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Potential energy curves and analytical potential energy functions of the metastable states of B_2^{++}

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The multi-reference configuration interaction method and aug-cc-pvqz (AVQZ) have been used to calculate potential energy curves (PECs) of the singlet and triplet states of the $\prod_u$ and $\prod_g$ symmetry of B_2^{++}. All of the four states ($^1\prod_u$, $^1\prod_g$, $^3\prod_u$ and $^3\prod_g$) are found to be metastable states, though the potential well of $^3\prod_u$ symmetry is very shallow. Based on the PECs, the analytical potential energy functions (APEFs) of these states have been fitted using the least square fitting method and two models of function. The spectroscopic parameters of each state are also calculated, and are compared with other investigations in the literature. The credibility and veracity of the two functions are evaluated. Some ideas to improve the fitting accuracy are presented. Also the vibrational levels for each state are predicted by solving the Schrödinger equation of nuclear motion.

Keywords: potential energy curves, analytical potential energy function, spectroscopic parameter, metastable state

PACC: 1240Q, 3120A, 3150

1. Introduction

Studies of boron cluster ions and boron-rich materials are currently very active areas in both experiment and theory,[1−5] for these systems have many important technological applications, including thermally and chemically stable insulators and high modulus boron fibre composites.[6] However, the number of experimental and theoretical studies of boron clusters has been rather limited. This is surprising because boron exhibits some of the most interesting chemistry of all elements in the periodic table.[7] Also the calculation studies of it are not abundant. Langhoff and Bauschlicher[8] worked out the spectroscopic parameters of B_2 with multi-reference configuration interaction (MRCI) method. Niu *at al*[9] studied some ions of boron and boron-rich clusters with B3LYP method and MP4 method with basis set (10s, 5p, 1d/3s, 2p, 1d). For the ion B_2^{++}, Bruna and Wright (BW) [10] have investigated it using MRCI method. The dissociation limits, potential energy curves and vibrational frequencies were reported, but the analytical potential energy functions (APEFs) were not given. Yang[11] has dealt with the $^3\prod_g$ state with the single-reference configuration interaction method (a quadratic CI calculation, including single and double substitutions) and 6-311G** basis set, and worked out the APEF and spectroscopic parameters. Because of the Coulombic repulsion, all the investigated states are metastable states, and the potential energy curves (PECs) have a maximum. So the usual potentials for binding states are not effective to fit APEF. Even the Murrell–Sorbie (MS) function, which has been employed to deal with the ground state and some low-lying excited states successfully,[12−16] is invalid. In 1997, Zhu and Wang (ZW)[17] proposed a function to fit this kind of PEC. However, it is proven to work well only in very small range of interatomic distance. In 2004, Wang, Yang and Zhu (WYZ)[18] presented another function. It is more effective when applied to BH^{2+}, He_2^{2+} and HF^{2+}.[19] However, in their work, the range of the interatomic distance is still limited, and the states treated are ground states. So it is necessary to apply the two functions to more molecules and more states to test them. In the present paper, we use the PECs of $\prod$ symmetry of B_2^{++} in a very large range of interatomic distance to test the two functions.

With the development of computer, numerous theoretical models and algorithmic progress have been made to take advantage of large inexpensive computer storage devices as well as enhanced parallel programming methods.[20] In the aspect of computational speed, more and more parallel computers are used. So

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we can obtain more credible results based on higher computational levels. In the present paper, the PECs of high accuracy are obtained by using MRCI method and aug-cc-pvqz (AVQZ) basis set. Then the PECs are fitted into APEFs using the least square fitting method. Based on the APEFs, the spectroscopic parameters are determined. Also vibrational levels for each state are predicted based on the PECs. Since the data of this body system are scarce, our present work can provide useful information for further experimental and theoretical studies.

2. The principle

All of the calculations are carried out on our supercomputer Dawning 4000 A[1)] by MOLPRO program. The MRCI[21,22] method and the AVQZ basis set have been used in all the calculations. As is known, the single-reference state methods are usually employed, because the calculation is less CPU time-consuming. However, their accuracy is not very good. MRCI is a way to systematically include those configuration state functions (CSFs) that contribute most significantly to the correlation energy. It is regarded as the best method to treat problems of correlation energy carefully, and is suitable for the calculation of PECs.[23] For the basis set, in the work of BW, it corresponds to Dunning's 5s3p(TZ) contraction of Huzinaga's 10s6p primitive set, and has been expanded by diffuse *s*- and *p*- functions and two uncontracted *d* functions.[10] Our AVQZ basis set is larger than theirs. It includes dispersion primary function, and can describe the interactions of large interatomic distance well.[23] So the MRCI/AVQZ computational level can give credible and accurate PECs. In the calculation, the interatomic distance is given in angstrom, and total energies are given in Hartree. For each state the interatomic distance ranges from 1.20 Å to 6.15 Å. Based on the computational energies, the APEFs are determined using potential energy function and least square fitting method. Then the spectroscopic parameters are determined according to the relations between APEF and spectroscopic parameters. Also the reliabilities of the ZW and WYZ functions are examined by comparing the root mean square (RMS) errors. Based on the PECs of each state, the vibrational levels are determined by solving Schrödinger equation of nuclear motion.

3. Interatomic potential models

The ZW potential energy function was proposed by Zhu and Wang in 1997, in order to treat the metastable state. It can describe the potential energy function of HCL^{++}, HBr^{++}, HI^{++}well,[11] but the nuclear distances considered are limited. Its form is simple. The common ZW function is

$$V(\rho) = a_1/(\rho - a_2) - a_3/(\rho - a_4)\,, \tag{1}$$

where $\rho = R - R_{\rm e}$, R and $R_{\rm e}$ are the interatomic distance and the equilibrium bond length, respectively. In order to improve the fitting accuracy, we add a parameter to it. So the function we use is

$$V(\rho) = a_1/(\rho - a_2) - a_3/(\rho - a_4) + a_5\,. \tag{2}$$

In 2004, Wang Yang and Zhu[18] proposed a new function for diatomic cations to describe the metastable state. The function includes two parts, the Coulomb potential term and the Varandas potential term. They can be written as

$$V_{\rm Coul} = C/R\,, \tag{3}$$

$$V_{\rm Var} = \Big(\sum_{n=0}^{k} a_n R_n\Big)\exp(-a_{k+1}R)\,. \tag{4}$$

So the general function is

$$V = C/R + \Big(\sum_{n=0}^{k} a_n R_n\Big)\exp(-a_{k+1}R)\,, \tag{5}$$

where C, a_n, and a_{k+1} are parameters to be determined, and R is the interatomic distance. In fact, as we can see from Eq.(5), it can be regarded as a modified form of MS function. Wang *at al* apply the function to BH^{2+}, He_2^{2+} and HF^{2+}.[23] However, in their work, k is fixed at 3. According to our experience, the number of multinomial can influence the fitting quality. So we suggest that for different molecules, the value of k should be different. For B_2^{++}, after a series of tries, we find that better results can be obtained when $k = 9$. Also we have used the functions with $k = 3, 6$ to compare their accuracies in describing metastable states.

We can calculate the spectroscopic parameters with the equations as follows:

$$B = \frac{h}{8\pi c\mu R_{\rm e}^2}\,, \tag{6}$$

[1)] Dawning 4000 A is a large parallel computer containing 134 CPUs (AMD Opteron 64-bit 1.8GHz) in Yantai Normal University. It is based on Turbo Linux 8.0 and implements with Molpro2002, Gaussian03, Molcas 5.0 and so on.

$$\omega = \sqrt{\frac{f_2}{4\pi^2 mc^2}}\,, \tag{7}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3 R_e}{3f_2} + 1\right), \tag{8}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4 R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)\right], \tag{9}$$

where f_2, f_3 and f_4 are the quadratic, cubic and quartic force constants which could be derived from the potential function (5).

4. Results and discussion

4.1. The analytical potential energy functions and spectroscopic parameters

For each state, beginning from 1.2 Å, 100 points are calculated at 0.05 Å intervals. The computational PECs based on MRCI/AVQZ level are plotted in Fig.1, in which all the curves have maximum, so these states are metastable states. Also we can see that for larger R, the PECs of $^3\prod_u$ and $^3\prod_g$ symmetry are almost overlapped, indicating that the two states have the same dissociation limit. In the same measure, the $^1\prod_u$ and $^1\prod_g$ states have the same dissociation limit.

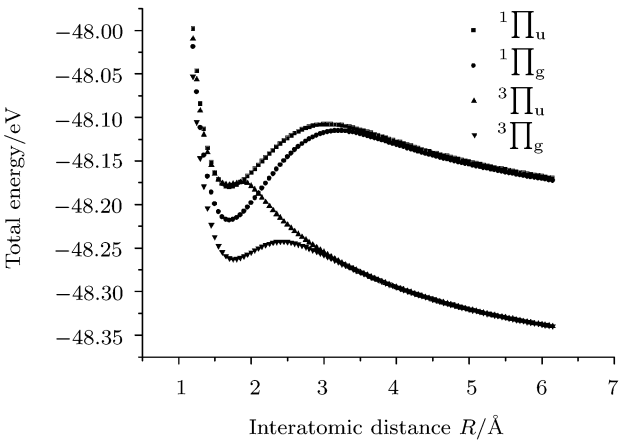


Fig.1. PECs of the 4 states ($^1\prod_u$,$^1\prod_g$, $^3\prod_u$ and $^3\prod_g$) for B_2^{++} (*ab initio* calculation at MRCI/AVQZ level).

The fitted PECs for each state using WYZ function are shown in Fig.2 and those using ZW function are shown in Fig.3. From Fig.2, we can see that the curves fitted with WYZ function are in good agreement with the results of *ab initio* calculations. However, as can be seen in Fig.3, the fitted curves with ZW function cannot accord well with the calculated results. The parameters for states $^1\prod_u$, $^1\prod_g$ and $^3\prod_g$ obtained using WYZ and ZW functions are listed in Table 1 and Table 2 respectively.

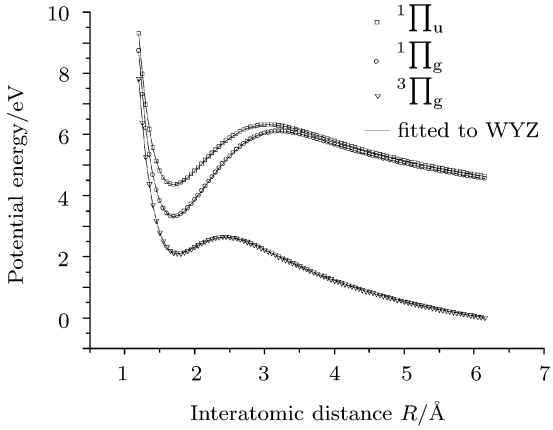


Fig.2. PECs of the states ($^1\prod_u$,$^1\prod_g$ and $^3\prod_g$) for B_2^{++} (*ab initio* calculation and fit to WYZ potentials).

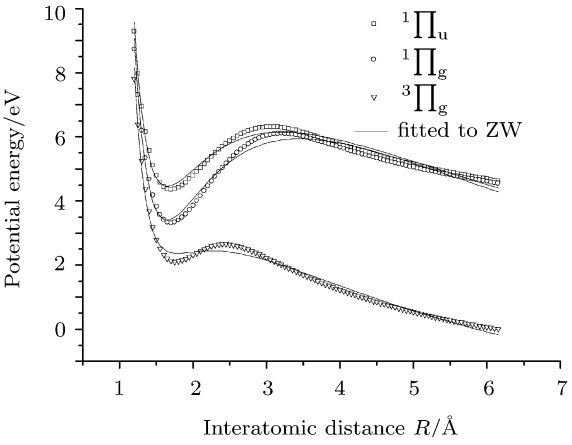


Fig.3. PECs of the states ($^1\prod_u$,$^1\prod_g$ and $^3\prod_g$) for B_2^{++} (*ab initio* calculation and fit to ZW potentials).

In order to evaluate the quality of fitting process quantificationally, we also calculate the RMS error as follows:

$$\mathrm{RMS} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(V_{\mathrm{APEF}} - V_{ab\ initio})^2}\,, \tag{10}$$

where V_{APEF} and $V_{ab\ initio}$ are energies given by the fitting and *ab initio* calculations, respectively. The RMS errors for each state by using the two functions are listed in Table 3. As can be seen, the RMS errors obtained using ZW function are obviously larger than those by using the WYZ function. The RMS errors of the former even exceed the chemical accuracy

(1.0 kcal/mol or 0.0433641 eV) which indicates that the deduced APEFs using the ZW function are not creditable. While, all the RMS errors for the states $^1\prod_u$ $^1\prod_g$ and $^3\prod_g$ by using the WYZ function are tolerable, indicating that the deduced APEFs are creditable and can be used for further studies. For the states of $^3\prod_u$, the potential energy well is very shallow (only 0.0841 eV). The RMS errors for this state calculated with the two models are large in comparison with the chemical accuracy (0.0433641 eV) and the depth of potential energy well (0.0841 eV) . For example, the RMS error obtained using WYZ function is 0.0219 eV. Neither of the two functions is suitable to reproduce this kind of state. So the APEF for the state of $^3\prod_u$ are incredible, and the parameters are not listed in Table 1 and Table 2.

Table 1. Parameters for states ($^1\prod_u$, $^1\prod_g$ and $^3\prod_g$) of B_2^{++} using the WYZ function.

parameters	$^1\prod_u$	$^1\prod_g$	$^3\prod_g$
a_0/eV	4.3753	3.3192	2.0980
a_1/eV·Å^{-1}	6.3272	4.7925	3.8986
a_2/eV·Å^{-2}	14.5495	13.3461	9.8027
a_3/eV·Å^{-3}	2.2167	1.2246	1.0645
a_4/eV·Å^{-4}	4.5366	4.0416	–1.9353
a_5/eV·Å^{-5}	0.4848	0.1815	–0.8298
a_6/eV·Å^{-6}	–1.9239	–1.7974	2.6716
a_7/eV·Å^{-7}	1.3060	1.133	–1.4166
a_8/eV·Å^{-8}	–0.3050	–0.2484	0.3203
a_9/eV·Å^{-9}	0.0302	0.0215	–0.0281
a_{10}/Å^{-1}	1.6463	1.5224	1.8450
$C/10^{-5}$eV·Å	–0.00071	–7.0000	–6.0000
R_e/Å	1.6500	1.6844	1.7610

Based on the relationship between spectroscopic parameters and APEFs, i.e. Eqs.(6)–(9), the spectroscopic parameters can be calculated. Furthermore, the results can be compared with those in Refs.[5] and [6]. The parameters used for the WYZ function are listed in Table 4. For the state of $^3\prod_u$, whose potential energy well is shallow, based on the fitted results, the obtained spectroscopic parameters are imaginary numbers which do not have physical meaning. The parameters for $^1\prod_u$, $^1\prod_g$ and $^3\prod_g$ are listed in Table 4. As can be seen in the table, the calculated values of R, ω_e, $\omega_e\chi_e$ and α_e, for $^3\prod_g$ symmetry have some little gap compared with that by Yang and BW. Data for other states are absent, so the calculated values are only listed for further study. For the results obtained using the ZW function, the RMS errors for all the four states exceed the chemical accuracy, so they cannot provide credible dada for further study. Just for this, the spectroscopic parameters used in the ZW function are not listed. As both the method and basis set are more advanced than those reported formerly, our results will be more credible, although other states of $\prod$ symmetry have not been treated. APEFs for $^1\prod_u$, $^1\prod_g$ and $^3\prod_g$, which are not reported in the former work, are given here. Since the values for these states are limited, our work can provide information for experimental and theoretical investigations for B_2^{++} ion.

Table 2. Parameters for states ($^1\prod_u$, $^1\prod_g$ and $^3\prod_g$) of B_2^{++} using the ZW function.

parameters	$^1\prod_u$	$^1\prod_g$	$^3\prod_g$
a_1/eV·Å	76.4440	90.5051	40.7805
a_2/Å	−1.1699	−1.2212	−0.9947
a_3/eV·Å	236.5879	332.2050	89.7574
a_4/Å	2.0257	2.14152	1.6402
a_5/eV	−3.6407	−5.6166	−5.2446

Table 3. RMS errors with the two potential energy functions (in eV).

functions used	$^1\prod_u$	$^1\prod_g$	$^3\prod_u$	$^3\prod_g$
WYZ	1.68×10^{-3}	3.16×10^{-3}	2.19×10^{-2}	2.34×10^{-3}
ZW	1.31×10^{-1}	1.60×10^{-1}	1.25×10^{-1}	1.41×10^{-1}

Table 4. Calculated spectroscopic parameters of B_2^{++} with the WYZ function.

parameters	$^1\prod_u$	$^1\prod_g$	$^3\prod_g$	$^3\prod_g$[6]	$^3\prod_g$[5]
R_e/Å	1.6500	1.6844	1.7610	1.7723	1.7752
B_e/cm^{-1}	1.1456	1.0993	1.006	0.975	
ω_e/cm^{-1}	1006.2	997.89	788.5	666.8	674
$\omega_e\chi_e$/cm^{-1}	7.5578	6.9768	16.90	37.18	
$\alpha_e/10^{-2}$cm^{-1}	1.32	1.19	1.99	4.21	

It should be noted that the two potential models have different applicable ranges. In fact, in the fitting process, we find that for a small range of R, the gap between the RMS errors of the two functions is not very large, and the two functions can give tolerable results. However, for larger R, the ZW function cannot give tolerable results, while the WYZ function

still can. We can see this clearly in Table 3 by comparing their RMS errors. So we can conclude that the WYZ function is more effective than the ZW function, especially for large R.

For the WYZ function, we also compare its reliability with different values of k. For $k = 3, 6$ and 9, the RMS errors are listed in Table 5, from which we can see obviously that the larger the k, the smaller the RMS error. So we suggest that for the WYZ function a larger value of k can give better results.

Table 5. RMS errors for the four states obtained with WYZ function when $k = 3$, 6 and 9 (in eV).

K	$^1\prod_u$	$^1\prod_g$	$^3\prod_u$	$^3\prod_g$
3	3.63×10^{-2}	2.97×10^{-2}	1.84×10^{-1}	7.62×10^{-2}
6	4.47×10^{-3}	8.37×10^{-3}	4.67×10^{-2}	1.05×10^{-2}
9	1.68×10^{-3}	3.16×10^{-3}	2.19×10^{-2}	2.34×10^{-3}

4.2. The vibrational levels

Based on the calculated PECs, we can predict the vibrational levels of each state. The vibrational levels are determined by solving the Schrödinger equation of nuclear motion, and can be used to identify the molecule. The vibrational levels for states $^1\prod_u$, $^1\prod_g$ and $^3\prod_g$ are collected in Table 6. From the table we can see that 23, 31 and 6 vibrational levels are found respectively. However, for the $^3\prod_u$ state, only 33 rotational energy levels are found and no excited vibrational level is found due to the shallow well in the PEC. As there are no experimental vibrational levels of B_2^{++} reported to date, we hope that the present calculated results can be used as a reference for further study.

Table 6. Vibrational levels of the $^1\prod_u$, $^1\prod_g$ and $^3\prod_g$ states based on the PECs (in cm^{-1}).

v	$^1\prod_u$	$^1\prod_g$	$^3\prod_g$
1	871.98	948.9298	738.9959
2	1727.1955	1883.9466	1444.3294
3	2565.5443	2805.1867	2111.786
4	3386.9088	3712.4033	2735.1635
5	4191.1522	4604.9247	3304.0761
6	4978.1153	5483.1365	3794.0357
7	5747.6134	6347.4542	
8	6499.4314	7197.2512	
9	7233.3176	8032.4646	
10	7948.9775	8853.0438	
11	8646.0641	9658.7939	
12	9324.1663	10449.596	
13	9982.7934	11225.2376	
14	10621.355	11985.5141	
15	11239.1308	12730.1782	
16	11835.2299	13458.9532	
17	12408.5298	14171.5204	
18	12957.5813	14867.5114	
19	13480.4513	15546.5006	
20	13974.4379	16207.9892	
21	14435.4789	16851.3904	
22	14856.6258	17476.0037	
23	15221.1401	18080.9843	
24		18665.2953	
25		19227.6378	
26		19766.3413	
27		20279.1812	
28		20763.0535	
29		21213.3270	
30		21622.1396	
31		21968.9635	

5. Conclusion

We have investigated the four states of $\prod$ symmetry of B_2^{++} with MRCI method and AVQZ basis set. All the states are found to be metastable ones and the PECs have maximum. The ZW function and WYZ function are employed to fit the APEFs of the PECs. The APEFs and spectroscopic parameters for state $^1\prod_u$, $^1\prod_g$ and $^3\prod_g$ are determined. By comparison, we find that the WYZ function is more credible for dealing with the metastable states than the ZW function, especially for larger R. Also we find that increasing k in WYZ function can significantly improve the fitting quality. Based on the calculated PECs, the vibrational levels of each state are predicted for further study of this ion.

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