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The Determination of Electronic Ground and Singlet State Wavefunctions of BH

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An extensive series of CI calculations have been carried out for the BH molecule using averaged natural orbitals. It is shown that energy profiles yielding accurate spectroscopic constants are obtainable for several states simultaneously. Energy values and spectroscopic data for the five lowest singlet states $X^1\Sigma^+$, $A^1\Pi$, $C^1\Delta$, $B^1\Sigma^+$, and $C^1\Sigma^+$ have been calculated.

Key words: BH, electronic ground and singlet states of ∼

1. Introduction

In a previous paper [1], a method was outlined which permits accurate state wavefunctions to be calculated efficiently. In this paper the same method is applied to the BH molecule for the lowest five singlet states $X^1\Sigma^+$, $A^1\pi$, $C^1\Delta$, $B^1\Sigma^+$, $C^1\Sigma^+$. Recent interest has developed in this system due to the prediction of the presence of a maximum in the $B^1\Sigma^+$ state [2, 3] in addition to that observed in the $A^1\pi$ state [4]. Spectroscopic constants were calculated for all states including $C^1\Sigma^+$ for which constants have not previously been reported.

2. Self Consistent Field (SCF) Calculations

The use of atomic orbitals augmented with orbitals having higher electron density in the bonding region of molecules was shown to lead to accurate state wavefunctions [1]. The orbitals chosen for the present calculations were the same as those used previously [1] except that further augmenting functions were added. In these calculations an additional set of d-type gaussian orbitals centred on Boron were included. An exponent of 0.4829 was selected using the same method as previously described [1].

The SCF calculation at a separation of 2.3291 bohr yielded an energy of -25.1292 hartree which is 0.0022 hartree above Cade's and Huo's value of -25.1314 hartree [5]. This latter energy is taken to be the Hartree Fock limit of BH. Our SCF energy is also only 0.0006 hartree above Kaufman's and

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⋆ Taken in part from a Ph. D. thesis submitted to the University of Toronto in 1971.
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Table 1. LCAO–MO (SCF) energy profile of BH

r (bohr)	E (hartree)
1.75	− 25.0692
2.3291	− 25.1292
2.75	− 25.1148
3.25	− 25.0827
3.75	− 25.0491
4.50	− 25.0046
6.00	− 24.9403

Table 2. Transition energies of the first three $^1\Sigma^+$ excited states calculated by the virtual orbital technique

	Energy ($r = 2.3291$ bohr)		
	$B\,^1\Sigma^+$	$^1\Sigma_3^+$	$^1\Sigma_4^+$
Calculated	0.250	0.374	0.401
experimental	0.238	—	—

Burnell's value of − 25.1298 hartree [6]; the lowest SCF energy of BH that has been reported using gaussian orbitals.

The energies obtained for several internuclear separations of BH are given in Table 1. This energy profile is obviously in error since the system is predicted to dissociate to atomic states much higher in energy than the observed $B(^2P) + H(^2S)$ dissociated products. Inspection of the molecular orbitals and comparison of the neutral and ionized atoms [7] indicates that the SCF calculations are predicting dissociation into the $B^+ + H^-$ system.

Excited states may similarly be constructed by replacing one of the occupied orbitals in the ground configuration with one of the virtual orbitals [8]. Since the virtual orbital was not optimized for this state it should be expected that this wavefunction will not be as accurate as the ground state wavefunction; however, single AOP functions form the logical starting point for CI state wavefunctions. Since results based on the single AOP functions are widely quoted in the literature, it is worth while to look at these states in the present analysis.

The determination of orthonormalized symmetry adapted functions for use as virtual orbitals for symmetries other than σ, has been explained [1]. It is also pointed out that these functions are adequate for virtual orbital calculations consequently only the lowest $^1\Sigma^+$ state energies were determined.

Table 2 lists the energies of the first three $^1\Sigma^+$ excited state wavefunctions at equilibrium geometry ($r = 2.3291$ bohr). The results are unchanged from the smaller calculation [1]. Only the first excited state wavefunction can be identified with any of observed states since the $C^1\Sigma^+$ state has principal terms requiring double replacement of orbitals to be accurately represented.

3. CI Calculations on BH

3.1. Full Double Valence Shell CI[1]

Initially, full double valence shell CI calculations were carried out for seven different internuclear separations for the six states of interest. 521 configurations of symmetry $^1\Sigma^+$ and 490 of $^1\Pi$ were generated for these points. The energy profiles obtained are included in Table 3, while Fig. 1 shows the same results in graphic form.

Table 3. Five lowest energy singlet state energy profiles for BH. Single and double valence shell CI

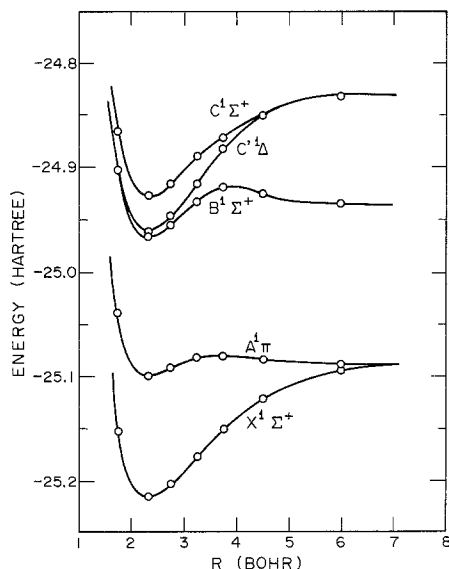| r	Energy $X^1\Sigma^+$	$A^1\Pi$	$C^1\Delta$	$B^1\Sigma^+$	$C^1\Sigma^+$
1.75	− 25.1470	− 25.0242	− 24.8816	− 24.8832	− 24.8400
2.3291	− 25.2063	− 25.0829	− 24.9343	− 24.9403	− 24.9141
2.75	− 25.1915	− 25.0737	− 24.9223	− 24.9264	− 24.8977
3.25	− 25.1644	− 25.0601	− 24.8838	− 24.9023	− 24.8589
3.75	− 24.1420	− 24.0525	− 24.8438	− 24.8872	− 24.8251
4.50	− 25.1129	− 25.0516	− 24.7886	− 24.9074	− 24.7766
6.00	− 24.0759	− 25.0526	− 24.7089	− 24.9389	− 24.7067
ΔE ($r=2.3291$ bohr)	0.0	0.123	0.263	0.2662	0.291

Fig. 1. Singlet state energy profiles for BH. Full Double Valence Shell CI

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[1] For explanation of different types of CI calculations referred to in this paper see [1].

Table 4. Spectroscopic properties of BH calculated from the full double valence shell CI wavefunctions

Property	State				
	$^1\Sigma^+$	$^1\Pi$ [a]	$^1\Delta$	$^1\Sigma^+$ [b]	$^1\Sigma^+$
r_e	2.30	2.266	2.328	2.267	2.351
D_e	0.138	—[c]	0.278	—[d]	0.239
$\omega_e (\times 10^2)$	1.255	1.225	1.371	1.353	1.355
$\omega_e X_e (\times 10^4)$	2.860	1.036	1.692	1.69	1.920
$E_{r=\infty}$	-25.0673	-25.053^3	-24.6631	-24.960^e	-24.6735

[a] Lowest 6 separations only used to fit Morse curve.
[b] Lowest 5 separations only used to fit Morse curve.
[c] Maximum-minimum energy is 0.031.
[d] Maximum-minimum energy is 0.053.
[e] Estimated from Fig. 1.

These results will only be discussed briefly. The energy of the ground state at $r = 2.3291$ bohr is -25.2063 hartree which represents a lowering of 0.0772 hartree (68 % of the valence shell correlation energy[2], 51 % of the total correlation energy. Since the SCF energy is only 0.0022 hartree above the HF limit, this improvement can all be claimed to be recovered correlation energy. The transition energies for the states are of qualitative use only.

Morse curves were fitted to the calculated points, yielding the spectroscopic data listed in Table 4. A comparison of this table with experimented values included in Tables 6 and 7 shows that a quite reasonable qualitative picture is given by these calculations.

It can be seen that both the $A^1\Pi$ and $B^1\Sigma^+$ states occur with maxima. The $B^1\Sigma^+$ maximum has not yet been observed and will be discussed later in this paper. The maximum of the $A^1\Pi$ state is predicted to occur at $r = 4.2$ bohr and is 0.0311 hartree above the minimum of the state; this may be compared to experimental values of $r = 4.32$ bohr and $\Delta E = 0.0262$ hartree respectively.

3.2. Restricted Valence Shell CI Using Natural Orbitals

The preceding calculations for the $^1\Sigma^+$ ground state and $^1\Pi$ state represent full double valence shell CI calculations for 7 internuclear separations. The density matrices for these fourteen wavefunctions were then constructed and their Natural Orbitals (NO) formed. When ordered in terms of their occupation numbers it was found that for the $^1\Sigma^+$ wavefunctions, the first twelve NO included 8 of σ symmetry and 4 of π symmetry.

The $5\pi'$ wavefunctions of closest separation had 6 NO of σ symmetry, 5 of π symmetry and 1 of δ symmetry while the two wavefunctions at furthest separation had a seventh σ type NO occurring before the fifth π type (which was the twelfth NO for the first five wavefunctions). In order to retain the same basis for all calculations this extra σ type NO was ignored and the next (i.e. the thirteenth) NO selected which was the fifth π type.

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[2] For a discussion of the partitioning of correlation energy into core correlation energy and valence shell correlation energy see Ref. [12].

Table 5. Electronic energies for the five lowest energy singlet states of BH. $X^1\Sigma^{1+}$ and $A^1\Pi$ calculated with full valence shell CI on 12 NO of their respective full double valence shell CI wavefunctions. $C^1\Delta$, $B^1\Sigma^+$ and $C^1\Sigma^+$ calculated with full valence shell CI on 12 ANO of the full double valence shell CI wavefunctions

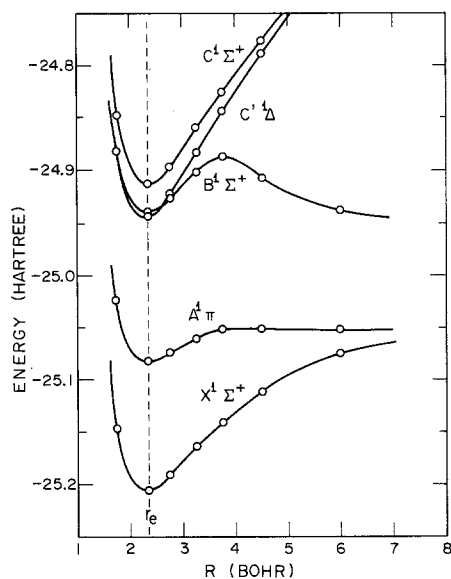| r(bohr)	Energy (hartree)				
	$X^1\Sigma^+$	$A^1\pi$	$C'^1\Delta$	$B^1\Sigma^+$	$C^1\Sigma^+$
1.75	−25.1523	−25.0386	−24.9013	−24.9028	−24.8655
2.3291	−25.2150	−25.0991	−24.9615	−24.9655	−24.9275
2.75	−25.2033	−25.0919	−24.9467	−24.9556	−24.9163
3.25	−25.1771	−25.0813	−24.9160	−24.9337	−24.8903
3.75	−25.1515	−25.0801	−24.8820	−24.9184	−24.8722
4.50	−25.1215	−25.0844	−24.8501	−24.9252	−24.8516
6.00	−25.0949	−25.0884	−24.8310	−24.9333	−24.8350
$\Delta E\ (r = 2.3291)$	0.0000	0.1159	0.2354	0.2304	0.2685

Fig. 2. Energy profiles of five lowest energy singlet states of BH. $X^1\Sigma^+$ and $A^1\Pi$ calculated with full valence shell CI on 12 NO of their respective full double valence shell CI wavefunctions. $C^1\Delta$, $B^1\Sigma^+$ and $C^1\Sigma^+$ calculated with full valence shell CI on 12 ANO of the full double valence shell CI wavefunctions

The first 2 columns in Table 5 give the results of the restricted valence shell CI calculations using these 12 NO. These calculations involved 622 configurations for $X^1\Sigma^+$ and 590 configurations for $A^1\Pi$. The energy profiles were also plotted as the lower 2 curves in Fig. 2. The ground state energy at $r = 2.3291$ bohr represents a recovery of 0.0858 hartree of the correlation energy which is 76% of the valence shell correlation energy or 57% of the total correlation energy.

Both states are clearly converging on the same dissociation state, while the $A^1\Pi \leftarrow X^1\Sigma^+$ transition energy is close to the experimental value. The maximum

of the $A^1\Pi$ state is predicted to occur at approximately $r = 3.7$ bohr and is 0.0190 hartree above the minimum. This maximum is 0.135 hartree above the $X^1\Sigma^+$ minimum which effectively yields the experimental D_e (0.137 hartree).

3.3. Restricted Valence Shell CI Using Averaged National Orbitals

A set of averaged NO were formed by averaging together the density matrices for the three lowest $^1\Sigma^+$ and the two degenerate $C^1\Delta$ states of the full double valence shell CI wavefunctions described previously. For the first 4 geometries (shorter bond lengths), the set of 12 NO with largest occupation numbers included 6σ and 6π type NO. The NO for the larger separations included an additional σ type NO occuring before the 5th and 6th π type NO. Nevertheless, the 6σ and 6π NO with largest occupation numbers were chosen in every case. These 12 averaged NO were then used in a restricted valence shell CI which resulted in 620 configurations with $^1\Sigma^+$ symmetry.

The energy profiles for the $C^1\Delta$, $B^1\Sigma^+$ and $C^1\Sigma^+$ states formed from $^1\Sigma^+$ co-detors are presented in Table 5 and Fig. 2. The ground state energy which was obtained at equilibrium separation, -25.1970 hartree, is only 0.0180 hartree above that obtained for the NO calculation. This indicate that only a slight loss of absolute accuracy in total energy is encountered.

In agreement with experimental, the $C^1\Delta$ and $C^1\Sigma^+$ states are correctly predicted to dissociate to the same state; in fact, the profiles for these states are superimposed above 4.5 bohr separation. The transition energies of the ground state to all of the above states are quite reasonable. As for the small basis set [1], the order of the $C^1\Delta$ and the $B^1\Sigma^+$ states is interchanged from experimental; however, these states occur very close together and the actual numerical error is very small.

Table 6 also includes the total energy of published calculations on BH. Only calculations obtaining a total energy below the HF limit are included. To this list should be added a calculation by Bender and Davidson [13] in which they obtained an energy of -25.2621 hartree. This latter energy represents the lowest energy calculated for BH to date and is only 0.021 hartree above the non relativistic limit for BH. This represents 86% of correlation energy recovered. By comparison, the best energy reported in this work is -25.2150 hartree. This is 0.068 hartree above the non-relativistic limit of BH and represents a yield of 57% of the correlation energy recovered. In the present calculation, however, only substitutions into the four valence electrons were allowed thus only valence shell correlation energy is determined. The correlation energy of BH is taken to be 0.113 hartree [12]. Thus in the present calculation 76% of the valence shell correlation energy has been recovered.

4. Spectroscopic Constants

Spectroscopic constants for the $X^1\Sigma^+$, $A^1\Pi$, $C^1\Delta$, $B^1\Sigma^+$ and $C^1\Sigma^+$ states for BH are recorded in Table 6 and 7 together with experimental values [4] and other calculated values reported. Values from this work were obtained by fitting the energy values to Morse curves.

Table 6. Spectroscopic constants for the $X^1\Sigma^+$ state of BH (a.u.)

Calculation	Ref.	E	r_e	D_e	$\omega_e(\times 10^2)$	$\omega_e X_e(\times 10^4)$
Hartree-Fock	5	−25.1315	2.268	0.102	1.140	2.234
Valence Bond	2	−25.1454	2.527	0.110	1.258	6.619
Valence Bond	9	−25.1453	2.536	0.107	—	—
Spin-optimized SCF	10	−25.1664	2.360	0.121	—	—
Bethe-Goldstone	11	−25.1723	2.331	0.169	1.139	1.924
CI	2	−25.1797	2.412	0.120	0.984	2.221
Separated Pair	12	−25.2054	2.343	0.142	1.324	2.166
This work	—	−25.2150	2.357	0.131	1.259	3.034
Experimental	4	−25.289	2.336	0.131	1.078	2.251

Table 7. Spectroscopic constants for the $A^1\Pi$, $C'^1\Delta$, $B^1\Sigma^+$ and $C^1\Sigma^+$ states of BH

Calculation	Ref.	E	r_e	D_e	ω_e ($\times 10^2$)	$\omega_e X_e$ ($\times 10^4$)	T_e	r^a_{max}	ΔE^a_{max}
$A^1\Pi$									
Valence Bond	9	−25.0357	2.536	0.003	—	—	0.1067	3.13	0.0044
This work		−25.0991	2.261	—[b]	1.164	1.422	0.1159	3.70	0.0191
Experimental	4	−25.184	2.311	0.026	1.026	2.582	0.1051	4.32	0.0262
$C^1\Delta$									
Valence Bond	9	−24.9216	2.35	0.116	—	—	0.2212		
This work		−24.9615	2.305	0.145	1.383	3.306	0.235[c]		
Experimental	4	−25.079	—	0.139	1.189	2.124	0.2105		
$B^1\Sigma^+$									
Valence Bond	2	−24.9235	2.361	—	1.063	4.483	0.220	3.74	0.0301
CI	3	−24.9443	2.270	0.062	1.181	2.942	0.236	3.63	0.0517
This work		−24.9655	2.331	—[c]	1.236	5.016	0.230[c]	3.77	0.0531
Experimental	4	−25.051	2.298	0.067	1.093	3.167	0.2382	—	—
$C^1\Sigma^+$									
This work		−24.9275	2.326	0.096	1.280	4.249	0.269[d]		
Experimental	4	−25.037	2.213	0.097	1.128	2.479	0.252		

[a] position and height of maximum above first minimum; $A^1\Pi$ and $B^1\Sigma^+$ states only.
[b] Maximum-minimum energy is 0.019.
[c] Maximum-minimum energy is 0.047.
[d] Computed using energy for $X^1\Sigma^+$ state calculated using ANO (−25.1970 hartree).

Of particular interest is the maximum in the $B^1\Sigma^+$ profile since this state has not yet been observed. Other calculation have also indicated its existence [2, 3] with close agreement as to position and height above the minimum (see Table 7). For comparative purposes the energy profiles for the $X^1\Sigma^+$ and $B^1\Sigma^+$ for all three works have been included in Fig. 3.

The energy profiles obtained in this work can be used to determine the harmonic force constant associated with the vibration of the BH bond. On the assumption of harmonic behaviour for the energy near equilibrium geometry,
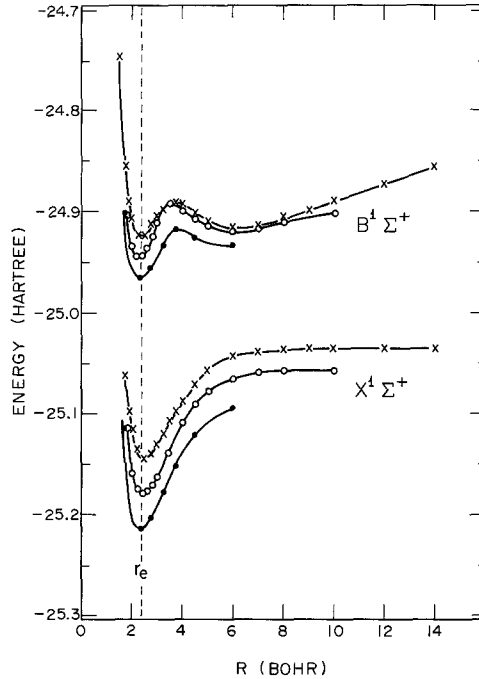
Fig. 3. Potential energy curves for the $X^1\Sigma^+$ and $B^1\Sigma^+$ of BH ($-\times-$ Ref. [2], $-\bigcirc-$ Ref. [3], $-\bullet-$ this work)

the harmonic force constant, k, is defined by the relation

$$E = 1/2\, k(r - r_e)^2 + E_e$$

or

$$\left(\frac{\partial^2 E}{\partial r^2}\right)_{r \to r_e} = k\,.$$

For a Morse curve this relation yields

$$k = 2\beta^2 D_e\,.$$

The value of this force constant calculated for the Morse curves fitted to the energy profile for the $X^1\Sigma^+$ state of BH is 0.1954 a.u.

The experimental force constant can be evaluated from the above equation using the experimental values of D_e and ω_e [4] and the value of β calculated [14] from

$$\beta = 2.5993 \times 10^4\, \omega_e \sqrt{\frac{\mu A}{D_e}}$$

The experimental value is 0.1959 a.u. almost identical to the calculated value.

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