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Ab initio calculation of accurate dissociation energy, potential energy curve and dipole moment function for the $A^1\Sigma^+$ state ^{7}LiH molecule*

Shi De-Heng(施德恒)[a)b)c)†], Liu Yu-Fang(刘玉芳)[b)], Sun Jin-Feng(孙金锋)[b)c)], Yang Xiang-Dong(杨向东)[c)], and Zhu Zun-Lue(朱遵略)[b)c)]

[a)] *College of Physics & Electronic Engineering, Xinyang Normal University, Xinyang 464000, China*
[b)] *College of Physics & Information Engineering, Henan Normal University, Xinxiang 453007, China*
[c)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*

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The reasonable dissociation limit of the $A^1\Sigma^+$ state ^{7}LiH molecule is obtained. The accurate dissociation energy and the equilibrium geometry of this state are calculated using a symmetry-adapted-cluster configuration-interaction method in complete active space for the first time. The whole potential energy curve and the dipole moment function for the $A^1\Sigma^+$ state are calculated over a wide internuclear separation range from about 0.1 to 1.4 nm. The calculated equilibrium geometry and dissociation energy of this potential energy curve are of R_e=0.2487 nm and D_e=1.064 eV, respectively. The unusual negative values of the anharmonicity constant and the vibration-rotational coupling constant are of $\omega_e\chi_e$=–4.7158cm^{-1} and α_e=–0.08649cm^{-1}, respectively. The vertical excitation energy from the ground to the $A^1\Sigma^+$ state is calculated and the value is of 3.613 eV at 0.15875 nm (the equilibrium position of the ground state). The highly anomalous shape of this potential energy curve, which is exceptionally flat over a wide radial range around the equilibrium position, is discussed in detail. The harmonic frequency value of 502.47cm^{-1} about this state is approximately estimated. Careful comparison of the theoretical determinations with those obtained by previous theories about the $A^1\Sigma^+$ state dissociation energy clearly shows that the present calculations are much closer to the experiments than previous theories, thus represents an improvement.

Keywords: *ab initio* calculation, dissociation energy, dipole moment, potential energy curve
PACC: 3420

1. Introduction

Recent progress in trapping of cold atoms in ultracold samples[1–7] has needed the determination of diatomic interaction potentials with high precision. Because, on the one hand, in the collision processes between atoms and molecules, the relatively slow nuclear motion is very sensitive to the details of the electronic potential energy curve (PEC);[2] on the other hand, collisions at ultracold temperatures are major factors in determining the behaviour of trapped atoms and the formation of Bose–Einstein condensation (BEC).[1] In order to produce trustworthy dynamics such as the behaviour of trapped atoms and BEC formation, accurate PEC, particularly accurate PEC over a large internuclear separation range, is always wanted in calculations of the various cross sections and scattering length at ultralow energies.[1,2] Though PEC calculation for small molecules can be made by solving the electronic Schrödinger equation, the computation of highly accurate PEC, especially highly accurate PEC for an excited state, is still a very formidable task.

There are several methods for obtaining the PECs of a molecule in excited states, which avoid directly solving the electronic Schrödinger equation. In this paper, we are interested in a symmetry adapted cluster configuration interaction (SAC-CI) method[8–11] in complete active space in the Gaussian 03 program

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†Corresponding author. E-mail: scattering@sina.com.cn

package.[12] The ^{7}LiH molecule is selected as target molecule, because, on the one hand, mixtures of the alkali metal atoms ^{7}Li with the hydrogen atoms H may be effective in enhancing the cooling efficiency;[2,3] with the BEC discovery in ultracold hydrogen,[4] lithium,[5] sodium[6] and rubidium,[7] the alkali metal hydrides, especially lithium hydride, have renewedly attracted extensive attention. On the other hand, the highly anomalous PEC shape of the $A^1\Sigma^+$ state ^{7}LiH molecule, has long been a source of fascination to theoreticians and experimentalists.[13] To our knowledge, previous studies on the $A^1\Sigma^+$ state about this molecule have been incomplete in some aspect such as having larger difference[14] between the computed dissociation energy and experimentally determined value, or only considering a narrow range of interaction internuclear separations.[15] And most of the work done mainly focuses on the ground state,[16−19] or has been devoted to understanding its other properties such as the dipole moment functions.[18−23] To date, only a few researches[14,15,24−26] involve the $A^1\Sigma^+$ state PEC of this molecule. Here, we attempt to obtain the accurate dissociation energy, equilibrium geometry and PEC over a wide internuclear separation range and improve the accuracy of the *ab initio* potentials of this state. Comparing the theoretical determinations with those obtained by previous theories about the $A^1\Sigma^+$ state dissociation energy, the work described here is in excellent agreement with experiments, thus represents an improvement.

In this paper, the accurate dissociation energy and equilibrium geometry of the $A^1\Sigma^+$ state is calculated using SAC-CI method[8−11] in complete active space. In the next section, we describe in detail the dissociation limit of this state. In Section 3, we present the calculated results for the dissociation energy, the equilibrium internuclear separation, the whole PEC and the dipole moment function over a wide internuclear separation range from about 0.1 to 1.4 nm, the vertical excitation energy from the ground to $A^1\Sigma^+$ state and the approximately estimated harmonic frequency, and make some useful discussion about them. Concluding remarks are made in Section 4.

2. Dissociation limit and electronic state

We first determine the reasonable dissociation limit about this state. When both Li and H atoms are in the ground state ^2S_g,[27] based on the group theory and atomic and molecular reaction statics,[28] the representation ^2S_g of the atomic group is resolved into those of $C_{\infty v}$(LiH) as follows:

$$^2S_g \rightarrow {}^2\Sigma^+. \tag{1}$$

Their direct product and its reduction are

$$^2\Sigma^+ \otimes {}^2\Sigma^+ \rightarrow {}^1\Sigma^+ \oplus {}^3\Sigma^+. \tag{2}$$

We instantly find that Eq.(2) contains $^1\Sigma^+$. Thus according to the principle of reversibility for the microscopic process,[28] the possible dissociation limit for the $A^1\Sigma^+$ state may be

$$\mathrm{LiH}(A^1\Sigma^+) \rightarrow \mathrm{Li}(^2S_g) + \mathrm{H}(^2S_g). \tag{3}$$

When one atom is in the ground state ^2S_g and the other in the first excited state ^2P_u, based on the above-mentioned reason, the representation ^2P_u of the atomic group is resolved into those of $C_{\infty v}$(LiH) as follows:

$$^2P_u \rightarrow {}^2\Sigma^+ \oplus {}^2\Pi. \tag{4}$$

Their direct product and its reduction are

$$^2\Sigma^+ \otimes ({}^2\Sigma^+ \oplus {}^2\Pi) \rightarrow {}^1\Sigma^+ \oplus {}^3\Sigma^+ \oplus {}^1\Pi \oplus {}^3\Pi. \tag{5}$$

Obviously, Eq.(5) contains $^1\Sigma^+$. Thus the possible dissociation limit for the $A^1\Sigma^+$ state may be

$$\mathrm{LiH}(A^1\Sigma^+) \rightarrow \mathrm{H}(^2S_g) + \mathrm{Li}(^2P_u), \tag{6}$$

$$\mathrm{LiH}(A^1\Sigma^+) \rightarrow \mathrm{Li}(^2S_g) + \mathrm{H}(^2P_u). \tag{7}$$

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 $A^1\Sigma^+$ state,

$$\mathrm{LiH}(A^1\Sigma^+) \rightarrow \mathrm{H}(^2P_u) + \mathrm{Li}(^2P_u). \tag{8}$$

Compared with the possible dissociation limits described by Eqs.(6)–(8), Eq.(3) is the most optimal according to the principle of the optimum energy dissociation.[28] It would be doubtless if we take it into consideration only according to that principle. However, the possible dissociation limit described by Eq.(3) does not obey the selection rule for the excited state.[29]

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

$$E_a = D_e^* + \Delta T_e - D_e^0, \tag{9}$$

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, which takes into consideration the vibrational zero energy.[30] T_e is the adiabatic excitation energy for a given state. ΔT_e is the difference between the ground and the excited state. And E_a is the atomic excitation energy sum of the separated atoms in the dissociation limit. Using Eq.(9) and the experimental data,[30] we obtain $E_a \approx 1.848$ eV for the $A^1\Sigma^+$ 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 atoms,[27] but greatly smaller than the one between the ground state ^2S_g and the first excited state ^2P_u for H atoms, and 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.[27] Thus we conclude that the reasonable dissociation limit for the $A^1\Sigma^+$ state is Eq.(6).

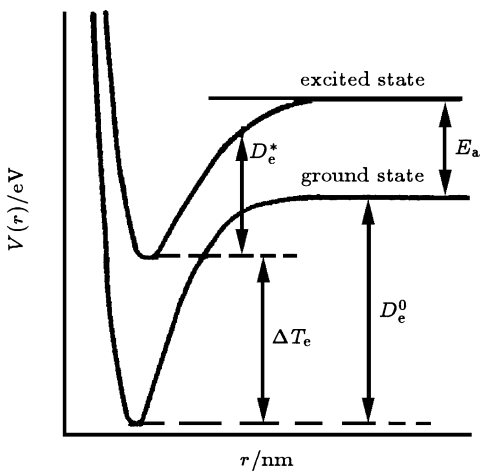


Fig.1. Potential energy curves of the ground and excited state.

3. Results and discussion

The calculations described here are carried out using Gaussian 03 program package.[12] Firstly, by comparing a large number of computed results about the dissociation energy and equilibrium geometry of the $A^1\Sigma^+$ state between theories and experiments[13,30] at numerous basis sets such as D95, D95(d), D95++, D95V(d,p), 6-311G(d,p), D95V++, 6-311G++, DGDZVP and cc-PVTZ, we select 6-311G(3df,3pd) basis set[31,32] for further calculations in complete active space. Then, using the selected 6-311G(3df,3pd) basis set, we calculate the potential energies of this state over the internuclear separation range from about 0.1 to 1.4 nm. The calculated potential energies at selected values of the internuclear separation are tabulated in Table 1, and the curve of the *ab initio* calculated points over this range is shown in Fig.2. In order to investigate the PEC details of this state, the curve around the equilibrium position from about 0.15 to 0.35 nm is shown in Fig.3, too.

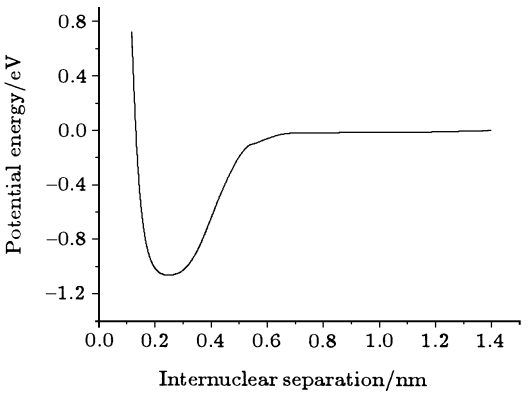


Fig.2. Potential energy curve of the first excited singlet state of ^{7}LiH molecule at internuclear separation from 0.1 to 1.4nm.

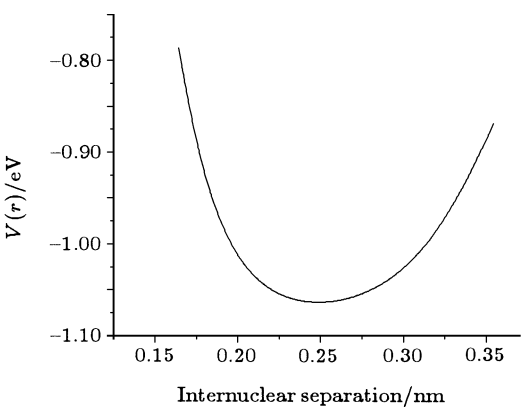


Fig.3. Potential energy curve of the first excited singlet state of ^{7}LiH molecule around the equilibrium position.

Table 2 shows that the computed dissociation energy of the $A^1\Sigma^+$ state is equal to 1.064 eV at 6-311G(3df,3pd) basis set level. It is easy to be calculated that the difference between this computed value and the experimentally determined one[13,30] is only about 1.1%. According to the difference value, we can say that our computed dissociation energy is in excellent agreement with the measurements,[13,30] and represents an significant improvement over the previous theories.[14,15,24–26]

Table 1. Potential energies $E(R)$ at different internuclear separations R for the $A^1\Sigma^+$ state.

R/nm	$E(R)$/hartree	R /nm	$E(R)$/hartree	R /nm	$E(R)$/hartree
0.1058354	−7.822091	0.2804639	−7.917628	0.5820949	−7.881678
0.1164190	−7.852427	0.2910475	−7.917221	0.6508880	−7.879954
0.1322943	−7.881613	0.3016310	−7.916662	0.6826386	−7.879816
0.1428778	−7.893839	0.3122146	−7.915927	0.7143892	−7.879724
0.1534614	−7.902228	0.3227981	−7.914996	0.7461399	−7.879678
0.1640449	−7.907915	0.3386734	−7.913205	0.7778905	−7.879654
0.1746285	−7.911715	0.3545487	−7.910945	0.8096411	−7.879641
0.1852120	−7.914214	0.3704240	−7.908277	0.8413918	−7.879629
0.1957956	−7.915832	0.3862994	−7.905324	0.8731424	−7.879603
0.2063791	−7.916861	0.4021747	−7.902222	0.9048930	−7.879600
0.2169627	−7.917500	0.4180500	−7.899103	0.9366437	−7.879593
0.2275462	−7.917875	0.4339253	−7.896074	0.9789778	−7.879582
0.2381297	−7.918068	0.4815513	−7.888296	1.0266038	−7.879576
0.2487133	−7.918125	0.5080101	−7.885133	1.1112721	−7.879561
0.2592968	−7.918069	0.5344690	−7.882763	1.1641899	−7.879552
0.2698804	−7.917906	0.5556361	−7.882698	1.3970278	−7.879017

Table 2. The excitation energy, dissociation energy and equilibrium geometry of the $A^1\Sigma^+$ state (With the supposition that the adiabatic excitation energy for the ground state equals zero, the adiabatic excitation energy for the first excited state listed in this table actually equals the difference between the ground and the first excited state.)

Dissociation limit	Source	T_e/eV	R_e/nm	D_e/eV
$LiH(A^1\Sigma^+) \rightarrow H(^2S_g) + Li(^2P_u)$	This work	3.2657	0.2487	1.064
	Exp.[13]	—	0.2597	1.076
	Exp.[30]	3.2876	0.2605	1.075
	Theory[14]	3.2723	0.2530	1.121
	Theory[15]	3.1179	0.2476	1.018
	Theory[24]	—	0.2540	1.121
	Theory[25]	—	0.2598	1.047
	Theory[26]	3.2044	0.2709	1.048

From Figs.2 and 3, we can easily see that the $A^1\Sigma^+$ state potential energy curve of ^{7}LiH molecule is exceptionally flat over a wide radial range around the equilibrium position R_e, which is quite different from the general cases of diatomic molecules.[33−36] The highly unusual PEC 'square-well' shape of the $A^1\Sigma^+$ state ^{7}LiH molecule leads to unusual negative values of the unharmonicity constant $\omega_e\chi_e$ and the vibration-rotational coupling constant α_e predicted in Ref.[37].

In order to elucidate the 'square-well' shape of the $A^1\Sigma^+$ state, we further calculate dipole moment function of this state over the internuclear separation range from about 0.1 to 1.4 nm at present basis set, and the calculated results are shown in Fig.4. From Fig.4 we clearly see that the calculated dipole moment presents anomalous negative values at the internuclear separation R shorter than about 0.31 nm. This shows that the dipole of the $A^1\Sigma^+$ state is affirmatively of ionic character. When the internuclear separation R varies from about 0.31 nm to 0.42 nm, the magnitude of the dipole moment goes up as R increases; when the internuclear separation R is greater than 0.42 nm, the magnitude of the dipole moment goes down as the $Li(^2P_u)$+$H(^2S_g)$ asymptote is approached. According to these, we think that the highly unusual shape may arise from the avoided crossing of two zero-order curves, one of covalent (LiH), the other of ionic (Li^+H^-) character, as was firstly predicted by Mulliken in 1936.[37] The strongly bonded ionic state Li^+H^- dissociates to $Li^+(^1S_g)$+ $H^-(^1S_g)$, whereas the weakly bound covalent state LiH dissociates to $Li(^2S_g)$+$H(^2S_g)$ (Eq.(3)). Thus, an avoided crossing at $R \approx 0.31$ nm[37,38] takes place between the strongly bonded ionic state Li^+H^- dissociating to the ground-state atomic ions and the weakly bound covalent state

LiH dissociating to the ground-state atoms. However, before the ionic dissociation limit, a second avoided crossing[37] ensures that the $A^1\Sigma^+$ state actually dissociates to neutral atoms, Li(^2P_u)+H(^2S_g) (Eq.(6)), rather than to ions.[13] Although the dipole of the $A^1\Sigma^+$ state also has Li^-H^+ polarity, further calculations show that the $Li^-(^1S_g)$+$H^+(^1S_g)$ ionic curve does not significantly affect the shape of the $A^1\Sigma^+$ state potential curve. In addition, an explanation is afforded for the observed dissociation energy of the $A^1\Sigma^+$ state ^{7}LiH molecule, which is anomalously small relative to that expected for dissociation to the $Li^+(^1S_g)$+ $H^-(^1S_g)$ ion pair limit.[13]

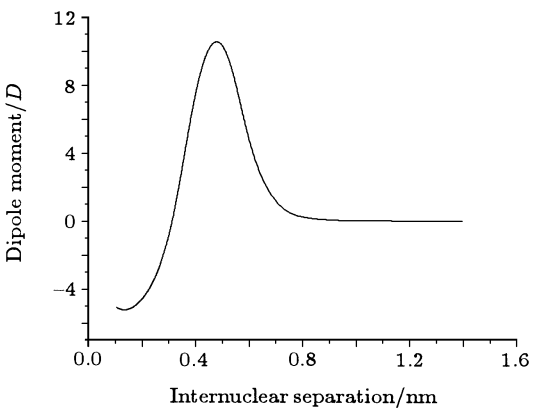


Fig.4. Dipole moment function of the first excited singlet state of ^{7}LiH molecule.

Numerous theories[23,39−41] and experiments[42−44] have supported the above-mentioned analysis, too, such as the large dipole moment[39,40] in v=0 of the $X^1\Sigma^+$ state, the relatively small and rapidly varying dipole moments[42,43] for low-v levels of the $A^1\Sigma^+$ state and the *ab initio* calculations of the positive dipole moment functions about the $A^1\Sigma^+$ state.[23,41]

Our computed results about T_e and D_e listed in Table 2 affirmatively support that the dissociation limit of this state is Eq.(6). To be specific, $\Delta T_e = T_e(A^1\Sigma^+) - T_e(X^1\Sigma^+)$=3.2657 eV–0.0 eV=3.2657 eV, D_e^*=1.064 eV, D_e^0=2.515 eV, thus employing the ground-state experimental dissociation energy[30] and Eq.(9), we can easily calculate the excitation energy sum of the two atoms, Li and H, in the dissociation limit. And the computed value equals 1.814 eV. Obviously, this value approximately equals the difference between the ground state ^2S_g and the first excited state ^2P_u for the atom Li, thus further affirms that the atom Li is in the first excited state ^2P_u, and the atom H is in the ground state ^2S_g. So, the reasonable dissociation limit of the $A^1\Sigma^+$ state is only Eq.(6).

The computed equilibrium internuclear separation of the $A^1\Sigma^+$ state obtained by geometry optimization is found to be different from the one obtained by single-point energy scanning (SPES) at 6-311G(3df,3pd) basis set. The geometry optimization result equals 0.2637 nm, whereas the SPES one is 0.2487 nm. Further calculations find that obvious differences exist at numerous basis sets such as D95, D95(d), D95++, D95V(d,p), 6-311G(d,p), D95V++, 6-311G++, DGDZVP and cc-PVTZ for this state at present SAC-CI theory level. Because the unique GSUM (group-sum of the linked and unlinked operations at different geometries) method used in the SPES calculations is not completely identical with the one used in the geometry optimization calculations,[11,12] the difference of the above-mentioned results is easily understood. In detail, the GSUM method is not automatically done in the geometry optimization in this SAC-CI Gaussian version,[11,12] since it is difficult in general to say where is the unknown optimized geometry. Furthermore, by comparison between our computed results and the experimental data,[13,30] we have found that the equilibrium internuclear distance obtained by SPES is closer to the experiments[13,30] than the one obtained by geometry optimization at the same basis set. Thus we can say that the result obtained by SPES is more accurate than the one obtained by geometry optimization. So, in present work, in order to obtain accurate equilibrium geometry, we make SPES calculations around the equilibrium position of the $A^1\Sigma^+$ state by a very small step at different basis sets. Finally, we find that the lowest potential energy lies at R_e=0.2487 nm and the 6-311G(3df,3pd) basis set is the most suitable one. Obviously, the value is in good agreement with the experiments.[13,30] The smallest difference between our computed R_e value and the experimentally determined one is about 4.2%,[13] and the largest difference is only about 4.5%.[30] Our calculated value is superior in accuracy to the one given by Sasagane *et al*,[15] who employed a multiconfiguration time-dependent Hartree–Fock approximation method and a 20-CGTO basis set in their calculations, equivalent to the one given by Docken *et al*,[26] who employed an *ab initio* self-consistent-field plus configuration-interaction method and a $22\sigma12\pi7\delta$ Slater-type function (STF) basis set in their calculations, but inferior to the one given by Partridge *et al*,[14] who employed an *ab initio*

multiconfiguration self-consistent-field method and a $23\sigma 8\pi 4\delta$ STF basis set in their calculations, Mendéz *et al*[24] who employed a model potential method, and Ben-Shlomo and Kaldor,[25] who employed an open-shell coupled-cluster method and a $22\sigma 12\pi 7\delta$ STF basis set in their calculations. However, the calculation method in present work is much simpler than that in Ref.[14,24–26].

By the way, employing our present computed PEC values, the experimental harmonic frequency[30] and the calculation method presented in Ref.[34], we obtain the negative values of $\omega_e\chi_e$=–4.7158 cm^{-1} and α_e=–0.08649cm^{-1}.

Table 3. Vertical excitation energy (in unit of eV) from the ground to the $A^1\Sigma^+$ state.

Excitation	This work	Theory[14]	Theory(FCI)[15]	Theory[45]	Theory[46]	Theory (QHCC)[47]
$X^1\Sigma^+ \rightarrow A^1\Sigma^+$	3.613	3.60	3.524	3.61	3.57	3.72

In order to compare further with previous theories, employing the ground-state PEC, we calculate the vertical excitation energy from the ground to the $A^1\Sigma^+$ state and list it in Table 3 together with the recent *ab initio* calculated results.[14,15,45–47] From Table 3 we obviously see that our computed result (obtained at R=0.15875 nm) is in excellent agreement with the one given in Ref.[45], (obtained at R=0.15875 nm) in which Boutalib and Gadéa[45] employed a very complicated basis set, and is in good agreement with the one given in Ref.[14] (obtained at R=0.15957 nm), but is slightly larger than the ones given in Ref.[15,46] (obtained at R=0.15957 nm), and slightly smaller than the one given in Ref.[47] (obtained at R=0.15957 nm). Unfortunately, to our knowledge there is no experimental information to be compared with about the vertical excitation energy from the ground to the $A^1\Sigma^+$ state.

We can get a definite harmonic frequency value of this $A^1\Sigma^+$ state by means of geometry optimization, but we cannot regard this value as an accurate one, since the equilibrium internuclear separation obtained by geometry optimization is different from the one obtained by SPES. In measurements, we have found an experimental frequency value[30] of 280.96cm^{-1}. And in theories, we have surprisingly found no calculations in literatures to our knowledge. But then, employing the Rydberg–Klein–Rees (RKR) method and the analytic Murrell–Sorbie function,[48] we can attain the following relationship:

$$\omega_e = \left[\frac{D_e(a_1^2 - 2a_2)}{4\pi^2\mu c^2}\right]^{1/2}. \qquad (10)$$

Here, μ is the reduced mass of ^{7}LiH molecule. ω_e is the harmonic frequency of the $A^1\Sigma^+$ state. c is the light speed in vacuum space. a_1 and a_2 are the coefficients of the analytic Murrell–Sorbie function[48] derived from a least-squares fit. Using the calculation method presented in Ref.[34], we can approximately estimate the ω_e value of 502.47cm^{-1}.

4. Conclusions

Figures 2 and 3 show the anomalous 'square-well' PEC and Fig.4 presents the dipole moment function of the $A^1\Sigma^+$ state. Through SPES calculations around the equilibrium position of the $A^1\Sigma^+$ state by a very small step, we have accurately determined the equilibrium internuclear separation. Compared with previous theories,[14,15,24–26] the computed dissociation energy and equilibrium internuclear separation of the $A^1\Sigma^+$ state, especially the computed dissociation energy at present, is obviously in better agreement with experiments, thus represents an improvement over the previous theories.[14,15,24–26] In addition, the computed vertical excitation energy from the ground to the $A^1\Sigma^+$ state is in excellent agreement with the previous theoretical results,[14,15,45–47] too.

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