Ab initio VB Studies of the Ground and Low-lying Excited States of BeH and BH

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A scheme has been proposed to classify valence bond (VB) wave functions for the calculations of ground and excited states, according to the symmetry properties of one-electron orbitals which are involved in the construction of VB wave functions. This scheme is illustrated by the examples of BeH and BH. *Ab initio* VB computations of these two test molecules in combination with the present classification scheme give reliable results. For example, calculation results show that the state $C^2\Sigma^+$ of BeH is stable, with the bonding energy 0.87 eV and bond length 0.238 nm, which are in good agreement with those obtained by Gerratt *et al*. The bonding features of ground and low-lying excited states of BeH and BH are discussed.

Keywords   valence bond theory, excited state, BeH, BH

Introduction

Bonded Tableau Unitary Group Approach (BTUGA)[1-4] falls in the spin-free modern valence bond (VB) theory. The key idea of VB theory is that two electrons are paired to form a chemical bond, and each VB function corresponds to one unique VB structure. Although the classical VB theory is closely related to the conventional chemical concepts and can present an intuitive chemical bonding picture appealing to chemists, the symmetry of an individual VB structure is a subset of the overall point group of the system and different VB structures have different symmetries. This imposes difficulties to the study of exited states of specific symmetries with *ab initio* VB methods. At our early stage of the VB study of excited states with BTUGA,[5,6] the usual procedure to calculate the energies of excited states includes two steps: (1) taking a combination of all linearly independent bonded tableau (BT) functions as a wave function of a molecule, and (2) solving the secular equation to derive the eigenvalues and eigenfunctions, where the lowest value corresponds to the ground state, the second lowest one to the first excited state, and so on. In this way, however, sometimes it is extremely difficult to meet the request of an avoided crossing between two energy curves, because only the wave

functions of the ground state could be optimized in the calculations of excited states.

Recently, our group[7,8] proposed two methods to overcome the above-mentioned difficulties. One method is based on the correspondence between the molecular orbital (MO) theory and VB theory in describing chemical bonds,[7] the other is based on the symmetry properties of BTs and the projection operator associated with a point group.[8] These two methods made the *ab initio* VB calculations of the excited states possible. However, in cases of diatomic molecules an even simpler procedure than the above two methods exists in the efficient computation of low-lying excited states with the *ab initio* VB approach. In this work, we proposed a scheme to classify the VB functions, according to the symmetry properties of one-electron basis functions, which are used to construct BT functions. This scheme has been applied to the study of BeH and BH molecules in the ground and low-lying excited states, whose potential energy surfaces have been evaluated and compared with the available theoretical data. Bonding pictures for the ground and low-lying excited states are also presented and discussed.

Methodology

Bonded tableau unitary group approach (BTUGA)

As a simple spin-free VB method, BTUGA adopts bonded tableaus (BTs) as state functions of a system. These state functions are used to describe conventional resonance structures. Thus, the BTUGA method is much closer to classical concepts and ideas than other many-body theories. For an N electron system, a BT is defined as

$$\Phi^{[\lambda]}(k) = A_k e_{11}^{[\lambda]}\Omega(k)$$
$$= A_k e_{11}^{[\lambda]}[u_1(1)u_2(2)\cdots u_n(n)] \qquad (1)$$

where A_k is a normalization constant, $e_{11}^{[\lambda]}$ is a standard

projection operator for the irreducible representation $[\lambda] = [2^{N/2-S}, 1^{2S}]$ of permutation group corresponding to the desired spin multiplicity $2S + 1$ and u_i is a one-electron basis function. Eq. (1) describes a VB structure where two one-electron basis u_{2i-1} and u_{2i} overlap to form a bond ($i \leqslant N/2^{-S}$ and the 'bond' is a lone electron pair if $u_{2i-1} = u_{2i}$) and the last $2S$ one-electron functions are unpaired. Thus the wave function of the system can be expressed as a superimposition of all possible BTs, namely

$$\Psi_i = \sum_{k=1}^{M} C_{ki}\Phi_i(k) \qquad (2)$$

The structural weight of a BT$\Phi_i(k)$ in the Ψ_i can be defined as

$$T_i(k) = \sum_{l=1}^{M} C_{ki}C_{li}S_{kl} \qquad (3)$$

where S_{kl} is the overlap between the two BTs $\Phi_i(k)$ and $\Phi_i(l)$.

The condition of normalization requires

$$\sum_{k=1}^{M} T_i(k) = 1 \qquad (4)$$

where M is the number of linearly independent bonded tableaux.

The VB charge population $P(u_i)$ on the one-electron orbital u_i is defined as

$$P(u_i) = \sum_{k=1}^{M} T_i(k)m_i(k) \qquad (5)$$

where $m_i(k) = 0$, 1 or 2, depending on whether the one-electron orbital u_i in the $\Phi(k)$ is filled with zero, one or two electrons, respectively.

Classification of valence bond wave functions

According to the MO theory, for a molecule whose nuclear framework has elements of symmetry, the subsequent molecular orbitals belong to irreducible representa-

tions of the corresponding point group, and can be classified accordingly. Similarly, a total VB wave function corresponding to a specific state of the molecule should have the symmetry of the system. Moreover, analogous to the MO theory, where the irreducible representations of the Rydberg states belong to the irreducible representations of the open-shell orbitals, the symmetry of VB wave functions is determined by the symmetries of one-electron oribitals. In this way, overall VB wave functions can be classified according to the symmetry of one-electron oribitals. For AB type diatomic molecules, their molecular symmetry group belongs to $C_{\infty v}$, and we introduce three criterions for the classification of BTs as follows: (1) if no π-orbital or only doubly-occupied π-orbitals are involved in the construction of a BT function, the corresponding BT function belongs to the subspace Σ^+; (2) if only a singly-occupied π-orbital or odd numbers of π-orbitals are involved in the construction of a BT function, the corresponding BT function belongs to the subspace Π; (3) if two singly-occupied π-orbitals are involved in the construction of a BT function, the corresponding BT function belongs to the subspace Σ^-.

Take BeH with 6-31G basis set as an example, where the 1s orbital of Be keeps frozen to reduce the computational cost. Atomic hybrid orbitals (AHOs) are taken as one-electron orbitals. For simplicity, three σ-symmetry one-electron orbitals, whose dominant components are $2s + 2p_z$ (Be), $2s - 2p_z$ (Be) and $2s$ (H), are denoted as σ_1, σ_2 and σ_3, while the two π-symmetry ones, whose dominant compotents are $2p_x$ (Be), $2p_y$ (Be), are denoted as π_1 and π_2. According to the criteria, totally 40 BTs are classified as listed in the Table 1.

Computational details

Xiamen package[9] was used for all VB calculations in this paper. 6-31G basis set was used, with the 1s orbitals of Be and B being frozen to reduce the computational cost. In the VB wavefunctions, atomic hybrid orbitals (AHOs) are taken as one-electron orbitals to ensure an unambiguous definition of a covalent or an ionic bond. Similar to multiconfigurational self-consistent field (MCSCF) calculations, in valence bond self-consistent field (VBSCF) calculations, expansion coefficients of AHOs are simultaneously optimized with coefficients of the VB structures.

Table 1 Classifications of 40 BTs (BeH)

Subspace	Configuration
$^2\Sigma^+$	$\sigma_1\sigma_1\sigma_2$, $\sigma_1\sigma_1\sigma_3$, $\sigma_2\sigma_2\sigma_1$, $\sigma_2\sigma_2\sigma_3$, $\sigma_3\sigma_3\sigma_1$, $\sigma_3\sigma_3\sigma_2$, $\sigma_1\sigma_3\sigma_2$, $\sigma_2\sigma_3\sigma_1$, $\pi_1\pi_1\sigma_1$ $\pi_1\pi_1\sigma_2$, $\pi_1\pi_1\sigma_3$, $\pi_2\pi_2\sigma_1$, $\pi_2\pi_2\sigma_2$, $\pi_2\pi_2\sigma_3$
$^2\Pi$	$\sigma_1\sigma_2\pi_1$, $\sigma_2\sigma_3\pi_1$, $\sigma_1\sigma_3\pi_1$, $\sigma_1\sigma_3\pi_2$, $\sigma_2\sigma_3\pi_2$, $\sigma_2\sigma_2\pi_1$, $\sigma_2\sigma_2\pi_2$, $\sigma_3\sigma_3\pi_1$, $\sigma_3\sigma_3\pi_2$ $\pi_1\sigma_1\sigma_3$, $\sigma_1\pi_2\sigma_3$, $\sigma_2\pi_1\sigma_3$, $\sigma_1\pi_2\sigma_3$, $\sigma_2^2\pi_1\sigma_1$, $\sigma_1\sigma_2\pi_2$, $\sigma_2\pi_2\sigma_1$, $\pi_1\pi_1\pi_2$, $\pi_2\pi_2\pi_1$
$^2\Sigma^-$	$\pi_1\pi_2\sigma_3$, $\sigma_3\pi_1\pi_2$, $\sigma_1\pi_2\pi_1$, $\pi_2\pi_1\sigma_1$, $\pi_2\sigma_2\pi_1$, $\pi_2\pi_1\sigma_2$, $\pi_2\sigma_1\pi_1$, $\sigma_1\pi_1\pi_2$

Results and discussion

Potential curves of the serveral $^2\Sigma^+$ states of BeH

The VBSCF calculations on BeH were carried out at 21 points of the internuclear distance R between 0.063 and 1.058 nm. Total energy curves for the ground state $(X^2\Sigma^+)$ and the first excited state $(C^2\Sigma^+)$, as a function of R are plotted in Fig. 1. For comparison, the ground state energy curves at the HF and MP2 levels are also shown. It can be seen that the potential curve obtained by VBSCF is the lowest, whereas that of HF is the highest. This indicates that our 14BTSCF calculation can recover more electron correlation energy than MP2.
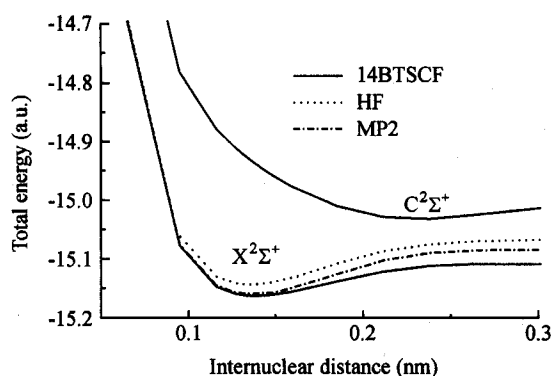

Fig. 1 Potential energy curves for BeH in the $X^2\Sigma^+$ and $C^2\Sigma^+$ states, the former being compared with those obtained from HF and MP2 calculations.

There are two kinds of description for the first excited state $(C^2\Sigma^+)$. According to Chan and Davidson,[10] the potential energy curve of the $C^2\Sigma^+$ state has no minimum and is purely repulsive; on the contrary, Gerratt and Raimondi[11] found that this state is reasonably stable with the binding energy D_e of 0.92 eV and the equilibrium internuclear distance R_e of 0.228 nm, which differs considerably from the ground state value (0.136 nm) and consequently explains why the $C^2\Sigma^+$ state has so far not been observed directly. In the present work, our calculations show that the $C^2\Sigma^+$ state is stable with D_e of 0.87 eV relative to Be $(sp_z;\ ^3P) + H(^2S)$ and R_e of 0.238 nm, in good agreement with results of Gerratt and Raimondi .[11] The results

confirm that $C^2\Sigma^+$ state is stable and a long R_e accounts for the fact that $C^2\Sigma^+$ has not been observed directly.

For a further comparison, we adopt the reduced potential energy surface introduced by Bartlett *et al* .,[12] defined by $U(X) = 1.0 + [E(X) - E_0]/D_e$, where $X = 1.0 + R/R_e$, and E_0 is the total energy of the reaction products. In this way, the comparisons among 14BTSCF, 80SCVB[11] and CISD are shown in Fig. 2. It is obvious that the curve of 14BTSCF almost coincides with that of 80SCVB, except for being a slightly steep in the range of 0.265—0.317 nm. This implies that the 14BTSCF calculations can provide comparable results with a fewer VB structures, compared with 80SCVB. Moreover, although the curve of CISD is a little wider than those of 14BTSCF and 80SCVB, the CISD and 14BTSCF calculations recover comparable electron correlation by using the same basis set.
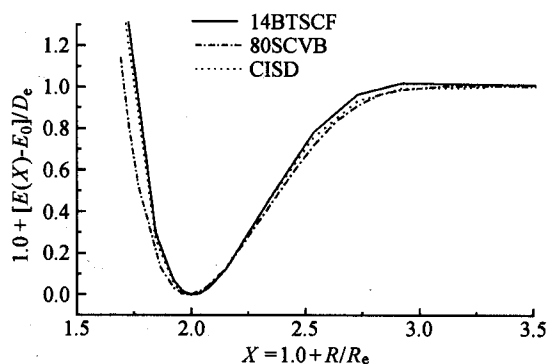

Fig. 2 Reduced potential curves for the $X^2\Sigma^+$ state obtained by 14BTSCF, CISD/6-31G and 80-SCVB[11] calculations.

Table 2 lists the calculated equilibrium distances (R_e), dissociation energies (D_e) and dissociative products (P, at $R = 1.058$ nm) of several $^2\Sigma^+$ states of BeH, together with available values from the literature. For the ground state $(X^2\Sigma^+)$, our dissociative products are consistent with those of the SCVB calculations.[11] For the first excited state $(C^2\Sigma^+)$, our results show that the $C^2\Sigma^+$ state is stable with D_e of 0.87 eV relative to Be $(sp_z;\ ^3P) + H$ (^2S), in good agreement with the work by Gerratt and Raimondi.[11] The resulting dissociative product for the state is also consistent with those of Gerratt and Raimondi.[11] The $F^2\Sigma^+$ state is weakly bound state, with D_e of 0.24 eV.

Table 2 Equilibrium bond lengths (R_e), dissociation energies (D_e) and dissociative products

State	R_e(nm)	D_e (eV)	Dissociative product	Reference
	0.138	1.25	$Be(s^2;\ ^1S) + H(^2S)$	14BTSCF (this work)
	0.136	1.87	$Be(s^2 + p^2;\ ^1S) + H(^2S)$	SCVB[11]
$X^2\Sigma^+$	0.135	2.115	—	Bagus *et al*.[12]
	—	1.48	—	Chan & Davidson[10]
	0.134	2.16	—	Experimental[13]
$C^2\Sigma^+$	0.238	0.87	$Be(sp_z;\ ^3P) + H(^2S)$	14BTSCF (this work)
	0.228	0.92	$Be(sp_z;\ ^3P) + H(^2S)$	SCVB[11]
$F^2\Sigma^+$	0.265	0.24	$Be(sp_z;\ ^1P) + H(^2S)$	this work

Potential curves of the $X^1\Sigma^+$ *and excitation energies of the* $A^1\Pi$ *states of* BH

Potential energy curves obtained from different methods for the ground state $(X^1\Sigma^+)$ are shown in Fig. 3. It is very encouraging to find that our VB calculations can describe the dissociation process correctly, whereas both HF and MP2 fail to provide an appropriate description of the bonding.
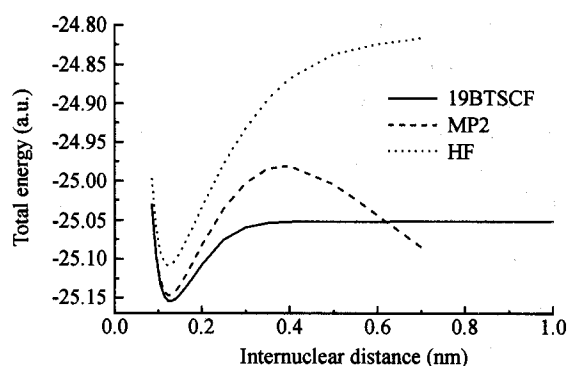

Fig. 3 Comparison among the potential curves obtained by several methods for the BH in the $X^1\Sigma^+$ state.

Comparison between the excitation energies obtained by the 11BTSCF and CIS calculations for the BH in the $A^1\Pi$ state is shown in Fig. 4. Our 11BTSCF can describe the excitation process correctly even when the internuclear distance (R) becomes very large, whereas the CIS calculations give a negative excitation energy when R is larger than 0.5 nm.
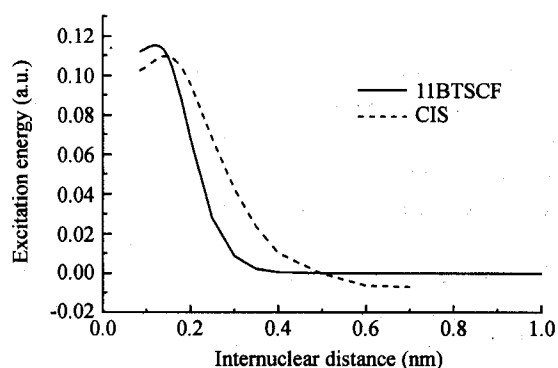

Fig. 4 Comparison between the excitation energies obtained by the 11BTSCF and CIS calculations for the BH in the $A^1\Pi$ state.

VB structural weights and charge distributions of the $X^2\Sigma^+$, $C^2\Sigma^+$ *and* $F^2\Sigma^+$ *states of* BeH

Fig. 5 shows the curves of VB structural weights versus the internuclear distances for the three lowest Σ^+ states. It can be seen that for the $F^2\Sigma^+$ state, the ionicity is predominant at R is 0.064 nm, and the bonds for three lowest states $(X^2\Sigma^+, C^2\Sigma^+, F^2\Sigma^+)$ are chiefly covalent when R is larger than 0.159 nm.

The variations of net charge on H atom with the internuclear distance are listed in Table 3. For the $X^2\Sigma^+$, $C^2\Sigma^+$ and $F^2\Sigma^+$ states, the charge transfer behaviors are similar: first from H to Be, then from Be to H as R arrives at a critical point (R_c), *i.e.* H→Be→H. The R_c values for the three states are 0.095, 0.159 and 0.159 nm, respectively.

VB structural weights and charge distributions of $X^1\Sigma^+$, $a^3\Pi$ *and* $A^1\Pi$ *states of* BH

Fig. 6 shows the variations of the calculated structural weights with the internuclear distance. It is seen that the bond-types of B—H for the $X^1\Sigma^+$, $a^3\Pi$ and $A^1\Pi$ states are similar to one another: the covalent character first decreases slowly, then increases as R become large, except for the B—H bond in the $a^3\Pi$ state, which shows a complete covalent character in the range of 0.140—0.180 nm.

The values of net charges on the H atom of BH for various states versus the nuclear distance between B and H are listed in Table 4. For the $X^1\Sigma^+$ state, the H atom bears negative charge for $R < 0.40$ nm. This implies that charge transfer from B to H during the bonding process is in good agreement with electronegativity rule. Interestingly, it is seen that the situation in the excited states differs from the case of the ground state $(X^1\Sigma^+)$. The behavior of the $A^1\Pi$ state is similar to that of the $a^3\Pi$ state. In the dissociation process, H bears positive charges except that for the $a^3\Pi$ state, the net charges of H are zero in the range of 0.140—0.160 nm. In other words, there is a charge transfer from B to H during the bonding process, showing that the electronegativity rule is invalid for the excited states.

Conclusions

A simple scheme to classify the valence bond wave functions for the calculations of the excited states has been suggested. The new scheme has been used to study the bonding processes of the ground and low-lying excited states of BeH and BH. The calculated results not only are in good agreement with the previous theoretical results, but also can account for some foundational bonding phenomena in a visual way. Besides, there are two predominant advantages in our scheme: (1) It may ensure the calculated results possess physical meanings. For every energy curve, the contribution from a specific set of BT functions is continuous so that the change of a chemical bond is continuous. (2) It is convenient to obtain a series of energy levels for a molecule in a specific state, since each subspace of BT functions corresponds to a specific state of a molecule. For example, if the Σ states of a molecule are concerned, then the calculation with the BTs belonging to Σ subspace can provide the energy levels of Σ states.
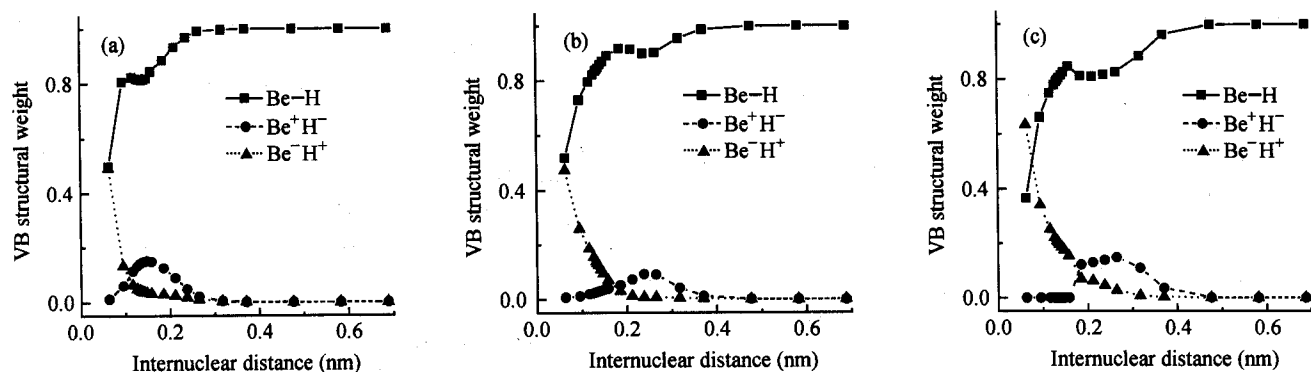
Fig. 5   VB structural weights versus the internuclear distances between H and Be for the three lowest Σ^+ states: (a) $X^2\Sigma^+$, (b) $C^2\Sigma^+$ and (c) $F^2\Sigma^+$.
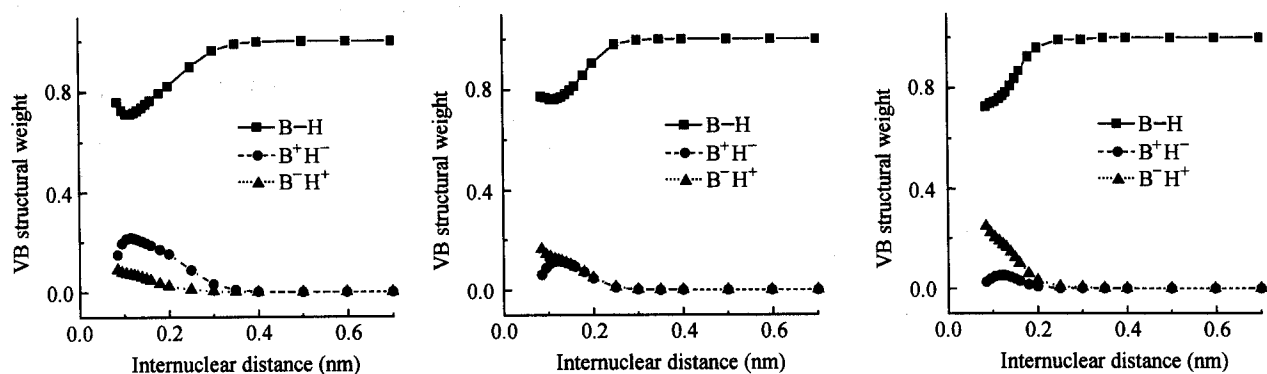

Fig. 6   VB structural weights versus the internuclear distances between H and B for the three lowest Σ^+ states: (a) $X^1\Sigma^+$, (b) $a^3\Pi$ and (c) $A^1\Pi$.

Table 3   Net charges on atom for the several $X^2\Sigma^+$, $C^2\Sigma^+$ and $F^2\Sigma^+$ states of BeH

Internuclear distance R (nm)	$X^2\Sigma^+$	$C^2\Sigma^+$	$F^2\Sigma^+$
0.064	+ 0.485	+ 0.469	+ 0.634
0.095	+ 0.074	+ 0.249	+ 0.339
0.116	− 0.051	+ 0.168	+ 0.251
0.127	− 0.087	+ 0.131	+ 0.221
0.132	− 0.100	+ 0.114	+ 0.208
0.134	− 0.103	+ 0.107	+ 0.204
0.138	− 0.109	+ 0.096	+ 0.196
0.143	− 0.113	+ 0.077	+ 0.185
0.148	− 0.117	+ 0.061	+ 0.174
0.159	0.118	+ 0.031	+ 0.153
0.185	− 0.098	− 0.023	− 0.052
0.211	− 0.065	− 0.061	− 0.068
0.238	− 0.031	− 0.085	− 0.094
0.265	− 0.010	− 0.083	− 0.123
0.317	− 0.001	− 0.037	− 0.102
0.370	0.000	− 0.009	− 0.033
0.476	0.000	− 0.001	− 0.001
0.582	0.000	0.000	0.000
0.688	0.000	0.000	0.000

Table 4   Net charges on atom for the $X^1\Sigma^+$, $a^3\Pi$ and $A^1\Pi$ states of BH

Internuclear distance R (nm)	$X^1\Sigma^+$	$a^3\Pi$	$A^1\Pi$
0.085	− 0.161	+ 0.105	+ 0.224
0.095	− 0.119	+ 0.056	+ 0.187
0.105	− 0.142	+ 0.027	+ 0.159
0.115	− 0.151	0.012	+ 0.139
0.123	− 0.150	+ 0.006	+ 0.125
0.130	− 0.149	+ 0.003	+ 0.115
0.140	− 0.147	+ 0.001	+ 0.101
0.150	− 0.144	0.000	+ 0.086
0.160	− 0.142	− 0.001	+ 0.070
0.180	− 0.138	0.000	+ 0.044
0.200	− 0.130	+ 0.002	+ 0.025
0.250	− 0.078	+ 0.002	+ 0.006
0.300	− 0.028	+ 0.001	− 0.089
0.350	− 0.007	+ 0.001	− 0.001
0.400	− 0.002	0.000	0.000
0.500	0.000	0.000	0.000
0.600	0.000	0.000	0.000
0.700	0.000	0.000	0.000

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