Two-electron atoms. The Kinoshita expansion

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Kinoshita has pointed out that the famous Hylleraas expansion, $\psi = \sum A_{l,m,n}\, s^l u^m t^n$, is unable to furnish a formal solution to the Schrödinger equation for the two-electron atom. He further noted that the source of the difficulty is the arbitrary restriction of the indices l and m to positive values. The Kinoshita variables $s = s$, $p = u/s$, and $q = t/u$ alleviate this difficulty, and a Kinoshita expansion $\psi = \sum C_{l,m,n}\, s^l p^m q^n$ seems capable of furnishing formal solutions. It is shown here for S states that $C_{l,m,n} = 0$ for all $C_{l,m,n}$ with $n > m$. This result is equivalent to the statement that negative powers of u are not needed. This result, when applied to the $1\,^1S$ ground state, allows the determination of all coefficients of the form $C_{2,2\mu+1,n}$. The implied infinite series are summed and explicit closed-form expressions are found which involve a novel logarithmic term. Conditions which must be imposed on that part of ψ constructed from $C_{2,2\mu,n}$ are discussed.

I. INTRODUCTON

The Hamiltonian equation for two electrons of charge e and a nucleus of charge $-Ze$ moving only under the influence of their mutual Coulombic interactions is given in atomic units[1] by

$$\{-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + 1/r_{12}\}\psi = E\psi. \qquad (1)$$

The nucleus is taken to be infinitely massive, and relativistic effects are ignored. The eigenfunctions and eigenvalues of this equation have been studied intensively over the past 50 years by various powerful methods of approximation, yet surprisingly little of an exact nature is known. Thus in 1937, Barlett[2] pointed out, using elementary arguments, that for small values of the interparticle distances, the ground-state solution has the form

$$\psi \approx 1 - Z(r_1 + r_2) + \tfrac{1}{2} r_{12} + \cdots . \qquad (2)$$

Fock[3] has given a rigorous proof of Bartlett's result. Fock employed an expansion in the so-called hyperspherical coordinates. Certain of the coefficients in these expansions, or parts of the coefficients, have been obtained exactly,[4] but results have been meager.

Kinoshita[5] has studied an expansion of the form

$$\psi \approx \sum C_{l,m,n} s^l p^m q^n, \qquad (3a)$$

where

$$s = r_2 + r_1, \quad p = r_{12}/s, \quad q = (r_2 - r_1)/r_{12}. \qquad (3b)$$

If this expansion is substituted into Eq. (1), a recursion relation between the $C_{l,m,n}$ is obtained as follows:

$$\begin{aligned}(n+1)(n+2)C_{l,m+2,n+2} &+ (m-n+2)(m+n+3)C_{l,m+2,n} \\ &+ (n+m-l)(n-m-l-3)C_{l,m,n} \\ &- (n-m-2)(n+m-2l-3)C_{l,m,n-2} \\ &- (l-m+2)(l-m+1)C_{l,m-2,n-2} + 4ZC_{l-1,m,n} \\ &- C_{l-1,m+1,n} + C_{l-1,m-1,n-2} + EC_{l-2,m,n} \\ &- EC_{l-2,m-2,n-2} = 0 . \end{aligned} \qquad (4)$$

On the basis of this relation and of conditions of continuity and single valuedness, Kinoshita found relations between certain of the coefficients, the $C_{l,m,n}$, but did not pursue his studies systematically.

Kinoshita initially proposed his expansion as a generalization of the famous Hylleraas expansion[6]

$$\psi = \sum A_{l,m,n} s^l u^m t^n, \qquad (5a)$$

where

$$s = r_1 + r_2, \quad u = r_{12}, \quad t = r_2 - r_1. \qquad (5b)$$

Kinoshita noticed that Eq. (5a) is unable to furnish a formal solution to Eq. (1). Kinoshita pointed out that negative powers of s and of u seemed to be allowed by the boundary conditions, so that the restriction of l and m to positive values was an arbitrary restriction. In the present paper it is shown that negative powers of u are not needed, and, in fact, that they violate the boundary conditions.

Further, in the expression for the 1^1S ground state of the two-electron atom, all coefficients of the form $C_{2,2\mu+1,n}$ have been determined. That part of the total wave function which is constructed from these terms,

$$\psi_{2,\,\mathrm{odd}} = s^2 \sum_{\mu,\, n} C_{2,\, 2\mu+1,\, n} p^{2\mu+1} q^n ,$$

has been explicitly summed to give a closed-form expression for $\psi_{2,\mathrm{odd}}$. The expression includes a novel logarithmic term of an unexpected and complicated form.

II. $C_{l,m,n}$ FOR $n > m$

The basic contribution of the present paper is the establishment of the following result, valid for all S states,

$$C_{l,m,n} = 0 , \quad n > m . \tag{6}$$

The result is established by an induction. The induction proceeds as follows. Suppose Eq. (6) holds for all $m \leqslant m_0$. There are two cases. Either m_0 and n have the same parity or they do not. The easiest case to establish is m_0 and n have different parities. In this case, substitute into the recursion relation Eq. (5),

$$m = m_0 - 1 ,$$
$$n = m_0 + 2\nu + 1 , \quad \nu = 0, 1, 2, \ldots . \tag{7}$$

There results

$$(m_0 + 2\nu + 2)(m_0 + 2\nu + 3) C_{l,\, m_0+1,\, m_0+2\nu+3}$$
$$- 2\nu(2m_0 + 2\nu + 3) C_{l,\, m_0+1,\, m_0+2\nu+1}$$
$$- 2\nu(2m_0 + 2\nu - 2l - 3) C_{l,\, m_0-1,\, m_0+2\nu-1} = 0 . \tag{8}$$

For $\nu = 0$, there follows immediately,

$$C_{l,\, m_0+1,\, m_0+3} = 0 , \tag{9}$$

and for $\nu \geqslant 1$,

$$C_{l,\, m_0+1,\, m_0+2\nu+3} = [2\nu/(m_0 + 2\nu + 2)] C_{l,\, m_0+1,\, m_0+2\nu+1} . \tag{10}$$

Repeated application of this formula to the term on its own right-hand side leads to

$$C_{l,\, m_0+1,\, m_0+2\nu+3} \sim C_{l,\, m_0+1,\, m_0+3} . \tag{11}$$

The right-hand side is zero by virtue of Eq. (9), and hence

$$C_{l,\, m_0+1,\, m_0+2\nu+3} = 0 , \quad \nu = 0, 1, 2, \ldots . \tag{12}$$

The case in which m_0 and n have the same parity is approached by substituting into the recursion relation the parameter values

$$m = m_0 - 1 ,$$
$$n = m_0 + 2\nu + 2 . \tag{13}$$

There results

$$(m_0 + 2\nu + 3)(m_0 + 2\nu + 4) C_{l,\, m_0+1,\, m_0+2\nu+4}$$
$$- (2\nu + 1)(2m_0 + 2\nu + 4) C_{l,\, m_0+1,\, m_0+2\nu+2} = 0 . \tag{14}$$

Straightforward manipulation of this expression leads to

$$C_{l,\, m_0+1,\, m_0+2\nu+4}$$
$$= 2(m_0 + 2) \frac{(\nu+1)(\nu+2)\cdots(m_0+\nu+2)}{(2\nu+2)(2\nu+3)\cdots(m_0+2\nu+4)}$$
$$\times C_{l,\, m_0+1,\, m_0+2} . \tag{15}$$

At this point it is convenient to continue the proof with an n of a definite parity, say n even, the case of principal interest. A parallel argument can be made to apply *mutatis mutandis* to odd n also. The numerator of Eq. (15) consists of $m_0 + 2$ factors involving ν. The denominator consists of $m_0 + 3$ such factors. There are $\frac{1}{2} m_0 + 2$ even terms in the denominator, and each even factor in the denominator divides a factor in the numerator. Thus, after cancellation, the numerator is given by a polynomial of degree $\frac{1}{2} m_0$ in ν. Then Eq. (15) becomes

$$C_{l,\, m_0+1,\, n} = \frac{R_\mu(n) C_{l,\, m_0+1,\, m_0+2}}{(n-1)(n-3)\cdots(n-m_0+1)(n-m_0-1)} . \tag{16}$$

Note that this new version of Eq. (15) is now valid for $\nu = -1$, and that n has been redefined as $m_0 + 2\nu + 4$. The numerator is a polynomial of degree μ in n, where $2\mu = m_0$. The denominator is a polynomial of degree $\mu = 1$. Thus the right-hand side of Eq. (16) may be written as a sum of partial fractions as follows:

$$C_{l,\, m_0+1,\, n} = C_{l,\, m_0+1,\, m_0+2} \sum_{i=0}^{\mu} \frac{A_i(m_0)}{n - 2i - 1} . \tag{17}$$

That part of the total wave function which arises from these $C_{l,\, m_0+1,\, n}$ is given by

$$s^l p^{m_0+1} \sum_{n=m_0+2}^{\infty} C_{l,\, m_0+1,\, n} q^n = s^l p^{m_0+1} C_{l,\, m_0+1,\, m_0+2} \Phi(m_0) , \tag{18}$$

where

$$\Phi(m_0) = \sum_{n=m_0+2}^{\infty} \sum_{i=0}^{\mu} \frac{A_i(m_0) q^n}{n - 2i - 1}$$
$$= \sum_{i=0}^{\mu} A_i(m_0) \sum_{n=m_0+2}^{\infty} \frac{q^n}{n - 2i - 1} . \tag{19}$$

Let $n_0 = m_0 + 2$. Then

$$\sum_{n=n_0}^{\infty} \frac{q^n}{n - 2i - 1} = \tfrac{1}{2} q^{2i+1} \ln \frac{1+q}{1-q} - q^{2i+1} \sum_{n=0}^{n_0-2i-4} \frac{q^{n+1}}{n+1} . \tag{20}$$

Thus

$$\Phi(m_0) = P_\mu(q^2) q \ln[(1+q)/(1-q)] + Q_\mu(q^2) , \tag{21}$$

where

$$P_\mu(q^2) = \sum_{i=0}^{\mu} A_i(m_0) q^{2i} , \tag{22}$$

$$Q_\mu(q^2) = \sum_{i=0}^{\mu} \sum_{n=0}^{n_0-2i-4} \frac{q^{n+1}}{n+1} . \tag{23}$$

The logarithmic term diverges as q approaches ± 1.

On the other hand, both P and Q are well-behaved functions of q^2 for all values of q. Further, as q^2 goes to 1, P_μ has the value

$$P_\mu(1)=\sum_{i=0}^{\mu} A_i(m_0). \tag{24}$$

The sum on the right-hand side of Eq. (24) is exactly the coefficient of n^μ in R_μ as defined in Eq. (16), and hence is necessarily not zero. It follows then that

$$P_\mu(1)\neq 0, \tag{25}$$

and hence $\Phi(m_0)$ as given in Eq. (21) diverges logarithmically. This singularity can not be removed by forming linear combinations of terms involving the different $\Phi(m_0)$, as their coefficients, the $s^l p^{m_0+1}$, are independent variables. There are no other sources of bad behavior remaining as q^2 goes to 1. Hence, the only way to remove the singularity is to require

$$C_{l,m_0+1,n}=0, \quad n>m_0+1, \tag{26}$$

which establishes the second case.

The two inductions proved above can now be combined to establish the desired result, Eq. (6). Assume that Eq. (6) is valid for all $m\leq m_0$ for a particular parity of m_0. Application of the relevant case, one or the other of the two inductions above, will establish that Eq. (6) is valid for $m\leq m_0+1$. Then application of the other induction will establish the validity of Eq. (6) for $m\leq m_0+2$, and so on.

It remains to demonstrate that the lemma holds for the initial cases. Kinoshita has shown that

$$C_{l,0,n}=0, \quad n\geq 1, \tag{27}$$

$$C_{l,1,n}=0, \quad n\geq 1. \tag{28}$$

Equation (27) follows directly from the requirement of continuity and single valuedness, and Eq. (28) from Kato's second theorem [see Ref. 5, Eq. (A6)]. Kinoshita's version of Eq. (28) only claimed validity for $n\geq 2$. The slight (but vital) extension to $n=1$ may be verified directly from Kato's second theorem, or mediately from Kinoshita's own Eq. (A10). Insertion of $m=0$ into the recursion relation leads to the result

$$C_{l,2,n}=0, \quad n \text{ even and } n\geq 4.$$

This same substitution ($m=0$) shows that already the $C_{l,2,n}$ series with n odd leads to a divergence of the type in Eq. (21). The singularity can only be removed by requiring $C_{l,2,1}$ be zero, so that

$$C_{l,2,n}=0, \quad n\neq 0,2 \tag{29}$$

This concludes the induction.

III. RESULTS FOR THE SECOND-ORDER TERM ($l=2$)

On the basis of the exactly known zero- and first-order terms for the ground state, i.e., Eq. (2), and on the basis of the result established above, Eq. (6), it is now productive to investigate the recursion relation for the case $l=2$. A complete solution is not to be expected, of course, because the behavior at each singularity has not been considered. The form of the expansion Eq. (3) ensures correct behavior at $s\to 0$ and at $p\to 0$, but it remains to extract further information from the case variables that are large and from the case $p,q\to 1$. Because of the symmetry with respect to interchange of r_1 and r_2, the expansion for the $1\,^1S$ state of helium is written

$$\psi=\sum C_{l,m,2\nu}s^l p^m q^{2\nu}, \tag{30}$$

where ν is an integer. Systematic substitution into the recursion relation gives explicit results for $C_{2,2\mu+1,2\nu}$ (i.e., for odd m). These results may be summarized as follows:

$$C_{2,2\mu+1,2\nu}=\frac{Z}{3\times 2^{2\mu}}\,\frac{(-)^\nu(\mu-\nu)}{(2\mu-1)(2\nu-1)\mu}\binom{\mu}{\nu}\binom{2\mu}{\mu}+A_{01},$$

$$A_{01}=\frac{Z}{6}\,\frac{(2\mu+3)}{(2\mu-1)(2\mu+1)} \quad \text{if } \nu=0, \tag{31}$$

$$=-\frac{Z}{6}\,\frac{1}{(2\mu-1)} \quad \text{if } \nu=1,$$

where the factor $(\mu-\nu)/\mu$ is taken as zero when $\mu=0$. Alternately, note that

$$\frac{\mu-\nu}{\mu}\binom{\mu}{\nu}=\binom{\mu-1}{\nu},$$

and take this factor as zero when $\mu-1$ is negative. Let the second-order wave function ($l=2$) be denoted by

$$\psi_2=\psi_{2,\text{odd}}+\psi_{2,\text{even}}, \tag{32}$$

where

$$\psi_{2,\text{odd}}=s^2\sum_{\mu,\nu} C_{2,2\mu+1,2\nu}p^{2\mu+1}q^{2\nu} \tag{33}$$

and $\psi_{2,\text{even}}$ is a similar summation involving the even powers of p. It is possible to carry out the indicated summations in Eq. (33) and to obtain $\psi_{2,\text{odd}}$ in closed form. The required summations are outlined in the appendix. The final result is

$$\psi_{2,\text{odd}}=\tfrac{1}{3}Zs^2\{\tfrac{1}{4}(2p^2-1-p^2q^2)\ln[(1+p)/(1-p)] +pu-2p-pq\ln[(1+r)/(1-r)]\}, \tag{34}$$

where

$$u^2=1-p^2+p^2q^2, \tag{35}$$

and

$$r = q(1-\lambda)/(u+\lambda), \quad (36)$$

with

$$\lambda^2 = 1 - p^2. \quad (37)$$

The final form, Eq. (34), has been extensively checked by a direct reexpansion, by numerical methods, and by substitution into Eq. (1) as described in Sec. IV.

The logarithmic term involving r is rather complicated, and does not resemble any logarithmic term suggested for the helium-atom wave function by previous investigators. These suggestions include terms which contain[7,8] $\ln s$, terms which contain[9] $\ln s(1+p)$ and $\ln sp(1+q)$, and of course the famous Bartlett-Fock terms[2,3] which contain $\ln s^2(1+p^2q^2)$.

IV. CONDITIONS ON $\psi_{2,\text{even}}$

In general,

$$T\psi_l + V\psi_{l-1} + E\psi_{l-2} = 0, \quad (38)$$

where T is the kinetic energy term and V is the potential energy term of Eq. (1). In view of Eq. (32), it follows that

$$T\psi_{2,\text{even}} + 4Z/(1-p^2q^2) + E + \tfrac{1}{2} = 0, \quad (39)$$

$$T\psi_{2,\text{odd}} - Z/p - 2Zp/(1-p^2q^2) = 0. \quad (40)$$

Equation (40) furnished an excellent and thorough check on the result presented in Eq. (34). In the limit as p approaches unity, both of the logarithmic terms in $\psi_{2,\text{odd}}$ contain terms that diverge like $\ln(1-p)$. Hence, $\psi_{2,\text{even}}$ must also contain a divergence of this form, as it is the only part of ψ capable of combining with $\psi_{2,\text{odd}}$ to eliminate the singularity. Thus

$$\lim_{p\to 1} \psi_{2,\text{even}} = s^2 f(p,q)\ln(1-p) + s^2 g(p,q), \quad (41)$$

where f and g are well-behaved as p approaches unity. The function f must also remain finite (nonzero).

APPENDIX: SUMMATION OF EQ. (33)

The summations needed to establish Eq. (34) from Eqs. (33) and (31) are not so much difficult as devious. Most of the summations may be obtained from the following easily verified evaluations:

$$\sum_{n=0}^{m} \binom{m}{n}(-q^2)^n = (1-q^2)^m \quad (A1)$$

$$\sum_{m=1}^{\infty} \binom{2m}{m} \frac{x^m}{m(2m-1)} = \sum_{m=1}^{\infty} \binom{2m}{m}\left(\frac{2}{2m-1} - \frac{1}{m}\right)x^m = 2 - 2u + 2\ln(1+u)/2, \quad (A2)$$

where u is the same u as in Eq. (35) and is related to x by

$$u = (1-4x)^{1/2} \quad (A3)$$

$$\sum_{m=0}^{\infty} \frac{2m+3}{(2m-1)(2m+1)} p^{2m+1} = (p^2 - \tfrac{1}{2})\ln\frac{1+p}{1-p} - 2p \quad (A4)$$

$$\sum_{m=1}^{\infty} \frac{p^{2m+1}}{2m-1} = \tfrac{1}{2}p^2 \ln\frac{1+p}{1-p}. \quad (A5)$$

There remains

$$\phi = \sum_{m=1}^{\infty} \left(\frac{p}{2}\right)^{2m} \binom{2m}{m} \frac{1}{m} \sum_{n=0}^{m} \binom{m}{n} \frac{(-q^2)^n}{2n-1}. \quad (A6)$$

There follows immediately

$$q^2 \frac{\partial}{\partial q}\left(\frac{\phi}{q}\right) = \sum_{m=1}^{\infty} \left(\frac{p}{2}\right)^{2m} \binom{2m}{m} \frac{(1-q^2)^m}{m} = -2\ln(1+u)/2. \quad (A7)$$

Thus

$$\phi = -2q \int \frac{dq}{q^2} \ln\tfrac{1}{2}(1+u). \quad (A8)$$

Let $z = pq$. There follows

$$\phi = -2z \int \frac{dz}{z^2} \ln\tfrac{1}{2}(1+u). \quad (A9)$$

It is easily shown then that

$$\phi = 2\ln(1+u) - 2pq\ln\lambda - 2pqG, \quad (A10)$$

where

$$G = \int \frac{d\theta}{\lambda + \cos\theta}, \quad z = \lambda\tan\theta. \quad (A11)$$

G is a standard integral, and may be obtained from tables.

$$G = (1/p)\ln[(1+r)/(1-r)] + \kappa(p), \quad (A12)$$

where

$$r = q(1-\lambda)/(u+\lambda), \quad (A13)$$

and κ is the constant of integration and turns out to be zero.

[1]Units of length a_0, units of energy $2Rhc$, where a_0 is the Bohr radius and R is the Rydberg.

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