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# On the Exact Helium Wave Function Expansion

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A  $^1S$  wave function's expansion for 2 electron atoms and ions is obtained and the leading coefficients are reported.

## I. INTRODUCTION

The ground electronic state of Helium (and its iso-electronic ions) has been studied extensively since the original work of Hylleraas [1]. Absent an exact solution, efforts have been expended to find compact approximate wave functions which give increasingly better energy eigenvalues for the energy [2].

The  $^1S$  wave function for Helium's two electrons is not a power series in  $r_1, r_2$  and  $r_{12}$ , as shown by Bartlett, Gibbons and Dunn [3] who demonstrated that a unique solution for  $\psi(r_1, r_2, r_{12})$  of the form

$$\psi = \sum_{i,j,k} C_{i,j,k} r_1^i r_2^j r_{12}^k$$

does not exist. They showed that the coefficient of  $\frac{r_2^2}{r_1 r_{12}} \leftrightarrow C_{101} = 0$ , that the coefficients of  $\frac{1}{r_1} \leftrightarrow 2c_{100} + c_{010} = 0$  and that the coefficients of  $\frac{r_1}{r_{12}} \leftrightarrow 5C_{101} - \frac{1}{2}C_{100} = 0$ .

Fock [4–6] showed that there must be logarithmic terms in the expansion, and gave the form the expansion had to take. Defining  $R = \sqrt{r_1^2 + r_2^2}$ , he wrote (in current but mixed notation)

$$\begin{aligned} \psi = & 1 - Z(r_1 + r_2) + \frac{1}{2}r_{12} + \\ & R(\psi_{2,1}\ell nR + \psi_{2,0}) + \\ & R^{1/2}(\psi_{5/2}R\ell nR + R\psi_{5/2,0}) + \\ & R^2(\psi_{3,2}\ell n^2R + \psi_{3,1}\ell nR + \psi_{3,0}) + \dots \end{aligned} \quad (1.1)$$

with  $Z = 2$  for Helium.  $\psi_{2,1}$  was shown by Fock to be a linear combination of  $\cos \alpha$  and  $\sin \alpha \cos \vartheta$  where  $\cos \alpha \leftrightarrow r_1^2 - r_2^2$  and  $\sin \alpha \cos \vartheta \leftrightarrow r_{12} - 1$   $R^{1/2} \cos(\alpha/2)$  and  $R^{1/2} \sin(\alpha/2)$  are equal to  $r_1$  and  $r_2$  respectively, while  $r_{12}$  is equal to  $R^{1/2}(1 - \sin \alpha \cos \vartheta)$ .

## II. ANSATZ

It is hard to fit the Fock form coherently into the Bartlett et al. formulation of an *Ansatz* for the Schrödinger Equation's possible solution.

The idea that the coefficients of  $\psi_{2,1}$  are a linear combination of  $\sin \alpha \sin \vartheta$  and  $\cos \alpha$  is worrisome, as  $\cos \alpha$  is

an odd function of  $r_1$  and  $r_2$  and the ground state of 2-electron systems should be even with respect to these two variables. If the coefficient of  $\cos \alpha$  in  $\psi_{2,1}$  is indeed zero, then  $\psi_{2,1} = r_1^2 + r_2^2 - r_{12}^2$ . But then what is  $\psi_{2,0}$ ?

The following expansion is proposed:

$$\begin{aligned} & 1 + C_{1,0,0}r_1 + C_{0,1,0}r_2 + C_{0,0,1}r_{12} + \\ & + C_{1,1,0}r_2r_2 + C_{1,0,1}r_1r_{12} + C_{0,1,1}r_2r_{12} + \\ & \text{constant} * (r_1r_{12}\ell n r_1r_{12} + r_2r_{12}\ell n r_2r_{12}) + \dots \end{aligned} \quad (2.1)$$

as the first few terms. The last term shown in Equation 2.1 mitigates the Bartlett, Gibbons and Dunn conundrum. This suggests the following Ansatz:

$$\psi = \sum_{i,j,k,\ell} C_{i,j,k,\ell} r_1^i r_2^j r_{12}^k \left[ (r_1r_{12}\ell n r_1r_{12})^\ell + (r_1r_{12}\ell n r_2r_{12})^\ell \right] \quad (2.2)$$

(with restrictions on  $i, j, k$  and  $\ell$ ), but it fails the Bartlett Gibbons and Dunn criterion. Instead, the following is proposed:

$$\begin{aligned} \psi = & \sum_{i,j,k=0} C_{i,j,k,0} r_1^i r_2^j r_{12}^k \\ & + \sum_{\{i,j,k\}=0, \ell=1} C_{i,j,k,\ell} r_1^i r_2^j r_{12}^k \left( r_1r_{12} (\ell n r_1r_{12})^\ell + r_2r_{12} (\ell n r_2r_{12})^\ell \right) \end{aligned}$$

with  $C_{0,0,0,0} = 1$ .

## III. THE HAMILTONIAN AND LEADING TERMS IN THE EXPANSION

The Hamiltonian Operator used in the best calculation to date [7] applicable to the ground state of the Helium-like atom's/ion's two electrons is:

$$\begin{aligned} & -\frac{1}{2} \left( \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) \right) - \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( r_{12}^2 \frac{\partial}{\partial r_{12}} \right) \\ & - \frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_2r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \\ & - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{\lambda}{r_{12}} \end{aligned}$$

where  $\lambda = 1$  and  $Z$  is the atomic number of the nucleus. We obtain  $C_{1,0,0,0} = C_{0,1,0,0} = -Z$ , and  $C_{0,0,1,0} = \lambda/2$  as expected.

TABLE I. Sequential coefficients

$\frac{r_1^2}{r_1 r_{12}}$	$C_{1,0,1,0} = -2 * (C_{0,0,0,1} + C_{0,0,0,2})$
$\frac{r_2^2}{r_1 r_{12}}$	$C_{0,1,1,0} = -2 * (C_{0,0,0,1} + C_{0,0,0,2})$
$\frac{1}{r_1}, \frac{1}{r_2}$	$C_{1,1,0,0} = Z^2$
$\frac{r_1^2 \ln(r_1 r_{12})}{r_2 r_{12}}, \frac{r_2^2 \ln(r_2 r_{12})}{r_1 r_{12}}$	$C_{0,0,0,1} = -(4C_{0,0,0,2} + 6C_{0,0,0,3})$
$\frac{r_2 r_{12}}{r_1}, \frac{r_1 r_{12}}{r_2}$	$C_{1,1,1,0} = -(12ZC_{0,0,0,2} + 24ZC_{0,0,0,3})/3$
$\frac{r_{12}}{r_1}, \frac{r_{12}}{r_2}$	$C_{0,0,0,2} = 2(Z\lambda/2 + 3C_{0,0,0,3})$

#### IV. RESULTS AND DISCUSSION

Table 1 indicates the beginning sequence of coefficients determined sequentially substituting beginning terms of the expansion of the wave function Ansatz (Eqn. 2.3) into the Hamiltonian (Eqn. 3.1) of the Schrödinger equation.

##### A. Demurral

The continuation of developments with respect to coefficient recursion relationships, variational calculations based on wave function choices shaped by the results shown here, and the ultimate finding of simple functional forms for which this series is the expansion, exceeds the ability and timeline of the author.

It is not apparent what sequence one needs to solve the succeeding equations.

However, approximate calculations which include logarithmic terms such as those indicated above, should allow smaller expansions with increased accuracy and a well

defined path for improvement. It is worth noting that literature statements that equate more accurate energy values (to more digits) to more accurate wave functions is not, in fact, true. The contrary is expected to be true however, i.e., the more accurate the wave function the better the eigenenergy.

##### V. ACKNOWLEDGEMENTS

The mathematics employed herein was done in part using SageMath/CoCalc.

##### VI. SAGEMATH/COCALC CODE

The following code was used. It can be cut and pasted directly into Sage. The lines containing "ELIMINATES" (and the four lines below them) have been commented out. The reader should then reactivate them serially to see the choices made.

```

r1,r2,Z,r12,k,a,b,c,d,L,e,f,g,h, E= var('r1 r2 Z r12 k a b c d L e f g h E');
v = (r1*r12*log(r1*r12))+r2*r12*log(r2*r12));
v1 = (r1*r12*log(r1*r12));
v2=(r2*r12*log(r2*r12));
var('c1000 c0100 c0010 c1010 c0110 c1100 c2000 c0200 c0020 c2010 c1200 c2100 c0210 c1020 c0120 c1110');
var('c0001 c0002 c0003 c0004 c0005');
var('c1001 c0101 c0011 c1011 c0111 c1101 c2001 c0201 c0021 c2011 c0211 c1021 c0121 c1111');
var('c1002 c0102 c0012 c1012 c0112 c1102 c2002 c0202 c0022 c2012 c0212 c1022 c0122 c1112');
function('psi')(r1,r2,r12);
#function('psiext')(r1,r2,r12);
psi(r1,r2,r12) = 1+c1000*r1+c0100*r2+c0010*r12+c1010*r1*r12+c0110*r2*r12+c1100*r1*r2;
var('c2000 c0200 c0020 c0002');
psi(r1,r2,r12) = psi(r1,r2,r12)+c0001*(r1*r12*log(r1*r12)+r2*r12*log(r2*r12))+c0002*(r1*r12*(log(r1*r12))^2+
psi(r1,r2,r12) = psi(r1,r2,r12)+c0003*(r1*r12*(log(r1*r12))^3+(r2*r12*(log(r2*r12))^3));

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psi(r1,r2,r12) = psi(r1,r2,r12)+c0004*(r1*r12*(log(r1*r12))^4+(r2*r12*(log(r2*r12))^4));
psi(r1,r2,r12) = psi(r1,r2,r12)+c2000*r1^2+c0200*r2^2 + c0020*r12^2;
psi(r1,r2,r12) = psi(r1,r2,r12)+c2010*r12*r1^2+c0210*r12*r2^2 + c1020*r1*r12^2+ c0120*r2*r12^2+ c1110*r1*r12*r2;
psi(r1,r2,r12) = psi(r1,r2,r12)+c1200*r1*r2^2+c2100*r1^2*r2 ;
#var('h1 h2 h3');
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0001*(r1*r12*log(r1*r12)+r2*r12*log(r2*r12));
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0002*((r1*r12*log(r1*r12))^2+(r2*r12*log(r2*r12))^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1001*r1*v;
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0101*r2*v;
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0011*r12*v;
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1101*r1*r2*v;
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1011*r1*r12*v;
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0111*r2*r12*v;
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0002*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1002*r1*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0102*r2*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0012*r12*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c0112*r2*r12*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1012*r1*r12*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1102*r1*r2*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1112*r1*r2*r12*(v1^2+v2^2);
#psi(r1,r2,r12) = psi(r1,r2,r12)+c1111*r1*r2*r12*v;

show("psi (final) = ",psi);

show("=====");
t1 = expand(((1/(r1^2))*(derivative((r1^2)*derivative(psi(r1,r2,r12),r1),r1)))));
#show("t1 = ",t1)
t2 = expand(((1/(r2^2))*(derivative((r2^2)*derivative(psi(r1,r2,r12),r2),r2)))));
#show("t2 = ",t2)

t3 = expand(((1/(r12^2))*(derivative((r12^2)*derivative(psi(r1,r2,r12),r12),r12)))));
#show("t3 = ",t3)
t4 = ((r1^2+r12^2-r2^2)/(2*r1*r12))*derivative(derivative(psi(r1,r2,r12),r1),r12);
#show("t4 = ",t4)
t5 = ((r2^2+r12^2-r1^2)/(2*r2*r12))*derivative(derivative(psi(r1,r2,r12),r2),r12);
#show("t5 = ",t5)
t = -(1/2)*(t1+t2)-t3-t4-t5;
#show("t = ",t)
#t = expand(t+(-Z/r1-Z/r2+L/r12- E)*psi(r1,r2,r12));
#t= expand(t.substitute(c1000=-Z));#ELIMINATES 1/r1 and 1/r2 TERMS
#t= expand(t.substitute(c0100=-Z));#ELIMINATES 1/r1 and 1/r2 TERMS
#t= expand(t.substitute(c0010=L/2));#ELIMINATES 1/r12
#t= expand(t.substitute(c1010= -2*(c0001+c0002)));#ELIMINATES r2^2/r1r12
t= expand(t.substitute(c0110= -(c0002+c0001)*2));#ELIMINATES r1^2/r2r12
t= expand(t.substitute(c1100=Z^2));#ELIMINATES r2/r1 and r1/r2 terms
#apr 7, 2022: verified 5/12
#t = expand(t.substitute(c0001=-Z*L-2*c0002));#apr 9
#t = expand(t.substitute(c0001=-(4*c0002+6*c0003)));#may 15 after factor of 2 ; r2^2*ln(r1*r12)/(r1r12)
#t = expand(t.substitute(c0002=2*(Z*L/2+3*c0003)));#may 15 r12/r1
#t = expand(t.substitute(c1110=-(12*Z*c0002+24*Z*c0003)/3));#may 16, (r12r2)/r1
#
#
# FINALIZED MAY 17, 2022
#
#
#t = t.collect_common_factors();t

```

```

#t = expand(t.substitute(e= L*Z/2-2*f));
#t = t.canonicalize_radical();
#t = t.simplify();
#t = t.numerator();
#show("t = ",t);
#s0 = t.coefficient(E);
#t= expand(t.substitute("(r1*r12)^c*r1 + (r12*r2)^c*r2"=tsp));
#s0 = t.coefficient(1/(r12*r12)).collect(r1);
#show ("s0, r12^(-2) coefficient = ",s0);
show("-----+++++-----");
s1 = t.coefficient(1/(r1*r12));
t = expand(t - s1/(r1*r12));#cleanup
#s1 = numerator(s1).collect_common_factors();
s1 = s1.collect(r2);
show("=====");
show ("s1, 1/(r1*r12) coeff numerator = ",s1);
show("=====");
#-----
s1 = t.coefficient(1/(r2*r12));
t = expand(t - s1/(r2*r12));#cleanup
#n1 = numerator(s1);
s1 = s1.collect(r1);
show("=====");
show ("1/(r2*r12) coeff = ",s1);

#-----
show("=====");
show("=====");
s1 = t.coefficient(1/(r1));
t = expand(t - s1/(r1)).collect(r2);#cleanup
show ("s1, 1/r1 coeff = ",s1.collect(r2));
s2 = t.coefficient(1/(r2));
t = expand(t - s2/(r2)).collect(r1);#cleanup
show("=====");
show ("s2, 1/r2 coeff = ",s2.collect(r1));
show("=====");

#show("t with a, b and e computed) = ",t);

#t = expand(t - s1/(r1));
#t = expand(t - s2/(r2));
#show("t reduced = ",t);
s1 = t.coefficient(1/(r12));
t = expand(t - s1/(r12));#cleanup
#s1 = s1.simplify();
show ("s1, 1/r12 coeff = ",s1);

show("=====");
show("term (after 1/r1, 1/r2, & 1/r12 removal)= ",expand(t));

```

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This manuscript has not been referee'd. it has been rejected by editors who act as gatekeepers. They believe that the topic is not relevant to Phys. Rev. Letters, Phys. Rev. A, and J. Chem. Phys.. How this is possible is beyond me!

I can not continue submitting to lower and lower journals, when gatekeepers are allowed veto power. If the work is actually in error, please contact me. Thank you.