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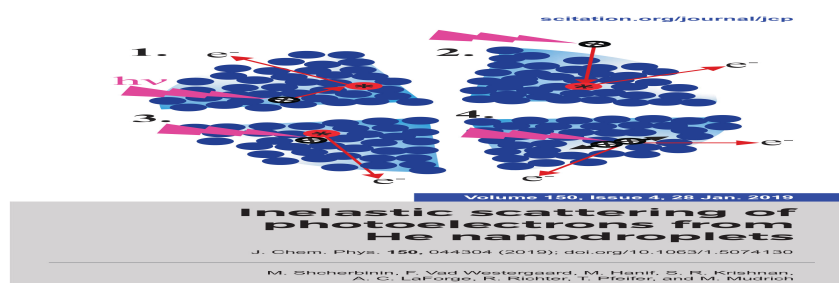Integral partition bounds for fast and effective screening of general one-, two-, and many-electron integrals
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Solving the Schrödinger equation with the free-complement chemical-formula theory: Variational study of the ground and excited states of Be and Li atoms

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ABSTRACT

The chemical formula theory (CFT) proposed in Paper I of this series [H. Nakatsuji *et al.*, J. Chem. Phys. **149**, 114105 (2018)] is a simple variational electronic structure theory for atoms and molecules. The CFT constructs simple, conceptually useful wave functions for the ground and excited states, simultaneously, from the ground and excited states of the constituent atoms, reflecting the spirits of the chemical formulas. The CFT wave functions are also designed to be used as the initial wave functions of the free complement (FC) theory, that is, the exact theory producing the exact wave functions of the Schrödinger accuracy. This combined theory is referred to as the FC-CFT. We aim to construct an exact wave function theory that is useful not only quantitatively but also conceptually. This paper shows the atomic applications of the CFT and the FC-CFT. For simplicity, we choose the small atoms, Be and Li, and perform variational calculations to essentially exact levels. For these elements, a simple Hylleraas CI type formulation is known to be potentially highly accurate: we realize it with the CFT and the FC-CFT. Even from the CFT levels, the excitation energies to the Rydberg excited states were calculated satisfactorily. Then, with increasing the order of the FC theory in the FC-CFT, all the absolute energies and the excitation energies of the Be and Li atoms were improved uniformly and reached rapidly to the essentially exact levels in order 3 or 4 with moderately small calculational labors.

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I. INTRODUCTION

Chemical formulas that represent molecular structural formulas and chemical reaction formulas as illustrated in Fig. 1 of Ref. 1 are used in chemistry like a language of the chemists for describing their chemistry: this is seen in any textbook of chemistry and chemical biology. What are central to chemical formulas are the local atomic concept, from-atoms-to-molecule concept, three-dimensional atomic arrangements, and the transferability of these basic concepts. Among them, what is most important is the atomic concept that has long history from Dalton. In the chemical formulas, atoms are shown by dots and chemical formulas are essentially the

assembly of the dots representing the constituent atoms. They are connected by lines that indicate chemical bonds, but their meanings are vague. This situation is clear considering the history: only quantum mechanics can describe the nature of these lines, but its birth was much later than that of the chemical formulas. Furthermore, quantum mechanics has clarified that these dots in chemical formulas are not simply the dots, but they represent the many atomic electronic states associated with these dots that characterize the nature of the atoms.

Although the chemical formulas provide useful conceptual basis and tools for chemists, the basic principles of chemistry are provided by the principles of quantum mechanics

like the Schrödinger equation and the Dirac equation. These equations describe the governing principles of chemistry. Our laboratory has already a history of the research aiming to solve these basic equations of chemistry. One of the authors initiated the studies on the structure of the exact wave function and proposed a general method of constructing the wave functions that have the exact structure from some approximate wave functions.[2,3] When we apply the variational principle to the wave functions having the exact structure, it is guaranteed that we get the exact solutions of the Schrödinger equation as their solutions. However, for atoms and molecules whose Hamiltonians include the Coulombic potentials that diverge at the position of the charged particles, we encountered the divergence difficulty, but this was resolved by introducing the scaled Schrödinger equation[4]

$$g(H - E)\psi = 0 \tag{1}$$

that is free from the diverging difficulty originating from the existence of the Coulombic potentials, where g is the scaling operator defined by

$$g = \sum_{i,A} r_{iA} + \sum_{i>j} r_{ij}. \tag{2}$$

Since g is always positive, the Schrödinger equation and the scaled Schrödinger equation have the same set of solutions of the wave functions and the energies. This research became a basis for us to formulate a general theory of solving the Schrödinger and Dirac equations in the way that is useful for chemists both quantitatively and conceptually.[1–14] It was easy to show that the following recursion formulas[4]

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n,$$
$$\psi^{exact} = \prod_n [1 + C_n g(H - E_n)] \cdot \psi_0, \tag{3}$$

which were referred to as the simplest iterative complement (or configuration) interaction (ICI) formulas, give the exact wave function starting from some approximate initial wave function ψ_0 without meeting the divergence difficulty. The second equation of Eq. (3) can be rewritten in the form

$$\psi^{exact} = \sum_I c_I \phi_I, \tag{4}$$

with the use of the independent analytical functions $\{\phi_i\}$ that consist of the right-hand side of Eq. (3) attached with the individual coefficients $\{c_i\}$. We refer to the functions $\{\phi_i\}$ as the complement functions (cf's) since they are the element of the complete set of the functions that describes the exact wave function as given by Eq. (4). Since these complement functions are dealt freely in Eq. (4), we call this theory free-complement (FC) theory. Thus, the FC theory is the theory that gives the exact wave function from any approximate wave function ψ_0 of the system, which may be expressed as

$$\psi^{exact} = FC(\psi_0). \tag{5}$$

The formation of the cf's of Eq. (4) is a very rapid step, and this wave function ψ^{exact} has an exact structure. Namely, it is guaranteed that the exact wave function is included in Eq. (5) to the accuracy of the order n. Therefore, when we optimize the set of the coefficients $\{c_i\}$ by the variational method or the sampling type method like the local Schrödinger equation (LSE) method,[8] we are guaranteed to obtain the exact wave functions of the system to the accuracy of the order n.

After this theoretical breakthrough reported in 2004,[4] we have already published many examples obtained by the variational method[6,7,9,11] and the LSE method.[8,10–13] As expected from Eq. (5), the choice of ψ_0 is very important since the exact wave function has the mathematical structure characteristic to ψ_0 and the convergence speed and the calculational labors are dependent on the choice of ψ_0. Furthermore, if ψ_0 has the structure that is easily understandable, then we may be able to understand conceptually the chemical implication from the exact wave function ψ^{exact}. We think this feature to be important.

In Ref. 1, we have proposed to take the chemical formulas widely used in chemical studies as the conceptual basis of our FC theory and proposed the chemical formula theory (CFT or ChFT) of atomic and molecular electronic structures. The CFT is an approximate general variational theory that describes the electronic structures of atoms and molecules based on the concepts of the chemical formulas. The central concept of the CFT is the from-atomic-states-to-molecular-states (FASTMS) concept that is based on the from-atoms-to-molecules (FATM) concept of the chemical formulas. This concept means that from all the atomic electronic states of the constituent atoms, the ground and excited states of the molecule under consideration are formed. This implies that we may use all the atomic states of the constituent atoms as if they are the elements of the basis set to form, through their interactions governed by the variational principle, the ground and excited states of the molecule under consideration. Therefore, the CFT deals with the ground and excited states at the same time from the beginning.

Referring to the Moore's books of atomic energy levels and more advanced versions published by NIST,[15] we can get the detailed information on the energy levels of the atomic electronic states associated with each atom. For example, our most familiar atom, carbon has the atomic states, the $^3P(0)$, $^1D(10\,193)$, and $^1S(21\,648)$ states arising from the $2s^2 2p^2$ configuration, the $^5S(33\,735)$, $^3D(64\,090)$, and $^3P(75\,256)$ states arising from the $2s2p^3$ configuration, where the energies from the ^3P ground state are shown in the parentheses in cm^{-1}, and then the 3s, 3p Rydberg states from 60 333 to 73 976 cm^{-1}. On the other hand, the hydrogen atom has a very discrete electronic structure: the ground state is the valence 1s state and the degenerate 2s and 2p states are very high (82 259 cm^{-1}) and diffuse to form chemical bonds with other atoms.

When we use the variational principle in the course of the formation of the atomic and molecular electronic states from the elemental atomic electronic states, the resultant ground and excited electronic states $\{\psi_I\}$ of the system under consideration satisfy the very important relations

$$\langle \psi_I | \psi_J \rangle = \delta_{IJ},$$
$$\langle \psi_I | H | \psi_J \rangle = E_I \delta_{IJ} \tag{6}$$

between different electronic states. This is the fundamental relation that characterizes the excited states among themselves and against the ground state. For example, the excited states calculated by the SAC-CI (symmetry-adapted-cluster configuration-interaction) theory[16,17] satisfy this relation among themselves and against the ground state calculated by the SAC theory.

In this paper, we apply CFT and FC-CFT to efficiently calculate the ground and excited states of small atoms, three and four electron lithium and beryllium atoms. Sims and Hagstrom[18] performed the Hylleraas CI calculations for the ground state of the Be atom and showed that the Hylleraas CI could give the energy correct to the chemical accuracy. Based on this fact, we assumed that highly accurate results would be obtained for both of the ground and excited states of the Be and Li atoms within the Hylleraas CI type approach that does not include the functions of the type $r_{ij}r_{kl}$ and higher difficult correlation-type functions within the wave functions. This assumption will turn out to be correct as will be seen in this paper. We must note however that this assumption does not hold for the heavier elements. For example, for the boron atom, Ruiz[19] could not get the chemical accuracy within the Hylleraas CI type approach. Similar results were also published by Clary and Handy many years ago for the ground state of the neon atom.[20] We note that at the CFT level of the study, we do not include any r_{ij} correlation type functions. At the FC-CFT level of the study, we produce our complement functions by applying the FC theory to the functions obtained with the CFT where we limit our r_{ij} correlation type functions to be of only Hylleraas CI type, though for the r_i type functions, we include even up to order 5. The FC theory systematically generates the complement functions as explained with Eq. (3). The FC theory is completely different from the Hylleraas CI theory.

From theoretical interest, we start from the larger atom, Be, instead of the Li atom. In Sec. II, we first construct the complement functions of the CFT for the ground and excited states of the Be atom and then apply the FC theory to the CFT wave functions to obtain essentially exact wave functions of all the ground and excited states. For the smallness of the Li and Be atoms and for the simplicity of the integral evaluations for the linear r_{ij} type functions, we can use the variational method at all levels of the calculations so that the important relations given by Eq. (6) are satisfied from the CFT level to the essentially exact FC-CFT levels.

II. CFT FOR GROUND AND EXCITED STATES OF BERYLLIUM ATOM

The CFT may be considered as a theory for molecules and not for atoms because the chemical formula for an atom is simply a dot. This is not the case, however, since even an atom has many different electronic states:[15] we start from their approximate functions and let them interact with each other to give the best CFT wave function for each state through the variational calculation. The principle expressed by Eq. (6) is the same for both atoms and molecules.

The Be atom is a simple closed-shell many-electron atom so that many accurate theoretical calculations have been published. In the historical study by Sims and Hagstrom,[18] the Hylleraas CI calculations were performed for the ground state of the Be atom which gave the energy correct to the chemical accuracy. There are also studies[21–25] that clarified the electronic structures of the Be atom to high accuracy. Stanke et al.[24] performed highly accurate explicitly correlated-Gaussian (ECG) calculations for the ground and $2s \rightarrow ns$ (n = 3-6) Rydberg excited states. Their results are essentially exact so that we choose their energies at the Born-Oppenheimer (BO) or fixed-nucleus level as the exact theoretical references to compare with our results of the BO level of calculations. They examined further the finite-nuclear mass effect, relativistic effect, quantum electrodynamics (QED) effect, and higher QED effects.[24]

In Ref. 1, we have explained the CFT for atoms using the example of the Be atom. In the ground state of the Be atom, the 1s and 2s orbitals are occupied by two electrons, which is designated by the complement function (cf)

$$\phi_{0,G}^{Be} = A[(1s)^2\alpha\beta \cdot (2s)^2\alpha\beta]. \tag{7}$$

The valence-like excited state having the same ^1S symmetry lies as high as at 76 190 cm^{-1} (Ref. 15) as the two-electron excited state from 2s to 2p orbital, and the cf of this state is written as

$$\phi_{0,2p^2}^{Be} = A[(1s)^2\alpha\beta \cdot \{(2p_x)^2 + (2p_y)^2 + (2p_z)^2\}\alpha\beta]. \tag{8}$$

We include this state in our calculations, considering the interaction with the ground state to be important. Between these ground and doubly excited states, there are many Rydberg excited states of the same ^1S symmetry: they are $2s \rightarrow ns$ (n = 3, 4, 5, 6, . . .) states and their cf's are written as

$$\phi_{0,ns}^{Be} = A[(1s)^2\alpha\beta \cdot (2sns + ns2s)\alpha\beta]. \tag{9}$$

We study here only the first four states lying at 54 677(3s), 64 245(4s), 69 322(5s), and 71 321(6s) cm^{-1}, though there are more states below the doubly excited 2p state. So, we deal with the above six electronic states in our study, and our CFT wave function of Be for its I-th electronic state is written as

$$\psi_I^{Be,CFT} = \sum_{m=0}^{M} c_m^I \phi_{0,m}^{Be}$$
$$= c_0^I \phi_{0,G}^{Be} + c_1^I \phi_{0,2p^2}^{Be} + c_2^I \phi_{0,3s}^{Be} + c_3^I \phi_{0,4s}^{Be} + c_4^I \phi_{0,5s}^{Be} + c_5^I \phi_{0,6s}^{Be}, \tag{10}$$

with m and I from 0 to 5 (= M). The suffix 0 of the primitive cf's means that it will be used later as the initial function when we apply the FC theory to this set of the cf's of the CFT. The CFT wave functions of the ground and excited states are obtained by applying the variational principle, and the solutions satisfy the important relation given by Eq. (6). We note that the highest state in the above calculations, the $(2s)^2 \rightarrow (2p)^2$ state, does not have the interaction counterpart at the higher energy part so that this state tends to be calculated higher because of the absence of the push-down effect as seen from Eq. (6).

Anyway, this state was added as a kind of dummy state to improve the lower states through Eq. (6) in the variational calculations.

The orbital around the Be nucleus to which each electron is accommodated is written by a single Slater orbital. First, the 2p orbital in Be($1s^2 2p^2$) is simply written as

$$2p_x = x \exp(-\alpha_{2p} r), \quad 2p_y = y \exp(-\alpha_{2p} r), \quad 2p_z = z \exp(-\alpha_{2p} r) \tag{11}$$

because the orbital of the p symmetry appears only in this cf. For the s orbitals, we may write them in the following form:

$$ns = (\sum_{i=0}^{n-1} b_i r^i) \exp(-\alpha_{ns} r) \tag{12}$$

or

$$ns = \sum_{i=0}^{n-1} b_i r^i \exp(-\alpha_{(i+1)s} r). \tag{13}$$

Equation (12) follows the expressions of the exact hydrogenic orbitals. Equation (13) is another possibility. We may fix the coefficients b_i to the optimal values, or we may deal with each term independently. In the latter case, Eq. (12) gives a larger number of independent terms than Eq. (13). In Ref. 1, we have written only the former type of the orbitals, but we will examine both possibilities, though the inner 1s-like orbital of the 2s orbital was assumed to have the form of Eq. (12). Most calculations were done with Eq. (13), dealing with the elements independently. In the Appendix, we will give the results obtained by using Eq. (12).

The Slater exponents $\{\alpha\}$ in these orbitals were optimized at the present CFT level: we first optimized the exponents of the 1s and 2s orbitals by the variational method applied to the single CFT wave function given by Eq. (12). Then, the Rydberg orbital exponents were optimized variationally for each cf of $\phi_{0,ns}^{Be}$ in Eq. (9), fixing the 1s and 2s orbital exponents. The 2p orbital exponent was optimized similarly for the

TABLE I. Optimized orbital exponents used in the present calculations for the ground state and the valence and Rydberg excited states of ^1S for the Be atom.

Orbital	$^1S: \alpha_{ns}$
1s	3.6915
2s	1.0090
2p for $(2p)^2$	0.7594
3s	0.3940
4s	0.2733
5s	0.2046
6s	0.1626

cf $\phi_{0,2p^2}^{Be}$, fixing the 1s orbital exponent. The optimized exponents for this system are shown in Table I. The orbital exponents of the 1s and 2s orbitals optimized by Clementi[26] for the ground state of the Be atom were 3.6848 and 0.9560, though their 2s orbital did not have the inner 1s-like orbital.

In Table II, we show the energies of the ground and excited states calculated by CFT that satisfy Eq. (6), together with the energy expectation values of the primitive cf's, $\left\langle \phi_{0,m}^{Be} \left| H \right| \phi_{0,m}^{Be} \right\rangle$ ($m = 0 \ldots 5$). We also gave the difference from the estimated exact energy, ΔE, in kcal/mol. Similarly, we summarized the corresponding quantity of the excitation energy, ΔEX, in eV. Note that, in Tables II–V and VII–XIII, something noteworthy is given in boldface.

We see that at the level of the primitive cf's, the difference from the exact energy shown as ΔE is oscillating depending on the states, but at the CFT level, it becomes stable at around 46 kcal/mol, except for the $(2s)^2 \rightarrow (2p)^2$ excited state that does not have the interaction counterparts at the higher energy side so that it is calculated higher than the other states. The same is true for the excitation energy: though the excitation energies calculated from the primitive complement functions do not agree with the experimental values, the calculated excitation energies at the CFT level agree well with the exact BO values of Adamowitz *et al.*[24] and the NIST

TABLE II. Energy expectation value of the primitive cf's, $\left\langle \phi_{0,m}^{Be} \left| H \right| \phi_{0,m}^{Be} \right\rangle$, and the energies of the CFT for the ^1S states of the Be atom; absolute energy in a.u., difference from the exact energy ΔE (kcal/mol), excitation energy in eV, and difference from the exact excitation energy ΔEX (eV) are shown. Noteworthy results indicated in boldface.

	$\left\langle \phi_{0,m}^{Be} \middle\| H \middle\| \phi_{0,m}^{Be} \right\rangle$				CFT				Exact excitation energy (Adamowicz *et al.*)[a] (eV)	Experimental excitation energy (NIST)[b] (eV)
	Absolute energy (a.u.)	ΔE (kcal/mol)	Excitation energy (eV)	ΔEX (eV)	Absolute energy (a.u.)	ΔE (kcal/mol)	Excitation energy (eV)	ΔEX (eV)		
Ground $(1s)^2(2s)^2$	−14.560 059 7	67.330			−14.593 503 4	46.343				
2s → 3s	−14.387 397 8	19.354	**4.698**	−2.080	−14.340 009 7	49.090	**6.898**	0.119	**6.779**	**6.779**
2s → 4s	−14.318 118 2	32.611	**6.584**	−1.506	−14.296 985 3	45.873	**8.069**	−0.020	**8.089**	**8.089**
2s → 5s	−14.293 150 9	36.622	**7.263**	−1.332	−14.279 844 9	44.972	**8.535**	−0.059	**8.595**	**8.595**
2s → 6s	−14.280 446 9	38.878	**7.609**	−1.234	−14.271 276 7	44.633	**8.768**	−0.074	**8.842**	**8.843**
$(2s)^2 \rightarrow (2p)^2$	−14.220 759 9	(62.405)[c]	**9.233**	(−0.214)[c]	−14.188 020 2	(82.950)[c]	**11.034**	(1.587)[c]		**9.446**

[a] Reference 24.
[b] Reference 15.
[c] Since E_{exact} does not exist for the $(2s)^2 \rightarrow (2p)^2$ state, these values were estimated from the exact ground-state energy of Adamowicz *et al.*[24] and the NIST experimental excitation energy.[15]

experimental values to within 0.1 eV, in average. This is an encouraging result, considering the simplicity of the CFT calculations. If this is general, the CFT would be a good approximate tool for the studies of the excitation phenomena and photochemistry involving different electronic states. The agreement is not good for the $(2s)^2 \to (2p)^2$ excited state because of the absence of the push-down effect as expressed by Eq. (6).

After finishing the CFT calculations, we proceed to the FC-CFT to obtain accurate wave functions of the level of the solutions of the Schrödinger equation order by order. The FC theory produces the rapidly converging set of functions, called complement functions (cf's) that are the exact set of the functions for solving the Schrödinger equations of the system under consideration. We apply this FC theory to the CFT wave function, and so we are automatically led to the exact solutions of the Schrödinger equations for both ground and excited states, since the CFT wave functions span both ground and excited states of interest. Thus, in our FC-CFT, we must be careful only in the stage of the CFT. Thereafter, the FC theory takes care of almost everything toward solving the Schrödinger equations.

III. FC-CFT FOR GROUND AND EXCITED STATES OF BERYLLIUM ATOM

We apply the FC theory to the CFT wave functions $\psi_I^{\text{Be,CFT}}$ given by Eq. (10). However, since these wave functions are given by a linear combination of the set of the cf's $\{\phi_{0,m}^{\text{Be}}\}$, we actually apply the FC theory to each cf of the CFT $\phi_{0,m}^{\text{Be}}$ and obtain L_m cf's, $\phi_{l_m,m}^{\text{Be}}$ ($l_m = 0 \dots L_m$). Then, the wave function of the FC-CFT is written as

$$\psi_I^{\text{Be,FC-CFT}} = \sum_m^M \sum_{l_m}^{L_m} c_{l_m,m}^I \phi_{l_m,m}^{\text{Be}} \quad (I, m = 0, \cdots, M), \quad (14)$$

where I denotes the electronic states of the Be atom, i.e., the ground state, the $2s \to ns$ ($n = 3, 4, 5, 6$) Rydberg excited states, and the $(2s)^2 \to (2p)^2$ two-electron excited state. In comparison with the CFT wave function given by the first equation of Eq. (10), the FC-CFT wave functions include the sum over the cf's produced by applying the FC theory. The total number of the cf's included in this FC-CFT wave function, $N_{\text{FC-CF}}^{\text{Be}}$, is given by

$$N_{\text{FC-CF}}^{\text{Be}} = \sum_{m=0}^M L_m. \quad (15)$$

The cf's of the FC-CFT are produced by the standard method of the FC theory[1,4,11] applied to the wave functions obtained by the CFT calculations. Using the cf's of the CFT, $\phi_{0,m}^{\text{Be}}$, they are written to the second order of the FC theory as

$$\{\phi_{l_m,m}^{\text{Be}}\} = \phi_{0,m}^{\text{Be}}, r_i \phi_{0,m}^{\text{Be}}, r_j r_i \phi_{0,m}^{\text{Be}}, r_{ij} \phi_{0,m}^{\text{Be}}, r_k r_{ij} \phi_{0,m}^{\text{Be}}, r_{kl} r_{ij} \phi_{0,m}^{\text{Be}}, \cdots. \quad (16)$$

We use the variational principle so that we calculate the overlap and Hamiltonian integrals. For the Hamiltonian integrals,

among the cf's given by Eq. (16), the cf's including only one-electron functions are integratable and for atoms, the cf's including r_{ij} are also integratable. Those including r_{ij}^2 are also integratable, since they are expressed with the one-electron functions as

$$r_{ij}^2 = r_i^2 + r_j^2 - 2(x_i x_j + y_i y_j + z_i z_j), \quad (17)$$

but those including different r_{ij}'s, like the last term of Eq. (16), are non-integratable. Thus, for using the variational principle, we classify the cf's to those that are integratable and to those that are non-integratable. The former set is called i-set and the latter the n-set. In the cf's given in Eq. (16), only the last term is non-integratable, except when they are written as r_{ij}^2. All others are integratable. For atoms, the analytical integration methods of the two-, three-, and four-electron integrals that appear in the variational calculations are well established[27-32] and we have developed our own code for evaluating the three and four electron integrals necessary for the present calculations.[33] For the ground state of the Be atom, Sims and Hagstrom[18] showed that with the Hylleraas CI method including r_{ij} terms only linearly, we can get the energy correct to chemical accuracy. So, assuming this fact to be true even for the excited states, we generated the cf's of the FC theory up to the order three and discarded the cf's belonging to the n-set. Then, we calculate the linear parameters $\{c_{l_m,m}^I\}$ in Eq. (14) using the variational principle and obtain the energies and the wave functions of the ground and excited states. This is a kind of the FC-CFT-variational (FC-CFT-V) proposed in Ref. 1, but for the present Be case, this method gives highly accurate results exceeding the chemical accuracy and essentially exact as shown below. It is true, however, that if we can calculate the integrals for the cf's of the last terms of Eq. (16) that include two different r_{ij} functions, then we would also be able to get high accuracy results even within the order two of the FC theory. This is expected from the results of the integral-free local Schrödinger equation (LSE) method[8] applied to the second-order FC-CFT wave functions of the first-row atoms including such $r_{ij}r_{kl}$ terms that were published in a review article[11] and in a recent paper of this series.[14]

In Table III, we summarized the results of the calculations of the CFT and the FC-CFT both performed with the variational principle. For the ns orbitals of the Rydberg states, we used the Slater orbitals given by Eq. (13). Table III gives the groups of the results in different "drawers," grouped into the first two upper drawers and the second lower three drawers. The first upper two drawers give the energetic results, from the left to right, the order 0 (CFT), order 1 to 3, and the reference data in the last column, and from up to down, the ground state, the $(2s) \to (ns)$ Rydberg states, and the $(2s)^2 \to (2p)^2$ valence excited state. The first drawer gives the absolute energy in a.u., and the second drawer gives the difference from the known exact energy, $\Delta E = E_{FC} - E_{exact}$, in kcal/mol, where the exact energy is due to the BO values from Adamowicz et al.[24] with the ECG method. The lower three drawers give the information on the calculated excitation energy, abbreviated as EX: the first drawer gives the excitation energies in cm^{-1}, the second and third give the difference from the

TABLE III. FC-CFT for the ground state and the valence and Rydberg excited states of the ^{1}S states of the Be atom; absolute energy (E_{FC-CFT}), difference from the exact energy $\Delta E = E_{FC-CFT} - E_{exact}$, excitation energies ($EX_{FC-CFT}$), and difference from the exact excitation energy $\Delta EX = EX_{FC-CFT} - EX_{exact}$ (eV and cm^{-1} units). Noteworthy results indicated in boldface.

	FC-CFT					
n (order)[a]	0 (CFT)	1	2	3		
M (dimension)[b]	12	84	317	1049		Reference
Absolute energy (a.u.)					**Exact energy (a.u.) Adamowicz et al.[c]**	
Ground $(1s)^2(2s)^2$	−14.593 503 4	−14.653 808 0	−14.665 949 0	−14.667 111 9	−14.667 356 486	
2s → 3s	−14.340 009 7	−14.403 700 2	−14.446 564 5	−14.417 978 6	−14.418 240 328	
2s → 4s	−14.296 985 3	−14.356 451 9	−14.368 718 5	−14.369 842 8	−14.370 087 876	
2s → 5s	−14.279 844 9	−14.338 111 8	−14.350 229 5	−14.351 269 4	−14.351 511 654	
2s → 6s	−14.271 276 7	−14.328 994 3	−14.341 057 4	−14.342 137 8	−14.342 403 552	
$(2s)^2 → (2p)^2$	−14.188 020 2	−14.299 795 7	−14.313 175 9	−14.319 685 7	. . .[d]	
$\Delta E = E_{FC-CFT} - E_{exact}$ **(kcal/mol)**						
Ground $(1s)^2(2s)^2$	46.343	8.502	0.883	**0.153**		
2s → 3s	49.090	9.124	1.052	**0.164**		
2s → 4s	45.873	8.557	0.859	**0.154**		
2s → 5s	44.972	8.409	0.805	**0.152**		
2s → 6s	44.633	8.414	0.845	**0.167**		
$(2s)^2 → (2p)^2$	(82.950)[d]	(12.810)[d]	(4.413)[d]	**(0.329)[d]**		
Excitation energy (cm^{-1})					**Excitation energy (cm^{-1})**	
					Exact (Adamowicz et al.)[c]	Experiment (NIST)[e]
2s → 3s	55 635.43	54 892.31	54 733.58	54 678.44	54 674.68	54 677.26
2s → 4s	65 078.21	65 262.11	65 234.56	65 243.02	65 242.92	65 245.33
2s → 5s	68 840.08	69 287.31	69 292.43	69 319.43	69 319.93	69 322.20
2s → 6s	70 720.58	71 288.37	71 305.46	71 323.58	71 318.93	71 321.15
$(2s)^2 → (2p)^2$	88 993.28	77 696.72	77 424.74	76 251.25		76 190
$\Delta EX = EX_{FC-CFT} - EX_{exact}$ **(eV)**						
2s → 3s	0.119 118	0.026 984	0.007 303	**0.000 466**		
2s → 4s	−0.020 422	0.002 379	−0.001 036	**0.000 013**		
2s → 5s	−0.059 493	−0.004 044	−0.003 410	**−0.000 062**		
2s → 6s	−0.074 186	−0.003 788	−0.001 670	**0.000 577**		
$(2s)^2 → (2p)^2$	(1.587 405)[d]	(0.186 809)[d]	(0.153 089)[d]	**(0.007 594)[d]**		
$\Delta EX = EX_{FC-CFT} - EX_{exact}$ **(cm^{-1})**						
2s → 3s	960.75	217.64	58.90	**3.76**		
2s → 4s	−164.71	19.19	−8.36	**0.10**		
2s → 5s	−479.84	−32.62	−27.50	**−0.50**		
2s → 6s	−598.35	−30.55	−13.47	**4.65**		
$(2s)^2 → (2p)^2$	(12 803.28)[d]	(1506.72)[d]	(1234.74)[d]	**(61.25)[e]**		

[a]Order of FC-CFT.
[b]Number of complement functions.
[c]Reference 24.
[d]Since E_{exact} does not exist for the $(2s)^2 → (2p)^2$ state, these values were estimated from the exact ground-state energy of Adamowicz[24] and the NIST experimental excitation energy.[15]
[e]Reference 15.

theoretical exact value, $\Delta EX = EX_{FC} - EX_{exact}$ in eV and in cm^{-1}, respectively.

We note that since Be and Li atoms dealt with in this paper are small atoms, we have highly accurate theoretical results in the literature that are essentially the exact solutions of the Schrödinger equation at the fixed nucleus level. We use such theoretical results as our reference exact energies in this paper, since these values do not include the

effects of finite-nuclear mass, relativities, and QED, as our calculations.

Now, we examine the results shown in Table III. In the first column, the results of the CFT, which is the order 0 theory for the FC-CFT, are given, but they have already been discussed in Table II. However, we want to emphasize again that with the CFT, we could obtain reasonable quality results for all the ground and excited states studied. We will see that this is

the origin of the constant stabilities and the high qualities of the FC-CFT results for all the ground and excited states of the Be atom shown in Table III.

When we apply the FC theory to the CFT wave functions, the theory leads the wave functions up to the exact level of the Schrödinger equation order by order. The order n is zero for the CFT initial functions, and we performed the one, two, and three orders of the FC theory. As seen from the first drawer, the calculated absolute energies of our theory approach the essentially exact results of Adamowicz et al.[24] The energies at order 3 agree with the exact results to within milli-hartrees. The numbers given in kcal/mol unit in the second drawer confirm this fact: the accuracy of our results approach surprisingly rapidly to the exact level. At the orders two and three, the FC-CFT results are in chemical accuracy. At order 3, the first 4 states, ground and Rydberg states, are constantly close to the exact energies to less than 0.17 kcal/mol. The energy of the $(2s)^2 \rightarrow (2p)^2$ excited state is a bit worse because for this state there are no states that work to push down from the above through Eq. (6).

Accurate variational calculations for the ground state of the Be atom have been performed by the Hylleraas-CI method of Sims and Hagstrom[18,21] and the ECG method of Komasa,[22] Pachucki and Komasa,[23] and Adamowicz et al.[24] However, for the excited states, only a few accurate studies exist, the calculations with the ECG method by Adamowicz et al.[24] and those with the variational Monte Carlo method by Sarsa et al.[25] In particular, Adamowicz et al.[24] provided highly accurate results for the ground state and the $2s \rightarrow ns$ (n up to 6) Rydberg excited states of the ^1S symmetry, where each state was calculated separately with a large number of basis sets (over 10 000 functions): we do not know whether their results strictly satisfy the orthogonality and the Hamiltonian orthogonality given in Eq. (6). In the present calculations, our purpose is not to give the landmark calculations, but to

examine the possibility of the general methods of the CFT and the FC-CFT. It is of course possible to aim the landmark calculations with the present methodology, as we have done for some systems,[6,7,9,11,14] but it will be postponed to the future studies.

Next, let us see the excitation energies from the ground state. The NIST Atomic Spectra Database[15] summarizes highly accurate experimental excitation energies in cm^{-1} unit. The third drawer shows the excitation energy in the absolute value. The BO "exact" values by Adamowicz et al.[24] were also summarized. The present theoretical results quickly approach the theoretical exact values and the NIST experimental values. The closeness is shown from the fourth and fifth drawers in eV and cm^{-1} units, respectively. Our results of order 3 give the excitation energies for the Rydberg states as accurate as to less than 0.0006 eV and 5 cm^{-1} from the reference exact values. This is an encouraging result, considering the easiness of our calculations. Again, the result for the $(2s)^2 \rightarrow (2p)^2$ excited state is a bit worse by the reason stated above.

Now let us compare the present results of excitation energies with the NIST experimental values: due to the report of the measurements of the Be spectra by Johansson,[34] the experimental error should be less than 0.05 cm^{-1}. Table IV gives the summary. So far, the comparisons were done with the theoretical BO exact energy because the experimental values include other effects like relativistic effects. In Table V, we compared our BO FC-CFT results with the NIST experimental values and the results of the BO and extended calculations of Adamowicz et al.[24] including the non-BO effects, relativistic effects, QED effects, and higher QED corrections for the $2s \rightarrow ns$ (n = 3, 4, 5, 6) Rydberg excited states. Our results for the $2s \rightarrow 4s$, 5s states agree well with those of Adamowicz et al. For the agreement to be more than a few cm^{-1} with the experimental values, the inclusion of the relativistic and other effects is necessary.

TABLE IV. Comparison of the FC-CFT BO results for the excitation energy with those of Adamowicz and of the NIST experimental values for the ^1S states of the Be atom: $\Delta EX_{\text{expt.}} = EX - EX_{\text{expt.}}$ (cm^{-1}). Noteworthy results indicated in boldface.

| | FC-CFT, n(order) = 3, BO | | | Theoretical exact Adamowicz et al.[a] | | | |
| | | | | | $\Delta EX_{\text{expt.}}$ (cm^{-1}) | | Experimental excitation energy |
	Excitation energy: $EX_{\text{FC-CFT}}$ (cm^{-1})	ΔEX_{exact} (cm^{-1})	$\Delta EX_{\text{expt.}}$ (cm^{-1})	Excitation energy: EX_{exact} (cm^{-1})	BO level	Best value[c]	(NIST)[b] (cm^{-1})
$2s \rightarrow 3s$	54 678.44	**3.76**	**1.18**	54 674.68	−2.58	**0.12**	54 677.26
$2s \rightarrow 4s$	65 243.02	**0.10**	−2.31	65 242.92	−2.41	**0.10**	65 245.33
$2s \rightarrow 5s$	69 319.43	−0.50	−2.77	69 319.93	−2.27	**0.15**	69 322.20
$2s \rightarrow 6s$	71 323.58	**4.65**	**2.43**	71 318.93	−2.22	**0.22**	71 321.15
$(2s)^2 \rightarrow (2p)^2$	(76 251.25)[d]		(61.25)[d]				76 190

[a]Reference 24.
[b]Reference 15.
[c]The best value includes further the finite-nuclear mass effect, relativistic effect, QED effect, and higher QED effects for ^{9}Be.
[d]This state does not have the push-down effect from the higher states in the FC-CFT calculations.

TABLE V. Convergences of the FC calculations for the ground state of the Be atom with the initial functions (2s)² $\psi_0 = \phi_{0,G}^{Be}$; (2s)² + (2p)² $\psi_0 = \phi_{0,G}^{Be} + \phi_{0,2p^2}^{Be}$, and valence + Rydberg $\psi_0 = \phi_{0,G}^{Be} + \phi_{0,2p^2}^{Be} + \phi_{0,3s}^{Be} + \phi_{0,4s}^{Be} + \phi_{0,5s}^{Be} + \phi_{0,6s}^{Be}$. Noteworthy results indicated in boldface.

ψ_0;	(2s)²: $\psi_0 = \phi_{0,G}^{Be}$			(2s)² + (2p)²: $\psi_0 = \phi_{0,G}^{Be} + \phi_{0,2p^2}^{Be}$			Valence + Rydberg: $\psi_0 = \phi_{0,G}^{Be} + \phi_{0,2p^2}^{Be} + \phi_{0,3s}^{Be} + \phi_{0,4s}^{Be} + \phi_{0,5s}^{Be} + \phi_{0,6s}^{Be}$		
n (order)[a]	M (dimension)[b]	Absolute energy (a.u.)	$\Delta E = E_{FC} - E_{exact}$ (kcal/mol)	M (dimension)[b]	Absolute energy (a.u.)	$\Delta E = E_{FC} - E_{exact}$ (kcal/mol)	M (dimension)[b]	Absolute energy (a.u.)	$\Delta E = E_{FC\text{-}CFT} - E_{exact}$ (kcal/mol)
0	3	−14.560 059 7	67.330	4	−14.593 186 8	46.542	12	−14.593 503 4	46.343
1	18	−14.649 118 1	11.445	24	−14.652 942 0	9.045	84	−14.653 808 0	8.502
2	61	−14.661 402 4	3.736	83	−14.665 843 3	**0.949**	317	−14.665 949 0	**0.883**
3	190	−14.666 922 5	**0.272**	260	−14.667 061 8	**0.185**	1049	−14.667 111 9	**0.153**
Estimated exact (E_{exact})[c]		−14.667 356 486			−14.667 356 486				

[a]Order of FC calculations.
[b]Number of complement functions.
[c]Reference 24.

IV. COMPARISON OF THE EFFICIENCIES WITH AND WITHOUT THE (2S)² → (2P)² EXCITED STATE

In the CFT and FC-CFT calculations, we use the ground and excited states as if they constitute the basis set for each other through the orthogonality and Hamiltonian orthogonality relations given by Eq. (6). We showed the efficiency of this method in Table II within the CFT calculations. In this section, we examine this idea by performing the comparative calculations up to the FC-CFT level. We calculated the ground state of the Be atom using the FC-CFT method to orders 1, 2, and 3 starting from the initial function $\phi_{0,G}^{Be}$ for the ground state alone, from the initial functions $\phi_{0,G}^{Be}$ and $\phi_{0,2p^2}^{Be}$ for the valence set, the ground and (2s)² → (2p)² excited state, and further from the initial functions $\phi_{0,G}^{Be}$, $\phi_{0,2p^2}^{Be}$ $\phi_{0,3s}^{Be}$, $\phi_{0,4s}^{Be}$, $\phi_{0,5s}^{Be}$, and $\phi_{0,6s}^{Be}$ for all the valence and Rydberg states. The last choice of the initial functions is the one used in Sec. III. In Table V, we compared the results of these three different sets of calculations, and in Fig. 1, we depicted the convergence speeds of the three sets of the different calculations.
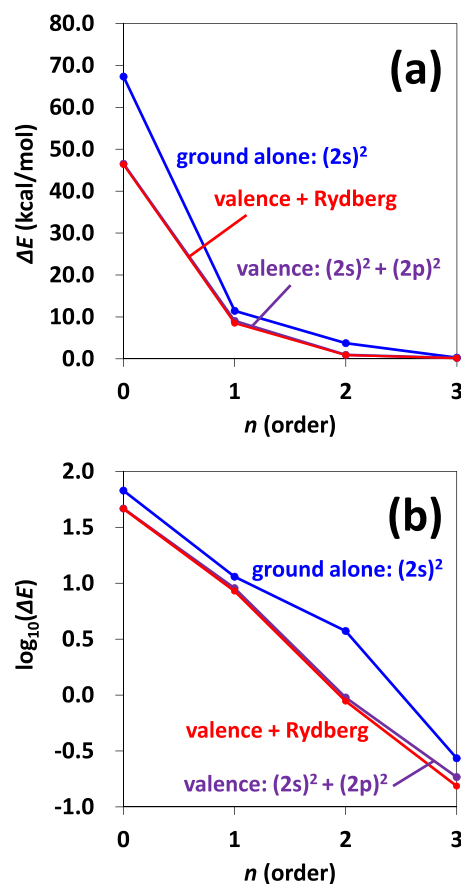

FIG. 1. Plots of (a) $\Delta E = E_{FC} - E_{exact}$ (kcal/mol) and (b) $\log_{10}\Delta E$ against the order n of the FC calculations for the ground state of the Be atom for the different initial functions, (2s)² $\psi_0 = \phi_{0,G}^{Be}$ (blue), (2s)² + (2p)² $\psi_0 = \phi_{0,G}^{Be} + \phi_{0,2p^2}^{Be}$ (purple), and all valence + Rydberg $\psi_0 = \phi_{0,G}^{Be} + \phi_{0,2p^2}^{Be} + \phi_{0,3s}^{Be} + \phi_{0,4s}^{Be} + \phi_{0,5s}^{Be} + \phi_{0,6s}^{Be}$ (red).

When we compare three different sets of calculations at the same order, the accuracy increases as we consider the larger number of the ground and excited states at the same time. This is particularly the case when we consider the $(2s)^2 \rightarrow (2p)^2$ excited state additionally to the ground state. Since these two states are both valence states, they interact strongly. On the other hand, when we add further the Rydberg excited states to the above valance-state calculations, the effects are not so remarkable. Because the Rydberg states are diffused, the interactions with the valence states are not so large. This is clearly seen from Fig. 1: the effect of the addition of the $(2s)^2 \rightarrow (2p)^2$ excited state is large, but the effects of adding the Rydberg excited states are small: they are seen only in Fig. 1(b) given in the logarithmic scale.

V. CFT AND FC-CFT FOR THE LITHIUM ATOM

Next, we study the CFT and the FC-CFT for the ground and excited states of the Li atom, which include only three electrons, so that the subjects must be simpler than the previous Be case. Because of this simplicity, many highly accurate quantum-chemical calculations have been performed particularly for the ground state.

Pachucki et al.[35,36] and Drake et al.[37,38] performed highly accurate calculations with a huge number of the Hylleraas basis set. Sims and Hagstrom[39] and Ruiz et al.[40] also performed accurate Hylleraas-CI calculations. They also gave the results for the excited states of ^{2}S symmetry. For higher angular momentum symmetries, Adamowicz et al. gave the accurate results of the excited states of ^{2}P[41] and ^{2}D[42] by the ECG method and King performed the calculations for the ^{2}F states with the Hylleraas basis set.[43] Ruiz et al. reported the excited states of higher angular momentums: ^{2}S to ^{2}I symmetries by the full-CI calculations and ^{2}S to ^{2}D symmetries by the Hylleraas-CI method.[40] Although all the above calculations need to prepare basis functions, they did not construct them without very much considering target states: for instance, they used non-linear exponents optimized with a brute-force way.[35–38,41,42] We choose their essentially exact energies at the BO level as the exact theoretical references to compare with our calculations. Further physical effects for the excitation energies, finite-nuclear mass effect, relativistic effect, QED effect, and higher QED effects were examined by Drake et al.[44] for the $2s \rightarrow 3s$ and $2s \rightarrow 2p$ states, by Adamowicz et al.[45] for the $2s \rightarrow 3s$ state, and by Pachucki et al.[36] for the $2s \rightarrow ns$ ($n = 3$ to 9) states.

In contrast to these calculations, the CFT calculations are intuitively designed and very simple. The calculations themselves are also very small and easy. Then, after the CFT calculations, we use the FC theory to produce highly accurate basis functions (called complement functions) that lead to the exact wave functions of the system.

A. CFT for the ground and excited states of the Li atom

Now, let us start the CFT for the Li atom. The ground state is expressed by the cf as

$$\phi_{0,G}^{Li} = A[(1s)^2 \alpha\beta \cdot 2s\alpha], \tag{18}$$

which is composed of the two 1s and one 2s electrons and belongs to the ^{2}S symmetry. Referring to the Moore's table and the Atomic Spectra Database by NIST,[15] all the excited states below the ionization limit are characterized by the $2s \rightarrow 2p$ intra-valence excitation and the Rydberg excitations of the types, $2s \rightarrow ns, np, nd, nf, \ldots$ ($n = 3, 4, 5, \ldots$). These electronic states are written in our cf's as

$$\phi_{0,2s\rightarrow nq}^{Li} = A[(1s)^2 \alpha\beta \cdot nq\alpha], \tag{19}$$

where q represents s, p, d, f, $\ldots$ for the ^{2}S, ^{2}P, ^{2}D, ^{2}F, $\ldots$ symmetries, respectively. Thus, the CFT wave functions for the ^{2}S, ^{2}P, ^{2}D, and ^{2}F symmetries are given, respectively, by

$$
\begin{aligned}
^2\text{S} &: \psi_m^{\text{Li}(^2\text{S}),\text{CFT}} = c_0\phi_{0,G}^{Li} + \sum_{n=3}^{10} c_{n-2}\phi_{0,2s\rightarrow ns}^{Li}, \\
^2\text{P} &: \psi_m^{\text{Li}(^2\text{P}),\text{CFT}} = c_1\phi_{0,2s\rightarrow 2p}^{Li} + \sum_{n=3}^{10} c_{n-1}\phi_{0,2s\rightarrow np}^{Li}, \\
^2\text{D} &: \psi_m^{\text{Li}(^2\text{D}),\text{CFT}} = \sum_{n=3}^{10} c_{n-2}\phi_{0,2s\rightarrow nd}^{Li}, \\
^2\text{F} &: \psi_m^{\text{Li}(^2\text{F}),\text{CFT}} = \sum_{n=4}^{10} c_{n-3}\phi_{0,2s\rightarrow nf}^{Li}.
\end{aligned}
\tag{20}
$$

We consider the states within up to $n = 10$ as our subject of this section.

The orbitals that accommodate electrons around the Li nucleus in the ground and excited states may be expressed as

$$
\begin{aligned}
1s &= e^{-\alpha_{1s} r}, \\
2s &= (b_0^{(2s)} + r)e^{-\alpha_{2s} r}, \\
ns &= b_0^{(ns)}e^{-\alpha_{1s} r} + b_1^{(ns)}re^{-\alpha_{2s} r} + b_2^{(ns)}r^2 e^{-\alpha_{3s} r} + \cdots + b_{n-1}^{(ns)}r^{n-1}e^{-\alpha_{ns} r}, \\
np_x &= x \cdot \left(b_0^{(np)}e^{-\alpha_{2p} r} + b_1^{(np)}re^{-\alpha_{3p} r} + b_2^{(np)}r^2 e^{-\alpha_{4p} r} + \cdots \right. \\
&\quad \left. + b_{n-2}^{(np)}r^{n-2}e^{-\alpha_{np} r} \right), \\
nd_{xy} &= xy \cdot \left(b_0^{(nd)}e^{-\alpha_{3d} r} + b_1^{(nd)}re^{-\alpha_{4d} r} + b_2^{(nd)}r^2 e^{-\alpha_{5d} r} + \cdots \right. \\
&\quad \left. + b_{n-3}^{(nd)}r^{n-3}e^{-\alpha_{nd} r} \right), \\
nf_{xyz} &= xyz \cdot \left(b_0^{(nf)}e^{-\alpha_{4f} r} + b_1^{(nf)}re^{-\alpha_{5f} r} + b_2^{(nf)}r^2 e^{-\alpha_{6f} r} + \cdots \right. \\
&\quad \left. + b_{n-4}^{(nf)}r^{n-4}e^{-\alpha_{nf} r} \right).
\end{aligned}
\tag{21}
$$

These orbitals are similar to those given in Eq. (13) rather than Eq. (12) of the previous Be case. Similarly, we dealt with all the terms in Eq. (20) independently in actual calculations, since it gives better accuracy with similar labors of calculations.

TABLE VI. Optimized orbital exponents used in the present calculations of the ^{2}S, ^{2}P, ^{2}D, and ^{2}F ground, valence, and Rydberg excited states of the Li atom.

n[a]	^{2}S: α_{ns}	^{2}P: α_{np}	^{2}D: α_{nd}	^{2}F: α_{nf}
1	2.6895			
2	0.6920	0.5227		
3	0.3634	0.3011	0.3334	
4	0.2510	0.2169	0.2276	0.2500
5	0.1908	0.1689	0.1751	0.1852
6	0.1531	0.1377	0.1422	0.1487
7	0.1272	0.1156	0.1194	0.1242
8	0.1083	0.0990	0.1024	0.1066
9	0.0938	0.0862	0.0893	0.0930
10	0.0824	0.0758	0.0788	0.0822

[a]Principal quantum numbers.

The optimized exponents of the independent Slater orbitals included above are summarized in Table VI.

Now, let us first examine the CFT results in comparison with the energy expectation values of the primitive cf's given on the right-hand-side of Eq. (20), which are the elements of the CFT. Table VII gives a summary. The excitation energies at the primitive cf level are randomly deviated from the exact excitation energies and the NIST experimental excitation energies shown in the two columns of the right-hand-side of Table VII. However, at the CFT level that satisfies Eq. (6), the excitation energies agree with the exact values constantly and the deviations are less than 0.04 eV for all the symmetries of the ^{2}S, ^{2}P, ^{2}D, and ^{2}F. The deviations are much smaller than the primitive level: this is the result of applying the variational principle to Eq. (20). We will see later that this accuracy of the CFT theory is already satisfactory for practical use for calculating the excitation energies of atoms and molecules.

B. FC-CFT calculations for the ground and excited states of the Li atom

After finishing the CFT calculations, we applied the FC theory to the CFT wave functions as the initial functions of the FC theory. The cf's of the FC-CFT thus obtained have the forms like those given in Eq. (16). We applied the FC theory up to the order 5 for the ^{2}S state and to the order 4 for the ^{2}P, ^{2}D, and ^{2}F states. However, for the computational practical reason stated in Sec. III, we included the r_{ij} functions only to the linear ones, though we included the r_{ij}^2 terms since it is integrable. Then, we used the variational principle to calculate the FC-CFT wave functions so that the present results satisfy the orthogonality and the Hamiltonian orthogonality relations between the different states as expressed in Eq. (6). The results of the FC-CFT calculations for the ^{2}S, ^{2}P, ^{2}D, and ^{2}F symmetries of the Li atom are given in Tables VIII–XI, respectively.

Table VIII gives the results of the CFT and the FC-CFT calculations for the ^{2}S states of the Li atom. For this symmetry, we have performed up to the order 5 of the FC theory.

Table VIII has the same structure as Table III for the Be atom. It consists of the five drawers: two upper ones give the information on the absolute energies for the ground state and for the 2s → 3s ~ 10s Rydberg states, and the three lower drawers summarize the excitation energies from the ground state to these Rydberg states.

The first column of Table VIII gives the results of the CFT. We notice that the CFT results of the absolute energies differ from the exact values by almost a constant value (~36.1 kcal/mol) except for the ground state (36.9 kcal/mol). For this reason, the excitation energies of the CFT differ from the exact values again constantly by about −0.037 eV except for the 2s → 3s excitation (−0.032 eV). These behaviors are similar to the Be case.

The FC theory improves largely the results of the CFT. By performing the FC calculations to the orders 1 to 5, all the calculated results steadily approach the exact values reported by Drake et al.[38] and Pachucki et al.[36] As seen from the second drawer, the absolute energies of all the ns Rydberg states are improved systematically by an order of magnitude as increasing the order of the FC theory. The accuracies are almost the same at each order of the FC-CFT starting from the CFT: independent of the excitations, the average deviations from the exact values are 36.1, 7.86, 0.454, 0.102, and 0.028 kcal/mol at the order 0, 1, 2, 3, and 4, respectively, and finally at order 5, they differ by only 0.010 kcal/mol, by less than 0.1 milli-hartree in average from the highly accurate results of Drake and Pachucki. This is a satisfactory result, considering the labor of the present calculations. The number of the cf's is about 900 with order 4 (about twice at order 5) of the FC theory including all the ground and 2s → ns Rydberg excited states (n up to 10). Although the purpose is different, the landmark calculations by Drake et al.[38] used 26 520 functions for the ground state alone. With the FC theory, we would be able to perform more accurate calculations than the present ones by increasing the order of the FC theory, but it will be done elsewhere.

When we move to the excitation energies, which are the energy difference from the ground state, the accuracy of our results much increases. They are given in the lower three drawers of Table VIII. The accuracies of the present FC-CFT results are easily seen from the last two drawers. It is interesting to note that the deviations from the exact values are almost constants independent of the excitations: all the excited states are calculated to almost the same accuracies at each order, which is an important feature of the FC-CFT starting from the CFT. The average deviations from the exact excitation energies of Drake et al.[38] and Pachucki et al.[36] are −0.036, −0.000 17, −0.001 323, −0.000 07, 0.000 01, and 0.000 01 (in eV), and −292.6, −1.4, −10.7, −0.6, 0.1, and 0.1 (in cm^{-1}), at the orders 0, 1, 2, 3, 4, and 5, respectively. The results seem to be at convergence at about order 4, and the average value for the order 2 is not meaningful because the difference values change sign depending on the excitations. It is a practically useful news that we could get much less than 1 cm^{-1} accuracy, when we used the higher orders of the FC-CFT.

TABLE VII. Energy expectation values of the primitive cf's, $\langle\phi^{Li}_{0,m}|H|\phi^{Li}_{0,m}\rangle$, and the energies of the CFT for ^2S, ^2P, ^2D, and ^2F states of the Li atom; absolute energy in a.u., difference from the exact energy ΔE (kcal/mol), excitation energy in eV, and difference from the exact excitation energy ΔEX (eV) are given. Noteworthy results indicated in boldface.

	$\langle\phi^{Li}_{0,m}|H|\phi^{Li}_{0,m}\rangle$				CFT				Exact excitation energy[a-e] (eV)	Experimental excitation energy (NIST)[f] (eV)
	Absolute energy (a.u.)	ΔE (kcal/mol)	Excitation energy (eV)	ΔEX (eV)	Absolute energy (a.u.)	ΔE (kcal/mol)	Excitation energy (eV)	ΔEX (eV)		
					^{2}S states					
Ground (1s)²(2s)	−7.419 183 47	36.946			−7.419 192 07	36.940				
2s → 3s	−7.330 326 23	14.917	**2.418**	−0.955	−7.296 424 76	36.191	**3.341**	−0.033	**3.373**[a]	3.373
2s → 4s	−7.280 901 11	23.610	**3.763**	−0.578	−7.260 998 12	36.102	**4.305**	−0.036	**4.341**[a]	4.341
2s → 5s	−7.258 782 69	28.093	**4.365**	−0.384	−7.246 044 69	36.086	**4.712**	−0.037	**4.749**[a]	4.749
2s → 6s	−7.247 109 66	30.591	**4.682**	−0.276	−7.238 356 34	36.084	**4.921**	−0.037	**4.958**[a]	4.958
2s → 7s	−7.240 205 44	32.120	**4.870**	−0.209	−7.233 885 49	36.086	**5.042**	−0.037	**5.080**[b]	5.079
2s → 8s	−7.235 797 68	33.115	**4.990**	−0.166	−7.231 058 18	36.089	**5.119**	−0.037	**5.156**[b]	5.156
2s → 9s	−7.232 819 99	33.794	**5.071**	−0.137	−7.229 164 26	36.088	**5.171**	−0.037	**5.208**[b]	5.208
2s → 10s	−7.230 710 78	(34.278)[g]	**5.129**	(−0.116)[g]	−7.227 815 32	(36.095)[g]	**5.208**	(−0.037)[g]		5.244
					^{2}P states					
2s → 2p	−7.350 382 61	37.509	**1.872**	0.024	−7.350 400 78	37.497	**1.872**	0.024	**1.848**[a]	1.848
2s → 3p	−7.301 861 52	22.145	**3.192**	−0.642	−7.279 108 55	36.423	**3.812**	−0.022	**3.834**[c]	3.834
2s → 4p	−7.270 147 13	26.193	**4.055**	−0.466	−7.254 158 49	36.226	**4.491**	−0.031	**4.522**[c]	4.522
2s → 5p	−7.253 577 94	29.311	**4.506**	−0.331	−7.242 640 43	36.174	**4.804**	−0.033	**4.837**[c]	4.837
2s → 6p	−7.244 161 49	31.287	**4.763**	−0.245	−7.236 395 68	36.160	**4.974**	−0.034	**5.008**[c]	5.008
2s → 7p	−7.238 353 78	32.568	**4.921**	−0.190	−7.232 630 60	36.160	**5.077**	−0.034	**5.110**[c]	5.110
2s → 8p	−7.234 540 73	33.432	**5.024**	−0.152	−7.230 183 91	36.166	**5.143**	−0.034	**5.178**[c]	5.177
2s → 9p	−7.231 911 32	34.036	**5.096**	−0.126	−7.228 513 25	36.168	**5.189**	−0.033	**5.222**[c]	5.222
2s → 10p	−7.230 023 48	34.474	**5.147**	−0.107	−7.227 325 31	36.167	**5.221**	−0.034	**5.255**[c]	5.254
					^{2}D states					
2s → 3d	−7.278 212 39	35.963	**3.836**	−0.043	−7.278 212 39	35.963	**3.836**	−0.042	**3.879**[a]	3.879
2s → 4d	−7.264 745 83	29.144	**4.202**	−0.338	−7.253 879 08	35.963	**4.498**	−0.042	**4.541**[d]	4.541
2s → 5d	−7.251 874 30	30.154	**4.553**	−0.295	−7.242 584 70	35.983	**4.806**	−0.042	**4.847**[d]	4.847
2s → 6d	−7.243 594 94	31.511	**4.778**	−0.236	−7.236 431 67	36.006	**4.973**	−0.041	**5.014**[d]	5.014
2s → 7d	−7.238 219 99	32.570	**4.924**	−0.190	−7.232 707 75	36.029	**5.075**	−0.040	**5.114**[d]	5.114
2s → 8d	−7.234 580 67	(33.356)[g]	**5.023**	(−0.156)[g]	−7.230 279 50	(36.055)[g]	**5.141**	(−0.038)[g]		5.179
2s → 9d	−7.232 028 27	(33.928)[g]	**5.093**	(−0.131)[g]	−7.228 613 48	(36.071)[g]	**5.186**	(−0.038)[g]		5.224
2s → 10d	−7.230 171 01	(34.357)[g]	**5.143**	(−0.112)[g]	−7.227 424 65	(36.080)[g]	**5.218**	(−0.037)[g]		5.256
					^{2}F states					
2s → 4f	−7.253 902 33	35.935	**4.498**	−0.044	−7.253 902 33	35.935	**4.498**	−0.044	**4.541**[e]	4.542
2s → 5f	−7.248 663 19	32.179	**4.641**	−0.207	−7.242 645 02	35.939	**4.804**	−0.043	**4.848**[e]	4.848
2s → 6f	−7.242 411 26		**4.810**		−7.236 515 24		**4.971**			
2s → 7f	−7.237 771 76		**4.936**		−7.232 805 17		**5.072**			
2s → 8f	−7.234 455 35		**5.027**		−7.230 384 52		**5.138**			
2s → 9f	−7.232 049 28		**5.092**		−7.228 718 90		**5.183**			
2s → 10f	−7.230 265 21		**5.141**		−7.227 527 05		**5.215**			

[a]Reference 38.
[b]Reference 36.
[c]Reference 41.
[d]Reference 42.
[e]Reference 43.
[f]Reference 15.
[g]Since the exact energies E_{exact} do not exist for the 2s → 10s and 2s → nd (n = 8, 9, and 10) states, these values were estimated from the exact ground-state energy of Drake et al.[38] and the NIST experimental excitation energies.[15]

TABLE VIII. FC-CFT for the ^{2}S ground and Rydberg excited states of the Li atom; absolute energy (E_{FC-CFT}), difference from the exact energy $\Delta E = E_{FC-CFT} - E_{exact}$, excitation energies ($EX_{FC-CFT}$), and difference from the exact excitation energy $\Delta EX = EX_{FC-CFT} - EX_{exact}$ (eV and cm^{-1} units). Noteworthy results indicated in boldface.

n (order)[a] M (dimension)[b]	0 (CFT) 10	1 49	2 155	FC-CFT 3 404	4 908	5 1855	Reference Exact energy (a.u.) Drake et al.[c] and Pachucki et al.[d]
Absolute energy (a.u.)							
Ground (1s)²(2s)	−7.419 192 07	−7.465 532 52	−7.477 294 27	−7.477 895 26	−7.478 015 00	−7.478 045 46	−7.478 060 323 910 146 894[c]
2s → 3s	−7.296 424 76	−7.341 602 33	−7.353 392 25	−7.353 937 13	−7.354 053 08	−7.354 083 21	−7.354 098 421 444 364 045[c]
2s → 4s	−7.260 998 12	−7.306 033 13	−7.317 829 62	−7.318 370 27	−7.318 485 51	−7.318 515 58	−7.318 530 845 998 906 901[c]
2s → 5s	−7.246 044 69	−7.291 042 25	−7.302 845 35	−7.303 390 91	−7.303 506 18	−7.303 536 28	−7.303 551 579 226 734 650[c]
2s → 6s	−7.238 356 34	−7.283 336 77	−7.295 145 23	−7.295 698 37	−7.295 813 99	−7.295 844 17	−7.295 859 510 844 131 039[c]
2s → 7s	−7.233 885 49	−7.278 857 65	−7.290 669 77	−7.291 230 51	−7.291 346 60	−7.291 376 90	−7.291 392 274 160[d]
2s → 8s	−7.231 058 18	−7.276 027 93	−7.287 841 02	−7.288 407 41	−7.288 524 01	−7.288 554 41	−7.288 569 832 747[d]
2s → 9s	−7.229 164 26	−7.274 125 94	−7.285 932 37	−7.286 507 57	−7.286 626 82	−7.286 657 91	−7.286 673 586 71[d]
2s → 10s	−7.227 815 32	−7.272 730 39	−7.284 516 17	−7.285 134 16	−7.285 280 36	−7.285 319 61	...[e]
ΔE = E$_{FC-CFT}$ − E$_{exact}$ (kcal/mol)							
Ground (1s)²(2s)	36.940	7.861	0.481	0.104	0.028	**0.009**	
2s → 3s	36.191	7.841	0.443	0.101	0.028	**0.010**	
2s → 4s	36.102	7.842	0.440	0.101	0.028	**0.010**	
2s → 5s	36.086	7.850	0.443	0.101	0.028	**0.010**	
2s → 6s	36.084	7.858	0.448	0.101	0.029	**0.010**	
2s → 7s	36.086	7.866	0.453	0.102	0.029	**0.010**	
2s → 8s	36.089	7.870	0.457	0.102	0.029	**0.010**	
2s → 9s	36.088	7.874	0.465	0.104	0.029	**0.010**	
2s → 10s	(36.095)[e]	(7.910)[e]	(0.515)[e]	(0.127)[e]	(0.035)[e]	**(0.011)[e]**	

n (order)[a] M (dimension)[b]	0 (CFT) 10	1 49	2 155	3 404	4 908	5 1855	Excitation energy (cm^{-1}) Exact (Drake et al.[c] and Pachucki et al.[d])	Experiment (NIST[f])
Excitation energy (cm^{-1})								
2s → 3s	26 944.31	27 199.53	27 193.35	27 205.66	27 206.50	27 206.57	27 206.49[c]	27 206.12
2s → 4s	34 719.56	35 006.07	34 998.45	35 011.83	35 012.68	35 012.76	35 012.67[c]	35 012.06
2s → 5s	38 001.46	38 296.19	38 287.11	38 299.42	38 300.26	38 300.34	38 300.24[c]	38 299.50
2s → 6s	39 688.85	39 987.34	39 977.09	39 987.74	39 988.50	39 988.56	39 988.46[c]	39 987.64
2s → 7s	40 670.09	40 970.40	40 959.34	40 968.32	40 968.98	40 969.02	40 968.90[d]	40 967.9
2s → 8s	41 290.61	41 591.45	41 580.18	41 587.92	41 588.47	41 588.48	41 588.36[d]	41 587.1
2s → 9s	41 706.28	42 008.89	41 999.08	42 004.89	42 004.85	42 004.71	42 004.53[d]	42 003.3
2s → 10s	42 002.34	42 315.18	42 309.90	42 306.32	42 300.37	42 298.44		42 298

TABLE VIII. (Continued.)

n (order)[a] M (dimension)[b]	0 (CFT) 10	1 49	2 155	3 404	4 908	5 1855	Reference
			$\Delta EX = EX_{FC\text{-}CFT} - EX_{exact}$ (eV)				
2s → 3s	−0.032 507	−0.000 863	−0.001 629	−0.000 103	0.000 001	**0.000 010**	
2s → 4s	−0.036 342	−0.000 819	−0.001 764	−0.000 104	0.000 000	**0.000 011**	
2s → 5s	−0.037 045	−0.000 503	−0.001 628	−0.000 101	0.000 002	**0.000 012**	
2s → 6s	−0.037 146	−0.000 138	−0.001 409	−0.000 089	0.000 006	**0.000 013**	
2s → 7s	−0.037 048	0.000 186	−0.001 185	−0.000 072	0.000 010	**0.000 014**	
2s → 8s	−0.036 915	0.000 384	−0.001 013	−0.000 054	0.000 014	**0.000 015**	
2s → 9s	−0.036 978	0.000 540	−0.000 676	0.000 044	0.000 039	**0.000 022**	
2s → 10s	(−0.036 657)[e]	(0.002 130)[e]	(0.001 476)[e]	(0.001 031)[e]	(0.000 293)[e]	**(0.000 054)[e]**	
			$\Delta EX = EX_{FC\text{-}CFT} - EX_{exact}$ (cm^{-1})				
2s → 3s	−262.18	−6.96	−13.14	−0.83	0.01	0.08	
2s → 4s	−293.11	−6.60	−14.23	−0.84	0.00	0.09	
2s → 5s	−298.79	−4.05	−13.13	−0.82	0.02	0.10	
2s → 6s	−299.60	−1.11	−11.36	−0.72	0.04	0.10	
2s → 7s	−298.81	1.50	−9.56	−0.58	0.08	0.11	
2s → 8s	−297.74	3.10	−8.17	−0.43	0.11	0.12	
2s → 9s	−298.25	4.36	−5.45	0.36	0.32	0.18	
2s → 10s	(−295.66)[e]	(17.18)[e]	(11.90)[e]	(8.32)[e]	(2.37)[e]	(0.44)[e]	

FC-CFT

[a]Order of FC-CFT.
[b]Number of complement functions.
[c]Reference 38.
[d]Reference 36.
[e]Since E_{exact} does not exist for the 2s → 10s state, this value was estimated from the exact ground-state energy of Drake *et al.*[38] and NIST experimental excitation energy.[15]
[f]Reference 15.

TABLE IX. FC-CFT for the ^{2}P valence and Rydberg excited states of the Li atom; absolute energy (E_{FC-CFT}), difference from the exact energy $\Delta E = E_{FC-CFT} - E_{exact}$, excitation energies ($EX_{FC-CFT}$), and difference from the exact excitation energy $\Delta EX = EX_{FC-CFT} - EX_{exact}$ (eV and cm^{-1} units). Noteworthy results indicated in boldface.

	FC–CFT					
n (order)[a]	0 (CFT)	1	2	3	4	
M (dimension)[b]	9	45	144	378	855	Reference
Absolute energy (a.u.)						Exact energy (a.u.) Drake *et al.*[c] and Adamowicz *et al.*[d]
2s → 2p	−7.350 400 78	−7.396 542 12	−7.409 201 54	−7.409 924 66	−7.410 078 68	−7.410 156 532 652 370[c]
2s → 3p	−7.279 108 55	−7.324 307 90	−7.336 375 05	−7.336 968 20	−7.337 095 85	−7.337 151 707 93[d]
2s → 4p	−7.254 158 49	−7.299 229 64	−7.311 148 87	−7.311 718 59	−7.311 839 15	−7.311 889 059 38[d]
2s → 5p	−7.242 640 43	−7.287 676 24	−7.299 550 39	−7.300 121 82	−7.300 240 29	−7.300 288 164 88[d]
2s → 6p	−7.236 395 68	−7.281 416 09	−7.293 274 76	−7.293 854 84	−7.293 972 92	−7.294 020 052 93[d]
2s → 7p	−7.232 630 60	−7.277 647 42	−7.289 500 81	−7.290 089 75	−7.290 208 04	−7.290 254 908 09[d]
2s → 8p	−7.230 183 91	−7.275 208 50	−7.287 058 44	−7.287 652 57	−7.287 771 26	−7.287 818 068 01[d]
2s → 9p	−7.228 513 25	−7.273 541 82	−7.285 377 20	−7.285 979 49	−7.286 102 66	−7.286 150 973 21[d]
2s → 10p	−7.227 325 31	−7.272 291 07	−7.284 090 31	−7.284 736 20	−7.284 896 34	−7.284 960 529 60[d]
$\Delta E = E_{FC-CFT} - E_{exact}$ (kcal/mol)						
2s → 2p	37.497	8.543	0.599	0.146	**0.049**	
2s → 3p	36.423	8.060	0.487	0.115	**0.035**	
2s → 4p	36.226	7.944	0.464	0.107	**0.031**	
2s → 5p	36.174	7.914	0.463	0.104	**0.030**	
2s → 6p	36.160	7.909	0.468	0.104	**0.030**	
2s → 7p	36.160	7.911	0.473	0.104	**0.029**	
2s → 8p	36.166	7.913	0.477	0.104	**0.029**	
2s → 9p	36.168	7.912	0.486	0.108	**0.030**	
2s → 10p	36.167	7.950	0.546	0.141	**0.040**	
Excitation energy (cm^{-1})						Excitation energy (cm^{-1}) Exact (Drake *et al.*[c] and Adamowicz *et al.*[d]) / Experiment (NIST)[e]
2s → 2p	15 097.94	15 141.64	14 944.63	14 917.82	14 910.30	14 903.16[c] / 14 903.66
2s → 3p	30 744.78	30 995.22	30 928.20	30 929.91	30 928.18	30 925.87[d] / 30 925.38
2s → 4p	36 220.68	36 499.26	36 464.70	36 471.56	36 471.38	36 470.38[d] / 36 469.55
2s → 5p	38 748.60	39 034.94	39 010.27	39 016.76	39 017.04	39 016.48[d] / 39 015.56
2s → 6p	40 119.17	40 408.88	40 387.61	40 392.20	40 392.57	40 392.17[d] / 40 390.84
2s → 7p	40 945.51	41 236.01	41 215.90	41 218.55	41 218.86	41 218.52[d] / 41 217.35
2s → 8p	41 482.50	41 771.30	41 751.94	41 753.44	41 753.68	41 753.35[d] / 41 751.63
2s → 9p	41 849.16	42 137.09	42 120.93	42 120.64	42 119.89	42 119.23[d] / 42 118.27
2s → 10p	42 109.89	42 411.59	42 403.37	42 393.51	42 384.65	42 380.51[d] / 42 379.16
$\Delta EX = EX_{FC-CFT} - EX_{exact}$ (eV)						
2s → 2p	0.024 150	0.029 568	0.005 141	0.001 818	**0.000 885**	
2s → 3p	−0.022 452	0.008 599	0.000 289	0.000 502	**0.000 287**	
2s → 4p	−0.030 958	0.003 581	−0.000 704	0.000 147	**0.000 125**	
2s → 5p	−0.033 212	0.002 289	−0.000 769	0.000 035	**0.000 070**	
2s → 6p	−0.033 848	0.002 072	−0.000 565	0.000 004	**0.000 049**	
2s → 7p	−0.033 850	0.002 168	−0.000 325	0.000 003	**0.000 042**	
2s → 8p	−0.033 581	0.002 225	−0.000 175	0.000 012	**0.000 040**	
2s → 9p	−0.033 485	0.002 214	0.000 210	0.000 174	**0.000 082**	
2s → 10p	−0.033 553	0.003 854	0.002 835	0.001 613	**0.000 514**	

TABLE IX. (*Continued.*)

	FC-CFT					
n (order)[a]	0 (CFT)	1	2	3	4	
M (dimension)[b]	9	45	144	378	855	Reference
$\Delta EX = EX_{FC\text{-}CFT} - EX_{exact}$ (cm^{-1})						
$2s \rightarrow 2p$	194.78	238.48	41.47	14.66	**7.14**	
$2s \rightarrow 3p$	−181.09	69.36	2.33	4.05	**2.31**	
$2s \rightarrow 4p$	−249.69	28.89	−5.68	1.19	**1.01**	
$2s \rightarrow 5p$	−267.87	18.46	−6.21	0.28	**0.56**	
$2s \rightarrow 6p$	−273.00	16.71	−4.56	0.03	**0.40**	
$2s \rightarrow 7p$	−273.02	17.49	−2.62	0.02	**0.34**	
$2s \rightarrow 8p$	−270.85	17.95	−1.41	0.09	**0.33**	
$2s \rightarrow 9p$	−270.07	17.85	1.69	1.41	**0.66**	
$2s \rightarrow 10p$	−270.62	31.09	22.86	13.01	**4.14**	

[a]Order of FC-CFT.
[b]Number of complement functions.
[c]Reference 38.
[d]Reference 41.
[e]Reference 15, where data of $J = 1/2$ were employed.

Next, we examine comparatively all the ns, np, nd, and nf states shown in Tables VIII–XI, respectively. We note that among these excited states, only one state, the $2s \rightarrow 2p$ state in Table IX is different from all other excited states in nature: the $2s \rightarrow 2p$ state is the valence excited state, but all others are the Rydberg excited states. Usually, the Rydberg excited states are more easily described by the theoretical methods than the valence excited states. One of the authors has such experiences in his extensive studies of many valence and Rydberg excitations of molecules with his SAC-CI (symmetry-adapted-cluster configuration-interaction) theory.[16,17,46–48] This is natural from the simplicity of the Rydberg states in comparison with the valence states: Rydberg states are like the hydrogenic atoms in both atomic and molecular cases. This experience is also seen here: the differences from the exact values are a bit larger for the $2s \rightarrow 2p$ state than for other Rydberg states. For example, referring to Table IX, the difference in the calculated absolute energy from the exact value is 0.049 kcal/mol at order 4 for the $2s \rightarrow 2p$ state, but for other Rydberg excitations, the differences are 0.029–0.035 kcal/mol for the $2s \rightarrow 3 \sim 9p$ states, except for 0.040 kcal/mol for the $2s \rightarrow 10p$ state for which the value may be worse than the others because of the absence of the push-down effect from the higher states. Similar behavior is also seen in Table IX for the results of the lower-order calculations.

So, we examine the $2s \rightarrow 2p$ valence excited state right here. Although the description of this valence state is more difficult than other Rydberg states at all orders, at the order 4 of the FC theory, the accuracy of the description is already satisfactory. For the excitation energy, the difference from the exact value is 0.000 89 eV for the $2s \rightarrow 2p$ valence excited state, which is larger in comparison with 0.000 04–0.000 29 eV for the other normal Rydberg states of $2s \rightarrow 3 \sim 9p$, but is acceptable as a predictive quantum chemistry. Thus, the description of the present theory for the $2s \rightarrow 2p$ valence excited state is fine.

Now we come back to the examinations of the absolute energies of the Rydberg excited states from the 2s to the ns, np, nd, and nf states shown in the first two drawers of Tables VIII–XI, respectively. We limit our discussions only to the "normal" excited states: by "normal," we mean that we do not deal with the highest excited state because it does not have the push-down effect from the higher excited states through the variational relations given by Eq. (6). From Tables VIII–XI, we see that the deviations of the CFT energies from the exact values are almost constant, for all the different states: the accuracies of the CFT are quite constant for any excited states of any symmetries of S, P, D, and F. This is something quite nice for CFT. The average values and the standard deviations within the "normal" excited states are 36.104 ± 0.036, 36.211 ± 0.089, 35.989 ± 0.025, and 35.937 ± 0.002 (in kcal/mol) for the ns, np, nd, and nf Rydberg states, respectively. From the smallness of the standard deviations, we see that the difference from the exact values is almost constant, 36 kcal/mol, not only for the different principal n states, but also for different angular l states. This is rather surprising, considering the level of the theory of the CFT. Because of this constancy from the starting CFT calculations, the differences of the calculated energies at the different orders of the FC-CFT are again quite a constant. At order 1, the average deviations from the exact energies are 7.857 ± 0.012, 7.938 ± 0.051, 7.832 ± 0.019, and 7.806 ± 0.002, which are about 7.86, for the ns, np, nd, and nf Rydberg states and the deviations from this average are small; at order 2, they are 0.4501 ± 0.0084, 0.4740 ± 0.0090, 0.4461 ± 0.0097, and 0.4335 ± 0.0005, which are about 0.45; at order 3, they are 0.1016 ± 0.0011, 0.1065 ± 0.0039, 0.1012 ± 0.0006, and 0.1010 ± 0.0000, which are about 0.10; and at order 4, they are 0.0287 ± 0.0003, 0.0307 ± 0.0019, 0.0287 ± 0.0001, and 0.0294 ± 0.0000, which are about 0.029. These results show that the stable uniform descriptions of all the Rydberg states by the FC-CFT are steadily improved as the order of

TABLE X. FC-CFT for the ^{2}D Rydberg excited states of the Li atom; absolute energy ($E_{\text{FC-CFT}}$), difference from the exact energy $\Delta E = E_{\text{FC-CFT}} - E_{\text{exact}}$, excitation energies ($EX_{\text{FC-CFT}}$), and difference from the exact excitation energy $\Delta EX = EX_{\text{FC-CFT}} - EX_{\text{exact}}$ (eV and cm^{-1} units). Noteworthy results indicated in boldface.

	FC–CFT					
n (order)[a]	0 (CFT)	1	2	3	4	
M (dimension)[b]	8	40	128	336	760	Reference
	Absolute energy (a.u.)					Exact energy (a.u.) Drake *et al.*[c] and Adamowicz *et al.*[d]
2s → 3d	−7.278 212 39	−7.323 076 89	−7.334 827 40	−7.335 362 75	−7.335 477 73	−7.335 523 543 524 685[c]
2s → 4d	−7.253 879 08	−7.298 734 96	−7.310 493 04	−7.311 029 25	−7.311 144 00	−7.311 189 578 43[d]
2s → 5d	−7.242 584 70	−7.287 453 02	−7.299 222 11	−7.299 766 97	−7.299 882 00	−7.299 927 555 94[d]
2s → 6d	−7.236 431 67	−7.281 310 96	−7.293 091 15	−7.293 649 20	−7.293 765 00	−7.293 810 713 64[d]
2s → 7d	−7.232 707 75	−7.277 596 21	−7.289 386 36	−7.289 959 86	−7.290 076 84	−7.290 122 856 24[d]
2s → 8d	−7.230 279 50	−7.275 178 38	−7.286 977 48	−7.287 564 93	−7.287 683 17	...[e]
2s → 9d	−7.228 613 48	−7.273 523 50	−7.285 327 47	−7.285 922 47	−7.286 042 01	...[e]
2s → 10d	−7.227 424 65	−7.272 319 66	−7.284 109 98	−7.284 722 39	−7.284 860 27	...[e]
	$\Delta E = E_{\text{FC-CFT}} - E_{\text{exact}}$ (kcal/mol)					
2s → 3d	35.963	7.810	0.437	0.101	**0.029**	
2s → 4d	35.963	7.815	0.437	0.101	**0.029**	
2s → 5d	35.983	7.828	0.443	0.101	**0.029**	
2s → 6d	36.006	7.844	0.452	0.101	**0.029**	
2s → 7d	36.029	7.861	0.462	0.102	**0.029**	
2s → 8d	(36.055)[e]	(7.880)[e]	(0.476)[e]	(0.108)[e]	**(0.033)**[e]	
2s → 9d	(36.071)[e]	(7.889)[e]	(0.482)[e]	(0.109)[e]	**(0.034)**[e]	
2s → 10d	(36.080)[e]	(7.908)[e]	(0.509)[e]	(0.125)[e]	**(0.039)**[e]	
	Excitation energy (cm^{-1})					Excitation energy (cm^{-1}) Exact (Drake *et al.*[c] and Adamowicz *et al.*[d]) / Experiment (NIST)[f]
2s → 3d	30 941.46	31 265.40	31 267.86	31 282.27	31 283.32	31 283.21[c] / 31 283.08
2s → 4d	36 282.01	36 607.83	36 608.64	36 622.86	36 623.95	36 623.90[d] / 36 623.38
2s → 5d	38 760.84	39 083.93	39 082.32	39 094.64	39 095.68	39 095.62[d] / 39 094.93
2s → 6d	40 111.27	40 431.96	40 427.91	40 437.33	40 438.20	40 438.12[d] / 40 437.31
2s → 7d	40 928.58	41 247.25	41 241.02	41 247.05	41 247.66	41 247.51[d] / 41 246.5
2s → 8d	41 461.52	41 777.90	41 769.71	41 772.68	41 773.01	/ 41 771.3
2s → 9d	41 827.16	42 141.11	42 131.84	42 133.16	42 133.20	/ 42 131.3
2s → 10d	42 088.08	42 405.32	42 399.05	42 396.54	42 392.56	/ 42 389
	$\Delta EX = EX_{\text{FC-CFT}} - EX_{\text{exact}}$ (eV)					
2s → 3d	−0.042 371	−0.002 208	−0.001 902	−0.000 116	**0.000 014**	
2s → 4d	−0.042 389	−0.001 991	−0.001 891	−0.000 129	**0.000 007**	
2s → 5d	−0.041 508	−0.001 450	−0.001 649	−0.000 122	**0.000 006**	
2s → 6d	−0.040 524	−0.000 763	−0.001 265	−0.000 097	**0.000 011**	
2s → 7d	−0.039 542	−0.000 031	−0.000 804	−0.000 056	**0.000 019**	
2s → 8d	(−0.038 408)[e]	(0.000 819)[e]	(−0.000 197)[e]	(0.000 171)[e]	**(0.000 212)**[e]	
2s → 9d	(−0.037 708)[e]	(0.001 216)[e]	(0.000 067)[e]	(0.000 230)[e]	**(0.000 236)**[e]	
2s → 10d	(−0.037 309)[e]	(0.002 024)[e]	(0.001 246)[e]	(0.000 935)[e]	**(0.000 442)**[e]	
	$\Delta EX = EX_{\text{FC-CFT}} - EX_{\text{exact}}$ (cm^{-1})					
2s → 3d	−341.74	−17.81	−15.34	−0.94	**0.11**	
2s → 4d	−341.89	−16.06	−15.26	−1.04	**0.06**	
2s → 5d	−334.79	−11.69	−13.30	−0.98	**0.05**	
2s → 6d	−326.84	−6.16	−10.20	−0.78	**0.09**	
2s → 7d	−318.93	−0.25	−6.49	−0.45	**0.15**	
2s → 8d	(−309.78)[e]	(6.60)[e]	(−1.59)[e]	(1.38)[e]	**(1.71)**[e]	
2s → 9d	(−304.14)[e]	(9.81)[e]	(0.54)[e]	(1.86)[e]	**(1.90)**[e]	
2s → 10d	(−300.92)[e]	(16.32)[e]	(10.05)[e]	(7.54)[e]	**(3.56)**[e]	

[a]Order of FC-CFT.
[b]Number of complement functions.
[c]Reference 38.
[d]Reference 42.
[e]Since E_{exact} does not exist for the 2s → nd (n = 8, 9, and 10) states, this value was estimated from the exact ground-state energy of Drake *et al.*[38] and NIST experimental excitation energy.[15]
[f]Reference 15, where data of J = 3/2 were employed.

TABLE XI. FC-CFT for the ^{2}F Rydberg excited states of the Li atom; absolute energy ($E_{\text{FC-CFT}}$), difference from the exact energy $\Delta E = E_{\text{FC-CFT}} - E_{\text{exact}}$, excitation energies ($EX_{\text{FC-CFT}}$), and difference from the exact excitation energy $\Delta EX = EX_{\text{FC-CFT}} - EX_{\text{exact}}$ (eV and cm^{-1} units). Noteworthy results indicated in boldface.

	FC-CFT					
n (order)[a]	0 (CFT)	1	2	3	4	
M (dimension)[b]	7	35	112	294	665	Reference
Absolute energy (a.u.)						Exact energy (a.u.) King[c]
2s → 4f	−7.253 902 33	−7.298 732 60	−7.310 478 70	−7.311 007 84	−7.311 121 84	−7.311 168 7
2s → 5f	−7.242 645 02	−7.287 475 82	−7.299 225 36	−7.299 756 19	−7.299 870 29	−7.299 917 1
2s → 6f	−7.236 515 24	−7.281 351 15	−7.293 106 62	−7.293 643 76	−7.293 758 27	. . .[d]
2s → 7f	−7.232 805 17	−7.277 646 94	−7.289 409 45	−7.289 957 38	−7.290 072 77	. . .[d]
2s → 8f	−7.230 384 52	−7.275 232 37	−7.287 002 13	−7.287 563 74	−7.287 680 52	. . .[d]
2s → 9f	−7.228 718 90	−7.273 573 12	−7.285 349 30	−7.285 922 28	−7.286 040 31	. . .[d]
2s → 10f	−7.227 527 05	−7.272 380 05	−7.284 154 51	−7.284 738 17	−7.284 863 92	. . .[d]
$\Delta E = E_{\text{FC-CFT}} - E_{\text{exact}}$ (kcal/mol)						
2s → 4f	35.935	7.804	0.433	0.101	**0.029**	
2s → 5f	35.939	7.807	0.434	0.101	**0.029**	
2s → 6f	(35.951)[e]	(7.816)[e]	(0.440)[e]	(0.103)[e]	**(0.031)[e]**	
Excitation energy (cm^{-1})						Excitation energy (cm^{-1})
						Exact (King)[c] Experiment (NIST)[f]
2s → 4f	36 276.90	36 608.35	36 611.79	36 627.55	36 628.82	36 628.48 36 630.2
2s → 5f	38 747.60	39 078.93	39 081.61	39 097.01	39 098.25	39 097.92 39 104.5
2s → 6f	40 092.93	40 423.14	40 424.52	40 438.53	40 439.68	40 438.90[g]
2s → 7f	40 907.20	41 236.12	41 235.95	41 247.60	41 248.55	
2s → 8f	41 438.47	41 766.06	41 764.30	41 772.94	41 773.59	
2s → 9f	41 804.03	42 130.22	42 127.05	42 133.20	42 133.58	
2s → 10f	42 065.61	42 392.07	42 389.28	42 393.08	42 391.76	
$\Delta EX = EX_{\text{FC-CFT}} - EX_{\text{exact}}$ (eV)						
2s → 4f	−0.043 590	−0.002 496	−0.002 069	−0.000 115	**0.000 042**	
2s → 5f	−0.043 434	−0.002 355	−0.002 022	−0.000 113	**0.000 041**	
2s → 6f	(−0.042 895)[e]	(−0.001 954)[e]	(−0.001 783)[e]	(−0.000 046)[e]	**(0.000 097)[e]**	
$\Delta EX = EX_{\text{FC-CFT}} - EX_{\text{exact}}$ (cm^{-1})						
2s → 4f	−351.57	−20.13	−16.69	−0.92	**0.34**	
2s → 5f	−350.32	−18.99	−16.31	−0.91	**0.33**	
2s → 6f	(−345.97)[e]	(−15.76)[e]	(−14.38)[e]	(−0.37)[e]	**(0.78)[e]**	

[a] Order of FC-CFT.
[b] Number of complement functions.
[c] Reference 43.
[d] E_{exact} does not exist for the 2s → nf (n = 6 to 10) state.
[e] Since E_{exact} does not exist for the 2s → 6f state, this value was estimated from the exact ground-state energy of Drake et al.[38] and experimental excitation energy.[51]
[f] Reference 15, where data of J = 5/2 were employed.
[g] Reference 51.

the FC theory increases from 0 of CFT and that finally all the results of the FC-CFT reach the essentially exact results uniformly.

We next examine the excitation energies from 2s to Rydberg ns, np, nd, and nf states shown in the last three drawers of Tables VIII–XI, respectively. From the second lower drawers, we see the differences from the exact excitation energies for all the Rydberg excitations of all different symmetries from order 0 to order 4 of the FC theory. From the last bottom drawers, we see that the accuracies are in cm^{-1}. Again, we see that at each order, the accuracies are almost the same among all the excitations of all the symmetries for each order

of the FC theory. The accuracies are improved dramatically as the order of the FC theory increases. Finally, at order 4, the accuracy of the FC-CFT excitation energies is to within a few cm^{-1} for all the excitations of different principal and angular quantum numbers. This accuracy would be useful for most quantum chemical studies.

In Table XII, we give a summary of the FC-CFT studies of the Li atom, together with the comparison of the experimental NIST values.[15] More accurate experimental data were reported for some states by Radziemski et al.,[49] Reinhardt et al.,[50] Sanchez et al.,[51] Lorenzen and Niemax,[52] DeGraffenreid and Sansonetti,[53] and Sansonetti et al.[54] Some

TABLE XII. Summary and comparison with the NIST experimental values of the FC-CFT calculations at n(order) = 5, 4, 4, and 4 for the ^{1}S, ^{2}P, ^{2}D, and ^{2}F states of the Li atom. $\Delta EX_{expt.} = EX - EX_{expt.}$ (cm^{-1}). Noteworthy results indicated in boldface.

	FC-CFT					Theoretical exact[a–f]			Experimental excitation energy (cm^{-1})	
	Absolute energy:		Excitation energy:			Excitation energy:	$\Delta EX_{expt.}$ (cm^{-1})			
	$E_{FC\text{-}CFT}$ (cm^{-1})	ΔE_{exact} (kcal/mol)	$EX_{FC\text{-}CFT}$ (cm^{-1})	ΔEX_{exact} (cm^{-1})	$\Delta EX_{expt.}$ (cm^{-1})	EX_{exact} (cm^{-1})	BO level	Best value[g]	NIST[h]	Other[i–l]
^{2}S states										
Ground (1s)^2(2s)	−7.478 045 46	**0.009**								
2s → 3s	−7.354 083 21	**0.010**	27 206.57	**0.08**	**0.45**	27 206.49[a]	0.37	**−0.0002**[a,m,n]	27 206.12	27 206.094 082[i]
2s → 4s	−7.318 515 58	**0.010**	35 012.76	**0.09**	**0.70**	35 012.67[a]	0.61	**0.0000**[b,n]	35 012.06	35 012.033 582[j]
2s → 5s	−7.303 536 28	**0.010**	38 300.34	**0.10**	**0.84**	38 300.24[a]	0.74	**0.0061**[b,n]	38 299.50	38 299.4627[k]
2s → 6s	−7.295 844 17	**0.010**	39 988.56	**0.10**	**0.92**	39 988.46[a]	0.82	**0.0155**[b,n]	39 987.64	39 987.586[k]
2s → 7s	−7.291 376 90	**0.010**	40 969.02	**0.11**	**1.12**	40 968.90[b]	1.00	**0.09**[b]	40 967.9	
2s → 8s	−7.288 554 41	**0.010**	41 588.48	**0.12**	**1.38**	41 588.36[b]	1.26	**0.31**[b]	41 587.1	
2s → 9s	−7.286 657 91	**0.010**	42 004.71	**0.18**	**1.41**	42 004.53[b]	1.23	**0.25**[b]	42 003.3	
2s → 10s	−7.285 319 61	**(0.011)**[o]	42 298.44		0.44				42 298	
^{2}P states										
2s → 2p	−7.410 078 68	**0.049**	14 910.30	**7.14**	**6.64**	14 903.16[a]	−0.50	**0.0004**[f,n]	14 903.66	14 903.648 130[l]
2s → 3p	−7.337 095 85	**0.035**	30 928.18	**2.31**	**2.80**	30 925.87[c]	0.49		30 925.38	30 925.5530[k]
2s → 4p	−7.311 839 15	**0.031**	36 471.38	**1.01**	**1.83**	36 470.38[c]	0.83		36 469.55	36 469.7542[k]
2s → 5p	−7.300 240 29	**0.030**	39 017.04	**0.56**	**1.48**	39 016.48[c]	0.92		39 015.56	39 015.6988[k]
2s → 6p	−7.293 972 92	**0.030**	40 392.57	**0.40**	**1.73**	40 392.17[c]	1.33		40 390.84	40 391.283[k]
2s → 7p	−7.290 208 04	**0.029**	41 218.86	**0.34**	**1.51**	41 218.52[c]	1.17		41 217.35	
2s → 8p	−7.287 771 26	**0.029**	41 753.68	**0.33**	**2.05**	41 753.35[c]	1.72		41 751.63	
2s → 9p	−7.286 102 66	**0.030**	42 119.89	**0.66**	**1.62**	42 119.23[c]	0.96		42 118.27	
2s → 10p	−7.284 896 34	**0.040**	42 384.65	**4.14**	**5.49**	42 380.51[c]	1.35		42 379.16	
^{2}D states										
2s → 3d	−7.335 477 73	**0.029**	31 283.32	**0.11**	**0.24**	31 283.21[a]	0.13		31 283.08	31 283.0505[k]
2s → 4d	−7.311 144 00	**0.029**	36 623.95	**0.06**	**0.57**	36 623.90[d]	0.52		36 623.38	36 623.3360[k]
2s → 5d	−7.299 882 00	**0.029**	39 095.68	**0.05**	**0.75**	39 095.62[d]	0.69		39 094.93	39 094.861[k]
2s → 6d	−7.293 765 00	**0.029**	40 438.20	**0.09**	**0.89**	40 438.12[d]	0.81		40 437.31	40 437.220[k]
2s → 7d	−7.290 076 84	**0.029**	41 247.66	**0.15**	**1.16**	41 247.51[d]	1.01		41 246.5	
2s → 8d	−7.287 683 17	**(0.033)**[o]	41 773.01		1.71				41 771.3	
2s → 9d	−7.286 042 01	**(0.034)**[o]	42 133.20		1.90				42 131.3	
2s → 10d	−7.284 860 27	**(0.039)**[o]	42 392.56		3.56				42 389	
^{2}F states										
2s → 4f	−7.311 121 84	**0.029**	36 628.82	**0.34**	**−1.38**	36 628.48[e]	−1.72		36 630.2	36 628.329[k]
2s → 5f	−7.299 870 29	**0.029**	39 098.25	**0.33**	**−6.25**	39 097.92[e]	−6.58		39 104.5	39 097.499[k]
2s → 6f	−7.293 758 27	**(0.031)**[o,p]	40 439.68		0.78[p]					40 438.90[k]
2s → 7f	−7.290 072 77		41 248.55							
2s → 8f	−7.287 680 52		41 773.59							
2s → 9f	−7.286 040 31		42 133.58							
2s → 10f	(−7.284 863 92)[q]		(42 391.76)[q]							

[a]Reference 38.
[b]Reference 36.
[c]Reference 41.
[d]Reference 42.
[e]Reference 43.
[f]Reference 44.
[g]The best value includes further the finite-nuclear mass effect, relativistic effect, QED effect, and higher QED effects for ^{7}Li.
[h]Reference 15.
[i]Reference 51.
[j]Reference 53.
[k]Reference 49.
[l]Reference 54.
[m]For other theoretical data[36,45] that could not be cited, see the text.
[n]Difference from the best precise experimental data[49–54] available.
[o]Since E_{exact} does not exist for 2s → 10s and 2s → nd (n = 8, 9, and 10) states, E_{exact} estimated using the exact ground-state energy of Drake et al.[38] and NIST experimental excitation energy.[15]
[p]Experimental excitation energy of Ref. 49 was used.
[q]For the 2s → 10f state, there are no push-down effects from the higher states as expressed by Eq. (6).

of their data are also shown in Table XII. For the FC-CFT data, we obtained the results of the order n of 5, 4, 4, and 4 for the ^1S, ^2P, ^2D, and ^2F states. The column under ΔE_{exact} gives the accuracies of the absolute energies of the present BO FC-CFT calculations in kcal/mol for all the different states. For the S symmetry, the accuracy is more stable and better than other symmetries, since it is order 5 instead of order 4 for other symmetries. The column under ΔEX_{exact} gives the accuracies of the excitation energies of the present BO FC-CFT calculations in cm^{-1}, which are discussed above. The columns under $\Delta EX_{expt.}$ of the FC-CFT and of "BO level" of "Theoretical exact" give the differences from the NIST experimental values for the BO FC-CFT and for the theoretical BO exact values of Drake et al.,[38] and Pachucki et al.,[36] both in cm^{-1}. We notice that under FC-CFT, the values of ΔEX_{exact} are mostly smaller than the values of $\Delta EX_{expt.}$. Also, the values of BO level $\Delta EX_{expt.}$ of "Theoretical exact" are close to those of FC-CFT. These behaviors seem to indicate the existence of some other factors not included in the present FC-CFT and "Theoretical exact" calculations of Drake and Pachucki. Further finite-nuclear mass effect, relativistic effect, QED effect, and higher QED effects were examined by Drake et al.,[44] Adamowicz et al.,[45] and Pachucki et al.:[36] these reference values are also given in the column under $\Delta EX_{expt.}$ as "Best value," which were calculated using the best precise experimental data available.[49-54] For the 2s → 3s excitation energy, Drake, Adamowicz, and Pachucki reported

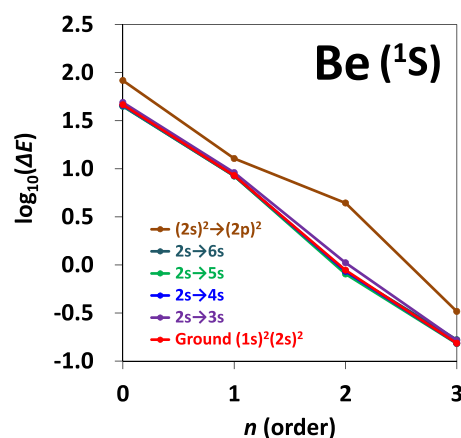**FIG. 2.** Plots of $\log_{10} \Delta E$ [$\Delta E = E_{FC\text{-}CFT} - E_{exact}$ (kcal/mol)] against the order n of the FC-CFT calculations for the ^1S states of the Be atom.

independently the values −0.0002, −0.0016, and −0.0004 cm^{-1}, respectively, as the value of $\Delta EX_{expt.}$. Pachucki also reported the theoretical 2s → ns (n = 3 to 9) excitation energies that agreed with the experimental values within 0.0155 cm^{-1} for n = 3 to 6, and for n = 7 to 9, where very precise experimental data are not available, the differences were within 0.31 cm^{-1} from the old existing data, while Drake
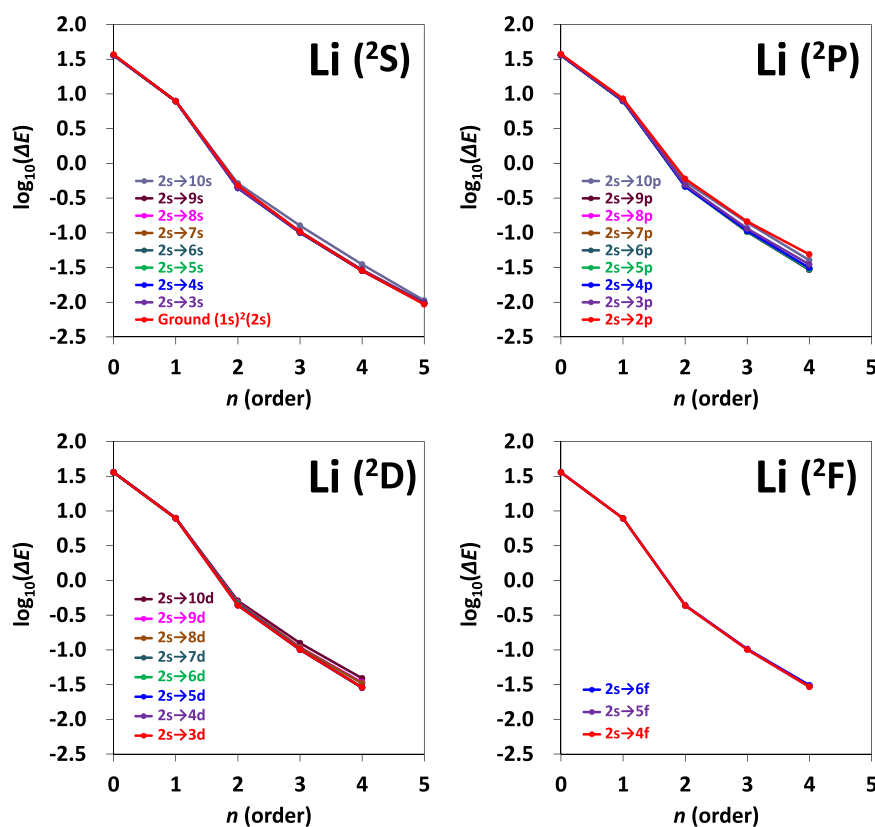

FIG. 3. Plots of $\log_{10} \Delta E$ [$\Delta E = E_{FC\text{-}CFT} - E_{exact}$ (kcal/mol)] against the order n of the FC-CFT calculations for the ^2S, ^2P, ^2D, and ^2F states of the Li atom.

reported the 2s → 2p excitation energy within the difference of 0.004 cm⁻¹. Thus, these highly accurate theoretical data beyond the BO Schrödinger equation can explain their individual physical origins and their magnitudes.

VI. CONVERGENCE SPEED OF THE FC-CFT TO THE EXACT ENERGY

We have applied the CFT and the FC-CFT to the very small atoms, Li and Be, three and four electron atoms. Because of practical reasons of the integrals available for the calculations, our theory was the Hylleraas-CI type formulation of the FC theory: the r_{ij}-type cf's were limited only to those including them only linearly, though r_{ij}^2 type functions are integratable and included. We examine here the convergence behavior of such variational FC-CFT calculations toward the exact limit.

In Fig. 2, we give a plot of $\log_{10}\Delta E$ with $\Delta E = E_{FC-CFT} - E_{exact}$ in kcal/mol against the order n of the present FC-CFT calculations for the ^1S states of the Be atom. We have given the calculations for the ground state, Rydberg 2s → ns ($n = 3$–6) excited states, and valence $(2s)^2 \to (2p)^2$ excited state. We see that all the ground and Rydberg excited states converge to the exact energies in the same speeds. This behavior starts from the CFT level ($n = 0$). However, for the $(2s)^2 \to (2p)^2$ excited state, the convergence speed is a bit slower than those of the other states. The reason is clear: this state lies as high as 76 190 cm⁻¹ (9.44 eV) so that in the variational calculations, this state does not have the push-down effects from the higher states as seen from Eq. (6). For this reason, we may not include the highest-energy state in the calculational purpose or add some dummy higher-energy state to the calculations of the CFT.

Figure 3 shows the similar plots for all the states of the Li atom. Again, all the states converge to the exact level at the same speed. Although we gave the states, S, P, D, and F, separately, all the four graphs of different symmetry in Fig. 3 overlap with each other. Thus, with the FC-CFT, all the states within the CFT calculations are improved to the same extent order by order, if the states are similar electronically. This feature of the CFT and FC-CFT is a very important and useful merit from a theoretical point of view because as far as this relation is kept from the beginning (CFT) to the final, the difference quantities must be close to the exact values. For example, the excitation energies are the difference property so that the excitation energies calculated from any levels of the FC-CFT calculations must be close to the exact values and consequently to the experimental values. In other words, to the calculated excitation energies, the FC-CFT theory is approximation-independent. This was certainly so even from the CFT level of the theory, as have been shown in all the tables of the FC-CFT calculation results (Tables III, IV, and VIII–XII). Furthermore, if one studies the potential energy surfaces along the chemical reactions, this insensible nature to the approximations used is a valuable merit of the theory.

Let us examine the CFT and FC-CFT results more intuitively. Figure 4 shows the plots of the excitation energies of the Be atom calculated by the CFT and FC-CFT against the
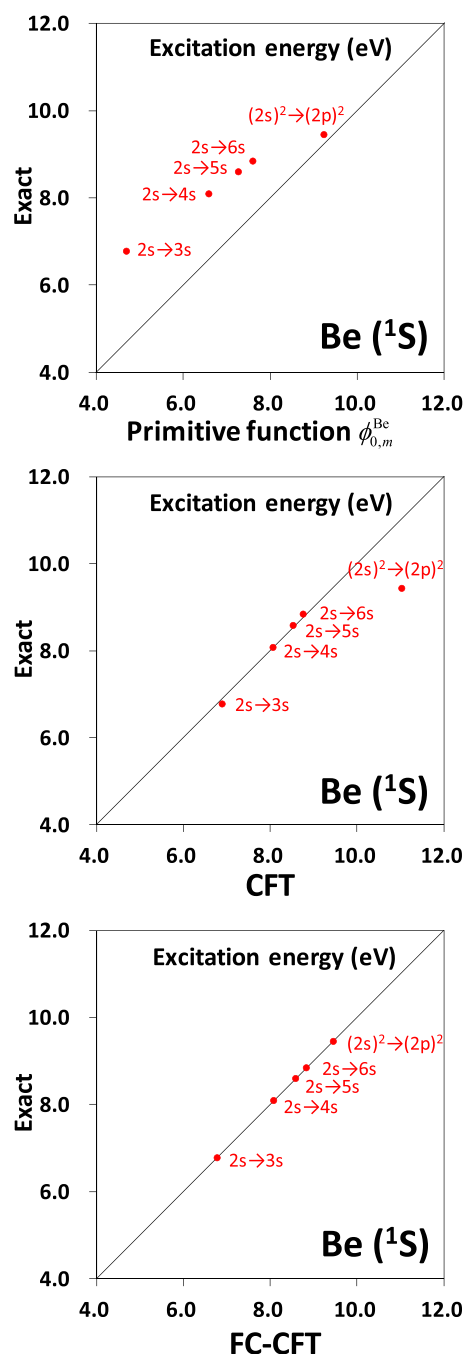

FIG. 4. Plots of excitation energies (eV) of the primitive function (top), CFT (middle) and FC-CFT at n(order) = 3 (bottom) for the ^1S states of the Be atom against the theoretical exact excitation energy[24] and the NIST experimental excitation energy[15] for the $(2s)^2 \to (2p)^2$ state.

exact values. We first examine the energy expectation values of the primitive cf's that compose the CFT wave functions as Eq. (10): the top figure shows their values against the exact results of Adamowicz et al.[24] and for the $(2s)^2 \to (2p)^2$ state, the
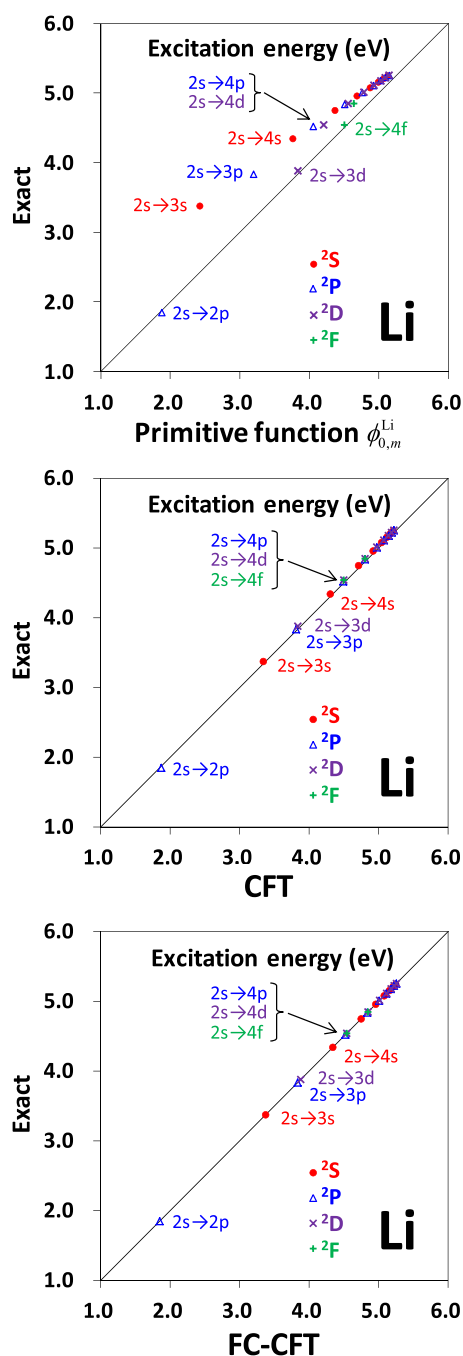
FIG. 5. Plots of excitation energies (eV) of the primitive function (top), CFT (middle), FC-CFT at n(order) = 5, 4, 4, and 4 (bottom) for the ^{2}S, ^{2}P, ^{2}D, and ^{2}F states of the Li atom against the theoretical exact excitation energy[36,38,41–43] and the NIST experimental excitation energy[15] for the 2s → 10s and 2s → nd (n = 8, 9, and 10) states.

estimated exact value by using the NIST experimental excitation energy. We see that the approximate results deviate considerably from the 45-degree line, though the order of the

states is correctly calculated. However, when we use the CFT result, we obtain the middle figure. The excitation energies calculated by the CFT are all on the 45-degree line for the Rydberg excited states. For the $(2s)^2 \rightarrow (2p)^2$ doubly excited state, the CFT energy is too high: a reason is that for this highest state of the CFT, there is no push down-effect from the above. However, with the FC-CFT at order 3, all the calculated excited states are exactly on the 45-degree line, including the $(2s)^2 \rightarrow (2p)^2$ doubly excited state.

In Fig. 5, we show the similar results for the Li atom for the excitation energies of all the excitations studied in this paper. With the primitive cf's that compose the CFT wave functions as Eq. (20), the results deviate considerably from the 45-degree line. However, when we see the middle figure, we notice that the CFT results are all on the 45-degree line. The CFT is simply the results that diagonalize the contributions of the primitive cf's. Thus, we understand how important the relations given by Eq. (6) are: this equation adjusts the energy of each state through the variational principle, and each state works as if they form the basis set for each other. Of course, at the FC-CFT level, all the calculated results are exactly on the 45-degree line.

Thus, the results of Figs. 4 and 5 show the surprisingly nice feature of the CFT calculations of the excitation properties. From the computational point of view, the CFT is an easy approximate theory, like MO and VB theories. It simply diagonalizes the primitive cf's which are treated like the basis functions of each other. To use all the real states to describe the excitation properties is probably very important to make balanced descriptions for all the states under consideration. At the FC-CFT level, we can anyway perform the exact descriptions of all the ground and excited states.

VII. SUMMARY

The free-complement chemical formula theory (FC-CFT) is composed of the two steps of the theories. First, we construct simple but conceptually useful wave functions with the chemical formula theory (CFT), considering the spirits of the chemical formulas, which chemists use daily as their working concepts. The essence of the CFT is the from-atomic-states-to-molecular-states (FASTMS) concept instead of the from-atoms-to-molecules (FATM) concept of the chemical formulas. For an atom, the chemical formula is simply a dot, but many atomic states are associated with this dot, as seen from the Moore's tables of atomic energy levels or NIST data book.[15] Therefore, the aim of the CFT for atoms is to construct simple and conceptually useful wave functions for the set of atomic states of interest. First, we choose such n set of atomic states, referring to the Moore's book, for example, and from such an n set, we construct the CFT wave functions using the variational principle given in Eq. (6). We recommend adding one more state for accuracy because the highest state does not have the push-down effect from the higher states, but they do not exist in the present calculations. We have seen that even the simple approximate set of the CFT wave functions describes well the difference properties of the ground and excited states, like excitation energies.

Next stage is to apply the free-complement (FC) theory to the simple CFT wave functions to obtain the set of the exact solutions of the Schrödinger equation for the n states of the atom or molecule. The FC theory is a useful theory that constructs the exact wave functions from any approximate wave functions used as the initial wave functions of the FC theory: the exact wave functions thus obtained have the mathematical structure similar to the wave functions used as the initial functions. The FC theory produces a set of the complement functions (cf's) that span the exact wave function: by calculating the linear parameters with the variational principle, we obtain the exact wave functions of the ground and excited states that satisfy Eq. (6). However, we often have the cf's that are not integratable so that some inventions are necessary. For the atoms studied here, we limited our formulation to the Hylleraas CI type for the r_{ij} functions as explained in some detail in the Introduction. However, except for the r_{ij}-type functions, we produced with the FC theory the higher-order complement functions that are integratable: the orders of the present FC calculations are not in balance between the integratable set and the non-integratable sets of the cf's. For the Li and Be atoms, we could obtain the essentially exact results with this prescription. With increasing the order of the FC theory for the integratable functions, the accuracies of all the states of the Li and Be atoms were improved rapidly and consistently. This rapid and consistent convergence behavior resulted since all the states satisfy Eq. (6) at each level of the FC-CFT from the initial CFT level.

Through the present studies, we have shown that our theories, CFT, FC-CFT, and FC-CFT-V, consist a unified comprehensive theory that covers from approximate to exact levels and both ground and excited states. We have shown in Ref. 1 that this is true also from small to giant molecules,

and for both numerical and conceptual understanding. We will show the unified and comprehensive nature of our theories in the succeeding papers. Although we used here only the variational method, we have also prepared the LSE method[8,11,14] which is the sampling-type methodology that does not require the integral evaluations. For applying our theory to large and giant molecules, the knowledge of the inter-exchange theory,[13] which shows that the antisymmetrization requirement for a pair of electrons decays as the distance between the two electrons increases, is necessary.

ACKNOWLEDGMENTS

APPENDIX: CFT AND FC-CFT FOR BERYLLIUM ATOM USING EQ. (12)

Table XIII shows the results of the variational calculations of the CFT and the FC-CFT, where we used the Slater orbitals given by Eq. (12) for the ns orbitals of the Rydberg states. In comparison with the expressions given by Eq. (13), this expression gives a larger number of functions when we deal all the elements independently. For this reason, the results shown in Table XIII are better than those given in Table III. In this paper, we have mainly adopted the expression given by Eq. (13) to make the calculations more compact.

TABLE XIII. FC-CFT using the independent orbitals given by Eq. (13) for the ground state and the valence and Rydberg excited states of the ^{1}S states of the Be atom; absolute energy (E_{FC-CFT}), difference from the exact energy $\Delta E = E_{FC-CFT} - E_{exact}$, excitation energies ($EX_{FC-CFT}$), and difference from the exact excitation energy $\Delta EX = EX_{FC-CFT} - EX_{exact}$ (eV and cm^{-1} units). Noteworthy results indicated in boldface.

n (order)[a]	FC-CFT			
	0 (CFT)	1	2	
M (dimension)[b]	40	266	917	Reference
Absolute energy (a.u.)				Exact energy (a.u.) Adamowicz *et al.*[c]
Ground $(2s)^2$	−14.594 838 5	−14.654 573 4	−14.666 100 8	−14.667 356 486
$2s \rightarrow 3s$	−14.340 354 5	−14.404 120 6	−14.416 708 5	−14.418 240 328
$2s \rightarrow 4s$	−14.297 271 7	−14.356 652 4	−14.368 773 7	−14.370 087 876
$2s \rightarrow 5s$	−14.280 108 4	−14.338 258 0	−14.350 284 8	−14.351 511 654
$2s \rightarrow 6s$	−14.271 546 1	−14.329 219 3	−14.341 211 6	−14.342 403 552
$(2s)^2 \rightarrow (2p)^2$	−14.188 139 0	−14.297 507 3	−14.315 161 8	. . .[d]
$\Delta E = E_{FC-CFT} - E_{exact}$ (kcal/mol)				
Ground $(2s)^2$	45.506	8.021	**0.788**	
$2s \rightarrow 3s$	48.874	8.860	**0.961**	
$2s \rightarrow 4s$	45.693	8.431	**0.825**	
$2s \rightarrow 5s$	44.806	8.317	**0.770**	
$2s \rightarrow 6s$	44.464	8.273	**0.748**	
$(2s)^2 \rightarrow (2p)^2$	(82.875)[d]	(14.246)[d]	**(3.167)[d]**	

TABLE XIII. (*Continued.*)

n (order)[a] M (dimension)[b]	FC-CFT			Reference	
	0 (CFT) 40	1 266	2 917		
	Excitation energy (cm^{-1})			**Excitation energy (cm^{-1})** Exact (Adamowicz *et al.*)[c]	Experiment (NIST)[e]
$2s \to 3s$	55 852.79	54 968.03	54 735.28	54 674.68	54 677.26
$2s \to 4s$	65 308.37	65 386.11	65 255.76	65 242.92	65 245.33
$2s \to 5s$	69 075.27	69 423.20	69 313.60	69 319.93	69 322.20
$2s \to 6s$	70 954.48	71 406.97	71 304.94	71 318.93	71 321.15
$(2s)^2 \to (2p)^2$	89 260.22	78 366.94	77 022.20		76 190
	$\Delta EX = EX_{FC\text{-}CFT} - EX_{exact}$ (eV)				
$2s \to 3s$	0.146 067	0.036 371	**0.007 514**		
$2s \to 4s$	0.008 115	0.017 754	**0.001 592**		
$2s \to 5s$	−0.030 333	0.012 804	**−0.000 784**		
$2s \to 6s$	−0.045 185	0.010 916	**−0.001 734**		
$(2s)^2 \to (2p)^2$	(1.620 501)[d]	(0.269 906)[d]	(0.103 179)[d]		
	$\Delta EX = EX_{FC\text{-}CFT} - EX_{exact}$ (cm^{-1})				
$2s \to 3s$	1178.11	293.35	**60.60**		
$2s \to 4s$	65.45	143.19	**12.84**		
$2s \to 5s$	−244.66	103.27	**−6.32**		
$2s \to 6s$	−364.44	88.04	**−13.99**		
$(2s)^2 \to (2p)^2$	(13 070.22)[d]	(2176.94)[d]	(832.20)[d]		

[a]Order of FC-CFT.
[b]Number of complement functions.
[c]Reference 24.
[d]Since E_{exact} does not exist for the $(2s)^2 \to (2p)^2$ state, these values were estimated from the exact ground-state energy of Adamowicz *et al.*[24] and the NIST experimental excitation energy.[15]
[e]Reference 15.

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