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Coordinate systems and analytic expansions for three-body atomic wavefunctions: II. Closed form wavefunction to second order in r

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Abstract. Several coordinate systems for solving the few-electron Schrödinger equation are presented. Formal solutions corresponding to each coordinate system are given in terms of the Fock expansion and their interrelationships and general structure are examined. Attention is focused on the solutions obtained using spherical polar coordinates for a Coulomb potential of arbitrary symmetry. The wavefunction is obtained up to second order in the hyperradius $r=(r_1^2+r_2^2)^{1/2}$, and the special case of ^{1}S states is then reduced to a closed form using classical techniques. The insight gained from this reduction suggests methods for solving the wavefunction to all orders. The results hint at the existence of closed form wavefunctions for few-body systems.

1. Introduction

Closed form helium wavefunctions have been discussed since the Schrödinger equation (SE) was postulated. After Bartlett *et al* (1935) showed that the ^{1}S helium wavefunction could not be expanded as an analytic series in interparticle coordinates, more emphasis was placed on approximate techniques. However Bartlett (1937) and Fock (1954, 1958) proposed a formally correct expansion for solving the SE for ^{1}S He, utilising hyperspherical coordinates (HC), by including logarithmic functions of the hyperradius. Ermolaev (1958) and Demkov and Ermolaev (1959) extended the Fock expansion (FE) to the N-electron SE. Recently Leray (1982a, b, 1983, 1984) and Morgan (1986) have rigorously justified the FE using functional analytic methods.

Newman (1973) modified the FE and, working in spherical polar coordinates (SPC), converted the SE to a recurrence relation with derivative continuity as an additional boundary condition. Newman did not attempt algebraic summation of his expansion. However, his series may be summed by analytic techniques and progress in this direction is presented here.

Pluvinage (1982, 1985), also working in SPC, solved the FE to second order in r not by conversion into a recurrence relation but instead, using a partial separation of variables, reduced the equations to be solved to ordinary second-order differential equations in one variable. This method is incorporated in recent work by Gottschalk and Maslen (1987).

Previously, workers in this area have resorted to approximate techniques when they considered that further algebraic simplification was unlikely. However this paper illustrates that the wavefunction to second order in r may be completely reduced to a

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finite sum of polynomial and logarithmic functions of the interparticle coordinates in addition to one irreducible integral. This reduction removes the convergence problems of infinite series expansions. Work in progress indicates similar, though algebraically more difficult, simplification for the third-order wavefunction. Moreover, the relative simplicity of the final results hints at the existence of straightforward techniques for obtaining the wavefunction to all orders.

In the preceding paper (Abbott and Maslen 1987, to be referred to hereafter as I), HC systems for treating the few-body SE were described and analytic methods for treating the wavefunction by expansion into an infinite series of hyperspherical harmonics (HH) were presented. In § 2 alternative coordinate systems for solving the SE are introduced. Formal solutions to the few-body wavefunctions are examined in § 3. The analytic structure of few-body wavefunctions is discussed in § 4. Using SPC the ^{1}S wavefunction to second order in r is written in closed form (§§ 5 and 6). The closed form expression is then studied to provide further information on the derivation of the wavefunctions to all orders in § 7.

2. Coordinate systems

This section collects together the properties of several coordinate systems that are widely used for treating the few-body SE. As discussed in I, different coordinate systems have advantages when treating specific aspects of few-body wavefunctions.

2.1. Cartesian coordinates

In the fixed nucleus approximation, the positions of N electrons require $n=3N$ coordinates. In cartesian coordinates, the configuration of the electrons is specified by an n-dimensional vector, $\boldsymbol{r}=(x_1, x_2, \ldots, x_n)\equiv(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ where $\boldsymbol{r}_i\in\mathbb{R}^3$ is the position vector of each electron. However, since the Coulomb potential is rotationally invariant under SO(3), the Laplacian $\Delta_n=\Sigma\,\partial^2/\partial x_i^2$ is more conveniently factored into operators consistent with this invariance.

2.2. Spherical polar coordinates

SPC are trivially generalised to $N>1$. Specifying the position of each electron by its own SPC, $\boldsymbol{r}_i=(r_i, \theta_i, \phi_i)$, the n-dimensional Laplacian becomes $\Delta_n=\Sigma\Delta_i$, where

$$\Delta_i = r_i^{-2}\frac{\partial}{\partial r_i}r_i^2\frac{\partial}{\partial r_i} - r_i^{-2}l_i^2(\theta_i, \phi_i) \tag{1}$$

and

$$l_i^2(\theta_i, \phi_i) = -\left((\sin\theta_i)^{-1}\frac{\partial}{\partial\theta_i}\sin\theta_i\frac{\partial}{\partial\theta_i} + (\sin\theta_i)^{-2}\frac{\partial^2}{\partial\phi_i^2}\right). \tag{2}$$

Here l_i^2 is the squared (ordinary) angular momentum operator. For details on the SE in SPC see Newman (1973), Pluvinage (1982), Davis and Maslen (1982, 1983a, b, c) and Gottschalk and Maslen (1985).

2.3. Internal and external coordinates

Hylleraas (1928) commenced his treatment of helium, $N=2$, in SPC. He showed that the six coordinates 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. The external coordinates are usually chosen to be the Eulerian angles (α, β, γ) specifying the orientation of the principal axes of inertia of the three particles with respect to a space-fixed coordinate frame (Kalotas 1965, Johnson 1980). Moreover, a rotationally invariant potential only depends on the internal coordinates. For example, choosing the internal coordinates to be r_1, r_2 and θ, the angle subtended at the nucleus by the two electrons, the wavefunction may be written in the separable form:

$$\Psi_{LM}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{K=-L}^{L} \Psi_L^K(r_1, r_2, \theta) D^L{}_{MK}(\alpha, \beta, \gamma) \tag{3}$$

where the $D^L{}_{MK}$ are rotation matrices which are eigenfunctions of the total angular momentum operator (see I, equation (8)). Restricting attention to S states, $L = M = 0$, one need not consider the external coordinates and the Laplacian becomes (Breit 1930)

$$\Delta = r_1^{-2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + r_2^{-2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + [r_1^{-2} + r_2^{-2}](\sin\theta)^{-1}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}. \tag{4}$$

Note that the partitioning of the coordinates is reflected in the simple form of the wavefunction (3) and the Laplacian (4). This analysis may be generalised to lithium ($N = 3$). After removal of the motion of the centre of mass, nine coordinates are required. It is easily seen that there are six internal coordinates and three external coordinates since the Coulomb potential, which depends on all internal coordinates, is a function of r_1, r_2, r_3, r_{12}, r_{13} and r_{23} in obvious notation. The three external coordinates may also be realised by Eulerian angles, in this case describing the orientation of the tetrahedron formed by the nucleus and the three electrons (Kalotas *et al* 1968).

For general $N \geq 2$ there are three external, $3N-3$ internal coordinates and $N(N+1)/2$ interparticle coordinates (IC). For $N \geq 4$, $N(N+1)/2 > 3N-3$ and some of the IC are redundant. Note that partitioning into internal and external coordinates automatically yields states with good angular momentum. For any other partition the total angular momentum must be constructed by standard coupling techniques (Morse and Feshbach 1953).

2.4. Interparticle and elliptic coordinates

In his classic paper, Hylleraas (1929) examined the S-state wavefunction of helium using IC, r_1, r_2 and r_{12}. In these coordinates the S-state Laplacian (4) becomes

$$\begin{aligned}\Delta = {} & r_1^{-2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + r_2^{-2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + 2r_{12}^{-2}\frac{\partial}{\partial r_{12}} r_{12}^2 \frac{\partial}{\partial r_{12}} \\ & + \frac{(r_1^2 + r_{12}^2 - r_2^2)}{r_1 r_{12}} \frac{\partial^2}{\partial r_1\, \partial r_{12}} + \frac{(r_2^2 + r_{12}^2 - r_1^2)}{r_2 r_{12}} \frac{\partial^2}{\partial r_2\, \partial r_{12}}\end{aligned} \tag{5}$$

in which the functions multiplying the cross-terms have a simple interpretation. By examining figure 1, it is seen that

$$\cos\theta_1 = (r_1^2 + r_{12}^2 - r_2^2)/2r_1 r_{12}$$

and

$$\cos\theta_2 = (r_2^2 + r_{12}^2 - r_1^2)/2r_2 r_{12}.$$

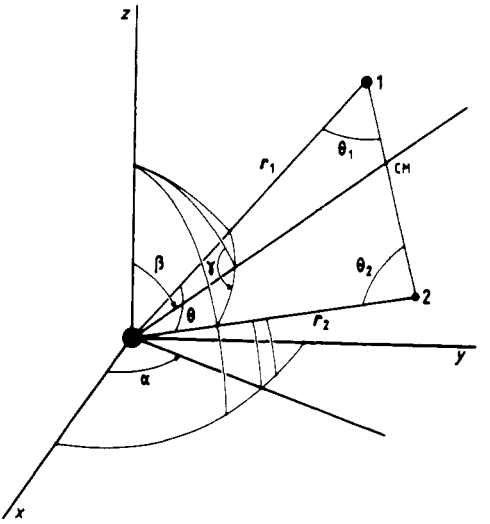

Figure 1. Specification of the Eulerian angles (α, β, γ) and the internal angles θ, θ_1 and θ_2. CM indicates the centre of mass of particles 1 and 2.

Hylleraas, realising that the helium wavefunction has definite symmetry under particle interchange, introduced the elliptic coordinates (EC)

$$s = r_1 + r_2 \qquad t = r_1 - r_2 \qquad u = r_{12} \tag{6}$$

which reflect this symmetry. Following Hylleraas (1932), the S-state Laplacian in EC becomes

$$\Delta = 2\left[\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + u^{-2}\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u} + \frac{4}{(s^2-t^2)}\left(s\frac{\partial}{\partial s} - t\frac{\partial}{\partial t}\right)\right.$$
$$\left. + \frac{2}{u(s^2-t^2)}\left(s(u^2-t^2)\frac{\partial^2}{\partial s\,\partial u} - t(u^2-s^2)\frac{\partial^2}{\partial t\,\partial u}\right)\right]. \tag{7}$$

2.5. Hyperspherical coordinates

The use of HC for few-body wavefunctions is discussed in I. Here we restrict attention to $N = 2$ and choose the HC r, α, θ as the internal coordinates, where

$$r = (r_1^2 + r_2^2)^{1/2} \qquad y = \sin\alpha = 2r_1r_2/r^2. \tag{8}$$

3. Formal solutions to the Schrödinger equation

A formal solution to the SE is defined to be an expansion that is capable of satisfying the SE term by term, without requiring the physical boundary conditions to be satisfied. Some expansions can be ruled out by general considerations. For instance Bartlett *et al* (1935) showed that power series solutions in IC were inadequate for helium. A formal solution cannot be an eigenfunction unless it is capable of satisfying the physical boundary conditions. These physical boundary conditions are discussed in Kato (1957) and Abbott (1986).

3.1. The Fock expansion in hyperspherical coordinates r, α, θ

Bartlett (1937) and later Fock (1954, 1958) propòsed a formal solution for the ^{1}S states of helium in HC, now known as the FE, which is

$$\Psi(r, \alpha, \theta) = \sum_{k=0}^{\infty} r^k \sum_{m=0}^{[k/2]} \ln^m r \Psi_{km}(\alpha, \theta). \tag{9}$$

Expanding $\Psi_{km}(\alpha, \theta)$ in hyperspherical harmonics (HH) as discussed in I, one obtains

$$\Psi_{km}(\alpha, \theta) = \sum_{nl} \mathscr{C}_{knlm} Y_{nl}(\alpha, \theta). \tag{10}$$

Recently Leray (1982a, b, 1983, 1984) outlined a proof that every solution of the N-electron SE may be written in the form of the FE. Morgan (1986), generalising the work of Macek (1967), proved that, for the S states of helium, the FE converges pointwise for all r. These results are examined in more detail in Abbott (1986).

3.2. Formal solution in spherical polar coordinates r_1, r_2 and $P_l(\Omega)$

In SPC the three internal coordinates are chosen as r_1, r_2 and $\Omega = \cos\theta$. Following Newman (1973) and Davis and Maslen (1982) the formal solution to the SE in SPC, termed the NDM expansion, is written in the region-dependent form:

$$\Psi(r_1, r_2, \Omega) = \begin{cases} \exp(-\lambda_1 r_1 - \lambda_2 r_2) \sum_{ijlp} C_{ijlp} r_1^i r_2^j [\exp(qr_1)\mathrm{Ei}(-qr_1)]^p P_l(\Omega)/p! & r_1 > r_2 \\ \exp(-\lambda_2 r_1 - \lambda_1 r_2) \sum_{ijlp} C'_{ijlp} r_1^j r_2^i [\exp(qr_2)\mathrm{Ei}(-qr_2)]^p P_l(\Omega)/p! & r_1 < r_2 \end{cases} \tag{11}$$

where l, p, $q \geqslant 0$ and $i + j \geqslant 0$, $j \geqslant l$. Note that the expansion (11) depends on the ratio r_1/r_2. For $q = 0$, the exponential integral term (Abramowitz and Stegun 1972) $\exp(qr)\mathrm{Ei}(-qr)$ is replaced by $\ln r$. The exponential terms multiplying the summations in (11) are included so that the asymptotic form may be factored from the wavefunction (Fock 1954, 1958, Ermolaev 1961, Morgan 1977, Davis and Maslen 1982, 1983b). Setting $q = 0$, $\lambda_1 = \lambda_2 = 0$, $r_> = \max\{r_1, r_2\}$, $r_< = \min\{r_1, r_2\}$ and

$$\mathbb{C}_{ijlp} = \begin{cases} C_{ijlp} & r_1 > r_2 \\ C'_{ijlp} & r_1 < r_2 \end{cases}$$

one may write

$$\Psi(r_1, r_2, \Omega) = \sum_{ijlp} \mathbb{C}_{ijlp} r_>^i r_<^j (\ln r_>)^p P_l(\Omega)/p!. \tag{12}$$

For $q > 0$ (Abramowitz and Stegun 1972, p 228)

$$\mathrm{Ei}(-qr) = \gamma + \ln(qr) + \sum_{n=1}^{\infty} \frac{(-qr)^n}{nn!}$$

where γ is Euler's constant and, using series rearrangement, the NDM expansion (11) may be written in the form of the FE (9) and (10). Hence the two expansions are formally equivalent. Note, however, that using $\mathrm{Ei}(-qr)$ instead of $\ln r$ removes the (unphysical) zero of the logarithmic terms of the FE at $r = 1$, since $\mathrm{Ei}(-qr) < 0$ for $r \geqslant 0$.

3.3. Fock expansion in the coordinates r, y and Ω

One system, currently being studied, utilises r, y and Ω (for symmetric states only). The wavefunction may be expanded as

$$\Psi(r, y, \Omega) = \sum_{ijkp} D_{ijkp} y^i \Omega^j r^k (\ln r)^p. \tag{13}$$

To transform between the different formal expansions (9), (11)-(13), one notes that r_1, r_2 and r each have the dimension of length, and hence $k = i + j$. The logarithmic function may be considered formally homogeneous of degree zero in r and thus does not have dimensions. Note that all expansions are to be solved in order of increasing k and decreasing p or m. Comparison of expansions for the wavefunction derived using different internal coordinates involves comparing terms with the same value of k.

Writing $\rho = r_< / r_>$ then

$$\ln r = \ln r_> + \tfrac{1}{2} \ln(1 + \rho^2). \tag{14}$$

Using (9), (10), (12), (14) and I the transformation between $\mathbb{C}_{ijlp}$ and $\mathscr{C}_{knlm}$ may be obtained. Since $Y_{nl}(\alpha, \theta)$, defined in I, is proportional to $P_l(\Omega)$, the transformation between (10) and (11), (12) for each value of l is trivial. However this relationship does not hold for an arbitrary set of internal coordinates.

4. Analytic structure of few-body atomic wavefunctions

The analytic structure of few-body atomic wavefunctions may be discussed in terms of region dependence (§ 4.1), continuity and derivative continuity (§§ 4.2 and 4.4) and symmetry and antisymmetry (§ 4.3).

4.1. Region-dependent expansions

Before examining the NDM expansion, it is helpful to consider the archetypal case of the Laplace expansion of $1/r_{12} = 1/(r_> R)$ where $R = (1 - 2\Omega\rho + \rho^2)^{1/2}$, into Legendre polynomials (Gradshteyn and Ryzhik 1980, p 1027), namely

$$r_{12}^{-1} = \begin{cases} r_1^{-1} \sum_{l=0}^{\infty} \left(\dfrac{r_2}{r_1}\right)^l P_l(\Omega) & r_1 > r_2 \\ r_2^{-1} \sum_{l=0}^{\infty} \left(\dfrac{r_1}{r_2}\right)^l P_l(\Omega) & r_1 < r_2 \end{cases} \equiv r_>^{-1} \sum_{l=0}^{\infty} \rho^l P_l(\Omega). \tag{15}$$

The expansion (15) is uniformly convergent for $\Omega \in [-1, 1]$, $\rho \in [0, R]$ with $R < 1$ and absolutely convergent for $\Omega \in [-1, 1]$ with $\rho \in [0, 1)$. For $\Omega \in (-1, 1)$, $\rho = 1$ it is pointwise convergent. For $\Omega = -1$, $\rho = 1$ it is Abel summable and does not converge for $\Omega = 1$, $\rho = 1$.

Alternatively, using $r_{12} = r(1 - y\Omega)^{1/2}$, expanding r_{12}^{-1} as hypergeometric series in Ω (Srivastava and Manocha 1984, p 281) yields

$$r_{12}^{-1} = r^{-1} \sum_{l=0}^{\infty} \left(\frac{y}{2}\right)^l {}_2F_1\left[\begin{matrix} l/2 + \frac{1}{4}, l/2 + \frac{3}{4} \\ l + \frac{3}{2} \end{matrix}; \; y^2\right] P_l(\Omega). \tag{16}$$

Generalised expansions which include (15) and (16) are given by Sack (1964). Furthermore, Sack shows that the transformation between region-dependent expansions like

(15) and region-independent expansions like (16) is given by a quadratic transformation of the (Gaussian) hypergeometric function in (16).

To make the relationship between (15) and (16) explicit we consider the quadratic transformation (Gradshteyn and Ryzhik 1980, p 1043)

$$ {}_2F_1\left[\begin{matrix} a, b \\ a+b+\frac{1}{2}; \end{matrix} \quad 4z(1-z)\right] = {}_2F_1\left[\begin{matrix} 2a, 2b \\ a+b+\frac{1}{2}; \end{matrix} \quad z\right] \tag{17} $$

where z is complex. The region of analyticity of each ${}_2F_1$ is shown in figure 2. Figure 2 and (17) show that for $x \in \mathbb{R}$

$$ {}_2F_1\left[\begin{matrix} a, b \\ a+b+\frac{1}{2}; \end{matrix} \quad 4x(1-x)\right] = \begin{cases} {}_2F_1\left[\begin{matrix} 2a, 2b \\ a+b+\frac{1}{2}; \end{matrix} \quad x\right] & x \in [0, \frac{1}{2}) \\ {}_2F_1\left[\begin{matrix} 2a, 2b \\ a+b+\frac{1}{2}; \end{matrix} \quad 1-x\right] & x \in (\frac{1}{2}, 1]. \end{cases} \tag{18} $$

The left-hand hypergeometric in (17) is invariant under $z \to 1 - z$ whereas the right-hand hypergeometric is not. However both sides of (18) are invariant under $x \to 1 - x$.

To make (18) physically significant we put $x = (r_2/r)^2$. Hence $4x(1-x) = y^2$ and $x \in [0, \frac{1}{2})$ corresponds to $r_1 > r_2$, $x \in (\frac{1}{2}, 1]$ to $r_1 < r_2$. Setting $a = l/2 + \frac{1}{4}$, $b = l/2 + \frac{3}{4}$ leads to

$$ {}_2F_1\left[\begin{matrix} l/2+\frac{1}{4}, l/2+\frac{3}{4} \\ l+\frac{3}{2} \end{matrix}; \quad y^2\right] = \begin{cases} (r/r_1)^{2l+1} & r_1 > r_2 \\ (r/r_2)^{2l+1} & r_1 < r_2 \end{cases}. \tag{19} $$

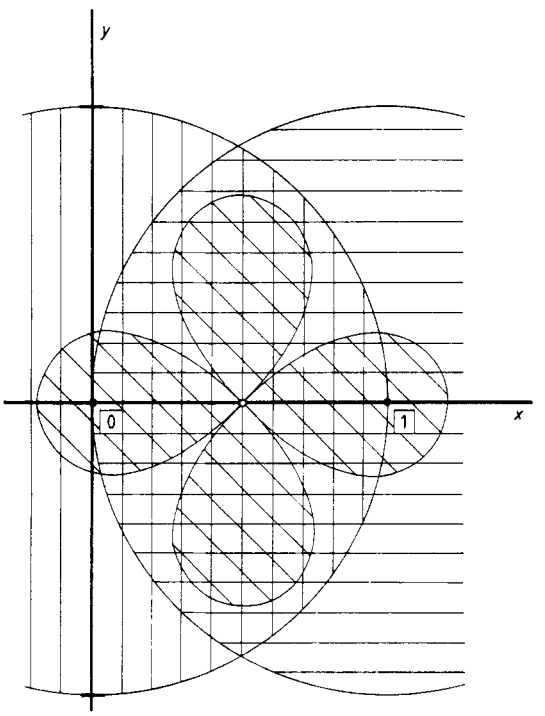

Figure 2. Regions $|z| \leq 1$ ▥, $|1-z| \leq 1$ ▤ and $|4z(1-z)| \leq 1$ ▧.

Substituting (19) into (16) yields (15). This transformation is typical of those found in the expansions of many-body wavefunctions. A region-dependent form is often simpler analytically, as the right-hand side of (19) demonstrates.

4.2. Continuity and derivative continuity of the wavefunction

When a non-physical boundary is introduced into an expansion of a well behaved function, continuity and derivative continuity are required at the boundary. In the case of a many-body system, the wavefunction and its derivatives are continuous except at the points where particles coalesce, namely $\boldsymbol{r}_1 = \boldsymbol{r}_2$, $r_1 = 0$ or $r_2 = 0$ (Kato 1957). At these coalescences, the wavefunction and its derivatives satisfy cusp conditions (Pack and Byers-Brown 1966). However, for all r_1, $r_2 \neq 0$ and $\theta \neq 0$, the wavefunction and its derivatives are continuous. Commencing with the region-dependent NDM expansion, Gottschalk and Maslen (1985) derived the continuity and derivative continuity conditions satisfied by C_{ijlp} and C'_{ijlp}. In contrast, the HH $Y_{nl}(\alpha, \theta)$ and their derivatives are finite and continuous on the hypersphere. Hence the region-independent expansion (10) has continuous derivatives everywhere except for the particle coalescences and there are no continuity or derivative continuity conditions applying to $\mathscr{C}_{knlm}$.

Care is required in obtaining continuity conditions for region-dependent forms, as Dirac delta functions may appear when differentiating the expansions term by term. For instance, the derivative of the Heaviside step function is the Dirac delta function (Schiff 1968, p 306).

Consider r_{12}^{-1}; from (15) it is seen that

$$\left.\frac{\partial r_{12}^{-1}}{\partial r_1}\right|_{r_1 \to r_2} = \begin{cases} -\dfrac{1}{r_2^2}\displaystyle\sum_{l=0}^{\infty}(l+1)P_l(\Omega) & r_1 \to r_2^+ \qquad (20a) \\ \dfrac{1}{r_2^2}\displaystyle\sum_{l=1}^{\infty} lP_l(\Omega) & r_1 \to r_2^-. \qquad (20b) \end{cases}$$

Both sums are divergent in the usual sense. However they have meaning in the space of generalised functions (Kay *et al* 1969). Here these limits are equal; subtracting (20*a*) from (20*b*) involves (Schiff 1968, p 143)

$$\sum_{l=0}^{\infty}(2l+1)P_l(\Omega) = 4\delta(1-\Omega). \qquad (21)$$

For $\Omega \neq 1$, (21) is zero and hence $\partial r_{12}^{-1}/\partial r_1$ is continuous at $r_1 = r_2$. Furthermore, the presence of delta functions indicates that the convergence near $\boldsymbol{r}_1 = \boldsymbol{r}_2$ will be slow. This is expected as r_{12}^{-1} is infinite and $\partial r_{12}^{-1}/\partial r_1$ is discontinuous near $\boldsymbol{r}_1 = \boldsymbol{r}_2$ (Lakin 1965). In comparison, using the region-independent expansion (16) one finds that

$$\left.\frac{\partial r_{12}^{-1}}{\partial r_1}\right|_{r_1 \to r_2} = -\frac{1}{2r_2^2}\sum_{l=0}^{\infty}P_l(\Omega). \qquad (22)$$

Series (20*a*) equals (20*b*) except for $\Omega = 1$, from (21) above, and thus by adding (20*a*) and (20*b*), (22) is seen to be equivalent to (20). Furthermore (15) shows that (20*a*), (20*b*) and (22) are all equal to $-2^{-3/2}r_2^{-2}(1-\Omega)^{-1/2}$ for $\Omega \neq 1$.

These characteristics of region-dependent and independent expansions of r_{12}^{-1} are typical of many-particle wavefunctions.

4.3. Symmetry and antisymmetry of the wavefunction

For a symmetric potential the wavefunction has definite symmetry. However, using a general Coulomb potential for a system of nuclear charge Z and N charges Z_i

$$V = \sum_{i=1}^{N} \frac{\mu_i}{r_i} + \sum_{i<j=1}^{N} \frac{\mu_{ij}}{r_{ij}} \qquad \mu_i = ZZ_i,\ \mu_{ij} = Z_iZ_j \tag{23}$$

leads to asymmetric states. It is desirable to decompose these into symmetric and antisymmetric pieces. Two points are especially relevant to the discussion of many-body wavefunctions.

(i) Infinite expansions of symmetric or antisymmetric functions may not possess the same symmetry as the individual terms. This depends in particular on the domain within which the expansion is defined.

(ii) An antisymmetric function may be made to appear symmetric by taking its absolute value. Square roots with fixed sign lead to absolute value functions.

Consider the Coulomb potential (23) for $N=2$:

$$V(r_1, r_2, r_{12}) = \frac{\mu_1}{r_1} + \frac{\mu_2}{r_2} + \frac{\mu_{12}}{r_{12}} \equiv \left(\frac{\mu_S(r_1+r_2)}{r_1r_2} + \frac{\mu_{12}}{r_{12}}\right) - \frac{\mu_A(r_1-r_2)}{r_1r_2} \tag{24}$$

where $\mu_S = (\mu_1+\mu_2)/2$ and $\mu_A = (\mu_1-\mu_2)/2$. This factorisation clearly displays the symmetry of the terms in (24). Using (24) is no more complicated than working with a symmetric potential. Moreover, the final result includes all the special cases of interest. To preserve invariance of the potential (24) under the interchange of r_1 and r_2 one must also swap μ_1 and μ_2. This must apply when transforming a region-dependent expansion of the wavefunction for $r_1 > r_2$ into one for $r_1 < r_2$.

For example, in §6 the region-dependent expansion for $r_1 > r_2$, $k=2$, $l \geqslant 2$ contains

$$r^2(\mu_1+\mu_2)y^l\,{}_2F_1\left[\begin{matrix} l/2-\frac{1}{2},\ l/2+\frac{3}{2} \\ l+\frac{3}{2} \end{matrix};\ y^2\right] \tag{25}$$

and

$$r^2(\mu_1-\mu_2)y^l\,{}_2F_1\left[\begin{matrix} l/2-\frac{1}{2},\ l/2+\frac{3}{2} \\ l+\frac{3}{2} \end{matrix};\ y^2\right]. \tag{26}$$

Both (25) and (26) appear superficially to be symmetric. Note that (25) is region independent, but for $r_1 < r_2$ (26) is multiplied by -1. This region dependence can be removed by using Euler's transformation for Gaussian hypergeometric functions (Rainville 1960, p 60) and

$$(1-y^2)^{1/2} \equiv |r_1^2 - r_2^2|/r^2$$

yielding

$${}_2F_1\left[\begin{matrix} l/2-\frac{1}{2},\ l/2+\frac{3}{2} \\ l+\frac{3}{2} \end{matrix};\ y^2\right] = \frac{|r_1^2-r_2^2|}{r^2}\,{}_2F_1\left[\begin{matrix} l/2,\ l/2+2 \\ l+\frac{3}{2} \end{matrix};\ y^2\right].$$

Hence (26) becomes

$$(\mu_1-\mu_2)(r_1^2-r_2^2)y^l\,{}_2F_1\left[\begin{matrix} l/2,\ l/2+2 \\ l+\frac{3}{2} \end{matrix};\ y^2\right] \tag{27}$$

which is antisymmetric and region independent. Note that $(\mu_1-\mu_2)|r_1^2-r_2^2|$ for $r_1 > r_2$ is just $(\mu_1-\mu_2)(r_1^2-r_2^2)$ and for $r_1 < r_2$ becomes $(\mu_2-\mu_1)|r_1^2-r_2^2|$ which also equals $(\mu_1-\mu_2)(r_1^2-r_2^2)$.

The Euler transformation is not valid for $r_1 = r_2$ and in the limit $r_1 \to r_2$ the ${}_2F_1$ in (27) is divergent. However the correct limit can be obtained from the original series (26) yielding

$$\frac{(\mu_1 - \mu_2)2r_2^2\Gamma(l+\frac{3}{2})\Gamma(\frac{1}{2})}{\Gamma(l/2+2)\Gamma(l/2)}.$$

4.4. Derivative continuity of the Fock expansion in HC

The Fock expansion in HC requires no additional derivative continuity conditions (§ 4.2). From I the $k=2$ term of the wavefunction, Ψ_{20}, contains $|x| = |r_1^2 - r_2^2|/r^2$, $\alpha = \sin^{-1} y$ and $\rho = r_</r_>$ that separately have discontinuous derivatives. However

$$\left.\frac{\partial |x|}{\partial r_1}\right|_{r_1 \to r_2} = \begin{cases} r_2^{-1} & r_1 \to r_2^+ \\ -r_2^{-1} & r_1 \to r_2^- \end{cases}$$

$$\left.\frac{\partial}{\partial r_1}\left(\frac{(1-2y^2)\alpha}{y}\right)\right|_{r_1 \to r_2} = \begin{cases} r_2^{-1} & r_1 \to r_2^+ \\ -r_2^{-1} & r_1 \to r_2^- \end{cases}$$

and hence $(1-2y^2)\alpha/y - |x|$ has a continuous derivative. Derivative continuity is satisfied for the region-independent Fock expansion generally, even though the partial summations in I contain terms that are separately region dependent and possess discontinuous derivatives. This provides a useful check on the results presented in I and is helpful when examining higher k lines.

5. The wavefunction in spherical polar coordinates

The wavefunction in HC has been described in detail in I. Here we concentrate on SPC. The formal solution to the SE in SPC is given by (11). A recurrence equation for coefficients C_{ijlp} is obtained by substituting the trial solution (11) into the SE and equating the multipliers of powers of r_1, r_2 and $\exp(qr_1)\mathrm{Ei}(-qr_1)$ for each of the Legendre polynomials. The Coulomb potential in SPC requires the expansion of r_{12}^{-1} given by (15) or (16). To enable the indices of $P_l(\Omega)$ to be evaluated the product of Legendre polynomials is linearised (Gradshteyn and Ryzhik 1980, p 1026)

$$P_n(\Omega)P_m(\Omega) = \sum_l a_l^{mn} P_l(\Omega)$$

where $|n-m| \leqslant l \leqslant n+m$ and a_l^{mn} is a squared Clebsch-Gordan coefficient which may be evaluated yielding

$$a_l^{mm-s} = \frac{(2l+1)\Gamma(l/2-s/2+\frac{1}{2})\Gamma(l/2+s/2+\frac{1}{2})\Gamma(m+l/2-s/2+1)\Gamma(m-l/2-s/2+\frac{1}{2})}{2\pi\Gamma(l/2-s/2+1)\Gamma(l/2+s/2+1)\Gamma(m-l/2-s/2+1)\Gamma(m+l/2-s/2+\frac{3}{2})}.$$

Since the recurrence relation is obtained from term by term differentiation, the validity of the resulting solution must be justified. It is assumed that the solution is uniformly convergent in a region of non-zero size, permitting term by term differentiation in that region. The range of validity can be extended by analytic continuation to the interval for which the series solution converges. The form of the coefficients

presented later in this paper indicates that the solution obtained converges to the true wavefunction everywhere.

The recurrence equation does not specify all the coefficients. Most of these remaining are specified by the requirement that the wavefunction and its derivatives be continuous. If the potential multipliers μ_1 and μ_2 are equal, and the wavefunction is either symmetric or antisymmetric in r_1 and r_2, further coefficients are specified. The values of coefficients not yet determined are related to the normalisation of the wavefunction. To evaluate these algebraically requires a knowledge of the asymptotic form of the wavefunction, as described by Davis and Maslen (1982, 1983b) who calculated the coefficients for the ground state of helium numerically.

The equations specifying the coefficients, apart from those determined by normalisability, are summarised in the appendix. Using these equations any C_{ijlp} and C'_{ijlp} can be written as nested infinite sums, increasing in number with k. This procedure is suitable for numerical calculation but it is desirable to reduce the number of infinite series when the analytic form of the wavefunction is derived.

The coefficients with $k=0$ and $k=1$ follow from a straightforward application of equations (A1), (A2) and (A4). For $k=0$ $C'_{0000}=C_{0000}$. If μ_1 equals μ_2, and an antisymmetric wavefunction is required, $C_{0000}=0$; otherwise its value is determined when the wavefunction is normalised.

For $k=1$ the non-zero coefficients are

$$C_{1000}=(\lambda_1+\mu_1+\mu_{12}/2)C_{0000} \qquad C_{0100}=(\lambda_2+\mu_2)C_{0000} \qquad C_{-1200}=\mu_{12}/6C_{0000}$$
$$C_{1-ll10}=-\mu_{12}C_{0000}/[2(2l-1)] \qquad C_{-1-l+210}=\mu_{12}C_{0000}/[2(2l+3)] \qquad l\geqslant 1. \tag{28}$$

Coefficients C'_{ijlp} are the same as these with μ_1 and μ_2 interchanged (see § 4.3).

The $k=2$ coefficients with $l\geqslant 2$ are completely specified by (A1) and (A2). All coefficients with $p\geqslant 1$ vanish. To evaluate the $p=0$ coefficients the summation due to the interparticle potential terms in $R(2, l, g, 0)$ and $R'(2, l, g, 0)$ must be reduced. For $g\geqslant 4$ this potential term in $R(2, l, g, 0)$ is

$$-\mu_{12}^2/2C_{0000}\sum_{s=0}^{l} a_l^{s-1+g/2l-s-1+g/2}/(2l-2s-3+g)$$
$$+\mu_{12}^2/2C_{0000}\sum_{s=0}^{l} a_l^{s-2+g/2l-s-2+g/2}/(2l-2s-1+g). \tag{29}$$

Davis and Maslen (1983a) showed that the sum vanishes by repeated application of a binomial identity. A simpler proof involves writing (29) in terms of generalised hypergeometric functions (Bailey 1935):

$$\frac{C_{0000}\mu_{12}^2\Gamma(l+g/2)\Gamma(g/2-1)\Gamma(l+\frac{3}{2})}{2\Gamma(l+g/2)\Gamma(g/2)\Gamma(\frac{1}{2})l!(3-g-2l)}{}_3F_2\left[\begin{matrix}\frac{1}{2}, -l, \frac{3}{2}-g/2-l \\ \frac{5}{2}-g/2-l, \frac{1}{2}-l\end{matrix}; \quad 1\right]$$
$$\frac{-C_{0000}\mu_{12}^2\Gamma(l+g/2-1)\Gamma(g/2-2)\Gamma(l+\frac{3}{2})}{2\Gamma(l+g/2-1)\Gamma(g/2-1)\Gamma(\frac{1}{2})l!(1-g-2l)}{}_3F_2\left[\begin{matrix}\frac{1}{2}, -l, \frac{1}{2}-g/2-l \\ \frac{3}{2}-g/2-l, \frac{1}{2}-l\end{matrix}; \quad 1\right].$$

The ${}_3F_2(1)$ reduce to single terms using Saalschutz's theorem (Rainville 1960) and the sums of the ${}_3F_2$ vanish.

This result is important because it enables the infinite sum over g to be truncated. The zero value for this term results in $R(2, l, g, 0)$ and $R'(2, l, g, 0)$ being zero for $g\geqslant 5$.

This emphasises the need to simplify the infinite sums containing the Clebsch-Gordan coefficients associated with the potential term. The non-zero $l \geqslant 2$ coefficients are

$$C_{2-lll0} = -\mu_{12}\left(\frac{\mu_1}{6l(2l-1)} + \frac{\mu_1}{3(l-1)} + \frac{\lambda_1}{2(2l-1)}\right)C_{0000} + A(2, l, 0) \qquad l \geqslant 2$$

$$C_{1-ll+1l0} = -\mu_{12}\left(\frac{\mu_2}{2(l+1)(2l-1)} + \frac{\lambda_2}{2(2l-1)}\right)C_{0000} \qquad l \geqslant 0$$

$$C_{-ll+2l0} = \mu_{12}\left(\frac{\lambda_1}{2(2l+3)} - \frac{\mu_1}{2l(2l+3)}\right)C_{0000} + A(2, l, 2) \qquad l \geqslant 1$$

$$C_{-l-1l+3l0} = \mu_{12}\left[\frac{\lambda_2}{2(2l+3)} - \frac{\mu_2}{3(l+2)}\left(\frac{1}{2(l+1)} - 1 - \frac{1}{2(2l+3)}\right)\right]C_{0000} \qquad l \geqslant 0$$

$$C_{2-l-2nl+2nl0} = A(2, l, 2n) \qquad l \geqslant 0,\ n \geqslant 2 \tag{30}$$

where

$$A(2, l, 2n) = \frac{\mu_{12}(2l+1)(-1)^n \Gamma(n-\frac{3}{2})\Gamma(l+n-1)}{32\Gamma(\frac{1}{2})\Gamma(n+1)\Gamma(l+n+\frac{3}{2})}$$
$$\times\left((\mu_1+\mu_2)\frac{\Gamma(l/2+\frac{1}{2})}{\Gamma(l/2+1)} + 2(\mu_1-\mu_2)\frac{\Gamma(l/2+1)}{\Gamma(l/2+\frac{1}{2})}\right)C_{0000}.$$

When the $l = 0$ and 1 coefficients are calculated using (A1), (A3) and (A4) it is seen that the expressions for some $l \geqslant 2$ coefficients extend into the lower l values. The expression for $C_{2-l-2n\,2n+l10}$ is valid for all $l \geqslant 0$. This term also forms part of the expression for C_{2-lll0} and $C_{-ll+2l0}$. The other non-zero coefficients are

$$C_{2000} + C'_{2000} = \{\mu_{12}^2/6 + \mu_{12}[(3-\ln 2)(\mu_1+\mu_2) + 6\lambda_1]/6 + (\mu_1^2+\mu_2^2)/3 + (7\lambda_1^2+\lambda_2^2)/6$$
$$+ \lambda_1(\mu_1+\mu_2) - \varepsilon/3\}C_{0000}$$

$$C_{1100} = (\lambda_1+\mu_1)(\lambda_2+\mu_2)C_{0000} + \mu_{12}(\lambda_2+\mu_2)/2C_{0000}$$

$$C_{0200} = (\lambda_2+\mu_2)(2\lambda_2+\mu_2)/3C_{0000} + (\lambda_1+\mu_1)(2\lambda_1+\mu_1)/3C_{0000}$$
$$+ \mu_{12}[2\lambda_1 + \tfrac{3}{2}\mu_1 + 5(\pi-2)(\mu_1-\mu_2)/(12\pi)]/3C_{0000}$$
$$+ (\mu_{12}^2/6 - \varepsilon/3)C_{0000} - C_{2000}$$

$$C_{2001} = -\mu_{12}(\pi-2)(\mu_1-\mu_2)/(6\pi)C_{0000}$$

$$C_{0201} = \mu_{12}(\pi-2)(\mu_1-\mu_2)/(6\pi)C_{0000}$$

$$C_{1110} - C'_{1110} = -\mu_{12}(\mu_1-\mu_2)(3-2\ln 2)/6C_{0000}$$

$$C_{1111} = -\mu_{12}(2-\pi)(\mu_1+\mu_2)/(3\pi)C_{0000} \tag{31}$$

where $\varepsilon = E + \lambda_1^2/2 + \lambda_2^2/2$.

The values of C'_{ijlp} are obtained from the expression for C_{ijlp} by interchanging μ_1 and μ_2 in (30) and (31). The coefficients listed above specify the $k = 0$, 1 and 2 terms

in the three-particle S-state wavefunction (11) completely, except for the values determined by normalisation of the wavefunction.

6. Summation of series arising in the spherical polar expansion

The formal series (11) contains a fourfold summation. The sums over i, j and l are infinite while that over p is finite, terminating at $[k/2]$. It is desirable to express the wavefunction in a more compact form.

6.1. The $k=0$, 1 terms of the wavefunction

The $k=0$ series contains one term only. The $k=1$ series is reduced using the expansion

$$r_{12}=\sum_{l=0}^{\infty} P_l(\Omega)[r_2\rho^{l+1}(2l+3)^{-1}-r_1\rho^l(2l-1)^{-1}] \qquad r_1>r_2. \tag{32}$$

The $k=1$ terms in series (11) simplify to

$$C_{0000}[(\lambda_1+\mu_1)r_1+(\lambda_2+\mu_2)r_2+\mu_{12}r_{12}/2]\exp(-\lambda_1 r_1-\lambda_2 r_2) \qquad r_1>r_2 \tag{33}$$

in agreement with Slater (1968) and Abbott and Maslen (1986).

6.2. Reduction of the $k=2$ terms

The $k=2$ terms in (11),

$$\sum_{l,p=0}^{\infty}\sum_{j=l}^{\infty} C_{2-jjlp}r_1^{2-j}r_2^j[\exp(qr_1)\mathrm{Ei}(-qr_1)]^p P_l(\Omega)/p! \qquad r_1>r_2$$

separate into three main groups. The $l=0$ and 1 terms contain the infinite series, in hypergeometric notation,

$$\begin{aligned} &r_1^2 C_{0000}\rho^4\mu_{12}[2(\mu_1-\mu_2)+\pi(\mu_1+\mu_2)]_3F_2(1,1,\tfrac{1}{2};3,\tfrac{7}{2};-\rho^2)/(120\pi)\\ &\quad -r_1^2\Omega C_{0000}\rho^5\mu_{12}[2(\mu_1+\mu_2)+\pi(\mu_1-\mu_2)]_3F_2(1,2,\tfrac{1}{2};3,\tfrac{9}{2};-\rho^2)/(140\pi). \end{aligned} \tag{34}$$

There is no unified form for the coefficients C_{2-jjl0} with $l\geqslant 2$ and $j=l$, $l+1$, $l+2$ or $l+3$, but for $j\geqslant l+4$ all C_{2-jjl0} have the same form. The series

$$\sum_{l=2}^{\infty}\sum_{j=l}^{\infty} C_{2-jjl0}r_1^{2-j}r_2^j P_l(\Omega)$$

is best written in two parts:

$$\begin{aligned} -\mu_{12}C_{0000}\sum_{l=2}^{\infty}\Bigg\{&\left(\frac{\mu_1}{6l(2l-1)}+\frac{\mu_1}{3(l-1)}+\frac{\lambda_1}{2(2l-1)}\right)r_1^2\\ &+\left(\frac{\mu_2}{2(l+1)(2l-1)}+\frac{\lambda_2}{2(2l-1)}\right)r_1r_2-\left(\frac{\lambda_1}{2(2l+3)}-\frac{\mu_1}{2l(2l+3)}\right)r_2^2\\ &+\left[-\frac{\lambda_2}{2(2l+3)}+\frac{\mu_2}{3(l+2)}\left(\frac{1}{2(l+1)}-1-\frac{1}{2(2l+3)}\right)\right]r_2^3r_1^{-1}\Bigg\}\rho^l P_l(\Omega) \end{aligned} \tag{35}$$

and

$$\mu_{12}/12C_{0000}r_1^2 \sum_{l=2}^{\infty} \frac{\Gamma(l-1)\rho^l P_l(\Omega)}{\Gamma(l+\frac{1}{2})}\left[\frac{(\mu_1+\mu_2)\Gamma(l/2+\frac{1}{2})}{\Gamma(l/2+1)}+\frac{2(\mu_1-\mu_2)\Gamma(l/2+1)}{\Gamma(l/2+\frac{1}{2})}\right]$$

$$\times {}_2F_1\left[\begin{matrix}-\frac{3}{2}, l-1 \\ l+\frac{3}{2}\end{matrix}; \quad -\rho^2\right]. \tag{36}$$

The infinite series (34) may be related to hypergeometric functions of the type ${}_2F_1(1, a; a+1; z)$ by the use of the contiguous relation (Rainville 1960, p 82)

$$(a_i - a_j)F = a_i F(a_i+1) - a_j F(a_j+1)$$

where the abbreviated notation

$$F = {}_pF_q(a_1, a_2, \ldots, a_p; b_1, \ldots, b_q; z)$$

$$F(a_i+1) = {}_pF_q(a_1, \ldots, a_i+1, \ldots, a_p; b_1, \ldots, b_q; z)$$

has been used.

Abramowitz and Stegun (1972) list the evaluation of this ${}_2F_1$ in terms of logarithmic or $\tan^{-1}$ functions for particular values of a. This extends to more general values of a yielding

$${}_2F_1(1, a; a+1; z) = -az^{-a}\ln(1-z) - az^{-a}\sum_{i=0}^{a-2} z^{i+1}/(i+1)$$

where $a \in \mathbb{Z}^+$, $|z|<1$ or $z=-1$,

$${}_2F_1(1, a; a+1; -z^2) = 2az^{-2a}(-1)^{a-1/2}\tan^{-1} z + 2a(-z^2)^{1/2-a}\mathop{\mathscr{S}}_{i=a-1/2}^{-1}(-z^2)^i/(2i+1)$$

where $(2a) \in \mathbb{Z}$, but $a \notin \mathbb{Z}$, $|z| \leqslant 1$. $\mathscr{S}_{r=p}^{q-1}$ is the *generalised sum* interpreted as $\Sigma_{r=p}^{q-1}$ for $p<q$, $-\Sigma_{r=q}^{p-1}$ for $p>q$, and as zero when $p=q$. These relations enable (34) to be written in terms of logarithmic and $\tan^{-1}$ functions.

Part of the infinite series (35) reduces using (32). The remainder may be written in terms of the series

$$\sum_l \rho^l P_l(\Omega)/(l+n)$$

where n is an integer. For $n \geqslant 1$ this can be summed using (15) and interchanging the sum and integral yielding

$$\sum_{l=0}^{\infty} \rho^l P_l(\Omega)/(l+n) = \rho^{-n}\int_0^{\rho} t^{n-1}/(1-2\Omega t+t^2)^{1/2}\,\mathrm{d}t. \tag{37}$$

Expressions for $n \in \{-2, \ldots, 4\}$ are listed by Gradshteyn and Ryzhik (1980, pp 83, 85). McIsaac *et al* (1987) obtained a general expression valid for all n.

The reduction of the infinite series of Legendre polynomials and hypergeometric functions (36) is the most complex part of this work. The transformation of the $(\mu_1+\mu_2)$ multiplier in the series is analogous to that for the $(\mu_1-\mu_2)$ term, but the latter is marginally more complicated. Therefore only the reduction of the $(\mu_1-\mu_2)$ multiplier is described except for differences between the two series which are indicated.

The $(\mu_1-\mu_2)$ series (denoted by $\mathscr{A}$ below) is first cast in a region-independent form using (27) from § 4.3

$$\mathscr{A}=\frac{\mu_{12}(\mu_1-\mu_2)(r_1^2-r_2^2)}{12\Gamma(\frac{1}{2})}\sum_{l=2}^{\infty}\frac{\Gamma(l/2)\Gamma(l/2+1)P_l(\Omega)y^l}{\Gamma(l+\frac{1}{2})(l-1)}{}_2F_1\left[\begin{matrix}l/2+2,\,l/2\\ l+\frac{3}{2}\end{matrix};\quad y^2\right].$$

Euler's transformation is valid for $r_1>r_2$ but not for $r_1=r_2$. The following assumes that r_2 is strictly less than r_1 and an expression defined on the boundary is then sought. This difficulty does not arise for the $(\mu_1+\mu_2)$ term.

Elementary series rearrangement yields

$$\mathscr{A}=\mu_{12}(\mu_1-\mu_2)(r_1^2-r_2^2)/(6\pi)\sum_{l=2}^{\infty}y^l\Gamma(l/2+2)\Gamma(l/2)f_l(\Omega) \tag{38}$$

where

$$f_l(\Omega)=\sum_{t=0}^{[l/2-1]}\frac{P_{l-2t}(\Omega)(2l-4t+1)}{(\frac{3}{2})_{l-t}(l-2t+2)(l-2t-1)t!}$$

where should be compared with (A1) of I. Substituting the expansion for Legendre polynomials yields

$$f_l(\Omega)=\sum_{t=0}^{[l/2-1]}\frac{(2l-4t+1)}{(\frac{3}{2})_{l-t}(l-2t+2)(l-2t-1)t!}\sum_{k=0}^{[l/2-t]}\frac{(-1)^k(\frac{1}{2})_{l-2t-k}(2\Omega)^{l-2t-2k}}{k!(l-2t-2k)!}. \tag{39}$$

This double series is reducible to single series by rearranging so that the exponent of Ω contains only one summation index, using identities such as

$$\sum_{t=0}^{n}\sum_{k=0}^{n-t}f(t,k)=\sum_{u=0}^{n}\sum_{v=-u,2}^{u}f(u/2+v/2,\,u/2-v/2)$$

where f is an arbitrary function. Application to (39) requires the separation of the Ω^0 and Ω^1 terms from the double sum. For even l this gives a single series in t, representing the Ω^0 term, and a double series over the indices u and v. Reversing the u and v parts and using hypergeometric notation yields, for even l,

$$f_l(\Omega)=\frac{-5\pi^{1/2}}{16\Gamma(l/2+\frac{5}{2})\Gamma(l/2)}{}_4F_3\left[\begin{matrix}1-l/2,\,\frac{9}{4},\,\frac{1}{2},\,1\\ \frac{5}{2}+l/2,\,\frac{5}{4},\,3\end{matrix};\quad 1\right]$$

$$+\sum_{u=0}^{l/2-1}\frac{(2\Omega)^{l-2u}(2l-4u+1)\Gamma(l-2u+\frac{1}{2})}{u!(l-2u)!(l-2u-1)(l-2u+2)\Gamma(l-u+\frac{3}{2})2}$$

$$\times{}_5F_4\left[\begin{matrix}-u,\,l/2-u-\frac{1}{2},\,l-2u+\frac{1}{2},\,l/2-u+1,\,l/2-u+\frac{5}{4}\\ \frac{1}{4}-u+l/2,\,\frac{1}{2}-u+l/2,\,\frac{3}{2}-u+l,\,2-u+l/2\end{matrix};\quad 1\right].$$

Using standard identities one obtains

$$f_l(\Omega)=\sum_{u=2,2}^{l}\frac{\Omega^u 2^l(l+1)}{(u-1)\Gamma(l+3)}-\frac{2^l l}{2\Gamma(l+3)}.$$

The reduction in complexity when compared to the previous expression for $f_l(\Omega)$ (39) is dramatic. The hypergeometric series multiplying the Ω^u part of $f_l(\Omega)$ for odd l and $u\geqslant 2$ is as for even l. The function multiplying Ω^1 is a ${}_6F_5(1)$. Writing this as a well

poised ${}_7F_6(1)$ and applying the transformations to Saalschutzian ${}_4F_3(1)$ (Bailey 1935, ch 7) yields

$$ {}_7F_6\left[\begin{matrix}1, 1, \frac{5}{2}, \frac{5}{2}, \frac{11}{4}, \frac{3}{2}-l/2, \frac{7}{2} \\ \frac{7}{2}, \frac{7}{2}, 2, 2, \frac{7}{4}, 3+l/2\end{matrix}; \quad 1\right] = \frac{4(l+4)}{7(l-1)} {}_4F_3\left[\begin{matrix}1, 1, \frac{5}{2}, \frac{3}{2}-l/2 \\ 2, \frac{7}{2}, \frac{3}{2}-l/2\end{matrix}; \quad 1\right]. $$

This is a simple finite summation. Substitution into (39) reduces $f_l(\Omega)$ to

$$ f_l(\Omega) = \sum_{u=3,2}^{l} \frac{\Omega^u 2^l (l+1)}{(u-1)\Gamma(l+3)} - \frac{3\Omega\pi^{1/2}}{2\Gamma(l/2+2)\Gamma(l/2+\frac{1}{2})} \sum_{t=0}^{(l-3)/2} \frac{1}{(2t+2)(2t+5)}. $$

A useful form for $f_l(\Omega)$ involves the integral representation, achieved using a transformation similar to (37). Taking the summations inside the integrals gives finite geometric progressions. Inserting this representation for $f_l(\Omega)$ into the expression for series $\mathscr{A}$ (38), and exchanging the order of integration and summation over l, enables the summation to be written as ${}_2F_1$ of variable argument. These reduce to elementary functions using standard transformation formulae (Abramowitz and Stegun 1972, ch 15).

It is instructive to describe this procedure for part of the expression for $\mathscr{A}$. For even l the Ω^u, $u \geqslant 2$ part of $f_l(\Omega)$ becomes

$$ \sum_{u=2,2}^{l} \frac{\Omega^u 2^l (l+1)}{(u-1)\Gamma(l+3)} = \frac{(l+1)2^l \Omega}{\Gamma(l+3)} \int_0^{\Omega} \frac{(1-x^l)}{(1-x^2)} \, dx. \tag{40} $$

This part of $\mathscr{A}$ simplifies by interchanging the summations with the integral and reducing the l sum. This requires the evaluation of two series of the form

$$ \sum_{l=2,2}^{\infty} \frac{\Gamma(l/2+2)\Gamma(l/2)(l+1)z^l}{\Gamma(l+3)} $$

with $z = 2y$ in one case and $z = 2yx$ in the other. Writing this as a ${}_2F_1$ and reducing these functions by standard formulae yields

$$ z/(4-z^2)^{1/2} \sin^{-1}(z/2). $$

The resulting integral can be partly reduced, leaving an irreducible integral, resulting in

$$ (r_1^2 - r_2^2) \sum_{l=2,2}^{\infty} y^l \Gamma(l/2+2)\Gamma(l/2) \sum_{u=2,2}^{l} \frac{\Omega^u 2^l (l+1)}{(u-1)\Gamma(l+3)} $$

$$ = (r^2 - r_{12}^2)^{\frac{1}{2}} \sin^{-1} y \ln\left(\frac{1+\Omega}{1-\Omega}\right) - (r^2 - r_{12}^2)/r^2 \int_0^{\Omega} \frac{x \sin^{-1}(yx)}{(1-x^2)(1-y^2x^2)^{1/2}} \, dx. \tag{41} $$

Note that

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

$$ = -\ln(-r_1 + r_2 + r_{12}) + \ln(r_1 + r_2 - r_{12}) - \ln(r_1 - r_2 + r_{12}) + \ln(r_1 + r_2 + r_{12}) $$

where Q_0 is a Legendre function of the second kind (Abramowitz and Stegun 1972, p 333).

Series (36) can be reduced completely using this technique. Combining the simplified forms of (33)-(36) with the remaining terms yields the compact form for the three-particle wavefunction to second order in r:

$$\begin{aligned}\Psi(r_1, r_2, r_{12}) = \exp(-\lambda_1 r_1 - \lambda_2 r_2)\Bigg[\Bigg[C_{0000}\Bigg\{ & 1 + (\lambda_1+\mu_1)r_1 \\ & + (\lambda_2+\mu_2)r_2 + \frac{\mu_{12}}{2} r_{12} + \frac{\mu_{12}}{6}(2\mu_S \boldsymbol{Y}_{21} - \mu_A \boldsymbol{Y}_{20}) \\ & \times \left[\ln(r_1+r_2+r_{12}) - \frac{2}{\pi}\ln r + \left(\frac{\pi-2}{\pi}\right)[\exp(qr_1)\mathrm{Ei}(-qr_1) - \ln r_1]\right] \\ & + \frac{\mu_{12}}{6}(\mu_S \boldsymbol{Y}_{20} - 2\mu_A \boldsymbol{Y}_{21})\left[\tfrac{1}{2}\ln[r_{12}(2r^2 - r_{12}^2)^{1/2} + r_1^2 - r_2^2] - \ln(r_1 - r_2 + r_{12})\right. \\ & \left. - \frac{1}{2\pi}\sin^{-1} y \ln\left(\frac{1+\Omega}{1-\Omega}\right) + \frac{(1-y^2)^{1/2}}{\pi}\int_0^{\Omega} \frac{x \sin^{-1}(yx)\,\mathrm{d}x}{(1-x^2)(1-y^2x^2)^{1/2}}\right] \\ & - \frac{\mu_S \mu_{12}}{6}\left[r_{12}(2r^2 - r_{12}^2)^{1/2}\left(1 + \frac{2}{\pi}\sin^{-1}(y\Omega)\right) + 2r_1 r_2 - 4r_{12}(r_1+r_2)\right] \\ & + \frac{\mu_A \mu_{12}}{3}\left[r_1 r_2\left(1 - \frac{2}{\pi}\sin^{-1} y\right) + 2r_{12}(r_1 - r_2)\right] \\ & + (\lambda_1+\mu_1)(\lambda_2+\mu_2)r_1 r_2 + \frac{\mu_{12}}{2} r_{12}(\lambda_1 r_1 + \lambda_2 r_2) \\ & + \left((\lambda_1+\mu_1)(2\lambda_1+\mu_1) + (\lambda_2+\mu_2)(2\lambda_2+\mu_2) - \varepsilon + \frac{\mu_{12}^2}{2}\right)\frac{r^2}{6}\Bigg\} \\ & + \left\{\frac{C_{0000}}{12}\left[\mu_{12}\left(\frac{8\mu_S}{\pi} - 4\mu_S \ln 2 - 2\mu_A \ln 2 + 3\mu_S + 3\mu_A + 3\lambda_1\right)\right] + \frac{C_{1110}}{2}\right\}\boldsymbol{Y}_{21} \\ & + \left[\frac{C_{0000}}{12}\left(\mu_{12}(\mu_S \ln 2 + 2\mu_A \ln 2 - 3\mu_S - 4\mu_A - 3\lambda_1) + \varepsilon - \frac{\mu_{12}^2}{2}\right.\right. \\ & \left.\left. - (\lambda_1+\mu_1)(2\lambda_1+\mu_1) - (\lambda_2+\mu_2)(2\lambda_2+\mu_2)\right) + \frac{C_{2000}}{2}\right]\boldsymbol{Y}_{20}\Bigg]\Bigg] \qquad r_1 > r_2\end{aligned} \tag{42}$$

where $\boldsymbol{Y}_{20} = 2(r_1^2 - r_2^2)$ and $\boldsymbol{Y}_{21} = r^2 - r_{12}^2$ are *solid harmonics* tabulated in I. This may be compared with the work of Pluvinage (1950) and Hylleraas (1960), whose results are incorrect in not having a continuous derivative at $r_1 = r_2$. Gottschalk and Maslen (1987) commence with the (unphysical) solutions of Pluvinage and Hylleraas and show, using solutions to the homogeneous differential equation (i.e. Laplace's equation—see equation (54)), how to construct the physical eigenfunction given by (42).

The multiplier of the integral in (42) is proportional to $(\mu_S \boldsymbol{Y}_{20} - 2\mu_A \boldsymbol{Y}_{21})(r_1^2 - r_2^2)/r^2$, differing from the multipliers of the other terms because of the $(r_1^2 - r_2^2)/r^2$ factor. This is the only term with a length variable in the denominator. The anomaly is removed by transforming into an expression containing Lobachevskiy's function (Gradshteyn and Ryzhik 1980, p 933),

$$L(x) = -\int_0^x \ln|\cos t|\,\mathrm{d}t.$$

The resulting expression is more useful when differentiating the wavefunction.

Integration by parts yields

$$\int_0^{\Omega} \frac{x \sin^{-1}(xy)\,dx}{(1-x^2)(1-x^2y^2)^{1/2}} = \frac{r^2}{2(r_1^2-r_2^2)} \sin^{-1}\left(\frac{r^2-r_{12}^2}{r^2}\right)$$
$$\times \{\ln[r_{12}(2r^2-r_{12}^2)^{1/2}+r_1^2-r_2^2]-\ln[r_{12}(2r^2-r_{12}^2)^{1/2}-r_1^2+r_2^2]\}$$
$$-\frac{r_1 r_2}{(r_1^2-r_2^2)} \int_0^{\Omega} \frac{1}{(1-y^2x^2)^{1/2}} \ln\left(\frac{(1-y^2x^2)^{1/2}+(1-y^2)^{1/2}}{(1-y^2x^2)^{1/2}-(1-y^2)^{1/2}}\right) dx.$$

Using $y = \sin\alpha$ and $yx = \sin\beta'$ yields the integral in the required form, and the complete term in (42) becomes

$$\frac{\mu_{12}}{6\pi}\frac{(r_1^2-r_2^2)}{r^2}(\mu_S \boldsymbol{Y}_{20}-2\mu_A \boldsymbol{Y}_{21}) \int_0^{\Omega} \frac{x \sin^{-1}(yx)\,dx}{(1-x^2)(1-x^2y^2)^{1/2}}$$
$$= \frac{\mu_{12}}{12\pi}(\mu_S \boldsymbol{Y}_{20}-2\mu_A \boldsymbol{Y}_{21})\beta\{\ln[r_{12}(2r^2-r_{12}^2)^{1/2}+r_1^2-r_2^2]$$
$$-\ln[r_{12}(2r^2-r_{12}^2)^{1/2}-r_1^2+r_2^2]\}$$
$$-\frac{\mu_{12}}{6\pi}(\mu_S \boldsymbol{Y}_{20}-2\mu_A \boldsymbol{Y}_{21})\left[L\left(\frac{\alpha-\beta}{2}\right)-L\left(\frac{\alpha+\beta}{2}\right)\right.$$
$$\left.+L\left(\frac{\pi-\alpha+\beta}{2}\right)-L\left(\frac{\pi-\alpha-\beta}{2}\right)\right] \tag{43}$$

where $\beta = \sin^{-1}(y\Omega)$. The result agrees with Pluvinage (1985).

6.3. Examination of the second-order wavefunction

Kato (1957) showed that the wavefunction for a system of particles interacting via the Coulomb potential cannot be singular at any point. In the compact form of the wavefunction to second order several terms are singular for particular values of r_1, r_2 and r_{12}. Such singularities must cancel since the total wavefunction is well behaved.

Four cases require examination.

(i) Three-particle coalescence, $r_1 \to r_2 \to r_{12} \to 0$. The log terms are multipled by vanishing polynomials.

(ii) One particle at the nucleus, $r_2 \to 0$, $r_1 \to r_{12}$ ($y \to 0$ and $\Omega \to 0$). The singular $\ln[(1+\Omega)/(1-\Omega)]$ is multiplied by a vanishing $\sin^{-1}y$.

(iii) Two-particle coalescence, $r_1 \to r_2^+$, $r_{12} \to 0$, ($\Omega \to 1$). For $r_1 \to r_2$, i.e. $y \to 1$, the integral in (42) becomes

$$\int_0^{\Omega} \frac{\sin^{-1} x\,dx}{(1-x^2)^{3/2}} = \frac{\sin^{-1}\Omega}{(1-\Omega^2)^{1/2}} - \frac{1}{2}\ln\left(\frac{1+\Omega}{1-\Omega}\right).$$

However this term, being multiplied by $(r_1^2-r_2^2)$, vanishes in this limit. (This can also be deduced from (43).) The singular terms are

$$\frac{\mu_{12}}{12}(\mu_S \boldsymbol{Y}_{20}-2\mu_A \boldsymbol{Y}_{21})\left[2\ln(r_1-r_2+r_{12})+\sin^{-1}y \ln\left(\frac{1+\Omega}{1-\Omega}\right)\pi^{-1}\right.$$
$$\left.-\ln[r_{12}(2r^2-r_{12}^2)^{1/2}+r_1^2-r_2^2]\right]$$

yielding for $r_1 \to r_2$

$$\frac{\mu_{12}}{24}(\mu_S Y_{20} - 2\mu_A Y_{21})\left[4 \ln r_{12} + \ln\left(\frac{1+\Omega}{1-\Omega}\right) - 2 \ln[r_{12}(2r^2 - r_{12}^2)^{1/2}]\right]. \tag{44}$$

As $\ln r_{12} \to \frac{1}{2}\ln(1-\Omega) + \ln r$ and $\ln[r_{12}(2r^2 - r_{12}^2)^{1/2}] \to 2 \ln r + \frac{1}{2}\ln(1-\Omega^2)$, expression (44) vanishes for all Ω.

(iv) The particles colinear, $r_{12} = r_1 \pm r_2$, ($\Omega = \mp 1$). The singular terms are $\ln[(1+\Omega)/(1-\Omega)]$ and the integral in (42). Using integration by parts with respect to $(1-x^2)^{-1}$

$$\int_0^\Omega \frac{x \sin^{-1}(xy)\,dx}{(1-x^2)(1-x^2y^2)^{1/2}} = \frac{\Omega}{2}\ln\left(\frac{1+\Omega}{1-\Omega}\right)\frac{\sin^{-1}(y\Omega)}{(1-y^2\Omega^2)^{1/2}}$$
$$-\frac{1}{2}\int_0^\Omega \ln\left(\frac{1+x}{1-x}\right)\left(\frac{xy}{(1-x^2y^2)} + \frac{\sin^{-1}(xy)}{(1-x^2y^2)^{3/2}}\right) dx. \tag{45}$$

The last integral is simplified by noting that

$$2z\,{}_2F_1(1, 2; \tfrac{3}{2}; z^2) = z(1-z^2)^{-1} + (1-z^2)^{-3/2} \sin^{-1} z.$$

The integral containing this ${}_2F_1$ is well behaved in the limits of $r_{12} \to r_1 \pm r_2$. Thus the singular part of the integral (45) has been factored out. With the correct multipliers the singularity in (45) cancels with the $\sin^{-1} y \ln[(1+\Omega)/(1-\Omega)]$ term in the limit, leaving the integral

$$\int_0^{\pm 1} x \ln\left(\frac{1+x}{1-x}\right) {}_2F_1(1, 2; \tfrac{3}{2}; x^2y^2)\,dx. \tag{46}$$

This has not been simplified but a less complex form is obtained from the original double summation (41) for $\Omega = \pm 1$.

The integral representation (40) for the innermost sum can be evaluated for $\Omega = 1$ (Gradshteyn and Ryzhik 1980, p 301) yielding

$$\int_0^1 \frac{(1-x^l)}{(1-x^2)}\,dx = [\psi(l/2 + \tfrac{1}{2}) - \psi(\tfrac{1}{2})]/2.$$

This also gives the value for $\Omega = -1$ as the integrand is symmetric for even l. The double sum in (41), evaluated using Erdelyi (1954), is

$$[\psi(l/2 + \tfrac{1}{2}) - \psi(\tfrac{1}{2})]\frac{\Gamma(l/2)\pi^{1/2}}{\Gamma(l/2 + \tfrac{1}{2})} = \int_0^\infty \exp(-t/2)t(1 - e^{-t})^{l/2-1}\,dt.$$

Hence, for $\Omega = \pm 1$,

$$4 \sum_{l=2,2}^{\infty} y^l \Gamma(l/2+2)\Gamma(l/2) \sum_{u=2,2}^{l} \frac{\Omega^u 2^l (l+1)}{(u-1)\Gamma(l+3)}$$
$$= \sum_{l=0}^{\infty} y^{2l+2} \int_0^\infty \exp(-t/2)t(1-e^{-t})^l\,dt = -4y^2 \int_0^1 (1 - y^2 + y^2x^2)^{-1} \ln x\,dx$$

using Abramowitz and Stegun (1972). This yields the reduced form of the right-hand side of (41) in the limit of $r_{12} \to r_1 \pm r_2$.

This integral may be compared with (46), the equivalence being

$$\int_0^{\pm 1} x \ln\left(\frac{1+x}{1-x}\right) {}_2F_1(1, 2; \tfrac{3}{2}; x^2y^2)\,dx = \mp \int_0^1 (1 - y^2 + y^2x^2)^{-1} \ln x\,dx \qquad y \in [0, 1).$$

This relation has not been proved directly but has been checked by numerical quadrature.

The results here should be contrasted with the discussion of the FE in HC (§ 4.4). There the expansion of the wavefunction is continuous and region independent but appears to have a discontinuous derivative. Closer inspection shows that the wavefunction indeed has a continuous derivative except at the particle coalescences. Here the wavefunction itself appears singular but in the relevant limits all singularities cancel. Furthermore, the derivatives of the wavefunction may also be shown to be continuous.

7. Insight from the $k=2$ reduction

The reduction of the $k=2$ line using the HC in I and that using SPC given in § 5 above is tortuous, and in contrast to the simplicity of the compact form (42). One may ask whether equation (42) for $k=2$ is in the form 'best' suited to solving higher k lines. We consider 'best' to be a form consistent with the structure deduced for the higher k lines which minimises complexity in their reduction. Several characteristics of the $k=2$ line given by (42) are relevant in deriving that structure.

7.1. Simple expansions for the Coulomb potential

In the derivation of $k=2$ in HC (§ 5.3 of I) one expands the Coulomb potential in HH. A double summation over HH with complicated coefficients must then be reduced to compact form. After one summation the expansion is in Legendre polynomials. This could be obtained more directly by proposing an expansion in Legendre polynomials at the outset (§ 3.4 of I). In SPC one expands the Coulomb potential in Legendre polynomials and then, since the expansion of the wavefunction is similar, linearises the product of two Legendre polynomials obtaining Clebsch-Gordan coefficients. Summation over the Clebsch-Gordan coefficients is required to obtain a compact form. The difficulty common to HC and SPC is that the expansion of the potential leads to complicated coefficients. This would be alleviated in coordinate systems with simpler potential expansions. For example, in the coordinates r, y, $\Omega=\cos\theta$ (§ 3.3), the (symmetric) Coulomb potential is

$$V(r,y,\Omega)=\frac{2\mu_S(1+y)^{1/2}}{ry}+\frac{\mu_{12}}{r}(1-y\Omega)^{-1/2} \tag{47}$$

and the coefficient of Ω in the product of the wavefunction (13) and the potential (47), required for computing the $k=2$ line (see equation (38) from I), is trivial. Moreover the solution for $k=2$ in this system obtained by rewriting (42) is also simple. From (41) one sees that the expansion in r, y and Ω of the irreducible integral in (42) is straightforward. Substituting (13) into the SE produces a three-term recurrence relation, compared with the two-term one for (11). This has been solved for all k (McIsaac and Maslen 1987).

The form of the potential is simplest in IC or EC. One may ask therefore if the wavefunction should be expanded in those systems. This is feasible in a formal sense; the difficulties are twofold. The lesser problem is the complexity of the Laplacian given by equations (5) or (7). The more important difficulty is that a straightforward expansion of the irreducible integral in (42) in IC or EC has not been obtained. This suggests that the form of the wavefunction in these coordinates is not simple. Note

however that all other terms of (42) are simple functions of IC and the problems with IC would decrease dramatically if the irreducible integral could be expressed in a suitable form.

Summarising, difficulties associated with determining $k=2$, and hence higher k lines, arise from the complexity of the potential expansion. However, there is a trade-off in complexity between the kinetic energy (Laplacian) and potential energy terms. One must look for an 'optimum' coordinate system. Workers using HC often emphasise the simplicity of the Laplacian (Knirk 1974). This simplicity is important for functional analytic methods which rely on the fact that the kinetic energy 'dominates' the potential energy (Kato 1957, Morgan 1986). However, even though the Laplacian appears simple in HC (equation (3) of I), expansions into HH are complicated and are not suitable for analytic computation. Both r, y, Ω and IC have advantages when compared with HC or SPC because both avoid sums over Clebsch-Gordan coefficients.

7.2. Propagation of $k=2$ into $k=3$: avoiding the potential expansions

In § 5 of I the propagation of the solid harminics $\boldsymbol{Y}_{kl}$ for even k into the succeeding k line involves determining the coefficients in a polynomial of degree $(k+1)$ in IC, from

$$\Delta \boldsymbol{\Psi}_{k+1}^{[k,l]} = 2\boldsymbol{V}\boldsymbol{Y}_{kl}. \tag{48}$$

The results are tabulated as $\boldsymbol{\Psi}_{k+1}^{[k,l]}$ in table 4 of I. This technique may be generalised.

From (42) and (43) one sees that the $k=2$ line can be written as

$$\boldsymbol{\Psi}_2 = \boldsymbol{\Phi}_2 + C_{20}(r_1, r_2, r_{12})\boldsymbol{Y}_{20} + C_{21}(r_1, r_2, r_{12})\boldsymbol{Y}_{21}. \tag{49}$$

This suggests that for $k=3$

$$\boldsymbol{\Psi}_3 = \boldsymbol{\Phi}_3 + C_{20}(r_1, r_2, r_{12})\boldsymbol{\Psi}_3^{[2,0]} + C_{21}(r_1, r_2, r_{12})\boldsymbol{\Psi}_3^{[2,1]} \tag{50}$$

where $\boldsymbol{\Phi}_3$ is presently undetermined and C_{20} and C_{21} are obtained from (42) and (49). To determine $\boldsymbol{\Phi}_3$ one substitutes (49) into the $k=3$ differential equation (equation (36) of I)

$$\Delta \boldsymbol{\Psi}_3 = 2\boldsymbol{V}\boldsymbol{\Psi}_2 - 2E\boldsymbol{\Psi}_1. \tag{51}$$

Consider for example, the term from the $k=2$ line, $\ln(r_1+r_2+r_{12})\boldsymbol{Y}_{21}$. Using (5), one obtains

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

Examining the function

$$\ln(r_1+r_2+r_{12})\boldsymbol{\Psi}_3^{[2,1]} \tag{52}$$

since any derivative of $\ln(r_1+r_2+r_{12})$ is proportional to $(r_1+r_2+r_{12})^{-1}$ and $\Delta\ln(r_1+r_2+r_{12}) = (r_1+r_2)/(r_1r_2r_{12})$, one sees that using (48)

$$\Delta[\ln(r_1+r_2+r_{12})\boldsymbol{\Psi}_3^{[2,1]}] = 2\boldsymbol{V}[\ln(r_1+r_2+r_{12})\boldsymbol{Y}_{21}] + \boldsymbol{R}(r_1, r_2, r_{12}) \tag{53}$$

where $\boldsymbol{R}$ is a rational function of r_1, r_2 and r_{12}.

Solving for $\boldsymbol{\Phi}_3$ in (50) may be simpler than solving $\boldsymbol{\Psi}_3$ in (51) directly. Comparing (53) and (51) one sees that (52) solves the potential piece of (51) while avoiding some

of the complicated potential expansions. The logarithmic function is also replaced by the rational function $\boldsymbol{R}$. This analysis may be generalised to include the irreducible integral in (42). Hence the calculation of the propagation of $k=2$ into $k=3$ is simplified using (50). Note however that this approach must be modified for the propagation of $k=3$ into $k=4$ since, for each even k line, there arises $k/2+1$ HH. Furthermore, care must be taken to ensure that the solution $\boldsymbol{\Phi}_3$ has a continuous derivative. This is discussed by Gottschalk and Maslen (1987).

7.3. Variation of parameters

Ordinary non-homogeneous second-order differential equations may be solved by variation of parameters (Boyce and DiPrima 1969), if one knows the fundamental set of solutions of the corresponding homogeneous differential equation. From I, the non-homogeneous (partial) differential equation for $k=2$ is

$$\Delta\boldsymbol{\Psi}_2 = 2\boldsymbol{V}\boldsymbol{\Psi}_1 - 2E\boldsymbol{\Psi}_0 \tag{54}$$

and the general well behaved solution to the homogeneous equation, which is Laplace's equation, becomes

$$\boldsymbol{\Psi}_2^{\mathrm{c}} = C_{20}\boldsymbol{Y}_{20} + C_{21}\boldsymbol{Y}_{21}$$

where $\boldsymbol{\Psi}_2^{\mathrm{c}}$ is the complementary solution and C_{20} and C_{21} are constants. Note that since (54) is a partial differential equation the HH $\boldsymbol{Y}_{2l}(l=0,1)$ are selected from all possible solutions by requiring them to be finite and continuous on the hypersphere. Assuming that the method of variation of parameters extends to partial differential equations one may propose that the particular solution, $\boldsymbol{\Psi}_2^{\mathrm{p}}$, is of the form

$$\boldsymbol{\Psi}_2^{\mathrm{p}} = C_{20}(r_1, r_2, r_{12})\boldsymbol{Y}_{20} + C_{21}(r_1, r_2, r_{12})\boldsymbol{Y}_{21}. \tag{55}$$

$C_{2l}(r_1, r_2, r_{12})$ for $l=0,1$ could be determined by substituting (55) into (54), imposing additional conditions as required. Equations (42) and (49) confirm that the majority of terms have the form (55). The additional term $\boldsymbol{\Phi}_2$ must arise in generalising the method of variation of parameters to partial differential equations.

Alternatively, one can consider not only the well behaved solutions to the homogeneous equation (i.e. the HH), but also more general solutions to Laplace's equation obtained by relaxing the requirement that they must be well behaved everywhere. These solutions are therefore unphysical. However Gottschalk and Maslen (1987) show that, by firstly solving equation (54) *without* requiring derivative continuity at $r_1 = r_2$, and then adding appropriate linear combinations of (unphysical) solutions to Laplace's equation possessing cancelling discontinuities, one may construct the physical solution to (54) in a straightforward fashion.

7.4. Mixed coordinate representation for the wavefunction

The discussion on the compact form (42) indicates that different terms in the $k=2$ wavefunction simplify when expressed in the most appropriate system of coordinates. This is not just a cosmetic alteration, for it gives insight into the structure of higher k lines. For example, § 7.1 shows that the irreducible integral is simpler when expressed in terms of r, y and Ω. Section 7.2 extends the methods of I, proposing the propagation of even k lines into odd k lines by construction from the even k wavefunction and polynomials of suitable degree in IC. Section 7.3 suggests that the wavefunction for

even k lines could be obtained by variation of parameters utilising the HH. That is, we suggest that several coordinate systems and methods be used when determining the terms in the wavefunction as classified in §§ 7.1, 7.2 and 7.3. Pluvinage (1982) examined the two-electron wavefunction from this point of view but does not classify the terms in the $k = 2$ line explicitly. The techniques of Pluvinage and § 5 both utilise SPC. However, whereas in § 5 the wavefunction is expanded into a multiply infinite summation of $P_l(\Omega)$, Pluvinage utilises a (partial) separation of variables, reducing the equations to *ordinary* differential equations involving a single sum of $P_l(\Omega)$. Pluvinage recognised that solving $k = 3$ in SPC involves summing over Clebsch-Gordan coefficients. The method of § 7.2 which generalises techniques proposed by Ermolaev (1961) may resolve these difficulties by avoiding summations. Once higher k lines have been compacted, additional structure that has not previously been classified may emerge.

7.5. Alternate methods for obtaining the few-body wavefunction

So far the methods applied to solving the few-body wavefunction are all generalisations of classical techniques for ordinary differential equations. In I, power series solutions are generalised to include logarithmic functions. The wavefunction to $k = 2$ resembles a solution obtained by variation of parameters. Another technique applicable to this problem is the conversion of the partial differential equations into equivalent integral equations using Green functions (Dettman 1969). Since variation of parameters and Green function techniques are closely related (Whitten and McCormick 1975), one expects from § 7.2 that Green functions will be useful for many-body wavefunctions. Investigation along these lines by Bartlett (1937) reached the discouraging conclusion that to solve the resulting integral equation one would be forced to expand the wavefunction. This would have no advantage compared to solving the differential equation directly. However Pluvinage (1985) recently used the Green functions given by Fock (1954, 1958) to evaluate the symmetric $k = 2$ wavefunction. This should encourage further work using Green functions.

7.6. Use of the wavefunction up to $k = 2$

The wavefunction up to $k = 1$ has been examined by Abbott and Maslen (1986) where it is shown that the first-order wavefunction is determined by its form at the Coulombic poles, or equivalently, by the cusp conditions (Kato 1957). The ground-state energy from the first-order wavefunction is in good agreement with the exact value. One expects that the second-order wavefunction will give a much better value for the ground-state energy, which should converge rapidly to the exact value as k increases. Furthermore, any physical property involving matrix elements of the wavefunction to order k will also be a rapidly convergent function of k.

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Appendix. The spherical polar treatment

Gottschalk and Maslen (1985) described the procedure for evaluation of the coefficients appearing in the series solution (11) of the three-body S-state SE using SPC. The method is summarised here.

The coefficients vanish in the region with $j<l$ and $i+j<0$. Coefficients with $j=l$ are determined by requiring the wavefunction and its derivatives to be continuous or by the requirement of a normalisable wavefunction. The recurrence equations obtained by substituting the trial solution into the SE specify the remaining coefficients in terms of the $j=l$ coefficients.

Introducing variables g and k such that $j=l+g$, $g\geq 0$ and $i+j=k$, $k\geq 0$, the order of solution is that of increasing k starting at $k=0$. For every k line the order is of decreasing p and for every p the order is of increasing g starting at $g=0$. Rearranging the recurrence equation relates coefficients with $g>0$ to those with either $g=0$, higher values of p or lower k:

$$C_{k-l-2n-1l+2n+1lp}$$
$$=\frac{(-1)^n\Gamma(n+l-k/2+\frac{1}{2})\Gamma(n-k/2)}{\Gamma(n+\frac{3}{2})2\Gamma(n+l+2)}$$
$$\times\sum_{t=0}^{n}\frac{(-1)^t\Gamma(t+\frac{1}{2})\Gamma(t+l+1)}{\Gamma(t+l-k/2+\frac{1}{2})\Gamma(t-k/2)}$$
$$\times R(k,l,2t+1,p)\qquad n\geq 0 \tag{A1a}$$

and

$$C_{k-l-2nl+2nlp}=\frac{(-\frac{1}{2}-k/2)_n(l-k/2)_n(-1)^n}{(l+\frac{3}{2})_n n!}C_{k-lllp}$$
$$-\frac{(-1)^n\Gamma(n-\frac{1}{2}-k/2)\Gamma(n+l-k/2)}{2\Gamma(n+\frac{3}{2}+l)n!}$$
$$\times\sum_{t=0}^{n-1}\frac{(-1)^t\Gamma(t+1)\Gamma(t+l+\frac{3}{2})}{\Gamma(t+l-k/2+1)\Gamma(t-k/2+\frac{1}{2})}$$
$$\times R(k,l,2t+2,p)\qquad n\geq 1 \tag{A1b}$$

where

$$R(k,l,g,p)=[(k-l-g+2)(\lambda_1-qp)+\mu_1]C_{k-l-g+1l+g-2lp}$$
$$+[\lambda_2(l+g)+\mu_2]C_{k-l-gl+g-1lp}$$
$$+(\lambda_1 pq-p^2q^2/2-E-\lambda_1^2/2-\lambda_2^2/2)C_{k-l-gl+g-2lp}$$
$$-(2k-2l-2g+5)/2C_{k-l-g+2l+g-2lp+1}$$
$$+[\lambda_1-q(p+\tfrac{1}{2})]C_{k-l-g+1l+g-2lp+1}-\tfrac{1}{2}C_{k-l-g+2l+g-2lp+2}$$
$$+\mu_{12}\sum_{s=-l,2}^{l}\sum_{m=(l+s)/2}^{(l+g+s-2)/2}a_l^{mm-s}C_{k-l-g+m+1l+g-2-mm-sp}.$$

As this function contains coefficients with higher p or lower k, it is already determined. The double sum, calculated using the linearised product of Legendre polynomials, results from the interaction between the two finite mass particles. In the case of helium

it is the electron-electron interaction term. As is well known this term results in non-separability of the SE. The equations for coefficients C'_{ijlp} are the same as (A1) with $R(k, l, g, p)$ replaced by $R'(k, l, g, p)$. $R'(k, l, g, p)$ is identical to $R(k, l, g, p)$ except that C_{ijlp} is replaced by C'_{ijlp} and μ_1 and μ_2 interchanged.

Using

$$Y(k, l, g) = [X(k, l, g) + kW(k, l, g)]/2$$
$$Z(k, l, g) = [X(k, l, g) - kW(k, l, g)]/2$$

where

$$X(k, l, g) = (k-2g-2l)_4F_3\left[\begin{matrix}1, l/2-k/4+g/2+1, g/2-k/2-\frac{1}{2}, l+g/2-k/2 \\ l/2-k/4+g/2, g/2+1, l+g/2+\frac{3}{2}\end{matrix}; \quad -1\right]$$

and

$$W(k, l, g) = {}_3F_2\left[\begin{matrix}-k/2+g/2-\frac{1}{2}, l-k/2+g/2, 1 \\ g/2+1, l+g/2+\frac{3}{2}\end{matrix}; \quad -1\right]$$

are generalised hypergeometric functions, the equations specifying the $g = 0$ coefficients when $k \neq 2l+2m$, $m = 0, 1, 2, \ldots$, are

$$Y(k, l, 0)C_{k-lllp} + Z(k, l, 0)C'_{k-lllp}$$
$$= -2\sum_{g=1}^{\infty} g^{-1}(2l+g+1)^{-1}[Y(k, l, g)R(k, l, g, p)$$
$$+ Z(k, l, g)R'(k, l, g, p)] - D(k, l, p) \qquad \text{(A2}a\text{)}$$
$$Z(k, l, 0)C_{k-lllp} + Y(k, l, 0)C'_{k-lllp}$$
$$= -2\sum_{g=1}^{\infty} g^{-1}(2l+g+1)^{-1}[Z(k, l, g)R(k, l, g, p)$$
$$+ Y(k, l, g)R'(k, l, g, p)] - D'(k, l, p). \qquad \text{(A2}b\text{)}$$

Note that the definitions for $X(k, l, g)$ and $W(k, l, g)$ given by Gottschalk and Maslen (1985) are valid for restricted values of k, l and g whereas in the above definitions there are no restrictions on k, l and g. These are related by standard transformations (Bailey 1935). Functions $D(k, l, p)$ and $D'(k, l, p)$ are defined by

$$D(k, l, p) = \sum_k C_{ijlp+1} + pq\sum_{k-1} C_{ijlp} - \sum_{k-1}(\lambda_1 C_{ijlp} - \lambda_2 C'_{ijlp})$$
$$D'(k, l, p) = \sum_k C'_{ijlp+1} + pq\sum_{k-1} C'_{ijlp} - \sum_{k-1}(\lambda_1 C'_{ijlp} - \lambda_2 C_{ijlp})$$

where Σ_k is shorthand for $\Sigma_{i,j(i+j=k)}$.

For $k = 2l+4m+2$ the equations determining C_{ijlp} and C'_{ijlp} are

$$\sum_{g=1}^{\infty} \frac{W(k, l, g)}{g(2l+g+1)}[R(k, l, g, p) - R'(k, l, g, p)] = 0 \qquad \text{(A3}a\text{)}$$

and

$$X(k, l, 0)(C_{k-lllp+1} + C'_{k-lllp+1})$$
$$= -2\sum_{g=1}^{\infty} \frac{X(k, l, g)}{g(2l+g+1)}[R(k, l, g, p+1) + R'(k, l, g, p+1)] - 2D(k, l, p+1). \qquad \text{(A3}b\text{)}$$

Setting $p+1=0$ gives a value for $C_{k-111\,0}+C'_{k-111\,0}$. These are specified completely if the wavefunction is symmetric, and in other cases by requiring the wavefunction to be normalisable. For $k=2l+4m$ the equations determining C_{ijlp} and C'_{ijlp} are

$$\sum_{g=1}^{\infty}\frac{X(k,l,g)}{g(2l+g+1)}[R(k,l,g,p)+R'(k,l,g,p)]+D(k,l,p)=0 \qquad \text{(A4}a\text{)}$$

and

$$W(k,l,0)(C_{k-111p+1}-C'_{k-111p+1})$$
$$=-2\sum_{g=1}^{\infty}\frac{W(k,l,g)}{g(2l+g+1)}[R(k,l,g,p+1)-R'(k,l,g,p+1)]. \qquad \text{(A4}b\text{)}$$

Setting $p+1=0$ determines $C_{k-111\,0}-C'_{k-111\,0}$. These coefficients are determined completely either by the requirement of antisymmetry or normalisability of the wavefunction.

The infinite series used to simplify the coefficients, denoted $X(k,l,g)$ where $g=j-l$, was reduced to a finite series and the elementary infinite series π and $\ln 2$ by Davis and Maslen (1983a). They defined a function $S(k,l,b)$ such that

$$X(k,l,g)=-(2l+g+1)+(2l-k-2)c(k,l,g)S(k,l,b)$$

where $b=(g-k)/2$ and

$$c(k,l,g)=\frac{82^k\Gamma(g/2+1)\Gamma(l+g/2+\frac{3}{2})}{\Gamma(g/2-k/2-\frac{1}{2})\Gamma(l-k/2+g/2)}.$$

Noting that

$$W(k,l,g)=1-c(k,l,g)S(k,l+1,b)$$

the reduction of $W(k,l,g)$ is also achieved using the simplification of $S(k,l,b)$.

The values of $X(k,l,g)$ and $W(k,l,g)$ required for the calculation of the coefficients with $k=0,1,2$ are

$X(0,0,0)=0 \qquad W(0,0,0)=1$

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

$W(1,l,0)=(4l+2)/(2l+3) \qquad W(1,0,1)=1 \qquad W(1,l,2)=1 \qquad l\geqslant 0.$

For $l>1$

$$X(2,l,0)=\frac{-\Gamma(l+\frac{3}{2})8\pi^{1/2}}{2^l\Gamma(l/2+\frac{3}{2})\Gamma(l/2-\frac{1}{2})} \qquad X(2,l,1)=2(1-5l)/3$$

$$X(2,l,2)=2(2l+3)/3-\frac{\Gamma(l+\frac{5}{2})\pi^{1/2}8}{3\Gamma(l/2+\frac{1}{2})\Gamma(l/2+\frac{3}{2})2^l} \qquad X(2,l,3)=-2(l+2)$$

$$X(2,l,4)=20(2l+5)/3+\frac{8(2l+5)}{3l}\left(3-\frac{\Gamma(l+\frac{5}{2})\pi^{1/2}2}{\Gamma(l/2+\frac{1}{2})\Gamma(l/2+\frac{3}{2})2^l}\right)$$

$$W(2,l,0)=\frac{\Gamma(l+\frac{3}{2})2\pi^{1/2}}{\Gamma(l/2+2)\Gamma(l/2)2^l} \qquad W(2,l,1)=\frac{5(l+1)}{3(l+2)}$$

$$W(2,l,2)=\frac{4\Gamma(l+\frac{5}{2})\pi^{1/2}}{3(l-1)\Gamma(l/2+2)\Gamma(l/2)2^l}-\frac{(2l+3)}{3(l-1)} \qquad W(2,l,3)=1$$

$$W(2,l,4)=\frac{8\Gamma(l+\frac{7}{2})\pi^{1/2}}{3(l-1)\Gamma(l/2+2)\Gamma(l/2+1)2^l}-\frac{10(2l+5)}{3(l-1)}.$$

If l is treated as a continuous variable the $l=0$ and 1 values of $X(2, l, g)$ and $W(2, l, g)$ are the limits of the $l>1$ expressions.

Note there are typographical errors in the transformed expressions for $S(k, l, b)$ reported by Davis and Maslen (1983a). Using their notation the correct expressions are, for k even and $k/2-l$ even,

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

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

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

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