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On the Exact Helium Wave Function Expansion, II, an exponential modulated form

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Abstract

A 1^1S wave function's expansion for 2 electron atoms and ions is proposed employing an appropriate exponential factor and Fock's logarithmic terms. The leading coefficients are presented.

I. INTRODUCTION

The ground electronic state of Helium (and its isoelectronic ions) has been studied extensively since the original work of Hylleraas [1]. However, the 1^1S 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 [2] who demonstrated that a unique solution for $\psi(r_1, r_2, r_{12})$ of the Hylleraas 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 coefficient of $\frac{1}{r_1} \leftrightarrow 2c_{100} + c_{010} = 0$ and that the coefficient of $\frac{r_1}{r_{12}} \leftrightarrow 5C_{101} - \frac{1}{2}C_{100} = 0$.

Fock [3–5] showed that there must be logarithmic terms in the expansion, and gave the form the expansion had to take. Defining $R = r_1^2 + r_2^2$, he wrote (in current but mixed notation)

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

with $Z = 2$ for Helium. $R^{1/2} \cos(\alpha/2)$ and $R^{1/2} \sin(\alpha/2)$ are equal to r_1 and r_2 respectively, while r_{12} is equal to $R^{1/2} \sqrt{(1 - \sin \alpha \cos \vartheta)}$.

Myers et al [6] argued that the Fock expansion should be used as a template for shaping basis functions for future calculations on the Helium ground state. Here, it is suggested that a certain re-formulation of the Fock expression allows us to understand and obviate the Bartlett conundrum and thereby suggest an appropriate wave function expansion for future investigations.

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II. ANSATZ

The following expansion is proposed:

$$\begin{aligned}
& 1 + C_{1,0,0}r_1 + C_{0,1,0}r_2 + C_{0,0,1}r_{12} + \\
& + C_{1,1,0}r_2r_2 + C_{1,0,1}r_1r_{12} + C_{0,1,1}r_2r_{12} + \\
& \text{constant} * (r_1r_{12}\ell nr_1r_{12} + r_2r_{12}\ell nr_2r_{12}) + \dots
\end{aligned} \tag{2.1}$$

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

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

(with restrictions on i, j, k and ℓ), but it fails the Bartlett Gibbons and Dunn criterion.

Here, we propose a (unfortunately) more complicated expansion which, with appropriate conditions, actually achieves cancellation of offending terms in the resultant equation resulting from substitution into the Schrödinger equation.

We have:

$$\begin{aligned}
\psi_{proposed} = e^{-Z(r_1+r_2)+r_{12}/2} \times \\
\left\{ \sum_{i,j,k} C_{i,j,k} r_1^i r_2^j r_{12}^k + \right. \\
\left. \sum_{i=1,j=0,k=1,\ell=1} d_{i,j,k,\ell} r_1^i r_2^j r_{12}^k (\ell n r_1 r_{12})^\ell + \sum_{i=0,j=1,k=1,\ell=1} e_{i,j,k,\ell} r_1^i r_2^j r_{12}^k (\ell n r_2 r_{12})^\ell \right\} \tag{2.2}
\end{aligned}$$

with $i+j+k \leq 2\ell$. Traditionally, we leave $C_{1,0,0} = 1$, deferring normalization considerations.

This notation is itself in-elegant but the indices of "d" and "e" reflect the powers of r_1, r_2 and r_{12} properly.

The only thing excluded from this form are terms of mixed logarithms of $r_1 r_{12}$ and $r_2 r_{12}$. There is little reason to believe that these mixed logarithmic terms are required, as the separate operators never mix r_1 terms and r_2 terms together inside the partial derivatives.

The choice of pre-exponential is intentional, since using this term removes the triple collision singularity and it is wiser than making the subsequent power series undo the damage of having reciprocal distances occurring throughout the forthcoming calculation.

A. Some coefficients of wavefunctions

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:

$$\begin{aligned}
& -\frac{1}{2} \left(\frac{1}{r_1^2} \frac{\partial \left(r_1^2 \frac{\partial}{\partial r_1} \right)}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial \left(r_2^2 \frac{\partial}{\partial r_2} \right)}{\partial r_2} \right) - \frac{1}{r_{12}^2} \frac{\partial \left(r_{12}^2 \frac{\partial}{\partial r_{12}} \right)}{\partial r_{12}} \\
& - \frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \\
& - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{\lambda}{r_{12}}
\end{aligned} \tag{2.3}$$

where $\lambda = 1$ and Z is the atomic number of the nucleus.

Substituting 2.2 into this Hamiltonian results in an set of equations for coefficients. As expected, $c_{1,0,0} = 0$ and does $c_{0,1,0}$ and $c_{0,0,1} = -(1 - \lambda)/2$.

The situation becomes murkier the deeper into the terms we proceed. $C_{1,0,1} = (\lambda * Z - 4 * D_{1,0,1,1} - 4 * D_{1,0,1,2})/2$ with an equivalent expression for $C_{0,1,1} = (\lambda * Z - 4 * E_{0,1,1,1} - 4 * E_{0,1,1,2})/2$.

The Appendix shows the SageMath/CoCalc coding that was used in this effort.

Clearly, better programming would result in extending the set of relations which determine the wave function's eigenfunctionality.

B. Accuracy of wavefunctions

The fact that the eigenenergy for this problem is known to more then 40 significant figures [7] (-2.903 724 377 034 119 598 ...) does not mean that the associated wave function is "exact".

All the expansions proposed to date fail this test(see, for example, Aznabaev et al) [8]. Even those which include logarithmic terms fail the test, as they have not been properly constructed to cancel relevant terms generated elsewhere in the expansion as shown above. As an example,

$$\psi_0^{new \ log} = [1 + \ln(r_1 + r_2) + \beta r_{12}] e^{-\alpha(r_1+r_2)}$$

is used in the best calculation [7] to obtain a spectacular energy, but an unknown local energy profile.

It would seem that incorporating logarithmic terms of the type described, into approximate wave functions for use in computations of many electron systems would also improve the accuracy of such calculations.

III. RESULTS AND DISCUSSION

These results suggest that a simple variational calculation carried out analytically would result in a good first approximation to the "true" value. The simplest one parameter *Ansatz*, $e^{-\alpha(r_1+r_2)}$, is known to yield a value of -2.84765 au. However, such a wave function yields local energies varying from minus to plus infinity.

Extending the proposed series in standard variational calculations to include more terms (including properly constructed logarithmic ones) should rapidly give an approximate eigenenergy to any desired number of digits with minimal or no local energy divergences.

It would appear that a reasonable wavefunction *Ansatz* might be:

$$\psi = e^{-Z(r_1+r_2)+\frac{1}{2}r_{12}} \left(e^{A*(r_1r_{12})\ell nr_1r_{12}} + e^{A*(r_2r_{12})\ell nr_2r_{12}} \right) f(r_1, r_2, r_{12})$$

This *Ansatz* keeps the correlation functions separated in the same way they are separated in the Hamiltonian.

In any case, no matter what the *Ansatz*, the resultant integrals required for variational calculations are quite daunting. It is not clear whether these computations are practical in execution.

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.

IV. ACKNOWLEDGEMENTS

The mathematics employed herein was done using SageMath/CoCalc. Using SageMath on a remote server has limited the ability to carry out very large sample size computations.

In addition, chatGPT has helped immeasurably in dealing with SageMath problems.

A. Appendix

```
# 2023-11-07-revisiting
# 2021-09-03-WORKING SERIES-GENERATED exp version
reset();

sage_server.MAX_HTML_SIZE = 150000;

var('r1 r2 Z r12 L E');
function('psi')(r1,r2,r12);

N = 3
show("N = ",N)

R.<r1,r2,r12> = PolynomialRing(QQ)

psi(r1,r2,r12) = R.sum([var("C"+str(i)+str(j)+str(k))*r1^i*r2^j*r12^k
for i in range(0,N) for j in range(0,N) for k in range(0,N)])
+ sum([var("D"+str(i)+str(j)+str(k)+str(l))*r1^i*r2^j*r12^k*((log(r1*r12))^l)
for i in range(1,N) for j in range(0,N)for k in range(1,N) for l in range(1,N)])+
sum([var("E"+str(i)+str(j)+str(k)+str(l))*r1^i*r2^j*r12^k*(log(r2*r12))^l
for i in range(0,N) for j in range(1,N)for k in range(1,N) for l in range(1,N)])

psiexp= exp(-Z*(r1+r2)+r12/2);

psi(r1,r2,r12)=psi(r1,r2,r12)*psiexp;
show("psi (before substitutions) = ",psi);

psi(r1,r2,r12)=psi(r1,r2,r12).substitute(C000=1)
psi(r1,r2,r12)=psi(r1,r2,r12).substitute(C100= 0)
```



```

psi(r1,r2,r12)=psi(r1,r2,r12).substitute(C010= 0)
psi(r1,r2,r12)=psi(r1,r2,r12).substitute(C001= - (1-L)/2)
psi(r1,r2,r12)=psi(r1,r2,r12).substitute(C101 = (L*Z-4*D1011-4*D1012)/2)#ok up to n=4
show("=====");
psi(r1,r2,r12)=psi(r1,r2,r12).substitute(C011 = (L*Z-4*E0111-4*E0112)/2)#ok up to n=4
show("=====");
show("psi (final) = \n",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)/(r1*r12))*derivative(derivative(psi(r1,r2,r12),r1),r12);
#show("t4 = ",t4)
t5 = ((r2^2+r12^2-r1^2)/(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/psiexp);

s1 = t.coefficient(1/(r1*r12));
t = expand(t - s1/(r1*r12));#cleanup
#s1 =numerator(s1).collect_common_factors();
s1 = s1.collect(r2);
show ("s1, 1/(r1*r12) coeff numerator = ",expand(s1));
#show ("s1, 1/(r1*r12) coeff numerator = ",(s1));

```

```

#show("r1*r12 coefficient in final t using mycoeff")
#show(expand(mycoeff(t, (r1*r12),-1)))
show("=====1");
#exit()
#-----
s1 = t.coefficient(1/(r2*r12));
t = expand(t - s1/(r2*r12));#cleanup
#n1 = numerator(s1);
s1 = s1.collect(r1);
show("=====2");
show ("\n 1/(r2*r12) coeff = ",expand(s1));

#-----
show("=====3");
show("=====");
s1 = t.coefficient(1/(r1));
t = expand(t - s1/(r1));#cleanup
show ("s1, 1/r1 coeff = ",s1.collect(r2));

s2 = t.coefficient(1/(r2));
t = expand(t - s2/(r2));#cleanup
show("=====4");
show ("s2, 1/r2 coeff = ",s2);
show("=====5");
s1 = t.coefficient(1/r12);
t = expand(t - s1/r12);#cleanup
#s1 = s1.simplify();
show ("s1, 1/r12 coeff = ",s1);

show("=====6");
t = t.collect(r1);
show("term (after 1/r1, 1/r2, & 1/r12 removal)= ",t);

```

```
show("=====");
```

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