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Formal Solution for the Three Body Problem in Helium Theoretical Chemistry

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The theory of co-ordinates r_a, r_b, with $r_b = \max(r_1, r_2)$ and $r_a = \min(r_1, r_2)$ is developed to yield formal solutions for Schroedinger equations of helium theoretical chemistry. The correction for nuclear motion is included. Four most significant sets of terms in the ground state for the radial equation give a good approximation for the radial limit independently of the variation theorem. Thirteen most significant terms from the four sets are the basis for accurate variation calculations. A new radial limit is obtained.

Es wird eine Theorie für die Koordinaten r_a und r_b ($r_b = \max(r_1, r_2)$, $r_a = \min(r_1, r_2)$) entwickelt, um formale Lösungen der Schrödingergleichung von heliumartigen Systemen zu erhalten. Die Kernbewegung wird durch eine Korrektur berücksichtigt. Vier sehr wichtige Termgruppen des Grundzustandes ergeben im Falle der Radialgleichung eine gute Näherung für das Grenzverhalten, und zwar unabhängig vom Variationstheorem. Dreizehn sehr wichtige Terme aus den erwähnten vier Termgruppen bilden die Grundlage für exakte Variationsrechnungen.

1. Introduction

We develop the theory of co-ordinates r_a, r_b with $r_b = \max(r_1, r_2)$ and $r_a = \min(r_1, r_2)$. This is done to yield formal solutions for Schroedinger equations of helium theoretical chemistry.

An atomic model is introduced in Section 2. This treats electron correlation and by inspection has advantages over more conventional treatments. The work described in this paper is the simplest application of the model. The model is fundamental enough to produce series solutions for radial and angular correlation.

The difficulties of using co-ordinates r_a, r_b, have been mentioned in the literature [1–3]. The behaviour of functions in r_a, r_b, to operators $\partial/\partial r_i$, $\partial^2/\partial r_i^2$, $(i = 1, 2)$, operating in singular space defined by $r = r_1 = r_2$, is of special interest. This is because of the possible discontinuity in the first derivatives of such functions. In the general case the first and second derivatives of $f(r_a, r_b)$ are undefined in singular space. Because the Hamiltonian operator contains $\Sigma\partial^2/\partial r_i^2$, $(i = 1, 2)$, the basis for treatment of such functions becomes important.

In Section 4 we derive expansions in r_1, r_2, for functions $f(r_a, r_b)$. We compare the operand behaviour of functions $f(r_a, r_b)$ and their expansions in r_1, r_2. It is demonstrated that the discontinuities in the first derivatives of $f(r_a, r_b)$ exist in the first derivatives of the expansions. The second derivatives of $f(r_a, r_b)$ in singular space are infinite and undefinable. It is shown that the second derivatives of the corresponding expansions gives a divergent series for singular space. Therefore $f(r_a, r_b)$ is not analytically equivalent to its expansion in r_1, r_2. $\partial^2/\partial r_i^2 \cdot f(r_a, r_b)$

is undefined in singular space and is to be correlated with a divergent expansion in r_1, r_2.

The idea of variation calculations for the radial limit is considered in Sections 5, 6. Simulation functions $\psi_0 f(r_a, r_b)$ are defined where ψ_0 is the Kellner function from (7). These functions are outside the Domain of H. Nevertheless they can be used successfully in variation calculations. This is because functions $\psi_0 f(r_a, r_b)$ can be expanded in r_1, r_2. Every term in the expansion is in the Domain of H. Despite the analytical differences between $\psi_0 f(r_a, r_b)$ and the expansions, the former can be used for the latter in the calculation of matrix elements provided delta functions are used. More general simulation functions are derived.

A further boundary condition is developed in Section 7. This is that the discontinuities in the first derivatives of all terms $\psi_0 C_{p,q} r_a^p / r_b^q$ in a function should cancel. The constants $C_{p,q}$ may be adjusted for this condition. These functions are no longer simulation functions. They come into the Domain of H.

The coefficients $C_{p,q}$ can be sorted into sets according to the value of $p-q$. The four most significant sets correspond to values 0, 1, 2, 3. A recursion formula is developed in Section 8 for these four most significant sets of coefficients in the series solution of the ground state for the radial Schroedinger equation. The estimate of the eigenvalue obtained from these coefficients is -2.8788 H. This result is accurate to 9 parts in 10^5 and is independent of the variation theorem.

The series from the recursion formula and boundary conditions fails to continue to the fifth most significant set of coefficients while remaining in the Domain of H. The unique way out of this difficulty is to make the series more general with a typical term $\psi_0 C_{p,q,j} r_a^p / r_b^q \cdot (\log r_b)^j \cdot j \geqq 0$. $C_{p,q,j} = 0$ when $p - q < 4j$.

In Section 9 Kato's cusp theorems are discussed. The cusp relation at the nucleus is shown to follow from the recursion formulae in Section 8. Some difficulty arises when H is defined in $r_1, r_2, \cos\theta$, and $0.5\,\psi_0 r_{12}$ is regarded as part of the solution to helium when $r_{12} = 0$. r_{12} is better replaced by its expansion in $r_a, r_b, P_l(\cos\theta)$.

In Section 10 terms are obtained for the ground state of the SP and Complete Schroedinger equations. The latter shows the correct cusp behaviour when r_{12} tends to zero. From a consideration of the need for logarithmic terms similar to that in Section 8 an analytical form is produced for angular as well as radial correlation. Recursion formulae are produced for the formal solutions to the SP, SPD and Complete Schroedinger equations defined in Section 3. Coefficients from the Complete equation are corrected for the motion of the nucleus in Section 12. The correction though a small one does enable the series solution for the helium three body problem.

Successful and economic variation results are described in Section 11. The thirteen most significant terms of the solution to the radial Schroedinger equation are implemented variationally. This calculation produces a new radial limit of $-2.879{,}028{,}59$ H.

2. An Atomic Model

Instead of a conventional model wave function:

$$\psi_0^{\text{det}}\{1 + \sigma g(r_1, r_2, r_3 \ldots \cos\theta_{12}, \cos\theta_{13} \ldots)\} \tag{1}$$

we propose:

$$\psi_0^{\text{det}}\{1 + f(r_a, r_b, r_c \ldots \cos\theta_{ab}, \cos\theta_{ac} \ldots)\} \tag{2}$$

with $r_a \leqq r_b \leqq r_c \ldots$ and θ_{ij} the angle between r_i and r_j. ψ_0^{det} is a variational form of the determinantal solution from the appropriate zero order problem. This problem is that of non-interacting electrons moving in a central field. A single variation constant is envisaged which is the single exponential constant. f and g are functions not usually symmetrical to the interchange of subscripts. σ is the corresponding symmetrising operator. f is a more flexible form than σg. If a particular case of f is symmetrical to the interchange of subscripts it is identical to a particular case σg. More generally the symmetrising operator must not be included in (2). This is because any f is intrinsically symmetrical in r_1, r_2. f has the advantage of yielding functions which are shown to require an infinite series of functions σg.

Electron zoning has been introduced in (2) precisely and compactly by using co-ordinates which are useful for the expression of the interelectron potential operator. Our present concern is with the small set of co-ordinates r_a, r_b, θ_{ab}. These are co-ordinates for the helium problem.

3. Basic Definitions and Results in the Helium Problem

The Hamiltonian operator in the zero order helium problem is:

$$H^0 = -1/2 \cdot \nabla_1^2 - 1/2 \cdot \nabla_2^2 - 2/r_1 - 2/r_2 \tag{3}$$

if operands to H^0 are expressed in the form ΣC_l (radial part)$_l \cdot P_l(\cos\theta)$ with $\theta = \theta_{12} = \theta_{ab}$ in (1), (2) then ∇_i^2 is conveniently replaced by:

$$\partial^2/\partial r_i^2 + 2/r_i \cdot \partial/\partial r_i - l(l+1)/r_i^2 \tag{4}$$

H' the interelectron potential operator is usually taken as first order to H^0. This is here defined as:

$$H' = \sum_l^{0,\infty} r_a^l / r_b^{l+1} \cdot P_l(\cos\theta); \quad r_a = \min(r_1, r_2); \quad r_b = \max(r_1, r_2); \tag{5}$$

The series in (5) has the following properties:

i) absolute convergence for all parts of space $r_b > r_a$.

ii) uniform convergence for any closed part of space with $r_b > r_a$.

iii) convergence for any part of space with $r_b = r_a$, $|\cos\theta| < 1$.

We are to use the series in (5) to form the Hamiltonian operator $H = H^0 + H'$. The resulting Schroedinger equation is to be solved formally. Intermediate Schroedinger equations are defined for formal solution. These are the S, SP, SPD..., Schroedinger equations as H' in H is expanded to the first, second, third..., term. The Schroedinger equation for the complete expansion of H' is called the Complete Schroedinger equation.

H' fails to converge when $r_a = r_b = r$, $\cos\theta = -1$. The series oscillates between 0 and $1/r$ instead of giving $1/(2r)$. If this difficulty prevents the numerical processing for any series solution for helium, (5) could be replaced by (5a).

$$H' = \sum_l^{0,n} r_a^l / r_b^{l+1} \cdot P_l(\cos\theta) + 1/2 \cdot r_a^{n+1} / r_b^{n+2} \cdot P_{n+1}(\cos\theta) \tag{5a}$$
$$n \to \infty$$

As n increases from zero to infinity H' is always $1/(2r)$ when $r_a = r_b$, $\cos\theta = -1$. It will be shown in Section 10 that one important series of terms in the helium eigenfunction is given correctly when (5) is used. This is true when $r_a = r_b$, $\cos\theta = -1$. It seems probable therefore that (5a) will never need to be substituted for (5).

As the electrons approach the same point H' tends to infinity. When the electrons occupy the same point the series for H' diverges. This divergence may be associated with the natural infinity of $1/r_{12}$. If Ψ is a series solution such that $(H^0 + H')\Psi = E\Psi$, then the result of $(H^0 + H')\Psi$ leads to a cancellation of the terms of $H'\Psi$. This is true when the separation of the electrons is infinitesmal. When the separation is zero $H'\Psi$ becomes undefined but $(H^0 + H')\Psi$ may be defined by a continuity argument.

No practical difficulty appears to arise from the use of H' if Ψ can be deduced.

The solutions to the zero order problem defined in (3) form an incomplete set of square integrable orthonormal functions, the pth element of which is ψ_p^0. The inclusion of the functions from the continuum makes the set complete. The configuration interaction method for helium uses trial wave functions:

$$\Sigma C_p \psi_p^0 \tag{6}$$

For the singlet ground state of helium the space spin Kellner variation form is used for ψ_0^{det} with the space part given in (7).

$$\psi_0 = \exp\{-\zeta(r_1 + r_2)\} \tag{7}$$

Because of the interelectron energy the average potential energy for helium is less negative than in the zero order problem. It follows from the virial theorem that the average kinetic energy of the former is less positive. If we regard ζ as a variation constant in the context of (7), (1) or (2), the average kinetic energy is reduced by reducing ζ from 2. Further it is often convenient to give ζ the value of minus the sequare root of the eigenvalue. Under this condition the functions in (7), (1), and (2) have the proper operand behaviour to $H(=H^0 + H')$ when both electrons are at infinity. ψ_0 is an eigenfunction of H^0 only if $\zeta = 2$.

A set of square integrable functions with the ith element ψ_i is said to be in the Domain of H if all $H\psi_i$ are square integrable and the relationship between matrix elements in (8) is satisfied.

$$\int \psi_i H \psi_j \, d\tau = \int \psi_j H \psi_i \, d\tau \tag{8}$$

ψ_i and $H\psi_i$ are well formed in Hilbert space. The Ritz variation principle may be applied to functions in the Domain of H. It follows that:

$$\int \left(\sum_n c_i \psi_i\right) H \left(\sum_n c_i \psi_i\right) d\tau \Big/ \int \left(\sum_n c_i \psi_i\right)^2 d\tau \geqq E_0 \tag{9}$$

where E_0 is the ground state eigenvalue of the system defined in H. The constants c_i can be varied to produce a minimum value for the left hand side of (9). If the functions ψ_i form a complete set then the left hand side of (9) tends to E_0 if the constants c_i are optimised and n tends to infinity.

It is noteworthy that ψ_0 is in the Domain of H but $H\psi_0$ is not. It is not unexpected therefore that $\int (H\psi_0) H(H\psi_0) \, d\tau$ is indeterminately large and negative.

4. The Operand Behaviour of $f(r_a, r_b)$

Let us consider the simple cases of $f_1 = r_a^2$, $f_2 = 1/r_b$:

$$\begin{aligned} \partial f_1/\partial r_{1_{r_1<r_2}} &= 2r_a; \quad & \partial f_1/\partial r_{1_{r_1>r_2}} &= 0\,; \\ \partial f_2/\partial r_{1_{r_1<r_2}} &= 0; \quad & \partial f_2/\partial r_{1_{r_1>r_2}} &= -1/r_b^2\,; \end{aligned} \tag{10}$$

We see that the first derivatives of f_1, f_2, are discontinuous when $r_1 = r_2$. Further differentiation at the discontinuity is undefined. Because first and second derivatives of r_a^2 and $1/r_b$ are not analytic in the space $r_1 = r_2$ we call this space singular space.

Three results are stated and then demonstrated.

i) Any continuous function $f_j(r_a, r_b)$ in (2) may in general be expanded as an infinite series of terms. These terms are symmetrical in r_1, r_2. Further the first and second derivates of these terms with respect to r_1, r_2, are analytic. So we write:

$$f_j(r_a, r_b) = \sum_k C_{k,j}\chi_{k,j}(r_1, r_2) \tag{11a}$$

ii) The equality:

$$\partial/\partial r_i \cdot f_j(r_a, r_b) = \partial/\partial r_i \cdot \sum_k C_{k,j}\chi_{k,j}(r_1, r_2) \tag{11b}$$

with $i = 1$ or 2, holds for all functions f_j and $\chi_{k,j}$ from (11a). This is so for all of space including what is singular space when $r_1 = r_2$. If the left hand side of (11b) is discontinuous when $r_1 = r_2$ then also is the right hand side.

(iii) The inequality:

$$\partial^2/\partial r_i^2 \cdot f_j(r_a, r_b) \neq \partial^2/\partial r_i^2 \cdot \sum_k C_{k,j}\chi_{k,j}(r_1, r_2) \tag{11c}$$

holds where the left hand and right hand sides of (11b) are discontinuous. At any discontinuity from (11b), the right hand of (11c) diverges while the left hand side of (11c) cannot be formed.

The results in (11) are demonstrated by comparing two expansions for $1/r_{12}$, (5) and (12).

with
$$\begin{aligned} 1/r_{12} &= (1 + 1/2\cdot\xi\cos\theta + 1/2\cdot 3/4\cdot\xi^2\cos^2\theta\ldots)(r_1^2 + r_2^2)^{-1/2} \\ \xi &= 2r_1 r_2/(r_1^2 + r_2^2) \end{aligned} \tag{12}$$

Our interest is to rewrite (12) in Legendre harmonics. To do this we expand $\cos^m\theta$ in Legendre harmonics. By comparing the l th harmonic parts of (5) and the re-expansion of (12), we obtain a series for r_a^l/r_b^{l+1} in r_1, r_2, ξ. For $l = 0$ we have (13).

$$1/r_b = (1 + 1/2\cdot 3/4\cdot 1/3\cdot\xi^2 + 1/2\cdot 3/4\cdot 5/6\cdot 7/8\cdot 1/5\cdot\xi^4 + \cdots)(r_1^2 + r_2^2)^{-1/2} \tag{13}$$

Fortunately the series in (13) converges absolutely for all ξ; $\xi \leqq 1$. Thus the result in (11a) is proved for the particular case: $f(r_a, r_b) = 1/r_b$.

We compare the operand behaviour of the two sides of (13) to $\partial/\partial r_i$ with $i = 1$ or 2. We obtain (14) from the right hand side of (13) by operating with $\partial/\partial r_1$.

$$\begin{aligned} &-\{1 + 1/2\cdot 3/4\cdot 1/3\cdot\xi^2 + 1/2\cdot 3/4\cdot 5/6\cdot 7/8\cdot 1/5\cdot\xi^4 + \cdots\}\, r_1(r_1^2 + r_2^2)^{-3/2} \\ &\quad + 2\{1/2\cdot 3/4\cdot 2/3\cdot\xi + 1/2\cdot 3/4\cdot 5/6\cdot 7/8\cdot 4/5\cdot\xi^3 + \cdots\}\, r_2(r_2 - r_1)(r_1 + r_2) \\ &\qquad \cdot(r_1^2 + r_2^2)^{-5/2} \end{aligned} \tag{14}$$

The series factor of the second term in (14) tends to infinity as ξ approaches 1. The binomial expansion of $1/2\cdot(1-\xi)^{-1/2}-1/2\cdot(1+\xi)^{-1/2}$ tends to infinity in the same way. In the limit the series factor can be replaced by $1/2(1-\xi)^{-1/2}$. Let us consider an interval $\Delta r = r_2 - r_1$ which is very small so that r_2 and r_1 are considered to approach r. In the limit (14) converges to (15).

$$-1/2\cdot 1/r^2 + 1/2\cdot 1/r^2\cdot \Delta r/|\Delta r| \tag{15}$$

(15) shows just the discontinuous behaviour shown by $\partial/\partial r_1(1/r_b)$ in (10). Thus the result in (11b) is justified for the particular case: $f(r_a, r_b) = 1/r_b$.

We may repeat the analysis for $l>0$ in any r_a^l/r_b^{l+1} from before (13). More generally series may be obtained for $f(r_a, r_b)$. This justifies the results in (11a) and (11b). For example the series for r_a may be obtained by multiplying the right hand side of (13) by $r_1 r_2$ and that for r_b may be obtained by using:

$$r_b = r_1 + r_2 - r_a\,.$$

The second derivative of (13) with respect to r_1 is the first derivative of (14). The factor $(r_2 - r_1)$ in the second term of (14) prevents the series from diverging when $r_1 = r_2$. The differentiation of the factor $(r_2 - r_1)$ will cause the second derivative of (13) to diverge when $r_1 = r_2$. This divergence in general is to be correlated with the undefined first derivative of a discontinuity. The result in (11c) is justified.

5. Variation Calculations, Dirac Delta Functions, The Finite Contribution to Matrix Elements from Singular Space of Zero Volume and Simulation

We consider the terms of the series in (15) as a basis for variation calculations.

$$\psi_0 \sum_{p}^{0,\infty} \sum_{q}^{-\infty,p} \sum_{l}^{0,\infty} C_{p,q,l} r_a^p/r_b^q \cdot P_l(\cos\theta) \tag{16}$$

The Hylleraas expansion can be re-expanded in terms which are a subset of those in (16). The functions in the Hylleraas expansion have been shown to be complete [4]. Therefore the functions in (16) are complete. So are the functions in (17).

$$\psi_0 \sum_{p}^{0,\infty} \sum_{q}^{-\infty,p} C_{p,q} r_a^p/r_b^q\,. \tag{17}$$

Our interest is firstly to implement (17) variationally to estimate the radial limit and secondly to find the series solution for the S-equation defined after (5). There are two difficulties however.

i) Because of (11c) and the second derivative in (4) the functions $\psi_0 r_a^p/r_b^q$ are not the same operators to H as their expansions in (18).

$$\psi_0 r_a^p/r_b^q = \psi_0 \sum_k C_{k,j}\chi_{k,j}(r_1, r_2)\,. \tag{18}$$

The calculation of the left hand side of (19) presents difficulties.

$$\int \psi_0 r_a^p/r_b^q \cdot H\psi_0 r_a^{p'}/r_b^{q'}\cdot d\tau = \sum_k \sum_{k'} C_{k,j} C_{k',j'} \int \psi_0 \chi_{k,j} H \psi_0 \chi_{k',j'}\, d\tau\,. \tag{19}$$

The evaluation of the right hand side of (19) presents no such difficulties.

ii) We shall see that functions $\psi_0 r_a^p/r_b^q$ are not in the Domain of H.

However if we find some way of evaluating matrix elements such that the matrix relationships in (20) and (21) are satisfied we conclude that functions $\psi_0 r_a^p/r_b^q$ simulate functions $\psi_0 \sum_k C_{k,j}\chi_{k,j}(r_1, r_2)$ for the evaluation of matrix elements provided that the functions $\psi_0 \chi_{k,j}$ are in the Domain of H.

$$\int \psi_0 H \psi_0 r_a^p/r_b^q \, d\tau = \int \psi_0 r_a^p/r_b^q H \psi_0 \, d\tau \,, \tag{20}$$

$$\int \psi_0 r_a^{p'}/r_b^{q'} \cdot H \psi_0 r_a^p/r_b^q \, d\tau = \int \psi_0 r_a^p/r_b^q \cdot H \psi_0 r_a^{p'}/r_b^{q'} \, d\tau \,. \tag{21}$$

If all relevent cases of (20) and (21) hold and all corresponding functions $\psi_0 \chi_{k,j}$ are in the Domain of H it follows from after (9) that the Ritz variation method can be used with (17).

Dirac δ-functions [5] are used for the evaluation of the unexpanded matrix elements in (20), (21). From (3), (4) we consider

$$1/2 \cdot \psi_0 \, \partial/\partial r_1 (r_a^p/r_b^q), \; 1/2 \cdot \psi_0 \, \partial^2/\partial r_1^2 (r_a^p/r_b^q)$$

for a fixed value of r_2. The first derivative term shows the discontinuity in (22) when $r_1 = r_2$.

$$\Delta_1 = -1/2 \cdot (p+q) \, r_2^{p-q-1} [\psi_0]_{r_1 = r_2} \,. \tag{22}$$

Therefore over this singular space of zero volume the second derivative is infinite. The integration of the second derivative term over singular space can be redistributed over r_1 space. The result is given in (23).

$$\int_0^\infty \psi_0 r_a^{p'}/r_b^{q'} \, r_1^2 \Delta_1 \, \delta(r_1 - r_2) \, dr_1 = [\psi_0]_{r_1 = r_2} r_2^{p'-q'+2} \, \Delta_1 \tag{23}$$

$\delta(r_1 - r_2)$ is a δ-function. It has the value zero for all values of r_1 except where $r_1 = r_2$. $\delta(r_1 - r_2)$ then becomes indeterminately large. We integrate the right hand side of (23) for all values of r_2. The contribution to the left hand side of (21) from the total singular space is:

$$(p+q) \int_0^\infty [\psi_0^2]_{r_1 = r_2} \, r_2^{p+p'-q-q'+3} \, dr_2 \,. \tag{24}$$

With the aid of δ-functions we can evaluate the integrals in (20), (21). However there is no way of evaluating (25). From this follows (ii) after (19).

$$\int [H \psi_0 r_a^p/r_b^q]^2 \, d\tau \tag{25}$$

6. Acceptable Terms $\psi_0 r_a^p/r_b^q$ for the Ritz Variation Method and Successful Simulation

From Section 5 we require the ranges for integers p and q for which the matrix relations in (20), (21) hold and all corresponding functions $\psi_0 \chi_{k,j}$ are in the Domain of H. The contributions to matrix elements from singular space are calculated according to Section 5. We now state the result for a basis set from (17)

to form a valid wave function. The sufficient conditions for all p and q are:

$$q-p\leqq 0\,;\quad p\geqq 0\,; \tag{26}$$

Given (26) we draw conclusions.

(i) With "simulation" defined before (20), the series in (17) successfully "simulates" its expansion according to (18) for the evaluation of matrix elements. This expansion is the proper wave function. The terms of (17) are simulation functions.

(ii) The treatment of singularities in Section 5 is successful and effectively treats the divergence from the right hand side of (11c).

We now sketch the derivation of (26). From (13) it follows that infinitely many functions $\psi_0\chi_{k,j}$ for any value j in (11a) are of the form $\psi_0(r_1r_2)^m/(r_1^2+r_2^2)^{n/2}$. For these functions to be in the Domain of H it is necessary and sufficient for $m-n\geqq 0$. It follows that:

$$p-q\geqq 0\,. \tag{27}$$

A generalisation of (27) is that $\psi_0 f(r_a, r_b)$ must not tend to infinity near $r_1=r_2=0$. The second consideration is the effect of the indices p, q, p', q', on the matrix relations (20), (21). We need only consider the Laplacian parts of H in (28).

$$-1/2\cdot\int r_a^{p'}/r_b^{q'}\cdot\psi_0(\nabla_1^2+\nabla_2^2)\,\psi_0 r_a^p/r_b^q\,d\tau\,. \tag{28}$$

All contributions to (28) are first considered excluding those from singular space examined in Section 5. From (7), (3) and (4) with $l=0$, we represent (28) as:

$$\begin{aligned}&-\int_0^\infty \exp(-2\zeta r_2)r_2^{p+p'+2}dr_2\int_0^\infty \exp(-\zeta r_1)/r_1^{q'-1}\cdot\partial^2/\partial r_1^2\{\exp(-\zeta r_1)/r_1^{q-1}\}\,dr_1\\&-\int_0^\infty \exp(-2\zeta r_1)/r_1^{q+q'-2}dr_1\int_0^{r_1} \exp(-\zeta r_2)r_2^{p'+1}\cdot\partial^2/\partial r_2^2\{\exp(-\zeta r_2)r_2^{p+1}\}\,dr_2\,.\end{aligned} \tag{29}$$

The integration of (29) by parts gives:

$$\begin{aligned}&-\int_0^\infty \exp(-2\zeta r_2)r_2^{p+p'+2}dr_2[\exp(-\zeta r_1)/r_1^{q'-1}\cdot\partial/\partial r_1\{\exp(-\zeta r_1)/r_1^{q-1}\}]_{r_2}^\infty\\&+\int_0^\infty \exp(-2\zeta r_2)r_2^{p+p'+2}dr_2\int_{r_2}^\infty \partial/\partial r_1\{\exp(-\zeta r_1)/r_1^{q'-1}\}\cdot\partial/\partial r_1\{\exp(-\zeta r_1)/r_1^{q-1}\}\,dr_1\\&-\int_0^\infty \exp(-2\zeta r_1)/r_1^{q+q'-2}\,dr_1[\exp(-\zeta r_2)r_2^{p'+1}\cdot\partial/\partial r_2\{\exp(-\zeta r_2)r_2^{p+1}\}]_0^{r_1}\\&+\int_0^\infty \exp(-2\zeta r_1)r_1^{q+q'-2}\,dr_1\int_0^{r_1} \partial/\partial r_2\{\exp(-\zeta r_2)r_2^{p'+1}\}\cdot\partial/\partial r_2\{\exp(-\zeta r_2)r_2^{p+1}\}\,dr_2\,.\end{aligned} \tag{30}$$

We consider the single integral terms in (30) which are unsymmetrical in index pairs pp' and qq'. If and only if $p+p'\geqq 0$, these unsymmetrical terms can be combined together to give:

$$-(p+q)\int_0^\infty \exp(-4\zeta r_1)\,r_1^{p+p'-q-q'+3}\,dr_1\,, \tag{31}$$

$$p+p'\geqq 0 \tag{32}$$

We add the remaining contribution to (28) which is (24). This if (32) holds, the result from (28) is symmetrical in pp' and qq'. In the evaluation of all matrix elements for a variation calculation using (17), the same values occur for p as for p'. p and p' must have the same minimum value. Therefore $p \geqq 0$. (26) is derived. From (26) it follows that the integrands in (30) tend to zero near $r_1 = r_2 = 0$. Because of (26) all terms in (17) are simulation functions. These make a complete set.

It is of interest to compare the expansions of $\psi_0 r_a/r_b$ and $\psi_0 r_b/r_a$ according to (18). From (26) $\psi_0 r_a/r_b$ is a simulation function and must yield terms all in the Domain of H. $\psi_0 r_b/r_a$ is not a simulation function and must yield at least one term not in the Domain of H. The condition that the matrix relation in (8) is satisfied with $\psi_j = \psi_o$ is:

$$\psi_0 r_k \partial/\partial r_k(\psi_i r_k)|_{r_k=0,\infty} = \psi_i r_k \, \partial/\partial r_k(\psi_0 r_k)|_{r_k=0,\infty} = 0 \tag{33}$$

with $k = 1, 2$.

Squaring the series in (13) and multiplying each term by $\psi_0 r_1 r_2$ we obtain the expansion of $\psi_0 r_a/r_b$. All terms satisfy ψ_i in (33). Now considering $\psi_0 r_a/r_b$ we have (34).

$$\psi_0 r_b/r_a = \psi_0 r_1/r_2 + \psi_0 r_2/r_1 - (\text{the terms for } \psi_0 r_a/r_b). \tag{34}$$

According to (33) the first two terms on the right hand side of (34) are not in the Domain of H.

Finally we consider just what functions $\psi(r_a, r_b)$ are valid simulation functions. By arguments similar to those used for the condition for p in (26) we obtain an analogue to (33) for functions $\psi(r_a, r_b)$ which are continuous and square integrable. This analogue is (35).

$$\psi_0 r_a \partial/\partial r_a\{r_a \psi(r_a, r_b)\}|_{r_a=0} = \psi(r_a, r_b)\, r_a \partial/\partial r_a\{\psi_0 r_a\}|_{r_a=0} = 0\,, \tag{35a}$$

$$\psi_0 r_b \partial/\partial r_b\{r_b \psi(r_a, r_b)\}|_{r_b=\infty} = \psi(r_a, r_b)\, r_b \partial/\partial r_b\{\psi_0 r_b\}|_{r_b=\infty} = 0\,. \tag{35b}$$

The similarity between (33) and (35) means that simulation functions can be generated by taking any unsymmetrical function in r_1, r_2, which is in the Domain of H and substituting r_a, r_b for r_1, r_2 or r_2, r_1.

A second sort of simulation function can be formed from (35). This is of the general type $f(r_a, r_b)\exp(-\zeta r_b)$. The simplest example is $\exp(-\zeta r_b)$. We note that $\exp(-\zeta r_a)$ is not acceptable according to (35). This function is not even square integrable.

7. Two Different Types of Model Wave Functions

The first derivatives of the terms in (17) have discontinuities in singular space. These discontinuities have been characterised in Section 4, 5. It is critical to distinguish two types of functions (17) for which the conditions in (26) hold. This is done according to the sum of the discontinuities. The two different types of functions are referred to as functions of the First Type and functions of the Second Type.

(i) We define a function of the First Type. For such a function the discontinuities from the operation of $\partial/\partial r_i$, $(i=1,2)$, on all terms sum to zero in all singular space.

(ii) For a function of the Second Type the discontinuities do not sum to zero in all singular space.

Because of (26) we write (17) in the form:

$$\psi_0 \sum_{n}^{0,\infty} \sum_{m}^{0,\infty} C_{m,m-n} r_a^m / r_b^{m-n} \tag{36}$$

The condition for (36) to represent a general form of the First Type is (37) for all the values of n in (36).

$$\sum_{m}^{0,\infty} (2m-n)\, C_{m,m-n} = 0 \tag{37}$$

There are three results for functions of the First Type which do not extend to functions of the Second Type.

$$\text{(i)} \quad \psi_0\, \partial^2/\partial r_i^2 \cdot f_j(r_a, r_b) = \psi_0\, \partial^2/\partial r_i^2 \cdot \sum_k C_{k,j} \chi_{k,j}(r_1, r_2); \qquad \text{c.f. (11c)} \tag{38}$$

The result in (38) holds even for singular space. The first derivatives of $f(r_a, r_b)$ are no longer discontinuous. If both sides of (38) are undefined because of discontinuities they contain what is the same discontinuity. This occurs in a similar way to the result in (15).

(ii) $\psi_0 f(r_a, r_b)$ is now in the Domain of H {c.f. (25)}. Matrix elements are evaluated without the use of δ-functions. From the definition of simulation functions after (26), $\psi_0 f(r_a, r_b)$ is no longer merely a simulation function. In general it may be assumed to be analytically equivalent to $\psi_0 \sum_k C_{k,j} \chi_{k,j}(r_1, r_2)$ for the evaluation of matrix elements.

(iii) $\psi_0 \sum_i \partial^2/\partial r_i^2 \cdot f(r_a, r_b)$, $(i=1,2)$, is analytically defined for a function of the First Type. This is because any undefined part is proportional to $\Delta r/|\Delta r| - \Delta r/|\Delta r| = 0$; c.f. (15).

It follows from the discussion in this section that any formal solution to a Schroedinger equation will be a function of the First Type. This is because the eigenfunctions of H are in the Domain of H. Similarly any complete model wave function of the Second Type will tend towards a function of the First Type.

8. The Series Solution for the Ground State of the Radial Helium Schroedinger Equation

We consider the radial helium Schroedinger equation and derive early sets of terms in the series solution for the ground state. These are processed to give an estimate of the eigenvalue. This estimate for what is the radial limit is independent of the variation theorem. From (3), (4) and after (5) the equation is:

$$(H^0 + 1/r_b - E_0)\Psi_0 = 0 \tag{39}$$

We obtain a recursion formula. From this and boundary conditions we produce the four most significant sets of terms in the series solution. This approach fails to produce later sets of terms. From this failure we are able to deduce the general form of the formal solution. This includes logarithmic terms.

The recursion formula used for the partial solution of (39) is simple. To obtain it we take Ψ_0 from the complete expansion in (17). The corresponding recursion formula is:

$$\begin{aligned} p(p+1)\,C_{p,q} + (q-2)(q-3)\,C_{p-2,q-2} \\ = -2\{1+\zeta(q-2)\}\,C_{p-2,q-1} + 2\{p\zeta - 2\}\,C_{p-1,q} \\ -2(\zeta^2 + E_0)\,C_{p-2,q} \end{aligned} \tag{40}$$

Suppose $p-q=n$. For smaller values of $p-q$ all $C_{p,q}$ have been determined. We are to use (40) to determine all $C_{p,q}$ with the same value of n. When $p=n+2$, $n+3$, then $C_{p,q}$ is obtained in terms of already determined coefficients with $p-q=n-1$ and $n-2$. When $p>n+3$ then a non zero already determined term $(q-2)(q-3)\,C_{p-2,q-2}$, with $p-q=n$, contributes to the left hand side of (40). From (26) we have the result:

$$C_{p,q}=0 \quad \text{for} \quad p<0 \quad \text{or} \quad q>p \tag{41}$$

When $p=0$ both sides of (40) are zero. When $p<n+2$ and odd $C_{p,q}$ can be determined in a similar way to terms $p \geqq n+2$. For $p<n+2$ and even there results a set of m consistent simultaneous equations. m is given in (42):

$$m = \text{integer part } \{(n+1)/2\} \tag{42}$$

The simultaneous equations have $m+1$ coefficients $C_{p,q}$, with $p-q=n$, to be determined. Therefore an extra equation is needed. This derives from Section 7. The series solution must be a function of the First Type in the Domain of H. So from (37) we obtain:

$$\begin{aligned} \sum_{p}^{0,m} (4p-n)\,C_{2p,2p-n} = -\sum_{p}^{0,m} (4p+2-n)\,C_{2p+1,2p+1-n} \\ -\sum_{p}^{2m+2,\infty} (2p-n)\,C_{p,p-n}; \quad n \neq 0 \end{aligned} \tag{43}$$

From (40) the evaluation of E_0 is necessary for the solution of Ψ_0 in (39). The consideration is of an approximation to Ψ_0 made from a series of most significant sets of terms. Each set corresponds to a particular value of n. An approximation to the eigenvalue is E_0'. The corresponding approximate eigenfunction is Ψ_0'. E_0' is obtained by successive approximations in (44).

$$E_0' = \int \Psi_0'(H^0 + 1/r_b)\,\psi_0\,d\tau \Big/ \int \Psi_0'\psi_0\,d\tau \tag{44}$$

We indicate the determination of the four most significant sets of coefficients in (40) and (43). These correspond to $n=0, 1, 2, 3$.

$C_{p,p}=0$ for $p>0$. $C_{0,0}$ is undetermined in (43) and is arbitrarily given the value unity: $C_{0,0}=1$.

From all $C_{p,p-1}$ we obtain just three non-zero coefficients:

$$C_{2,1}=1/6,\ C_{1,0}=\zeta-2,\ C_{0,-1}=\zeta-1.5 \tag{45}$$

From all $C_{p,p-2}$ we obtain an infinite set of non-zero coefficients. We obtain: $C_{p,p-2}=0$ for $p\geqq 5$, $p=$ odd, otherwise $C_{p,p-2}\neq 0$ for $p\geqq 0$. $C_{p,p-3}\neq 0$ for all values of $p\geqq 0$.

Values for E_0' in (44) will depend on the selected value for ζ in (7) and (40). We take $\zeta=(-E_0')^{1/2}$. The result is an approximate eigenvalue of -2.8788 H. This result shows an error of 9 parts in 10^5. This value can be obtained with as few as 29 terms from (36) in (44). All matrix elements in (44) are simple off-diagonal matrix elements. The Ritz variation method requires diagonal matrix elements. The variational method favours the eigenvalue for a comparable eigenfunction. Nevertheless the 29 terms in (44) yield a comparable eigenvalue to a 15-term Ritz variation calculation [6]. The latter employs terms from a complete set of square integrable functions closely related to the functions in (6). The series calculation is shorter and simpler.

Four approximations to the eigenvalue can be obtained usefully from (36) and (44). These correspond to $n=0$; $n=0, 1$; $n=0, 1, 2$; $n=0, 1, 2, 3$. The approximations are:

$$-2.8477,\ -2.8689,\ -2.8777,\ -2.8788\ \text{H} \tag{46}$$

The eigenvalue to five figures is -2.8790 H. These results improve in the rations of 1:3:24:156.

The simple method of series solution becomes more complex for $n\geqq 4$. Whenever n is a multiple of 4 the m equations before (42) can be combined together to give the left hand side of (43). This makes the $m+1$ equations needed for the simple solution inconsistent. The m equations give an infinite set of solutions. (43) can no longer be used to select the set which puts the terms $\psi_0 \sum_{p}^{0,\infty} C_{p,p-n} r_a^p/r_b^{p-n}$ in the Domain of H. Despite the completeness of (17) it becomes necessary to introduce logarithmic terms.

We require an auxiliary series to (36) to be able to remove the discontinuity in first derivatives when $n=4$. Such a series must differ in form from (36) and yet give terms of the sort in (36) on differentiating with respect to r_i, $(i=1$ or $2)$. The form must be logarithmic and is:

$$\psi_0 \sum_{n}^{4,\infty} \sum_{p}^{0,\infty} C_{p,p-n,1}\, r_a^p/r_b^{p-n}\cdot\log r_b \tag{47}$$

From (47) and considerations similar to those which lead to (26), we obtain (48) with $j=1$. (40) is replaced by (49).

$$C_{p,p-n,j}=0 \quad \text{for} \quad p<0 \quad \text{or} \quad n<4j\,. \tag{48}$$

$$\begin{aligned} p(p+1)\,C_{p,p-n,j}&+(p-n-2)(p-n-3)\,C_{p-2,p-n-2,j}\\ &=-2\{1+\zeta(p-n-2)\}\,C_{p-2,p-n-1,j}+2(p\zeta-2)\,C_{p-1,p-n,j}\\ &\quad-2(\zeta^2+E_0)\,C_{p-2,p-n,j}+2\zeta(j+1)\,C_{p-2,p-n-1,j+1}\\ &\quad+(j+1)(2p-2n-5)\,C_{p-2,p-n-2,j+1}\\ &\quad-(j+1)(j+2)\,C_{p-2,p-n-2,j+1} \end{aligned} \tag{49}$$

$C_{p,q}$ from (40) corresponds to $C_{p,q,0}$ in (48), (49), (50). (43) is replaced by (50).

$$\sum_{p}^{0,m}(4p-n)\,C_{2p,2p-n,j}=-\sum_{p}^{0,m}(4p+2-n)\,C_{2p+1,2p+1-n,j} - \sum_{p}^{2m+2,\infty}(2p-n)\,C_{p,p-n,j}+(j+1)\sum_{p}^{0,\infty}C_{p,p-n,j+1} \tag{50}$$

When $j=1$ and $n=4$ the right hand sides of (49) and (50) are zero. This means that (49) and (50) are interdependent but consistent. Both equations are satisfied by whatever value may be chosen for say $C_{0,-4,1}$. When $j=0$, $n=4$, (49) and (50) can be made consistent by adjusting the value of $C_{0,-4,1}$. (49), (50) become inconsistent when n is a multiple of 4 ($n \geqq 8$) and $j=0$ unless $C_{0,-n,1}$ is adjusted to make these consistent. When $n=8$, $j=1$ (49), (50) are again inconsistent unless an auxiliary series from $n=8$ with $j=2$ is started. The total requirement is for the triple series in (51).

$$\psi_0 \sum_{j}^{0,\infty}\sum_{n}^{4j,\infty}\sum_{p}^{0,\infty} C_{p,p-n,j}\, r_a^p/r_b^{p-n}\cdot(\log r_b)^j \tag{51}$$

There is a remaining problem. $C_{2,-2,0}$, $C_{2,-6,0}$, $C_{2,-10,0}$, etc. for example remain undetermined. This will be treated in a subsequent paper. The functions in (17) are in fact overcomplete. The terms corresponding to the undetermined coefficients can be removed from (17). The resultant functions still form an overcomplete set.

9. Cusp Behaviour in the Ground State Solutions of Helium Schroedinger Equations

The cusp behaviour of Ψ_0 from (39) in the limit of r_a tending to zero is known to be:

$$1/\Psi_0\cdot(\partial\Psi_0/\partial r_a)=-2\,; \quad r_a\to 0\,; \tag{52}$$

From (17) and (52) we obtain the following recursion formula:

$$(2-\zeta)\,C_{0,q}+C_{1,q}=0 \tag{53}$$

The relationship in (53) is also obtained from (40), (41). This proves (52) for any series from (40), (41). (48), (49) produce the analogous result. The correct cusp behaviour at the origin can be shown similarly for the series generated in Section 10.

We now consider the ground state solution Ψ of the Complete Schroedinger equation for helium defined after (5). We have:

$$(H^0+H'-E_0)\,\Psi=0\,; \quad \text{c.f. (39)} \tag{54}$$

In particular we consider the cusp behaviour of Ψ as r_{12} tends to zero. The cusp theorem first formally stated by Kato can be written:

$$\Psi^{-1}(\partial\Psi/\partial r_{12})=0.5\,; \quad r_{12}\to 0\,; \tag{55}$$

From (55) it follows [7] that when r_{12} tends to zero Ψ contains r_{12} in the forms:

$$\exp(0.5\, r_{12}) = 1 + 0.5\, r_{12} + \cdots \tag{56}$$

The result in (56) confirms the use of r_{12} as a useful co-ordinate for the helium problem. There is a difficulty however. It is that both sides of (56) do not show all the correct properties when $r_{12} = 0$. From the right hand side of (56) when $\cos\theta = 1$, Ψ will contain $r_b - r_a$. Ψ becomes a radial function of the Second Type in Section 7. This is not acceptable. Let us consider the expansion of r_{12}.

$$u = \sum_{l}^{0,\infty} [1/(2l+3)\cdot r_a^{l+2}/r_b^{l+1} - 1/(2l-1)\cdot r_a^l/r_b^{l-1}]\, P_l(\cos\theta) \tag{57}$$

Summing the first $l+1$ terms of (57) we obtain (58) when $\cos\theta = 1$.

$$r_b - r_a + 1/(2l+3)\cdot r_a^{l+2}/r_b^{l+1} + 1/(2l+1)\cdot r_a^{l+1}/r_b^l \tag{58}$$

As l tends to infinity the terms in l become zero. u is identical to r_{12}. On taking radial derivatives however the terms in l contribute to $\partial/\partial r_i$, $(i = 1, 2)$, when $r_1 = r_2$ and l tends to infinity. The radial derivatives of the expansion are non-uniformly convergent near $r_1 = r_2$ when $\cos\theta = 1$. Because of this Ψ contains $0.5\, u$ and is still a radial function of the First Type when $\cos\theta = 1$. Ψ will then have the correct cusp behaviour as r_{12} approaches zero.

Let us consider the operation $\partial/\partial r_1$ on $0.5\, r_{12}$ and $0.5\, u$ as these functions tend to zero and actually equal zero.

$$\begin{aligned} &0.5(\partial r_{12}/\partial r_1)_{r_1<r_2} = -0.5; \quad 0.5(\partial r_{12}/\partial r_1)_{r_1=r_2} = \text{undefined}; \\ &0.5(\partial r_{12}/\partial r_1)_{r_1>r_2} = 0.5 \end{aligned} \tag{59}$$

$$\begin{aligned} &0.5(\partial u/\partial r_1)_{r_1<r_2} = -0.5; \quad 0.5(\partial u/\partial r_1)_{r_1=r_2} = 0; \\ &0.5(\partial u/\partial r_1)_{r_1>r_2} = 0.5 \end{aligned} \tag{60}$$

When describing the properties of Ψ for $r_1 = r_2$, $\cos\theta = 1$, it is better to use $0.5\, u$ rather than $0.5\, r_{12}$.

Given the importance of $0.5\, u$ we expect to find terms from $0.5\, u$ in any series obtained from Ψ. This expectation is confirmed in Section 10. However we obtain from (45) and before (45) the most significant terms in the solution of (39):

$$\psi_0\{1 + (\zeta - 2)(r_a + r_b) + 0.5(r_b + 1/3\cdot r_a^2/r_b)\} \tag{61}$$

The third term of the right hand factor in (61) corresponds to the term in (57) with $l = 0$. The constant 0.5 is confirmed.

10. The Formal Solutions for the Ground States of the SP, SPD, etc. and Complete Helium Schroedinger Equations

The SP helium Schroedinger equation is defined after (5). For this we use an analogous expression to (17). This is:

$$\Psi_1 = \psi_0 \sum_{l}^{0,\infty} \sum_{p}^{0,\infty} \sum_{q}^{-\infty,p} C_{p,q,l}\, r_a^p/r_b^q \cdot P_l(\cos\theta) \tag{62}$$

The recursion formula analogous to (40) is:

$$\begin{aligned}-(l-p)(l+p+1)\,C_{p,q,l} = &-2\{1+\zeta(q-2)\}\,C_{p-2,q-1,l}\\ &+2(p\zeta-2)\,C_{p-1,q,l}-2(E_1+\zeta^2)\,C_{p-2,q,l}\\ &+(l+q-2)(l-q+3)\,C_{p-2,q-2,l}\\ &+2l/(2l-1)\cdot C_{p-3,q-2,l-1}\\ &+2(l+1)/(2l+3)\cdot C_{p-3,q-2,l+1}\end{aligned} \tag{63}$$

From (26) and (63) we have:

$$C_{p,q,l}=0 \quad \text{for} \quad p<l \quad \text{or} \quad q>p-l \tag{64}$$

The analogue to (43) is:

$$C_{l,l-n,l} = -1/(2l-n)\cdot \sum_{p}^{l+1,\infty} (2p-n)\,C_{p,p-n,l}; \qquad n\neq 2l \tag{65}$$

Using (63), (64) and (65) subsets of coefficients may be extracted. These correspond to the following values for l and n:

$$l=0, n=0, 1, 2; \; l=1, n=1; \; l\geqq 2, n=l \tag{66}$$

There are an infinite number of subsets in (66). There are however significant gaps because of difficulties similar to those which lead to (47).

We concern ourselves with the three most significant subsets in (66). With these are no gaps. The subsets correspond to $l=0, n=0, 1$; $l=1, n=1$. We obtain the following non-zero terms:

$$\psi_0\{1+(\zeta-2)(r_a+r_b)+0.5\sum_{l}^{0,k}[1/(2l+3)\cdot r_a^{l+2}/r_b^{l+1}-1/(2l-1)\cdot r_a^l/r_b^{l-1}]\cdot P_l(\cos\theta)\} \tag{67}$$

with $k=1$. In the case of Ψ from (54) which is Ψ_∞ in the notation of (62) we obtain (67) with $k=\infty$. From (57) this proves the cusp condition in (55) and (56) with the special singular properties in (60).

Fock [8] has shown that the terms of (67) for Ψ up to the linear terms are:

$$1-2(r_1+r_2)+0.5\,r_{12} \tag{68}$$

These terms can be obtained from (67) by expanding ψ_0 from (7). This shows how the terms in (68) belong to a square integrable series.

It is clear that the form in (62) is inadequate for the complete evaluation of $\Psi_1, \Psi_2, \ldots, \Psi_\infty$. When $n=2l$ $(l\neq 0), 2l+4, 2l+8, 2l+12$ etc. the combination of (63), (64), (65), gives sets of inconsistent simultaneous equations. It is necessary to find the analogue to (51) for total correlation including angular correlation. From arguments similar to those for (51) this is:

$$\psi_0 \sum_{l}^{0,\infty}\sum_{j}^{0,\infty}\sum_{n}^{2j,\infty}\sum_{p}^{l,\infty} C_{p,p-n,j,l}\, r_a^p/r_b^{p-n}\cdot(\log r_b)^j\, P_l(\cos\theta) \tag{69}$$

The analogue to (49) for the SP problem is:

$$\begin{aligned}-(l-p)(l+p+1)\,C_{p,p-n,j,l} = &-2\{1+\zeta(p-n-2)\}\,C_{p-2,p-n-1,j,l}\\ &+2(p\zeta-2)\,C_{p-1,p-n,j,l}-2(E_1+\zeta^2)\,C_{p-2,p-n,j,l}\\ &+(l+p-n-2)(l-p+n+3)\,C_{p-2,p-n-2,j,l}\\ &+2l/(2l-1)\cdot C_{p-3,p-n-2,j,l-1}\\ &+2(l+1)/(2l+3)\cdot C_{p-3,p-n-2,j,l+1}\\ &+2\zeta(j+1)\,C_{p-2,p-n-1,j+1,l}\\ &+(j+1)(2p-2n-5)\,C_{p-2,p-n-2,j+1,l}\\ &-(j+1)(j+2)\,C_{p-2,p-n-2,j+2,l}\end{aligned} \tag{70}$$

The analogue to (49) for the SPD problem is:

$$\begin{aligned}-(l-p)(l+p+1)\,C_{p,p-n,j,l} = &\{\text{terms on the right hand side of (70)}\}\\ &+3(l-1)/(2l-3)\cdot l/(2l-1)\,C_{p-4,p-n-3,j,l-2}\\ &+3\{(l+1)/(2l+1)\cdot(l+1)/(2l+3)\\ &+l/(2l+1)\cdot l/(2l-1)-1/3\}\,C_{p-4,p-n-3,j,l}\\ &+3(l+2)/(2l+5)\cdot(l+1)/(2l+3)\cdot C_{p-4,p-n-3,j,l+2}\end{aligned} \tag{71}$$

Recursion formulae like (71) can be built up for the evaluation of Ψ_3, Ψ_4 etc. For Ψ_u, $(u \geqq 3)$, we obtain (72):

$$\begin{aligned}-(l-p)(l+p+1)\,C_{p,p-n,j,l} = &\{\text{terms on the right hand side of (71)}\}\\ &+(2l+1)\sum_{v}^{3,u}\sum_{w}^{0,v} I_{l-v+2w,v,l}\,C_{p-v,p-n-v-1,j,l-v+2w}\end{aligned} \tag{72}$$

where

$$I_{a,b,c} = \int_{-1}^{1} P_a(x)\,P_b(x)\,P_c(x)\,dx$$

When $u=\infty$ (72) yields the recursion formula for the complete Schroedinger equation. (69) can be used to solve any of this infinite sequence of Schroedinger equations. This confirms Fock's general conclusion [8, 9] that the formal solution of (54) contains logarithmic terms.

The analogue to (50) for Ψ_1, Ψ_2 etc. is:

$$\sum_{p}^{l,\infty}(2p-n)\,C_{p,p-n,j,l}-(j+1)\sum_{p}^{l,\infty}C_{p,p-n,j+1,l}=0 \tag{73}$$

The operation of (73) is similar to that of (50). It is used to ensure that the sets of terms with different values of p and j but with the same values of l and n are kept within the Domain of H.

There is the difficulty of undetermined coefficients similar to that mentioned after (51). These coefficients are for example:

(i) for $l>0$, $C_{l,-l-s,0,l}$ where $s=0, 4, 8\ldots$,

(ii) for $l=0$, $C_{2,-2-s,0,0}$ where $s=0, 4, 8\ldots$.

The terms corresponding to these coefficients can be removed from (69) without the loss of completeness for the functions in (69).

11. Variational Estimates for the Radial Limit

The variational calculations so far undertaken have been small but accurate. These take the expansion in (17) to no more than thirteen terms. Following the series solution in Section 8 the general form (74) was used:

$$\psi_0(1 + d_1 r_b + d_2 r_a + d_3 r_b^2 + d_4 r_a^2 + d_5 r_a r_b + d_6 r_a^2/r_b + d_7 r_a^3/r_b + d_8 r_a^4/r_b^2 + d_9 r_b^3 + d_{10} r_a^3 + d_{11} r_b^2 r_a + d_{12} r_a^2 r_b) \tag{74}$$

For the variation of thirteen independent parameters including ζ from (7) an eigenvalue of -2.879028589 H was obtained. This compares with -2.8790248 H obtained by Davis [10] from the variation of 66 independent parameters in a configurational interaction calculation of the sort mentioned before (46). Our value also provides a more precise upper bound than was obtained by Davis from the implementation of up to 66 terms and extrapolating for infinite terms. Not only is the eigenvalue from (74) the best estimate of the radial limit ever obtained but it also represents the most successful eigenvalue obtained in thirteen or so terms for an electron correlation problem. The error from (74) is probably less than 2 parts in 10^7. The result from 14 terms [11, 12] in the Hylleraas expansion for the Complete helium problem shows an error of 2 parts in 10^5. The high accuracy of the present calculation is due partly to the simplicity of the problem and partly to the technique of choosing terms which are important in a series solution.

We obtain the six most interesting trial wave functions from (74) each characterised by a vector of coefficients which are a subset of d. Optimum results are tabulated below. These are the relevent d-subscripts; optimum ζ values; m, the number of terms implemented by Davis which give a comparable eigenvalue.

Table 1

m	ζ	Subscripts for d_i	$E_{\min}$
55	1.598	1, 2, 3...7	−2.879,023,10 H
55	1.5941	1, 2, 3...8	−2.879,023,47 H
55	1.5132	1, 2, 3...9	−2.879,025,55 H
66	1.4842	1, 2, 3...10	−2.879,025,93 H
∞	1.4419	1, 2, 3...11	−2.879,027,31 H
∞	1.5899	1, 2, 3...12	−2.879,028,59 H

The coefficients d_1 to d_{12} for the most accurate function are: 0.0918435727; −0.4126805604; 0.0269466033; 0.0046643072; −0.0354601186; 0.1679732815; 0.0182867438; −0.0038330449; 0.0013156847; −0.0111772241; −0.0122628367; 0.0218323572.

The accuracy of these results and those in (46) reflect favourably the convergence characteristics of (17) and (51). More extensive calculations need to be carried out. These should be well ordered so as to be extensible by extrapolation procedures.

12. The Motion of the Nucleus

The helium three body problem has a feature resulting from the finite mass of the nucleus. (54) is replaced by:

$$(H^0 + H' + H'' - E_0)\,\Psi = 0 \tag{75}$$

where:

$$H'' = -\mu/M \cdot (\partial^2/\partial x_1\,\partial x_2 + \partial^2/\partial y_1\,\partial y_2 + \partial^2/\partial z_1\,\partial z_2) \tag{76}$$

μ is the reduced mass of the electron. M is the mass of the nucleus. The atomic units of length and energy in (75), (76) are defined using the reduced mass of the electron [13].

The recursion formula for the helium three body problem is given in (77), (78).

$$\begin{aligned} -(l-p)(l+p+1)\,C_{p,p-n,j,l} &= \{\text{terms on the right hand side of (72)}\} \\ &\quad -2\mu/M \cdot \{\text{terms in (78)}\} \end{aligned} \tag{77}$$

$$\begin{aligned} &C_{p+1,p-n-1,j,l+1} \cdot (l+1)/(2l+3) \cdot (l^2 + 6l + nl + 3n + 9 + pn - p^2) \\ &\quad - C_{p+1,p-n-1,j,l-1} \cdot l/(2l-1) \cdot (-l^2 + 4l + p^2 - pn + ln - 2n - 4) \\ &\quad - C_{p,p-n-1,j,l+1} \cdot (l+1)/(2l+3) \cdot \zeta(l-p+n+3) \\ &\quad + C_{p,p-n-1,j,l-1} \cdot l\zeta/(2l-1) \cdot (l+p-n-2) \\ &\quad - C_{p+1,p-n,j,l+1} \cdot (l+1)\,\zeta/(2l+3) \cdot (l+p+3) \\ &\quad + C_{p+1,p-n,j,l-1} \cdot l\zeta/(2l-1) \cdot (l-p-2) \\ &\quad + C_{p+1,p-n-1,j+1,l+1} \cdot (l+1)(j+1)/(2l+3) \cdot (l+p+3) \\ &\quad + C_{p+1,p-n-1,j+1,l-1} \cdot l(j+1)/(2l-1) \cdot (-l+p+2) \\ &\quad + l/(2l-1) \cdot \zeta^2\, C_{p,p-n,j,l-1} + (l+1)/(2l+3) \cdot \zeta^2\, C_{p,p-n,j,l+1} \\ &\quad - l/(2l-1) \cdot \zeta(j+1)\, C_{p,p-n-1,j+1,l-1} \\ &\quad - (l+1)/(2l+3) \cdot \zeta(j+1)\, C_{p,p-n-1,j+1,l+1} \end{aligned} \tag{78}$$

An approximation for the two body helium problem may be obtained using (72). The expectation is that this may be refined by successive approximations in (77). Limiting values for E_0 from (72) and (77) will be the eigenvalues for the helium two body and three body problems.

13. Conclusions

i) A method has been developed for the series solution of the two and three body problems in helium theoretical chemistry. The analytical form for the problems of radial and angular correlation has been derived. The convergence

of the solution to the radial Schroedinger equation seems satisfactory. More of this series solution remains to be investigated numerically. The series solutions for the SP, SPD, etc. and Complete equations require processing.

(ii) This work requires extension to those excited states of helium in which electrons are described in different orbitals. In these cases the space part of ψ_0^{det} from (2) is more complicated than for the ground state and other states in which electrons are paired in the same orbitals. Such work is to be carried out to facilitate the extension of present techniques to lithium for which ψ_0^{det} is still more complicated.

(ii) Another problem should be tackled as a prelude to lithium. This is the problem of three negatively charged bosons in the same $1s$ orbital centred on the nucleus.

(iv) We have made some progress with problems of series solution for Schroedinger equations. The corresponding Rayleigh-Schroedinger perturbation equations appear a parallel field of investigation.

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