Computational method of many-electron integrals over explicitly correlated Cartesian Gaussian functions

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Derivation of recurrence formulas for general many-electron overlap, nuclear attraction, and electron repulsion integrals over explicitly correlated Cartesian Gaussian functions is presented. The recurrence formulas are derived in a similar way as the derivation of molecular two-electron integrals over Cartesian Gaussian functions by Obara and Saika. As a result, the formulas expressing the many-electron integrals of higher angular momentum as a linear combination of those of lower angular momentum are obtained. An algorithm for computation of the general many-electron integrals by means of the recurrence formulas is also shown. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1332990]

I. INTRODUCTION

To compute accurate atomic and molecular wave functions, one must take electron correlation effects into account. The configuration interaction (CI) method[1] is used extensively for this purpose. The CI wave function is a linear combination of antisymmetrized products of one-electron functions, and its coefficients are determined by the Ritz variational method. The CI method is conceptually very simple, and is mathematically exact if a complete set of one-electron functions is used. However, in actual computations, the CI wave function must be confined to expansion by finite one-electron functions. This restriction causes the slow convergence of the CI wave functions and total energies. The main source of the slow convergence is that the description of probability amplitude at small interelectronic distance by one-electron functions is difficult. One must use functions explicitly including interelectronic distances to obtain compact and energetically accurate wave functions.

In 1928, Hylleraas obtained a very accurate ground state energy of the He atom by a wave function explicitly including powers of the interelectronic distance r_{12} and showed that the interelectronic distance enables extremely compact and energetically accurate wave functions to be obtained.[2] This method, referred to as Hylleraas-type method, has been extended to two-electron molecules by James and Coolidge,[3] Kołos and Wolniewicz,[4] and Clementi *et al.*[5] For application to larger systems, there have been calculations of Li and Be atoms by Kleindienst and Lüchow[6] and Sims and Hagstrom,[7] respectively. However, application of the Hylleraas-type method to many-electron systems is very difficult due to the appearance of many-electron integrals, the calculation of which being very laborious. For example, the formulas of three- and four-electron integrals for molecular systems obtained by Clementi *et al.*[5] include multidimensional numerical integrations.

Another function explicitly including the interelectronic distances is the ''explicitly correlated Gaussian function''

(ECGF), which was independently introduced by Boys[8] and Singer.[9] ECGF is defined as a product of Gaussian functions and Gaussian-type correlation factors. In particular, ECGF with Cartesian angular factors are called ''explicitly correlated Cartesian Gaussian function'' (ECCGF). As a variant of ECCGFs, there is the Gaussian-type geminal (GTG), which is ECCGF with only one Gaussian-type correlation factor, $\exp(-\beta r_{12}^2)$. The advantage of ECGFs is that the many-electron integrals needed in calculations of atomic and molecular wave functions can be expressed in compact forms involving the incomplete Gamma function. There have been many applications of ECGFs because of this advantage. Early applications are calculations of two-electron systems by Lester and Krauss[10] and Longstaff and Singer.[11] Subsequent applications of ECGFs have been made by Pan and King,[12] Salmon and Poshusta,[13] Adamowicz and Sadlej,[14] Szalewicz *et al.*,[15–17] Kozlowski and Adamowicz,[18] and Cencek and Rychlewski.[19] In particular, weak orthogonal (WO) pair correlation techniques for the use of GTGs developed by Szalewicz *et al.*[15] are suitable for application to many-electron systems, and have been applied to ten-electron systems.[16,17] Since computational methods using ECGFs are suitable for application to many-electron systems, further development of those is hoped.

There have been several formulas of the many-electron integrals over ECGFs needed in atomic and molecular computations. Boys,[8] Singer,[9] Kozlowski and Adamowicz,[18] and Cencek and Rychlewski[19] have obtained formulas of the many-electron integrals over ECGFs with zero angular momenta. These formulas can only be applied to restricted systems. Formulas of the many-electron integrals over ECCGFs with higher angular momenta have been obtained by three groups. Lester and Krauss[10] and Persson and Taylor[20] have obtained formulas of up to three- and four-electron integrals over GTGs, respectively. Persson and Taylor have derived the formulas in a similar manner to McMurchie and Davidson.[21] The general many-electron integrals over EC-

CGFs for an arbitrary number of electrons have been obtained by Kozlowski and Adamowicz by using the raising operators that transform spherical ECGFs into ECCGFs.[22] Their formulas are very complicated, and evaluation of them would be laborious.

In the present paper, we derive recurrence formulas of the general many-electron integrals over ECCGFs for an arbitrary number of electrons, and establish an efficient recursive computational method of them. These recurrence formulas have recursive forms with respect to the angular momenta of ECCGFs in the integrals. For derivation of the recurrence formulas, we employ the method of Obara and Saika[23,24] and Honda et al.,[25] i.e., the derivation method of efficient recurrence formulas for molecular two-electron integrals over Cartesian Gaussian functions.

In the next section, the characteristics of ECCGF are presented, and recurrence formulas for many-electron overlap, nuclear attraction, and electron repulsion integrals over ECCGFs are derived by the aid of the characteristics of ECCGF. Then, Sec. III discusses our recurrence formulas for the many-electron integrals over ECCGFs and outlines an algorithm for the recursive computation of the many-electron integrals by means of them.

II. RECURRENCE FORMULAS FOR MANY-ELECTRON INTEGRALS OVER EXPLICITLY CORRELATED CARTESIAN GAUSSIAN FUNCTIONS

A. Explicitly correlated Cartesian Gaussian function

An N-electron explicitly correlated Cartesian Gaussian function (ECCGF) $G_N(\{\mathbf{l}\})$ is denoted as a product of the Cartesian Gaussian functions with centers $\{\mathbf{R}_k\}$ and Gaussian-type correlation factors as follows:

$$G_N(\{\mathbf{l}\}) = \prod_{k=1}^{N} \prod_{\mu=x,y,z} (\mathbf{r}_k - \mathbf{R}_k)_\mu^{l_{k\mu}} \exp(-\alpha_k |\mathbf{r}_k - \mathbf{R}_k|^2)$$

$$\times \exp\left(-\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \beta_{ij} |\mathbf{r}_i - \mathbf{r}_j|^2\right), \quad (1)$$

where the correlation exponents $\{\beta_{ij}\}$ satisfy

$$\beta_{ij} = \begin{cases} \beta_{ji} & (i \neq j) \\ 0, & (i = j) \end{cases}, \quad (2)$$

$\{\mathbf{l}\} \equiv (\mathbf{l}_1, \ldots, \mathbf{l}_N)$, and $\mathbf{l}_k$ is a set of three nonnegative integers l_{kx}, l_{ky}, and l_{kz},

$$\mathbf{l}_k = (l_{kx}, l_{ky}, l_{kz}). \quad (3)$$

$\mathbf{l}_k$ is closely related to the angular momentum quantum number, and $|\mathbf{l}_k| = l_{kx} + l_{ky} + l_{kz}$ is equal to the angular momentum quantum number of the k-th electron. Hereafter, we refer to ECCGF with $\Sigma_{k=1}^{N} |\mathbf{l}_k| = 0$ and 1 as s- and p-type ECCGF, respectively.

ECCGFs satisfy the differential relation

$$\frac{\partial}{\partial r_{k\mu}} G_N(\{\mathbf{l}\}) = -2\alpha_k G_N(\mathbf{l}_1, \ldots, \mathbf{l}_k + \mathbf{1}_\mu, \ldots, \mathbf{l}_N)$$

$$+ l_{k\mu} G_N(\mathbf{l}_1, \ldots, \mathbf{l}_k - \mathbf{1}_\mu, \ldots, \mathbf{l}_N)$$

$$- 2\sum_{i=1}^{N} \beta_{ki}(\mathbf{r}_k - \mathbf{r}_i)_\mu G_N(\{\mathbf{l}\}), \quad (4)$$

where $r_{k\mu}$ is the μ component of $\mathbf{r}_k$, and $\mathbf{1}_\mu$ is defined by

$$\mathbf{1}_\mu = (\delta_{\mu,x}, \delta_{\mu,y}, \delta_{\mu,z}) \quad (5)$$

with Kronecker's deltas. Using the decomposition relation

$$(\mathbf{r}_k - \mathbf{r}_i)_\mu = (\mathbf{r}_k - \mathbf{R}_k)_\mu - (\mathbf{r}_i - \mathbf{R}_i)_\mu + (\mathbf{R}_k - \mathbf{R}_i)_\mu, \quad (6)$$

Eq. (4) can be rewritten as

$$\frac{\partial}{\partial r_{k\mu}} G_N(\{\mathbf{l}\})$$

$$= -2\left(\alpha_k + \sum_{i=1}^{N} \beta_{ki}\right) G_N(\mathbf{l}_1, \ldots, \mathbf{l}_k + \mathbf{1}_\mu, \ldots, \mathbf{l}_N)$$

$$+ 2\sum_{i=1}^{N} \beta_{ik} G_N(\mathbf{l}_1, \ldots, \mathbf{l}_i + \mathbf{1}_\mu, \ldots, \mathbf{l}_N) + l_{k\mu} G_N(\mathbf{l}_1, \ldots,$$

$$\mathbf{l}_k - \mathbf{1}_\mu, \ldots, \mathbf{l}_N) - 2\sum_{i=1}^{N} \beta_{ik}(\mathbf{R}_k - \mathbf{R}_i)_\mu G_N(\{\mathbf{l}\}). \quad (7)$$

As $|r_{k\mu}|$ goes to infinity, the exponential factor of ECCGF decreases to zero much faster than the increase of the angular factor $\Pi_{k=1}^{N} \Pi_{\mu=x,y,z} (\mathbf{r}_k - \mathbf{R}_k)_\mu^{l_{k\mu}}$. Then we have

$$G_N(\{\mathbf{l}\}) \rightarrow 0 \quad \left(|r_{k\mu}| \rightarrow \infty, \alpha_k + \sum_{i=1}^{N} \beta_{ik} > 0\right). \quad (8)$$

Relation (8) leads to

$$\int_{-\infty}^{\infty} dr_{k\mu} \frac{\partial}{\partial r_{k\mu}} G_N(\{\mathbf{l}\}) = 0. \quad (9)$$

This relation plays an important role in the derivation of the recurrence formulas of the manyelectron integrals over ECCGFs.

B. Derivation of recurrence formulas

When one computes the matrix elements of the nonrelativistic Hamiltonian of N-electron systems by ECCGFs the N-electron overlap integral (S_N), nuclear attraction integral (U_N), electron repulsion integral (E_N), and kinetic integral (K_N) are required:

$$S_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N G_N(\{\mathbf{l}\}) G'_N(\{\mathbf{l}'\}), \quad (10)$$

$$U_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N$$

$$\times G_N(\{\mathbf{l}\}) |\mathbf{r}_p - \mathbf{V}|^{-1} G'_N(\{\mathbf{l}'\}), \quad (11)$$

$$E_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N$$

$$\times G_N(\{\mathbf{l}\}) |\mathbf{r}_p - \mathbf{r}_q|^{-1} G'_N(\{\mathbf{l}'\}), \quad (12)$$

and

$$K_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N$$
$$\times G_N(\{\mathbf{l}\})(-\tfrac{1}{2}\nabla_p^2)G_N'(\{\mathbf{l}'\}), \qquad (13)$$

where $p \neq q$, $\mathbf{V}$ is any nuclear center, $G_N'(\{\mathbf{l}'\})$ is an ECCGF having $\{\alpha_k'\}$, $\{\beta_{ij}'\}$, $\{\mathbf{R}_k'\}$, and $\{\mathbf{l}'\}$. For the sake of simplicity, hereafter we abbreviate $S_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, $U_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, $E_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, and $K_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$ as S_N, U_N, E_N, and K_N,

respectively. When some of the angular momentum indices are different from those in $S_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, $U_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, $E_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, and $K_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, only the distinct indices will be given, and thus $S_N(\mathbf{l}_1,\dots,\mathbf{l}_k+\mathbf{1}_\mu,\dots,\mathbf{l}_N|\{\mathbf{l}'\})$, for instance, will be designated as $S_N(\mathbf{l}_k+\mathbf{1}_\mu|)$. The kinetic integral can be reduced a linear combination of the overlap integrals as follows:

$$K_N = \sum_{\mu=x,y,z} K_{N\mu}, \qquad (14)$$

$$K_{N\mu} = 2\sum_{i=1}^{N} C_{pi} \sum_{j=1}^{N} C_{pj}' S_N(\mathbf{l}_i+\mathbf{1}_\mu|\mathbf{l}_j'+\mathbf{1}_\mu) + 2D_{p\mu}' \sum_{i=1}^{N} C_{pi} S_N(\mathbf{l}_i+\mathbf{1}_\mu|) + 2D_{p\mu} \sum_{i=1}^{N} C_{pi}' S_N(|\mathbf{l}_i'+\mathbf{1}_\mu)$$

$$-l_{p\mu}D_{p\mu}' S_N(\mathbf{l}_p-\mathbf{1}_\mu|) - l_{p\mu}' D_{p\mu} S_N(|\mathbf{l}_p'-\mathbf{1}_\mu) + 2D_{p\mu}D_{p\mu}' S_N$$

$$-l_{p\mu}' \sum_{i=1}^{N} C_{pi} S_N(\mathbf{l}_i+\mathbf{1}_\mu|\mathbf{l}_p'-\mathbf{1}_\mu) - l_{p\mu} \sum_{i=1}^{N} C_{pi}' S_N(\mathbf{l}_p-\mathbf{1}_\mu|\mathbf{l}_i'+\mathbf{1}_\mu) + \tfrac{1}{2}l_{p\mu}l_{p\mu}' S_N(\mathbf{l}_p-\mathbf{1}_\mu|\mathbf{l}_p'-\mathbf{1}_\mu), \qquad (15)$$

where

$$C_{pi} = \left(\alpha_p + \sum_{j=1}^{N} \beta_{pj}\right)\delta_{p,i} - \beta_{pi}, \qquad (16)$$

$$C_{pi}' = \left(\alpha_p' + \sum_{j=1}^{N} \beta_{pj}'\right)\delta_{p,i} - \beta_{pi}', \qquad (17)$$

$$D_{p\mu} = \sum_{i=1}^{N} \beta_{pi}(\mathbf{R}_p - \mathbf{R}_i)_\mu, \qquad (18)$$

and

$$D_{p\mu}' = \sum_{i=1}^{N} \beta_{pi}'(\mathbf{R}_p' - \mathbf{R}_i')_\mu. \qquad (19)$$

We derive recurrence formulas for the integrals Eqs. (10), (11), and (12). Although the recurrence formula for the kinetic integral can be derived (see the Appendix), it is more effective to compute the kinetic integral as the linear combination of the overlap integrals. To accomplish our aim, we define a common integrand I_N and reduction operators for S_N, U_N, and E_N. The common integrand is defined as

$$I_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \exp[i\mathbf{k}_p(\mathbf{r}_p - \mathbf{V}) + i\mathbf{k}_{pq}(\mathbf{r}_p - \mathbf{r}_q)]$$
$$\times G_N(\{\mathbf{l}\})G_N'(\{\mathbf{l}'\}). \qquad (20)$$

Equation (20) includes two Fourier kernels $\exp[i\mathbf{k}_p(\mathbf{r}_p - \mathbf{V})]$ and $\exp[i\mathbf{k}_{pq}(\mathbf{r}_p - \mathbf{r}_q)]$ of the Fourier transformation of the Coulomb interactions

$$|\mathbf{r}_p - \mathbf{V}|^{-1} = (2\pi^2)^{-1}\int d\mathbf{k}_p \mathbf{k}_p^{-2} \exp[i\mathbf{k}_p(\mathbf{r}_p - \mathbf{V})] \qquad (21)$$

and

$$|\mathbf{r}_p - \mathbf{r}_q|^{-1} = (2\pi^2)^{-1}\int d\mathbf{k}_{pq}\mathbf{k}_{pq}^{-2} \exp[i\mathbf{k}_{pq}(\mathbf{r}_p - \mathbf{r}_q)], \qquad (22)$$

respectively, where $i = \sqrt{-1}$, $\mathbf{k}_p = (k_{px}, k_{py}, k_{pz})$, and $\mathbf{k}_{pq} = (k_{pqx}, k_{pqy}, k_{pqz})$. The reduction operators for S_N, U_N, and E_N are defined as

$$\mathcal{R}_S \equiv \lim_{\mathbf{k}_p \to \mathbf{0}} \lim_{\mathbf{k}_{pq} \to \mathbf{0}}, \qquad (23)$$

$$\mathcal{R}_U(\mathbf{n}) \equiv (2\pi^2)^{-1}\int d\mathbf{k}_p \mathbf{k}_p^{-2} \prod_{\mu=x,y,z}(ik_{p\mu})^{n_\mu} \lim_{\mathbf{k}_{pq}\to\mathbf{0}} \qquad (24)$$

and

$$\mathcal{R}_E(\mathbf{n}) \equiv (2\pi^2)^{-1}\int d\mathbf{k}_{pq}\mathbf{k}_{pq}^{-2} \prod_{\mu=x,y,z}(ik_{pq\mu})^{n_\mu} \lim_{\mathbf{k}_p\to\mathbf{0}}, \qquad (25)$$

respectively, where $\mathbf{0} = (0,0,0)$, $\mathbf{n}$ denotes a set of nonnegative integers n_x, n_y, and n_z,

$$\mathbf{n} = (n_x, n_y, n_z), \qquad (26)$$

and we refer to $\mathbf{n}$ as the auxiliary index. Using the integrand Eq. (20) and the reduction operators Eqs. (23), (24), and (25), the integrals Eqs. (10), (11), and (12) can be written as

$$S_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \mathcal{R}_S[\{\mathbf{l}\}|\{\mathbf{l}'\}]_N, \qquad (27)$$

$$U_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \mathcal{R}_U(\mathbf{0})[\{\mathbf{l}\}|\{\mathbf{l}'\}]_N, \qquad (28)$$

and

$$E_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \mathcal{R}_E(\mathbf{0})[\{\mathbf{l}\}|\{\mathbf{l}'\}]_N, \qquad (29)$$

with

$$[\{\mathbf{l}\}|\{\mathbf{l}'\}]_N \equiv \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N I_N(\{\mathbf{l}\}|\{\mathbf{l}'\}). \tag{30}$$

We refer to $[\{\mathbf{l}\}|\{\mathbf{l}'\}]_N$ as the N-electron basic integral. It is notice that the target integrals Eqs. (28) and (29) have $\mathbf{n}=\mathbf{0}$.

First, we differentiate the integrand Eq. (20) with respect to $r_{k\mu}$ ($k=1,\dots,N$ and $\mu=x,y,z$). Using Eq. (7), we obtain

$$\frac{\partial I_N}{\partial r_{k\mu}} = -2\left(\alpha_k + \sum_{i=1}^{N} \beta_{ki}\right) I_N(\mathbf{l}_k+\mathbf{1}_\mu|)$$

$$-2\left(\alpha_k' + \sum_{i=1}^{N} \beta_{ki}'\right) I_N(|\mathbf{l}_k'+\mathbf{1}_\mu) + l_{k\mu} I_N(\mathbf{l}_k-\mathbf{1}_\mu|)$$

$$+ l_{k\mu}' I_N(|\mathbf{l}_k'-\mathbf{1}_\mu) - 2\sum_{i=1}^{N} \{\beta_{ki}(\mathbf{R}_k-\mathbf{R}_i)_\mu + \beta_{ki}'$$

$$\times (\mathbf{R}_k'-\mathbf{R}_i')_\mu\} I_N + \{ik_{k\mu}\delta_{p,k} + ik_{pq\mu}(\delta_{p,k}-\delta_{q,k})\} I_N. \tag{31}$$

$I_N(|\mathbf{l}_k'+\mathbf{1}_\mu)$ can be transformed into

$$I_N(|\mathbf{l}_k'+\mathbf{1}_\mu) = (\mathbf{r}_k-\mathbf{R}_k')_\mu I_N$$

$$= \{(\mathbf{r}_k-\mathbf{R}_k)_\mu + (\mathbf{R}_k-\mathbf{R}_k')_\mu\} I_N$$

$$= I_N(\mathbf{l}_k+\mathbf{1}_\mu|) + (\mathbf{R}_k-\mathbf{R}_k')_\mu I_N. \tag{32}$$

Substituting Eq. (32) into Eq. (31), Eq. (31) becomes

$$\frac{\partial I_N}{\partial r_{k\mu}} = -2\left(A_k + \sum_{i=1}^{N} B_{ki}\right)\{I_N(\mathbf{l}_k+\mathbf{1}_\mu|) + R_{k\mu} I_N\}$$

$$+ 2\sum_{i=1}^{N} B_{ki}\{I_N(\mathbf{l}_i+\mathbf{1}_\mu|) + R_{i\mu} I_N\} + l_{k\mu} I_N(\mathbf{l}_k-\mathbf{1}_\mu|)$$

$$+ l_{k\mu}' I_N(|\mathbf{l}_k'-\mathbf{1}_\mu) + \{2P_{k\mu} + ik_{p\mu}\delta_{p,k}$$

$$+ ik_{pq\mu}(\delta_{p,k}-\delta_{q,k})\} I_N, \tag{33}$$

where $A_i = \alpha_i + \alpha_i'$, $B_{ij} = \beta_{ij} + \beta_{ij}'$, and $P_{k\mu}$ is the μ component of a vector

$$\mathbf{P}_k = \alpha_k \mathbf{R}_k + \alpha_k' \mathbf{R}_k'. \tag{34}$$

Next, we integrate both sides of Eq. (33) over $\mathbf{r}_1,\dots,\mathbf{r}_N$. The left-hand side of Eq. (33) becomes zero due to the relation Eq. (9). Then we can obtain one set of equations for $[\mathbf{l}_k+\mathbf{1}_\mu|]_N$ ($k=1,2,\dots,N$):

$$0 = \left(A_k + \sum_{i=1}^{N} B_{ki}\right)\{[\mathbf{l}_k+\mathbf{1}_\mu|]_N + R_{k\mu}[|]_N\}$$

$$-\sum_{i=1}^{N} B_{ki}\{[\mathbf{l}_i+\mathbf{1}_\mu|]_N + R_{i\mu}[|]_N\} - \tfrac{1}{2}\{l_{k\mu}[\mathbf{l}_k-\mathbf{1}_\mu|]_N$$

$$+ l_{k\mu}'[|\mathbf{l}_k'-\mathbf{1}_\mu]_N - \tfrac{1}{2}\{2P_{k\mu} + ik_{p\mu}\delta_{p,k}$$

$$+ ik_{pq\mu}(\delta_{p,k}-\delta_{q,k})\}[|]_N. \tag{35}$$

In matrix representation, Eq. (35) ($k=1,2,\dots,N$) is written as follows:

$$\begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \mathbf{Z}_N \begin{pmatrix} [\mathbf{l}_1+\mathbf{1}_\mu|]_N + R_{1\mu}[|]_N \\ [\mathbf{l}_2+\mathbf{1}_\mu|]_N + R_{2\mu}[|]_N \\ \vdots \\ [\mathbf{l}_N+\mathbf{1}_\mu|]_N + R_{N\mu}[|]_N \end{pmatrix}$$

$$-\frac{1}{2} \begin{pmatrix} l_{1\mu}[\mathbf{l}_1-\mathbf{1}_\mu|]_N + l_{1\mu}'[|\mathbf{l}_1'-\mathbf{1}_\mu]_N \\ l_{2\mu}[\mathbf{l}_2-\mathbf{1}_\mu|]_N + l_{2\mu}'[|\mathbf{l}_2'-\mathbf{1}_\mu]_N \\ \vdots \\ l_{N\mu}[\mathbf{l}_N-\mathbf{1}_\mu|]_N + l_{N\mu}'[|\mathbf{l}_N'-\mathbf{1}_\mu]_N \end{pmatrix}$$

$$- \begin{pmatrix} P_{1\mu}[|]_N + \tfrac{1}{2}\{ik_{p\mu}\delta_{p,1} + ik_{pq\mu}(\delta_{p,1}-\delta_{q,1})\}[|]_N \\ P_{2\mu}[|]_N + \tfrac{1}{2}\{ik_{p\mu}\delta_{p,2} + ik_{pq\mu}(\delta_{p,2}-\delta_{q,2})\}[|]_N \\ \vdots \\ P_{N\mu}[|]_N + \tfrac{1}{2}\{ik_{p\mu}\delta_{p,N} + ik_{pq\mu}(\delta_{p,N}-\delta_{q,N})\}[|]_N \end{pmatrix}, \tag{36}$$

with

$$\mathbf{Z}_N \equiv \begin{pmatrix} A_1 + \Sigma_{i=1}^{N} B_{1i} & -B_{12} & \cdots & -B_{1N} \\ -B_{12} & A_2 + \Sigma_{i=1}^{N} B_{2i} & \cdots & -B_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ -B_{1N} & -B_{2N} & \cdots & A_N + \Sigma_{i=1}^{N} B_{Ni} \end{pmatrix}. \tag{37}$$

$\mathbf{Z}_N$ is an $N \times N$ nonsingular symmetric matrix which consists of the exponents of $G_N(\{\mathbf{l}\})$ and $G_N'(\{\mathbf{l}'\})$. Hence, the inverse matrix $\mathbf{Z}_N^{-1}$ of $\mathbf{Z}_N$ exists, which is a symmetric matrix. Multiplying both sides of Eq. (36) by $\mathbf{Z}_N^{-1}$ from the left, we obtain the recurrence formulas for $[\mathbf{l}_k+\mathbf{1}_\mu|]_N$:

$$[\mathbf{l}_k+\mathbf{1}_\mu|]_N = \frac{1}{2}\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{kj}\{l_{j\mu}[\mathbf{l}_j-\mathbf{1}_\mu|]_N$$

$$+ l_{j\mu}'[|\mathbf{l}_j'-\mathbf{1}_\mu]_N\} + \left\{\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{kj}P_{j\mu}\right.$$

$$\left. - R_{k\mu}\right\}[|]_N + \frac{1}{2}\{(\mathbf{Z}_N^{-1})_{kp}ik_{p\mu}$$

$$+ ik_{pq\mu}((\mathbf{Z}_N^{-1})_{kp} - (\mathbf{Z}_N^{-1})_{kq})\}[|]_N. \tag{38}$$

Operation of the reduction operators Eqs. (27), (28), and (29) on both sides of Eq. (38) yields the recurrence formulas for S_N, U_N, and E_N, respectively. As a result, the recurrence formulas for S_N, U_N, and E_N can be written as

$$X_N(\mathbf{l}_k+\mathbf{1}_\mu|) = \frac{1}{2}\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{kj}\{l_{j\mu}X_N(\mathbf{l}_j-\mathbf{1}_\mu|)$$

$$+ l_{j\mu}'X_N(|\mathbf{l}_j'-\mathbf{1}_\mu)\}$$

$$+ \left\{\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{kj}P_{j\mu} - R_{k\mu}\right\} X_N + Y_N, \tag{39}$$

where $X_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$ stands for $S_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, $U_N(\{\mathbf{l}\}|\{\mathbf{l}'\}:\mathbf{n})$, and $E_N(\{\mathbf{l}\}|\{\mathbf{l}'\}:\mathbf{n})$, and $Y_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$ is defined as follows:

$$X_N = S_N : \quad Y_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = 0, \tag{40}$$

$$X_N = U_N : \quad Y_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \tfrac{1}{2}(\mathbf{Z}_N^{-1})_{kp} U_N(\{\mathbf{l}\}|\{\mathbf{l}'\}:\mathbf{n}+\mathbf{1}_\mu), \tag{41}$$

$$X_N = E_N : \quad Y_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \tfrac{1}{2}\{(\mathbf{Z}_N^{-1})_{kp} - (\mathbf{Z}_N^{-1})_{kq}\}$$

$$\times E_N(\{\mathbf{l}\}|\{\mathbf{l}'\}:\mathbf{n}+\mathbf{1}_\mu). \tag{42}$$

Equation (39) is called the ''vertical recurrence relation.'' Operation of the reduction operators Eqs. (23), (24), and (25) on both sides of Eq. (32) integrated over $\mathbf{r}_1,\ldots,\mathbf{r}_N$ yields

$$X_N(|\mathbf{l}_k' + \mathbf{1}_\mu) = X_N(\mathbf{l}_k + \mathbf{1}_\mu|) + (\mathbf{R}_k - \mathbf{R}_k')_\mu X_N. \tag{43}$$

This is the so-called ''horizontal recurrence relation.'' Substituting Eq. (39) into Eq. (43), we obtain another vertical recurrence formula

$$X_N(|\mathbf{l}_k' + \mathbf{1}_\mu) = \frac{1}{2}\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{kj}\{l_{j\mu} X_N(\mathbf{l}_j - \mathbf{1}_\mu|)$$

$$+ l'_{j\mu} X_N(|\mathbf{l}_j' - \mathbf{1}_\mu)\}$$

$$+ \left\{\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{kj} P_{j\mu} - R'_{k\mu}\right\} X_N + Y_N. \tag{44}$$

The recursive computation of the N-electron integrals is carried out by Eqs. (39) and (44) or by Eqs. (39) and (43).

C. Initial integrals for the recurrence formulas

Initial integrals for recursive computations of $S_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$, $U_N(\{\mathbf{l}\}|\{\mathbf{l}'\}:\mathbf{0})$, and $E_N(\{\mathbf{l}\}|\{\mathbf{l}'\}:\mathbf{0})$ are $S_N(\{\mathbf{0}\}|\{\mathbf{0}\})$, $U_N(\{\mathbf{0}\}|\{\mathbf{0}\}:\mathbf{n})$, and $E_N(\{\mathbf{0}\}|\{\mathbf{0}\}:\mathbf{n})$, respectively. The initial integrals are closely related to the N-electron integrals over s-type ECCGFs. We derive the N-electron basic integral first. It is straightforward to obtain the initial N-electron basic integral. Integrating the integrand Eq. (20) with $\mathbf{l}_k = \mathbf{l}_k' = \mathbf{0}$ ($k=1,\ldots,N$) over $\mathbf{r}_1,\ldots,\mathbf{r}_N$, we obtain the initial N-electron basic integral

$$[\{\mathbf{0}\}|\{\mathbf{0}\}]_N = \left(\frac{\pi^N}{|\mathbf{Z}_N|}\right)^{3/2} \exp\left[\sum_{ij} (\mathbf{Z}_N^{-1})_{ij} \mathbf{P}_i \mathbf{P}_j - \sum_{i=1}^{N} (\alpha_i \mathbf{R}_i^2 + \alpha_i' \mathbf{R}_i'^2) + i\mathbf{k}_p\left\{\sum_j (\mathbf{Z}_N^{-1})_{jp} \mathbf{P}_j - \mathbf{V}\right\} + i\mathbf{k}_{pq} \sum_j \{(\mathbf{Z}_N^{-1})_{jp} \right.$$

$$\left. - (\mathbf{Z}_N^{-1})_{jq}\} \mathbf{P}_j - \frac{1}{4}(\mathbf{Z}_N^{-1})_{pp} \mathbf{k}_p^2 - \frac{1}{2}\{(\mathbf{Z}_N^{-1})_{pp} - (\mathbf{Z}_N^{-1})_{pq}\} \mathbf{k}_p \mathbf{k}_{pq} - \frac{1}{4}\{(\mathbf{Z}_N^{-1})_{pp} - 2(\mathbf{Z}_N^{-1})_{pq} + (\mathbf{Z}_N^{-1})_{qq}\} \mathbf{k}_{pq}^2\right], \tag{45}$$

where $|\mathbf{Z}_N|$ is the determinant of $\mathbf{Z}_N$. Operating the reduction operator Eq. (23) on both sides of Eq. (45), we obtain the initial integral

$$S_N(\{\mathbf{0}\}|\{\mathbf{0}\}) = \left(\frac{\pi^N}{|\mathbf{Z}_N|}\right)^{3/2} \exp\left[\sum_{ij} (\mathbf{Z}_N^{-1})_{ij} \mathbf{P}_i \mathbf{P}_j \right.$$

$$\left. - \sum_{i=1}^{N} (\alpha_i \mathbf{R}_i^2 + \alpha_i' \mathbf{R}_i'^2)\right]. \tag{46}$$

This is the same as the overlap integral obtained by Boys.[8] In a similar way, operation of the reduction operators Eqs. (24) and (25) on both sides of Eq. (45) yields

$$U_N(\{\mathbf{0}\}|\{\mathbf{0}\}:\mathbf{n})$$

$$= (2\pi^2)^{-1} S_N(\{\mathbf{0}\}|\{\mathbf{0}\}) \int d\mathbf{k}_p \mathbf{k}_p^{-2}$$

$$\times \prod_{\mu=x,y,z} (ik_{p\mu})^{n_\mu} \times \exp\left[-\frac{1}{4}(\mathbf{Z}_N^{-1})_{pp} \mathbf{k}_p^2 \right.$$

$$\left. + i\mathbf{k}_p\left\{\sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{jp} \mathbf{P}_j - \mathbf{V}\right\}\right], \tag{47}$$

and

$$E_N(\{\mathbf{0}\}|\{\mathbf{0}\}:\mathbf{n})$$

$$= (2\pi^2)^{-1} S_N(\{\mathbf{0}\}|\{\mathbf{0}\}) \int d\mathbf{k}_{pq} \mathbf{k}_{pq}^{-2} \prod_{\mu=x,y,z} (ik_{pq\mu})^{n_\mu}$$

$$\times \exp\left[-\frac{1}{4}\{(\mathbf{Z}_N^{-1})_{pp} - 2(\mathbf{Z}_N^{-1})_{pq} + (\mathbf{Z}_N^{-1})_{qq}\} \mathbf{k}_{pq}^2 \right.$$

$$\left. + i\mathbf{k}_{pq} \sum_{j=1}^{N} \{(\mathbf{Z}_N^{-1})_{jp} - (\mathbf{Z}_N^{-1})_{jq}\} \mathbf{P}_j\right], \tag{48}$$

respectively. Since these integrals mutually have the same structure, we can write these integrals as the common form

$$X_N(\{\mathbf{0}\}|\{\mathbf{0}\}:\mathbf{n}) = (2\pi^2)^{-1} S_N(\{\mathbf{0}\}|\{\mathbf{0}\}) W(\mathbf{n}) \tag{49}$$

with

$$W(\mathbf{n}) = \int d\mathbf{k} \mathbf{k}^{-2} \prod_{\mu=x,y,z} (ik_\mu)^{n_\mu} \exp\left[-\frac{Z}{4}\mathbf{k}^2 + i\mathbf{k}\mathbf{Q}\right], \tag{50}$$

where $\mathbf{Q}$ and Z depend on U_N or E_N as follows:

$$X_N = U_N: \quad \mathbf{Q} = \sum_{j=1}^{N} (\mathbf{Z}_N^{-1})_{jp} \mathbf{P}_j - \mathbf{V}, \tag{51}$$

$$Z = (\mathbf{Z}_N^{-1})_{pp}, \tag{52}$$

$$X_N = E_N: \quad \mathbf{Q} = \sum_{j=1}^{N} \{(\mathbf{Z}_N^{-1})_{jp} - (\mathbf{Z}_N^{-1})_{jq}\} \mathbf{P}_j, \tag{53}$$

$$Z = (\mathbf{Z}_N^{-1})_{pp} - 2(\mathbf{Z}_N^{-1})_{pq} + (\mathbf{Z}_N^{-1})_{qq}. \tag{54}$$

Equation (50) is rewritten as

$$W(\mathbf{n}) = \prod_{\mu=x,y,z} \left(\frac{\partial}{\partial Q_\mu}\right)^{n_\mu} \int d\mathbf{k} \, \mathbf{k}^{-2} \exp\left[-\frac{Z}{4} \mathbf{k}^2 + i\mathbf{k}\mathbf{Q}\right]. \tag{55}$$

Integrating Eq. (55) over $\mathbf{k}$ by the aid of the relation

$$\exp(-ak^2) = 2ak^2 \int_0^1 dt \, t^{-3} \exp(-at^{-2}k^2), \tag{56}$$

and rewriting by the incomplete Gamma function

$$F_m(a) = \int_0^1 t^{2m} \exp(-at^2) dt, \tag{57}$$

the function W becomes

$$W(\mathbf{n}) = 4\pi^{3/2} Z^{-1/2} \prod_{\mu=x,y,z} \left(\frac{\partial}{\partial Q_\mu}\right)^{n_\mu} F_0\left(\frac{\mathbf{Q}^2}{Z}\right). \tag{58}$$

To obtain the recurrence formula for the auxiliary index $\mathbf{n}$, we replace F_0 by F_m of the function Eq. (58) as follows:

$$W_m(\mathbf{n}) = 4\pi^{3/2} Z^{-1/2} \prod_{\mu=x,y,z} \left(\frac{\partial}{\partial Q_\mu}\right)^{n_\mu} F_m\left(\frac{\mathbf{Q}^2}{Z}\right). \tag{59}$$

$W(\mathbf{n})$ is equal to $W_0(\mathbf{n})$. We obtain the recurrence relation

$$W_m(\mathbf{n}+\mathbf{1}_\mu) = -\frac{2Q_\mu}{Z} W_{m+1}(\mathbf{n}) - \frac{2n_\mu}{Z} W_{m+1}(\mathbf{n}-\mathbf{1}_\mu) \tag{60}$$

after differentiation of the integrand of $F_m(\mathbf{Q}^2/Z)$ with respect to Q_μ. $W_0(\mathbf{n})$ can be evaluated from the values of $W_m(\mathbf{0})$, which are $F_m(\mathbf{Q}^2/Z)$ $(m=0,1,2,...,|\mathbf{n}|)$. Then, the initial integrals for U_N and E_N are evaluated by Eqs. (49) and (60). Although evaluation of F_m is a time-consuming step, there are efficient computation methods for F_m.[21,23,26]

III. DISCUSSION

We have derived the recurrence formulas (39), (43), and (44) for the N-electron integrals over ECCGFs by means of the method of Obara and Saika[23,24] and Honda *et al.*,[25] i.e., the derivation method of efficient recurrence formulas for molecular two-electron integrals over Cartesian Gaussian functions. Our vertical recurrence formula for E_2 with $\beta_{12} = 0$ is essentially the same as that obtained by Honda *et al.* The vertical recurrence formula Eq. (39) [or Eq. (44)] expresses the N-electron integrals of higher angular momentum as a linear combination of the N-electron integrals of lower angular momentum. The first two terms in Eq. (39) are the same forms as in the case of any N-electron integrals. On the

other hand, the last term in Eq. (39) depends on the same type of N-electron integral as in Eqs. (40)–(42). The horizontal recurrence formula Eq. (43) only depends on centers of ECCGFs, and its structure does not depend on the type of N-electron integral. Equation (43) is an extension of the horizontal recurrence formula obtained by Head-Gordon and Pople.[27]

The N-electron integrals Eqs. (10)–(12) are calculated recursively by Eqs. (39) and (44) or by Eqs. (39) and (43). The use of Eqs. (39) and (43), i.e., the use of the vertical and horizontal recurrence formulas, has been shown as an efficient computation algorithm of molecular two-electron integrals over contracted Gaussian functions by Head-Gordon and Pople.[27] The advantages of employing the horizontal recurrence formula are as follows: (1) determination of the required intermediate integrals is straightforward; (2) computation of the intermediate integrals is reduced if one uses contracted functions. Here we employ the method which combined the vertical and horizontal recurrence formulas.
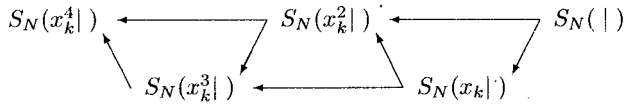
We show an algorithm for computation of the N-electron integrals Eqs. (10)–(13). Computation of the N-electron integrals is carried out in the following three steps: First, the parameters $\mathbf{Z}_N^{-1}$, $|\mathbf{Z}_N|$, and $\sum_{i=1}^{N}(\mathbf{Z}_N^{-1})_{ki}\mathbf{P}_i$ $(k=1,...,N)$ needed in the recursive computation are calculated and stored. Subsequently, the overlap and kinetic integrals are computed. Since the kinetic integral is the linear combination of the overlap integrals, the kinetic integrals should be evaluated along with the overlap integrals. Finally, the nuclear attraction and electron repulsion integrals are computed after evaluation of the overlap integrals because the initial integrals of U_N and E_N require $S_N(\{\mathbf{0}\}|\{\mathbf{0}\})$.

Calculation of $\mathbf{Z}_N^{-1}$ and $|\mathbf{Z}_N|$ is straightforward if $N \le 3$. However, calculation of $\mathbf{Z}_N^{-1}$ and $|\mathbf{Z}_N|$ becomes more laborious as N increases. In $N \ge 4$, calculation of $\mathbf{Z}_N^{-1}$ and $|\mathbf{Z}_N|$ has to be performed by an efficient method, e.g., the LU decomposition method, unless $\mathbf{Z}_N$ has a special structure.
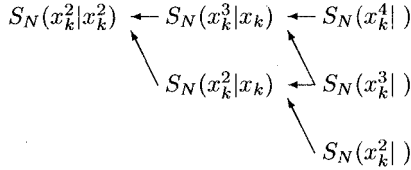
The overlap integrals are calculated in the following two steps:

(1) Computation of the initial integrals $S_N(\{\mathbf{0}\}|\{\mathbf{0}\})$.
(2) Computation of the target integrals by means of the vertical and horizontal recurrence formulas.

The initial overlap integrals must be stored because they are required in the computation of the initial U_N and E_N. If only s-type ECCGFs are used, evaluation of S_N's by means of the recurrence formula is needless. However, since the kinetic integral is built up by the overlap integrals over ECCGFs with higher angular momenta, the overlap integrals over p-type ECCGFs must be computed even if only s-type ECCGFs are used. To obtain the target integral $S_N(\mathbf{l}_1,...,\mathbf{l}_N|\mathbf{l}_1',...,\mathbf{l}_N')$, one has to generate the intermediate integrals $S_N(\mathbf{l}_1,...,\mathbf{l}_N|\mathbf{0},...,\mathbf{0}) \sim S_N(\mathbf{l}_1+\mathbf{l}_1',...,\mathbf{l}_N+\mathbf{l}_N'|\mathbf{0},...,\mathbf{0})$ by the vertical recurrence formula Eq. (39), and the target integral is calculated from the intermediate integrals by the horizontal recurrence formula Eq. (43). As an illustration, we have shown calculation scheme of $S_N(x_k^2|x_k^2)$ by means of the vertical and horizontal recurrence formulas in Fig. 1.

$$S_N(x_k^4|\ ) \longleftarrow S_N(x_k^2|\ ) \longleftarrow S_N(\ |\ )$$
$$S_N(x_k^3|\ ) \qquad S_N(x_k|\ )$$

(a) Vertical recursive calculation

$$S_N(x_k^2|x_k^2) \longleftarrow S_N(x_k^3|x_k) \longleftarrow S_N(x_k^4|\ )$$
$$S_N(x_k^2|x_k) \longleftarrow S_N(x_k^3|\ )$$
$$S_N(x_k^2|\ )$$

(b) horizontal recursive calculation

FIG. 1. Recursive calculation scheme of the target overlap integral $S_N(x_k^2|x_k^2)$.

Here we abbreviated $S_N(\{0\}|\{0\})$ as $S_N(|)$, and explicitly wrote angular factors in S_N. We will use the same notation for U_N and E_N below.

It is more complicated than the case of the overlap integral to generate the initial and intermediate integrals for U_N and E_N. The target integral $E_N(\{l\}|\{l'\})$ requires $\prod_{\mu=x,y,z}(L_\mu+1)$ initial integrals with the auxiliary indices resulting from all possible combinations of $n_\mu=0,...,L_\mu(\mu=x,y,z)$, where $L_\mu=\Sigma_{k=1}^{N}(l_k+l_k')_\mu$. For example, initial integrals $E_N(|:n_x n_y n_z)$ needed in computation of $E_N(x_k|y_k)$ are $E_N(|:000)$, $E_N(|:100)$, $E_N(|:010)$, and $E_N(|:110)$. The target $U_N(\{l\}|\{l'\})$ also requires $\prod_{\mu=x,y,z}(L_\mu+1)$ initial integrals with the same auxiliary indices as $E_N(|:n)$ for $E_N(\{l\}|\{l'\})$. The initial integrals for U_N and E_N are generated by Eqs. (49) and (60), and the target U_N and E_N are evaluated by the recurrence formulas Eqs. (39) and (43) in the same way as S_N. As an illustration, we have shown calculation scheme of $E_N(x_k^2|x_k^2)$ by the vertical and horizontal recurrence formulas in Fig. 2.

The recurrence formulas can be applied to calculation of the expectation values of $\delta(\mathbf{r}_p-\mathbf{V})$ and $\delta(\mathbf{r}_p-\mathbf{r}_q)$ because these two operators can be expressed with the Fourier transformations

$$\delta(\mathbf{r}_p-\mathbf{V})=(2\pi)^{-3}\int d\mathbf{k}_p\exp[i\mathbf{k}_p(\mathbf{r}_p-\mathbf{V})] \quad (61)$$

and

$$\delta(\mathbf{r}_p-\mathbf{r}_q)=(2\pi)^{-3}\int d\mathbf{k}_{pq}\exp[i\mathbf{k}_{pq}(\mathbf{r}_p-\mathbf{r}_q)], \quad (62)$$

which are similar to those of $|\mathbf{r}_p-\mathbf{V}|^{-1}$ and $|\mathbf{r}_p-\mathbf{r}_q|^{-1}$, respectively. Integrals required in calculation of the expectation values of $\delta(\mathbf{r}_p-\mathbf{V})$ and $\delta(\mathbf{r}_p-\mathbf{r}_q)$ are

$$D_{\delta_p}=\int d\mathbf{r}_1...\int d\mathbf{r}_N G_N(\{l\})\delta(\mathbf{r}_p-\mathbf{V})G_N'(\{l'\}) \quad (63)$$

and

$$D_{\delta_{pq}}=\int d\mathbf{r}_1...\int d\mathbf{r}_N G_N(\{l\})\delta(\mathbf{r}_p-\mathbf{r}_q)G_N'(\{l'\}), \quad (64)$$

respectively. The reduction operators for D_{δ_p} and $D_{\delta_{pq}}$ are

$$\mathcal{R}_{\delta_p}(\mathbf{n})\equiv(2\pi)^{-3}\int d\mathbf{k}_p\prod_{\mu=x,y,z}(ik_{p\mu})^{n_\mu}\lim_{\mathbf{k}_{pq}\to\mathbf{0}} \quad (65)$$

and

$$\mathcal{R}_{\delta_{pq}}(\mathbf{n})\equiv(2\pi)^{-3}\int d\mathbf{k}_{pq}\prod_{\mu=x,y,z}(ik_{pq\mu})^{n_\mu}\lim_{\mathbf{k}_p\to\mathbf{0}}, \quad (66)$$

respectively. Calculation of D_{δ_p} and $D_{\delta_{pq}}$ is carried out the same recurrence formulas as U_N and E_N, respectively. Operating the reduction operators Eqs. (65) and (66) on Eq. (45), initial integrals of D_{δ_p} and $D_{\delta_{pq}}$ become

$$D_X(\{0\}|\{0\}:\mathbf{n})=(2\pi)^{-3}S_N(\{0\}|\{0\})W'(\mathbf{n}) \quad (67)$$

with

$$W'(\mathbf{n})=\int d\mathbf{k}\prod_{\mu=x,y,z}\left(\frac{\partial}{\partial Q_\mu}\right)^{n_\mu}\exp\left(-\frac{Z}{4}\mathbf{k}^2+i\mathbf{k}\mathbf{Q}\right), \quad (68)$$

where $X=\delta_p$ or δ_{pq}, Z and $\mathbf{Q}$ are the same as those of U_N and E_N for D_{δ_p} and $D_{\delta_{pq}}$, respectively, i.e., Eqs. (51)–(54). Evaluation of the initial integrals is carried out by the relation

$$W'(\mathbf{n}+\mathbf{1}_\mu)=-\frac{2Q_\mu}{Z}W'(\mathbf{n})-\frac{2n_\mu}{Z}W'(\mathbf{n}-\mathbf{1}_\mu) \quad (69)$$

with

$$W'(\mathbf{0})=\left(\frac{4\pi}{Z}\right)^{3/2}\exp\left(-\frac{\mathbf{Q}^2}{Z}\right). \quad (70)$$

The relation Eq. (69) is the same form as Eq. (60).

Finally, we suggest a modification of two interesting Hylleraas-type wave functions by the use of Gaussian-type correlation factors. One of them is a Hylleraas-type molecular wave function Ψ_{OH} by Obara and Hirao.[28] Ψ_{OH} is defined as a product of a correlation factor $F_{symmetric}$ which is symmetric with respect to exchange of electrons and an antisymmetrized product of orbitals $\Phi_{antisymmetric}$:

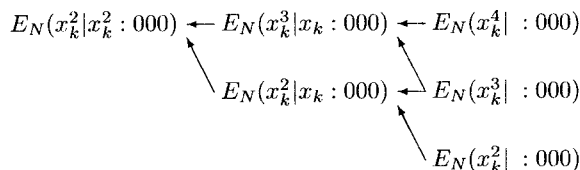$$\Psi_{OH}=F_{symmetric}\Phi_{antisymmetric}. \quad (71)$$

They have written $F_{symmetric}$ as

$$F_{symmetric}=\exp\left(\sum_p\sum_{i<j}c_{ijp}|\mathbf{r}_i-\mathbf{r}_j|^p\right.$$
$$\left.+\sum_p^{nuclei}\sum_I\sum_i c_{iIp}|\mathbf{r}_i-\mathbf{R}_I|^p\right), \quad (72)$$

where c_{ijp} and c_{iIp} are variational constants. We suggest replacing $F_{symmetric}$ as follows:
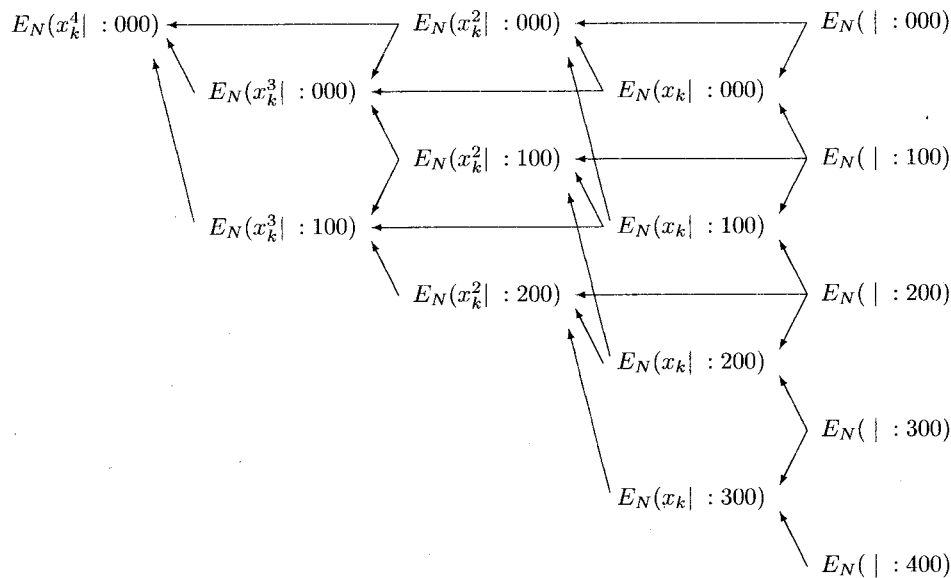
(a) vertical recursive calculation

(b) horizontal recursive calculation

FIG. 2. Recursive calculation scheme of the target electron repulsion integral $E_N(x_k^2|x_k^2)$.

$$F_{\text{symmetric}} = 1 + \exp\left(-\sum_p \sum_{i<j} c_{ijp}|\mathbf{r}_i - \mathbf{r}_j|^2 \right.$$
$$\left. -\sum_p \sum_I^{\text{nuclei}} \sum_i c_{iIp}|\mathbf{r}_i - \mathbf{R}_I|^2 \right). \quad (73)$$

The other is ''linked Hylleraas-CI'' wave function Ψ_{KL} by Kleindienst and Lüchow,[6] which is defined as

$$\Psi_{\text{KL}} = \Phi_0 + \sum_p \sum_{i<j} \Phi_{ij}^{(p)} f(ijp)$$

$$+ \sum_{p,q} \sum_{i<j,k<l} \Phi_{ijkl}^{(pq)} f(ijp)f(klq), \quad (74)$$

with

$$f(ijp) = |\mathbf{r}_i - \mathbf{r}_j|^p. \quad (75)$$

Similarly, we suggest employing

$$f(ijp) = \exp(-\beta_{ij}^{(p)}|\mathbf{r}_i - \mathbf{r}_j|^2). \quad (76)$$

Applications of the original Ψ_{OH} and Ψ_{KL} to many-electron systems are not practical due to cumbersome many-electron integrals over Hylleraas-type functions. On the other hand, the modified Ψ_{OH} and Ψ_{KL} require many-electron integrals over ECCGFs, and can be more easily applied to many-electron systems.

APPENDIX: RECURRENCE FORMULAS FOR KINETIC INTEGRAL

In this Appendix, we derive recurrence formula for the kinetic integral. Let us define an integrand of the kinetic integral as

$$T_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = G_N(\{\mathbf{l}\})\left(-\frac{1}{2}\nabla_p^2 \right) G_N'(\{\mathbf{l}'\}); \quad (A1)$$

then the kinetic integral is

$$K_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N T_N(\{\mathbf{l}\}|\{\mathbf{l}'\}). \quad (A2)$$

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The recurrence formula for the kinetic integral can be derived in a similar way as derivation for the other integrals.

First, we differentiate the integrand Eq. (A1) with respect to $r_{k\mu}$ ($k=1,...,N$ and $\mu=x,y,z$). Then we obtain

$$\frac{\partial T_N}{\partial r_{k\mu}} = -2\left(A_k + \sum_{j=1}^{N} B_{kj}\right)\{T_N(\mathbf{l}_k+\mathbf{1}_\mu|) + R_{k\mu}T_N\}$$

$$+ 2\sum_{j=1}^{N} B_{kj}\{T_N(\mathbf{l}_j+\mathbf{1}_\mu|) + R_{j\mu}T_N\} + l_{k\mu}T_N(\mathbf{l}_k-\mathbf{1}_\mu|)$$

$$+ l'_{k\mu}T_N(|\mathbf{l}'_k-\mathbf{1}_\mu) + 2P_{k\mu}T_N + 2C'_{pk}L_N, \qquad (A3)$$

where

$$L_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) = G_N(\{\mathbf{l}\})\frac{\partial}{\partial r_{p\mu}}G'_N(\{\mathbf{l}'\}). \qquad (A4)$$

For above manipulation, we used the relation

$$-\tfrac{1}{2}\nabla_p^2 r_{k\mu}G'_N = r_{k\mu}(-\tfrac{1}{2}\nabla_p^2)G'_N - \delta_{p,k}\frac{\partial}{\partial r_{p\mu}}G'_N. \qquad (A5)$$

Integrating both sides of Eq. (A3) over $\mathbf{r}_1,...,\mathbf{r}_N$, the left hand side of Eq. (A3) becomes zero due to the relation Eq. (9). Then we can obtain one set of equations for $K_N(\mathbf{l}_k+\mathbf{1}_\mu|)$ ($k=1,...,N$) as follows:

$$0 = \left(A_k + \sum_{j=1}^{N} B_{kj}\right)\{K_N(\mathbf{l}_k+\mathbf{1}_\mu|) + R_{k\mu}K_N\}$$

$$- \sum_{j=1}^{N} B_{kj}\{K_N(\mathbf{l}_j+\mathbf{1}_\mu|) + R_{j\mu}K_N\} - \tfrac{1}{2}\{l_{k\mu}K_N(\mathbf{l}_k-\mathbf{1}_\mu|)$$

$$+ l'_{k\mu}K_N(|\mathbf{l}'_k-\mathbf{1}_\mu)\} - P_{k\mu}K_N - C'_{pk}M_N, \qquad (A6)$$

where

$$M_N(\{\mathbf{l}\}|\{\mathbf{l}'\}) \equiv \int d\mathbf{r}_1 ... \int d\mathbf{r}_N L_N(\{\mathbf{l}\}|\{\mathbf{l}'\}). \qquad (A7)$$

We refer to $M_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$ as the auxiliary kinetic integral. Solving one set of Eq. (A6) for $K_N(\mathbf{l}_k+\mathbf{1}_\mu|)$, we obtain

$$K_N(\mathbf{l}_k+\mathbf{1}_\mu|)$$

$$= \frac{1}{2}\sum_{j=1}^{N}(\mathbf{Z}_N^{-1})_{kj}\{l_{j\mu}K_N(\mathbf{l}_j-\mathbf{1}_\mu|)$$

$$+ l'_{j\mu}K_N(|\mathbf{l}'_j-\mathbf{1}_\mu)\} + \left\{\sum_{j=1}^{N}(\mathbf{Z}_N^{-1})_{kj}P_{j\mu} - R_{k\mu}\right\}$$

$$\times K_N + \sum_{j=1}^{N}(\mathbf{Z}_N^{-1})_{kj}C'_{pj}M_N. \qquad (A8)$$

Subsequently, we derive recurrence formula for $M_N(\{\mathbf{l}\}|\{\mathbf{l}'\})$. Differentiating the integrand Eq. (A4) of M_N with respect to $r_{k\mu}$, we obtain

$$\frac{\partial L_N}{\partial r_{k\mu}} = -2\left(A_k + \sum_{j=1}^{N} B_{kj}\right)\{L_N(\mathbf{l}_k+\mathbf{1}_\mu|) + R_{k\mu}L_N\}$$

$$+ 2\sum_{j=1}^{N} B_{kj}\{L_N(\mathbf{l}_j+\mathbf{1}_\mu|) + R_{j\mu}L_N\}$$

$$+ l_{k\mu}L_N(\mathbf{l}_k-\mathbf{1}_\mu|) + l'_{k\mu}L_N(|\mathbf{l}'_k-\mathbf{1}_\mu)$$

$$+ 2P_{k\mu}L_N - 2C'_{pk}G_N(\{\mathbf{l}\})G'_N(\{\mathbf{l}'\}). \qquad (A9)$$

In the same way, we obtain the recurrence formula for $M_N(\{\mathbf{l}\}|\{\mathbf{l}\})$ as follows:

$$M_N(\mathbf{l}_k+\mathbf{1}_\mu|) = \frac{1}{2}\sum_{j=1}^{N}(\mathbf{Z}_N^{-1})_{kj}\{l_{j\mu}M_N(\mathbf{l}_j-\mathbf{1}_\mu|) + l'_{j\mu}M_N$$

$$\times(|\mathbf{l}'_j-\mathbf{1}_\mu)\} + \left\{\sum_{j=1}^{N}(\mathbf{Z}_N^{-1})_{kj}P_{j\mu} - R_{k\mu}\right\}M_N$$

$$- \sum_{j=1}^{N}(\mathbf{Z}_N^{-1})_{kj}C'_{pj}S_N. \qquad (A10)$$

The target kinetic integral can be calculated by means of the recurrence formulas Eqs. (A8) and (A10).

The initial auxiliary integral $M_N(\{\mathbf{0}\}|\{\mathbf{0}\})$ is obtained by integration of the integrand Eq. (A4) with $\mathbf{l}_k=\mathbf{l}'_k=\mathbf{0}$ ($k=1,...N$) over $\mathbf{r}_1,...,\mathbf{r}_N$ as follows:

$$M_N(\{\mathbf{0}\}|\{\mathbf{0}\}) = 2\sum_{i=1}^{N} C_{pi}S_N(\{\mathbf{1}_{p\mu}\}|\{\mathbf{0}\})$$

$$+ 2D_{p\mu}S_N(\{\mathbf{0}\}|\{\mathbf{0}\}), \qquad (A11)$$

where $\{\mathbf{1}_{p\mu}\} \equiv (\mathbf{0}_1,...,\mathbf{1}_{p\mu},...,\mathbf{0}_N)$. We find the initial integral $K_N(\{\mathbf{0}\}|\{\mathbf{0}\})$ from Eq. (15) as follows:

$$K_N(\{\mathbf{0}\}|\{\mathbf{0}\}) = \sum_{\mu=x,y,z} K_{N\mu}(\{\mathbf{0}\}|\{\mathbf{0}\}) \qquad (A12)$$

$$= 2\sum_{i=1}^{N} C_{pi}\sum_{j=1}^{N} C'_{pj}S_N(\{\mathbf{1}_{i\mu}\}|\{\mathbf{1}_{j\mu}\})$$

$$+ 2D'_{p\mu}\sum_{i=1}^{N} C_{pi}S_N(\{\mathbf{1}_{i\mu}\}|\{\mathbf{0}\})$$

$$+ 2D_{p\mu}\sum_{i=1}^{N} C'_{pi}S_N(\{\mathbf{0}\}|\{\mathbf{1}_{i\mu}\})$$

$$+ 2D_{p\mu}D'_{p\mu}S_N(\{\mathbf{0}\}|\{\mathbf{0}\}). \qquad (A13)$$

$M_{N\mu}(\{\mathbf{0}\}|\{\mathbf{0}\})$ and $M_N(\{\mathbf{0}\}|\{\mathbf{0}\})$ are built up by the overlap integrals over s- and p-type ECCGFs.

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