

An *ab initio* study of the ground and low-lying excited states of LiBe^+

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Abstract. By using multi-reference configuration interaction method and large all-electron basis sets aug-cc-pwCV5Z, we have calculated the dense potential energy curves (PECs) of $1^1\Sigma^+$, $1^3\Sigma^+$, $1^1\Pi$, and $1^3\Pi$ states of LiBe^+ molecule. Based on the obtained PECs, the analytical potential energy functions (APEF) have been constructed with a Morse long-range potential function and nonlinear least squares method. The rotational and vibrational energy levels of the four states are determined by solving Schrödinger equation of nuclear movement with the APEFs. The spectroscopic parameters are deduced with the obtained rotational and vibrational energy levels.

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Key words: analytical potential energy function, excited state, spectroscopic parameters.

1 Introduction

Ultra-cold molecules have been brought in a great deal of interests in the past twenty years [1, 2], and now still arouse many researchers' interesting. Recently, some researchers have started to pay attention to the diatoms comprise of alkali and alkaline-earth metal elements. In 1993, using several theoretical methods and basis sets, Boldyrev *et al.* [1] studied the electronic structures of lithium containing diatomic molecules and ions. The equilibrium internuclear distance R_e and the harmonic vibrational frequency ω_e were obtained by using correlated second-order Moller-Plesset (MP2) with 6-311+G* For the dissociation energy D_e , they used two methods, PMP4 and quadratic configuration interaction with single and double (triplet) (QCISD (T)) excitation, with the basis sets 6-311+G (2df). They found the QCISD (T) can give better results than PMP4 when compared with

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the experimental values. Marino *et al.* [2] reported the potential energy curves (PEC) for the ground state and fourteen excited states of LiBe and LiBe⁺. Several spectroscopic parameters were also presented in their work. Safonov *et al.* [3] also performed a study on LiBe and LiBe⁺ by using self-consistent field method. The PECs and some spectroscopic parameters of 1¹Σ⁺, 1³Σ⁺, and 2¹Σ⁺ states of LiBe⁺ are also obtained. Using MRCI+Q and multi-reference averaged quadratic coupled-cluster (MRAQCC) methods including Davidson correction, Sun *et al.* [4] calculated the PECs for the X¹Σ⁺, a³Σ⁺, A¹Σ⁺, c³Σ⁺, C¹Σ⁺, B¹Π, and b³Π states. Their results showed that X¹Σ⁺, a³Σ⁺, B¹Π, and b³Π are weakly bound, while A¹Σ⁺, c³Σ⁺, and C¹Σ⁺ states are repulsive. The calculated spectroscopic parameters for the bound states with two methods show a little difference.

Beyond all question, these investigations should not be ignored and have made a significant effort for the later theoretical work. However, obvious differences occur in the reported spectroscopic parameters from the different author, especially for the D_e in the ground state. Besides, the analytical potential energy functions (APEF) of the PECs, which are very important for constructing an analytical function for the system containing more atoms or dynamical calculations such as photoassociation or photoassociation dissociation investigation, have not constructed. Therefore, the present paper focus on performing high accurate *ab initio* calculations for the PECs of LiBe⁺ and constructing the APEF for both the ground and the low-lying states.

2 Theoretical details

2.1 Computational details

The multi-reference configuration interaction (MRCI) [5, 6] method shows a good performance in dealing with the electron correlation. Combined with suitable basis sets and active space, MRCI can give the accurate PEC for molecule. The MRCI calculations are based on the optimized orbitals with the complete-active-space-self-consistent field (CASSCF) method. In the present work, the all-electron basis sets aug-cc-pwCV5Z [7] are used, which implies that (9s,4p,1d) [3s,2p,1d] for both Li and Be atoms. Orbitals and occupation schemes are referring to the irreducible representation (A₁/B₁/B₂/A₂) of C_{2v} group. All calculations are performed in the C_{2v} subgroup of the C_{∞v} point group because of the limit of the program. No core orbitals is used to include the correlation effect of the inner 1s electrons. That is to say, the orbitals of 2p of Li and Be are included in the active space for the excited states, which mean the active space consisted of 2 closed-shell orbitals (2,0,0,0) and 8 active orbitals (4,2,2,0). Hence there are 2 active electrons in 8 orbitals in the correlation energy calculations. The PECs spanning a range from 1.50 to 21.45 Å with a step of 0.05 Å are used for both the ground and the low-lying excited states. All calculations are carried out with MOLPRO package [8].