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## POTENTIAL ENERGY SURFACES OF THE GROUND AND EXCITED STATES OF $^{11}\text{BH}$ MOLECULE IN THE MULTIREFERENCE COUPLED CLUSTER THEORY

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The multireference state-specific coupled cluster theory is used for the calculation of the potential energy surfaces (PES) of  $^{11}\text{BH}$  molecule in the ground and excited states. The PESs are approximated by a number of analytical functions generalizing the Morse potential. The solution of a radial Schrödinger equation and the values of spectroscopic constants depending on the accuracy of the PES approximation are analyzed.

### 1. Introduction

Calculations of potential curves (or potential energy surfaces) and molecular spectroscopic constants (SC) still remain rather a complicated problem of quantum chemistry. The main difficulties are related to the investigation of PESs of electronically excited states, dissociation processes, and processes of formation and decay of chemical bonds. An important peculiarity of these structural-chemical situations consists in the presence of a set of degenerate or quasidegenerate energy levels and, rather often, the open-shell character of an electron state. As a result, there arise the considerable correlation effects that cannot be described, in principle, in the framework of the single-determinant approximation. In this connection, a special attention is paid to the development of multiconfiguration methods involving the electron correlation. At the present time, there exists a number of computer programs realizing different versions of quantum-chemical methods in the framework of the non-empirical (*ab initio*) methodology allowing one to take both dynamic and non-dynamic components of the electron correlation into account (in varying levels of accuracy). A special interest is attracted by study-

ing the approaches based on the Coupled Cluster (CC) theory.

During the recent decade, the CC method has acquired a reputation as a high-precision technique involving the electron correlation in non-empirical calculations of small- and medium-size molecular systems. The guaranteed size extensivity makes the CC theory an attractive instrument for the description of various physical-chemical processes and effects (intermolecular interaction, spectroscopy, nonlinear optical properties, and so on). However, a considerable success of this theory is related, first of all, to the calculation of closed shells near an equilibrium geometry. When describing the degenerate or quasi-degenerate chemical systems, the traditional CC method encounters a number of problems. It is caused by the fact that, with increase in internuclear distances or in the presence of quasidegeneracy effects, the electron wave function of a molecular system can include several determinants with large weights. In these situations, it is necessary to accurately consider the contributions of some most important configurations. Thus, the corresponding generalization of the CC theory represents an urgent problem.

The majority of the up-to-date quantum-chemical calculations involving the electron correlation is based on the Hartree-Fock determinant as an initial reference state. This means that all excitations are generated relative to this Hartree-Fock determinant. An alternative to this approach is presented by the method in the multidimensional model space (multireference, MR), where a set of reference determinants is constructed. All necessary excitations are generated relative to this set of reference determinants. A comparative review of the

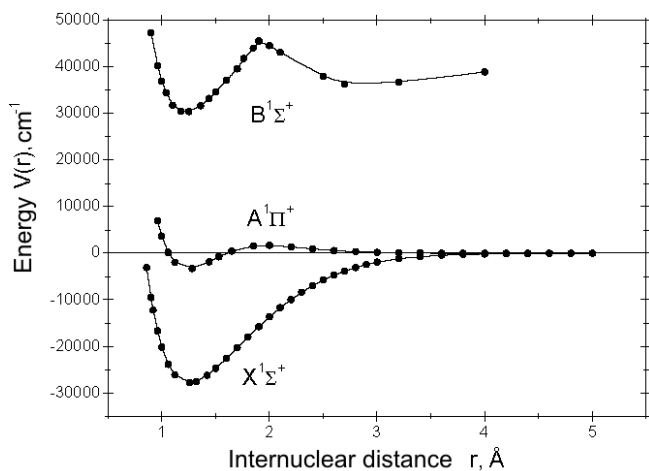


Fig. 1. CAS(2,2)CCSD/cc-pVDZ curves of the potential energy of the ground and excited states of  $^{11}\text{BH}$  molecule (zero line corresponds to the dissociation limit of the ground state)

MR approaches can be found, for example, in [1]. It is worth noting that the MRCC ideology as the most general method of solving the correlation problem can potentially solve any problem related to the dissociation of a chemical bond.

A considerable part of the up-to-date MRCC calculations is based upon the so-called complete active space (CAS). An active single-electron space is the minimal set of molecular orbitals (or spin orbitals) that must be taken into account in order to obtain a qualitatively correct solution of the investigated chemical problem. Using active orbitals, one constructs a model (reference) space – a set of determinants or their superpositions generated by various ways of the distribution of active orbitals by electrons. In the zero-order approximation of the method, the electron correlation is taken into account with participation of only the group of “active” orbitals.

In the given work, we proceed with testing our earlier proposed multireference CC method using the active orbital space (CAS Coupled Cluster Singles and Doubles, CASCCSD) [2–4]. We realized this method as an additional package of the well-known program complex GAMESS [6]. Our previous calculations have demonstrated a high accuracy of the CASCCSD method in the description of the energy and the wave function as compared to the accurate Full Configuration Interaction (FCI) method. In this work, we perform calculations of the PESs and SCs for three singlet states of  $^{11}\text{BH}$  molecule: the ground  $X^1\Sigma^+$ , the lowest totally symmetric  $B^1\Sigma^+$ , and the lowest degenerate  $A^1\Pi$  ones (Fig. 1).

We also study the influence of the accuracy of approximation of the PESs on the SC values, as well as the energies of the lowest vibrational terms with available experimental values.

## 2. Theory

### 2.1. Multireference state-specific coupled cluster theory

In the standard CC method, the reference state is presented by the only determinant constructed on the spin-orbitals in the Hartree–Fock approximation. In the general case, the wave function of the method has the following form:

$$|\Psi_{\text{CC}}\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_n)|0\rangle, \quad (1)$$

where  $|0\rangle$  is the reference state (Hartree–Fock determinant),  $\hat{T}_1, \dots, \hat{T}_n$  are the operators of generation of a superposition of excited determinants of the corresponding multiplicity relative to the reference determinant. We have

$$\hat{T}_1|0\rangle = \sum_{i,a} t_i^a |i^a\rangle, \quad (2)$$

$$\hat{T}_2|0\rangle = \sum_{i>j,a>b} t_{ij}^{ab} |ij^{ab}\rangle, \quad (3)$$

$$\hat{T}_3|0\rangle = \sum_{i>j>k,a>b>c} t_{ijk}^{abc} |ijk^{abc}\rangle, \dots, \quad (4)$$

where  $t_i^a$ ,  $t_{ij}^{ab}$ ,  $t_{ijk}^{abc}$ , and so on stand for the amplitudes characterizing the contribution of the corresponding configurations  $(|i^a\rangle, |ij^{ab}\rangle, |ijk^{abc}\rangle, \text{etc.})$ . The indices  $i, j, k$  correspond to occupied spin-orbitals, while  $a, b, c$  – to vacant spin-orbitals in the reference state  $|0\rangle$ .

In practical applications of the CC theory, the sum of the operators  $\hat{T}$  in expansion (1) is terminated at some member resulting in different approximations of the theory. The most widespread among them are the theory explicitly taking only doubly excited configurations into account (Coupled Cluster Doubles – CCD), that explicitly taking singly and doubly excited configurations into account (Coupled Cluster Singles Doubles – CCSD), that allowing for singly, doubly, and triply excited configurations (Coupled Cluster Singles Doubles and Triples – CCSDT), and so on. Each approximation implies the corresponding expansion of the exponential

function into a series. For example, in the CCSD case ( $\hat{T} = \hat{T}_1 + \hat{T}_2$ ), one obtains

$$|\Psi_{\text{CCSD}}\rangle = (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \dots)|0\rangle. \quad (5)$$

Expansion (5) includes both linear and nonlinear terms. On the one hand, this fact complicates the procedure of solving the Schrödinger equation, but, on the other hand, these nonlinear terms provide the accuracy and the additive energy separability of the method. The working equations of the CCSD method explicitly deal with amplitudes of only singly and doubly excited configurations. However, due to the nonlinear components of the wave function, the configurations of higher multiplicity are also approximately taken into account (emulated). For example, the terms ( $\hat{T}_1\hat{T}_2$  and  $\hat{T}_1^3$ ) correspond to the approximate description of triply excited configurations. The component ( $\hat{T}_2\hat{T}_2$ ) corresponds to the approximate description of quadruply excited configurations relative to the reference Hartree–Fock determinant ( $|0\rangle$ ). It is worth emphasizing once again that the mentioned configurations of higher multiplicities are taken into account only approximately, since they do not correspond to definite amplitudes.

A direct generalization of (1) to the case of a many-dimensional model space (multireference theory, MRCC) yields the expression

$$|\Psi_{\text{MRCC}}\rangle = \sum_{I=1,M} \exp(\hat{T}_1^{(I)} + \hat{T}_2^{(I)} + \dots)|\Phi_I\rangle, \quad (6)$$

where the set of determinants  $|\Phi_I\rangle, I = 1, M$  forms a reference space. The operators  $\hat{T}_i^{(I)}$  in the MRCC theory act on the corresponding selected reference determinants. Real calculations are usually confined to double excitations.

The choice of the reference space represents a key moment for the calculation of PESs of excited states. To form the space, it is necessary to choose a set of active orbitals. For this purpose, the complete set of molecular orbitals is divided into core *nonactive* and valent *active* ones (Fig. 2). The reference determinants are those only, for which core orbitals are doubly occupied, while active ones are populated by electrons in all possible ways. A reference space formed in such a manner is complete (Complete Active Space, CAS). In the case where two valent electrons are distributed among two active orbitals (four spin-orbitals), the active space is denoted as  $(2 \times 2)$  and has a dimension of 4.

In our calculations of the ground and excited states of  $^{11}\text{BH}$  molecule, the active space includes two orbitals

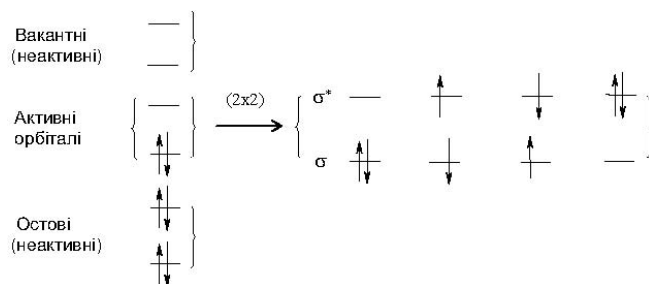


Fig. 2. Active space of orbitals of BH molecule used for the calculation of the  $\Sigma^+$  states

with two distributed electrons. In this case, the description of the ground ( $X^1\Sigma^+$ ) and excited ( $B^1\Sigma^+$ ) states requires the consideration of the bonding ( $3\sigma$ ) and antibonding ( $4\sigma$ ) molecular orbitals. Four determinants appearing due to such a distribution of electrons are reference ones (Fig. 2). Calculating the excited ( $A^1\Pi$ ) states, one should use the ( $3\sigma$ ) and ( $1\pi$ ) molecular orbitals as active ones. Due to the symmetry, the distribution of electrons among them generates only two determinants.

Our approach to the MRCC calculation (state-specific method) consists in the choice of one of the reference determinants as the so-called “formal reference” state. Electron excitations relative to this determinant form the rest of determinants of the reference state and the corresponding excitations relative to the latter.

Thus, the wave function of our method (CASCCSD) can be described in the following way (considering that the formal reference determinant is  $|0\rangle$ ):

$$|\Psi_{\text{CAS}(2,2)\text{CCSD}}\rangle = \exp(\hat{T}_1^{(\text{ext})} + \hat{T}_2^{(\text{ext})})(1 + \hat{C}_1 + \hat{C}_2)|0\rangle. \quad (7)$$

Here, the operators  $\hat{C}_1$  and  $\hat{C}_2$  generate the electron distribution among the active orbitals (by forming superpositions of reference determinants),

$$\hat{C}_1|0\rangle = \sum_{I,A} c_{I,A}^A |I^A\rangle, \quad (8)$$

$$\hat{C}_2|0\rangle = \sum_{I>J,A>B} c_{IJ}^{\text{AB}} |IJ^{\text{AB}}\rangle, \quad (9)$$

while the operators  $\hat{T}_1^{(\text{ext})}$  and  $\hat{T}_2^{(\text{ext})}$  form superpositions of single and double excitations beyond the reference space relative to all reference determinants. In our approach, these excitations represent excitations of higher multiplicity with respect to  $|0\rangle$ . For example, double excitations relative to the reference determinant

$|\frac{AB}{IJ}\rangle$  are realized as quadruple ones with respect to the “formal reference” determinant  $|0\rangle$ :

$$\hat{T}_2^{(\text{ext})}(\frac{cd}{kl})|\frac{AB}{IJ}\rangle = \hat{T}_4(\frac{ABcd}{IJkl})|0\rangle. \quad (10)$$

The practical choice of the “formal reference” determinant depends on the type of the investigated specific state. For example, in the case of calculating the  $^1\Sigma^+$  electron state, the reference function has the form

$$|0\rangle + x|\frac{4\sigma\bar{4}\sigma}{3\sigma\bar{3}\sigma}\rangle + y\left(|\frac{4\sigma}{3\sigma}\rangle + |\frac{\bar{4}\sigma}{3\sigma}\rangle\right), \quad (11)$$

where the determinant  $|0\rangle$  corresponds to a closed shell, in which the  $3\sigma$  molecular orbital is doubly occupied. The rest of determinants of the reference function represent excitations with respect to  $|0\rangle$ . The coefficients  $x$  and  $y$  can be found solving the Schrödinger equation. Our calculations show that, when describing the ground state ( $X^1\Sigma^+$ ), one should take the  $|0\rangle$  state as a “formal reference” one, as this determinant makes the dominant contribution to the wave function within the multireference method of configuration interaction. When calculating the ( $B^1\Sigma^+$ ) excited state, one can use one of the singly excited determinants ( $|\frac{4\sigma}{3\sigma}\rangle$  or  $|\frac{\bar{4}\sigma}{3\sigma}\rangle$ ).

The calculation of the  $^1\Pi$  state requires one to use the following reference function:

$$|\frac{1\pi}{3\sigma}\rangle + |\frac{\bar{1}\pi}{3\sigma}\rangle. \quad (12)$$

One of the determinants of this superposition (for example,  $|\frac{1\pi}{3\sigma}\rangle$ ) can serve as a formal reference one. The second determinant appears automatically, when the operator  $\hat{C}_2$  acts on  $|\frac{1\pi}{3\sigma}\rangle$ .

As was already noted above, all excitations in our realization of the multireference theory (CASCCSD) are constructed relative to one determinant. Due to this fact, it is necessary to take the chosen set of configurations of higher multiplicity into account. The search for the energies and the corresponding amplitudes of the sought states follows the standard projection scheme of the CC theory, according to which the Schrödinger equation is projected on the most important configurations, whose contributions are characterized by definite amplitudes:

$$\langle 0|H - E_{\text{CAS}(2,2)\text{CCSD}}|\Psi_{\text{CAS}(2,2)\text{CCSD}}\rangle = 0, \quad (13)$$

$$\langle_i^a|H - E_{\text{CAS}(2,2)\text{CCSD}}|\Psi_{\text{CAS}(2,2)\text{CCSD}}\rangle = 0, \quad (14)$$

$$\langle_{ij}^{ab}|H - E_{\text{CAS}(2,2)\text{CCSD}}|\Psi_{\text{CAS}(2,2)\text{CCSD}}\rangle = 0, \dots \quad (15)$$

In these expressions,  $E_{\text{CAS}(2,2)\text{CCSD}}$  stands for the total energy of the system. Our calculation scheme is described in [2, 3], and [4] in detail.

## 2.2. Analytical form of the PES function

In order to describe a molecular state in the nonrelativistic adiabatic approximation, it is necessary to find a “realistic potential function” describing the dependence of the energy on the internuclear distance  $V(r)$ . In this case, the form of the potential  $V(r)$  represents a source of considerable errors in calculating SCs and energies of vibrational-rotational terms. In our previous works [6], we proposed a generalization of the Morse potential (GM) in the following form:

$$V_{\text{GM}}(r) = \sum_{m=2}^q \alpha_m [1 - \exp(-\beta_m(r - R_e))]^m, \quad (16)$$

where  $\alpha_m$  and  $\beta_m$  are fitting parameters,  $R_e$  is the equilibrium internuclear distance. Function (16) at  $q = 2$  (standard Morse potential) gives a qualitatively correct form of the curve, but it is too rough for the accurate approximation of data of *ab initio* calculations. One also uses other functions generalizing the Morse potential, for example, in the form of the Murrell–Sorbie (MS) potential [7]:

$$V_{\text{MS}}(r) = -\alpha \sum_{m=1}^{6 \geq q} \beta_m (r - R_e)^{m-1} \exp(-\beta_1(r - R_e)), \quad (17)$$

and the James–Coolidge–Vernon (JCV) potential [8]:

$$V_{\text{JCV}}(r) = \sum_{m=2}^q \alpha_m [1 - \exp(-\beta(r - R_e))]^m. \quad (18)$$

Here,  $\alpha$  and  $\beta$  with the corresponding indices are the fitting parameters.

Potentials (16)–(18) exponentially decrease at large internuclear distances. However, it is known that, at large distances, functions of the intermolecular (interatomic) interaction take the form of power sums:

$$V(r \rightarrow \infty) \approx \alpha - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \dots \quad (19)$$

In this expression,  $C_6, C_8, \dots$  are the dispersion constants determined by the nature of interacting atoms (molecules). The generalized Lennard-Jones (LJ) function [9] satisfies this condition:

$$V_{\text{LJ}}(r) = T^{\text{dis}} - \alpha y [2 - y],$$

$$y = \left(\frac{R_e}{r}\right)^n \left(1 + \sum_{m=1}^q \beta_m \cdot z^m\right),$$

$$z = \frac{r/R_e - 1}{r/R_e + 1}, \quad (20)$$

where  $n = 6$ , while  $T^{\text{dis}}$  corresponds to the dissociation energy.

Searching for the parameters  $\alpha$  and  $\beta$  with the help of an iterative procedure, one minimizes the sum of squared deviations of *ab initio* theoretical energies from the values obtained by the approximation in the whole PES region (least square technique):

$$\chi^2 = \frac{1}{(N-p)} \sum_i [E_i - V_i]^2, \quad (21)$$

where  $E_i$  is the theoretical value of the energy  $E_{\text{CAS}(2,2)\text{CCSD}}$  at the point  $r_i$ ,  $V_i = V_i(r_i)$  is the value of the potential function (the result of approximation of the set  $E_i$ ) at the same point  $r_i$ ,  $N$  is the number of points used in the approximation, and  $p$  is the total number of the fitting parameters.

### 2.3. Calculation of molecular parameters

The complete description of a molecular state and the calculation<sup>1</sup> of a wide set of SCs require the solution of the radial Schrödinger equation with the chosen potential  $V(r)$ :

$$\varphi''_{\nu,J}(r) - \frac{J(J+1)\varphi_{\nu,J}(r)}{r^2} + 2\mu(E_{\nu,J} - V(r))\varphi_{\nu,J}(r) = 0, \quad (22)$$

where  $E_{\nu,J}$  denotes the eigenvalue corresponding to the vibrational-rotational level,  $\varphi_{\nu,J}(r)$  is the wave function of nuclear motion,  $\nu$  is the vibrational quantum number,  $J$  is the rotational quantum number, and  $\mu$  is the reduced mass. The explicit form of the function  $V(r)$  allows one to estimate the SCs of the investigated molecule generally determined as the corresponding coefficients of the Dunham expansion [10]:

$$E_{\nu,J} = \sum_{\ell} \sum_m Y_{\ell m} \left( \nu + \frac{1}{2} \right)^{\ell} J^m (J+1)^m. \quad (23)$$

The Dunham coefficients  $Y_{\ell m}$  are expressed in terms of different derivatives of the corresponding potential function  $V(r)$  (16)–(20) at the point  $r = R_e$  calculated by analytical or numerical differentiation. The error related to the number of levels in the molecular spectrum taken into account when searching for the equilibrium

vibrational frequency  $\omega_e$  and the anharmonicity  $\omega_e x_e$  can vary between  $20 \text{ cm}^{-1}$  and  $100 \text{ cm}^{-1}$ . The theoretical calculation of the SCs consists in the numerical solution of the radial equation (22) with the potential approximated in one of the possible ways [11]. Calculating the constants with the use of Eqs. (22) and (23), it is necessary to take the experimental number of vibrational levels  $E_{\nu,J}$  into account. In this case, theoretical and experimental values can be compared. The numerical differentiation of the total energy of the system  $E_{\text{CASCCSD}}$  “point-by-point” is the simplest way to obtain the SCs. In this case, we used the standard formulas of numerical differentiation by five points (see, e.g., [12]):

$$F_5'' = \frac{1}{12h^2} [-E_{+2} + 16E_{+1} - 30E_0 + 16E_{-1} - E_{-2}],$$

$$F_5''' = \frac{1}{2h^3} [E_{+2} - 2E_{+1} + 2E_{-1} - E_{-2}],$$

$$F_5'''' = \frac{1}{h^4} [E_{+2} - 4E_{+1} + 6E_0 - 4E_{-1} + E_{-2}]. \quad (24)$$

Here,  $h$  is the step of differentiation (takes the values from  $0.01 \text{ a.u.}$  to  $0.1 \text{ a.u.}$ ),  $E_0$  corresponds to the energy of the system at the minimum point  $R_e$ , and  $E_{\pm n}$  is the energy of the system at the points  $R_e \pm nh$ .

It is worth noting that, generally speaking, the mentioned variants of calculating the SCs result in different values of the constants.

### 3. Calculation Results

Table 1 presents the results of the CAS(2,2)CCSD calculations of the SCs for three states of  $^{11}\text{BH}$  molecule. The PESs are approximated by functions (16)–(20). We also adduce the data of numerical differentiation. In order to find the accurate values of the SCs, we studied the accuracy of approximation in the narrow region of the PES curve close to the minimum. In addition to the equilibrium vibrational frequency  $\omega_e$  and the anharmonicity constant  $\omega_e x_e$ , Table 1 also presents the centrifugal distortion constant  $\bar{D}$ , the vibrational-rotational interaction constant  $\alpha_e$ , and the rotational constant  $B_e$ . These parameters are found by numerically integrating the energy  $E_{\text{CAS}(2,2)\text{CCSD}}$  with the use of 5 points. For comparison, we chose functions (16), (18), and (20) with the same number of the fitting parameters  $\alpha$  and  $\beta$ . The data of Table 1 exhibit some spread of the SC values caused by

<sup>1</sup> All calculations were performed in the atomic system of units.

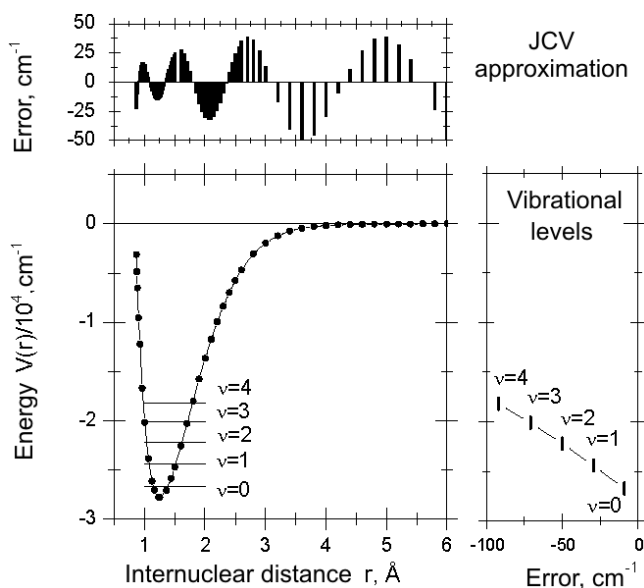


Fig. 3.  $^{11}\text{BH}(X^1\Sigma^+)$ , CAS(2,2)CCSD/cc-pVDZ, the accuracy of approximation by the JCV potential, and the calculation error of the vibrational terms

both the form of the potential and the mathematical method of obtaining the corresponding derivatives (analytically for the nonlinear approximation or numerically for the interpolation using five points). Nevertheless, the values obtained in the approximate CAS(2,2)CCSD method agree with the accurate FCI calculation for the ground state. For the lowest excited states, the CAS(2,2)CCSD calculation perfectly reproduces the values of equilibrium vibrational frequency and anharmonicity. However, a marked deviation from the experimental value is observed for the vibrational-rotational constants ( $\alpha_e$ ). In this case, one should take into account that the calculated value of  $\alpha_e$  depends on many factors and particularly depends on the quality of approximation of the potential function. This problem is studied in a number of works (see, e.g., [15]) stating among other things that none of the generalized Morse potentials can describe both most important molecular constants  $\alpha_e$  and  $\omega_e x_e$  with the same accuracy.

Figure 3 presents the  $X^1\Sigma^+$  PES curve and the accuracy of approximation by potential (18) calculated as the absolute deviation from the theoretical energies at separate PES points  $\Delta V$ . It is worth noting that such a behavior of the approximation accuracy is typical of all the investigated functions. In Fig. 3, one can see large absolute deviations in the region of the curve bend reach-

ing  $50\text{ cm}^{-1}$ , which can introduce an additional error in the calculation of the energy of vibrational terms.

The approximation of the  $A^1\Pi$  PES in the whole range of internuclear distances by functions (16)–(20) yielded the dissociation energies  $D_e^{\text{GM}} = 0.743\text{ eV}$ ,  $D_e^{\text{LJ}} = 0.766\text{ eV}$ ,  $D_e^{\text{JCV}} = 0.731\text{ eV}$ , and  $D_e^{\text{MS}} = 0.743\text{ eV}$  that agree with the experimental value  $D_e^{\text{exp}} = 0.697\text{ eV}$  [16]. It is worth noting that the approximation of *ab initio* data can considerably distort the accuracy of calculations reached by the quantum-chemical method.

The quality of the description of excited states by the CASCCSD method can be judged by the data of Table 2 displaying the results characterizing the  $A^1\Pi$  PES: the equilibrium internuclear distance  $R_e$ , the position of the barrier  $R^b$ , its height relative to the dissociation limit  $V^b$ , the dissociation energy  $D_e$ , the difference between the PES minimum and maximum energies  $V_{\text{max}} - \text{min}$ , and the transition energy  $T_e$ .

In addition, the accuracy of PES calculations depends on the basis set of atomic orbitals. According to the data of Table 2, the geometric PES parameters are systematically improved, when passing from the double to triple split-valence polarized basis set cc-pVTZ.

**Table 1.** CAS(2,2)CCSD and experimental values [17] of the molecular parameters for the  $X^1\Sigma^+$ ,  $A^1\Pi$ , and  $B^1\Sigma^+$  states of  $^{11}\text{BH}$ ,  $\text{cm}^{-1}$

Function	$R_e, \text{Å}$	$\omega_e$	$\omega_e x_e$	$\bar{D}, 10^{-3}$	$B_e$	$\alpha_e$
$N_{\alpha_i, \beta_i} = 6$						
$X^1\Sigma, R \in [0.9; 1.8], \text{cc-pVDZ}$						
LJ	1.2541	2343.5	49.26	1.140	11.61	0.4445
GM	1.2545	2346.8	50.75	1.134	11.60	0.4117
JCV	1.2548	2346.1	49.30	1.134	11.60	0.4010
FCI [18]	1.2559	2340.0	48.80	1.100	11.57	0.396
numerically						
“5 points”	1.2550	2348.9	43.20	1.127	11.58	0.396
Exper.	1.2324	2366.9	49.39	1.242	12.02	0.412
$A^1\Pi, R \in [0.9; 2.0], \text{cc-pVTZ}$						
LJ	1.2176	2250.52	56.833	1.48	12.316	0.467
GM	1.2169	2251.37	57.392	1.48	12.330	0.498
JCV	1.2200	2250.40	56.732	1.46	12.267	0.430
Exper.	1.2195	2250.99	56.665	1.45	12.295	0.835
$B^1\Sigma^+, R \in [0.9; 1.6], \text{cc-pVDZ}$						
GM	1.2309	2401.2	69.526	1.22	12.051	0.565
JCV	1.2073	2402.7	69.923	1.36	12.526	0.954
Exper.	1.2164	2399.9	69.51	1.26	12.339	0.485

The radial Schrödinger equation (22) was solved numerically using a mesh of 500–1000 values of  $\varphi_{\nu,J}$  in the interval  $r = [r_{\min}, r_{\max}]$ . Such a partition appears sufficient for the estimation of the energy of the lowest (to  $\nu = 7$ ) vibrational terms accurate to within  $0.01 \text{ cm}^{-1}$ . The corresponding experimental energies of the terms in the “zero” vibrational state  $G(\nu) = E_{\nu,0}$  were reproduced with the use of the RKR technique [13], and their values for the first five levels ( $\nu = 0 - 4$ ) amount to 1171.1, 3440.4, 5614.2, 7694.7, and 9684.0  $\text{cm}^{-1}$ , respectively.

Equation (22) was solved with the use of potentials (16) and (18). In this case, the accuracies of the description of vibrational states are comparatively equal provided that the number of fitting parameters is large enough. However, it is worth noting that, at  $q = 12$ , the number of variable parameters in the case of the Morse function is equal to 24, whereas it is only 13 for the James–Coolidge–Vernon function. The absolute deviations of the calculated values of  $\Delta G(\nu)$  from the experimental data for five first levels ( $\nu = 0 - 4$ ) are equal to  $-9.0$ ,  $-29.4$ ,  $-49.9$ ,  $-70.8$ , and  $-92.1 \text{ cm}^{-1}$ , respectively.

The transition energy  $T_e$  is usually calculated from the observed transitions with no regard for  $Y_{00}$  in the excited and ground states. According to the RKR data,  $T_e(B^1\Sigma^+) = 0.2384603 \text{ a.u.}$  ( $52\,336 \text{ cm}^{-1}$ ) [14]. We calculated the transition energy as  $T_e(B^1\Sigma^+) = E_{\min}(B^1\Sigma^+) - E_{\min}(X^1\Sigma^+) = 58\,256 \text{ cm}^{-1}$ . A considerable error in the excitation energy can be due to the drawback of the cc-pVDZ basis set. The corresponding transition energy obtained in the cc-pVTZ basis set  $T_e(B^1\Sigma^+) = 55\,830 \text{ cm}^{-1}$ . Moreover, it is worth noting that the calculation error irregularly varies along the curve, as the structure of the wave function fundamentally changes with increase in the interatomic distance.

The performed calculations have demonstrated a high efficiency of the CASCCSD technique. An active space

of dimension  $2 \times 2$  appears sufficient for qualitatively reproducing the PESs of the ground and excited states of BH (the existence of the potential barrier in the  $A^1\Pi$  state and the second minimum in the  $B^1\Sigma^+$  state). The SC values calculated as the corresponding coefficients of the Dunham expansion are in good agreement with the experimental data. The performed analysis of a number of analytical functions used for the approximation of the PESs testifies to the sensitivity of the calculated SC values to the form of the potential energy function and the number of fitting parameters.

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**Table 2. Theoretical and experimental parameters of the  $A^1\Pi$  state of  $^{11}\text{BH}$  molecule**

Parameter	CAS(2,2)CCSD		Experiment [16, 17]
	cc-pVDZ	cc-pVTZ	
$R_e$ (Å)	1.2424	1.2144	1.2195
$R^b$ (Å)	1.952	2.052	2.143
$V^b$ (eV)	0.22	0.14	$\geq 0.11$
$D_e$ (eV)	0.415	0.738	0.697
$V_{\max - \min}$ (eV)	0.632	0.88	$\geq 0.81$
$T_e$ ( $\text{cm}^{-1}$ )	24 445	23 436	23 136

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ПОВЕРХНІ ПОТЕНЦІАЛЬНОЇ ЕНЕРГІЇ ОСНОВНОГО  
ТА ЗБУДЖЕНИХ СТАНІВ МОЛЕКУЛИ  $^{11}\text{BH}$   
У МУЛЬТИРЕФЕРЕНСНІЙ ТЕОРІЇ  
ЗВ'ЯЗАНИХ КЛАСТЕРІВ

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Р е з ю м е

У методі мультуреференсної теорії зв'язаних кластерів проведено розрахунки поверхні потенціальної енергії (ППЕ) молекули  $^{11}\text{BH}$  в основному та збуджених станах. ППЕ апроксимовано за допомогою аналітичних функцій, що узагальнюють потенціал Морзе. Досліджено вплив точності апроксимації ППЕ на розв'язок радіального рівняння Шредінгера та значення спектроскопічних параметрів.