Compact 1^1S Helium Wave Functions; an 8-Parameter Wave Function and its Sensitivity Analysis

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A previously obtained approximate non-relativistic Helium wave function is improved significantly coming within 0.02% of the "exact" value with 8 terms. The sensitivity of this final result to the parameters in the wave function is examined.

Key words: Helium; Wave Function; Compact.

1. Introduction

We have found, vide infra, that the Hirschfelder [1, 2] function

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

not only satisfies all the cusp conditions (as promised by Hirschfelder) but provides a satisfying variational form for obtaining quite high accuracy predicted energies of the Helium ^{1}S 2-electron ground state. It employs a "to be determined" function $g(r_1,r_2,r_{12})$ to correct for all the errors induced by the cusp determined functions (i. e., those functions chosen to make sure that the total Ansatz has no poles and/or singularities). Hirschfelder never comments in his paper why he chose this form, but, serendipitously from our point of view, it works better than the standard $\mathrm{e}^{-r_{12}/2}$ term or variants thereof [3, 4]. In prior work, a 4-parameter expansion of this type gave an average energy of -2.9012 a. u. [2]. The associated wave function for this energy value was [5, 6].

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

2. Results

We have (using the same Maple code as used earlier [7]) obtained an approximate 7-term expansion

$$\psi = \mathrm{e}^{-2s}\left(1+\frac{1}{2}u\mathrm{e}^{-1.013u}\right)\cdot(1+0.206448s\,u+0.1528565957t^2-0.003u^2+0.076s-0.0025su^2+0.0027t^4) \quad (2)$$

using the 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 -2.902620761 a. u. Schwartz [8, 9] reports a 35-digit value of $-2.9037243770\ldots$, which means that our simple 7-parameter wave function is within ~ 0.001104 a. u. of the "exact" answer. This corresponds to 0.038% accuracy.

Clearly, one can continue to add terms to the expansion, and continue improving our results, but an end must be called if we are to stop arguing about the "angels on the head of a pin". Thus, we have gone on to an 8-parameter wave function as our last attempt to show that the central concept of this kind of wave function is incredibly apt.

In doing so, the Maple code has been altered to sequentially minimize the average energy as a function of each of the constants a_i $(i=1\ldots7)$ defined via

$$\psi_8 = \mathrm{e}^{-2s}\left(1+\frac{1}{2}u\mathrm{e}^{-a_0u}\right)\left(1+a_1su+a_2t^2+a_3u^2+a_4s-a_5su^2+a_6t^4+a_7s^2u\right). \quad (3)$$

We report an average energy of -2.903126912 a. u., which compares favorably with the Schwartz value as well as the Seelig and Becker [10] value.

The algorithm employed minimizes each coefficient $a_1\cdots a_7$ in turn (based on a fixed a_0 value), and then continues to the next iteration of minimization steps. Repeating the scheme while searching for a "best" value of a_0 results in our final reported results.

Table 1 indicates our results for the coefficients, based on 500 iterations of the sequential minimization at constant $a_0=0.68500$. Note that these coefficients have been arbitrarily truncated since the Maple program emphasizes too many digits in its printout. The "digits" held by the Maple program varied from 20 to 30, and the numbers in Table 1 reflect those digits

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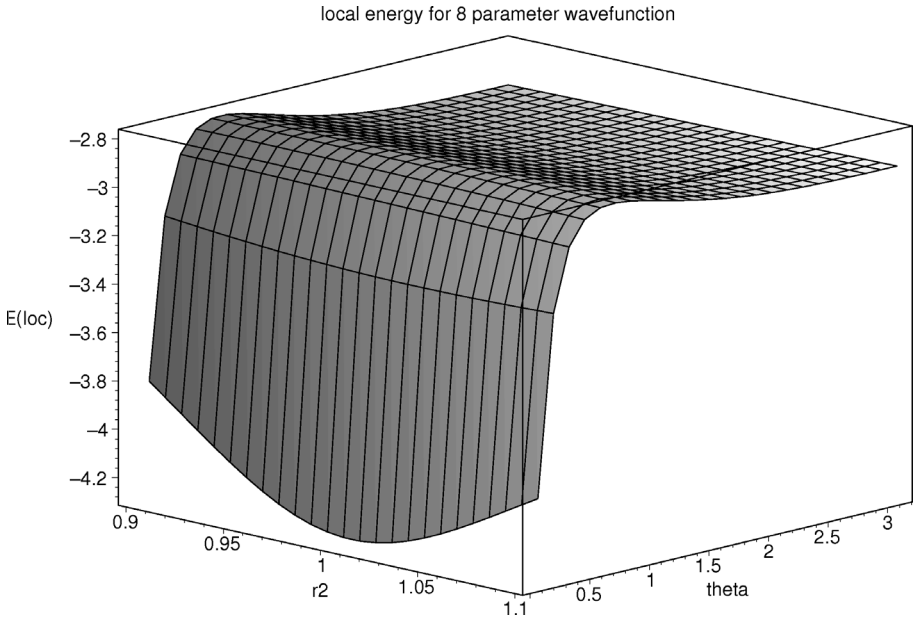

Fig. 1. Local energy at $r_1 = 0$.

which were unchanged in going from 20 to 30 "digits". Although it is possible, using more than 500 iterative steps to achieve a slight change in the last digits of the energy reported herein, the labor does not seem worth the effort.

Minimization of all coefficients $(a_1 \cdots a_7)$ while varying a_0 is very time-consuming, and our best efforts indicate that the reported value is very close to the "best" value.

The final value of the energy corresponds to an accuracy, relative to the "exact" answer, of 0.02%. Obviously, the "gain" in going from 7 to 8 parameters is minimal, and augers poorly for continuing this kind of quest mindlessly.

We have converted (3) to its more normal r_1, r_2, $\cos\vartheta$ form so that the local energy can be easily computed in terms of variables understandable to most readers. A plot of the local energy versus r_2, ϑ with $r_1 = 1$, showing that near the point $r_1 = r_2$ the expected singularity is replaced by a rather benign bounded minimum, can be seen in Figure 1.

We have also computed the sensitivity coefficients of the resultant average energy to the values of the wave functions parameters, and the results are presented in Table 1.

We defined the sensitivity coefficients as

$$s_i = \frac{1}{E_{\text{average}}} \times \left(\frac{\partial E_{\text{average}}}{\partial \text{parameter}_i} \right)_{j \neq i \text{ fixed}},$$

Table 1. Parameters and sensitivities of the 8-parameter wave function.

Parameter number	Value	Sensitivity
0	0.68500[a]	$4.3492 \cdot 10^{-3}$
1:su	0.03219366047	$-0.5309433870 \cdot 10^{-5}$
2:t^2	0.1473590731	$0.2610672187 \cdot 10^{-6}$
3:u^2	0.059911475936	$0.3070601670 \cdot 10^{-6}$
4:s	0.1475730155	$-0.3994775034 \cdot 10^{-6}$
5:su^2	0.01691368899	$0.1458383639 \cdot 10^{-4}$
6:t^4	0.002828848751	$0.17811217939 \cdot 10^{-5}$
7:s^2u	0.03565344040	$0.26331780286 \cdot 10^{-22}$[b]

[a] Obtained by hand trial and error.

[b] Since the a_7 value is the last one minimized in the sequential scheme employed, its value is artificially closest to zero.

which means that each has the units of inverse parameter. There are no outlandish sensitivities found in this set, although clearly the exponential coefficient a_0 is the most sensitive of this set.

3. Discussion

The execution time of computation at this level rises so high that an alternative method of global minimization would be preferable, especially if more terms are envisioned. Three factors are involved. First, the number of digits carried by the Maple program must be increased as one goes to larger and larger expansions, attempting to obtain better values at the "next" digit in the average energy. Second, as with all such computations, the time of execution becomes painfully long with larger and larger expansions. Finally, the variation

of a_0 requires heroic work of the Maple program, and therefore can not be carried out often enough. Since little is learned specifically about the wave function from knowing these coefficients, it suffices that the accuracy is spectacular given the small size of the expansion carried out.

It would appear that the Hirschfelder argument remains as valid now as it was in 1963. Wave functions which explicitly include r_{12} can be chosen to be cusp-free and yet give very good energies variationally.

It would be remiss to omit the fact that the 1s2s states 2^1S and 2^3S, when properly symmetrized and accompanied by a Hylleraas-Hirschfelder type correlation function do not give good results. For the singlet state, we have achieved average energy results of the order of -0.869 a. u. (expt $= -2.146$ a. u. [11]) and for the triplet, we have achieved average energy results of the order of -0.372 a. u. (expt $= -2.175$ a. u.). Not only are these results terrible, but they are in reversed order.

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