

A NEW TYPE OF WAVEFUNCTION FOR BH †

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The wavefunctions of BH have been obtained using a generalization of the valence bond and Hartree-Fock methods known as the Spin-Coupling Optimized GI (SOGI) method. The shapes of the bonding and especially the nonbonding orbitals are discussed as are several properties of the molecule.

1. INTRODUCTION

We report here the wavefunctions and properties of the BH molecule as obtained using the recently developed G1 [1-3] and spin-coupling optimized GI [4] (SOGI) methods. The G1 method can be viewed as a generalization of the valence bond (VB) method in which all orthogonality conditions are removed, the orbitals are allowed to be of any shape and spread over all the atoms, and the orbitals are functionally optimized in ab initio calculations [3,4]. Thus for BH there are six orbitals, none of which are orthogonal to another. However, the orbitals still divide into three groups: two core orbitals, two nonbonding orbitals, and two bonding orbitals. The SOGI method is a generalization of the G1 method in which the spin-coupling is optimized simultaneously with the orbital optimization rather than forced to be the spin coupling appropriate for the G1 or VB wavefunction [4].

The G1 wavefunction has the form

$$G\chi \Phi \chi, \quad (1)$$

where

$$\Phi = \phi_{1a}(1) \phi_{1b}(2) \phi_{2a}(3) \phi_{2b}(4) \phi_{3a}(5) \phi_{3b}(6) \quad (2)$$

and

$$\chi = \alpha(1) \beta(2) \alpha(3) \beta(4) \alpha(5) \beta(6)$$

are products of spatial and spin functions respectively. (In the following, electron numbers will be omitted from functions such as Φ and χ ; it will be understood that all functions are ordered by electron number.) Here G_1 is the group operator [5] (involving spatial and spin permutation operators) which ensures that for any Φ and χ , (1) describes a singlet state and satisfies Pauli's principle. The wavefunction in (1) can be re-expressed as [2,4]

$$c\mathcal{A}[(\phi_{1a} \phi_{1b} + \phi_{1b} \phi_{1a})(\phi_{2a} \phi_{2b} + \phi_{2b} \phi_{2a}) \times \\ (\phi_{3a} \phi_{3b} + \phi_{3b} \phi_{3a}) \alpha \beta \alpha \beta] = \\ c\mathcal{A}[\phi_{1a} \phi_{1b} \phi_{2a} \phi_{2b} \phi_{3a} \phi_{3b} \times \\ (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)], \quad (3)$$

which has the form of a generalized valence-bond wavefunction (c is just an arbitrary constant dependent upon normalization). In the G1 method it is required that each orbital, ϕ_k , be optimum (that is, that the energy be stationary under variations of ϕ_k). The result is a set of self-consistent equations analogous to the Hartree-Fock equations. However, the ϕ_k 's are allowed to be completely general (no double occupancy or orthogonality restrictions) and the G1 wavefunctions dissociate to the correct atomic limits.

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In the usual valence bond [6] (VB) or extended valence bond [7] (EVB) method, the wavefunction for BH would have the form in (3) except that we would take ϕ_{1a} and ϕ_{1b} to be identical core-like orbitals and ϕ_{2a} and ϕ_{2b} to be identical nonbonding orbitals. In this case (3) differs from the form of the Hartree-Fock wavefunction only by having a split ϕ_3 pair. Thus the G1 wavefunction is a generalization of the VB and EVB wavefunctions in which *all* orbitals are allowed to split and where the orbitals are allowed to be of any shape and spread over all the atoms, and the orbitals are functionally optimized in ab initio calculations.

Given a product of orbitals as in (2) we can construct five linearly independent many-electron wavefunctions satisfying Pauli's principle and describing a singlet state. These can be taken as [5]

$$G_i^\gamma \Phi \chi, \quad i = 1, 2, \dots, 5,$$

where the group operator G_i^γ simultaneously takes care of the Pauli and spin symmetries. The different i just correspond to the different spin couplings of 6 electrons to form a singlet, one of which is presented in (1) and (3). However the G_i^γ are expressed in terms of representation matrices for the symmetric group, and any linear combination of the operators $\sum_i C_i G_i^\gamma$ can be expressed as $G_1^{\gamma L}$ using a new set representation matrices [4],

$$U_\tau^L = L U_\tau L^{-1}.$$

Thus the optimum wavefunction constructable from the product of orbitals Φ in (2) can be written as [4]

$$G_1^{\gamma L} \Phi \chi. \quad (4)$$

The orbitals of (4) are optimized in the same way (using the same programs) as are the orbitals of (1) except that now we must also optimize the transformation matrices L in order to optimize the spin coupling. In order to distinguish these approaches the latter is called the spin-coupling optimized GI (SOGI) method [4]. The SOGI orbitals can also be interpreted as the states of electrons moving in the average field due to the other electrons (the independent particle interpretation). In fact since the SOGI wavefunction is the best possible wavefunction using just the product of orbitals (1), these SOGI orbitals are the optimum independent particle orbitals. Hence the SOGI method can be viewed as the generalization and synthesis of the other orbital methods, such as Hartree-Fock, valence bond, and G1.

Previous calculations with the G1 and SOGI methods have been limited to molecules [3,4] and

atoms [2,4,8] with up to four electrons. Here we will report the first such calculations on larger systems. A matter of particular interest will be the description of the nonbonding orbitals of BH since VB and HF calculations take the nonbonding orbitals to be doubly occupied and since the systems previously considered with the G1 and SOGI methods did not have nonbonding orbitals.

2. CALCULATIONAL DETAILS

The SCF calculations were carried out in the same way as described previously [1-4] except that each GI equation was expanded to first order in all six orbitals and the six coupled equations for the changes in all six orbitals were solved for the increments in each orbital each iteration. This generalized Newton-Raphson procedure [9] was found to lead to quadratic convergence in the orbitals*.

Only the first row of L is needed for constructing $U_{11}^L(\tau)$. In the case of a six-electron singlet state or a five-electron doublet state this row becomes

$$L_{11} = \cos \frac{1}{2}\Xi$$

$$L_{12} = \sin \frac{1}{2}\Xi_1 \cos \frac{1}{2}\Xi_2$$

$$L_{13} = \sin \frac{1}{2}\Xi_1 \sin \frac{1}{2}\Xi_2 \cos \frac{1}{2}\Xi_3$$

$$L_{14} = \sin \frac{1}{2}\Xi_1 \sin \frac{1}{2}\Xi_2 \sin \frac{1}{2}\Xi_3 \cos \frac{1}{2}\Xi_4$$

$$L_{15} = \sin \frac{1}{2}\Xi_1 \sin \frac{1}{2}\Xi_2 \sin \frac{1}{2}\Xi_3 \sin \frac{1}{2}\Xi_4.$$

Thus the spin-coupling is specified by the angles $\{\Xi_1, \Xi_2, \Xi_3, \text{ and } \Xi_4\}$. In some cases it is convenient to represent the spin-coupling in terms of the standard five spin-couplings (corresponding to the standard Young tableaux; these coefficients are denoted as $\{c_i\}$ and can be easily calculated from the $\{\Xi_i\}$).

The basis set consists of nine Slater orbitals on the boron (five s, three p, and one d) and two Slater orbitals on the hydrogen (one s and one p). The three core-like s functions of the B were chosen from a G1 B⁺⁺ calculation [2] and the other functions were chosen from Hartree-Fock [10,11] and GF [12] calculations. All SCF orbitals were *restricted* to be symmetry functions (σ for BH, s or p for B). Indeed, we have found that for

* Typically three to four iterations were required for the orbitals to converge to ten places. For six electrons and eleven basis functions this took 220 seconds/iteration on an IBM 360/75 computer.

Table 1
Calculated properties for the HF, G1 and SOGI wavefunctions of B and BH. Hartree atomic units are used unless otherwise specified

	B			BH		
	HF [13]	G1	SOGI	HF [10,14]	G1	SOGI
Total energy (E)	-24.52905	-24.54558	-24.54602	-25.13137	-25.16639	-25.16640
Kinetic energy (KE)	24.52837	24.53695	24.53800	25.11630	25.15858	25.15850
Virial ratio ($V/2E$)	0.99999	0.99982	0.99984	1.00030	0.99984	0.99984
Electric field gradient ^{b)}						
B nucleus	-0.62042	-0.62149	-0.63051	...	-0.74218	-0.74249
H nucleus	0.0	0.0	0.0	...	0.17671	0.17668
Dipole moment ^{c)}	0.0	0.0	0.0	0.682	0.70197	0.70200
Molecular quadrupole moment at boron ^{d)}	-2.45908	-2.44813	-2.42077	...	-2.32339	-2.32198
$\langle r^2 \rangle_B$ ^{e)}	15.853	15.90059	15.87240	22.75 ^{a)}	23.19517	23.19441
$\langle r^2 \rangle_H$ ^{e)}	3.0	3.0	3.0	47.70 ^{a)}	48.30235	48.30173
$\langle \frac{1}{r} \rangle_B$ ^{f)}	11.37930	11.37642	11.37727	11.81 ^{a)}	11.80471	11.80471
$\langle \frac{1}{r} \rangle_H$ ^{f)}	1.0	1.0	1.0	3.272 ^{a)}	3.26849	3.26847

a) Ref. [15].

b) 1 au = 3.24140×10^{15} esu/cm³.

c) 1 au = 2.54158 D.

d) 1 au = 1.34492×10^{-26} esu cm².

e) Multiply by -0.791985 to obtain diamagnetic susceptibility in ppm (cgs).

f) Multiply by 17.7497 to obtain diamagnetic shielding in ppm (cgs).

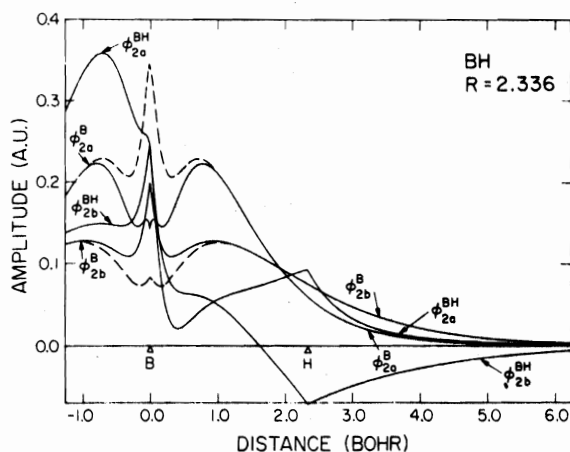


Fig. 1. The nonbonding SOGI orbitals of BH and the 2s valence pair SOGI orbitals of B. The dashed lines show the G1 orbitals of B, the G1 orbitals of BH superimpose upon the SOGI orbitals.

the UHF, GF, G1 and SOGI wavefunctions of such systems as Be, B, and BH, the SCF orbitals split so as to have lower symmetry than that of the atom and molecule. In this case, the spatial symmetry of the total wavefunction is not correct. The wavefunctions reported here are the optimum

ones leading to the correct spatial symmetry for the total wavefunction. These effects will be discussed more completely elsewhere.

Note in fig. 1 that the core parts of the non-bonding orbitals (2a and 2b) of B change significantly between SOGI and G1 (indicated by dashed lines in fig. 1). We have also noted that the shapes of the 2a and 2b orbitals in B for symmetry restricted calculations are quite sensitive to the description of the core potentials whereas this is not true for the unrestricted wavefunctions. Thus the changes in this B pair seem to be due to inadequacies in the basis being magnified by the symmetry restrictions. All the other orbitals of B and BH from the G1 and SOGI calculations nearly superimpose.

3. RESULTS AND DISCUSSION

The energies and properties of the (symmetry restricted) SOGI wavefunctions of B and BH are given in table 1. The optimum SOGI angles for BH are: $\frac{1}{2}\Xi_1 = 0.8165^\circ$, $\frac{1}{2}\Xi_2 = 94.65^\circ$, $\frac{1}{2}\Xi_3 = -39.44^\circ$, $\frac{1}{2}\Xi_4 = 23.1^\circ$ and the corresponding spin-coupling coefficients are:

$$c_1 = 0.99681, \quad c_2 = -0.01810, \quad c_3 = -0.07755, \\ c_4 = 0.00430 \quad \text{and} \quad c_5 = 0.00169.$$

Table 2
The SOGI wavefunctions for BH molecule ($R = 2.336 a_0$) and B atom

BH molecule	ϕ_{1a}	ϕ_{1b}	ϕ_{2a}	ϕ_{2b}	ϕ_{3a}	ϕ_{3b}
B 1s 5.0	1.143 246	0.706 898	0.037 763	0.039 543	0.033 893	0.011 822
B 3s 7.9	-0.172 579	0.203 322	-0.028 390	-0.009 537	-0.022 257	-0.006 118
B 3s 4.84	0.004 488	0.172 874	-0.042 033	-0.011 014	-0.036 046	-0.018 877
B 2s 0.979 64	-0.001 731	-0.002 108	0.016 565	0.732 485	0.151 871	-0.076 912
B 2s 1.565 74	0.009 075	-0.043 706	0.882 057	0.184 435	0.663 363	0.106 787
B 2p 0.910 77	0.000 284	0.012 328	-0.007 938	-0.690 080	0.089 509	0.053 472
B 2p 1.540 07	-0.001 014	-0.020 281	-0.382 704	0.451 711	0.275 117	0.016 676
B 2p 2.144 47	0.002 320	0.017 790	-0.023 835	-0.176 545	0.065 855	0.047 420
B 3d 1.080 34	0.000 511	-0.000 006	0.044 084	-0.146 639	0.066 574	0.005 197
H 1s 1.182 74	0.003 730	-0.000 816	0.102 911	-0.090 995	0.123 680	0.933 762
H 2p 1.699 99	-0.000 466	-0.001 868	-0.024 368	-0.002 887	-0.058 525	-0.013 321
ϵ	-7.887 418	-7.379 591	-0.492 456	-0.340 935	-0.619 464	-0.675 779
SOGI angles	$\frac{1}{2}\Xi_1 = 0.8165^\circ$		$\frac{1}{2}\Xi_2 = 94.65^\circ$	$\frac{1}{2}\Xi_3 = -39.44^\circ$	$\frac{1}{2}\Xi_4 = 23.13^\circ$	

B atom	(SOGI wavefunction)				
	ϕ_{1a}	ϕ_{1b}	ϕ_{2a}	ϕ_{2b}	ϕ_{3a}
B 1s 5.0	1.141 563	0.702 788	0.022 575	0.031 547	0.0
B 3s 7.9	-0.173 477	0.202 382	-0.034 825	-0.009 340	0.0
B 3s 4.84	0.002 680	0.172 992	-0.086 832	0.009 758	0.0
B 2s 1.11	0.004 485	0.013 193	0.121 019	1.109 207	0.0
B 2s 1.72	0.018 043	-0.032 001	0.054 425	-0.132 354	0.0
B 2p 0.931	0.0	0.0	0.0	0.0	0.691 758
B 2p 1.753	0.0	0.0	0.0	0.0	0.353 931
B 2p 4.558	0.0	0.0	0.0	0.0	0.017 740
ϵ	-7.916 911	-7.424 851	-0.588 972	-0.477 026	-0.312 538
SOGI angles	$\frac{1}{2}\Xi_1 = 4.673^\circ$		$\frac{1}{2}\Xi_2 = 76.00^\circ$	$\frac{1}{2}\Xi_3 = -3.748^\circ$	$\frac{1}{2}\Xi_4 = 21.56^\circ$

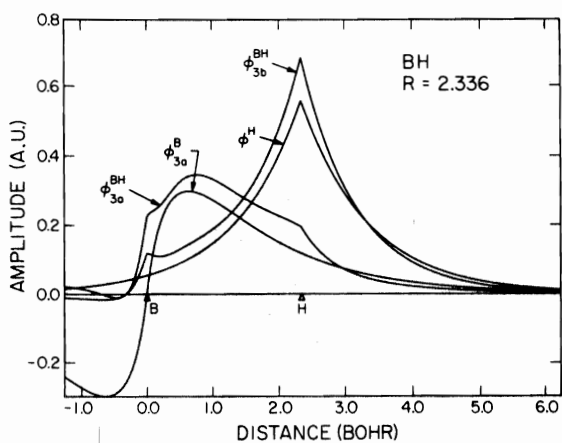


Fig. 2. The bonding SOGI orbitals of BH and the 2p valence SOGI orbital of B. The G1 orbitals superimpose upon the SOGI orbitals.

Thus we see that the SOGI wavefunction is essentially the G1 wavefunction. In fact, for BH the expansion coefficients of the G1 orbitals are the same as the SOGI coefficients (see table 2) to about four places and the plots of the G1 orbitals

would superimpose on the SOGI orbitals of figs. 1 and 2. The G1 energy is higher than the SOGI energy by 0.0004 for B and 0.00001 for BH and the G1 dipole moment of BH is lower by 0.0001 debye. This close comparison between G1 and SOGI was also observed for LiH [3] and is expected to occur often in the ground states of such stable, nonconjugated systems.

The SOGI energy of BH is 0.035 hartree lower than the best Hartree-Fock value [10] and the calculated dissociation energy is 91.5% of the experimental value as compared to 77.8% for Hartree-Fock. The Hartree-Fock and SOGI values for the dipole moment are nearly the same.

Next we will discuss the SOGI orbitals for B and BH, the expansion coefficients of which are given in table 2.

The boron atom ($2P$ state) has five orbitals. Two of these orbitals (ϕ_{1a} and ϕ_{1b}) are spherically symmetric s-like functions which are concentrated in the region close to the boron nucleus; these orbitals are similar to the Hartree-Fock core orbital and will be referred to as core functions. However, the SOGI orbitals are split significantly, that is, ϕ_{1a} is not equal to ϕ_{1b} as is

demonstrated by the 0.9625 overlap between the two orbitals. The second pair of orbitals, ϕ_{2a} and ϕ_{2b} , are also s-like functions, but are much more diffuse (see fig. 1), being concentrated in what will be called the valence region. These orbitals are similar to the Hartree-Fock 2s orbital in the valence region although they are significantly split (overlap 0.9084). However, in the core region they differ greatly from the HF 2s orbital since the HF 2s is forced to be orthogonal to the HF 1s whereas no orthogonality restrictions are imposed upon the SOGI orbitals. The remaining orbital, ϕ_{3a} (see fig. 2) is a p-type orbital which is nearly identical to the corresponding Hartree-Fock orbital. The resulting total energy for SOGI is 0.017 hartree lower than the Hartree-Fock value.

In the BH molecule ($^1\Sigma^+$ state at $R = R_e = 2.336 a_0$), the orbitals naturally group into three pairs. The first pair of orbitals, ϕ_{1a} and ϕ_{1b} , are s-type core functions concentrated mainly in the area of the boron nucleus and are essentially the same as in B atom. The pair of orbitals, ϕ_{3a} and ϕ_{3b} , are aptly termed as bonding orbitals and have evolved from the pairing of a boron atom orbital with the hydrogen 1s orbital (see fig. 2). We see that by $R = R_e$ these two orbitals have significantly increased their amplitude between the two nuclei. The ϕ_{3a} orbital has mixed in s character into the orbital so as to increase its amplitude between the two nuclei. The hydrogen orbital has also mixed in some s-like character from the boron center so as to increase its amplitude in the area between the nuclei. The remaining pair of orbitals, ϕ_{2a} and ϕ_{2b} , are clearly nonbonding orbitals (see fig. 1). Both of these orbitals have hybridized such that they have "moved" out of the area between the two nuclei. Additionally, these two orbitals have split more so that the overlap between the two orbitals is now 0.8350.

Although these changes in the orbitals from B to BH seem reasonable a more detailed comparison of the changes as a function of R shows disturbing features. Even for R as large as $7 a_0$ the H 1s orbital is coupled to one of the 2s orbitals (ϕ_2) of B rather than with the 2p orbital. Furthermore between 7.0 and 3.5 the nonbonding orbitals change drastically where it appears that these orbitals flip from one type of coupling appropriate for large R to one appropriate for small R . A further investigation showed that these strange

features were due to the symmetry restrictions and that unrestricted G1 and SOGI calculations lead to continuous changes of the orbitals for changing from ∞ to R_e .

The bonding orbitals of BH have shapes similar to the bonding orbitals of LiH and are closely related to what one might have guessed for hybridized valence-bond orbitals. However, the nonbonding orbitals are rather different from the previously discussed valence-bond orbitals primarily because the valence-bond nonbonding orbitals are usually taken as doubly occupied atomic orbitals. It will be of great interest to see what the nonbonding orbitals are like in larger molecules and perhaps determine how they affect and are affected by neighboring bonding orbitals.

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