An *ab initio* investigation of the low-lying electronic states of BeH

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Potential energy curves (PECs) for the ground state ($X^2\Sigma^+$) and the four excited electronic states ($A^2\Pi$, $B^2\Pi$, $C^2\Sigma^+$, $^4\Pi$) of a BeH molecule are calculated using the multi-configuration reference single and double excited configuration interaction (MRCI) approach in combination with the aug-cc-pVTZ basis sets. The calculation covers the internuclear distance ranging from 0.07 nm to 0.70 nm, and the equilibrium bond length R_e and the vertical excited energy T_e are determined directly. It is evident that the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Pi$, $C^2\Sigma^+$ states are bound and $^4\Pi$ is a repulsive excited state. With the potentials, all of the vibrational levels and inertial rotation constants are predicted when the rotational quantum number J is set to be equal to zero ($J = 0$) by numerically solving the radial Schrödinger equation of nuclear motion. Then the spectroscopic data are obtained including the rotation coupling constant ω_e, the anharmonic constant $\omega_e x_e$, the equilibrium rotation constant B_e, and the vibration–rotation coupling constant α_e. These values are compared with the theoretical and experimental results currently available, showing that they are in agreement with each other.

Keywords: multi-configuration reference single and double excited configuration interaction method, BeH potential curves, vibrational levels, spectroscopic constants

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1. Introduction

The BeH molecule, composed of two nuclei and five electrons, is radical with a very convenient number, and the advantage of studying this small system is that it is an ideal material for serving as a "touchstone" of testing new approaches in calculation.[1] Being a relatively simple system in beryllium hydride, BeH plays a significant role in constituting and researching the complex beryllium compounds, especially for the BeH_2 molecule, which is used as rocket solid fuel[2] and target molecules.[3−5] Therefore it is of vital significance to investigate the electronic structure and the spectral properties of the ground state and the excited states of BeH. Currently, studies of this molecule are very active in both experiment and theory.

Experimentally, although its spectra were observed more than a century ago, most of transition bands have been investigated in detail only in the past several decades. For example, the studies on the BeH molecule describing the $A^2\Pi$–$X^2\Sigma^+$ emission band system at 500 nm were first reported by Watson *et al.*[6] in the late 1920 s and early 1930 s.[7−9] Later, a sequence of strong degraded violet bands from 0–0 to 3–3 at 196 nm in an absorption spectrum was assigned by Watson and Humphreys.[10] De Greef and Colin[11] analysed the absorption and emission of a number of excited states of this molecule. Those detailed spectrum analyses have produced a lot of useful information and data, which will be compared with our calculation results. However, BeH has been less studied experimentally than other small systems because of the toxicity of beryllium. Up to now, a large number of theoretical investigations of BeH have been carried out. Jiang and Wu,[12] used a CCSD method to obtain the molecular structure and potential energy function for the ground state of BeH. Machado *et al.*[13] calculated the radiative transition probabilities and lifetimes for the band systems $A^2\Pi$–$X^2\Sigma^+$ and $C^2\Pi$–$X^2\Sigma^+$ of BeH molecule by employing the CASSCF method. Pitarch-Ruiz *et al.*[14] obtained the low-lying valence and Rydberg excited states of BeH by taking the FCI approach. Henriet and Verhaegen[15] calculated the five lowest states of both $^2\Pi$ and $^2\Sigma^+$ symmetries, including the dipole moments and the spec-

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troscopic constants at the LCAO-MO-SCF level.

However, limited by the calculation level, the spectroscopic parameters deviated from the experimental data greatly. In addition, the theoretical studies focused only on the ground state and the first excited state. The rest of the present paper is organized as follows. In Section 2 the computational method and specific steps will be discussed. In Section 3, the results of each state will be presented and compared with other available theoretical and experimental results. In the last section a summary of our calculations will be given.

2. Computational method

Nowadays *ab initio* methods are still under development and under improvement in the two important aspects, i.e., accuracy and application. Looking at a variety of *ab initio* methods, the single reference method is usually employed because the calculation is less CPU time-consuming. However, its accuracy is limited.[16] On the contrary, the full configuration interaction (FCI) method is successful in solving the Schrödinger equation, but usually too complicated to compute molecules containing more electrons. The multi-reference configuration interaction (MRCI)[17,18] method that is obtained by simplifying the FCI method is good at dealing with the abovementioned two aspects and it is a way to systematically include those configuration state functions (CSFs) that contribute most significantly to the correlation energy. As is well known, the correlation energy has an important effect on the quality of spectroscopic parameters and molecular constants in the quantum chemistry calculations. The MRCI is regarded as the best method to treat problems related to the correlation energy at present. Besides, the MRCI theory has been proved to be successful particularly in a number of high-quality spectroscopic results for a number of diatomic molecules in recent years.[19−21]

In the present paper, we are basically concerned with descriptions of the Σ^+ and Π symmetries with doublet and quartet spin multiplicities of the BeH molecule. First, we determine the equilibrium internuclear distance R_e of the ground state of the BeH molecule by the geometry optimization using the second-order electron correlation Moller–Plesst (MP2) perturbation method. Next, a common set of molecule orbitals for the next CI calculations of BeH is derived from a multi-configuration self-consistent field (MCSCF) solution, which is obtained by complete active space self-consistent field (CASSCF) method. In general, we choose and put the orbitals with electronic charges between $0.003e$ and $1.999e$ into the CASSCF active space. The use of the active space ensures that no important orbits exist in the subsequent MRCI calculation outside the reference space. Six valence orbitals, correlated in the MRCI treatment, are put into the full valence active space including three electrons and the remaining two electrons of the BeH molecule are put into the inner-shell orbitals. Therefore, within each spin symmetry, a common set of averaged natural orbitals to be used for all states is computed using the CASSCF (3,6) wavefunctions where all possible electronic excitations resulting from the distribution of 3 electrons into 6 active orbitals were allowed. Then, we use these molecular orbitals (MOs) to calculate the potential energy curves (PECs) by employing the MRCI approach over the internuclear distance range from about 0.07 nm to 0.7 nm. In order to obtain more reliable results, the PECs are made in steps of 0.008 nm and corrected for size-extensive errors by means of the Davidson modification (MRCI+Q).[22] Totally, 81 points are calculated separately for all states of the BeH molecule. We take into account that all single and double excitations from the reference sets generated by all CASSCF configurations and core orbitals are kept frozen in all calculations.

The basis set used in the present investigation is essentially of the correlation-consistent polarized-valence triple-zeta (cc-pVTZ) type developed by Dunning. For Be, the basis set is [21s6p3d2f] contracted to [5s4p3d2f] and for H, the basis set is [6s3p2d] contracted to [4s3p2d]. The basis set consists of 93 primitive Gaussian functions and 69 contracted basis functions. In addition, there are 50 configurations and 70 CSFs in the CASSCF calculation. All of the above calculations are carried out by using ORCA program package.[23]

Finally, the single point energies of the ground state and the excited states of BeH are scanned using the MRCI approach and then a series of single point energies are obtained. Based on the potentials, the radial Schrödinger equation of nuclear motion is numerically solved to predict all the vibrational states when the rotational quantum number J is set to be equal to zero ($J = 0$). And the spectroscopic data are also obtained. This calculation is performed with the LEVEL8.0 computer program package.[24]

3. Results and discussion

3.1. Potential energy curves

Figure 1 shows the lowest-lying electronic states with the doublet and quartet spin multiplicities of the BeH molecule. It is obvious that curves 2 and 3 as well as curves 5 and 6 are in complete coincidence, meaning that they are degenerate states. The potential energy curves of the ground state $X^2\Sigma^+$ and the excited states $A^2\Pi$, $B^2\Pi$, and $C^2\Sigma^+$ with the minimum energy points demonstrate that those states are stable bound states. However, the excited state $^4\Pi$ is a repulsive excited state. We find that the eight PECs smoothly tend to the three different dissociation limits respectively.

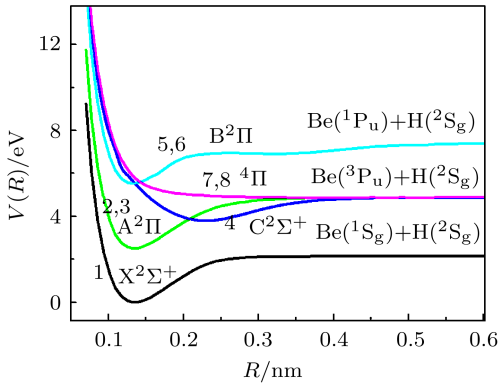


Fig. 1. (colour online) Low-lying potential energy curves of BeH, obtained from MRCI calculation.

Now we analyse the behaviour of the potential energy curves at the dissociation limit. The interaction between atoms within a molecule is governed by the electronic potential energy surface of the system. The electronic potential energy surface describes the molecular structure and molecular spectrum and acts as the base of researching the time-dependant process, which matches a definite electronic state of a molecule or radical. The potentials covered 81 single point energies for each curve are calculated using the MRCI method through solving the resulting Schrödinger equation for the electronic motion. The eight PECs represent the different states $X^2\Sigma^+$, $A^2\Pi$, $B^2\Pi$, $C^2\Sigma^+$, and $^4\Pi$ of BeH molecule respectively correlated with the three lowest-lying dissociation channels: $Be(^1S_g)+H(^2S_g)$, $Be(^3P_u)+H(^2S_g)$, and $Be(^1P_u)+H(^2S_g)$. According to the atomic and molecular reaction statics,[25] the possible electronic states can be determined. The ground electronic state of a Be atom is ^1S_g, and that of H is ^2S_g. When the $Be(^1S_g)$ atom reacts with $H(^2S_g)$ atom and thereby produces a BeH molecule, the systematic symmetry decreases. The irreducible representation of the atomic group can be decomposed into the direct sum of the irreducible representations of molecular $C_{\infty v}$ point group. Considering the spin multiplicity and eliminating the subscript g and u, we obtain the irreducible representation of $C_{\infty v}$ group, namely the possible electronic states, can be deduced using the direct product and reduction. The irreducible representations of ^1S_g and ^2S_g decomposed from $C_{\infty v}$ group are $^1S_g \rightarrow {}^1\Sigma_g^+$ and $^2S_g \rightarrow {}^2\Sigma_g^+$. It should be determined that the ground state $X^2\Sigma^+$ included in the combination of $^1\Sigma_g^+ \otimes {}^2\Sigma_g^+$ is the only electronic state correlated with the first dissociation channel, $Be(^1S_g)+H(^2S_g)$. Equally, when Be is in the symmetric states of ^3P_u and ^1P_u, the irreducible representations are $^3P_u \rightarrow {}^3\Sigma_u^+ + {}^3\Pi_u$ and $^1P_u \rightarrow {}^1\Sigma_u^+ + {}^1\Pi_u$, respectively. Whereas for the $A^2\Pi$, $C^2\Sigma^+$, and $^4\Pi$ states these fragments are $Be(^3P_u)+H(^2S_g)$, and the last molecule dissociation channel is determined. Using the invertible micro-process principle, the above can be expressed as

$$\begin{aligned}
&BeH(X^2\Sigma^+) \rightarrow Be(^1S_g) + H(^2S_g),\\
&BeH(A^2\Pi, C^2\Sigma^+, {}^4\Pi) \rightarrow Be(^3P_u) + H(^2S_g),\\
&BeH(B^2\Pi) \rightarrow Be(^1P_u) + H(^2S_g).
\end{aligned}$$

3.2. Vibrational levels

The vibrational energy levels are determined by solving the Schrödinger equation of nuclear motion with the Level 8.0 Program. Vibrational spectroscopy plays a fundamental role in molecular physics, specifically, vibrational molecular analysis provides important information about the structure of molecules. In order to investigate all the vibrational levels accurately for each state, only the PECs can be used for studying the asymptotic energies. Based on this criterion, we use PECs to calculate the vibrational levels of $X^2\Sigma^+$, $A^2\Pi$, $B^2\Pi$, $C^2\Sigma^+$ states, respectively.

We select the 81 potentials with the internuclear distances ranging from 0.07 nm to 0.70 nm for each state of BeH and take the radial integration mesh $RH = 0.0001$ nm with the integral area ranging from 0.06 nm to 9.90 nm. The cubic spline function is used as the interpolation function of the MRCI values in the integration range; on the other hand, the exponential function and the inverse power function as extrapolate potential energy functions for the outside values,

The predicted the vibrational level and rotational constants of the four states are listed in Table 1. In total, 14 vibrational levels are found for the ground state $X^2\Sigma^+$, 15 for the $A^2\Pi$ state, 12 for the $C^2\Sigma^+$ state, and 7 for the $B^2\Pi$ state. For the sake of concision, only 10 vibrational energy levels of each state are shown in the table. We can see that the energy gaps between the levels of the ground state are large enough to be clearly distinguished in experiment. As there are no experimental vibrational levels of a BeH dimer available up to date, we hope that the present calculation results can be helpful for further studies.

Table 1. Vibrational levels and rotational constants of BeH for the low-lying states.

υ	$X^2\Sigma^+$		$A^2\Pi$		$C^2\Sigma^+$		$B^2\Pi$	
	$G(\upsilon)/\mathrm{cm}^{-1}$	$B_\upsilon/\mathrm{cm}^{-1}$	$G(\upsilon)/\mathrm{cm}^{-1}$	$B_\upsilon/\mathrm{cm}^{-1}$	$G(\upsilon)/\mathrm{cm}^{-1}$	$B_\upsilon/\mathrm{cm}^{-1}$	$G(\upsilon)/\mathrm{cm}^{-1}$	$B_\upsilon/\mathrm{cm}^{-1}$
0	1014.1856	10.06549	1010.593	10.17224	499.0604	3.51705	1135.7005	10.45227
1	3018.4285	9.75657	2986.594	9.84196	1488.602	3.50763	3208.7424	10.11191
2	4921.9768	9.44249	4879.587	9.50019	2431.283	3.48591	5200.6419	9.70123
3	6742.6587	9.12007	6686.136	9.14641	3328.603	3.44895	7035.3773	9.28189
4	8481.2414	8.78111	8402.657	8.77872	4177.097	3.39308	8752.3367	8.69515
5	10132.7572	8.41665	10026.3	8.38469	4975.451	3.31993	10260.8205	7.88525
6	11685.8039	8.00775	11552.17	7.95974	5720.350	3.21603	11282.0844	5.50159
7	13133.4568	7.54022	12973.47	7.49490	6406.406	3.08327		
8	14452.8311	6.98218	14281.94	6.98688	7028.770	2.90982		
9	15614.4779	6.25776	15465.25	6.42493	7578.877	2.68737		
10	16565.7906	5.43441	16508.51	5.79873	8043.419	2.38605		

3.3. Spectroscopic parameters

In this work, we provide a useful way to obtain the spectroscopic parameters based on a series of vibrational levels of the ground state $X^2\Sigma^+$ and the excited states $A^2\Pi$, $B^2\Pi$, and $C^2\Sigma^+$ of BeH. Now, the spectroscopic parameters, ω_e, $\omega_\mathrm{e}x_\mathrm{e}$, B_e, and α_e, are fitted by employing the Origin 7.5 program package according to the equations given next in Ref. [26].

$$G(\upsilon) = \omega_\mathrm{e}(\upsilon + 0.5) - \omega_\mathrm{e}x_\mathrm{e}(\upsilon + 0.5)^2, \quad (1)$$

$$B_\upsilon = B_\mathrm{e} - \alpha_\mathrm{e}(\upsilon + 0.5) + \gamma_\mathrm{e}(\upsilon + 0.5)^2. \quad (2)$$

The calculated results are given in Table 2. In addition, we also collect the available measurements and other calculations in the table for convenient comparison.

Table 2. Spectroscopic constants of the low-lying electronic states of BeH.

State		R_e/nm	T_e/eV	$\omega_\mathrm{e}/\mathrm{cm}^{-1}$	$\omega_\mathrm{e}x_\mathrm{e}/\mathrm{cm}^{-1}$	$B_\mathrm{e}/\mathrm{cm}^{-1}$	$\alpha_\mathrm{e}/\mathrm{cm}^{-1}$
$X^2\Sigma^+$	MRCI	0.1336	0	2066.2	38.7	10.262	0.308
	EXP[27,28]	0.1343	0	2060.8	36.3	10.316	0.303
	THERO[29]	0.1354	0	2048.4	41.0	10.154	0.274
$A^2\Pi$	MRCI	0.1333	2.49	2073.8	40.1	10.328	0.311
	EXP[30]	0.1334	2.49	2088.6	40.1	10.457	0.322
	THERO[31]	0.1334	2.46	2080.7	45.3	9.3641	0.326
$C^2\Sigma^+$	MRCI	0.2300	3.80	1060.6	39.7	3.494	–0.029
	EXP[11]	0.2301	3.84	1061.2	42.2	3.514	–0.022
	THERO[32]	0.2307	3.83	1053.6	31.4	3.496	
$B^2\Pi$	MRCI	0.1302	6.00	2260.1	71.2	10.523	0.173
	EXP[27,28]	0.1310	6.31	2265.9	71.5	10.849	0.102

As may be seen, the agreement between the results using the MRCI approach and the experimental results is extremely good. In detail, the spectroscopic parameters, R_e and T_e, which are directly obtained from the PECs, are in excellent agreement with the measurements. The remaining spectroscopic parameters, such as ω_e, $\omega_\mathrm{e}x_\mathrm{e}$, B_e, and α_e, which are reproduced from the vibrational levels obtained in this paper, also accord well with the available measurements. For example, the largest deviation of the ground state

from the $\omega_e x_e$ is 6.6% and the others are less than 1% compared with the measurements. And the deviations of the $A^2\Pi$ state are also only 0.7%, 0.1%, 1.2%, and 3.4% for ω_e, $\omega_e x_e$, B_e, and α_e respectively. For the $B^2\Pi$ state, there appears to be no theoretical value for comparison, but we note that our data accord very well with the experimental values. It further proves that the present MRCI is credible and accurate, and can be used to perform the vibrational manifold calculations.

4. Conclusions

In this paper, we report on the potential energy curves, vibrational energy levels, and spectroscopic constants for four low-lying states of BeH. Based on the potentials obtained from the MRCI method and the cc-pVTZ basis set, all of the vibrational states and the spectroscopic constants are predicted when the rotational quantum number J equals zero, showing that the present spectroscopic constants are in excellent agreement with the available experimental values and more accurate as a whole than the previous theoretical investigations, which means that the calculation method presented in this paper is reliable and feasible. And our work can provide a reference for experiment and perform dynamic calculations in the future.

References

[1] Robert J, Le Roy, Dominique R T, Appadoo and Reginald Colin 2006 *J. Mol. Spectrosc.* **236** 175

[2] Luo J S, Wu W D and Tang Y J 2006 *High Power Laser and Particle Beams* **18** 85

[3] Henriet C and Verhaegen G 1984 *J. Mol. Struct.* **107** 68

[4] Shayesteh A, Tereszchuk K and Bernath P F 2003 *J. Phys. Chem.* **118** 3622

[5] Bernath P F, Shayesteh A and Tereszchuk K 2002 *Science* **297** 1323

[6] Watson W W 1928 *Phys. Rev.* **32** 600

[7] Watson W W and Parker A E 1931 *Phys. Rev.* **37** 167

[8] Olsson E 1932 *Z. Phys.* **73** 732

[9] Koontz P G 1935 *Phys. Rev.* **48** 707

[10] Watson W W and Humphreys R F 1937 *Phys. Rev.* **52** 318

[11] De Greef D and Colin R 1974 *J. Mol. Spectrosc.* **53** 455

[12] Jiang W S and Wu K Y 2005 *Journal of Sichuan University: Natural Science Edition* **28** 469 (in Chinese)

[13] Machado F B C, Roberto-Neto O and Ornellas F R 1999 *Chem. Phys. Lett.* **305** 156

[14] Pitarch-Ruiz J, Sanchez-Marin J and Velasco A M 2007 *J. Comput. Chem.* **29** 523

[15] Henriet C and Verhaegen G 1986 *Physica Scripta* **3** 299

[16] Zhang X Y, Yang C L, Gao F and Ren T Q 2007 *J. Mol. Struct.* **816** 97

[17] Wernal H J and Knowles P J 1988 *J. Phys. Chem.* **89** 5811

[18] Colin R, Dreze C and Steinhauer M 1983 *Can. J. Phys.* **61** 641

[19] Sherrill C D and Piecuch P 2005 *J. Phys. Chem.* **122** 124104

[20] Wang X Q, Yang C L, Su T and Wang M S 2009 *Acta Phys. Sin.* **58** 6873 (in Chinese)

[21] Shi D H, Liu H, Sun J F, Zhu Z L and Liu Y F 2010 *Acta Phys. Sin.* **59** 227 (in Chinese)

[22] Langhoff S R and Davidson E R 1974 *J. Quantum Chem.* **8** 61

[23] Neese F and Wennmohs F 2010 ORCA- An *ab initio*, DFT and semiempirical SCF-MO package, Version 2.8-20, Bonn, Germany

[24] Le Roy R J 2007 Level 8.0-A computer program for solving the radial Schrödinger equation for bound and quasibound levels, University of Waterloo Chemical Physics Research Report No. CP-663

[25] Zhu Z H 1996 *Atomic Reaction Statics* (Beijing: Science Press) pp. 15–31 (in Chinese)

[26] Herzberg G 1983 *Molecular Spectra and Structure: Spectra of Diatomic Molecules* Vol. 1 translated by Wang D C (Beijing: Science Press) p. 69

[27] Knight L B Jr and Weltner W Jr 1972 *J. Chem. Phys.* **56** 1152

[28] Horne R and Colin R 1972 *Bull. Soc. Chim. Belg.* **81** 93

[29] Xu M, Wang R K, LingHu R F and Yang X D 2007 *Acta Phys. Sin.* **56** 771 (in Chinese)

[30] Olsson E 1932 *Z. Phys.* **73** 732

[31] Lü B, LingHu R F and Song X S 2008 *Journal of Sichuan University: Natural Science Edition* **45** 924 (in Chinese)

[32] Petsalakis I D, Theodorakopoulos G and Nicolaides C A 1992 *J. Chem. Phys.* **97** 7625