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Solving the Schrödinger equation of atoms and molecules with the free-complement chemical-formula theory: First-row atoms and small molecules

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The free-complement chemical-formula theory (FC-CFT) for solving the Schrödinger equation (SE) was applied to the first-row atoms and several small molecules, limiting only to the ground state of a spin symmetry. Highly accurate results, satisfying chemical accuracy (kcal/mol accuracy for the absolute total energy), were obtained for all the cases. The local Schrödinger equation (LSE) method was applied for obtaining the solutions accurately and stably. For adapting the sampling method to quantum mechanical calculations, we developed a combined method of local sampling and Metropolis sampling. We also reported the method that leads the calculations to the accurate energies and wave functions as definite converged results with minimum ambiguities. We have also examined the possibility of the stationarity principle in the sampling method: it certainly works, though more extensive applications are necessary. From the high accuracy and the constant stability of the results, the present methodology seems to provide a useful tool for solving the SE of atoms and molecules. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5040377>

I. INTRODUCTION

For developing a predictive theory in chemistry, it is important to develop a general practical theory for solving the Schrödinger equation (SE) since it is a governing principle of chemistry.¹ The free-complement (FC) theory initiated in our laboratory²⁻⁸ is growing and becoming a candidate of such a theory.⁹⁻¹³ In Paper I,¹³ we have proposed an electronic structure theory for atoms and molecules, called chemical formula theory (CFT), which describes the essence of the chemical formula in a simple variational formalism. Here, the chemical formula stands for both a molecular structural formula and chemical reaction formula that are used widely by chemists as working theories for performing their chemistries. What is central to the chemical formula is the locality of the electronic structure, as represented by atoms, and their transferability among chemistry. In CFT, we describe with the variational principle the electronic structures of atoms and molecules based on the chemical formula through the interactions of the ground and excited electronic states of the constituent atoms using their free valences. Then, we apply the FC theory to the CFT wave functions to obtain the exact wave functions that have the local structures of the chemical formula. This theory was referred to as FC-CFT. Between the approximate CFT and the exact FC-CFT, there exists a useful and yet accurate variational theory, called FC-CFT-V. The FC-CFT-V is a flexible variational theory with which the basic chemistry of interest is extensively studied with reasonable accuracy. Then, if further

exact solutions of the SE are necessary, we perform the FC-CFT using the sampling type local Schrödinger equation (LSE) method.^{7,11} We believe that this way of utilization of the exact wave function theory is not only efficient but also useful for chemists.

In this paper, we apply the FC-CFT to solve the SE of the first-row atoms and small molecules. Different from the general theory given in Paper I,¹³ the calculations here were limited only to the ground state of a given spin symmetry. Therefore, the calculations here do not use the merits of the FC-CFT due to the interactions between the ground and excited states in the course of the calculations, but other central concepts of the chemical formula like locality, transferability, and from-atoms-to-molecule are common. The purpose is to show the accuracy and the reliability of the basic methods. At the same time, we want to show how the elementary theories are used and what are their basic physics. As we wrote before,²⁻¹³ the FC theory is an exact theory for solving the SE. The FC wave function has an exact structure, which implies that the FC wave function includes the exact wave function within its variational space. Therefore, when we optimize the linear parameters included in the FC wave function, we can get the exact wave function. However, since the FC theory produces the wave function in order, if we terminate at some order, the accuracy of the result stops at that order. This example was shown with the He atom: we could calculate the energy of the He atom to over 40 digits accuracy by determining the linear parameters with the variational principle. The method used there is like below, which is general. Starting from some initial function and applying the FC theory to it, we can write the exact wave function ψ in the form

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$$\psi = \sum_I c_I \phi_I, \quad (1)$$

where the functions $\{\phi_I\}$ are referred to as the complement functions (cf's), because as this equation shows, they are the elements of the complete set of functions that describes exactly the solution of the SE. In general, the number of cf's is infinite for obtaining the exact wave function, but if only the chemical accuracy (kcal/mol accuracy for the absolute total energy) is sufficient, about order 2 is necessary.

For general atoms and molecules, the variational principle cannot be applied because in the cf's above, there are many terms that include inter-electron functions r_{ij} for which the analytical integrals are difficult to be evaluated. Therefore, we have to use some other conditions that are equivalent to the SE and yet that does not include the integration method. As such a method, we used the SE itself at some given set of points $\{r_\mu\}$ in the space of the atoms and molecules under consideration,

$$H\psi(r_\mu) = E\psi(r_\mu). \quad (2)$$

This is the local Schrödinger equation (LSE) method reported in 2007.^{7,11} We refer to the set of points $\{r_\mu\}$ as sampling points. Inserting Eq. (1) into Eq. (2), the above equation is rewritten as

$$\mathbf{AC} = \mathbf{BCE}, \quad (3)$$

where the matrix elements of the \mathbf{A} and \mathbf{B} matrices are given by

$$A_{\mu i} = H\phi_i(r_\mu) \quad (4)$$

and

$$B_{\mu i} = \phi_i(r_\mu), \quad (5)$$

respectively, and \mathbf{C} and \mathbf{E} are the matrices of the coefficients and energies, respectively, where \mathbf{E} is diagonal. We referred to this expression, which is just the same as the original local SE, as the AB method. The matrices \mathbf{A} and \mathbf{B} are large rectangular matrices, when the number of sampling points, N_s , is large (like 2×10^6 in our case). To save the memory for such large matrices, let us multiply \mathbf{B}^T from the left of Eq. (3), and then we obtain

$$\mathbf{HC} = \mathbf{SCE}, \quad (6)$$

where $\mathbf{H} = \mathbf{B}^T \mathbf{A}$ and $\mathbf{S} = \mathbf{B}^T \mathbf{B}$. More explicitly, their elements are written as

$$H_{ij} = \sum_{\mu}^{N_s} \phi_i(r_\mu) \cdot H\phi_j(r_\mu) \quad (7)$$

and

$$S_{ij} = \sum_{\mu}^{N_s} \phi_i(r_\mu)\phi_j(r_\mu), \quad (8)$$

respectively. We called this method the HS method. Equation (6) has a form like an eigenvalue equation, but though the matrix \mathbf{S} is symmetric, \mathbf{H} is not. So, we solve this equation using the non-symmetric form of the secular equation. Thus, the LSE method has been developed to determine the parameters $\{c_I\}$ included in the potentially exact wave function given by the FC theory as Eq. (1). We used the SE itself as the condition since our wave function is potentially exact.

We noticed that this equation is very similar to the equation used in the variational Monte Carlo (VMC) method, in particular, to the non-symmetric method reported, for example, by

Toulouse and Umrigar.^{14,15} They reported that with the non-symmetric method, the statistical fluctuations are reduced by one or two orders of magnitude in comparison with those with the symmetric method, though the optimal energy does not correspond to the minimum value as the variational method implies. In the VMC calculations, the wave functions used, which are usually the product of the Jastrow function and the multideterminantal wave function, should be highly accurate but probably do not have the exact structure in the above sense. The VMC and quantum Monte Carlo (QMC) calculations^{14–25} reported accurate results for small molecules. Braida *et al.*^{23,24} reported QMC calculations with Jastrow-valence-bond (JVB) wave functions, giving impressive results using the VB functions.

Within our program calculating the \mathbf{A} and \mathbf{B} matrices as given above, it is easy to calculate the H-square error or the variance defined by

$$\sigma^2 = \langle \psi | (H - E)^2 | \psi \rangle / \langle \psi | \psi \rangle. \quad (9)$$

This quantity becomes zero for the exact wave function but is usually positive. We calculated this quantity in our code to investigate its possibility in the variational and stationarity calculations of the sampling-type methodology.

Thus, the LSE method is a simple, straightforward, and integral-free theory. It is the method for the potentially exact theory like the FC theory. As the wave function under study becomes closer to exact, the sampling-point dependences should become smaller and disappear at the exact limit. For example, e^{-ar} is a potentially exact wave function of the hydrogen atom. The LSE method using only two sampling points can determine the exact wave function, e^{-r} , together with the normalization factor. There are no sampling dependences: any two sampling points can determine the exact wave function unambiguously. In the practical applications at low orders of the FC theory, however, the sampling methodologies have some ambiguities originating from the statistical errors that are difficult to be rationalized but must be overcome. The SE is a quantum mechanical deterministic principle, while the sampling method involves some ambiguous aspects characteristic to the stochastic and random nature. To overcome these aspects, we have combined, in this paper, our local sampling method, which is a quantum-mechanical regular systematic method, with the Metropolis sampling method that is classical, but useful in sampling type methods. Using these methods, we want to develop a general theory that leads to the exact energy and the exact wave function as the definite converged results.

A purpose of this paper is to propose some practical methods for solving the SE's of atoms and molecules with the LSE method applied to the FC-CFT that has local structure. The accuracy of the solutions we aim is chemical accuracy for the absolute total energy. Then, any chemical phenomena can be described in chemical accuracy. The present applications to the first-row atoms and several small molecules are encouraging. They satisfy chemical accuracy and the computational processes were stable, which is probably due to the potentially exact structure of the FC theory combined with the local structure of the FC-CFT.

II. ADAPTING SAMPLING METHOD TO QUANTUM-MECHANICAL CALCULATIONS

The FC-LSE method is a sampling-type method for calculating the exact solution of the SE. We define the density of the N -electron sampling points by $\gamma(1 \cdots N)$ and the exact N -electron density $\Gamma(1 \cdots N)$ associated with the atomic and molecular wave function by

$$\Gamma(1 \cdots N) = \psi_{exact}^*(1 \cdots N)\psi_{exact}(1 \cdots N). \quad (10)$$

It is well known that when the density of the N -electron sampling points $\gamma(1 \cdots N)$ is proportional to the exact N -electron density $\Gamma(1 \cdots N)$, namely,

$$\gamma(1 \cdots N) \propto \Gamma(1 \cdots N), \quad (11)$$

then we can expect an accurate result from the sampling methodology.¹⁸ Since we do not know the exact N -electron density $\Gamma(1 \cdots N)$, we can imagine a necessity of the self-consistent iterative method between the assumed $\gamma^{(n)}(1 \cdots N)$ that gives the wave function $\psi^{(n)}(1 \cdots N)$, from which we estimate $\gamma^{(n+1)}(1 \cdots N)$ of the next step, \dots . For adapting the classical sampling points to the potentially exact quantum-mechanical wave function, we considered the combination of the local sampling method developed in our laboratory^{4,8,11} followed by the Metropolis sampling method developed by Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller (MRRTT).²⁶ Since we are dealing with quantum mechanics, not the statistical theory, the distribution of the sampling points must be regular, in some sense, and cover all regions of the atoms and molecules under study to satisfy Eq. (11) as much as possible. This method is referred to as the LMn method where L means the local sampling method that gives an initial set of sampling points and Mn means the Metropolis method with n being the number of the walker's steps, usually set to unity, within one cycle. The iteration actually proceeds as LMnMn. . ., until convergence. With the use of the LMn iteration processes, we will examine the possibility of the stationarity principle, the averaging method, and the accumulation method to obtain the definite results with minimum statistical ambiguities. Let us explain them in detail below.

A. Local sampling method

The local sampling method is a trial of using the quantum-mechanical principle directly in the sampling method because what we want to solve with the sampling method is the solution of the SE using the FC theory. With the local sampling method, the sampled points must cover all local regions of atoms and molecules in a regular manner, from the cusp regions to the high-density regions and to the tail regions. Since the FC-CFT is based on the local atomic concept, let us consider first the atomic sampling.

In atoms, the system is spherically symmetric, and the origin of the stability is the Coulombic force due to the positive charge of the nucleus centered at the origin. For the hydrogenic atom, the Coulombic nuclear potential is $-Z/r$, the exact wave function of the ground state is $\psi = \exp(-Zr)$, and the exact density is given by the radial distribution function, $\rho(r) = r^2 \exp(-2Zr)$. Then, the best sampling is produced

so that the density of the sampling points along r is proportional to the exact density. While, for the angular θ and φ distribution, no physical requirement exists: purely random distribution is ideal. This is the exact sampling for the hydrogen atom.

For the exponential orbital, an interesting formula exists. For the 1s Slater orbital, for example, the density is written in the form

$$d(r_i) = \exp(-ar_i). \quad (12)$$

Then, the sequence η_i on the r coordinate according to the weight distribution of Eq. (12) is given by

$$\eta_i = -\log(ar_i), \quad (13)$$

which is an inverse function of $d(r_i)$: a plane random number sequence on the r coordinate $\{r_i\}$ is mapped to the probability distribution $\{\eta_i\}$ of $d(r_i)$. This formula is simple, but we cannot use it directly because our density is the radial distribution function given by $4\pi r_i^2 d(r_i)$.

By using the atomic Hartree-Fock (HF) orbital with the Slater basis function, for example, the one-electron radial distribution function $\rho(r_i)$ for the s orbital is written in general as

$$\rho(r_i) = \sum_k b_k r_i^{n_k+2} \exp(-a_k r_i), \quad (14)$$

where $n_k \geq 0$ and k runs over the Slater basis functions used to describe the orbital to which the electron i belongs. b_k and a_k are some coefficient and exponent of the given orbital. A uniform distribution $\{\xi_i\}$ in the interval $[0,1]$ is mapped to the probability distribution $\{\eta_i\}$ according to $\rho(r_i)$ by the relation

$$\xi_i = \int_0^{\eta_i} \rho(r_i) dr_i. \quad (15)$$

From $\{\xi_i\}$, one obtains the corresponding η_i by solving Eq. (15). Since η_i is guaranteed to be a monotonically increasing function of ξ_i , Eq. (15) can be solved easily by the numerical method and η_i is obtained with one-to-one correspondence to ξ_i . Thus, we obtain the weighted radial distributions $\{\eta_i\}$ ($i = 1, \dots, N_s$) that are regularly and densely arranged along the radial coordinates of the atomic orbitals.

The electronic structure of the many electron atoms may be described well by the atomic Hartree-Fock theory. With the latter theory, we have in the literature the minimal Slater basis of Clementi²⁷ and the multi-exponent Slater functions reported by McLean and Yoshimine.²⁸ For the sp^3 state (5S) of the carbon atom, for example, the electronic structure is produced using the Aufbau principle as $(1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$. Therefore, we construct first the sampling points for the 1s electrons, and then for the 2s electrons, \dots , and afterward, we approximate the local sampling points for $C(sp^3)$ by a set of products of the sampling points of the six electrons in a set of orbitals, each sampling point being produced according to the radial density $\rho(r)$ of each orbital. For the 2s orbital, we take its node into account. For the 2p orbitals, we distributed spherically, ignoring the x, y, z angle, just like for the 2s orbital. This is because, when we later consider chemical reactions, for example, the spherical sampling points are easier to use since they are not dependent on the molecular geometry. Then, the angular distributions may be calculated as being due to the randomness origin as in the hydrogen atom. We then shuffled the

ordering of the sampling points and made a set of 6-electron sampling points by taking products of the shuffled sampling points of 6 electrons, like the Hartree products, arranged in the orbital sequence of 1s, 1s, 2s, 2p_x, 2p_y, 2p_z. We made N_s ($\sim 10^6$) sets of sampling points, instead of N_s^6 . The effects of the Pauli principle and the inter-electron repulsions will be taken into account in the Metropolis step done later.

Next, we consider the local sampling method for molecules. When we calculate molecules, usually we already have the best atomic sampling points associated with the best FC calculations for the atom. So, the method for the local sampling for molecules may have some selections. The first selection is to use the results of the quantum-chemical calculations for the molecule under consideration, like we did for atoms in the above paragraphs. Second is to use the result of the best atomic sampling calculations with the similar sampling method. Third is like the second one and is to use the result of the best calculations for the fragments of the molecule.

For the first method selected, a note may be necessary. When we use the results of the Hartree-Fock calculations, a problem arises from the multi-center nature of the MO's. For example, for the MO, $a + b$, where a and b are the atomic orbitals on centers A and B, respectively, its density becomes $\rho(\mathbf{r}) = (a + b)^2 = a^2 + 2ab + b^2$. For the first and last terms, we can use the method given above for atoms, but for the second term, such a method is not applicable because this is the two-center function. For the Gaussian functions, however, the second term can be transformed to the one-center Gaussian function, for which the above method is applicable. When the coefficient of b is negative, we have to delete the corresponding near-by sampling points of $a^2 + b^2$, which would be possible.

The second method is popular. We put the best atomic samplings to the coordinates of the atoms in the chemical formula. From them, we form the initial local sampling for the molecule. In the succeeding LMn steps, the reorganization from atomic distribution to molecular distribution occurs.

The third method is similar to the second one. We utilize the sampling points already calculated for the fragment of the molecule under study. We used this method in the calculations of acetylene: we used the best sampling of C₂ and the sampling of two H's.

B. Local sampling plus iterative Metropolis cycles: LMn method

The local sampling method explained above utilizes the quantum-chemical method for producing the sampling points, but it neglects many other conditions, like antisymmetry effect, inter-electron repulsions, accumulation of density in bonding regions, and other interactions within molecules. These points are improved by using the Metropolis method²⁶ which is done iteratively for satisfying the important relation given by Eq. (11).

The Metropolis method is designed to form Monte Carlo distributions of a state composed of interacting particles: it assumes classical statistics, only two-body forces, and homogenous fields. These assumptions do not hold for

the electrons in atoms and molecules that follow quantum mechanics, but this method is still a useful working method for adjusting the sampling distribution to satisfy Eq. (11).

The calculations are performed in an iterative way: (i) we first prepare the local sampling points as an initial distribution and perform the LSE calculations to get the wave function and energy, and (ii) a set of sampling points given by the local sampling method is updated to adapt to a given (previous cycle's) wave function and perform the LSE calculations again to get the solution. We continue this iteration process (ii) until we get the convergence. We refer to this iterative calculation process of (ii) as the LMn method: the Local (L) and Metropolis n -step (Mn) method, where n means the number of walks of the random walkers allowed in one Metropolis cycle. The calculations proceed in the form of LMnMn. . . . Since the local sampling points were prepared based on some quantum-chemical bases, while the Metropolis method does not stand on the quantum-mechanical principle, it is not recommended to choose the step size d and the number of walks n too large. We used n usually unity and d to be reasonably small. However, these parameters are the subjects of the experiences: the best choice will be obtained after accumulating the experiences of calculating many atoms and molecules.

We determined the step size d in the following manner. When the random walker i_A (i denotes the electron and A denotes the atom it belongs, but A is omitted below) moves in the atomic region of A, the step size should be chosen, depending on the nature of the orbital to which the electron i belongs. When the electron i belongs to the hydrogenic orbital χ_i with the principal quantum number n_i and the orbital exponent α_i , namely, $\chi_i = r^{n_i-1} \exp(-\alpha_i r)$, then the step size d_i of the walker may be defined by

$$d_i = \eta \frac{n_i}{\alpha_i}, \quad (16)$$

where η is an input parameter: when $\eta = 1$, $d_i = n_i/\alpha_i$ is the distance from the nucleus to the maximum of the radial distribution $4\pi r^2 \chi^2$. Therefore, the proportionality parameter η adjusts the walker's step size and normally should be much smaller than unity. In the CFT, each electron has its own orbital and center A for the local atomic concept. Therefore, the explanation here is common to both atoms and molecules.

Next is about the random walker's pass. As atoms are spherical, the pass along the r, θ, φ coordinate is a natural choice. In the pre-step of the local sampling, the regular and dense distributions of the sampling points were produced along the r coordinate based on the quantum mechanical origin, while for the angular θ and φ coordinates, the distribution was chosen purely randomly or with the reference to the HF single determinant or some other method. In the Metropolis method of atoms, we may keep the radial sampling fixed to those of the initial local sampling and consider the many-electron effects only with the θ, φ coordinates. Since the Metropolis method is suitable to adjust something of the randomness origin, this usage matches with the nature of the Metropolis method. We may refer to this method as the θ, φ method since the r -coordinates are fixed to the initial local sampling without

any modification. For this purpose, the quantum mechanical method that provides the local r -sampling must be of good quality. Actually, as shown below, this θ , φ method seems to work well. However, if the θ , φ method is restrictive, we can modify the radial distribution by relaxing the r coordinate at the same time. Actually, the atomic radial distribution used in the local sampling method is an approximate one, not including the correlation effects, if the Hartree-Fock orbitals were used for obtaining the initial local sampling points. Therefore, after some iterations of the θ , φ method, it should be changed to the r , θ , φ method, considering the modification of the sampling points on the r coordinate.

Even for molecules, we may start from the best atomic sampling and use only the θ , φ coordinates to adjust them for molecules, at least in the initial stage. After several cycles, it may be changed to the r , θ , φ pass or even to the local x , y , z pass near the atom to which the electron belongs. We note one thing. For atoms, each electronic state is uniquely related to the electronic configuration. For example, the valence 5S state is uniquely related to the sp^3 configuration. However, in molecules, the ground state of the C_2 molecule at the equilibrium state, for example, is a mixture of the sp^3 and s^2p^2 configurations of the carbon atom. Therefore, for the sampling of the C_2 molecule, for example, the radial distribution of the atomic sampling must also be an appropriate mixture of the two atomic states, if we keep the atomic radial distributions even in molecules. However, if we optimize them in molecules with the r , θ , φ coordinate, then this problem disappears.

In molecules, the above process may be done using the local x , y , z coordinate near the atoms or the local r , θ , φ coordinate of the atom to which the electron belongs. In molecules, the original spherical symmetry for atoms disappears, but from the local atomic concept, the local r , θ , φ coordinate may still be meaningful: inner-shell electrons are still well approximated to be in the spherical orbitals.

It is true that the convergence may be obtained whatever pass coordinate one may use. In the sampling calculations, there are the cases in our experiences where the theory and the actual practice look differently or even contradictory. A reason may lie in the number of the sampling points, N_s : if N_s is too small than necessary, the theory may not work. In most calculations of this report, N_s was 2×10^6 .

C. Possibility of the stationarity principle in the LSE calculations

Here, we consider a possibility of introducing a variational principle and a stationarity principle based on the inherent randomness of the sampling method. In the sampling methodology, a measure of the exactness of the calculated result may be given by the variance or the H-square error given by Eq. (9). Since it is always positive and becomes zero when the result is exact, the variance minimization may be a useful principle in the optimization process. However, in our experiences, the variance itself is not a good measure of the accuracy of the wave function, though it certainly becomes zero when the wave function becomes truly exact. On the other hand, when we know the exact energy E_{exact} for the system under study, the absolute value of the difference $|E(n) - E_{exact}|$ is positive and

becomes zero at the exact situation. Therefore, we may use the following quantity as a variational principle in the sampling method:

$$V(n) = a \cdot \sigma^2(n) + b \cdot |E(n) - E_{exact}|, \quad (17)$$

where n is the iteration number and a and b are the positive parameters. $V(n)$ should be minimum for the result obtained at the best iteration n . Since the variance is not a good measure, the above variational principle is essentially due to the second term. So, this is useful when we know the exact energy like in the calculations of the first-row atoms whose exact energies are estimated from the accurate spectroscopic data,²⁹ but in general cases, we do not know the exact energy. We note that the combination of variance and energy minimization method used in the VMC method^{18–20} is close to the above method.

Thus, in most cases, the above variational method is useless. However, when the results change due to the inherent randomness of the calculational method, like by the randomness in the LMn process explained above, we propose a “stationarity” principle as expressed by the minimization of the quantity defined by

$$S(n) = a \cdot \sigma^2(n) + b \cdot \overline{\sigma^2(n)} + c \cdot |\sigma^2(n) - \sigma^2(n-1)| + d \cdot \overline{E(n)} + e \cdot |E(n) - E(n-1)|, \quad (18)$$

where $S(n)$, which is always positive or zero when we get the exact result, represents the stationarity measure at the iteration cycle n . This equation is based on the fact that both variance and energy become stationary at the optimal position. At the minimum, the first derivative against the variation must also be zero. Then, $S(n)$ should be minimum for the result obtained at the best iteration n . For the first variance term, the reasoning is the same as above. The quantity with the bar above is the standard deviation that is positive by definition. The second term is zero when the variance is constant at the last five sampling steps of the n th iteration. The third term is zero when the variance is again constant at the $(n-1)$ th and n th iterations. These two terms represent the stationarity principle of the variance at the optimal position. The last two terms represent the similar behavior of the energy. At the variational minimum, the energy change caused by the small random fluctuations should be zero. This stationarity of the energy is complementary to the stationarity of the variance. It is true that if the wave function is exact, the SE must be satisfied at any sampling points so that all the terms of Eqs. (17) and (18) should be zero. We examined this idea using the limited number of molecular calculations reported in this paper. It should be examined for larger number of molecules.

D. Possibility of the averaging method and the accumulation method

Actual calculations of the FC-LSE calculations proceed as follows. We first produce N_s sampling points by the local sampling method, referring to the electron density distributions in atoms and molecules obtained by quantum chemical calculations. The first iteration is done using the local sampling points. The succeeding steps are to adjust the sampling points to fit the many-electron distribution Γ given by Eq. (10) using

the Metropolis method: each sampling point is examined with the Metropolis algorithm, and if necessary, it is replaced with a new sampling point. In each cycle of the iteration, we use the sampling points produced by the last step and calculate the energy and the wave function at each increment of the $N_s/10$ sampling points. One cycle of the iteration step finishes when we reach the N_s sampling points. When the self-consistent cycles get some stability after several Metropolis steps, there occurs a choice: one is to continue the same process, but we start averaging the calculated energy or other quantities of interest. This method may be called averaging method. The other is to start accumulations of the **H** and **S** matrices to get some continuity, which is referred to as the accumulation method.

First, we explain the averaging method, which is used popularly in the sampling-type methodologies. If the fluctuations of the sampling method come from the inherent randomness, the behavior would be the oscillation about the definite value. If this is the case, we would be able to get the definite value simply by taking the average. This averaging must be done when the self-consistent cycles get some stability after several Metropolis steps. Though this method is simple, we can get fairly good results. We note that with this averaging method, we cannot get the unique wave function: though we can make an average of the calculated energy values, it is difficult to take an average of the calculated wave functions. This is a demerit of this method, though we may use the wave function close to the average value.

Next, we explain the accumulation method. At the beginning of the iterations, both wave functions and sampling points may not be good. So, their information must be thrown out. But from some steps after reaching a stability, we may accumulate the **H** and **S** matrices. There are two reasons. One is the similarity of this method to increase the number of the sampling points, which merits the accuracy of the calculations. Second is that by accumulating them, the result of each diagonalization becomes more continuous than otherwise. With the accumulation method, we can reach the convergence by continuing the calculations: we can get both the exact energy and wave function from the converged results. However, we note that the accumulation method must be started only after the iteration process reaches a steady state.

III. SOLVING THE SCHRÖDINGER EQUATIONS OF THE FIRST-ROW ATOMS

We now apply the methods explained above to solving the SE's of the first-row atoms. We limited our calculations here only to the ground state of the symmetry. We did not calculate the excited states of the same symmetry. Therefore, we used only one initial function for the ground state for all the first-row atoms. We employed the LM1 method and N_s was 2×10^6 . At each $N_s/10$ sampling points, we calculated the **H** and **S** matrices, diagonalized, and recorded the calculated wave function, energy, and H-square error. For the energy and the H-square error, the average value and the standard deviation from the average value were recorded for the results of the last five diagonalizations.

A. Results of the LM1 method applied to all first-row atoms

The electronic structure of the first-row atom may be written as

$$(1s)^2(2s)^{1-2}(2p_x)^{0-2}(2p_y)^{0-2}(2p_z)^{0-2}. \quad (19)$$

We studied here the ground state of each atom. We calculated the $^2P(s^2p)$ and $^4P(sp^2)$ states of the boron atom and the $^3P(s^2p^2)$ and $^5S(sp^3)$ states of carbon atom for their special importance in their chemistries. The initial function is written correspondingly to the electronic configuration given above. For example, for the nitrogen atom, it is written as

$$\phi_0 = A[(1s)^2(2s)^2 2p_x 2p_y 2p_z] \alpha \beta \alpha \beta \alpha \alpha \alpha. \quad (20)$$

It is easy to write the initial function for each state of the first-row atom, referring to the electronic configuration given by Eq. (19). We used Slater orbitals of the single-zeta level as $1s = \exp(-\alpha_{1s}r)$, $2s = r \exp(-\alpha_{2s}r)$, and $2p_{(x,y,z)} = (x, y, z) \exp(-\alpha_{1s}r)$. For the 2s orbital, an additional orbital, $\exp(-\alpha_{2s}r)$, was used with the same exponent, but the cf's generated therefrom were limited to only order 1. For the inner cores and the doubly occupied orbitals, we considered the in-out correlations,¹³ and for this reason, we optimized the orbital exponents of all the orbitals for the initial functions. For the N, O, and F atoms, the in-out correlations are considered for the 1s, 2s, and closed-2p orbitals. The optimized values are summarized in Table I.

Now, we apply the FC theory to the initial functions of the first-row atoms like the ϕ_0 given by Eq. (20) for the nitrogen atom and generate the cf's which are generally written as

$$\{\phi_I\} = \phi_0, r_i \phi_0, r_{ij} \phi_0, r_j r_i \phi_0, r_k r_{ij} \phi_0, r_{kl} r_{ij} \phi_0, \dots, \quad (21)$$

to the second order. For the N, O, and F atoms, in addition to the in-out correlations for all doubly occupied orbitals, all possible r_{ij} terms between 2s-2s, 2s-2p, and 2p-2p electrons were included. Therefore, the number of their cf's became large compared to the other smaller atoms since the number of electrons belonging to these orbitals is large for these atoms. In addition, some additional higher-order functions with respect to r_i and r_{ij} were added.

With the use of these cf's, the FC wave function is written as Eq. (1). In the LM1 calculations, we used a simple x, y, z method. For the first-row atoms, the estimated exact energies are known from the literatures³⁰⁻³³ and the spectroscopic experiments.²⁹ Therefore, after the stabilization, the best theoretical energy was selected by the variational method given by Eq. (17) with $a = 0$. Table II shows the summary of the results: these results are partially the same as those reported already for the IMS Computer Center Reports.³⁴

Table II shows that the energies calculated by the present FC theory differ from the estimated exact energies²⁹⁻³³ by less than one kcal/mol for all the first low atoms: the chemical accuracy was achieved. Here and below, the boldface value shows such a case. This is a necessary condition that the present method is useful as an accurate theory for chemistry: with these data, we can predict the dissociation energies and the heats of formations of molecules, for example, in chemical accuracy. Table II shows also the standard deviations of the calculated energies: they were calculated from the energies

TABLE I. Optimized exponents of the single Slater orbitals in the initial functions of the first-row atoms with including the in-out correlations for the doubly occupied orbitals.

Atom, state	No. of electrons ^a	Orbital exponents							
		$\alpha_{1s}^{(in)}$	$\alpha_{1s}^{(out)}$	$\alpha_{2s}^{(in)}$	$\alpha_{2s}^{(out)}$	α_{2s}	$\alpha_{2p}^{(in)}$	$\alpha_{2p}^{(out)}$	α_{2p}
Li, ² S(s)	3	3.2990	2.0674			0.6390			
Be, ¹ S(s ²)	4	4.3981	2.9531	1.1058	0.8057				
B, ² P(s ² p)	5	5.4816	3.8554	1.4703	1.1021				1.2189
B, ⁴ P(sp ²) ^b	5	4.6760	4.6754			1.3276			1.2385
C, ³ P(s ² p ²)	6	6.5581	4.7627	1.8278	1.3826				1.5747
C, ⁵ S(sp ³)	6	6.5585	4.7685			1.6626			1.5847
N, ⁴ S(s ² p ³)	7	7.6292	5.6744	2.1815	1.6572				1.9230
O, ³ P(s ² p ⁴)	8	8.6952	6.5862	2.5424	1.9515		2.8803	1.4376	2.2910
F, ² P(s ² p ⁵)	9	9.7597	7.4989	2.9004	2.2369		3.3423	1.6988	2.6447

^aNumber of electrons.^bOptimized values for the 1s in and out orbitals were almost identical.

of the last five diagonalizations of the final LM1 step using $16\text{-}20 \times 10^5$ sampling points. The standard deviations are all far below kcal/mol, showing the reliability of the calculated results.

Some reference calculations are cited on the right-hand side of Table II: the values shown are the differences in kcal/mol from the reference estimated exact energies. The first column shows the Diffusion Monte Carlo (DMC) results due to Buendia *et al.*:³⁵ they do not reach the chemical accuracy, while the DMC calculations due to Brown *et al.*:³⁶ are more accurate, though again the results for N to F do not reach the chemical accuracy. In the last column, we refer to the R12/F12 calculations due to Noga *et al.*:³⁷ who used quite extensive bases like 19s14p8d6f4g3h and obtained the results

of the chemical accuracy. The present results give stably the chemical accuracy for all the first-row atoms with less than 1100 complement functions at most.

B. Averaging and accumulation methods applied to C(sp³) and O(s²p⁴)

We show here the results of the averaging and accumulation methods applied to the carbon ⁵S(sp³) state and the oxygen ³P(s²p⁴) state. The initial functions and the cf's are the same as described above. The number of cf's was 187 for C ⁵S(sp³) and 662 for O ³P(s²p⁴). For the local sampling, the radial distributions were generated according to the densities of the Hartree-Fock orbitals with the McLean-Yoshimine Slater basis set,²⁸ while the angular distributions were produced in

TABLE II. FC-CFT with LSE-LM1 method applied to the first-row atoms.

Atom, state	No. of electrons ^a	FC-CFT with LSE-LM1 ^{b,c}					Reference energy ΔE (kcal/mol)			
		Dimension ^d	H-square error (a.u.)	Energy (a.u.)		ΔE (kcal/mol) ^e	Estimated exact energy (a.u.)	Buendia DMC ^f	Brown DMC ^g	Noga R12/F12 ^h
				Std. dev.						
Li, ² S(s)	3	25	0.039 975	-7.477 772	$\pm 0.000\ 023$	0.181	-7.478 060 ⁱ	0.013	0.001	
Be, ¹ S(s ²)	4	105	0.118 825	-14.666 436	$\pm 0.000\ 069$	0.577	-14.667 356 ^j	6.373	0.023	
B, ² P(s ² p)	5	203	0.347 766	-24.653 734	$\pm 0.000\ 103$	0.083	-24.653 866 ^k	8.827	0.186	
B, ⁴ P(sp ²) ^a	5	109	0.493 243	-24.522 622	$\pm 0.000\ 050$	0.014	-24.522 6 ^l			
C, ³ P(s ² p ²)	6	236	0.924 209	-37.845 004	$\pm 0.000\ 282$	-0.002	-37.845 0 ^m	9.726	0.722	0.418
C, ⁵ S(sp ³)	6	187	0.972 810	-37.690 998	$\pm 0.000\ 099$	0.001	-37.691 ⁿ			
N, ⁴ S(s ² p ³)	7	396	2.005 442	-54.588 954	$\pm 0.000\ 103$	0.154	-54.589 2 ^m	8.471	1.192	0.357
O, ³ P(s ² p ⁴)	8	662	3.332 498	-75.067 207	$\pm 0.000\ 087$	0.058	-75.067 3 ^m	9.287	3.514	0.390
F, ² P(s ² p ⁵)	9	1069	4.445 421	-99.733 637	$\pm 0.000\ 476$	0.102	-99.733 8 ^m	10.668	4.016	0.217

^aNumber of electrons.^bOptimal results selected by the variational method (V).^cAveraged values of the five results at the sampling: 16×10^5 to 20×10^5 and their standard deviations (Std. dev.).^dDimension (number of cf's).^eEnergy difference between the energies of the FC-CFT with LSE-LM1 method and estimated exact value. When it is smaller than 1 kcal/mol, it is written by boldface.^fReference 35.^gReference 36.^hReference 37.ⁱReference 31.^jReference 32.^kReference 33.^lEstimated exact energy of ²B(s²p)³³ + experimental excitation energy of ⁴B(sp²) from the atomic spectra database.²⁹^mReference 30.ⁿEstimated exact energy of ³C(s²p²)³⁰ + experimental excitation energy of ⁵C(sp³) from the atomic spectra database.²⁹

TABLE III. Converging process of the FC-CFT calculations with LSE-LM5 method for the $^5S(sp^3)$ state of the carbon atom. The results of the averaging and accumulation methods are shown. We adjusted only the θ , φ coordinates of the sampling points fixing the r coordinates to the initial radial local sampling points obtained from the Hartree-Fock orbital densities of the McLean-Yoshimine basis set.

Iteration ^a	LM5 process			Accumulation process			
	Energy (a.u.) ^b		ΔE (kcal/mol) ^c	Energy (a.u.) ^b		ΔE (kcal/mol) ^c	
	Std. dev.		Averaging ^d	Std. dev.			
Local	-37.300 595	±0.536 840	244.983				

Metropolis							
1	-37.648 647	±0.000 539	26.577				
2	-37.636 722	±0.000 278	34.060				
3	-37.673 314	±0.000 348	11.098				
4	-37.680 145	±0.000 329	6.812				
5	-37.685 102	±0.000 156	3.701				
6	-37.688 870	±0.000 213	1.337				
7	-37.688 802	±0.000 129	1.379				
8	-37.688 994	±0.000 204	1.259				
9	-37.691 028	±0.000 023	-0.018				
10	-37.692 601	±0.000 426	-1.005	-1.005	-37.690 917	±0.000 027	0.052
11	-37.690 656	±0.000 214	0.216	-0.394	-37.689 876	±0.000 030	0.705
12	-37.691 715	±0.000 076	-0.448	-0.412	-37.691 437	±0.000 114	-0.274
13	-37.691 619	±0.000 291	-0.388	-0.406	-37.692 849	±0.000 076	-1.160
14	-37.690 287	±0.000 086	0.448	-0.236	-37.691 060	±0.000 127	-0.038
15	-37.691 460	±0.000 247	-0.289	-0.244	-37.691 213	±0.000 049	-0.133
16	-37.691 567	±0.000 345	-0.356	-0.260	-37.691 059	±0.000 112	-0.037
17	-37.690 729	±0.000 170	0.170	-0.207	-37.691 137	±0.000 268	-0.086
18	-37.689 843	±0.000 158	0.726	-0.103	-37.691 615	±0.000 021	-0.386
19	-37.689 890	±0.000 197	0.696	-0.023	-37.692 022	±0.000 058	-0.641
20	-37.690 824	±0.000 192	0.111	-0.011	-37.691 387	±0.000 038	-0.243
21	-37.691 823	±0.000 220	-0.516	-0.053	-37.691 671	±0.000 030	-0.421
22	-37.689 184	±0.000 325	1.140	0.039	-37.691 449	±0.000 050	-0.282
23	-37.692 296	±0.000 185	-0.813	-0.022	-37.691 515	±0.000 059	-0.323
24	-37.690 269	±0.000 293	0.459	0.010	-37.691 577	±0.000 085	-0.362
25	-37.688 371	±0.000 277	1.650	0.112	-37.691 327	±0.000 017	-0.205
26	-37.690 228	±0.000 125	0.484	0.134	-37.691 045	±0.000 043	-0.028
27	-37.690 876	±0.000 052	0.078	0.131	-37.691 607	±0.000 079	-0.381
28	-37.692 145	±0.000 427	-0.718	0.086	-37.691 638	±0.000 024	-0.400
29	-37.691 446	±0.000 207	-0.280	0.068	-37.691 463	±0.000 061	-0.291
30	-37.690 048	±0.000 109	0.597	0.093	-37.691 060	±0.000 025	-0.038
31	-37.690 648	±0.000 304	0.221	0.099	-37.691 027	±0.000 007	-0.017
32	-37.691 061	±0.000 260	-0.038	0.093	-37.690 899	±0.000 031	0.064
33	-37.691 241	±0.000 135	-0.151	0.083	-37.691 063	±0.000 050	-0.040
34	-37.691 256	±0.000 125	-0.161	0.073	-37.691 241	±0.000 024	-0.151
35	-37.692 007	±0.000 151	-0.632	0.046	-37.691 219	±0.000 023	-0.137
36	-37.690 537	±0.000 094	0.291	0.055	-37.691 077	±0.000 030	-0.048
37	-37.689 374	±0.000 074	1.020	0.090	-37.690 779	±0.000 045	0.138
38	-37.689 142	±0.000 219	1.166	0.127	-37.690 957	±0.000 039	0.027
39	-37.691 597	±0.000 334	-0.375	0.110	-37.691 146	±0.000 023	-0.091
40	-37.691 006	±0.000 250	-0.004	0.106	-37.691 136	±0.000 028	-0.086
41	-37.690 781	±0.000 194	0.137	0.107	-37.691 130	±0.000 019	-0.082
42	-37.690 186	±0.000 437	0.510	0.120	-37.690 963	±0.000 028	0.023
43	-37.692 599	±0.000 166	-1.004	0.087	-37.690 869	±0.000 027	0.082
44	-37.691 899	±0.000 178	-0.564	0.068	-37.690 988	±0.000 030	0.008
45	-37.692 362	±0.000 191	-0.854	0.042	-37.690 991	±0.000 031	0.006
46	-37.691 054	±0.000 164	-0.034	0.040	-37.690 965	±0.000 016	0.022
47	-37.689 024	±0.000 287	1.240	0.072	-37.691 329	±0.000 023	-0.206

TABLE III. (Continued.)

Iteration ^a	LM5 process				Accumulation process			
	Energy (a.u.) ^b		ΔE (kcal/mol) ^c		Energy (a.u.) ^b		ΔE (kcal/mol) ^c	
	Std. dev.		Averaging ^d		Std. dev.			
48	-37.691 860	$\pm 0.000\ 276$	-0.539	0.056	-37.691 077	$\pm 0.000\ 035$	-0.048	
49	-37.693 337	$\pm 0.000\ 244$	-1.467	0.018	-37.691 083	$\pm 0.000\ 039$	-0.052	
50	-37.691 177	$\pm 0.000\ 359$	-0.111	0.015	-37.690 899	$\pm 0.000\ 031$	0.063	
Est. exact energy ^e	-37.691				-37.691			

^aAveraging and accumulation methods start from iteration = 10. The step size parameters for θ and φ coordinates were 10° and 20° , respectively, and M5 calculations were done for each iteration cycle.

^bAveraged values of the five results at the sampling: 16×10^5 to 20×10^5 and their standard deviations (Std. dev.).

^cEnergy difference between the energies of the FC-CFT with the LSE-LM5 method and estimated exact value. When it is smaller than 1 kcal/mol, it is written by boldface.

^dAverage from iteration 10 to iteration n .

^eEstimated exact energy of ${}^3\text{C}(\text{s}^2\text{p}^2)$ ³⁰ + experimental excitation energy of ${}^5\text{C}(\text{sp}^3)$ from the atomic spectra database.²⁹

a purely random manner. Since these radial distribution functions were believed to be accurate, we fixed them to the initial distributions: in the Metropolis step, the walker moved only on the θ, φ coordinates. The step size parameters for θ and φ coordinates were 10° and 20° , respectively, and here M5 calculations were done for each iteration cycle. N_s was again 2×10^6 .

Table III shows the converging processes of the LM5 and accumulation methods in the FC-LSE calculations applied to the ${}^5\text{S}(\text{sp}^3)$ state of the carbon atom. The first row indicated by ‘‘Local’’ shows the result of the initial local sampling points. At this stage, the sampling points do not include the many-electron effects like the antisymmetry principle and the inter-electron correlations. They are incorporated from the next Metropolis step by adjusting only the angular coordinates, θ and φ . We continued the initial stabilization process to iteration = 9, and from the next step, we initiated the averaging and accumulation methods since we could observe the stationarity from the steady decrease of the energy standard deviation and the small changes in the energy values.

From iteration = 10, we examined the averaging and accumulation methods for comparison. Details of the changes in the energy and in its standard deviation are shown in Table III and they are depicted in Fig. 1. The behavior of the LMn process is a random oscillation within about one kcal/mol changes. This deviation range is dependent on the magnitudes

of the applied perturbation: $\theta = 10^\circ$, $\varphi = 20^\circ$, and M5. When we decrease these parameters, the range of deviations should become smaller, but we did not change these parameters in the present calculations.

We can get a remarkable result when we take an average of the energy of the iteration process, i.e., the averaging method. We start this averaging after the 10th cycle of the Metropolis steps, which is the same iteration cycle that the accumulation method starts, and the averaged results for ΔE were shown at the column under ‘‘Averaging.’’ The average energy value differs from the exact energy by less than 1 kcal/mol throughout, and at the 50th cycle, it becomes 0.015 kcal/mol which is very accurate. However, with this method, we cannot get the wave function corresponding to this energy, though we may choose the one whose energy is close to the averaged value.

On the other hand, when the accumulation method is switched on, the behavior changed. The changes in the energy values and in their standard deviation values both become much smaller than those of the iteration process, and the energy converges to the value of $-37.690\ 899$ a.u. at the 50th cycle: the energy difference from the known exact energy is only 0.063 kcal/mol. Even with the sampling methodology based on the randomness origin, we could get the convergence of the energy within 1 kcal/mol accuracy for the absolute value as large as -37.691 a.u. = 2.363×10^7 kcal/mol. At the same time, we could get the wave function corresponding

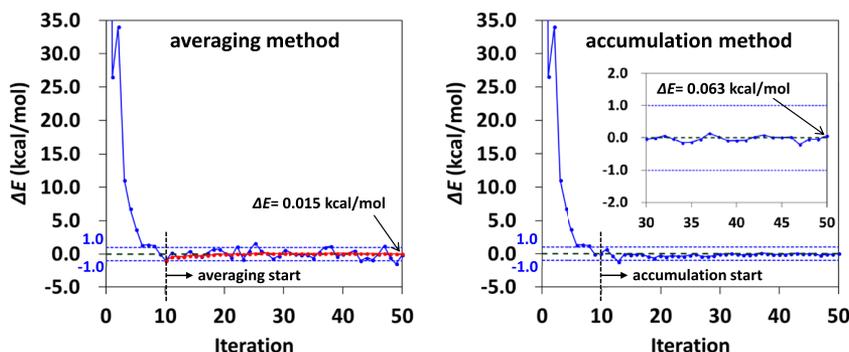


FIG. 1. Converging process of ΔE (kcal/mol) for the ${}^5\text{S}(\text{sp}^3)$ state of the carbon atom by the FC-CFT with the LSE-LM5 method: the averaging (left with red line) and accumulation (right) methods with adjusting only θ, φ coordinates without changing the initial radial distributions. The averaging and accumulation start from iteration 10. See Table III for more details.

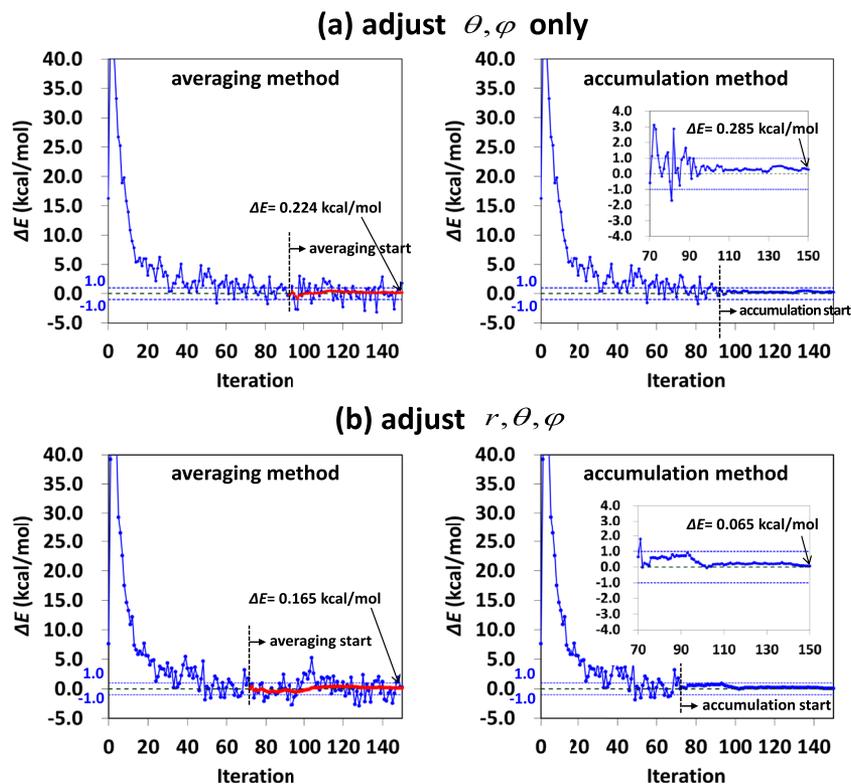


FIG. 2. Converging process of ΔE (kcal/mol) for the ground state of the oxygen atom by the FC-CFT with the LSE-LM5 method; the averaging (left with red line) and accumulation (right) methods are shown. (a) Results by adjusting only θ , φ coordinates without changing the initial radial distributions. The averaging and accumulation start from iteration 92. (b) Results by adjusting r , θ , φ coordinates with $\eta = 0.00001$ for changing radial distributions. The averaging and accumulation start from iteration 72.

to the converged energy. We can calculate many properties from this wave function. It is noteworthy that the present convergence to the exact value was realized with the random walks within only the angular coordinates θ and φ and without any reoptimization of the initial radial distribution due to the Hartree-Fock orbitals with the McLean-Yoshimine Slater basis set.²⁸

The accumulation method was invented to get the continuity in the sampling-type methodology, though we must switch on it after some convergence behavior is observed in the iteration process. Otherwise, the convergence may be slow. The merit is that we can obtain both the energy and the wave function at the convergence.

We also performed the similar calculations for the $^3P(s^2p^4)$ ground state of the oxygen atom. Figure 2(a) shows the converging processes of the averaging and accumulation method applied to the LM5 iteration process moving only the θ , φ coordinate without changing the initial radial distributions. We continued the initial stabilization process up to iteration = 91, and from the next step, we initiated the averaging and accumulation methods since we could observe the stationarity from the steady decrease of the energy standard deviation and the small changes in the energy values. With the accumulation method, we could get the energy -75.066850 a.u., which was 0.285 kcal/mol higher than the estimated exact energy, -75.0673 a.u.^{29,30} On the other hand, from the averaging method, we get the energy of -75.066943 ± 0.000673 a.u. with the ΔE value of 0.224 kcal/mol, which is satisfactory also.

For oxygen, we also examined the r , θ , φ method with a slight reoptimization of the radial distributions with the parameters of $\eta = 0.00001$ in Eq. (16): other parameters are the

same as above, $\theta = 10^\circ$, $\varphi = 20^\circ$, and M5. Figure 2(b) shows the results: the initial stabilization process was done up to iteration = 71 and, after that, the averaging and the accumulation methods were started. From the averaging method, we obtained the energy -75.067038 ± 0.000615 a.u. with $\Delta E = 0.165$ kcal/mol higher than the estimated exact energy,^{29,30} and with the accumulation method, we obtained the energy -75.067196 a.u. with $\Delta E = 0.065$ kcal/mol. Thus, by slightly reoptimizing the radial distributions, both the energy results and the stability were slightly improved. However, large changes of the radial distributions by the Metropolis method would cause a problem when exactly solving the SE because the distributions may get away from their initial quantum-mechanical distributions that regularly cover from the cusp regions to the dissociation regions. Therefore, we need more experiences about the optimal sets of appropriate parameters for the Metropolis walks.

IV. FC-CFT APPLIED TO SMALL MOLECULES

Next, we apply the FC theory to small molecules. Earlier applications of the FC theory to small molecules were reported in the review paper⁸ and the reports to the computer centers whose computers were used for the calculations.^{34,38,39} In the earlier stage of the calculations, we could not overcome the fluctuations due to the inherent randomness of the sampling points produced. In this paper, we have reported some progresses in overcoming these problems.

In the present calculation, we focus only on the ground state of the molecules and therefore, we did not fully follow the CFT proposed in Paper I.¹³ We considered the locality and transferability concept of the chemical formula but did not

consider well the effects of the ground and excited states of atoms on the electronic structure of molecules. For example, for the carbon atom, the initial functions were constructed using the conventional knowledge of atomic configurations and hybrid orbitals. We considered only the s^2p^2 configuration for the carbon of the CH molecule and only the sp^3 configuration for the carbons of CH_3 , C_2 , $HCCCH$, and H_2CO . This is OK with the FC theory since the purpose is the ground state of these molecules. The FC theory is a very flexible theory and its initial wave function is permissible if it has an overlap with the exact wave function. In this sense, the present calculations are standard as the ground-state calculations.

The initial local sampling points for molecules were constructed using the results of the FC calculations of the corresponding atoms based on the transferability concept. For example, if we calculate a hydrocarbon molecule C_nH_m , we have n carbons and m hydrogens. When we have N_s sampling points for each atom, we prepare n and m different shuffled sets of carbon and hydrogen sampling points, respectively, put them on the center of each atom, and produce N_s sets (instead of N_s^{n+m}) of sampling points by taking the products of the sampling points of each atom. Other choice is to use the fragment sampling method. For example, for acetylene, the fragments may be two CH molecules or C_2 plus two hydrogen atoms: the latter choice was used in the calculations shown below, together with the products of the atomic samplings.

A. FC-CFT study of small molecules using the variational and stationarity principles

We have performed the FC-CFT LM1 calculations for the ground state of nine small molecules. The molecules are LiH (4), BH (6), CH (7), CH_3 (9), OH (9), OH_2 (10), C_2 (12), $HCCCH$ (14), and H_2CO (16), where the number of the electrons is given in the parentheses. In Table IV, we summarize the initial functions used in the present calculations. For LiH, both $^2Li(2s)-H(1s)$ and $^2Li(2p_x)-H(1s)$ configurations were considered. For BH, CH, and OH, $^2B(s^2p)-H(1s)$, $^3C(s^2p^2)-H(1s)$, and $^3O(s^2p^4)-H(1s)$ were employed as ψ_0 . For other carbons, we used only the $^5C(sp^3)$ state. This is because we know that

the $^5C(sp^3)$ state is most important for the bonding of carbon at their equilibrium geometries. For the CH molecule, however, the $^5C(sp^3)$ state does not contribute for the symmetry and therefore the $^3C(s^2p^2)$ state was used. These choices are permissible when we consider the flexible nature of the FC theory, but the use of both configurations of carbons would be a better choice for the initial functions. For the $^5C(sp^3)$ state, we used the popular hybrid orbitals appropriate for each molecule. For C_2 , the nature of the C–C bond is an interesting topic.^{40–44} However, since we used only the sp^3 configuration in the present study, we do not focus on this subject.

Now, we apply the FC theory to the initial functions given in Table IV. We generate the cf's of the FC theory to essentially order 2 as explained in Paper I.¹³ The dimensions of the molecules including the O atom are large in comparison with our current calculations because here we have included rather carefully the r_{ij} terms of the valence electrons as already explained in the atomic section. In Table V, we summarize the results. The calculations were done with the method similar to the one used for the first-row atoms shown in Table II. In the LM1 calculations, the random walks were done using the local x , y , z coordinate around each atom. We have applied both the variational method and the stationarity principle for the sampling method explained in Sec. II C. For the variational method, we set the parameter a in Eq. (17) to be zero because the exact energies of the molecules shown in this table are all available in the literature: after the calculations become stable, we chose the result whose energy is closest to the known exact energy. We have also applied the stationarity principle to examine its potentiality. The optimal values of the fitting parameters of Eq. (18) were $a = 1$, $b = 10$, $c = 10$, $d = 1000$, and $e = 100$. The results due to the stationarity principle were different from the variational results only for the three molecules, LiH, CH_3 , and $HCCCH$, and in Table V, we gave both results of the variational method (denoted as V) and the stationarity principle (denoted as S) for these three molecules. All the results of the variational method and the stationarity principle agreed with the exact energies in the literature to within the chemical accuracy (the differences are less than kcal/mol). The estimated exact energies shown in these tables are from

TABLE IV. Initial functions of the FC-CFT for small molecules.

Molecule	No. of electrons ^a	Initial function ψ_0 ^{b,c}	Atomic states ^d
LiH ^e	4	$A \left[(1s1s')(\sigma(2s^{(Li)}h))^2 \right] + A \left[(1s1s')(\sigma(2p_x^{(Li)}h))^2 \right]$	Li, $^2S(s)$
BH	6	$A \left[(1s1s') \cdot (2s2s') \cdot (\sigma(2p_x h))^2 \right]$	B, $^2P(s^2p)$
CH	7	$A \left[(1s1s') \cdot (2s2s') \cdot (\sigma(2p_x h))^2 (2p_y) \right]$	C, $^3P(s^2p^2)$
CH_3	9	$A \left[(1s1s')(\sigma(Ch_a))^2(\sigma(Ch_b))^2(\sigma(Ch_c))^2(2p_z) \right]$	C, $^5S(sp^3)$
OH	9	$A \left[(1s1s')(2s2s')(\sigma(2p_x h))^2(2p_y 2p_y')(2p_z) \right]$	O, $^3P(s^2p^4)$
H_2O	10	$A \left[(1s1s')(2s2s')(\sigma(Oh_a))^2(\sigma(Oh_b))^2(2p_z 2p_z') \right]$	O, $^3P(s^2p^4)$
C_2	12	$A \left[(1s_a 1s_a')(1s_b 1s_b')(\sigma(C_a C_b))^2(\sigma'(C_a C_b))^2(\pi(C_a C_b))^2(\pi'(C_a C_b))^2 \right]$	C, $^5S(sp^3)$
$HCCCH$	14	$A \left[(1s_a 1s_a')(1s_b 1s_b')(\sigma(h_a C_a))^2(\sigma(C_a C_b))^2(\pi(C_a C_b))^2(\pi'(C_a C_b))^2(\sigma(C_b h_b))^2 \right]$	C, $^5S(sp^3)$
H_2CO	16	$A \left[(1s_C 1s_C')(1s_O 1s_O')(2s_O 2s_O')(\sigma(h_a C))^2(\sigma(h_b C))^2(\sigma(CO))^2(\pi(CO))^2(2p_{yO} 2p_{yO}') \right]$	C, $^5S(sp^3)$, O, $^3P(s^2p^4)$

^aNumber of electrons.

^bFor diatomic molecule, the molecular axis is x and the CH_3 , H_2O , and H_2CO plane is x , y . One CH of CH_3 and CO of H_2CO is on x . For H_2O , two OH bonds are equivalently dealt with.

^cInner core and lone pair were described with the in-out correlation model and spin functions are omitted in the representation.

^dAtomic states used for constructing molecular initial functions.

^eTwo initial functions were used and the cf's were generated only up to order 1.

TABLE V. FC-CFT with the LSE-LM1 method applied to small molecules. Both the variational (V) method and stationarity (S) principle were examined, and when two methods gave different results, two results were shown.

Molecules	No. of electrons ^a	Dim. ^c	FC-CFT with LSE-LM1 ^b					Std. dev. of energy (a.u.)	ΔE (kcal/mol) ^e	Estimated exact	Timing (hour) ^f
			V, S ^d	H-square error	Energy (a.u.)						
LiH	4	78	V	0.253 474	-8.070 440	± 0.000 128	0.067	-8.070 547 3 ^g	0.07 (1.1) ^h		
			S	0.227 638	-8.069 904	± 0.000 110	0.404				
BH	6	346	V, S	0.989 326	-25.283 728	± 0.000 149	0.146	-25.283961 ⁱ	0.3 (7.0)		
CH	7	424	V, S	1.923 754	-38.478 607	± 0.000 261	0.247	-38.479 ^j	0.8 (6.4) ^h		
CH ₃	9	352	V	5.631 570	-39.833 344	± 0.000 321	-0.011	-39.834 6 ^j	0.4 (2.0)		
			S	5.657 196	-39.833 246	± 0.000 507	0.849				
H ₂ O	10	965	V, S	6.225 278	-76.437 295	± 0.000 151	0.066	-76.437 4 ^j	1.8 (21.3)		
C ₂	12	695	V,S	21.697 311	-75.925 958	± 0.000 603	0.340	-75.926 5 ^k	1.4 (14.0)		
HCCH (atomic sampling)	14	821	V, S	12.541 928	-77.336 747	± 0.000 702	-0.908	-77.335 3 ^j	2.1 (18.9)		
HCCH (C ₂ sampling)	14	821	V	11.631 268	-77.334 915	± 0.000 596	0.242	-77.335 3 ^j	2.2 (24.2)		
			S	12.300 341	-77.336 358	± 0.000 994	-0.664				
H ₂ CO	16	1098	V, S	28.508 543	-114.507 471	± 0.001 054	-0.044	-114.507 4 ^j	3.3 (62.7)		

^aNumber of electrons.^bAveraged values of the five results at the sampling: 16×10^5 to 20×10^5 and their standard deviations (Std. dev.).^cDimension (number of cf's).^dOptimal results with the variational method (V) or the stationarity principle (S).^eEnergy difference between the energies of the FC-CFT with the LSE-LM1 method and estimated exact value. When it is smaller than 1 kcal/mol, it is written by boldface.^fTime for one cycle of LM1 calculations and values in the parentheses are the time for total calculations. With 1036 core computers at IMS, Okazaki.^gReference 45.^hWith 112 core computers at IMS, Okazaki.ⁱEstimated with the atomization energy (0 K) from Ref. 47 and the zero-point vibrational energy from NIST Chemistry WebBook.⁴⁶^jEstimated by the atomization energy (0 K) and the zero-point vibrational energy, both obtained from NIST Chemistry WebBook.⁴⁶^kReference 48.

the explicitly correlated Gaussian calculations for LiH by Tung *et al.*,⁴⁵ from those estimated from the experimental values of the atomization energies at 0 K and of the zero-point vibrational energies, both from NIST Chemistry WebBook⁴⁶ for all the molecules except for BH by Curtiss *et al.*^{46,47} and C₂ by Bytautas and Ruedenberg.⁴⁸ In the last column of the tables, we have shown the computer times used for the calculations in hour. The values in the parentheses are the total time in hour used.

The results of Table V for all the molecules calculated here show that the FC-CFT gave the highly accurate results: the SE's of all the molecules are solved stably in the chemical accuracy with the FC-CFT using the LM1 sampling method. This result may be thought to be good news since until recently the SE was thought not to be soluble for ordinary molecules in chemistry.

Let us examine Table V more closely. ΔE is the difference between the calculated FC energy and the known exact energy, and all the results are smaller than 1 kcal/mol, satisfying chemical accuracy. The standard deviation of the calculated total energy of each molecule is smaller than a milli-hartree (0.56 kcal/mol). These facts show the stability of the present theory and calculations. For acetylene, we used two different sampling points, one from the best atomic sampling points and the other from the best C₂ fragment sampling and two H's: the latter gave a better result. In the last column, the computer times used for the calculations are shown: the value is for the one LM1 cycle and the value in the parentheses is total with the 1036-core super-parallel computers at the IMS computer center, Okazaki: the computers were updated recently and the ones we used are the older ones. The FC-CFT-LSE calculations are

suitable to the super-parallel computers since almost 100% parallelism could be realized for the most time-consuming steps. Even for the largest molecule, formaldehyde H₂CO, the time for one LM1 cycle was 3.3 h, which is now shorter with the better computers now available at IMS. In comparison with the calculations of organic molecules of similar size done about three years ago with the TSUBAME computer system at the Tokyo Institute of Technology,³⁸ our present theoretical level seems to be much improved.

We have applied the stationarity principle given by Eq. (18) to all the molecules calculated here, and the results were different only for the three molecules as shown in Table V. Though the variational principle given by Eq. (17) is straightforward, it is meaningless to assume the knowledge of the exact energy, particularly when we study unknown molecules and the courses of chemical reactions. We want to know the method that does not assume the knowledge of the exact energy. Then, we can imagine that when the result corresponds to the extremum, then the first derivative of the quantity against the variation must also be zero. Equation (18) is a mathematical expression of this principle, together with the fact that the variance should be minimum at the best solution. This principle has led to the results of chemical accuracy, as shown in Table V. Since the present test of this method is insufficient, we must examine this principle for a large number of examples.

B. Averaging and accumulation methods applied to CH₃ and acetylene

Finally, we apply the averaging and accumulation methods to the FC-CFT LM1 calculations of CH₃ and HCCH

TABLE VI. Converging process of the FC-CFT calculations with the LSE-LM1 method applied to CH₃. The results of the averaging and accumulation methods are shown.

Iteration ^a	LM1 process			Accumulation process			
	Energy (a.u.) ^b		ΔE (kcal/mol) ^c	Energy ^b (a.u.)			
	Std. dev.	Averaging ^d	Std. dev.	ΔE (kcal/mol) ^e			
Local	-39.853 931	$\pm 0.032\ 051$	-12.130				

Metropolis							
1	-39.866 495	$\pm 0.001\ 894$	-20.014				
2	-39.833 196	$\pm 0.000\ 989$	0.881				
3	-39.833 775	$\pm 0.000\ 765$	0.517				
4	-39.837 521	$\pm 0.000\ 294$	-1.833				
5	-39.836 069	$\pm 0.000\ 690$	-0.922				

6	-39.837 023	$\pm 0.000\ 597$	-1.520	-1.520	-39.837 160	$\pm 0.000\ 594$	-1.607
7	-39.836 136	$\pm 0.000\ 343$	-0.964	-1.242	-39.836 400	$\pm 0.000\ 209$	-1.130
8	-39.836 853	$\pm 0.001\ 271$	-1.414	-1.299	-39.836 724	$\pm 0.000\ 412$	-1.333
9	-39.834 533	$\pm 0.000\ 717$	0.042	-0.964	-39.835 777	$\pm 0.000\ 161$	-0.739
10	-39.834 741	$\pm 0.001\ 034$	-0.089	-0.789	-39.835 475	$\pm 0.000\ 187$	-0.549
11	-39.835 899	$\pm 0.000\ 405$	-0.815	-0.793	-39.835 613	$\pm 0.000\ 096$	-0.636
12	-39.834 391	$\pm 0.001\ 205$	0.131	-0.661	-39.835 306	$\pm 0.000\ 122$	-0.443
13	-39.833 344	$\pm 0.000\ 564$	0.788	-0.480	-39.835 027	$\pm 0.000\ 058$	-0.268
14	-39.834 617	$\pm 0.000\ 321$	-0.011	-0.428	-39.834 926	$\pm 0.000\ 040$	-0.205
15	-39.833 246	$\pm 0.000\ 507$	0.849	-0.300	-39.834 835	$\pm 0.000\ 035$	-0.147
16	-39.832 484	$\pm 0.000\ 513$	1.328	-0.152	-39.834 724	$\pm 0.000\ 037$	-0.078
17	-39.834 621	$\pm 0.000\ 377$	-0.013	-0.141	-39.834 862	$\pm 0.000\ 025$	-0.164
18	-39.835 178	$\pm 0.000\ 477$	-0.363	-0.158	-39.834 981	$\pm 0.000\ 046$	-0.239
19	-39.831 462	$\pm 0.001\ 856$	1.969	-0.006	-39.834 904	$\pm 0.000\ 100$	-0.191
20	-39.834 303	$\pm 0.000\ 693$	0.186	0.007	-39.834 984	$\pm 0.000\ 070$	-0.241
Est. exact energy ^e -39.834 6				-39.834 6			

^aM1 calculations were done for each iteration cycle with $\eta = 0.1$ up to iteration 5 and the averaging and accumulation methods start from iteration = 6 with $\eta = 0.01$.

^bThe averaged values of the five results at the sampling from 16×10^5 to 20×10^5 and their standard deviations.

^cEnergy difference between the energies of the FC-CFT with the LSE-LM1 method and the estimated exact value. When it is smaller than 1 kcal/mol, it is written by boldface.

^dAverage from iteration 6 to iteration n .

^eEstimated from the atomization energy (0 K) and the zero-point vibrational energy, both obtained from NIST Chemistry WebBook.⁴⁶

molecules. The initial functions and the cf's of the FC theory are the same as those shown in Tables IV and V, respectively. Other backgrounds are also the same as explained above.

In Table VI, the results of CH₃ were summarized. After the initial local sampling, 6 steps of the LM1 calculations were made for getting a stability, and from 7th step, both averaging and accumulation calculations were made up to the 20th iteration. Figure 3 illustrates the converging behaviors of both

calculations. For the averaging calculations, we showed the average for the energy difference ΔE from the 6th cycle of the Metropolis steps. The average value of ΔE became less than 1 kcal/mol after the 9th cycle, and at the 20th cycle, it became 0.007 kcal/mol, smaller than 1 kcal/mol. With the accumulation method, the calculated energy itself became steadily close to the known exact energy. After the 9th cycle, the value of ΔE became smaller than 1 kcal/mol, and at the 20th iteration,

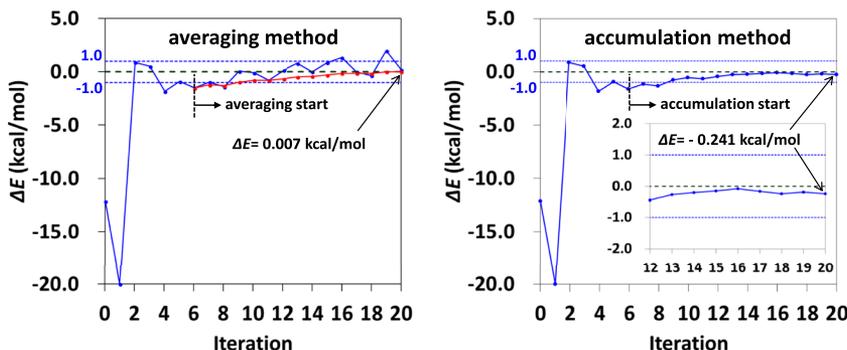


FIG. 3. Converging process of the ΔE value in kcal/mol for CH₃ by the FC-CFT with the LSE-LM1 method: the averaging (left with red line) and accumulation (right) methods starting from iteration 6 are shown. See Table VI for more details.

TABLE VII. Converging process of the FC-CFT calculations with the LSE-LM1 method applied to HCCH. The results of the averaging and accumulation methods are shown.

Iteration ^a	LM1 process		Accumulation process				
	Energy (a.u.) ^b	Std. dev.	ΔE (kcal/mol) ^c	Averaging ^d	Energy ^b (a.u.)	Std. dev.	ΔE (kcal/mol) ^e
Local ^e	-77.277 704	±0.056 252	36.142				

Metropolis							
1	-77.357 056	±0.032 755	-13.652				
2	-77.597 986	±0.006 781	-164.838				
3	-77.474 833	±0.002 548	-87.558				
4	-77.452 884	±0.000 871	-73.785				
5	-77.435 482	±0.000 503	-62.865				
6	-77.411 443	±0.001 429	-47.781				
7	-77.371 175	±0.001 561	-22.512				
8	-77.361 442	±0.001 142	-16.405				
9	-77.357 688	±0.001 408	-14.049				
10	-77.336 123	±0.001 750	-0.516				

11	-77.325 970	±0.000 720	5.855	5.855	-77.331 632	±0.000 349	2.302
12	-77.334 272	±0.000 559	0.645	3.250	-77.332 923	±0.000 212	1.492
13	-77.339 045	±0.000 857	-2.350	1.383	-77.333 449	±0.000 153	1.162
14	-77.340 124	±0.001 663	-3.027	0.281	-77.333 657	±0.000 260	1.031
15	-77.338 819	±0.000 941	-2.208	-0.217	-77.334 655	±0.000 141	0.405
16	-77.336 966	±0.001 247	-1.045	-0.355	-77.335 020	±0.000 202	0.176
17	-77.334 758	±0.001 698	0.340	-0.256	-77.335 399	±0.000 113	-0.062
18	-77.335 914	±0.001 177	-0.385	-0.272	-77.335 331	±0.000 121	-0.019
19	-77.335 028	±0.001 483	0.171	-0.223	-77.335 267	±0.000 091	0.021
20	-77.336 759	±0.001 201	-0.916	-0.292	-77.335 092	±0.000 090	0.131

Est. exact energy ^f	-77.335 3			-77.335 3			

^aM1 calculations were done for each iteration cycle with $\eta = 0.1$ up to iteration 10 and the averaging and accumulation methods start from iteration = 11 with $\eta = 0.01$.

^bAveraged values of the five results at the sampling from 16×10^5 to 20×10^5 and their standard deviations.

^cEnergy difference between the energies of the FC-CFT with the LSE-LM1 method and the estimated exact value. When it is smaller than 1 kcal/mol, it is written by boldface.

^dAverage from iteration 11 to iteration n .

^eSynthesized from the best molecular sampling points of the C₂ molecule and the local sampling points of H atom.

^fEstimated from the atomization energy (0 K) and the zero-point vibrational energy, both obtained from NIST Chemistry WebBook.⁴⁶

it was -0.241 kcal/mol. Examining the iteration results, we conclude that we should have continued the initial stabilization cycle more around 9 and 10 cycles. Even so, the present result is satisfactory, obtaining the energy and the wave function of the chemical accuracy as a converging result of the sampling methodology.

Table VII and Fig. 4 show again the behaviors of the averaging and accumulation methods for the acetylene molecule, HCCH. After the local sampling method, the initial stabilization cycles were done to 10 cycles, and then the averaging and accumulation calculations were done till the 20th cycle. With the averaging method, the average ΔE value was

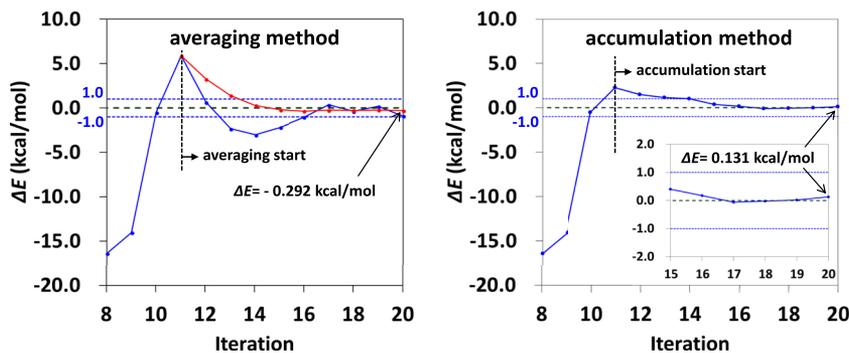


FIG. 4. Converging process of the ΔE value in kcal/mol for HCCH by the FC-CFT with the LSE-LM1 method: the averaging (left with red line) and accumulation (right) methods starting from iteration 11 are shown. See Table VII for more details.

-0.292 kcal/mol, and with the accumulation method, the ΔE value was 0.131 kcal/mol, both at the 20th cycle. Both results were obtained as the converged result without ambiguities. Thus, we could solve the SE of acetylene and get the wave function and energy of chemical accuracy with the FC-CF theory. Referring to Fig. 4, the convergence is smooth for both methods.

V. CONCLUDING REMARKS

In this paper, we have described the practical methods for calculating the accurate solutions of the Schrödinger equation based on the general method of solving the SE of atoms and molecules reported in 2004.⁴ The basic formalisms based on the local concept of the chemical formulas were given in Paper I.¹³ Here, our purpose was to solve the FC-CFT for the ground states of the first-row atoms and small molecules. Since our wave functions include non-integratable functions, we used the LSE method that utilizes the local SE's as the conditions to optimize the parameters involved in the FC wave functions. We developed the practical methods for actual applications of the LSE method: we combined the local sampling method and the Metropolis method in order to adapt the sampling method to the quantum mechanical calculations. The present results of our methodology with super-parallel computers were encouraging. We could obtain the solutions of the Schrödinger equations consistently within chemical accuracy for the first-row atoms and small molecules with reasonable labors.

The sampling methodology has inherent fluctuation behaviors originating from the random statistical natures of sampling processes. However, when the wave function has the exact structure, like the FC ones, and if the number of the parameters included are finite, then the LSE method with the appropriate number of sampling points will definitely give the exact wave function. The hydrogen atom and the two-electron Hooke's atom are such examples.¹¹ So, with the FC theory, the sampling dependences must decrease as we raise the order of the theory, but the computational labor increases rapidly.

Therefore, with the sampling-type methodology, it is favorable if we can have the method that gives the result as the definitely converging result. The averaging method and the accumulation method may be a candidate for such a method. For solving the SE, we think that it is very important to use the theory that has the exact structure to reduce the sampling ambiguity.

We have attempted in this paper to give some different trials to solve the SE for the first-row atoms and several small molecules. At least for these small systems, the calculations could give consistently the results of chemical accuracy in a rather stable manner. This is good news for future studies of solving the SE.

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