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Free-complement local-Schrödinger-equation method for solving the Schrödinger equation of atoms and molecules: Basic theories and features

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The free-complement (FC) method is a general method for solving the Schrödinger equation (SE): The produced wave function has the potentially exact structure as the solution of the Schrödinger equation. The variables included are determined either by using the variational principle (FC-VP) or by imposing the local Schrödinger equations (FC-LSE) at the chosen set of the sampling points. The latter method, referred to as the local Schrödinger equation (LSE) method, is integral-free and therefore applicable to any atom and molecule. The purpose of this paper is to formulate the basic theories of the LSE method and explain their basic features. First, we formulate three variants of the LSE method, the AB, HS, and $H^T Q$ methods, and explain their properties. Then, the natures of the LSE methods are clarified in some detail using the simple examples of the hydrogen atom and the Hooke's atom. Finally, the ideas obtained in this study are applied to solving the SE of the helium atom highly accurately with the FC-LSE method. The results are very encouraging: we could get the world's most accurate energy of the helium atom within the sampling-type methodologies, which is comparable to those obtained with the FC-VP method. Thus, the FC-LSE method is an easy and yet a powerful integral-free method for solving the Schrödinger equation of general atoms and molecules. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4909520]

I. INTRODUCTION

Chemistry and biology are governed by the quantum principle described by the Schrödinger equation (SE), relativistic Dirac equation (DE), and the Pauli principle.[1] Therefore, if we can establish a general method of solving these equations in a chemical accuracy and in a reasonable speed, we should be able to predict and even simulate various chemical phenomena. For this reason, much effort has been devoted in quantum science to solving the SE as accurately as possible and significant advancements have been achieved particularly in the recent decade.[2–70] In examining these advancements, it is important to distinguish different approaches based on the criterion of whether the central methodology is *guaranteed* to give the exact solutions of the SE, or *not guaranteed* although it is believed to be highly accurate.

The full configuration interaction (CI) method[2–7] is a *guaranteed method* and has often been considered as if it is an alternative of the SE, partially because the SE was believed not to be solvable. However, the full CI is exact only within the basis set used, which is usually far from complete. To apply to larger systems, many problems, particularly a huge dimensionality problem, must be overcome and several important methodologies have been introduced recently: the density matrix renormalization method,[8–12] the full CI quantum Monte Carlo method,[13,14] and related methods[15,16] have been developed and applied even to the large systems with impressive successes.

In his historical paper on the helium atom, Hylleraas[17] introduced explicit r_{12} terms and obtained very accurate results. This study is the basis of the explicitly correlated method that has been developed recently in the fields of the Hylleraas-CI[18–28] and the R12/F12[29–36] methods. However, based on the above criterion, these methods belong to the category of the *non-guaranteed* method. Although the Hylleraas-CI has a structure similar to the exact one[55] for the very small atoms like helium,[59] this does not apply to general atoms and molecules. Actually, it is difficult to assume the exact structure only with the integrable functions, even for atoms. The R12/F12 methods have achieved dramatic improvements on the basis-set convergence. In particular, the R12/F12 variants of the MP2, CCSD, and CCSD(T) methods have provided fairly accurate results.[29–36] However, these methods use the Gaussian basis sets that do not satisfy the cusp condition and limit to use only the special two-electron terms such as the linear-r_{12} and $\exp(\beta r_{12})$ terms. Further, the molecular orbital (MO) related theories have a common difficulty in describing the potential energy curves along homopolar dissociation reactions.[37]

The Monte Carlo method has a long history of use in accurate quantum chemistry.[38–48] It avoids integrations and uses flexible functions that are suitable for describing electron correlations. The variational Monte Carlo method uses a variational formula within the sampling methodology. The quantum Monte Carlo method[41–46] often introduces explicitly correlated terms in the form of totally symmetric Jastrow functions to avoid computational difficulties due to antisymmetrizations. The diffusion Monte Carlo method suffers from the theoretical nodal problem, although it is currently being improved by

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several new approaches such as the released-node Monte Carlo method.[47,48] In most calculations, the Monte Carlo methods do not assume their basic functions to be guaranteed to converge to the exact wave function.

In our laboratory, we are developing several different routes for solving the SE's of atoms and molecules,[49–70] but they belong to the guaranteed methods in the above criterion. They have been applied to many small atoms and molecules including the recent applications to some organic molecules like ethylene and formaldehyde, which were summarized in the review articles.[67–70]

The most representative general theory for solving the SE is the free complement (FC) theory published in 2004.[54] The FC wave function is generated as follows, using the simplest iterative complement (SIC) formula given by:

$$\psi_n = [1 + C_{n-1} g (H - E_{n-1})] \psi_{n-1}. \tag{1}$$

It was proven[54,55] that this SIC formula leads to the exact wave function at convergence. H is the Hamiltonian of the system and g is the scaling function given by

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

for general molecules without external fields: A denotes nucleus and i, j electrons. In Eq. (1), we start from some approximate wave function ψ_0, which we refer to the initial function. Any approximate wave function is all right as ψ_0 if it has an overlap with the exact wave function. For getting fast convergence, we usually choose valence bond (VB) or MO wave function composed of Slater orbitals. The subsequent iteration is done following Eq. (1): apply gH and g operators analytically, several times (orders). Then, from the results, we pick up all independent analytical functions $\{\phi_i\}$ and express the exact wave function as

$$\psi = \sum_i c_i \phi_i. \tag{3}$$

The basis functions $\{\phi_i\}$ of our theory are referred to as *complement functions* (cf's), because ϕ_i is an element of the complete functions that span the exact wave function ψ as Eq. (3) and the above theory was referred to as the FC theory. If we use a sufficient number of cf's $\{\phi_i\}$, this ψ is guaranteed to become exact. Although ψ is guaranteed to be exact, the coefficient c_i is not determined yet. We called this situation "*potentially exact*": the FC wave function has a potentially exact structure. In the FC theory, the Hamiltonian of the system generates with the initial function ψ_0 the analytical cf's $\{\phi_i\}$ that span its exact wave function. Thus, our theory produces a *unique guaranteed* basis set for each atom or molecule; this is very different from the basis set in the conventional theories. The cf's are composed of the products of not only the one-electron terms but also the two-electron terms since the Hamiltonian is composed of both one- and two-electron terms. We refer to Figure 4 of our review[68] for intuitive understanding.

When all the Hamiltonian and overlap integrals of the cf's $\{\phi_i\}$ are available, we can use the variational principle (VP) to determine the variables $\{c_i\}$ in the FC wave function and highly accurate energies are obtained almost automatically. We call this method FC-variational principle (FC-VP) method.

Actually, this method was proved to give highly accurate energies as shown for the helium atom,[54,59,60] hydrogen molecule ion,[63] hydrogen molecule,[56,70] Hooke's atoms,[55,71,72] and the hydrogen atom under magnetic fields.[65] These numerical results indicate that if the FC-VP method were always possible for any atom or molecule at a moderate speed, then the dream of solving the SE and DE for general chemistry has already been realized. Unfortunately, however, the analytical integrals over the cf's are not available for general atoms and molecules: we called this situation "*integration difficulty*." To overcome this difficulty, we proposed an integral-free approach;[58] since our wave function is potentially exact, the undetermined coefficients $\{c_i\}$ can be calculated by using *only some* necessary but exact conditions. As such conditions, we used the Schrödinger equation itself locally at the sampled points and referred it as the local Schrödinger equation (LSE) method. Because of the simplicity of the method itself, it is applicable to any type of the cf's including even the complex r_{ij} terms.

Thus, by combining the FC method with the LSE method, we obtain a general route for solving the SE. This method is referred to as the "*FC-LSE method*" and has the following features: (i) the FC method is a guaranteed method that converges to the exact wave function— its basis functions called cf's are uniquely defined by the Hamiltonian and the initial function of the system, and (ii) the LSE method is integral-free and therefore applicable to any atoms and molecules. The LSE method itself is popular but becomes powerful, we believe, when it is combined with the guaranteed FC theory. Otherwise, the LSE method itself would not be so accurate. Thus, the FC-LSE theory is a promising method that overcomes the principal problems common to the accurate quantum chemistry theories.

The purpose of this paper is to explain the basic aspects of the FC-LSE theory and particularly to clarify the nature of the sampling-type LSE part of the theory. For this purpose, complex systems were not appropriate and we chose physically very clear small systems like H, He, etc. To apply this method to larger systems, we have to understand clearly the basic physics of our methodology. We note that the FC-LSE method itself has been applied to many atoms and molecules, from small atoms and molecules[58,68] to small organic compounds composed of 16 electrons (ethylene and formaldehyde).[67–70] Further applications to larger molecules are in progress.[70]

In the next section, we will introduce the three variants of the LSE method, the AB, HS, and H^{T}Q methods. The AB method follows the original concept of the LSE method.[58] The HS and H^{T}Q methods are derived from the AB method (the reverse is not true) and mimics the variational principles, the normal and inverse[53] variation principles, respectively. In Sec. III, we explain the nature of the LSE method with the applications to the hydrogen atom and the Hooke's atom.[71,72] For these two systems, the exact solutions of the SE are analytically known. Therefore, the nature of the LSE method is clearly explained without ambiguities.

Finally, in Sec. IV, we apply the ideas on the FC-LSE method obtained here to the accurate calculations of the helium atom. Some years ago, we have published the highly accurate FC-VP calculations for the helium atom[59,60] with analytical integrations.[73] We reported the energy correct up to 41 digits[59] and even 43 digits[60] using the logarithmic function and the Ei

function, respectively. Here, by applying the FC-LSE method, we will show that we can get highly accurate results comparable to the earlier variational ones. It is important to show that not only the VP method, but also the LSE method can give accurate results when combined with the FC method. In the last section, we briefly give the conclusion of the present study.

II. LOCAL SCHRÖDINGER EQUATION METHOD

The exact wave function must satisfy the SE

$$(H - E)\psi = 0. \tag{4}$$

More explicitly, it must satisfy the LSE

$$H\psi(r_\mu) = E\psi(r_\mu) \tag{5}$$

at any coordinate $\{r_\mu\}$ of the system. Further, it must satisfy the differential Schrödinger equation defined by

$$\frac{\partial^n H\psi}{\partial q^n} = E\frac{\partial^n \psi}{\partial q^n}, \tag{6}$$

where $\partial^n/\partial q^n$ implies the n-th order differentiation with respect to a parameter q, which is the coordinate r_μ or some other parameters on which the wave function depends explicitly. From Eq. (5), we obtain

$$E_{loc}(r_\mu) \equiv \frac{H\psi(r_\mu)}{\psi(r_\mu)} = E, \tag{7}$$

where $E_{loc}(r_\mu)$ stands for the local energy. The SE requires the constancy of the local energy over all the coordinates.

Probably, Frost was the first who tried to use the local-energy constancy, as early as in 1942, to calculate the variables included in the wave function.[74] Mohrenstein[75] and Frost *et al.*[76] further applied this idea to the Hylleraas wave functions of the helium atom and to the James-Coolidge wave function of the hydrogen molecule. Now, we know that these choices were very clever, because these wave functions are certainly obtained by the FC formalism starting from the simple initial functions.[54,59] However, since then, this method was forgotten, probably because there were no general methods of producing the potentially exact wave functions of atoms and molecules.

Below, we formulate three variants of the LSE method, AB, HS, and H^TQ methods. Before that, we further want to note that the AB method is related to the collocation method used earlier for solving the SE's for molecular rotation-vibration problems.[77–81] The HS and H^TQ methods would also be similar to the methods used in the sampling-type methodology[38–48] for solving the SE, like the quantum Monte Carlo methods etc.[41–48] However, the point in this paper is that these methods become powerful accurate methods of solving the SE when combined with the FC method of generating the potentially exact wave function. Especially, when we want to solve the SE, we have to handle the functions for which Hamiltonian and overlap integrals are difficult to evaluate and therefore, only the integral-free sampling-type methodologies are useful in this field. However, in this accurate field, we have another important positive fact, that is, when the wave function is potentially exact, its local energy should be nearly constant; this fact helps us to improve the accuracy of our methodology even if it is a sampling type methodology, which is otherwise less clear

and less reliable than the variational principle. The FC-LSE method stands on this fact to get enough accuracy for doing chemistry of general molecules. We will explain below the FC-LSE method in comparison with the variational method and will see an application example of this methodology that gives the result of the accuracy comparable to the variational one.

A. AB method

The original idea of the LSE method started from the AB method.[58] Suppose there are M_c unknown coefficients $\{c_i\}$ in the potentially exact wave function given by Eq. (3). (We assume the case where the exact wave function is written with a finite number of cf's like in the Hooke's atom case. Otherwise, this exactness is within some accuracy, say, the chemical accuracy.) Then, because this expression is a *sufficient* expression for the solution of the SE, we should be able to determine these variables by using M_c *necessary* conditions for the solution of the SE. These M_c necessary conditions must be independent of each other. As such necessary conditions, we proposed to use the local SE at the M_c sampling points,[58] which is the LSE method. So, the number of the sampling points N_s is equal to the number of the variables, $N_s = M_c$. Inserting the FC wave function, Eq. (3) into the LSE equation Eq. (5), we obtain

$$\mathbf{AC} = \mathbf{BCE}, \tag{8}$$

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

$$A_{\mu i} = H\phi_i(r_\mu) \tag{9}$$

and
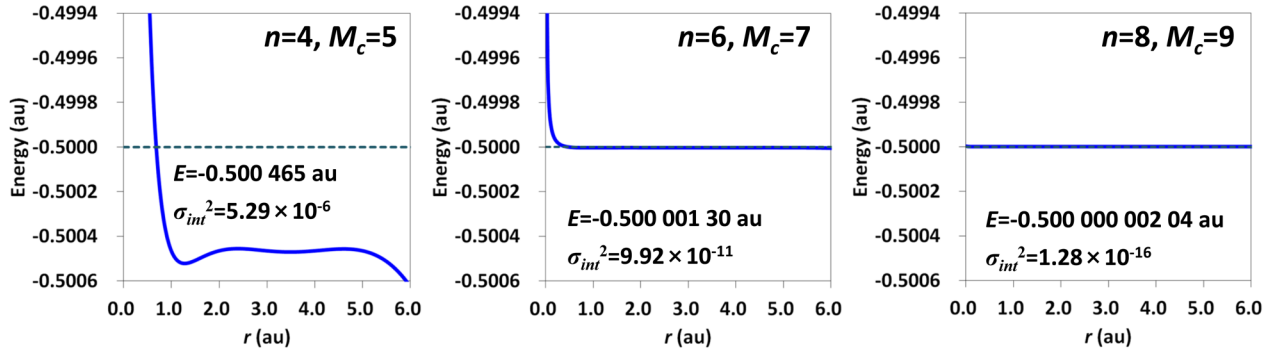
$$B_{\mu i} = \phi_i(r_\mu), \tag{10}$$

respectively. $\mathbf{E}$ is a diagonal matrix whose elements are E_0, $E_1, \ldots$ and $\mathbf{C} = \{\mathbf{c}^0, \mathbf{c}^1, \cdots\}$ represents different sets of coefficients corresponding to different eigenvalues, $E_0, E_1, \ldots$. The suffixes $0, 1, \ldots$ on E and $\mathbf{c}$ denote the ground, first excited, ... states. The coefficient vector $\mathbf{c}^k$ has the elements c_i^k for the k-th state. We refer to this expression of the LSE method as the "*AB method*."

We can utilize the local differential SE (LDSE) given by Eq. (6) as well in addition to the LSE given by Eq. (5). When the aimed property is related to the differentiation of the wave function, mixed use of the LSE and the LDSE would be a good idea. The formulations given below are also valid for such cases. This is true not only for the AB method, but also for the HS and H^TQ methods given below.

The $\mathbf{A}$ and $\mathbf{B}$ matrices are highly non-symmetric, i representing a cf and μ a sampling point. They are square matrices. When they are rectangular, $N_s > M_c$, we actually solve Eq. (8) after transforming it into the HS or H^TQ methods described below. The singular value decomposition for rectangular matrices[82] is related to the HS and H^TQ methods. Therefore, we limit here our AB method to the case where the $\mathbf{A}$ and $\mathbf{B}$ matrices are square matrices, namely, when N_s is "formally" equal to M_c. We use "formally" because we may use a linear combination of the sampling points as a "formal" sampling point; such case will be explained in the subsequent paper of this series.

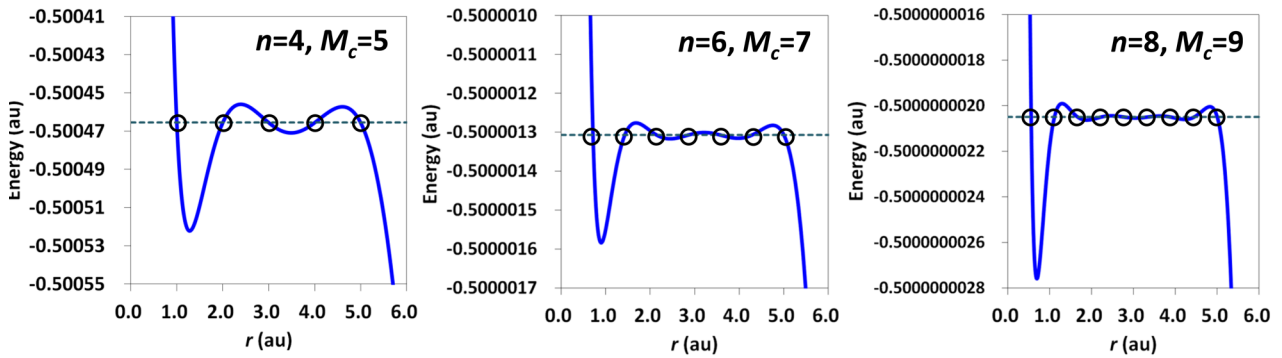## (a) Local energy plots with the AB method: *n*=4, 6, and 8

(b) Enlarged graphs

FIG. 1. (a) Local energy plots of the hydrogen atom calculated by the AB method for $n = 4$, 6, and 8. The calculated energy E and the H-square error with integration σ_{int}^2 are shown in the figures. (b) Enlarged graphs of (a). The circles represent the local energies at the sampled points: $r_\mu = 1, 2, 3, 4, 5$ a.u. for $n = 4$ for instance. The dotted lines in (a) and (b) represent the exact energy -0.5 a.u. and the calculated energy, respectively.

When the AB method is solved, the local energies at the sampled points are all equal to the calculated energy E (see Fig. 1, for example). So, the AB method is equi-local-energy principle. Since Eq. (5) is satisfied at all the sampling points, the H-square error explained below becomes zero with the AB method. Note that this holds only for the set of sampling points that is used to solve Eq. (8). For different sets of sampling points, the H-square error is usually non-zero. If the H-square error is zero for any set of sampling points, then the wave function is exact.

The AB equation, Eq. (8), is just a matrix representation of the LSE; it reflects the physics and the mathematical structure of the SE. As shown below, the HS method is closely related to the variational method and the $H^T Q$ method to the inverse variation method.[53] The HS and $H^T Q$ methods are derived from the AB method, but the converse is not true if $N_s > M_c$. This implies that the AB method should have more information than the other two methods.

B. HS method

We can transform the AB method into another useful expression. Multiplying $\mathbf{B}^T$ from the left of Eq. (8), we obtain

$$\mathbf{HC} = \mathbf{SCE}, \qquad (11)$$

where $\mathbf{H} = \mathbf{B}^T\mathbf{A}$ and $\mathbf{S} = \mathbf{B}^T\mathbf{B}$, both being the square matrices of the dimension M_c. The matrix elements of the H and S matrices are given by

$$H_{ij} = \sum_{\mu}^{N_s} \phi_i(r_\mu) \cdot H \phi_j(r_\mu) \qquad (12)$$

and

$$S_{ij} = \sum_{\mu}^{N_s} \phi_i(r_\mu) \phi_j(r_\mu), \qquad (13)$$

respectively. Note that here the number of the sampling points N_s need not to be equal to the number of the cf's M_c of the FC wave function; the matrices $\mathbf{A}$ and $\mathbf{B}$ can be rectangular and usually we take N_s to be much larger than M_c.

The $\mathbf{S}$ matrix is symmetric and positive semi-definite: the element S_{ij} is analogous to the overlap between the cf's ϕ_i and ϕ_j. Similarly, the $\mathbf{H}$ matrix is analogous to the Hamiltonian matrix, though it is not symmetric here. We refer to this method as the HS method. It is solved by the general diagonalization procedure.[82] Different from the AB method, the HS method has a similarity to the variational method; when the number of the sampling points is infinity covering all the possible spaces, the HS equation reduces to the variational equation applied to the FC wave function. The relation between the local energy and the energy E in Eq. (11) is given by

$$E = \frac{\sum\limits_{\mu} |\psi(r_\mu)|^2 \cdot E_{loc}(r_\mu)}{\sum\limits_{\mu} |\psi(r_\mu)|^2}. \qquad (14)$$

Thus, the energy of the HS method is the weighted average of the local energies at the sampled points with the weight of $|\psi(r_\mu)|^2$ at each sampling point r_μ.

In our FC calculations where analytical integrations are difficult, we have mostly used the HS method with 10^6-10^7 sampling points. In the previous publications of the LSE method,[58,68–70] we calculated small atoms and molecules and the results were fairly good. For Be and LiH, the results of the FC-LSE calculations were much better than the state-of-the-art full CI results.[58]

C. H^{T}Q method

When we multiply $\mathbf{A}^T$ from the left to Eq. (8), we obtain $\mathbf{QC} = \mathbf{H}^T\mathbf{CE}$ which is transformed to

$$\mathbf{H}^T\mathbf{C} = \mathbf{QCE}^{-1}, \tag{15}$$

where $\mathbf{H}^T = \mathbf{A}^T\mathbf{B}$ and $\mathbf{Q} = \mathbf{A}^T\mathbf{A}$. $\mathbf{Q}$ is symmetric but $\mathbf{H}^T$ is not, and both are square. More explicitly,

$$H^T{}_{ij} = \sum_\mu H\phi_i(r_\mu) \cdot \phi_j(r_\mu) \tag{16}$$

and

$$Q_{ij} = \sum_\mu H\phi_i(r_\mu) \cdot H\phi_j(r_\mu). \tag{17}$$

We call this method H^{T}Q method.

The physical meaning of Eq. (15) becomes clear when it is compared with the inverse variational principle.[53] The variational principle for the energy of the inverse Hamiltonian,

$$E^{-1} = \frac{\langle\Psi|H^{-1}|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \tag{18}$$

is given by

$$\langle\Psi|H^{-1} - E^{-1}|\delta\Psi\rangle = 0. \tag{19}$$

Although the inverse Hamiltonian itself is difficult to be handled analytically, we can eliminate it from the variation principle by redefining our variational space by[83]

$$\Psi = H\psi, \tag{20}$$

where Ψ is our formal space but our actual free variation is done for the space of ψ. Then, Eq. (19) is rewritten as

$$\langle\psi|(H - H^2E^{-1})^T|\delta\psi\rangle = 0, \tag{21}$$

which has the form of Eq. (15). We can expect this method to give better result than the HS method since Ψ is one rank higher than ψ in a Kryrov series of space.[52,53,83–86] This usage of the inverse Hamiltonian was first proposed by Hill and Krauthauser[83] in their study of the relativistic variational principle. Note that, in the formulation of the inverse Hamiltonian,[53] we have to shift the Hamiltonian into the positive Hamiltonian by adding some constant energy ε_P. We assume that such an energy shift has already been done for the Hamiltonian given by Eqs. (15) to (21). We note that the result and the convergence speed are dependent on the positive shift parameter ε_P.

The merits of introducing the inverse Hamiltonian were discussed in our previous papers[53] for the non-relativistic case, for the relativistic calculations of solving the Dirac-Coulomb equation,[57] and for the full-CI calculations.[52] We further note that the usage of the variational space defined by Eq. (20) is difficult in ordinary variational calculations because it requires the difficult integrals of H^2. However, in the sampling method, this is easy; after $H\phi_i(r_\mu)$ and $\phi_i(r_\mu)$ are evaluated, the calculations of the $\mathbf{H}^T$ and $\mathbf{Q}$ matrices given by Eqs. (16) and (17) are straightforward.

D. Importance sampling and the AB, HS, and H^{T}Q methods

In the HS and H^{T}Q methods, the concept of *importance sampling* is useful to obtain good results. This concept comes from the similarity to the integral method, like the HS method to the variational principle and the H^{T}Q method to the inverse variation method. We first choose some distribution function ρ that mimics the exact distribution $\psi * \psi$ and produces the set of the sampling points $\{r_\nu\}$ according to the weight (density) function ρ by well-known methods.[38,39,88] Then, we define the sampling weight $\omega(r_\nu)$ by

$$\omega(r_\nu) = \frac{1}{\rho(r_\nu)}. \tag{22}$$

Then, the HS equation given by Eq. (10) becomes, in the importance sampling case to

$$\sum_i c_i \sum_\nu \omega(r_\nu)\phi_j(r_\nu)H\phi_i(r_\nu)$$
$$= E\sum_i c_i \sum_\nu \omega(r_\nu)\phi_j(r_\nu)\phi_i(r_\nu) \tag{23}$$

which is dependent on the sampling weight $\omega(r_\nu)$ because this equation includes the sum over the sampling points ν produced by the importance sampling procedure. The same is true for the H^{T}Q method. Thus, when we use the importance sampling method, we have to modify the HS and H^{T}Q equations like Eq. (23) for the HS method. We note, however, that the AB method does not depend on the weight $\omega(r_\nu)$ because the AB method is not related to the integration method but is related to the SE itself.

E. Energy and H-square error in the LSE method

The H-square error is a significant quantity that defines the exactness of the wave function and is given by

$$\sigma_{int}^2 = \langle\psi|(H - E_{int})^2|\psi\rangle \tag{24}$$

in an integral form with the normalized wave function ψ,[49,87] where the subscript "int" represents "integration" and E_{int} is the energy expectation value given by, $E_{int} = \langle\psi|H|\psi\rangle$. σ_{int}^2 is always positive and becomes zero only for the exact wave function.

In the sampling procedure, the H-square error σ^2 over the sampled points is defined by

$$\sigma^2 = \frac{\sum\limits_{\nu} \omega(r_\nu) \cdot |(H - E)\psi(r_\nu)|^2}{\sum\limits_{\nu} \omega(r_\nu) \cdot |\psi(r_\nu)|^2}$$

$$= \frac{\sum\limits_{i=1}^{M_c} \sum\limits_{j=1}^{M_c} c_i \left[\mathbf{Q}_{ij} - E(\mathbf{H}_{ij} + \mathbf{H}^T{}_{ij}) + E^2 \mathbf{S}_{ij} \right] c_j}{\sum\limits_{i=1}^{M_c} \sum\limits_{j=1}^{M_c} c_i \mathbf{S}_{ij} c_j} \qquad (25)$$

with the energy given by

$$E = \frac{\sum\limits_{\nu} \omega(r_\nu) \cdot \psi(r_\nu) \cdot H\psi(r_\nu)}{\sum\limits_{\nu} \omega(r_\nu) \cdot |\psi(r_\nu)|^2} = \frac{\sum\limits_{i=1}^{M_c} \sum\limits_{j=1}^{M_c} c_i \mathbf{H}_{ij} c_j}{\sum\limits_{i=1}^{M_c} \sum\limits_{j=1}^{M_c} c_i \mathbf{S}_{ij} c_j}. \qquad (26)$$

In the HS method, the eigenvalue E of Eq. (11) is equal to the E of Eq. (26). In the $\mathrm{H^T Q}$ method, however, the eigenvalue E of Eq. (15) is slightly different from the E of Eq. (26), the values shown in this paper are from Eq. (15).

For the exact wave function, σ^2 must be zero with *any* set of the sampling points. However, even if σ^2 is zero with some set of the sampling points, ψ is not necessarily exact. Whereas the evaluation of σ_{int}^2 by the integration method is generally difficult due to the existence of the H^2 operator, σ^2 can be easily evaluated by the sampling method. So, we utilize this quantity to see the accuracy of the wave function.

III. NATURE OF THE LSE METHOD

We investigate here, the nature of the FC-LSE method for the potentially exact wave functions of the hydrogen atom and the Hooke's atom. Since the exact wave function is well known, the nature of the LSE method is clearly demonstrated.

A. Hydrogen atom

A detailed explanation of the FC-VP method was given before[62] for the hydrogen atom. Here, we explain the nature of the FC-LSE method. First, we create the cf's using the Hamiltonian, g function, and the initial wave function, $H = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}$, $g = r$ and $\psi_0 = \exp(-\alpha r)$ ($\alpha = 1.2$), respectively. We perform the iterative complement (IC) calculations to order n and obtain the FC wave function as

$$\psi_n = \sum_{i=1}^{n+1} c_i r^{i-1} \exp(-\alpha r), \qquad (27)$$

where $\phi_i = r^{i-1} \exp(-\alpha r)$. The number of the cf's is $M_c = n + 1$. Now, we calculate the coefficients $\{c_i\}$ using the three different LSE methods, AB, HS, and $\mathrm{H^T Q}$ methods.

1. AB method

In the AB method, the number of the sampling points is the same as the number of the cf's. We chose the order of the FC function to be $n = 3$ to 15 and the sampling points to be equally distributed within $r = 0\text{-}5$ a.u. as $r_\mu = 5\mu/(n + 1)$ ($\mu = 1, 2, \ldots, n + 1$). Table I shows the calculated energy, energy difference ΔE from the exact value, -0.5 a.u., and the H-square error σ^2 (total variance). We note that the H-square error calculated from the AB method is always zero by the definition since the local energies at the sampled points are always the calculated energy due to the equi-local energy principle. Therefore, we also show the H-square error σ_{int}^2 calculated by the *integral* method from the AB wave function obtained here, which is meaningful as a measure of the exactness of the wave function. The bold face in the energy indicates the correct number.

Even with such arbitrarily selected sampling points, the integral value of H-square error σ_{int}^2 smoothly approaches to

TABLE I. Energy convergence for the hydrogen atom calculated by the AB method. Equally distributed sampling points between $r = 0$ and 5 a.u. were used, $r_\mu = 5\mu/(n+1)(\mu = 1, 2, \ldots, n+1)$. The H-square errors calculated by the sampling method σ^2 and by the integration method σ_{int}^2 are also given.

				H-square error	
n[a]	M_c[b]	Energy (a.u.)	ΔE (a.u.)[c]	σ^2	σ_{int}^2
3	4	**−0.4**91 462 5[d]	8.54×10^{-3}	0	1.06×10^{-3}
4	5	**−0.500** 465 52	-4.66×10^{-4}	0	5.29×10^{-6}
5	6	**−0.499** 973 066	2.69×10^{-5}	0	2.77×10^{-8}
6	7	**−0.500 00**1 306 7	-1.31×10^{-6}	0	9.92×10^{-11}
7	8	**−0.499 999** 942 511	5.75×10^{-8}	0	2.81×10^{-13}
8	9	**−0.500 000 00**2 049 4	-2.05×10^{-9}	0	1.28×10^{-15}
9	10	**−0.499 999 999** 910 511	8.95×10^{-11}	0	2.71×10^{-17}
10	11	**−0.500 000 000 000** 743 41	-7.43×10^{-13}	0	8.99×10^{-19}
11	12	**−0.499 999 999 999** 747 07	2.53×10^{-13}	0	3.00×10^{-20}
12	13	**−0.499 999 999 999 9**81 684	1.83×10^{-14}	0	9.85×10^{-22}
13	14	**−0.499 999 999 999 99**7 771 6	2.23×10^{-15}	0	3.19×10^{-23}
14	15	**−0.499 999 999 999 999** 768 57	2.31×10^{-16}	0	1.02×10^{-24}
15	16	**−0.499 999 999 999 999 9**75 482	2.45×10^{-17}	0	3.21×10^{-26}
Exact		−0.5	0	0	0

[a]Order of the FC method.
[b]Number of the cf's.
[c]Difference between the calculated energy and the exact energy, -0.5 a.u.
[d]Throughout this paper, the boldface figure shows the value that is definitely correct.

zero as n increases. The energy also smoothly converges to the exact value as the order n increases. The energy of the AB method can be both higher and lower than the exact energy, but as n increases, the energy is always higher than the exact energy, like in the variational case.

Figure 1(a) shows the plots of the local energy defined by Eq. (7) for $n = 4$, 6, and 8. The local energy at $n = 4$ ($M_c = 5$) is lower than -0.5 a.u., at $n = 6$ ($M_c = 7$) it is much improved and looks to lie on the exact energy line except for the region close to the nucleus, and at $n = 8$ ($M_c = 9$) the local energy lies on the exact line everywhere within 0–5 a.u., though we do not impose any restriction on the wave function to satisfy the electron-nucleus cusp condition. Thus, as the order increases, the wave function certainly approaches the exact one. This behavior is very similar to the one reported previously for the helium atom.[59] Note that this result was obtained with only a few sampling points without doing any integral calculation.

Figure 1(b) is the enlarged graph of Figure 1(a) and shows the confirmation of the *equi-local-energy at the sampled points* in the AB method. The local energy curve crosses the horizontal axis of the calculated energy ($-0.500\,465\,52$ a.u. for $n = 4$, $-0.500\,001\,306\,7$ a.u. for $n = 6$, and $-0.500\,000\,002\,049\,4$ a.u. for $n = 8$) exactly at the sampled points, five times for $n = 4$, seven times for $n = 6$, and nine times for $n = 8$. Note in Figure 1(b) the vertical axis is scaled up as n increases.

From Figure 1(b), one may imagine that the local energy may diverge to minus infinity as r increases, but this is not the

case; the local energy curves converge to the value -0.72 at $r \to \infty$ for all the cases of Figure 1(b). When a single Slater function is used as the initial function, the FC wave function ψ_n given by Eq. (27) is produced. Using this ψ_n, we obtain the asymptotic value of the local energy as

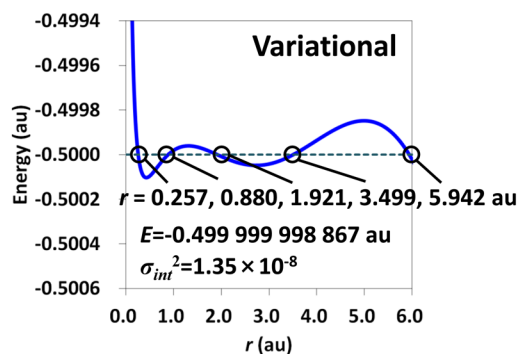$$\lim_{r \to \infty} \frac{H\psi_n}{\psi_n} = \frac{d_m}{c_m} = -\frac{\alpha^2}{2}, \quad (28)$$

where m is the maximum order of r and c_m and d_m are the coefficients of r^m in ψ_n and $H\psi_n$, respectively. Thus, the asymptotic value is finite and depends on the orbital exponent. It is -0.72 when $\alpha = 1.2$, the present case. Of course, it is -0.5 a.u. when $\alpha = 1.0$. In the case of the single Gaussian function in the initial function, the maximum order of r in $H\psi_n$ increases to $m + 2$ due to the differentiation in the kinetic operator, and we obtain

$$\lim_{r \to \infty} \frac{H\psi_n}{\psi_n} = \lim_{r \to \infty} \frac{d_{m+2}r^2}{c_m} = \lim_{r \to \infty} \left(-2\alpha^2 r^2\right) = -\infty. \quad (29)$$

Thus, in the case of the Gaussian function, the local energy diverges at $r \to \infty$.

We next show that the LSE calculation can reproduce the variational result. Figure 2(a) is the plot of the local energy calculated from the variational wave function at $n = 4$ against r. Since the 5-term variational wave function is not exact, its local energy is not flat. From this figure, we can identify the coordinates r_i that give the local energy that is equal to

(a) Local energy plot of the variational wave function
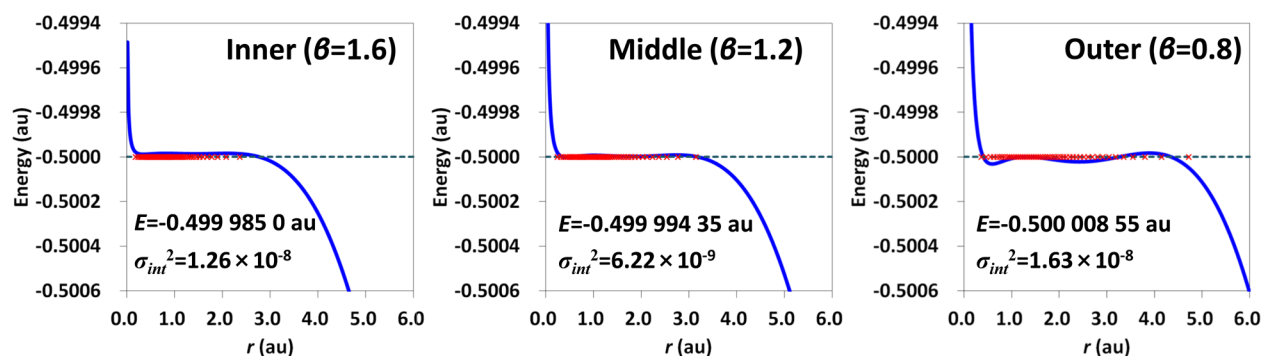

(b) Local energy plots with the HS method

FIG. 2. (a) Local energy plot for the variational wave function of the hydrogen atom for $n = 4$. (b) Local energy plots for the wave functions calculated with the HS method at $n = 4$ by using three different sets of the sampling points shown by the red cross points. The dotted lines represent the exact energy -0.5 a.u. The calculated energy E and the H-square error σ_{int}^2 calculated by the integration method are shown in the figures.

TABLE II. Sampling points for the AB method that reproduce the variational results for the hydrogen atom at $n = 4$ ($M_c = 5$).

	Variational	AB method
Sampling points: r_μ a.u.	∞	0.257, 0.880, 1.921, 3.499, 5.942
	−0.499 999 998 867	**−0.499 999 99**8 867
	−0.113 311 447 870	−0.113 311 447 870
All five eigenvalues	0.158 457 476 265	0.158 457 476 265
	1.064 741 960 618	1.064 741 960 618
	6.590 112 009 854	6.590 112 009 854

the variational energy at r_μ = 0.257, 0.880, 1.921, 3.499, and 5.942 a.u. Then, when we performed the AB calculation using these 5 sampling points, we obtained the LSE energy E_{LSE} = −0.499 999 998 867 a.u. that is completely equal to the variational energy, as shown in Table II. Moreover, the energies of the excited states obtained at the same time all agreed between the variational and this LSE calculations. Though this calculation is possible only after we know the variational results and therefore meaningless in practice, it is nice to know that the LSE playground includes even the variational results.

2. HS method

Next, let us consider the case where the number of the sampling points is larger than the number of the unknown coefficients $\{c_i\}$. In this case, we use the HS or H^{T}Q methods and here we explain the HS method. We prepared 50 sampling points distributed according to the weight function ρ = $|\exp(-\beta r)|^2$ using the local sampling method.[88] Three different sets of the sampling points were tested using β = 1.6, 1.2, and 0.8, which generate the sampling points in the inner, middle (well-spread), and outer regions, respectively. The sampling weight $\omega(r_\mu)$ of Eq. (22) is also used in the calculations. Table III shows the convergence behavior of the

calculated energy to −0.5 and of the H-square errors (σ^2 and σ^2_{int}) to zero as the order increases. The sampling points were generated using β = 1.2. Both the energy and H-square errors rapidly converge to the exact values as in the case of the AB method. σ^2 is not zero in the HS method since the number of the sampling points (necessary conditions) is larger than that of the unknowns. However, it is always smaller than σ^2_{int} and especially small in the higher orders since the number of the sampling points (50 points) is still quite small to mimic the integration. ΔE and σ^2_{int} in the HS method are slightly better than those in the AB method at small orders up to $n = 8$, but those in the AB method become better than those in the HS method at higher orders. Thus, the AB method effectively works well and becomes powerful as the wave function becomes close to the potential exactness.

Figure 2(b) represents the local energy plots of ψ_4 at $n = 4$ ($M_c = 5$) calculated by using the three different sets of the sampling points that lie in the inner, middle (well-spread), and outer regions (β = 1.6, 1.2, and 0.8). Comparing these three plots, one notices that the flatness of the local energy is realized well in the region of the sampled points. With the inner sampling, the local energy is well flat around the exact energy in the inner region but it deviates from the flat line at $r > 3$ a.u. With the middle- and outer-region samplings, the

TABLE III. Energy convergence for the hydrogen atom with the HS method. 50 sampling points distributed according to a weight function $\rho = |\exp(-\beta r)|^2$ ($\beta = 1.2$) were used. The H-square errors calculated by the sampling method σ^2 and by the integration method σ^2_{int} are also given.

n[a]	M_c[b]	Energy (a.u.)	ΔE (a.u.)[c]	H-square error σ^2	H-square error σ^2_{int}
3	4	**−0.499** 932 436	6.76×10^{-5}	9.35×10^{-9}	2.88×10^{-7}
4	5	**−0.499 994** 355 6	5.64×10^{-6}	1.22×10^{-11}	6.22×10^{-9}
5	6	**−0.499 99**9 096 0	9.04×10^{-7}	9.18×10^{-15}	2.19×10^{-10}
6	7	**−0.499 999** 894 50	1.05×10^{-7}	4.41×10^{-18}	7.92×10^{-12}
7	8	**−0.499 999 9**87 188	1.28×10^{-8}	1.44×10^{-21}	2.79×10^{-13}
8	9	**−0.499 999 99**8 515 6	1.48×10^{-9}	3.34×10^{-25}	9.62×10^{-15}
9	10	**−0.499 999 999** 831 06	1.69×10^{-10}	5.71×10^{-29}	3.25×10^{-16}
10	11	**−0.499 999 999 9**81 141	1.89×10^{-11}	7.41×10^{-33}	1.08×10^{-17}
11	12	**−0.499 999 999 997** 927 1	2.07×10^{-12}	7.46×10^{-37}	3.53×10^{-19}
12	13	**−0.499 999 999 999** 775 18	2.25×10^{-13}	5.94×10^{-41}	1.14×10^{-20}
13	14	**−0.499 999 999 999** 975 896	2.41×10^{-14}	3.79×10^{-45}	3.66×10^{-22}
14	15	**−0.499 999 999 999 99**7 441 8	2.56×10^{-15}	1.97×10^{-49}	1.16×10^{-23}
15	16	**−0.499 999 999 999 999** 730 90	2.69×10^{-16}	8.39×10^{-54}	3.65×10^{-25}
Exact		−0.5	0	0	0

[a]Order of the FC method.
[b]Number of the cf's.
[c]Difference between the calculated energy and the exact energy, −0.5 a.u.

flat regions get longer. One also notices that the local energy at the sampled region is even better than that of the variational case shown in Figure 2(a). Moreover, σ_{int}^2 with the inner- and middle-region samplings are better than the variational one. Thus, although the variational calculation can provide accurate energy, the LSE method is able to give better quality wave function than the variational one in the well-sampled region.

3. H^{T}Q method

We also applied the H^{T}Q method to the same FC wave function of the hydrogen atom. The same set of the sampling points was used as that of the HS method. Table IV shows the results that are similar to those of Table I (AB method) and Table III (HS method). The H^{T}Q method, however, needs an additional positive energy shift parameter ε_P, which we chose $\varepsilon_P = 0.6$ and 1.0 a.u. There were almost no significant differences in the energy and the H-square errors between the H^{T}Q and HS-methods, but for σ^2, the H^{T}Q method always gave smaller values than the HS method; in the H^{T}Q method the H-square matrix is diagonalized, which is related to the σ^2 minimization method. Therefore, the H^{T}Q method provides a better quality wave function than the HS method. When we compare the results of the different energy shifts, $\varepsilon_P = 0.6$ and 1.0 a.u., their dependencies were small. In general, however, the result slightly depends on the shifted energy, especially when the order n of the wave function is small.

B. Hooke's atom

The Hooke's atom is a model system for which the exact wave function is known in a closed form at some special conditions.[71,72] It is a two-electron system where the Coulomb potential function of the helium atom is replaced by the harmonic potential. There are several variations: (i) only the nuclear-electron potential is replaced by the harmonic potential, $-Z/r_1 - Z/r_2 \rightarrow k/2 \cdot (r_1^2 + r_2^2)$ and (ii) the electron-electron potential is also replaced by the harmonic potential, $1/r_{12} \rightarrow k'/2 \cdot r_{12}^2$, where Z is a nuclear charge, and k and k' are the force constants of the harmonic potentials. We here treat only the first case, and its Hamiltonian is given by

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{k}{2}\left(r_1^2 + r_2^2\right) + \frac{1}{r_{12}}. \quad (30)$$

The exact wave function is known in a closed form for $k = 1/4$ and $1/100$:[71,72] they are given by

$$\psi_{k=1/4}^{exact} = \left[1 + \frac{1}{2}r_{12}\right] \cdot \exp\left[-\frac{1}{4}\left(r_1^2 + r_2^2\right)\right] \quad (31)$$

and

$$\psi_{k=1/100}^{exact} = \left[1 + \frac{1}{2}r_{12} + \frac{1}{20}r_{12}^2\right] \cdot \exp\left[-\frac{1}{20}\left(r_1^2 + r_2^2\right)\right], \quad (32)$$

respectively.

We took the initial function and g function by $\psi_0 = \exp\left[-\alpha\left(r_1^2 + r_2^2\right)\right]$ and $g = r_{12}$ because the singularity exists only in the electron-electron potential. For $k = 1/4$ and $1/100$, $\alpha = 1/4$ and $1/20$ were employed, respectively, which are the exact values of the exponents in the Gaussian functions.

When one performs the SIC calculation according to Eq. (1), one notices that no more functions are generated when $n > 1$ and $n > 2$ for $k = 1/4$ and $1/100$, respectively. This indicates that the wave function has arrived the potentially exact one, which is

$$\psi_{k=1/4}^{exact} = [1 + c_1 r_{12}] \cdot \exp\left[-\frac{1}{4}\left(r_1^2 + r_2^2\right)\right], \quad (31a)$$

for $k = 1/4$ and

$$\psi_{k=1/100}^{exact} = \left[1 + c_1 r_{12} + c_2 r_{12}^2\right] \cdot \exp\left[-\frac{1}{20}\left(r_1^2 + r_2^2\right)\right], \quad (32a)$$

for $k = 1/100$. The potentially exact FC wave function has the same functional form as Eqs. (31) or (32), but the coefficients of the cf's are unknown. In this situation, any sampling point (necessary condition) should be able to give the exact wave function. We performed the AB method using the sampling points $r_1 = r_2 = r_{12} = 1/2 \cdot k$ ($k = 1, 2, \ldots, M_c$) that form an equilateral triangle and summarized in Table V the calculated energies and coefficients $\{c_i\}$ of the cf's of the FC wave functions. In the case of $k = 1/4$, the exact energy and coefficients were obtained at $n \geq 1$ and M_c does not increase further. Similarly, in the case of $k = 1/100$, the exact solution was obtained at $n \geq 2$. The exact coefficient $1/2$ for the cf, $r_{12}e^{-\alpha(r_1^2+r_2^2)}$, can also be determined by the electron-electron cusp condition,[84] which is another necessary condition. If the wave function is potentially exact, one can combine different necessary conditions, not only the LSE condition, but also the general cusp condition,[84–92] asymptotic condition at infinity, differentiated SE of Eq. (6), etc.

It would be necessary to remark that the above examples of the FC wave functions of Eqs. (31a) and (32a) are the special cases of choosing the initial function ψ_0 in the Gaussian form. For example, when we choose the Slater function for ψ_0, the FC wave function will not terminate at some order and will be composed of the infinite terms. This is similar to the case of the hydrogen atom starting from the Gaussian initial function.[62]

IV. ACCURATE FC-LSE CALCULATION OF THE HELIUM ATOM

For the helium atom, we already have published extremely accurate solutions[59,60] of the SE using the FC-VP method. In this section, we want to show that by applying the results obtained in this study, it is possible to calculate the highly accurate wave function and energy of this atom even with the sampling type LSE method applied to the same FC wave function.

A. Free complement wave function

In the FC method of generating the cf's, we employed the initial function given by

$$\psi_0 = [1 + \log(s + u)] \exp(-\alpha s), \quad (33)$$

where the Hylleraas coordinates, $s = r_1 + r_2$, $t = r_1 - r_2$, and $u = r_{12}$ are used as in our previous paper.[59] The logarithm function was employed for an efficient description of the three-particle coalescence.[93–95] We employed the g function given by

TABLE IV. Energy convergence of the hydrogen atom calculated by the H^TQ method. The positive-energy shifts $\varepsilon_P = 0.6$ and 1.2 a.u. were employed. 50 sampling points distributed according to a weight function $\rho = |\exp(-\beta r)|^2$ were used. The H-square errors calculated by the sampling method σ^2 and by the integration method σ_{int}^2 are also given.

| | | $\varepsilon_P = 0.6$ a.u. | | | | $\varepsilon_P = 1.0$ a.u. | | | |
| | | | | H-square error | | | | H-square error | |
n[a]	M_c[b]	Energy (a.u.)	ΔE (a.u.)[c]	σ^2	σ_{int}^2	Energy (a.u.)	ΔE (a.u.)[c]	σ^2	σ_{int}^2
3	4	**−0.499** 933 356	6.66×10^{-5}	5.53×10^{-9}	2.32×10^{-7}	**−0.499** 933 928	6.61×10^{-5}	5.58×10^{-9}	4.33×10^{-7}
4	5	**−0.499 9**93 019 5	6.98×10^{-6}	7.56×10^{-12}	6.95×10^{-9}	**−0.499 9**93 140 5	6.86×10^{-6}	7.60×10^{-12}	1.65×10^{-8}
5	6	**−0.499 99**9 019 66	9.80×10^{-7}	5.93×10^{-15}	2.47×10^{-10}	**−0.499 999** 026 72	9.73×10^{-7}	5.95×10^{-15}	5.96×10^{-10}
6	7	**−0.499 999** 884 56	1.15×10^{-7}	2.94×10^{-18}	8.74×10^{-12}	**−0.499 999** 885 22	1.15×10^{-7}	2.95×10^{-18}	2.09×10^{-11}
7	8	**−0.499 999** 986 262	1.37×10^{-8}	9.86×10^{-22}	3.03×10^{-13}	**−0.499 999** 986 314	1.37×10^{-8}	9.87×10^{-22}	7.17×10^{-13}
8	9	**−0.499 999 99**8 422 5	1.58×10^{-9}	2.34×10^{-25}	1.03×10^{-14}	**−0.499 999 99**8 427 0	1.57×10^{-9}	2.34×10^{-25}	2.41×10^{-14}
9	10	**−0.499 999 999** 822 00	1.78×10^{-10}	4.10×10^{-29}	3.44×10^{-16}	**−0.499 999 999** 822 38	1.78×10^{-10}	4.10×10^{-29}	7.95×10^{-16}
10	11	**−0.499 999 999 9**80 263	1.97×10^{-11}	5.42×10^{-33}	1.13×10^{-17}	**−0.499 999 999 9**80 296	1.97×10^{-11}	5.42×10^{-33}	2.59×10^{-17}
11	12	**−0.499 999 999 99**7 842 6	2.16×10^{-12}	5.55×10^{-37}	3.69×10^{-19}	**−0.499 999 999 99**7 845 4	2.15×10^{-12}	5.55×10^{-37}	8.35×10^{-19}
12	13	**−0.499 999 999 999** 767 10	2.33×10^{-13}	4.49×10^{-41}	1.19×10^{-20}	**−0.499 999 999 999** 767 35	2.33×10^{-13}	4.49×10^{-41}	2.66×10^{-20}
13	14	**−0.499 999 999 999** 975 129	2.49×10^{-14}	2.91×10^{-45}	3.78×10^{-22}	**−0.499 999 999 999** 975 150	2.48×10^{-14}	2.91×10^{-45}	8.43×10^{-22}
14	15	**−0.499 999 999 999 99**7 369 3	2.63×10^{-15}	1.53×10^{-49}	1.20×10^{-23}	**−0.499 999 999 999 99**7 371 1	2.63×10^{-15}	1.53×10^{-49}	2.65×10^{-23}
15	16	**−0.499 999 999 999 999** 724 08	2.76×10^{-16}	6.62×10^{-54}	3.75×10^{-25}	**−0.499 999 999 999 999** 724 24	2.76×10^{-16}	6.62×10^{-54}	8.26×10^{-25}
Exact		−0.5	0	0	0	−0.5	0	0	0

[a]Order of the FC method.

[b]Number of the complement functions.

[c]Difference between the calculated energy and the exact energy, −0.5 a.u.

TABLE V. Energy and the coefficients of the cf's of the FC wave functions of the Hooke's atom for the Hamiltonian of Eq. (30). The AB method was employed with the sampling points $r_1 = r_2 = r_{12} = 1/2 \cdot k \, (k = 1, 2, \ldots, M_c)$ forming an equilateral triangle.

			$\{c_i\}^c$		
n^a	$M_c{}^b$	Energy (a.u.)	$e^{-\alpha(r_1^2+r_2^2)d}$	$r_{12}e^{-\alpha(r_1^2+r_2^2)d}$	$r_{12}^2e^{-\alpha(r_1^2+r_2^2)d}$
$K = 1/4$					
0	1	3.5	1		
1	2	**2.0**	1	1/2	
2	2	**2.0**	1	1/2	
Exact		2.0			
$K = 1/100$					
0	1	2.3	1		
1	2	0.640 249	1	0.531 950	
2	3	**0.5**	1	1/2	1/20
3	3	**0.5**	1	1/2	1/20
Exact		0.5			

[a]Order of the FC method.
[b]Number of the cf's.
[c]The coefficient of $\psi_0 = e^{-\alpha(r_1^2+r_2^2)}$ is set to unity.
[d]cf's.

$$g = -\frac{1}{V_{Ne}} + \frac{1}{V_{ee}} = \frac{s^2 - t^2}{4sz} + u, \qquad (34)$$

where V_{Ne} represents the nucleus-electron attraction potential and V_{ee} is the electron-electron repulsive potential. The resultant FC wave function at order n has the form

$$\psi_n = \sum_{i=(a,b,c,d)}^{M_c} c_i s^a t^b u^c [\ln(s+u)]^d \exp(-\alpha s), \qquad (35)$$

where both a and c are integers including negative ones. This FC wave function is the same as that used in the FC-VP calculation and gave the energy correct to 42 digits.[59] For the present case, however, since the functions using negative integers of c were not very significant, their functions were neglected. b runs over only the positive even integer and d takes zero or unity. The index (a, b, c, d) is related to the order n. Its range is specified as satisfying the following equalities and inequalities: (i) $-2n \le a < -n, 0 \le c \le 2n + a, 0 \le a + b + c \le 2n + a - c, d = 0, 1$ (In case $c = n$, $b = 0$, and $d = 0$), (ii) $-n \le a \le -1$, $0 \le c \le n$, $0 \le a + b + c \le \min(n, 2n + a - c), d = 0, 1$ (In case $c = n$, $b = 0$, and $d = 0$), (iii) $0 \le a \le n$, $0 \le a + b + c \le n, d = 0, 1$, and (iv) In case $n = 1$, (a, b, c, d)

$= (-2, 2, 0, 1)$ is eliminated. α is an exponent of the Slater function and we used the optimal values[59] for different orders n.

Each cf is given by $\phi_i = \phi_{(a,b,c,d)} = s^a t^b u^c [\ln(s+u)]^d \exp(-\alpha s)$. We note that the cf with the logarithm term and/or negative powers of a has large amplitudes close to the nucleus. On the other hand, the functions having large positive powers a, b, and c are quite diffuse. As increasing the order n, a large number of such functions are generated. Thus, the present cf's cover quite a wide region from the nucleus to the outer region.

B. Sampling points

As seen from Fig. 2 for the hydrogen atom, a clever choice of the set of the sampling points is important in the practical calculations. Generally speaking, the distribution of the sampling points is recommended to be similar to the amplitude of the wave function to be calculated.[38]

We employed the local sampling method,[88] where the sampling points were generated according to the several different sets of $\rho = |\exp(-\beta r)|^2$. The exponents β used in the generation of the sampling points are summarized in Table VI. To investigate the dependence on the sampling-points

TABLE VI. Definition of the five different sampling sets: their exponents β and the numbers of the sampling points.

Sampling set	Number of the total sampling points	Exponents β (the number of the points)
(i)	1×10^6	1.6875^a (1×10^6)
(ii)	2×10^6	(i) +5.0, 10.0, 20.0, 30.0, 50.0 (each 2×10^5)
(iii)	2×10^6	(i) +1.2, 0.8, 0.4, 0.2, 0.1 (each 2×10^5)
(iv)	5×10^6	(i) +3.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 80.0, 100.0, 120.0, 140.0, 1.2, 0.8, 0.4, 0.2, 0.1, 0.05, 0.02, 0.01 (each 2×10^5)
(v)	6×10^6	(iv) +[1.6875,10],[b] [1.6875,30], [1.6875,60], [1.6875,100], [1.6875,0.8], [1.6875,0.4], [1.6875,0.2], [1.6875,0.1], [30,0,4], [60,0.2] (each 10^5)

[a]Same β values are used for electrons 1 and 2.
[b]Different β values in the square bracket are used for electrons 1 and 2.

distribution, we examined five different sets of the sampling points. Sampling set (i) is the simplest case composed of the 10^6 points according to the single $\beta = 27/16 = 1.6875$, which is energetically optimal for the single Slater wave function of the ground-state helium atom.[59] Set (ii) is composed of the five different sets of 2×10^5 points generated by $\beta = 5.0, 10.0, 20.0, 30.0, 50.0$ in addition to set (i), and the total number of the points is 2×10^6. Thus, set (ii) covers the region close to the nucleus. Similarly, set (iii) covers the outside area: $\beta = 1.2, 0.8, 0.4, 0.2, 0.1$ (each 2×10^5) in addition to set (i). It is composed of 2×10^6 points. Set (iv) includes wider inside and outside regions by $\beta = 3.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 80.0, 100.0, 120.0, 140.0, 1.2, 0.8, 0.4, 0.2, 0.1, 0.05, 0.02, 0.01$ (each 2×10^5) in addition to set (i). It is composed of 5×10^6 points. Finally, set (v) includes the different orbital effects for electrons 1 and 2 by $[\beta_1, \beta_2] = [1.6875, 10], [1.6875, 30], [1.6875, 60], [1.6875, 100], [1.6875, 0.8], [1.6875, 0.4], [1.6875, 0.2], [1.6875, 0.1], [30, 0.4], [60, 0.2]$ (each 10^5) in addition to set (v) and total 6×10^6 points. Thus, set (i) is an ordinary one and set (v) is the widest one that covers both regions of nuclear and outside regions.

C. FC-LSE calculations

The FC-LSE calculations of the helium atom were performed using the different sets of sampling points given above. To guarantee the numerical accuracy beyond double precision, all the calculations were performed in the 160 digits precision using the GMP library.[96] We employed the FC wave functions given by Eq. (35), which are the same as those in our previous study,[59] where we had performed the FC-VP calculations and obtained the extremely accurate energy, local energy, and H-square error σ_{int}^2. Their variational energies, the plots of the local energy, and the H-square error, σ_{int}^2 were summarized,[59,61] which are used as the references to examine the accuracy of the LSE calculations shown below.

We first performed the FC-LSE calculation using the HS method with the sampling set (i). Table VII summaries the

energy E, the energy difference ΔE from the exact energy ($\Delta E = E - E_{exact}$), and the H-square error σ^2 calculated by the sampling method. As increasing the order n, the energy converges to the exact one and σ^2 also rapidly converges to zero. At $n = 11$ ($M_c = 1861$), ΔE was 4.38×10^{-9} a.u. and thus, the accurate absolute energy correct to nano hartree was obtained without doing any integral evaluation. However, when we compare the results at $n = 9$ and $n = 11$, almost no improvement could be obtained. Therefore, we stopped the calculations at $n = 11$ with this sampling set (i).

To investigate the reason why further improvements could not be obtained at $n = 11$ above, we examined the other sets of the sampling points. Table VIII summarizes the results calculated with the sampling sets (i) to (v) at $n = 5$ ($M_c = 247$) and $n = 11$ ($M_c = 1861$) with the HS method. At $n = 5$, with set (ii), the result was much improved than the case of set (i); the sampling points close to the nucleus were important because the cf's include the logarithm and negative powers of a (see Eq. (35)). On the other hand, set (iii), i.e., diffuse sampling points, did not bring any significant improvement since the diffuse cf's were not much included in the cf's generated at $n = 5$. No further dramatic improvements could be obtained with set (iv) and (v) even though the sampling space was enlarged. Thus, set (i) was not optimal but set (ii) was suitable for the cf's at $n = 5$. On the other hand, at $n = 11$, we could not obtain an improvement with set (ii) but a moderate improvement was obtained with set (iii). This implies that the diffuse sampling points are energetically more important than the sampling points close to the nucleus for the cf's at $n = 11$. Further improvement was obtained with set (iv). This indicates that it is important to include the sampling points for both regions; close to the nucleus and diffuse area. Set (v) brought a slight improvement over set (iv) through the effect of the different densities for the different electrons: $\Delta E = -5.45 \times 10^{-16}$ a.u., i.e., more than 15 digits (femto hartree) accuracy was accomplished with set (v). We note that the improvement in the calculated energy in Table VI from above to below may partially reflect the increase in the number of the sampling points.

TABLE VII. Energy, energy difference ΔE, and H-square error σ^2 of the FC-LSE wave functions of the Hamiltonian calculated by the HS method with sampling set (i) (10^6 points) and (v) (6×10^6 points).

		Sampling set (i)			Sampling set (v)		
n[a]	M_c[b]	Energy (a.u.)	ΔE (a.u.)[c]	H-square error σ^2	Energy (a.u.)	ΔE (a.u.)[c]	H-square error σ^2
3	77	−2.903 725 106 7	−7.30×10⁻⁷	1.20×10⁻⁶	−2.903 724 253 89	1.23×10⁻⁷	4.36×10⁻⁵
5	247	−2.903 724 626 99	−2.50×10⁻⁷	1.49×10⁻¹¹	−2.903 724 379 666 9	−2.63×10⁻⁹	1.96×10⁻⁹
7	569	−2.903 724 361 814	1.52×10⁻⁸	7.01×10⁻¹⁶	−2.903 724 377 033 867 1	2.52×10⁻¹³	1.13×10⁻¹²
9	1091	−2.903 724 371 678 3	5.36×10⁻⁹	2.16×10⁻¹⁹	−2.903 724 377 034 102 002	1.76×10⁻¹⁴	9.77×10⁻¹⁷
11	1861	−2.903 724 372 649 2	4.38×10⁻⁹	7.08×10⁻²³	−2.903 724 377 034 120 143	−5.45×10⁻¹⁶	2.71×10⁻²⁰
13	2927				−2.903 724 377 034 119 851 25	−2.53×10⁻¹⁶	1.67×10⁻²³
15	4337				−2.903 724 377 034 119 594 481 6	3.83×10⁻¹⁸	3.74×10⁻²⁶
17	6139				−2.903 724 377 034 119 598 320 846	−9.69×10⁻²¹	2.59×10⁻²⁸
Exact energy[d]		−2.903 724 377 034 119			−2.903 724 377 034 119 598 311 159		

[a]Order of the FC method.
[b]Number of the cf's.
[c]Energy difference $\Delta E = E - E_{exact}$ between the calculated energy E and the exact energy E_{exact}.
[d]The variationally best energy was used for E_{exact} in Refs. 59 and 60.

TABLE VIII. Examinations of the appropriate sampling points for the helium wave functions of $n = 5$ and $n = 11$ using five different sampling sets defined in Table VI. Energy, energy difference ΔE, and H-square error σ^2 of the FC-LSE wave functions calculated by the HS method are given for $n = 5$ ($M_c = 247$) and $n = 11$ ($M_c = 1861$).

Sampling set[a]	Energy (a.u.)	ΔE (a.u.)[b]	H-square error σ^2
$n = 5$ ($M_c = 247$)[c]			
(i)	**−2.903 724** 626 99	-2.50×10^{-7}	1.49×10^{-11}
(ii)	**−2.903 724 374** 324 5	2.71×10^{-9}	1.22×10^{-9}
(iii)	**−2.903 724** 502 81	-1.26×10^{-7}	2.55×10^{-11}
(iv)	**−2.903 724 379** 099 5	-2.07×10^{-9}	1.94×10^{-9}
(v)	**−2.903 724 379** 666 9	-2.63×10^{-9}	1.96×10^{-9}
$n = 11$ ($M_c = 1861$)[c]			
(i)	**−2.903 724 372** 649 2	4.38×10^{-9}	7.08×10^{-23}
(ii)	**−2.903 724 372** 525 8	4.51×10^{-9}	1.59×10^{-21}
(iii)	**−2.903 724 377** 085 544	-5.14×10^{-11}	1.22×10^{-22}
(iv)	**−2.903 724 377 034** 038 45	8.11×10^{-14}	2.68×10^{-20}
(v)	**−2.903 724 377 034 1**20 143	-5.45×10^{-16}	2.71×10^{-20}
Exact energy[d]	−2.903 724 377 034 119 598		

[a]Sampling sets defined in Table VI.
[b]Energy difference $\Delta E = E - E_{exact}$ between the calculated energy E and the exact energy reference E_{exact}.
[c]Order of the FC method: n and number of the cf's: M_c.
[d]The variationally best energy was used for E_{exact} from Refs. 59 and 60.

Thus, it was confirmed that set (v) was appropriate for the higher order FC wave functions. We continued to perform the calculations with set (v) by the HS method up to $n = 17$ ($M_c = 6139$) and summarized the results on the right-hand side of Table VII. The energy with set (v) converges more rapidly to the exact one than the case with set (i). At $n = 17$ ($M_c = 6139$), the calculated energy was −**2.903 724 377 034 119 598 3**20 846 a.u. and $\Delta E = -9.69 \times 10^{-21}$ a.u., i.e., more than 20 digits (zepto hartree) accuracy, was accomplished only with the sampling methodology. Note that the potential exactness of the FC wave function was the strong reason of this success: near constancy of the local energy at any sampling point is a preferable feature. To the best of our knowledge, the present result should be most accurate among the sampling-type quantum mechanical calculations of atoms and molecules.

D. Local energy analysis

We also performed the local energy analysis of the calculated wave functions. Similar analysis was made before for the FC-VP wave function.[61] Instead of directly plotting the local energy $E_{loc}(\mathbf{r})$, one may plot the local energy difference $\Delta E_{loc}(\mathbf{r})$ with logarithm scale, defined by

$$\Delta E_{loc}(\mathbf{r}) = \log_{10} |E_{loc}(\mathbf{r}) - E|. \quad (36)$$

$\Delta E_{loc}(\mathbf{r})$ clearly shows the bad region where $E_{loc}(\mathbf{r})$ largely deviates from the energy constant E calculated from the corresponding wave function. For the helium atom, $\mathbf{r}$ is the two-electron coordinates (six variables) but, for the ground state, the wave function is represented by three independent coordinates; $\{r_1, r_2, r_{12}\}$ or $\{r_1, r_2, \theta_{12}\}$, or the Hylleraas coordinates $\{s, t, u\}$. θ_{12} is defined as the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$ vectors. We plotted $\Delta E_{loc}(\mathbf{r})$ as the two-dimensional surface of r_1 and r_2 with fixed $\theta_{12} = 0$, which means that both electrons locate on a same straight line. We took the three plotted ranges of r_1 and r_2: (a) [0.0, 0.1] with 1/5000 a.u. interval, (b) [0.0, 1.0] with

1/500 a.u. interval, and (c) [0.0, 10.0] with 1/50 a.u. interval. They show from the nuclear position to (a) the region close to the nucleus (up to 0.1 a.u.), (b) up to the middle (1.0 a.u.) area, and (c) up to the outside (10 a.u.) area, respectively.

Figure 3 shows the plots of $\Delta E_{loc}(\mathbf{r})$ for the FC-LSE wave functions obtained with the sampling sets (i) and (v) and, as a reference, for the FC-VP wave function at $n = 5$ ($M_c = 247$). The red color describes the bad region where $E_{loc}(\mathbf{r})$ largely deviates from the energy constant and the green and blue colors represent the region where the constancy of $E_{loc}(\mathbf{r})$ from E is improved. The indicator defining the colors is given at the right-hand side of the figure. For example, if $\Delta E_{loc}(\mathbf{r}) \approx -10$, then it means that the difference between $E_{loc}(\mathbf{r})$ and E is less than 10^{-10} a.u. Although we examined several different θ_{12}, we could not see any essential difference from that for $\theta_{12} = 0$. Therefore, we only show the result for $\theta_{12} = 0$. In this case, the diagonal lines in Fig. 3 correspond to the electron-electron coalescence position; this position is always bad since no constraint concerning the cusp condition was imposed to our wave functions.[61] The position of $r_1 = 0$ and $r_2 = 0$ is the three-particle coalescence point. In all the cases of the FC-LSE with sets (i) and (v) and FC-VP, the bad regions concentrate on the area close to the nucleus; r_1, $r_2 = 1$ and the diffuse area; r_1, $r_2 > 5$. The bad regions in the FC-LSE with set (i) are wider than that of the FC-VP. This indicates that taking more sampling points for these bad regions would improve the FC-LSE result. In fact, the plot with set (v) shows a large improvement: the result of set (v) is quite similar to the result from the FC-VP calculation.

Figure 4 shows similar plots of $\Delta E_{loc}(\mathbf{r})$ with the wave functions at $n = 11$ ($M_c = 1861$). For the FC-LSE with set (i), $\Delta E_{loc}(\mathbf{r})$ of the middle region, r_1, $r_2 \approx 1$ was much improved than the former $n = 5$ case. However, the inner r_1, $r_2 = 1$ and outer r_1, $r_2 > 5$ regions were not improved and even worse than the former case of $n = 5$. In contrast, $\Delta E_{loc}(\mathbf{r})$ of the FC-VP was considerably improved also for r_1, $r_2 = 1$ and r_1, $r_2 > 5$. Thus, we understand that set (i) should be in a lack of the
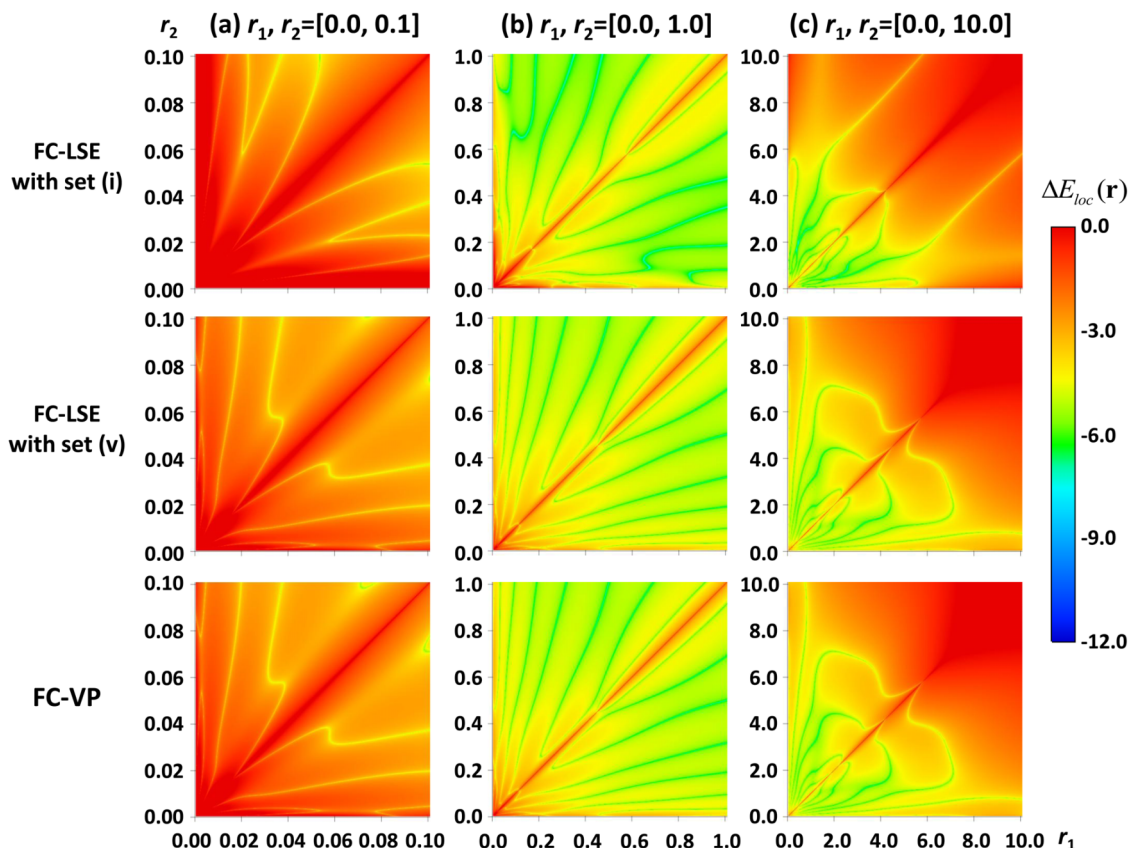
FIG. 3. Plots of $\Delta E_{loc}(\mathbf{r})$ as a two-dimensional surface of the coordinates r_1 and r_2 a.u. with fixed $\theta_{12} = 0$ for the FC-LSE wave functions with sampling sets (i) and (v) and the FC-VP wave function at $n = 5$ ($M_c = 247$). In the graphs, r_1 and r_2 within (a) [0.0, 0.1] with 1/5000 a.u. interval, (b) [0.0, 1.0] with 1/500 a.u. interval, and (c) [0.0, 10.0] with 1/50 a.u. interval were taken, respectively. The plots are described by color-coded maps and the red color represents worst region and the blue color excellent region of $\Delta E_{loc}(\mathbf{r})$ in logarithm scale from the right-side indicator.

sampling points for these regions since the distribution of set (i) was generated by a single $\beta = 1.6875$ which does not cover well the regions $r_1, r_2 = 1$ and $r_1, r_2 > 5$. While the cf's at $n = 11$ include the functions having large amplitudes close to the nucleus (logarithm and negative powers of a) and also very diffuse functions such as s^{11}, t^{10}, and u^{11}, there were not enough sampling points to correctly determine the coefficients of these cf's. Therefore, it is necessary to prepare the sampling points which cover these regions to correctly determine the coefficients of such cf's. The improvement, however, cannot be expected by simply increasing the number of the sampling points using a single $\beta = 1.6875$ of set (i) because the Slater-type density function decays exponentially. In contrast, with set (v), a drastic improvement was obtained even for these regions. The plots with set (v) were almost identical to those of the FC-VP for all three regions ($0 < r_1, r_2 < 10$). This implies that the variational wave function is almost-totally reproduced by the LSE method by preparing the appropriate sampling points. This is an important observation revealed from the local energy analysis shown in these figures.

Figure 5 shows the plots of $\Delta E_{loc}(\mathbf{r})$ further at $n = 17(M_c = 6139)$. Set (i) could not give the correct solution for the regions of $r_1, r_2 = 1$ and $r_1, r_2 > 5$, though this FC wave function at $n = 17$ is potentially much better than seen from the results of the set (i) sampling. Only the middle region, where enough sampling points exist, was improved. In contrast, with set (v), the plots of $\Delta E_{loc}(\mathbf{r})$ for the FC-LSE wave function at

$n = 17$ were much improved than those for $n = 11$. Surprisingly, again, the plots from the LSE calculation were almost identical to those of the VP calculation for all three regions. The present analysis shows that the correct wave function is obtained with the LSE method even for the higher order FC wave functions that have more complex cf's than the lower ones by taking the appropriate sampling points that cover all the functional spaces. The present local energy analysis also indicates that the FC wave function at $n = 17$ is nearly exact from the viewpoint of the local energy,[61] i.e., blue color for all the regions within $0 < r_1, r_2 < 10$, which is wide enough for the helium atom.

E. Exactness of the FC-LSE wave functions

We now analyze the energy and the H-square error quantities, using both sampling and integration methods. We examine the exactness of the FC-LSE wave functions calculated by the HS and H^{T}Q ($\varepsilon_P = 3.0$) methods at the orders $n = 11$ ($M_c = 1861$) and $n = 17$ ($M_c = 6139$) with sampling set (v). Table IX summarized the energy E, the energy difference ΔE from the exact energy, and the H-square error σ^2 calculated by the sampling method, together with the energy expectation value E_{int}, the energy difference ΔE_{int}, and the H-square error expectation value σ^2_{int} calculated by the integration method. They are also compared with these quantities calculated from the FC-VP wave functions of the orders $n = 11$ and 17.
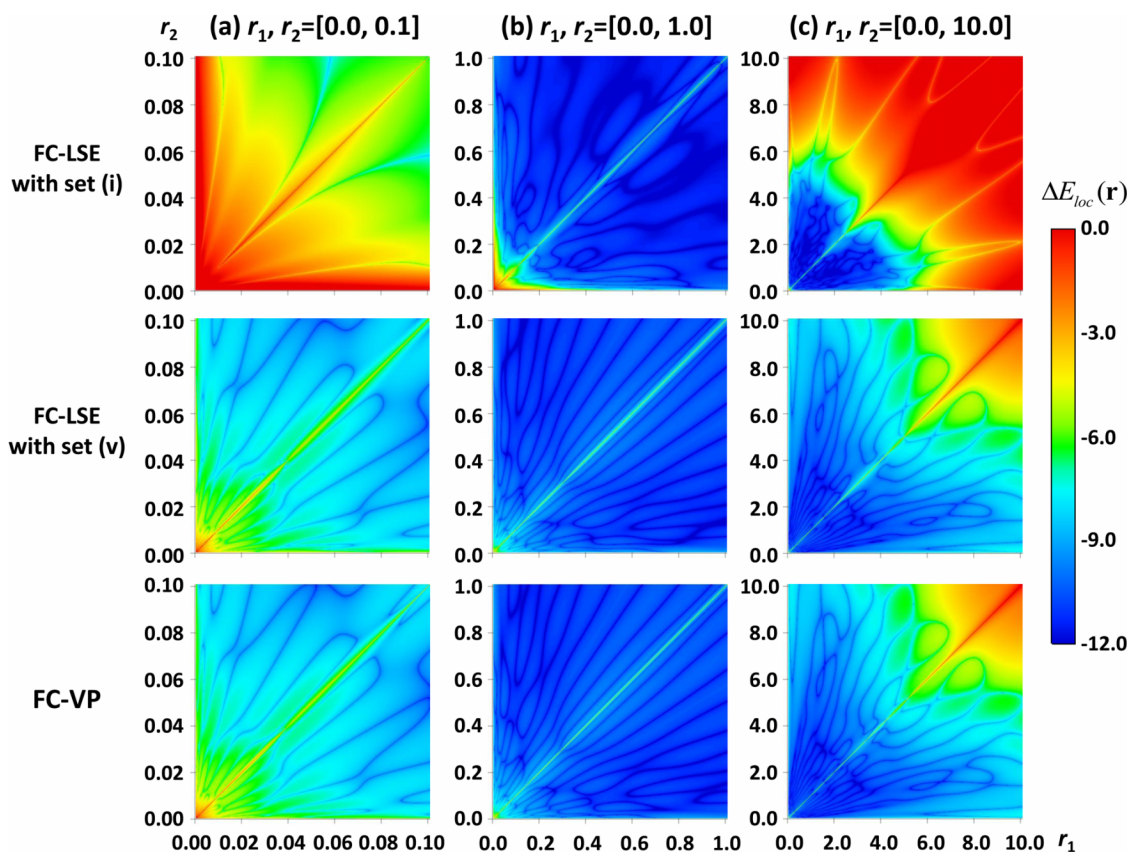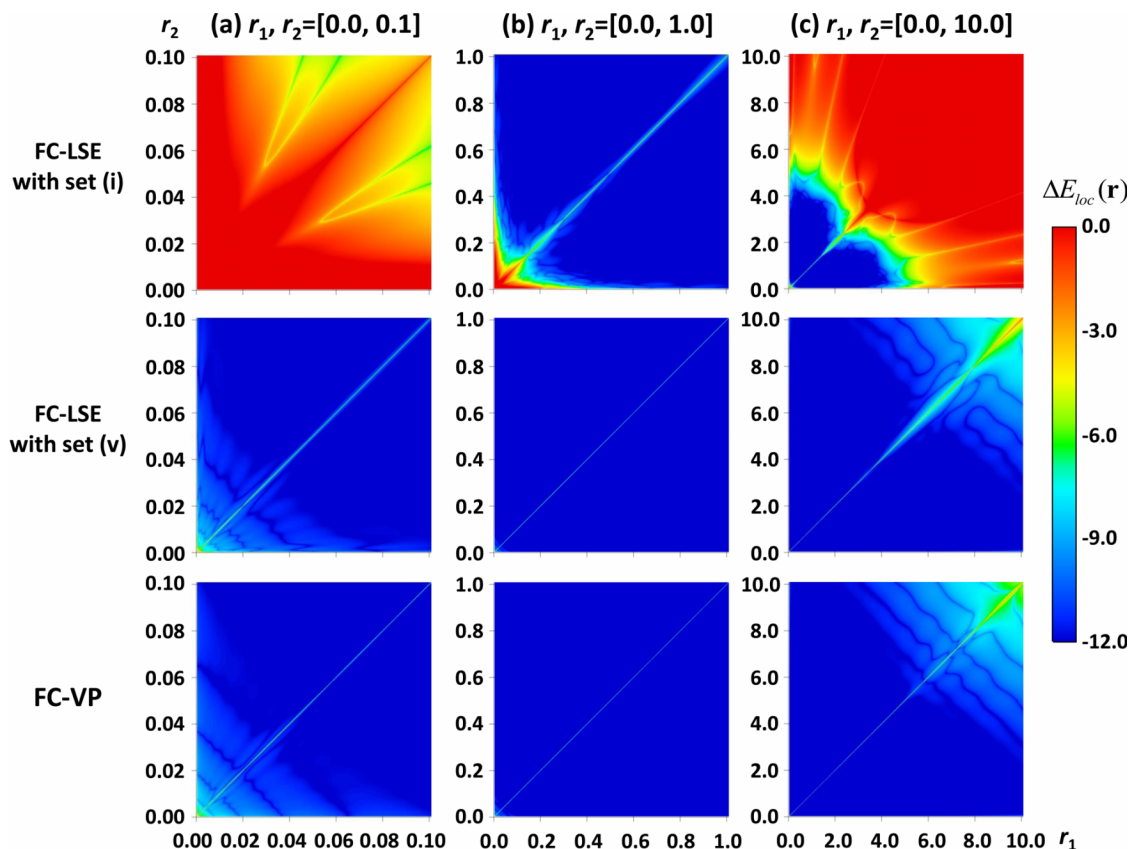
FIG. 4. Plots of $\Delta E_{loc}(\mathbf{r})$ as a two-dimensional surface of the coordinates r_1 and r_2 a.u. with fixed $\theta_{12} = 0$ for the FC-LSE wave functions with sampling sets (i) and (v) and the FC-VP wave function at $n = 11$ ($M_c = 1861$). Plotting condition is described in Figure 3.

FIG. 5. Plots of $\Delta E_{loc}(\mathbf{r})$ as a two-dimensional surface of the coordinates r_1 and r_2 a.u. with fixed $\theta_{12} = 0$ for the FC-LSE wave functions with sampling sets (i) and (v) and the FC-VP wave function at $n = 17$ ($M_c = 6139$). Plotting condition is described in Figure 3.

TABLE IX. Energy E, energy difference ΔE, and H-square error σ^2 of the helium FC-LSE wave functions obtained by the HS and H^{T}Q methods ($\varepsilon_P = 3.0$) with sampling set (v) (total 6×10^6 points) at $n = 11$ ($M_c = 1861$) and $n = 17$ ($M_c = 6139$). By integration, the energy expectation value E, energy difference ΔE from the exact energy reference, and H-square error σ_{int}^2 of the FC-LSE wave functions are also calculated and compared with those of the FC-VP results.

Wave function		Energy (E or E_{int}) (a.u.)[a]	ΔE or ΔE_{int} (a.u.)[b]	H-square error[c]
$n = 11$ ($M_c = 1861$)				
LSE (HS method)	Sampling	**−2.903 724 377 034 1**20 143	−5.45×10^{-16}	2.71×10^{-20}
	Integration	**−2.903 724 377 034 119 598 311 158** 733 69	5.11×10^{-25}	8.10×10^{-18}
LSE (H^{T}Q method)	Sampling	**−2.903 724 377 034 1**29 206	−9.61×10^{-15}	9.98×10^{-23}
	Integration	**−2.903 724 377 034 119 598 311 15**7 120 8	2.12×10^{-24}	1.24×10^{-21}
VP		**−2.903 724 377 034 119 598 311 158** 761 80	4.83×10^{-25}	3.66×10^{-19}
$n = 17$ ($M_c = 6139$)				
LSE (HS method)	Sampling	**−2.903 724 377 034 119 598 3**20 846	−9.69×10^{-21}	2.59×10^{-28}
	Integration	**−2.903 724 377 034 119 598 311 159 245 194 39**9 344 5	5.10×10^{-33}	1.79×10^{-24}
LSE (H^{T}Q method)	Sampling	**−2.903 724 377 034 119 598** 867 49	−5.56×10^{-19}	1.38×10^{-30}
	Integration	**−2.903 724 377 034 119 598 311 159 245 194** 332 75	7.17×10^{-32}	3.24×10^{-26}
VP		**−2.903 724 377 034 119 598 311 159 245 194** 403 526 60	9.19×10^{-34}	3.31×10^{-26}
Exact energy[d]		−2.903 724 377 034 119 598 311 159 245 194 404 446		

[a]Energy E by sampling or energy expectation value E_{int} by integration.
[b]Energy difference $\Delta E = E - E_{exact}$ between the calculated energy E or E_{int} and the exact energy reference E_{exact}.
[c]H-square error σ^2 by sampling or σ_{int}^2 by integration.
[d]The variationally best energy was used for E_{exact} from Refs. 59 and 60.

At $n = 11$ ($M_c = 1861$), although ΔE by sampling were -5.45×10^{-16} and -9.61×10^{-15} a.u., ΔE_{int} were as small as 5.11×10^{-25} and 2.12×10^{-24} a.u. with the HS and H^{T}Q methods, respectively, and that of the FC-VP wave function was 4.83×10^{-25} a.u. Thus, when we use the integration method, very accurate energy expectation values, which are almost identical with the FC-VP ones, were obtained from the wave function determined by the LSE method. Since the sampling (LSE) method is different from the variational method, the energy E calculated by the sampling method has the error to the same order as that of the wave function. On the other hand, the energy expectation value E_{int} calculated by the integration method is generally correct to the second order of the wave-function error and so more accurate than E of the sampling method. On the other hand, the H-square error σ^2 calculated by the sampling method was always smaller than σ_{int}^2. Since $\sigma_{int}^2 = 0$ means that the wave function is exact and satisfies the SE, we can use σ_{int}^2 as a definite value for the judgment of the exactness of the wave function. We see from Table IX that σ_{int}^2 by the HS, H^{T}Q, and VP methods were 8.10×10^{-18}, 1.24×10^{-21}, and 3.66×10^{-19}, respectively. It is quite remarkable that σ_{int}^2 by the H^{T}Q method was smaller than that of the VP method, showing that the FC wave function calculated by the LSE-H^{T}Q method is more exact than the FC-VP wave function from the judgment of the H-square error. This is reasonable since the H^{T}Q method is related to the inverse variational principle.[53]

At $n = 17$ ($M_c = 6139$), ΔE was -9.69×10^{-21} a.u. with the HS method and -5.56×10^{-19} a.u. with the H^{T}Q methods; the energies were correct about 20 digits with only the sampling method. Furthermore, the integral expectation value ΔE_{int} with the HS and H^{T}Q methods were as small as 5.10×10^{-33} and 7.17×10^{-32} a.u., respectively. Their absolute energies were almost 33 digits correct. The accuracy is almost equivalent to that of the VP method; 9.19×10^{-34} a.u. On the other hand, σ_{int}^2 by the HS, H^{T}Q, and VP methods were 1.79×10^{-24},

3.24×10^{-26}, and 3.31×10^{-26}, respectively. Again, the LSE-H^{T}Q sampling method gave more accurate wave function than the variational method in the viewpoint of the H-square error. Thus, for the approximately potentially exact FC wave function, the LSE sampling method can give the result comparable to the variational method.

F. Sampling points that reproduce the variational energy

Finally, let us consider whether the set of the sampling points that reproduces the variational energy and wave function can exist in the case of the helium atom. For the hydrogen atom, we already confirmed that there is such a set of the sampling points that reproduces the variational results (see Fig. 2(a)). We investigated this possibility for the FC wave function at the order $n = 3$ ($M_c = 77$). The variational energy of this wave function was **−2.903 724 375** 094 1 a.u.[59] in comparison with the present LSE energy **−2.903 725** 106 7 a.u. with sampling set (i). We found that there are essentially infinite number of sampling points that give the local energy that is equal to the variational energy. Since the variational energy is considered as the averaged energy over the infinite number of sampling points, the local energy of the variational wave function must cross the constant variational energy surface. Generally, when two d-dimensional surfaces cross each other, their intersection is represented by a $(d - 1)$-dimensional surface for $d > 2$, by a line for $d = 2$, or by a point for $d = 1$. Since the ground-state helium wave function is written by the three independent radial coordinates ($d = 3$), the intersection with the variational energy surface is represented by a two-dimensional surface and therefore essentially infinite number of points should exist where the local energy is equal to the variational energy. When arbitrary 77 sets of sampling points were selected from them, the AB method would reproduce the variational energy. Although we do not yet give a complete

proof, we feel that this is generally correct. This implies that the LSE method can give the wave function (not energy) comparable to the variational method in accuracy. To confirm this from the energy, the analytical integrations over the cf's are necessary, which can be done for the helium atom. This was certainly confirmed by the present study in Table IX.

V. CONCLUSION

We studied in this paper the LSE method combined with the FC method that produces the potentially exact wave function of the SE. First, the three variants of the LSE method, the AB, HS, and H^TQ methods were explained. The LSE method is the equi-local energy condition at the sampled points. The AB method is a direct expression of the local Schrödinger equation. It reflects the original idea of the LSE method.[58] In the AB methods, the unknown coefficients are determined using the same number of conditions (sampling points). This is possible when it is applied to the potentially exact FC wave function. The underlying concept is completely different from the variational one. On the other hand, the numbers of the sampling points used in the HS and H^TQ methods are usually much larger than the number of the variables. The **H**, **S**, and **Q** matrices correspond to the Hamiltonian, overlap, and H-square matrices, respectively, and therefore, the HS and H^TQ methods mimic the ordinary variational principle and the inverse variational principle,[53] respectively. For all of the three types of LSE method, we can easily calculate the H-square error which is a good indicator of the exactness of the wave function. This quantity has not been used in the variational calculations, because the integrals over the square of the Hamiltonian are difficult to evaluate. Generally speaking, the results of the H^TQ method are often slightly better than those of the HS method. Since the H^TQ method is related to the inverse variational principle, this is reasonable from the Krylov sense.[52,53] The H^TQ method can be applied as easily as the HS method.

We investigated the natures of the LSE method through the applications to the hydrogen atom and the Hooke's atom for which the potentially exact wave functions are available. In the application to the hydrogen atom, all three AB, HS, and H^TQ methods could provide very accurate solutions even with a few sampling points. The calculated local energies and the H-square errors showed that the wave functions calculated with the LSE method were even more accurate than those obtained by the variational method. In the application to the Hooke's atom, it was confirmed that the SIC process of Eq. (1) produces the exact wave function at some order and thereafter, no more cf's are produced. At this stage, any set of the sampling points, whose number is equal to the number of the variables, can give the exact solution. Note that, even when the wave function becomes exact, its cf's do not form a complete space. Thus, the cf's and the complete set of functions are different.

The ideas from the present study were applied to solving the SE of the helium atom with the FC-LSE method. We have shown that we can obtain highly accurate results even with the sampling-type LSE method, when the wave function is produced with the FC method. This was achieved by preparing the sampling points that are appropriate for the cf's under study. We could get the energy accurate to more than 20 digits

even with the sampling-type procedure. The energy expectation value E_{int} calculated by the integration method from the LSE wave function was quite accurate, to almost 33 digits accuracy, which was almost the same accuracy as the FC-VP energy obtained before.[59] The integral value of the H-square error σ_{int}^2 obtained from the wave function calculated with the LSE-H^TQ method was even better than that of the VP method in accordance with the fact that the H^TQ method is related to the inverse variational principle. The local error analyses for the LSE wave functions calculated with the differently distributed sampling points have revealed the important clue in generating the sampling points used in the LSE method. It was also shown that the set of the sampling points that reproduces the result of the variational calculation exists: this would be true for any atoms and molecules.

The referee asked the authors to address about the scaling of the method and guessed the bottleneck to be the generation of the cf's. As explained in many occasions (for example, see Ref. 70 pp. 25), the cf. generation step is a fast step. The most time-consuming step is the LSE step[70] which involves the handling of about 10^6 sampling points and their antisymmetrizations. Therefore, to make the LSE step efficient is very important and so is the subject of this paper. For the antisymmetrization, we have invented two useful theories: one is the determinant based Nk method,[66] and the other is the inter-exchange (iExg) theory[97] that breaks the Pauli dogma most people believe. They contribute much to reduce the computational time. Anyway, the computational time scales in a polynomial time and to reduce the scaling, it is important to understand the physical nature of the sampling-type methodology, which is a topic in this paper. There is no established efficient way of sampling[38–40] and therefore we have to seek for that.

The FC-LSE method would become a main stream in the calculations of highly accurate solutions of the Schrödinger equations of atoms and molecules, because the Hamiltonian and overlap integrals are not available for many functions that are necessary to describe highly accurate wave functions. In comparison with the variational method, the LSE method is simple, easy, and general. We have shown in this paper that the LSE method can give the wave functions as accurate as the variational method, if the sampling points are prepared carefully. It is very important to advance the LSE methodology to be always accurate, efficient, and usable for any FC wave functions of atoms and molecules. This is necessary to pave the way towards the accurately predictive quantum chemistry.

[1]P. A. M. Dirac, Proc. R. Soc. A **123**, 714 (1929).
[2]P. J. Knowles and N. C. Handy, J. Chem. Phys. **91**, 2396 (1989).
[3]I. Shavitt, Int. J. Quantum Chem. **S11**, 131 (1977).
[4]P. E. M. Siegbahn, J. Chem. Phys. **72**, 1647 (1980).

[5]E. Rossi, G. L. Bendazzoli, S. Evangelisti, and D. Maynau, Chem. Phys. Lett. **310**, 530 (1999).

[6]G. L. Bendazzoli and A. Monari, Chem. Phys. **306**, 153 (2004).

[7]C. X. Almora-Díaz and C. F. Bunge, Int. J. Quantum Chem. **110**, 2982 (2010).

[8]S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); S. R. White, Phys. Rev. B **48**, 10345 (1993); S. R. White and R. L. Martin, J. Chem. Phys. **110**, 4127 (1999).

[9]G. K. Chan and M. Head-Gordon, J. Chem. Phys. **116**, 4462 (2002); G. K. Chan, M. Kállay, and J. Gauss, *ibid.* **121**, 6110 (2004); G. K. Chan and T. V. Voorthis, *ibid.* **122**, 204101 (2005).

[10]U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005); Ann. Phys. **326**, 96 (2011).

[11]G. Moritz and M. Reiher, J. Chem. Phys. **124**, 034103 (2006); **126**, 244109 (2007).

[12]Y. Kurashige and T. Yanai, J. Chem. Phys. **135**, 094104 (2011).

[13]Y. Ohtsuka and S. Nagase, Chem. Phys. Lett. **463**, 431 (2008); **485**, 367 (2010).

[14]G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **131**, 054106 (2009); G. H. Booth, D. Cleland, A. Alavi, and D. P. Tew, *ibid.* **137**, 164112 (2012).

[15]G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature **493**, 365 (2013).

[16]S. Ten-no, J. Chem. Phys. **138**, 164126 (2013)

[17]E. A. Hylleraas, Z. Phys. **48**, 469 (1928); **54**, 347 (1929); **65**, 209 (1930); **71**, 739 (1931).

[18]J. S. Sims and S. Hagstrom, Phys. Rev. A **4**, 908 (1971).

[19]G. W. F. Drake and Z.-C. Yan, Chem. Phys. Lett. **229**, 486 (1994).

[20]*Explicitly Correlated Wave Functions in Chemistry and Physics - Theory and Applications*, edited by J. Rychlewski (Kluwer Academic, Dordrecht, 2003).

[21]C. Schwartz, Int. J. Mod. Phys. E **15**, 877 (2006).

[22]J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).

[23]M. B. Ruiz, J. Math. Chem. **46**, 1322 (2009).

[24]K. L. Sharkey, M. Pavanello, S. Bubin, and L. Adamowicz, Phys. Rev. A **80**, 062510 (2009).

[25]F. W. King, D. Quicker, and J. Langer, J. Chem. Phys. **134**, 124114 (2011).

[26]J. S. Sims and S. A. Hagstrom, Phys. Rev. A **83**, 032518 (2011).

[27]W. Cencek, M. Przybytek, J. Komasa, J. B. Mehl, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **136**, 224303 (2012).

[28]C. Wang, P. Mei, Y. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Rev. A **85**, 042512 (2012).

[29]W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).

[30]W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).

[31]S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).

[32]W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006).

[33]J. Noga, S. Kedžuch, J. Šimunek, and S. Ten-no, J. Chem. Phys. **128**, 174103 (2008).

[34]T. Shiozaki, M. Kamiya, S. Hirata, and E. F. Valeev, J. Chem. Phys. **130**, 054101 (2009).

[35]C. Hättig, D. P. Tew, and B. Helmich, J. Chem. Phys. **136**, 204105 (2012).

[36]R. Haunschild, S. Mao, D. Mukherjee, and W. Klopper, Chem. Phys. Lett. **531**, 247 (2013).

[37]P. Piecuch, S. A. Kucharski, and K. Kowalski, Chem. Phys. Lett. **344**, 176 (2001).

[38]B. L. Hammond, W. A. Lester, and Jr. Reynolds, *Monte Carlo Methods in ab initio Quantum Chemistry* (World Scientific, Singapore, 1994).

[39]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[40]H. Suwa and S. Todo, Phys. Rev. Lett. **105**, 120603 (2010).

[41]M. P. Nightingale and C. J. Umrigar, *Quantum Monte Carlo Methods in Physics and Chemistry* (Springer, 1998).

[42]J. B. Anderson, *Quantum Monte Carlo: Origins, Development, Applications* (Oxford University Press, 2007).

[43]B. M. Austin, D. Y. Zubarev, and W. A. Lester, Jr., Chem. Rev. **112**, 263 (2012).

[44]J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975).

[45]R. P. Subramaniam, M. A. Lee, K. E. Shmidt, and J. W. Moskowitz, J. Chem. Phys. **97**, 2600 (1992).

[46]F. Fracchia, C. Filippi, and C. Amovilli, J. Chem. Theory Comput. **8**, 1943 (2012).

[47]N. M. Tubman, J. L. Dubois, R. Q. Hood, and B. J. Alder, J. Chem. Phys. **135**, 184109 (2011).

[48]F. R. Petruzielo, J. Toulouse, and C. J. Umrigar, J. Chem. Phys. **136**, 124116 (2012).

[49]H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).

[50]H. Nakatsuji and E. R. Davidson, J. Chem. Phys. **115**, 2000 (2001)

[51]H. Nakatsuji, J. Chem. Phys. **115**, 2465 (2001); **116**, 1811 (2002).

[52]H. Nakatsuji and M. Ehara, J. Chem. Phys. **117**, 9 (2002); **122**, 194108 (2005); H. Nakatsuji, Phys. Rev. A **84**, 062507 (2011).

[53]H. Nakatsuji, Phys. Rev. A **65**, 052122 (2002).

[54]H. Nakatsuji, Phys. Rev. Lett. **93**, 030403 (2004).

[55]H. Nakatsuji, Phys. Rev. A **72**, 062110 (2005).

[56]Y. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Rev. A **72**, 062502 (2005).

[57]H. Nakatsuji and H. Nakashima, Phys. Rev. Lett. **95**, 050407 (2005); H. Nakashima and H. Nakatsuji, Theor. Chem. Acc. **129**, 567–574 (2011).

[58]H. Nakatsuji, H. Nakashima, Y. Kurokawa, and A. Ishikawa, Phys. Rev. Lett. **99**, 240402 (2007).

[59]H. Nakashima and H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007).

[60]Y. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Chem. Chem. Phys. **10**, 4486 (2008).

[61]H. Nakashima and H. Nakatsuji, Phys. Rev. Lett. **101**, 240406 (2008).

[62]H. Nakatsuji and H. Nakashima, Int. J. Quantum Chem. **109**, 2248 (2009).

[63]Y. Hijikata, H. Nakashima, and H. Nakatsuji, J. Chem. Phys. **130**, 024102 (2009); A. Ishikawa, H. Nakashima, and H. Nakatsuji, Chem. Phys. **401**, 62 (2012); H. Nakashima, Y. Hijikata, and H. Nakatsuji, Astrophys. J. **770**, 144 (2013); H. Nakashima and H. Nakatsuji, J. Chem. Phys. **139**, 074105 (2013).

[64]A. Bande, H. Nakashima, and H. Nakatsuji, Chem. Phys. Lett. **496**, 347 (2010).

[65]H. Nakashima and H. Nakatsuji, Astrophys. J. **725**, 528 (2010).

[66]H. Nakatshima and H. Nakatsuji, J. Chem. Phys. **139**, 044112 (2013).

[67]H. Nakatsuji, Bull. Chem. Soc. Jpn. **83**, 1705 (2005).

[68]H. Nakatsuji, Acc. Chem. Res. **45**, 1480 (2012).

[69]H. Nakatsuji, J. Jpn. Soc. Simul. Tech. **32**, 39 (2013), (in Japanese).

[70]H. Nakatsuji and H. Nakashima, TSUBAME e-Science J. **11**(08), 24 (2014); H. Nakatsuji, CRC-SU Symposium at Stockholm University, 31 November 2014.

[71]N. R. Kestner and O. Sinanoglu, Phys. Rev. **128**, 2687 (1962).

[72]M. Taut, Phys. Rev. A **48**, 3561 (1993).

[73]J.-L. Calaia and P.-O. Löwdin, J. Mol. Spectrosc. **8**, 203 (1962).

[74]A. A. Frost, J. Chem. Phys. **10**, 240 (1942).

[75]A. V. Mohrenstein, Z. Phys. **134**, 488 (1953).

[76]A. A. Frost, R. E. Kellogg, B. M. Gimarc, and J. D. Scargle, J. Chem. Phys. **35**, 827 (1961).

[77]W. Yang and A. C. Peet, Chem. Phys. Lett. **153**, 98 (1988).

[78]A. C. Peet and W. Yang, J. Chem. Phys. **90**, 1746 (1989).

[79]W. Yang and A. C. Peet, J. Chem. Phys. **92**, 522 (1990).

[80]S. Manzhos, M. Chan, and T. Carringtonn, Jr., J. Chem. Phys. **139**, 051101 (2013).

[81]G. Avila and T. Carrington, Jr., J. Chem. Phys. **139**, 134114 (2013).

[82]J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Oxford University Press, 1965); W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes 3rd Edition: The Art of Scientific Computing* (Cambridge University Press, 2007).

[83]R. N. Hill and C. Krauthauser, Phys. Rev. Lett. **72**, 2151 (1994).

[84]C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950).

[85]W. E. Arnoldi, Q. Appl. Math. **9**, 17 (1951).

[86]R. Chen and H. Guo, J. Comput. Phys. **136**, 494 (1997).

[87]H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).

[88]H. Nakatsuji and H. Nakashima, "Local sampling method for potentially exact wave functions"(unpublished).

[89]T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[90]R. T. Pack and W. B. Brown, J. Chem. Phys. **45**, 556 (1966).

[91]V. A. Rassolov and D. M. Chipman, J. Chem. Phys. **104**, 9908 (1996).

[92]Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, J. Chem. Phys. **139**, 044114 (2013); **140**, 214103 (2014).

[93]J. H. Bartlett, Jr., Phys. Rev. **51**, 661 (1937).

[94]T. H. Gronwall, Phys. Rev. **51**, 655 (1937).

[95]V. A. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 161 (1954).

[96]See http://gmplib.org/ for about the GMP library.

[97]H. Nakatsuji and H. Nakashima, "Solving Schrödinger equation of molecules by dissolving Pauli dogma: Inter-exchange theory," J. Chem. Phys. (submitted).