On exact analytical solutions for the few-particle Schrodinger equation. IV. The asymptotic form and normalisability of the wavefunction

1983 J. Phys. A: Math. Gen. 16 4255

(http://iopscience.iop.org/0305-4470/16/18/026)

J. Phys. A: Math. Gen. **16** (1983) 4255–4264. Printed in Great Britain

On exact analytical solutions for the few-particle Schrödinger equation: IV. The asymptotic form and normalisability of the wavefunction

C L Davis and E N Maslen

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

Received 7 December 1982, in final form 10 June 1983

Abstract. Formal series solutions for the Schrödinger equations of few-particle systems contain infinitely many parameters associated with the normalisability, i.e. square-integrability of the wavefunction. The energy is one of these parameters. A method for determining the parameters by examining the asymptotic behaviour of the series has been developed. No integration, matrix inversions or trial and error procedures are involved.

As described here the method is directly applicable to the ^1S states of two-electron atoms. If the wavefunction is expressed as a multipole expansion in spherical polar coordinates, the radial functions have asymptotic properties which give rise to relations between the parameters. Values assigned to the parameters not specified by these relations (one per multipole) ensure that the wavefunction is normalisable.

1. Introduction

Formal solutions for the Schrödinger equations of small atomic systems have been obtained in the form of infinite series expansions involving numerical coefficients (Knirk 1974a, b, c, d, Davis and Maslen 1982). Recurrence relations derived from the Schrödinger equation allow most of the coefficients to be determined recursively, subject to starting conditions which ensure correct behaviour of the solutions at the nucleus. Infinitely many coefficients are not determined by the recursion process, and may have arbitrary values in the formal solutions. These coefficients and the energy E must be chosen so that, at large distances from the nucleus, the solutions decrease sufficiently rapidly to have finite norms. Normalisable solutions exist only for special values of E, which are the eigenvalues.

As yet none of the methods proposed for determining the parameters associated with normalisability has realised the potential for computational efficiency and exact treatment offered by the formal solutions. Methods suggested by Knirk (1974c) and by Demiralp and Suhubi (1977) require the solution of determinantal equations with roots which are approximations to some of the energy eigenvalues. One would hope that the limitations of this procedure, which is a time-consuming part of the usual orbital-based wavefunction calculations, could be avoided in the use of formal solutions. A method described by Davis and Maslen (1982, hereafter referred to as II) involves least-squares analyses of the coefficients. This is also cumbersome, requiring matrix inversions.

The determination of the parameters associated with normalisability ideally requires a knowledge of the asymptotic form of each solution at large distances. Extraction of

this asymptotic form from the series would enable the energy and the arbitrary coefficients to be evaluated, by requiring the remaining series to truncate.

The methods mentioned above are not suited to the exact determination of the asymptotic forms of the series. A more suitable method, described below, results from a study of the problem in spherical polar coordinates. The study reveals that some of the components of the radial wavefunctions are asymptotically separable. An analysis of asymptotic behaviour, when combined with an algebraic treatment of the type described in the preceding paper (Davis and Maslen 1983, hereafter referred to as III), enhances the prospects for obtaining exact solutions of the Schrödinger equation.

In addition to its application to exact solutions, the asymptotic separability property leads to an efficient numerical method for estimating the energy and the arbitrary coefficients. The procedure does not require matrix inversions, solution of determinantal equations or the calculation of integrals. Trial and error estimates of the energy, of the type applied to approximate series solutions by Rosenthal and Wilson (1967, 1970) and McColm (1973), are not required. Although the calculations reported here are not of high accuracy, their purpose being merely to indicate the properties of the series solutions and to guide future analytical and computational work, high accuracy should be readily obtainable.

2. Formal solutions in spherical polar coordinates

Our procedure is illustrated here by application to the ^{1}S states of helium-like atoms for which the Schrödinger equation, in coordinates defined in III, becomes

$$\left[-\tfrac{1}{2}\sum_{\tau=1}^{2}\left(r_\tau^{-2}\frac{\partial}{\partial r_\tau}r_\tau^2\frac{\partial}{\partial r_\tau}+r_\tau^{-2}\frac{\partial}{\partial\Omega}(1-\Omega^2)\frac{\partial}{\partial\Omega}\right)-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{Zr_{12}}-E\right]\Psi=0. \tag{1}$$

Z is the nuclear charge in units of the proton charge and Ω is the cosine of the angle Θ between the position vectors of the electrons relative to the nucleus. Paper III describes the recursion procedure for the formal solution

$$\Psi=\sum_{l=0}^{\infty}\sum_{ijp}C_{ijlp}P_l(\Omega)r_1^i r_2^j\exp(-\lambda_1 r_1)\exp(-\lambda_2 r_2)\ln^p r_1 \qquad r_1>r_2 \tag{2}$$

where $P_l(\Omega)$ is a Legendre polynomial and the solution for $r_1<r_2$ is obtained by interchanging r_1 and r_2 in (2). Exact expressions for the coefficients C_{ijlp} with $i+j=0$, 1 and 2 were given there.

Equation (2) describes all bound states of ^1S symmetry. The wavefunction for a particular state is obtained by choosing appropriate values for the arbitrary coefficients. We make use of the fact that the coefficients are polynomials in Z^{-1}. The energy can also be expanded as a power series in Z^{-1}, $E=\Sigma_{n=0}^{\infty}E_n(Z^{-1})^n$. A particular state is selected by setting E_0 and the Z^0 components of the arbitrary coefficients at their values for the corresponding eigenfunction of the $Z^{-1}=0$ system. This fixes λ_1 and λ_2. The lambda dependence of the coefficients causes the terms of higher power in Z^{-1} in the energy and the arbitrary coefficients to assume values appropriate to the state under consideration when the normalisability condition is applied.

We illustrate the method by calculating some Z^{-1} terms for the ground state. The extension to other ^{1}S states and to higher powers of Z^{-1} is straightforward. For the ground state, $E_0=-1$. The Z^0 component of the series solution (2) truncates if

$\lambda_1 - \lambda_2 = 1$, representing a product of hydrogen 1s eigenfunctions. Only $p = 0$ and $p = 1$ terms appear in the Z^{-1} component of the solution (2) whose radial functions become, for each $l \geqslant 0$,

$$f_l(r_1, r_2) = \exp(-r_1)\exp(-r_2)\sum_{p=0}^{1}\sum_{i,j} C_{ijlp} r_1^i r_2^j \ln^p r_1 \qquad r_1 > r_2. \tag{3}$$

The $p = 1$ component of the solution (3) is an asymptotically increasing function. To make $f_l(r_1, r_2)$ asymptotically decreasing would involve adjusting the $p = 0$ component, which contains the arbitrary coefficients, so that it just cancelled the divergence of the $p = 1$ component. This difficult problem may be avoided by replacing the $\ln^p r_1$ factors with alternative functions, logarithmic in behaviour near $r_1 = 0$, but decreasing for large r_1. The existence of these alternative forms was discussed in II. A suitable form, obtained by a simple transformation of the coefficients, is

$$f_l(r_1, r_2) = \exp(-r_1)\exp(-r_2)\sum_{p=0}^{1}\sum_{i,j} C'_{ijlp}\,[\exp(r_1)\,\mathrm{Ei}(-r_1)]^p r_1^i r_2^j \qquad r_1 > r_2 \tag{4}$$

where $\mathrm{Ei}(-r_1)$ is the exponential integral function. For convenience in notation we rewrite this expression, suppressing the l index, as

$$\exp(-r_1)\exp(-r_2)\left(\sum_{i,j} C_{ij} r_1^i r_2^j + \exp(r_1)\,\mathrm{Ei}(-r_1)\sum_{i,j} D_{ij} r_1^i r_2^j\right) \qquad r_1 > r_2. \tag{5}$$

In this form, the Z^{-1} component of the solution corresponds exactly with the first-order perturbation of the ground state, described in II.

3. Asymptotic behaviour of the radial functions

When the potential terms are neglected, equation (1) is separable with eigenfunctions of the form $f(r_1)f(r_2)P_l(\Omega)$. The equation is no longer separable in the radial variables when the electron–electron interaction is reintroduced, but the following argument leads us to expect that the radial functions in the solution (2) may tend towards a separable form at large r_1 and r_2. Where the $1/r_{12}$ potential is small, the radial functions should be nearly separable. As r_1 and r_2 approach infinity, r_{12} can only be small (and $1/r_{12}$ large) for vanishingly small angles Θ. Thus the degree of separability should increase as r_1 and r_2 increase, until the radial function for each partial wave component becomes asymptotically separable.

Correlation between the motions of the electrons, which is responsible for a cusp in the wavefunction at $r_{12} = 0$, persists in the asymptotic region, especially when $\Theta \approx 0$. In that region the cusp is produced by a superposition of Legendre polynomials, each multiplied by a smooth, separable, radial function, much as the singularity in $1/r_{12}$ at $r_{12} = 0$ is produced by such a superposition (see equation (24) of III).

4. Properties of asymptotically separable series

The radial functions in (5) may be asymptotically separable as a function of r_1 multiplied by a function of r_2. Thus the C_{ij} and D_{ij} series should each be asymptotically separable

and the asymptotic form in r_2 for the two series should be identical. The r_2 dependence could then be extracted as a common factor.

In other words, we expect the asymptotic form of the radial function to be, for $r_1 > r_2$,

$$\exp(-r_1)\exp(-r_2)\left(\sum_i C_i r_1^i \sum_j C'_j r_2^j + \exp(r_1)\,\mathrm{Ei}(-r_1)\sum_i D_i r_1^i \sum_j D'_j r_2^j\right)$$

where $C'_j = aD'_j$ and a is independent of j. Terms with large i and j should dominate the asymptotic form, so we expect that $C_{ij} \approx C_i C'_j$ and $D_{ij} \approx D_i D'_j$ for large i and j. Hence the ratios $C_{i,j+1}/C_{ij}$ and $D_{i,j+1}/D_{ij}$ should be nearly independent of i for large i and j. We should also observe that, approximately,

$$C_{i,j+1}/C_{ij} = D_{i,j+1}/D_{ij} \tag{6}$$

with the approximation improving as j increases.

The ratios $C_{i,j+1}/C_{ij}$ and $D_{i,j+1}/D_{ij}$ have been evaluated for coefficients calculated by the method described in II, that is, with the arbitrary coefficients determined by a least-squares procedure. A sample of the ratios for $l = 1$ is shown in table 1. It may be observed that, even for low values of i and j, the ratios are nearly independent of i and that equation (6) holds to a good approximation. These relationships are not observed when the arbitrary coefficients deviate from the least-squares values. For higher values of l the agreement between the ratios is better, while for $l = 0$ it is slightly worse.

The radial functions are approximately separable even at small values of r_1 and r_2 for $l > 0$. It is not clear whether the degree of separability increases with r_1 and r_2, because the calculation of the coefficients involves approximations and errors (see II) which accumulate as $i+j$ increases. For $l = 0$ the separable form, if it holds, is approached far more slowly. Nevertheless equation (6) is valid asymptotically for all l. This property allows the values of many of the arbitrary coefficients in the formal solution to be determined.

5. Reduction of the number of undetermined coefficients

The coefficients $C_{l+4n,l}$ for non-negative integers n are not determined by the recurrence relation. Except for C_{00}, which is replaced by E_1, these must be chosen to make the norm of the solution finite. We now use equation (6) to reduce the number of undetermined coefficients to one for each l.

A coefficient $C_{i,j'+1}$ with $i \geq l$ and $j'+1 \geq l$ depends linearly on the arbitrary coefficients encountered earlier in the recursion process, that is, on those with $n \leq \frac{1}{4}(i+j'+1-2l)$ (see III). The D_{ij} coefficients are independent of the arbitrary coefficients. Setting $j = j'$ in (6) yields an equation linear in these arbitrary coefficients. Additional linear equations involving the same arbitrary coefficients may be obtained by substituting $j = j'-1$, $j'-2$, etc into (6), keeping i and l constant. The equations may be solved simultaneously by a straightforward elimination method.

Although it is possible to obtain more equations than the number of arbitrary coefficients in the $j = j'$ equation, the equations are not all independent. One coefficient always remains to be determined by normalisability. The equations give approximate expressions for the arbitrary coefficients in terms of C_{ll} (for $l > 0$) or E_1 (for $l = 0$). Including equations between ratios of higher-order coefficients, which display the

Table 1. Ratios of $l = 1$ coefficients. The arbitrary coefficients in the formal solution were determined by the least-squares method of II.

	$C_{i,j+1}/C_{ij}$					$D_{i,j+1}/D_{ij}$				
$j \backslash i$	1	2	3	4	5	1	2	3	4	5
1	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00	0.500 00
2	0.403 54	0.393 95	0.391 12	0.386 18	0.387 41	0.400 00	0.400 00	0.395 46	0.392 94	0.388 74
3	0.335 77	0.329 07	0.327 03	0.323 39	0.324 31	0.333 33	0.333 33	0.330 14	0.328 34	0.325 29
4	0.289 55	0.285 13	0.283 27	0.281 14	0.280 96	0.288 14	0.288 14	0.285 71	0.284 31	0.282 13
5	0.254 42	0.251 40	0.249 71	0.248 51	0.247 72	0.253 60	0.253 60	0.251 68	0.250 57	0.248 94
6	0.226 83	0.224 66	0.223 09	0.222 39	0.221 31	0.226 46	0.226 46	0.224 82	0.223 86	0.222 54
7	0.204 61	0.202 98	0.201 50	0.201 08	0.199 87	0.204 59	0.204 59	0.203 11	0.202 23	0.201 09
8	0.186 39	0.185 14	0.183 72	0.183 45	0.182 18	0.186 63	0.186 63	0.185 26	0.184 43	0.183 38
9	0.171 20	0.170 22	0.168 84	0.168 67	0.167 36	0.171 65	0.171 65	0.170 34	0.169 55	0.168 55
10	0.158 37	0.157 59	0.156 22	0.156 13	0.154 77	0.158 97	0.158 97	0.157 72	0.156 94	0.155 97
11	0.147 39	0.146 77	0.145 41	0.145 37	0.143 94	0.148 11	0.148 11	0.146 90	0.146 14	0.145 18
12	0.137 90	0.137 41	0.136 04	0.136 06	0.134 43	0.138 71	0.138 71	0.137 54	0.136 79	0.135 83
13	0.129 61	0.129 23	0.127 85	0.127 94	0.125 76	0.130 50	0.130 50	0.129 36	0.128 63	0.127 66
14	0.122 32	0.122 03	0.120 66	0.120 74	0.117 60	0.123 26	0.123 26	0.122 16	0.121 44	0.120 47
15	0.115 86	0.115 64	0.114 37	0.114 13	0.109 93	0.116 83	0.116 83	0.115 77	0.115 07	0.114 09
16	0.110 08	0.109 94	0.108 93	0.107 66	0.133 35	0.111 07	0.111 07	0.110 07	0.109 39	0.108 40
17	0.104 89	0.104 84	0.104 36	0.100 81		0.105 89	0.105 89	0.104 95	0.104 30	
18	0.100 16	0.100 30	0.095 43			0.101 20	0.101 20	0.100 32		
19	0.095 80	0.096 30				0.096 92	0.096 92			
20	0.092 35					0.093 00				

asymptotic separability of the radial functions more strongly for $l > 0$, leads to convergence of the approximate results towards the exact relationships. For reasons yet to be completely understood, the precise nature of this convergence differs in the $l > 0$ and $l = 0$ cases.

5.1. The $l > 0$ case

For $l > 0$, solution of the simultaneous equations provides the expressions

$$C_{l+4n,l} = a_{ln}C_{ll} + b_{ln} \qquad n \geq 1. \tag{7}$$

Our numerical solutions, based on C_{ij} and D_{ij} coefficients evaluated as in II, show that a_{ln} is independent of j' to high accuracy. This implies that a_{ln} should be obtainable exactly from the algebraic expressions for low-order coefficients.

The b_{ln} term in (7) converges to a limit as j' increases. Figure 1 displays this convergence for b_{11}, a component of C_{51}.

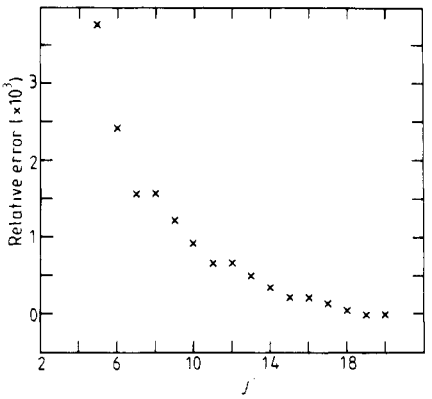

Figure 1. The relative error in b_{11} compared with the $j' = 20$ value.

The value of i in (6) is not important. The results in figure 1 are for $i = l$. Calculations using different values of i give apparently identical values for a_{ln}. The estimates of b_{ln} appear, as expected, to converge with increasing j' to limits independent of i.

A study of the transformation taking equation (3) into equation (4) shows that

$$C'_{ljl1} = C_{ljl1} \qquad \text{and} \qquad C'_{ljl0} = C_{ljl0} - \gamma C_{ljl1}$$

where γ is Euler's number (Abramowitz and Stegun 1965). Similar relations apply for transformations between solutions containing the alternative logarithmic functions described in II (except that γ must be replaced by a different constant). Thus, if equation (6) holds on the $i = l$ line for one form of the solution, it will also be true for the alternative forms. The same a_{ln} and limiting b_{ln} values will be obtained for all forms.

5.2. The $l = 0$ case

Solving the simultaneous equations with $i \geq 2$ gives expressions for the $l = 0$ arbitrary coefficients in the form

$$C_{4n,0} = a_{0n}E_1 + b_{0n} \qquad n \geq 1. \tag{8}$$

The $i=1$ equations cannot be used since the coefficients C_{1j} are independent of E_1 and the arbitrary coefficients. The $i=0$ equations provide incorrect estimates of E_1 and leave C_{40} undetermined. As $j' \to \infty$, however, E_1 becomes indeterminate, while a relation between E_1 and C_{40} emerges.

Provided $j' > i$, a_{0n} and b_{0n} appear to be independent of j'. For $j' < i$ the estimates of a_{0n} and b_{0n} are poor. Improved estimates of b_{0n} are obtained by increasing i in (6). The value of a_{0n} appears to be independent of i, and should be obtainable exactly from the $i=2$ equations.

Figure 2 shows the estimated value of C_{40} as a function of i', the value of i used in (6). These results were obtained with E_1 set at its exact value of 0.625 Z-scaled atomic units. The estimates oscillate about the least-squares value of II, converging as i' increases.

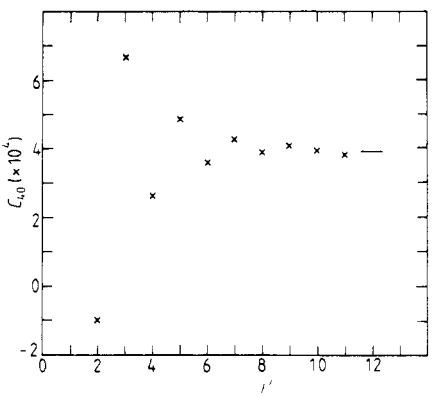

Figure 2. The coefficient C_{40} as a function of i' for $E_1 = 0.625$ Z-scaled atomic units. The least-squares value (——) from II is shown for comparison.

6. The asymptotic series in r_2

When the arbitrary coefficients are chosen in accordance with equations (7) and (8), the asymptotic form of the solution in r_2 is determined. The true asymptotic nature of the solution has not been proven, but we consider its probable form.

From our argument of § 3, we expect the formal solutions of the Schrödinger equation to approach separable solutions of the independent electron problem (in which the $1/r_{12}$ term is neglected) asymptotically. Such solutions exist for $l > 0$ and have the form

$$f_l^{\text{sep}} = \exp(-r_1)\exp(-r_2)\sum_{m=0}^{\infty}\frac{2^m(l+m-1)!}{m!(2l+m+1)!}r_1^{m+l}\sum_{n=0}^{\infty}\frac{2^n(l+n-1)!}{n!(2l+n+1)!}r_2^{n+l}. \tag{9}$$

Solutions of the full equation should have the same asymptotic form in r_2 as f_1^{sep}. In support of this proposition we note that the recurrence relation for the D_{ij}, considered in isolation, generates a separable series with the same r_2 behaviour as f_l^{sep} (the r_1 behaviour is the same as f_l^{sep} for the solution in (3), but different for the alternative forms of the solution). Numerical calculations show that the true D_{ij} series is very close to the separable form, and appears to be the same asymptotically. Equation (6) implies that the C_{ij} series should also have this asymptotic form.

For $l = 0$, the independent electron problem has no infinite-norm separable solutions with the physically correct behaviour at the origin. Only asymptotically separable solutions exist and the exact asymptotic form of the solution is not known.

7. Solution of the normalisability problem

The asymptotic form in r_2, proposed in (9), is a rapidly increasing function of r_2. This fact does not jeopardise the normalisability of the solutions, since the solutions apply to the $r_2 < r_1$ region. The asymptotic form in r_1 must, however, be a rapidly decreasing function if the norm of the wavefunction is to be finite.

We expect a finite-norm solution to be represented by an alternating series in r_1. The r_1 behaviour of the solution is controlled by the remaining undetermined parameters, C_{ll} (for $l > 0$) and E_1 (for $l = 0$). Examining a series having C_{ll} or E_1 near its correct value, we observe that initially the series alternates. With increasing i the series changes to a non-alternating form as infinite-norm solutions of the independent electron problem begin to dominate its behaviour. Improving the estimate of C_{ll} or E_1 extends the region of alternating behaviour—to infinity for exact estimates.

These properties of the series solution may be exploited to find estimates of C_{ll} and E_1. One method involves equating a coefficient C_{il} to zero for some $i = i^*$. This gives an approximate linear equation that can be solved for C_{ll} or E_1. The resulting series alternates for $i < i^*$ and is non-alternating for $i > i^*$. Increasing i^* improves the estimate of the undetermined parameter.

An alternative method giving more rapid convergence involves the minimisation of the product $C_{i,l}C_{i+1,l}$ as a function of C_{ll} or E_1. Figures 3 and 4 show the convergence of estimates of C_{11} and E_1 with increasing i^*, the value of i for which the product is minimised. The converged estimates in this relatively crude calculation are reasonably close to the least-squares value of C_{11} (from II) and the exact value of E_1. The discrepancies arise because the condition derived from the asymptotic behaviour has been applied in an approximate way (using only low-order coefficients) in this exploratory study.

The results obtained here are for the ground state of a helium-like atom. Excited states of ^{1}S symmetry may be treated in the same way by selecting other sets of λ_1,

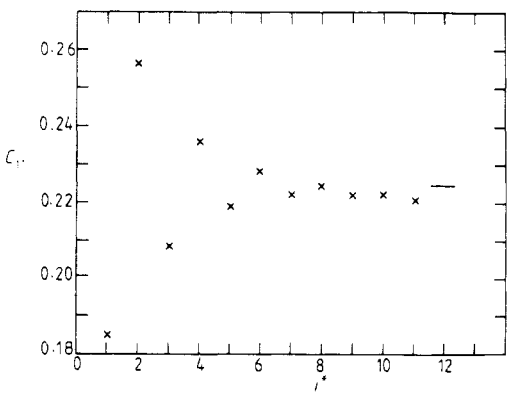

Figure 3. The value of C_{11} that minimises $C_{i^*,l}C_{i^*+1,l}$, shown as a function of i^*. The least-squares value (——) from II is shown for comparison.

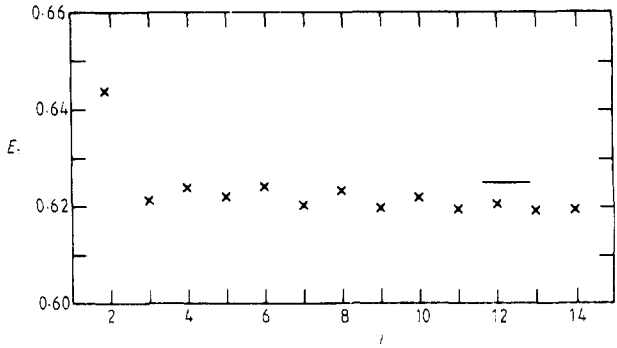

Figure 4. The value of E_1 that minimises $C_{i^*,0}C_{i^*+1,0}$, shown as a function of i^*. The exact value (——) is 0.625 Z-scaled atomic units.

λ_2 and E_0 values for which the Z^0 component of the series solution truncates. For each quantum state there is a unique choice of values for E_1 and the arbitrary coefficients that produces a finite-norm solution.

8. Conclusions

The radial functions for ^{1}S states of a helium-like atom, expressed in spherical polar coordinates, contain components that are asymptotically separable. The multiplier for a logarithmic contribution has the same asymptotic form as the polynomial component of the solution. Such asymptotic properties reduce the problem of finding finite-norm series solutions of the Schrödinger equation from one involving infinitely many parameters to a set of one-parameter problems.

A computational procedure for exploiting the asymptotic properties requires only simple algebraic steps, making a very efficient method for calculating the wavefunction possible. With careful programming, numerical results of far greater accuracy than those reported in this preliminary study could be obtained. Furthermore, the insight into the nature of the physical solutions provided by this property will be helpful in deriving the exact solutions.

We expect the properties and methods described here to be applicable to other states of the two-electron Coulomb problem, to systems with a greater number of particles, and to systems with other than Coulomb forces.

Acknowledgment

This work was supported by the Australian Research Grants Scheme.

References

Abramowitz M and Stegun I A (ed) 1965 *Handbook of Mathematical Functions* (New York: Dover)
Davis C L and Maslen E N 1982 *Proc. R. Soc.* A **384** 89–105
—— 1983 *J. Phys. A: Math. Gen.* **16** 4237–53

Demiralp M and Suhubi E 1977 *J. Math. Phys.* **18** 777–85
Knirk D L 1974a *J. Chem. Phys.* **60** 66–80
—— 1974b *J. Chem. Phys.* **60** 760–5
—— 1974c *Proc. Natl Acad. Sci. USA* **71** 1291–3
—— 1974d *Phys. Rev. Lett.* **32** 651–4
McColm D 1973 *Phys. Rev.* A **7** 1272–6
Rosenthal C M and Wilson E B 1967 *Phys. Rev. Lett.* **19** 143–5
——1970 *J. Chem. Phys.* **53** 388–91