Knirk 1974b, Klar 1985b, Feagin *et al* 1985). In general, proposing a polynomial of degree k in three variables leads to $(k+1)(k+2)/2$ linear equations for $(k+1)(k+2)/2$ unknown coefficients. Using the EC given by

$$s = r_1 + r_2 \qquad t = r_1 - r_2 \qquad u = r_{12}$$

Table 3. Table of the T_{nl}^{ijm}.

n	l	i	j	m	T_{nl}^{ijm}	n	l	i	j	m	T_{nl}^{ijm}
0	0	0	0	0	1	6	0	1	2	1	2/45π
						6	0	1	1	2	0
2	0	−1	1	0	−8/3π	6	0	2	3	−1	3/70π
2	0	−1	0	1	−2/3						
2	0	0	1	−1	−2/3π	6	1	−1	4	1	44/75 − 214/105π
						6	1	−1	3	2	−64/175π
2	1	−1	0	1	−8/3π	6	1	−1	2	3	26/175 − 24/25π
2	1	0	1	−1	2/3	6	1	−1	1	4	−128/225π
						6	1	−1	0	5	−24/35π
4	0	−1	3	0	8/5π	6	1	0	5	−1	0
4	0	−1	2	1	2/3 − 3/5π	6	1	0	3	1	−2/175π
4	0	−1	1	2	4/3π	6	1	0	2	2	0
4	0	−1	0	3	2/5	6	1	0	1	3	2/175
4	0	0	3	−1	0	6	1	0	0	4	0
4	0	0	2	0	0	6	1	1	4	−1	2/15 − 12/25π
4	0	0	1	1	−1/15π	6	1	1	2	1	2/75 − 22/525π
4	0	0	0	2	0	6	1	1	1	2	128/1575π
4	0	1	2	−1	−1/3π	6	1	2	3	−1	−2/25π
4	0	1	1	0	−4/15π						
						6	2	−1	4	1	−17/21 + 352/135π
4	1	−1	2	1	−9/20 + 2/π	6	2	−1	3	2	0
4	1	−1	1	2	16/15π	6	2	−1	2	3	−4/15 + 208/315π
4	1	−1	0	3	6/5π	6	2	−1	1	4	−2048/4725π
4	1	0	3	−1	−3/10π	6	2	−1	0	5	−4/21
4	1	0	1	1	1/20	6	2	0	5	−1	−8/63π
4	1	0	0	2	0	6	2	0	3	1	1/105
4	1	1	2	−1	−1/4 + 7/10π	6	2	0	2	2	0
						6	2	0	1	3	−16/315π
4	2	−1	2	1	2/3 − 12/5π	6	2	0	0	4	0
4	2	−1	1	2	0	6	2	1	4	−1	−2/5 + 376/315π
4	2	−1	0	3	2/5	6	2	1	2	1	−11/315 + 16/135π
4	2	0	3	−1	3/10	6	2	1	1	2	0
4	2	0	1	1	−4/15π						
4	2	0	0	2	0	6	2	2	3	−1	1/15 − 8/35π
4	2	1	2	−1	7/10 − 4/3π						
						6	3	−1	4	1	88/75 − 1184/315π
6	0	−1	5	0	−8/7π	6	3	−1	3	2	0
6	0	−1	4	1	−2/3 + 44/45π	6	3	−1	2	3	52/175 − 64/75π
6	0	−1	3	2	−16/15π	6	3	−1	1	4	0
6	0	−1	2	3	−2/5 + 26/105π	6	3	−1	0	5	−64/105π
6	0	−1	1	4	−304/315π	6	3	0	5	−1	1/7
6	0	−1	0	5	−2/7	6	3	0	3	1	−32/525π
6	0	0	5	−1	1/42π	6	3	0	2	2	0
6	0	0	4	0	0	6	3	0	1	3	4/175
6	0	0	3	1	0	6	3	0	0	4	0
6	0	0	2	2	0	6	3	1	4	−1	33/35 − 64/25π
6	0	0	1	3	−2/105π	6	3	1	2	1	4/75 − 352/1575π
6	0	0	0	4	0	6	3	1	1	2	0
6	0	1	4	−1	23/210π	6	3	2	3	−1	9/35 − 32/75π
6	0	1	3	0	8/105π						

leads to polynomials that are either symmetric or antisymmetric, only depending on the power of t. The $(k+1)(k+2)/2$ equations decouple into

$$\frac{(k+1)(k+2)}{4}+\frac{[(k+2)/2]}{2}$$

symmetric and

$$\frac{(k+1)(k+2)}{4}-\frac{[(k+2)/2]}{2}$$

antisymmetric equations simplifying the analysis. The symmetric and antisymmetric polynomials may be written explicitly as

$$\begin{aligned} \boldsymbol{P}_k^{[S]} &= \sum_{i=0}^{k} \sum_{j=0}^{[(k-i)/2]} C_{i\,2j\,k-i-2j} s^i t^{2j} u^{k-i-2j} \\ \boldsymbol{P}_k^{[A]} &= \sum_{i=0}^{k-1} \sum_{j=0}^{[(k-i-1)/2]} C_{i\,2j+1\,k-i-2j-1} s^i t^{2j+1} u^{k-i-2j-1}. \end{aligned} \tag{59}$$

Note that, for even k, equation (59) contains HH of order k. The HH vanish under the action of the Laplacian and may therefore be omitted, again reducing the number of coefficients.

In contrast to $\boldsymbol{\Psi}_1$, the polynomial terms do not generally account for the complete $\boldsymbol{\Psi}_k$ for $k>1$. One is faced with two alternatives: (a) choose the coefficients in (59) to put $\boldsymbol{I}_{k-2}$ defined by (36) into its 'simplest' form; (b) the Coulomb potential is singular for r_1, r_2 or $r_{12}=0$. By suitable choice of coefficients, the singular terms in $\boldsymbol{I}_{k-2}$ arising from $\boldsymbol{V}$ may be removed (Ermolaev 1961). Any series expansion for $\boldsymbol{I}_{k-2}$ will converge more rapidly. One may use the fact that $r_1 r_2 r_{12} \boldsymbol{V}$ is finite for finite values of r_1, r_2 and r_{12}. This is used in § 5.2 for removing the singular pieces of $\boldsymbol{I}_{k-2}$ by considering the following combinations:

$$\begin{aligned} u(s^2-t^2) &= 4r_1r_2r_{12} \\ u(u^2-t^2) &= 2r_1r_2r_{12}(1-\cos\theta) \\ u(s^2-u^2) &= 2r_1r_2r_{12}(1+\cos\theta) \\ s(u^2-t^2) &= 2r_1r_2r_{12}(\cos\theta_1+\cos\theta_2) \\ t(s^2-u^2) &= 2r_1r_2r_{12}(\cos\theta_1-\cos\theta_2) \end{aligned} \tag{60}$$

where θ_i is the angle between $\boldsymbol{r}_i$ and $\boldsymbol{r}_{12} (i=1,2)$. Since the cosine terms are finite for finite r_1, r_2 and r_{12}, the potential multiplied by any of (60) is also finite. One therefore chooses the coefficients in (59) so that only the combinations appearing in (60) arise.

In EC, it is helpful to modify the Laplacian using (Hylleraas 1932)

$$\begin{aligned} \Xi &= 2r_1r_2r_{12}\Delta \\ &= \left[u(s^2-t^2)\left(\frac{\partial^2}{\partial s^2}+\frac{\partial^2}{\partial t^2}+\frac{\partial^2}{\partial u^2}\right) + 4su\frac{\partial}{\partial s} - 4tu\frac{\partial}{\partial t} + 2(s^2-t^2)\frac{\partial}{\partial u} \right. \\ &\quad \left. + 2s(u^2-t^2)\frac{\partial^2}{\partial s\partial u} - 2t(u^2-s^2)\frac{\partial^2}{\partial t\partial u} \right]. \end{aligned}$$

Using (11) it can be seen that

$$\Xi r^k \Psi(\alpha,\theta) \equiv -r^{k-2} 2r_1r_2r_{12}[\Lambda^2 - k(k+4)]\Psi(\alpha,\theta). \tag{61}$$

Use of equations (5) and (61) allows the FRR (53) to be rewritten in terms of EC. For example, $k=3$, $p=1$ leads to

$$\Xi\boldsymbol{\Psi}_{31} = 4r_1r_2r_{12}V\boldsymbol{\Psi}_{21}. \tag{62}$$

Once $\boldsymbol{\Psi}_{21}$ is determined, $\boldsymbol{\Psi}_{31}$ is easily found by use of equations (59) and (62).

4.3. *Solution of the Fock recurrence relation for highest power of ln r*

The FRR (53) is easily generalised to include excited states and states of mixed symmetry by allowing $k'>0$, where k' is defined in § 3.3. Wavefunctions commencing at degree k' are denoted by a superscript k'. When $k'=0$ it will usually be omitted from the notation.

4.3.1. Even k. For even k, the highest power of ln r is

$$p' = (k-k')/2$$

and the FRR for p' and $p'-1$ becomes

$$[\Lambda^2 - k(k+4)]\Psi^{k'}_{kp'} = 0 \tag{63}$$

$$[\Lambda^2 - k(k+4)]\Psi^{k'}_{kp'-1} = (k-k')(k+2)\Psi^{k'}_{kp'} - 2V\Psi^{k'}_{k-1\,p'-1} + 2E\Psi^{k'}_{k-2\,p'-1}. \tag{64}$$

Equation (63) together with (21) implies that

$$\Psi^{k'}_{kp'} = \sum_{l=0}^{k/2} a^{k'}_{kl} Y_{kl}(\alpha, \theta) \tag{65}$$

where the $a^{k'}_{kl}$ are presently undetermined. The inhomogeneous term in a differential equation must be orthogonal to the solutions to its corresponding homogeneous equation. In our case the homogeneous solutions are the Y_{kl} ($l=0, 1, \ldots, k/2$), and the right-hand side of (64) must be orthogonal to each Y_{kl} separately. Noting that $\Psi^{k'}_{k-2\,p'-1}$ is analogous to $\Psi^{k'}_{kp'}$ and therefore contains only HH with lower k, one obtains

$$a^{k'}_{kl} = \frac{2}{(k-k')(k+2)} \int V\Psi^{k'}_{k-1\,p'-1} Y_{kl}(\alpha, \theta)\, d\Omega. \tag{66}$$

The particular case a^0_{21} is examined by Bartlett (1937), Ermolaev (1961), Knirk (1974b) and Morgan (1978a, b). The fact that $a^0_{21} \neq 0$ is equivalent to requiring logarithmic terms in the wavefunction.

4.3.2. Odd k. For odd k

$$p' = (k-k')/2 - 1$$

and the FRR for p' becomes

$$[\Lambda^2 - k(k+4)]\Psi^{k'}_{kp'} = -2V\Psi^{k'}_{k-1\,p'} \tag{67}$$

or equivalently, from (62),

$$\Xi\boldsymbol{\Psi}^{k'}_{kp'} = 4r_1r_2r_{12}V\boldsymbol{\Psi}^{k'}_{k-1\,p'}. \tag{68}$$

The $\Psi^{k'}_{k-1\,p'}$ are computed by § 4.3.1 and hence the $\Psi^{k'}_{kp'}$ may be evaluated by the method of § 4.2.

Expanding $V\Psi^{k'}_{k-1\,p'-1}$ in IC, it is seen that equation (66) becomes a sum of integrals of the type evaluated by equation (57). Moreover, since the Y_{kl} have a definite parity under interchange of r_1 and r_2, one only needs to consider either the symmetric or the antisymmetric terms of $V\Psi^{k'}_{k-1\,p'-1}$. Hence the $a^{k'}_{kl}$ are easily obtained.

The above approach may be compared with the treatment of § 3.3 leading to equation (44). There the coefficient of the highest power of ln r was $I^0_{2l}/8$, where I^0_{nl} was obtained by expanding $\boldsymbol{I}_0$ into HH. From equations (36), (39), (40), (44), (54) and (55) and comparison with equation (66), the methods are seen to be equivalent.

5. Applications

In what follows, the techniques of § 4 are applied to obtain several $\Psi^{k'}_{kp}$. One example of § 4.2 has already been given: $\boldsymbol{\Psi}_{10}$ was stated in equation (37).

5.1. $\Psi^{k'}_{kp'}$ for $k\leq 6$

From § 4.3, Ψ_{21} is completely determined by equations (65) and (66). To evaluate (66) we expand the integrand as follows:

$$V\Psi_{10}\equiv \boldsymbol{V\Psi}_{10}=\left\{2\mu_S^2+2\mu_A^2+\frac{\mu_{12}^2}{2}+(\mu_S^2-\mu_A^2)\frac{r^2}{r_1r_2}+\mu_S\mu_{12}\left[(r_1+r_2)\left(\frac{1}{r_{12}}+\frac{r_{12}}{2r_1r_2}\right)\right]\right\}$$
$$+\mu_A\mu_{12}\left[(r_1-r_2)\left(\frac{1}{r_{12}}-\frac{r_{12}}{2r_1r_2}\right)\right] \tag{69}$$

where

$$\mu_S=(\mu_1+\mu_2)/2 \qquad \mu_A=(\mu_1-\mu_2)/2.$$

This factorisation clearly displays the symmetry of the terms in (69). Functions not depending on r_{12} are orthogonal to $P_l(\cos\theta)$ for $l\geq 1$. Hence one sees that

$$a_{21}=\frac{\mu_S\mu_{12}}{4}\int(r_1+r_2)\left(\frac{1}{r_{12}}+\frac{r_{12}}{2r_1r_2}\right)Y_{21}(\alpha,\theta)\,d\Omega$$

$$a_{20}=\frac{\mu_A\mu_{12}}{4}\int(r_1-r_2)\left(\frac{1}{r_{12}}-\frac{r_{12}}{2r_1r_2}\right)Y_{20}(\alpha,\theta)\,d\Omega.$$

Evaluating these integrals by way of (57), one obtains from (65) that

$$\boldsymbol{\Psi}_{21}=\frac{\mu_{12}(\pi-2)}{3\pi}[\mu_S(r^2-r_{12}^2)-\mu_A(r_1^2-r_2^2)]\ln r. \tag{70}$$

By convention the 'solid function', for example $\boldsymbol{\Psi}_{21}$, includes not only the dependence on r but also the appropriate power of ln r. Once $\boldsymbol{\Psi}_{21}$ has been determined, it is straightforward to obtain $\boldsymbol{\Psi}_{31}$ by solving (62). More generally, the propagation of each HH into the next k line may be obtained by the method of § 4.2 applied to (67) or (68). The propagation of $\boldsymbol{Y}_{kl}$ will be denoted $\boldsymbol{\Psi}^{[k,l]}_{k+1}$ and is tabulated in table 4. For the HIS the results in table 4 agree with those of Pluvinage (1982).

Table 4. Propagation of the HH of order k into the next k line, $Y_{kl} \rightarrow \Psi^{[k,l]}_{k+1}$.

k l	$\Psi^{[k,l]}_{k+1}$
0 0	$\mu_S s + \mu_A t + \frac{1}{2}\mu_{12} u$
2 0	$\frac{1}{6}\mu_S t(9s^2 - t^2) + \frac{1}{6}\mu_A s(9t^2 - s^2) + \frac{1}{2}\mu_{12} stu$
2 1	$\frac{1}{2}(\mu_S s + \mu_A t + \mu_{12} u)(r^2 - u^2) + \frac{1}{12}\mu_{12} u^3$
4 0	$\frac{1}{30}\mu_S s(-4s^4 + 65s^2t^2 - 15t^4) + \frac{1}{30}\mu_A t(-4t^4 + 65s^2t^2 - 15s^4)$ $+ \frac{1}{90}\mu_{12} u(55r^2u^2 - 45r^4 + 60s^2t^2 - 22u^4)$
4 1	$\frac{1}{18}\mu_S t(15s^4 + 14s^2t^2 - 30s^2u^2 + 2t^2u^2 - t^4) + \frac{1}{18}\mu_A s(15t^4 + 14s^2t^2 - 30t^2u^2 + 2s^2u^2 - s^4)$ $+ \frac{1}{9}\mu_{12} stu(9r^2 - 8u^2)$
4 2	$\frac{1}{12}(\mu_S s + \mu_A t)[s^4 + 4s^2t^2 - 6u^2(s^2 + t^2 - u^2) + t^4] - \frac{1}{180}\mu_{12} u(89u^4 + 15s^2t^2 - 200u^2r^2 + 90r^4)$

From equation (65) and linearity, it is seen that for odd k

$$\Psi^{k'}_{kp'} = \sum_{l=0}^{(k-1)/2} a^{k'}_{k-1\,l} \Psi^{[k-1,l]}_{k}. \tag{71}$$

Once the $\Psi^{k'}_{kp'}$ for odd k has been determined then from (65) one can determine $\Psi^{k'}_{k+1\,p'}$. However, it is more convenient to define

$$b^{[k'',l'']}_{kl} = \frac{2}{(k+2)} \int V \Psi^{[k'',l'']}_{k-1} Y_{kl}(\alpha, \theta)\, d\Omega \tag{72}$$

where $k'' = k - 2$. The $b^{[k'',l'']}_{kl}$ are tabulated in table 5. They are independent of k' and

Table 5. Table of $b^{[k'',l'']}_{kl}$.

k l	k'' l''	0 0		
2 0		$-\mu_A\mu_{12}(\pi - 2)/3\pi$		
2 1		$2\mu_S\mu_{12}(\pi - 2)/3\pi$		
	k'' l''	2 0	2 1	
4 0		$\frac{-2\mu_A\mu_{12}(5\pi - 14)}{45\pi}$	$\frac{\mu_S\mu_{12}(5\pi - 14)}{45\pi}$	
4 1		$\frac{\mu_S\mu_{12}(7\pi - 20)}{15\pi}$	$\frac{-\mu_A\mu_{12}(7\pi - 20)}{30\pi}$	
4 2		$\frac{-8\mu_A\mu_{12}(5\pi - 14)}{45\pi}$	$\frac{4\mu_S\mu_{12}(5\pi - 14)}{30\pi}$	
	k'' l''	4 0	4 1	4 2
6 0		$\frac{-\mu_A\mu_{12}(5\pi - 14)}{35\pi}$	$\frac{\mu_S\mu_{12}(147\pi - 436)}{945\pi}$	$\frac{-\mu_A\mu_{12}(9\pi - 32)}{105\pi}$
6 1		$\frac{4\mu_S\mu_{12}(35\pi - 103)}{325\pi}$	$\frac{-2\mu_A\mu_{12}(89\pi - 276)}{325\pi}$	$\frac{\mu_S\mu_{12}(62\pi - 188)}{525\pi}$
6 2		$\frac{-2\mu_A\mu_{12}(73\pi - 224)}{315\pi}$	$\frac{8\mu_S\mu_{12}(237\pi - 730)}{2835\pi}$	$\frac{-4\mu_A\mu_{12}(19\pi - 58)}{315\pi}$
6 3		$\frac{4\mu_S\mu_{12}(315\pi - 1048)}{1573\pi}$	$\frac{-32\mu_A\mu_{12}(192\pi - 583)}{4725\pi}$	$\frac{4\mu_S\mu_{12}(189\pi - 572)}{1573\pi}$

are related to the $a_{kl}^{k'}$ by

$$a_{kl}^{k'} = \frac{1}{(k-k')} \sum_{l''=0}^{k''/2} b_{kl}^{[k'',l'']} a_{k''l''}^{k'} \tag{73}$$

where $a_{00}^{0} \equiv \boldsymbol{\Psi}_{00}$ corresponding to the overall normalisation of the wavefunction.

To illustrate these results it is seen from equations (66), (71)-(73) and tables 1, 4 and 5 that one recovers equations (37) and (70). Moreover, one may obtain

$$\boldsymbol{\Psi}_{31} = \frac{\mu_{12}(\pi-2)}{36\pi}[6\mu_S^2 s(r^2-u^2)+6\mu_S\mu_{12}u(r^2-u^2)+\mu_A^2 s(s^2-9t^2)+\mu_S\mu_{12}u^3$$
$$-2\mu_A\mu_S t(3s^2+3u^2-2t^2)-3\mu_A\mu_{12}stu]\ln r \tag{74}$$

$$\boldsymbol{\Psi}_{42} = \left(\frac{\mu_{12}^2(\pi-2)(5\pi-14)}{180\pi^2}(\mu_S^2+\mu_A^2)[r^4-8r_1^2r_2^2+2(r^2-u^2)^2]\right.$$
$$\left.-\frac{\mu_{12}^2(\pi-2)(7\pi-20)}{45\pi^2}\mu_S\mu_A(r^2-u^2)(r_1^2-r_2^2)\right)\ln^2 r \tag{75}$$

and

$$\boldsymbol{\Psi}_{41}^2 = \left(\frac{\mu_{12}(5\pi-14)}{30\pi}(\mu_S a_{21}^2-2\mu_A a_{20}^2)[r^4-8r_1^2r_2^2+2(r^2-u^2)^2]\right.$$
$$\left.-\frac{\mu_{12}(7\pi-20)}{15\pi}(\mu_A a_{21}^2-2\mu_S a_{20}^2)(r^2-u^2)(r_1^2-r_2^2)\right)\ln r. \tag{76}$$

In equation (76) the a_{20}^2 and a_{21}^2 are arbitrary coefficients (§ 3.5) corresponding to the independent particle states $n_1 s n_2 s\ ^3S$ and $n_1 p n_2 p\ ^1S$, respectively.

For the HIS, equation (74) agrees with Ermolaev (1961). However equation (75) differs slightly from that given by David (1975), (76) differs from Ermolaev (1968) and is exactly half that obtained by Pluvinage (1982). These results have been closely checked using the computer algebra system SMP (Wolfram 1985) and the earlier results are incorrect. From tables 1, 4 and 5, $\Psi_{kp'}^{k'}$ for $k \leq 6$, $k' \leq 6$ may be determined. The extension to higher k, k' is straightforward but tedious. A tabulation of all the known Fock coefficients is given by Abbott (1986).

5.2. Reduction of the equation for $\boldsymbol{\Psi}_{20}$ to simplest form

From the discussion of §§ 4.2 and 4.3.1 one may write

$$\boldsymbol{\Psi}_{20} = A_{20}\boldsymbol{Y}_{20} + A_{21}\boldsymbol{Y}_{21} + \boldsymbol{P}_2 + \chi_{20} \tag{77}$$

where A_{20} and A_{21} are arbitrary coefficients, analogous to a_{20}^2 and a_{21}^2, $\boldsymbol{P}_2$ is defined by (59) and χ_{20} is presently undetermined. Following § 4.2, the constants in $\boldsymbol{P}_2$ may be determined by substituting (77) into the FRR (53). Realising that two of the coefficients, here chosen to be C_{110} and C_{002}, are related to the arbitrary coefficients (as they multiply the HH of order 2), one only has to determine C_{200}, C_{020}, C_{101} and C_{011}. One finds that

$$C_{200} = \tfrac{1}{12}(\mu_1^2+\mu_2^2+\tfrac{1}{2}\mu_{12}^2-E+3\mu_1\mu_2) \tag{78a}$$

$$C_{020} = \tfrac{1}{12}(\mu_1^2+\mu_2^2+\tfrac{1}{2}\mu_{12}^2-E-3\mu_1\mu_2). \tag{78b}$$

Choosing

$$C_{101}^{(a)}=\mu_{12}\mu_S/3 \qquad C_{011}^{(a)}=\mu_{12}\mu_A/3 \tag{79}$$

(53) becomes

$$(\Lambda^2-12)\chi_{20}^{(a)}=8\Psi_{21}-\frac{\mu_{12}r^2}{3r_1r_2r_{12}}(\mu_S s-\mu_A t) \tag{80}$$

whereas choosing

$$C_{101}^{(b)}=\mu_{12}\mu_S/2 \qquad C_{011}^{(b)}=\mu_{12}\mu_A/2 \tag{81}$$

yields

$$(\Lambda^2-12)\chi_{20}^{(b)}=8\Psi_{21}+\mu_{12}\mu_S(\cos\theta_1+\cos\theta_2)+\mu_{12}\mu_A(\cos\theta_1-\cos\theta_2). \tag{82}$$

For the HIS, equation (82) has been given by Ermolaev (1961), David (1975) and Pluvinage (1982). It is emphasised that, from (77), (79) and (81), $\chi_{20}^{(a)}$ and $\chi_{20}^{(b)}$ are simply related by

$$\chi_{20}^{(a)}=\tfrac{1}{6}\mu_{12}u(\mu_S s+\mu_A t)+\chi_{20}^{(b)}. \tag{83}$$

Equations (80) and (82) may be solved by expanding both sides in HH. The inhomogeneous term in equation (80) is simple but not finite for r_1, r_2 or $r_{12}=0$. Expansion in HH is thus slowly convergent. However, if one can algebraically sum the expansion of $\chi_{20}^{(a)}$ in HH, obtained by solving (80), slow convergence is immaterial. The advantage of examining (80) is that its expansion is simpler than that associated with (82). For the HIS, the expansion of (82) is given by David (1975) but his results can be simplified, as in the general case described in the following section. Pluvinage (1982) solved (82) for the HIS by expansion, not into HH, but into a region-dependent series of SPC. This method is discussed in II.

5.3. Solution of Ψ_{20}

As discussed in § 5.2 we will solve Ψ_{20} by expanding (80) in HH. Consider

$$\frac{r^2(r_1\pm r_2)}{2r_1r_2r_{12}}=\frac{(\cos\alpha/2\pm\sin\alpha/2)}{\sin\alpha(1-\sin\alpha\cos\alpha)^{1/2}}=f^{\pm}(\alpha,\theta)=\sum_{nl}D_{nl}^{\pm}Y_{nl}(\alpha,\theta) \tag{84}$$

where Y_{nl} are the *unnormalised* HH. From (12), (54) and (55)

$$D_{nl}^{\pm}=N_{nl}^2\int f^{\pm}(\alpha,\theta)Y_{nl}(\alpha,\theta)\,d\Omega. \tag{85}$$

Following White and Stillinger (1970) it is usual to write

$$\frac{r}{r_{12}}=(1-\sin\alpha\cos\theta)^{-1/2}=\sum_{nl}P_l(\cos\theta)\begin{cases}\dfrac{\sin^l(\alpha/2)}{\cos^{l+1}(\alpha/2)} & \alpha\in[0,\pi/2)\\[2ex] \dfrac{\cos^l(\alpha/2)}{\sin^{l+1}(\alpha/2)} & \alpha\in(\pi/2,\pi].\end{cases} \tag{86}$$

However, this region-dependent expansion can be avoided by following Sack (1964), who expands an arbitrary function $f(r_{12})$ into a region-independent expansion. Equation (86) becomes (there is an error in Sack, equation (27*a*)) for $\nu>-2$

$$\left(\frac{r_{12}}{r}\right)^{\nu}=\sum_{l=0}^{\infty}P_l(\cos\theta)\frac{(-\nu/2)_l}{(1/2)_l}2^{-l}\sin^l\alpha\;{}_2F_1\left[\begin{matrix}l/2-\nu/4,\ l/2-\nu/4+\frac{1}{2}\\ l+\frac{3}{2}\end{matrix};\ \sin^2\alpha\right].$$

The integral over θ in (85) is now trivial and from the orthogonality of the Legendre polynomials

$$D^{\pm}_{nl}=N^2_{nl}\frac{\pi^2 2^{1-l}}{2l+1}\int_0^{\pi}\sin^{2l+1}\alpha C^{(l+1)}_{n/2-1}(\cos\alpha)$$
$$\times\left\{(\cos\alpha/2\pm\sin\alpha/2)\,{}_2F_1\left[\begin{matrix}l/2+\frac{1}{4},\,l/2+\frac{3}{4}\\ l+\frac{3}{2}\end{matrix};\ \sin^2\alpha\right]\right\}\mathrm{d}\alpha. \tag{87}$$

The term in $\{\ldots\}$, $f^{\pm}(\alpha)$, is simplified by theorem VI in Slater (1966, p 78), which may be written in the elegant form

$${}_2F_1\left[\begin{matrix}a,\,a+\frac{1}{2}\\ 2a+1\end{matrix};\ z\right]{}_2F_1\left[\begin{matrix}b,\,b+\frac{1}{2}\\ 2b+1\end{matrix};\ z\right]={}_2F_1\left[\begin{matrix}a+b,\,a+b+\frac{1}{2}\\ 2a+2b+1\end{matrix};\ z\right]. \tag{88}$$

Srivastava and Manocha (1984, p 200) show how a GHS is decomposed into even and odd powers

$${}_pF_q\left[\begin{matrix}(a)\\ (b)\end{matrix};\ z\right]={}_{2p}F_{2q+1}\left[\begin{matrix}(a/2),\,((a+1)/2)\\ (b/2),\,((b+1)/2),\,\frac{1}{2}\end{matrix};\ \frac{z^2}{4^{1-p+q}}\right]$$
$$+z\frac{((a)_p)_1}{((b)_q)_1}\,{}_{2p}F_{2q+1}\left[\begin{matrix}((a+1)/2),\,(a/2+1)\\ ((b+1)/2),\,(b/2+1),\,\frac{3}{2}\end{matrix};\ \frac{z^2}{4^{1-p+q}}\right].$$

Thus

$$(1\pm z)^{\nu}\equiv{}_1F_0\left[\begin{matrix}-\nu\\ -\end{matrix};\ \pm(-z)\right]={}_2F_1\left[\begin{matrix}-\nu/2,\,-(1-\nu)/2\\ \frac{1}{2}\end{matrix};\ z^2\right]$$
$$\pm\nu z\,{}_2F_1\left[\begin{matrix}(1-\nu)/2,\,1-\nu/2\\ \frac{3}{2}\end{matrix};\ z^2\right] \tag{89}$$

and hence we see that for the symmetric (+) case

$$\cos(\alpha/2)+\sin(\alpha/2)=(1+\sin\alpha)^{1/2}$$

implies that

$$f^{+}(\alpha)={}_2F_1\left[\begin{matrix}l/2,\,(l+1)/2\\ l+1\end{matrix};\ \sin^2\alpha\right]+\tfrac{1}{2}\sin\alpha\,{}_2F_1\left[\begin{matrix}(l+1)/2,\,l/2+1\\ l+2\end{matrix};\ \sin^2\alpha\right]. \tag{90}$$

For the antisymmetric (−) case we first apply Euler's transform (Rainville 1960, p 60) to the ${}_2F_1$ in (87) yielding

$${}_2F_1\left[\begin{matrix}l/2+\frac{1}{4},\,l/2+\frac{3}{4}\\ l+\frac{3}{2}\end{matrix};\ \sin^2\alpha\right]=|\cos\alpha|\,{}_2F_1\left[\begin{matrix}l/2+\frac{3}{4},\,l/2+\frac{5}{4}\\ l+\frac{3}{2}\end{matrix};\ \sin^2\alpha\right]. \tag{91}$$

Since

$$(\cos(\alpha/2)-\sin(\alpha/2))|\cos\alpha|=\cos\alpha(1-\sin\alpha)^{1/2}$$

then from (87)-(89) and (91)

$$f^{-}(\alpha)=\cos\alpha\left\{{}_2F_1\left[\begin{matrix}(l+1)/2,\,l/2+1\\ l+1\end{matrix};\ \sin^2\alpha\right]\right.$$
$$\left.-\tfrac{1}{2}\sin\alpha\,{}_2F_1\left[\begin{matrix}l/2+1,\,(l+3)/2\\ l+2\end{matrix};\ \sin^2\alpha\right]\right\}$$

(87) may be evaluated. For conciseness only D^+_{nl} will be examined and the modifications required for D^-_{nl} are indicated.

Writing $f^+(\alpha)$ as an infinite series one obtains integrals of the form (Gradshteyn and Ryzhik 1980, p 826)

$$\int_0^\pi \sin^{2a+1}\alpha C_n^{(\nu)}(\cos\alpha)\,d\alpha = \int_{-1}^1 (1-x^2)^a C_n^{(\nu)}(x)\,dx = \frac{\pi^{1/2}\Gamma(a+1)(\nu)_{n/2}(\nu-a-\frac{1}{2})_{n/2}}{\Gamma(a+\frac{3}{2})(a+\frac{3}{2})_{n/2}(1)_{n/2}} \tag{92}$$

for n even. For $f^-(\alpha)$ the analogous integral contains $xC_n^{(\nu)}(x)$ and may be put in the form of (92) using the recursion formula (Gradshteyn and Ryzhik 1980, p 1030)

$$xC_n^{(\nu)}(x) = \frac{1}{2(\nu+n)}[(n+1)C_{n+1}^{(\nu)}(x) + (2\nu+n-1)C_{n-1}^{(\nu)}(x)].$$

Hence

$$\int_0^\pi \sin^{2a+1}\alpha\cos\alpha C_n^{(\nu)}(\cos\alpha)\,d\alpha = \frac{\pi^{1/2}\Gamma(a+1)(\nu)_{(n+1)/2}(\nu-\alpha-\frac{1}{2})_{(n-1)/2}}{\Gamma(a+\frac{3}{2})(a+\frac{3}{2})_{(n+1)/2}(1)_{(n-1)/2}}$$

for n odd. Utilising (90) and (91), (87) may be evaluated yielding

$$D^+_{nl} = (-1)^m\left\{\frac{1}{2^{2m+l+1}}\frac{(\frac{1}{2})_m}{(l+2)_m}\,{}_3F_2\left[\begin{matrix} l/2+m+\frac{1}{2}, l/2+m+1, l/2+m+\frac{3}{2} \\ l+m+2, l+2m+2\end{matrix}; 1\right]\right.$$
$$\left. + \frac{4(1)_l(\frac{1}{2})_m((l+3)/2)_m}{\pi(\frac{3}{2})_l(l+\frac{3}{2})_m((l+1)/2)_m}\,{}_3F_2\left[\begin{matrix}-m, m+l+1, 1 \\ l/2+1, (l+3)/2\end{matrix}; 1\right]\right\} \tag{93}$$

where $m=n/4-l/2$. The second ${}_3F_2$ in (93) is a terminating sum. The first may be transformed into a finite series (Abbott 1986)

$${}_3F_2\left[\begin{matrix} l/2+m+\frac{1}{2}, l/2+m+1, l/2+m+\frac{3}{2} \\ l+m+2, l+2m+2\end{matrix}; 1\right] = (-1)^m 4^{m+l+1}$$
$$\times\begin{cases} 1 - \dfrac{2(L+1)_m(1)_L^2}{\pi(2L+\frac{3}{2})_m(\frac{3}{2})_{2L}}\,{}_2F_1\left[\begin{matrix}-\frac{1}{2}-L, -\frac{1}{2}-L-m \\ \frac{1}{2}\end{matrix}; 1\right]_{L+m+1} & L=l/2 \\ 1 - \dfrac{2(L+1)_m(1)_L^2}{\pi(2L+\frac{1}{2})_m(\frac{1}{2})_{2L}}\,{}_2F_1\left[\begin{matrix}\frac{1}{2}-L, \frac{1}{2}-L-m \\ \frac{3}{2}\end{matrix}; 1\right]_{L+m} & L=(l+1)/2 \end{cases} \tag{94}$$

where ${}_pF_q[\ldots]_n$ denotes the partial sum to n terms of ${}_pF_q[\ldots]$. We have one simple check on these results. The inhomogeneous part of equation (80) cannot contain any HH of degree $n=2$ since these are solutions to the homogeneous equation. From (70), (80) and (84), the symmetric terms are

$$\mu_S\mu_{12}\left(\frac{8(\pi-2)}{3\pi}Y_{21} - \frac{2}{3}\sum_{nl} D^+_{nl}Y_{nl}\right).$$

However, from (93) and (94), $D^+_{21} = 4(\pi-2)/\pi$ and hence the contribution of Y_{21} due to (84) cancels exactly with that in Ψ_{21} as required. Analogously, for the antisymmetric case, one finds that $D^-_{21} = 2(\pi-2)/\pi$ also cancels with Ψ_{21}. In summary, equation (80) may be written

$$[\Lambda^2 - 12]\chi_{20}^{(a)} = \frac{-2\mu_{12}}{3}\sum_{nl}{}' (\mu_S D^+_{nl} - \mu_A D^-_{nl})Y_{nl} \tag{95}$$

where the prime indicates that $n=2$ is omitted from the summation. It is seen from (21) that

$$[\Lambda^2-12]Y_{nl}=(n-2)(n+6)Y_{nl}$$

and hence equation (95) may be inverted to yield

$$\chi_{20}^{(a)}=\frac{-2\mu_{12}}{3}\sum_{nl}{}'\frac{\mu_S D_{nl}^+-\mu_A D_{nl}^-}{(n-2)(n+6)}Y_{nl}. \tag{96}$$

Since the $D_{nl}^{\pm}$ are finite series, we have derived a series expansion for χ_{20} with easily computable coefficients. This may be compared with David (1975) who obtained the coefficients in the expansion of χ_{20} as a doubly finite sum. A numerical check showed the equivalence of the two treatments.

Note that (96) requires a double summation and for numerical work the convergence will be slow due to the presence of the Legendre and Gegenbauer polynomials. In § 5.4 equation (96) is reduced to a single summation, using series rearrangement and equation (52), improving convergence. The reduction is completed in II.

5.4. *Reduction of* Ψ_{20}

For compactness we write $x=\cos\alpha$, $y=\sin\alpha$. Using elementary series rearrangement, (A3), (12) and (93) the double summation in (96) may be written

$$\sum_{l=0}^{\infty}P_l(\cos\theta)y^l\sigma_l(x,y)$$

where

$$\sigma_l(x,y)=\frac{-2\mu_{12}}{3}\sum_{m=\delta_{l,1}}^{\infty}\frac{\mu_S D_{4m+2l,l}^+-\mu_A D_{4m+2l,l}^-}{(2m+l-1)(2m+l+3)}C_{2m}^{(l+1)}(x). \tag{97}$$

In (97), $\delta_{l,1}$ arises because $n=2$ was excluded from equation (96). Restricting attention to the symmetric piece of (97), we examine

$$\sigma_l^+=\frac{-2\mu_S\mu_{12}}{3}\sum_{m=\delta_{l,1}}^{\infty}\frac{D_{4m+2l,l}^+}{(2m+l-1)(2m+l+3)}C_{2m}^{(l+1)}(x). \tag{98}$$

The reduction of (98) requires the expansion of general functions into Gegenbauer polynomials. This includes an extension of § 8.92 of Gradshteyn and Ryzhik (1980). Details are given in the appendix. The σ_l^+, given by (A19), (A22) and (A24) are

$$\sigma_0^+=\frac{\mu_S\mu_{12}}{12}\left[y+2+x\ln\left(\frac{1-x}{1+x}\right)-|x|+\frac{(1-2y^2)\alpha}{y}-|x|\ln(1-x^2)\right]$$

$$\sigma_1^+=\frac{-2\mu_S\mu_{12}}{3}\left(\frac{-\rho}{4}+\frac{\rho^2}{2}-\frac{\rho^3}{12}+\ln(1+\rho^2)-\frac{1}{\pi y^2}+\frac{(1+2y^2)|x|\alpha}{\pi y^3}\right)$$

$$\begin{aligned}\sigma_l^+=\frac{2^{1-l}\mu_S\mu_{12}}{3}\Bigg\{&(1+\rho^2)^{l-1}\left[\left(\frac{1}{l}-\frac{2}{l-1}\right)+\frac{\rho}{l+1}-\frac{\rho^2}{l}+\left(\frac{2}{l+2}-\frac{1}{l+1}\right)\rho^3\right]\\&+\frac{\Gamma(l-1)\Gamma((l+1)/2)}{\Gamma(l+\frac{1}{2})\Gamma(l/2+1)}\,{}_2F_1\left[\begin{matrix}(l-1)/2,(l+3)/2\\ l+\frac{3}{2}\end{matrix};\ y^2\right]\Bigg\}\qquad l\geqslant 2.\end{aligned}$$

Also

$$\frac{(r_1+r_2)r_{12}}{r^2}=\sum_{l=0}^{\infty} P_l(\cos\theta)\left(\frac{y}{2}\right)^l (1+\rho^2)^{l-1}\left(\frac{-(\rho+1)}{2l-1}+\frac{\rho^2(\rho+1)}{2l+3}\right). \tag{99}$$

Combining equations (77), (78), (79) and (96), one obtains

$$\begin{aligned}\Psi_{20}^{+}=A_{21}(r^2-r_{12}^2)+\mu_1\mu_2 r_1 r_2+\tfrac{1}{3}\mu_S\mu_{12}(r_1+r_2)r_{12}\\ +\tfrac{1}{6}r^2(\mu_1^2+\mu_2^2+\tfrac{1}{2}\mu_{12}^2-E)\\ +\sum_{l=0}^{\infty} P_l(\cos\theta)y^l\sigma_l^{+}(x,y).\end{aligned} \tag{100}$$

Using (83) and (99) it may be shown that equation (100) is equivalent to the result obtained by Pluvinage (1982). Moreover, Pluvinage proves the absolute convergence of (100), hence justifying the series rearrangement. In II, it is shown that equation (100) may be reduced to a finite sum of special functions.

It is important to note that the σ_l^+ must have continuous derivatives with respect to r_1 and r_2, across the boundary $r_1=r_2$, to satisfy Hermicity (Davis and Maslen 1982). It is apparent that $|x|$, α and r have discontinuous derivatives. However, it may be shown that these discontinuities cancel exactly.

All algebraic expansions in I and II were evaluated and checked with the aid of the algebraic computing package Symbolic Manipulation Program (SMP), available from Inference Corporation (Wolfram 1985). Where possible, numeric checks were also carried out.

6. Conclusions

The hyperspherical formalism for solving the N-electron SE has been introduced and the case $N=2$ is examined in detail. The relationship between the HH and the excited states has been made explicit.

Expansion of the wavefunction into a generalised power series PHE, where the logarithmic function is formally homogeneous of degree zero, leads naturally to the FE. Examination of the derivation reveals the link between treatments of PHE in alternate sets of internal coordinates. The particular case of HC is treated in detail. This connection is of prime importance since each system of internal coordinates is advantageous for studying particular aspects of the many-particle wavefunction. For example, the connection between the HH, excited states and arbitrary coefficients is best treated using HC, whereas the polynomial pieces and the asymptotic form are transparent in IC or EC, whilst the wavefunction is most simply solved in SPC.

The FE has been solved to second order and the expression simplified by partial summations. However, the final reduction is complicated and does not give a hint to the reduction for higher orders. This difficulty of HC is reduced by working with the PHE expansion in SPC (as described in II) and may be reduced further by alternative techniques (as described in Gottschalk and Maslen 1987).

Logarithmic terms in the exact helium wavefunction have been given to sixth order and the extension to higher orders is straightforward. Moreover, simple polynomial terms appearing in all orders are demonstrated and their identification reduces the complexity of the differential recurrence relation.

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Appendix

A1. Expansion of GHS of sin α, cos α into $C^{(n)}_{2m}(\cos\alpha)$

Put $x=\cos\alpha$, $y=\sin\alpha$, and require n, m, k non-negative integers; p and ν real. From Rainville (1960, p 283)

$$x^n=\frac{n!}{2^n}\sum_{m=0}^{[n/2]}\frac{\nu+n-2m}{m!\,(\nu)_{n+1-m}}\,C^{(\nu)}_{n-2m}(x). \tag{A1}$$

For n even we reverse the order of summation (Slater 1966, p 47) to obtain

$$x^{2n}=\frac{(\frac{1}{2})_n}{(\nu+1)_n}\sum_{m=0}^{n}\frac{(-n)_m(\nu/2+1)_m}{(\nu+n+1)_m(\nu/2)_m}(-1)^m C^{(\nu)}_{2m}(x). \tag{A2}$$

By series rearrangement, utilising Rainville (1960, p 56), we have for an arbitrary function f

$$\sum_{n=0}^{\infty}\sum_{m=0}^{n+k}f(n,m)=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}f(n+m,m+k)+\sum_{n=0}^{\infty}\sum_{m=0}^{k-1}f(n,m) \tag{A3a}$$

$$=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}f(n+m,m)+\sum_{n=0}^{\infty}\sum_{m=0}^{k-1}f(n,n+m+1) \tag{A3b}$$

where the second summation of (A3a) and (A3b) vanishes for $k=0$. Using (A2) and (A3) one obtains

$${}_pF_q\left[\begin{matrix}(a)\\(b)\end{matrix};\ x^2\right]=\sum_{m=0}^{\infty}\frac{((a)_p)_m(\frac{1}{2})_m}{((b)_q)_m(\nu)_m}\,{}_{p+1}F_{q+1}\left[\begin{matrix}(a)+m,\ m+\frac{1}{2}\\(b)+m,\ 2m+\nu+1\end{matrix};\ 1\right]C^{(\nu)}_{2m}(x). \tag{A4}$$

In particular, using Gauss's theorem (Slater 1966, p 243)

$$\begin{aligned}y^p&=(1-x^2)^{p/2}\\&={}_1F_0\left[\begin{matrix}-p/2\\-\end{matrix};\ x^2\right]\\&=\frac{\Gamma(\nu+1)\Gamma(\nu+p/2+\frac{1}{2})}{\Gamma(\nu+\frac{1}{2})\Gamma(\nu+p/2+1)}\sum_{m=0}^{\infty}\frac{(-p/2)_m(\frac{1}{2})_m(\nu/2+1)_m}{(\nu+p/2+1)_m(\nu/2)_m(\nu+\frac{1}{2})_m}C^{(\nu)}_{2m}(x).\end{aligned} \tag{A5}$$

Using (A3) and (A5) one obtains

$${}_pF_q\left[\begin{matrix}(a)\\(b)\end{matrix};\ y^2\right]=\sum_{m=0}^{\infty}\frac{((a)_q)_m(\frac{1}{2})_m(-1)^m}{((b)_q)_m(\nu)_{2m}}\,{}_{p+1}F_{q+1}\left[\begin{matrix}(a)+m,\ m+\nu+\frac{1}{2}\\(b)+m,\ 2m+\nu+1\end{matrix};\ 1\right]C^{(\nu)}_{2m}(x). \tag{A6}$$

Since $C_{2m}^{(\nu)}(x)$ is an even function of x, no expansion of x^{2n+1} exists. However, from (A6) one may show that

$$
\begin{aligned}
|x|^{2n+1} &= (1-y^2)^{n+1/2} \\
&= {}_1F_0\left[\begin{matrix}-n-\frac{1}{2} \\ -\end{matrix};\ y^2\right] \\
&= \frac{\Gamma(\nu+1)(1)_n}{\Gamma(\nu+\frac{3}{2})\Gamma(\frac{1}{2})(\nu+\frac{3}{2})_n}\sum_{m=0}^{\infty}\frac{(-n-\frac{1}{2})_m(\nu/2+1)_m}{(\nu/2)_m(n+\nu+\frac{3}{2})_m}(-1)^m C_{2m}^{(\nu)}(x)
\end{aligned}
\tag{A7}
$$

and moreover that

$$
\begin{aligned}
|x|^{2n+1}{}_pF_q\left[\begin{matrix}(a) \\ (b)\end{matrix};\ x^2\right]
&= \frac{\Gamma(\nu+1)(1)_n}{\Gamma(\nu+\frac{3}{2})\Gamma(\frac{1}{2})(\nu+\frac{3}{2})_n}\sum_{m=0}^{\infty}\frac{(-n-\frac{1}{2})_m(\nu/2+1)_m}{(\nu/2)_m(n+\nu+\frac{3}{2})_m}(-1)^m \\
&\quad\times {}_{p+2}F_{q+2}\left[\begin{matrix}(a),\ n+\frac{3}{2},\ n+1 \\ (b),\ n+\frac{3}{2}-m,\ n+m+\nu+\frac{3}{2}\end{matrix};\ 1\right]C_{2m}^{(\nu)}(x).
\end{aligned}
\tag{A8}
$$

When $(a)=0$, (A8) reduces to (A7). Furthermore, it is straightforward to show using (A3), (A5) and (A6) that

$$
\begin{aligned}
y^{2n+1}{}_pF_q\left[\begin{matrix}(a) \\ (b)\end{matrix};\ y^2\right]
&= \frac{\Gamma(\nu+1)^2(\nu+1)_n}{\Gamma(\nu+\frac{3}{2})\Gamma(\nu+\frac{1}{2})(\nu+\frac{3}{2})_n}\sum_{m=0}^{\infty}\frac{(\frac{1}{2})_m(\nu/2+1)_m(-n-\frac{1}{2})_m}{(\nu/2)_m(\nu+\frac{1}{2})_m(\nu+n+\frac{3}{2})_m} \\
&\quad\times {}_{p+2}F_{q+2}\left[\begin{matrix}(a),\ n+\frac{3}{2},\ n+\nu+1 \\ (b),\ n+\frac{3}{2}-m,\ n+m+\nu+\frac{3}{2}\end{matrix};\ 1\right]C_{2m}^{(\nu)}(x)
\end{aligned}
\tag{A9}
$$

and after some effort

$$
\begin{aligned}
y^{2n}{}_{p+1}F_q\left[\begin{matrix}(a),1 \\ (b)\end{matrix};\ y^2\right]
&= \frac{(-1)^n(\frac{1}{2})_n(1)_n}{(\nu)_{2n}}\sum_{m=0}^{\infty}\frac{((a)_p)_m(n+\frac{1}{2})_m(n+1)_m}{((b)_q)_m(\nu+2n)_{2m}}(-1)^m \\
&\quad\times {}_{p+2}F_{q+1}\left[\begin{matrix}(a)+m,\ m+n+1,\ m+n+\nu+\frac{1}{2} \\ (b)+m,\ 2n+2m+\nu+1\end{matrix};\ 1\right]C_{2(m+n)}^{(\nu)}(x) \\
&\quad+\frac{(\nu+\frac{1}{2})_n}{(\nu+1)_n}\sum_{m=0}^{n-1}\frac{(-n)_m(\frac{1}{2})_m(\nu/2+1)_m}{(n+\nu+1)_m(\nu+\frac{1}{2})_m(\nu/2)_m} \\
&\quad\times {}_{p+3}F_{q+2}\left[\begin{matrix}(a),\ 1,\ n+1,\ n+\nu+\frac{1}{2} \\ (b),\ n+1-m,\ n+m+\nu+1\end{matrix};\ 1\right]C_{2m}^{(\nu)}(x).
\end{aligned}
\tag{A10}
$$

In the special case $n=0$, (A10) reduces to (A6) and for $(a)=0$, (A9) and (A10) agree with (A5). Note that, since the Legendre polynomial is just a special case of the

Gegenbauer polynomial by way of the relation $P_n(x) = C_n^{(1/2)}(x)$, the results above generalise those given in Gradshteyn and Ryzhik (1980, pp 1027-9). The correspondence is

$$\begin{aligned}(\mathrm{A1}), (\mathrm{A2}) &\to 8.922\ (1), (2)\\ (\mathrm{A4}) &\to 8.922\ (3), (5)\\ (\mathrm{A5}) &\to 8.925\ (2), (4)\\ (\mathrm{A6}) &\to 8.928.\end{aligned}$$

These relationships provide an additional check on the validity of (A1), (A2), (A4)-(A6).

A2. Expansion of functions of $\rho = r_</r_>$

Using Abramowitz and Stegun (1972, p 556)

$$\rho = \frac{1-|x|}{y} = \frac{1-(1-y^2)^{1/2}}{y} = \frac{y}{2}\,{}_2F_1\left[\begin{matrix}\frac{1}{2}, 1\\ 2\end{matrix}; \quad y^2\right]. \tag{A11}$$

Applying (88) n times one obtains

$${}_2F_1\left[\begin{matrix}a, a+\frac{1}{2}\\ 2a+1\end{matrix}; \quad z\right]^n = {}_2F_1\left[\begin{matrix}na, na+\frac{1}{2}\\ 2na+1\end{matrix}; \quad z\right] \tag{A12}$$

and from (A11) we have

$$\rho^n = \left(\frac{y}{2}\right)^n {}_2F_1\left[\begin{matrix}n/2, (n+1)/2\\ n+1\end{matrix}; \quad y^2\right]. \tag{A13}$$

Furthermore from (A3) and (A13)

$$\ln(1+\rho^2) = \rho^2\,{}_2F_1\left[\begin{matrix}1, 1\\ 2\end{matrix}; \quad \rho^2\right] = \tfrac{1}{4}y^2\,{}_3F_2\left[\begin{matrix}1, 1, \frac{3}{2}\\ 2, 2\end{matrix}; \quad y^2\right]. \tag{A14}$$

Expansion of (A13) and (A14) may be accomplished by use of equations (A9) and (A10)

$$(1+\rho^2)^p = \left(\frac{2}{1+|x|}\right)^p = 2^p\,{}_1F_0\left[\begin{matrix}p\\ -\end{matrix}; \quad -|x|\right] = \sum_{m=0}^{\infty} S_m^{[p,\nu]} C_{2m}^{(\nu)}(x)$$

where

$$\begin{aligned}S_m^{[p,\nu]} = 2^p\Bigg(&\frac{\Gamma(\nu+1)\Gamma(\nu-p+\frac{1}{2})(\nu/2+1)_m(p/2)_m((p+1)/2)_m}{\Gamma(\nu-p/2+1)\Gamma(\nu-(p+1)/2)(\nu/2)_m(\nu-p/2+1)_m(\nu-(p+1)/2)_m}\\ &-\frac{p\Gamma(\nu+1)}{\Gamma(\frac{1}{2})\Gamma(\nu+\frac{3}{2})}\,\frac{((p+1)/2)_m(p/2+1)_m(\nu/2+1)_m}{(\nu/2)_m(\nu+\frac{3}{2})_{2m}}\\ &\times{}_3F_2\left[\begin{matrix}p/2+m+\frac{1}{2}, p/2+m+1, 1\\ \nu+2m+\frac{3}{2}, \frac{3}{2}\end{matrix}; \quad 1\right]\Bigg).\end{aligned} \tag{A15}$$

Use of (A6) and (A13) yields

$$\rho^{2n+1}(1+\rho^2)^p = \frac{\Gamma(\nu+1)^2(\nu+1)_n}{2^{2n+1}\Gamma(\nu+\frac{1}{2})\Gamma(\nu+\frac{3}{2})(\nu+\frac{3}{2})_n}$$
$$\times \sum_{m=0}^{\infty} \frac{(\frac{1}{2})_m(\nu/2+1)_m(-n-\frac{1}{2})_m}{(\nu/2)_m(\nu+\frac{1}{2})_m(\nu+n+\frac{3}{2})_m} C_{2m}^{(\nu)}(x)$$
$$\times \sum_{k=0}^{\infty} \frac{(-p)_k(\nu+n+1)_k(n+\frac{3}{2})_k(-1)^k}{(1)_k(n+\frac{3}{2}-m)_k(n+\nu+m+\frac{3}{2})_k 2^{2k}}$$
$$\times {}_4F_3\left[\begin{matrix} k+n+\frac{1}{2}, k+n+1, k+n+\frac{3}{2}, k+n+\nu+1 \\ 2k+2n+2, k+n+\frac{3}{2}-m, k+n+m+\nu+\frac{3}{2}\end{matrix}; \ 1\right]$$
$$\equiv \sum_{m=0}^{\infty} S_m^{[n,p,\nu]} C_{2m}^{(\nu)}(x). \tag{A16}$$

When $p=0$, $(-p)_k = \delta_{k,0}$ and (A16) gives the expansion of ρ^{2n+1} which agrees with (A9) and (A13). For p a non-negative integer, the sum over k in (A16) is finite. Moreover, the hypergeometric series in (A15) and (A16) may be transformed into finite summations by standard techniques (Abbott 1986).

A3. Reductions required for σ_l^+

The reductions required relate to three special cases.

A3.1. $l=0$. For $l=0$, from (A1)

$$y = \frac{8}{3\pi}\sum_{m=0}^{\infty}\frac{(-\frac{1}{2})_m}{(\frac{5}{2})_m} C_{2m}^{(1)}(x) \tag{A17a}$$

$$1+\frac{x}{2}\ln\left(\frac{1-x}{1+x}\right) = {}_2F_1\left[\begin{matrix}-\frac{1}{2}, 1\\ \frac{1}{2}\end{matrix}; \ x^2\right] = \frac{2}{3}\sum_{m=0}^{\infty}\frac{(-\frac{1}{2})_m(\frac{3}{2})_m}{(\frac{1}{2})_m(\frac{5}{2})_m} C_{2m}^{(1)}(x) \tag{A17b}$$

$$|x| = \frac{4}{3\pi}\sum_{m=0}^{\infty}\frac{(-\frac{1}{2})_m(\frac{3}{2})_m}{(\frac{1}{2})_m(\frac{5}{2})_m}(-1)^m C_{2m}^{(1)}(x) \tag{A17c}$$

$$|x|\ln(1-x^2) = \frac{-8}{15\pi}\sum_{m=0}^{\infty}\frac{(-\frac{3}{2})_m(\frac{3}{2})_m}{(\frac{1}{2})_m(\frac{7}{2})_m}(-1)^m {}_3F_2\left[\begin{matrix}1, 1, \frac{5}{2}\\ \frac{5}{2}-m, m+\frac{7}{2}\end{matrix}; \ 1\right] C_{2m}^{(1)}(x) \tag{A17d}$$

$$\frac{(1-2y^2)\alpha}{y} = (1-2y^2)\,{}_2F_1\left[\begin{matrix}\frac{1}{2}, \frac{1}{2}\\ \frac{3}{2}\end{matrix}; \ y^2\right] = \frac{-2}{\pi}\sum_{m=0}^{\infty}\left(\frac{(-\frac{1}{2})_m^2}{(\frac{1}{2})_m^2} + \frac{(\frac{3}{2})_m^2}{9(\frac{5}{2})_m^2}\right)(-1)^m C_{2m}^{(1)}(x). \tag{A17e}$$

The derivation of (A17*e*) uses the contiguous relations for GHS (Rainville 1960, p 80). By reducing equation (93) to its simplest form it may be verified that

$$\frac{D_{4m0}^+}{(2m-1)(2m+3)} = \frac{-1}{3\pi}\frac{(-\frac{1}{2})_m}{(\frac{5}{2})_m} - \frac{(-\frac{1}{2})_m(\frac{3}{2})_m}{6(\frac{1}{2})_m(\frac{5}{2})_m} + \frac{(-1)^m(-\frac{1}{2})_m(\frac{3}{2})_m}{6\pi(\frac{1}{2})_m(\frac{5}{2})_m}$$
$$+\frac{(-1)^m}{4\pi}\left(\frac{(-\frac{1}{2})_m^2}{(\frac{1}{2})_m^2} + \frac{(\frac{3}{2})_m^2}{9(\frac{5}{2})_m^2}\right)$$
$$-\frac{(-1)^m(-\frac{3}{2})_m(\frac{3}{2})_m}{15\pi(\frac{1}{2})_m(\frac{7}{2})_m}\,{}_3F_2\left[\begin{matrix}1, 1, \frac{5}{2}\\ \frac{5}{2}-m, m+\frac{7}{2}\end{matrix}; \ 1\right] \tag{A18}$$

and hence from (A17) and (A18)

$$\sigma_0^+ = \frac{\mu_S\mu_{12}}{12}\left[y+2+x\ln\left(\frac{1-x}{1+x}\right) - |x| + \frac{(1-2y^2)\alpha}{y} - |x|\ln(1-x^2)\right]. \tag{A19}$$

A3.2. $l=1$. For $l=1$, from (A1) and (A2)

$$\rho=\sum_{m=0}^{\infty} S_m^{[1]} C_{2m}^{(2)}(x) \tag{A20a}$$

$$\rho^2=\frac{5}{3}-\frac{32}{9\pi}+\sum_{m=1}^{\infty} S_m^{[2]} C_{2m}^{(2)}(x) \tag{A20b}$$

$$\rho^3=\sum_{m=0}^{\infty} S_m^{[3]} C_{2m}^{(2)}(x) \tag{A20c}$$

$$\ln(1+\rho^2)=\frac{5}{24}\,{}_4F_3\left[\begin{matrix}1,\frac{3}{2},\frac{7}{2},1\\ 2,4,2\end{matrix};\ 1\right]+\sum_{m=1}^{\infty} S_m^{[\ln]} C_{2m}^{(2)}(x) \tag{A20d}$$

$$\left(\frac{(1+2y^2)|x|\alpha}{y}-1\right)=\frac{1}{6\pi}+\sum_{m=1}^{\infty} S_m^{[\alpha]} C_{2m}^{(2)}(x) \tag{A20e}$$

where in (A20e) we have used 15.1.6 from Abramowitz and Stegun (1972, p 556) yielding

$$\frac{|x|\alpha}{y}=(1-y^2)\,{}_2F_1\left[\begin{matrix}1,1\\ \frac{3}{2}\end{matrix};\ y^2\right].$$

The $S_m^{[\ldots]}$ are given by

$$S_m^{[1]}=\frac{64(-\frac{1}{2})_m(\frac{1}{2})_m(2)_m}{45\pi(1)_m(\frac{5}{2})_m(\frac{7}{2})_m}\,{}_4F_3\left[\begin{matrix}\frac{1}{2},1,\frac{3}{2},3\\ 2,m+\frac{7}{2},\frac{3}{2}-m\end{matrix};\ 1\right]$$

$$S_m^{[2]}=\frac{(-1)^m(\frac{1}{2})_m^2}{2^{2m}(2)_m(\frac{3}{2})_m}\,{}_3F_2\left[\begin{matrix}m+1,m+\frac{1}{2},m+\frac{5}{2}\\ m+2,2m+3\end{matrix};\ 1\right]$$

$$S_m^{[3]}=\frac{32(-\frac{3}{2})_m(\frac{1}{2})_m(2)_m}{105\pi(1)_m(\frac{9}{2})_m(\frac{5}{2})_m}\,{}_3F_2\left[\begin{matrix}\frac{3}{2},2,\frac{5}{2}\\ m+\frac{9}{2},\frac{5}{2}-m\end{matrix};\ 1\right]$$

$$S_m^{[\ln]}=\frac{(-1)^{m+1}(\frac{3}{2})_m^2}{48\,2^{2m}(2)_m^2}\,{}_3F_2\left[\begin{matrix}m+1,m+\frac{3}{2},m+\frac{7}{2}\\ m+2,2m+5\end{matrix};\ 1\right]$$

$$S_m^{[\alpha]}=\frac{4(-1)^m(1)_m(\frac{3}{2})_m(3)_m^2}{15\pi(4)_m(\frac{7}{2})_m(2)_m^2}. \tag{A21}$$

It may be verified that for $m\geqslant 1$

$$\frac{D_{4m+2,1}^{+}}{2m(2m+4)}=\frac{-S_m^{[1]}}{4}+\frac{S_m^{[2]}}{2}-\frac{S_m^{[3]}}{12}+S_m^{[\ln]}+S_m^{[\alpha]}$$

and hence from (A20) and (A21) we have

$$\sigma_1^{+}=\frac{-2\mu_{\mathrm{S}}\mu_{12}}{3}\left(\frac{-\rho}{4}+\frac{\rho^2}{2}-\frac{\rho^3}{12}+\ln(1+\rho^2)+\frac{[(1+2y^2)|x|\alpha/y-1]}{\pi y^2}\right). \tag{A22}$$

A3.3. $l\geqslant 2$. From (A6) we have that

$${}_2F_1\left[\begin{matrix}(l-1)/2,(l+3)/2\\ l+\frac{3}{2}\end{matrix};\ y^2\right]=\frac{\Gamma(l+2)}{\Gamma((l+1)/2)\Gamma((l+5)/2)}$$
$$\times\sum_{m=0}^{\infty}\frac{((l-1)/2)_m((l+3)/2)_m^2(\frac{1}{2})_m(-1)^m}{(l+\frac{3}{2})_m((l+1)/2)_m^2((l+5)/2)_m}\,C_{2m}^{(l+1)}(x). \tag{A23}$$

It may be verified that

$$\frac{D^+_{4m+2l,l}}{(2m+l-1)(2m+l+3)} = -2^{-l}\left[\frac{\Gamma(l-1)\Gamma(l+2)((l-1)/2)_m((l+3)/2)^2_m(\frac{1}{2})_m(-1)^m}{\Gamma(l+\frac{1}{2})\Gamma(l/2+1)\Gamma((l+5)/2)(l+\frac{3}{2})_m((l+1)/2)^2_m((l+5)/2)_m} - \left(\frac{2S_m^{[l-1,l+1]}}{l(l-1)} + \frac{S_m^{[l,l+1]}}{l} + \frac{2S_m^{[1,l-1,l+1]}}{(l+1)(l+2)} - \frac{S_m^{[0,l,l+1]}}{(l+1)}\right)\right]$$

and hence from (A15), (A16) and (A23)

$$\sigma_l^+ = \frac{2^{1-l}\mu_S\mu_{12}}{3}\left\{(1+\rho^2)^{l-1}\left[\left(\frac{1}{l}-\frac{2}{l-1}\right)+\frac{\rho}{l+1}-\frac{\rho^2}{l}+\left(\frac{2}{l+2}-\frac{1}{l+1}\right)\rho^3\right] + \frac{\Gamma(l-1)\Gamma((l+1)/2)}{\Gamma(l+\frac{1}{2})\Gamma(l/2+1)}\,{}_2F_1\left[\begin{matrix}(l-1)/2,\,(l+3)/2\\ l+\frac{3}{2}\end{matrix};\ y^2\right]\right\}. \tag{A24}$$

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