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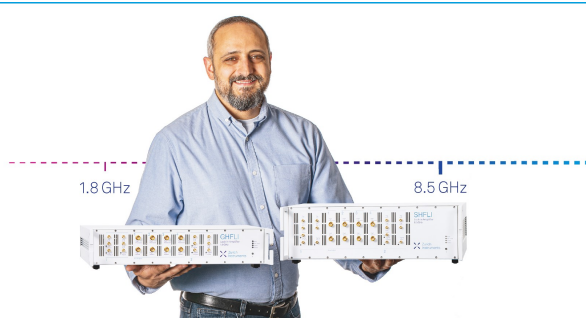
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Potential curves of the lower nine states of Li_2 molecule: Accurate calculations with the free complement theory and the comparisons with the SAC/SAC-CI results

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ABSTRACT

The free-complement (FC) theory proposed for solving the Schrödinger equation of atoms and molecules highly accurately was applied to the calculations of the potential curves of the lower nine states of the Li_2 molecule. The results were compared with the accurate experimental Rydberg–Klein–Rees potential curves available. They overlap completely with each other without any shift everywhere for all the states of Li_2 . At all the calculated points on the seven potential curves ranging between -14.83 and -15.00 hartree, the average difference was only 0.0583 kcal/mol and the maximum difference was only $+0.165$ kcal/mol. For the vertical excitation energies from the ground state curve to the seven excited states, the differences between theory and experiment were $0.000\,645$ eV in average and their maximum difference was $-0.007\,20$ eV. The potential properties calculated with the FC theory also agreed well with the experimental values. These results show a high potentiality of the FC theory as a highly predictive quantum chemistry theory. For comparison, as an example of the Hartree–Fock based theory popular in modern quantum chemistry, we adopted the symmetry-adapted-cluster (SAC)-configuration-interaction (CI) theory using a highly flexible basis set. While the FC theory gave the absolute agreements with experiments, the SAC-CI potential curves compare reasonably well with experiments only after shifting-down of the SAC-CI curves by 5.727 kcal/mol. The differences in the excitation energies between SAC-CI and experiments were $0.004\,28$ eV on average, and the maximum difference was $+0.109\,67$ eV. The SAC-CI results reported in 1985 were less accurate but still reasonable.

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I. INTRODUCTION

Li_2 molecule is a simple homopolar diatomic molecule whose simplicity is next to the hydrogen molecule. The equilibrium distance of H_2 molecule is 1.4011 a.u. ($0.741\,44$ Å), while that of Li_2 is 5.051 a.u. (2.673 Å).¹ This shows how large is the repulsive interaction between the inner $1s$ -shell electrons. The Li atom has the $(1s)^2(2s)^1$ structure and the $(1s)^1(2p)^1$ state is a very low excited state and mix strongly in the Li–Li bond so that the lower states of the Li_2 molecule have mixed bonding natures of $2s$ – $2s$, $2s$ – $2p$, and $2p$ – $2p$. In 1985, we reported a study of the potential curves of the lower nine states of Li_2 molecule.² We used the symmetry-adapted-cluster (SAC) configuration–interaction (CI)

theory, SAC/SAC-CI theory.^{3,4} From the next year of its publication, many accurate results of the Rydberg–Klein–Rees (RKR)^{5–7} potential curves of $^7\text{Li}_2$ were reported. First, in 1986, Barakat *et al.*⁸ reported extensive analyses of the potential curve of the $X^1\Sigma_g^+$ ground state by the laser-induced fluorescence Fourier-transform spectrometry. They observed the vibrational levels of up to $v = 40$, which allowed them to study the potential curve to $R = 12.6$ Å, only 2 cm^{-1} below the dissociation limit. They gave a precise dissociation energy, $D_e = 8516.78(54)$ cm^{-1} . Linton *et al.*⁹ reported a similar spectroscopy of the $b^3\Sigma_g^+ - a^3\Sigma_u^+$ states transition and by combining the results by Martin *et al.*¹⁰ determined the RKR potential curves and the dissociation energies of these states. For the $1^1\Pi_g$ state, Miller *et al.*¹¹ obtained

the RKR potential by a pulsed optical-optical double resonance spectroscopy and determined accurate properties associated with the potential curve. For the second $2^1\Sigma_g^+$ state, the RKR potential curve was reported by He, Gold, and Bernheim⁷ by the near infrared two-photon laser spectroscopy. The excitation energy T_e from the ground state was obtained as $20\,102.237\text{ cm}^{-1}$. The $A^1\Sigma_u^+$ state has been studied by Urbanski *et al.*¹³ using all optical triple resonance spectroscopy. The Born–Oppenheimer breakdown was observed in a combined-isotopomer analysis of the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ system of Li_2 .¹⁴ The high-lying vibrational levels and dissociation energy of the $a^3\Sigma_u^+$ state were additionally reported by Linton *et al.*¹⁵ A full description of the potential curve of the higher bound state $B^1\Pi_u$ was given in 2001 by Bouloufa *et al.*¹⁶ mainly by analyzing high resolution sub-Doppler $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ excitation spectra. Accurate analytic potentials for the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states of Li_2 were reported from accurate experimental data.¹⁷ Accurate potential curves of higher Rydberg states were also reported,^{18,19} but we restrict ourselves in this study to only the lower 9 states of Li_2 .

Theoretical studies on the potential curves of Li_2 molecule were done by Konowalow and Fish²⁰ and by Schmidt-Mink *et al.*²¹ They dealt with this system by using the effective core-potential (ECP) for the 1s core electrons of the Li atom and therefore like H_2 molecule. Similar method was applied extensively to many excited states of Li_2 by Jasik and Sienkiewicz.²² On the other hand, Hirao and one of the authors published in 1978 the symmetry-adapted coupled-cluster (SAC) theory for studying ground states³ and the SAC-CI theory for studying excited states, ionized states, and electron-attached states⁴ of molecules. These two theories have a beautiful Brillouin theoretic framework in common.^{4,23,24} This SAC/SAC-CI theory was applied in 1985 to the study of the potential curves of the lower 9 states of the Li_2 molecule.² Kaldor studied the ground and many excited states of Li_2 by the open-shell coupled cluster theory.²⁵ Shi, Ma, Sun, Zhu, Yu, Yang, and Liu used the SAC-CI theory for studying the potential curves of the excited states of Li_2 molecule and reported highly accurate results for many different states.^{26–30} Musiał and Kucharski reported extensive studies of the potential curves of the Li dimer³¹ using the multireference Fock space coupled cluster method.³² They could describe many states of different natures to high accuracy. Their theory has some similarity to the SAC-CI theoretical framework.

In this paper, we apply our free-complement (FC) theory^{33–35} that was proposed for solving the Schrödinger equation highly accurately to the calculations of the potential curves of the lower nine states of the Li_2 molecule. This theory is highly accurate³⁵ and could give almost exact solutions of the Schrödinger equation for small systems so far.³⁵ Some more recent applications are seen for the first-row atoms, small molecules,³⁶ and clusters.³⁷ Recently, we have generalized the scaling functions of the scaled Schrödinger equation³⁴ such that they obey the correct conditions at particle coalescence and asymptotic regions.³⁸ We use in the present study the correct g_{ij} function reported there.³⁸

II. METHOD

The FC theory leads to the exact solution of the Schrödinger equation from any initial wave function of the subject molecule that

has overlap with the exact wave function. It produces a potentially exact wave function in the form^{34,35}

$$\psi = \sum_{I=0} c_I \phi_I, \quad (1)$$

where the functions $\{\phi_I\}$ are referred to as complement functions (cf's). Here, we produced the cf's to order 3 from the initial wave functions. They can describe the lower nine states of the Li_2 molecule in all ranges of the inter-nuclear distances. We used the initial functions that consist of the covalent and ionic bonds between the two Li atoms in the 2s and 2p natures. For $^1\Sigma_g^+$ symmetry, the covalent ones are consisted of the three functions as

$$\begin{aligned} 2s-2s : \psi_0^{(1)} &= (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ &\quad \times (\alpha\beta - \beta\alpha) \cdot (2s_A 2s_B)(\alpha\beta - \beta\alpha), \\ 2s-2p : \psi_0^{(2)} &= (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ &\quad \times (\alpha\beta - \beta\alpha) \cdot (2s_A 2p_B)(\alpha\beta - \beta\alpha) + (A \leftrightarrow B), \\ 2p-2p : \psi_0^{(3)} &= (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ &\quad \times (\alpha\beta - \beta\alpha) \cdot (2p_A 2p_B)(\alpha\beta - \beta\alpha), \end{aligned} \quad (2)$$

where 2p is $2p_x$ -sigma orbital. The ionic functions are consisted of the functions given by

$$\begin{aligned} (2s)^2 : \psi_0^{(4)} &= (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ &\quad \times (\alpha\beta - \beta\alpha) \cdot (2s_A)^2(\alpha\beta) + (A \leftrightarrow B), \\ 2s2p : \psi_0^{(5)} &= (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ &\quad \times (\alpha\beta - \beta\alpha) \cdot (2s_A 2p_A)(\alpha\beta - \beta\alpha) + (A \leftrightarrow B), \\ (2p)^2 : \psi_0^{(6)} &= (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ &\quad \times (\alpha\beta - \beta\alpha) \cdot (2p_A)^2(\alpha\beta) + (A \leftrightarrow B), \end{aligned} \quad (3)$$

where the antisymmetrization operator was abbreviated. The orbitals are the Slater type as given by

$$\begin{aligned} 1s_{in,A} &= \exp(-\alpha_{1s,in} r_A), \quad 1s_{out,A} = \exp(-\alpha_{1s,out} r_A), \\ 2s_A &= r_A \exp(-\alpha_{2s}^{(r)} r_A) + d_{2s}^{(0)} \exp(-\alpha_{2s}^{(0)} r_A), \\ 2p_A &= x_A \exp(-\alpha_{2p} r_A). \end{aligned} \quad (4)$$

We considered the in-out correlation for the 1s electrons. The exponent parameters in Eq. (4) were optimized at the zeroth order, and the values are $\alpha_{1s,in} = 3.3029$, $\alpha_{1s,out} = 2.0674$, $\alpha_{2s}^{(r)} = 0.6785$, $\alpha_{2s}^{(0)} = 1.1832$, $d_{2s}^{(0)} = -0.096\,777$, and $\alpha_{2p} = 0.7979$. Based on the principle of the chemical formula theory that takes the Brillouin theorem into account,³⁶ the diffuse 3p functions of the exponent 0.55 that is slightly larger than that of the typical 3p function of around 0.3 were added in addition to the 2p orbital. The initial functions for other symmetries were adjusted based on the formulas given by Eqs. (2) and (3) for the $^1\Sigma_g^+$ symmetry.

The FC wave functions were produced from the above initial functions by using the scaling functions g_{iA} and g_{ij} to order 3 of the FC theory. For the electron nuclear term g_{iA} , we used the conventional form, $g_{iA} = r_{iA}$, but for the electron–electron term g_{ij} , we used

the “correct” scaling function introduced in the recent paper,³⁸ since it is more accurate than the conventional function r_{ij} that are not “correct” but only “reasonable.”³⁸ As such correct function, we used here a single Ei function given by

$$g_{ij} = \text{Ei}(-\gamma_1 r_{ij} - \gamma_2) - \text{Ei}(-\gamma_2), \quad (5)$$

where

$$\text{Ei}(-x) = \int_{-\infty}^{-x} \frac{\exp(t)}{t} dt. \quad (6)$$

The values of the parameters γ_1 and γ_2 were assumed to be transferable: we used the values, 0.001 21 and 0.000 238, respectively, that were optimized for the He atom at order 3.³⁸ The Ei function was used before³⁹ for the He atom for obtaining the world-best variational energy that was correct to over 43 digits by using the FC theory.

After generating the FC wave function,^{36,38} we optimized the linear parameters in the wave function by using the local Schrödinger equation (LSE) method.^{40,41} There, we used the HS method whose dimension is the number of the cfs considered and the energies are obtained as eigenvalues after the diagonalization. The sampling points used there were produced by the inverse transformation method or the direct method^{42,43} applied to the initial functions given by Eqs. (2) and (3). This method belongs to the local sampling method reported before³⁶ and gives directly the distributions of the sampling points proportional to the probability distributions of the wave function considered, though we limited ourselves from the integrability to use only the initial function set. This method is theoretically natural, and further, we can avoid the use of the Metropolis sampling method,⁴⁴ which assumes classical statistics and requires time-consuming iterative processes in producing the sampling points.³⁶ The direct or inverse transformation method⁴² gives the set of the sampling points directly from the appropriate wave functions and does not include the iterative processes like in the Metropolis method, and therefore, we can save the computer times. Details of the method will be published soon. The number of the sampling points used here was 3×10^6 .

For comparison with the popular methodology that starts from the Hartree–Fock theory, we also used the SAC/SAC-CI theory to obtain the potential curves of the nine lower states of Li_2 . Since our earlier calculations² published in 1985 are old, we have performed the recalculations using extended flexible basis sets, which are the uncontracted jorge-6ZP basis,⁴⁵ using the SAC/SAC-CI program in the GAUSSIAN set of programs.⁴⁶ In the SAC-CI calculations, we performed straightforward calculations without using the selection procedures, though we used them slightly in the old calculations.² In modern quantum chemistry calculations, the Hartree–Fock theory and the Hartree–Fock based correlation theories are popularly used. As a typical such theory, we have chosen the SAC/SAC-CI theory for comparison with the exact FC theory.

III. NUMERICAL RESULTS

A. Results of the FC theory

We summarize in Tables I and II the results of the present FC calculations of the ground (in Table I) and eight excited singlet and

TABLE I. Energies of the ground $X^1\Sigma_g^+$ state of Li_2 calculated by the FC theory at several inter-nuclear distances R^a . ΔE represents the energy difference in kcal/mol from the experimental RKR potential energy and bold face denotes less than 1 kcal/mol, i.e. satisfying chemical accuracy.^b

R (a.u.)	FC theory		RKR potential energy (a.u.)	ΔE (FC) (kcal/mol)
	H-square error	Energy (a.u.)		
4.0	0.018 109	−14.981 162	−14.981 401	0.150
4.5	0.016 033	−14.991 652	−14.991 846	0.122
4.8	0.014 234	−14.994 208	−14.994 355	0.092 2
5.051	0.013 885	−14.994 840	−14.994 926 ^c	0.054 0
5.2	0.013 568	−14.994 663	−14.994 757	0.058 5
5.5	0.011 969	−14.993 448	−14.993 533	0.053 5
6.0	0.010 922	−14.989 667	−14.989 740	0.045 7
6.5	0.010 331	−14.984 759	−14.984 839	0.050 1
8.0	0.008 047	−14.970 338	−14.970 393	0.034 4
9.0	0.007 277	−14.963 854	−14.963 893	0.024 3
10.0	0.007 220	−14.960 077	−14.960 078	0.000 320
12.0	0.007 237	−14.957 138	−14.957 147	0.005 93
Average ^d				0.057 6
Max.dif. ^e				0.150

^aThe FC theory at the order 3. The dimensions of the complement functions were 11098 for the $^1\Sigma_g^+$ symmetry.

^bRKR potentials are fitted by the spline interpolation from the reference experimental data.^{8–17}

^cExact total energy of $X^1\Sigma_g^+$ state of Li_2 at $R_{eq} = 5.051$ a.u. For details, see text.

^dAverage value of ΔE .

^eSigned maximum value of ΔE (largest difference from RKR), which was at $R = 4.0$ a.u.

triplet states (in Table II) of Li_2 at various internuclear distances, R . We also summarized the absolute values obtained from the experimental RKR potentials reported for the ground and various excited states of Li_2 .^{8–17} These values were obtained from the ground state RKR potential reported by Barakat *et al.*⁸ and the estimated exact energy of Li_2 at the equilibrium length.⁴⁷ This value of the absolute energy of Li_2 at the equilibrium distance $R_{eq} = 5.051$ a.u. was re-estimated as −14.994 926 a.u. as a refined value. Here, the estimation method is the same as the one used by Filippi and Umrigar,⁴⁷ but the experimental values used therein were updated: namely, we used the nonrelativistic exact energy of the ground state of Li atom reported by Drake *et al.*⁴⁸ and the experimental dissociation energy D_e by Barakat *et al.*⁸ Then, the absolute values of the RKR potential for the ground $X^1\Sigma_g^+$ state are obtained from the experimental RKR potential reported by Barakat *et al.*⁸ The values of the absolute RKR potentials of the excited states were obtained similarly by adding the experimental adiabatic excitation energies.^{8–17} The continuous curves were obtained by local spline fitting methods.

The first columns of Tables I and II show the Li–Li internuclear distances. Although we listed only 12 points between 4 and 12 a.u. first adopted in Ref. 2, we performed here the FC calculations at the 36 points to get smooth potential curves in the analyses. The next two columns show the results of the FC calculations: first is the H-square error defined by $\langle \psi | (H - E)^2 | \psi \rangle$ and next is the absolute energy of the FC theory, E_{FC} both in a.u. About the H-square error, if this value is zero for any set of sampling points, the results are strictly

TABLE II. Energies and vertical excitation energies of the excited states of Li_2 calculated by the FC theory at several inter-nuclear distances R . ΔE represents the energy difference in kcal/mol from the experimental RKR potential energy and bold face denotes less than 1 kcal/mol, i.e. satisfying chemical accuracy.⁵ ΔEX represents the difference in eV from the RKR excitation energy and bold face denotes their absolute values less than 0.01 eV.

R (a.u.)	$A^1\Sigma_u^+$ state					$2^1\Sigma_g^+$ state				
	FC theory			Vertical excitation energy (eV)		FC theory			Vertical excitation energy (eV)	
	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	ΔEX	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	ΔEX
4.0	0.009 964	-14.900 341	-14.900 315	-0.015 9	-0.007 20	0.020 412	-14.867 382			
4.5	0.009 784	-14.917 388	-14.917 380	-0.005 60	-0.005 53	0.018 335	-14.884 341			
4.8	0.009 099	-14.923 534	-14.923 512	-0.013 9	-0.004 60	0.017 915	-14.891 037	(-14.891 484) ^c	(0.280)	(0.008 14)
5.051	0.009 127	-14.926 896	-14.926 917	0.013 3	0.001 76	0.014 377	-14.894 865	-14.895 128	0.165	0.004 81
5.2	0.009 097	-14.928 311	-14.928 341	0.019 3	-0.001 70	0.014 029	-14.896 685	-14.896 928	0.153	0.004 08
5.5	0.008 947	-14.930 100	-14.930 135	0.021 6	-0.001 38	0.012 414	-14.899 373	-14.899 610	0.149	0.004 14
6.0	0.008 813	-14.930 709	-14.930 762	0.033 6	-0.000 524	0.012 194	-14.901 930	-14.902 116	0.116	0.003 06
6.5	0.008 980	-14.929 357	-14.929 437	0.050 4	0.000 013 7	0.012 460	-14.902 988	-14.903 139	0.094 9	0.001 94
8.0	0.008 503	-14.920 291	-14.920 366	0.047 0	0.000 549	0.011 878	-14.902 036	-14.902 201	0.103	0.002 99
9.0	0.008 272	-14.913 253	-14.913 338	0.053 6	0.001 27	0.011 572	-14.899 248	-14.899 445	0.123	0.004 29
10.0	0.008 010	-14.906 872	-14.906 946	0.046 3	0.001 99	0.011 306	-14.895 432	-14.895 596	0.103	0.004 46
12.0	0.006 449	-14.897 684	-14.897 796	0.069 8	0.002 77	0.008 307	-14.888 631		1.864 17	
Average ^d				0.026 6	-0.001 34				0.126	0.003 72
Max.dif. ^e				0.069 8	-0.007 20				0.165	0.004 81

R (a.u.)	$B^1\Pi_u$ state					$1^1\Pi_g$ state				
	FC theory			Vertical excitation energy (eV)		FC theory			Vertical excitation energy (eV)	
	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	ΔEX	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	ΔEX
4.0	0.012 813	-14.879 804	(-14.880 217) ^f	(0.259)	(0.004 73)	0.009 594	-14.854 880			
4.5	0.011 774	-14.893 462	-14.893 637	0.110	-0.000 538	0.009 488	-14.871 314			
4.8	0.011 401	-14.897 961	-14.898 124	0.102	0.000 426	0.009 129	-14.878 039			
5.051	0.010 790	-14.900 190	-14.900 340	0.094 6	0.001 76	0.009 028	-14.882 427			
5.2	0.010 683	-14.900 983	-14.901 132	0.093 7	0.001 52	0.008 892	-14.884 488			
5.5	0.010 110	-14.901 654	-14.901 799	0.091 2	0.001 64	0.008 747	-14.887 768			
6.0	0.009 961	-14.900 827	-14.900 983	0.098 2	0.002 27	0.008 252	-14.891 353	-14.891 605	0.158	0.004 86
6.5	0.009 516	-14.898 697	-14.898 801	0.064 9	0.000 640	0.008 476	-14.893 349	-14.893 466	0.073 2	0.001 00
8.0	0.008 286	-14.890 955	-14.891 027	0.045 2	0.000 472	0.006 964	-14.894 566	-14.894 646	0.0500	0.000 677
9.0	0.007 741	-14.887 810	-14.887 802	-0.004 99	-0.001 268	0.007 337	-14.894 080	-14.894 030	-0.031 4	-0.002 41
10.0	0.007 292	-14.886 403	-14.886 348	-0.034 3	-0.001 50	0.006 306	-14.893 173	-14.893 164	-0.005 49	-0.000 252
12.0	0.006 872	-14.886 086	-14.886 024	-0.038 6	-0.001 93	0.006 070	-14.891 512	-14.891 513	0.000 958	-0.000 215
Average ^d				0.056 5	0.000 317				0.040 9	0.000 610
Max.dif. ^e				0.110	0.002 27				0.158	0.004 86

TABLE II. (Continued.)

R (a.u.)	$^3\Sigma^+$ state				$1^3\Pi_u$ state			
	FC theory		Vertical excitation energy (eV)		FC theory		Vertical excitation energy (eV)	
	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)
4.0	0.007 293	-14.919 577						
4.5	0.006 903	-14.936 325						
4.8	0.006 710	-14.942 888						
5.051	0.006 482	-14.946 947						
5.2	0.006 381	-14.948 879						
5.5	0.006 322	-14.951 872						
5.0	0.006 006	-14.954 950						
5.5	0.005 946	-14.956 544						
6.0	0.005 828	-14.957 593						
6.8	0.005 708	-14.957 423						
9.0	0.005 637	-14.957 134						
10.0	0.005 502	-14.956 630						
12.0								
Average ^d								
Max.diff. ^e								

R (a.u.)	$b^1\Sigma_g^+$ state				$1^3\Pi_g$ state			
	FC theory		Vertical excitation energy (eV)		FC theory		Vertical excitation energy (eV)	
	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)
4.0	0.015887	-14.891080			0.017147	-14.841977		3.78740
4.5	0.015832	-14.908198			0.017460	-14.860781		3.56117
4.8	0.015677	-14.914071			0.016274	-14.867908		3.43681
5.051	0.015467	-14.917144	-14.914277	0.129	0.019281	-14.872440		3.33068
5.2	0.015193	-14.918425	-14.918627	0.148	0.023430	-14.874720		3.26382
5.5	0.014873	-14.919953	-14.920112	0.126	0.022268	-14.877747		3.14840
6.0	0.013837	-14.920204	-14.920378	0.00994	0.018115	-14.880326		2.97532
5.5	0.012763	-14.918769	-14.918927	0.110	0.014782	-14.881137		2.81970
8.0	0.010967	-14.911065		0.0997	0.009591	-14.881938		2.40550
9.0	0.009034	-14.905853			0.007241	-14.882985		2.20056
10.0	0.007678	-14.901512			0.006127	-14.883991		2.07043
12.0	0.006421	-14.895792			0.005842	-14.885553		1.94793
Average ^d				0.103				
Max.diff. ^e				0.148				
				0.00258				
				0.00406				

The FC theory at the order 3. The dimensions of the complement functions were 11 098, 9536, 10 688, 10 688, 8446, and 10 688 for ${}^1\Sigma_g^+$, ${}^1\Sigma_u^+$, ${}^1\Pi_g$, ${}^3\Sigma_g^+$, and ${}^3\Pi_g$ symmetries, respectively.

RRR potentials are fitted by the spline interpolation from the reference experimental data.

The shape of the RKR potential looks slightly unreasonable here.

Average values of ΔE and ΔEX of the same states. The total averages of ΔE and ΔEX for all the calculated states in this table were 0.0583 kcal/mol and 0.000 645 eV, respectively. The shape of the KKK potential looks slightly unreasonable here.

Signed maximum values of ΔE and ΔEX over all the states were 0.165 kcal/mol of the $2^1\Sigma_g^-$ state at $R = 5.051$ a.u. and -0.00720 eV of the $\Lambda^1\Sigma_u^-$ state at $R = 4.0$ a.u., respectively.

The RKR value might be

The RKR value might be not accurate enough here since the vibrational levels around this R are beyond the bound region.

exact as the solutions of the Schrödinger equation. Then, the fourth column shows the absolute values of the experimental RKR potential interpolated by spline fitting, and the fifth column shows the difference between the FC energy and the RKR potential, $E_{\text{FC}} - E_{\text{RKR}}$, in kcal/mol. If E_{FC} is higher than E_{RKR} , $\Delta E(\text{FC})$ is positive. We see from Table I that the absolute energy differs only slightly between theory and experiment: the FC energy was only 0.0576 kcal/mol in average higher than the absolute experimental energy (We note that the LSE method^{40,41} is not variational). The largest difference from the RKR value was +0.150 kcal/mol at $R = 4.0$ a.u.

Table II gives the results for the eight excited states: four singlet and four triplet states in increasing order of energy. For the $1^3\Pi_u$ and $1^3\Pi_g$ states, we could not find the experimental values. For the other seven states, the differences ΔE 's between theory and experiment were as small as 0.0266, 0.126, 0.0565, 0.0409, -0.00172 , and 0.103 kcal/mol in average of the different lengths R for the $A^1\Sigma_u^+$, $2^1\Sigma_g^+$, $B^1\Pi_u$, $1^1\Pi_g$, $a^3\Sigma_u^+$, and $b^3\Sigma_g^+$ states, respectively. All values were much less than 1 kcal/mol. The total average value of the ΔE values was 0.0583 kcal/mol (see footnote e of Table II), and the largest ΔE value for all the calculated points in Tables I and II was only +0.165 kcal/mol for the $2^1\Sigma_g^+$ state at $R = 5.051$ a.u. Thus, the FC theory of order 3 has reproduced the exact absolute potential curves of the seven different states of Li_2 highly accurately.

In addition to the data of the absolute potential curves, we gave in Table II (from 6th to 8th columns for the $A^1\Sigma_u^+$ state, for example) the vertical excitation energies of the seven excited states from the ground $X^1\Sigma_g^+$ state at each inter-nuclear distance R in eV for the FC theory and for the experimental RKR method and their differences are shown as ΔEX in eV unit. For the states for which the RKR values are known, the ΔEX values in eV unit were as small as -0.00134 , 0.00372, 0.000317, 0.000610, -0.00107 , and 0.00258 eV in average for the $A^1\Sigma_u^+$, $2^1\Sigma_g^+$, $B^1\Pi_u$, $1^1\Pi_g$, $a^3\Sigma_u^+$, and $b^3\Sigma_g^+$ states, respectively. The total average value of the ΔEX values was 0.000645 eV and its largest value was -0.00720 eV for the $A^1\Sigma_u^+$ state at $R = 4.0$ a.u. Thus, the FC theory was highly accurate for both the ground and excited states of any symmetry.

In conclusion, we feel it surprising that the completely different independent data from experiments and theory, the experimental spectroscopic RKR potential and the calculated energies of the FC theory for solving the Schrödinger equation agree well with each other in so wide ranges of the potential curves of so many different states of the Li_2 molecule. This certainly shows that the Schrödinger equation or more explicitly the variational formula [Eq. (8) of Ref. 34] of the scaled Schrödinger equation, from which the FC theory was derived, governs quantitatively the chemistry of the Li_2 molecule. Note that the corresponding variational formula of the Schrödinger equation itself diverges.³⁴

Finally, we briefly summarize the costs of the present FC calculations. We used the super-parallel computers consisted of the 3000 cores at the Institute of Molecular Sciences (IMS), Okazaki. For the $1^1\Sigma_g^+$ states that include the ground $X^1\Sigma_g^+$ and excited $2^1\Sigma_g^+$ states, the number of the cfs (namely, the dimension) at order 3 of the FC theory was 11 098 and the computational time for one distance was 83.6 min, consisted of 8.0 min for generating the FC wave function, 53.2 min for generating sampling points, and 22.4 min for evaluating H, S matrices of the LSE theory and diagonalization. For the excited

$A^1\Sigma_u^+$ state, the dimension of the order 3 was 9536 and the computational time for one distance was 73.2 min, where 7.2 min for generating the FC wave function, 47.3 min for generating sampling points, and 18.7 min for the H, S step. For other excited states, the costs were like those for the $A^1\Sigma_u^+$ state.

B. Comparative calculations with the SAC/SAC-CI theory

At present, many quantum chemistry theories are based on the Hartree-Fock theory. For studying closed-shell ground state, the coupled cluster theory gives a reliable tool. The SAC (Symmetry-Adapted Cluster) theory³ by Hirao and one of the authors is a spin-symmetry adapted coupled cluster theory, which was necessary for handling open-shell molecules because the coupled cluster theory is a non-linear expansion theory. The SAC-CI theory⁴ was a new reliable theory for constructing excited states, ionized states, and electron attached states using the subspace produced by the SAC theory: this subspace was found to satisfy the Brillouin-theorem conditions, namely, the orthogonality and Hamiltonian orthogonality conditions, with the SAC ground state.²³ Thus, the SAC/SAC-CI theory is a systematic theory for studying the ground, excited, ionized, and electron-attached states of molecules with a good reliability and useful performances even at that time.^{3,4,24} Using this SAC/SAC-CI theory, we could study many different chemistries of various excited states.^{23,24} Remarkable ones were the studies^{49–51} of the electronic spectra, electron-transfer routes, and their mechanisms of the photosynthetic reaction center of *rhodospseudomonas viridis*, a photosynthetic bacterium.⁵² More recently, we have studied the helical structure of DNA and RNA using the circular dichroism (CD) spectroscopic studies based on the SAC-CI theory.⁵³ We note here that the so-called EOM-CC was very similar or even identical to the SAC-CI,⁵⁴ though it was published more than a decade later than the original SAC-CI theory. For details, see Secs. I–E of the SAC-CI Guide.⁵⁴ Priority is important in our world of science.

This SAC/SAC-CI theory was applied to the study of the potential curves of nine lower states of Li_2 in 1985.² The published results of the potential curves were reasonably good, in comparison with the experimental RKR potentials published later,^{8–17} as will be shown below. But nowadays, the computational situations are much different from then, and so, we decided to do the recalculations, for comparison, using a modern extended basis set: we used the uncontracted primitive set of jorge-6ZP⁴⁵ and performed the SAC/SAC-CI calculations using the GAUSSIAN code⁴⁶ with no selections and no cut-off of the active space. We refer to this new results as SAC-CI(2022) and the old ones as SAC-CI(1985). The computational time for all 9 states at a single distance (for instance, $R = 5.051$ a.u.) was 4.7 h using a single node (40 cores) computer at the IMS computer center.

In Table III, we compare the SAC-CI(2022) data with the experimental RKR potential. The table format is essentially the same as that of Tables I and II, except that we did not cite the RKR potential because they were already given in Tables I and II. First, let us watch the absolute energy values and the ΔE values in kcal/mol for the ground state, $X^1\Sigma_g^+$. The calculated SAC-CI energy was higher than the experimental RKR value by $\Delta E = 5.617$ kcal/mol in average, which was very large in comparison with the results of the

TABLE III. Energies and the vertical excitation energies of Li_2 calculated by the SAC/SAC-Cl theory using the jorge-6ZP(uncontract) basis at several inter-nuclear distances R . ΔE represents the energy difference in kcal/mol from the RKR potential energy. ΔEX represents the difference in eV from the RKR excitation energy.

R (a.u.)	$X^1\Sigma_g^+$ state				$A^1\Sigma_u^+$ state				$2^1\Sigma_g^+$ state			
	SAC-Cl		ΔE		SAC-Cl		ΔE		SAC-Cl		ΔE	
	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	ΔEX
4.0	-14.972 780	5.410	-14.972 780	5.410	-14.890 997	5.847	2.225 43	0.018 98	-14.858 002	3.123 27	-14.858 002	
4.5	-14.983 459	5.263	-14.983 459	5.263	-14.908 308	5.692	2.044 96	0.018 62	-14.875 276	2.943 81	-14.875 276	
4.8	-14.986 055	5.208	-14.986 055	5.208	-14.914 536	5.632	1.946 13	0.018 39	-14.881 904	(6.011)	-14.881 904	(0.034 82)
5.051	-14.986 681	5.174	-14.986 681	5.174	-14.918 014	5.587	1.868 52	0.017 90	-14.885 877	5.805	-14.885 877	0.027 38
5.2	-14.986 535	5.159	-14.986 535	5.159	-14.919 479	5.561	1.824 69	0.017 44	-14.887 695	5.794	-14.887 695	0.027 52
5.5	-14.985 345	5.138	-14.985 345	5.138	-14.921 340	5.519	1.741 66	0.016 50	-14.890 386	5.788	-14.890 386	0.028 18
6.0	-14.981 556	5.136	-14.981 556	5.136	-14.922 035	5.477	1.619 65	0.014 78	-14.892 773	5.863	-14.892 773	0.031 52
6.5	-14.976 584	5.180	-14.976 584	5.180	-14.920 746	5.454	1.519 43	0.011 86	-14.893 481	6.061	-14.893 481	0.038 17
8.0	-14.961 452	5.610	-14.961 452	5.610	-14.911 617	5.490	1.356 08	-0.005 23	-14.890 464	7.365	-14.890 464	0.076 08
9.0	-14.954 147	6.116	-14.954 147	6.116	-14.904 441	5.583	1.352 57	-0.023 10	-14.885 879	8.513	-14.885 879	0.103 95
10.0	-14.949 504	6.635	-14.949 504	6.635	-14.897 840	5.714	1.405 85	-0.039 94	-14.880 992	9.164	-14.880 992	0.109 67
12.0	-14.945 399	7.372	-14.945 399	7.372	-14.888 222	6.008	1.555 87	-0.059 17	-14.875 721	1.896 03	-14.875 721	
Average ^a		5.617		5.617		5.630		0.000 586		6.794		0.055 31
Max.dif. ^b		7.372		7.372		6.008		-0.059 17		9.164		0.109 67

R (a.u.)	$B^1\Pi_u$ state				$1^1\Pi_g$ state				$a^3\Sigma_u^+$ state			
	SAC-Cl		ΔE		SAC-Cl		ΔE		SAC-Cl		ΔE	
	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	(kcal/mol)	Energy (a.u.)	ΔEX
4.0	-14.870 727	(5.955)	2.777 00	(0.023 65)	-14.844 579	3.488 53	-14.911 244		-14.911 244	1.674 48	-14.911 244	
4.5	-14.884 556	5.698	2.691 29	0.018 86	-14.861 740	3.312 14	-14.928 087		-14.928 087	1.506 75	-14.928 087	
4.8	-14.889 161	5.624	2.636 62	0.018 04	-14.868 742	3.192 25	-14.934 744		-14.934 744	1.396 24	-14.934 744	
5.051	-14.891 460	5.572	2.591 10	0.017 29	-14.873 159	3.089 09	-14.938 873		-14.938 873	1.300 92	-14.938 873	
5.2	-14.892 293	5.547	2.564 46	0.016 80	-14.875 275	3.027 54	-14.940 829		-14.940 829	1.243 72	-14.940 829	
5.5	-14.893 028	5.504	2.512 07	0.015 86	-14.878 616	2.904 24	-14.943 881		-14.943 881	1.128 29	-14.943 881	
6.0	-14.892 272	5.466	2.429 54	0.014 33	-14.882 150	2.704 97	-14.947 049	0.034 57	-14.947 049	0.938 98	-14.947 049	-0.011 66
6.5	-14.890 095	5.463	2.353 49	0.012 26	-14.884 018	2.518 85	-14.948 700	0.032 44	-14.948 700	4.911	-14.948 700	0.758 76
8.0	-14.882 067	5.622	2.160 18	0.000 520	-14.885 057	2.078 81	-14.949 856	0.017 63	-14.949 856	4.883	-14.949 856	0.315 54
9.0	-14.878 557	5.802	2.056 91	-0.013 62	-14.884 358	1.899 06	-14.949 649	-0.002 00	-14.949 649	4.879	-14.949 649	-0.053 65
10.0	-14.876 857	5.956	1.976 83	-0.029 46	-14.883 422	1.798 18	-14.949 334	-0.022 63	-14.949 334	4.880	-14.949 334	-0.076 12
12.0	-14.876 256	6.130	1.881 48	-0.053 87	-14.881 705	1.733 20	-14.948 826	-0.052 79	-14.948 826	4.886	-14.948 826	-0.107 82
Average ^a		5.671		0.001 55		6.036		0.001 20		4.888		-0.056 16
Max.dif. ^b		6.130		-0.053 87		6.155		-0.052 79		4.911		-0.107 82

TABLE III. (Continued.)

R (a.u.)	$1^3\Pi_u$ state			$b^3\Sigma_g^+$ state			$1^3\Pi_g$ state		
	SAC-CI Energy (a.u.)	Vertical excitation energy (eV)		SAC-CI Energy (a.u.)	Vertical excitation energy (eV)		SAC-CI Energy (a.u.)	Vertical excitation energy (eV)	
		ΔE (kcal/mol)	ΔEX		ΔE (kcal/mol)	ΔEX		ΔE (kcal/mol)	ΔEX
4.0	-14.926 932	1.247 59		-14.882 879	2.446 33		-14.833 336	3.794 46	
4.5	-14.934 265	1.338 64		-14.900 044	2.269 84		-14.852 322	3.568 42	
4.8	-14.935 649	1.371 62		-14.905 900	5.257	0.002 09	-14.859 619	3.440 50	
5.051	-14.935 565	1.390 94		-14.909 033	5.238	0.002 77	-14.864 015	3.337 91	
5.2	-14.935 095	1.399 75		-14.910 299	5.226	0.002 88	-14.866 036	3.278 94	
5.5	-14.933 406	1.413 33		-14.911 806	5.212	0.003 19	-14.869 052	3.164 49	
6.0	-14.929 053	1.428 68		-14.912 103	5.193	0.002 48	-14.871 807	2.986 42	
6.5	-14.923 620	1.441 22		-14.910 705	5.160	-0.000 896	-14.872 832	2.823 24	
8.0	-14.906 429	1.497 25		-14.902 869	1.594 12		-14.872 965	2.407 85	
9.0	-14.897 040	1.553 96		-14.897 506	1.541 28		-14.873 419	2.196 72	
10.0	-14.890 296	1.611 13		-14.892 994	1.537 72		-14.874 190	2.049 40	
12.0	-14.883 399	1.687 11		-14.886 798	1.594 61		-14.875 576	1.899 98	
Average ^a					5.214	0.002 09			
Max dif. ^b					5.257	0.003 19			

^aAverage values of ΔE and ΔEX from this SAC-CI calculations. Their total averages of ΔE and ΔEX for all the calculated points in this table were 5.727 kcal/mol and 0.00428 eV, respectively.
^bSigned maximum values of ΔE and ΔEX of the same states. The signed maximum values of ΔE and ΔEX over all the states were 9.164 kcal/mol of the $2^1\Sigma_g^+$ state at $R = 10.0$ a.u. and 0.10967 eV of the $2^1\Sigma_g^+$ state at $R = 10.0$ a.u., respectively.

FC theory, 0.0576 kcal/mol. Thus, the SAC-CI(2022) data do not satisfy the chemical accuracy for the absolute energy. At the equilibrium distance of the $X^1\Sigma_g^+$ state, ΔE was 5.174 kcal/mol, which was slightly smaller than the value 5.803 kcal/mol that Musiał and Kucharski reported with the Fock space-coupled cluster singles and doubles (FS-CCSD) method.³¹ When R becomes 8 a.u., ΔE becomes 5.610 kcal/mol and as R increases to 9, 10, and 12 a.u., the ΔE increases as 6.116, 6.632, and 7.372 kcal/mol. This is due to the well-known deficiency of the Hartree–Fock method in the bond-breaking region. Since the SAC-CI includes all singles and doubles in its active space, it is almost correct when the Hartree–Fock configuration is dominant, but at the distance larger than 9 a.u., the Hartree–Fock configuration is not dominant, so that this deficiency emerges. The same is true for the second state, $2^1\Sigma_g^+$: already from $R = 8$ a.u., ΔE increases to 7.365 kcal/mol, and then to 8.513 and 9.164 kcal/mol at $R = 9$ and 10 a.u., respectively. However, for other symmetries like $A^1\Sigma_u^+$ state, the Hartree–Fock configuration does not mix, and therefore such deficiency does not occur. For example, for the $A^1\Sigma_u^+$ state, the ΔE values at different distances are all about the average value, 5.630 kcal/mol. This is true for all the other states that does not mix with the Hartree Fock configuration. The average values of ΔE for other states are in kcal/mol 5.671, 6.036, 4.888, and 5.214, respectively, for the $B^1\Pi_u$, $1^1\Pi_g$, $a^3\Sigma_u^+$, and $b^3\Sigma_g^+$ states. The change in these average values is over chemical accuracy. The average of these average values was 5.727 kcal/mol.

For the excited states, the vertical excitation energy from the ground state at each inter-nuclear distance R is summarized for the SAC-CI(2022) data in Table III and the differences from the experimental values were compared with the exact experimental values under the column of ΔEX in eV unit. They were 0.000 586, 0.055 31, 0.001 55, 0.001 20, and 0.002 09 eV for the $A^1\Sigma_u^+$, $2^1\Sigma_g^+$, $B^1\Pi_u$, $1^1\Pi_g$, $a^3\Sigma_u^+$, and $b^3\Sigma_g^+$ states, respectively. The average of these

values was 0.004 28 (0.011 84) eV, which is reasonable, but much worse by an order of magnitude than the value, 0.000 645 eV of the FC theory. The largest difference was +0.109 67 eV in the $2^1\Sigma_g^+$ state at $R = 10.0$ a.u. In contrast, that of the FC theory was $-0.007 20$ eV. The FC theory is universally exact for any electronic states and at any R , but the Hartree–Fock based SAC/SAC-CI theory has a weakness for the Hartree–Fock dominant states near the bond-breaking region.

For comparison, we also summarized briefly the old SAC-CI(1985) data² in the [supplementary material](#). Table S1 shows the results like Table III.

Li_2 is a simple chemical system. Therefore, both the FC theory and the SAC/SAC-CI theory give reliable results and the theoretical calculations are also easy for both. We are performing similar examinations for more complex systems, whose results will be published soon.

IV. POTENTIAL CURVES

For the Li_2 molecule, highly accurate potential curves are known experimentally for many states. This helps us to examine the accuracy of the theory in detail. We could show that the FC theory can give the potential curves as accurately as the experiments. For some states, the experimental observations of the potential curves were limited. For example, because the RKR method is based on the accurate observations of many vibrational states, it is difficult to apply this method to the repulsive states because for such states, stable vibrational states do not exist. For such cases, the FC theory can provide the data that are reliable like the experimental data.

In this section, we compare the figures of the potential curves of Li_2 between theory and experiments. In Fig. 1, we show in the

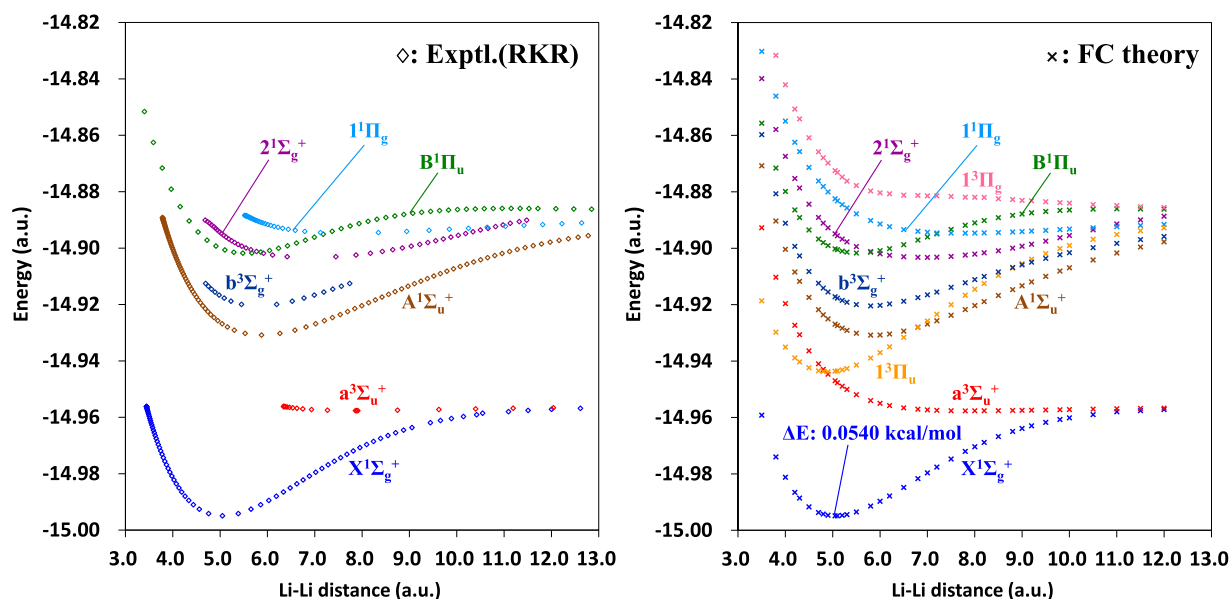


FIG. 1. Left is the experimentally determined RKR potential curves and right is the potential curves calculated by the free-complement (FC) theory, both for Li_2 .

left-hand side the experimentally determined potential curves of Li_2 . For the $X^1\Sigma_g^+$,⁸ $A^1\Sigma_u^+$,^{13,14} and $B^1\Pi_u$ ¹⁶ states, the potential curves are almost fully known, and for the $2^1\Sigma_g^+$ state,¹² the main parts were observed, but for the $1^1\Pi_g$,¹¹ $a^3\Sigma_u^+$,^{9,10,15} and $b^3\Sigma_g^+$ ¹⁰ states, the potential curves were obtained only partially. The $b^3\Sigma_g^+$ state is also referred to as the $1^3\Sigma_g^+$ state.¹⁰ For the $1^3\Pi_u$ and $1^3\Pi_g$ states, we could not find the experimental potential curves in the literature.

The right-hand side of Fig. 1 shows the theoretical potential curves of the lower nine states of Li_2 calculated by the FC theory. As we already seen from Tables I and II, the energies obtained from the FC theory agree almost absolutely with the experimental values and the average difference was as small as only 0.0583 kcal/mol at all the distances of all the seven states. Then, to compare these two figures more closely, we simply move the FC curves to the left until the vertical axes of the two figures overlap to each other. Then, we obtained Fig. 2.

In Fig. 2, the diamond shape shows the experimental value and the cross shows the FC value. At $R = 5.051$ a.u., the FC energy differs from the experimental RKR values by only 0.0540 kcal/mol. Actually, we could not see any meaningful difference between the experiment and the theory for all the seven states in this scale of the figure. This is the result we already expected from Tables I and II. Completely different approaches, the fine experiments using many fine apparatus and the calculated results using the FC theory gave such a fine agreement to each other. This shows that the Schrödinger equation describes completely the chemistry and physics of Li_2 . Furthermore, the FC theory could fill the empty space of the experimental figure, like the potential curves of the $1^3\Pi_u$ and $1^3\Pi_g$ states. Note that in the experimental curve of the $2^1\Sigma_g^+$ state, there is a small tilt on the last experimental diamonds near 4.7 a.u., but with the FC theoretical curve, we could not find such a small tilt. Finally, we note again that differently from the SAC-CI case we explain below, we simply moved the left theoretical figure to the right, without any vertical shift: we have compared the theory and the experiment simply with their total absolute energies.

We next compare the results of SAC-CI(2022) obtained by using the jorge-6ZP basis shown in the right-hand side of Fig. 3

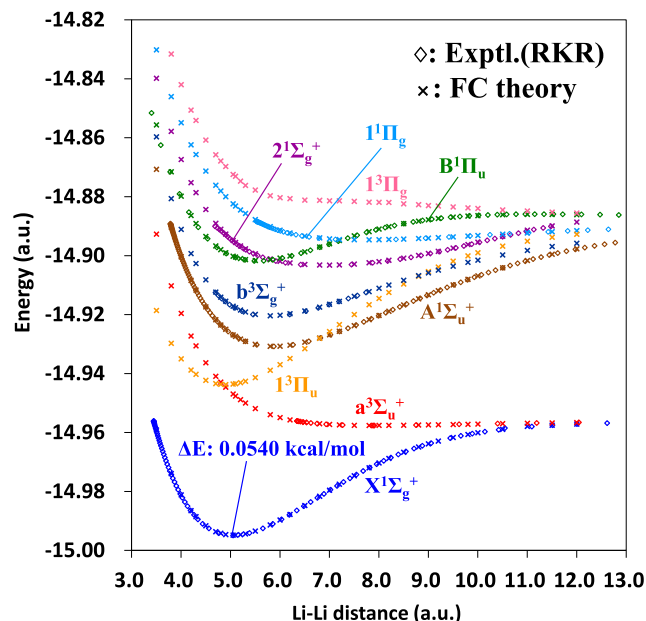


FIG. 2. Experimental RKR and FC theoretical potential curves of Li_2 on the common axes of the energy (vertical) and the Li-Li distance (horizontal).

with the experiments shown again in the left-hand side of Fig. 3. Differently from Fig. 1, the SAC/SAC-CI figure lies higher by 5.727 kcal/mol than the experimental figure in average, as shown in the footnote a of Table III. Therefore, to compare the two figures, we must shift down the SAC/SAC-CI figure by 5.727 kcal/mol and then moved it to the left to make overlap the two vertical lines. Then, we obtained Fig. 4, where the SAC/SAC-CI values are shown by the triangles. The SAC results for the ground state $X^1\Sigma_g^+$ shown in blue lie slightly lower than the experimental values shown by diamonds near the equilibrium length, but at larger separations around 9–12 a.u., the SAC results become higher and deviate much than

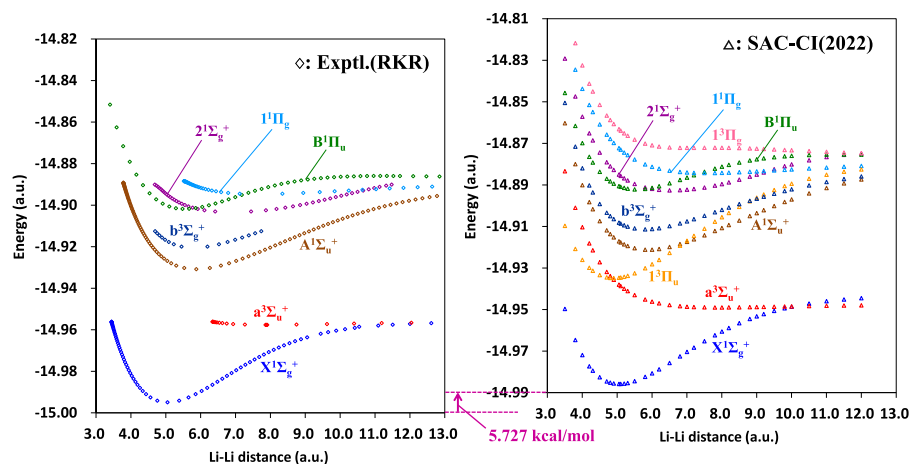


FIG. 3. Left is the experimentally determined RKR potential curves and right is the potential curves calculated by the SAC/SAC-CI theory using the jorge-6ZP basis, both for Li_2 .

the experimental values. For the $2^1\Sigma_g^+$ state, the SAC-CI results given by purple triangle deviate much from the experimental curve at the length larger than 7 a.u. This is quantitatively confirmed from Table III from the ΔE values shown for the $2^1\Sigma_g^+$ state. These two large deviations at large R for the two $1^1\Sigma_g^+$ states are due to the well know poor description of the homopolar covalent bond of the restricted Hartree–Fock method near the dissociation limit. For the other states for which the symmetry is different from $1^1\Sigma_g^+$, the deviations are moderate. Relatively large deviations are seen for the $a^3\Sigma_u^+$ state shown in red: the SAC-CI curve lies lower than the experimental curve.

Finally, let us see the SAC/SAC-CI results reported in 1985. The detailed numerical results were summarized in the supplementary material. In Fig. 5, we compare the experimental potential curve (left) with the SAC-CI(1985) curve (right) that lies by 56.953 kcal/mol higher (reference d of Table S1 of the supplementary material). Then, we shift down the SAC-CI(1985) curve by 56.953 kcal/mol and then move it to the left until the vertical axes of the two figures overlap to each other, and we obtain Fig. 6. Considering the quality of the basis set and the large overall shift, 56.953 kcal/mol, the general agreement is relatively good, except for the $2^1\Sigma_g^+$ curve in the region larger than 8 a.u. The SAC-CI(1985) points given by purple triangle lies much higher than the experimental curve given by purple diamond.

In Table IV, we summarize some spectroscopic data associated with the potential curves, such as the equilibrium distance R_e , the vertical excitation energy T_e from the ground state at R_e , and the dissociation energy D_e calculated for the ground and many excited states of the Li_2 molecule from the data of the potential curves given in Tables I–III for the FC theory and the SAC/SAC-CI(2022) calculations using Jorge-6ZP basis. Here, we also cited the data obtained by Musiał and Kucharski with their FS-CCSD theory³¹ as a representative result from the current quantum chemistry calculations.

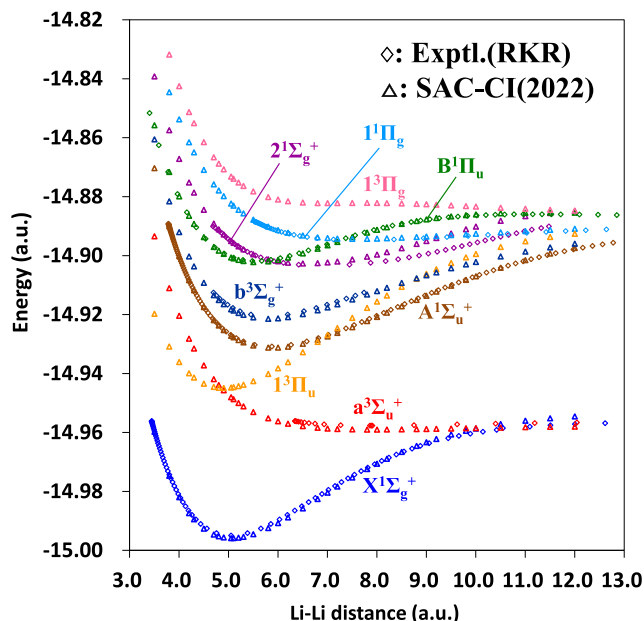


FIG. 4. Overlapped experimental RKR and present SAC/SAC-CI theoretical potential curves of Li_2 after shifting down the SAC/SAC-CI curves by 5.727 kcal/mol.

The FC theory is the theory that can solve the Schrödinger equation highly accurately and, therefore, gives the results that agree well with the experimental values for all the eight lower states of Li_2 . This theory has an absolute and comprehensive reliability among the theories presented here. The FS-CCSD theory also gives highly accurate results for all the states, though their absolute energy values

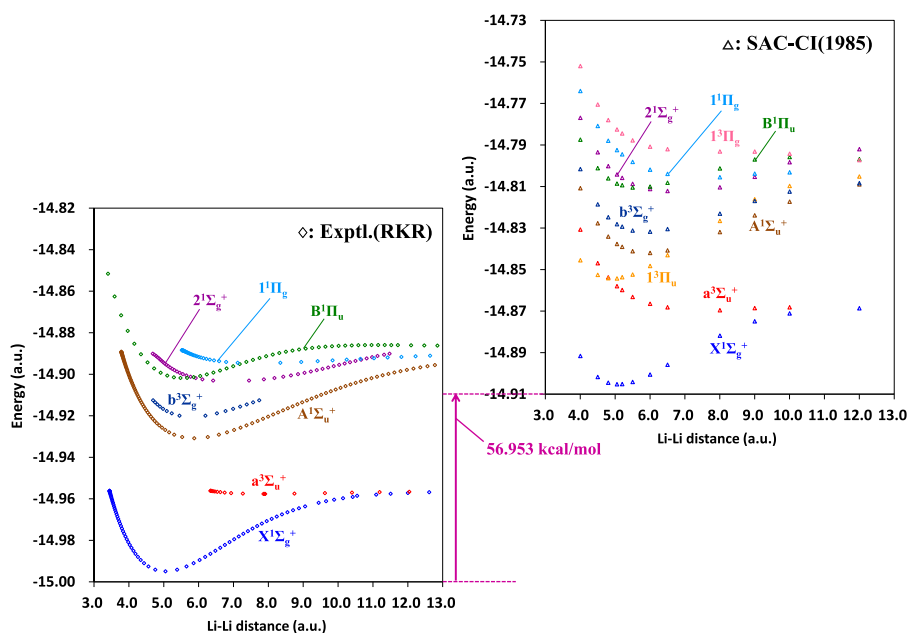


FIG. 5. Left is the experimentally determined RKR potential curves and right is the potential curves calculated by the SAC/SAC-CI theory published in 1985² both for Li_2 .

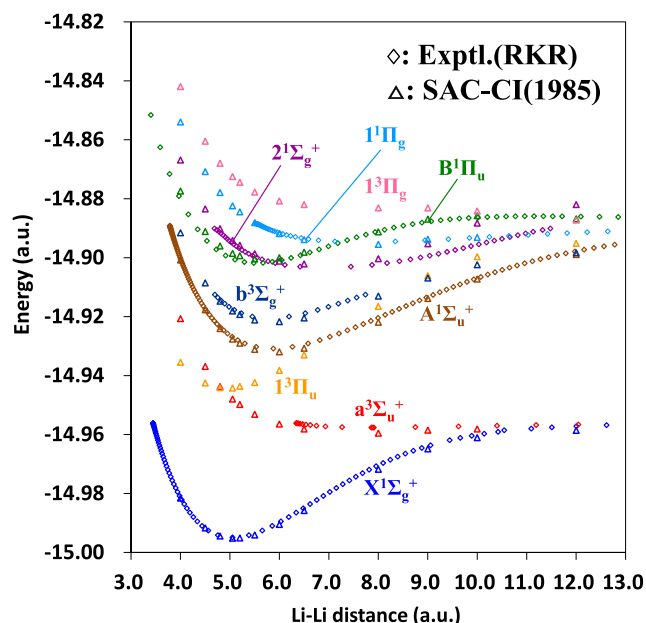


FIG. 6. Overlapped experimental RKR and SAC/SAC-CI (1985)² theoretical potential curves of Li_2 after shifting down the SAC/SAC-CI curves by 56.953 kcal/mol.

were still higher by about 5.803 kcal/mol at the equilibrium distance of $X^1\Sigma_g^+$ than the exact value like the present SAC/SAC-CI(2022) results shown in Fig. 3. The SAC/SAC-CI results are acceptable for the equilibrium distance and the vertical excitation energies, but not so for the dissociation energy, which is common for the theories based on the Hartree-Fock wave function.

Finally, we would like to discuss about the physics not included in the Schrödinger equation, but included in the experimental observations. With the FC theory, we have solved the Schrödinger equation of the Li_2 molecule, which is the non-relativistic equation, within the Born-Oppenheimer approximation. For comparisons with experiments, we must examine the relativistic effect and the nuclear quantum effect. For the H_2 molecule, Kołos and Roothaan reported the accurate non-relativistic wave functions.⁵⁵ Then, Kołos and Wolniewicz performed the detailed examinations on the relativistic and adiabatic effects.^{56–58} At the equilibrium distance, their contributions to the binding energy were -0.526 and 4.947 cm^{-1} ($1 \text{ cm}^{-1} = 0.0028572 \text{ kcal/mol}$), respectively.⁵⁷ Their dependences on the internuclear distance were also investigated. For the Li_2 molecule, Lesiuk *et al.*⁵⁹ studied the potential curve of the $a^3\Sigma_u^+$ state and reported the leading-order relativistic and adiabatic corrections to be -0.243 and 0.6803 cm^{-1} , respectively, near the equilibrium distance, 7.75 a.u. The adiabatic correction to the energy depends on κ^4 with $\kappa = (m/\mu)^{1/4}$ where m is the mass of the electron and μ is the reduced mass of the nuclei.⁶⁰ Therefore, this correction to the $^7\text{Li}_2$ molecule would be roughly seven times smaller than that of H_2 , as seen here from the result of H_2 and $^7\text{Li}_2$. Furthermore, these values were dependent on the Li-Li distance⁵⁹ and when it is 6.50 a.u., these values were -0.284 and -0.04866 cm^{-1} , respectively, and when it is 12.5 a.u., these values were -0.04 and

TABLE IV. Some spectroscopic data associated with the potential curves of the ground and excited states of Li_2 .

State	Method	Equilibrium distance R_e (Å)	Excitation energy T_e (eV)	Dissociation energy D_e (kcal/mol)
$X^1\Sigma_g^+$	FC	2.676		24.323
	Expt. ^a	2.673		24.351
	FS-CCSD ^b	2.677		24.206
	SAC-CI ^c	2.679		24.041
$A^1\Sigma_u^+$	FC	3.106	1.743	26.729
	Expt. ^{b,d}	3.108	1.744	26.742
	FS-CCSD ^b	3.112	1.739	26.750
	SAC-CI ^c	3.116	1.758	27.141
$2^1\Sigma_g^+$	FC	3.660	2.493	9.438
	Expt. ^e	3.651	2.492	9.489
	FS-CCSD ^b	3.655	2.491	9.404
	SAC-CI ^c	3.472	2.536	9.193
$B^1\Pi_u$	FC	2.937	2.535	8.456
	Expt. ^{b,f}	2.936	2.534	8.532
	FS-CCSD ^b	2.942	2.536	8.377
	SAC-CI ^c	2.945	2.548	8.919
$1^1\Pi_g$	FC	4.067	2.727	4.043
	Expt. ^g	4.058	2.726	4.069
	FS-CCSD ^b	4.061	2.722	4.077
	SAC-CI ^c	4.008	2.763	3.960
$a^3\Sigma_u^+$	FC	4.171	1.013	0.959
	Expt. ^h	4.171	1.014	0.952
	FS-CCSD ^b	4.169	1.008	0.955
	SAC-CI ^c	4.187	1.002	0.933
$1^3\Pi_u$	FC	2.591	1.390	34.861
	Expt. ⁱ	2.591		34.724
	FS-CCSD ^b	2.592	1.390	34.784
	SAC-CI ^c	2.594	1.386	35.704
$b^3\Sigma_g^+$	FC	3.065	2.026	20.190
	Expt. ^h	3.068	2.024	20.276
	FS-CCSD ^b	3.071	2.021	20.243
	SAC-CI ^c	3.073	2.025	20.966
$1^3\Pi_g$	Repulsive			

^aReference 8.

^bReference 31.

^cDe was calculated by considering $R = 20.0$ a.u. as a dissociation limit.

^dReference 62.

^eReference 12.

^fReference 16.

^gReference 11.

^hReference 9.

ⁱReference 63.

0.2148 cm^{-1} , respectively. So far, we could not find the examinations of these effects done for the potential curves of the other electronic states.

At present, we do not investigate the relativistic and adiabatic corrections on our FC-LSE results of the potential curves of the Li_2 molecule yet. From the study of Lesiuk *et al.*, if the orders of the magnitudes of these effects are similar for all the nine states of the Li_2 molecule, we might be able to ignore them for the present chemical-accuracy calculations with the FC-LSE theory. However, when we aim the spectroscopic accuracy, we must examine these contributions carefully. Such studies are possible by using the higher-order FC theory because the FC theory is exact. As an example of the highly accurate calculations with the FC theory, we may refer to the calculations performed for the He atom.^{39,61}

V. CONCLUSIONS

We applied the free complement (FC) theory that was developed for solving the Schrödinger equation highly accurately to the calculations of potential curves of the lower nine states of Li_2 molecule. For this molecule, accurate experimental Rydberg–Klein–Rees (RKR) potential curves are available for the ground and many excited states so that we could examine the accuracy of the theory in detail. The theoretical FC potential curves and the experimental RKR curves agreed very accurately in their absolute values in all regions of the Li–Li distances of all the states for which the experimental RKR potentials were reported. The differences between the absolute energies of the FC theory and the experiments were 0.0583 kcal/mol in average and the maximum difference was only $+0.165\text{ kcal/mol}$ for all the calculated lengths, $3\text{--}13\text{ a.u.}$, of all the states in the range of $-14.82 \sim -15.00\text{ hartree}$ ($1\text{ hartree} = 627.5096\text{ kcal/mol}$) directly compared. The potential properties calculated by the FC theory agreed well with the experimental results for all the ground and excited states.

We note that the experimental RKR potentials were determined through the careful experimental spectroscopy^{8–19} of the Li_2 molecule using the RKR method.^{5–7} The present theoretical potential curves of the Li_2 molecule were obtained from the free complement (FC) theory developed for solving the Schrödinger equation highly accurately.^{34,35} It was shown here that these completely independent experimental and theoretical data on the potential curves of the seven states of Li_2 molecule agreed almost completely with each other in wide range of the Li–Li distance and the energy. This may be considered as a proof of the statement that the Schrödinger equation governs the chemistry of the Li_2 molecule. More explicitly, we have solved the Schrödinger equation of the Li_2 molecule by using the free complement theory that was formulated from the variational formula of the scaled Schrödinger equation, since the variational formula of the Schrödinger equation itself diverges.³⁴

Furthermore, in Fig. 1, we notice that the experimental figure on the left-hand side has many empty spaces like no information for the $1^3\Pi_u$ and $1^3\Pi_g$ states and the incomplete information for the $a^3\Sigma_u^+$, $b^3\Sigma_g^+$, and $1^1\Pi_g$ states. These empty spaces may be an obstacle for predicting chemistry. On the other hand, the theoretical

figure by the FC theory given on the right-hand side is full of information, and if we need the potential curves shorter than 3.4 a.u. and longer than 12 a.u. , we can obtain highly reliable data only with computers. The same is true for the states lying higher than the given 9 states. With the FC theory, all that necessary is the computer time. Thus, the observations given in this paper certainly give the bases for the future development of the quantitatively predictive quantum chemistry. Truly reliable data can nurture the imagination that may lead to a big future. It is important to develop the FC theory to be applicable to a wide field of chemistry, including the structural and reaction chemistries and other related fields in physics and biology.

For comparison with the conventional Hartree–Fock based quantum chemistry, we performed the SAC/SAC-CI calculations using the flexible basis set and compared the results with the accurate experimental potential curves as we did for the results of the FC theory. Although the SAC/SAC-CI theory did not have the chemical accuracy (predictive power to within kcal/mol), the agreement between theory and experiment was reasonable for all the states except for the regions showing the deficiencies of the Hartree–Fock theory near the dissociation limit of a homopolar bond.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the detailed comparisons of the old SAC/SAC-CI data published in 1985 with the experimental RKR potential data published thereafter.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Hiroshi Nakatsuji: Conceptualization (equal); Methodology (equal); Writing – original draft (equal). **Hiroyuki Nakashima:** Investigation (equal); Software (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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