

# A full configuration interaction study of the low-lying states of the BH molecule

By LAURA GAGLIARDI, GIAN LUIGI BENDAZZOLI and  
STEFANO EVANGELISTI

Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale  
Risorgimento 4; I-40136 Bologna, Italy

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A full configuration interaction study on the BH molecule is presented. The potential energy curves of 20 different electronic states have been calculated correlating the four valence electrons. On the two most important states, i.e. the  $X^1\Sigma^+$  and  $A^1\Pi$  states, a complete study has been performed. This includes the effect of core electron correlation, estimated via truncated configuration interaction techniques. The dissociation energy of the molecule in the two states and the height of the predissociative barrier in the  $A^1\Pi$  state have been determined with basis sets of increasing quality.

## 1. Introduction

The BH molecule has been widely studied both by experimentalists and theoreticians, and a large quantity of data on the spectroscopic properties of various electronic states is available. Nevertheless it appears that, in some cases, the experimental and theoretical results are inconsistent, and it is thus interesting to perform calculations on a small system like this. In this paper a comprehensive study on the BH molecule at the full configuration interaction (FCI) level is presented. Twenty different electronic states of the molecule were studied at the FCI level, correlating the four valence electrons, and the electronic potential curves for all of them were determined. The results obtained at this level give useful information on the behaviour of the molecule in its different states, and can also be used as benchmarks to test approximate methods.

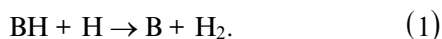
We then concentrated on the  $X^1\Sigma^+$  ground state and the  $A^1\Pi$  state, which is of considerable interest to both spectroscopists and quantum chemists because it has a barrier to dissociation, and performed FCI and string-truncated configuration interaction (TCI) calculations with basis sets of increasing quality, including the core-electron correlation. The results obtained with the largest basis set are of high accuracy and can be compared to experiment. The determination of the dissociation energy ( $D_0$ ) of the molecule in the  $X^1\Sigma^+$  state and of the height of a predissociative barrier ( $H_b$ ) present in the  $A^1\Pi$  state has been treated in several papers and the value obtained from recent theoretical predictions is not in agreement with the one reported in standard reference books like Huber and Herzberg [1]

The value reported by Huber and Herzberg,  $D_0 = 78.9 \pm 0.4 \text{ kcal mol}^{-1}$ , has been derived from the experimental predissociation limit of  $82.6 \pm 0.4 \text{ kcal mol}^{-1}$  for transitions from the  $X^1\Sigma^+$  to the  $A^1\Pi$  state [2] which presents an outer repulsive barrier. By combining this result with an early theoretical estimate [3] of the height of the maximum ( $H_b$ ) in the  $A^1\Pi$  state ( $3.7 \text{ kcal mol}^{-1}$ ), the value of  $D_0$  reported by Huber and Herzberg is obtained. To compare this value with the theoretical prediction, the zero-point energy  $E_0$  must be added ( $D_e = D_0 + E_0$ ). The harmonic approximation of  $E_0$ , derived from the experimental force constant  $\omega_e = 2367 \text{ cm}^{-1}$ , is of  $3.42 \text{ kcal mol}^{-1}$ , while an accurate computation by Botschwina gave  $E_0 = 3.36 \text{ kcal mol}^{-1}$  [4]. In any case the value  $D_e = 82.3 \pm 0.4 \text{ kcal mol}^{-1}$  is obtained. We note that an upper limit for  $D_e$  can be derived from the experimental data assuming a zero height for the barrier in the  $A^1\Pi$  state, and this is  $86.0 \pm 0.4 \text{ kcal mol}^{-1}$ .

On the experimental side, there have been several other investigations on these two electronic states of BH. Among the most recent works, Gustafsson and Rittby [5] have recorded the emission spectrum for the  $A^1\Pi \rightarrow X^1\Sigma^+$  transition and performed computations of the energy and width of the vibrational levels. The experimental values of the lifetimes are larger than the theoretical predictions and in order to obtain agreement, they have suggested a barrier of about  $7 \text{ kcal mol}^{-1}$  for the  $A^1\Pi$  state. Math and Savadatti [6] have also recorded the emission spectra of BH for the  $A^1\Pi \rightarrow X^1\Sigma^+$  transition and determined the rotational distributions in the  $A^1\Pi$  state from the intensities of the

rotational lines for the 0–0 band of the A–X system. Fernando and Bernath [7] have recorded the transitions of BH and BD molecules in emission near  $4330\text{ cm}^{-1}$  by Fourier transform spectroscopy, and determined improved line positions and molecular constants for BH.

On the theoretical side, several studies have been performed on the BH system. Most of them concern the  $X^1\Sigma^+$  and  $A^1\Pi$  states and give an estimate of  $D_e$  ( $X^1\Sigma^+$  state) and of  $H_b$  ( $A^1\Pi$  state). Curtiss and Pople have performed quadratic configuration interaction (QCI) calculations with a basis set of TDZ quality plus polarization functions [8]. They obtained a substantially larger value for  $D_e$ ,  $83.9\text{ kcal mol}^{-1}$ , that becomes even larger ( $D_e = 84.9\text{ kcal mol}^{-1}$ ) if it is evaluated via the isogyric reaction



In this way, the experimental value of the dissociation energy of  $\text{H}_2$  can be used to correct the corresponding *ab initio* value, reducing the error due to the incompleteness of the basis set of H [9]. Coupled cluster calculations, done by Martin *et al.* with a different basis set, have given a value  $D_e = 83.1\text{ kcal mol}^{-1}$  ( $D_e = 85.8\text{ kcal mol}^{-1}$  using the isogyric reaction) [10].

The most accurate computation is certainly the one done by Bauschlicher *et al.* [11]. These authors performed multireference configuration interaction (MRCI) calculations calibrated by FCI results to determine the  $D_0$  of the  $X^1\Sigma^+$  ground state and the  $H_b$  of  $A^1\Pi$ . In the FCI calculations they have correlated only the four valence electrons and used an atomic natural orbital (ANO) [12] type basis set with (13s8p6d4f)/[4s3p2d1f] on boron and (8s6p4d)/[4s2p1d] on hydrogen. At MRCI level they have also estimated the core–core and core–valence contributions to the binding energy and used the basis set with (13s10p8d4f)/[13s10p8d1f] on boron and (8s6p4d)/[4s2p1d] on hydrogen. With their largest basis set they obtained an estimate of  $D_0$  of  $81.5 \pm 0.5\text{ kcal mol}^{-1}$  and of  $H_b$  of  $1.9 \pm 0.2\text{ kcal mol}^{-1}$ . These results are in disagreement with the value of  $D_0$  reported by Huber and Herzberg and of  $H_b$  estimated by Hurley and that suggested by Gustafsson and Rittby.

The problem was not solved by Bauschlicher *et al.*, and Persico [13] in 1994, performed a rather complete study of the various decay channels of the  $A^1\Pi$  state of BH. Using the data from Gustafsson and Rittby [5] and CIPSI-MBP computations, he derived a value of  $D_e$  of  $84.12\text{ kcal mol}^{-1}$  for the  $X^1\Sigma^+$  state and a barrier height of about  $5.4\text{ kcal mol}^{-1}$  for the  $A^1\Pi$  state.

It thus seems that the determination of both these quantities  $D_e$  and  $H_b$  is still an open problem. Other theoretical contributions should be mentioned. Koch

*et al.* [14] have calculated the excitation energies for several electronic states of BH, in the coupled cluster model hierarchy CCS, CC2 and compared it with FCI results. Cimiraglia and Persico [15] have carried out some *ab initio* calculations on the  $X^1\Sigma^+$  and the  $A^1\Pi$  states and computed numerically the dissociative vibrational states to obtain the transition dipole moments of the discrete and continuum spectra. They have also determined the adiabatic and diabatic curves of the lowest  $1,3\Sigma^+$  states of BH [16], namely the first four singlets and the first three triplets. The first four singlet  $1\Sigma^+$  states have been investigated also by Broeckhove *et al.* [17]. They obtained the potential curves by SCF-CI calculations and showed that these states have strong non-adiabatic couplings, resulting in a complex topology of avoided crossing regions and double well potentials.

The double-minimum  $B^1\Sigma^+$  electronic state of BH has been studied by several authors [18–24]. In the computation of the boron quadrupole coupling constants of the rovibrational levels of this state, Šavrdra *et al.* [24] noticed that the double-minimum character of the potential profoundly influences the rovibrational dependence of these coupling constants.

Other studies, both experimental and theoretical, on some different states have also been performed. Pederson and co-workers [25] studied the decay of the  $b^3\Sigma^-$  state. They determined the lifetimes of rotational/fine-structure levels of this state, in vibrational levels  $v' = 0–4$ , from fluorescence decay waveforms with laser excitation on isolated rotational lines in the  $b^3\Sigma^- \leftrightarrow a^3\Pi \Delta v = 0$  sequence. Then the experimental lifetimes were compared with values obtained from a theoretical treatment of the excited state dynamics. Boehmer and Benard [26] monitored the highly metastable  $a^3\Pi$  state for the first time, directly by resonance absorption using a spin-allowed transition to the  $b^3\Sigma^-$  state.

## 2. Theoretical approach

Due to the small number of electrons of BH, this molecule can be studied by FCI techniques and a fairly large basis set, at least if only the four valence electrons are correlated. Using our FCI code, both in the scalar/vector version for IBM RISC and CRAY-C90 [27] and in the parallel version implemented for CRAY-T3D [28] we carried out some FCI calculations on 20 different electronic states of BH, correlating only the four valence electrons, and successively concentrated on the two most important ones, that is  $X^1\Sigma^+$  and  $A^1\Pi$ . On these two states we performed some FCI and TCI calculations, with a series of ANO-type basis sets of increasing quality, correlating all the six electrons. We

used the ANO basis optimized by Widmark *et al.* [29] that is a (14s9p4d3f)/[6s5p3d2f] gaussian basis set on boron and (8s4p3d)/[4s3p2d] on hydrogen. In our largest calculations, we also added to this basis a (2g)/[1g] orbital on boron and a (2f)/[1f] orbital on hydrogen. The exponents for boron g orbitals (0.537 59, 0.215 03) have been obtained as a geometrical mean of the exponents of those of f orbitals on boron, and those for hydrogen f orbitals (1.150 44, 0.460 15) as a geometrical mean of those on d orbitals on hydrogen. The first contraction coefficient on both atoms was set equal to 1. The second one for boron (0.058) was optimized for atomic boron, while for hydrogen (0.224) was optimized for molecular H<sub>2</sub> at experimental equilibrium distance.

The TCI calculations [30] are based on a truncation criterion on strings, which allows for a reduction of the CI space with a minimum loss of accuracy. Each Slater determinant of the CI expansion can be viewed as the product of two strings collecting the  $\alpha$  and  $\beta$  electrons, respectively [31]. The FCI space is thus the antisymmetrized tensor product  $S_\alpha \otimes S_\beta$ , where  $S_\alpha$  is the space spanned by all possible  $\alpha$  strings constructed by using the given set of orbitals and the given number  $n_\alpha$  of electrons with  $\alpha$  spin, and similarly for  $S_\beta$ . In a TCI space we restrict  $S_\alpha$  and  $S_\beta$  to be generated by the strings having an assigned level of excitation from a given set of reference strings. The price to pay for this simple truncation scheme is that the CI wave function is no longer an eigenfunction of the total spin operator  $\hat{S}^2$  and hence presents some spin contamination, which is negligible in energy calculations, at geometries far from the dissociation limit.

In table 1 we report the information on basis sets used in the various calculations and the dimensions of the corresponding CI expansions. By comparing B1, B2, respectively, to B1<sub>t</sub>, B2<sub>t</sub> we notice that there is a reduction of the dimension of the CI expansions in going from the FCI to the corresponding TCI, respectively, of 80, 87%, and it indicates that this truncation technique allows the treatment of cases which are dimensionally prohibitive at the FCI level.

### 3. Low-lying state calculations

We investigated all the states of BH that dissociate to one of the first five dissociation limits of the molecule. These limits correspond to the hydrogen atom in its ground state  ${}^2S(1s^1)$  and the boron atom in one of the following atomic states:  ${}^2P(1s^2 2s^2 2p^1)$ ,  ${}^4P(1s^2 2s^1 2p_x^1 2p_y^1)$ ,  ${}^2S(1s^2 2s^2 3s^1)$ ,  ${}^2P(1s^2 2s^2 3p^1)$ ,  ${}^2D(1s^2 2s^1 2p^2)$  respectively. Since the hydrogen atom is always in its ground state, in the following we will identify the dissociation limits only by the boron atomic states. The  ${}^2P$  boron states will be distinguished below by the notation  ${}^2P(2p)$  for the lowest and  ${}^2P(3p)$

Table 1. Information on the basis sets for boron and hydrogen atoms. The number of orbitals corresponding to each basis set and the number of determinants in the CI expansion. This last value refers to the calculations for  $X^1\Sigma^+$  state.

Basis set		Number of orbitals	Number of determinants	Label
B	H			
<i>FCI 4 electrons</i>				
4s3p1d	3s1p	23	17 215	b1
5s4p2d	4s2p	36	105 300	b2
5s4p2d1f	4s2p1d	48	327 684	b3
6s5p3d2f	4s3p2d	72	1 665 232	b4
6s5p3d2f1g	4s3p2d1f	88	3 706 938	b5
<i>TCI 6 electrons</i>				
14s3p1d	3s1p	34	2 068 378	B1 <sub>t</sub>
14s4p2d	4s2p	46	7 522 875	B2 <sub>t</sub>
14s4p2d1f	4s2p1d	58	19 850 440	B3 <sub>t</sub>
14s5p3d2f	4s3p2d	81	80 571 911	B4 <sub>t</sub>
<i>FCI 6 electrons</i>				
14s3p1d	3s1p	34	9 955 840	B1
14s4p2d	4s2p	46	57 608 100	B2

for the highest, while for the other states the unambiguous notation  ${}^4P$ ,  ${}^2S$ ,  ${}^2D$  will be used. There are a total of 20 molecular states that dissociate to one of these limits: four to  ${}^2P(2p)$  ( $X^1\Sigma^+$ ,  $c^3\Sigma^+$ ,  $A^1\Pi$  and  $a^3\Pi$ ), four to boron  ${}^4P$  ( ${}^5\Pi$ ,  $e^3\Pi$ ,  ${}^5\Sigma^-$ ,  $b^3\Sigma^-$ ), two to boron  ${}^2S$  ( $B^1\Sigma^+$ ,  $f^3\Sigma^+$ ), four to boron  ${}^2P(3p)$  ( $C^1\Sigma^+$ ,  $h^3\Sigma^+$ ,  $D^1\Pi$  and  $g^3\Pi$ ), and six to boron  ${}^2D$  ( $E^1\Sigma^+$ ,  $i^3\Sigma^+$ ,  $G^1\Pi$ ,  $l^3\Pi$ ,  $C^1\Delta$  and  $d^3\Delta$ ). Among these states the four singlets  ${}^1\Sigma^+$  and the first three triplets  ${}^3\Sigma^+$  have already been treated in several papers. The lowest  $\Pi$  singlet,  $A^1\Pi$ , presenting the predissociative barrier, has been the subject of several studies, as already mentioned, the lowest  $a^3\Pi$  has been investigated by Boehmer and Benard [26] and the  $b^3\Sigma^-$  has been studied by Pederson and co-workers [25]. All the remaining  ${}^1\Pi$  and  ${}^3\Pi$ , on the other hand, are investigated theoretically for the first time in this study to our knowledge.

We performed a series of FCI calculations, with only the 4 valence electrons correlated, to determine the potential energy curves of these 20 electronic states of different symmetry. We used molecular orbitals (MOs) obtained by a valence complete active space (CAS)-SCF calculation for the ground state, with one doubly occupied or inactive MO (corresponding essentially to the boron 1s orbital) and five active MO (deriving from boron 2s and 2p and hydrogen 1s orbitals). The preliminary CAS-SCF calculation was performed with the MOLPRO package of *ab initio* programs [32]. In the FCI calculation the 1s orbital was kept doubly occupied and frozen at the CAS-SCF level. The basis set used

Table 2. Valence FCI calculations on the low lying states of BH molecule with b5 basis set. Minimum depth  $D_e$ , equilibrium distance  $R_{\min}$ , harmonic fundamental frequency  $\omega_e$ , and electronic term  $T_e$ , for each state. The comparison with experiment [1] is reported when available.

	State					
	$X^1\Sigma^+$	$A^1\Pi$	$a^3\Pi$	$C^1\Delta$	$d^3\Delta$	$b^3\Sigma^-$
$D_e/\text{kcal mol}^{-1}$	84.23	17.39	53.49	89.43	13.17	58.89
$R_e/\text{\AA}$	1.2338	1.2256	1.1924	1.1993	1.2258	1.2197
Exp.	1.2324	1.2186	1.2006	1.1963	—	1.2271
$\omega_e/\text{cm}^{-1}$	2,254	2,275	2,615	2,604	2,181	2,428
Exp.	2,367	2,251	—	2,610	—	—
$T_e/\text{cm}^{-1}$	—	23,376	10,752	46,581	73,258	38,116
Exp.	—	23,136	—	45,981	—	—

was the [5s4p2d1f] on boron and [4s3p2d] on hydrogen (b3).

With a basis set of higher quality, [6s5p3d2f1g] on boron, and [4s3p2d] on hydrogen (b5), we studied the lowest attractive state in each symmetry, namely the  $X^1\Sigma^+$ ,  $A^1\Pi$ ,  $a^3\Pi$ ,  $C^1\Delta$ ,  $d^3\Delta$  and  $b^3\Sigma^-$  states. For each of them we determined the equilibrium distance ( $R_e$ ), the minimum energy ( $E_{\min}$ ), and the harmonic fundamental frequency constant ( $\omega_e$ ), using a cubic interpolation near the minimum (step  $0.01 a_0$ ). (The absolute energies at the geometries used for the interpolation are not reported, but they are available upon request.) We also calculated  $D_e$  as the difference between the isolated-atom energy and the minimum energy. The energies of the atoms were obtained with separate FCI calculations on boron and hydrogen.

In table 2 we report these values together with the electronic term ( $T_e$ ) that, for each state, is the difference between the minimum energy of that state and of the  $X^1\Sigma^+$  state, and also the experimental values, when available.

#### 4. $X^1\Sigma^+$ and $A^1\Pi$ state calculations

Among all the states studied, the  $X^1\Sigma^+$  and  $A^1\Pi$  are certainly the most interesting. Our aim is, in fact, to determine  $D_e$  of BH in  $X^1\Sigma^+$  state and  $H_b$  in  $A^1\Pi$ , and this implies the investigation of the minimum region of  $X^1\Sigma^+$  curve and the barrier region of  $A^1\Pi$  curve. We decided to perform some further calculations on these two states in which all six electrons were correlated, to take into account the  $1s^2$  correlation. Because of the huge size of the CI space, FCI calculations with six correlated electrons can be performed only with relatively small basis sets. However, it is possible to have a

good approximation of the FCI result by using string-TCI.

In these calculations we used as reference the CAS-SCF MO space split into six active orbitals (those deriving from combinations of boron 1s, 2s, 2p, and hydrogen 1s atomic orbitals) and the remaining virtual orbitals. Only strings with, at most, two virtual orbitals are kept, while the others are discarded. In this way, we include all the determinants of the four-electron FCI space, plus a large fraction of those determinants where one or both the 1s electrons of boron are excited. Of course the TCI energy computed in this way is a rigorous *upper bound* to the six-electron FCI energy computed with the same basis set. Since for the two separated atoms we used the exact FCI energies, our TCI value for  $D_e$  is a *lower bound* to the corresponding FCI result obtained with the same basis set.

Using both the CRAY-C90 and CRAY-T3D version of our code, we performed TCI calculation on  $X^1\Sigma^+$  and  $A^1\Pi$  states with all the basis sets previously used for the valence FCI calculations, except the largest one. In order to correlate the boron 1s orbital, all the 14 s-type gaussians of the original ANO basis set were left completely uncontracted.

#### 5. Low-lying state results

The potential energy curves of the 20 states obtained with the b3 basis set are reported in figures 1 to 5, according to symmetry.

Figure 1 shows the  $^1\Sigma^+$  states. We notice that the  $X^1\Sigma^+$  state lies rather below the others and dissociates to boron in its  $^2P(2p)$  state. The  $B^1\Sigma^+$  presents a double minimum, already analysed in a number of publications [18–23]. As discussed in these studies, the double minimum arises from a complex interplay of avoided crossings between diabatic states of different character. Some portions of the curve have a well defined character, e.g. between 4.0–7.0 Å the curve is essentially described by the ionic configuration  $B^+H^-$ . At about 7.0 Å there is an avoided crossing with a Rydberg state and the ionic  $B^+H^-$  goes over to the next state  $C^1\Sigma^+$ . This state presents the ionic character between 7.0 and 9.5 Å and it dissociates as boron  $^2P(3p)$ . It undergoes two avoided-crossings, the one already mentioned with the previous  $B^1\Sigma^+$  state, and a second one at about 2.3 Å with the upper  $E^1\Sigma^+$ . This last state dissociates to boron  $^2D$ . In figure 1 we also report the  $F^1\Sigma^+$  curve, even though it does not dissociate to one of the dissociation limits considered in the present study. From 9.6 Å on, this curve shows the ionic character that was present in the lower states, and at shorter distance, 2.0–4.0 Å, it has a broad predissociative barrier.

In figure 2 the  $^3\Sigma^+$  states are reported. The  $c^3\Sigma^+$  state is completely repulsive and dissociates to the same

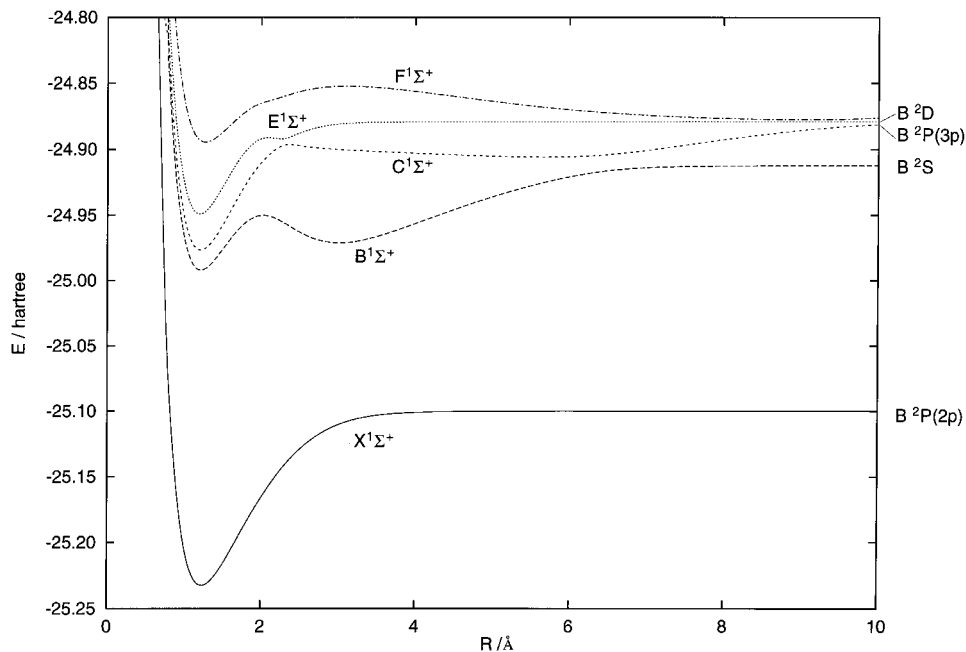


Figure 1. Potential energy curves of  ${}^1\Sigma^+$  states.

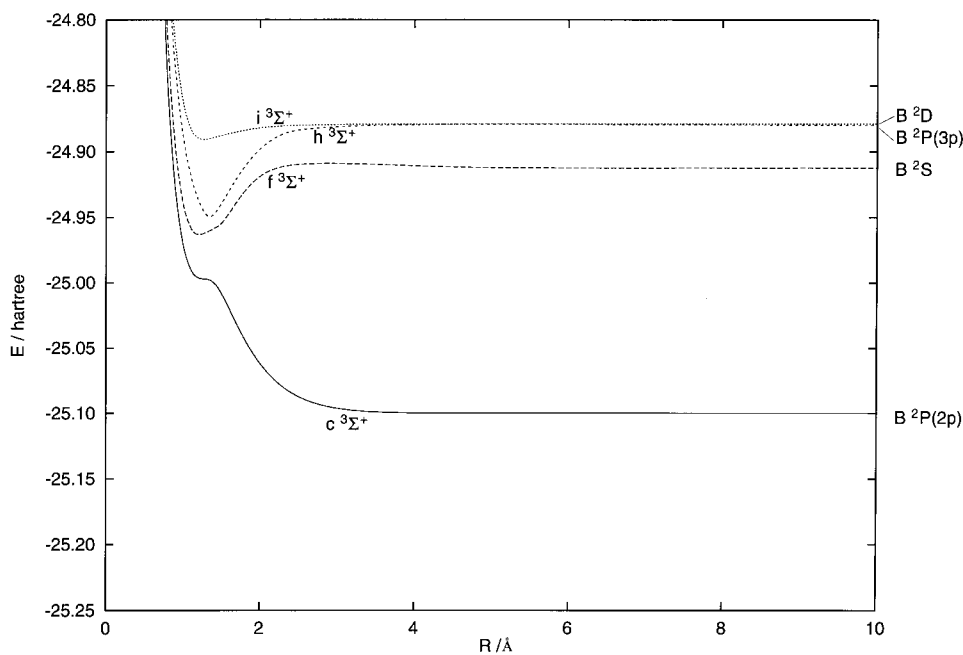


Figure 2. Potential energy curves of  ${}^3\Sigma^+$  states.

dissociation limit of  $X^1\Sigma^+$ , that is boron  ${}^2P(2p)$ . The three other states present a minimum and dissociate, respectively, to boron  ${}^2S$ ,  ${}^2P(3p)$  and  ${}^2D$ . An avoided crossing between the  $f^3\Sigma^+$  and  $h^3\Sigma^+$  occurs at 1.3–1.6 Å, which is responsible for the flat shape of the  $f^3\Sigma^+$  curve in that region.

Figure 3 shows the  ${}^1\Pi$  states together with the  ${}^5\Pi$  one. The  $A^1\Pi$  state lies somewhat below the others and presents a predissociation barrier at about 2.6 Å. The  $D^1\Pi$  and  $G^1\Pi$  present a particular shape due to

an avoided crossing that occurs at 1.6–1.9 Å. There is also another avoided crossing between these two states at about 3.0 Å. The three  ${}^1\Pi$  states dissociate respectively to boron  ${}^2P(2p)$ ,  ${}^2P(3p)$  and  ${}^2D$ . The  ${}^5\Pi$  curve is completely repulsive and dissociates to boron  ${}^4P$ .

In figure 4 we report the  ${}^3\Pi$  states. The lowest curve dissociates to boron  ${}^2P(2p)$ . The  $e^3\Pi$  presents a weak avoided crossing with the  $g^3\Pi$  state at about 1.4 Å and a minimum at about 1.9 Å, and dissociates to boron  ${}^4P$ . The  $g^3\Pi$  and  $l^3\Pi$  states dissociate respectively to boron

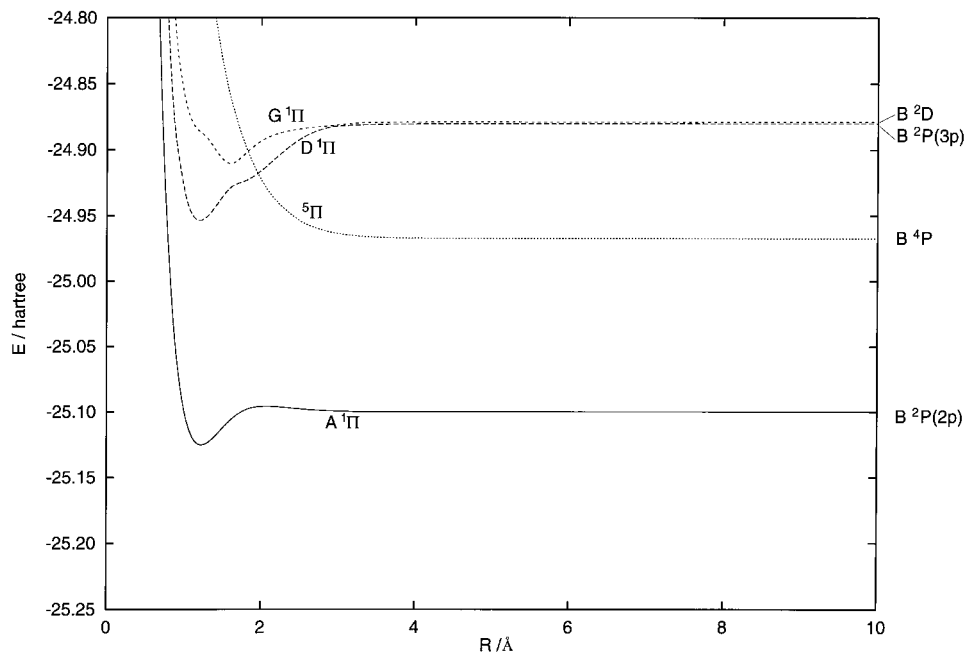


Figure 3. Potential energy curves of  $1\Pi$  states and the  $5\Pi$  one.

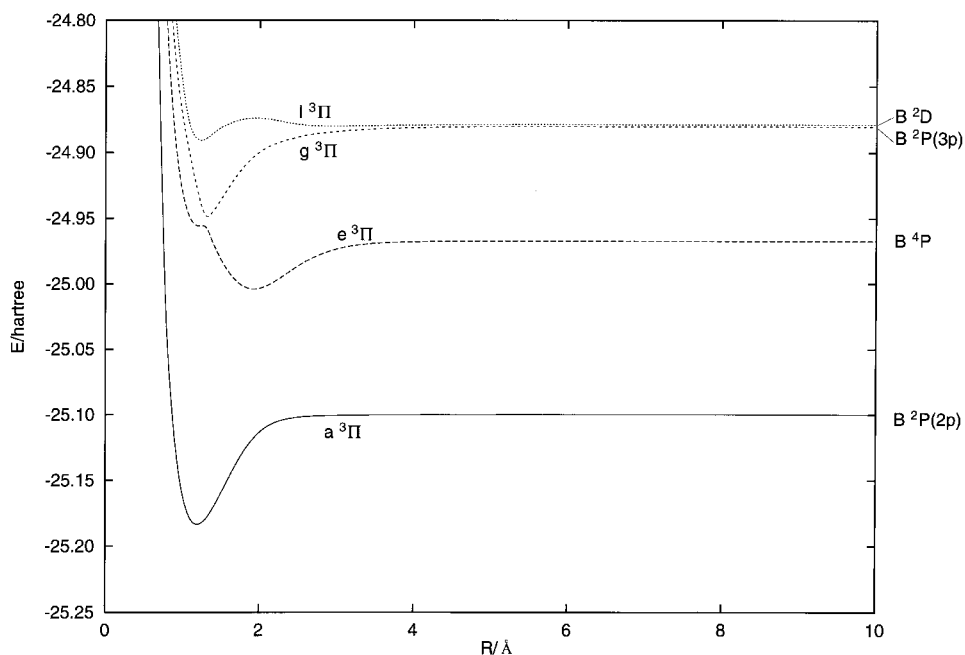


Figure 4. Potential energy curves of  $3\Pi$  states.

$2P(3p)$  and  $2D$ . The  $l^3\Pi$  curve presents a high predissociation barrier between 1.5 and 2.5 Å.

In figure 5 the curves of  $C^1\Delta$ ,  $d^3\Delta$ ,  $5\Sigma^-$  and  $b^3\Sigma^-$  states are presented. The  $3\Sigma^-$  curve presents a flat minimum and dissociates together with the  $b^3\Sigma^-$  one to boron  $4P$ . The  $\Delta$  states dissociate to boron  $2D$  and  $d^3\Delta$  presents a deep minimum, while  $C^1\Delta$  presents a shallow one.

As already mentioned, with the basis set b5, we studied the lowest state in each symmetry, that is the

$X^1\Sigma^+$ ,  $A^1\Pi$ ,  $a^3\Pi$ ,  $C^1\Delta$ ,  $l^3\Delta$  and  $l^3\Sigma^-$  states. In table 2 we report the results. Some of them can be compared to experiment. As regards the equilibrium distance, the experimental values are available for all the states, with the exception of the  $d^3\Delta$ , and they are in substantial agreement with our results. The difference goes from a minimum of 0.0014 Å for  $X^1\Sigma^+$ , to a maximum of 0.0082 Å for  $a^3\Pi$ . The experimental values for the harmonic fundamental frequency constant are available only for the states  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $C^1\Delta$  and the differ-

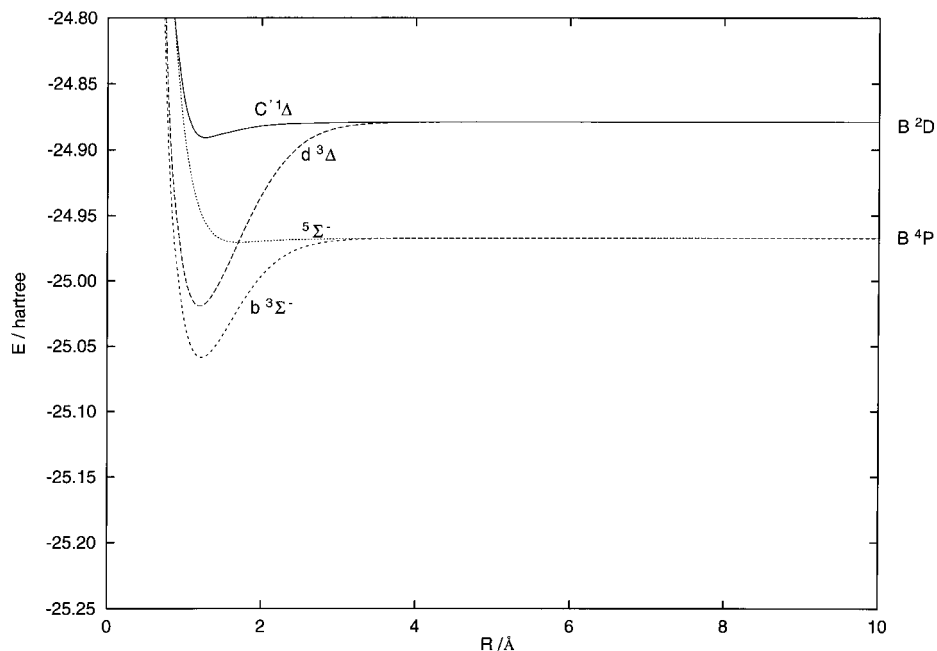


Figure 5. Potential energy curves of  $C^1\Delta$ ,  $d^3\Delta$ ,  $5\Sigma^-$  and  $b^3\Sigma^-$  states.

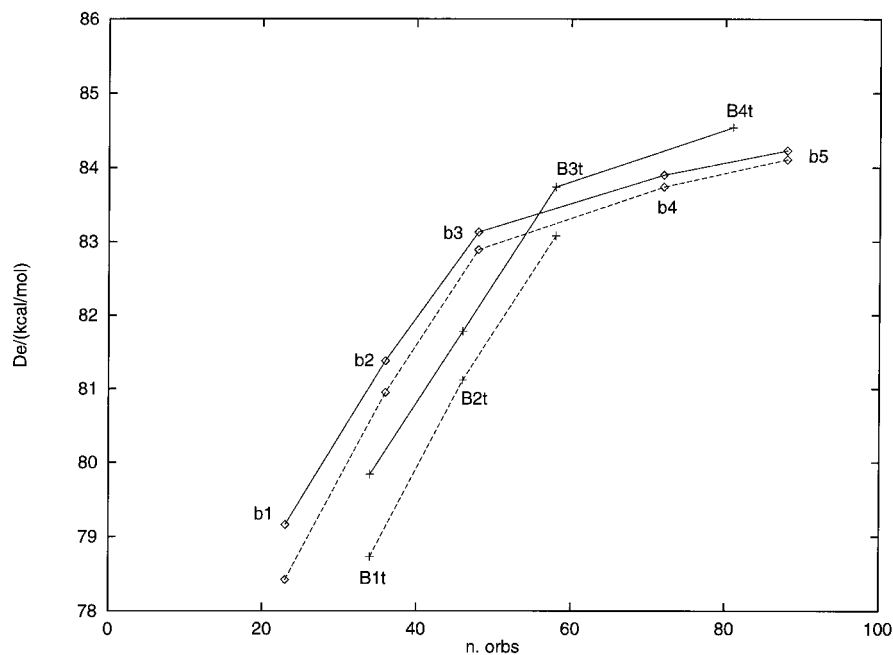


Figure 6.  $D_e$  for  $X^1\Sigma^+$  state with the different basis sets, without BSSE correction (full line), and with (dashed line).

ence from the calculated values are respectively 13, 24 and  $6\text{ cm}^{-1}$ . As regards the electronic term,  $T_e$ , we can compare our results with the experimental values of  $A^1\Pi$  and  $C^1\Delta$  states, from which the difference is respectively 240 and  $600\text{ cm}^{-1}$ . It would be interesting to repeat all these calculations with a larger basis set and the inclusion of the correlation of  $1s^2$  electrons. However, the most important states to investigate, also from an experimental point of view, are the  $X^1\Sigma^+$  and  $A^1\Pi$ . We thus studied, with more extended basis sets, only

these two states, to determine to better accuracy the values of the spectroscopic constants.

## 6. $X^1\Sigma^+$ and $A^1\Pi$ state results

The complete set of results concerning these two states is reported in tables 3 to 7 and in figures 6 and 7. The results obtained with the basis set superposition error (BSSE) correction are also reported in each table.

In table 3 we report the FCI results obtained with the b5 basis set for both states. The whole trend of the FCI

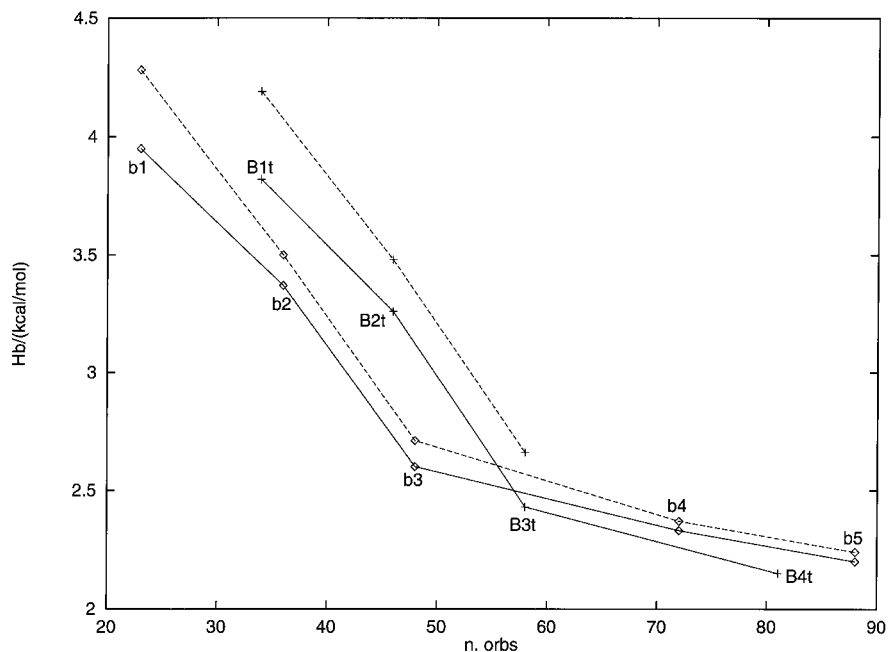


Figure 7.  $H_b$  for  ${}^1\Pi$  state with the different basis sets, without BSSE correction (full line), and with (dashed line).

Table 3. Valence FCI results (4 electrons correlated) for  ${}^1\Sigma^+$  and  $A^1\Pi$  states, obtained with the b5 basis set. The results with the BSSE correction are those on the second line. Minimum energy  $E_{\min}$ , separated-atom energy  $E_{\infty}$  and maximum energy  $E_{\max}$  ( $E_h$ ). Equilibrium distance  $R_e$  (Å),  $D_e = E_{\infty} - E_{\min}$  ( $\text{kcal mol}^{-1}$ ), harmonic fundamental frequency in the harmonic approximation  $\omega_e$  ( $\text{cm}^{-1}$ ),  $D_0 = D_e - \omega_e/2$  ( $\text{kcal mol}^{-1}$ ), maximum distance  $R_{\max}$  (Å) and  $H_b = E_{\max} - E_{\infty}$  ( $\text{kcal mol}^{-1}$ ).

${}^1\Sigma^+$ State								
$E_{\min}$	$E_{\infty}$	$R_e$	$D_e$	$\omega_e$	$D_0$			
- 25.235 654	- 25.101 420	1.2338	84.23	2354	80.83			
- 25.235 456	- 25.101 420	1.2342	84.11	2353	80.71			
Exp. —	—	1.2324	—	2376	—			
${}^1\Pi$ State								
$E_{\min}$	$E_{\infty}$	$E_{\max}$	$R_e$	$D_e$	$\omega_e$	$D_0$	$R_{\max}$	$H_b$
- 25.129 146	- 25.101 420	- 25.097 911	1.2256	17.39	2275	14.119	2.0946	2.20
- 25.128 945	- 25.101 420	- 25.097 854	1.2261	17.27	2272	13.99	2.0929	2.24
Exp. —	—	—	1.2186	—	2251	—	—	—

results as a function of the basis set is resumed in figures 6 and 7, respectively, and in the following discussion we will refer to these figures when mentioning the FCI values of  $D_e$  and  $H_b$  obtained with the different basis sets.

The FCI calculations with the b5 basis set have been performed also at long internuclear distances, namely at 10.00, 20.00 and 30.00 au. (In the tables we do not report the absolute value of the energy at these distances, which are available upon request.) These calculations indicate that the energy of the molecule in both  $X^1\Sigma^+$  and  $A^1\Pi$  states converges monotonically to the

sum of the separated-atom energies, and they thus confirm that the method used is accurate at long distance.

The TCI results for the  $X^1\Sigma^+$  are reported in table 4. It can be noted that  $D_e$  increases as a function of the basis sets.

For the first two basis sets the TCI results can be compared to the corresponding FCI ones obtained by correlating all the six electrons, ( $B1_t$  to B1 and  $B2_t$  to B2). The difference between FCI and TCI is less than  $0.01 \text{ kcal mol}^{-1}$  and it indicates that the TCI results are a good approximation to the FCI ones.



Table 4. TCI and FCI calculations (6 electrons correlated) for  $X^1\Sigma^+$  state without (first line) and with (second line) the BSSE correction. Equilibrium distance (Å), minimum energy and separated-atom energy ( $E_h$ ),  $D_e$  (kcal mol<sup>-1</sup>), harmonic fundamental frequency in the harmonic approximation (cm<sup>-1</sup>), and  $D_0$  (kcal mol<sup>-1</sup>). The same symbols as in table 3 are used.

Basis set	$R_e$	$E_{\min}$	$E_{\infty}$	$D_e$	$\omega_e$	$D_0$
<i>TCI</i>						
B1 <sub>t</sub>	1.2455	-25.237 450	-25.110 215	79.84	2303	76.52
	1.2505	-25.235 679	-25.110 215	78.73	2281	75.44
B2 <sub>t</sub>	1.2363	-25.247 399	-25.117 080	81.78	2338	78.41
	1.2383	-25.246 352	-25.117 080	81.12	2329	77.76
B3 <sub>t</sub>	1.2331	-25.252 022	-25.118 581	83.74	2351	80.34
	1.2356	-25.250 974	-25.118 581	83.08	2346	79.69
B4 <sub>t</sub>	1.2301	-25.259 225	-25.124 510	84.54	2364	81.12
<i>FCI</i>						
B1	1.2455	-25.237 463	-25.110 215	79.85	2303	76.52
	1.2505	-25.235 692	-25.110 215	78.74	2281	75.45
B2	1.2363	-25.247 421	-25.117 080	81.79	2338	78.42
	1.2383	-25.246 374	-25.117 080	81.13	2331	77.77
Exp.	1.2324	—	—	—	2367	—

The TCI results have to be compared with the FCI ones (4 electrons) to assess the effect of 1s correlation. With the basis set including the highest angular momentum orbitals (b5), only the FCI calculations correlating the four valence electrons were performed. To have an idea of the effect of the correlation of 1s orbitals for this basis set, we consider how it affects the previous-basis results. In going from b1, b2, b3, b4, respectively, to B1<sub>t</sub>, B2<sub>t</sub>, B3<sub>t</sub>, B4<sub>t</sub>, the value of  $D_e$  increases of 0.68, 0.40, 0.61, 0.64 kcal mol<sup>-1</sup>, respectively. This indicates that, for the effect of the 1s correlation, the value of  $D_e$  probably should be increased by a quantity in the range of 0.6–0.8 kcal mol<sup>-1</sup>.

Let us now consider the correction to BSSE for the value of  $D_e$ . To estimate the BSSE we used the standard counterpoise method [33] in which the separated-fragment energies are computed in the total basis set of the system. In the valence FCI results it goes from 0.74 (b1) to 0.12 kcal mol<sup>-1</sup> (b5), while at TCI level it has been determined only for the first three basis, and it is slightly larger: from 1.11 (B1) to 0.66 (B3). According to Bauschlicher *et al.* [11] for a basis set of the size of our largest one (b5), a reasonable estimate of the basis set incompleteness error is 1.5 times the magnitude of the BSSE. That is, instead of subtracting the BSSE correction, we add 1.5 times this value to  $D_e$  to account for the basis set incompleteness. Our best estimate for  $D_e$  of 85.11 kcal mol<sup>-1</sup> is thus obtained by adding to the value computed with b5 (84.23), 0.7 kcal mol<sup>-1</sup> for the

Table 5.  $X^1\Sigma^+$ :  $\bar{D}_e$  (kcal mol<sup>-1</sup>) via isogyric reaction at FCI level (4 correlated electrons) and TCI (6 correlated electrons).

Basis set	$\bar{D}_e$	Basis set	$\bar{D}_e$
FCI	(4 electrons)	TCI	(6 electrons)
b1	82.35	B1 <sub>t</sub>	83.04
b2	83.44	B2 <sub>t</sub>	83.83
b3	84.15	B3 <sub>t</sub>	84.70
b4	84.47	B4 <sub>t</sub>	85.11
b5	84.68	—	—

1s correlation and  $0.12 \times 1.5 = 0.18$  kcal mol<sup>-1</sup> for the basis set incompleteness.

In figure 6 the information about  $D_e$  are presented. We report  $D_e$  as a function of the number of orbitals for the valence FCI calculations and TCI ones, without and with the BSSE correction. The slope of all the curves decreases after the inclusion of the second f orbital in the basis set, and a further decrease occurs with the inclusion of the g orbital in the b-basis curves, which means that the basis is reasonably close to completeness.

The value of  $D_e$  has been determined also via the isogyric reaction ( $D_e$ , and in this way, it is more stable within the basis sets (table 5). The final value, corresponding to b5 and including about 0.7 kcal mol<sup>-1</sup> for the 1s correlation, is 85.38 kcal mol<sup>-1</sup>, which is slightly higher than the value obtained in the traditional way (including also that for BSSE).

We come now to discuss the results for the  $A^1\Pi$  state (tables 6 and 7) with particular attention to the value of  $H_b$ . In table 3 we report the valence FCI results obtained

Table 6. TCI and FCI calculations (6 electrons correlated) for  $A^1\Pi$  state without (first line) and with (second line) the BSSE correction. Minimum energy, separated-atom energy, and maximum energy ( $E_h$ ). The same symbols as in table 6 are used.

Basis	$E_{\min}$	$E_{\infty}$	$E_{\max}$
<i>TCI</i>			
B1 <sub>t</sub>	-25.127 692	-25.110 215	-25.104 124
	-25.125 915	-25.110 215	-25.103 541
B2 <sub>t</sub>	-25.139 092	-25.117 080	-25.111 889
	-25.138 038	-25.117 080	-25.111 538
B3 <sub>t</sub>	-25.145 357	-25.118 581	-25.114 712
	-25.144 297	-25.118 581	-25.114 336
B4 <sub>t</sub> <sup>a</sup>	-25.153 142	-25.124 510	-25.121 076
<i>FCI</i>			
B1	-25.127 745	-25.110 215	-25.104 155
	-25.125 968	-25.110 215	-25.103 5737

<sup>a</sup>A single point calculation was performed in the minimum region at  $R = 1.23$  Å and in the maximum region at  $R = 2.10$  Å.

Table 7. TCI and FCI calculations (6 electrons correlated) for  $A^1\Pi$  state without (first line) and with (second line) the BSSE correction. Equilibrium distance ( $\text{\AA}$ ),  $D_e$  ( $\text{kcal mol}^{-1}$ ), harmonic fundamental frequency in the harmonic approximation ( $\text{cm}^{-1}$ ),  $D_0$  ( $\text{kcal mol}^{-1}$ ), maximum distance ( $\text{\AA}$ ), and  $H_b$  ( $\text{kcal mol}^{-1}$ ). The same symbols as in table 7 are used.

Basis	$R_e$	$D_e$	$\omega_e$	$D_0$	$R_{\text{max}}$	$H_b$
<i>TCI</i>						
B1 <sub>t</sub>	1.2434	10.97	2150	7.86	1.9882	3.82
	1.2492	9.85	2116	6.80	1.9861	4.19
B2 <sub>t</sub>	1.2315	13.81	2223	10.60	2.0233	3.26
	1.2336	13.15	2211	9.96	2.0233	3.48
B3 <sub>t</sub>	1.2259	16.80	2265	13.53	2.0791	2.43
	1.2288	16.14	2363	12.73	2.0726	2.66
B4 <sub>t</sub> <sup>a</sup>	—	17.97	—	—	—	2.15
<i>FCI</i>						
B1	1.2434	11.00	2150	7.90	1.9885	3.80
	1.2492	9.89	2118	6.83	1.9805	4.17
Exp.	1.2186	—	2251	—	—	—

<sup>a</sup>A single point calculation was performed in the minimum region at  $R=1.23\text{ \AA}$  and in the maximum region at  $R=2.10\text{ \AA}$ .

with the b5 basis, while in tables 6 and 7 those obtained at TCI including the 1s correlation.

For the first basis, B1<sub>t</sub>, the corresponding FCI calculation (B1) was performed and the difference in the value of  $H_b$  is only of  $0.02\text{ kcal mol}^{-1}$ .

The inclusion of 1s correlation (TCI) (compare table 7 with table 3) implies a decrease in  $H_b$  of  $0.13\text{ kcal mol}^{-1}$  from b1 to B1<sub>t</sub>,  $0.11$  from b2 to B2<sub>t</sub>,  $0.17$  from b3 to B3<sub>t</sub>, and  $0.18$  from b4 to B4<sub>t</sub>. We can thus say that the 1s correlation decreases the value of  $H_b$  by about  $0.2\text{ kcal mol}^{-1}$ .

The BSSE on the value of  $H_b$  is not negligible for the smaller basis sets, while it reduces to  $0.04\text{ kcal mol}^{-1}$  for b5, and in any case it is lower than in the region close to the minimum, since the barrier occurs at longer distance than the minimum. Taking into account a correction of about  $0.2\text{ kcal mol}^{-1}$  for the 1s correlation and  $0.04 \times 1.5 = 0.06$  for the basis set incompleteness, to subtract from the value of  $H_b$  obtained with b5, the final estimate of  $H_b$  is in the range of  $1.95\text{--}2.00\text{ kcal mol}^{-1}$ .

The value of  $H_b$  for  $A^1\Pi$  is reported in figure 7 as a function of the number of orbitals, within the different methods. As in the case for  $D_e$ , we note that the slope of the curves decreases after the inclusion of the second f orbital in the basis set (b4, B4<sub>t</sub>), indicating that the basis set approaches completeness.

If we consider the upper limit for  $D_e$  of  $86.0 \pm 0.4\text{ kcal mol}^{-1}$ , derived from the experimental predissociation data [2] assuming a zero height for the barrier, we note that it slightly differs from the sum of  $D_e$  and  $H_b$ ,

$86.43\text{ kcal mol}^{-1}$  ( $86.35$  with BSSE correction) obtained with the b5 basis.

## 7. Conclusions

In this FCI study on the BH molecule, the potential energy curves of 20 electronic states have been computed, some of which had never been published before. For the two most important states,  $X^1\Sigma^+$  and  $A^1\Pi$ , the spectroscopic constants have been determined with basis sets of increasing quality, including the 1s correlation. The results obtained for  $D_e$  and  $H_b$  are not in agreement with those reported by Huber and Herzberg [1], Gustaffson and Rittby [5] and Persico [13] while they confirm the results of Bauschlicher *et al.* [11]. Our estimate of the  $D_e$  value for  $X^1\Sigma^+$  is  $85.1\text{ kcal mol}^{-1}$ , and that of  $H_b$  for the  $A^1\Pi$  state is  $2.0\text{ kcal mol}^{-1}$ .

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