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Free complement s_{ij}-assisted r_{ij} theory: Variational calculation of the quintet state of a carbon atom

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The free complement s_{ij}-assisted r_{ij} (FC $r_{ij}s_{ij}^n$) theory was developed as a variational method for solving the Schrödinger equations of atoms and molecules. This theory permits only a single correlated r_{ij} term in each complement function (cf) and the other r_{ij} terms are replaced with $s_{ij} = r_{ij}^2$ terms so that the variational calculations are performed within one- to four-electron integrals. We developed the r_{ij}-extended Löwdin formula for the antisymmetrization of r_{ij}-included nonorthogonal functions and implemented one- to four-electron Slater atomic integral codes necessary for the present calculations. The cf selection technique was introduced to reduce the number of degrees of freedom efficiently without much loss of accuracy. These methods were applied to the lowest quintet ${}^5S^o(sp^3)$ state of a carbon atom, which is an excited state of a carbon atom but most important for chemical bonds. The chemical accuracy was achieved with the absolute solution of $\Delta E = 0.215$ kcal/mol from the estimated exact energy: The number of the cf's used was 4577 but reduced to only 129 after utilizing the cf selection technique for obtaining the chemical accuracy $\Delta E < 1$ kcal/mol. Thus, the present theory can realize accurate variational calculations of many-electron systems with compact wave functions if the required three- and four-electron integrals are practically available.

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I. INTRODUCTION

Solving the Schrödinger equations (SE) of atoms and molecules is one of the most important subjects of quantum chemistry [1]. In 2004, one of the authors proposed the free complement (FC) theory based on the scaled SE (SSE) [2–4],

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

where H, E, and ψ are the Hamiltonian, energy, and wave function, respectively. In Eq. (1), the scaling operator, g function, was introduced to overcome the divergence difficulty of the integrals of the Hamiltonian in the variational formulas. A popular choice of this g function is

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

where r_{iA} is a distance between electron i and nucleus A and r_{ij} is a distance between electrons i and j. The method using Eq. (2) or related functions is referred to as FC r_{ij} theory. This g function does not eliminate the information at the particle coalescences, i.e., $gV|_{r\to 0} \neq 0$, where V is the potential operators and r is r_{iA} or r_{ij}. Therefore, the electron-nucleus and electron-electron cusp conditions are satisfied. We have applied the FC r_{ij} theory to the variational calculations of small atoms and molecules, such as He, ${H_2}^+$, H_2, Li, Be, etc., with analytical integrations and obtained highly accurate results [5–8]; especially the energy accurate over 40 digits were obtained for the He atom [5]. For general systems, however, the FC r_{ij} theory often requires many-electron integrals unfeasible to evaluate analytically since the multiple-linked non-separable r_{ij} terms are generated at higher FC order. Alternatively, we also performed the sampling calculations by the local Schrödinger equation (LSE) method with the FC r_{ij} wave functions [9,10]. The chemical accuracies, within 1 kcal/mol error as an absolute solution, were obtained for all the first-row atoms and small molecules, such as C_2, C_2H_2, H_2CO, etc. [11,12]. The LSE method is free from the integration difficulty.

On the other hand, the FC s_{ij} theory was recently proposed [13] where the g function was approximated by

$$g = \sum_{i,A} r_{iA} + \sum_{i<j} s_{ij}, \tag{3}$$

with $s_{ij} \equiv {r_{ij}}^2 = (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2$. Since s_{ij} can be transformed into one-electron terms, this theory has great merit that all the integrals necessary for the matrix elements can be calculated by only one- and two-electron integrals. The demerit is not to satisfy the electron-electron cusp condition due to $gV|_{r_{ij}\to 0} = 0$ though the electron-electron coalescence regions are not majorly important due to the repulsive character of the Coulomb potential. We applied the FC s_{ij} theory to He, Li, and the quintet ${}^5S^o(sp^3)$ state of a carbon atom and a H_2 molecule and the chemical accuracies as absolute solutions were obtained [13]. The convergence to the exact solution was, however, less efficient than that of the FC r_{ij} theory although the computational labors were much smaller.

In the present paper, we introduce an intermediate theory between the FC r_{ij} and the s_{ij} theories. We limit our calculations to include only up to a single correlated r_{ij} term in each cf defined in Sec. II, and the other r_{ij} terms are replaced with

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the s_{ij} terms in the FC r_{ij} wave function. Since the s_{ij} terms can be converted into the one-electron functions, the present variational calculations require one- to four-electron integrals at most, which are feasible. We call this method the FC s_{ij}-assisted r_{ij}(FC $r_{ij}s_{ij}^n$) theory. This theory may be similar to the Hyllerass-configuration interaction (CI) method [14–18]. However, the Hylleraas-CI method has not been successful yet for more than four-electron systems to obtain the chemical accuracy as absolute solution. For example, Ruiz performed the high-level calculations for the boron atom, but the calculated energy was still 3.6 kcal/mol higher than the estimated exact energy [18]. The FC $r_{ij}s_{ij}^n$ theory, on the other hand, is based on the FC theory which guarantees the convergence to the exact solutions [2–4]. In the present paper, we examine the FC $r_{ij}s_{ij}^n$ theory with solving the SE for the lowest quintet $^5S^o(sp^3)$ state of a carbon atom (six-electron system): This state is an excited state of a carbon atom but is most important for chemical bonds. Recently, Strasburger performed very accurate calculations of the ^3P and $^5S^o$ states of a carbon atom with the explicitly correlated Gaussian (ECG) lobe functions and gave variationally best energies for these states [19]. This method is powerful and accurate but needs to optimize a large number of linear and nonlinear parameters. We also note here the other accurate approaches for calculating atomic states although they may not calculate the $^5S^o$ state of a carbon atom; the ECG methods [20–25], the F12 theory [26], the full CI method [27], the recent development of the quantum Monte Carlo [28], etc.

In the present paper, for general applications of the FC $r_{ij}s_{ij}^n$ theory, we extended the determinant-based Löwdin formula [29] to evaluate the matrix elements for the nonorthogonal orbitals including explicit r_{ij} terms [30]. We also implemented one- to four-electron Slater atomic integral code necessary for the FC $r_{ij}s_{ij}^n$ calculations of general atoms. We also introduced the cf selection technique to reduce the number of degrees of freedom efficiently without much loss of accuracy. These computational techniques would be useful for the present theory to be applicable to many-electron systems.

In the present paper, Sec. II describes the FC $r_{ij}s_{ij}^n$ theory and the variational computational techniques of the r_{ij}-extended Löwdin formula, the implementation of the required integrals, and the cf selection technique. In Sec. III, the applications to the $^5S^o(sp^3)$ state of a carbon atom is discussed and, in Sec. IV, the concluding remarks are given.

II. THEORY AND COMPUTATIONAL TECHNIQUES

A. Free complement s_{ij}-assisted r_{ij} (FC $r_{ij}s_{ij}^n$) theory

Here, we briefly summarize the FC $r_{ij}s_{ij}^n$ theory. First, we construct the FC wave function using the simplest iterative complement formula as given by the recurrence formula [2–4],

$$\psi_n = [1 + C_n g(H - E_{n-1})]\psi_{n-1}, \tag{4}$$

where n represents the order of the FC theory and C_n and E_{n-1} denote a variational parameter and the expectation energy of ψ_{n-1}. With the SSE, g is a scaling function necessary to get rid of the Coulomb singularity problem. This recurrence series is proved to converge to the exact solution of the SE [2–4]. The FC wave function is defined by

$$\psi_n = \sum_{I=1}^{M} c_I \phi_I, \tag{5}$$

where the analytical independent functions are collected from the right-hand side of Eq. (4). ϕ_I is referred to as the cf that spans the target exact solution, c_I is the correspondent variational coefficient, and M is the number of the independent cf's. $\{c_I\}$'s are determined by the variational method with integrations or the LSE method [9,10]: the present paper employs the former.

The cf's are generally denoted by

$$\phi_I = A\Omega[f_I(\{r_{iA}, x_{iA}, y_{iA}, z_{iA}\}, r_{ij})\varphi_0], \tag{6}$$

where the operators A and Ω represent the antisymmetrization and spatial symmetrization operators, respectively. The initial function of the FC theory is given by $\psi_0 = A\Omega[\varphi_0]$, where φ_0 consists of a spatial part and a spin eigenfunction of the S^2 and S_z operators. f_I is a spatial function that characterizes each complement function generated by the FC theory. The choice of ψ_0 is an important key point for constructing the accurate FC wave functions efficiently and understandably with physical and chemical intuitions. One of the proper choices we have mainly examined is to construct ψ_0 based on the local atomic concept, transferability, and from-atoms-to-molecule concept, that is theoretically summarized as the chemical formula theory for general atoms and molecules in our previous work [11]. Based on this theory, the present paper employs ψ_0 using the nonorthogonal local atomic orbitals as given in Sec. III.

f_I in Eq. (6) is the function of one-electron coordinates $\{r_{iA}, x_{iA}, y_{iA}, z_{iA}\}$ and two-electron coordinates r_{ij}, where i and j denote electrons and A represents the nucleus. The FC r_{ij} theory generates the f_I including multiple linked odd-power r_{ij} terms, such as r_{ij}, $r_{ij}r_{kl}$, and $r_{ij}r_{kl}r_{mn}$, etc., at the FC order $n = 1 - 3$, respectively. Although this theory can produce accurate results with fast convergences to the exact solutions, analytical integrations for these functions are generally difficult. The FC s_{ij} theory [13], on the other hand, generates the f_I including s_{ij} terms, such as s_{ij}, $s_{ij}s_{kl}$, $s_{ij}s_{kl}s_{mn}$, etc., but does not contain any odd-power r_{ij} terms. s_{ij} is separable into one-electron functions by

$$\begin{aligned} s_{ij} &= (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \\ &= (x_{iA} - x_{jB})^2 + (y_{iA} - y_{jB})^2 + (z_{iA} - z_{jB})^2 \\ &\quad - 2(X_A - X_B)(x_{iA} - x_{jB}) - 2(Y_A - Y_B)(y_{iA} - y_{jB}) \\ &\quad - 2(Z_A - Z_B)(z_{iA} - z_{jB}), \end{aligned} \tag{7}$$

where the right-hand side is denoted by the electron-nucleus interparticle coordinates and capital (X_A, Y_A, Z_A) and (X_B, Y_B, Z_B) are the nuclear geometries, i.e., constant values. Thus, f_I is a function of $\{r_{iA}, x_{iA}, y_{iA}, z_{iA}\}$ and does not contain any interelectron coordinates, and only one- and two-electron integrals are enough for the variational calculations. However, the convergence to the exact solutions is generally slower than the FC r_{ij} case due to the loss of information at the electron-electron coalescence regions, i.e., for $gV|_{r_{ij}\to 0} = 0$.

We here introduce the FC $r_{ij}s_{ij}^n$ theory as a simple hybrid method of the FC r_{ij} and s_{ij} theories. The formulation is

TABLE I. Classifications of the Hamiltonian and overlap matrix elements for the cf's generated by the FC $r_{ij}s_{ij}^n$ theory.

Pattern	Matrix elements[a]	Origin	Most complicated type of primitive integral
1	$\langle U \mid V\rangle$	Overlap	One-electron
2	$\langle U\vert h_1(\Lambda)\vert V\rangle$	Hamiltonian	One-electron
3	$\langle U\vert 1/r_{\Lambda \mathrm{M}}\vert V\rangle$	Hamiltonian	Two-electron
4	$\langle U \mid r_{KL}V\rangle$	Overlap	Two-electron
5	$\langle U\vert h_1(\Lambda)\vert r_{KL}V\rangle$	Hamiltonian	Two-electron
6	$\langle U\vert 1/r_{\Lambda \mathrm{M}}\vert r_{KL}V\rangle$	Hamiltonian	Three-electron (type I)
7	$\langle U r_{IJ} \mid V\rangle$	Overlap	Two-electron
8	$\langle U r_{IJ}\vert h_1(\Lambda)\vert V\rangle$	Hamiltonian	Two-electron
9	$\langle U r_{IJ}\vert 1/r_{\Lambda \mathrm{M}}\vert V\rangle$	Hamiltonian	Three-electron (type I)
10	$\langle U r_{IJ} \mid r_{KL}V\rangle$	Overlap	Three-electron (type I)
11	$\langle U r_{IJ}\vert h_1(\Lambda)\vert r_{KL}V\rangle$	Hamiltonian	Three-electron (type I)
12	$\langle U r_{IJ}\vert 1/r_{\Lambda \mathrm{M}}\vert r_{KL}V\rangle$	Hamiltonian	Three-electron (types I and II), Four-electron (types I and II)

[a] Antisymmetrization operator is abbreviated.

very simple; the cf's are first generated by the FC r_{ij} theory, the even-power r_{ij}^{2t} (t is a positive integer) was rewritten by s_{ij}^t, and then, transform the remaining single-odd-power $r_{ij}r_{kl}r_{mn}\cdots$ terms as a single r_{ij} term retained and the others are replaced by s_{ij} termsas as given by

$$\begin{aligned} r_{ij} &\rightarrow r_{ij} \\ r_{ij}r_{kl} &\rightarrow r_{ij}s_{kl}, \quad s_{ij}r_{kl} \\ r_{ij}r_{kl}r_{mn} &\rightarrow r_{ij}s_{kl}s_{mn}, \quad s_{ij}r_{kl}s_{mn}, \quad s_{ij}s_{kl}r_{mn} \\ &\cdots . \end{aligned} \tag{8}$$

Since the transformed s_{ij} can be described by one-electron functions, each term of f_I includes only a single inseparable electron pair. As long as both FC r_{ij} and s_{ij} theories guarantee the exactness, this theory also guarantees the exactness. The important merit of this theory has a form to satisfy $gV|_{r_{ij}\rightarrow 0} \neq 0$, similar to the FC r_{ij} theory. Therefore, the convergence to the exact solution is expected to be improved than that of the FC s_{ij} theory. However, the evaluations of the matrix elements are much more complicated than the FC s_{ij} case especially for the required three- and four-electron integrals. Therefore, some useful formulations are necessary before entering into the calculations.

B. r_{ij}-Extended Löwdin formula for the matrix elements over partially correlated nonorthogonal functions

For the variational FC $r_{ij}s_{ij}^n$ theory, one needs to compute the Hamiltonian and overlap matrix elements over the cf's with one- to four-electron integral evaluations. The present cf's include local nonorthogonal orbitals and partially correlated r_{ij} terms so that an efficient antisymmetrization procedure for these functions is necessary. In 1955, Löwdin provided the formulations to evaluate the matrix elements for the overlap, one-electron, and two-electron operators [29]. In the present paper, we extended the Löwdin formula to the cases including partially correlated single-r_{ij} term. We simply apply the Laplace expansion as the r_{ij} term outside of the determinant. With this method, the antisymmetrization process can be evaluated with a polynomial computational cost. Despite its simpleness, there is no reference that explicitly provides its formulations as far as we know. The formulations should be useful not only for the present theory, but also for the Hylleraas-CI method.

We denote a general expression for a single term contained in bra- and ket-side cf's of the FC $r_{ij}s_{ij}^n$ theory,

$$\begin{aligned} \phi_{\mathrm{bra}} &= A[f_{IJ}U] = A\big[f_{IJ}u_1(1)u_2(2)\cdots u_{N_e}(N_e)\big], \\ \phi_{\mathrm{ket}} &= A[f_{KL}V] = A\big[f_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]. \end{aligned} \tag{9}$$

For simplicity, we omit a spin function in Eq. (9) without loss of generality. U and V represent the Hartree products of one-electron nonorthogonal orbitals u_i and v_i of electron i for the bra and ket sides, respectively. f_{IJ} and f_{KL} are unity or inseparable two-electron terms; r_{IJ} and r_{KL} in the present case. With ϕ_{bra} and ϕ_{ket}, the Hamiltonian one-electron and two-electron terms and the overlap are given by

$$\langle\phi_{\mathrm{bra}}|h_1(\Lambda)|\phi_{\mathrm{ket}}\rangle,\ \langle\phi_{\mathrm{bra}}|1/r_{\Lambda \mathrm{M}}|\phi_{\mathrm{ket}}\rangle,\ \langle\phi_{\mathrm{bra}}|\phi_{\mathrm{ket}}\rangle, \tag{10}$$

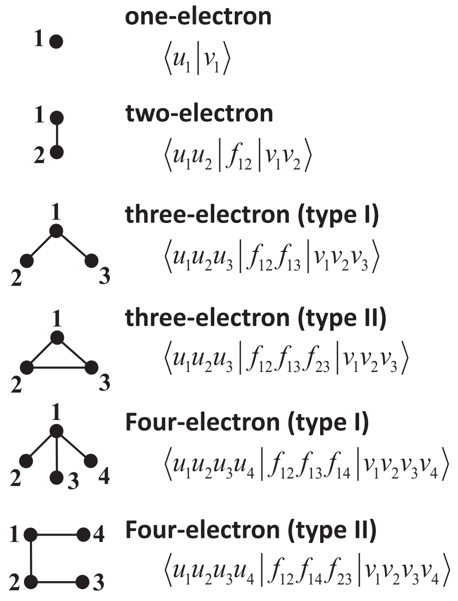

FIG. 1. Diagrams classified the primitive integrals where a dot and a line represent an electron and an inseparable f_{ij} function which is r_{ij} or r_{ij}^{-1} in the present paper, respectively.

TABLE II. Classifications of the primitive integrals that appear in the FC $r_{ij}s_{ij}^n$ wave functions.

No.	Type	Primitive integrals	Origin
1	One-electron	$\langle u_p \mid v_q\rangle$	Overlap
2	One-electron	$\langle u_p\lvert h_1\rvert v_q\rangle$	Hamiltonian
3	Two-electron	$\langle u_pu_q\lvert f_{12}\rvert v_rv_s\rangle[f_{12}=1/r_{12}, r_{12}, (r_{12}^2)]$	Hamiltonian, overlap
4	Two-electron	$\langle u_pu_q\lvert f_{12}^{(b)}h_1f_{12}^{(k)}\rvert v_rv_s\rangle(f_{12}^{(b)},\ f_{12}^{(k)}=1,\ r_{12})$	Hamiltonian
5	Three-electron (type I)	$\langle u_pu_qu_r\lvert f_{12}f_{13}\rvert v_sv_tv_u\rangle(f_{12}=1/r_{12},\ r_{12},\ f_{13}=r_{13})$	Hamiltonian, overlap
6	Three-electron (type I)	$\langle u_pu_qu_r\lvert f_{12}h_1(1)f_{13}\rvert v_sv_tv_u\rangle(f_{12}=r_{12},\ f_{13}=r_{13})$	Hamiltonian
7	Three-electron (type I)	$\langle u_pu_qu_r\lvert f_{12}h_1(2)f_{13}\rvert v_sv_tv_u\rangle(f_{12}=r_{12},\ f_{13}=r_{13})$	Hamiltonian
8	Three-electron (type I)	$\langle u_pu_qu_r\lvert f_{12}h_1(3)f_{13}\rvert v_sv_tv_u\rangle(f_{12}=r_{12},\ f_{13}=r_{13})$	Hamiltonian
9	Three-electron (type II)	$\langle u_pu_qu_r\lvert f_{12}f_{13}f_{23}\rvert v_sv_tv_u\rangle(f_{12}=r_{12},\ f_{13}=r_{13},\ f_{23}=1/r_{23})$	Hamiltonian
10	Four-electron (type I)	$\langle u_pu_qu_ru_s\lvert f_{12}f_{13}f_{14}\rvert v_tv_uv_vv_w\rangle(f_{12}=r_{12},\ f_{13}=r_{13},\ f_{14}=1/r_{14})$	Hamiltonian
11	Four-electron (type II)	$\langle u_pu_qu_ru_s\lvert f_{12}f_{14}f_{23}\rvert v_tv_uv_vv_w\rangle\begin{pmatrix}f_{12}=r_{12},\ f_{14}=r_{14},\ f_{23}=1/r_{23}\\ f_{12}=1/r_{12},\ f_{14}=r_{14},\ f_{23}=r_{23}\end{pmatrix}$	Hamiltonian

respectively, where $h_1(\Lambda)$ contains a kinetic operator and electron-nuclear Coulomb potential and $1/r_{\Lambda\mathrm{M}}$ is an electron-repulsion Coulomb potential.

Equation (10) is classified into 12 patterns summarized in Table I by whether nonunity f_{IJ} and f_{KL}, i.e., r_{IJ} and r_{KL}, terms, exist or not. Table I indicates the types of matrix elements, their origins (Hamiltonian or overlap), and the type of the most complicated primitive integrals. The types of the primitive integrals are classified as shown in Fig. 1 which is discussed in the next subsection. In Table I, patterns 1 to 3 are the matrix elements without any r_{IJ} and/or r_{KL} terms, and they can be evaluated by the Löwdin's original formulas [29] with one- and two-electron integrals. Any other patterns include the correlation terms, at least, one of r_{IJ} and/or r_{KL} terms in the bra and/or ket wave functions. Patterns 4, 5, 7, and 8 can be still evaluated within one- and two-electron integrals. Patterns 6, 9–11 require three-electron (type-I) integrals which are not very difficult compared to the other types of three- and four-electron integrals. Pattern 12 originates from the electron-repulsive Coulomb potential with the r_{IJ} and r_{KL} terms in both bra and ket sides, and it requires three-electron (type-I and type -II) and even four-electron (type-I and -II) integrals. In the present paper, we formulated their matrix elements based on the Laplace expansion of the determinant-based algorithm extended from Löwdin's formulas [29] for all the patterns 1–12 where patterns 7–9 are the same as patterns 4–6 by exchanging the bra and ket sides. Since their formulations were simple but lengthy, we provided them in the Appendix.

C. Implementation of the primitive atomic one- to four-electron integrals necessary for the FC $r_{ij}s_{ij}^n$ theory

The matrix elements in Table I are further decomposed to the primitive one- to four-electron integrals as given in Table II. They are classified according to the connection of the inseparable f_{ij} (r_{ij} or r_{ij}^{-1}) terms as illustrated in Fig. 1. The diagrams of one- and two-electron integrals are trivial. Three-electron integrals has two types; type I and II. Three-electron (type-I) $\langle f_{12}f_{13}\rangle$ has only a single-linked electron but all three electrons are linked in three-electron (type-II) $\langle f_{12}f_{13}f_{23}\rangle$. Four-electron integrals are also classified into type I and II. Four-electron (type-I) $\langle f_{12}f_{13}f_{14}\rangle$ has only a single-linked electron and four-electron (type-II) $\langle f_{12}f_{14}f_{23}\rangle$ has two linked electrons. Generally, three-electron (type II) is most difficult to evaluate. Four-electron (type II) is the next difficulty. Four-electron (type I) and three-electron (type I) are not so very difficult to evaluate. In actual computations, the memory required is also a serious problem, which is discussed in the last paragraph of this subsection. A direct and disposable method and/or something approximate methods for their integrations should be required for the calculations of many-electron systems.

For the present accurate atomic calculations, we implemented one- to four-electron atomic integrals over Slater orbitals. The closed-form integration methods of these integrals have been proposed in several references [31–35]. However, accurate calculations of the FC $r_{ij}s_{ij}^n$ theory further need to cover higher-order radial and angular momentum functions with the explicit r_{ij} functions. In the present paper, we employed, for instance, the Laplace series expansion of r_{ij} and/or $1/r_{ij}$ terms for two-electron integrals which is well suitable for higher angular momentum cases. The method that converts angular parts into radial integrals was also employed for three-electron (type I) and four-electron (types I and II). This basic idea is given by Calais and Löwdin [31] and it is extended by Ruiz for the three- and four-electron cases [32]. For the fully linked three-electron integral (type II), after converting the angular part into the radial part using the rotational invariant [36], we employed the method using a closed-form recursion formula of the radial r_i and r_{ij} parts. This idea was originally given by Fromm and Hill [33] with the mathematically complicated form, but it was simplified by Pachucki and Puchalski [34]. In our paper, we also developed a closed-form integration method for three- (type-I) and four-electron (type-I and -II) integrals in case including exponential-type $\exp(-\beta r_{ij})$ functions [35]. We unified the above integration methods and originally implemented a general code of Slater atomic integrals for the accurate FC $r_{ij}s_{ij}^n$ calculations of atoms [37]. Here, all the integrals are calculated with the closed forms to keep high accuracies and adapted to higher-order radial and angular momentum functions. A general integral code that satisfies these requirements seems not exist except for the present program.

The memory requirement is generally a crucial problem in the variational calculations. Simply, the number of two-, three-, and four-electron integrals seem to scale with $O(K^4)$, $O(K^6)$, and $O(K^8)$, respectively, where K is the number of one-electron functions in the cf's. However, when the FC $r_{ij}s_{ij}^n$ wave function is constructed based on the local description [11], the number of necessary integrals can be much reduced. For instance, in a simple case of lithium atom, the Hartree-Fock delocalized molecular orbital theory requires all the two-electron integrals: $\langle 1s1s|1s1s\rangle, \langle 1s1s|1s2s\rangle, \langle 1s2s|1s2s\rangle, \langle 1s2s|2s1s\rangle, \langle 1s2s|2s2s\rangle$, and $\langle 2s2s|2s2s\rangle$, where 1s and 2s denote the atomic (basis set) orbitals. On the other hand, the local atomic theory only needs the integrals: $\langle 1s1s|1s1s\rangle$, $\langle 1s1s|1s2s\rangle$, $\langle 1s2s|1s2s\rangle$, and $\langle 1s2s|2s1s\rangle$ since there are at most two atomic $2s$ orbitals in the bra and ket sites. Such an observation works much more effectively in large systems, three- and four-electron integrals, and higher FC order calculations. In addition, for large systems, the exchange integrals among distant atoms become negligible. Thus, the development of the FC $r_{ij}s_{ij}^n$ theory based on the local concept is very important for its extension to large systems.

D. Complement function selection technique

We proposed the cf selection technique to construct the wave function with a compact set of cf's without much loss of accuracy. The proposed scheme is very simple as shown below: (i) Calculate Hamiltonian and overlap matrices: $H^{(1)}$ and $S^{(1)}$ for the initial cf and set $m = 1$. (ii) Add the i th cf candidate (add the i th row and column to $H^{(m)}$ and $S^{(m)}$), solve the secular equation, obtain its energy $E(i)$ for the target state, and this step is repeated over all the remaining candidates. (iii) Select the variationally best $E(i_{\text{best}})$, update $H^{(m+1)}$ and $S^{(m+1)}$ by adding the i_{best} th row and column, and increment m. (iv) Repeat steps (ii) and (iii) until convergence or enough accuracy is obtained.

Thus, the energetically important cf's are successively chosen from all the M cf's (candidates for selection) at order n. Since the loop can be truncated if the solution reaches to the enough accuracy, we do not have to calculate all the matrix elements for all the M cf's. The time-consuming part is a huge number of solving the secular equations (diagonalizations). This step requires $O(m^3)$ for $H^{(m)}$ and $S^{(m)}$. However, if the determinant and inverse matrix update algorithm are employed [30], the calculation of this step is reduced to $O(m^2)$.

III. APPLICATION TO THE LOWEST QUINTET $^5S^o(sp^3)$ STATE OF A CARBON ATOM

We applied the above methods to the lowest quintet $^5S^o(sp^3)$ state of a carbon atom. We employed the initial function $\psi_0 = A\Omega[\varphi_0]$ of the FC theory, given by

$$\varphi_0 = (1s1s' + 1s'1s)\alpha\beta(2s)(2p_x)(2p'_y)(2p''_z)\alpha\alpha\alpha\alpha, \qquad (11)$$

where each orbital is defined by

$$\begin{aligned}
1s &= N_{1s}\exp(-\alpha_{1s}r), \quad 1s' = N_{1s'}\exp(-\alpha_{1s'}r),\\
2s &= N_{2s,1}r\ \exp(-\alpha_{2s}r) + d_{2s}N_{2s,2}\exp(-\alpha_{2s}r),\\
2p_x &= N_{2p}x\ \exp(-\alpha_{2p}r), \quad 2p'_x = N_{2p'}x\ \exp(-\alpha_{2p'}r),\\
2p''_x &= N_{2p''}x\ \exp(-\alpha_{2p''}r),\\
2p_y &= N_{2p}y\ \exp(-\alpha_{2p}r), \quad 2p'_y = N_{2p'}y\ \exp(-\alpha_{2p'}r),\\
2p''_y &= N_{2p''}y\ \exp(-\alpha_{2p''}r),\\
2p_z &= N_{2p}z\ \exp(-\alpha_{2p}r), \quad 2p'_z = N_{2p'}z\ \exp(-\alpha_{2p'}r),\\
2p''_z &= N_{2p''}z\ \exp(-\alpha_{2p''}r). \qquad (12)
\end{aligned}$$

Equation (11) is constructed by the concept of "each electron to each orbital." The inner shell $1s$ pair is represented with the in-out correlation and $2p$ orbitals also include the effect similar to the in-out correlation. The spatial symmetrization operator is given by

$$\begin{aligned}
\Omega = 1 &+ (x, y, z \to x, z, y)\\
&+ (x, y, z \to y, x, z) + (x, y, z \to z, y, x)\\
&+ (x, y, z \to y, z, x) + (x, y, z \to z, x, y), \qquad (13)
\end{aligned}$$

which is necessary for the $2p_x$, $2p_y$, and $2p_z$ orbitals having the different exponents. In Eq. (12), $(\alpha_{1s}, \alpha_{1s'}, \alpha_{2s}, \alpha_{2p}, \alpha_{2p'}, \alpha_{2p''}, d_{2s}) = (6.5770, 4.7565, 1.7820, 2.2778, 1.4180, 1.0705, -0.167\,979\,829)$ were used. These parameters were variationally roughly optimized by minimizing the total energy of ψ_0 with the energy convergence threshold 10^{-8} a.u.N in Eq. (12) are the normalization factors of each term. Starting from this ψ_0, the FC $r_{ij}s_{ij}^n$ theory was applied with the modified g function of Eq. (2), where the r_{ij} terms were applied up to $n = 2$ to reduce the computational cost and the r_i^2 terms were also used to get ahead of s_{ij} terms, i.e., $g = \sum_i (r_i + r_i{}^2) + \sum_{i<j} r_{ij}$ at $n = 1$ and 2 and $g = \sum_i (r_i + r_i{}^2)$ at $n = 3$.

Table III summarizes the results for the FC orders $n = 0$–3. ΔE denotes the energy difference from the estimated exact energy given by Strasburger [19]. At $n = 0$, the energy of ψ_0 was $-37.611\,214$ a.u. and $\Delta E = 50.538$ kcal/mol. As increasing the FC order, the variational energies rapidly converge to the exact value. At $n = 1$ with $M = 28$, ΔE was 9.746 kcal/mol and, at $n = 2$ with $M = 505$, ΔE was 1.140 kcal/mol. At $n = 3$ with $M = 4577$, ΔE reached to 0.215 kcal/mol and achieved the chemical accuracy, i.e., less than 1 kcal/mol.

We further applied the cf selection technique to the FC wave function at $n = 3$. Figure 2 plots ΔE on the cf selection process. As shown in this figure, ΔE decreased monotonically and showed the exponentially rapid convergence to the limit value, i.e., the energy at $n = 3$ with $M = 4577$. Table III picks up some snapshots of this process. For instance, ΔE less than 3 kcal/mol was accomplished with $M = 45$, and $\Delta E < 2$ kcal/mol was performed with $M = 63$. The chemical accuracy, $\Delta E < 1$ kcal/mol, was accomplished only with $M = 129$ even for the present six-electron correlated system. Furthermore, $\Delta E < 0.8$, 0.5, and 0.3 kcal/mol were also obtained with small number of cf's; $M = 162$, 285, and 668, respectively. These results imply that small number of cf's are

TABLE III. Energy convergence of the FC $r_{ij}s_{ij}^n$ theory applied to the lowest quintet $^5S^o(sp^3)$ state of a carbon atom.

n[a,b]	M[c]	Energy (a.u.)	$\Delta E = E_{\mathrm{FC}} - E_{\mathrm{exact}}$ (kcal/mol)[d]
0	1	−37.611 214	50.538
1	28	−37.676 220	9.746
2	505	−37.689 935	1.140
3	4577	−37.691 409	**0.215**
	(cf selection from $n = 3$, $M = 4577$)		
	45	−37.687 059	2.944 (<3)
	63	−37.688 597	1.979 (<2)
	129	−37.690 159	**0.999 (<1)**
	162	−37.690 481	**0.797 (<0.8)**
	285	-37.690 956	**0.498 (<0.5)**
	668	−37.691 274	**0.299 (<0.3)**
Estimated exact energy		−37.691 751[e]	

[a] Order of FC theory.

[b] r_{ij} terms are restricted up to $n = 2$ to reduce the computational cost.

[c] Number of complement functions (dimension).

[d] Energy difference from the estimated exact energy by Ref. [19]. The values less than 1 kcal/mol are denoted by boldface.

[e] Reference [19].

enough to describe accurate wave functions due to the local natures of the cf's. If one chooses the higher-order cf's as candidates, the efficiency of the selection should be more improved, but the cf selection process needs more computational costs.

In Table IV, we compared the present results with the other calculations of the $^5S^o$ state of a carbon atom. Table IV indicates the absolute energy and ΔE by each method with the number of degrees of freedom. The definitions of degrees of freedom for each method is given in the footnote of this table. The Hartree-Fock energy was −37.597 60 a.u. and $\Delta E = 59.081$ kcal/mol with the McLean-Yoshimine Slater basis set given in Table I of Ref. [38]. The ψ_0 energy, −37.611 214 a.u. ($\Delta E = 50.538$ kcal/mol) in Table III, was lower than the Hartree-Fock energy. The in-out-like correlations in 1s electrons and 2p electrons effectively lowered the variational energy. Next, we examined the full CI calculations with the ordinary Gaussian and Slater basis sets using the MOLPRO WITH SMILES package [39]. The full CI calculation with the aug-cc-pVTZ (Gaussian) basis set [40] shows quite large $\Delta E = 31.718$ kcal/mol even with 8×10^6 configurations. The full CI result with the CVB3 (Slater) basis set [41] was much improved, but ΔE still remains 3.329 kcal/mol despite using the huge number of configurations almost 180×10^6. Thus, the convergence of the full CI method to the absolute exact energy of the SE was basically very slow with respect to the freedom. On the other hand, Sasaki and Yoshimine performed the single, double, triple, and quadruple (STDQ) -CI calculation with the selected configurations on the Slater basis set including higher angular momentum ($l_{\max} = 6$) [42]. Their results were surprisingly accurate, $\Delta E = 1.538$ kcal/mol and efficient with only 607 selected configurations. Since 1974, their variational best energy had not been updated until recently. As a sampling method, the diffusion Monte Carlo method was applied by Maldonado *et al.* [43] and $\Delta E = 0.936$ kcal/mol satisfying chemical accuracy was reported. Recently, the most precise energy, −37.691 747 780 a.u. and $\Delta E = 0.002$ kcal/mol, was reported by Strasburger with the ECG lobe function method [19] where the exact energy was estimated by extrapolation in this reference. This calculation is very accurate, but the wave function includes a lot of linear and nonlinear parameters to be optimized. With the FC LSE calculations [12], we obtained $\Delta E = 0.472$ kcal/mol satisfying the chemical accuracy only with 187 cf's though this is not a variational result. Recently, we also applied the FC s_{ij} theory and obtained $\Delta E = 0.837$ kcal/mol which is a variational energy satisfying the chemical accuracy [13]. After the cf selection technique was applied, $\Delta E < 1$ kcal/mol was obtained with 2942 cf's. These results are also remarkable because this calculation was performed only within one- and two-electron integrals. Compared with all above calculations, we can remarkably say that the present results were not only accurate as the solution of the SE, but also efficient to achieve the chemical accuracy with very small number of degrees of freedom.

In Table V, we summarized first 140 selected cf's through the cf selection technique. Each line indicates f_I of the selected cf on the selection process, the corresponding energy, ΔE, and $\Delta\Delta E$, which is the difference between the successive ΔE's. $\Delta\Delta E$ is also an important indicator for judgment of the importance of the selected cf. The first term is fixed as the initial function. The second most important cf for energy lowering was $r_{ij(1s,1's')}$, which is the r_{ij} correlation term between 1s electrons. By adding only this function to ψ_0, ΔE lowered almost 10 kcal/mol. The third energetically important cf was also 1s contribution of $r_{(1s')}$, which lowered the energy almost 8 kcal/mol. These may be reasonable because large energy contributions appear in 1s electrons. However, the fourth and fifth cf's related to 2p electrons. Although these features can-

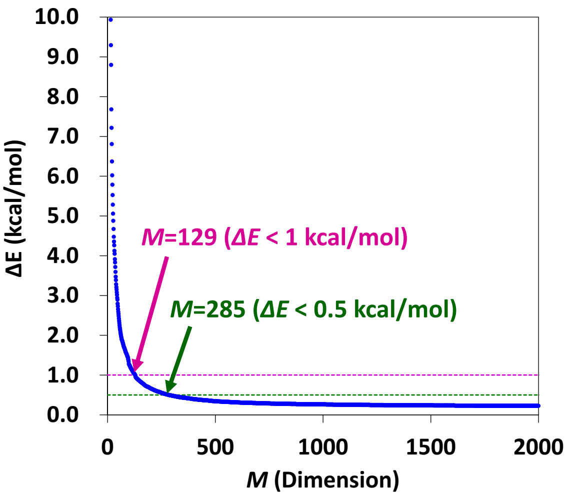

FIG. 2. Process of the cf selection technique applied to the FC $r_{ij}s_{ij}^n$ wave function at $n = 3$ for the lowest quintet $^5S^o(sp^3)$ state of a carbon atom.

TABLE IV. Comparison of the present results with the other calculations for the lowest quintet $^5S^o(sp^3)$ state of a carbon atom.

Method	The number of degrees of freedom (M)	Energy (a.u.)	$\Delta E = E_{\mathrm{FC}} - E_{\mathrm{exact}}$ (kcal/mol)[a]
Hartree-Fock (variational)[b,c]	1	−37.597 60	59.081
Full CI (variational)[c,d]			
aug-cc-pVTZ basis	7892868	−37.641 204	31.718
CVB3 basis (variational)	175576284	−37.686 446	3.329
SDTQ-CI (selected CI)[c,e]	607	−37.689 3	1.538
Diffusion Monte Carlo (sampling)[f]		−37.690 26(3)	**0.936**
ECG lobe function (variational)[g,h]			
$K = 129$	3612	−37.690 127 107	1.019
$K = 4023$	112644	−37.691 747 780	**0.002**
FC LSE (sampling)[i,j]	187	−37.690 998	**0.472**
FC s_{ij} theory (variational)[k,j]			
Step 9	13814	−37.690 418	**0.837**
cf selection	2942	−37.690 162	**0.997 (<1)**
This work: FC $r_{ij}s_{ij}^n$ theory (variational)			
Order $n = 3$	4577	−37.691 409	**0.215**
cf selection	129	−37.690 159	**0.999 (<1)**
Estimated exact energy		−37.691 751[g]	

[a] Energy difference from the estimated exact energy by Ref. [19]. The values less than 1 kcal/mol are denoted by boldface.

[b] McLean-Yoshimine (Slater) basis set [38].

[c] The number of degrees of freedoms is counted as the number of the configuration state functions or determinants.

[d] Full CI calculations were performed using the MOLPRO with the SMILES package [39] on the D_{2h} Abelian group. The numbers of basis functions of aug-cc-pVDZ (Gaussian) [40] and CVB3 (Slater) [41] basis sets are 46 and 76, respectively.

[e] Reference [42].

[f] Reference [43].

[g] Reference [19].

[h] The number of degrees of freedoms is counted according to Eqs. (2) and (3) of Ref. [19] where the number of linear parameters is denoted by K and the nonlinear parameters $\alpha_{I,i}$, $\beta_{I,ij}$, and $\mathbf{R}_{I,i}$ are used for each for each primitive function. Therefore, we count the freedom by $K + K \times (6 + 6 \times 5/2 + 6)$ for a six-electron carbon atom where the calculated number may be overestimated because the symmetry is not considered.

[i] Reference [12].

[j] The number of degrees of freedoms is the number of complement functions.

[k] Reference [13].

not be understood straightforwardly, we need broader insight into the selected cf's by analyzing more details. Up to 129 cf's which achieved the chemical accuracy, the number of cf's without any r_{ij} and s_{ij} terms was 30 and that of cf's including r_{ij} or s_{ij} terms was 99. The number of cf's whose f_I included $1s$ electrons was 78, that including $2s$ electrons was 63, and that including $2p$ electrons was 98. The number of cf's whose f_I was composed of only $1s$ electrons was 13, that composed of only valence electron was 50, and that including $1s$-valence inter-r_{ij} or -s_{ij} terms was 52. In the early stage of the selection process, most of the selected cf's include f_I related to $1s$ electrons. The cf's around $M = 100$, on the other hand, consist of f_I having only valence electrons. Further analysis may be performed using the artificial intelligence (AI) technique with various kinds of descriptors that relate to physical and chemical properties in the local concept. If we can accumulate much more experiences for various atomic states and molecules and use the AI technique, the important cf's might be predicted without calculations.

IV. CONCLUDING REMARKS

We formulated the FC $r_{ij}s_{ij}^n$ theory as a variational method for solving the Schrödinger equations and applied to the lowest quintet $^5S^o(sp^3)$ state of a carbon atom. For these calculations, we developed the r_{ij}-extended Löwdin formula to perform the antisymmetrization for the r_{ij}-included nonorthogonal functions efficiently and implemented one- to four-electron integrals necessary for the FC $r_{ij}s_{ij}^n$ theory over atomic Slater functions. The integrations are implemented in our original code to support higher-order radial and angular momentums required for the FC calculations. We also proposed a naive method to select the important cf's without much loss of accuracy.

These methods were applied to the lowest quintet $^5S^o(sp^3)$ state of a carbon atom and obtained $\Delta E = 0.215$ kcal/mol from the estimated exact energy at $n = 3$ with $M = 4577$. By the cf selection technique, only $M = 129$ cf's were enough to achieve the chemical accuracy; $\Delta E < 1$ kcal/mol. That is sur-

TABLE V. First 140 selected cf's through the cf selection technique for the lowest quintet $^5S^{\mathrm{o}}(sp^3)$ state of a carbon atom.

M[a]	f_I of cf[b]	Energy (a.u.)	$\Delta E = E_{\mathrm{FC}} - E_{\mathrm{exact}}$ (kcal/mol)[c]	$\Delta\Delta E$ (kcal/mol)[d]	M[a]	f_I of cf[b]	Energy (a.u.)	$\Delta E = E_{\mathrm{FC}} - E_{\mathrm{exact}}$[c] (kcal/mol)[c]	$\Delta\Delta E$ (kcal/mol)[d]
1	1	−37.611 214	50.537		71	$r_{(1s')}r_{ij(1s,1s')}s_{ij(1s,2px)}$	−37.688 863	1.812	0.021
2	$r_{ij(1s,1s')}$	−37.627 177	40.521	10.016	72	$r^2_{(1s')}r_{ij(1s',2px)}$	−37.688 893	1.793	0.019
3	$r_{(1s')}$	−37.640 184	32.359	8.162	73	$r^2_{(1s')}r_{ij(1s,1s')}$	−37.688 919	1.777	0.016
4	$r_{ij(1s',2px)}s_{ij(2px,2py)}$	−37.647 065	28.041	4.318	74	$r_{(1s)}r^2_{(1s')}r_{(2px)}$	−37.688 955	1.755	0.023
5	$r_{(2px)}r_{(2py)}$	−37.655 339	22.849	5.192	75	$r^2_{(1s)}r^2_{(2px)}r_{ij(1s,1s')}$	−37.688 993	1.731	0.024
6	$r_{(2s)}r_{ij(1s',2pz)}s_{ij(2px,2py)}$	−37.657 713	21.359	1.490	76	$r^2_{(1s')}s_{ij(1s',2px)}r_{ij(2px,2py)}$	−37.689 019	1.715	0.016
7	$r_{ij(2s,2px)}$	−37.660 625	19.532	1.827	77	$r^2_{(2py)}r_{(2pz)}r_{ij(1s',2px)}$	−37.689 040	1.701	0.014
8	$r_{(2s)}r_{(2px)}$	−37.662 863	18.127	1.404	78	$r_{(2s)}r^2_{(2py)}r_{ij(2px,2pz)}$	−37.689 062	1.688	0.013
9	$r_{(2px)}s_{ij(1s,1s')}$	−37.664 942	16.823	1.305	79	$r^4_{(1s)}r^2_{(2px)}$	−37.689 082	1.675	0.013
10	$r_{(2px)}r_{ij(2px,2py)}$	−37.666 844	15.629	1.194	80	$r_{(1s)}s_{ij(1s,1s')}r_{ij(1s',2py)}$	−37.689 104	1.661	0.013
11	$r_{ij(1s',2px)}s_{ij(2s,2py)}$	−37.670 489	13.342	2.287	81	$r^2_{(1s')}r_{ij(1s,2py)}$	−37.689 146	1.635	0.026
12	$r_{(1s)}r_{ij(1v,1s')}s_{ij(1s',2px)}$	−37.671 760	12.544	0.798	82	$r_{(1s')}s_{ij(1s,1s')}$	−37.689 167	1.622	0.013
13	$r_{(2px)}r_{(2py)}r_{(2pz)}$	−37.672 769	11.911	0.633	83	$r^2_{(1s)}s_{ij(1s,1s')}$	−37.689 203	1.599	0.023
14	$r_{ij(1s',2px)}$	−37.674 595	10.766	1.145	84	$r^2_{(1s')}$	−37.689 235	1.579	0.020
15	$r^2_{(2px)}r_{ij(1s',2s)}$	−37.675 922	9.933	0.833	85	$r^2_{(1s')}r^2_{(2px)}r_{ij(1s,1s')}$	−37.689 254	1.567	0.012
16	$r_{(2pz)}s_{ij(1s',2px)}r_{ij(2px,2py)}$	−37.676 939	9.295	0.638	86	$r^3_{(1s')}r_{ij(2s,2px)}$	−37.689 273	1.555	0.012
17	$r_{(2s)}r_{(2py)}$	−37.677 730	8.799	0.496	87	$r_{(1s)}r^2_{(1s')}r_{ij(1s,2px)}$	−37.689 290	1.544	0.011
18	$r_{(2px)}$	−37.679 513	7.680	1.119	88	$r^3_{(2py)}$	−37.689 306	1.534	0.010
19	$r_{ij(2py,2pz)}$	−37.680 253	7.215	0.465	89	$s_{ij(2py,2pz)}$	−37.689 324	1.523	0.011
20	$s_{ij(1s,2px)}$	−37.680 901	6.808	0.407	90	$r^4_{(2py)}r_{ij(1s',2s)}$	−37.689 352	1.505	0.018
21	$r_{(2pz)}$	−37.681 598	6.371	0.437	91	$r_{(2s)}r_{(2pz)}r_{ij(2py,2pz)}$	−37.689 374	1.492	0.014
22	$r_{(2px)}r_{ij(2s,2pz)}$	−37.682 152	6.023	0.348	92	$s_{ij(2px,2py)}r_{ij(2py,2pz)}$	−37.689 400	1.475	0.016
23	$r_{(2px)}s_{ij(2s,2px)}$	−37.682 531	5.786	0.238	93	$r_{(2py)}r_{ij(1s',2s)}s_{ij(1s',2px)}$	−37.689 418	1.464	0.011
24	$r_{(2px)}r_{(2pz)}r_{ij(2px,2py)}$	−37.682 945	5.526	0.260	94	$r^2_{(2s)}s_{ij(1s',2s)}r_{ij(2s,2pz)}$	−37.689 439	1.451	0.013
25	$r^2_{(2px)}$	−37.683 328	5.285	0.241	95	$r^4_{(2s)}r_{ij(1s',2s)}$	−37.689 465	1.435	0.016
26	$r^3_{(s)}$	−37.683 689	5.059	0.226	96	$r^4_{(2s)}$	−37.689 523	1.398	0.036
27	$r_{(1s)}r^2_{(2px)}r_{ij(1s',2px)}$	−37.683 975	4.880	0.180	97	$r^2_{(2s)}$	−37.689 557	1.377	0.021
28	$s_{ij(1s',2s)}$	−37.684 302	4.674	0.205	98	$r^5_{(2s)}$	−37.689 612	1.342	0.035
29	$r_{(2px)}s_{ij(1s',2px)}r_{ij(2s,2px)}$	−37.684 616	4.477	0.197	99	$r_{(2s)}$	−37.689 706	1.283	0.059
30	$r_{(2s)}r^2_{(2pz)}r_{ij(2px,2py)}$	−37.684 809	4.356	0.121	100	$r_{(2s)}r_{(2py)}r_{ij(2s,2px)}$	−37.689 727	1.270	0.013
31	$s_{ij(1s,1s')}$	−37.684 960	4.262	0.094	101	$r_{(1s')}s_{ij(1s,1s')}r_{ij(2s,2px)}$	−37.689 745	1.259	0.011
32	$r_{(1s)}r^2_{(1s')}$	−37.685 178	4.125	0.137	102	$r_{(2py)}s_{ij(2px,2py)}r_{ij(2px,2pz)}$	−37.689 762	1.248	0.010
33	$r_{ij(1s',2s)}$	−37.685 295	4.051	0.074	103	$r_{(2py)}r_{ij(2px,2py)}$	−37.689 778	1.238	0.010
34	$r^2_{(2px)}r_{ij(1s',2px)}$	−37.685 515	3.913	0.138	104	$r_{(2s)}s_{ij(1s,1s')}r_{ij(1s,2py)}$	−37.689 792	1.229	0.009
35	$r_{ij(2px,2py)}$	−37.685 641	3.834	0.079	105	$r^3_{(2s)}r_{ij(1s,1s')}$	−37.689 815	1.215	0.015
36	$r_{(2py)}r_{ij(1s',2px)}$	−37.685 825	3.719	0.116	106	$r_{(2px)}r_{ij(1s,1s')}s_{ij(2px,2py)}$	−37.689 834	1.203	0.012
37	$r_{(2s)}r_{(2px)}r_{(2py)}$	−37.686 021	3.596	0.123	107	$r_{(2s)}r^2_{(2py)}r_{ij(1s,1s')}$	−37.689 856	1.189	0.014
38	$r^2_{(2s)}s_{ij(1s',2px)}r_{ij(1s',2pz)}$	−37.686 217	3.472	0.123	108	$r_{(2s)}s_{ij(1s,1s')}r_{ij(1s',2s)}$	−37.689 876	1.177	0.012
39	$r^4_{(2s)}r_{ij(2s,2pz)}$	−37.686 351	3.389	0.084	109	$r^2_{(2s)}r_{(2py)}r_{ij(2s,2py)}$	−37.689 890	1.168	0.009
40	$r_{(2s)}s_{ij(1s',2s)}$	−37.686 518	3.284	0.105	110	$s_{ij(2s,2py)}r_{ij(2px,2py)}$	−37.689 903	1.160	0.008
41	$s_{ij(1s,1s')}r_{ij(1s,2px)}$	−37.686 634	3.211	0.073	111	$r_{ij(2s,2px)}s_{ij(2py,2pz)}$	−37.689 919	1.149	0.010
42	$r_{(2px)}s_{ij(1s',2px)}$	−37.686 729	3.151	0.059	112	$r^2_{(2pz)}r_{ij(1s',2)}s_{ij(1s',2py)}$	−37.689 933	1.141	0.008
43	$r_{(2px)}s_{ij(1s',2py)}r_{ij(2s,2py)}$	−37.686 839	3.082	0.069	113	$r^2_{(1s')}s_{ij(1s,1s')}r_{ij(1s,2px)}$	−37.689 945	1.133	0.008

TABLE V. *(Continued).*

M[a]	f_I of cf[b]	Energy (a.u.)	$\Delta E = E_{\mathrm{FC}} - E_{\mathrm{exact}}$ (kcal/mol)[c]	$\Delta\Delta E$ (kcal/mol)[d]	M[a]	f_I of cf[b]	Energy (a.u.)	$\Delta E = E_{\mathrm{FC}} - E_{\mathrm{exact}}$[c] (kcal/mol)[c]	$\Delta\Delta E$ (kcal/mol)[d]
44	$s_{ij(2px,2py)}$	−37.686 937	3.021	0.061	114	$r^4_{(1s')}r_{ij(1s',2s)}$	−37.689 960	1.124	0.009
45	$r_{(2s)}r^2_{(2py)}r_{ij(2s,2pz)}$	−37.687 059	2.944	0.077	115	$r^2_{(1s)}r_{(1s')}$	−37.689 976	1.114	0.010
46	$r_{(2s)}r_{ij(1s',2s)}$	−37.687 135	2.896	0.048	116	$r^2_{(1s')}s_{ij(1s,1s')}r_{ij(1s',2s)}$	−37.689 993	1.103	0.010
47	$r^2_{(2s)}s_{ij(1s',2s)}$	−37.687 295	2.796	0.100	117	$r^2_{(1s)}$	−37.690 009	1.093	0.010
48	$r^6_{(2s)}$	−37.687 399	2.731	0.065	118	$r_{(1s')}r_{ij(1s,2s)}s_{ij(1s',2s)}$	−37.690 020	1.086	0.007
49	$r_{(2py)}$	−37.687 519	2.656	0.075	119	$r_{(1s')}r^2_{(2s)}r_{ij(1s',2py)}$	−37.690 038	1.075	0.011
50	$r_{(2pz)}s_{ij(2px,2py)}r_{ij(2px,2pz)}$	−37.687 620	2.592	0.064	120	$r_{(2py)}r_{ij(1s,1s')}s_{ij(1s,2s)}$	−37.690 053	1.065	0.010
51	$r_{(1s)}s_{ij(1s,1s')}$	−37.687 698	2.543	0.049	121	$r_{(1s')}r_{ij(2s,2px)}s_{ij(2px,2py)}$	−37.690 066	1.058	0.008
52	$r^2_{(1s)}r_{(1s')}r_{ij(1s,1s')}$	−37.687 794	2.483	0.060	122	$r_{(2s)}r^2_{(2px)}r_{ij(2px,2py)}$	−37.690 076	1.051	0.006
53	$r^3_{(1s)}$	−37.687 889	2.423	0.060	123	$r^2_{(2s)}r_{ij(2py,2pz)}$	-37.690 090	1.043	0.009
54	$s_{ij(1s,1s')}r_{ij(1s',2px)}$	−37.687 987	2.362	0.061	124	$r^2_{(2s)}r_{ij(1s,1s')}s_{ij(2s,2px)}$	−37.690 100	1.036	0.006
55	$r_{ij(2s,2py)}$	−37.688 066	2.312	0.050	125	$r_{(2px)}r^2_{(2py)}r_{ij(1s',2py)}$	−37.690 109	1.030	0.006
56	$s_{ij(2s,2py)}$	−37.688 162	2.252	0.060	126	$r_{(2s)}\ r^2_{(2py)}r_{ij(2py,2pz)}$	−37.690 119	1.024	0.006
57	$r_{(2s)}r_{(2py)}r_{(2pz)}$	−37.688 243	2.202	0.051	127	$r_{(2px)}r_{ij(1s,2s)}s_{ij(1s',2s)}$	-37.690 128	1.018	0.006
58	$r_{(2pz)}r_{ij(1s',2s)}s_{ij(2py,2pz)}$	−37.688 304	2.163	0.038	128	$r_{(2px)}s_{ij(1s',2s)}r_{ij(1s',2px)}$	−37.690 143	1.009	0.009
59	$r^2_{(2px)}s_{ij(2s,2px)}$	−37.688 356	2.130	0.033	129	$r^2_{(2px)}s_{ij(1s',2px)}$	−37.690 159	**0.999**	0.010
60	$r^2_{(2s)}r^2_{(2px)}$	−37.688 429	2.084	0.046	130	$r^3_{(2px)}r_{ij(1s',2px)}$	−37.690 208	**0.968**	0.031
61	$r_{(2px)}\ r^2_{(2py)}$	−37.688 486	2.049	0.035	131	$r^4_{(2px)}$	−37.690 243	**0.946**	0.022
62	$r^2_{(1s)}r_{ij(1s,1s')}s_{ij(1s,2px)}$	−37.688 538	2.016	0.033	132	$r^2_{(2px)}r_{(2py)}r_{ij(2s,2px)}$	−37.690 257	**0.938**	0.009
63	$r^2_{(1s)}s_{ij(1s,2px)}r_{ij(1s',2py)}$	−37.688 597	1.979	0.037	133	$r^2_{(2py)}r_{ij(1s,2s)}s_{ij(2s,2pz)}$	−37.690 266	**0.932**	0.006
64	$r_{(1s')}s_{ij(1s,1s')}r_{ij(1s,2px)}$	−37.688 635	1.955	0.024	134	$r_{(1s')}s_{ij(1s,2s)}$	−37.690 274	**0.927**	0.005
65	$s_{ij(2s,2px)}r_{ij(2px,2py)}$	−37.688 672	1.932	0.023	135	$r_{(1s')}s_{ij(1s,1s')}r_{ij(1s',2s)}$	−37.690 283	**0.921**	0.006
66	$r^2_{(2s)}r_{(2py)}$	−37.688 719	1.902	0.030	136	$r^2_{(1s)}s_{ij(1s,1s')}r_{ij(1s,2px)}$	−37.690 292	**0.915**	0.006
67	$r^2_{(2px)}r_{(2py)}$	−37.688 749	1.884	0.019	137	$r_{(2px)}r_{ij(1s,1s')}$	−37.690 301	**0.910**	0.005
68	$r^3_{(1s)}r_{ij(1s',2py)}$	−37.688 773	1.869	0.015	138	$r_{(1s)}s_{ij(1s,1s')}r_{ij(1s',2px)}$	−37.690 307	**0.906**	0.004
69	$s_{ij(1s',2px)}r_{ij(1s',2py)}$	−37.688 800	1.852	0.017	139	$s_{ij(1s',2s)}r_{ij(1s',2px)}$	−37.690 313	**0.902**	0.004
70	$r_{(2px)}s_{ij(1s,1s')}r_{ij(2px,2py)}$	−37.688 830	1.833	0.019	140	$r_{(2s)}r_{(2py)}r_{ij(1s',2px)}$	−37.690 327	**0.894**	0.009
	Estimated exact	−37.691 751[e]					−37.691 751[e]		

[a] Number of complement functions (dimension).

[b] Each cf is written as $\phi_I = A\Omega[f_I\varphi_0]$, where $r_{(\mathrm{a})}$ denotes one-electron r term of electron a and $r_{ij(\mathrm{a,b})}$ and $s_{ij(\mathrm{a,b})}$ denote two-electron r_{ij} and s_{ij} terms of electrons a and b, respectively. Each electron is assigned to each orbital defined in Eq. (11).

[c] Energy difference from the estimated exact energy of Ref. [19]. The values less than 1 kcal/mol are denoted by boldface.

[d] Difference between ΔE at $M - 1$ and ΔE at M.

[e] Reference [19].

prisingly small degrees of freedom. Thus, the present results numerically prove that the FC $r_{ij}s^n_{ij}$ theory successfully works if the three- and four-electron integrals can be practically evaluated.

As future perspectives for the applications to general atoms and molecules, we need to further develop the FC $r_{ij}s^n_{ij}$ theory based on the local concept [11] and some numerical methods to compute three- and four-electron integrals more efficiently. Alternatively, the FC s_{ij} theory, which requires only one- and two-electron integrals, should also be useful for chemical studies if the relative energies, such as potential-energy curves, excitation energies, etc., are precisely calculated in chemical accuracy. The sampling method, i.e., LSE theory, is also powerful because it is integral free and any type of cf's for general systems are available without any restrictions. We continue to develop all these methods to take advantage of their merits.

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APPENDIX: r_{ij}-EXTENDED LÖWDIN FORMULA FOR THE FC $r_{ij}s_{ij}^n$ THEORY

The complement function of the FC $r_{ij}s_{ij}^n$ theory is generally expressed by Eq. (6), and we use a primitive expression denoted by Eq. (9) using Löwdin's original notation [29]. All the patterns of the matrix elements necessary in the present method was classified in Table I. We provided their concrete formulations according to the case with the classifications of Table I. Note that the antisymmetrizaion operator can be applied only to the ket site, but this operator is abbreviated in the equations.

Pattern 1. This is the overlap matrix elements without r_{ij} in both bra and ket sites. This can be trivially evaluated with the determinant, given by

$$\begin{aligned}\langle U \mid V\rangle &= \big\langle u_1(1)u_2(2)\cdots u_{N_e}(N_e)\;\big|\,A\big[v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle\\ &= |D| = \begin{vmatrix} \langle u_1 \mid v_1\rangle & \langle u_1 \mid v_2\rangle & \cdots & \langle u_1 \mid v_{N_e}\rangle \\ \langle u_2 \mid v_1\rangle & \langle u_2 \mid v_2\rangle & \cdots & \langle u_2 \mid v_{N_e}\rangle \\ \cdots & \cdots & \cdots & \cdots \\ \langle u_{N_e} \mid v_1\rangle & \langle u_{N_e} \mid v_2\rangle & \cdots & \langle u_{N_e} \mid v_{N_e}\rangle \end{vmatrix},\end{aligned} \tag{A1}$$

where $|D|$ is the overlap determinant whose element $\langle u_p \mid v_q\rangle$ is the one-electron overlap integral.

Pattern 2. This formulation is also given in Löwdin's formulations [29]. The idea is very simple, i.e., the row and column applied $h_1(\Lambda)$ are the outside of the determinant by the Laplace expansion. The resultant formula is given by

$$\langle U|h_1(\Lambda)|V\rangle = \big\langle u_1(1)u_2(2)\cdots u_{N_e}(N_e)\;\big|\,h_1(\Lambda)A\big[v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle = \sum_{\lambda=1}^{N_e}(-1)^{\Lambda+\lambda}\langle u_\Lambda|h_1|v_\lambda\rangle D(\Lambda|\lambda), \tag{A2}$$

where $\langle u_\Lambda|h_1|v_\lambda\rangle$ is the one-electron primitive integral for the kinetic and nucleus-electron potentials. $D(\Lambda|\lambda)$ is the minor which is the determinant of the matrix where the Λ row and the λ column are eliminated from D.

Pattern 3. This formulation is also given in Löwdin's formulations [29]. The idea is also based on the Laplace expansion where the Λ, M rows and the λ, μ columns are located on the outside of the determinant matrix. So, this can be represented by

$$\begin{aligned}\langle U|1/r_{\Lambda\mathrm{M}}|V\rangle &= \big\langle u_1(1)u_2(2)\cdots u_{N_e}(N_e)\;\big|\,1/r_{\Lambda\mathrm{M}}A\big[v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle\\ &= \sum_{\lambda=1}^{N_e-1}\sum_{\mu>\lambda}^{N_e}(-1)^{\Lambda+M+\lambda+\mu}\times[\langle u_\Lambda u_\mathrm{M}|1/r_{12}|v_\lambda v_\mu\rangle - \langle u_\mathrm{M}u_\Lambda|1/r_{12}|v_\lambda v_\mu\rangle]D(\Lambda, M|\lambda, \mu).\end{aligned} \tag{A3}$$

The following patterns are not given in Löwdin's formulations [29]. But, the idea is the same, i.e., the correlated electrons are put out from the determinant matrix by the Laplace expansion.

Pattern 4. This is similar to Eq. (A3) but the r_{KL} function is within the antisymmetrization operator in the ket site. Therefore, the formulation is given by

$$\begin{aligned}\langle U \mid r_{KL}V\rangle &= \big\langle u_1(1)u_2(2)\cdots u_{N_e}(N_e)\;\big|\,A\big[r_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle\\ &= \sum_{k=1}^{N_e-1}\sum_{l>k}^{N_e}(-1)^{k+l+K+L}[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle]D(k, l|K, L),\end{aligned} \tag{A4}$$

where $\langle u_k u_l|r_{12}|v_K v_L\rangle$ is a two-electron integral but surely not same as the ordinary electron repulsive potential integral.

Pattern 5. In this case, the Λ, K, and L electrons are outside but one must be careful the electrons K and L are within the antisymmetrization operator. So, the formulation is given by part by part,

$$\begin{aligned}&\langle U|h_1(\Lambda)|r_{KL}V\rangle\\ &\quad= \big\langle u_1(1)u_2(2)\cdots u_{N_e}(N_e)\;\big|\,h_1(\Lambda)A\big[r_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle\\ &= \sum_{k=1}^{N_e-1}\sum_{l>k}^{N_e}\begin{cases}(\Lambda = k)\\ \qquad\times(-1)^{\Lambda+l+K+L}[\langle u_\Lambda u_l|h_1(1)r_{12}|v_K v_L\rangle - \langle u_\Lambda u_l|h_1(1)r_{12}|v_L v_K\rangle]D(\Lambda, l|K, L)\\ (\Lambda = l)\\ \qquad\times(-1)^{k+\Lambda+K+L}[\langle u_k u_\Lambda|h_1(2)r_{12}|v_K v_L\rangle - \langle u_k u_\Lambda|h_1(1)r_{12}|v_L v_K\rangle]D(k, \Lambda|K, L)\\ (\Lambda \neq k, l)\\ \qquad\times\sum_{\lambda=1\ (\lambda\neq K,L)}^{N_e}(-1)^{k+l+K+L}(-1)^{\Lambda'+\lambda'}\\ \qquad\times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle]\\ \qquad\times\langle u_\Lambda|h_1|v_\lambda\rangle\\ \qquad\times D(\Lambda, k, l|\lambda, K, L),\end{cases}\end{aligned} \tag{A5}$$

where $\langle u_\Lambda u_l|h_1(1)r_{12}|v_K v_L\rangle$ is another two-electron integral. This case can be still computed within one- and two-electron integrals.

Pattern 6. Similarly, the Λ, M, K, and L electrons are outside. Note that Λ and M are outside of the antisymmetrization, but K and L electrons are within the antisymmetrization. These formulas are given by

$$\begin{aligned}
&\langle U|1/r_{\Lambda\mathrm{M}}|r_{KL}V\rangle \\
&\quad = \big\langle u_1(1)u_2(2)\cdots u_{N_e}(N_e)\ \big|\ 1/r_{\Lambda\mathrm{M}}A\big[r_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle \\
&\quad = \sum_{k=1}^{N_e-1}\sum_{l>k}^{N_e}\left\{\begin{array}{l}
(\Lambda = k, M = l) \\
\qquad \times(-1)^{\Lambda+M+K+L}[\langle u_\Lambda \mid v_K\rangle\langle u_\mathrm{M} \mid v_L\rangle - \langle u_\Lambda \mid v_L\rangle\langle u_\mathrm{M} \mid v_K\rangle]D(\Lambda, M|K, L) \\
(\Lambda = k, M \neq l) \quad \text{(and other patterns)} \\
\qquad \times \sum_{\mu=1\ (\mu\neq K,L)}^{N_e} (-1)^{\Lambda+l+K+L}(-1)^{M'+\mu'} \\
\qquad \times[\langle u_\Lambda u_\mathrm{M} u_l|1/r_{12}r_{13}|v_K v_\mu v_L\rangle - \langle u_\Lambda u_\mathrm{M} u_l|1/r_{12}r_{13}|v_L v_\mu v_K\rangle] \\
\qquad \times D(\Lambda, M, l|K, \mu, L) \\
(\Lambda \neq k, M \neq l) \\
\qquad \times \sum_{\lambda=1}^{N_e-1}\sum_{\mu>\lambda\ [(\lambda,\mu)\neq(K,L)]}^{N_e} (-1)^{k+l+K+L}(-1)^{\Lambda'+M'+\lambda'+\mu'} \\
\qquad \times[\langle u_\Lambda u_\mathrm{M}|1/r_{12}|v_\lambda v_\mu\rangle - \langle u_\mathrm{M} u_\Lambda|1/r_{12}|v_\lambda v_\mu\rangle] \\
\qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle] \\
\qquad \times D(\Lambda, M, k, l|\lambda, \mu, K, L),
\end{array}\right.
\end{aligned} \tag{A6}$$

This formulation contains $\langle u_\Lambda u_\mathrm{M} u_l|1/r_{12}r_{13}|v_K v_\mu v_L\rangle$ which is a three-electron (type-I) integral.

Patterns 7–9. This can be evaluated by the same as patterns 4–6 by exchanging the bra and ket sites.

Pattern 10. The formulation is similar to pattern 6 but $1/r_{ij}$ is replaced by r_{ij} and given by

$$\begin{aligned}
&\langle U r_{IJ} \mid r_{KL}V\rangle \\
&\quad = \big\langle r_{IJ}u_1(1)u_2(2)\cdots u_{N_e}(N_e)\ \big|A\big[r_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle \\
&\quad = \sum_{k=1}^{N_e-1}\sum_{l>k}^{N_e}\left\{\begin{array}{l}
(I = k, J = l) \\
\qquad \times(-1)^{I+J+K+L}\big[\langle u_I u_J|r_{12}^2|v_K v_L\rangle - \langle u_I u_J|r_{12}^2|v_L v_K\rangle\big]D(I, J|K, L) \\
(I = k, J \neq l) \text{ (and other patterns)} \\
\qquad \times \sum_{j=1\ (j\neq K,L)}^{N_e} (-1)^{I+l+K+L}(-1)^{J'+j'} \\
\qquad \times[\langle u_I u_J u_l|r_{12}r_{13}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}r_{13}|v_L v_j v_K\rangle] \\
\qquad \times D(I, J, l|K, j, L) \\
(I \neq k, J \neq l) \\
\qquad \times \sum_{i=1}^{N_e-1}\sum_{j>i\ [(i,j)\neq(K,L)]}^{N_e} (-1)^{k+l+K+L}(-1)^{I'+J'+i'+j'} \\
\qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle] \\
\qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle] \\
\qquad \times D(I, J, k, l|i, j, K, L),
\end{array}\right.
\end{aligned} \tag{A7}$$

$\langle u_\Lambda u_\mathrm{M} u_l|r_{12}r_{13}|v_K v_\mu v_L\rangle$ is also a three-electron (type-I) integral.

Pattern 11. In this case, the electrons I, J, Λ, and K, L electrons must be outside by the Laplace expansion. Similar to pattern 10, the Laplace expansion for r_{ij} and r_{KL} is first applied and then $h_1(\Lambda)$ is applied. This is given by

$$\begin{aligned}
&\langle U r_{IJ}|h_1(\Lambda)|r_{KL}V\rangle \\
&\quad = \big\langle r_{IJ}u_1(1)u_2(2)\cdots u_{N_e}(N_e)\ \big|\ h_1(\Lambda)A\big[r_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle \\
&\quad = \sum_{k=1}^{N_e-1}\sum_{l>k}^{N_e}\left\{\begin{array}{l}
(I = k, J = l) \\
\qquad \times(-1)^{I+J+K+L}I_1^{(11)}(I, J, \Lambda|K, L) \\
(I = k, J \neq l) \quad \text{(and other patterns)} \\
\qquad \times \sum_{j=1\ (j\neq K,L)}^{N_e} (-1)^{I+l+K+L}(-1)^{J'+j'}I_2^{(11)}(I, J, \Lambda, l|K, L, j) \\
(I \neq k, J \neq l) \\
\qquad \times \sum_{i=1}^{N_e-1}\sum_{j>i\ [(i,j)\neq(K,L)]}^{N_e} (-1)^{k+l+K+L}(-1)^{I'+J+i'+j'}I_3^{(11)}(I, J, \Lambda, k, l|K, L, i, j),
\end{array}\right.
\end{aligned} \tag{A8}$$

where

$$I_1^{(11)}(I, J, \Lambda|K, L) = \left\{\begin{array}{l} (\Lambda = I) \\ \qquad \times[\langle u_I u_J|r_{12}h_1(1)r_{12}|v_K v_L\rangle - \langle u_I u_J|r_{12}h_1(1)r_{12}|v_L v_K\rangle]D(I, J|K, L) \\ (\Lambda = J) \\ \qquad \times[\langle u_J u_I|r_{12}h_1(1)r_{12}|v_L v_K\rangle - \langle u_J u_I|r_{12}h_1(1)r_{12}|v_K v_L\rangle]D(I, J|K, L) \\ (\Lambda \neq I, J) \\ \qquad \times \sum_{\lambda=1\ (\lambda\neq K,L)}^{N_e} (-1)^{\Lambda'+\lambda'} \\ \qquad \times[\langle u_I u_J|r_{12}^2|v_K v_L\rangle - \langle u_I u_J|r_{12}^2|v_L v_K\rangle]\cdot \\ \qquad \times\langle u_\Lambda|h_1|v_\lambda\rangle D(I, J, \Lambda|K, L, \lambda), \end{array}\right. , \tag{A9}$$

$$I_2^{(11)}(I, J, \Lambda, l|K, L, j)$$

$$= \left\{\begin{array}{l} (\Lambda = I) \\ \qquad \times[\langle u_I u_J u_l|r_{12}h_1(1)r_{13}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}h_1(1)r_{13}|v_L v_j v_K\rangle]D(I, J, l|K, j, L) \\ (\Lambda = J) \\ \qquad \times[\langle u_I u_J u_l|r_{12}h_1(2)r_{13}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}h_1(2)r_{13}|v_L v_j v_K\rangle]D(I, J, l|K, j, L) \\ (\Lambda = l) \\ \qquad \times[\langle u_I u_J u_l|r_{12}h_1(3)r_{13}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}h_1(3)r_{13}|v_L v_j v_K\rangle]D(I, J, l|K, j, L) \\ (\Lambda \neq I, J, l) \\ \qquad \times \sum_{\lambda=1\ (\lambda\neq K,L,j)}^{N_e} (-1)^{\Lambda'+\lambda'} \\ \qquad \times[\langle u_I u_J u_l|r_{12}r_{13}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}r_{13}|v_L v_j v_K\rangle] \\ \qquad \times\langle u_\Lambda|h_1|v_\lambda\rangle \\ \qquad \times D(I, J, l, \Lambda|K, j, L, \lambda), \end{array}\right. \tag{A10}$$

and

$$I_3^{(11)}(I, J, \Lambda, k, l|K, L, i, j) = \left\{\begin{array}{l} (\Lambda = I) \\ \qquad \times[\langle u_I u_J|r_{12}h_1(1)|v_i v_j\rangle - \langle u_J u_I|r_{12}h_1(1)|v_i v_j\rangle] \\ \qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle] \\ \qquad \times D(I, J, k, l|i, j, K, L) \\ (\Lambda = J) \\ \qquad \times[\langle u_J u_I|r_{12}h_1(1)|v_j v_i\rangle - \langle u_I u_J|r_{12}h_1(1)|v_j v_i\rangle] \\ \qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle] \\ \qquad \times D(I, J, k, l|i, j, K, L) \\ (\Lambda = k) \\ \qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle] \\ \qquad \times[\langle u_k u_l|h_1(1)r_{12}|v_K v_L\rangle - \langle u_k u_l|h_1(1)r_{12}|v_L v_K\rangle] \\ \qquad \times D(I, J, k, l|i, j, K, L) \\ (\Lambda = l) \\ \qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle] \\ \qquad \times[\langle u_l u_k|h_1(1)r_{12}|v_L v_K\rangle - \langle u_l u_k|h_1(1)r_{12}|v_K v_L\rangle] \\ \qquad \times D(I, J, k, l|i, j, K, L) \\ (\Lambda \neq I, J, k, l) \\ \qquad \times \sum_{\lambda=1\ (\lambda\neq K,L,i,j)}^{N_e} (-1)^{\Lambda'+\lambda'} \\ \qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle] \\ \qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle] \\ \qquad \times\langle u_\Lambda|h_1|v_\lambda\rangle \\ \qquad \times D(I, J, k, l, \Lambda|i, j, K, L, \lambda), \end{array}\right. , \tag{A11}$$

$\langle u_I u_J u_l|r_{12}h_1(1)r_{13}|v_K v_j v_L\rangle$ is necessary to be evaluated. It is also a three-electron (Type-I) integral.

Pattern 12. In this case, the electrons I, J, Λ, M, and K, L electrons must be outside by the Laplace expansion. The Laplace expansion is first applied to r_{IJ} and r_{KL}. Later, $1/r_{\Lambda\mathrm{M}}$ is applied. The formulation is given by

$$\begin{aligned}\langle U r_{IJ}|1/r_{\Lambda\mathrm{M}}|r_{KL}V\rangle &= \big\langle r_{IJ}u_1(1)u_2(2)\cdots u_{N_e}(N_e)\big|\ 1/r_{\Lambda\mathrm{M}}A\big[r_{KL}v_1(1)v_2(2)\cdots v_{N_e}(N_e)\big]\big\rangle \\ &= \sum_{k=1}^{N_e-1}\sum_{l>k}^{N_e}\left\{\begin{array}{l} (I=k, J=l) \\ \qquad \times(-1)^{I+J+K+L} I_1^{(12)}(I,J,\Lambda,M|K,L) \\ (I=k, J\neq l)\quad \text{(and other patterns)} \\ \qquad \times\sum_{j=1\ (j\neq K,L)}^{N_e}(-1)^{I+l+K+L}(-1)^{J'+j'} I_2^{(12)}(I,J,\Lambda,M,l|K,L,j) \\ (I\neq k, J\neq l) \\ \qquad \times\sum_{i=1}^{N_e-1}\sum_{j>i\ [(i,j)\neq(K,L)]}^{N_e}(-1)^{k+l+K+L}(-1)^{I'+J'+i'+j'} I_3^{(12)}(I,J,\Lambda,,k,l|K,L,i,j), \end{array}\right.\end{aligned} \tag{A12}$$

where

$$I_1^{(12)}(I,J,\Lambda,M|K,L) = \left\{\begin{array}{l} (\Lambda=I, M=J) \\ \qquad \times[\langle u_I u_J|r_{12}|v_K v_L\rangle - \langle u_I u_J|r_{12}|v_L v_K\rangle] \\ \qquad \times D(I,J|K,L) \\ (\Lambda=I, M\neq J)\quad \text{(and other patterns)} \\ \qquad \times\sum_{\mu=1\ (\mu\neq K,L)}^{N_e}(-1)^{M'+\mu'} \\ \qquad \times[\langle u_I u_J u_\mathrm{M}|r_{12}1/r_{13}|v_K v_L v_\mu\rangle - \langle u_I u_J u_\mathrm{M}|r_{12}1/r_{13}|v_L v_K v_\mu\rangle] \\ \qquad \times D(I,J,|K,L,\mu) \\ (\Lambda\neq I, M\neq J) \\ \qquad \times\sum_{\lambda=1}^{N_e-1}\sum_{\mu>\lambda\ (\lambda,\mu\neq K,L)}^{N_e}(-1)^{\Lambda'+M'+\lambda'+\mu'} \\ \qquad \times[\langle u_I u_J|r_{12}^2|v_K v_L\rangle - \langle u_I u_J|r_{12}^2|v_L v_K\rangle] \\ \qquad \times[\langle u_\Lambda u_\mathrm{M}|1/r_{12}|v_\lambda v_\mu\rangle - \langle u_\mathrm{M} u_\Lambda|1/r_{12}|v_\lambda v_\mu\rangle] \\ \qquad \times D(I,J,\Lambda,M|K,L,\lambda,\mu), \end{array}\right. \tag{A13}$$

$$I_2^{(12)}(I,J,\Lambda,M,l|K,L,j) = \left\{\begin{array}{l} (\Lambda=I, M=J) \\ \qquad \times[\langle u_J\mid v_j\rangle\langle u_I u_l|r_{13}|v_K v_L\rangle - \langle u_J\mid v_j\rangle\langle u_I u_l|r_{13}|v_L v_K\rangle] \\ \qquad \times D(I,J,l|K,j,L) \\ (\Lambda=I, M=l)\quad \text{(and other patterns)} \\ \qquad \times[\langle u_l\mid v_L\rangle\langle u_I u_J|r_{12}|v_K v_j\rangle - \langle u_I\mid v_L\rangle\langle u_I u_J|r_{12}|v_j v_K\rangle] \\ \qquad \times D(I,J,M|K,j,L) \\ (\Lambda=J, M=l)\quad \text{(and other patterns)} \\ \qquad \times[\langle u_I u_J u_l|r_{12}r_{13}1/r_{23}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}r_{13}1/r_{23}|v_L v_j v_K\rangle] \\ \qquad \times D(I,J,l|K,j,L) \\ (\Lambda=I, M\neq J,l)\quad \text{(and other patterns)} \\ \qquad \times\sum_{\mu=1\ (\mu\neq K,L,j)}^{N_e}(-1)^{M'+\mu'} \\ \qquad \times[\langle u_I u_J u_l u_\mathrm{M}|r_{12}r_{13}1/r_{14}|v_K v_j v_L v_\mu\rangle - \langle u_I u_J u_l u_\mathrm{M}|r_{12}r_{13}1/r_{14}|v_L v_j v_K v_\mu\rangle] \\ \qquad \times D(I,J,l,M|K,j,L,\mu) \\ (\Lambda=J, M\neq I,l)\quad \text{(and other patterns)} \\ \qquad \times\sum_{\mu=1\ (\mu\neq K,L,j)}^{N_e}(-1)^{M'+\mu'} \\ \qquad \times[\langle u_I u_J u_l u_\mathrm{M}|r_{12}r_{13}1/r_{24}|v_K v_j v_L v_\mu\rangle - \langle u_I u_J u_l u_\mathrm{M}|r_{12}r_{13}1/r_{24}|v_L v_j v_K v_\mu\rangle] \\ \qquad \times D(I,J,l,M|K,j,L,\mu) \\ (\Lambda=l, M\neq I,J)\quad \text{(and other patterns)} \\ \qquad \times\sum_{\mu=1\ (\mu\neq K,L,j)}^{N_e}(-1)^{M'+\mu'} \\ \qquad \times[\langle u_I u_J u_l u_\mathrm{M}|r_{12}r_{13}1/r_{34}|v_K v_j v_L v_\mu\rangle - \langle u_I u_J u_l u_\mathrm{M}|r_{12}r_{13}1/r_{34}|v_L v_j v_K v_\mu\rangle] \\ \qquad \times D(I,J,l,M|K,j,L,\mu) \\ (\Lambda, M\neq I,J,l)\quad \text{(and other patterns)} \\ \qquad \times\sum_{\lambda=1}^{N_e-1}\sum_{\mu>\lambda\ (\lambda,\mu\neq K,L,j)}^{N_e}(-1)^{\Lambda'+M'+\lambda'+\mu'} \\ \qquad \times[\langle u_I u_J u_l|r_{12}r_{13}|v_K v_j v_L\rangle - \langle u_I u_J u_l|r_{12}r_{13}|v_L v_j v_K\rangle] \\ \qquad \times[\langle u_\Lambda u_\mathrm{M}|1/r_{12}|v_\lambda v_\mu\rangle - \langle u_\mathrm{M} u_\Lambda|1/r_{12}|v_\lambda v_\mu\rangle] \\ \qquad \times D(I,J,l,\Lambda,M|K,j,L,\lambda,\mu), \end{array}\right. \tag{A14}$$

and

$$
I_3^{(12)}(I,J,\Lambda,k,l|K,L,i,j) = \left\{\begin{array}{l}
(\Lambda = I, M = J)\\
\qquad \times[\langle u_I \mid v_i\rangle\langle u_J \mid v_j\rangle - \langle u_J \mid v_i\rangle\langle u_I \mid v_j\rangle]\\
\qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle]\\
\qquad \times D(I,J,k,l|i,j,K,L)\\
(\Lambda = k, M = l)\\
\qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle]\\
\qquad \times[\langle u_k \mid v_K\rangle\langle u_l \mid v_L\rangle - \langle u_k \mid v_L\rangle\langle u_l \mid v_K\rangle]\\
\qquad \times D(I,J,k,l|i,j,K,L)\\
(\Lambda = I, M = k) \quad \text{(and other patterns)}\\
\qquad \times\left[\begin{array}{l}\langle u_I u_J u_k u_l|r_{12}r_{34}1/r_{13}|v_i v_j v_K v_L\rangle - \langle u_J u_I u_k u_l|r_{12}r_{34}1/r_{13}|v_i v_j v_K v_L\rangle\\ -\langle u_I u_J u_l u_k|r_{12}r_{34}1/r_{13}|v_i v_j v_K v_L\rangle + \langle u_J u_I u_l u_k|r_{12}r_{34}1/r_{13}|v_i v_j v_K v_L\rangle\end{array}\right]\\
\qquad \times D(I,J,k,l|i,j,K,L)\\
(\Lambda = I, M \neq J,k,l)\\
\qquad \times \sum_{\mu=1\ (\mu\neq K,L,i,j)}^{N_e} (-1)^{M'+\mu'}\\
\qquad \times[\langle u_I u_J u_{\mathrm{M}}|r_{12}1/r_{13}|v_i v_j v_\mu\rangle - \langle u_J u_I u|r_{12}1/r_{13}|v_i v_j v_\mu\rangle]\\
\qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle]\\
\qquad \times D(I,J,k,l,M|i,j,K,L,\mu)\\
(\Lambda = k, M \neq I,J,l)\\
\qquad \times \sum_{\mu=1\ (\mu\neq K,L,i,j)}^{N_e} (-1)^{M'+\mu'}\\
\qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle]\\
\qquad \times[\langle u_k u_l u_{\mathrm{M}}|r_{12}1/r_{13}|v_K v_L v_\mu\rangle - \langle u_k u_l u|r_{12}1/r_{13}|v_L v_K v_\mu\rangle]\\
\qquad \times D(I,J,k,l,M|i,j,K,L,\mu)\\
(\Lambda, \neq I,J,k,l)\\
\qquad \times \sum_{\lambda=1}^{N_e-1} \sum_{\mu>\lambda\ (\lambda,\mu\neq K,L,i,j)}^{N_e} (-1)^{\Lambda'+M'+\lambda'+\mu'}\\
\qquad \times[\langle u_I u_J|r_{12}|v_i v_j\rangle - \langle u_J u_I|r_{12}|v_i v_j\rangle]\\
\qquad \times[\langle u_k u_l|r_{12}|v_K v_L\rangle - \langle u_k u_l|r_{12}|v_L v_K\rangle]\\
\qquad \times[\langle u_\Lambda u_{\mathrm{M}}|1/r_{12}|v_\lambda v_\mu\rangle - \langle u_\times u_\Lambda|1/r_{12}|v_\lambda v_\mu\rangle]\\
\qquad \times D(I,J,k,l,\Lambda,M|i,j,K,L,\lambda,\mu),
\end{array}\right. \tag{A15}
$$

where three-electron (type-II) and four-electron (type-I and -II) integrals are necessary in addition to one-, two-, and three-electron (type-I) integrals.

Determinant update. The above formulations require a lot of calculations of the minor $D(\cdots|\cdots)$ which roughly requires $O({N_e}^3/3)$ operations, where N_e is the number of electrons. However, in the matrix of $D(\cdots|\cdots)$, only a few columns and rows are changed from the original determinant matrix. The determinant update algorithm [30], therefore, is useful especially for many electron systems; (i) evaluate $|D|$ and same time keep D^{-1} and (ii) by using $|D|$ and D^{-1}, the minor $D(\cdots|\cdots)$ can be evaluated with $O(N_e)$. This process can much reduce the computational costs.

All these formulations require the computational costs of polynomial orders. These formulations are also valid for a general f_{ij} (not restricted to r_{ij}) and molecular case if their three-electron (types I and II) and four-electron (types-I and -II) integrals can be practically computed.

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