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Molecular Integrals in the Equation of a Correlated Electronic Wave Function Including Interparticle Distances[#]

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An equation has been derived for a correlated electronic wave function satisfying the two-particle correlation cusp condition. Molecular integrals of spatial operators in the equation have been formulated based on the recursive formulations of general molecular integrals given by Honda, Sato, and Obara. An efficient scheme of computing them is proposed by taking advantage of the recursive and translational relations of the integrals.

The electron correlation remains one of laborious tasks of taking into account at the *ab initio* calculations of electronic wave functions of atoms and molecules. Much work have been done by the use of the configuration interaction (CI) methods and/or the perturbation theory for various sizes of molecular systems. The method employing correlated functions, which explicitly depend on the interparticle distances, is, however, limited to atoms, atomic ions, and small molecules.[1—14] One of the causes is the complexity of the formulas of the molecular integrals necessary for the method and the resulting complicated computations involved in the method. The purpose of the present work is, thus, to give a simple formulation and an efficient scheme of computing these molecular integrals.

Largo-Cabrerizo and Clementi[9] have formulated the molecular integrals necessary for the Hylleraas-CI method. These integrals have a close relation to the molecular integrals. Their formulas of the molecular integrals, however, are written in terms of primitive parameters and, therefore, take very much complicated forms. Their formulas do not readily lead us to an efficient method of computing them.

The molecular integrals treated in this paper are those over cartesian Gaussian functions, which are usually used in the *ab initio* calculations. The present formulation is based on the recursive formulation given by Honda, Sato, and Obara.[15] The recursive formulas of molecular integrals, as well as their horizontal relations,[16] lead us to an efficient computation. The present computational scheme takes into account of the contracted basis functions usually used in the *ab initio* calculations, so that, the scheme is of practical use.

In the subsequent section the correlated electronic wave function, the equation satisfied by the function, and spatial operators, whose molecular integrals are to be calculated, are given. In the 2nd section the molecular integrals over cartesian Gaussian functions are expressed in terms of those over hypergaussian functions, and in the 3rd section the recurrence formulas are reduced from those given by Honda, Sato, and Obara. In the 4th section the formulas of molecular integrals over the contracted basis functions are assembled. In the 5th section computational strategy is discussed, and a summary is added in the last section.

I. Equation of Correlated Electronic Wave Function

The approximate wave function treated in this paper takes a form of

$$\Psi = C\psi. \tag{1}$$

Here C is a "correlation part" depending on the interparticle distances;

$$C = \exp\,[D], \tag{2}$$

$$D = \sum_{i<j}^{\text{electrons}} P_{ij}(r_{ij}) + \sum_{I}^{\text{nuclei}} \sum_{i}^{\text{electrons}} P_{iI}(r_{iI}), \tag{3}$$

where $r_{ij}(r_{iI})$ is the distance between electron i and electron j (nucleus I with its charge Z_I)

$$r_{ij} = |\,\boldsymbol{r}_{ij}\,|,\ \boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j, \tag{4}$$

$$r_{iI} = |\,\boldsymbol{r}_{iI}\,|,\ \boldsymbol{r}_{iI} = \boldsymbol{r}_i - \boldsymbol{R}_I, \tag{5}$$

and $P_{ij}(P_{iI})$ in D is a polynomial of $r_{ij}(r_{iI})$ whose lowest order is one

$$P_{ij}(r_{ij}) = c_{ij1}r_{ij} + c_{ij2}r_{ij}^2 + \cdots, \tag{6}$$

$$P_{iI}(r_{iI}) = c_{iI1}r_{iI} + c_{iI2}r_{iI}^2 + \cdots. \tag{7}$$

The two-particle correlation cusp condition[3] requires the coefficients c_{ij1} and c_{iI1} of the first order terms to be

$$c_{ij1} = \frac{1}{2}, \tag{8}$$

$$c_{iI1} = -Z_I. \tag{9}$$

The function ψ in Eq. 1 is a "noncorrelation part" which does not depend explicitly on the interparticle distances.

Substitution of Ψ into the Schrödinger equation

$$\mathscr{H}\Psi = E\Psi \tag{10}$$

leads us to the equation of ψ

$$\mathscr{H}C\psi = EC\psi, \tag{11}$$

[#] This paper is dedicated to the Memory of Professor Hiroshi Kato.

$$C^{-1}\mathscr{H}C\psi = E\psi, \tag{12}$$

which is farther reducible by virtue of the exponential form of C to

$$\exp[-D]\mathscr{H}\exp[D]\psi = E\psi, \tag{13}$$

$$\left\{\mathscr{H} + [\mathscr{H}, D] + \frac{1}{2!}[[\mathscr{H}, D], D] + \cdots\right\}\psi = E\psi \tag{14}$$

with a commutator $[A, B]$

$$[A, B] = AB - BA. \tag{15}$$

Only noncommutative operators in $\mathscr{H}$ with D are the kinetic operators

$$T_i = -\frac{1}{2}\nabla_i^2 = -\frac{1}{2}\sum_{\mu=x,y,z}\frac{\partial^2}{\partial r_{i\mu}^2}, \tag{16}$$

then the term $[\mathscr{H}, D]$ of the above equation becomes

$$\begin{aligned}[\mathscr{H}, D] = \sum_{i>j}\Bigg\{&-\frac{1}{r_{ij}} - \frac{\boldsymbol{r}_{ij}\cdot(\nabla_i - \nabla_j)}{2r_{ij}} \\ &- \sum_{n=2} n c_{ijn}[r_{ij}^{n-2}\boldsymbol{r}_{ij}\cdot(\nabla_i - \nabla_j) + (n+1)r_{ij}^{n-2}]\Bigg\} \\ +\sum_{i,I}\Bigg\{&\frac{Z_I}{r_{iI}} + \frac{Z_I\boldsymbol{r}_{iI}\cdot\nabla_i}{r_{iI}} \\ &- \sum_{n=2} n c_{iIn}[r_{iI}^{n-2}\boldsymbol{r}_{iI}\cdot\nabla_i + (n+1)r_{iI}^{n-2}]\Bigg\}.\end{aligned} \tag{17}$$

The first terms $-1/r_{ij}$ and Z_I/r_{iI} in the braces cancel out the terms $1/r_{ij}$ and $-Z_I/r_{iI}$ in the original Hamiltonian $\mathscr{H}$, which would lead us to avoid the divergence difficulty of the inverse distance potentials taking place when two particles collapse. The term $[[\mathscr{H}, D], D]$ reduces for two-electron systems to

$$\begin{aligned}[[\mathscr{H}, D], D] &= -\sum_{i<j}\sum_{n,m=1} nm c_{ijn} c_{ijm} r_{ij}^{n+m-2} \\ &\quad -\sum_{iI}\sum_{n,m=1} nm c_{iIn} c_{iIm} r_{iI}^{n+m-2}.\end{aligned} \tag{18}$$

Higher order commutators than the second, such as $[[[\mathscr{H}, D], D], D]$, become identically naught, since the second order commutator $[[\mathscr{H}, D], D]$ already commutes with D.

The molecular integrals we should formulate are those for the following one-electron operators

$$\mathscr{O}_{1,2n} = r_{1I}^{2n}, \tag{19}$$

$$\mathscr{O}_{1,2n+1} = r_{1I}^{2n+1} = \frac{r_{1I}^{2n+2}}{r_{1I}}, \tag{20}$$

$$\mathscr{O}_{2,2n} = r_{1I}^{2n}\boldsymbol{r}_{1I}\cdot\nabla_1, \tag{21}$$

$$\begin{aligned}\mathscr{O}_{2,2n-1} &= r_{1I}^{2n-1}\boldsymbol{r}_{1I}\cdot\nabla_1 = r_{1I}^{2n}\frac{\boldsymbol{r}_{1I}\cdot\nabla_1}{r_{1I}}, \\ &(r_{1I} = |\,\boldsymbol{r}_{1I}\,|,\ \boldsymbol{r}_{1I} = \boldsymbol{r}_1 - \boldsymbol{R}_1,\ n \geq 0)\end{aligned} \tag{22}$$

and two-electron operators

$$\mathscr{O}_{3,2n} = r_{12}^{2n}, \tag{23}$$

$$\mathscr{O}_{3,2n+1} = r_{12}^{2n+1} = \frac{r_{12}^{2n+2}}{r_{12}}, \tag{24}$$

$$\mathscr{O}_{4,2n} = r_{12}^{2n}\boldsymbol{r}_{12}\cdot(\nabla_1 - \nabla_2), \tag{25}$$

$$\begin{aligned}\mathscr{O}_{4,2n-1} &= r_{12}^{2n-1}\boldsymbol{r}_{12}\cdot(\nabla_1 - \nabla_2) = r_{12}^{2n}\frac{\boldsymbol{r}_{12}\cdot(\nabla_1 - \nabla_2)}{r_{12}}. \\ &(r_{12} = |\,\boldsymbol{r}_{12}\,|, \boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2,\ n \geq 0)\end{aligned} \tag{26}$$

In the subsequent section we shall give the formulas of molecular integrals over unnormalized cartesian Gaussian functions ϕ for the above operators based on the general recurrence formula over hypergaussian functions[15,17] employing their notations as much as possible. The unnormalized cartesian Gaussian function ϕ

$$\begin{aligned}\phi &= \phi(\boldsymbol{r} - \boldsymbol{R}; \boldsymbol{n}, \zeta) \\ &= (r_x - R_x)^{n_x}(r_y - R_y)^{n_y}(r_z - R_z)^{n_z}\exp[-\zeta(\boldsymbol{r} - \boldsymbol{R})^2],\end{aligned} \tag{27}$$

$$\boldsymbol{n} = (n_x, n_y, n_z) \tag{28}$$

can be expressed in terms of hypergaussian function Φ

$$\begin{aligned}\Phi &= \Phi(\boldsymbol{r} - \boldsymbol{R}; \zeta, \boldsymbol{k}; \boldsymbol{n}, \boldsymbol{l}) \\ &= (\frac{\partial}{\partial R_x})^{l_x}(\frac{\partial}{\partial R_y})^{l_y}(\frac{\partial}{\partial R_z})^{l_z} \\ &\times \phi(\boldsymbol{r} - \boldsymbol{R}; \boldsymbol{n}, \zeta)\exp[i\boldsymbol{k}\cdot(\boldsymbol{r} - \boldsymbol{R})],\end{aligned} \tag{29}$$

$$\boldsymbol{k} = (k_x, k_y, k_z), \tag{30}$$

$$\boldsymbol{l} = (l_x, l_y, l_z) \tag{31}$$

as

$$\phi(\boldsymbol{r} - \boldsymbol{R}; \boldsymbol{n}, \zeta) = \Phi(\boldsymbol{r} - \boldsymbol{R}; \zeta, \boldsymbol{0}; \boldsymbol{n}, \boldsymbol{0}). \tag{32}$$

Note that the cartesian Gaussian function ϕ is the hypergaussian function with $\boldsymbol{k} = \boldsymbol{l} = \boldsymbol{0}$. Also note that the hypergaussian function with the parameters ζ, $\boldsymbol{k}$, $\boldsymbol{n}$, and $\boldsymbol{l}$ being zero is unity;

$$\Phi(\boldsymbol{r} - \boldsymbol{R}; 0, \boldsymbol{0}; \boldsymbol{0}, \boldsymbol{0}) = 1 \tag{33}$$

These relations will be used to rewrite molecular integrals over cartesian Gaussian functions into those over hypergaussian functions, and to reduce recurrence formulas over hypergaussian functions to those over cartesian Gaussian functions.

II. Molecular Integrals over Hypergaussians

In order to use recurrence formulas given by Honda, Sato, and Obara[15] the molecular integrals over cartesian Gaussian functions should be expressed in terms of the hypergaussian functions. This section is devoted to give these expressions.

A. One-Electron Operators $\mathscr{O}_{1,2n}$ and $\mathscr{O}_{2,2n}$. The one-electron operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, and

$\mathscr{O}_{2,2n-1}$ contain the factor of a form r_{1I}^{2N}, which can be written in its cartesian components as

$$\begin{aligned} r_I^{2N} &= (\boldsymbol{r} - \boldsymbol{R}_I)^{2N} \\ &= (r_{Ix}^2 + r_{Iy}^2 + r_{Iz}^2)^N \\ &= \sum_{k=0}^{N} \sum_{l=0}^{k} \binom{N}{k} \binom{k}{l} r_{Ix}^{2N-2k} r_{Iy}^{2k-2l} r_{Iz}^{2l}, \end{aligned} \tag{34}$$

where the subscript 1 is omitted for simplicity. The factor of a form $r_{Ix}^{n_{Ix}} r_{Iy}^{n_{Iy}} r_{Iz}^{n_{Iz}}$ in the last expression is a moment operator and is expressible in terms of the hypergaussian function as

$$r_{Ix}^{n_{Ix}} r_{Iy}^{n_{Iy}} r_{Iz}^{n_{Iz}} = \Phi(\boldsymbol{r} - \boldsymbol{R}_I; 0, \boldsymbol{0}; \boldsymbol{n}_I, \boldsymbol{0}), \tag{35}$$

then the molecular integrals of the operator $\mathscr{O}_{1,2n}$

$$\int \mathrm{d}\boldsymbol{r} \phi_a \mathscr{O}_{1,2n} \phi_b$$

are reducible by the use of one-electron moment integrals (OEMIs) denoted as $[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b]$

$$\begin{aligned} [\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b] &\equiv \int \mathrm{d}\boldsymbol{r} \phi_a \Phi(\boldsymbol{r} - \boldsymbol{R}_I; 0, \boldsymbol{0}; \boldsymbol{n}_I, \boldsymbol{0}) \phi_b \\ &= \int \mathrm{d}\boldsymbol{r} \Phi(\boldsymbol{r} - \boldsymbol{R}_a; \zeta_a, \boldsymbol{0}; \boldsymbol{n}_a, \boldsymbol{0}) \\ &\quad \times \Phi(\boldsymbol{r} - \boldsymbol{R}_I; 0, \boldsymbol{0}; \boldsymbol{n}_I, \boldsymbol{0}) \\ &\quad \times \Phi(\boldsymbol{r} - \boldsymbol{R}_b; \zeta_b, \boldsymbol{0}; \boldsymbol{n}_b, \boldsymbol{0}) \end{aligned} \tag{36}$$

as

$$\int \mathrm{d}\boldsymbol{r} \phi_a \mathscr{O}_{1,2n} \phi_b = \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} [\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b] \tag{37}$$

with angular momentum indices n_{Ix}, n_{Iy}, and n_{Iz} taking values of

$$n_{Ix} = 2n - 2k, \ n_{Iy} = 2k - 2l, \ n_{Iz} = 2l. \tag{38}$$

The operator $\mathscr{O}_{2,2n}$ contains $\boldsymbol{r}_I \cdot \nabla$

$$\boldsymbol{r}_I \cdot \nabla = \sum_{\nu=x,y,z} r_{I\mu} \frac{\partial}{\partial r_\mu}, \tag{39}$$

whose effect on ϕ_{b} is

$$\begin{aligned} \frac{\partial}{\partial r_\mu} \phi_b &= -\frac{\partial}{\partial R_{b\mu}} \phi_b \\ &= -2\zeta_b \phi_b(\boldsymbol{r} - \boldsymbol{R}_b; \boldsymbol{n}_b + \boldsymbol{1}_\mu, \zeta_b) \\ &\quad + N_\mu(\boldsymbol{n}_b) \phi_b(\boldsymbol{r} - \boldsymbol{R}_b; \boldsymbol{n}_b - \boldsymbol{1}_\mu, \zeta_b) \\ &= -2\zeta_b \Phi_b(\boldsymbol{r} - \boldsymbol{R}_b; \zeta_b, \boldsymbol{0}; \boldsymbol{n}_b + \boldsymbol{1}_\mu, \boldsymbol{0}) \\ &\quad + N_\mu(\boldsymbol{n}_b) \Phi_b(\boldsymbol{r} - \boldsymbol{R}_b; \zeta_b, \boldsymbol{0}; \boldsymbol{n}_b - \boldsymbol{1}_\mu, \boldsymbol{0}). \end{aligned} \tag{40}$$

Here $N_\mu(\boldsymbol{n}_b)$ means the μ component of $\boldsymbol{n}_b = (n_{bx}, n_{by}, n_{bz})$. Then the molecular integrals of the operator $\mathscr{O}_{2,2n}$ is reducible in terms of the OEMI defined by Eq. 36 to

$$\begin{aligned} \int \mathrm{d}\boldsymbol{r} \phi_a \mathscr{O}_{2,2n} \phi_b = &- \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} \\ &\times \sum_{\mu=x,y,z} \{2\zeta_b [\boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b + \boldsymbol{1}_\mu] \\ &- N_\mu(\boldsymbol{n}_b) [\boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b - \boldsymbol{1}_\mu]\} \end{aligned} \tag{41}$$

with the same angular momentum indices n_{Ix}, n_{Iy}, and n_{Iz} given in Eq. 38.

B. One-Electron Operators $\mathscr{O}_{1,2n+1}$ and $\mathscr{O}_{2,2n-1}$. The one-electron operators $\mathscr{O}_{1,2n+1}$ and $\mathscr{O}_{2,2n-1}$, contain the factor r_I^{-1} which is the only essential difference from the operators $\mathscr{O}_{1,2n}$, and $\mathscr{O}_{2,2n}$ in the previous subsection. This factor is rewritten by the use of the hypergaussian function as

$$\begin{aligned} r_I^{-1} &= \frac{2}{\pi^{1/2}} \int_0^\infty \mathrm{d}u \ \exp[-u^2(\boldsymbol{r} - \boldsymbol{R}_I)^2] \\ &= \mathscr{R} \Phi(\boldsymbol{r} - \boldsymbol{R}_I; u^2, \boldsymbol{0}; \boldsymbol{0}, \boldsymbol{0}) \end{aligned} \tag{42}$$

with a reduction operator $\mathscr{R}$ including an integration over u as

$$\mathscr{R} = \frac{2}{\pi^{1/2}} \int_0^\infty \mathrm{d}u. \tag{43}$$

The integration variable u will be termed an *integration exponent* in later sections. A multiplication of factor $r_{Ix}^{n_{Ix}} r_{Iy}^{n_{Iy}} r_{Iz}^{n_{Iz}}$ to r_I^{-1} results in an increase of the angular momentum indices in the above hypergaussian function from $\boldsymbol{0}$ to $\boldsymbol{n}_I$

$$r_{Ix}^{n_{Ix}} r_{Iy}^{n_{Iy}} r_{Iz}^{n_{Iz}} r_I^{-1} = \mathscr{R} \Phi(\boldsymbol{r} - \boldsymbol{R}_I; u^2, \boldsymbol{0}; \boldsymbol{n}_I, \boldsymbol{0}), \tag{44}$$

then the molecular integral of $\mathscr{O}_{1,2n+1}$ finally takes a form of

$$\int \mathrm{d}\boldsymbol{r} \phi_a \mathscr{O}_{1,2n+1} \phi_b = \sum_{k=0}^{n+1} \sum_{l=0}^{k} \binom{n+1}{k} \binom{k}{l} \mathscr{R} [\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b] \tag{45}$$

with angular momentum indices n_{Ix}, n_{Iy}, and n_{Iz} being

$$n_{Ix} = 2n - 2k + 2, \ n_{Iy} = 2k - 2l, \ n_{Iz} = 2l, \tag{46}$$

and generalized nuclear attraction integrals (GNAIs) defined by

$$\begin{aligned} \mathscr{R} [\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b] &= \mathscr{R} \int \mathrm{d}\boldsymbol{r} \Phi(\boldsymbol{r} - \boldsymbol{R}_a; \zeta_a, \boldsymbol{0}; \boldsymbol{n}_a, \boldsymbol{0}) \\ &\quad \times \Phi(\boldsymbol{r} - \boldsymbol{R}_I; u^2, \boldsymbol{0}; \boldsymbol{n}_I, \boldsymbol{0}) \\ &\quad \times \Phi(\boldsymbol{r} - \boldsymbol{R}_b; \zeta_b, \boldsymbol{0}; \boldsymbol{n}_b, \boldsymbol{0}). \end{aligned} \tag{47}$$

Note that the true nuclear attraction integral corresponds to the GNAI with $\boldsymbol{n}_I = \boldsymbol{0}$.

The effect of $\boldsymbol{r}_I \cdot \nabla$ in $\mathscr{O}_{2,2n-1}$ is similar to that discussed in the previous subsection, then the molecular integral of $\mathscr{O}_{2,2n-1}$ becomes

$$\begin{aligned} \int \mathrm{d}\boldsymbol{r} \phi_a \mathscr{O}_{2,2n-1} \phi_b = &- \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} \\ &\times \sum_{\mu=x,y,z} \{2\zeta_b \mathscr{R} [\boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b + \boldsymbol{1}_\mu] \\ &- N_\mu(\boldsymbol{n}_b) \mathscr{R} [\boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b - \boldsymbol{1}_\mu]\} \end{aligned} \tag{48}$$

with angular momentum indices n_{Ix}, n_{Iy}, and n_{Iz} now taking values of

$$n_{Ix} = 2n - 2k, \ n_{Iy} = 2k - 2l, \ n_{Iz} = 2l. \tag{49}$$

C. Two-Electron Operators $\mathscr{O}_{3,2n}$ and $\mathscr{O}_{4,2n}$. The factor of a form r_{12}^{2N} in the two-electron operators

$\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$ is rewritten in terms of its cartesian components as

$$\begin{aligned} r_{12}^{2N} &= (\boldsymbol{r}_1 - \boldsymbol{r}_2)^{2N} \\ &= (r_{12x}^2 + r_{12y}^2 + r_{12z}^2)^N \\ &= \sum_{k=0}^{N}\sum_{l=0}^{k} \binom{N}{k}\binom{k}{l} r_{12x}^{2N-2k} r_{12y}^{2k-2l} r_{12z}^{2l}, \end{aligned} \tag{50}$$

and the factor of a form $r_{12x}^{n_{12x}} r_{12y}^{n_{12y}} r_{12z}^{n_{12z}}$ in the last expression is a two-electron moment operator which is expressible in terms of two-electron hypergaussian function as

$$r_{12x}^{n_{12x}} r_{12y}^{n_{12y}} r_{12z}^{n_{12z}} = \Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; 0, \boldsymbol{0}; \boldsymbol{n}_{12}, \boldsymbol{0}). \tag{51}$$

The molecular integrals of the operator $\mathscr{O}_{3,2n}$

$$\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a(\boldsymbol{r}_1)\phi_c(\boldsymbol{r}_2)\mathscr{O}_{3,2n}\phi_b(\boldsymbol{r}_1)\phi_d(\boldsymbol{r}_2)$$

are reducible by the use of two-electron moment integrals (TEMIs) denoted as $[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d]$

$$\begin{aligned} &[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d] \\ &\quad\equiv \int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a\phi_c \Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; 0, \boldsymbol{0}; \boldsymbol{n}_{12}, \boldsymbol{0})\phi_b\phi_d \\ &\quad= \int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \Phi(\boldsymbol{r}_1 - \boldsymbol{R}_a; \zeta_a, \boldsymbol{0}; \boldsymbol{n}_a, \boldsymbol{0}) \\ &\qquad\times \Phi(\boldsymbol{r}_2 - \boldsymbol{R}_c; \zeta_c, \boldsymbol{0}; \boldsymbol{n}_c, \boldsymbol{0}) \\ &\qquad\times \Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; 0, \boldsymbol{0}; \boldsymbol{n}_{12}, \boldsymbol{0}) \\ &\qquad\times \Phi(\boldsymbol{r}_1 - \boldsymbol{R}_b; \zeta_b, \boldsymbol{0}; \boldsymbol{n}_b, \boldsymbol{0})\Phi(\boldsymbol{r}_2 - \boldsymbol{R}_d; \zeta_d, \boldsymbol{0}; \boldsymbol{n}_d, \boldsymbol{0}) \end{aligned} \tag{52}$$

as

$$\begin{aligned} &\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a(\boldsymbol{r}_1)\phi_c(\boldsymbol{r}_2)\mathscr{O}_{3,2n}\phi_b(\boldsymbol{r}_1)\phi_d(\boldsymbol{r}_2) \\ &\qquad= \sum_{k=0}^{n}\sum_{l=0}^{k}\binom{n}{k}\binom{k}{l}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d] \end{aligned} \tag{53}$$

with angular momentum indices n_{12x}, n_{12y}, and n_{12z} taking values of

$$n_{12x} = 2n - 2k,\ n_{12y} = 2k - 2l,\ n_{12z} = 2l. \tag{54}$$

Taking into account of the effect of $\boldsymbol{r}_{12}\cdot(\nabla_1 - \nabla_2)$ in the operator $\mathscr{O}_{4,2n}$ on the cartesian Gaussian functions ϕ_b and ϕ_d, we have the expression of the molecular integrals of operator $\mathscr{O}_{4,2n}$ as

$$\begin{aligned} &\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a(\boldsymbol{r}_1)\phi_c(\boldsymbol{r}_2)\mathscr{O}_{4,2n}\phi_b(\boldsymbol{r}_1)\phi_d(\boldsymbol{r}_2) \\ &\quad= -\sum_{k=0}^{n}\sum_{l=0}^{k}\binom{n}{k}\binom{k}{l} \\ &\qquad\times \sum_{\mu=x,y,z}\{2\zeta_b[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b + \boldsymbol{1}_\mu, \boldsymbol{n}_d] \\ &\qquad -2\zeta_d[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b, \boldsymbol{n}_d + \boldsymbol{1}_\mu] \\ &\qquad -N_\mu(\boldsymbol{n}_b)[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b - \boldsymbol{1}_\mu, \boldsymbol{n}_d] \\ &\qquad +N_\mu(\boldsymbol{n}_d)[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b, \boldsymbol{n}_d - \boldsymbol{1}_\mu]\} \end{aligned} \tag{55}$$

with the same angular momentum indices n_{12x}, n_{12y}, and n_{12z} given in Eq. 54.

D. Two-Electron Operators $\mathscr{O}_{3,2n+1}$ and $\mathscr{O}_{4,2n-1}$. The two-electron operator r_{12}^{-1} in $\mathscr{O}_{3,2n+1}$ and $\mathscr{O}_{4,2n-1}$ is expressible as

$$\begin{aligned} r_{12}^{-1} &= \frac{2}{\pi^{1/2}}\int_0^\infty \mathrm{d}u\ \exp[-u^2(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2] \\ &= \mathscr{R}\Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; u^2, \boldsymbol{0}; \boldsymbol{0}, \boldsymbol{0}) \end{aligned} \tag{56}$$

with the reduction operator $\mathscr{R}$ given in Eq. 43. The product $r_{12x}^{n_{12x}} r_{12y}^{n_{12y}} r_{12z}^{n_{12z}} r_{12}^{-1}$ reduces to

$$r_{12x}^{n_{12x}} r_{12y}^{n_{12y}} r_{12z}^{n_{12z}} r_{12}^{-1} = \mathscr{R}\Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; u^2, \boldsymbol{0}; \boldsymbol{n}_{12}, \boldsymbol{0}) \tag{57}$$

The molecular integral of $\mathscr{O}_{3,2n+1}$ becomes

$$\begin{aligned} &\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a(\boldsymbol{r}_1)\phi_c(\boldsymbol{r}_2)\mathscr{O}_{3,2n+1}\phi_b(\boldsymbol{r}_1)\phi_d(\boldsymbol{r}_2) \\ &\qquad= \sum_{k=0}^{n+1}\sum_{l=0}^{k}\binom{n+1}{k}\binom{k}{l}\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d] \end{aligned} \tag{58}$$

with generalized electron repulsion integrals (GERIs) defined by

$$\begin{aligned} &\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d] \\ &\quad= \mathscr{R}\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a\phi_c \Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; u^2, \boldsymbol{0}; \boldsymbol{n}_{12}, \boldsymbol{0})\phi_b\phi_d \\ &\quad= \mathscr{R}\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \Phi(\boldsymbol{r}_1 - \boldsymbol{R}_a; \zeta_a, \boldsymbol{0}; \boldsymbol{n}_a, \boldsymbol{0}) \\ &\qquad\times \Phi(\boldsymbol{r}_2 - \boldsymbol{R}_c; \zeta_c, \boldsymbol{0}; \boldsymbol{n}_c, \boldsymbol{0}) \\ &\qquad\times \Phi(\boldsymbol{r}_1 - \boldsymbol{r}_2; u^2, \boldsymbol{0}; \boldsymbol{n}_{12}, \boldsymbol{0}) \\ &\qquad\times \Phi(\boldsymbol{r}_1 - \boldsymbol{R}_b; \zeta_b, \boldsymbol{0}; \boldsymbol{n}_b, \boldsymbol{0})\Phi(\boldsymbol{r}_2 - \boldsymbol{R}_d; \zeta_d, \boldsymbol{0}; \boldsymbol{n}_d, \boldsymbol{0}), \end{aligned} \tag{59}$$

(the true electron repulsion integral is the GERI with $\boldsymbol{n}_{12}$=$\boldsymbol{0}$), and angular momentum indices n_{12x}, n_{12y}, and n_{12z} being

$$n_{12x} = 2n - 2k + 2,\ n_{12y} = 2k - 2l,\ n_{12z} = 2l. \tag{60}$$

Taking into account of the effect of $\boldsymbol{r}_{12}\cdot(\nabla_1 - \nabla_2)$ in $\mathscr{O}_{4,2n-1}$ we have the expression of the molecular integrals of $\mathscr{O}_{4,2n-1}$ as

$$\begin{aligned} &\int\!\!\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_a(\boldsymbol{r}_1)\phi_c(\boldsymbol{r}_2)\mathscr{O}_{4,2n-1}\phi_b(\boldsymbol{r}_1)\phi_d(\boldsymbol{r}_2) \\ &\quad= -\sum_{k=0}^{n}\sum_{l=0}^{k}\binom{n}{k}\binom{k}{l} \\ &\qquad\times \sum_{\mu=x,y,z}\{2\zeta_b\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b + \boldsymbol{1}_\mu, \boldsymbol{n}_d] \\ &\qquad -2\zeta_d\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b, \boldsymbol{n}_d + \boldsymbol{1}_\mu] \\ &\qquad -N_\mu(\boldsymbol{n}_b)\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b - \boldsymbol{1}_\mu, \boldsymbol{n}_d] \\ &\qquad +N_\mu(\boldsymbol{n}_d)\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b, \boldsymbol{n}_d - \boldsymbol{1}_\mu]\} \end{aligned} \tag{61}$$

with angular momentum indices n_{12x}, n_{12y}, and n_{12z} being

$$n_{12x} = 2n - 2k,\ n_{12y} = 2k - 2l,\ n_{12z} = 2l. \tag{62}$$

III. Recurrence Formulas

For the calculation of molecular integrals of operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, $\mathscr{O}_{2,2n-1}$, $\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$ we need OEMIs $[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b]$ in Eq. 36, GNAIs $\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b]$ in Eq. 47, TEMIs $[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d]$ in Eq. 52, and GERIs $\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d]$

in Eq. 59. We give the recurrence formulas for these integrals in this section.

First we note that the following equality, which we call "horizontal relation",[16]

$$(\boldsymbol{r}-\boldsymbol{R}_I)_\mu = (\boldsymbol{r}-\boldsymbol{R}_a)_\mu + (\boldsymbol{R}_a-\boldsymbol{R}_I)_\mu \tag{63}$$

allows us to rewrite $[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b]$ as

$$\begin{aligned}[][\boldsymbol{n}_a,\boldsymbol{n}_I,\boldsymbol{n}_b] &= [\boldsymbol{n}_a+\mathbf{1}_\mu,\boldsymbol{n}_I-\mathbf{1}_\mu,\boldsymbol{n}_b] \\ &\quad +(\boldsymbol{R}_a-\boldsymbol{R}_I)_\mu[\boldsymbol{n}_a,\boldsymbol{n}_I-\mathbf{1}_\mu,\boldsymbol{n}_b],\end{aligned} \tag{64}$$

where the angular momentum $\boldsymbol{n}_I$ in the right hand side is now decreased to $\boldsymbol{n}_I-\mathbf{1}_\mu$. Repeatedly using this relation for both $\boldsymbol{n}_I$ and $\boldsymbol{n}_b$, we arrive at the integrals $[\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b]$, namely, both $\boldsymbol{n}_I$ and $\boldsymbol{n}_b$ are reduced to zero. In other words, if we have a set of the integrals $[\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b]$ for $\boldsymbol{n}'_a$ from $\boldsymbol{n}_a$ to $\boldsymbol{n}_a+\boldsymbol{n}_I+\boldsymbol{n}_b$, we can calculate $[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b]$ by the use of the above horizontal relation.

Similarly the GNAIs, TEMIs, and GERIs can be calculated from sets of integrals $\mathscr{R}[\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b]$, $[\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d]$, and $\mathscr{R}[\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d]$, respectively, by the use of the horizontal relation. Furthermore the last two sets of the integrals are obtainable from another sets of $[\boldsymbol{n}''_a, \boldsymbol{n}''_c, \mathbf{0}_{12}, \mathbf{0}_b, \mathbf{0}_d]$, and $\mathscr{R}[\boldsymbol{n}''_a, \mathbf{0}_c, \mathbf{0}_{12}, \mathbf{0}_b, \mathbf{0}_d]$ by the use of equalities given in later subsections. Then we shall give the recurrence formulas for these latter integrals based on the work given by Honda, Sato, and Obara.[15] The equations in their paper will be denoted with "HSO-", such as Eq. (HSO-100).

A. OEMIs. The recurrence formula for the one-electron moment integrals (OEMIs) [Eq. 36] with both $\boldsymbol{n}_I$ and $\boldsymbol{n}_b$ being zero, $[\boldsymbol{n}_a, \mathbf{0}_I, \mathbf{0}_b]$, is reducible from Eqs. (HSO-114) and (HSO-115). The terms including $N_\mu(\boldsymbol{l}_i)$, $M_{uu}+1$, or $\boldsymbol{q}_i+\mathbf{1}_\mu$ $(i=a,I,b)$ will become naught after the reduction. That $N_\mu(\boldsymbol{l}_i)$ is zero comes from becaue the index $\boldsymbol{l}_i$ is zero in the OEMI [Eq. 36]. The index $q_{i\mu}$ (μ component of $\boldsymbol{q}_i$) is the power of $k_{i\mu}$ [Eq. (HSO-113)], then a positive value of $q_{i\mu}$ reduces the integral to naught since $k_{i\mu}$ (μ component of $\boldsymbol{k}_i$) is also zero in the OEMI. The index M_{uu} is the power of an integration exponent ζ_u [Eq. (HSO-113)], although there is no integration exponent in the OEMI. If we multiply the integrand of the OEMI by $[\Phi(\boldsymbol{r}-\boldsymbol{R}_u;\ \zeta_u,\ \mathbf{0};\ \mathbf{0},\ \mathbf{0})]_{\zeta_u=0}$, which is identically unity [Eq. 33], the OEMI, now, includes the integration exponent ζ_u. A positive value of M_{uu} reduces the integral to zero since ζ_u is zero. Finally noting that $N_\mu(\boldsymbol{n}_I)$ and $N_\mu(\boldsymbol{n}_b)$ are zero because of $\boldsymbol{n}_I=\boldsymbol{n}_b=\mathbf{0}$, we have

$$[\boldsymbol{n}_a+\mathbf{1}_\mu] = (\boldsymbol{R}_G-\boldsymbol{R}_a)_\mu[\boldsymbol{n}_a] + \frac{1}{2\zeta_G}N_\mu(\boldsymbol{n}_a)[\boldsymbol{n}_a-\mathbf{1}_\mu]. \tag{65}$$

Here $\mathbf{0}_I$ and $\mathbf{0}_b$ in the integral $[\boldsymbol{n}_a, \mathbf{0}_I, \mathbf{0}_b]$ have been omitted for simplicity. $\boldsymbol{R}_G$ and ζ_G reduce from Eq. (HSO-50) and Eq. (HSO-49), respectively, to

$$\boldsymbol{R}_G = \frac{1}{2\zeta_G}(\zeta_a\boldsymbol{R}_a+\zeta_b\boldsymbol{R}_b), \tag{66}$$

$$\zeta_G = \zeta_a+\zeta_b. \tag{67}$$

The initial integral of the recursive calculation is found from Eqs. (HSO-120) and (HSO-98) to be

$$[\mathbf{0}_a,\mathbf{0}_I,\mathbf{0}_b] = \mathscr{S}_G, \tag{68}$$

$$\mathscr{S}_G = \left(\frac{\pi}{\zeta_G}\right)^{3/2} \exp\left[-\frac{\zeta_a\zeta_b}{\zeta_G}(\boldsymbol{R}_a-\boldsymbol{R}_b)^2\right], \tag{69}$$

by noting that the factors including $\boldsymbol{k}_i$ ($i=a$, I, or b), M_{uu}, or M_{uv} become unity since $\boldsymbol{k}_i=\mathbf{0}$ and the integration exponent ζ_u is zero.

B. GNAIs. The generalized nuclear attraction integrals (GNAIs) $\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b]$ involve the integration over u in $\mathscr{R}$[Eq. 43], so that we are to employ auxiliary GNAIs which will be denoted as $[\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b|M]$

$$[\boldsymbol{n}_a,\boldsymbol{n}_I,\boldsymbol{n}_b \mid M] = \mathscr{R}\left(\frac{u^2}{\zeta_G+u^2}\right)^M [\boldsymbol{n}_a,\boldsymbol{n}_I,\boldsymbol{n}_b] \tag{70}$$

with ζ_G defined by Eq. 67. As can be seen from this definition, the auxiliary GNAIs with $M=0$ are the true GNAIs.

The recurrence formula for the auxiliary GNAIs with both $\boldsymbol{n}_I$ and $\boldsymbol{n}_b$ being $\mathbf{0}=(0,0,0)$, $[\boldsymbol{n}_a, \mathbf{0}_I, \mathbf{0}_b|M]$, is reducible from Eqs. (HSO-114) and (HSO-115). Noting that the terms including $\boldsymbol{l}_i-\mathbf{1}_\mu$ or $\boldsymbol{q}_i+\mathbf{1}_\mu$ ($i=a$, I, or b) become naught because of $\boldsymbol{l}_i=\boldsymbol{k}_i=\mathbf{0}$, we have

$$\begin{aligned}&[\boldsymbol{n}_a+\mathbf{1}_\mu \mid M] \\ &\quad = (\boldsymbol{R}_G-\boldsymbol{R}_a)_\mu[\boldsymbol{n}_a \mid M] - (\boldsymbol{R}_G-\boldsymbol{R}_I)_\mu[\boldsymbol{n}_a \mid M+1] \\ &\qquad +\frac{1}{2\zeta_G}N_\mu(\boldsymbol{n}_a)\{[\boldsymbol{n}_a-\mathbf{1}_\mu \mid M] - [\boldsymbol{n}_a-\mathbf{1}_\mu \mid M+1]\}\end{aligned} \tag{71}$$

with the definition of $\boldsymbol{R}_G$ given in Eq. 66, and $\mathbf{0}_I$ and $\mathbf{0}_b$ have been omitted. The initial integrals of the auxiliary GNAIs are reduced from Eqs. (HSO-120), (HSO-98), and (HSO-99) to be

$$\begin{aligned}[][\mathbf{0}_a,\mathbf{0}_I,\mathbf{0}_b \mid M] &= \mathscr{R}\left(\frac{u^2}{\zeta_G+u^2}\right)^M [\mathbf{0}_a,\mathbf{0}_I,\mathbf{0}_b] \\ &= 2\left(\frac{\zeta_G}{\pi}\right)^{1/2} \mathscr{S}_G F_M(U),\end{aligned} \tag{72}$$

where $F_M(U)$ comes from the integration over u in $\mathscr{R}$ of the factor $\mathscr{E}(\zeta_u/Z,\ \zeta_G(\boldsymbol{R}_G-\boldsymbol{R}_u)^2,\ M_{uu})$ in Eq. (HSO-120). Replacing ζ_u, Z, $\boldsymbol{R}_u$, and M_{uu} in the factor by u^2, (ζ_G+u^2), $\boldsymbol{R}_I$, and M, respectively, we arrive at

$$F_M(U) = \int_0^1 \mathrm{d}t\ t^{2M}\ \exp[-Ut^2], \tag{73}$$

with

$$U = \zeta_G(\boldsymbol{R}_G-\boldsymbol{R}_I)^2. \tag{74}$$

$\mathscr{S}_G$ has been given in Eq. 69.

C. TEMIs. The two-electron moment integrals (TEMIs) with $\boldsymbol{n}_{12}=\mathbf{0}$, $[\boldsymbol{n}_a, \boldsymbol{n}_c, \mathbf{0}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d]$, are actually the product of one-electron overlap integrals

$$\begin{aligned}[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{0}_{12},\boldsymbol{n}_b,\boldsymbol{n}_d] &= \int\int \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\phi_a\phi_c\phi_b\phi_d \\ &= \left(\int \mathrm{d}\boldsymbol{r}_1\phi_a\phi_b\right)\left(\int \mathrm{d}\boldsymbol{r}_2\phi_c\phi_d\right) \\ &= [\boldsymbol{n}_a,\boldsymbol{n}_b][\boldsymbol{n}_c,\boldsymbol{n}_d]. \qquad (75)\end{aligned}$$

The one-electron overlap integrals $[\boldsymbol{n}_a, \boldsymbol{0}_b]$ satisfy the recurrence relation[17)]

$$[\boldsymbol{n}_a+\boldsymbol{1}_\mu,\boldsymbol{0}_b]=(\boldsymbol{R}_G-\boldsymbol{R}_a)_\mu[\boldsymbol{n}_a,\boldsymbol{0}_b]+\frac{1}{2\zeta_G}N_\mu(\boldsymbol{n}_a)[\boldsymbol{n}_a-\boldsymbol{1}_\mu,\boldsymbol{0}_b] \qquad (76)$$

and so as to $[\boldsymbol{n}_c, \boldsymbol{0}_d]$ with $\boldsymbol{n}_c$, $\boldsymbol{R}_G^{(2)}$, and $\boldsymbol{\zeta}_G^{(2)}$ instead of $\boldsymbol{n}_a$, $\boldsymbol{R}_G$, and $\boldsymbol{\zeta}_G$, respectively, where $\boldsymbol{\zeta}_G^{(2)}$ and $\boldsymbol{R}_G^{(2)}$ mean

$$\zeta_G^{(2)}=\zeta_c+\zeta_d \qquad (77)$$

$$\boldsymbol{R}_G^{(2)}=\frac{1}{\zeta_G^{(2)}}(\zeta_c\boldsymbol{R}_c+\zeta_d\boldsymbol{R}_d). \qquad (78)$$

Then the evaluation of the TEMIs $[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{0}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d]$ is readily accomplished by taking a product of $[\boldsymbol{n}_a, \boldsymbol{0}_b]$ and $[\boldsymbol{n}_c, \boldsymbol{0}_d]$. In order to increase $\boldsymbol{n}_{12}$ in the integrals $[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d]$, we use Eq. (HSO-62). Noting $\boldsymbol{k}_{12}=\boldsymbol{0}$ and $\Theta=0$ (since ζ_{12} is zero), we have

$$\begin{aligned}[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{n}_{12}+\boldsymbol{1}_\mu] = {}&(\boldsymbol{R}_G-\boldsymbol{R}_G^{(2)})_\mu[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{n}_{12}] \\ &+\frac{1}{2\rho_G}N_\mu(\boldsymbol{n}_{12})[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{n}_{12}-\boldsymbol{1}_\mu] \\ &+\frac{1}{2\zeta_G}N_\mu(\boldsymbol{n}_a)[\boldsymbol{n}_a-\boldsymbol{1}_\mu,\boldsymbol{n}_c,\boldsymbol{n}_{12}] \\ &-\frac{1}{2\zeta_G^{(2)}}N_\mu(\boldsymbol{n}_c)[\boldsymbol{n}_a,\boldsymbol{n}_c-\boldsymbol{1}_\mu,\boldsymbol{n}_{12}], \qquad (79)\end{aligned}$$

$$\rho_G=\frac{\zeta_G\zeta_G^{(2)}}{\zeta_G+\zeta_G^{(2)}}, \qquad (80)$$

where $\boldsymbol{0}_b$ and $\boldsymbol{0}_d$ have been omitted for simplicity.

D. GERIs. The generalized electron repulsion integrals (GERIs) $\mathscr{R}[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d]$ involve the integration over u in $\mathscr{R}$[Eq. 43], so that we are to employ auxiliary GERIs which will be denoted as $[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d|m]$

$$[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{n}_{12},\boldsymbol{n}_b,\boldsymbol{n}_d \mid m]=\mathscr{R}\Theta^m[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{n}_{12},\boldsymbol{n}_b,\boldsymbol{n}_d], \qquad (81)$$

$$\Theta=\frac{u^2}{\rho_G+u^2}. \qquad (82)$$

The auxiliary GERIs with $m=0$ are the true GERIs.

The recurrence formula for the auxiliary GERIs with only $\boldsymbol{n}_a$ being nonzero, $[\boldsymbol{n}_a, \boldsymbol{0}_c, \boldsymbol{0}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d|m]$, is reducible from Eq. (HSO-150). Since $\boldsymbol{l}_i$ ($i=a$, c, 12, b, d) are zero, the factor $N_\mu(\boldsymbol{l}_i)$ becomes naught. The recurrence formula takes finally a form of

$$\begin{aligned}&[\boldsymbol{n}_a+\boldsymbol{1}_\mu \mid m] \\ &=(\boldsymbol{R}_G-\boldsymbol{R}_a)_\mu[\boldsymbol{n}_a \mid m]-(\boldsymbol{W}_G-\boldsymbol{R}_G)_\mu[\boldsymbol{n}_a \mid m+1] \\ &\quad+\frac{1}{2\zeta_G}N_\mu(\boldsymbol{n}_a)\left\{[\boldsymbol{n}_a-\boldsymbol{1}_\mu \mid m]-\frac{\rho_G}{\zeta_G}[\boldsymbol{n}_a-\boldsymbol{1}_\mu \mid m+1]\right\}, \qquad (83)\end{aligned}$$

with $\boldsymbol{0}_c$, $\boldsymbol{0}_{12}$, $\boldsymbol{0}_b$, and $\boldsymbol{0}_d$ being omitted. $\boldsymbol{W}_G$ denotes

$$\boldsymbol{W}_G=\frac{1}{\zeta_G+\zeta_G^{(2)}}(\zeta_G\boldsymbol{R}_G+\zeta_G^{(2)}\boldsymbol{R}_G^{(2)}). \qquad (84)$$

The initial integrals of the auxiliary GERIs are reducible from Eq. (HSO-97) to

$$\begin{aligned}[\boldsymbol{0}_a,\boldsymbol{0}_c,\boldsymbol{0}_{12},\boldsymbol{0}_b,\boldsymbol{0}_d \mid m] &= \mathscr{R}\Theta^m[\boldsymbol{0}_a,\boldsymbol{0}_c,\boldsymbol{0}_{12},\boldsymbol{0}_b,\boldsymbol{0}_d] \\ &= 2\left(\frac{\rho_G}{\pi}\right)^{\frac{1}{2}}\mathscr{S}_G\mathscr{S}_G^{(2)}F_m(T), \qquad (85)\end{aligned}$$

where $\mathscr{S}_G$ and $F_m(T)$ have been given in Eqs. 69 and 73, respectively, and $\mathscr{S}_G^{(2)}$ and T mean

$$\mathscr{S}_G^{(2)}=\left(\frac{\pi}{\zeta_G^{(2)}}\right)^{3/2}\exp\left[-\frac{\zeta_c\zeta_d}{\zeta_G^{(2)}}(\boldsymbol{R}_c-\boldsymbol{R}_d)^2\right], \qquad (86)$$

$$T=\rho_G(\boldsymbol{R}_G-\boldsymbol{R}_G^{(2)})^2. \qquad (87)$$

In order to increase the angular momentum $\boldsymbol{n}_{12}$ in $[\boldsymbol{n}_a, \boldsymbol{0}_c, \boldsymbol{0}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d|m]$ we use Eq. (HSO-91). Noting $\boldsymbol{l}_i=\boldsymbol{k}_i=\boldsymbol{0}$ ($i=a$, c, 12, b, d), we have

$$\begin{aligned}&[\boldsymbol{n}_a,\boldsymbol{n}_{12}+\boldsymbol{1}_\mu \mid m] \\ &\quad=(\boldsymbol{R}_G-\boldsymbol{R}_G^{(2)})_\mu\{[\boldsymbol{n}_a,\boldsymbol{n}_{12} \mid m]-[\boldsymbol{n}_a,\boldsymbol{n}_{12} \mid m+1]\} \\ &\quad\quad+\frac{1}{2\rho_G}N_\mu(\boldsymbol{n}_{12})\{[\boldsymbol{n}_a,\boldsymbol{n}_{12}-\boldsymbol{1}_\mu \mid m] \\ &\quad\quad-[\boldsymbol{n}_a,\boldsymbol{n}_{12}-\boldsymbol{1}_\mu \mid m+1]\} \\ &\quad\quad+\frac{1}{2\zeta_G}N_\mu(\boldsymbol{n}_a)\{[\boldsymbol{n}_a-\boldsymbol{1}_\mu,\boldsymbol{n}_{12} \mid m] \\ &\quad\quad-[\boldsymbol{n}_a-\boldsymbol{1}_\mu,\boldsymbol{n}_{12} \mid m+1]\}. \qquad (88)\end{aligned}$$

Here the indices $\boldsymbol{0}_c$, $\boldsymbol{0}_b$, and $\boldsymbol{0}_d$ have been omitted. For the increase of angular momentum $\boldsymbol{n}_c$ in $[\boldsymbol{n}_a, \boldsymbol{0}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d|m]$ the horizontal relation given by Hamilton and Schaefer[18)] is applicable

$$\begin{aligned}&[\boldsymbol{n}_a,\boldsymbol{n}_c+\boldsymbol{1}_\mu,\boldsymbol{n}_{12} \mid m] \\ &\quad=-\frac{\zeta_G}{\zeta_G^{(2)}}[\boldsymbol{n}_a+\boldsymbol{1}_\mu,\boldsymbol{n}_c,\boldsymbol{n}_{12} \mid m] \\ &\quad\quad-\left\{\frac{\zeta_G}{\zeta_G^{(2)}}(\boldsymbol{R}_G-\boldsymbol{R}_a)+(\boldsymbol{R}_G^{(2)}-\boldsymbol{R}_c)\right\}_\mu[\boldsymbol{n}_a,\boldsymbol{n}_c,\boldsymbol{n}_{12} \mid m] \\ &\quad\quad+\frac{\zeta_a}{\zeta_G^{(2)}}[\boldsymbol{n}_a-\boldsymbol{1}_\mu,\boldsymbol{n}_c,\boldsymbol{n}_{12} \mid m] \\ &\quad\quad+\frac{\zeta_c}{\zeta_G^{(2)}}[\boldsymbol{n}_a,\boldsymbol{n}_c-\boldsymbol{1}_\mu,\boldsymbol{n}_{12} \mid m]. \qquad (89)\end{aligned}$$

(The indices $\boldsymbol{0}_b$ and $\boldsymbol{0}_d$ are omitted.) This relation is derived for true electron repulsion integrals, namely, both $\boldsymbol{n}_{12}$ and m being zero in the auxiliary GERIs, however, holds for nonzero values of these indices.

IV. Contracted Integrals

In usual *ab initio* calculations the contracted Gaussian functions are used. The contracted Gaussian function χ_a takes a form of

$$\chi_a=\sum_s D_{as}\phi_{as}. \qquad (90)$$

Here the primitive Gaussian functions ϕ_{as} have the common function center $\boldsymbol{R}_a$ and angular momentum $\boldsymbol{n}_a$ while distinct orbital exponents ζ_{as}. We discuss how the integrals over the primitive Gaussian functions ϕ given in the previous section are to be transformed for the calculation of molecular integrals of the operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, $\mathscr{O}_{2,2n-1}$, $\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$ over the contracted Gaussian functions. In order to distinguish the contracted integrals from the integrals over the primitive Gaussian functions we use brackets (<>).

One-electron moment integrals over the contracted Gaussian functions, $<\boldsymbol{n}_a,\ \boldsymbol{n}_I,\ \boldsymbol{n}_b>$, can be obtained from $<\boldsymbol{n}_a,\ \boldsymbol{0}_I,\ \boldsymbol{0}_b>$

$$< \boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b >= \sum_s \sum_t D_{as} D_{bt} [\boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b] \qquad (91)$$

by making use of the horizontal relation (63) as

$$\begin{aligned} &< \boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b > \\ &\quad =< \boldsymbol{n}_a + \boldsymbol{1}_\mu, \boldsymbol{n}_I, \boldsymbol{n}_b > +(\boldsymbol{R}_a - \boldsymbol{R}_I)_\mu < \boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b >, \end{aligned} \qquad (92)$$

$$\begin{aligned} &< \boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b + \boldsymbol{1}_\mu > \\ &\quad =< \boldsymbol{n}_a + \boldsymbol{1}_\mu, \boldsymbol{n}_I, \boldsymbol{n}_b > +(\boldsymbol{R}_a - \boldsymbol{R}_b)_\mu < \boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b > . \end{aligned} \qquad (93)$$

Then the molecular integrals of $\mathscr{O}_{1,2n}$ over the contracted Gaussian functions are readily calculated by the use of a set of $<\boldsymbol{n}_a,\ \boldsymbol{n}_I,\ \boldsymbol{n}_b>$ [see Eq. 37] as

$$\begin{aligned} &\int \mathrm{d}\boldsymbol{r} \chi_a \mathscr{O}_{1,2n} \chi_b \\ &= \sum_s \sum_t D_{as} D_{bt} \int \mathrm{d}\boldsymbol{r} \phi_{as} \mathscr{O}_{1,2n} \phi_{bt} \\ &= \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} \sum_s \sum_t D_{as} D_{bt} [\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b] \\ &= \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} < \boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b > . \end{aligned} \qquad (94)$$

If we multiply $2\zeta_{bt}$ at the calculation of $<\boldsymbol{n}_a,\ \boldsymbol{0}_I,\ \boldsymbol{0}_b>$ in Eq. 91

$$< \boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b; \zeta_b >= \sum_s \sum_t D_{as} D_{bt} 2\zeta_{bt} [\boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b], \qquad (95)$$

and use the horizontal relation (63), we can get a set of contracted integrals taking a form of $<\boldsymbol{n}_a,\ \boldsymbol{n}_I,\ \boldsymbol{n}_b;\ \zeta_b>$ then we have the molecular integrals of $\mathscr{O}_{2,2n}$ [Eq. 41] as

$$\begin{aligned} \int \mathrm{d}\boldsymbol{r} \chi_a \mathscr{O}_{2,2n} \chi_b = &- \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} \\ &\times \sum_{\mu=x,y,z} \{< \boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b + \boldsymbol{1}_\mu; \zeta_b > \\ &- N_\mu(\boldsymbol{n}_b) < \boldsymbol{n}_a, \boldsymbol{n}_I + \boldsymbol{1}_\mu, \boldsymbol{n}_b - \boldsymbol{1}_\mu >\}. \end{aligned} \qquad (96)$$

Similarly we can obtain the remaining molecular integrals over the contracted Gaussian functions. Necessary contracted integrals are sets of

$$\begin{array}{ll} <\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b \mid 0>, & <\boldsymbol{n}_a, \boldsymbol{n}_I, \boldsymbol{n}_b \mid 0; \zeta_b>, \\ <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d>, & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d; \zeta_b>, \\ & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d; \zeta_d>, \\ <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d \mid 0>, & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d \mid 0; \zeta_b>, \\ \text{and} & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{n}_b, \boldsymbol{n}_d \mid 0; \zeta_d>, \end{array}$$

which are obtainable by the use of the horizontal relation (63) from sets of corresponding integrals with some angular momenta being zero, namely,

$$\begin{array}{ll} <\boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b \mid 0>, & <\boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b \mid 0; \zeta_b>, \\ <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d>, & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d; \zeta_b>, \\ & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d; \zeta_d>, \\ <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d \mid 0>, & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d \mid 0; \zeta_b>, \\ \text{and} & <\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d \mid 0; \zeta_d> . \end{array}$$

The integrals of $\mathscr{O}_{4,2n-1}$, for instance, become

$$\begin{aligned} &\int\int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \chi_a(\boldsymbol{r}_1) \chi_c(\boldsymbol{r}_2) \mathscr{O}_{4,2n-1} \chi_b(\boldsymbol{r}_1) \chi_d(\boldsymbol{r}_2) \\ &\quad = - \sum_{k=0}^{n} \sum_{l=0}^{k} \binom{n}{k} \binom{k}{l} \\ &\qquad \times \sum_{\mu=x,y,z} \{< \boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b + \boldsymbol{1}_\mu; \boldsymbol{n}_d \mid 0; \zeta_b > \\ &\qquad - < \boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b, \boldsymbol{n}_d + \boldsymbol{1}_\mu; \mid 0; \zeta_d > \\ &\qquad - N_\mu(\boldsymbol{n}_b) < \boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_b - \boldsymbol{1}_\mu, \boldsymbol{n}_d \mid 0 > \\ &\qquad + N_\mu(\boldsymbol{n}_d) < \boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{n}_{12} + \boldsymbol{1}_\mu, \boldsymbol{n}_d, \boldsymbol{n}_d - \boldsymbol{1}_\mu \mid 0 >\}, \end{aligned} \qquad (97)$$

with $<\boldsymbol{n}_a,\ \boldsymbol{n}_c,\ \boldsymbol{n}_{12}+\boldsymbol{1}_\mu,\ \boldsymbol{n}_b+\boldsymbol{1}_\mu,\ \boldsymbol{n}_d|0;\ \zeta_b>$, for example, obtained by the use of the horizontal relation from $<\boldsymbol{n}'_a,\ \boldsymbol{n}'_c,\ \boldsymbol{n}'_{12},\ \boldsymbol{0}_b,\ \boldsymbol{0}_d,\ |0;\ \zeta_b>$ which has been calculated by

$$\begin{aligned} &< \boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d \mid 0; \zeta_b > \\ &\quad = \sum_s \sum_t \sum_u \sum_v D_{as} D_{bt} D_{cu} D_{dv} \\ &\qquad \times 2\zeta_{bt} [\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d \mid 0]. \end{aligned} \qquad (98)$$

V. Strategy of Computation

The calculation of molecular integrals of the operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, $\mathscr{O}_{2,2n-1}$, $\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$ should be carried out with the following scheme:

1) calculate primitive integrals with some angular momenta of basis functions being zero;

OEMIs	$[\boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b]$,
GNAIs	$[\boldsymbol{n}_a, \boldsymbol{0}_I, \boldsymbol{0}_b \mid M]$,
TEMIs	$[\boldsymbol{n}_a, \boldsymbol{n}_c, \boldsymbol{0}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d]$,
and GERIs	$[\boldsymbol{n}_a, \boldsymbol{0}_c, \boldsymbol{0}_{12}, \boldsymbol{0}_b, \boldsymbol{0}_d \mid m]$,

by the use of the recurrence formulas Eqs. 65, 71, 76, and 83, respectively,

2) then increase angular momentum $\boldsymbol{n}_{12}$ in TEMIs to $[\boldsymbol{n}'_a,\ \boldsymbol{n}'_c,\ \boldsymbol{n}'_{12},\ \boldsymbol{0}_b,\ \boldsymbol{0}_d]$ by making use of the equality (79), and $\boldsymbol{n}_c$ and $\boldsymbol{n}_{12}$ in the GERIs to $[\boldsymbol{n}'_a,\ \boldsymbol{n}'_c,\ \boldsymbol{n}'_{12},\ \boldsymbol{0}_b,\ \boldsymbol{0}_d,\ |0]$ with the helps of equalities (89) and (88), respectively,

3) transform the primitive integrals into contracted ones

OEMIs; $<\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b>$ and $<\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b; \zeta_b>$,
GNAIs; $<\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b|0>$ and $<\boldsymbol{n}'_a, \mathbf{0}_I, \mathbf{0}_b|0; \zeta_b>$,
TEMIs; $<\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d>$, $<\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d; \zeta_b>$,
and $<\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d; \zeta_d>$,
and
GERIs; $<\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d|0>$,$<\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d|0; \zeta_b>$,
and $<\boldsymbol{n}'_a, \boldsymbol{n}'_c, \boldsymbol{n}'_{12}, \mathbf{0}_b, \mathbf{0}_d|0; \zeta_d>$,

such as in Eqs. 91 and 98,

4) increase the remaining zero angular momenta of basis functions in the contracted integrals by the use of the horizontal relation (63), and finally

5) multiply the binomial coefficients and take sums of them in order to get the contracted molecular integrals of the operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, $\mathscr{O}_{2,2n-1}$, $\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$.

It is to be noted that the use of the recurrence and horizontal relations is one of keys to efficient calculations in the above procedure. We also note that when we have prepared integrals for the maximum value $n_{\max}$ of n in the operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, $\mathscr{O}_{2,2n-1}$, $\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$ we can reuse them for lower values of n. This feature also makes the present scheme efficient.

The formulas are complicated, but their computation can be made simple. All the calculations can be decomposed into a set of the following basic operation,

$$\text{(integral)} \xleftarrow{\text{addition}} \text{(coefficient)} \times \text{(integral)}, \tag{99}$$

namely, an addition of a product of a coefficient and an integral to another integral. If we assign serial numbers to all the coefficients and integrals for a particular set of angular momenta $\boldsymbol{n}_a$, $\boldsymbol{n}_b$, $\boldsymbol{n}_c$, and $\boldsymbol{n}_d$ of the basis functions, and express necessary basic operations in terms of the serial numbers;

$$\begin{aligned}&\text{(serial number of integral)}\\ &\xleftarrow{\text{addition}} \text{(serial number of coefficient)}\\ &\qquad \times\text{(serial number of integral)},\end{aligned} \tag{100}$$

all the calculations are expressible as a set of three serial numbers. This scheme simplifies the management of intermediate data in the calculation and the removement of unnecessary arithmetic operations in the basic operations. The generation of the basic operations in terms of the serial numbers is not time-consuming, so that it can be carried out for each set of angular momenta $\boldsymbol{n}_a$, $\boldsymbol{n}_b$, $\boldsymbol{n}_c$, and $\boldsymbol{n}_d$ before actual evaluation of molecular integrals without sacrificing the computer time. Of course, it is more efficient to store the basic operations as a data or as arithmetic codes in the program.

VI. Summary

We have formulated the molecular integrals over the cartesian Gaussian functions of the spatial operators $\mathscr{O}_{1,2n}$, $\mathscr{O}_{1,2n+1}$, $\mathscr{O}_{2,2n}$, $\mathscr{O}_{2,2n-1}$, $\mathscr{O}_{3,2n}$, $\mathscr{O}_{3,2n+1}$, $\mathscr{O}_{4,2n}$, and $\mathscr{O}_{4,2n-1}$ in the equation of correlated electronic wave function satisfying the two-particle correlation cusp condition. The molecular integrals of these operators have been classified into one-electron moment integrals, generalized nuclear attraction integrals, two-electron moment integrals, and generalized electron repulsion integrals, and their recurrence formulas are reduced from those of the integrals over hypergaussian functions given by Honda, Sato, and Obara.[15] An efficient computational method is proposed by decomposing necessary calculations into five steps, which allows us to carry out recursive calculations, to make use of the horizontal relation, to reuse intermediate integrals as much as possible, and to employ the contracted basis functions. Decomposition of all the calculations into a set of basic operations, which consist of a set of three serial numbers of integrals and coefficients, is also proposed in order to avoid cumbersome tasks at the coding of programs, such as, whether right integrals and coefficients are referred, evaluated values are added to right integrals, and unnecessary arithmetic operations are included.

The present formulas for the molecular integrals are closely related to those given by Largo-Cabrerizo and Clementi.[9] Their formulas, however, are given in terms of primitive parameters without using intermediate integrals, which is in contrast to the present formulation. Therefore their formulas are not readily useable for an efficient computation of the molecular integrals.

The calculations based on the present formulation of molecular integrals are in progress.

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