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Variational Calculations with a Hyperspherical Basis on Atomic Helium*

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We have recently formulated an expansion of the N electron wavefunction in an appropriate set of harmonics on the 3N-dimensional hypersphere. Angular correlation appears in the usual way, while radial correlation appears as a "generalized angular" correlation. Calculations on ^1S helium have been performed to explore the convergence of this expansion. Energies for various angular approximations have been compared with Bunge's angular limits and show a fractional error $< 3.5 \times 10^{-4}$. A theoretical contraction procedure is shown to usefully reduce basis size without forfeiting accuracy.

Key words: Hyperspherical coordinates – Atomic wavefunctions

We report results from variational calculations on the ground state of ^1S helium using the hyperspherical expansion suggested previously [1]. The angular basis for these calculations consists of functions $\mathscr{S}(\gamma, l|\eta, \theta)$ with γ even [2]. The number γ describes radial correlation in terms of the γth order Gegenbauer polynomial of $\cos 2\eta = (r_2^2 - r_1^2)/r^2$, while l describes angular correlation in terms of the lth order Legendre polynomial of $\cos \theta = \hat{r}_1 \cdot \hat{r}_2$.

We think this is the first actual calculation with such a trial wavefunction. An earlier calculation with hyperspherical coordinates was performed by Ermolaev and Sochilin [3] with basis functions dictated by available analytical results from the Fock approach [4]. Their results on several two-electron systems were quite good. No similar analytical results are known for N-electron systems to guide wavefunction construction; our purpose in doing these calculations is to assess the behavior of a general form not specifically tailored to the system. A calculation in this spirit has been reported recently by Whitten and Sims [5], but their results are not directly comparable to ours because they used a quite different angular basis.

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We have factored ψ as $e^{-\zeta r}\,\phi$ and dealt primarily with the form

$$\phi = D_0 \pi^{-3/2} + \sum_{l=0}^{\bar{l}} \sum_{\gamma=0}^{\bar{\gamma}} \sum_{n=1}^{\bar{n}} D_{n\gamma l}\, r^n \mathscr{S}(\gamma, l|\eta, \theta). \tag{1}$$

Three aspects of this expansion have been investigated: convergence of n and γ summations for $l=0$ to the s limit, contraction of basis functions, and convergence to the ground state.

Using only the constant term in Eq. (1), the wavefunction $e^{-\zeta r}$ has an energy of -2.49797 a.u., with the best exponent satisfying $\zeta^2 = -2E$ [2]. Following this qualitative guidance, we set ζ equal to 2.3 for all calculations here. For the s limit, we keep $l=0$. The energy for $\bar{n}=1$ and $\bar{\gamma}=4$ is -2.81996; energies for other combinations of $\bar{n}$ and $\bar{\gamma}$ are in Table 1. A noteworthy feature of these results is their gentle convergence. We have made no selection of terms here. Indeed, there are no dominant terms beyond the first, just a gradual lessening of importance. Similar behavior occurred in the results of Whitten and Sims [5].

Table 1. Dependence of s limit energy on $\bar{n}$ and $\bar{\gamma}$. Exact result is -2.87903 ([10])

$\bar{n}$ \ $\bar{\gamma}$	12	20	28
1	−2.85812	−2.86134	−2.86206
2	−2.87125	−2.87588	−2.87690
3	−2.87202	−2.87690	−2.87810
4	−2.87205		

The seven terms with $n=4$ gave a fractional energy lowering of only 10^{-5}. This can be explained through the "adiabatic" approach of Macek [6]. In both our work and that of Lin and Fano [7], we find the radial potential of the ground state to be deep and narrow (classical region $0.40 \leqq r \leqq 2.64$, minimum near $r=0.68$.) Hence, $r^4 e^{-\zeta r}$ contributes very little in the energetically important region.

We have investigated the possibility of contracting our functions into a smaller variational basis. Previous study of the ^{1}S wavefunction [8] showed that all coefficients $D_{1\gamma l}$ are fixed by the cusp condition; call these $u_{\gamma l}$. Defining an s limit cusp function $\chi_{10} = \Sigma u_{\gamma 0} \mathscr{S}(\gamma, 0|\eta, \theta)$, we used the s limit trial function

$$\phi = D_0 \pi^{-3/2} + d_{10}\, r \chi_{10} + \sum_{\gamma=0}^{\bar{\gamma}} \sum_{n=2}^{\bar{n}} D_{n\gamma 0}\, r^n \mathscr{S}(\gamma, 0|\eta, \theta). \tag{2}$$

This has the same terms as Eq. (1) with $l=0$, but now a single variational coefficient d_{10} replaces all the $D_{1\gamma 0}$. The variational energy must increase, and we show this increase in Table 2 for various $\bar{n}$ and $\bar{\gamma}$. The results indicate that a considerable reduction of computational effort needs not significantly compromise the accuracy of the result. Generally, as $\bar{n}$ increases, the variationally determined cusp approaches the theoretical one closely.

Results for the full expansion in Eq. (1) are in Table 3, where the γ and n summation limits are given for each type of l term. Energies of Weiss' 35 con-

Table 2. Increase in s limit energy when cusp coefficients have been fixed

$\bar{n}$ $\bar{\gamma}$	12	20	28
1	0.01988	0.02115	0.02145
2	0.00095	0.00113	0.00115
3	0.00016	0.00020	0.00028

Table 3. Energies for various angular limits

l	$\bar{\gamma}$	$\bar{n}$	E_l	E_l ([9])	Limit ([10])
0	28	3	−2.87810	−2.87896	−2.87903
1	8	2	−2.89954	−2.90036	−2.90052
2	8	2	−2.90178	−2.90258	−2.90277
3	2	1	−2.90230	−2.90307	−2.90331
4	0	1	−2.90250	−2.90320	−2.90347

figuration wavefunction [9] are shown, as well as Bunge's angular limits [10]. Neither changing ζ nor scaling ψ brought significant improvements. Our error is almost all in the s limit; differences $E_{l+1} - E_l$ are nearly identical to differences in the limits. The spdf calculation was repeated with the theoretical term $r^2 \ln r \mathscr{S}(1, 1|\eta, \theta)$ included and yielded an energy of -2.90241, reducing the spdf error by 10%.

This test of the general hyperspherical expansion shows it is capable of good accuracy. Using results from the recursive solution of the Schrödinger equation [8] to contract the basis offers the possibility of performing more extensive calculations with less work.

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