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Ab initio calculations of accurate dissociation energy and analytic potential energy function for the second excited state $B^1\Pi$ of ^7LiH*

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The reasonable dissociation limit of the second excited singlet state $B^1\Pi$ of ^7LiH molecule is obtained. The accurate dissociation energy and equilibrium geometry of the $B^1\Pi$ state are calculated using a symmetry-adapted-cluster configuration–interaction method in full active space. The whole potential energy curve for the $B^1\Pi$ state is obtained over the internuclear distance ranging from about 0.10 nm to 0.54 nm, and has a least-square fit to the analytic Murrell–Sorbie function form. The vertical excitation energy is calculated from the ground state to the $B^1\Pi$ state and compared with previous theoretical results. The equilibrium internuclear distance obtained by geometry optimization is found to be quite different from that obtained by single-point energy scanning under the same calculation condition. Based on the analytic potential energy function, the harmonic frequency value of the $B^1\Pi$ state is estimated. A comparison of the theoretical calculations of dissociation energies, equilibrium interatomic distances and the analytic potential energy function with those obtained by previous theoretical results clearly shows that the present work is more comprehensive and in better agreement with experiments than previous theories, thus it is an improvement on previous theories.

Keywords: *ab initio* calculation, dissociation energy, analytic potential energy function
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1. Introduction

The analytic potential energy function (PEF) plays a fundamental role in understanding collision processes between atoms and molecules[1] since the relatively slow nuclear motion is very sensitive to the details of the electronic PEF. In order to produce trustworthy dynamics such as the behaviour of trapped atoms and formation of Bose–Einstein condensation (BEC), the accurate PEF, or even highly accurate PEF, is always requisite for the calculation of the scattering of atoms at ultralow energies.[2] Though the PEF calculation for small molecules can be made by solving the electronic Schrödinger equation, the computation of highly accurate PEF, especially highly accurate PEF for excited states, is still a very formidable task.

There have been suggested several methods of obtaining the PEF of a molecule in an excited state, which avoid directly solving the electronic Schrödinger equation. Here, we are interested in a symmetry-adapted-cluster configuration–interaction (SAC-CI) method[3−5] in full active space in the Gaussian 03 program package.[6] ^7LiH is selected as a target molecule, because, on the one hand, mixtures of the alkali metal atoms ^7Li with the hydrogen atoms may be effective in enhancing the cooling efficiency.[7,8] Thus, with the BEC discovery in ultracold lithium,[9] hydrogen,[10] sodium[2,11] and rubidium,[2] the alkali metal hydrides, especially lithium hydride molecules, have attracted extensive attention; on the other hand, the $B^1\Pi$ state of ^7LiH molecule presents a problem in its own right because one is confronted with a very shallow potential. In the past decades it has been difficult to obtain accurate potential energy curves of such weakly bound states within any sort of spectro-

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scopic precision due to its specialties.

The theoretical work on ^{7}LiH molecule concentrated mainly on describing the ground state[12−17] and its properties such as the dipole moment functions.[15−18] The first calculations about the $B^1\Pi$ state, to obtain a bound potential energy curve, were given by Docken *et al*[19] in 1972, whose computed dissociation energy of 0.0175 eV is only half the experimental value[20] of 0.0357 eV. To date, only several theories have involved the $B^1\Pi$ state,[19,21−24] in which very few analytic PEFs can be found. Thus in this paper, we attempt to obtain the analytic PEF and improve the accuracy of the *ab initio* potentials. Compared with previous theories, the work described here is in good agreement with experiments, and is more comprehensive to deal with the analytic PEF of $B^1\Pi$ state of ^{7}LiH molecule than previous theories, thus it represents an improvement on the previous theories.

In this paper, the accurate dissociation energy and equilibrium geometry of the $B^1\Pi$ state are calculated using the SAC-CI method in full active space. In the next section, we describe in detail the dissociation limit of this $B^1\Pi$ state. In Section 3, we present the calculated results for the dissociation energy, the equilibrium internuclear distance, the vertical excitation energy from the ground state to the $B^1\Pi$ state, the harmonic frequency and the analytic PEF, and carry out some useful discussion about them. Concluding remarks are made in Section 4.

2. Dissociation limit and electronic state

For the calculation of the full PEF about the $B^1\Pi$ state, first and foremost, we must determine its reasonable dissociation limit. When one atom is in the ground state ^2S_g and the other in the first excited state ^2P_u,[25] based on the group theory and atomic and molecular reaction statics,[26] the representations ^2S_g and ^2P_u of the atomic group are resolved into those of $C_{\infty v}$(LiH) as follows:

$$^2S_g \to {}^2\Sigma^+, \tag{1}$$

$$^2P_u \to {}^2\Sigma^+ \oplus {}^2\Pi, \tag{2}$$

respectively. Their direct product and its reduction are

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

Obviously, Eq.(3) contains the $^1\Pi$ state. According to the principle of reversibility for the microscopic process,[26] the possible dissociation limit for the $B^1\Pi$ state may be

$$\mathrm{LiH}(B^1\Pi) \to \mathrm{H}(^2S_g) + \mathrm{Li}(^2P_u), \tag{4}$$

$$\mathrm{LiH}(B^1\Pi) \to \mathrm{Li}(^2S_g) + \mathrm{H}(^2P_u). \tag{5}$$

When both Li and H atoms are in their first excited state ^2P_u, we can also derive the following possible dissociation limit about the $B^1\Pi$| state:

$$\mathrm{LiH}(B^1\Pi) \to \mathrm{H}(^2P_u) + \mathrm{Li}(^2P_u). \tag{6}$$

As shown in Fig.1, the atomic excitation energy E_a for an excited state equals[27]

$$E_a = D_e^* + \Delta T_e - D_e^0. \tag{7}$$

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}LiH molecule, which takes into consideration the vibrational zero energy.[20] ΔT_e is the energy level difference between the ground state and the excited state. Using Eq.(7) and the measurements[28] listed in Table 1, we obtain $E_a \approx 1.848$ eV for the excited $B^1\Pi$ state. The value is just equal to the energy level difference between the ground state ^2S_g and the first excited state ^2P_u for Li atom,[25] but much smaller than that between the ground state ^2S_g and the first excited state ^2P_u for H atom,[25] and that between the sum of their ground state ^2S_g and the sum of their first excited state ^2P_u for Li and H atoms.[25] Thus we conclude that the reasonable dissociation limit for the $B^1\Pi$ state of ^{7}LiH molecule is the expression (4), not (5) or (6).

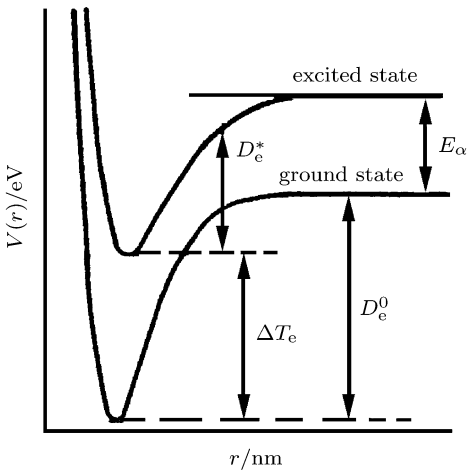


Fig.1. Potential energy curves of the ground and excited states.

3. Results and discussion

In the SAC-CI calculations, in order to investigate the molecular properties over different geometries using perturbation selection, it is needed to take a group-sum (GSUM) of the linked and unlinked operators selected at different geometries. Otherwise, the properties may be calculated discontinuously.[29] In order to keep the continuous properties of all the calculation points, the single-point energy scanning calculations are divided into three steps: BeforeGSUM, CalcGSUM, and AfterGSUM. Specifically, the BeforeGSUM is used to initialize a series of GSUM calculations and only used at the first geometry of the GSUM calculations. The CalcGSUM is used to add the operators selected at the current geometry to the GSUM set for all geometries except for the first one. And the AfterGSUM is used to perform SAC/SAC-CI calculations using the GSUM operators collected at all geometries.[29]

In order to obtain the accurate equilibrium geometry and dissociation energy of the $B^1\Pi$ state using this SAC-CI method, our calculation is divided into three parts. Firstly, the geometry optimization[29,30] is adopted so as to attain the equilibrium internuclear distances at numerous basis sets such as D95, D95(d), D95V(d,p), 6-311G(d,p), DGDZVP, cc-PVTZ, TZVP and the complete basis set (CBS) listed in Ref.[23]. By comparing the computed equilibrium internuclear distances with the experimental ones,[20,28] we select some of them for further calculations. Secondly, we make single-point energy scanning calculations near the experimental equilibrium position by a tiny step at the above-selected basis sets. When we determine the equilibrium internuclear distance for a certain basis set, we proceed with single-point energy scanning by a relatively large step to attain the dissociation energy. By comparing our computed results about the dissociation energies and equilibrium internuclear distances of this state with those obtained from other theory and experiments in Refs.[19-24, 28], we find that the 6-311G(3df,3pd) basis set[31,32] is a most suitable one in full active space. And lastly, using the selected basis set, we calculate its potential energy curve over the internuclear distances ranging from about 0.10 nm to 0.54 nm by a very small scanning step. The curves of the *ab initio* calculated points are shown in Fig.2, where the solid curve is fitted by the Murrell–Sorbie function[33]

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

Here $\rho = R - R_e$, R is the interatomic distance between the two atoms, and R_e is its equilibrium distance.

By iterating a system of normal equations based on a least-square fit, the parameters a_1, a_2 and a_3 in Eq.(8) are calculated for the $B^1\Pi$ state and listed in Table 1 together with the dissociation energies and the equilibrium interatomic distances obtained from experiments[20,28] and other theories.[19,21−24]

Table 1. Parameters of the analytical potential function (8) of the $B^1\ \Pi$ state.

dissociation limit	source	T_e/eV	R_e/nm	D_e/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
$LiH(B\ ^1\Pi) \rightarrow H(^2S_g) + Li(^2P_u)$	This work	4.2960	0.2434	0.0345	19.461	−40.657	1045.3
	Exp.[20]	4.3286	0.2378	0.0357	—	—	—
	Exp.[28]	4.3279	0.2383	0.0357	—	—	—
	Theory[19]	4.2349	0.2514	0.0175	—	—	—
	Theory[21]	—	0.2484	0.0110	—	—	—
	Theory[22]	—	0.2484	0.0110	—	—	—
	Theory[23]	4.3179	0.2394	0.0320	—	—	—
	Theory[24]	4.1131	0.2606	0.0233	—	—	—

In Fig.2, the zero reference energy is taken as the dissociation limit of the $B^1\Pi$ state. From Fig.2 we clearly see that the solid curve fitted by the Murrell–Sorbie function and the circle curve plotted by the single-point energy scanning results coincide very well. Thus we can say that the analytic Murrell–Sorbie function form is suitable for fitting the second excited singlet state $B^1\Pi$ of ^{7}LiH molecule. From Table 1, we can easily calculate that the difference between our computed dissociation energy and the experimentally determined value in Refs.[20,28] is only about 3.3%, thus we can say that they are in excellent agreement at the present SAC-CI/6-311G(3df,3pd) theory level. Obviously, our computed dissociation energy is much

closer to the experimental value[20,28] than those dissociated energies obtained by previous theories,[19,21−24] thus it is an improvement on the previous theoretical results.

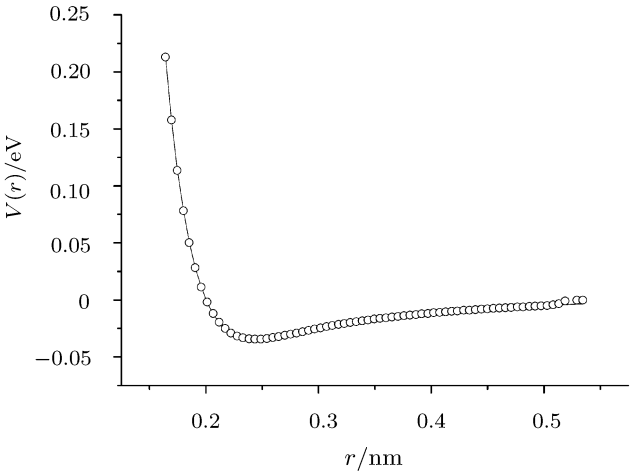


Fig.2. Potential energy curve of the second excited state of ^{7}LiH molecule. Solid line: curve fitted by Murrell–Sorbie function; circle line: single-point energy scanning results.

The computed equilibrium internuclear distance of the $B^1\Pi$ state obtained by the geometry optimization is found to be quite different from that obtained by the single-point energy scanning at the same basis set and present SAC-CI theory level. For example, at the 6-311G(3df,3pd) basis set, our geometry optimization gives an internuclear distance of 0.2521 nm, whereas the internuclear distance given by our single-point energy scanning is 0.2434 nm. Through careful examinations it has been found that the unique GSUM method used in the single-point energy scanning is incompletely identical with that used in the geometry optimization,[29,30] thus the difference between the above-mentioned results is easy to understand. In detail, the GSUM method is not automatically executed in the geometry optimization method in this SAC/SAC-CI Gaussian version,[6,29] because it is difficult in general to say where the unknown optimized geometry is. Though after optimization, we can again make perturbation selection and repeat optimization using freshly selected operators, the geometry optimization method only make an additional single-point SAC-CI calculation.[6,29] Furthermore, by comparing the results from theories and experiments in Refs.[20,28], we find that the equilibrium internuclear distances obtained from the single-point energy scanning are closer to the experimental ones than those obtained from the geometry optimization for the $B^1\Pi$ state of this molecule. Thus the results obtained from the single-point energy scanning are more accurate. Therefore, in the present work, in order to obtain the accurate equilibrium geometry, we perform the single-point energy scanning near the equilibrium position of the $B^1\Pi$ state by a very small step at different basis sets. Finally, we find that the lowest potential energy occurs at $R_e = 0.2434$ nm and the 6-311G(3df,3pd) basis set is a most suitable one in full active space. It is easy to see that this value is in good agreement with the measurements in Refs. [20,28]. The difference between our computed R_e value and the experimentally determined one in Ref.[20] is about 2.35%, and the difference between our R_e value and the experimental one in Ref.[28] is only about 2.14%. Our equilibrium internuclear distance is superior in accuracy to all the existing theoretical results[19,21,22,24] except for the result given by Boutalib *et al.*[23] However, the computed dissociation energy in the present work is much closer to the measurements in Refs.[20,28] than the dissociation energy presented in Ref.[23]. So, our computed results are very encouraging. Compared with the previous theories,[19,21−24] the present work is obviously comprehensive to deal with the analytic PEF about this $B^1\Pi$ state and can be directly used in collision processes between atoms and molecules.[34]

In order to compare further with previous theories, employing the ground-state potential energy curve, we calculate the vertical excitation energy from the ground state to the $B^1\Pi$ state and list it in Table 2 together with the recent *ab initio* calculated results.[23,24,35] From Table 2 we obviously see that our computed result (obtained at $R = 0.15875$ nm) is in excellent agreement with that given in Ref.[23] (obtained at $R = 0.15875$ nm) in which Boutalib *et al*[23] employed a very complicated basis set, and that presented in Ref.[35] (obtained at $R = 0.15957$ nm), but slightly larger than that given in Ref.[24] (obtained at $R = 0.15957$ nm). Unfortunately, to our knowledge there is no experimental information about the vertical excitation energy from the ground state to the $B^1\Pi$ state, which can be compared with our results.

Table 2. Vertical excitation energy (in units of eV) from the ground state to the $B^1\Pi$ state.

excitation	this work	theory[23]	theory[24] (DQ)	theory[24] (FCI)	Theory[35]
$X^1\Sigma^+ \rightarrow B^1\Pi$	4.612	4.62	4.516	4.547	4.63

We cannot obtain the accurate harmonic frequency of the $B^1\Pi$ state of this molecule since the geometry optimization cannot give the accurate equilibrium internuclear distance. An experimental value[20] of 130.73 cm^{-1} is found, but no theoretical harmonic frequency is available from literature to our knowledge. Then, employing the analytic PEF given by Eq.(8), we derive the expression of the force constant f_2 at the equilibrium position as follows:

$$f_2 = D_e(a_1^2 - 2a_2). \tag{9}$$

The following relationship exists according to the Rydberg–Klein–Rees (RKR) method:[36]

$$f_2 = 4\pi^2\omega_e^2\mu c^2. \tag{10}$$

Combing Eq.(9) with Eq.(10), we have

$$\omega_e = \Big[\frac{D_e(a_1^2 - 2a_2)}{4\pi^2\mu c^2}\Big]^{1/2}. \tag{11}$$

Here, μ is the reduced mass of ^{7}LiH molecule, and ω_e is the harmonic frequency of the $B^1\Pi$ state. Employing the known $B^1\Pi$ state parameters, we estimate the ω_e value to be 221.42 cm^{-1}.

4. Conclusions

Figure 2 shows that the Murrell–Sorbie function is suitable for fitting very shallow potential well of the $B^1\Pi$ state of ^{7}LiH molecule. Through single-point energy scanning near the equilibrium position of the $B^1\Pi$ state by a very small step, we have obtained the accurate equilibrium separation. Compared with previous theoretical results,[19,21–24] the computed dissociation energy and equilibrium internuclear distance of the $B^1\Pi$ state, especially the computed dissociation energy at present, are obviously in better agreement with measurements than those previous theoretical results,[19,21–24] which implies that the present work is an improvement on the previous theoretical work[19,21–24] In addition, the computed vertical excitation energy from the ground state to the $B^1\Pi$ state is in excellent agreement with the previous theoretical results,[23,34] too.

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