AP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **139**, 044112 (2013); doi: 10.1063/1.4815821 View online: http://dx.doi.org/10.1063/1.4815821 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v139/i4 Published by the AIP Publishing LLC.

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Efficient antisymmetrization algorithm for the partially correlated wave functions in the free complement-local Schrödinger equation method

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(Received 27 March 2013; accepted 2 July 2013; published online 25 July 2013)

We propose here fast antisymmetrization procedures for the partially correlated wave functions that appear in the free complement-local Schrödinger equation (FC-LSE) method. Pre-analysis of the correlation diagram, referred to as *dot analysis*, combined with the determinant update technique based on the Laplace expansion, drastically reduces the orders of the antisymmetrization computations. When the complement functions include only up to single-correlated terms, the order of computations is $O(N^3)$, which is the same as the non-correlated case. Similar acceleration is obtained for general correlated functions as a result of dot analysis. This algorithm has been successfully used in our laboratory in actual FC-LSE calculations for accurately solving the many-electron Schrödinger equations of atoms and molecules. The proposed method is general and applicable to the sampling-type methodology of other partially correlated wave functions like those in the quantum Monte Carlo and modern Hylleraas-type methods. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4815821]

I. INTRODUCTION

The Schrödinger equation (SE), $H\psi = E\psi$, is the most fundamental equation that governs most physical and chemical phenomena of atoms and molecules with high predictive power.¹ In addition, the exact wave function ψ must satisfy the Pauli exclusion principle.² The ultimate goal of quantum chemistry is to set up a general method of solving the SE under the condition of the Pauli principle.³ We assume in this paper that our Hamiltonian *H* is spin-independent.

When the wave function is constructed only with oneelectron orbitals, the antisymmetrization is done using the Slater determinant,^{3–5}

$$\phi(1, 2, \dots, N) = A [o_1(1) \cdot o_2(2) \cdots o_N(N)]$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} o_1(1) & o_1(2) & o_1(3) & \cdots & o_1(N) \\ o_2(1) & o_2(2) & o_2(3) & \cdots & o_2(N) \\ o_3(1) & o_3(2) & o_3(3) & \cdots & o_3(N) \\ \cdots & \cdots & \cdots & \cdots \\ o_N(1) & o_N(2) & o_N(3) & \cdots & o_N(N) \end{vmatrix}, \quad (1)$$

where ϕ represents an *N*-electron single configuration, *A* the antisymmetrizer, and $o_i(j)$ a one-electron function of electron *j* with spatial and spin coordinates. As is well-known, the evaluation of the Slater determinant of Eq. (1) (the evaluation

of the value in a full coordinate space) is an $N^3/3$ process. We refer to the antisymmetrization algorithm using the Slater determinant as the "*Det algorithm*."

In 1929, Hylleraas⁶ found that the inclusion of the twoelectron explicitly correlated term, r_{12} , in the helium wave function described very efficiently the major part of the electron-electron correlation: he calculated an accurate helium wave function only three years after the publication of the SE. Recently, a general method of solving the SE has been proposed by one of the authors.⁷⁻²² The antisymmetrization method proposed here has been developed to be useful for this general method applied to many-electron systems. The review articles^{7,8} published recently will be helpful for understanding the background of the present paper. There, we first construct the wave function space that is guaranteed to include the exact wave function. We call such space to have an exact structure. It is spanned by the "complement func*tions*" $\{\phi_i\}$ that are produced by the Hamiltonian itself of the system by applying to some approximate wave function ψ_0 . We referred to the function ϕ_i as complement function, since it is an element of the complete functions that describes the exact wave function as

$$\psi_n = \sum_i^{M_n} c_i \phi_i, \qquad (2)$$

where *n* stands for the order (times) of applications of the Hamiltonian to the function ψ_0 . As *n* increases, ψ_n approaches the exact wave function. We refer to the wave function given by Eq. (2) as *free complement* (FC) wave function. Since the electronic Hamiltonian contains only one- and two-body operators, the complement function generally has the form,

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$$\phi_i(1, 2, \dots, N) = A[\{f_{kl}(k, l) \cdots f_{mn}(m, n)\} \\ \cdot \{o_1(1) \cdot o_2(2) \cdots o_N(N)\} \cdot \chi_i], \quad (3)$$

where $f_{kl}(k, l)$ (k, l = 1, 2, ..., N) are the two-electron functions composed of the inter-electron coordinates r_{kl} , and $\{f_{kl}(k, l) \cdots f_{mn}(m, n)\}$ are the products of such two-electron functions. We note that three-, four-, and more-electron correlated functions, $f_{ijk}(i, j, k)$, $f_{ijkl}(i, j, k, l)$, etc., are not necessary for the exact structure. χ_i is a spin function and should be the exact spin eigenfunction of the target spin state. The unknown coefficients $\{c_i\}$ in Eq. (2) are determined by the variational method¹⁴⁻¹⁷ or by the local Schrödinger equation (LSE) method.^{7,8,15,19} The latter method is an integrationfree method using a sampling procedure and therefore can be applied to any atoms and molecules. Other parameters in ϕ_i like orbital exponents may be optimized for a fast convergence.

The antisymmetrization operator A in Eq. (3) generally involves N! permutations of electronic coordinates. This antisymmetrization procedure is referred to as "NF-algorithm." It is straightforward but not practical when N becomes larger than 8 or 9. However, when ϕ_i does not include any twoelectron function f_{kl} , the antisymmetrization can be done using the Det algorithm of Eq. (1) that includes only $N^3/3$ processes. This implies that depending on the types of the f_{ii} terms included in the complement functions ϕ_i , the antisymmetrization procedure could be simplified to the procedure including from $N^3/3$ to N! processes. In the ordinary FC calculations of chemical accuracy, the wave function contains only partially correlated complement functions, including usually from zero to three or four f_{ii} terms at most, so that much reduction of the operation counts should be possible in actual antisymmetrization procedure, which is the subject of the present paper.

In this paper, we propose new efficient algorithms for the antisymmetrization of the partially correlated wave functions of Eq. (3) at a given set of coordinates (grid or sampling points). In the free complement-local Schrödinger equation (FC-LSE) calculations of many-electron systems, the evaluations of ϕ_i and $H\phi_i$ at the sampling points are the rate-determining steps where the antisymmetrization for each N-electron sampling point is the most time-consuming process. So, the efficiency of the antisymmetrization process is of crucial importance for solving the SE of many electron atoms and molecules. The operation counts of the algorithms proposed here are much faster than the N! (NF) ones and are in the lower polynomial orders of N. In our approach, we start our formulation with the Laplace expansion of a Slater determinant. We distinguish correlated and non-correlated electrons, apply Laplace expansion, and use the NF-algorithm for the correlated-electron part and the Det algorithm for the non-correlated part. We refer to this simple algorithm as "Nm-algorithm." Because of the simplicity, the similar methods have been used in various situations of the treatment of the antisymmetrization. In 1960s, using the similar treatment with the Laplace expansion, Szasz et al. formulated the efficient evaluations of the integrals for the Hartree-Fock-based singe correlated wave functions.²³⁻²⁶ However, their purpose was to give the formulations of matrix elements: they did not generalize his formulations for more highly correlated cases and did not mention the possibility of any further acceleration.

The goal of this paper is to show that much further acceleration of the antisymmetrization is possible than the Nmalgorithm, using the fact that the wave function is composed of only one- and two-body terms. We have developed a further efficient algorithm introducing the pre-analysis named dot analysis of the correlation diagram and the determinant update technique. This algorithm can drastically reduce the computational cost to a lower polynomial order. We refer to this algorithm as "*Nk-algorithm*."

The focus of this paper is the fast antisymmetrization procedure of the FC-LSE wave function;¹⁵ however, the proposed methods are general and applicable to the sampling-type methodologies using other partially correlated wave functions like those used in the quantum Monte Carlo method,²⁷⁻³⁰ the Hylleraas-CI (Hy-CI)³¹⁻³⁴ and extended (exponential) Hylleraas-CI (EHy-CI) wave functions,²⁰ and other explicitly correlated wave functions.^{31,35}

II. TREATMENT OF THE SPIN PART

The non-relativistic wave function is often written using a linear combination of the antisymmetrized *N*electron configurations. A single spin-adapted configuration is expressed by using a spatial function φ and a spin function χ as

$$\phi = A \left[\varphi \chi \right], \tag{4}$$

where χ is the spin eigenfunction of the spin state we want to solve. The antisymmetrization operator *A* applies to both space and spin coordinates. Here, we first summarize the treatment of the spin part.

Generally, χ is expressed by a linear combination of the primitive spin functions composed of the one-electron spin functions α and β . For *N*-electron cases, χ can be expressed as

$$\chi = \sum_{i}^{s} \xi_{i}(1, 2, \dots, N),$$
 (5)

where $\xi_i(1, 2, ..., N)$ is a single primitive spin function. The number of terms that construct a single spin eigenfunction is denoted by *s*. For instance, one of the doublet spin eigenfunctions of a three-electron system with $s_z = 1/2$ is given by $\chi = [\alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)]/\sqrt{2}$, and so s = 2.

Once a spin function is given, it is possible to reorganize the linear combination of the spin part to that of the spatial part due to the equivalence of electrons in the antisymmetrization operator. For example, for the above three-electron doublet case, the total wave function can be rewritten as $\phi = A[\varphi(1, 2, 3) \cdot [\alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)]/\sqrt{2}] = A$ $[[\varphi(3, 2, 1) - \varphi(1, 3, 2)]/\sqrt{2} \cdot \alpha(1)\alpha(2)\beta(3)]$. For general

case, using Eq. (5), our wave function is expressed by

$$\phi = A \left[\varphi \chi \right] = A \left[\varphi(1, 2, \dots, N) \cdot \left\{ \sum_{i}^{s} \xi_{i}(1, 2, \dots, N) \right\} \right]$$
$$= A \left[\left\{ \sum_{i}^{s} (-1)^{q_{i}} Q_{i} \varphi(1, 2, \dots, N) \right\} \cdot \alpha(1) \dots \alpha(N_{\alpha}) \beta(N_{\alpha} + 1) \dots \beta(N) \right]$$
$$= \sum_{i}^{s} A [\lambda^{(i)}(1, 2, \dots, N) \cdot \alpha(1) \dots \alpha(N_{\alpha}) \beta(N_{\alpha} + 1) \dots \beta(N)]$$
$$= A \left[\zeta(\mathbf{r}_{1}, \mathbf{r}_{2}, \dots, \mathbf{r}_{N}) \cdot \vartheta(\sigma_{1}, \sigma_{2}, \dots, \sigma_{N}) \right],$$
(6)

where the numbers of α and β spin electrons are denoted as N_{α} and N_{β} ($N = N_{\alpha} + N_{\beta}$), respectively, and Q_i (with parity q_i) is a corresponding permutation operator which transforms ξ_i to $\alpha(1)\alpha(2)...\alpha(N_{\alpha})\beta(N_{\alpha} + 1)\beta(N_{\alpha} + 2)...\beta(N_{\alpha} + N_{\beta})$. {**r**_{*i*}} and { σ_i } represent the spatial and spin coordinates, respectively. Thus, the linear combination in the spin part was transformed into the linear combination in the spatial part as

$$\lambda^{(i)}(1, 2, \dots, N) = (-1)^{q_i} Q_i \varphi(1, 2, \dots, N),$$
(7)

$$\zeta(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i}^{s} \lambda^{(i)}(1, 2, \dots, N), \qquad (8)$$

and

$$\vartheta(\sigma_1, \sigma_2, \dots, \sigma_N) = \alpha(1)\alpha(2)\dots\alpha(N_\alpha)\beta(N_\alpha + 1)$$
$$\times \beta(N_\alpha + 2)\dots\beta(N_\alpha + N_\beta). \quad (9)$$

Since most of the physical operators of interest are independent of spin, we consider an expectation value (or matrix elements) of a spin-free operator for ordinary non-relativistic wave functions. This has been discussed in the spin-free formalism³⁶ and also realized with the Young operator.³⁷ For a spin-free operator, we only need to consider the permutations of the spatial coordinates within the same spin particles, i.e., within α or β , as given by

$$\phi' = A_{\alpha} A_{\beta} [\zeta(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)]$$
$$= \sum_{i}^{s} A_{\alpha} A_{\beta} [\lambda^{(i)}(1, 2, \dots, N)], \qquad (10)$$

instead of Eq. (6), where A_{α} and A_{β} are the antisymmetrization operators within α and β spin electrons. ϕ' here does not contain any spin coordinates, but the expectation value of a spin-free operator is the same as that of ϕ of Eq. (6).

For a singlet *N*-electron system (*N* is even) with the spin eigenfunction of the form: $(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)(\alpha\beta)$ - $\beta\alpha$)..., the value of *s* in Eq. (6) or Eq. (10) becomes $2^{N/2}$. However, when two paired α and β electrons occupy the same special orbital, i.e., $o_{\alpha} = o_{\beta}$ (closed shell), the spin-related exchange can be omitted and the computation is greatly simplified as

$$A[o_{\alpha}(1)o_{\beta}(2) \cdot (\alpha(1)\beta(2) - \beta(1)\alpha(2)) / \sqrt{2}]$$

= $A[(o_{\alpha}(1)o_{\beta}(2) + o_{\alpha}(2)o_{\beta}(1)) / \sqrt{2} \cdot \alpha(1)\beta(2)]$
= $\sqrt{2} \cdot A[o_{\alpha}(1)o_{\beta}(2) \cdot \alpha(1)\beta(2)].$ (11)

The double occupancy of orbitals simplifies notably the spinrelated exchanges.

Thus, the antisymmetrized wave function including both spatial and spin coordinates can be replaced by a linear combination of the antisymmetrized spatial functions. Therefore, our problem is reduced to developing the antisymmetrization method for each spatial function to each of the A_{α} and A_{β} operators in Eq. (10). We shall formulate this in Sec. III.

III. FORMULATION OF THE ANTISYMMETRIZATION

First, let us define a general partially correlated function φ , which is going to be antisymmetrized. It corresponds only to α or β spin electrons, as explained in Sec. II. Each function is represented by a Hartree product of one-electron functions with some correlated terms over two- or more-electron functions as

$$\varphi(1, 2, \dots, N) = f^{(m)}(1, 2, \dots, m)$$
$$\cdot d^{(N-m)}(m+1, m+2, \dots, N), \quad (12)$$

where $f^{(m)}$ is the *m*-electron correlated term which is composed of the product of two-electron functions $f_{kl}(k, l)$ and the one-electron terms of the first *m* electrons as described in Eq. (3), and $d^{(N-m)}$ is constructed by the product of the rest of the one-electron terms,

$$d^{(N-m)}(m+1, m+2, ..., N)$$

= $o_{m+1}(m+1) \cdot o_{m+2}(m+2) \cdot \cdots \cdot o_N(N)$, (13)

where $o_i(j)$ is the one-electron function o_i occupied by electron j. For convenience, the electrons are numbered, without loss of generality, so that the first m electrons are correlated. We assume $m \ll N$, but we do not assume the orthogonality between the one-electron functions o_i . Any type of orbitals

arising from the valence bond or molecular orbital methods is acceptable for the proposed formulation.

We formulate an efficient antisymmetrization procedure for φ defined in Eq. (12). We introduce three algorithms, NF-, Nm-, and Nk-algorithms, in which N stands for the number of electrons N, "F" for "factorial", "m" for the number of correlated electrons as defined in Eq. (12), and "k" for a number smaller or equal to m, as explained in detail in Subsections III A–III C.

A. NF-algorithm: Straightforward application of *N*! permutations

The NF-algorithm performs *N*! straightforward permutations as defined by the antisymmetrization operator,

$$\phi(1, 2, ..., N) = A [\varphi(1, 2, ..., N)]
= \frac{1}{\sqrt{N!}} \sum_{I=1}^{N!} (-1)^{p_I} \cdot P_I [f^{(m)}(1, 2, ..., m)
\cdot d^{(N-m)}(m+1, m+2, ..., N)]
= \frac{1}{\sqrt{N!}} \sum_{I=1}^{N!} (-1)^{p_I} \cdot f^{(m)} (t_1^{(I)}, t_2^{(I)}, ..., t_m^{(I)})
\cdot d^{(N-m)} (t_{m+1}^{(I)}, t_{m+2}^{(I)}, ..., t_N^{(I)}),$$
(14)

where ϕ is an antisymmetrized single *N*-electron function or a complement function and *P*_I is the *I*th permutation operator defined by

$$P_{I} = \begin{pmatrix} 1 & 2 & \cdots & N \\ t_{1}^{(I)} & t_{2}^{(I)} & \cdots & t_{N}^{(I)} \end{pmatrix},$$
(15)

with the corresponding parity $(-1)^{p_I}$. This representation of P_I is a two-line notation for permutation; the first row lists the elements before permutation and the second row describes the list after the permutation. This NF-algorithm is computationally too expensive and in practice it is limited at most to 6- or 7-electron cases. The computational time grows in an order of O(N!).

B. Nm-algorithm: Antisymmetrization for a general partially correlated function

For partially correlated functions, we can avoid the NFalgorithm. This idea is based on the Laplace expansion of the determinant. We use the Det algorithm for the Slater determinant, as explained for Eq. (1), and the NF-algorithm for the correlated electrons. For this purpose, we introduce the partial permutation operator defined by

$$\overline{P}_{I}^{(m)} = \begin{pmatrix} 1 & 2 & \cdots & m & m+1 & m+2 & \cdots & N \\ t_{1}^{(I)} & t_{2}^{(I)} & \cdots & t_{m}^{(I)}; & t_{m+1}^{(I)} & t_{m+2}^{(I)} & \cdots & t_{N}^{(I)} \end{pmatrix},$$
(16)

where the electrons $t_1^{(I)}$, $t_2^{(I)}$, ..., $t_m^{(I)}$ are chosen from the *N* electrons (combination ${}_NC_m$) and the NF-algorithm is adopted for this chosen *m* electrons (*m*! permutations). Thus, the total number of the $\overline{P}_I^{(m)}$ operators is ${}_NC_m \cdot m! = {}_NP_m$. The permutations for the other electrons, $t_{m+1}^{(I)}$, $t_{m+2}^{(I)}$, ..., $t_N^{(I)}$, are not considered in the $\overline{P}_I^{(m)}$ operator; instead, the Det algorithm is used for the antisymmetrization of $t_{m+1}^{(I)}$, $t_{m+2}^{(I)}$, ..., $t_N^{(I)}$ of the *N*-*m* dimension. So, the antisymmetrization of φ can be performed by

$$\phi(1, 2, \dots, N) = A \left[\varphi(1, 2, \dots, N) \right]$$

$$= \sqrt{\frac{(N-m)!}{N!}} \sum_{I=1}^{N^{P_m}} (-1)^{\overline{p}_I^{(m)}} \cdot \overline{P}_I^{(m)} [f^{(m)}(1, 2, \dots, m) \cdot D^{(N-m)}(m+1, m+2, \dots, N)]$$

$$= \sqrt{\frac{(N-m)!}{N!}} \sum_{I=1}^{N^{P_m}} (-1)^{\overline{p}_I^{(m)}} \cdot f^{(m)} (t_1^{(I)}, t_2^{(I)}, \dots, t_m^{(I)}) \cdot D^{(N-m)} (t_{m+1}^{(I)}, t_{m+2}^{(I)}, \dots, t_N^{(I)}), \qquad (17)$$

where $(-1)^{\overline{p}_{I}^{(m)}}$ is the parity of $\overline{P}_{I}^{(m)}$, and $D^{(N-m)}$ is the Slater determinant for the *N*-*m* electrons,

$$D^{(N-m)}(m+1, m+2, \dots, N) = A^{(N-m)}[d^{(N-m)}(m+1, m+2, \dots, N)]$$

$$= \frac{1}{\sqrt{(N-m)!}} \begin{vmatrix} o_{m+1}(m+1) & o_{m+1}(m+2) & o_{m+1}(m+3) & \cdots & o_{m+1}(N) \\ o_{m+2}(m+1) & o_{m+2}(m+2) & o_{m+2}(m+3) & \cdots & o_{m+2}(N) \\ o_{m+3}(m+1) & o_{m+3}(m+2) & o_{m+3}(m+3) & \cdots & o_{m+3}(N) \\ \cdots & \cdots & \cdots & \cdots \\ o_{N}(m+1) & o_{N}(m+2) & o_{N}(m+3) & \cdots & o_{N}(N) \end{vmatrix},$$
(18)

where $A^{(M)}$ denotes the *M*-electron antisymmetrization operator. Note that in this algorithm, the explicit form of $f^{(m)}$ does not play any role. $f^{(m)}$ is not only limited to the two-electron

inseparable correlated term $f_{ij}(i, j)$, but also three-, four-, and more-electron inseparable correlated terms $(f_{ijk}(i, j, k), f_{ijkl}(i, j, k, l), etc.)$ are acceptable. Such a multi-particle interaction might be important in nuclear physics although it may cause very complicated situations.³⁸ In the FC method for solving the electronic SE, the complement function includes only two-electron separable correlated term, $f_{ij}(i, j)$, etc.

This algorithm of antisymmetrization of a partially correlated function is referred to as the "Nm-algorithm." The number of operation steps in Eq. (17) is $_NP_m$, in which the calculation order is much less than N!, as long as m is not large. If $m \ll N$, then the operation count is roughly

$${}_{N}P_{m} \cdot O((N-m)^{3}) \Rightarrow O(N^{m+3}),$$
(19)

i.e., polynomial order operations, where the determinant evaluation in the summation loop requires $O(M^3)$ operations with the matrix dimension M.

C. Nk-algorithm: Further efficient algorithm with the pre-analysis of the correlation diagram

1. Simple example with three-electron correlated term $f_{12}(1, 2) f_{13}(1, 3)$

Although the Nm-algorithm is a general method, the calculation order depends directly on *m*, i.e., $O(N^{m+3})$; therefore, the cost of the calculation grows rapidly as *m* increases. However, if one carefully analyzes the structure of the correlated function $f^{(m)}$, then it is possible to achieve faster accelerations. To illustrate this new algorithm, let us take a simple example of Eq. (12), where $f^{(3)}(1, 2, 3) = f_{12}(1, 2)f_{13}(1, 3)$ (i.e., m = 3: three electrons are correlated). $f_{ij}(i, j)$ represents a two-electron inseparable correlated term such as r_{ij} , exp $(-\alpha r_{ij})$, log $(r_{iA} + r_{jA})$, etc., where r_{ij} is the radial distance between electrons *i* and *j*, and r_{iA} is the distance between electron *i* and nucleus *A*. We are going to antisymmetrize φ , which is represented by

$$\varphi(1, 2, \dots, N) = f_{12}(1, 2) \cdot f_{13}(1, 3) \cdot o_1(1) \cdot o_2(2) \cdot o_3(3)$$
$$\cdot o_4(4) \cdot \dots \cdot o_N(N). \tag{20}$$

If the Nm-algorithm is employed, then the calculation order becomes $O(N^6)$ because m = 3. This computational cost is still high. However, in the actual case where $f^{(3)}(1, 2, 3)$ $= f_{12}(1, 2)f_{13}(1, 3)$, there is no explicit correlation between electrons 2 and 3, which correlate only through electron 1. Therefore, we may rewrite the one-electron functions $o_2(2)$ and $o_3(3)$ by $o'_2(2; 1^*) = f_{12}(1^*, 2) \cdot o_2(2)$ as a function of electron 2, and similarly, $o'_{3}(3; 1^{*}) = f_{13}(1^{*}, 3) \cdot o_{3}(3)$ as a function of electron 3. In $o'_2(2; 1^*)$ and $o'_3(3; 1^*)$, electron 1 is considered to be just a parameter in the Slater determinant (we denote such a parametric electron with an asterisk). When the parametric coordinate of electron 1 is fixed (by its sampling), then $o'_2(2; 1^*)$, $o'_3(3; 1^*)$, $o_4(4), \ldots, o_N(N)$ can be treated as one-electron functions and the antisymmetrization within electrons 2 to N can be performed through the Det algorithm. The function of electron 1, $o_1(1^*)$, must be out of the determinant. Thus, the total antisymmetrization can be performed as

$$\begin{split} \phi(1,2,\ldots,N) &= A\left[\varphi(1,2,\ldots,N)\right] \\ &= \sqrt{\frac{(N-1)!}{N!}} \sum_{I=1}^{N} (-1)^{\overline{p}_{I}^{(1)}} \cdot \overline{P}_{I}^{(1)} [o_{1}(1^{*}) \cdot A^{(N-1)} [o_{2}^{\prime}(2;1^{*}) \cdot o_{3}^{\prime}(3;1^{*}) \cdot o_{4}(4) \cdots o_{N}(N)]] \\ &= \sqrt{\frac{(N-1)!}{N!}} \sum_{I=1}^{N} (-1)^{\overline{p}_{I}^{(1)}} \cdot \overline{P}_{I}^{(1)} [o_{1}(1^{*}) \cdot \widetilde{D}^{(N-1)} (2^{\prime},3^{\prime},4,\ldots,N;1^{*})] \\ &= \sqrt{\frac{(N-1)!}{N!}} \sum_{I=1}^{N} (-1)^{\overline{p}_{I}^{(1)}} \cdot o_{1} (t_{1}^{(I)^{*}}) \cdot \widetilde{D}^{(N-1)} (t_{2^{\prime}}^{(I)},t_{3^{\prime}}^{(I)},t_{4}^{(I)},\ldots,t_{N}^{(I)};t_{1}^{(I)^{*}}). \end{split}$$
(21)

We call these parametric electrons "dot electrons," (electron 1 was the dot electron in the above example) and call the analysis for these dot electrons the "dot analysis." The number of dot electrons is defined as d, with d = 1 in the above example. In Eq. (21), $A^{(N-1)}$ is the antisymmetrization operator for N - 1 electrons, electron 2 to N, and it can be replaced by the Slater determinant which contains electron 1 as a parameter through $f_{12}(1^*, 2)$ and $f_{13}(1^*, 3)$. The primes for electrons 2 and 3 in $\tilde{D}^{(N-1)}(2', 3', 4, ..., N; 1^*)$ represent that these electrons correlate through the dot electrons (electron 1). In the present example, $\tilde{D}^{(N-1)}$ is represented by

$$\tilde{D}^{(N-1)}(2', 3', 4, \dots, N; 1^*)$$

$$= \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} o_2'(2; 1^*) & o_2'(3; 1^*) & o_2'(4; 1^*) & \cdots & o_2'(N; 1^*) \\ o_3'(2; 1^*) & o_3'(3; 1^*) & o_3'(4; 1^*) & \cdots & o_3'(N; 1^*) \\ o_4(2) & o_4(3) & o_4(4) & \cdots & o_4(N) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ o_N(2) & o_N(3) & o_N(4) & \cdots & o_N(N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} f_{12}(1^*, 2) \cdot o_2(2) & f_{12}(1^*, 3) \cdot o_2(3) & f_{12}(1^*, 4) \cdot o_2(4) & \cdots & f_{12}(1^*, N) \cdot o_2(N) \\ f_{13}(1^*, 2) \cdot o_3(2) & f_{13}(1^*, 3) \cdot o_3(3) & f_{13}(1^*, 4) \cdot o_3(4) & \cdots & f_{13}(1^*, N) \cdot o_3(N) \\ o_4(2) & o_4(3) & o_4(4) & \cdots & o_4(N) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ o_N(2) & o_N(3) & o_N(4) & \cdots & o_N(N) \end{vmatrix} .$$
(22)

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The determinant $\widetilde{D}^{(N-1)}$ contains the explicitly correlated functions in their matrix elements, and we call such a generalized Slater determinant the "correlated Slater determinant." Figure 1 displays an example in the case of N = 6, where the summation in Eq. (21) includes six terms.

For comparison, the evaluation of the present example by the Nm-algorithm is given by

$$\phi(1, 2, ..., N)$$

$$= A \left[\varphi(1, 2, ..., N) \right]$$

$$= \sqrt{\frac{(N-3)!}{N!}} \sum_{I=1}^{N^{P_3}} (-1)^{\overline{p}_I^{(3)}} \cdot \overline{P}_I^{(3)} [\{f_{12}(1, 2) \cdot f_{13}(1, 3) \\ \cdot o_1(1) \cdot o_2(2) \cdot o_3(3)\} \cdot D^{(N-3)}(4, 5, ..., N)]. \quad (23)$$

The number of steps of the summation loop is much reduced, from $_NP_3$ of Eq. (17) (Nm-algorithm) to just N of Eq. (21). Thus, by analyzing the correlated function, the rank of the determinant can be enlarged also by introducing the correlated Slater determinant. As a result, the operation steps that are $O(N^6)$ in the Nm-algorithm can be reduced to $O(N^4)$ in the new algorithm, which is a big acceleration when N is large. We refer to this new algorithm (generalized later) as the "*Nk-algorithm*" ("k" appears faster than "m" in alphabetical order).

2. Nk-algorithm for the general case

Here, we formulate the Nk-algorithm for the general case. The most significant part of the Nk-algorithm is the analysis of the correlated function $f^{(m)}$ in a pre-calculation step, which we call the dot analysis to create the connection map of the correlated electrons. The number of dot electrons, *d*, should be determined as small as possible, since *d* directly corresponds to the number of electrons outside the determinant, and it directly determines the calculation order.

Our interest is to solve the electronic Schrödinger equation in which the Hamiltonian contains only one- and two-body operators. As a result, the correlated function is composed of only inseparable two-electron terms as given by

$$f^{(m)}(1, 2, ..., m)$$

= $\prod_{i < j}^{m} f_{ij}(i, j)$
= $f_{12}(1, 2) \cdot f_{13}(1, 3) \cdot \dots \cdot f_{m-1,m}(m-1, m),$ (24)

where we assume $f_{ji}(j, i) = f_{ij}(i, j)$ without loss of generality. Equation (24) is a general expression; usually it does not contain all the pair functions within 1 to *m* electrons: many of $f_{ij}(i, j)$ $(i, j \in 1, 2, ..., m)$ should be unity $(f_{ij}(i, j) = 1)$.

Figure 2 shows the correlation diagrams for all the cases in which one to four inseparable two-electron terms $f_{ii}(i, j)$ are included in the correlated function. In Fig. 2, the lines represent the existence of non-unity $f_{ii}(i, j)$ and the edges of the line represent electrons. After drawing the diagram, the dot electrons are simply determined according to the following rules: (i) the electron(s) of either (or both) side(s) of the line must be set as dot electron(s), (ii) the number of dot electrons should be set as small as possible, and (iii) the electron numbering should be reordered, for convenience, as the dot electrons locate in the first d electrons without loss of generality. In Fig. 2, the dot electrons are given by the black filled circles in each diagram. For instance, for the simplest case $f^{(2)} = f_{12}(1, 2), d$ = 1. Even for the case $f^{(4)} = f_{12}(1, 2) f_{13}(1, 3) f_{14}(1, 4)$, where three inseparable correlated terms are included and four electrons are correlated, the number of dot electrons is unity, d = 1. The computer algorithm of the dot analysis is very simple, looking at the correlation diagram, the electron that connects to the larger number of other electrons is assigned to the dot electron. This process is performed sequentially so that it satisfies the above rules (i) to (iii). In some cases of the above processes, there may be redundancies in the selection of the dot electron, but this is not a problem and any patterns will give the same result with the same calculation order.

After the dot analysis, a general expression of the antisymmetrization of the Nk-algorithm can be written by

$$\begin{split} \phi(1,2,\ldots,N) &= A\left[\varphi(1,2,\ldots,N)\right] \\ &= \sqrt{\frac{(N-d)!}{N!}} \sum_{I=1}^{N^{P_d}} (-1)^{\overline{p}_{I}^{(d)}} \cdot \overline{P}_{I}^{(d)}[\eta^{(d)}(1^*,2^*,\ldots,d^*) \cdot \widetilde{D}^{(N-d)}(d+1,d+2,\ldots,N;\,1^*,2^*,\ldots,d^*)] \\ &= \sqrt{\frac{(N-d)!}{N!}} \sum_{I=1}^{N^{P_d}} (-1)^{\overline{p}_{I}^{(d)}} \cdot \eta^{(d)}(t_1^{(I)^*},t_2^{(I)^*},\ldots,t_d^{(I)^*}) \cdot \widetilde{D}^{(N-d)}(t_{d+1}^{(I)},t_{d+2}^{(I)},\ldots,t_N^{(I)};\,t_1^{(I)^*},t_2^{(I)^*},\ldots,t_d^{(I)^*}). \end{split}$$
(25)

 $\phi =$

	(+1)· <i>o</i> ₁(1 [*])	$f_{12}(1^*,2)o_2(2)$	$f_{12}(1^*,3)o_2(3)$	$f_{12}(1^*,4)o_2(4)$	$f_{12}(1^*,5)o_2(5)$	$f_{12}(1^*,6)o_2(6)$
$A\varphi = \frac{1}{\sqrt{N!}}$		$f_{13}(1^*, 2)o_3(2)$	$f_{13}(1^*,3)o_3(3)$	$f_{13}(1^*, 4)o_3(4)$	$f_{13}(1^*,5)o_3(5)$	$f_{13}(1^*,6)o_3(6)$
		<i>o</i> ₄ (2)	<i>o</i> ₄ (3)	<i>o</i> ₄ (4)	o4(5)	<i>o</i> ₄ (6)
		o ₅ (2)	o ₅ (3)	o ₅ (4)	o ₅ (5)	<i>o</i> ₅ (6)
		<i>o</i> ₆ (2)	0 ₆ (3)	<i>o</i> ₆ (4)	06(5)	<i>o</i> ₆ (6)
	$+(-1) \cdot o_1(2^*)$	$f_{12}(2^*,1)o_2(1)$	$f_{12}(2^*,3)o_2(3)$	$f_{12}(2^*,4)o_2(4)$	$f_{12}(2^*,5)o_2(5)$	$f_{12}(2^*,6)o_2(6)$
		$f_{13}(2^*,1)o_3(1)$	$f_{13}(2^*,3)o_3(3)$	$f_{13}(2^*,4)o_3(4)$	$f_{13}(2^*,5)o_3(5)$	$f_{13}(2^*,6)o_3(6)$
) o ₄ (1)	<i>o</i> ₄ (3)	<i>o</i> ₄ (4)	<i>o</i> ₄ (5)	<i>o</i> ₄ (6)
		<i>o</i> ₅ (1)	<i>o</i> ₅ (3)	<i>o</i> ₅ (4)	<i>o</i> ₅ (5)	<i>o</i> ₅ (6)
		<i>o</i> ₆ (1)	<i>o</i> ₆ (3)	<i>o</i> ₆ (4)	<i>o</i> ₆ (5)	<i>o</i> ₆ (6)
	$+(-1) \cdot o_1(3^*)$	$f_{12}(3^*,2)o_2(2)$	$f_{12}(3^*,1)o_2(1)$	$f_{12}(3^*,4)o_2(4)$	$f_{12}(3^*,5)o_2(5)$	$f_{12}(3^*,6)o_2(6)$
		$f_{13}(3^*,2)o_3(2)$	$f_{13}(3^*, 1)o_3(1)$	$f_{13}(3^*,4)o_3(4)$	$f_{13}(3^*,5)o_3(5)$	$f_{13}(3^*,6)o_3(6)$
		0 04(2)	<i>o</i> ₄ (1)	<i>o</i> ₄ (4)	o ₄ (5)	<i>o</i> ₄ (6)
		<i>o</i> ₅ (2)	<i>o</i> ₅ (1)	<i>o</i> ₅ (4)	$o_{5}(5)$	<i>o</i> ₅ (6)
		<i>o</i> ₆ (2)	<i>o</i> ₆ (1)	<i>o</i> ₆ (4)	<i>o</i> ₆ (5)	<i>o</i> ₆ (6)
	$+(-1) \cdot o_1(4^*)$	$f_{12}(4^*,2)o_2(2)$	$f_{12}(4^*,3)o_2(3)$	$f_{12}(4^*,1)o_2(1)$	$f_{12}(4^*,5)o_2(5)$	$f_{12}(4^*,6)o_2(6)$
		$f_{13}(4^*,2)o_3(2)$	$f_{13}(4^*,3)o_3(3)$	$f_{13}(4^*, 1)o_3(1)$	$f_{13}(4^*,5)o_3(5)$	$f_{13}(4^*,6)o_3(6)$
				(1)	1.00	10
	$+(-1) \cdot o_1(4)$	$o_4(2)$	<i>o</i> ₄ (3)	$o_4(1)$	$o_4(5)$	<i>o</i> ₄ (6)
	$+(-1)\cdot o_1(4)$	$o_4(2) = o_5(2)$	$o_4(3)$ $o_5(3)$	$o_4(1) o_5(1)$	$o_4(5) o_5(5)$	$o_4(6)$ $o_5(6)$
	$+(-1)\cdot o_1(4)$	$\begin{array}{c c} & o_4(2) \\ & o_5(2) \\ & o_6(2) \end{array}$	$o_4(3)$ $o_5(3)$ $o_6(3)$	$o_4(1)$ $o_5(1)$ $o_6(1)$	$o_4(5)$ $o_5(5)$ $o_6(5)$	$o_4(6)$ $o_5(6)$ $o_6(6)$
	+(-1)·0 ₁ (4)	$ \begin{array}{c} $	$\begin{array}{c} o_4(3) \\ o_5(3) \\ o_6(3) \\ \hline f_{12}(5^*,3)o_2(3) \end{array}$	$\begin{array}{c} o_4(1) \\ o_5(1) \\ o_6(1) \\ f_{12}(5^*, 4)o_2(4) \end{array}$	$o_4(5)$ $o_5(5)$ $o_6(5)$ $f_{12}(5^*,5)o_2(1)$	$o_4(6)$ $o_5(6)$ $o_6(6)$ $f_{12}(5^*, 6)o_2(6)$
	$+(-1)\cdot o_1(4)$	$ \int \begin{array}{c} o_4(2) \\ o_5(2) \\ o_6(2) \\ f_{12}(5^*, 2)o_2(2) \\ f_{13}(5^*, 2)o_3(2) \end{array} $	$\begin{array}{c} o_4(3) \\ o_5(3) \\ \hline f_{12}(5^*,3)o_2(3) \\ f_{13}(5^*,3)o_3(3) \end{array}$	$\begin{array}{c} o_4(1) \\ o_5(1) \\ \hline \\ f_{12}(5^*, 4)o_2(4) \\ f_{13}(5^*, 4)o_3(4) \end{array}$	$f_{12}(5^*,5)o_2(1)$ $f_{13}(5^*,5)o_3(1)$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $f_{12}(5^*, 6)o_2(6) \\ f_{13}(5^*, 6)o_3(6) \end{array}$
	$+(-1)\cdot o_{1}(4)$ $+(-1)\cdot o_{1}(5^{*})$	$ \begin{array}{c} & o_4(2) \\ & o_5(2) \\ & o_6(2) \end{array} \\ f_{12}(5^*, 2)o_2(2) \\ f_{13}(5^*, 2)o_3(2) \\ & o_4(2) \end{array} $	$\begin{array}{c} o_4(3) \\ o_5(3) \\ c_6(3) \\ f_{12}(5^*,3)o_2(3) \\ f_{13}(5^*,3)o_3(3) \\ o_4(3) \end{array}$	$\begin{array}{c} o_4(1) \\ o_5(1) \\ \hline \\ f_{12}(5^*, 4)o_2(4) \\ f_{13}(5^*, 4)o_3(4) \\ \hline \\ o_4(4) \end{array}$	$\begin{array}{c} o_4(5) \\ o_5(5) \\ o_6(5) \\ f_{12}(5^*,5)o_2(1) \\ f_{13}(5^*,5)o_3(1) \\ o_4(1) \end{array}$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $f_{12}(5^*, 6)o_2(6) \\ f_{13}(5^*, 6)o_3(6) \\ o_4(6) \end{array}$
	$+(-1) \cdot o_1(4)$ $+(-1) \cdot o_1(5^*)$	$ \begin{array}{c} & o_4(2) \\ & o_5(2) \\ & o_6(2) \end{array} \\ f_{12}(5^*, 2)o_2(2) \\ f_{13}(5^*, 2)o_3(2) \\ & o_4(2) \\ & o_5(2) \end{array} $	$\begin{array}{c} o_4(3)\\ o_5(3)\\ \hline\\ f_{12}(5^*,3)o_2(3)\\ f_{13}(5^*,3)o_3(3)\\ \hline\\ o_4(3)\\ o_5(3) \end{array}$	$\begin{array}{c c} & o_4(1) \\ & o_5(1) \\ & & 0_6(1) \\ \hline f_{12}(5^*, 4)o_2(4) \\ & f_{13}(5^*, 4)o_3(4) \\ & & o_4(4) \\ & & o_5(4) \end{array}$	$\begin{array}{c} o_4(5) \\ o_5(5) \\ o_6(5) \\ f_{12}(5^*,5)o_2(1) \\ f_{13}(5^*,5)o_3(1) \\ o_4(1) \\ o_5(1) \end{array}$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $f_{12}(5^*, 6)o_2(6) \\ f_{13}(5^*, 6)o_3(6) \\ o_4(6) \\ o_5(6) \end{array}$
	$+(-1)\cdot o_1(4)$ $+(-1)\cdot o_1(5^*)$	$ \begin{array}{c} o_4(2) \\ o_5(2) \\ o_6(2) \\ \hline f_{12}(5^*,2)o_2(2) \\ f_{13}(5^*,2)o_3(2) \\ o_4(2) \\ o_5(2) \\ o_6(2) \end{array} $	$\begin{array}{c} o_4(3)\\ o_5(3)\\ \hline\\ f_{12}(5^*,3)o_2(3)\\ \hline\\ f_{13}(5^*,3)o_3(3)\\ o_4(3)\\ o_5(3)\\ o_6(3) \end{array}$	$\begin{array}{c c} & o_4(1) \\ & o_5(1) \\ & & o_6(1) \\ \hline f_{12}(5^*, 4)o_2(4) \\ & f_{13}(5^*, 4)o_3(4) \\ & & o_4(4) \\ & & o_5(4) \\ & & o_6(4) \end{array}$	$\begin{array}{c} o_4(5) \\ o_5(5) \\ o_6(5) \\ \hline f_{12}(5^*,5)o_2(1) \\ f_{13}(5^*,5)o_3(1) \\ o_4(1) \\ o_5(1) \\ o_6(1) \\ \end{array}$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $f_{12}(5^*, 6)o_2(6) \\ f_{13}(5^*, 6)o_3(6) \\ o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$
	$+(-1)\cdot o_1(4)$ $+(-1)\cdot o_1(5^*)$	$ \begin{array}{c} o_4(2) \\ o_5(2) \\ o_6(2) \\ \hline f_{12}(5^*, 2)o_2(2) \\ f_{13}(5^*, 2)o_3(2) \\ \hline o_4(2) \\ o_5(2) \\ o_6(2) \\ \hline f_{12}(6^*, 2)o_2(2) \\ \end{array} $	$\begin{array}{c} o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline f_{12}(5^*,3)o_2(3)\\ f_{13}(5^*,3)o_3(3)\\ o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline f_{12}(6^*,3)o_2(3)\\ \end{array}$	$\begin{array}{c c} & o_4(1) \\ & o_5(1) \\ & o_6(1) \\ \hline f_{12}(5^*, 4)o_2(4) \\ f_{13}(5^*, 4)o_3(4) \\ & o_4(4) \\ & o_5(4) \\ & o_6(4) \\ \hline f_{12}(6^*, 4)o_2(4) \end{array}$	$\begin{array}{c c} o_4(5) \\ o_5(5) \\ o_6(5) \\ \hline f_{12}(5^*,5)o_2(1) \\ f_{13}(5^*,5)o_3(1) \\ o_4(1) \\ o_5(1) \\ o_6(1) \\ \hline f_{12}(6^*,5)o_2(5) \\ \hline \end{array}$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $\begin{array}{c} f_{12}(5^*, 6)o_2(6) \\ f_{13}(5^*, 6)o_3(6) \\ o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$
	$+(-1)\cdot o_{1}(4)$ $+(-1)\cdot o_{1}(5^{*})$	$ \begin{array}{c} o_4(2) \\ o_5(2) \\ o_6(2) \\ \hline f_{12}(5^*,2)o_2(2) \\ f_{13}(5^*,2)o_3(2) \\ \hline o_4(2) \\ o_5(2) \\ o_6(2) \\ \hline f_{12}(6^*,2)o_2(2) \\ f_{13}(6^*,2)o_3(2) \\ \end{array} $	$\begin{array}{c} o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline f_{12}(5^*,3)o_2(3)\\ f_{13}(5^*,3)o_3(3)\\ o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline f_{12}(6^*,3)o_2(3)\\ f_{13}(6^*,3)o_3(3)\\ \end{array}$	$\begin{array}{c c} & o_4(1) \\ & o_5(1) \\ & o_6(1) \\ \hline f_{12}(5^*, 4)o_2(4) \\ f_{13}(5^*, 4)o_3(4) \\ & o_4(4) \\ & o_5(4) \\ & o_6(4) \\ \hline f_{12}(6^*, 4)o_2(4) \\ f_{13}(6^*, 4)o_3(4) \end{array}$	$ \begin{array}{c} o_4(5) \\ o_5(5) \\ o_6(5) \\ f_{12}(5^{\bullet},5)o_2(1) \\ f_{13}(5^{\bullet},5)o_3(1) \\ o_4(1) \\ o_5(1) \\ o_6(1) \\ 0_6(1) \\ f_{12}(6^{\bullet},5)o_2(5) \\ f_{13}(6^{\bullet},5)o_3(5) \end{array} $	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $\begin{array}{c} f_{12}(5^*,6)o_2(6) \\ f_{13}(5^*,6)o_3(6) \\ o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $\begin{array}{c} f_{12}(6^*,1)o_2(1) \\ f_{13}(6^*,1)o_3(1) \end{array}$
	+(-1) $\cdot o_1(5^*)$ +(-1) $\cdot o_1(5^*)$	$ \begin{array}{c} o_4(2) \\ o_5(2) \\ o_6(2) \\ \end{array} \\ f_{12}(5^*, 2)o_2(2) \\ f_{13}(5^*, 2)o_3(2) \\ o_4(2) \\ o_5(2) \\ o_6(2) \\ \end{array} \\ f_{12}(6^*, 2)o_2(2) \\ f_{13}(6^*, 2)o_3(2) \\ o_4(2) \\ \end{array} $	$\begin{array}{c} o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline\\f_{12}(5^*,3)o_2(3)\\ f_{13}(5^*,3)o_3(3)\\ o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline\\f_{12}(6^*,3)o_2(3)\\ f_{13}(6^*,3)o_3(3)\\ o_4(3)\\ \end{array}$	$\begin{array}{c c} & o_4(1) \\ & o_5(1) \\ & o_6(1) \\ \hline f_{12}(5^*, 4)o_2(4) \\ f_{13}(5^*, 4)o_3(4) \\ & o_4(4) \\ & o_5(4) \\ & o_6(4) \\ \hline f_{12}(6^*, 4)o_2(4) \\ f_{13}(6^*, 4)o_3(4) \\ \hline o_4(4) \\ \hline \end{array}$	$\begin{array}{c c} o_4(5) \\ o_5(5) \\ o_6(5) \\ f_{12}(5^{\bullet}, 5)o_2(1) \\ f_{13}(5^{\bullet}, 5)o_3(1) \\ o_4(1) \\ o_5(1) \\ o_6(1) \\ 0_6(1) \\ f_{12}(6^{\bullet}, 5)o_2(5) \\ f_{13}(6^{\bullet}, 5)o_3(5) \\ o_4(5) \end{array}$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $\begin{array}{c} f_{12}(5^*,6)o_2(6) \\ f_{13}(5^*,6)o_3(6) \\ o_4(6) \\ o_5(6) \\ o_6(6) \end{array}$ $\begin{array}{c} o_4(6) \\ o_6(6) \\ f_{12}(6^*,1)o_2(1) \\ f_{13}(6^*,1)o_3(1) \\ o_4(1) \end{array}$
	+(-1) $\cdot o_1(5^*)$ +(-1) $\cdot o_1(5^*)$	$ \begin{array}{c} & o_4(2) \\ & o_5(2) \\ & o_6(2) \end{array} \\ f_{12}(5^*,2)o_2(2) \\ f_{13}(5^*,2)o_3(2) \\ & o_4(2) \\ & o_5(2) \\ & o_6(2) \end{array} \\ f_{12}(6^*,2)o_2(2) \\ f_{13}(6^*,2)o_3(2) \\ & o_4(2) \\ & o_5(2) \end{array} $	$\begin{array}{c} o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline\\f_{12}(5^*,3)o_2(3)\\ f_{13}(5^*,3)o_3(3)\\ o_4(3)\\ o_5(3)\\ o_6(3)\\ \hline\\f_{12}(6^*,3)o_2(3)\\ f_{13}(6^*,3)o_3(3)\\ o_4(3)\\ o_5(3)\\ \end{array}$	$\begin{array}{c c} & o_4(1) \\ & o_5(1) \\ & o_6(1) \\ \hline f_{12}(5^*, 4)o_2(4) \\ f_{13}(5^*, 4)o_3(4) \\ & o_4(4) \\ & o_5(4) \\ \hline f_{12}(6^*, 4)o_2(4) \\ f_{13}(6^*, 4)o_3(4) \\ \hline o_4(4) \\ & o_5(4) \\ \hline \end{array}$	$\begin{array}{c c} o_4(5) \\ o_5(5) \\ o_6(5) \\ \hline f_{12}(5^{\bullet},5)o_2(1) \\ f_{13}(5^{\bullet},5)o_3(1) \\ o_4(1) \\ o_5(1) \\ o_6(1) \\ \hline f_{12}(6^{\bullet},5)o_2(5) \\ f_{13}(5^{\bullet},5)o_3(5) \\ o_4(5) \\ o_5(5) \\ \end{array}$	$\begin{array}{c} o_4(6) \\ o_5(6) \\ o_6(6) \\ \end{array}$ $\begin{array}{c} f_{12}(5^*,6)o_2(6) \\ f_{13}(5^*,6)o_3(6) \\ o_4(6) \\ o_5(6) \\ o_6(6) \\ \end{array}$ $\begin{array}{c} o_4(6) \\ o_6(6) \\ \hline f_{12}(6^*,1)o_2(1) \\ o_4(1) \\ o_5(1) \end{array}$

FIG. 1. The example of the Nk-algorithm for the case $f^{(3)}(1, 2, 3) = f_{12}(1, 2)f_{13}(1, 3)$ and N = 6. Here, the antisymmetrization can be performed with six terms. In the second to sixth terms, the first two rows (surrounded by red lines) and the single column (surrounded by blue dashed lines) show the difference from the first term.



FIG. 2. Correlation diagrams for all the cases in which one to four inseparable two-electron terms $f_{ij}(i, j)$ are included in the correlated function. For each diagram, the lines describe the non-unity two-electron terms, the edges of the line show electrons, and the circle points describe the dot electrons.

Equation (25) looks similar to Eq. (17), but *m* and $f^{(m)}$ in Eq. (17) are replaced by *d* and $\eta^{(d)}$ in Eq. (25), respectively, and the correlated Slater determinant $\widetilde{D}^{(N-d)}$ is newly introduced instead of $D^{(N-m)}$. $\eta^{(d)}$ is a function of 1^* , 2^* , ..., d^* and does not contain any coordinates of d + 1, d + 2, ..., N. Thus, $\eta^{(d)}$ consists of the one-electron functions $o_i(i^*)$ and the inseparable correlated functions $f_{ij}(i^*, j^*)$ which cannot be included in the determinant. It is generally written as

$$\eta^{(d)}(1^*, 2^*, \dots, d^*) = \prod_{\{(i < j) \le d\}} f_{ij}(i^*, j^*) \cdot \prod_{i=1}^d o_i(i^*)$$
$$= [f_{12}(1^*, 2^*) \cdot f_{13}(1^*, 3^*) \cdot \dots \cdot f_{d-1,d}((d-1)^*, d^*)] \cdot [o_1(1^*) \cdot o_2(2^*) \cdot \dots \cdot o_d(d^*)],$$
(26)

where the brace notation under the multiplication of \prod means that (i, j) pairs of non-unity f_{ij} are included. The correlated Slater determinant $\widetilde{D}^{(N-d)}$ is a function of d + 1, d + 2, ..., N and it realizes the permutations of the electrons d + 1, d + 2, ..., N, but it also contains the coordinates $1^*, 2^*, ..., d^*$ as parameters through the correlated terms. $\widetilde{D}^{(N-d)}$ is generally expressed by

$$\vec{D}^{(N-d)}(d+1, d+2, \dots, N; 1^{*}, 2^{*}, \dots, d^{*}) = \frac{1}{\sqrt{(N-d)!}} \begin{vmatrix} o'_{d+1}(d+1; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{d+1}(d+2; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{d+1}(d+3; 1^{*}, 2^{*}, \dots, d^{*}) & \cdots & o'_{d+1}(N; 1^{*}, 2^{*}, \dots, d^{*}) \\ o'_{d+2}(d+1; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{d+2}(d+2; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{d+2}(d+3; 1^{*}, 2^{*}, \dots, d^{*}) & \cdots & o'_{d+2}(N; 1^{*}, 2^{*}, \dots, d^{*}) \\ o'_{d+3}(d+1; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{d+3}(d+2; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{d+3}(d+3; 1^{*}, 2^{*}, \dots, d^{*}) & \cdots & o'_{d+3}(N; 1^{*}, 2^{*}, \dots, d^{*}) \\ \dots & \dots & \dots & \dots & \dots \\ o'_{N}(d+1; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{N}(d+2; 1^{*}, 2^{*}, \dots, d^{*}) & o'_{N}(d+3; 1^{*}, 2^{*}, \dots, d^{*}) & \cdots & o'_{N}(N; 1^{*}, 2^{*}, \dots, d^{*}) \end{vmatrix} ,$$

$$(27)$$

where $o'_i(j; 1^*, 2^*, ..., d^*)$ is a function of *j* but includes parametrically the coordinates of electrons $1^*, 2^*, ..., d^*$. It is composed of the one-electron functions $o_i(j)$ and the correlated terms containing electron *j* as expressed by

$$o'_{i}(j; 1^{*}, 2^{*}, \dots, d^{*}) = o_{i}(j) \cdot \prod_{\{k=1, 2, \dots, d\}} f_{kj}(k^{*}, j), \quad (28)$$

where *i* and *j* run over d + 1, d + 2, ..., N. The brace notation under the multiplication of \prod again means that (k, j) pairs for non-unity f_{kj} are included.

The operation count for Eq. (25) is given by

$$_{N}P_{d} \cdot O\left((N-d)^{3}/3\right) \Rightarrow O(N^{d+3}),$$
(29)

which is actually much faster than that of Eq. (17), because the inequality d < m is always satisfied (except for the two extreme cases where all electrons correlate or no electron correlates).

The present Nk-algorithm are applied independently to the A_{α} and A_{β} for the α and β spin electrons in Eq. (10), and the additional formulations for the functions across different spins are given in Appendix A.

The physically important many-electron correlated functions often appear, for instance, for *d*-shell electrons in transition metals. In the Nm-algorithm, however, their antisymmetrizations require very high computational costs. As an example, the chromium atom has the septet ground state whose six electrons singly occupy the 4s orbital and all the *d*-shell orbitals (d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, and d_{z^2}). Their radial distributions are almost similar so that their electrons have chances to be located close to each other. Therefore, even a six-electron correlated function, $r_{12}r_{13}r_{14}r_{15}r_{16}$, where electron 1 interacts with all others, would be still important. For the antisymmetrization of this function, whereas the Nmalgorithm requires $O(N^9)$ due to m = 6, the Nk-algorithm just requires $O(N^4)$ because d = 1, their calculation orders can be further improved to $O(N^3)$ using the determinant update method described in Sec. IV.

Up to here, we have considered the partially correlated functions of the type of Eq. (3) or Eq. (12). One may also consider the wave function that contains the totally symmetric term, $\exp(J)$,^{27–30} where *J* consists of the totally symmetric two-body terms with respect to the permutations of electrons. Since the antisymmetrization operator commutes with the totally symmetric term $\exp(J)$, such a wave function can be represented by

$$\phi_i(1, 2, \dots, N) = \exp(J) \cdot A[\{f_{12}(1, 2) \\ \cdot f_{13}(1, 3) \cdot \dots \cdot f_{N-1, N}(N-1, N)\} \\ \cdot \{o_1(1) \cdot o_2(2) \cdot \dots \cdot o_N(N)\} \cdot \chi_i].$$
(30)

Note that in Eq. (30), $\exp(J)$ does not cause any additional difficulties with respect to the antisymmetrization. This form may have a merit that the electron dynamical correlations are included in average through $\exp(J)$, but we believe that the different contributions from the different electron pairs are important: they are described by the partially correlated terms.

IV. FURTHER ACCELERATION WITH THE DETERMINANT UPDATE METHOD

In both of the Nm- and Nk-algorithms (Eqs. (17) and (25)), the determinant evaluation on each element of the permutation loop requires a computation of $O(M^3)$ (*M* is the matrix dimension). However, since each determinant in the loop varies only in a few rows and/or columns, the so-called determinant update technique based on the Laplace expansion is efficient and available for both Nm- and Nk-algorithms if $m \ll N$. In the quantum Monte Carlo method, this method is often used in sampling point differences.^{27–30}

The key equations of the determinant update method are well known by the matrix determinant lemma and the Sherman-Morrison formula,³⁹ and their mathematical formulations are given in Appendix B. With this method, it is not necessary to evaluate independently each determinant in the permutation loop, but the sequential updates of only a few lines are necessary. Therefore, the calculation order for the determinant evaluation part can be reduced from $O(M^3)$ to $O(M^2)$. In addition, there is another interesting property in the case where only several rows (or columns) change (but not both rows and columns): the calculation order becomes O(M)instead of $O(M^2)$, because the evaluation of the matrix-dense vector product $\mathbf{v}^T \mathbf{D}^{-1}$ or $\mathbf{D}^{-1} \mathbf{u}$ is not necessary (see Eq. (B6)). In the Nm-algorithm, this property is available because only columns change for each element of the loop (see Eq. (17)) and it can reduce the order from $O(M^3)$ to O(M) for the determinant evaluation. In the Nk-algorithm, unfortunately, this feature is not available and the reduction is to $O(M^2)$, since both rows and columns simultaneously change even for the simplest case.

Figure 1 shows a concrete example of the Nk-algorithm for the case $f^{(3)}(1, 2, 3) = f_{12}(1, 2)f_{13}(1, 3)$ with N = 6. The antisymmetrization can be accomplished with six terms. In the second to sixth terms, the first two rows (surrounded by red lines) and single column (surrounded by the blue dashed line) are different from those of the first term, and the other matrix elements are the same as those of first term. The determinant update method is efficiently applicable for evaluating the differences of these three lines.

V. SUMMARY OF THE CALCULATION ORDERS

As discussed above, the orders of the calculation for the Nm- and Nk-algorithms without the determinant update method were $O(N^{m+3})$ and $O(N^{d+3})$, respectively. In the case where N is sufficiently large compared to m, these can be reduced to $O(N^{m+1})$ and $O(N^{d+2})$, respectively, with the determinant update method, except for the non-correlated case. We call the latter cases (with the determinant update method) the "NmD-algorithm" and "NkD-algorithm" ("D" means "determinant update"), respectively. Table I summarizes the calculation orders for the Nm- and Nk-algorithms without and with the determinant update method for each type of the correlated function shown in Fig. 2, where one to four inseparable twoelectron terms $f_{ij}(i, j)$ are included.

For the non-correlated function, the evaluation of the determinant is $O(N^3)$. For both the NmD- and NkD-algorithms, the function that includes a single $f_{12}(1, 2)$ correlated term is again evaluated only with $O(N^3)$; this is the same as the non-correlated case, even in the existence of the correlated function. For this simplest case, which is obviously the case for the most dominant correlated functions in the FC or Hy-CI and EHy-CI wave functions, the present algorithms do not increase the computational cost for the antisymmetrization.

For more complicated correlated functions, the calculation order of the Nk-algorithm increases less rapidly than that for the Nm-algorithm, both without and with the determinant update method. In any case, the calculation order of the Nk-algorithm is always equal to or less than that for the Nmalgorithm. Even for the case in which eight electrons are correlated with four f_{ij} terms (see the last line in Table I), the evaluation can be performed with a calculation order of $O(N^6)$ in

	Nm-algorithm			Nk-algorithm			
Correlated functions	<i>m</i> (Number of correlated electrons)	Without determinant update: $O(N^{m+3})$	With determinant update: $O(N^{m+1})$ (NmD-algorithm)	d (Number of dot electrons)	Without determinant update: $O(N^{d+3})$	With determinant update: $O(N^{d+2})$ (NkD-algorithm)	
No correlated function:	0	$O(N^3)$		0	$O(N^3)$		
One f_{ij} : $f_{12}(1, 2)$	2	$O(N^5)$	$O(N^3)$	1	$O(N^4)$	$O(N^3)$	
Two f_{ij} : $f_{12}(1, 2)f_{13}(1, 3)$ $f_{13}(1, 3)f_{24}(2, 4)$	3 4	$O(N^6)$ $O(N^7)$	$O(N^4)$ $O(N^5)$	1 2	$O(N^4)$ $O(N^5)$	$O(N^3)$ $O(N^4)$	
Three f_{ij} : $f_{12}(1, 2)f_{13}(1, 3)f_{14}(1, 4)$ $f_{13}(1, 3)f_{14}(1, 4)f_{25}(2, 5)$ $f_{12}(1, 2)f_{13}(1, 3)f_{23}(2, 3)$ $f_{14}(1, 4)f_{25}(2, 5)f_{36}(3, 6)$	4 5 3 6	$O(N^7)$ $O(N^8)$ $O(N^6)$ $O(N^9)$	$O(N^5)$ $O(N^6)$ $O(N^4)$ $O(N^7)$	1 2 2 3	$O(N^4)$ $O(N^5)$ $O(N^5)$ $O(N^6)$	$O(N^3)$ $O(N^4)$ $O(N^4)$ $O(N^5)$	
Four f_{ij} : $f_{12}(1, 2)f_{13}(1, 3)f_{14}(1, 4)f_{15}(1, 5)$ $f_{13}(1, 3)f_{14}(1, 4)f_{15}(1, 5)f_{26}(2, 6)$ $f_{13}(1, 3)f_{14}(1, 4)f_{25}(2, 5)f_{26}(2, 6)$ $f_{12}(1, 2)f_{13}(1, 3)f_{14}(1, 4)f_{23}(2, 3)$ $f_{12}(1, 2)f_{13}(1, 3)f_{24}(2, 4)f_{34}(3, 4)$ $f_{14}(1, 4)f_{15}(1, 5)f_{26}(2, 6)f_{37}(3, 7)$	5 6 4 4 7	$O(N^8)$ $O(N^9)$ $O(N^9)$ $O(N^7)$ $O(N^{7})$	$O(N^6)$ $O(N^7)$ $O(N^7)$ $O(N^5)$ $O(N^5)$	1 2 2 3 3	$O(N^4)$ $O(N^5)$ $O(N^5)$ $O(N^5)$ $O(N^6)$ $O(N^6)$	$O(N^{3}) O(N^{4}) O(N^{4}) O(N^{5}) O(N^{5}) $	

TABLE I. The calculation orders of the Nm- and Nk-algorithms without and with the determinant update method for each type of correlated function

the NkD-algorithm. The correlated functions shown in Table I or in Fig. 2 cover all the complement functions in the ordinary FC wave function up to order = 4, which is a sufficient order to obtain chemical accuracy.^{7,8,16} Moreover, the numbers of the correlated functions with the worst calculation order of $O(N^6)$ are actually quite limited. Thus, for ordinary FC calculations, the antisymmetrization has the computational cost of lower polynomial orders.

VI. EVALUATION OF THE HAMILTONIAN APPLIED TO ϕ

To solve the SE with the FC-LSE method, we have to evaluate $H\phi$ or its local energy form $H\phi/\phi$ at the sampling point, where the local energy is more feasible in the sampling method than for $H\phi$ itself. Although the evaluation of the local energy requires more computational effort than for ϕ , the present antisymmetrization techniques can also be combined with the evaluation of the local energy.

The Hamiltonian of the SE for atoms and molecules is written as

$$H = K + V = -\frac{1}{2} \sum_{\kappa} \frac{1}{M_{\kappa}} \nabla_{\kappa}^2 + \sum_{\kappa < \lambda} \frac{Z_{\kappa} Z_{\lambda}}{r_{\kappa\lambda}}, \qquad (31)$$

where M_{κ} and Z_{κ} are the mass (or the reduced mass) and the charge, respectively, of the particle κ . The first and second terms (*K* and *V*) represent the kinetic and potential operators, respectively. Equation (31) is a general expression not only for electron coordinates but also for general fermions, and it is also valid for non-Born-Oppenheimer systems.²² For electrons, M_{κ} is unity in atomic units. Note that the potential term can be easily evaluated by $V\phi/\phi = V$, since it is a scalar operator.

Because Hamiltonian is totally symmetric, the antisymmetrization operator commutes with it,

$$[H, A] = 0. (32)$$

Therefore, we have two choices to apply the Hamiltonian either after or before the antisymmetrization. The former algorithm is more complicated than the latter but it is straightforward to implement and can also be extended to nonsymmetric operators besides Hamiltonian. The calculation of the latter algorithm is faster than the former, especially for the complement functions with small partial correlation number min Eq. (12).

The former algorithm is given in Appendix C and we show here the simpler latter case. Since the Hamiltonian and the antisymmetrization operator commute, $H\phi$ is given by

$$H\phi = H[A\varphi] = A[H\varphi]$$

= $A[H[f^{(m)}(1, 2, ..., m)$
 $\cdot d^{(N-m)}(m+1, m+2, ..., N)]].$ (33)

We should note that the differential operator of the kinetic operator does not increase the complexity of the correlation diagram. The number of the expanded terms in Eq. (33) is not large if *m* is comparably smaller than *N*. Therefore, the calculation order is an additional O(N) due to the summation

part of $\sum_{\kappa} \nabla_{\kappa}^2$. If *m* is not large, this order should be smaller than that in the former algorithm (Appendix C).

In the case where exp (J) (exp(J) = $\sum_{i,j} u(i, j)$) exists, Eq. (33) becomes

$$H\phi = H [A\varphi] = A [H\varphi]$$

= $A[H[\exp(J) \cdot f^{(m)}(1, 2, ..., m) \cdot d^{(N-m)}(m+1, m+2, ..., N)]].$ (34)

This requires the differentiation,

$$\nabla_{\kappa} \left[\sum_{i,j} u(i,j) \right] = \sum_{i} \nabla_{\kappa} u(i,\kappa), \quad (35)$$

but the right hand term can be considered to be a one-electron function of κ due to the total symmetry of $u(i, \kappa)$ in terms of *i*, and so it does not increase the complexity.

In the evaluations of ϕ and $H\phi$, it is obviously efficient to save all the elements of the primitive one- and two-electron functions and their derivatives into core memory, since they are used repeatedly in the complement functions. These are

$$o_i(k), \ \nabla_k^2 o_i(k), \ \nabla_k o_i(k)$$
 (36)

with $i = 1, 2, ..., M_1$ and k = 1, 2, ..., N for the one-electron functions, and

$$f_{(i)}(j,k), \ \nabla_k^2 f_{(i)}(j,k), \ \nabla_k f_{(i)}(j,k)$$
 (37)

with $i = 1, 2, ..., M_2$ and j, k = 1, 2, ..., N for the twoelectron functions. Here, $\{o_i\}$ and $\{f_{(i)}\}$ represent the different types of one- and two-electron functions, respectively, that appear in all the complement functions in the FC wave function, and M_1 and M_2 are their numbers. The inner products $\nabla_k o_i(k) \cdot \nabla_k f_{(j)}(k, l)$ and $\nabla_k f_{(i)}(k, l) \cdot \nabla_k f_{(j)}(k, m)$ are evaluated with the third elements of Eqs. (36) and (37). The evaluations of the terms in Eqs. (36) and (37) cost $O(M_1N)$ and $O(M_2N^2)$, respectively, and they are not dominant in the total computational cost.

VII. PERFORMANCE

Here, we examine the performance of the proposed antisymmetrization procedures: the NF-algorithm, the Nmalgorithm without the determinant update method, the Nmalgorithm with the determinant update method (NmDalgorithm), the Nk-algorithm without the determinant update method, and the Nk-algorithm with the determinant update method (NkD-algorithm). Figures 3 and 4 show the timing results (relative central processing unit (CPU) times) of the antisymmetrization with the test functions:

$$\varphi = f_{12}(1,2)f_{13}(1,3) \cdot o_1(1) \cdot o_2(2) \cdot o_3(3)$$
$$\cdot o_4(4) \cdot \cdots \cdot o_N(N)$$
(38)

and

$$\varphi = f_{13}(1,3) f_{24}(2,4) \cdot o_1(1) \cdot o_2(2) \cdot o_3(3)$$
$$\cdot o_4(4) \cdot \cdots \cdot o_N(N), \tag{39}$$

respectively. Equation (38) contains two correlated terms with the single linked electron (electron 1), i.e., the case m = 3



FIG. 3. Timing test for the antisymmetrization of Eq. (38) with the five different algorithms: NF-algorithm (black line), Nm-algorithm without the determinant update method (light blue dashed line), NmD-algorithm (blue line), Nk-algorithm without the determinant update method (orange dashed line), and NkD-algorithm (red line). The relative CPU time (the time in the NFalgorithm (N = 10) is set to unity) is shown for N.

and d = 1 (see Table I and Fig. 2). Equation (39) is for the case m = 4 and d = 2. Here, $o_i(\mathbf{r}) = \sqrt{\alpha_i^3/\pi} \cdot \exp(-\alpha_i r)$ with $\alpha_i = 1 + 0.2(i - 1)$ and $f_{ij}(\mathbf{r}_1, \mathbf{r}_2) = r_{12}$ were used. The *N*-electron coordinates (sampling points) are randomly generated in (x, y, z) = [0, 1]. The test was performed on a HP Z800 Workstation (Intel Xeon CPU and 48 GB core memory) with the test program written using the Maple13 package,⁴⁰ where the matrix evaluation library "LinearAlgebra" was used to evaluate the determinant.

In Figs. 3 and 4, as easily noticed, the NF-algorithm is completely unusable. For Eq. (38) (Fig. 3), the Nm-algorithm without the determinant update method still requires a high computational cost, $O(N^6)$, but the additional determinant update method (the NmD-algorithm) can greatly reduce the cost to $O(N^4)$. The Nk-algorithm without the determinant update method also requires $O(N^4)$, which is the same as the NmD-algorithm, but the pre-factor is favorable for the Nkalgorithm. The NkD-algorithm is most efficient with $O(N^3)$, so that even for N = 100-200, the required computational



FIG. 4. Timing test for the antisymmetrization of Eq. (39) with the five different algorithms: NF-algorithm (black line), Nm-algorithm without the determinant update method (light blue dashed line), NmD-algorithm (blue line), Nk-algorithm without the determinant update method (orange dashed line), and NkD-algorithm (red line). The relative CPU time (the time in the NFalgorithm (N = 10) is set to unity) is shown for N.

cost is quite small. The same situation also occurred for Eq. (39) (Fig. 4). The computational costs for the above five algorithms are O(N!), $O(N^7)$, $O(N^5)$, $O(N^5)$, and $O(N^4)$. Therefore, the evaluation requires more time than the case of Eq. (38).

In the actual applications to general atoms and molecules, the functions of one f_{ij} and two f_{ij} in Table I, i.e., noncorrelated case, $f_{12}(1, 2)$, $f_{12}(1, 2)f_{13}(1, 3)$ (Eq. (38)), and $f_{13}(1, 3)f_{24}(2, 4)$ (Eq. (39)), should dominantly determine the accuracy of the wave function. In the ordinary FC wave function, they are generated by order = 2. As shown in the above examinations, the NkD-algorithm requires the computational costs of only $O(N^3)$ or $O(N^4)$ even for the correlated functions and so it realizes the applications to highly accurate calculations of many-electron systems. Although more complicated correlated functions are generated at higher orders of the FC method, their contributions are smaller than those of the lower order ones.

VIII. CONCLUDING REMARKS

We have proposed here new antisymmetrization procedures for the partially correlated wave functions that appear in the FC-LSE method and other methods for accurately solving the Schrödinger equation. The Nm-algorithm is based on the simple concept of the Laplace expansion: all the correlated electrons are placed outside of the Slater determinant. Although the Nm-algorithm can avoid N! operations, the calculation order is still high. Alternatively, the Nk-algorithm can minimize the number of electrons that must be put outside of the determinant by performing the dot analysis and introducing the correlated Slater determinant. This pre-analysis of the correlation diagram is based on the fact that the electronic Hamiltonian and its exact FC wave function of the SE are composed of only one- and two-body inseparable terms. By combining the determinant update method with the Nkalgorithm, the computational cost could be further reduced. In the case where the wave function includes only up to single correlated terms (actually this type should be most important for describing the correlations in the FC wave function and the Hy-CI and EHy-CI wave functions), the computation could be performed with only $O(N^3)$ (the same order as the non-correlated case), despite of the existence of the correlated terms. Even with the case that includes four kinds of correlated terms with eight correlated electrons, the computational cost is just $O(N^6)$. The evaluations of the Hamiltonian-applied wave function and the local energy have been discussed for practical applications. The handling of the spin part of the spin eigenfunction wave function has also been discussed.

The presented methods are general and applicable not only to the FC wave functions we have actually applied for some years, but also to any partially correlated wave functions that appear in the explicitly correlated wave function theories aiming to get highly accurate wave functions. In addition to the antisymmetrization of electrons, the present methods are applicable to any fermion systems, for example, like proton nuclear systems in the non-Born-Oppenheimer calculations and the antisymmetrization of the relativistic Dirac wave functions including explicitly correlated terms.²¹

The presented antisymmetrization algorithms have actually been used in our laboratory for some years since 2008 in practical applications of the FC-LSE calculations of many different atoms and molecules. The FC-LSE method has been shown to be very accurate for solving the SE of many-electron atoms and molecules.^{7,8,15,19} In addition, the sampling procedures in the FC-LSE calculations are very easily addressable to massively parallel computing and the performance has been proved to be actually very high. These facts shed a good light to the future development of the method of solving the Schrödinger equation.^{7,8} For example, this method has recently been applied to 42-electron benzene molecule, showing that these size of molecules are really accessible from compu-

tational points of view. The achieved results for general atoms and molecules will be discussed in forthcoming papers.⁴¹ We hope that the present method will be useful in the development of highly accurate quantum chemistry in Schrödinger and Dirac accuracies.

APPENDIX A: ADDITIONAL FORMULATIONS OF THE Nk-ALGORITHM FOR THE α AND β SPIN ELECTRONS

In the spin-free formalism, the dot analysis in the Nkalgorithm is performed independently for α and β spin electrons, and each term of Eq. (10) is expressed as

$$\begin{split} &A_{\alpha}A_{\beta}\left[\lambda(1,2,\ldots,N)\right] \\ &= \sqrt{\frac{(N_{\alpha}-d_{\alpha})!\cdot(N_{\beta}-d_{\beta})!}{N_{\alpha}!N_{\beta}!}} \sum_{I=1}^{N_{\alpha}P_{d_{\beta}}} \sum_{J=1}^{N_{\beta}P_{d_{\beta}}} (-1)^{\overline{p}_{I}^{(d_{\alpha})}} (-1)^{\overline{p}_{I}^{(d_{\beta})}} \\ &\cdot \overline{P}_{I}^{(d_{\alpha})}\left[\eta_{\alpha}^{(d_{\alpha})}(1^{*},2^{*},\ldots,d_{\alpha}^{*}) \\ &\cdot \widetilde{D}_{\alpha}^{(M_{\alpha}-d_{\alpha})}(d_{\alpha}+1,d_{\alpha}+2,\ldots,N_{\alpha};1^{*},2^{*},\ldots,d_{\alpha}^{*},(N_{\alpha}+1)^{*},(N_{\alpha}+2)^{*},\ldots,(N_{\alpha}+d_{\beta})^{*})\right] \\ &\cdot \overline{P}_{I}^{(d_{\beta})}\left[\eta_{\beta}^{(d_{\alpha})}((N_{\alpha}+1)^{*},(N_{\alpha}+2)^{*},\ldots,(N_{\alpha}+d_{\beta})^{*}) \\ &\cdot \widetilde{D}_{\beta}^{(N_{\beta}-d_{\beta})}(N_{\alpha}+d_{\beta}+1,N_{\alpha}+d_{\beta}+2,\ldots,N;1^{*},2^{*},\ldots,d_{\alpha}^{*},(N_{\alpha}+1)^{*},(N_{\alpha}+2)^{*},\ldots,(N_{\alpha}+d_{\beta})^{*})\right] \\ &\cdot \overline{P}_{I}^{(d_{\alpha})}\overline{P}_{J}^{(d_{\beta})}\left[\eta_{\alpha,\beta}^{(d_{\alpha},d_{\beta})}(1^{*},2^{*},\ldots,d_{\alpha}^{*},(N_{\alpha}+1)^{*},(N_{\alpha}+2)^{*},\ldots,(N_{\alpha}+d_{\beta})^{*})\right] \\ &= \sqrt{\frac{(N_{\alpha}-d_{\alpha})!\cdot(N_{\beta}-d_{\beta})!}{N_{\alpha}!N_{\beta}!}\sum_{I=1}^{N_{\alpha}P_{d_{\alpha}}}\sum_{J=1}^{N_{\beta}P_{d_{\beta}}}\left(-1\right)^{\overline{p}_{I}^{(d_{\beta})}}\left(-1\right)^{\overline{p}_{I}^{(d_{\beta})}}\right) \\ &\cdot \eta_{\alpha,\beta}^{(d_{\alpha},d_{\beta})}(t_{1}^{(I,J)^{*}},\ldots,t_{d_{\alpha}}^{(I,J)^{*}})\cdot\eta_{\beta}^{(d_{\beta})}(t_{N_{\alpha}+1}^{(I,J)^{*}},t_{N_{\alpha}+2}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)^{*}}\right) \\ &\cdot \overline{D}_{\alpha}^{(N_{\alpha}-d_{\alpha})}(t_{d_{\alpha}+1}^{(I,J)},t_{d_{\alpha}+2}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+1}^{(I,J)^{*}},t_{N_{\alpha}+1}^{(I,J)^{*}},t_{N_{\alpha}+2}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)}\right) \\ &\cdot \overline{D}_{\alpha}^{(N_{\alpha}-d_{\alpha})}(t_{d_{\alpha}+1}^{(I,J)},t_{d_{\alpha}+1}^{(I,J)^{*}},t_{N_{\alpha}+1}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)}\right) \\ &\cdot \overline{D}_{\alpha}^{(N_{\alpha}-d_{\alpha})}(t_{d_{\alpha}+1}^{(I,J)},t_{d_{\alpha}+2}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+1}^{(I,J)^{*}},t_{N_{\alpha}+1}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}+2}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)^{*}},\ldots,t_{N_{\alpha}+1}^{(I,J)},t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)},t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)},t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)},t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)},t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+d_{\beta}}^{(I,J)},\ldots,t_{N_{\alpha}+1}^{(I,J)},t_{$$

where the index *i* for $\lambda^{(i)}$ was neglected for simplicity. In Eq. (A1), α electrons are assigned to 1, 2, ..., N_{α} and β electrons to $N_{\alpha} + 1$, $N_{\alpha} + 2$, ..., *N*. The α dot electrons are located in the first d_{α} electrons of the α electrons, and the β dot electrons are in the first d_{β} electrons in the β electrons. $\eta_{\alpha}^{(d_{\alpha})}$ and $\eta_{\beta}^{(d_{\beta})}$ correspond to Eq. (26) and $\widetilde{D}_{\alpha}^{(N_{\alpha}-d_{\alpha})}$ and $\widetilde{D}_{\beta}^{(N_{\beta}-d_{\beta})}$ correspond to Eq. (27), each for α or β spin, but they may also include the other spin dot electron indices. The additional $\eta_{\alpha,\beta}^{(d_{\alpha},d_{\beta})}$ consists of the inseparable terms between the α and β dot electrons, given by

$$\eta_{\alpha,\beta}^{(d_{\alpha},d_{\beta})}(1^{*},2^{*},\ldots,d_{\alpha}^{*},(N_{\alpha}+1)^{*},$$

$$(N_{\alpha}+2)^{*},\ldots,(N_{\alpha}+d_{\beta})^{*})$$

$$=\prod_{i=1}^{d_{\alpha}}\prod_{j=N_{\alpha}+1}^{N_{\alpha}+d_{\beta}}f_{ij}(i^{*},j^{*}),$$
(A2)

where some of the $f_{ij}(i^*, j^*)$ (i, j < d) would be constant. The matrix element in $\widetilde{D}_{\alpha}^{(N_{\alpha}-d_{\alpha})}$ and $\widetilde{D}_{\beta}^{(N_{\beta}-d_{\beta})}$ is given by

$$o'_{i}(j; 1^{*}, 2^{*}, \dots, d^{*}_{\alpha}, (N_{\alpha} + 1)^{*}, (N_{\alpha} + 2)^{*}, \dots, (N_{\alpha} + d_{\beta})^{*})$$

= $o_{i}(j) \cdot \prod_{\{k=1, 2, \dots, d_{\alpha}\}} f_{kj}(k^{*}, j) \cdot \prod_{\{k=N_{\alpha}+1, \dots, N_{\alpha}+d_{\beta}\}} f_{kj}(k^{*}, j),$
(A3)

where $j = d_{\alpha} + 1$, $d_{\alpha} + 2$, ..., N_{α} , $N_{\alpha} + d_{\beta} + 1$, $N_{\alpha} + d_{\beta} + 2$, ..., N and some of the $f_{ij}(i^*, j)$ would also be constant.

APPENDIX B: FORMULATION OF THE DETERMINANT UPDATE METHOD

The well-known matrix determinant lemma and the Sherman-Morrison formula³⁹ are given by

$$D' = \left| \mathbf{D}' \right| = \left| \mathbf{D} + \mathbf{u} \mathbf{v}^T \right| = \left[1 + \mathbf{v}^T \mathbf{D}^{-1} \mathbf{u} \right] \left| \mathbf{D} \right|, \qquad (B1)$$

and

$$\mathbf{D}^{\prime-1} = (\mathbf{D} + \mathbf{u}\mathbf{v}^T)^{-1} = \mathbf{D}^{-1} - \frac{(\mathbf{D}^{-1}\mathbf{u})(\mathbf{v}^T\mathbf{D}^{-1})}{1 + \mathbf{v}^T\mathbf{D}^{-1}\mathbf{u}}$$
$$= \mathbf{D}^{-1} - \frac{|\mathbf{D}|}{|\mathbf{D}^{\prime}|}(\mathbf{D}^{-1}\mathbf{u})(\mathbf{v}^T\mathbf{D}^{-1}), \qquad (B2)$$

respectively, where the updated and original determinants are defined as D' and D, and their matrices are defined as D' and **D**, respectively. **u** and **v** are the vectors that determine the updated components in the matrix. As shown in Eq. (B1), the new determinant can be evaluated using the original determinant and inverse matrix. The updated inverse matrix can be obtained using Eq. (B2). If the unit vector **u** is given, in which only the *n*th component is unity and the others are zero, then the updated matrix in which only the *n*th row changes is obtained by **v**. Similarly, if the unit vector **v** is given, in which only the *n*th component is unity and the others are zero, then the updated matrix in which the *n*th column changes is obtained by **u**, i.e.,

$$\mathbf{u} = (0 \ 0 \ \cdots \ 0 \ 1 \ 0 \ \cdots \ 0) ,$$

$$\mathbf{v} = (v_1 \ v_2 \ \cdots \ v_N)^T,$$

$$\Rightarrow \mathbf{u}\mathbf{v}^T = \begin{pmatrix} 0 \ 0 \ \cdots \ 0 \\ 0 \ 0 \ \cdots \ 0 \\ \cdots \ \cdots \ \cdots \\ 0 \ 0 \ \cdots \ 0 \\ v_1 \ v_2 \ \cdots \ v_N \\ 0 \ 0 \ \cdots \ 0 \\ \cdots \ \cdots \\ 0 \ 0 \ \cdots \ 0 \end{pmatrix},$$
(B3)

T

and

$$\mathbf{u} = (u_1 \ u_2 \ \cdots \ u_N)^T,$$
$$\mathbf{v} = (0 \ 0 \ \cdots \ 0 \ 1 \ 0 \ \cdots \ 0)^T,$$

$$\Rightarrow \mathbf{u}\mathbf{v}^{T} = \begin{pmatrix} 0 & 0 & \cdots & 0 & u_{1} & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 & u_{2} & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & u_{N} & 0 & \cdots & 0 \end{pmatrix}.$$
(B4)

Sequentially applying Eqs. (B1)–(B4), the updated determinant and inverse matrix that change multiple lines are obtained.

With the present formulas, the updated determinant and inverse matrix can be evaluated with a lower-order computation than the full $O(M^3)$ (*M* is the matrix dimension). In case only one line needs to be updated, then either **u** or **v** is just a sparse unit vector given in Eq. (B3) or Eq. (B4), and therefore the evaluation of $\mathbf{v}^T \mathbf{D}^{-1} \mathbf{u}$ appearing in Eq. (B1) requires just O(M). However, if another line needs to be changed, then the updated inverse matrix is necessary and it requires $O(M^2)$. This is because, in Eq. (B2), either $\mathbf{D}^{-1}\mathbf{u}$ or $\mathbf{v}^T \mathbf{D}^{-1}$ requires O(M), but the other requires $O(M^2)$ due to the matrix – dense vector (**v** or **u**) product. As a result, the calculation order for the determinant update (a few lines updated) can be generally reduced from $O(M^3)$ to $O(M^2)$.

For convenience, we formulate a recursion formula based on Eqs. (B1) and (B2) to evaluate the updated determinant that is changed by the multiple *n* lines from the initial matrix \mathbf{D}_0 . The determinant we want to evaluate is given by

$$D_n = |\mathbf{D}_n| = \left|\mathbf{D}_0 + \mathbf{u}_1\mathbf{v}_1^T + \mathbf{u}_2\mathbf{v}_2^T + \dots + \mathbf{u}_n\mathbf{v}_n^T\right|, \quad (B5)$$

where \mathbf{D}_n is the matrix of the determinant D_n that changes *n* lines from \mathbf{D}_0 . We also define

$$F(k, i, l) = \mathbf{v}_k^T \mathbf{D}_i^{-1} \mathbf{u}_l, \qquad (B6)$$

where k, l = 1, 2, ..., n. Applying Eqs. (B1) and (B2), the following sequence can be obtained:

$$F(k, i, l) = F(k, i - 1, l) - \frac{D_{i-1}}{D_i}$$

 $\cdot F(k, i - 1, i) \cdot F(i, i - 1, l).$ (B7)

With this *F*, one can easily obtain the recursion formula:

$$D_n = [1 + F(n, n - 1, n)] D_{n-1}.$$
 (B8)

APPENDIX C: EVALUATION OF $H\phi$ WITH THE ALGORITHM APPLYING THE HAMILTONIAN AFTER THE ANTISYMMETRIZATION

Since the evaluation of the potential part is trivial, we only need to formulate the kinetic part, i.e., the ∇_{κ}^2 operation. In the kinetic operator, ∇_{κ}^2 is symmetrically summed over electron κ , so that we may reorder the electron numbering as

$$\sum_{\kappa} \nabla_{t_{\kappa}^{(I)}}^2 = \sum_{\kappa} \nabla_{\kappa}^2.$$
(C1)

In the Nm- and Nk-algorithms of Eqs. (17) and (25), respectively, we can therefore apply $\nabla_{l_k^{(I)}}^2$ to each term in the loop after \overline{P}_I is applied. Herein we omit the index *I* to simplify the expression. Fortunately, $\nabla_{l_k}^2$ does not increase the complexity of the correlation diagram, since it is a one-electron operator.

In the Nk-algorithm, the local energy form of each term in the summation loop of Eq. (25) is given by

$$\frac{\nabla_{t_{\kappa}}^{2}[\eta^{(d)} \cdot \widetilde{D}^{(N-d)}]}{\eta^{(d)} \cdot \widetilde{D}^{(N-d)}} = \frac{\nabla_{t_{\kappa}}^{2}\eta^{(d)}(t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})}{\eta^{(d)}(t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})} + \frac{\nabla_{t_{\kappa}}^{2}\widetilde{D}^{(N-d)}(t_{d+1}, t_{d+2}, \dots, t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})}{\widetilde{D}^{(N-d)}(t_{d+1}, t_{d+2}, \dots, t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})} \\
+ 2\frac{\left[\nabla_{t_{\kappa}}\eta^{(d)}(t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})\right] \cdot \left[\nabla_{t_{\kappa}}\widetilde{D}^{(N-d)}(t_{d+1}, t_{d+2}, \dots, t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})\right]}{\eta^{(d)}(t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) \cdot \widetilde{D}^{(N-d)}(t_{d+1}, t_{d+2}, \dots, t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})}.$$
(C2)

In the case when t_{κ} is not a dot electron (i.e., $t_{\kappa} \in \{t_{d+1}, t_{d+2}, \dots, t_N\}$), only the second term remains in Eq. (C2), $\nabla_{t_{\kappa}}^2 \widetilde{D}^{(N-d)} / \widetilde{D}^{(N-d)}$, because $\eta^{(d)}$ does not include the electron t_{κ} . It is represented by

$$\frac{\nabla_{t_{\kappa}}^{2}\widetilde{D}^{(N-d)}}{\widetilde{D}^{(N-d)}} = \frac{1}{\widetilde{D}^{(N-d)}} \frac{1}{\sqrt{(N-d)!}} \begin{vmatrix} o_{d+1}'(t_{d+1}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & o_{d+1}'(t_{d+2}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & \cdots & \nabla_{t_{\kappa}}^{2} o_{d+1}'(t_{\kappa}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & \cdots & o_{d+1}'(t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) \\ o_{d+2}'(t_{d+1}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & o_{d+2}'(t_{d+2}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & \cdots & \nabla_{t_{\kappa}}^{2} o_{d+2}'(t_{\kappa}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & \cdots & o_{d+2}'(t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) \\ & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ o_{N}'(t_{d+1}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & o_{N}'(t_{d+2}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & \cdots & \nabla_{t_{\kappa}}^{2} o_{N}'(t_{\kappa}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) & \cdots & o_{N}'(t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*}) \\ \end{pmatrix}$$

$$(C3)$$

where it can be noticed that $\nabla_{t_{\kappa}}^2$ changes only the single column from the original matrix. The determinant update method can be used again here to evaluate the right hand side of Eq. (C3). Therefore, the calculation requires just an additional O(N). In Eq. (C3), the local energy form of $\nabla_{t_{\kappa}}^2 o'_i(t_{\kappa}; t_1^*, t_2^*, \dots, t_d^*)$ $(i = d + 1, d + 2, \dots, N)$ is evaluated by

$$\frac{\nabla_{t_{\kappa}}^{2}[o_{i}'(t_{\kappa};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*})]}{o_{i}'(t_{\kappa};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*})} = \frac{\nabla_{t_{\kappa}}^{2}o_{i}(t_{\kappa})}{o_{i}(t_{\kappa})} + \sum_{j=1}^{d} \frac{\nabla_{t_{\kappa}}^{2}f_{j\kappa}(t_{j}^{*},t_{\kappa})}{f_{j\kappa}(t_{j}^{*},t_{\kappa})} + 2\sum_{j=1}^{d} \frac{\nabla_{t_{\kappa}}o_{i}(t_{\kappa}) \cdot \nabla_{t_{\kappa}}f_{j\kappa}(t_{j}^{*},t_{\kappa})}{o_{i}(t_{\kappa})f_{j\kappa}(t_{j}^{*},t_{\kappa})} + 2\sum_{j$$

where the (i, j) pairs for the constant f_{ij} are neglected in the loop.

In the case when t_{κ} is a dot electron, i.e., $t_{\kappa} \in \{t_1, t_2, \dots, t_d\}$, then the electron t_{κ} is included in both $\eta^{(d)}$ and $\widetilde{D}^{(N-d)}$, and all three terms in Eq. (C2) are retained. The first term of Eq. (C2) is the differentiation of $\eta^{(d)}(t_1^*, t_2^*, \dots, t_d^*)$, which involves one-electron and some correlated two-electron functions of dot electrons. Therefore, this term is expressed by

$$\frac{\nabla_{t_{\kappa}}^{2}[\eta^{(d)}(t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})]}{\eta^{(d)}(t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})} = \sum_{i=1}^{d} \frac{\nabla_{t_{\kappa}}^{2} f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*})}{f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*})} + \sum_{i=1}^{d} \frac{\nabla_{t_{\kappa}}^{2} o_{i}(t_{\kappa}^{*})}{o_{i}(t_{\kappa}^{*})} + 2\sum_{i=1}^{d} \frac{\nabla_{t_{\kappa}} f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) \cdot \nabla_{t_{\kappa}} o_{i}(t_{\kappa}^{*})}{f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) o_{i}(t_{\kappa}^{*})} + 2\sum_{i=1}^{d} \frac{\nabla_{t_{\kappa}} f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) \cdot \nabla_{t_{\kappa}} o_{i}(t_{\kappa}^{*})}{f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) o_{i}(t_{\kappa}^{*})} + 2\sum_{i=1}^{d} \frac{\nabla_{t_{\kappa}} f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) \cdot \nabla_{t_{\kappa}} f_{j\kappa}(t_{j}^{*}, t_{\kappa}^{*})}{f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) o_{i}(t_{\kappa}^{*})} + 2\sum_{i=1}^{d} \frac{\nabla_{t_{\kappa}} f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) \cdot \nabla_{t_{\kappa}} f_{j\kappa}(t_{j}^{*}, t_{\kappa}^{*})}{f_{i\kappa}(t_{i}^{*}, t_{\kappa}^{*}) f_{j\kappa}(t_{j}^{*}, t_{\kappa}^{*})}.$$
(C5)

The second term of Eq. (C2) appears to be similar to Eq. (C3), but $\nabla_{t_{\kappa}}^2$ is applied to the dot electron in the determinant and therefore $\nabla_{t_{\kappa}}^2 \widetilde{D}^{(N-d)}$ changes some rows (not columns) that include t_{κ} . It is given by

$$\begin{split} & \nabla_{t_{k}}^{2}[\widetilde{D}^{(N-d)}(t_{d+1},t_{d+2},\ldots,t_{N};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*})] \\ & \widetilde{D}^{(N-d)}(t_{d+1},t_{d+2},\ldots,t_{N};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) \\ & = \frac{1}{\widetilde{D}^{(N-d)}} \frac{1}{\sqrt{(N-d)!}} \sum_{i=1}^{N-d} \begin{vmatrix} o_{d+1}'(t_{d+1};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) & o_{d+1}'(t_{d+2};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) & \cdots & o_{d+1}'(t_{N};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) \\ & o_{d+2}'(t_{d+1};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) & o_{d+2}'(t_{d+2};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) & \cdots & o_{d+2}'(t_{N};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) \\ & \ddots & \ddots & \ddots & \ddots \\ & \nabla_{t_{k}}^{2} o_{d+i}'(t_{d+1};t_{1}^{*},t_{2}^{*},\ldots,t_{k}^{*},\ldots,t_{d}^{*}) & \nabla_{t_{k}}^{2} o_{d+i}'(t_{d+2};t_{1}^{*},t_{2}^{*},\ldots,t_{k}^{*},\ldots,t_{d}^{*}) & \cdots & \nabla_{t_{k}}^{2} o_{d+i}'(t_{N};t_{1}^{*},t_{2}^{*},\ldots,t_{k}^{*},\ldots,t_{d}^{*}) \\ & \ddots & \ddots & \ddots & \ddots \\ & o_{N}'(t_{d+1};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) & o_{N}'(t_{d+2};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) & \cdots & o_{N}'(t_{N};t_{1}^{*},t_{2}^{*},\ldots,t_{d}^{*}) \\ \end{matrix}$$

$$+\frac{1}{\widetilde{D}^{(N-d)}}\frac{2}{\sqrt{(N-d)!}}\sum_{i$$

where each term for *i* and *j* runs over the case where o'_{d+i} (or o'_{d+j}) includes the electron t_{κ}^* in $o'_{d+i}(t_{d+1}; t_1^*, t_2^*, \dots, t_{\kappa}^*, \dots, t_d^*)$. Each term in Eq. (C6) can also be evaluated by the determinant update method, since only one or two lines are changed from the original determinant. By the additional theorem of the matrix determinant lemma of Eqs. (B5)–(B8) in Appendix B, the calculation can also be performed with the additional O(N). The differentiations of o'_{d+i} in Eq. (C6) (its local energy form) are evaluated by

$$\frac{\nabla_{t_{\kappa}}^{2}[o_{d+i}'(t_{l};t_{1}^{*},t_{2}^{*},\ldots,t_{\kappa}^{*},\ldots,t_{d}^{*})]}{o_{d+i}'(t_{l};t_{1}^{*},t_{2}^{*},\ldots,t_{\kappa}^{*},\ldots,t_{d}^{*})} = \frac{\nabla_{t_{\kappa}}^{2}f_{\kappa,l}(t_{\kappa}^{*},t_{l})}{f_{\kappa,l}(t_{\kappa}^{*},t_{l})}$$
(C7)

and

$$\frac{\nabla_{t_{\kappa}}[o'_{d+i}(t_{l}; t_{1}^{*}, t_{2}^{*}, \dots, t_{\kappa}^{*}, \dots, t_{d}^{*})]}{o'_{d+i}(t_{l}; t_{1}^{*}, t_{2}^{*}, \dots, t_{\kappa}^{*}, \dots, t_{d}^{*})} = \frac{\nabla_{t_{\kappa}} f_{\kappa,l}(t_{\kappa}^{*}, t_{l})}{f_{\kappa,l}(t_{\kappa}^{*}, t_{l})}$$
(C8)

for Laplacian and nabla (first derivative), respectively, where i, l = d + 1, d + 2, ..., N - d. For the third term of Eq. (C2), we only have to evaluate the next two vectors of the first derivatives:

$$\frac{\nabla_{t_{\kappa}}[\eta^{(d)}(t_1^*, t_2^*, \dots, t_d^*)]}{\eta^{(d)}(t_1^*, t_2^*, \dots, t_d^*)} = \sum_{i=1}^d \frac{\nabla_{t_{\kappa}} f_{i,\kappa}(t_i^*, t_{\kappa}^*)}{f_{i,\kappa}(t_i^*, t_{\kappa}^*)} + \sum_{i=1}^d \frac{\nabla_{t_{\kappa}} o_i(t_{\kappa}^*)}{o_i(t_{\kappa}^*)}$$
(C9)

and

$$= \frac{1}{D^{(N-d)}(t_{d+1}, t_{d+2}, \dots, t_N; t_1^*, t_2^*, \dots, t_d^*)} \begin{bmatrix} o'_{d+1}(t_{d+1}; t_1^*, t_2^*, \dots, t_d^*) & o'_{d+1}(t_{d+2}; t_1^*, t_2^*, \dots, t_d^*) & \cdots & o'_{d+1}(t_N; t_1^*, t_2^*, \dots, t_d^*) \\ o'_{d+2}(t_{d+1}; t_1^*, t_2^*, \dots, t_d^*) & o'_{d+2}(t_{d+2}; t_1^*, t_2^*, \dots, t_d^*) & \cdots & o'_{d+2}(t_N; t_1^*, t_2^*, \dots, t_d^*) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \nabla_{t_k} [o'_{d+i}(t_{d+1}; t_1^*, t_2^*, \dots, t_k^*, \dots, t_d^*)] \nabla_{t_k} [o'_{d+i}(t_{d+2}; t_1^*, t_2^*, \dots, t_k^*, \dots, t_d^*)] \cdots \nabla_{t_k} [o'_{d+i}(t_N; t_1^*, t_2^*, \dots, t_k^*, \dots, t_d^*)] \\ \cdots & \cdots & \cdots & \cdots \\ o'_N(t_{d+1}; t_1^*, t_2^*, \dots, t_d^*) & o'_N(t_{d+2}; t_1^*, t_2^*, \dots, t_d^*) & \cdots & o'_N(t_N; t_1^*, t_2^*, \dots, t_d^*) \end{bmatrix}$$

$$(C10)$$

which are evaluated similarly to the Laplacian cases of Eqs. (C5) and (C6), respectively. With these first derivatives, the third term is evaluated by the inner products for the x, y, and z coordinates.

In all cases of Eq. (C2), if N is sufficiently larger than d, then the determinant update method is applicable and efficient, with each term requiring only O(N).

 $\nabla_{t_{e}}[\widetilde{D}^{(N-d)}(t_{d+1}, t_{d+2}, \dots, t_{N}; t_{1}^{*}, t_{2}^{*}, \dots, t_{d}^{*})]$

Finally, we note the case when $\exp(J)$ exists in Eq. (C2), where J is a totally symmetric operator with respect to the electron permutations. In this case, Eq. (C2) becomes

$$= \frac{\nabla_{t_{\kappa}}^{2} \eta^{(d)}}{\eta^{(d)}} + \frac{\nabla_{t_{\kappa}}^{2} \widetilde{D}^{(N-d)}}{\widetilde{D}^{(N-d)}} + 2 \frac{\nabla_{t_{\kappa}} \eta^{(d)} \cdot \nabla_{t_{\kappa}} \widetilde{D}^{(N-d)}}{\eta^{(d)} \widetilde{D}^{(N-d)}} + \frac{\nabla_{t_{\kappa}}^{2} e^{J}}{e^{J}} + 2 \frac{\nabla_{t_{\kappa}} e^{J} \cdot \nabla_{t_{\kappa}} \widetilde{D}^{(N-d)}}{e^{J} \widetilde{D}^{(N-d)}} + 2 \frac{\nabla_{t_{\kappa}} e^{J} \cdot \nabla_{t_{\kappa}} \eta^{(d)}}{e^{J} \eta^{(d)}},$$
(C11)

where the first three terms are the same as those in Eq. (C2). The latter three terms are also easily handled after performing the analytic differentiations of $\exp(J)$.

 $\frac{\nabla_{t_{\kappa}}^2 [e^J \cdot \eta^{(d)} \cdot \widetilde{D}^{(N-d)}]}{e^J \cdot \eta^{(d)} \cdot \widetilde{D}^{(N-d)}}$

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