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Ab initio calculations on the $a^3\Sigma_u^+$ state properties of dimer $^7Li_2$*

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

[a)] *College of Physics & Electronic Engineering, Xinyang Normal University, Xinyang* 464000, *China*

[b)] *College of Physics & Information Engineering, Henan Normal University, Xinxiang* 453007, *China*

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The comparison between single-point energy scanning (SPES) and geometry optimization (OPT) in determining the equilibrium geometry of the $a^3\Sigma_u^+$ state for $^7Li_2$ is made at numerous basis sets such as 6-311++G(2df), cc-PVTZ, 6-311++G(2df,p), 6-311G(3df,3pd), 6-311++G(2df,2pd), D95(3df,3pd), 6-311++G, DGDZVP, 6-311++G(3df,2pd), 6-311G(2df,2pd), D95V++, CEP-121G, 6-311++G(d,p), 6-311++G(2df,pd) and 6-311++G(3df,3pd) in full active space using a symmetry-adapted-cluster/ symmetry-adapted-cluster configuration-interaction (SAC/SAC-CI) method presented in Gaussian03 program package. The difference of the equilibrium geometries obtained by SPES and by OPT is reported. Analyses show that the results obtained by SPES are more reasonable than those obtained by OPT. We have calculated the complete potential energy curves at these sets over a wide internuclear distance range from about $3.0a_0$ to $37.0a_0$, and the conclusion is that the basis set cc-PVTZ is the most suitable one. With the potential obtained at cc-PVTZ, the spectroscopic data (T_e, D_e, D_0, ω_e, $\omega_e\chi_e$, α_e and B_e) are computed and they are 1.006 eV, 338.71 cm^{-1}, 307.12 cm^{-1}, 64.88 cm^{-1}, 3.41 cm^{-1}, 0.0187 cm^{-1} and 0.279 cm^{-1}, respectively, which are in good agreement with recent measurements. The total 11 vibrational states are found at J=0. Their corresponding vibrational levels and classical turning points are computed and compared with available RKR data, and good agreement is found. One inertial rotation constant (B_v) and six centrifugal distortion constants (D_v H_v, L_v, M_v, N_v and O_v) are calculated. The scattering length is calculated to be –$27.138a_0$, which is in good accord with the experimental data.

Keywords: *ab initio*, potential energy curve, spectroscopic data, vibrational state, scattering length
PACC: 3520G, 3120D

1. Introduction

From a theoretical view point, the dimer $^7Li_2$ is interesting since it is the simplest and smallest stable homonuclear metal molecule. Thus it is not surprising that the dimer is usually used for testing and applications of new methodologies.[1−5] A great amount of theoretical results[6−21] about its spectroscopic constants and potential energy curves (PECs) has been reported during the last decades. In theories, following the observation by Bradley *et al*[22] of the Bose–Einstein condensation (BEC), there has been considerable interest in determining the scattering length[23] of two-ground-state Li atoms from an accurate PEC of the lowest triplet state, $a^3\Sigma_u^+$, of the dimer, since the scattering length, which can be deduced from the potential of the $a^3\Sigma_u^+$ state, determines the stability of the BEC. In experiments, atomic densities are sufficiently low so that two-body interactions dominate and BEC formation for $^7Li_2$ is dependent on the interaction potential of the $a^3\Sigma_u^+$ state. But to the best of our knowledge, previous investigations[6−16] on this state have been incomplete in some aspect, such as inadequate treatment of electron correlation, use of limited basis sets and/or considering only a small range of internuclear separation. Compared with the previous theories,[6−16] the present work is considered to be the most complete effort in dealing with the potential, spectroscopic data, vibrational levels and scattering length, and the present result is in excellent agreement with the measurements[23−26] wherever available.

In this paper, the accurate equilibrium geometry, dissociation energy and PEC for $^7Li_2(a^3\Sigma_u^+)$ have been calculated using the SAC/SAC-CI method[27] presented in Gaussian03 program package.[28] With the potential obtained at cc-PVTZ, the spectroscopic data ($\omega_e, \omega_e\chi_e$, α_e and B_e), the vibrational levels and their corresponding classical turning points, the inertial rotation constant, the centrifugal distortion constants and the scattering length are computed.

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

We will show that the single-point energy scanning (SPES) are more reasonable than the geometry optimization (OPT) method in determining the equilibrium internuclear separation, R_e, and thus the accurate harmonic frequency, ω_e, is obtained only by fitting the PEC near the equilibrium position. In the next section, we will make a wide comparison between the SPES and the OPT in determining the R_e values at a number of basis sets, discuss the drawbacks of this methodology in obtaining the R_e value, and select the most suitable basis set for further calculations. In Section 3, we employ the potential obtained at cc-PVTZ over a wide interatomic distance range from $3.05a_0$ to $37.05a_0$ to perform some interesting calculations and make some discussion. Conclusion remarks are made in Section 4.

2. Methodological details

To obtain the accurate equilibrium geometry, our calculations are made in two stages. First, the OPT calculations[27,28] are performed so as to attain the equilibrium internuclear distance at a number of basis sets such as 6-311++G(2df), D95(3df,3pd), 6-311G(3df,3pd), 6-311G(2df,2pd), 6-311++G(2df,pd), 6-311++G(2df,2pd), 6-311++G, DGDZVP, 6-311++G(3df,2pd), cc-PVTZ, D95V++, 6-311++G(2df,p), CEP-121G, 6-311++G(d,p) and 6-311++G(3df,3pd). Then, we make the SPES calculations near the experimental equilibrium position by a very tiny step under the same conditions. The results obtained by OPT (R_e-OPT) and by SPES (R_e-SPES) are given in Table 1.

Table 1. Equilibrium constants for the $a^3\Sigma_u^+$ state of $^7Li_2$.

Source	T_e/eV	D_e/cm^{-1}	D_0/cm^{-1}	R_e-SPES/nm	R_e-OPT/nm	ω_e/cm^{-1}
experiments[24]	1.0148	333.69	301.83	0.4173		
cc-PVTZ	1.0060	338.71	307.12	0.4154	0.4212	64.88
6-311++G(2df,pd)	0.9912	315.81	283.74	0.4196	0.4238	65.91
6-311G(2df,2pd)	0.9870	329.83	295.27	0.4117	0.4241	70.75
CEP-121G	0.8621	174.90	151.65	0.4503	0.4524	48.59
6-311++G(3df,2pd)	0.9850	310.48	277.29	0.4154	0.4265	68.42
6-311++G(3df,3pd)	0.9830	310.97	280.07	0.4233	0.4265	63.46
6-311++G	0.8651	166.94	142.50	0.4445	0.4520	51.05
6-311++G(2df)	0.9890	315.16	280.63	0.4117	0.4238	71.17
cc-PVDZ	0.9499	259.39	228.35	0.4191	0.4226	64.35
6-311++G(d,p)	0.9542	225.40	196.98	0.4255	0.4290	59.02
D95V++	0.8446	155.15	135.21	0.4551	0.4597	41.91
6-311++G(2df,p)	0.9908	315.35	282.61	0.4170	0.4238	67.35
6-311G(3df,3pd)	0.9834	321.05	290.99	0.4255	0.4249	61.71
6-311++G(2df,2pd)	0.9908	314.44	281.72	0.4170	0.4238	67.31
DGDZVP	0.8754	173.39	147.57	0.4440	0.4457	53.88
D95(3df,3pd)	0.9831	326.76	295.73	0.4202	0.4233	63.83

Generally speaking, at the same level of theory, method and basis set, the two approaches, OPT and SPES, are expected to produce the very same R_e result. If not, one of them is not robust enough to determine R_e. From Table 1, one can easily find that the R_e value obtained by OPT is different from that obtained by SPES under the same conditions. For example, at cc-PVTZ and 6-311++G(2df,2pd) basis sets, the R_e values obtained by OPT equal to 0.4212 and 0.4238 nm, whereas those obtained by SPES are 0.4154 and 0.4170 nm, respectively. Careful examinations have found that the unique method of group sum of operators (GSUM) used in the SPES is incompletely identical with that used in the OPT method,[27] thus the differences among the above results are easily understood. In detail, the GSUM method is not automatically done in OPT calculations in this SAC-CI Gaussian version,[27,28] because it is difficult in general to ascertain where the unknown optimized geometry is. Though after optimization, we can again make perturbation selection and repeat optimization using freshly selected operators, the OPT method can only do an additional single-point SAC-CI calculation.[27,28] This is the reason why the result obtained by SPES is quite integrated into the PEC, and all the spectroscopic data including R_e can be

derived from the PEC. Thus the result obtained by SPES is more reasonable, and the accurate R_e value is obtained only by performing the SPES near the experimental equilibrium position at a very small step.

Since the two approaches, OPT and SPES at the same level of theory, give different R_e values, we cannot directly calculate the frequency after we have performed the OPT calculations. And it is obviously unreliable to judge whether or not a basis set is suitable for PEC computations only by R_e accuracy, thus in order to select a most suitable basis set for further investigations, we must make the D_e calculations. Our calculated results are given in Table 1, too.

For the $a^3\Sigma_u^+$ state, the most recent experimental D_e and R_e values obtained by Linton *et al*,[24] who calculated an improved Rydberg–Klein–Rees (RKR) PEC using data from high-resolution fluorescence measurements of transitions from the $2^3\Pi_g$ to the $a^3\Sigma_u^+$ state of $^7Li_2$, are 333.69 cm^{-1} and 0.4173 nm, respectively. By comparing our D_e and R_e results tabulated in Table 1 with these experimental data,[24] we find that the basis set cc-PVTZ is a most suitable one. In this paper, calculations of the vibrational states and the scattering length are based on the potential obtained at this basis set.

3. Results and discussion

Using the basis sets tabulated in Table 1, we have calculated the PECs for $^7Li_2(a^3\Sigma_u^+)$ in full active space at a $0.2a_0$ step over the internuclear separation range from about $3.0a_0$ to $37.0a_0$. In order to be convenient for further calculations at cc-PVTZ, we tabulate the computed potential energies at selected values of the internuclear separation in Table 2 and plot the curve of the *ab initio* calculated points over this range in Fig.1.

Table 2. Potential energies $E(R)$ at different interatomic distances R for the $a^3\Sigma_u^+$ state at the basis set cc-PVTZ.

R/a_0	$E(R)$/hartree	E/a_0	$E(R)$/hartree	E/a_0	$E(R)$/hartree	E/a_0	$E(R)$/hartree
3.05	−14.795505	8.45	−14.893363	15.85	−14.892003	25.45	−14.891917
3.85	−14.849791	8.65	−14.893308	16.65	−14.891976	26.25	−14.891916
4.65	−14.876024	9.25	−14.893118	17.45	−14.891957	27.05	−14.891915
5.45	−14.887355	9.85	−14.892918	18.25	−14.891944	28.05	−14.891914
6.05	−14.891069	10.45	−14.892733	19.05	−14.891935	29.05	−14.891914
6.65	−14.892732	11.05	−14.892571	19.85	−14.891928	30.05	−14.891913
7.05	−14.893216	11.65	−14.892435	20.65	−14.891925	31.05	−14.891913
7.45	−14.893419	12.25	−14.892324	21.45	−14.891923	32.05	−14.891912
7.65	−14.893454	12.85	−14.892234	22.25	−14.891921	33.05	−14.891912
7.85	−14.893460	13.45	−14.892163	23.05	−14.891920	34.05	−14.891911
8.05	−14.893442	14.25	−14.892090	23.85	−14.891919	35.05	−14.891911
8.25	−14.893409	15.05	−14.892040	24.65	−14.891918	37.05	−14.891910

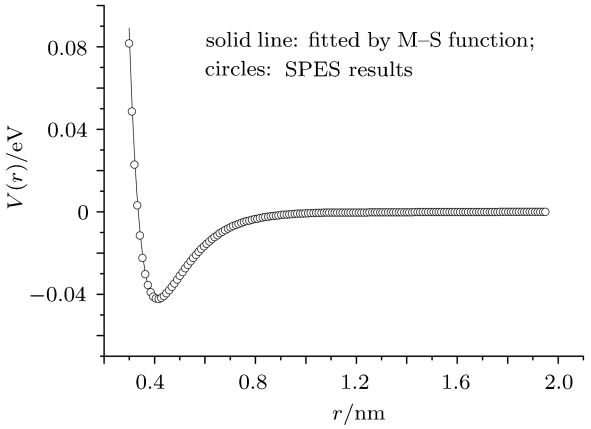


Fig.1. PEC of the lowest triplet excited state of spin-aligned dimer $^7Li_2$.

3.1. Main spectroscopic constants

The Murrell–Sorbie (M–S) function is a widely used potential energy function. It describes interaction potential energies of neutral diatomic molecules well. The common M–S function is of the form[29]

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

where $\rho = R - R_e$, and R is the internuclear distance of the diatom. R_e is regarded as a fixed parameter in the fitting process, which is obtained by SPES in this paper. The parameters a_i and D_e are determined by fitting. Generally, satisfactory results can be obtained

when n equals 3. Thus, Eq.(1) can be rewritten as

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

Such molecule as $^7Li_2(a^3\Sigma_u^+)$, for which the potential well is shallow, is usually fitted by a piecewise function. The piecewise function is often composed of at least two parts. One is the M–S function or another one, the other is the asymptotic van der Waals function.[17] The former is suitable when R is not very large. The latter is used when R is very large so as to guarantee the correct long-range form.[17] Because the spectroscopic data (ω_e, $\omega_e\chi_e$, α_e and B_e) are determined only by the properties of the PEC near the internuclear equilibrium position of the diatomic molecule, whereas the M–S function can give accurately fitting results near this position, we employ the simple Eq.(2) to fit the analytic potential energy function (APEF) in the present investigation.

By iterating a system of normal equations based on a least-squares fit, the parameters a_1, a_2, a_3 and D_e in Eq.(2) are fitted at each basis set. Here, we only tabulate the fitting results at cc-PVTZ in Table 3 together with the R_e value obtained by SPES for integrality. At the same time, the fitting results over this range are intuitively shown in Fig.1. In order to evaluate the fitting quality of PEC, we calculate the root-mean-square error (RMSE),

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(V_{\mathrm{APEF}} - V_{ab\,initio})^2}, \quad (3)$$

where V_{APEF} and $V_{ab\,initio}$ are energies attained by the fitting and the *ab initio* calculations, respectively. N is the number of fitting points (here N=115). The present RMSE for $^7Li_2(a^3\Sigma_u^+)$ is only 2.927 cm^{-1}. Thus we say that the M–S function is well suitable for the fitting of the APEF of $^7Li_2(a^3\Sigma_u^+)$ around the equilibrium position.

Table 3. Parameters of M–S APEF for dimer $^7Li_2(a^3\Sigma_u^+)$ at the SAC-CI/cc-PVTZ level of theory.

D_e/cm^{-1}	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	RMSE/cm^{-1}
338.71	0.4154	14.045	29.786	92.364	2.927

Now, we calculate the ω_e values according to the APEFs obtained at various basis sets. Using Eq.(2), we can derive the expression of the force constant f_2 at the equilibrium position as follows:

$$f_2 = D_e(a_1^2 - 2a_2). \quad (4)$$

The following relationship exists according to the RKR method:[30,31]

$$f_2 = 4\pi^2\omega_e^2\mu c^2. \quad (5)$$

Combining Eqs.(4) and (5), we have

$$\omega_e = \left[\frac{D_e(a_1^2 - 2a_2)}{4\pi^2\mu c^2}\right]^{1/2}. \quad (6)$$

Here, μ and c are the reduced mass of the dimer $^7Li_2$ and the light speed in vacuum, respectively. Employing Eq.(6), we obtain the ω_e values at various basis sets and present them in Table 1, too.

Table 4. Derived spectroscopic data for the $a^3\Sigma_u^+$ state of the dimer $^7Li_2$.

Source	T_e/eV	R_e/nm	D_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
this work	1.006	0.415	338.71	64.88	3.41	0.279	0.0187
exp.[24]	1.015	0.417	333.69	—	—	—	—
exp.[25]	1.015	0.417	333	65.13	3.27	0.276	0.0188
exp.[26]	1.014	0.413	336	67.58	—	—	—
theory[6]	—	0.488	363	85.2	—	—	—
theory[7]	1.023	0.405	306	75.0	—	—	—
theory[9]	—	0.423	292	61.0	3.20	—	—
theory[11]	—	0.411	340.6	65.6	3.16	—	—
theory[12]	—	0.407	354	66.4	3.11	—	—
theory[13]	1.010	0.418	322	63.72	3.20	0.274	0.0186
theory[14]	1.015	0.416	321	66.1	—	—	—
theory[15]	—	0.419	315	65.24	—	—	—

Having obtained the ω_e values and the APEFs near the equilibrium position, we can calculate easily the force constants (f_3 and f_4), and then the spectroscopic data ($\omega_e\chi_e$, B_e, α_e and D_0) using the following equations (7)–(12). Due to length limitation, here we only give the $\omega_e\chi_e$, B_e and α_e values at cc-PVTZ in Table 4 and the D_0 results at various basis sets in Table 1. We also give the T_e, R_e, D_e and ω_e values at cc-PVTZ in Table 4 for convenient comparison:

$$f_3 = -6D_e(a_3 - a_1a_2 + a_1^3/3), \tag{7}$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3), \tag{8}$$

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \tag{9}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\Big(\frac{f_3R_e}{3f_2} + 1\Big), \tag{10}$$

$$\omega_e\chi_e = \frac{B_e}{8}\Big[-\frac{f_4R_e^2}{f_2} + 15\Big(1 + \frac{\omega_e\alpha_e}{6B_e^2}\Big)^2\Big], \tag{11}$$

$$D_0 = D_e - \Big(\frac{1}{2}\omega_e - \frac{1}{4}\omega_e\chi_e\Big). \tag{12}$$

In theories, numerous calculations[6−16] have been performed for the $a^3\Sigma_u^+$ state. The earlier investigation was carried out by Watson *et al*,[6] who used a model potential method with 29 molecular orbitals consisting of eight σ_g, five σ_u, eight π_g and eight π_u. Their R_e value is too large by 17.0% as compared with the most recent experimental one.[24] Kaldor[7] used the coupled-cluster method including single and double substitutions (CCSD) with a 74-CGTO basis set to compute a small section of PEC (about 0.2–0.6 nm), and their derived results are obviously poorer than those obtained in this paper. Balková *et al*[8] used the basis sets of double-ζ quality and the single-reference CCSD approach and compared it with the results obtained from a multireference-CCSD and a full configuration interaction (FCI) calculation, also considering only a limited section of PEC (about 0.2–0.7 nm). Konowalow *et al*[11] combined the results of three previous calculations[9,10,16] so as to obtain an estimated 'most likely' PEC for this state, but compared with the most recent experimental findings,[24] their R_e and D_e results[11] are worse than those obtained in this paper. At the same time, Konowalow and Fish[12] employed a model potential combined configuration interaction (CI) with their compact basis set comprising 5s, 3p, 2d and 1f functions on each atom by a combination of energy and polarizability criteria. Their R_e result is smaller than the experimental one[24] by 2.4%, and the D_e result is larger than the experimental value by 6.0%. Whereas at the SAC-CI/cc-PVTZ level of theory in full active space, our calculated D_e value is in agreement with the experimental one[24] within 5.0 cm^{-1} or 1.5%, and the R_e is in accord with the experimental data[24] within 0.0019 nm or 0.46%. To compute the R_e, D_e and other spectroscopic constants accurately, Schmidt–Mink *et al*[13] have used a valence CI approach along with the effective core polarizability potentials (ECPP) and the molecular basis set consisting of 12s, 7p, 2d Gaussian-type functions for each Li atom, further augmented by 1s, $1p_\sigma$, $2p_\pi$, and $2d_{\pi,\delta}$ functions at the bond centre (90 contracted Gaussians). However, their D_e result is far inferior to ours at present. Lately, Poteau and Spiegelmann[14] have used the effective core pseudopotential (ECP) and the 7s5p3d1f basis set centred on the two Li atoms (88 contracted Gaussians), and Danovich *et al*[15] have used CCSD(T,full)/cc-pCVTZ to carry out the sophisticated correlated calculations so as to attain accurate R_e, D_e and ω_e. However, we can see clearly that their calculated D_e result compared with the most recent experimental one[24] is too small by 3.8%[14] and 5.6%.[15]

From Table 4 we can see easily that the value of ω_e attained at present is in good agreement with the measurements, which is only 0.38% smaller than the experimental one.[25] As to the spectroscopic constants B_e, α_e and $\omega_e\chi_e$, there have been only one group of experimental results[25] and one group of theoretical determinations[13] so far. Obviously, our calculations are in excellent agreement with those in Refs.[13,25] except that our result of $\omega_e\chi_e$ is somewhat larger than the experimental value by 4.28% and the theoretical one[13] by 6.56% (it should be noted that the theoretical value[13] is lower than the measurements[25] by 2.14%). This deviation implies that the fitted APEF near the equilibrium position is not satisfactory enough to give all the spectroscopic parameters accurately.

From the above discussion we can see that the value of D_e obtained in this paper is in good agreement with the measurements,[24−26] and the value R_e attained by SPES is also much inspiring. Combining the RMSE and the comparison of our calculated spectroscopic constants with the experimental and other theoretical ones, we find that the M–S function is well suitable for the fitting of the APEF around the equilibrium position of this state. Of course, we must employ the asymptotic van der Waals function if we want to make a more stringent fitting at a rather large R. The

above calculations prove that which function is chosen to fit the APEF should be determined in the light of the calculation emphasis.

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

$$\Big[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\Big]\Psi_{\nu.J}(r) = E_{\nu,J}\,\Psi_{\nu.J}(r). \quad (13)$$

Here $V(r)$ is the adiabatic rotationless potential ν and J are the vibrational and rotational quantum numbers, respectively. Generally speaking, the potential $V(r)$ in Eq.(13) can be given in two forms. One is analytic, for example, the function tabulated in Table 3. The other is a group of *ab initio* calculated points, for example, the points tabulated in Table 2. In the former case, the analytic function must be accurate enough for a fairly large internuclear separation. In the latter case, the interpolation between the calculated points must be performed so as to produce the data required in the numerical integration of Eq.(13).

The M–S APEF tabulated in Table 3 is accurate enough only near the equilibrium position. Thus we cannot use it when solving Eq.(13) for a rather large internuclear separation range. In order to reduce as far as possible the fitting errors arising either from the fitting process or from the fitted function, here we directly employ the potential tabulated in Table 2 and select the cubic spline function for data interpolation when we solve the radial Schrödinger equation. By numerically solving Eq.(13), we obtain the total 11 vibrational levels for $^7\mathrm{Li}_2(a^3\Sigma_\mathrm{u}^+)$ when J=0. The rotational sublevels of a given vibrational level are represented by the following power series,[32]

$$E_{\nu,J} = G(\nu)+B_\nu[J(J+1)]-D_\nu[J(J+1)]^2 + H_\nu[J(J+1)]^3+L_\nu[J(J+1)]^4 + M_\nu[J(J+1)]^5+O_\nu[J(J+1)]^6. \quad (14)$$

For each vibrational level $G(\upsilon)$, one inertial rotation constant B_υ and six centrifugal distortion constants D_υ, H_υ, L_υ, M_υ, N_υ and O_υ are attained. These vibrational levels together with the corresponding classical turning points, R_max and R_min, are tabulated in Table 5. And one inertial rotation constant and six centrifugal distortion constants when J=0 are tabulated in Table 6.

Table 5. Comparisons of vibrational level and classical turning point between our calculations and RKR data for $^7\mathrm{Li}_2(a^3\Sigma_\mathrm{u}^+)$ when $J=0$ at the SAC-CI/cc-PVTZ level of theory.

υ	SAC-CI/CC-PVTZ			RKR data[24]		
	$G(\upsilon)$/cm^{-1}	R_min/nm	R_max/nm	$G(\upsilon)$/cm^{-1}	R_min/nm	R_max/nm
0	32.432	0.3831	0.4603	31.857	0.3846	0.4630
1	92.162	0.3654	0.5051	90.453	0.3668	0.5092
2	145.309	0.3556	0.5459	142.523	0.3571	0.5503
3	191.992	0.3489	0.5890	188.240	0.3505	0.5922
4	231.279	0.3441	0.6328	227.679	0.3458	0.6373
5	265.179	0.3405	0.6833	260.837	0.3422	0.6885
6	291.616	0.3378	0.7440	287.665	0.3395	0.7501
7	312.395	0.3359	0.8224	308.098	0.3377	0.8297
8	326.108	0.3347	0.9359	322.155	0.3365	0.9441
9	333.824	0.3340	1.1283	330.170	0.3358	1.1392
10	337.747	0.3337	1.5895	333.269	0.3356	1.6052

From Table 5 we see that the $a^3\Sigma_\mathrm{u}^+$ potential obtained at cc-PVTZ is predicted to support 11 vibrational states. Having compared the total 11 vibrational levels with the corresponding classical turning points with the RKR data,[24] we find that the largest deviations do not exceed 1.8% for the vibrational levels and 1.0% for the classical turning points. These show that the present potential is valid up to the dissociation limit. According to these, we say that our calculations tabulated in Table 6 are accurate.

Table 6. One inertial rotation constant and six centrifugal distortion constants for $^7Li_2(a^3\Sigma_u^+)$ when $J = 0$ at the SAC-CI/cc-PVTZ level in theory.

v	$G(v)$/cm^{-1}	B_v/cm^{-1}	D_v/cm^{-1}	H_v/cm^{-1}	L_v/cm^{-1}	M_v/cm^{-1}	N_v/cm^{-1}	O_v/cm^{-1}
0	32.432	0.26933	1.99798×10^{-5}	-9.58997×10^{-10}	-2.06503×10^{-13}	-6.36055×10^{-17}	-1.54541×10^{-20}	-5.48378×10^{-24}
1	92.162	0.25096	2.09713×10^{-5}	-1.30126×10^{-9}	-3.04092×10^{-13}	-1.09386×10^{-16}	-3.52509×10^{-20}	-1.60347×10^{-23}
2	145.309	0.23235	2.22574×10^{-5}	-1.84304×10^{-9}	-5.11162×10^{-13}	-2.32417×10^{-16}	-8.67887×10^{-20}	-4.72737×10^{-23}
3	191.992	0.21332	2.40054×10^{-5}	-2.73753×10^{-9}	-9.56362×10^{-13}	-5.16210×10^{-16}	-2.42129×10^{-19}	-1.52863×10^{-22}
4	231.279	0.19360	2.65148×10^{-5}	-4.29323×10^{-9}	-1.89819×10^{-12}	-1.24910×10^{-15}	-7.83201×10^{-19}	-5.96929×10^{-22}
5	265.179	0.17279	3.03695×10^{-5}	-7.24604×10^{-9}	-4.16880×10^{-12}	-3.27007×10^{-15}	-3.12357×10^{-18}	-3.12000×10^{-21}
6	291.616	0.15019	3.68619×10^{-5}	-1.37858×10^{-8}	-1.06573×10^{-11}	-107411×10^{-14}	-1.79196×10^{-17}	-2.61076×10^{-20}
7	312.395	0.12449	4.65893×10^{-5}	-3.00545×10^{-8}	-2.77891×10^{-11}	-4.33328×10^{-14}	-2.12196×10^{-16}	-5.40335×10^{-19}
8	326.108	0.09233	6.46694×10^{-5}	-6.04458×10^{-7}	-1.18599×10^{-10}	-2.07430×10^{-13}	-1.72320×10^{-15}	-4.21195×10^{-18}
9	333.824	0.06029	9.39574×10^{-5}	-1.84119×10^{-7}	-8.11754×10^{-10}	-5.15483×10^{-12}	-1.01959×10^{-13}	-7.45699×10^{-17}
10	337.747	0.03823	1.11001×10^{-4}	-8.16905×10^{-6}	-7.74772×10^{-9}	-6.81296×10^{-11}	-7.10320×10^{-12}	-6.89408×10^{-16}

3.3. The scattering length

With the rapid development of laser cooling and trapping techniques, the scattering length has important applications in the BEC investigations. It is defined in terms of the zero energy s-wave phase shift δ_0 as

$$a = -\lim_{k\to 0}\frac{\tan\delta_0}{k}, \tag{15}$$

where (in atomic units) a is the scattering length, k is the wave number, $k = \sqrt{2\mu E}$, with diatom reduced mass, μ, and collision energy, E. The scattering length depends very sensitively on the binding energy of the last bound state of the interaction potential. Now we use the potential obtained above to calculate the a value.

The lth partial-wave phase shift δ_l is given by

$$\tan\delta_l = \frac{u_l(r_b)s(r_a) - u_l(r_a)s(r_b)}{u_l(r_a)s(r_b) - u_l(r_b)s(r_a)}. \tag{16}$$

Here (in atomic units) r_a and r_b are two distinct points in the asymptotic region, $s(r) = krj_l(kr)$ and $c(r) = krn_l(kr)$, where j_l and n_l are the spherical Bessel and Neumann functions, respectively. To obtain the δ_l, we solve the following radial Schrödinger equation in atomic unit at very low energies,

$$\Big[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + k^2 - \frac{l(l+1)}{r^2} - U(r)\Big] = 0. \tag{17}$$

Under the boundary condition $r \to \infty$, we have

$$u_l(r) \sim j_l(kr) + \tan\delta_l n_l(kr). \tag{18}$$

Here $U(r) = 2\mu V(r)/\hbar^2$, and $V(r)$ is the potential obtained in this paper. To obtain the best value for the scattering length, similarly to solving Eq.(13), we also directly employ the potential tabulated in Table 2 and select the cubic spline function for data interpolation when we numerically solve the Eq.(17) by the Numerov method. Our calculated result is –$27.138a_0$, which is very close to the experimental result,[23] $-27.6a_0$. It further proves that the potential obtained here is accurate, especially that the long-range behaviour of this potential is reliable. As a further investigation, we will employ our derived analytic PEFs to calculate the various cross sections,[33] especially at very low energies.

4. Conclusion

We have gained the conclusion that the R_e values obtained in this paper by SPES at a number of basis sets are more reliable than those obtained by OPT under the same conditions at SAC/SAC-CI level in theory in full active space in Gaussian03 program package, and found that the best potential can be obtained at cc-PVTZ basis set. We think that the frequency calculation method after OPT is disabled since OPT calculations cannot give reliable R_e results. Employing present potential obtained at cc-PVTZ and the RKR method, we obtain the ω_e value for the $a^3\Sigma_u^+$ state of dimer $^7Li_2$. Favourable agreement is found in comparing with the experimental data. And it is shown that other spectroscopic constants can also be accurately determined only by fitting the *ab initio* data around the equilibrium position of $^7Li_2(a^3\Sigma_u^+)$ using the M–S function. Employing the present potential obtained at cc-PVTZ, we have calculated the vibrational levels, classical turning points and the scattering length, which are in good accord with the mea-

surements wherever available. In addition, we have also computed one inertial rotation constant and six centrifugal distortion constants for $^7Li_2(a^3\Sigma_u^+)$ when J=0 for the first time so far as we know. The results at present are more complete than previous investigations, and can be regarded as an improvement.

References

[1] Kobus J, Moncrieff D and Wilson S 2001 *J. Phys.* B **34** 5127

[2] Maniero A M and Acioli P H 2005 *Int. J. Quant. Chem.* **103** 711

[3] Euboudali F and Joulakian B 2001 *J. Phys.* B **34** 4877

[4] Glushkov V N and Theophilou A K 2002 *J. Phys.* B **35** 2313

[5] Shi D H, Sun J F, Ma H and Zhu Z L 2007 *Acta Phys. Sin.* **56** 2085

[6] Watson D K, Cerjan C J, Guberman S and Dalgarno A 1997 *Chem. Phys. Lett.* **50** 181

[7] Kaldor U 1990 *Chem. Phys.* **140** 1

[8] Balková A, Kucharski S A and Bartlett R J 1991 *Chem. Phys. Lett.* **182** 511

[9] Olson M L and Konowalow D D 1977 *Chem. Phys.* **21** 393

[10] Kutzelnigg W, Staemmler V and Gélus M 1972 *Chem. Phys. Lett.* **13** 496

[11] Konowalow D D, Regan R M and Rosenkrantz M E 1984 *J. Chem. Phys.* **81** 4534

[12] Konowalow D D and Fish J L 1984 *Chem. Phys.* **84** 463

[13] Schmidt-Mink I, Müller W and Meyer W 1985 *Chem. Phys.* **92** 263

[14] Poteau R and Spiegelmann F 1995 *J. Mol. Spectrosc.* **171** 299

[15] Danovich D, Wu W and Shaik S 1999 *J. Am. Chem. Soc.* **121** 3165

[16] Konowalow D D and Fish J L 1983 *Chem. Phys.* **77** 435

[17] Huxley P, Knowles D B, Murrell J N and Watts J D 1984 *J. Chem. Soc. Faraday Trans.* **80** 1349

[18] Jastrzębski W and Pashov A 2001 *J. Chem. Phys.* **113** 6624

[19] Pashov A, Jastrzębski W and Kowalczyk P 2000 *J. Chem. Phys.* **114** 10725

[20] Huang Y and Le Roy R J 2003 *J. Chem. Phys.* **119** 7398

[21] Russier I, Martin F, Linton C, Crozet P, Ross A J, Bacis R and Churassy S 1994 *J. Mol. Spectrosc.* **168** 39

[22] Bradley C C, Sackett C A and Hulet R J 1997 *Phys. Rev. Lett.* **78** 985

[23] Abraham E R I, McAlexander W I, Gerton J M, Hulet R G, Côté R and Dalgarno A 1997 *Phys. Rev.* A **55** R3299

[24] Linton C, Martin F J, Ross A, Russier I, Crozet P, Yiannopoulou A, Li L and Lyyra A M 1999 *J. Mol. Spectrosc.* **196** 20

[25] Linton C, Murphy T L, Martin F, Bacis R and Verges J 1989 *J. Chem. Phys.* **91** 6036

[26] Xie X and Field R W 1985 *J. Chem. Phys.* **83** 6193

[27] Nakatsuji H, Hada M, Ehara M, Toyata K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O and Nakai H 2002 *SAC/SAC-CI Program Combined with Gaussian for Calculating Ground, Excited, Ionized, and Electron-Attached States and Singlet, Doublet, Triplet, Quartet, Quintet, Sextet, and Septet Spin States and their Analytical Energy Gradients* (Kyoto: Kyoto University) p19, p20, p38, p40

[28] Frisch M J, Trucks G W and Schlegel H B 2003 *Gaussian03* Revision A1 (Pittsburgh PA: Gaussian Inc) p149

[29] Murrell J N and Sorbie K S 1974 *J. Chem. Soc. Faraday Trans.* **70** 1552

[30] Shi D H, Liu Y F, Sun J F, Yang X D and Zhu Z L 2006 *Chin. Phys.* **15** 1015

[31] Yan S Y and Zhu Z H 2006 *Chin. Phys.* **15** 1517

[32] Herzberg G 1951 *Molecular Spectra and Molecular Structure*, vol.**1** (New York: Van Nostrand Reinhold)

[33] Shi D H, Sun J F, Liu Y F, Ma H and Zhu Z L 2006 *Acta Phys. Sin.* **55** 4096 (in Chinese)