

VARIATIONAL CALCULATIONS ON THE $^2P_{1/2}$ GROUND STATE OF BORON ATOM USING HYDROGENLIKE ORBITALS*

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Abstract: Variational calculations of the $^2P_{1/2}$ ground state of boron atom are performed using a single-term reference wave function and a 150-term wave function expansion without interelectronic distances. The wave function is constructed with hydrogenlike orbitals. These orbitals are superior to Slater orbitals, because the orbital 2s contains nodes. The calculated energy -24.550233 a.u. is compared with -24.541246 a.u. using Slater orbitals and the same basis function expansion, and with -24.5689998 a.u. obtained from full-CI calculations using a 4-31G basis set. The single-term wave function constructed with hydrogenlike orbitals leads to an energy value of -24.501187 a.u., which is lower than the Hartree-Fock energy using a single-zeta basis set of Slater orbitals and it is also lower than with a single-term wave function with Slater orbitals, both lead to an energy of -24.498369 a.u. The behavior of the node of the 2s orbital and its radial distribution function of the wave function series are discussed.

1. INTRODUCTION

Hydrogenlike orbitals contain a polynomial in r while the Slater orbitals are monomial. In addition, the hydrogenlike orbitals have nodes. Hydrogenlike orbitals have been used in calculations of the first row atoms by Zener [1] and Eckart [2]. The energy results were equivalent to the ones obtained with Slater orbitals [3]. Indeed, a hydrogenlike orbital is a linear combination of Slater ones [4]. Other similar orbitals were used by Morse [5] and Tubis [6]. In this article we use a 2s orbital of Morse-type with two adjustable parameters.

The purpose of this work is to use hydrogenlike atomic orbitals to improve the quality of the orbitals of a single-term and many-term wave functions, in order to have a good starting reference wave function for a full-Hylleraas calculation. The Hylleraas method [7] is a variational method which introduces the correlation effects by including explicitly the interelectronic distances in the wave function.

The Hylleraas-type wave functions are linear expansions of basis functions containing interelectronic coordinates whose coefficients are determined variationally. The calculations of the atoms helium [8] (other sets of basis functions have been also used), lithium [9-11, 14], and beryllium [12, 13] yielded energies close to the experiments. Parallel to the Hylleraas

* Dedicated to the memory of Professor Jacek Rychlewski

method, Hylleraas-CI and exponentially correlated wave functions yielded highly accurate energy results for helium [15], lithium [16], beryllium [17-19] and boron [20] atoms.

Recently, calculations on the ground state of boron atom have been made using the single-term and 150-term wave functions constructed with Slater orbitals [21]. The obtained energies lie between the Hartree-Fock and the CI energies, including about 28 per cent of the correlation energy. In this paper we use the same wave function but constructed with hydrogenlike orbitals and we compare with the results using Slater ones.

2. THEORY

The wave function of the ${}^2P_{1/2}$ state of boron atom is written:

$$\Psi = \hat{A}\phi\chi, \quad (1)$$

where ϕ is the spatial function, \hat{A} is the 5-particle antisymmetrization operator, χ is the spin function $\alpha\beta\alpha\beta\alpha$. Since it is possible to make the restriction of using the same spatial function for two electrons in the same shell, the single-determined wave function is eigenfunction of \hat{S}^2 with eigenvalue $M_s = M_z$, M_z being the eigenvalue of \hat{S}_z . Moreover, the spatial functions may be chosen such that the total wave function is eigenfunction of \hat{L}^2 .

We construct a trial wave function as the expansion [10]

$$\Psi = \sum_{\mu=1}^N C_{\mu} \hat{A}\phi_{\mu}\chi = \sum_{\mu=1}^N C_{\mu} \Psi_{\mu}, \quad (2)$$

where the constants C_{μ} , are determined variationally. The N basis functions ϕ_{μ} , are products of radial and angular functions of hydrogenlike orbitals:

$$\varphi_{1s}(1) = r_1^{i_1} e^{-\alpha r_1}, \quad \varphi_{1s}(2) = r_2^{i_2} e^{-\alpha r_2}, \quad (3)$$

$$\varphi_{2s}(3) = (1 - br_3^{i_3}) e^{-\beta r_3}, \quad \varphi_{2s}(4) = (1 - br_4^{i_4}) e^{-\beta r_4}, \quad (4)$$

$$\varphi_{2p}(5) = r_5^{i_5} e^{-\gamma r_5} \cos\theta_5, \quad (5)$$

with b as a constant to be optimized and i_1, i_2, i_3, i_4 , and i_5 are integers $i_i \geq 0$. The orbital exponents should be optimized. For the case of boron atom, with $n = 5$, the unpaired electron is in a p -orbital, and in the non-relativistic theory, the three p -orbitals are degenerate in energy.

The Hylleraas ground state wave function is a function of distance coordinates of every electron and the interelectronic coordinates. In the case $n \geq 5$ the Hylleraas wave function is also function of the polar angles θ_i and ϕ_i of the electrons [21]. As a first step of a full-Hylleraas calculation, the wave function will not yet include r_{ij} terms.

The single-term wave function of five-electrons is:

$$\phi_1 = e^{-\alpha r_1} e^{-\alpha r_2} (1 - br_3) e^{-\beta r_3} (1 - br_4) e^{-\beta r_4} r_5 e^{-\gamma r_5} \cos \theta_5 \quad (6)$$

A general basis function ϕ_μ with the powers of the $2s$ orbital inside of the bracket, (and not outside of the bracket as would be with truly hydrogen atomic orbitals) is:

$$\phi_\mu = r_1^{i_{1\mu}} e^{-\alpha r_1} r_2^{i_{2\mu}} e^{-\alpha r_2} \left(1 - br_3^{i_{3\mu}}\right) e^{-\beta r_3} \left(1 - br_4^{i_{4\mu}}\right) e^{-\beta r_4} r_5^{i_{5\mu}} e^{-\gamma r_5} \cos \theta_5, \quad (7)$$

where $i_{i\mu}$ are integers with $i_{i\mu} \geq 0$. The restriction for a given basis function (using for simplicity i_j instead $i_{j\mu}$), $i_1 = i_2$ and $i_3 = i_4$, and i_5 independent of the others, ensures that the wave function is spin-eigenfunction. The wave functions (6), (7) can be evaluated into a linear combination of four basis functions constructed with Slater orbitals¹ with factors in b . The orbital exponents a , β , γ and the constant b are parameters which are optimized using a simple parabolic procedure.

The nonrelativistic Hamiltonian for n electrons in the field of a fixed nucleus of charge Z is (in a.u.):

$$\hat{H} = -\sum_{i=1}^n \frac{1}{2} \nabla_i^2 - \sum_{i=1}^n \frac{Z}{r_i} + \sum_{i<j}^n \frac{1}{r_{ij}}. \quad (9)$$

As the general Hylleraas wave function has explicit angular dependence (and also depends on r_{ij}) it is convenient to transform the kinetic energy part into mutually independent distance coordinates r_i , r_{ij} and polar angles θ_j and φ_i . The derivation is given in detail in [21]:

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^n \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^n \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^n \frac{Z}{r_i} + \sum_{i<j}^n \frac{1}{r_{ij}} - \sum_{i<j}^n \frac{\partial^2}{\partial r_{ij}^2} - \sum_{i<j}^n \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \\ & -\frac{1}{2} \sum_{i \neq j}^n \frac{r_i^2 + r_{ij}^2 - r_j^2}{r_i r_{ij}} \frac{\partial^2}{\partial r_i \partial r_{ij}} - \frac{1}{2} \sum_{i \neq j}^n \sum_{k>j}^n \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{r_{ij} r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} + \\ & -\frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i} + \\ & -\sum_{i \neq j}^n \left(\frac{r_j}{r_i r_{ij}} \frac{\cos \theta_j}{\sin \theta_i} + \frac{1}{2} \cot \theta_i \frac{r_{ij}^2 - r_i^2 - r_j^2}{r_i^2 r_{ij}} \right) \frac{\partial^2}{\partial \theta_i \partial r_{ij}} + \\ & -\sum_{i \neq j}^n \frac{r_j}{r_i r_{ij}} \frac{\sin \theta_j}{\sin \theta_i} \sin(\varphi_i - \varphi_j) \frac{\partial^2}{\partial \varphi_i \partial r_{ij}}. \end{aligned} \quad (10)$$

¹ This fact makes the calculation of matrix elements more cumbersome as if one uses the basis function with Slater orbitals [21]

$$\phi_\mu = r_1^{i_{1\mu}} e^{-\alpha r_1} r_2^{i_{2\mu}} e^{-\alpha r_2} r_3^{i_{3\mu}} e^{-\beta r_3} r_4^{i_{4\mu}} e^{-\beta r_4} r_5^{i_{5\mu}} e^{-\gamma r_5} \cos \theta_5. \quad (8)$$

The partial derivatives operate on the corresponding coordinates only where they appear explicitly in the wave function. For a basis function of the type of Eqs. (6), (7) which does not depend on the interelectronic coordinates, the Hamiltonian of Eq. (10) is effectively reduced to

$$\hat{H} = -\sum_{i=1}^5 \left(\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} + \frac{5}{r_i} \right) + \sum_{i < j}^5 \frac{1}{r_{ij}} + \frac{1}{2} \left(\frac{1}{r_5^2} \frac{\partial^2}{\partial \theta_5^2} + \frac{1}{r_5^2} \cot \theta_5 \frac{\partial}{\partial \theta_5} \right). \quad (11)$$

The volume element is:

$$d\tau = \prod_{i=1}^n r_i^2 \sin \theta_i dr_i d\theta_i d\phi_i. \quad (12)$$

From the variational principle one obtains the matrix eigenvalue problem

$$(\mathbf{H} - E\Delta)\mathbf{C} = 0 \quad (13)$$

where the matrix elements are

$$H_{\mu\nu} = \int \psi_\mu \hat{H} \psi_\nu d\tau, \quad \Delta_{\mu\nu} = \int \psi_\mu \psi_\nu d\tau. \quad (14)$$

As the antisymmetrization operator commutes with the Hamiltonian and is idempotent, after "spin integration" we have:

$$H_{\mu\nu} = \left\langle \sum_{j=1}^{12} \phi_{\mu j} \left| \hat{H} \right| \phi_\nu \right\rangle. \quad (15)$$

On the left-hand side, the different terms are generated by the following permutations of the initial one ϕ_μ :

$$\begin{aligned} & \left\langle \left(\hat{e} - \hat{P}_{13} - \hat{P}_{24} + \hat{P}_{13}\hat{P}_{24} - \hat{P}_{15} - \hat{P}_{35} + \hat{P}_{15}\hat{P}_{24} + \hat{P}_{35}\hat{P}_{13} + \right. \right. \\ & \left. \left. + \hat{P}_{35}\hat{P}_{24} + \hat{P}_{35}\hat{P}_{15} - \hat{P}_{24}\hat{P}_{35}\hat{P}_{13} - \hat{P}_{24}\hat{P}_{35}\hat{P}_{15} \right) \phi_\mu \right| \hat{H} \left| \phi_\nu \right\rangle \end{aligned} \quad (16)$$

where \hat{e} is the unit operator and \hat{P}_{ij} is the permutation operator which interchanges the spatial coordinates of electrons i and j . If we evaluate now $H_{\mu\nu}$ we have four terms on the right hand side and 12 x 4 terms on the left hand side, which are products of Slater orbitals.

As in the case with Slater orbitals [21], the evaluation of the matrix element of Eq. (16) leads to the types of integrals: one-electron integrals, two-electron integrals, two-electron one-angle integrals:

$$\left\langle \frac{\cos \theta_i}{r_{ij}} \right\rangle = 0, \quad \left\langle \frac{\cos^2 \theta_i}{r_{ij}} \right\rangle = 0, \quad \forall_{i < j} \quad (17)$$

and two-electron two-angle integrals:

$$\left\langle \frac{\cos \theta_i \cos \theta_j}{r_{ij}} \right\rangle = \frac{(4\pi)^2}{9} \left\langle \frac{s_{ij}}{g_{ij}^2} \right\rangle, \quad \forall_{i < j} \quad (18)$$

where s_{ij} is the smallest of r_i and r_j , and g_{ij} the largest of r_i and r_j .

The resulting integrals in the Hylleraas method have been developed into programmable expressions using the MAPLE [22] program package. The one-electron and two-electron Slater integrals are solved with the help of auxiliary integrals [9]. They are once calculated and stored, and read when it is necessary.

The optimization procedure is simple. The three orbital exponents and the constant b are optimized one after the other using a numerical one-dimensional procedure. A three-point parabolic fitting is mixed with two other procedures which are the selection of the point with lower energy and the best virial coefficient. Each variable is changed with a different step-size which decreases with the cycles of optimization. For each energy calculation the virial coefficient is calculated to check the accuracy of the calculation.

3. CALCULATIONS

The first basis function ϕ_1 , Eq. (6), can be considered as an approximation to the Hartree-Fock wave function constructed with medium size basis set of orbitals.

Then the energy is given by

$$E_1 = \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle}{\langle \psi_1 | \psi_1 \rangle} \quad (19)$$

where $\psi_1 = \hat{A}\phi_1\chi$. We need a condition to calculate the energy of the state. The condition is that the virial theorem should be fulfilled. Therefore a factor η , the ratio between potential $\langle V \rangle$ and kinetic energies $\langle T \rangle$ should be precisely 2 ± 10^{-10} . This factor η is evaluated in every calculation to ensure that the state is the appropriate one:

$$\eta = -\frac{\langle V \rangle}{\langle T \rangle}. \quad (20)$$

The optimization of the exponents α , β , γ and the constant b leads to the energy

$E_1 = 24.501187$ a.u., virial factor $\eta = 1.999999999$, $\alpha = 4.688051$, $\beta = 1.357372$, $\gamma = 1.204539$ and $b = 6.5242$. This energy is lower than the energy the calculated with Slater orbitals [21] -24.498369 a.u. The optimized exponents α , γ , of the wave function with hydrogen-like

orbitals are very close to those obtained using the wave function with Slater orbitals, $\alpha = 4.6794196$, $\gamma = 1.2106724$. The reason is that the $1s$ and $2p$ orbitals have the same form in both wave functions and they are only weakly dependent on the form of the $2s$ orbital. As it is expected, the exponent of the $2s$ orbital is different compared with $\beta = 1.2880853$ for Slater orbitals. In the optimization of b one finds a very flat parabola.

The energy lies between the Hartree-Fock energy -24.498369 a.u. calculated using a single-zeta basis set and -24.527920 a.u. obtained with a double-zeta basis set [23]. Other results are given in Table IV. The energy obtained using hydrogenlike orbitals is lower than using Slater orbitals.

In this method the energy is improved by adding new basis functions in a systematic way, from $i_j = 0$ until $i_j = 7$, in some cases $i_j = 9$, ordered by similarity to facilitate the optimization of the exponents. The orbital exponents and the constant b have been optimized for every group of similar basis functions which is added. We have used the same basis function expansion than in the previous calculations with Slater orbitals [21]. In Table 1, the powers of the orbitals of the basis functions are given. For example, the basis functions 1 to 38 introduce flexibility to the outer electrons. The basis functions 39 to 57 give flexibility to the inner electrons. The rest of the basis functions introduces some correlation effects due to the use of more extended orbitals.

The energy results are shown in Table 2, together with the energies of those basis function expansions using Slater orbitals. For the first eight basis functions we have $i_3, i_4 = 0$, as the basis set is the same, the form of the hydrogenlike orbital $2s$ coincides with the Slater one for these basis functions except for a factor, therefore the energy results for both wave functions are equal. Taking more basis functions, the wave function of hydrogenic orbitals lead to an energy about 1 mhartree lower than the energy calculated with Slater orbitals. The difference increases with increasing number up to 150 basis functions. The final energy for $N = 150$ is $E_{150} = -24.550233$ a.u., 8.98 mhartree lower than the energy with Slater basis functions. This energy includes about 33 per cent of the total correlation energy for boron atom. 6 per cent more correlation energy have been obtained using hydrogenlike orbitals instead of Slater ones. This is due that they are physically more appropriate and to the presence of one more variational parameter, the constant b .

The optimized exponents and constants are given in Table 3. The final exponents are $\alpha = 4.520884$, $\beta = 1.338861$, and $\gamma = 0.750846$, and the constant is fitted to $b = 2.398$. These exponents are slightly smaller than the ones calculated using Slater orbitals. In the first basis functions α and γ coincide with the ones of Slater, but not β . Adding more basis functions the exponents became more different. In contrary, the β exponent became more close to the Slater one.

In Figure 1 the radial distribution functions of the Slater and hydrogenic $2s$ orbital using the optimized parameters of the 150-term wave function are shown. The hydrogenic orbital

Table 1. Basis function powers: $\phi_{\mu} = r_1^{i_1} r_2^{i_2} (1 - br_3^{i_3})(1 - br_4^{i_4}) r_5^{i_5} \cos \theta_5 e^{(-\alpha r_1 - \alpha r_2 - \beta r_3 - \beta r_4 - \gamma r_5)}$.

No.	i_1, i_2	i_3, i_4	i_5	No.	i_1, i_2	i_3, i_4	i_5	No.	i_1, i_2	i_3, i_4	i_5	No.	i_1, i_2	i_3, i_4	i_5
1	0	0	0	39	1	0	0	77	3	4	1	115	4	4	2
2	0	0	1	40	2	0	0	78	4	2	1	116	4	4	3
3	0	0	2	41	3	0	0	79	4	3	1	117	4	4	4
4	0	0	3	42	4	0	0	80	1	2	2	118	0	0	8
5	0	0	4	43	1	1	0	81	1	2	3	119	0	0	9
6	0	0	5	44	2	1	0	82	1	2	4	120	1	5	0
7	0	0	6	45	3	1	0	83	1	2	5	121	1	6	0
8	0	0	7	46	4	1	0	84	1	3	2	122	2	5	0
9	0	1	0	47	1	2	0	85	1	3	3	123	2	6	0
10	0	2	0	48	1	3	0	86	1	3	4	124	3	5	0
11	0	3	0	49	1	4	0	87	1	4	4	125	3	6	0
12	0	4	0	50	2	2	0	88	2	2	2	126	4	4	0
13	0	5	0	51	2	3	0	89	2	2	3	127	4	5	0
14	0	1	1	52	2	4	0	90	2	2	4	128	1	5	1
15	0	1	2	53	3	2	0	91	2	2	5	129	1	6	1
16	0	1	3	54	3	3	0	92	2	3	2	130	2	5	1
17	0	1	4	55	3	4	0	93	2	3	3	131	2	6	1
18	0	1	5	56	4	2	0	94	2	3	4	132	3	5	1
19	0	1	6	57	4	3	0	95	2	3	5	133	3	6	1
20	0	1	7	58	1	1	1	96	3	3	2	134	4	5	1
21	0	2	1	59	1	1	2	97	3	3	3	135	4	5	2
22	0	2	2	60	1	1	3	98	3	3	4	136	4	5	3
23	0	2	3	61	1	1	4	99	3	3	5	137	5	4	1
24	0	2	4	62	1	1	5	100	3	2	2	138	5	4	2
25	0	2	5	63	1	1	6	101	3	2	3	139	5	4	3
26	0	2	6	64	1	1	7	102	3	2	4	140	5	4	4
27	0	3	1	65	1	1	8	103	3	2	5	141	5	5	0
28	0	3	2	66	2	1	1	104	2	4	2	142	5	5	1
29	0	3	3	67	3	1	1	105	2	4	3	143	5	5	2
30	0	3	4	68	4	1	1	106	2	4	4	144	5	5	3
31	0	3	5	69	1	2	1	107	3	4	2	145	1	5	2
32	0	4	1	70	1	3	1	108	3	4	3	146	1	6	2
33	0	4	2	71	1	4	1	109	3	4	4	147	2	5	2
34	0	4	3	72	2	2	1	110	4	3	2	148	2	6	2
35	0	4	4	73	2	3	1	111	4	3	3	149	3	5	2
36	0	5	1	74	2	4	1	112	4	3	4	150	3	6	2
37	0	5	2	75	3	2	1	113	4	3	5				
38	0	5	3	76	3	3	1	114	4	4	1				

Table 2. Energies (in a.u.) for a given number of basis functions, using Slater orbitals [21], and hydrogenlike orbitals in the wave function, respectively. In addition the difference $E(\text{hydrogenlike}) - E(\text{Slater})$ is given

No.	E (Slater)	E (hydrogenlike)	Difference	No.	E (Slater)	E (hydrogenlike)	Difference
1	-24.348104	-24.351385	-0.003281	77	-24.540131	-24.542418	-0.002287
8	-24.432419	-24.432427	-0.000008	79	-24.540146	-24.542464	-0.002318
13	-24.491764	-24.494885	-0.003121	87	-24.540156	-24.542582	-0.002426
20	-24.516098	-24.516143	-0.000045	91	-24.540246	-24.542602	-0.002356
26	-24.518749	-24.518898	-0.000149	95	-24.540293	-24.542609	-0.002316
31	-24.519192	-24.519968	-0.000776	99	-24.540292	-24.542609	-0.002317
35	-24.519215	-24.520470	-0.001255	103	-24.540305	-24.542613	-0.002308
38	-24.519225	-24.520575	-0.001350	109	-24.540309	-24.542621	-0.002312
42	-24.525574	-24.528064	-0.002490	117	-24.540337	-24.542628	-0.002291
46	-24.535417	-24.536589	-0.001172	127	-24.540697	-24.545418	-0.004721
49	-24.536008	-24.537109	-0.001101	129	-24.540700	-24.545960	-0.005260
52	-24.536502	-24.538329	-0.001827	131	-24.540719	-24.545987	-0.005268
55	-24.536553	-24.538352	-0.001799	136	-24.540730	-24.545990	-0.005260
57	-24.536607	-24.538491	-0.001884	137	-24.540762	-24.546496	-0.005734
65	-24.539255	-24.540783	-0.001528	140	-24.540753	-24.547476	-0.006723
68	-24.539624	-24.540786	-0.001162	144	-24.541177	-24.549774	-0.008597
71	-24.539974	-24.542265	-0.002291	150	-24.541246	-24.550233	-0.008987
74	-24.540018	-24.542364	-0.002346				

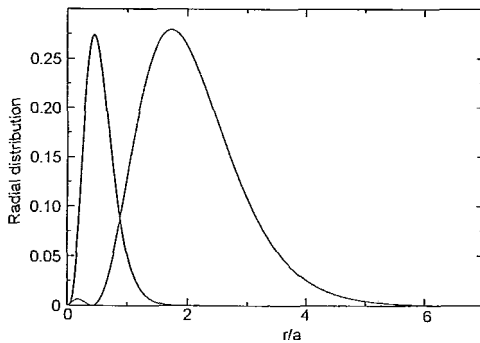


Fig. 1. Radial distribution function of the 2s hydrogenlike orbital (with a node) and the Slater type one calculated with the optimized exponents of a 150-term wave function

has a node and the maximal probability at larger distance. For $i_3, i_4 = 1$ the hydrogenlike orbital coincides with the hydrogenic orbital.

In Figures 2 and 3 the radial distribution functions of the 2s orbitals with different powers i_3, i_4 show different behavior at small r . The hydrogenlike orbitals present nodes, which move to large r with increasing powers. The Slater orbitals have a maximum at nearer distances to

the nucleus than the hydrogenlike ones. In both Figures the probability to find the electron is higher for power 1 and decreases with increasing power.

Table 3. Results using hydrogenlike orbitals: energies in (a. u.) for a given number of basis functions, optimized orbital exponents and orbital coefficient b , and virial coefficient

No.	E (hydrogenlike)	α	β	γ	b	virial ratio
1	-24.351385	4.62183388	0.74896367	0.47489419	7.136869	2.000000344
8	-24.432427	4.62670884	0.72026697	1.65453049	5.852452	2.0000080293
13	-24.494885	4.67718391	1.05324185	0.64033174	2.753014	2.0000000000
20	-24.516143	4.68590000	1.24058271	0.63399000	4.599031	2.0000000000
26	-24.518898	4.68620737	1.27517474	0.88807764	6.834067	2.0000000000
31	-24.519968	4.68641492	1.24694281	1.60862117	5.470780	2.0000000000
35	-24.520470	4.68641492	1.22935089	1.61343967	4.077469	2.0000000000
38	-24.520575	4.68676343	1.21088914	1.61937951	3.785341	1.9999999971
42	-24.528064	4.55953982	1.23382125	0.72695372	2.919047	2.0000000000
46	-24.536589	4.45773982	1.25648021	0.69123238	3.517716	2.0000000000
49	-24.537109	4.44461335	1.23386413	0.68764275	3.571725	2.0000000000
52	-24.538329	4.44841053	1.21365925	0.69109923	3.030002	2.0000000000
55	-24.538352	4.44975485	1.20919613	0.69322458	2.948800	1.9999999034
57	-24.538491	4.44701898	1.20534653	0.69306467	2.949590	1.9999998022
65	-24.540784	4.42490154	1.20982109	0.74509752	3.108249	2.0000000015
68	-24.540786	4.42490154	1.21082109	0.74841752	3.125801	2.0000000015
71	-24.542265	4.41928966	1.21987149	1.00909552	2.872800	1.9999999081
74	-24.542364	4.41762286	1.21987149	1.00909552	2.872800	1.9999999131
77	-24.542418	4.41653618	1.21987149	1.00909552	2.867022	1.9999999894
79	-24.542464	4.41660018	1.21987149	1.00909552	2.855222	2.0000000509
87	-24.542582	4.42267218	1.21987149	1.00909552	2.783861	1.9999999919
91	-24.542602	4.42237993	1.21987149	1.00909552	2.780100	1.9999999989
95	-24.542609	4.42239693	1.21987149	1.00909552	2.778428	1.9999999999
99	-24.542609	4.42226869	1.21986069	1.00909732	2.779800	1.9999999917
103	-24.542613	4.42214949	1.21986133	1.00908742	2.779000	1.9999999980
109	-24.542621	4.42229789	1.21984899	1.00898732	2.771000	1.9999999973
117	-24.542628	4.42206969	1.21985069	1.00909738	2.778000	1.99999996485
127	-24.545419	4.39900000	1.27000160	0.83784000	2.599200	1.9999999171
129	-24.545960	4.40000000	1.26016160	0.89900000	2.498000	1.9999999659
131	-24.545987	4.40101164	1.27035180	0.91071746	2.509400	2.0000001621
136	-24.545990	4.40116722	1.28307195	0.92082000	2.504400	1.9999998322
137	-24.546496	4.40426969	1.23087969	0.89209732	2.578000	2.0000000398
140	-24.547476	4.41000000	1.24979687	0.88833184	2.388000	2.0000002533
144	-24.549774	4.51281980	1.33886068	0.71579732	2.398000	2.0000000454
150	-24.550233	4.52088419	1.33886068	0.75084613	2.398000	2.0000000481

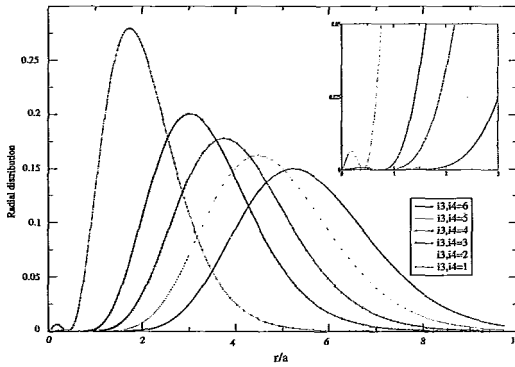


Fig. 2. Radial distribution functions of the 2s hydrogenlike orbitals with different powers of r , $i_3 = i_4$ from Eq. (7). Calculated with the optimized exponents of the 150-term wave function

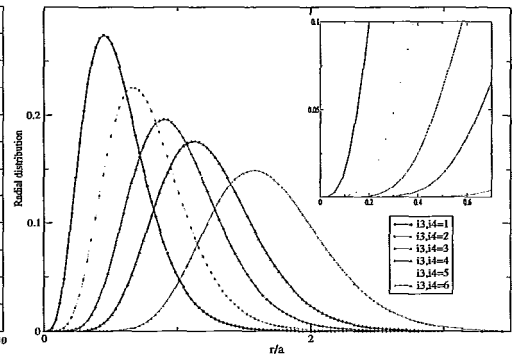


Fig. 3. Radial distribution functions of the 2s Slater orbitals with different powers in r , $i_3 = i_4$ from Eq. (8). Calculated with the optimized exponents of the 150-term wave function

Table 4. Comparison of the energies for boron atom calculated with different methods and the nonrelativistic energy (all values in a.u.)

Reference	Year	Method	Basis Set	Energy
Clementi [23]	1989	HF	c-GTO small geom.	-24.495670
Clementi, Roetti [24]	1974	HF	STO single zeta	-24.498369
Ruiz [21]	2004	ref Hy	(1-term)	-24.498369
Present Work	2004	ref Hy hydrog.	(1-term)	-24.501187
Clementi, Raimondi [25]	1963	HF	STO minimal basis	-24.498370
Clementi, Roetti [24]	1974	HF	STO double zeta	-24.527920
Clementi [23]	1989	HF	GTO large geom.	-24.528486
Huzinaga [26]	1977	HF	STO	-24.528709
Froese-Fisher <i>et La</i> [29]	1993	numerical HF		-24.529036
Clementi, Roetti [24]	1974	HF	STO extended	-24.529057
Clementi, Chakravorty [23]	1989	HF	GTO extra large	-24.52906
	2004	HF-Gaussian-98	cc-pVSZ	-24.5291094
Mayer [28]	2004	full-CI	4-31G	-24.530874
Ruiz [21]	2004	Hylleraas	150 (without r_{ij})	-24.541246
Present Work	2004	Hylleraas	150 (without r_{ij})	-24.550233
Froese-Fisher <i>et la</i> [30]	1994	multiref. CI		-24.560354
Mayer [28]	2004	full-CI	DZV	-24.568999
Mayer [28]	2004	full-CI	DZP	-24.585533
Estimated nonrelativistic [31]	1993			-24.65391

Small geom. stands for small geometrical basis set, large geom. for large geometrical basis set, DZV for valence double zeta basis and DZP for double zeta basis with polarization functions. In the literature, usually the best HF energy value is quoted as only HF, this is -24.52905 a.u.

Finally, in Table 4 we compare our energy results with the ones of other methods. The 150-term energy obtained using hydrogenlike orbitals is lower by 19.3 mhartrees than the energy of a full-CI wave function with 4-31G basis set [28]. It is also lower than numerical HF calculations. The calculated energy is higher by 10.1 mhartrees than the multireference CI energy [29], and 18.7 mhartrees higher than the full-CI energy using a double-zeta basis set. The energy using polarization basis functions is still lower. A similar energy to the full-CI using medium size basis set (DZV) could probably be achieved if the expansion serie would be extended to a larger number of basis functions. Nevertheless, our purpose is to introduce more correlation energy introducing interelectronic coordinates into the wave function, this work is in progress.

4. CONCLUSIONS

Substituting the $2s$ Slater orbital by the hydrogenlike $2s$ one into the reference Hylleraas wave function the energy result improves by 6 per cent for a large number of basis functions. This is due, on the one hand, to the higher quality of the $2s$ orbital, which has a node, as the exact solution of Schrödinger equation of the hydrogen atom. On the other hand, it is due to the presence of an additional variational parameter. The orbitals with high powers in r of the expansion series are not exactly Slater neither hydrogenic, they are of s -type. It can be understood as a basis function set inside of a shell. The obtained energy approaches the full-CI calculations using valence double-zeta basis set. We expect to introduce more correlation effects by introducing in this reference wave function interelectronic variables. This work is in progress.

Finally, the calculated energy is comparable with the energy of full-CI calculations.

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