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Approximate Wave Functions for the Ground State of Helium*

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Approximate ^1S electronic wave functions for the ground state of the helium atom have been obtained by the method of superposition of configurations. Parameters determining the radial factors of orbitals, with spherical harmonic angular factors up to $l=3$, were varied to minimize the calculated energy. For each choice of the ten parameters varied in this way, a complete calculation was carried out, involving the construction and diagonalization of the twenty-by-twenty configuration interaction matrix obtained from all independent ^1S functions determined by the ten independent orbital radial factors. The best energy obtained was -2.90276 atomic units, differing from the experimental value by 0.001 atomic unit.

I. INTRODUCTION

THE helium atom is perhaps the simplest example of a quantum mechanical many-body problem which cannot be reduced by separation of variables to a set of one-body problems. After carrying out a center of mass transformation, there still remains a nonseparable Schrödinger equation for two interacting electrons moving in a common central field. The most successful approach to integrating this equation has been the method of Hylleraas.[1] This consists of a variational calculation with a trial wave function depending explicitly on the separation between the two electrons, r_{12}. Recent calculations by this method have obtained a value of the total electronic energy within the current experimental error (an error of less than 0.00001 atomic unit).[2]

Unfortunately, the method of Hylleraas cannot easily be applied to systems with more than a very small number (three or four) of interacting particles. This is true primarily because the number of relative coordinates $\mathbf{r}_{ij}$ increases quadratically with the number of particles, while the number of independent coordinates $\mathbf{r}_i$ increases only linearly. For this reason, either there will have to be significant developments in methods for dealing with Hylleraas wave functions or it will be necessary to use different methods for systems with a larger number of particles.

The most promising method generally applicable to systems with a finite number of fermions is the method of superposition of configurations. This is a variational calculation with a trial wave function which is a linear combination of Slater determinants (orthonormal antisymmetrized product wave functions). The Slater determinants are constructed from an orthonormal set of one-particle wave functions (orbitals). For a given set of Slater determinants, the coefficients in a linear combination of these chosen to have stationary energy are just the components of an eigenvector of a matrix eigenvalue equation. For a finite set of Slater determinants, this eigenvalue equation can be solved by standard methods.

A more significant problem is that of determining the set of orthonormal orbitals from which the particular set of Slater determinants under consideration are to be constructed. The number of Slater determinants, which must be considered for a given degree of accuracy in a perturbation calculation, can be significantly decreased by choosing these orthonormal orbitals to include those which are occupied in a Slater determinant of stationary energy.[3] Such orbitals satisfy the Hartree-Fock equations appropriate to a wave function expressed as a single Slater determinant.

Because this method can be applied without practical difficulty to systems with a considerably greater number of particles, it was felt to be desirable to carry out similar calculations on the helium atom in order to compare results with the Hylleraas method and to obtain information on the rate of convergence of the general method.

The present paper reports the results of such calculations, carried out to a greater degree of accuracy than that of earlier work on helium by the same method,[4] but with no intention of exhausting the resources of this method.[5] The reported calculations were carried out on

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[5] After this paper had been submitted for publication, Tycko, Thomas, and King [Phys. Rev. **109**, 369 (1958)] reported work on He resulting in a much better ^1S energy (-2.903443 a.u.). For the case of a helium-like ion, their method leads to results of the same form as ours. Their better energy resulted from using more l values. For atomic systems with more than two electrons, their method is more difficult than and not identical with the method of superposition of configurations as described here.

TABLE I. The radial basis orbitals (R_i) in terms of their parameters l, A_i, and a_i.

	Case (a)			Case (b)		
	l	A_i	a_i	l	A_i	a_i
R_1	0	0	+2.675	0	0	+2.0
R_2	0	0	+1.437	0	1	+2.0
R_3	0	1	+5.390	0	2	+2.0
R_4	0	1	+3.125	0	3	+2.0
R_5	1	0	+4.006	1	0	+3.0
R_6	1	0	+2.314	1	1	+3.0
R_7	1	1	+4.125	1	2	+3.0
R_8	2	0	+5.844	2	0	+4.0
R_9	2	0	+3.620	2	1	+4.0
R_{10}	3	0	+4.860	3	0	+5.0

the Whirlwind Computer at MIT with digital computer programs which were already in existence, and were carried to the point where it would have been necessary to design new programs, specialized to the helium calculation, to proceed efficiently to a higher degree of approximation.

II. PROCEDURE AND RESULTS

The basis orbitals were chosen to be functions of the form

$$\eta_i(l,m,m_s)=R_{il}(r)Y_l^m(\theta,\phi)v(m_s),$$

where Y_l^m is a normalized spherical harmonic and $v(m_s)$ is one of the two possible elementary spin functions. The radial functions were of the form

$$R_{il}=r^{A_i+l}e^{-a_ir},$$

where A_i is an integer. Ten different sets of parameters (A_i, a_i, and l) were used, with four independent radial functions for $l=0$, three for $l=1$, two for $l=2$, and one for $l=3$ (see Table I). This distribution was found to give about equal weight in a variational calculation to the effects of the last radial function in each set of given l. The choice of A_i was based on preliminary calculations.

From this set of orbitals, twenty orthonormal two-electron ^1S wave functions could be constructed. In general, these are linear combinations of Slater determinants (see Table III). The matrix of the two-electron Hamiltonian (the configuration interaction matrix) was diagonalized in stages, first 1×1, then 10×10 to include all s orbitals, then 16×16 to include all s and

TABLE II. The orthonormalized ψ's in terms of the η_i's.

Case (a)

$\psi(s_1)=+\ 1.94757\eta_1+2.81013\eta_2-0.06280\eta_3-0.29053\eta_4$

$\psi(s_2)=-\ 15.38638\eta_1+10.15471\eta_2+41.31016\eta_3-36.05458\eta_4$

$\psi(s_3)=-\ 2.05146\eta_1+7.07248\eta_2+149.53752\eta_3-69.60687\eta_4$

$\psi(s_4)=-\ 71.67213\eta_1+4.47994\eta_2+440.18944\eta_3+33.98275\eta_4$

$\psi(p_1)=-\ 11.07721\eta_5+20.08616\eta_6-63.32703\eta_7$

$\psi(p_2)=-\ 5.29740\eta_5+20.81242\eta_6-161.35987\eta_7$

$\psi(p_3)=-108.43400\eta_5-18.13522\eta_6+270.76519\eta_7$

$\psi(d_1)=-107.39902\eta_8+52.74214\eta_9$

$\psi(d_2)=-338.53038\eta_8+40.40129\eta_9$

$\psi(f_1)=\ 138.59193\eta_{10}$

Case (b)

$\psi(s_1)=+\ 4.73436\eta_1+0.12685\eta_2+0.88428\eta_3+0.07755\eta_4$

$\psi(s_2)=-\ 3.03463\eta_1+6.31806\eta_2-11.64329\eta_3+6.60030\eta_4$

$\psi(s_3)=+\ 2.47709\eta_1+18.07539\eta_2-34.24766\eta_3+10.89368\eta_4$

$\psi(s_4)=-\ 24.54078\eta_1+79.30618\eta_2-64.43750\eta_3+14.20752\eta_4$

$\psi(p_1)=+\ 7.26487\eta_5-22.48513\eta_6+27.81103\eta_7$

$\psi(p_2)=+\ 10.26822\eta_5-75.21197\eta_6+47.38958\eta_7$

$\psi(p_3)=+\ 81.52165\eta_5-155.44751\eta_6+63.09454\eta_7$

$\psi(d_1)=-\ 35.01400\eta_8+91.17156\eta_9$

$\psi(d_2)=-148.57894\eta_8+135.34486\eta_9$

$\psi(f_1)=\ 157.48520\eta_{10}$

TABLE III. The twenty ^1S wave functions constructed from the ψ's.

$\Psi_1=\psi(s_1;0),\psi(s_1;0)$

$\Psi_2=(2^{-\frac{1}{2}})[\psi(s_1;0),\psi(s_2;0)+\psi(s_2;0),\psi(s_1;0)]$

$\Psi_3=\psi(s_2;0),\psi(s_2;0)$

$\Psi_4=(2^{-\frac{1}{2}})[\psi(s_1;0),\psi(s_3;0)+\psi(s_3;0),\psi(s_1;0)]$

$\Psi_5=(2^{-\frac{1}{2}})[\psi(s_2;0),\psi(s_3;0)+\psi(s_3;0),\psi(s_2;0)]$

$\Psi_6=\psi(s_3;0),\psi(s_3;0)$

$\Psi_7=(2^{-\frac{1}{2}})[\psi(s_1;0),\psi(s_4;0)+\psi(s_4;0),\psi(s_1;0)]$

$\Psi_8=(2^{-\frac{1}{2}})[\psi(s_2;0),\psi(s_4;0)+\psi(s_4;0),\psi(s_2;0)]$

$\Psi_9=(2^{-\frac{1}{2}})[\psi(s_3;0),\psi(s_4;0)+\psi(s_4;0),\psi(s_3;0)]$

$\Psi_{10}=\psi(s_4;0),\psi(s_4;0)$

$$\begin{aligned}\Psi_{11}=(3^{-\frac{1}{2}})[&\psi(p_1;1),\psi(p_1;-1)-\psi(p_1;0),\psi(p_1;0)\\&+\psi(p_1;-1),\psi(p_1;1)]\end{aligned}$$

$$\begin{aligned}\Psi_{12}=(6^{-\frac{1}{2}})[&\psi(p_1;1),\psi(p_2;-1)-\psi(p_1;0),\psi(p_2;0)\\&+\psi(p_1;-1),\psi(p_2;1)+\psi(p_2;1),\psi(p_1;-1)\\&-\psi(p_2;0),\psi(p_1;0)+\psi(p_2;-1),\psi(p_1;1)]\end{aligned}$$

$$\begin{aligned}\Psi_{13}=(3^{-\frac{1}{2}})[&\psi(p_2;1),\psi(p_2;-1)-\psi(p_2;0),\psi(p_2;0)\\&+\psi(p_2;-1),\psi(p_2;1)]\end{aligned}$$

$$\begin{aligned}\Psi_{14}=(6^{-\frac{1}{2}})[&\psi(p_1;1),\psi(p_3;-1)-\psi(p_1;0),\psi(p_3;0)\\&+\psi(p_1;-1),\psi(p_3;1)+\psi(p_3;1),\psi(p_1;-1)\\&-\psi(p_3;0),\psi(p_1;0)+\psi(p_3;-1),\psi(p_1;1)]\end{aligned}$$

$$\begin{aligned}\Psi_{15}=(6^{-\frac{1}{2}})[&\psi(p_2;1),\psi(p_3;-1)-\psi(p_2;0),\psi(p_3;0)\\&\psi(p_2;-1),\psi(p_3;1)+\psi(p_3;1),\psi(p_2;-1)\\&-\psi(p_3;0),\psi(p_2;0)+\psi(p_3;-1),\psi(p_2;1)]\end{aligned}$$

$$\begin{aligned}\Psi_{16}=(3^{-\frac{1}{2}})[&\psi(p_3;1),\psi(p_3;-1)-\psi(p_3;0),\psi(p_3;0)\\&+\psi(p_3;-1)\psi(p_3;1)]\end{aligned}$$

$$\begin{aligned}\Psi_{17}=(5^{-\frac{1}{2}})[&\psi(d_1;2),\psi(d_1;-2)-\psi(d_1;1),\psi(d_1;-1)\\&+\psi(d_1;0),\psi(d_1;0)-\psi(d_1;-1),\psi(d_1;1)\\&+\psi(d_1;-2),\psi(d_1;2)]\end{aligned}$$

$$\begin{aligned}\Psi_{18}=(10^{-\frac{1}{2}})[&\psi(d_1;2),\psi(d_2;-2)-\psi(d_1;1),\psi(d_2;-1)\\&+\psi(d_1;0),\psi(d_2;0)-\psi(d_1;-1),\psi(d_2;1)\\&+\psi(d_2;2),\psi(d_1;-2)-\psi(d_2;1),\psi(d_1;-1)\\&+\psi(d_2;0),\psi(d_1;0)-\psi(d_2;-1),\psi(d_1;1)\\&+\psi(d_1;-2),\psi(d_2;2)+\psi(d_2;-2),\psi(d_1;2)]\end{aligned}$$

$$\begin{aligned}\Psi_{19}=(5^{-\frac{1}{2}})[&\psi(d_2;2),\psi(d_2;-2)-\psi(d_2;1),\psi(d_2;-1)\\&+\psi(d_2;0),\psi(d_2;0)-\psi(d_2;-1),\psi(d_2;1)\\&+\psi(d_2;-2),\psi(d_2;2)]\end{aligned}$$

$$\begin{aligned}\Psi_{20}=(7^{-\frac{1}{2}})[&\psi(f_1;3),\psi(f_1;-3)-\psi(f_1;2),\psi(f_1;-2)\\&+\psi(f_1;1),\psi(f_1;-1)-\psi(f_1;0),\psi(f_1;0)\\&+\psi(f_1;-1),\psi(f_1;1)-\psi(f_1;-2),\psi(f_1;2)\\&+\psi(f_1;-3),\psi(f_1;3)]\end{aligned}$$

p orbitals, then 19×19 to include all s, p, and d orbitals, and finally the full 20×20 matrix (see Table IV). The improvement in energy obtained at each stage gave information on the contribution from each symmetry type of orbital.

A preliminary transformation was carried out which obtained the best linear combination of the s orbitals in an approximate Hartree-Fock calculation. In all cases the Hartree-Fock energy was obtained to five significant decimals. This number is quoted as the 1×1 stage in diagonalizing the 20×20 configuration interaction matrix. The other orbitals were orthonormalized and all necessary one- and two-electron integrals calculated before the configuration interaction matrix was constructed. The particular methods used for this numerical work have been described elsewhere in connection with the digital computer programs used.[6]

Although it would have been desirable to carry out a complete calculation to obtain values of the ten a_i parameters by the method of steepest descents, this was not practicable because of the large number of variables. Preliminary calculations and previously reported work[4] provided good initial values of these parameters, so they were varied in small sets or one at a time.

Parameters and results of two calculations are reported here. The second [case (b)], with all a_i the same for given l, is remarkable in that variations away from this extremely simple choice of parameters did not give an improvement in calculated energy at all significant in comparison with the difference between the experimental energy and that of our best calculation. As an empirical rule, the best choices of parameters appear to describe trial orbitals which have maximum radial densities near the same value of the radius. They differ markedly from parameters needed to describe the spectroscopic He orbitals, which spread away from the nucleus as either the angular momentum or the number of radial nodes increases. This agrees with the results of other atomic wave function calculations where the orbital basis was chosen by a variational criterion.[7]

It is estimated that further variation of parameters, with the same number of basis orbitals, would not improve the best energy given here by more than 0.00005 atomic unit.

TABLE IV. Configuration interaction energies.

Matrix diagonalized	Energy (a.u.)	Value of l contributing	Contribution to energy (a.u.)
	Case (a)		
1×1	−2.86168		
		0	−0.01719
10×10	−2.87887		
		1	−0.02142
16×16	−2.90029		
		2	−0.00209
19×19	−2.90238		
		3	−0.00038
20×20	−2.90276		
	Case (b)		
1×1	−2.86158		
		0	−0.01702
10×10	−2.87860		
		1	−0.02132
16×16	−2.89992		
		2	−0.00211
19×19	−2.90203		
		3	−0.00039
20×20	−2.90242		

Table I lists the parameters of the R_i's for the two cases reported. Table II gives the one-electron functions (ψ's) which result from orthonormalization and the approximate Hartree-Fock calculation involving the orbitals with $l=0$. The ψ's have been indexed according to l value (s for $l=0$, p for $l=1$, etc.), with a subscript to cover the cases of more than one ψ for a particular l value. A subscript has been used rather than the common notation to emphasize that only the s_1 orbital resembles a "normal" He one-electron wave function. $\psi(s_1)$ is the approximate Hartree-Fock 1s He wave function resulting from the preliminary calculations while, for example, the $\psi(p_1)$, which might have been labeled 2p instead, has a radically different radial distribution than the function normally referred to by the description "a 2p He orbital." The ψ's also have the quantum numbers m_l and m_s, which have been omitted in Table II but have been included in Table III which lists the twenty ^1S wave functions (Ψ) which were constructed from the ψ's. The m_l assignments are included with l assignments inside the brackets while the following convention is used for spin assignment. If a ψ precedes the comma in a particular term, it has $+\frac{1}{2}$ spin; and if it follows the comma, it has $-\frac{1}{2}$ spin. For example, $\psi(p_1;1),\psi(p_2;-1)$ means the product of a p_1 orbital with $m_l=1$ and $m_s=+\frac{1}{2}$ with a p_2 orbital

TABLE V. C_i's resulting from 20×20 diagonalizations.

i	Case (a)	Case (b)	i	Case (a)	Case (b)
1	+0.99596	+0.99596	11	+0.05010	+0.04420
2	−0.00026	+0.00179	12	−0.03086	−0.03478
3	−0.05671	−0.03329	13	+0.02259	+0.02655
4	+0.00175	+0.00153	14	−0.00165	+0.00362
5	+0.02220	+0.03943	15	+0.00521	−0.00847
6	−0.01229	−0.03198	16	+0.00362	+0.00581
7	−0.00011	−0.00107	17	−0.01211	−0.01173
8	−0.00019	−0.00602	18	+0.00291	+0.00407
9	+0.00113	+0.01095	19	−0.00325	−0.00464
10	−0.00075	−0.00607	20	+0.00411	+0.00399

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with $m_l=-1$ and $m_s=-\frac{1}{2}$. Table IV gives the energies resulting from diagonalizing the configuration interaction matrices. The final ^1S wave functions are a linear combination of the Ψ's of the form

$$\sum_i C_i \Psi_i,$$

and Table V gives the C_i's resulting from the 20×20 diagonalizations. All energies are quoted in Hartree atomic units (a.u.), where 1 a.u.$\cong$27.205 ev.

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Mass, Half-Life, and Excited States of B^8

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The mass of B^8 has been determined by measuring the threshold energy of the reaction $Li^6(He^3,n)B^8$. Observations were made on both the neutrons from the reaction and the positrons from the decay of B^8. The threshold energy is 2.9661 ± 0.0017 Mev, giving a mass of 8.027157 ± 0.000008 amu for B^8. The half-life of B^8 was measured to be 0.78 ± 0.01 sec. Evidence was found for possible excited states in B^8 at 0.6 ± 0.1 and 0.80 ± 0.05 Mev with respective widths of 0.2 ± 0.1 and 0.07 ± 0.04 Mev. Assuming that the decay proceeds exclusively to the 2.9-Mev state of Be^8, the log *ft* value is 5.7.

I. INTRODUCTION

THE first experimental evidence for the nuclide B^8 was reported by Alvarez,[1] who found it to be a delayed alpha-emitter decaying by means of a 13.7-Mev positron (0.65-sec half-life) to the same excited state of Be^8 as does Li^8. He produced B^8 in the reactions $B^{10}(p,H^3)B^8$, $Be^9(p,2n)B^8$, and $C^{12}(p,n\alpha)B^8$.

Sheline[2] observed B^8 in the following reactions: $B^{10}(\gamma,2n)B^8$, $B^{11}(\gamma,3n)B^8$, and $C^{12}(\gamma,p3n)B^8$, and measured the half-life for the positron activity to be 0.61 ± 0.11 sec.

We have used the reaction $Li^6(He^3,n)B^8$ to determine the ground-state mass of B^8, to search for excited states in B^8, and to measure the half-life of the positron activity associated with the decay of B^8.

II. EXPERIMENTAL PROCEDURE

The neutrons emitted in the reaction $Li^6(He^3,n)B^8$ just above the ground-state threshold have energies in the neighborhood of 110 kev due to the motion of the center of mass. Neutrons that are emitted at bombarding energies just above possible excited-state thresholds (energetically available to us) do not exceed 225 kev. Neutrons in the energy range 110 to 225 kev will be referred to as "slow" neutrons to distinguish them from "fast" neutrons of energies greater than 225 kev, such as those emitted from the beam-defining diaphragms and from the target at bombarding energies well above the ground-state threshold.

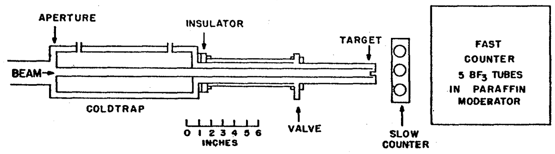

FIG. 1. Schematic representation of target and counter arrangement.

The neutron detectors and their relation to the target are shown in Fig. 1. The detectors and the techniques for observing "slow" neutrons associated with the states of B^8 have been described in a previous paper.[3] The target (near room temperature) was supported just inside the end of a metal tube which is attached to a reservoir containing liquid nitrogen. We have evidence from other experiments[4] to show that this arrangement is extremely effective in preventing the buildup of contaminants on the target. The vacuum jacket to the right of the cold trap may be slid to the right on an "O"-ring seal, the valve closed, and the target changed without losing vacuum inside the cold trap.

The beam emerges from the output slit of the magnetic analyzer, 25 ft from the target, with an energy spread of 0.1%, passes through an 18-in. concrete shielding wall, through a strong-focusing lens, and (as it nears the target) through a 0.1-in. aperture before entering the cold tube. The magnetic analyzer was carefully calibrated using the reactions $Al^{27}(p,\gamma)Si^{28}$ and $Li^7(p,n)Be^7$ with monatomic, diatomic, and triatomic beams. The mean energy of the beam was determined to

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