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Ab initio calculations on the spectroscopic constants, vibrational levels and classical turning points for the $2^1\Pi_u$ state of dimer $^7Li_2$*

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The accurate dissociation energy and harmonic frequency for the highly excited $2^1\Pi_u$ state of dimer $^7Li_2$ have been calculated using a symmetry-adapted-cluster configuration-interaction method in complete active space. The calculated results are in excellent agreement with experimental measurements. The potential energy curves at numerous basis sets for this state are obtained over a wide internuclear separation range from about $2.4a_0$ to $37.0a_0$. And the conclusion is gained that the basis set 6-311++G(d,p) is a most suitable one. The calculated spectroscopic constants D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e at 6-311++G(d,p) are 0.9670 eV, 0.3125 nm, 238.6 cm^{-1}, 1.3705 cm^{-1}, 0.0039 cm^{-1} and 0.4921 cm^{-1}, respectively. The vibrational levels are calculated by solving the radial Schrödinger equation of nuclear motion. A total of 53 vibrational levels are found and reported for the first time. The classical turning points have been computed. Comparing with the measurements, in which only the first nine vibrational levels have been obtained so far, the present calculations are very encouraging. A careful comparison of the present results of the parameters D_e and ω_e with those obtained from previous theories clearly shows that the present calculations are much closer to the measurements than previous theoretical results, thus representing an improvement on the accuracy of the *ab initio* calculations of the potentials for this state.

Keywords: *ab initio* calculation, dissociation energy, vibrational level, turning point
PACC: 3410, 3420

1. Introduction

Analytic potential energy functions (APEFs) of diatomic molecules are very important in atomic and molecular physics, because, on the one hand, accurate APEF plays a crucial role in investigating various molecular properties, such as determining the accurate spectroscopic constants, and acquiring the trustworthy vibrational levels and classical turning points; on the other hand, detailed knowledge of APEF is very useful to the understanding of collision processes between atoms and molecules since the relatively slow nuclear motion is very sensitive to the details of the electronic APEF. In order to determine the trustworthy collision dynamics at ultralow energies,[1] accurate APEF, particularly highly accurate APEF over a large internuclear separation range, is especially desirable. Though APEF calculation for small molecules can be made directly by solving the electronic Schrödinger equation, the computation of highly accurate APEF, especially highly accurate APEF for highly excited states, is still a very formidable task.

As to the lithium dimer $^7Li_2$, the second smallest homonuclear molecule next to H_2, its APEFs have been studied extensively both theoretically and experimentally.[2−9] However, only a few theoretical researches[10−12] and experimental investigations[13] have been devoted to the highly excited $2^1\Pi_u$ state to date to our knowledge. The earlier investigations on this state were carried out by Watson *et al*,[10] using a model potential method with 29 molecular orbitals consisting of eight σ_g, five σ_u, eight π_g and eight π_u. Their dissociation energy D_e, harmonic frequency ω_e and equilibrium internuclear separation R_e were greatly deviated from the most recent measurements.[13] Afterward, Konowalow and Fish[11] used the valence configuration interaction method with a compact basis set comprising 5s, 3p, 2d and 1f functions on each atom by a combination of energy and polarizability criteria to calculate D_e, ω_e and R_e.

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However, large discrepancies exist between their results and the measurements.[13] Lately, Poteau and Spiegelmann[12] used the effective core pseudopotential and the 7s5p3d1f basis set centred at the two Li atoms (88 contracted Gaussians) to compute D_e, ω_e and R_e. Though the R_e value is very close to the measurement,[13] the D_e and ω_e results have obvious deviations.[13] In this paper, we attempt to improve the accuracy of the *ab initio* potentials for this state. By comparing the present theoretical calculations of D_e and ω_e with those obtained from previous theories,[10−12] the present calculations described here are in excellent agreement with measurements,[13] implying that the present study is more complete effort on the APEF and other spectroscopic constants than previous theories, thus represents an improvement on the calculations in this respect.

In this paper, the spectroscopic constants, vibrational levels, and classical turning points for the $2^1\Pi_u$ state of dimer $^7Li_2$ are calculated. And the reasonable dissociation limit of this state is deduced. In the next section, we describe the methodological details. In Section 3, we present the calculated results for the spectroscopic constants, a total of 53 vibrational levels and their classical turning points, and make some useful discussion about them. Concluding remarks are made in Section 4.

2. Methodological details

The calculations about the potential energy curves (PECs) of the $2^1\Pi_u$ state are performed using a symmetry-adapted-cluster configuration-interaction (SAC-CI) method[14,15] in complete active space in Gaussian03 program package.[15] In addition, numerous basis sets, such as 6-311++G(df,pd), 6-311++G(2df,2pd), 6-311++G (3df,2pd), 6-311++G(d,p), cc-PVTZ, 6-311++G, 6-311++G(3df,3pd), 6-311++G(2df,pd), Aug-cc-PVTZ, 6-311G(3df,3pd), D95(d,p), D95V++, D95 (3df,3pd), DGDZVP, D95V and TZVP, are employed. Because the R_e value obtained by the fine single-point energy scanning (SPES) is more reasonable than that obtained by geometry optimization at the SAC-CI level of theory at the same basis set,[16] our calculations are divided into three steps to obtain the accurate R_e results. Firstly, the fine SPES calculations near the experimental equilibrium position are carried out by a very tiny step so as to achieve the accurate R_e values at various basis sets. Secondly, we calculate the PECs of this state through the equilibrium positions obtained by SPES at $0.2a_0$ intervals over the internuclear separation range from about $2.4a_0$ to $37.0a_0$. And lastly, the *ab initio* data of PECs at various basis sets are all fitted to the analytic Murrell–Sorbie (M–S) function with the least square fitting method, thus the dissociation energies D_e and the APEFs are obtained. Based on the APEFs obtained here, the force parameters, quadratic f_2, cubic f_3 and quartic f_4, are determined. And then the spectroscopic constants, ω_e, $\omega_e\chi_e$, α_e and B_e, are calculated. By comparing the computed D_e, ω_e and R_e with the measurements,[13] a most suitable basis set, 6-311++G(d,p),[17−19] is selected. Using the APEF obtained at the theoretical SAC-CI/6-311++G(d,p) level, the radial Schrödinger equation of nuclear motion is solved to acquire all the vibrational levels and their classical turning points, R_{min} and R_{max}.

3. Results and discussion

Through fine SPES calculations near the experimental equilibrium position at a very tiny interval of $0.01a_0$, we can obtain the accurate R_e values at different basis sets. Some of them are listed in Table 1.

Table 1. Equilibrium constants for the $2^1\ \Pi_u$ state of $^7Li_2$.

Source	T_e/eV	D_e/eV	R_e/nm	ω_e/cm^{-1}
Experiments[13]	3.7881	0.9642	0.3074	239.1
SAC-CI/6-311++G(d,p)	3.7766	0.9670	0.3125	238.6
SAC-CI/6-311++G(2df,2pd)	3.7766	0.9801	0.3101	240.8
SAC-CI/6-311++G(df,pd)	3.7777	0.9530	0.3127	240.7
SAC-CI/6-311++G(3df,2pd)	3.7794	1.0072	0.3112	237.1
SAC-CI/AUG-cc-PVTZ	3.8065	1.0172	0.3080	236.3
SAC-CI/6-311++G(2df,pd)	3.7766	0.9801	0.3101	240.8
SAC-CI/6-311++G(3df,3pd)	3.7794	1.0072	0.3106	235.1

The M–S function is a widely used potential energy function. It describes interaction potential energies of neutral diatomics well. The common M–S function is[20]

$$V(\rho) = -D_{\rm e}\Big(1 + \sum_{i=1}^{n} a_i \rho^i\Big)\exp(-a_1\rho), \qquad (1)$$

where $\rho = R - R_{\rm e}$, R is the internuclear distance of diatomics, and $R_{\rm e}$ is regarded as a fixed parameter in the fitting process, which is acquired by fine SPES calculations in this paper. The parameters a_i are determined by the fitting method using *ab initio* data. Generally, satisfactory results can be obtained when n equals 3. Thus, Eq.(1) can be simplified into the following form:

$$V = -D_{\rm e}(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho). \qquad (2)$$

By iterating a system of normal equations based on a least-squares fit, the parameters a_1, a_2, a_3 and $D_{\rm e}$ in Eq.(2) are calculated at various basis sets. From these we can calculate the quadratic force constant f_2,

$$f_2 = D_{\rm e}(a_1^2 - 2a_2). \qquad (3)$$

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

$$\omega_{\rm e} = \sqrt{\frac{f_2}{8\pi c\mu R_{\rm e}^2}}\,. \qquad (4)$$

Here, μ and c are the reduced mass of dimer $^7Li_2$ and the light speed in vacuum space, respectively. The calculated $\omega_{\rm e}$ values are also listed in Table 1.

Table 1 lists only the encouraging results. Some results at these basis sets, such as cc-PVTZ, 6-311++G, D95(3df,3pd) and 6-311G(3df,3pd), are not included in Table 1 since either $D_{\rm e}$ or $\omega_{\rm e}$ values at these basis sets is greatly deviated from the measurements.[13] From Table 1 one can easily find that the basis set 6-311++G(d,p) is an excellent one, since the calculated values of $D_{\rm e}$, $\omega_{\rm e}$ and $T_{\rm e}$ at this basis set are in agreement with the measurements[13] within 0.0028 eV or 0.29%, 0.5 cm^{-1} or 0.21%, and 0.0115 eV or 0.30%, respectively, though $R_{\rm e}$ is somewhat larger than the measurement[13] by 0.0051 nm or 1.66%.

The APEF parameters at 6-311++G(d,p) are all listed in Table 2 for integrality. At the same time, both the fitting results and the curve of the *ab initio* calculated points over this range are also intuitively shown in Fig.1.

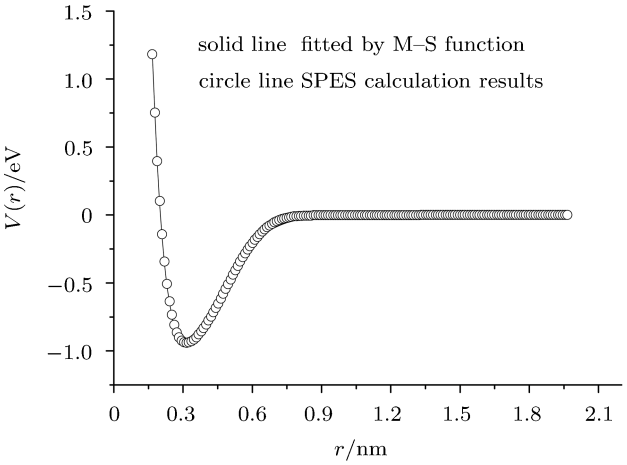


Fig.1. PEC of the excited dimer $^7Li_2$.

Table 2. Parameters of M–S PEF for dimer $^7Li_2(2\,^1\Pi_u)$ at the theoretical SAC-CI/6-311++G(d,p) level.

$D_{\rm e}$/eV	$R_{\rm e}$/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	RMS/eV
0.9670	0.3125	14.12526	59.33019	111.73137	0.017

In order to evaluate the fitting quality of APEF at 6-311++G(d,p), we calculate the root means square error (RMSE),

$$\mathrm{RMSE} = \frac{1}{N}\sqrt{\sum_{i=1}^{N}(V_{\rm APEF} - V_{ab\ initio})^2}\ , \qquad (5)$$

where $V_{\rm APEF}$ and $V_{ab\ initio}$ are energies obtained by the fitted and *ab initio* calculations, respectively. N is the number of fitted points (here $N = 174$). The present RMSE for $^7Li_2(2^1\Pi_u)$ is only 1.7×10^{-2} eV (~ 0.3927 kcal/mol). Obviously, our fitting accuracy is superior to the chemical accuracy (1.0 kcal/mol). Thus we can say that the APEF of dimer $^7Li_2(2\,^1\Pi_u)$ is credible.

3.1. Spectroscopic constants

Based on the following Eqs.(6)–(10), one can easily calculate the force constants f_3 and f_4, then calculate the spectroscopic constants $B_{\rm e}$, $\alpha_{\rm e}$ and $\omega_{\rm e}\chi_{\rm e}$. The calculated results are listed in Table 3. At the same time, we also give the present $T_{\rm e}$, $R_{\rm e}$, $D_{\rm e}$ and $\omega_{\rm e}$ values together with the measurements[13] and other theoretical results[10−12] in Table 3 for convenient comparison.

$$f_3 = -6D_{\rm e}(a_3 - a_1a_2 + a_1^3/3) \qquad (6)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3), \quad (7)$$

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad (8)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\Big(\frac{f_3R_e}{3f_2} + 1\Big), \quad (9)$$

$$\omega_e\chi_e = \frac{B_e}{8}\Big[-\frac{f_4R_e^2}{f_2} + 15(1 + \frac{\omega_e\alpha_e}{6B_e^2})^2\Big]. \quad (10)$$

From Table 3 one can easily find that the best values of D_e and ω_e, obtained from the previous theories, are given by Poteau and Spiegelmann.[12] Their deviations from the measurements[13] are 1.73% for D_e and 3.35% for ω_e. These discrepancies are greatly larger than ours in this paper. As to R_e, the accuracy of the present calculation is somewhat lower than that in Ref.[12], but greatly higher than the ones given in Refs.[10,11]. Thus present calculations represent an improvement as a whole. We cannot make any comparison about B_e and α_e because no measurements and theories about them are available from the existing literature to the best of our knowledge.

Table 3. Comparison between measurements and other calculations about T_e, R_e, D_e, ω_e, $\omega_e\chi_e$, B_e and α_e for dimer $^7Li_2(2\,^1\Pi_u)$ at the theoretical SAC-CI/6-311++G(d,p) level.

Source	T_e/eV	R_e/nm	D_e/eV	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
This work	3.7766	0.3125	0.9670	238.6	1.3705	0.4921	0.0039
Exp.[13]	3.7881	0.3074	0.9642	239.1			
Theory[11]	—	0.3697	0.5012	146.5	1.33		
Theory[10]	—	0.3620	0.5196	144.8	1.33		
Theory[12]	3.8040	0.3089	0.9475	231.3			

3.2. Vibrational levels and classical turning points

In the adiabatic approximation, the vibrational levels of a given electronic state of a diatomic molecule are obtained by solving the following radial Schrödinger equation of nuclear motion

$$\Big[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\hbar^2}{2\mu r^2}J(J+1) + V(r)\Big]\Psi_{\nu,J}(r) = E_{\nu,J}\,\Psi_{\nu,J}(r). \quad (11)$$

Here $V(r)$ is the adiabatic rotational potential energy function given by Eq.(2). ν and J are the vibrational and rotational quantum numbers, respectively. By solving Eq.(11), we can obtain a total of 53 vibrational levels for dimer $^7Li_2(2^1\Pi_u)$ when $J = 0$. These values together with the classical turning points, R_{max} and R_{min}, are all given in Tables 4 and 5.

Table 4 shows the first nine vibrational levels, classical turning points and the only measurements.[13] From Table 4 one can find that the calculated results are in good agreement with the measurements[13] as a whole.

There are no vibrational level measurements to be compared with when $\nu \geq 9$. We collect the rest 44 vibrational levels and their classical turning points from $\nu = 9$ to $\nu = 52$ in Table 5. These levels and classical turning points are reported for the first time.

Table 4. Comparison between our calculations and the measurements of vibrational level and classical turning point for the $2^1\Pi_u(J = 0)$ state of $^7Li_2$.

v	SAC-CI/6-311++G(d,p)			measurements[13]		
	$G(v)$/cm^{-1}	R_{min}/nm	R_{max}/nm	$G(v)$/cm^{-1}	R_{min}/nm	R_{max}/nm
0	120.736	0.29388	0.33316	118.592	0.28894	0.32928
1	359.079	0.28144	0.34969	350.742	0.27712	0.34785
2	591.010	0.27351	0.36172	576.405	0.26968	0.36207
3	813.494	0.26751	0.37176	796.068	0.26400	0.37485
4	1037.189	0.26242	0.38103	1010.220	0.25934	0.38602
5	1253.354	0.25811	0.38950	1219.347	0.25536	0.39680
6	1458.834	0.25444	0.39723	1423.936	0.25187	0.40707
7	1668.503	0.25101	0.40495	1624.476	0.24876	0.41691
8	1875.003	0.24790	0.41239	1821.452	0.24596	0.42638

Table 5. Vibrational levels and classical turning points from the theoretical SAC-CI/6-311++G(d,p) level for the $2^1\Pi_u(J=0)$ state of $^7Li_2$.

v	$E(v)$/ cm^{-1}	R_{min}/nm	R_{max}/nm	v	$E(v)$/ cm^{-1}	R_{min}/nm	R_{max}/nm
9	2129.093	0.24437	0.42145	31	6153.879	0.20883	0.60374
10	2375.727	0.24120	0.43020	32	6287.163	0.20800	0.61403
11	2609.158	0.23840	0.43850	33	6415.853	0.20721	0.62472
12	2849.338	0.23570	0.44710	34	6539.853	0.20647	0.63585
13	3056.220	0.23349	0.45459	35	6659.060	0.20576	0.64747
14	3259.753	0.23141	0.46207	36	6773.369	0.20509	0.65966
15	3459.888	0.22946	0.46955	37	6882.664	0.20446	0.67248
16	3656.574	0.22761	0.47706	38	6986.823	0.20387	0.68603
17	3849.759	0.22587	0.48461	39	7085.716	0.20331	0.70042
18	4039.388	0.22422	0.49221	40	7179.201	0.20279	0.71578
19	4225.408	0.22265	0.49988	41	7267.124	0.20230	0.73228
20	4407.763	0.22117	0.50764	42	7349.317	0.20185	0.75014
21	4586.394	0.21975	0.51551	43	7425.596	0.20144	0.76965
22	4761.243	0.21841	0.52349	44	7495.756	0.20106	0.79118
23	4932.248	0.21713	0.53160	45	7559.568	0.20072	0.81526
24	5099.347	0.21591	0.53987	46	7616.771	0.20041	0.84266
25	5262.474	0.21474	0.54837	47	7667.066	0.20015	0.87456
26	5421.562	0.21363	0.55694	48	7710.100	0.19992	0.91286
27	5576.542	0.21258	0.56578	49	7745.448	0.19974	0.96106
28	5727.341	0.21157	0.57485	50	7772.576	0.19960	1.02662
29	5873.883	0.21061	0.58418	51	7790.771	0.19950	1.13119
30	6016.090	0.20970	0.59380	52	7798.932	0.19946	1.43313

3.3. Dissociation limit of dimer $^7Li_2(2\,^1\Pi_u)$

As shown in Fig.2, the atomic excitation energy E_a for an excited state of a molecule equals

$$E_a = D_e^* + \Delta T_e - D_e^0. \tag{12}$$

Here, D_e^* is the dissociation energy for a given excited state. D_e^0 is the dissociation energy for the ground state and equals 1.0561 eV for dimer $^7Li_2$, with the vibrational energy taken as zero.[21] ΔT_e is the adiabatic excitation energy from the ground state to a given state. And E_a is the atomic excitation energy sum of the separated atoms for a given excited state in the dissociation limit when we let the atomic excitation energy sum of the separated atoms in the dissociation limit for the ground state equal zero.

The dissociation limit of the ground state[22] of $^7Li_2$ is

$$Li_2(X^1\Sigma_g^+) \rightarrow Li(^2S_g) + Li(^2S_g). \tag{13}$$

Obviously, the two separated atoms in the dissociation limit for the ground state are both in the ground state. Thus their atomic excitation energy sum in the dissociation limit equals zero.

We obtain $E_a \approx 3.68754$ eV (~ 29738 cm^{-1}) for the $2^1\Pi_u$ state using Eqs.(12) and (13). According to these we conclude that the two Li atoms in the dissociation limit for this state must be both in the excited $2P$ state, that is to say, $^7Li_2(^2P_u)$, according to the atomic energy levels.[23] So, the possible states of $^7Li_2$ corresponding to this dissociation limit are

$$^1\Sigma_g^+(2), {}^1\Sigma_u^-, {}^1\Pi_g, {}^1\,\Pi_u, {}^1\Delta_g,$$
$$^3\Sigma_u^+(2), {}^3\Sigma_g^-, {}^3\Pi_g, {}^3\,\Pi_u, {}^1\Delta_u \tag{14}$$

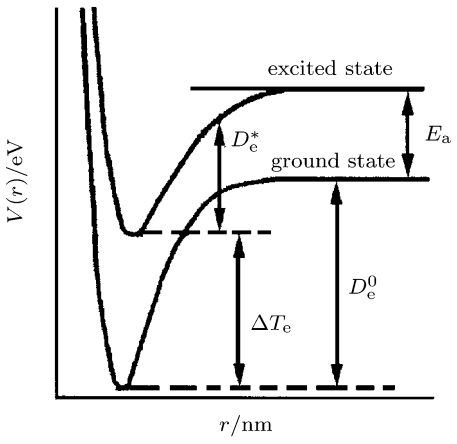


Fig.2. PECs of the ground and excited states.

According to the principle of the reversibility for the microscopic process, we conclude that the reasonable dissociation limit for this excited $2^1\Pi_u$ state must be

$$Li_2(2^1\Pi_u) \rightarrow Li(^2P_u) + Li(^2P_u). \quad (15)$$

4. Conclusions

We have calculated the interaction potentials of the $2^1\Pi_u$ state for dimer $^7Li_2$ using the SAC-CI method at numerous basis sets and found that the best potential can be obtained at the basis set 6-311++G(d,p). We have employed the calculated potential to compute the spectroscopic constants, vibrational levels and classical turning points for dimer $^7Li_2(2^1\Pi_u)$. Favourable agreement has been found in comparing with experimental data. The results obtained here are more complete and in better agreement than previous theoretical investigations as a whole. Also, the reasonable dissociation limit for dimer $^7Li_2(2^1\Pi_u)$ is obtained. As a further investigation, we will employ our derived analytic potential energy function to calculate various scattering cross sections,[24,25] especially at very low energies.

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