

# *Ab initio* calculations on accurate dissociation energy, equilibrium geometry, and analytic potential energy function for the $b^3\Pi$ state of ${}^7\text{LiH}$ molecule

Deheng Shi (施德恒)<sup>1,2,3</sup>, Yufang Liu (刘玉芳)<sup>2</sup>,  
Jinfeng Sun (孙金锋)<sup>2,3</sup>, Zunlue Zhu (朱遵略)<sup>2,3</sup>, and Xiangdong Yang (杨向东)<sup>3</sup>

<sup>1</sup>College of Physics & Electronic Engineering, Xinyang Normal University, Xinyang 464000

<sup>2</sup>College of Physics & Information Engineering, Henan Normal University, Xinxiang 453007

<sup>3</sup>Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065

Received August 10, 2005

The accurate dissociation energy and equilibrium geometry of the  $b^3\Pi$  state of  ${}^7\text{LiH}$  molecule is calculated using a symmetry-adapted-cluster configuration-interaction method in full active space. And the calculated results are 0.2580 eV and 0.1958 nm for the dissociation energy and equilibrium geometry, respectively. The whole potential energy curve for the  $b^3\Pi$  state is also calculated over the internuclear separation range from about 0.10 to 0.54 nm. The results are fitted by the Murrell-Sorbie function. It is found that the Murrell-Sorbie function form, which is mainly used to fit the ground-state potential energy function, is well suitable for the excited triplet  $b^3\Pi$  state. The vertical excitation energy from the ground state to the  $b^3\Pi$  state is calculated to be 4.233 eV. Based on the analytic potential energy function, the harmonic frequency of  $610.88\text{ cm}^{-1}$  about this state is firstly estimated. Compared with other theoretical results, this work is the most complete effort to deal with the analytic potential energy function and the harmonic frequency of this state.

OCIS codes: 020.2070, 020.7010.

Recent progress in trapping cold atoms in ultracold samples<sup>[1,2]</sup> has required the determination of diatomic interaction potentials with high precision. On the one hand, in the collision processes between atoms and molecules, the relatively slow nuclear motion is very sensitive to the electronic potential energy function (PEF)<sup>[3–5]</sup>; on the other hand, collisions at ultracold temperatures are major factors in determining the trapped atoms and the formation of Bose-Einstein condensation (BEC)<sup>[6]</sup>. In order to produce trustworthy dynamics such as trapped atoms and BEC formation, accurate PEF, particularly highly accurate PEF, is always wanted in calculations of the various cross sections and scattering length at ultralow energies<sup>[2,3]</sup>. Though PEF for small molecules can be calculated by solving the electronic Schrödinger equation, the highly accurate PEF, especially highly accurate PEF for an excited state, is still difficult to be attained.

There are several methods for obtaining the PEF of a molecule in the excited state, which avoid directly solving the electronic Schrödinger equation. Here, we are interested in a symmetry-adapted-cluster configuration-interaction method in full active space.  ${}^7\text{LiH}$  is selected as target molecule since mixtures of the alkali metal atoms  ${}^7\text{Li}$  with the hydrogen atoms H may be effective in enhancing the cooling efficiency<sup>[3,7]</sup>. Thus, with the BEC in ultracold lithium<sup>[8]</sup>, hydrogen<sup>[9]</sup>, sodium<sup>[1,6]</sup>, and rubidium<sup>[1]</sup>, the alkali metal hydrides, especially lithium hydride molecule, have renewedly attracted extensive attention. But to our knowledge, no PEF and harmonic frequency in this state are experimentally found. And up to now only the lowest four singlet electronic states ( $X^1\Sigma^+$ ,  $A^1\Sigma^+$ ,  $B^1\Pi$  and  $C^1\Sigma^+$ )<sup>[10,11]</sup>, have been identified and well characterized by convention or by laser

spectroscopy<sup>[12–18]</sup>; whereas in theories, only several calculations have involved the  $b^3\Pi$  state<sup>[19–21]</sup>, in which no analytic PEF and harmonic frequency are found. Thus in this letter, we attempt to attain the analytic PEF and the harmonic frequency.

For calculating the analytic PEF about the  $b^3\Pi$  state, its dissociation limit is firstly determined. When one atom is in the ground state  ${}^2S_g$  and the other in the first excited state  ${}^2P_u$ , based on the group theory and atomic and molecular reaction statics<sup>[22]</sup>, the representations  ${}^2S_g$  and  ${}^2P_u$  of the atomic group are resolved into those of  $C_{\infty v}(\text{LiH})$  as

$${}^2S_g \rightarrow {}^2\Sigma^+, \quad (1)$$

$${}^2P_u \rightarrow {}^2\Sigma^+ \oplus {}^2\Pi, \quad (2)$$

respectively. Their direct product and reduction are

$${}^2\Sigma^+ \otimes ({}^2\Sigma^+ \oplus {}^2\Pi) \rightarrow {}^1\Sigma^+ \oplus {}^3\Sigma^+ \oplus {}^1\Pi \oplus {}^3\Pi. \quad (3)$$

Obviously, expression (3) contains the  ${}^3\Pi$  state. According to the principle of reversibility for the microscopic process<sup>[22]</sup>, the possible dissociation limit for the  $b^3\Pi$  state may be

$$\text{LiH}(b^3\Pi) \rightarrow \text{H}({}^2S_g) + \text{Li}({}^2P_u), \quad (4)$$

$$\text{LiH}(b^3\Pi) \rightarrow \text{Li}({}^2S_g) + \text{H}({}^2P_u). \quad (5)$$

When both Li and H atoms are in their excited state  ${}^2P_u$ , we can also derive the following possible dissociation limit for the  $b^3\Pi$  state

$$\text{LiH}(b^3\Pi) \rightarrow \text{H}({}^2P_u) + \text{Li}({}^2P_u). \quad (6)$$

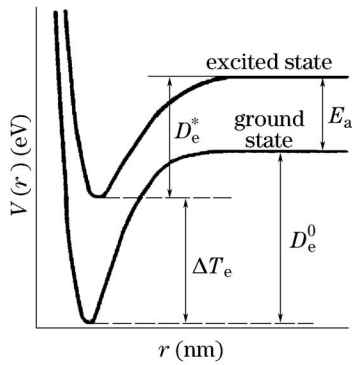


Fig. 1. Potential energy curves of the ground and excited states.

As shown in Fig. 1, the atomic excitation energy  $E_a$  for an excited state equals

$$E_a = D_e^* + \Delta T_e - D_e^0, \quad (7)$$

here  $D_e^*$  is the dissociation energy for the excited state.  $D_e^0$  is the dissociation energy for the ground state and equals 2.515 eV for  ${}^7\text{LiH}$  molecule, which takes into account the vibrational zero energy<sup>[23]</sup>.  $\Delta T_e$  is the energy level difference between the ground state and the excited state. Using Eq. (7),  $D_e^*$  and  $\Delta T_e$ , we obtain  $E_a \approx 1.815$  eV for the excited  $b^3\Pi$  state. The value approximately equals to the energy level difference between the ground state  ${}^2S_g$  and the excited state  ${}^2P_u$  for Li atom<sup>[24]</sup>, but smaller than the one between the ground state  ${}^2S_g$  and the excited state  ${}^2P_u$  for H atom<sup>[24]</sup>, and greatly smaller than the one between the sum of their ground state  ${}^2S_g$  and the sum of their excited state  ${}^2P_u$  for Li and H atoms<sup>[24]</sup>. Thus we conclude that the dissociation limit for the  $b^3\Sigma^+$  state is expression (4), not (5) or (6).

The calculations described are carried out in Gaussian 03 program package<sup>[25]</sup>. Firstly, we calculate the dissociation energies and equilibrium geometries about the  $A^1\Sigma^+$  and  $B^1\Pi$  states at the different basis sets, such as D95, D95(d), D95V(d,p), 6-311G(d,p), 6-311G(3df,3pd), DGDZVP, and cc-PVTZ. Here, because there are no experimental dissociation energy and equilibrium geometry about the  $b^3\Pi$  state, the comparison of the calculation results with the experimental data cannot be made. So, in order to select the most suitable basis set for the calculation of the  $b^3\Pi$  state, we use the experimental results of  $A^1\Sigma^+$  and  $B^1\Pi$  states for comparison. Then, by comparing our calculation results of  $A^1\Sigma^+$  and  $B^1\Pi$  states with the experimental data<sup>[23,26,27]</sup>, we select 6-311G(3df, 3pd) basis set for further  $b^3\Pi$  state calculation in full active space. And last, using the selected basis set, we calculate the  $b^3\Pi$  state potential energy curve over the internuclear separation range from about 0.10 to 0.54 nm.

The curve of the *ab initio* calculated points are shown in Fig. 2, where the solid curve is fitted by the Murrell-Sorbie (M-S) function<sup>[28]</sup>

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3) \exp(-a_1\rho), \quad (8)$$

where  $\rho = R - R_e$ ,  $R$  is the interatomic separation of the diatomic molecule, and  $R_e$  is its equilibrium separation.

By iterating a system of normal equations based on a least-squares fit, the parameters  $a_1$ ,  $a_2$ , and  $a_3$  of Eq. (8) have been calculated for the  $b^3\Pi$  state and listed in Table 1 together with the dissociation energies and the equilibrium interatomic separations obtained by other theories<sup>[19-21]</sup>.

In Fig. 2, the zero reference energy is taken to the dissociation limit of  $b^3\Pi$  state. From it, we clearly see that the solid curve fitted by the M-S function coincides well with the circle curve plotted by the single-point energy scanning results. Thus we can say that the analytic M-S function form is suitable to fit the second excited triplet state  $b^3\Pi$  of  ${}^7\text{LiH}$  molecule, though the M-S function is mainly used to fit diatomic ground state PEF. From Table 1, we can easily calculate that the dissociation energy difference between our calculation results and the theoretical data<sup>[19]</sup> with a complicated method is only about 0.12%. And we can also calculate that the equilibrium separation difference between our calculation value and the one in Ref. [19] is about 0.62%. Thus we can say that they are in excellent agreement at present basis set level.

Table 2 presents some recent *ab initio* calculations<sup>[19,29]</sup> about the vertical excitation energies from the ground state  $X^1\Sigma^+$  to the  $b^3\Pi$  state. Obviously, our result (obtained at the ground-state equilibrium separation of 0.1587 nm) is in excellent agreement with that given in Ref. [19] (obtained at 0.1587 nm) in which a complicated basis set was employed, but is slightly smaller than that

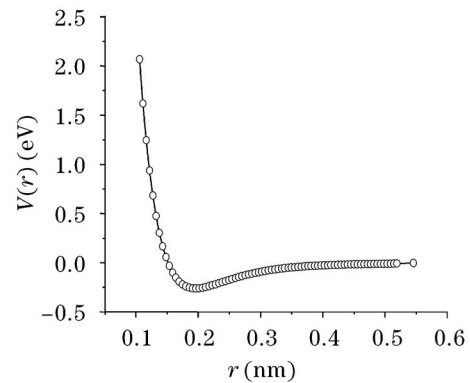


Fig. 2. Potential energy curve of the second excited triplet state of  ${}^7\text{LiH}$  molecule. Solid line: curve fitted by M-S function; circles: single-point energy scanning results.

Table 1. Parameters of the Analytical PEF (8) of the Second Excited Triplet State  $b^3\Pi$

Dissociation Limit	Source	$T_e$ (eV)	$R_e$ (nm)	$D_e$ (eV)	$a_1$ (nm <sup>-1</sup> )	$a_2$ (nm <sup>-2</sup> )	$a_3$ (nm <sup>-3</sup> )
$\text{LiH}(b^3\Pi) \rightarrow \text{H}({}^2S_g) + \text{Li}({}^2P_u)$	This Paper	4.0721	0.1958	0.2580	18.832	-72.278	287.77
	Ref. [19]	4.0908	0.1946	0.2583	—	—	—
	Ref. [20]	—	0.1989	0.2010	—	—	—
	Ref. [21]	—	0.1979	0.2160	—	—	—

**Table 2. Vertical Excitation Energy (in eV) from the Ground State  $X^1\Sigma^+$  to the State  $b^3\Pi$** 

Excitation	This Paper	Ref. [19]	Ref. [29]
$X^1\Sigma^+ \rightarrow b^3\Pi$	4.233	4.23	4.27

given in Ref. [29] (obtained at 0.1595 nm). Unfortunately, to our knowledge there is no experimental information about the vertical excitation energy from the ground state to the  $b^3\Pi$  state.

We do not attain the accurate harmonic frequency of the  $b^3\Pi$  state of  $^7\text{LiH}$  molecule since the geometry optimization cannot give the accurate equilibrium internuclear separation. At the same time, no theoretical and experimental harmonic frequencies about this state is found in literatures to our knowledge. But then, employing the analytic PEF given by Eq. (8), we can derive the expression of the force constant  $f_2$  at the equilibrium separation

$$f_2 = D_e(a_1^2 - 2a_2). \quad (9)$$

According to the Rydberg-Klein-Rees (RKR) method, we have

$$f_2 = 4\pi^2\omega_e^2\mu c^2. \quad (10)$$

Combining Eqs. (9) and (10), we have

$$\omega_e = \left[ \frac{D_e(a_1^2 - 2a_2)}{4\pi^2\mu c^2} \right]^{1/2}, \quad (11)$$

where  $\mu$  is the reduced mass of  $^7\text{LiH}$  molecule, and  $\omega_e$  is the harmonic frequency of the  $b^3\Pi$  state. Employing the known  $b^3\Pi$  state parameters listed in Table 1, we obtain the  $\omega_e$  value of  $610.88 \text{ cm}^{-1}$ .

In a word, compared with other theoretical results<sup>[19–21]</sup>, there is the most complete effort to deal with the analytic PEF and the harmonic frequency of this state.

This work was supported by the National Natural Science Foundation of China (No. 10574039) and Henan Innovation Fund for University Prominent Research Talents (No. 2006KYCX002). D. Shi's e-mail address is scattering@sina.com.cn or dehengshi@yahoo.com.cn.

## References

- J. Weiner, V. S. Bagnato, S. Zilio, and P. S. Julienne, *Rev. Mod. Phys.* **71**, 1 (1999).
- R. Côté, A. Dalgarno, Y. Sun, and R. G. Hulet, *Phys. Rev. Lett.* **74**, 3581 (1995).
- R. Côté, M. J. Jamieson, Z.-C. Yan, N. Geum, G.-H. Jeung, and A. Dalgarno, *Phys. Rev. Lett.* **84**, 2806 (2000).
- J. Sun, D. Shi, Z. Zhu, and Y. Liu, *Chin. Opt. Lett.* **1**, 624 (2003).
- D. Shi, J. Sun, X. Yang, Z. Zhu, and Y. Liu, *Chin. Opt. Lett.* **3**, 1 (2005).
- F. Dalfovo, S. Giorgini, L. P. Pitaevskii, and S. Stringari, *Rev. Mod. Phys.* **71**, 463 (1999).
- A. Derevienko, R. Côté, A. Dalgarno, and G.-H. Jeung, *Phys. Rev. A* **64**, 011404 (2001).
- D. G. Fried, T. C. Killian, L. Willmann, D. Landhuis, S. C. Moss, D. Kleppner, and T. J. Greytak, *Phys. Rev. Lett.* **81**, 3811 (1998).
- C. C. Bradley, C. A. Sackett, J. J. Tollett, and R. G. Hulet, *Phys. Rev. Lett.* **75**, 1687 (1995).
- J. A. Coxon and C. S. Dickinson, *J. Chem. Phys.* **121**, 9378 (2004).
- Y.-L. Huang, W.-T. Luh, G.-H. Jeung, and F. X. Gadéa, *J. Chem. Phys.* **113**, 683 (2000).
- P. H. Wine and L. A. Melton, *J. Chem. Phys.* **64**, 2692 (1976).
- P. J. Dagdigian, *J. Chem. Phys.* **73**, 2049 (1980).
- K. K. Verma and W. C. Stwalley, *J. Chem. Phys.* **77**, 2350 (1982).
- G. Ennen, B. Fiedler, and Ch. Ottinger, *J. Chem. Phys.* **75**, 59 (1981).
- Y. C. Chan, D. R. Harding, W. C. Stwalley, and C. R. Vidal, *J. Chem. Phys.* **85**, 2436 (1986).
- J. J. Chen, W. T. Luh, and G. H. Jeung, *J. Chem. Phys.* **110**, 4402 (1999).
- W. C. Lin, J. J. Chen, and W. T. Luh, *J. Phys. Chem. A* **101**, 6709 (1997).
- A. Boutalib and F. X. Gadéa, *J. Chem. Phys.* **97**, 1144 (1992).
- X. C. Wang and K. F. Freed, *J. Chem. Phys.* **91**, 3002 (1989).
- S. Ben-Shlomo and U. Kaldor, *J. Chem. Phys.* **89**, 956 (1988).
- Z. Zhu and H. Yu, *Molecular Structure and Potential Energy Function* (in Chinese) (Science Press, Beijing, 1997) p.41, 43.
- K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. Vol.4, Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979) p.382.
- C. E. Moore, *Atomic Energy Levels* (US Governments Printing Office, Washington, 1971) p.9.
- M. J. Frisch, G. W. Trucks, and H. B. Schlegel, *2003 Gaussian 03 Revision A.1* (Gaussian Inc. Pittsburgh).
- K. R. Way and W. C. Stwalley, *J. Chem. Phys.* **59**, 5298 (1973).
- C. R. Vidal and W. C. Stwalley, *J. Chem. Phys.* **80**, 2697 (1984).
- J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and J. C. Varandas, *Molecular Potential Energy Functions* (John Wiley & Sons, New York 1984) p.9.
- A. Balková, S. A. Kucharski, L. Meissner, and P. J. Bartlett, *J. Chem. Phys.* **95**, 4311 (1991).