

MRCI potential energy curves and analytical potential energy functions for the $X^2\Sigma^+$ and $^2\Pi$ states of BO molecule

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The potential energy curves (PECs) of BO molecule, including Σ^+ and Π symmetries with doublet spin multiplicities, are obtained employing multi-reference configuration interaction (MRCI) method and Dunning's correlation consistent basis sets. The analytical potential energy functions (APEFs) are fitted using the Murrell-Sorbie (MS) function and the least square method. Based on the PECs, the spectroscopic constants of the states have been determined and compared with the theoretical and experimental results available to affirm the accuracy and liability of the calculations. The root-mean-square (RMS) errors between the fitted results and the *ab initio* values are too little in comparison with the chemical accuracy (349.755 cm^{-1}). It is shown that the present APEFs are accurate and can display the interaction between the atoms well. The present APEFs can be used to construct more complicated APEF or do some dynamic investigations.

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Boron clusters and boron-rich materials are very important species and have been widely used in industry and technology, including thermally and chemically stable insulators and high modulus boron-fiber composites. Currently, the studies of this system are very active in both experiment and theory. Langhoff *et al.*^[1] reported the spectroscopic parameters of B_2 molecule with multi-reference configuration interaction (MRCI) method^[2,3]. Yang *et al.* have performed investigations for the potential energy curves (PECs) and spectroscopic properties of B_2^+ ion at the quadratic single and double excitation configuration interaction (QCISD) level, and fitted the analytical potential energy functions (APEFs) with least square method^[4]. They also studied the geometrical and electronic properties of B_3^{+5} and B_4^{+6} clusters. Very recently, the ground and low-lying excited states of B_2^{++} have been studied by Zhang *et al.* employing MRCI method^[7]. The spectroscopic properties and APEFs of four metastable states have been reported in their work.

The determination of accurate data for bond dissociation energies as well as spectroscopic properties is very important for the interpretation of many spectroscopic and chemical phenomena. The tasks considering the chemical bonding in elemental boron alloy clusters on this system have also been completed over the past few years^[8-9]. Niu *et al.* studied some ions of boron and boron-rich clusters with the Becke 3-parameter (exchange), Lee, Yang, and Parr (correlation; density functional theory) (B3LYP) method and Moller-Plesset (MP_n) method with the basis sets (10s, 5p, 1d/3s, 2p, 1d). In 2004, *ab initio* methods with 6-311G* and cc-pVTZ basis sets have been used to calculate the equilibrium geometries and vibrational properties of nine electronic states of MgB_2 molecule by Yang *et al.*^[11]. They distinguished the ground state from the $^1A^1$ and $^3B^1$

states successfully and gave a preferred dissociation channel in their work.

Boron monoxide is the simplest boron oxide and has attracted persistent interest over the past four decades, primarily due to their roles in the combustion of boron and boranes. In 1981, Nemukhin *et al.*^[12] calculated the ground state and some low-lying excited electronic states ($^2,^4\Sigma$, $^2,^4\Pi$, and $^2,^4\Delta$) of BO molecule by using the complete active space self-consistent-field (CASSCF) method in conjunction with the basis sets of contracted Gaussian-type orbitals (CGTOs). PECs and some spectroscopic constants of these states were reported in their work. However, limited by the calculation level, the spectroscopic parameters deviated from the experimental data significantly. Taking the ground state as an example, the percentage error of the dissociation energy D_e was larger than 4.5% and the difference for the harmonic frequency ω_e was 23 cm^{-1} compared with the experimental value. In 2001, the theoretical study of the ground state of BO molecule was implemented by Papakondylis *et al.* using coupled cluster calculations (CCSD(T)) method in conjunction with a series of basis sets^[13]. As we all know, the APEFs are an effective way to research the spectroscopic properties of diatomic molecules^[14,15]. However, both Nemukhin *et al.*^[12] and Papakondylis *et al.*^[13] only paid attention to the spectroscopic constants, and the APEFs of the excited states were not considered in their studies.

In this letter, valence internally contracted MRCI including those configuration state functions (CSFs) that contribute most significantly to the correlation energy, is employed in our calculation to obtain PECs of the ground state $X^2\Sigma^+$ and one excited state $^2\Pi$. The MRCI calculations are preceded by the CASSCF calculations, in which all valence molecular orbitals are optimized and it is

regarded as the best method to treat the problems referring to correlation energy at present. The APEFs of these states are fitted using Murrell-Sorbie (MS) function^[16] and least square method. Based on the credible PECs and APEFs, the spectroscopic constants of the two states are determined. It is expected that our results can provide a thorough understanding for the electronic and spectroscopic properties of the two states. All calculations are carried out with MOLPRO program package.

The sequence of augmented basis sets aug-cc-pVnZ ($n=T, Q, 5$)^[17–19] is employed to generate the *ab initio* potential energy points for the ground state. Compared with experimental values in the literatures, the big basis set aug-cc-pV5Z is chosen in our calculation, although the basis sets play a little influence on the total energies. The basis set consists of (15s, 9p, 5d, 4f, 3g, 2h) primary Gaussian functions, which are contracted to (7s, 6p, 5d, 4f, 3g, 2h). For the linear molecule with $C_{\infty v}$ symmetry, it will be substituted by C_{2v} symmetry with the order of the irreducible representations as $a_1/b_1/b_2/a_2$ because MOLPRO can use Abelian point group symmetry only. In the CASSCF and subsequent MRCI calculation, eight molecular orbitals (MOs) are put into active space, including four a_1 , two b_1 , two b_2 symmetry MOs, which correspond to the $2s2p$ shells of the B atom and $2s2p$ shells of the O atom. The MOs which consist of $1s$ of both B and O atoms are always closed occupation.

The Σ^+ and Π symmetries with doublet spin multiplicities of BO molecule, which result in the $X^2\Sigma^+$ and $^2\Pi$ states, are considered in this work. We computed them with the same basis sets and occupation orbitals. The energy points of PECs are computed using a step of 0.005 nm. The positions and energies of the minima on the PECs are determined by interpolation method. The MS function seems to be useful to reproduce diatomic PECs, and has been widely used to deduce APEFs of many diatomic molecules^[20–22]. The common MS function is

$$V(\rho) = -D_e \left(1 + \sum_{i=1}^n a_i \rho^i \right) \exp(-a_1 \rho), \quad (1)$$

where $\rho = R - R_e$, R is the internuclear distance, R_e is the equilibrium bond length; D_e is the dissociation energy; the constants D_e and a_i are determined by fitting.

Usually, R_e is regarded as a fixed constant in the fitting process. Now, in order to obtain more satisfactory fitting

results, we let it join the fitting process. The term number of multinomial n , according to our experience, can influence the fitting quality. In some cases, satisfactory results can be obtained when it equals 9^[23–26]. However, after a series of attempts, we find that 11 should be employed as the value of n when fitting results of very high accuracy are expected. The spectroscopic constants can be determined by the relationship equations among spectroscopic constants and APEFs. The force constant can be calculated from the constants of MS potential energy function:

$$f_2 = D_e(a_1^2 - 2a_2), \quad (2)$$

$$f_3 = 6D_e \left(a_1 a_2 - a_3 - \frac{a_1^3}{3} \right), \quad (3)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3 - 24a_4), \quad (4)$$

where f_2 , f_3 , and f_4 are quadratic, cubic, and quartic force constants, respectively. Then the spectroscopic constants are

$$B_e = \frac{h}{8\pi c \mu R_e^2}, \quad (5)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 \mu c^2}}, \quad (6)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e} \left(\frac{f_3 R_e}{3f_2} + 1 \right), \quad (7)$$

$$\omega_e \chi_e = \frac{B_e}{8} \left[-\frac{f_4 R_e^2}{f_2} + 15 \left(1 + \frac{\omega_e \alpha_e}{6B_e^2} \right) \right], \quad (8)$$

where B_e is the rotational constant, h is the Planck constant, c is the velocity of light, μ is the reduced mass, α_e is the vibration-rotation coupling constant, $\omega_e \chi_e$ is the anharmonic vibrational frequency. Based on Eqs. (5)–(8) and the constants of MS potential energy functions, the spectroscopic constants of a diatomic molecule can be determined.

The PECs of the ground states ($X^2\Sigma^+$) are computed using MRCI method for three different basis sets, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z with the purpose of observing the effect of basis sets on the molecular properties. The total energies, dissociation energies, equilibrium positions, and vibrational frequencies based on the

Table 1. Spectroscopic Constants of Two Low-Lying States ($X^2\Sigma^+$, $^2\Pi$) of BO

		R_e (nm)	D_e (eV)	ω_e (cm ⁻¹)	$\omega_e \chi_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
$X^2\Sigma^+$	Present MRCI/BS1	0.12091	8.415	1876.23	10.1283	1.7872	1.642×10^{-2}
	MRCI/BS2	0.12105	8.370	1872.38	10.1177	1.7833	1.63×10^{-2}
	MRCI/BS3	0.12166	8.196	1885.29	10.0097	1.7654	1.608×10^{-2}
	Experiment ^[27]	0.12049	8.395	1885.69	11.8100	1.7820	1.660×10^{-2}
	Nemukhin's ^[12]	0.12200	7.970	1909.00	–	–	–
	Papakondylis ^[13]	0.12079	8.367	1862.80	–	–	–
$^2\Pi$	Present	0.13568	5.719	1271.91	10.1495	1.4193	1.736×10^{-2}
	Experiment ^[27]	0.13533	–	1260.70	11.1570	1.4018	1.960×10^{-2}
	Nemukhin's ^[12]	0.13800	4.800	1238.00	–	–	–

BS1, BS2, BS3 stand for the basis sets aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z, respectively.

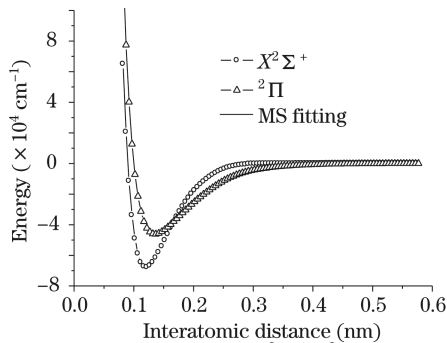


Fig. 1. PECs of the two states ($X^2\Sigma^+$, $^2\Pi$) for BO molecule (*ab initio* calculation at MRCI/aug-cc-pV5Z).

Table 2. Constants of MS Potential Energy Function for Two Low-Lying States ($X^2\Sigma^+$, $^2\Pi$) of BO

	$X^2\Sigma^+$	$^2\Pi$
D_e (cm $^{-1}$)	67878.73717	46130.12799
R_e (nm)	1.20919	1.35686
a_1 (nm $^{-1}$)	4.54914	4.41545
a_2 (nm $^{-2}$)	5.38572	6.39296
a_3 (nm $^{-3}$)	3.82102	6.52276
a_4 (nm $^{-4}$)	-0.84371	4.71097
a_5 (nm $^{-5}$)	-2.23797	4.64199
a_6 (nm $^{-6}$)	9.64322	2.91207
a_7 (nm $^{-7}$)	2.01371	-4.93681
a_8 (nm $^{-8}$)	-20.33698	-2.44484
a_9 (nm $^{-9}$)	15.94659	5.03335
a_{10} (nm $^{-10}$)	-4.65358	-1.87704
a_{11} (nm $^{-11}$)	0.47138	0.21937
RMS (cm $^{-1}$)	3.52908	0.01974

PECs are collected in Table 1, and the available experimental values are also presented. From the table, one can find that the basis sets have a little influence on the total energies. Comparing the spectroscopic constants with the experimental values, we find that the results based on aug-cc-pV5Z basis set is better, therefore it is chosen as the best basis set in the following analysis.

For each state, beginning from 0.082 nm, 100 points are calculated at 0.005-nm intervals. The computed PECs based on MRCI/aug-cc-pV5Z level are plotted in Fig. 1. The *ab initio* calculated energy points are fitted to APEFs employing the MS potential function and least square method. The fitted parameters are listed in Table 2.

In order to appreciate the quality of the fitting process, we also calculate the root mean square (RMS) error^[4]. RMS can be calculated with

$$\text{RMS} = \frac{1}{N} \sqrt{\sum_{i=1}^N (V_{\text{APEF}} - V_{\text{ab initio}})^2}, \quad (9)$$

where V_{APEF} and $V_{\text{ab initio}}$ are energies given by the fitting results and *ab initio* calculations, respectively. For the MS function, the calculated RMS values for the two states $X^2\Sigma^+$ and $^2\Pi$ are also listed in Table

1. As shown in the table, the smallest RMS is only 0.01974 cm $^{-1}$, and even the larger RMS is only 3.52908 cm $^{-1}$, which are much smaller than the chemical accuracy (349.755 cm $^{-1}$). It shows that our fitting process is of high quality, and the MS function is very suitable for reproducing the PECs of the two electronic states of BO molecule.

Based on the fitted parameters and Eqs. (5) – (8), the spectroscopic constants of the two states can be calculated. All of the calculated and experimental values are collected in Table 1. Furthermore, the credibility and precision of the APEFs can be evaluated by comparing the calculated spectroscopic constants with the available experimental and theoretical results. Compared with the previous theoretical results, our spectroscopic values obtained at the calculation MRCI/aug-cc-pV5Z are improved obviously. For the ground state $X^2\Sigma^+$, our calculated value of dissociation energy D_e is 8.415 eV, which is in excellent agreement with the experimental value of 8.395 eV by Huber *et al.*^[27]. Note that our harmonic frequency ω_e of 1876.23 cm $^{-1}$ is larger than the experimental value of 1885.69 cm $^{-1}$, but the percentage error is only 0.5%. The gap of equilibrium position R_e between our calculated value of 0.12091 nm and the experimental value of 0.12049 nm is only 0.00042 nm. For $\omega_e\chi_e$, B_e , and α_e , our theoretical results are also in good agreement with experimental values on the whole.

As can be seen from Table 1, for the excited state $^2\Pi$, our R_e value of 0.13568 nm is almost the same with the experimental value of 0.13533 nm, better than the theoretical value of 0.138 nm of Nemukhin *et al.*^[15]; the calculated ω_e value of 1271.91 cm $^{-1}$ is very close to the experimental value of 1260.70 cm $^{-1}$, better than the theoretical result of 1238.00 cm $^{-1}$ of Nemukhin *et al.*^[15]. The constants of $\omega_e\chi_e$, B_e , α_e also accord with the experimental values well. To our knowledge, the experimental dissociation energy of the $^2\Pi$ state has not been reported. Therefore we are unable to compare the present results with experimental work. From the comparison above, we have reason to believe that our calculated value of dissociation energy is credible. Therefore, it is concluded that the PEC calculations and APEF fitting are helpful way to obtain accurate spectroscopic constants.

In summary, the ground state ($X^2\Sigma^+$) as well as one excited states ($^2\Pi$) of BO molecule have been investigated employing the MRCI method and the augmented big basis set aug-cc-pV5Z. The PECs spanning the ranges of internuclear distances enough to determine the properties of the two states are obtained. The APEFs are deduced from the *ab initio* results using MS potential energy function and least square method. Based on the reliable APEFs, the spectroscopic constants have been obtained. The present spectroscopic constants are in excellent agreement with the available experimental values, which implicates that the calculations in the present work are reliable to investigate the BO molecule. The present APEFs display the interaction between B and O atoms well, and can be used to construct more complicated APEF or perform dynamic calculations.

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