



Direct local sampling method for solving the Schrödinger equation with the free complement - local Schrödinger equation theory

Hiroshi Nakatsuji^{*}, Hiroyuki Nakashima

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

ARTICLE INFO

This paper is dedicated to the Late Professor Kozo Kuchitsu

Keywords:

Schrödinger equation
Free complement theory
Local Schrödinger equation theory
Direct local sampling method
Accurate solutions of the Schrödinger equation of atoms and molecules

ABSTRACT

In the free complement (FC) - local Schrödinger equation (LSE) theory for solving the Schrödinger equation, we need an efficient sampling methodology in the LSE step. We propose here the *direct* or *inverse transformation* local sampling method for use in the FC-LSE calculations. This method is mathematically straightforward, deterministic, and fast as a sampling method for solving the Schrödinger equation of atoms and molecules, in comparison with the Metropolis or related method. We showed the capabilities of this method for obtaining the solutions of the Schrödinger equations of the beryllium, carbon (⁵S(sp³) state) and nitrogen atoms and the CH⁺ molecule.

1. Introduction

Recently, sampling-based approaches attracted a lot of attentions for highly accurate electronic structure calculations. A reason is that the variational calculations are difficult when the wave functions include explicitly the inter-electron functions. Examples are the variational, diffusion, and other variants of the Monte Carlo methods [1–9] and the recent neural-network representations such as PauliNet [10] and FermiNet [11]. Interestingly, in the projector or full configuration interaction (CI) quantum Monte Carlo methods [12–14], which are variational without explicit inter-electron functions, they employed the configuration space as a sampling point instead of the real position-space sampling points. Most of these methods employed stochastic simulation methods based on the so-called Metropolis algorithm and related ones [15–18] to generate a set of sampling points that fit well to a given probability density function. Our purpose is, however, to solve the Schrödinger equation as accurately as possible using the sampling-type methodology. Therefore, we want to propose the sampling-points-generation method that is not stochastic, but closely deterministic based straightforwardly on the first-principle.

Now, our central objective is to develop the free complement (FC) - local Schrödinger equation (LSE) theory [19–32]. The FC theory is an exact theory for solving the Schrödinger equation (SE) of atoms and

molecules and was derived from the variational expression of the scaled Schrödinger equation (SSE) [22,23,32]. Because the FC wave function includes the functions that depend explicitly on the inter-electron distance, like the scaled function g_{ij} [32], the integral-based method is difficult to apply. Therefore, we introduced the method that uses the LSE's at many sampling points as the conditions that determine the parameters included in the wave function, which was called LSE method [24,28]. For small atoms and molecules, the sampling points were generated with the local sampling method [24–28,30] in which the sampling points were generated according to the electron density distributions in atoms and molecules. Then, in Ref. [30], we introduced a sampling-point generation scheme referred to as LMn method. In this method, an initial sampling distribution was prepared by the local sampling method. This was the L step. Then, the sampling points were adjusted using the Metropolis algorithm, i.e. M step, trying to make their arrangements closer to the density of the wave function, which were referred to as the LM1, LM2, ... processes. With this method, accurate solutions of the SE were obtained for the first-row atoms and several small organic and inorganic molecules [30]. This LMn method, however, caused several problems for the exact-level accurate calculations: (i) It was often difficult to generate the sampling points where the probability densities were small but certainly necessary, such as around cusp regions at particle coalescences, long-distant asymptotic regions, near-

^{*} Corresponding author.

E-mail address: h.nakatsuji@qcri.or.jp (H. Nakatsuji).

nodal regions, etc. (ii) The continuous quantities, such as potential energy curves, might not be described smoothly due to its strong randomness dependences. (iii) It was also difficult to judge the convergence of the LMn iteration processes due to the random deviations of the Metropolis steps. (iv) Large computational costs were required for the repetitive processes like random-walker processes to reach at an equilibrium after a lot of accept-reject processes. Thus, the Metropolis simulations would require an artisanship by accumulating experiences to obtain accurate results. Mathematically straightforward and deterministic sampling-point generation method with which the resultant sampling points reflect correctly the density distributions of the wave function under consideration is, therefore, necessary especially for the exact-level accurate quantum mechanical methodologies like the FC-LSE theory

2. Local sampling method and its direct or inverse-transformation algorithm

In the LSE method [24], the parameters in the FC wave function are determined using the local SE's $H\psi(r_\mu) = E\psi(r_\mu)$ at given sampling points $\{r_\mu\}$ as conditions. Then, if the sampling points are distributed according to ψ^2 , these local conditions should efficiently work to determine ψ accurately because the sampling-points distribution matches the solution itself. However, ψ is unknown because ψ is indeed the solution we want to calculate. Then, we considered the sampling-point generation scheme where the density distributions of the sampling points were parallel *locally* to those of the electron density distribution of the system. This scheme was referred to as local sampling method and used successfully in the FC-LSE calculations of many small atoms and molecules [24–26].

For example, in the Hartree Fock and related methods, the electron density $\rho(r)$ is written as.

$$\rho(r) = \sum_i n_i \rho_i(r) = \sum_i n_i \varphi_i(r)^* \varphi_i(r) \quad (1)$$

where $\rho_i(r)$ is the orbital density of the molecular orbital φ_i and n_i is the occupation number. In the local sampling method, the sampling points of the electron i belonging to φ_i were so produced that the density of the sampling points at r was proportional to the electron density at r , $\rho_i(r)$.

A purpose of this paper is to show a general, mathematically accurate, and straightforward sampling-point generation method with minimum randomness dependency as possible without repetitive simulations. Recently, we found an integral-based sampling-generation scheme based on the “direct” or “inverse transformation” method

[33–35], whose basic formula is written as.

$$\xi = \int_0^\xi dx = \int_a^\eta dx f(x) \quad (2)$$

This method can be a candidate of such method. Fig. 1 gives an illustration for this formula. ξ is a sampling point in the uniform distribution shown on the left-hand side. The right-hand side shows a distribution given by the normalized function $f(x)$ and η is the sampling point that is produced by the sampling method we want to introduce here. Both sides of this equation are positive and monotonously increasing functions. Therefore, one to one correspondence is guaranteed between ξ and η . The area of $f(x)$ from a to η of the right-side figure just correspond to the area of the uniform distribution from 0 to ξ . Clearly, η is just the sampling point we want to obtain for the distribution function $f(x)$. So, this equation gives a general way of producing the desirable sampling point associated to the distribution function $f(x)$. This method is referred to as inverse transformation method or direct method; if we have an inverse function of $f(x)$ as $f^{-1}(x)$, then $\eta = f^{-1}(\xi)$. The meaning of direct is also self-explanatory. Since this equation realizes what we wanted to do with the local sampling method, we refer to the method based on this equation as direct local sampling (DLS) method or inverse-transformation local sampling (ITLS) method. We found this equation through Tsuda's book in Japanese [33], but it is also written in Devroye's book [34]. This method is referred to also in the book of the field of financial engineering [35].

Thus, the direct or inverse transformation method given by Eq. (2) defines a unique mapping method of the sampling point ξ on the uniform distribution into the sampling point η on the distribution function given by $f(x)$. This method is applicable when the definite integral in the last term of Eq. (2) is possible, except for the rare case that the inverse function $f^{-1}(x)$ is known. As the distribution function $f(x)$, we can use the orbital density function $\rho_i(r)$ and the electron density function $\rho(r)$ as given by Eq. (1), and the N -electron density function $\psi^* \psi$, which is the total density matrix $\Gamma^{(N)}(1, \dots, N)$ defined below. For multi-dimensional case, some general discussions are found in the Devroye's book [34].

Let us consider the generation of the sampling points according to a p -electron density function $f^{(p)}(x_1, x_2, \dots, x_p)$ where x_i denotes i -th electron coordinate. Suppose that we want to produce N_s set of sampling points. Then, first, we set up the set of sampling points on the uniform distribution as $\xi_1^{(\mu)}, \xi_2^{(\mu)}, \dots, \xi_p^{(\mu)}$ where μ runs from 1 to N_s . For electron 1, we integrate $f^{(p)}$ over the coordinates x_2, \dots, x_p , apply Eq. (2), and from $\xi_1^{(\mu)}$, we obtain η_1^μ which we write as x_1^μ . We then insert the number x_1^μ into $f^{(p)}$ and obtain $f^{(p)}(x_1^\mu, x_2, x_3, \dots, x_p)$. Next, we proceed to electron 2. We

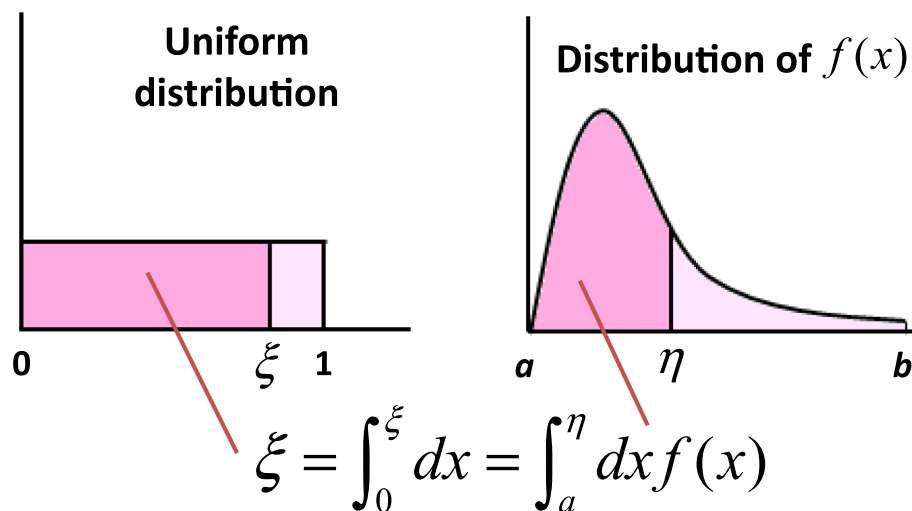


Fig. 1. Illustration of the inverse transformation method for one-dimensional density function $f(x)$. The deep-colored area of the left-hand side represents the area of a simple rectangle of the uniform distribution $\xi \in [0, 1]$. The right-hand side represents the integrated area of the function $f(x)$ in the region: $x \in [a, \eta]$ ($a \leq \eta \leq b$). Imposing both sides to be equal as shown by the equation, η is obtained as a desired sampling point obeying the distribution $f(x)$. Thus, a sampling point ξ on a uniform distribution is mapped onto the sampling point η on the distribution given by $f(x)$.

integrate $f^{(p)}(x_1^\mu, x_2, x_3, \dots, x_p)$ over the coordinates x_3, \dots, x_p , apply Eq. (2), obtain from ξ_2^μ, η_2^μ which we write as x_2^μ , and obtain $f^{(p)}(x_1^\mu, x_2^\mu, x_3, \dots, x_p)$. We continue this process up to x_p and obtain the μ -th set of sampling points $x_1^\mu, x_2^\mu, \dots, x_p^\mu$ on the $f^{(p)}$ distribution function. We repeat this calculation till we get N_s set of sampling points. Since x_i is usually a three-dimensional vector, we must repeat actually $3N_s$ times. We will see later in Fig. 2 the effect of inserting the number x_1^μ into $f^{(p)}$ as $f^{(p)}(x_1^\mu, x_2, x_3, \dots, x_p)$ on the electron distributions of x_2, x_3, \dots, x_p in $f^{(p)}(x_1^\mu, x_2, x_3, \dots, x_p)$. Such exclusion effect is actually very important in the sampling point generation steps.

Here, it would be useful to define the k -th order density matrix $\Gamma^{(k)}(1, \dots, k)$ [36,37] by.

$$\Gamma^{(k)}(1, \dots, k) = \int \psi^*(1, \dots, k, k+1, \dots, N) \psi(1, \dots, k, k+1, \dots, N) dx_{k+1} \dots dx_N \quad (3)$$

with $1 < k < N$, where N is the number of the electrons of the system. These density matrices are N -representable [37], because they are obtained from the total wave function ψ as given by Eq. (3). Actually, the electron density function $\rho(r)$ is $\Gamma^{(1)}$. It is said that in this world, there are only up-to-two physical operators, so that $\Gamma^{(2)}$ (a bit more general one) is enough to describe this world [37]. Therefore, it is wonderful, if we can produce the sampling points that correctly correspond to the exact $\Gamma^{(2)}$. However, from the integrability problem, the application of the direct or inverse transformation method is difficult because, generally, the exact $\Gamma^{(2)}$ includes the variables that are not integrable.

For the integrability condition, the direct or inverse transformation method is used, in the FC theory, only for the initial functions. This method is also useful for the functions obtained from the FC s_{ij} formalism [31], because there all the functions are integrable. It may be a good idea to use the FC s_{ij} functions for the sampling-points generation step. More

generally, this method will be useful for the Hartree-Fock and post-Hartree-Fock wave functions like configuration interaction (CI) and coupled cluster theories. The SAC/SAC-CI wave functions would be useful, since the wave functions are available not only for the ground state, but also for the excited, ionized and electron-attached states of different symmetries. The densities from these post-Hartree-Fock theories are interesting, because they include the effects of electron correlations.

3. Applications of the FC-LSE DLS (direct local sampling) method

We examine here the present direct local sampling (DLS) method in the applications of the FC-LSE calculations, which are performed for the beryllium (Be) atom, the $^5S^0(sp^3)$ state of the carbon (C) atom, the nitrogen (N) atom, and the CH^+ molecule.

3.1. Ground state of the Be atom

We applied the FC-LSE theory to the ground (1S) state of the Be atom using the present DLS method. We used $\Gamma^{(N)}$ as the reference density function: for the four-electron system this does not cause any difficulty. For the ground state, we employed the following two initial functions,

$$\begin{aligned} \psi_0^{(1)} &= A[(1s_{in} 1s_{out})(\alpha\beta - \beta\alpha) \cdot (2s_{in} 2s_{out})(\alpha\beta - \beta\alpha)] \\ \psi_0^{(2)} &= A\left[(1s_{in} 1s_{out})(\alpha\beta - \beta\alpha) \cdot [(2p_x)^2 + (2p_y)^2 + (2p_z)^2] \alpha\beta\right] \end{aligned} \quad (4)$$

where A represents the antisymmetrization operator, for generating the complement functions (cf's) of the FC theory. We considered the so-called in-out correlations for the 1 s and 2 s electrons and the angular correlations through $\psi_0^{(2)}$ using the two-electron excitation, $(2s)^2 \rightarrow (2p)^2$. Similar initial functions were employed in our previous study by the variational FC calculations [38]. Each orbital in Eq. (4) is

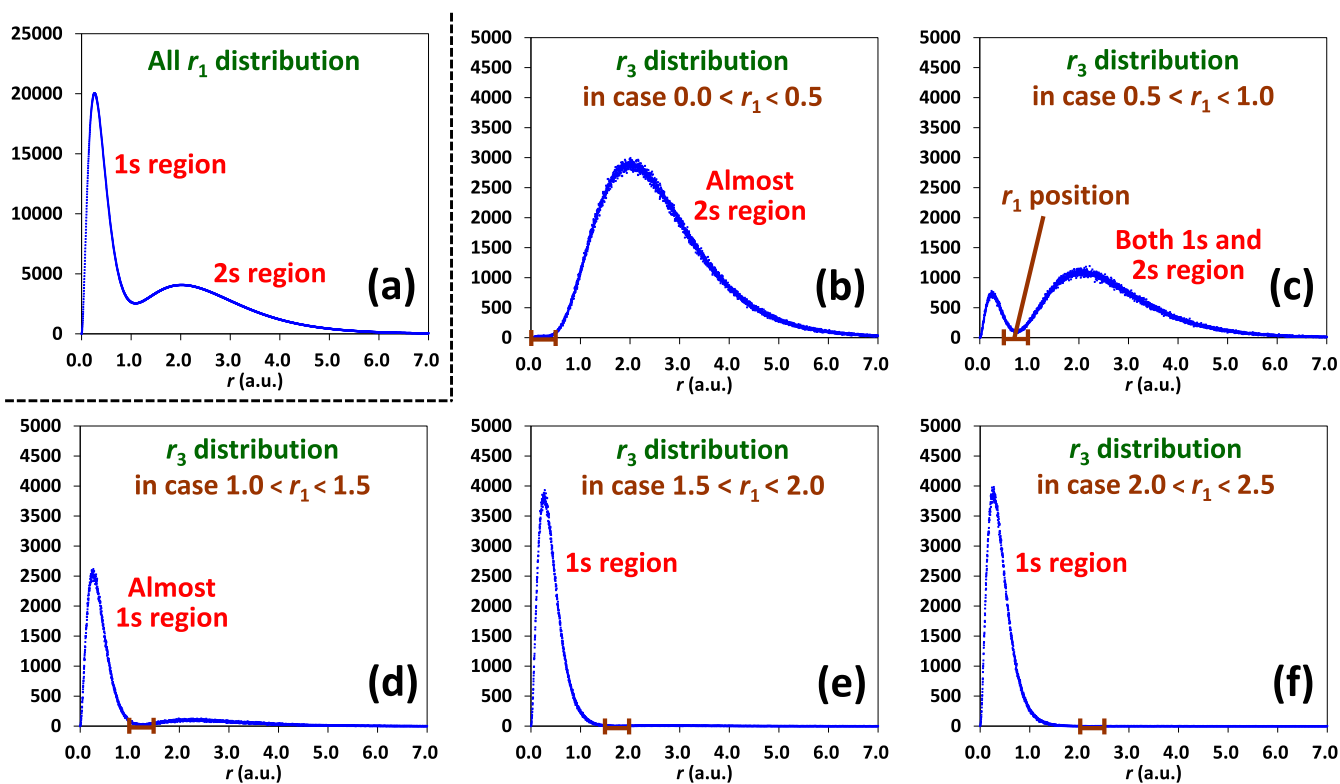


Fig. 2. Distributions of the generated sampling points for a Be atom. (a) represents the radial distribution of the coordinate of electron 1. (b) to (f) show the conditional radial distributions of electron 3 when electron 1 locates in some region denoted by charcoal color. These plots are drawn as the numbers of sampling points are counted in every 0.002 interval.

the Slater orbital given by.

$$\begin{aligned} 1s_{in} &= \exp(-\alpha_{1s,in}r) \\ 1s_{out} &= \exp(-\alpha_{1s,out}r) \\ 2s_{in} &= \text{rexp}(-\alpha_{2s,in}^{(1)}r) + d_{2s,in}^{(0)}\exp(-\alpha_{2s,in}^{(0)}r) \\ 2s_{out} &= \text{rexp}(-\alpha_{2s,out}^{(1)}r) + d_{2s,out}^{(0)}\exp(-\alpha_{2s,out}^{(0)}r) \\ 2p_x &= x\exp(-\alpha_{2p}r), \quad 2p_y = y\exp(-\alpha_{2p}r), \quad 2p_z = z\exp(-\alpha_{2p}r) \end{aligned} \quad (5)$$

where $\alpha_{1s,in}$, $\alpha_{1s,out}$, $\alpha_{2s,in}^{(1)}$, $\alpha_{2s,in}^{(0)}$, $d_{2s,in}^{(0)}$, $\alpha_{2s,out}^{(1)}$, $\alpha_{2s,out}^{(0)}$, $d_{2s,out}^{(0)}$, and α_{2p} were 4.4140, 2.9642, 1.2601, 1.6372, -0.228785 , 0.8281, 4.0054, 0.213761, and 0.9868, respectively. Actually, we employed the spin-free formalism, i.e., α and β spin electrons were separately treated in the antisymmetrization: $A \rightarrow A_\alpha A_\beta$. This is often used in the sampling-type methodology like the quantum Monte Carlo method [1–9] and, even with this formalism, the expectation value of the spin-free operator is unchanged. Here, we assigned electrons 1 and 3 to α spin and electrons 2 and 4 to β spin.

We employed $\Gamma^{(N)} = \psi_0^2$ with $\psi_0 = -0.9511 \psi_0^{(1)} + 0.3089 \psi_0^{(2)}$ in the sampling-points generation DLS step. Fig. 2 shows the distributions of the resultant sampling points. Fig. 2(a) shows the number of the sampled points along the radial coordinate r of electron 1. This distribution corresponds to the electron density function $f^{(1)}(x_1) = \Gamma^{(1)}(x_1|x_1)$ in both 1 s and 2 s regions. On the other hands, Fig. 2(b) to (f) show the conditional radial distributions of electron 3 (belonging to α spin like electron 1) when the electron 1 lies in a special region denoted in each figure. In case (b), electron 1 lies in $0.0 < r_1 < 0.5$, which is almost the 1 s-orbital region, then, electron 3 almost lies in the 2 s-orbital region and does not locate in the region, $0.0 < r_3 < 0.5$. In case (c), electron 1 lies in $0.5 < r_1 < 1.0$, which is a middle area between the 1s- and 2s-regions, then, electron 3 locates in both 1s- and 2s-orbital regions, but avoiding the region $0.5 < r_3 < 1.0$. In case (d), electron 1 lies in $1.0 < r_1 < 1.5$, which is the region where the 2s-orbital region starts, then, the amplitude of electron 3 is almost in the 1 s region. In cases (e) and (f), electron 1 lies in $1.5 < r_1 < 2.0$ and $2.0 < r_1 < 2.5$, respectively, then electron 3 is almost completely in the 1s-orbital region even though the 2s-orbital region is broad, i.e. there was no case that both electrons were in the 2s region. Thus, the generated sampling points reflect the Pauli-hole antisymmetrization effect. Interestingly, such a Pauli exclusion principle works not like point-to-point repulsions or coalescence-exclusive different positions of electrons, but regionals repulsions. Two electrons exist regionally-separated manner, so that they do not collide to each other. This may be different from the classical Coulomb-repulsion concept.

Using the sampling points generated as above, we performed the FC-LSE calculations at the order, $n = 0$ to 5. We employed the scaling functions [22,23,32] given by.

$$g = \sum_{i=1}^N r_i + \sum_{i<j}^N g_{ij} \quad \text{with} \quad (6)$$

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

where Ei denotes exponential integral function and γ_1 and γ_2 are the parameters given in the footnote of Table II of Ref. [32] at $n = 3$. Table 1 summarizes the convergence behaviours of the FC-LSE calculations. As increasing the FC order n , the energy difference from the estimated exact energy [39], ΔE , rapidly reduced toward zero. At $n = 2$ with the dimension of only $M = 108$, ΔE was 0.155 kcal/mol, which already satisfies the chemical accuracy, i.e. less than 1 kcal/mol error. At $n = 5$ with $M = 4635$, ΔE was 0.00464 kcal/mol, almost close to the spectroscopic accuracy. In the FC variational calculations previously performed [38], ΔE was 0.153 kcal/mol at $n = 3$ with $M = 1049$, though the Rydberg configurations were also included in the initial functions. Thus,

Table 1

Convergence of the FC-LSE direct local sampling calculations for the ground state of the Be atom with 10^7 sampling points generated by the $\Gamma^{(N)}$ scheme.

n^a	M^b	H-square error ^c	Energy (a.u.)	ΔE (kcal/mol) ^d
0	2	(variational) ^e	-14.629 417	23.807
1	19	0.355 268	-14.663 577	2.372
2	108	0.026 923 5	-14.667 109	0.155
3	454	0.004 902 2	-14.667 326 6	0.018 8
4	1562	0.001 019 25	-14.667 343 08	0.008 41
5	4635	0.000 341 010	-14.667 349 09	0.004 64
FC variational calculation ^e in Ref. [38] with $n = 3$ and $M = 1049$			-14.667 111 9	0.153
Estimated exact energy			-14.667 356 486	

^a Order of the FC theory.

^b Number of complement functions (Dimension).

^c Defined in Ref. [28].

^d Energy difference from the estimated exact energy [39]. Boldface means satisfying the chemical accuracy, i.e. $\Delta E < 1$ kcal/mol.

^e Variational calculations with analytical integrations.

the present results seemed to be more accurate than the previous variational calculations. A reason would lie in employing the general g_{ij} function [32] given by Eq. (6) instead of r_{ij} in the former variational calculations [38]. The H-square error, which is a good indicator of the exactness [28], also quickly approached to zero. Thus, with the present direct local sampling method, the FC-LSE calculations were stably and accurately performed with the direct sampling generation scheme without any repetitive simulations like those in the Metropolis algorithm.

3.2. $^5S^0(sp^3)$ state of the C atom

Next, we applied the FC-LSE theory to the $^5S^0(sp^3)$ excited state of the C atom again with the $\Gamma^{(N)}$ DLS method. We employed a set of initial functions of the FC theory given by.

$$\psi_0 = A \left[(1s_{in}1s_{out})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2s' \\ 2s \end{pmatrix} \cdot \begin{pmatrix} 2p_x^{(1)}2p_y^{(1)}2p_z^{(1)} \\ 2p_x^{(2)}2p_y^{(2)}2p_z^{(2)} \end{pmatrix} \alpha\alpha\alpha\alpha \right] \quad (7)$$

where the in-out correlation was introduced for 1 s electrons and the double sets of exponents were used for 2 s and 2p electrons. Eq. (7) is abbreviately described by the tensor product form and this includes four kinds of initial functions. The orbitals, Slater orbitals, in Eq. (7) are given by.

$$\begin{aligned} 1s_{in} &= \exp(-\alpha_{1s,in}r) \\ 1s_{out} &= \exp(-\alpha_{1s,out}r) \\ 2s &= \text{rexp}(-\alpha_{2s}^{(1)}r) \\ 2s' &= \exp(-\alpha_{2s}^{(0)}r) \\ 2p_x^{(1)} &= x\exp(-\alpha_{2p}^{(1)}r), \quad 2p_y^{(1)} = y\exp(-\alpha_{2p}^{(1)}r), \quad 2p_z^{(1)} = z\exp(-\alpha_{2p}^{(1)}r) \\ 2p_x^{(2)} &= x\exp(-\alpha_{2p}^{(2)}r), \quad 2p_y^{(2)} = y\exp(-\alpha_{2p}^{(2)}r), \quad 2p_z^{(2)} = z\exp(-\alpha_{2p}^{(2)}r) \end{aligned} \quad (8)$$

where $\alpha_{1s,in}$, $\alpha_{1s,out}$, $\alpha_{2s}^{(1)}$, $\alpha_{2s}^{(0)}$, $\alpha_{2p}^{(1)}$, and $\alpha_{2p}^{(2)}$ were 6.5817, 4.7577, 1.7456, 3.4063, 2.0742 and 1.5125, respectively. 2s represents the major term of the 2s orbital and 2s' represents the 1s-like function without r term in front of exponent. As the inter-electron scaling function g_{ij} , we used single and double type as given by.

$$\begin{aligned} g^{(\text{single})} &= \sum_{i=1}^N r_i + \sum_{i<j}^N g_{ij}^{(1)} \\ g^{(\text{double})} &= \sum_{i=1}^N r_i + \sum_{i<j}^N (g_{ij}^{(1)} + g_{ij}^{(2)}) \end{aligned} \quad (9)$$

Table 2

Convergence of the FC-LSE direct local sampling calculations for the $^5S^o(sp^3)$ state of the C atom with 10^7 sampling points generated by the $\Gamma^{(N)}$ scheme using single and double g_{ij} functions.

n_i^a	n_{ij}^a	M^b	H-square error ^c	Energy (a.u.)	ΔE (kcal/mol) ^d
$g_{ij}^{(single)}: g_{ij}^{(1)} = Ei(-\gamma_1 r_{ij} - \gamma_2) - Ei(-\gamma_2)$					
0	0	4	(variational) ^e	-37.560 729	82.218
1	1	48	1.262 832	-37.639 634	32.704
2	2	372	0.244 706	-37.686 718	3.158
3	2	1620	0.099 099 9	-37.689 968	1.119
4	2	5192	0.026 833 3	-37.691 396	0.223
$g_{ij}^{(double)}: g_{ij}^{(1)} = Ei(-\gamma_1 r_{ij} - \gamma_2) - Ei(-\gamma_2)$ and $g_{ij}^{(2)} = 1 - \exp(-\gamma r_{ij})$					
0	0	4	(variational) ^e	-37.560 729	82.218
1	1	76	1.295 203	-37.649 781	26.336
2	2	680	0.233 291	-37.688 768	1.872
3	2	3076	0.052 409 9	-37.690 968	0.491
4	2	10,020	0.015 720 9	-37.691 612 8	0.086 7
FC s_{ij} -assisted r_{ij} method (variational) in Ref. [41] with $n = 3$ and $M = 4577$				-37.691 409	0.215
Estimated exact energy				-37.691 751	

^a Order of the FC theory with n_i and n_{ij} for r_i and g_{ij} parts, respectively.

^b Number of complement functions (Dimension).

^c Defined in Ref. [28].

^d Energy difference from the estimated exact energy [39]. Boldface means satisfying chemical accuracy, i.e. $\Delta E < 1$ kcal/mol.

^e Variational calculations with analytical integrations.

up to 2) with $g^{(single)}$ and $g^{(double)}$. In the calculations with $g^{(single)}$, the chemical accuracy ($\Delta E < 1$ kcal/mol) to the estimated exact energy [40] was obtained at $n_i = 4$ and $n_{ij} = 2$ with $M = 5192$. When we use $g^{(double)}$, the chemical accuracy was obtained from $n_i = 3$ and $n_{ij} = 2$ with $M = 3076$ as $\Delta E = 0.491$ kcal/mol and at $n_i = 4$ and $n_{ij} = 2$ with $M = 10020$ as $\Delta E = 0.0867$ kcal/mol. Thus, the use of the two different types of g_{ij} functions was shown to be very efficient. Although the integral evaluations in such calculations including different $g_{ij}^{(1)}$ and $g_{ij}^{(2)}$ functions are generally very difficult in the variational calculations, there is no such computational difficulty in the LSE method. In our previous study by the variational calculations of the FC s_{ij} -assisted r_{ij} method [41], ΔE was 0.215 kcal/mol at $n = 3$ with $M = 4577$ though the initial function and the FC generation process were different from the present study. The H-square error also rapidly approached to zero as increasing n . Like the Be case, the FC-LSE DLS calculations were done very smoothly also for the $^5S^o(sp^3)$ state of the C atom.

3.3. Ground state of the N atom

Next, we examine the FC-LSE DLS method for the ground (4S) state of the N atom with the $\Gamma^{(1)}$ sampling scheme, which was faster than the $\Gamma^{(N)}$ sampling scheme. We employed a set of initial functions of the FC theory as given by.

$$\psi_0 = A \left[(1s_{in} 1s_{out})(\alpha\beta - \beta\alpha) \cdot (2s_{in} 2s_{out}) \begin{pmatrix} 2p_x^{(1)} 2p_y^{(1)} 2p_z^{(1)} \\ 2p_x^{(2)} 2p_y^{(2)} 2p_z^{(2)} \end{pmatrix} \begin{pmatrix} (\alpha\beta - \beta\alpha)\alpha\alpha \\ ((\alpha\beta + \beta\alpha)\alpha - 2\alpha\beta)\alpha \\ ((\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta)\alpha - 3\alpha\alpha\beta)\alpha \\ (\alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha + \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta)\alpha \end{pmatrix} \right] \quad (11)$$

with.

$$\begin{aligned} g_{ij}^{(1)} &= Ei(-\gamma_1 r_{ij} - \gamma_2) - Ei(-\gamma_2) \\ g_{ij}^{(2)} &= 1 - \exp(-\gamma r_{ij}). \end{aligned} \quad (10)$$

In $g^{(single)}$, we used a single g_{ij} function Ei. In $g^{(double)}$, we used two sets of g_{ij} functions of Ei and 1-exp types [32], but the cross terms $g_{ij}^{(1)} g_{ij}^{(2)}$ were eliminated from $n = 2$. In the FC process, we decomposed the FC orders as n_i and n_{ij} for r_i and g_{ij} parts in Eq. (9), respectively, and the latter one was set up to $n_{ij} = 2$. The sampling points were generated according to $\Gamma^{(N)} = \psi_0^2$, where ψ_0 was variationally determined and given as $n = 0$ in Table 2.

Table 2 summarizes the results with the FC orders from $n = 0$ to 4 (n_{ij}

where the in-out correlations were introduced for the 1s and 2s electrons and the double set of exponents were used for the 2s and 2p electrons. Further, for the 2s and 2p electrons, we introduced four spin functions, which are already known to efficiently work for accelerating the convergence to the exact solution. The notation of the orbitals in Eq. (11) are same as Eqs. (5) and (8) and we optimized the parameters $\alpha_{1s,in}$, $\alpha_{1s,out}$, $\alpha_{2s,in}^{(1)}$, $\alpha_{2s,in}^{(0)}$, $\alpha_{2s,in}^{(1)}$, $\alpha_{2s,out}^{(1)}$, $\alpha_{2s,out}^{(0)}$, $\alpha_{2s,out}^{(1)}$, $\alpha_{2p}^{(1)}$, and $\alpha_{2p}^{(2)}$ as 7.6767, 5.6493, 2.4137, 4.5826, -0.292745, 1.4876, 1.5620, 0.119322, 2.3609, and 1.7313, respectively. We used a single g function given by Eq. (6). The sampling points were generated using $\Gamma^{(1)}$ for ψ_0 which was variationally determined at $n = 0$.

Table 3 shows the converging process of the FC-LSE DSL calculations. In this process, we employed the so-called complement function (cf)

Table 3

Convergence of the FC-LSE direct local sampling calculations for the ground (4S) state of the N atom with 10^6 sampling points generated by the $\Gamma^{(1)}$ scheme using the cf selection technique.

n^a	cf selection	M^b	H-square error ^c	Energy (a.u.)	ΔE (kcal/mol) ^d
0	(variational)	8		-54.329 849	162.745
1		154	2.906 112	-54.491 462	61.331
new 2	$m_1 = 63 \rightarrow$ cf generation	1166	0.906 324	-54.577 222	7.516
new 3	$m_2 = 119 \rightarrow$ cf generation	3386	0.348 180	-54.587 011	1.373
new 4	$m_3 = 53 \rightarrow$ cf generation	4519	0.205 527	-54.589 066	0.0840
Estimated exact energy				-54.589 2	

^a Order of the FC theory. After $n = 1$, $m_1 = 63$ functions are selected by the cf selection from $M = 154$ functions of $n = 1$ and are used for the cf generation of order 2. New set of this order 2 is defined as 'new 2'. Other 'new n ' are similar.

^b Number of complement functions (Dimension).

^c Defined in Ref. [28].

^d Energy difference from the estimated exact energy [42]. Boldface means satisfying chemical accuracy, i.e. $\Delta E < 1$ kcal/mol.

selection technique that has been used in our previous variational calculations [31,41] to reduce the dimension efficiently without much loss of the accuracy. The cf's at $n = 1$ were ordinarily generated starting from ψ_0 of Eq. (1). After the cf selection applied, 63 functions were selected from the energy-lowering criterion and they were used for the cf gen-

dissociation, but the excited states, $2^1\Sigma^+$ and $3^1\Sigma^+$ states, dissociate into the neutral C atom (1D and 1S , respectively) and H^+ ion, i.e. ionic dissociation. For the FC-LSE calculations, therefore, we constructed the initial functions for these states based on the VB type local picture. We used the covalent-type functions, given by.

$$\begin{aligned}\psi_0^{(1)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2s_{in,C}^{(r)} 2s_{out,C}^{(r)})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{x,C}^{(1)} 1s_H \\ 2p_{x,C}^{(2)} 1s_H \end{pmatrix} (\alpha\beta - \beta\alpha) \right] \\ \psi_0^{(2)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{x,C}^{(1)} 2p_{x,C}^{(2)} \\ 2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \cdot (2s_{out,C}^{(r)} 1s_H)(\alpha\beta - \beta\alpha) \right] \\ \psi_0^{(3)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{x,C}^{(1)} 1s_H \\ 2p_{x,C}^{(2)} 1s_H \end{pmatrix} (\alpha\beta - \beta\alpha) \right]\end{aligned}\quad (12)$$

eration of new $n = 2$ shown in the table. Similar selection method was also performed at higher order n . Then, as increasing the orders, ΔE rapidly approached to zero with avoiding large dimensions. At new $n = 4$ with $M = 4519$, ΔE satisfied the chemical accuracy, even < 0.1 kcal/mol, against the estimated exact energy [42]. The computations were very stable with the $\Gamma^{(1)}$ sampling scheme. Thus, the cf selection technique combined with the FC-LSE DLS method would be effective for practical FC-LSE calculations of larger atoms and molecules.

3.4. Ground ($X^1\Sigma^+$) and excited ($2^1\Sigma^+$ and $3^1\Sigma^+$) states of CH^+ molecule

We next applied the FC-LSE DLS method to the ground ($X^1\Sigma^+$) and

where the molecular axis is x -axis. The notations of the orbitals in Eq. (12) are the same as those in Eqs. (5) and (8) with added atom indices of 'C' or 'H'. The parameters we used are: $\alpha_{1s,in,C}$, $\alpha_{1s,out,C}$, $\alpha_{2s,in,C}^{(1)}$, $\alpha_{2s,in,C}^{(0)}$, $\alpha_{2s,in,C}^{(0)}$, $\alpha_{2s,out,C}^{(1)}$, $\alpha_{2s,out,C}^{(0)}$, $\alpha_{2s,out,C}^{(0)}$, $\alpha_{2p,C}^{(1)}$, $\alpha_{2p,C}^{(2)}$, and $\alpha_{1s,H}$ are 6.5978, 4.7456, 2.0363, 3.7586, -0.248955 , 1.3148, 4.7236, -0.0178340 , 2.0258, 1.1261, and 1.0, respectively. $\psi_0^{(1)}$, $\psi_0^{(2)}$, and $\psi_0^{(3)}$ represent the covalent bonds corresponding to the $C^+(s^2p: ^2P)$ -H, $C^+(sp^2)$ -H, and $C^+(p^3)$ -H configurations, respectively, according to the chemical formula theory [29]. The ionic functions we employed are written as.

$$\begin{aligned}\psi_0^{(4)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2s_{in,C}^{(r)} 2s_{out,C}^{(r)})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{x,C}^{(1)} 2p_{x,C}^{(2)} \\ 2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \right] \\ \psi_0^{(5)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2s_{out,C}^{(r)} 2p_{x,C}^{(1)} \\ 2s_{out,C}^{(r)} 2p_{x,C}^{(2)} \end{pmatrix} (\alpha\beta - \beta\alpha) \right] \\ \psi_0^{(6)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{x,C}^{(1)} 2p_{x,C}^{(2)})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)})(\alpha\beta - \beta\alpha) \right] \\ \psi_0^{(7)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)})(\alpha\beta - \beta\alpha) \cdot (2p_{z,C}^{(1)} 2p_{z,C}^{(2)})(\alpha\beta - \beta\alpha) \right]\end{aligned}\quad (13)$$

excited ($2^1\Sigma^+$ and $3^1\Sigma^+$) states of CH^+ molecule at the equilibrium internuclear distance $R_{eq} = 2.137$ a.u. We used the $\Gamma^{(N)}$ sampling scheme. CH^+ is a simple six-electron molecule and known as an important astrophysical molecule: it was the first molecular ion detected in the interstellar medium [43]. In the $^1\Sigma^+$ symmetry, the ground ($X^1\Sigma^+$) state dissociates to the $C^+(^2P)$ ion and $H(^2S)$ atom, i.e. homopolar

They correspond to $C(s^2p^2: ^1D$ and $^1S)$ - H^+ , $C(sp^3)$ - H^+ , $C(p^4)$ - H^+ and, $C(p^4)$ - H^+ configurations, respectively. To describe the dissociation correctly, we also introduced the other singlet spin functions in addition to Eqs. (12) and (13). They are.

$$\begin{aligned}
\psi_0^{(8)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2s_{in,C}^{(r)} 2s_{out,C}^{(r)}) \begin{pmatrix} 2p_{x,C}^{(1)} 1s_H \\ 2p_{x,C}^{(2)} 1s_H \end{pmatrix} \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right] \\
\psi_0^{(9)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot \begin{pmatrix} 2p_{x,C}^{(1)} 2p_{x,C}^{(2)} \\ 2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)} \end{pmatrix} \begin{pmatrix} 2s_{out,C}^{(r)} 1s_H \\ 2s_{out,C}^{(r)} 1s_H \end{pmatrix} \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right] \\
\psi_0^{(10)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)}) \begin{pmatrix} 2p_{x,C}^{(1)} 1s_H \\ 2p_{x,C}^{(2)} 1s_H \end{pmatrix} \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right] \\
\psi_0^{(11)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2s_{in,C}^{(r)} 2s_{out,C}^{(r)}) \begin{pmatrix} 2p_{x,C}^{(1)} 2p_{x,C}^{(2)} \\ 2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)} \end{pmatrix} \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right] \\
\psi_0^{(12)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)}) \begin{pmatrix} 2s_{out,C}^{(r)} 2p_{x,C}^{(1)} \\ 2s_{out,C}^{(r)} 2p_{x,C}^{(2)} \end{pmatrix} \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right] \\
\psi_0^{(13)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{x,C}^{(1)} 2p_{x,C}^{(2)}) (2p_{y,C}^{(1)} 2p_{y,C}^{(2)} + 2p_{z,C}^{(1)} 2p_{z,C}^{(2)}) \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right] \\
\psi_0^{(14)} &= A \left[(1s_{in,C} 1s_{out,C})(\alpha\beta - \beta\alpha) \cdot (2p_{y,C}^{(1)} 2p_{y,C}^{(2)}) (2p_{z,C}^{(1)} 2p_{z,C}^{(2)}) \begin{pmatrix} \alpha(\alpha\beta\beta - \beta\beta\alpha) \\ -\beta(\alpha\alpha\beta - \beta\alpha\alpha) \end{pmatrix} \right]
\end{aligned} \tag{14}$$

Again, we used the Ei function as an inter-electron scaling function.

$$\begin{aligned}
g &= \sum_{i=1}^N \sum_{A=1}^{N_A} r_{iA} + \sum_{i<j}^N g_{ij} \quad \text{with} \\
g_{ij} &= Ei(-\gamma_1 r_{ij} - \gamma_2) - Ei(-\gamma_2)
\end{aligned} \tag{15}$$

where A denotes nuclear index and N_A is the number of nuclei, i.e. $N_A = 2$ in the present case. In the FC calculation process, we show the FC orders by n_{iA} and n_{ij} , respectively, for the orders of r_{iA} and g_{ij} . For the g function of Eq. (15) for molecules, the so-called inter- r_{iA} and inter- $g_{iA|B}$ functions are generated. r_{iA} , for example, means that the electron i belongs to the local orbital on A but the colliding nucleus is the nucleus B . Such function works for the improvements of the coalescence condition of electron i at nucleus B . It also works like a polarization function. Inter- $g_{iA|B}$ function works also similarly. The functions such as inter- $r_{iA|B}$ and inter- $g_{iA|B}$ were never generated in atomic calculations. These terms are not used in ordinary quantum chemistry because their integrals are generally difficult, but they are easily treated in the LSE sampling theory. They should be important for molecules because they are automatically generated by the FC theory for solving the Schrödinger equation.

Table 4 summarizes the converging process of the FC-LSE DLS calculations. The sampling points were generated using the $\Gamma^{(N)}$ scheme from each term of the initial function given by Eqs. (12) to (14) to efficiently determine the coefficients of the FC wave function having different natures of covalent and ionic terms. To reduce the computational costs, order 3 was only applied to the major initial functions of $\psi_0^{(1)}$, $\psi_0^{(4)}$, $\psi_0^{(8)}$ and $\psi_0^{(11)}$ above for the $X^1\Sigma^+$, $2^1\Sigma^+$, and $3^1\Sigma^+$ states. At $n = 3$ ($n_{iA} = 3$ and $n_{ij} = 2$) with $M = 18156$, ΔE of the $X^1\Sigma^+$ state was 0.427 kcal/mol satisfying the chemical accuracy as absolute solution to the estimated exact energy, which was estimated from the atomic energies of the $C^+(^2P)$ [44] and H atoms and the experimental dissociation energy D_e [45]. In the theoretical computation references by the full CI in 1989 [46] and the multi-reference CI (MRCI) in 2014 [47]

calculations, ΔE were 42.646 and 34.685 kcal/mol, respectively, whose absolute energies were much higher than the estimated exact energy and even higher than our $n = 1$ energy with $M = 536$. The $2^1\Sigma^+$ and $3^1\Sigma^+$ excited states were also computed accurately. The vertical excitation energies to these states from $X^1\Sigma^+$ were 8.218 and 13.382 eV at $n_{iA} = 3$ and $n_{ij} = 2$, respectively, though the corresponding experimental data were unfortunately not available. The data by the Full CI (1989) were slightly larger than our values and the data by the MRCI (2014) were close to our values. Thus, the present DLS method was also effective for molecular calculations. More detailed study of the present CH^+ molecule will be reported soon with the potential energy curves of the ground and excited states.

4. Concluding remarks

We developed the *direct* or *inverse transformation* local sampling method for calculating the accurate solutions of the Schrödinger equations of atoms and molecules based on the FC-LSE theory. We developed the *direct* or *inverse transformation* method to generate the sampling points obeying the distribution function defined by the initial functions of the FC theory. This method is mathematically straightforward, deterministic, and fast in comparison with the Metropolis method. We applied the present FC-LSE direct local sampling method to the calculations of the Be, C ($^5S^0(sp^3)$ state), and N atoms and the CH^+ molecule. The calculations proceeded quite smoothly and more rapidly than the Metropolis-scheme we used before [29] without any repetitive processes. The results were highly accurate for all the systems presently applied. The proposed method will be a standard method in the FC-LSE methodology for solving the Schrödinger equation.

Data availability

The data that support the findings of this study are available within the article.

Table 4
Convergence of the FC-LSE direct local sampling calculations for the ground ($X^1\Sigma^+$) state and the excited ($2^1\Sigma^+$ and $3^1\Sigma^+$) states of the CH^+ molecule at the equilibrium inter-nuclear distance $R_{\text{eq}} = 2.137$ a.u. with 4×10^6 sampling points generated by the $\Gamma^{(N)}$ scheme.

n_A^a	n_{ij}^b	M^c	$X^1\Sigma^+$ state			$2^1\Sigma^+$ state			$3^1\Sigma^+$ state		
			Energy (a.u.)	ΔE (kcal/mol) ^d	H-square error ^e	Energy (a.u.)	Excitation energy (eV)	H-square error ^e	Energy (a.u.)	Excitation energy (eV)	
0	0	24	-37.874 649	133.628	(variational) ^e	-37.558 157	8.612	(variational) ^e	-37.227 992	17.596	
1	1	536	-38.050 739	23.129	2.250 509	-37.733 933	8.621	3.104 273	-37.519 517	14.455	
2	2	6412	-38.083 639	2.484	0.476 537	-37.779 927	8.264	0.723 250	-37.585 964	13.542	
3	2	18156	-38.086 918	0.427	0.182 915	-37.784 907	8.218	0.157 072	-37.595 138	13.382	
Full CI (1989) ^f			-38.019 638	42.646			8.549 2			13.5246	
MRCI (2014) ^g			-38.032 324	34.685			8.198			13.375	
Estimated exact energy of $X^1\Sigma^+$			-38.087 598								

^a Order of the FC theory with n_A and n_{ij} for r_{iA} and g_{ij} parts, respectively.

^b Number of complement functions (Dimension).

^c Defined in Ref. [28].

^d Energy difference from the estimated exact energy, see text. Boldface means satisfying chemical accuracy, i.e. $\Delta E < 1$ kcal/mol.

^e Variational calculations with analytical integrations.

^f Ref. [46].

^g Ref. [47], where we interpolated the result at R_{eq} by a spline fitting from the potential energy data in the reference.

CRediT authorship contribution statement

Hiroshi Nakatsuji: Conceptualization, Methodology, Software, Validation, Formal analysis, Supervision, Writing – original draft, Writing – review & editing. **Hiroiyuki Nakashima:** Methodology, Software, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

We acknowledge the computer centers of the Research Center for Computational Science, Okazaki, Japan for their generous supports and encouragements to our research project (Project: 22-IMS-C012). We also used the computational resources of supercomputer Fugaku provided by the RIKEN Center for Computational Science, Japan and the super-computer system at the Information Initiative Center, Hokkaido University, Sapporo, Japan through the HPCI System Research Project (Project ID: hp210100). This work was also supported by JSPS KAKENHI grant numbers 17H06233, 20K20295, 20K21182, and 22H02045.

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