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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២ Hiroshi Nakatsuji and ២ Hiroyuki Nakashima



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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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Hiroshi Nakatsuji^{a)} 🔟 and Hiroyuki Nakashima^{b)} 🔟

AFFILIATIONS

Quantum Chemistry Research Institute, Kyoto Technoscience Center 16, 14 Yoshida Kawara-machi, Sakyo-ku, Kyoto 606-8305, Japan

^{a)} Author to whom correspondence should be addressed: h.nakatsuji@qcri.or.jp ^{b)} Electronic mail: h.nakashima@qcri.or.jp

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 Li₂ 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 Li₂. 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

Li₂ molecule is a simple homopolar diatomic molecule whose simplicity is next to the hydrogen molecule. The equilibrium distance of H₂ molecule is 1.4011 a.u. (0.741 44 Å), while that of Li₂ 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 Li₂ 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 Li₂ 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 ⁷Li₂ were reported. First, in 1986, Barakat *et al.*⁸ reported extensive analyses of the potential curve of the X¹Σ_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 b³Σ_g⁺-a³Σ_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 1¹Π_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 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 Li2.14 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 $X^1\boldsymbol{\Sigma_g}^+$ and $A^{1}\Sigma_{u}^{+}$ states of Li₂ 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 Li2.

Theoretical studies on the potential curves of Li2 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 H₂ molecule. Similar method was applied extensively to many excited states of Li2 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 Li₂ molecule.² Kaldor studied the ground and many excited states of Li2 by the open-shell coupled cluster theory.² Shi, Ma, Sun, Zhu, Yu, Yang, and Liu used the SAC-CI theory for studying the potential curves of the excited states of Li2 molecule and reported highly accurate results for many different states.²⁶ 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 Li₂ 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

$$\psi = \sum_{I=0} c_I \phi_I, \tag{1}$$

where the functions $\{\phi_l\}$ 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 Li₂ 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

$$2s - 2s : \psi_{0}^{(1)} = (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ \times (\alpha\beta - \beta\alpha) \cdot (2s_{A} 2s_{B})(\alpha\beta - \beta\alpha),$$

$$2s - 2p : \psi_{0}^{(2)} = (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ \times (\alpha\beta - \beta\alpha) \cdot (2s_{A} 2p_{B})(\alpha\beta - \beta\alpha) + (A \leftrightarrow B),$$

$$2p - 2p : \psi_{0}^{(3)} = (1s_{in,A} 1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B} 1s_{out,B}) \\ \times (\alpha\beta - \beta\alpha) \cdot (2p_{A} 2p_{B})(\alpha\beta - \beta\alpha),$$

$$(2)$$

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

$$(2s)^{2}: \psi_{0}^{(4)} = (1s_{in,A}1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B}1s_{out,B}) \times (\alpha\beta - \beta\alpha) \cdot (2s_{A})^{2}(\alpha\beta) + (A \leftrightarrow B),$$

$$2s2p: \psi_{0}^{(5)} = (1s_{in,A}1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B}1s_{out,B}) \times (\alpha\beta - \beta\alpha) \cdot (2s_{A}2p_{A})(\alpha\beta - \beta\alpha) + (A \leftrightarrow B),$$

$$(2p)^{2}: \psi_{0}^{(6)} = (1s_{in,A}1s_{out,A})(\alpha\beta - \beta\alpha) \cdot (1s_{in,B}1s_{out,B}) \times (\alpha\beta - \beta\alpha) \cdot (2p_{A})^{2}(\alpha\beta) + (A \leftrightarrow B),$$

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

$$1s_{in,A} = \exp(-\alpha_{1s,in}r_A), \quad 1s_{out,A} = \exp(-\alpha_{1s,out}r_A),$$

$$2s_A = r_A \, \exp(-\alpha_{2s}^{(r)}r_A) + d_{2s}^{(0)} \, \exp(-\alpha_{2s}^{(0)}r_A), \qquad (4)$$

$$2p_A = x_A \, \exp(-\alpha_{2p}r_A).$$

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 $\alpha_{1s,in} = 3.3029$, $\alpha_{1s,out} = 2.0674$, $\alpha_{2s}^{(r)} = 0.6785$, $\alpha_{2s}^{(0)} = 1.1832$, $d_{2s}^{(0)} = -0.096777$, 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

1 kcal/mol, i.e. satisfying chemical accuracy.

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

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

where

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

The values of the parameters y_1 and y_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 cf's 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 Li₂. 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

	FC	theory		
R (a.u.)	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	$\Delta E (FC)$ (kcal/mol)
4.0	0.018 109	-14.981 162	-14.981 401	0.150
4.5	0.016 033	-14.991 652	-14.991846	0.122
4.8	0.014234	-14.994208	-14.994 355	0.0922
5.051	0.013 885	-14.994840	-14.994 926 ^c	0.0540
5.2	0.013 568	-14.994 663	-14.994757	0.0585
5.5	0.011 969	-14.993 448	-14.993 533	0.0535
6.0	0.010 922	-14.989 667	-14.989740	0.0457
6.5	0.010 331	-14.984759	-14.984839	0.0501
8.0	0.008047	-14.970338	-14.970393	0.0344
9.0	0.007 277	-14.963 854	-14.963 893	0.0243
10.0	0.007 220	-14.960077	-14.960078	0.000 320
12.0	0.007 237	-14.957 138	-14.957 147	0.005 93
Average ^d				0.0576
Max.dif. ^e				0.150

TABLE I. Energies of the ground $X^1\Sigma_g^+$ state of Li₂ 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

 a The FC theory at the order 3. The dimensions of the complement functions were 11098 for the $^1\Sigma _g{}^+$ symmetry.

 $^{\rm b}{\rm RKR}$ potentials are fitted by the spline interpolation from the reference experimental data. $^{\rm 8-17}$

^cExact total energy of X¹ Σ_g^+ state of Li₂ 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 Li₂ 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 Li2.⁸⁻¹⁷ These values were obtained from the ground state RKR potential reported by Barakat et al.8 and the estimated exact energy of Li2 at the equilibrium length.⁴⁷ This value of the absolute energy of Li₂ 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 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, $E_{\rm FC}$ both in a.u. About the H-square error, if this value is zero for any set of sampling points, the results are strictly

is of the excited states of Li ₂ calculated by the FC theory at several inter-nuclear distances R^a ΔE represents
from the experimental RKR potential energy and bold face denotes less than 1 kcal/mol, i.e. satisfying chemical accuracy. ^D ΔEX represents the difference in eV from the RKR excitation energy and bold
face denotes their absolute values less than 0.01 eV.

			\mathbf{A}^{1}	$\Sigma_{\rm u}^{+}$ state						2	$2^{1}\Sigma_{g}^{+}$ state			
	FCt	FC theory			Vertica	l excitation	Vertical excitation energy (eV)	FC 1	FC theory			Vertical	excitation (Vertical excitation energy (eV)
R (a.u.)	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	FC	RKR	$\Delta E X$	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	FC	RKR	$\Delta E X$
4.0		-14.900 341	-14.900315	-0.0159		2.20645	-0.007 20	0.020412	-14.867 382					
4.5		-14.917 388	-14.917380	-0.005 60		2.02634	-0.005 53	0.018 335	-14.884 341					
4.8		-14.923534	-14.923512	-0.013 9	1.92314	1.92774	-0.00460	0.017915	-14.891037	$(-14.891484)^{\circ}$	(0.280)	2.80742	(2.799 27)	(0.00814)
5.051		-14.926896	-14.926917	0.0133	1.84886	1.85062	-0.00176	0.014377	-14.894865	-14.895128	0.165	2.72045	2.715 64	0.00481
5.2		-14.928311	-14.928341	0.0193	1.805555	1.80725	-0.00170	0.014029	-14.896685	-14.896928	0.153	2.666 13	2.662 05	0.00408
5.5	0.008 947	-14.930100	-14.930135	0.0216	1.72379	1.72517	-0.00138	0.012414	-14.899373	-14.899610	0.149	2.559 92	2.55578	0.00414
6.0	0.008 813	-14.930709	-14.930762	0.0336	1.60435	1.60487	-0.000524	$0.012\ 194$	-14.901930	$-14.902\ 116$	0.116	2.387 46	2.38439	0.003 06
6.5	0.008 980	-14.929357	-14.929437	0.0504	1.50758	1.50757	0.000 013 7	0.012460	-14.902988	$-14.903\ 139$	0.0949	2.225 12	2.223 18	0.00194
8.0	0.008 503	-14.920291	-14.920366	0.0470	1.36186	1.36131	0.000549	0.011878	-14.902036	$-14.902\ 201$	0.103	1.85860	1.85560	0.00299
9.0	0.008 272	-14.913253	-14.913338	0.0536	1.37694	1.37567	0.00127	0.011572	-14.899248	-14.899445	0.123	1.75802	1.75372	0.00429
10.0	0.008 010	-14.906872	-14.906946	0.0463	1.44778	1.44578	0.00199	0.011 306	-14.895432	-14.895596	0.103	1.75909	1.75463	0.00446
12.0	0.006 449	-14.897684	-14.897796	0.0698	1.61780	1.61504	0.00277	0.008 307	-14.888631			1.86417		
Average ^d				0.0266			-0.00134				0.126			0.00372
Max.dif. ^e				0.0698			-0.00720				0.165			0.00481
			B	lΠ _u state							1 ¹ ∏g state			
	FCt	FC theory			Vertica	l excitation	Vertical excitation energy (eV)	FC 1	FC theory			Vertical	excitation e	Vertical excitation energy (eV)
R (a.u.)	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	FC	RKR	$\Delta E X$	H-square error	Energy (a.u.)	RKR potential energy (a.u.)	ΔE (kcal/mol)	FC	RKR	$\Delta E X$
4.0	0.012 813	-14.879 804	(-14.880 217) ^f	(0.259)	2.758 08	(2.753 35)	(0.00473)	0.009 594	-14.854880			3.436.31		
4.5	0.011774	-14.893462	-14.893637	0.110	2.671 89	2.672 43	-0.000538	0.009488	-14.871314			3.274 58		
4.8	0.011401	-14.897961	-14.898124	0.102	2.61901	2.61858	0.000426	0.009 129	-14.878039			3.161 12		
5.051	0.010790	-14.900190	-14.900340	0.0946	2.57557	2.57381	0.00176	0.009 028	-14.882427			3.05892		
5.2	0.010 683	-14.900983	$-14.901\ 132$	0.0937	2.54918	2.547 66	0.00152	0.008 892	-14.884488			2.99801		
5.5	0.010 110	-14.901654	-14.901799	0.0912	2.49784	2.49621	0.00164	0.008747	-14.887768			2.87571		
6.0	0.009 961	-14.900827	-14.900983	0.0982	2.41748	2.41521	0.00227	0.008 252	-14.891353	-14.891605	0.158	2.675 27	2.67040	0.00486
6.5		-14.898697	-14.898801	0.0649	2.341 87	2.341 23	0.000640	0.008476	-14.893349	-14.893466	0.0732	2.48741	2.48641	0.00100
8.0		-14.890955	$-14.891\ 027$	0.0452		2.159 66	0.000472	0.006964	-14.894566	-14.894646	0.0500	2.06186	2.061 19	0.000 677
9.0		-14.887810	-14.887802	-0.00499		2.07053	-0.001268	0.007 337	-14.894080	-14.894030	-0.0314	1.89864	1.90106	-0.00241
10.0		-14.886403	-14.886348	-0.0343	2.00479	2.00629	-0.00150	0.006306	-14.893 173	-14.893164	-0.00549	1.82056	1.82081	-0.000252
12.0	0.006 872	-14.886086	-14.886024	-0.0386	1.93342	1.93535	-0.00193	0.006070	-14.891512	-14.891513	0.000958	1.78578	1.78599	-0.000215
Average ^d				0.0565			0.000317				0.0409			0.000610
Max.dif. ^e				0.110			0.00227				0.158			0.00486

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	FC theory FC theory Vertical excitation energy (eV) H-square Energy RK potential ΔE ΔE H= 4.0 0.007293 -14916577 energy (au.u) (kcal/mod) FC RK R H= 4.5 0.0067103 -14936535 -14936555 -14936555 0.000			1 ³]	1 ³ ∏ _u state			
	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	R (a.u.) H-square Energy (a.u.) (kcal/mol) FC RKR ΔEX H-square 4.0 0.007293 -14919577 energy (a.u.) (kcal/mol) FC RKR ΔEX ere 4.5 0.006432 -14919577 i.157580 0.00 0.00 5.2 0.006432 -1495632 i.139559 0.00 0.00 5.5 0.00632 -14956527 -0.0108 0.75778 0.00 0.00 5.5 0.005321 -14957533 -14957638 0.0347 -0.000269 0.00 5.6 0.005321 -14957638 0.03829 0.015657 -0.001269 0.00 5.0 0.005537 -14957638 0.035763 0.04577 0.00 0.00 6.5 0.005537 -14957638 0.03250 0.001457 -0.000254 0.00 10.0 0.005537 -14957638 0.03250 0.000210 0.1752 0.00001657 1.000159 0.00 0.000 0.0005474 0.000 <th> </th> <th>FC theory</th> <th></th> <th></th> <th>Vertical exc</th> <th>citation energy</th> <th>gy (eV)</th>		FC theory			Vertical exc	citation energy	gy (eV)
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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4.0 0.007233 -14.919577 1655 11.65580 0.007 4.8 0.006693 -14.946947 11.505 51 0.00 5.006938 -14.948879 11.505 50 0.00 5.1365 50 0.006328 -14.956544 -14.956554 -14.956554 0.00 5.5 0.005346 -14.9556544 -14.955654 -14.956564 0.00 6.5 0.005508 -14.957533 -14.957638 0.0286 0.00 0.0447 2 0.000 559 0.00 0.005502 -14.956530 -14.956652 0.00108 0.7677 8 0.77042 0.000 0.005502 -14.956530 -14.956630 -14.957638 0.0287 0.001067 0.00 0.005502 -14.956630 -14.956630 -14.956652 0.00172 0.013 82 0.014 57 -0.000 555 0.00 0.005502 -14.956630 -14.956612 -0.0114 0.013 82 0.014 57 -0.000 555 0.00 0.005502 -14.956630 -14.956612 -0.0112 0.013 82 0.014 57 -0.000 555 0.00 0.005502 -14.956630 -14.956612 -0.0112 0.013 82 0.014 57 -0.000 555 0.00 0.005502 -14.956630 -14.956612 -0.0112 0.013 82 0.014 57 -0.000 555 0.00 0.005502 -14.956630 -14.956612 -0.0112 0.013 82 0.014 57 -0.000 555 0.00 0.005502 -14.956630 -14.91457 0.0128 0.0128 0.00 0.005502 -14.916680 -14.914277 0.02024 0.00 4.0 0.015887 -14.891080 0.0148 0.0148 0.00 4.0 0.015887 -14.91080 0.0148 0.0148 0.000 59 0.00 4.0 0.015687 -14.911407 0.126 2.179 40 0.00159 0.00 4.0 0.015687 -14.911427 0.126 2.179 49 0.000 59 0.00 4.0 0.015687 -14.911427 0.128 0.0148 0.000 59 0.000 54 0.00 4.0 0.015687 -14.911465 0.01267 0.126 2.074 54 2.07160 0.000 294 0.00 5.5 0.015193 -14.919955 -14.911827 0.0999 1.9999 1.9979 1.0001 59 0.00 5.5 0.015193 -14.919955 -14.91165 0.000 59 0.000 59 0.000 59 0.000 59 5.5 0.015193 -14.919955 -14.91165 0.000 59 0.000 57 0.000 59 0.000 59 5.5 0.015193 -14.919955 -14.91165 0.000 59 0.000 59 0.000 59 0.000 56 5.5 0.015193 -14.919955 -14.91165 0.000 59 0.000 59 0.000 59 0.000 55 5.5 0.015193 -14.919955 -14.91165 0.000 59 0.000 59 0.000 55 5.5 0.015193 -14.919955 -14.91165 0.000 59 0.000 55 5.5 0.015673 -14.919955 -14.91165 0.000 59 0.000 59 0.000 55 5.5 0.015673 -14.919955 -14.91165 0.000 59 0.000 59 0.000 56 5.5 0.015673 -14.919955 -14.91165 0.000 59 0.000 57 0.125 0.000 55 5.5 0.015674 -14.911955 0.000 56 0.000 56 0.0000 56 0.14.900 58 0							
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$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	a.s. 0.000 530 - 14395 53 1.239 53 0.000 536 - 14395 563 1.135 53 1.135 53 5.5 0.006 335 - 14395 759 14395 557 1131 55 1131 56 1131 56 5.5 0.006 335 - 14395 759 14395 557 1131 57 0.006 354 1434 56 1131 57 5.6 0.006 358 - 14395 759 14395 557 0.001 20 0.005 36 1439 56 1131 59 6.0 0.005 358 - 14397 391 1430 567 0.001 20 0.006 592 1439 563 1131 25 0.0 0.005 352 - 14395 630 -1439 561 0.001 20 0.006 252 1430 561 1132 53 0.0 0.005 362 - 1439 640 0.001 25 0.001 25 0.001 25 0.001 25 0.001 25 1130 54 1.0 0.005 592 - 1439 640 0.001 25 0.001 25 0.001 25 0.001 25 1.149 51 1.153 53 1.0 0.005 592 - 1439 106 0.001 25 0.001 25 0.001 25 1.149 57 1.153 53 1.0 0.001 25 0.001 25 0.001 25 0.001 25 1.149 57 </td <td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td> <td>C 000.0</td> <td></td> <td></td> <td></td> <td>1.343 00</td> <td></td> <td></td>	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	C 000.0				1.343 00		
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$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$							
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	FC theory Vertical excitation energy (eV) H-square Energy RKR potential ΔE H-sectination energy (eV) 4.0 error (a.u.) energy (a.u.) (kcal/mol) FC RKR $\Delta E X$ error 4.0 0.015 887 -14.910 80 energy (a.u.) (kcal/mol) FC RKR $\Delta E X$ error 4.0 0.015 887 -14.914 071 -14.914 277 0.129 2.179 04 0.001 5.5 0.015 677 -14.917 144 -14.917 380 0.148 2.114 20 0.001 5.5 0.015 677 -14.918 627 0.129 2.180 63 2.179 04 0.001 5.5 0.015 677 -14.919 827 0.129 2.074 54 0.002 0.00 5.5 0.013 837 -14.918 627 0.129 2.107 60 0.002 0.00 5.5 0.010 967 -14.911 065 0.110 1.890 20 1.887 43 0.00 0.00 5.5 0.010 967 -14.918 627 <td< td=""><td></td><td></td><td>13.</td><td>Πg state</td><td></td><td></td><td></td></td<>			13.	Πg state			
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H-square Energy RKR potential ΔE R(a.u) error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) erregy (a.u) (kcal/mol) FC RKR ΔEX error (a.u) (kcal/mol) FC RKR ΔEX error (a.u) (kcal/mol) FC RKR ΔEX (a.u) (kcal/mol) FC RKR ΔEX (a.u) (a.u) (kcal/mol) FC RKR ΔEX (a.u) (a.u) (kcal/mol) FC RKR (a.u) (a.u) <t< td=""><td>H-square Energy RKR potential ΔE H-square Energy RKR potential ΔE R(a.u) error (a.u) error (a.u) error (a.u) rergy (a.u) (real/mol) FC 45 0.01587<</td> -14480198 2.45124 0.01746 -1486197 3.56117 45 0.01567 -1491714 -1491734 0.129 2.11043 0.001240 0.01746 -148677 3.5617 5551 0.015677 -1491071 -14917380 0.148 2.11420 2.11420 3.3068 552 0.015677 -1491071 -1491734 0.129 2.1904 0.00199 0.002430 3.3368 555 0.015677 -1491074 -1491744 -1491734 3.3368 3.3368 560 0.013837 -14920738 0.1109 1.8900 1.487729 3.1487420 3.3468 560 0.013837 -14920758 0.1099 1.8900 0.00129 0.0012411 -14877420 3.14877532<!--</td--><td>H-square Energy RKR potential ΔE H-square Energy (a.u.) cenergy (a.u.) K (a.u.) FC RKR ΔEX energy 40 0.015 887 -14.891 080 2.451 24 0.01 45 0.015 887 -14.891 080 2.451 24 0.01 45 0.015 887 -14.910 180 2.270 89 0.01 55 0.015 467 -14.917 144 -14.917 380 0.01 55.2 0.015 467 -14.918 627 0.0126 2.010 199 0.01 55.5 0.013 837 -14.918 627 0.126 2.074 54 0.00 0.01 55.5 0.013 837 -14.918 627 0.126 2.074 54 0.00 0.00 55.5 0.013 837 -14.920 112 0.010 9.00 0.00 0.00 0.01 55.5 0.013 837 -14.91 1065 0.110 1.890 20 1.887 43 0.00 60 0.012 653 -14.91 1065 0.190 97 1.795 70 1.793 55 0.001</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>	H-square Energy RKR potential ΔE H-square Energy RKR potential ΔE R(a.u) error (a.u) error (a.u) error (a.u) rergy (a.u) (real/mol) FC 45 0.01587<	H-square Energy RKR potential ΔE H-square Energy (a.u.) cenergy (a.u.) K (a.u.) FC RKR ΔEX energy 40 0.015 887 -14.891 080 2.451 24 0.01 45 0.015 887 -14.891 080 2.451 24 0.01 45 0.015 887 -14.910 180 2.270 89 0.01 55 0.015 467 -14.917 144 -14.917 380 0.01 55.2 0.015 467 -14.918 627 0.0126 2.010 199 0.01 55.5 0.013 837 -14.918 627 0.126 2.074 54 0.00 0.01 55.5 0.013 837 -14.918 627 0.126 2.074 54 0.00 0.00 55.5 0.013 837 -14.920 112 0.010 9.00 0.00 0.00 0.01 55.5 0.013 837 -14.91 1065 0.110 1.890 20 1.887 43 0.00 60 0.012 653 -14.91 1065 0.190 97 1.795 70 1.793 55 0.001							
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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, $E_{\rm FC}-E_{\rm RKR}$, in kcal/mol. If $E_{\rm FC}$ is higher than $E_{\rm RKR}$, $\Delta E(\rm FC)$ 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 Li₂ 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 Li₂ 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 Li₂ 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 ${}^{1}\Sigma_{g}{}^{+}$ states that include the ground $X^{1}\Sigma_{g}{}^{+}$ and excited $2{}^{1}\Sigma_{g}{}^{+}$ states, the number of the cf's (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 rhodopseudomonas 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 Li₂ 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

	$X^{1}\Sigma_{g}^{+}$ state	state				$A^{1}\Sigma_{u}^{+}$ state	tate			$2^{1}\Sigma_{g}^{+}$ state	state	
	SAC-CI	ΔE			SAC-CI	ΔE	Vertical ener£	Vertical excitation energy (eV)	SAC-CI	ΔE	Vertical e	Vertical excitation energy (eV)
R (a.u.)	Energy (a.u.)	(kcal/mol)			Energy (a.u.)	(kcal/mol)	SAC-CI	$\Delta E X$	Energy (a.u.)	(kcal/mol)	SAC-CI	$\Delta E X$
4.0	-14.972780	5.410			-14.890 997	5.847	2.225 43	0.01898	$-14.858\ 002$		3.123 27	
4.5	-14.983459	5.263			$-14.908\ 308$	5.692	2.044 96	0.01862	-14.875276		2.943 81	
4.8	-14.986055	5.208			-14.914536	5.632	1.946 13	0.01839	-14.881904	(6.011)	2.83409	(0.03482)
5.051	-14.986681	5.174			-14.918014	5.587	1.86852	0.01790	-14.885877	5.805	2.743 02	0.02738
5.2	-14.986535	5.159			-14.919479	5.561	1.82469	0.01744	-14.887695	5.794	2.689 57	0.02752
5.5	-14.985345	5.138			-14.921340	5.519	1.74166	0.01650	-14.890386	5.788	2.583 97	0.02818
6.0	-14.981556	5.136			-14.922035	5.477	1.61965	0.01478	-14.892773	5.863	2.41591	0.03152
6.5	-14.976584	5.180			-14.920746	5.454	1.51943	0.01186	-14.893481	6.061	2.261 35	0.03817
8.0	-14.961452	5.610			-14.911617	5.490	1.35608	-0.00523	-14.890464	7.365	1.93168	0.07608
9.0	-14.954147	6.116			-14.904441	5.583	1.35257	-0.02310	-14.885879	8.513	1.85767	0.10395
10.0	-14.949504	6.635			-14.897840	5.714	1.40585	-0.03994	-14.880992	9.164	1.86431	0.10967
12.0	-14.945399	7.372			-14.888222	6.008	1.55587	-0.05917	-14.875721		1.89603	
Average ^a		5.617				5.630		0.000586		6.794		0.05531
Max.dif. ^b		7.372				6.008		-0.05917		9.164		0.10967
		$B^{1}\Pi_{u}$ state	ate			$1^{1}\Pi_{g}$ state	ate			$a^3 \Sigma_u^+$ state	state	
			Vertical ex	cal excitation			Vertical	Vertical excitation			Vertical o	Vertical excitation
	SAC-CI	ΔE	energ	energy (eV)	SAC-CI	ΔE	ener£	energy (eV)	SAC-CI	ΔE	energ	energy (eV)
R (a.u.)	Energy (a.u.)	(kcal/mol)	SAC-CI	ΔEX	Energy (a.u.)	(kcal/mol)	SAC-CI	ΔEX	Energy (a.u.)	(kcal/mol)	SAC-CI	$\Delta E X$
4.0	-14.870727	(5.955)	2.777 00	(0.02365)	-14.844 579		3.488 53		-14.911 244		1.674 48	
4.5	-14.884556	5.698	2.691 29	0.01886	-14.861740		3.312 14		-14.928087		1.506 75	
4.8	-14.889161	5.624	2.636 62	0.01804	-14.868742		3.19225		-14.934744		1.39624	
5.051	-14.891460	5.572	2.591 10	0.01729	-14.873159		$3.089\ 09$		-14.938873		1.30092	
5.2	$-14.892\ 293$	5.547	2.56446	0.01680	-14.875275		3.027 54		-14.940829		1.24372	
5.5	-14.893028	5.504	2.512 07	0.01586	-14.878616		2.904 24		-14.943881		1.12829	
6.0	$-14.892\ 272$	5.466	2.42954	0.01433	-14.882150	5.933	2.70497	0.03457	-14.947049		0.93898	
6.5	$-14.890\ 095$	5.463	2.353 49	0.01226	-14.884018	5.928	2.518 85	0.03244	-14.948700	4.911	0.75876	-0.01166
8.0	-14.882067	5.622	2.160 18	0.000520	-14.885057	6.017	2.078 81	0.01763	-14.949856	4.883	0.31554	-0.03154
9.0	-14.878557	5.802	2.05691	-0.01362	-14.884358	6.070	1.89906	$-0.002\ 00$	-14.949649	4.879	0.12240	-0.05365
10.0	-14.876857	5.956	1.97683	-0.02946	-14.883422	6.113	1.79818	-0.02263	-14.949334	4.880	0.00463	-0.07612
12.0	-14.876256	6.130	1.88148	-0.05387	-14.881 705	6.155	1.73320	-0.05279	-14.948826	4.886	-0.09325	-0.10782
Average ^a		5.671		0.00155		6.036		0.00120		4.888		-0.05616

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		$1^3 \Pi_{\mathrm{u}}$ state	tate			$b^3 \Sigma_g^+$ state	tate			1 ³ ∏g state	ate	
	SAC-CI	ΔE	Vertical excitation energy (eV)	itation	SAC-CI	ΔE	Vertical energ	Vertical excitation energy (eV)	SAC-CI	ΔE	Vertical excitation energy (eV)	xcitation r (eV)
R (a.u.)	Energy (a.u.)	(kcal/mol)	SAC-CI	ΔEX	Energy (a.u.)	(kcal/mol)	SAC-CI	ΔEX	Energy (a.u.)	(kcal/mol)	SAC-CI	$\Delta E X$
4.0	-14.926932		1.247 59		-14.882 879		2.446 33		-14.833336		3.79446	
4.5	-14.934265		1.33864		-14.900044		2.26984		-14.852322		3.568 42	
4.8	-14.935649		1.371 62		-14.905900	5.257	2.181 13	0.00209	-14.859619		3.44050	
5.051	-14.935565		1.39094		-14.909033	5.238	2.11291	0.00277	-14.864015		3.33791	
5.2	-14.935095		1.39975		-14.910299	5.226	2.07449	0.00288	-14.866036		3.27894	
5.5	-14.933406		1.41333		-14.911806	5.212	2.001 10	0.00319	-14.869052		3.16449	
6.0	-14.929053		1.42868		-14.912103	5.193	1.88991	0.00248	-14.871807		2.98642	
6.5	-14.923620		1.44122		-14.910705	5.160	1.79266	-0.000896	-14.872832		2.823 24	
8.0	-14.906429		1.49725		-14.902869		1.59412		-14.872965		2.40785	
9.0	-14.897040		1.55396		-14.897506		1.54128		-14.873419		2.19672	
10.0	-14.890296		1.611 13		-14.892994		1.53772		-14.874190		2.04940	
12.0	-14.883399		1.68711		-14.886798		1.59461		-14.875576		1.899.98	
Average ^a						5.214		0.00209				
Max.dif. ^b						5.257		0.003 19				

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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 bondbreaking 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 0.000586, 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 Li₂ 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.

-14.82 -14.82 **◊: Exptl.(RKR) ×: FC theory** -14.84 -14.84 1¹Π **1**¹Π -14.86 -14.86 $B^1\Pi_{\mu}$ B¹Π_u -14.88 -14.88 Energy (a.u.) Energy (a.u.) -14.90 -14.90 -14.92 -14.92 -14.94 -14.94 -14.96 -14.96 AE: 0.05 -14.98-14.98 -15.00 -15.00 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 3.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 Li-Li distance (a.u.) Li-Li distance (a.u.)

In this section, we compare the figures of the potential curves of Li₂ 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 Lip.

left-hand side the experimentally determined potential curves of Li₂. 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 Li₂. 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

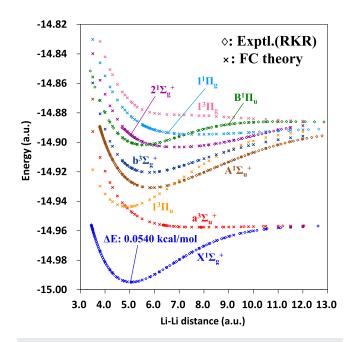


FIG. 2. Experimental RKR and FC theoretical potential curves of Li_2 on the common axes of the energy (vertical) and the Li–Li distance (horizontal).

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

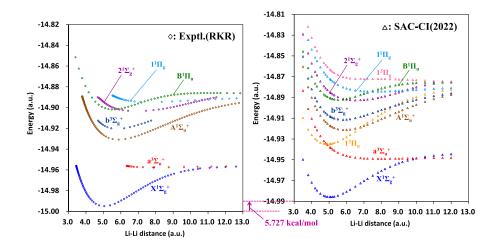


FIG. 3. Left is the experimentally determined RKR potential curves and right is the potential curves calculated by the SAC/SAC-CI theory using the jorge-6ZP basis, both for Li₂.

J. Chem. Phys. **157**, 094109 (2022); doi: 10.1063/5.0101315 Published under an exclusive license by AIP Publishing 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 ${}^{1}\Sigma_{g}^{+}$ 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 ${}^{1}\Sigma_{g}^{+}$, 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 Li₂ 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.

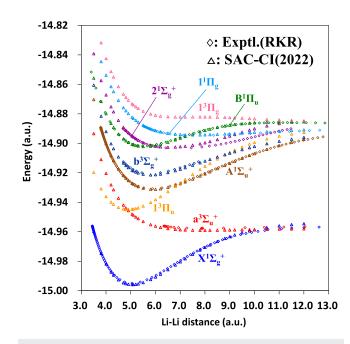


FIG. 4. Overlapped experimental RKR and present SAC/SAC-CI theoretical potential curves of Li_2 after shifting down the SAC/SAC-CI curves by 5.727 kcal/mol.

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 Li₂. 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

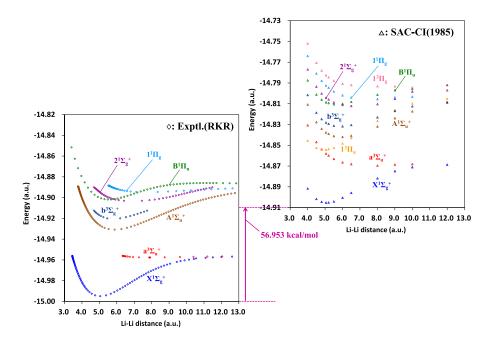


FIG. 5. Left is the experimentally determined RKR potential curves and right is the potential curves calculated by the SAC/SAC-CI theory published in 1985² both for Li₂.

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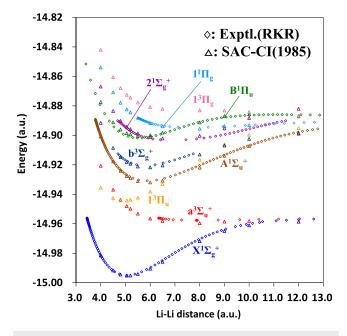


FIG. 6. Overlapped experimental RKR and SAC/SAC-Cl $(1985)^2$ theoretical potential curves of Li_2 after shifting down the SAC/SAC-Cl curves by 56.953 kcal/mol.

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 Li2 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 H₂ 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 cm⁻¹ = 0.002 857 2 kcal/mol), respectively.⁵⁷ Their dependences on the internuclear distance were also investigated. For the Li₂ 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 ⁷Li₂ molecule would be roughly seven times smaller than that of H₂, as seen here from the result of H₂ and ⁷Li₂. 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 excite	d states of Li2.								

		Equilibrium	Excitation	Dissociation
		distance	energy	energy
State	Method	R_e (Å)	T_e (eV)	D_e (kcal/mol)
$\overline{X^1 \sum_g^+}$	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
$A^1 \sum_u^+$	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
$2^1 \sum_{g^+}$	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
$\mathbf{B}^{1}\Pi_{\mathbf{u}}$	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
$a^3 \sum_u^+$	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
$b^3 \sum_{g^+}$	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.

^fReerence 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 Li₂ 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 Li₂ 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 Li2 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 kcal/mol for all the calculated lengths, 3-13 a.u., of all the states in the range of -14.82 ~ -15.00 hartree (1 hartree = 627.5096 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 spectroscopy⁸⁻¹⁹ of the Li₂ molecule using the RKR method.⁵⁻⁷ The present theoretical potential curves of the Li₂ 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 Li2 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 Li₂ molecule. More explicitly, we have solved the Schrödinger equation of the Li2 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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