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Compact Singlet S Helium Wave functions(corrected)

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Abstract

A highly compact 4-parameter form for Helium's approximate non-relativistic wave function is proposed and shown to yield an energy expectation value within 0.0025 au of the "exact" value. The wave function employs proper atomic number parameterized hydrogenic orbitals, a correlation function whose form is $\left(1+\frac{1}{2}r_{12}e^{-\alpha r_{12}}\right)$, coupled with a variationally determined expansion in r_1, r_2, and r_{12}.

I. INTRODUCTION

The Schrödinger Equation for this two-electron problem has the form

$$-\frac{1}{2}\left(\nabla_2^2+\nabla_2^2\right)\psi-\frac{2}{r_1}\psi-\frac{2}{r_2}\psi+\frac{1}{r_{1,2}}\psi=E\psi$$

where the subscripts refer to electron 1 and 2 respectively.

Since the 1926, solutions to this equation have been predicated on using an exponential decay factor dominated by a term

$$e^{-a(r_1+r_2)}$$

where "a" was regarded as a variational parameter whose value was to be adjusted to make the computed total energy a minimum.

The groundbreaking work in this area was conducted by Hylleraas [1–3]. The simplest Hylleraas wave function

$$\psi=e^{-A(r_1+r_2)}\left(1+C_{0,0,1}r_1^0r_2^0r_{1,2}^1\right)$$

has coefficients (obtained variationally)

$$\psi=e^{-1.36(r_1+r_2)}\left(1+0.365796r_{1,2}\right)$$

and average energy (-2.89112 a.u.) but the local energy ($\frac{H_{op}\psi}{\psi}$) [4] associated with this approximate function is singular both when r_1 or $r_2\rightarrow 0$ and also when $r_{12}\rightarrow 0$.

Bartlett showed that expansions such as these could not possibly work [5] although Coolidge and James [6] showed that the Bartlett finding does not sound the death knell for Hylleraas type wave functions when employed in variational computations.

Over the years since Hyllerass' original work, tremendous efforts have been made to improve upon that work, using larger and larger expansions, adding more complicated terms, etc., with the net result that the non-relativistic ground state energy of Helium's electrons is now known, to 35 significant figures to be [7, 8]E $=-2.903\ 72\ldots$ a.u., a truly remarkable result. This and similar results come from using increasingly more complicated wave functions containing enormous numbers of terms in the wave function expansion, seeking greater and greater accuracy of the resultant energy: 230 term [9], 246 term [10], 308 term [11], 616 term [12] and 1078 term [13] expansions have all been reported. A recent is from Korobov [14] who reports a result to 25 significant digits using 5200 functions while Goldman recent work [15] employed 8066 functions (Schwartz [7, 8] used 10257 terms). Computations based

on expansions including logarithmic terms include those of Frankowski and Pekeris [10, 16] up to the latest due to Forrey [17].

An alternative approach has attempted to find the "most compact" forms possible [18], at the expense of good energy accuracy.

Finally, there are two other avenues of approach to this problem which have contributed to our understanding. First, it is known [19–21] that the exact wave function's expansion has the analytic form

$$\psi = 1 - Z(r_1 + r_2) + \frac{1}{2} r_{12} - \left(\frac{2(\pi - 2)}{6\pi} \right) r_1 r_2 \cos\theta \ell n(r_1^2 + r_2^2) + \cdots$$

(Z=2 for Helium). This has lead to a subset of proposed wave functions, with accompanying variational calculations, which include logarithms, although not the form employed by Fock. One of these is an amazing calculation by Boumerzoug and Miletic [22] which included a $\ell n(r_{12} + e)$ term in their trial wave function and obtained -2.9024 a.u. with only two variational parameters, a truly spectacular result. Unfortunately, they did not publish the coefficients of their resultant wave function, and the computation has proven resistant to verification. One notes, in passing, that their wave function displays the standard improper local energy behavior characteristic of many currently employed Helium wave functions.

It is well known that there are a set of cusp conditions [23], which should be, *a priori*, fulfilled. Usually, these are cited with respect to the $r_{12} \rightarrow 0$ collision, where the Coulomb repulsive energy grows without bound, but there are cusp conditions also at the nucleus (origin) for each electron individually, as well as the "triple collision" cusp condition.

We therefore propose to revisit the Hylleraas scheme using wave functions which obey both the origin and r_{12} cusp conditions, including the "triple collision", *a priori*, reserving any deviation for a "correlation" function which is variationally adjustable.

But the r_{12} cusp condition can be satisfied in more than one way. We have found, *vide infra*, that the Hirschfelder [24]

$$\psi = e^{-2(r_1 + r_2)} \left(1 + \frac{1}{2} r_{12} e^{-\alpha r_{12}} \right) g(r_1, r_2, r_{12}) \tag{1}$$

satisfies all the cusp conditions, and employs a "to be determined" function "g" to correct for all the errors induced by the cusp determined functions and trumps the $e^{r_{12}/2}$ form [25]. Hirschfelder never comments in his paper why he chose this form, but, serendipitously from our point of view, it works better than the standard $e^{-r_{12}/2}$ term or variants thereof.

As an operational *Ansatz* for the Helium Ground State wave function Equation 1 clearly displays standard orbital characteristics while also employing one of the functional forms for the primary correlation function [25, 26] known to be the leading (dominant) term in the true complete correlation function (although other terms are not only possible, but may actually speed the rate of convergence of the approximate calculations undertaken herein, *vide infra*).

II. RESULTS

If one computes the energy, using the Hylleraas scheme [27], for various wave functions of the type indicated by Equation 1 one obtains, for a first case, with g=1, $E = -2.878$ a.u., with $\alpha = -0.08$.

Next, we attempt

$$\psi = e^{-2s}\left(1 + \frac{1}{2}ue^{-1.013u}\right)\left(1 + 0.2119s\ u + 0.1406t^2 - 0.003u^2\right)$$

where we have converted over to standard Hylleraas notation ($s = r_1 + r_2$,$t = r_1 - r_2$, and $u = r_{12}$). This wave function gives a variational energy of -2.901188 au. Schwartz [7, 8] reports a 35 digit value of $-2.9037243770\ldots$, which means that our simple 4-parameter wave function is within ~ 0.003 a.u. of the "exact" answer.

III. DISCUSSION

If a 4-parameter wave function can achieve a result within $\sim 0.1\%$ of the "exact" answer, and exhibit local energy behavior which is demonstrably free of pathological behaviour, there appears to be a reason to re-open the question of whether or not the pursuit of high accuracy atomic and molecular quantum mechanical calculations could be better pursued using proper atomic number parameterized hydrogenic orbital products (which would eliminate local energy problems at the nucleus) accompanied by a product of Hirschfelder correlation functions (which would eliminate local energy problems in the electron-electron collision regions), topped off with extra-Hirschfelder correlation functions of the Hylleraas type, suitably enhanced.

IV. APPENDIX

```
restart:
psi0 := exp(-2*s):
psi_corr := 1+u/2*exp(-1.013*u):
psi := psi0*psi_corr*(1+.2119256858*s*u+a*t^2-alpha*u^2);
alpha_last_cycle := 0.002;
last_cycle :=0.1;
t1 := diff(psi,s):
t2 := diff(psi,t):
t3 := diff(psi,u):
i1 := u*(s**2-t**2)*(t1**2+t2**2+t3**2)+2*t3*\n(s*(u**2-t **2)*t1+
       t*(s**2-u**2)*t2)-\npsi**2*(4*2*s*u - s**2+t**2):
i1 := expand(i1,exp):
i1 := simplify(i1,power):
i1_eval := subs(s=0,int(int(int(i1,t=0..u),u=0..s),s)):
i1_eval := simplify(i1_eval):
n1 := u*(s**2-t**2)*psi**2:
n1_eval := subs(s=0,int(int(int(n1,t=0..u),u=0..s),s)):
n1_eval := simplify(n1_eval):
energy := i1_eval/n1_eval:
E := simplify(i1_eval/n1_eval):
Ealpha := subs(alpha=alpha_last_cycle,E):
Ea := subs(a=a_last_cycle,E):
for k from 1 to 10 do
min_Ealpha := minimize(Ealpha, a=a_last_cycle/2..3*a_last_cycle,location);
#fixed alpha
min_Ea := minimize(Ea,alpha=alpha_last_cycle/2..50*alpha_last_cycle,location);
#fixed a
print(‘min_Ealpha = ‘,min_Ealpha);
print (‘min_Ea = ‘,min_Ea);
temp := min_Ealpha[2]:
```

```
ans := temp[1]:ans1 := ans[1]:ans2 := ans1[1]:
tempa := min_Ea[2]:
ansa := tempa[1]:ansa1 := ansa[1]:ans2a := ansa1[1]:
Ealpha := subs(ans2a,E):#function of a
Ea := subs(ans2,E):#functions of alpha
od;
```

Note added in proof.

Since the initial report, the program (above) has been enhanced from the original (into its current form) which allowed a slight improvement in the reported result.

$$\psi = e^{-2s}\left(1+\frac{1}{2}ue^{-1.013u}\right)\left(1+0.2119256858s\ u+0.1416353426t^2-0.0113074102u^2\right)$$

with an "improved" value of -2.901332805 a.u.

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[1] E. A. Hylleraas, Zeits. f. Physik **48**, 469 (1928).

[2] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

[3] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).

[4] W. J. Deal, Int. J. Quant. Chem. **35**, 513 (1989).

[5] J. H. Bartlett Jr., J. J. Gibbons Jr., and C. G. Dunn, Phys. Rev. **47**, 679 (1935).

[6] A. S. Coolidge and H. M. James, Phys. Rev. **51**, 855 (1937).

[7] C. Schwartz, Experiment and Theory in Computations of the He Atom Ground State, http://lanl.arxiv.org/PS_cache/physics/pdf/0208/0208005.pdf.

[8] C. Schwartz, Int. J. Mod. Phys. **E15**, 877 (2006).

[9] D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. **A29**, 980 (1984).

[10] K. Frankowski and C. F. Pekeris, Phys. Rev. **146**, 46 (1966).

[11] A. J. Thankkar and T. Koga, Phys. Rev. A. **50**, 854 (1994).

[12] G. W. F. Drake, Nucl. Inst. Meth. Phys. Res. **B31**, 7 (1988).

[13] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **11**, 1479 (1975).

[14] V. I. Korobov, Phys. Rev. A. **66**, 24501 (2002).

[15] S. P. Goldman, Phys. Rev. A. **57**, R677 (1998).

[16] K. Frankowski and C. F. Pekeris, Phys. Rev. **150**, 366E (1966).

[17] R. C. Forrey, Phys. Rev. A. **69**, 22504 (2004).

[18] D. N. Tripathy, B. Padhy, and D. K. Rai, J. Phys. B. **28**, L41 (1995).

[19] V. A. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 161 (1954).

[20] V. A. Fock, Det Koneglige Norske Videnskabers Selskabs Forhandlinger **31**, 138 (1958).

[21] A. M. Ermolaev and G. B. Sochilin, Sov. Physics, Dokl. **9**, 292 (1964).

[22] M. S. Boumerzoug and J. Miletic, J. Chem. Phys. **91**, 5129 (1989).

[23] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[24] J. O. Hirschfelder, J. Chem. Phys. **39**, 3145 (1963).

[25] C. F. Lebeda and D. M. Schrader, J. Chem. Phys. **49**, 2547 (1968).

[26] H.-J. Flad and A. Savin, J. Chem. Phys. **103**, 691 (1995).

[27] C. W. David, Computers and Chemistry **12**, 229 (1988).