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General recurrence formulas for molecular integrals over Cartesian Gaussian functions

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General recurrence formulas for various types of one- and two-electron molecular integrals over Cartesian Gaussian functions are derived by introducing *basic* integrals. These formulas are capable of dealing with (1) molecular integrals with any spatial operators in the nonrelativistic forms of the relativistic wave equations, (2) those with the kernel of the Fourier transform, (3) those with arbitrarily defined spatial operators so far as the integrals can be expressed in terms of the basic integrals, and (4) any order of their derivatives with respect to the function centers in the above integrals. Thus, the present formulation can cover a large class of molecular integrals necessary for theoretical studies of molecular systems by *ab initio* calculations, and furthermore provides us with an efficient scheme of computing them by virtue of its recursive nature.

I. INTRODUCTION

The basic step in *ab initio* calculations of molecular electronic structure is the computation of molecular integrals. Recent developments in theoretical chemistry require various types of molecular integrals, such as the Fourier transformed ones necessary for the calculations with the momentum–space representation, analytical derivatives of molecular integrals needed for the study of chemical reactions, and molecular integrals for the relativistic interactions as well as for the nonrelativistic ones. Several types of molecular integrals have been formulated as reviewed by Saunders,[1] and special efforts have been continued for the time-consuming calculation of electron repulsion integrals.[2–13] These formulations are useful for some types of molecular integrals, but not applicable to others. Thus, it is desirable to have a general formulation of molecular integrals, which gives an efficient computational scheme applicable to any type of molecular integral. This paper is aimed at such a generalization over Cartesian Gaussian functions introduced by Boys[2] and now extensively in use.

There are available a couple of schemes, which can be readily generalized. The first one proposed by Boys[2] differentiates the expression for the target molecular integrals over *s*-type functions with respect to the function centers to get expressions over higher angular momentum functions. This scheme is formally simple, but actually tedious mathematical manipulations are involved for higher angular momentum functions than *p*. The second is that by McMurchie and Davidson.[4] They proposed to use the Hermite Gaussian functions as the intermediaries for molecular integrals over Cartesian Gaussian functions. The differential relation of the Hermite Gaussian functions leads to simple expressions for molecular integrals over the Hermite Gaussian functions. Although this step is efficient computationally, the scheme is indirect in the sense that these integrals have to be transformed to those over the Cartesian Gaussian functions, and the transformation would demand careful consideration for efficient computations. Recently we have given[13] recurrence formulas for several types of molecular integrals over Cartesian Gaussian functions in terms of three-center overlap integrals. This scheme is a direct one, and has been found to be efficient for calculating electron repulsion integrals and their first derivatives both on scalar and vector computers.[13] In the present work we generalize this recursive formulation so as to be suitable to general types of molecular integrals over Cartesian Gaussian functions.

First we introduce *basic* one- and two-electron integrals, which allow us to formulate various types of one- and two-electron molecular integrals on the same ground, and then give recurrence relations satisfied by the basic integrals. Since many of general molecular integrals can be given as a linear combination of the basic integrals, the recurrence relations for these molecular integrals can be readily obtained from those for the basic integrals. The present formulation is applicable to molecular integrals (1) having any spatial operator in the nonrelativistic forms of the relativistic wave equations in addition to ordinary nonrelativistic operators, (2) of the Fourier transform, which would be necessary for theoretical study in the momentum–space representation, (3) of arbitrarily defined spatial operators as far as the molecular integrals can be expressed in terms of the basic integrals, e.g., the spherically symmetric part of the effective core potential[14] proposed by Kahn, Baybutt, and Truhlar, and (4) having any order of their derivatives with respect to the function centers of the Cartesian Gaussian functions, required for the "analytical derivative method."[15,16] The resulting expressions for the target molecular integrals take recursive forms, thus leading to efficient computation.[13]

In the next section the basic integrals are defined and then the recurrence formulas for the basic two-electron integrals are derived. In Sec. III mathematical properties of the basic two-electron integrals are discussed from the computational viewpoint, and concluding remarks are drawn in the last section. Expressions for the basic one-electron integrals, which are reducible from those for the basic two-electron integrals, are collected in the Appendix.

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II. GENERAL RECURRENCE FORMULAS FOR MOLECULAR INTEGRALS OVER CARTESIAN GAUSSIAN FUNCTIONS

A. Cartesian Gaussian functions

We shall closely follow the definitions and notation of Ref. 13. The unnormalized Cartesian Gaussian function with origin at $\mathbf{R}$ has the form

$$\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)=(r_x-R_x)^{n_x}(r_y-R_y)^{n_y}(r_z-R_z)^{n_z}\times\exp[-\zeta(\mathbf{r}-\mathbf{R})^2] \tag{1}$$

with the normalization constant

$$\mathcal{N}(\mathbf{n},\zeta)=\left(\frac{2\zeta}{\pi}\right)^{3/4}(4\zeta)^{(n_x+n_y+n_z)/2}\times[(2n_x-1)!!(2n_y-1)!!(2n_z-1)!!]^{-1/2}. \tag{2}$$

Here $\mathbf{n}$ denotes a set of nonnegative integers n_x, n_y, and n_z,

$$\mathbf{n}=(n_x,n_y,n_z), \tag{3}$$

and let us define

$$|\mathbf{n}|=n_x+n_y+n_z, \tag{4}$$

which is closely related to the total angular momentum quantum number. $|\mathbf{n}|$ and $\mathbf{n}$ will be, hereafter, termed the *angular momentum* and the *angular momentum index*, respectively.

We begin with the basic equations for the Cartesian Gaussian functions that will be utilized in the following derivations of molecular integrals. With the definition Eq. (1) of the Cartesian Gaussian function, one can write the Cartesian Gaussian function having an angular momentum higher by one as

$$\varphi(\mathbf{r}-\mathbf{R};\mathbf{n}+\mathbf{1}_\mu,\zeta)=(\mathbf{r}-\mathbf{R})_\mu\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)\quad(\mu=x,y,z). \tag{5}$$

Decomposing a Cartesian Gaussian function $\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)$ into a product of an "exponential" factor g_e,

$$g_e=\exp[-\zeta(\mathbf{r}-\mathbf{R})^2] \tag{6}$$

and an "angular" factor $g_a(\mathbf{n})$,

$$g_a(\mathbf{n})=(r_x-R_x)^{n_x}(r_y-R_y)^{n_y}(r_z-R_z)^{n_z}, \tag{7}$$

we find the following differential relations:

$$\frac{\partial}{\partial r_\mu}g_e=-2\zeta(\mathbf{r}-\mathbf{R})_\mu g_e \tag{8}$$

and

$$\frac{\partial}{\partial r_\mu}g_a(\mathbf{n})=N_\mu(\mathbf{n})g_a(\mathbf{n}-\mathbf{1}_\mu), \tag{9}$$

where $N_\mu(\mathbf{n})$, standing for n_μ, is meant to take the value of the μ component of the angular momentum index $\mathbf{n}$, and thus $N_\mu(\mathbf{1}_\nu)$ plays the same role as Kronecker's delta $\delta_{\mu\nu}$. It follows readily that

$$N_\mu(\mathbf{n}+\mathbf{n}')=N_\mu(\mathbf{n})+N_\mu(\mathbf{n}'). \tag{10}$$

Combining Eqs. (5), (8), and (9) together with the relation

$$\frac{\partial}{\partial R_\mu}\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)=-\frac{\partial}{\partial r_\mu}\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta), \tag{11}$$

one gets the differential relation of the Cartesian Gaussian functions with respect to the function center R_μ:

$$\frac{\partial}{\partial R_\mu}\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)=2\zeta\varphi(\mathbf{r}-\mathbf{R};\mathbf{n}+\mathbf{1}_\mu,\zeta)-N_\mu(\mathbf{n})\varphi(\mathbf{r}-\mathbf{R};\mathbf{n}-\mathbf{1}_\mu,\zeta). \tag{12}$$

As $|r_\mu|$ goes to infinity the exponential factor g_e decreases to zero much faster than the increase of the angular factor $g_a(\mathbf{n})$. Thus we have

$$\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)\to 0\quad(|r_\mu|\to\infty,\zeta>0), \tag{13}$$

which will be utilized in integration by part over the electron coordinate.

A product of a Cartesian Gaussian function and the kernel $\exp[i\,\mathbf{k}\cdot\mathbf{r}]$ of the Fourier transform can be reduced[17] to a linear combination of Cartesian Gaussian functions having a *complex* function center $\mathbf{R}^\dagger$:

$$\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)=\sum_{s_x=0}^{n_x}\sum_{s_y=0}^{n_y}\sum_{s_z=0}^{n_z}C(\mathbf{R},\mathbf{b},\mathbf{n},\mathbf{s})\varphi(\mathbf{r}-\mathbf{R}^\dagger;\mathbf{s},\zeta), \tag{14}$$

where

$$\mathbf{R}^\dagger=\mathbf{R}+\mathbf{b}, \tag{15}$$

$$\mathbf{b}=\frac{i}{2\zeta}\mathbf{k}, \tag{16}$$

$$\mathbf{s}=(s_x,s_y,s_z), \tag{17}$$

and the coefficient $C(\mathbf{R},\mathbf{b},\mathbf{n},\mathbf{s})$,

$$C(\mathbf{R},\mathbf{b},\mathbf{n},\mathbf{s})=\exp[2\zeta\mathbf{b}\cdot\mathbf{R}+\zeta\mathbf{b}^2]\binom{n_x}{s_x}\binom{n_y}{s_y}\binom{n_z}{s_z}\times b_x^{n_x-s_x}b_y^{n_y-s_y}b_z^{n_z-s_z} \tag{18}$$

comes from the following expression for $(r_\mu-R_\mu)^n$ in the angular factor $g_a(\mathbf{n})$:

$$(r_\mu-R_\mu)^n=\{(r_\mu-R_\mu^\dagger)+b_\mu\}^n=\sum_{s=0}^{n}\binom{n}{s}b_\mu^{n-s}(r_\mu-R_\mu^\dagger)^s. \tag{19}$$

Differentiation of Eq. (14) with respect to $\mathbf{R}$ leads to

$$\mathcal{D}_d(\mathbf{l})\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)=\mathcal{D}_{\mathrm{EF}}(\mathbf{t},\mathbf{s})\mathcal{D}_d^\dagger(\mathbf{t})\varphi(\mathbf{r}-\mathbf{R}^\dagger;\mathbf{s},\zeta), \tag{20}$$

where $\mathcal{D}_d(\mathbf{l})$ is a product of differential operators with respect to $\mathbf{R}$,

$$\mathcal{D}_d(\mathbf{l})=\left(\frac{\partial}{\partial R_x}\right)^{l_x}\left(\frac{\partial}{\partial R_y}\right)^{l_y}\left(\frac{\partial}{\partial R_z}\right)^{l_z}, \tag{21}$$

$$\mathbf{l}=(l_x,l_y,l_z), \tag{22}$$

and the operator $\mathcal{D}_d^\dagger(\mathbf{t})$ on the right-hand side of Eq. (20) denotes a similar product of differential operators with respect to $\mathbf{R}^\dagger$ rather than $\mathbf{R}$. Here we have utilized the following relation:

$$\mathcal{Q}_d(\mathbf{t})\varphi(\mathbf{r}-\mathbf{R}^{\dagger};\mathbf{s},\zeta)=\mathcal{Q}_d^{\dagger}(\mathbf{t})\varphi(\mathbf{r}-\mathbf{R}^{\dagger};\mathbf{s},\zeta). \quad (23)$$

We refer to $\mathbf{l}$ or $\mathbf{t}$ as the *derivative index*. $\mathcal{Q}_{\mathrm{EF}}(\mathbf{t},\mathbf{s})$ in Eq. (20) is an abbreviated expression for the sixfold summation over the derivative index $\mathbf{t}$ and the angular momentum index $\mathbf{s}$:

$$\mathcal{Q}_{\mathrm{EF}}=\sum_{t_x=0}^{l_x}\sum_{t_y=0}^{l_y}\sum_{t_z=0}^{l_z}\sum_{s_x=0}^{n_x}\sum_{s_y=0}^{n_y}\sum_{s_z=0}^{n_z}D(2\zeta\mathbf{b},\mathbf{l},\mathbf{t})C(\mathbf{R},\mathbf{b},\mathbf{n},\mathbf{s}), \quad (24)$$

where the coefficient $D(2\zeta\mathbf{b},\mathbf{l},\mathbf{t})$ follows from the differentiations of $C(\mathbf{R},\mathbf{b},\mathbf{n},\mathbf{s})$;

$$D(2\zeta\mathbf{b},\mathbf{l},\mathbf{t})=\binom{l_x}{t_x}\binom{l_y}{t_y}\binom{l_z}{t_z}\times(2\zeta b_x)^{l_x-t_x}(2\zeta b_y)^{l_y-t_y}(2\zeta b_z)^{l_z-t_z}. \quad (25)$$

Equations (14) and (20) provide us with four useful equations which allow us to rewrite molecular integrals containing the real Cartesian Gaussian functions and the kernel $\exp[i\,\mathbf{k}\cdot\mathbf{r}]$ in their integrands into those containing the complex Cartesian Gaussian functions, or vice versa. Multiplying Eq. (14) by $(\mathbf{r}-\mathbf{R}^{\dagger})_{\mu}$, rewriting it with the aid of Eqs. (5) and (15), and then finally operating $\mathcal{Q}_d(\mathbf{l})$, we get the first equation increasing the angular mementum index $\mathbf{s}$ of the complex Cartesian Gaussian function to $\mathbf{s}+\mathbf{1}_{\mu}$:

$$\begin{aligned}\mathcal{Q}_{\mathrm{EF}}\,\mathcal{Q}_d^{\dagger}(\mathbf{t})\varphi(\mathbf{r}-\mathbf{R}^{\dagger};\mathbf{s}+\mathbf{1}_{\mu},\zeta)&=\mathcal{Q}_d(\mathbf{l})\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n}+\mathbf{1}_{\mu},\zeta)\\&\quad-b_{\mu}\mathcal{Q}_d(\mathbf{l})\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta). \quad (26)\end{aligned}$$

Differentiating Eq. (14) with respect to R_{μ}, rewriting it by the use of Eqs. (12) and (14) as well as Eq. (26) having $\mathbf{l}=(0,0,0)$, and finally operating $\mathcal{Q}_d(\mathbf{l})$, we have the second equation decreasing the angular momentum index $\mathbf{s}$ of the complex function to $\mathbf{s}-\mathbf{1}_{\mu}$:

$$\begin{aligned}\mathcal{Q}_{\mathrm{EF}}N_{\mu}(\mathbf{s})\mathcal{Q}_d^{\dagger}(\mathbf{t})\varphi(\mathbf{r}-\mathbf{R}^{\dagger};\mathbf{s}-\mathbf{1}_{\mu},\zeta)&=N_{\mu}(\mathbf{n})\mathcal{Q}_d(\mathbf{l})\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n}-\mathbf{1}_{\mu},\zeta). \quad (27)\end{aligned}$$

Differentiating Eq. (20) with respect to R_{μ} and then rewriting it by the use of Eq. (20), we find the third equation in which the derivative index is $\mathbf{t}+\mathbf{1}_{\mu}$:

$$\begin{aligned}&\mathcal{Q}_{\mathrm{EF}}\mathcal{Q}_d^{\dagger}(\mathbf{t}+\mathbf{1}_{\mu})\varphi(\mathbf{r}-\mathbf{R}^{\dagger};\mathbf{s},\zeta)\\&=\{\mathcal{Q}_d(\mathbf{l}+\mathbf{1}_{\mu})-2\zeta b_{\mu}\mathcal{Q}_d(\mathbf{l})\}\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta). \quad (28)\end{aligned}$$

Replacing $\mathbf{l}$ in Eq. (20) by $\mathbf{l}-\mathbf{1}_{\mu}$, and multiplying by $N_{\mu}(\mathbf{l})$, we arrive at the final equation in which the derivative index is $\mathbf{t}-\mathbf{l}_{\mu}$:

$$\begin{aligned}\mathcal{Q}_{\mathrm{EF}}N_{\mu}(\mathbf{t})\mathcal{Q}_d^{\dagger}(\mathbf{t}-\mathbf{1}_{\mu})\varphi(\mathbf{r}-\mathbf{R}^{\dagger};\mathbf{s};\zeta)&=N_{\mu}(\mathbf{l})\mathcal{Q}_d(\mathbf{l}-\mathbf{1}_{\mu})\exp[i\,\mathbf{k}\cdot\mathbf{r}]\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta), \quad (29)\end{aligned}$$

where the following relations have been used:

$$N_{\mu}(\mathbf{l})D(2\zeta\mathbf{b},\mathbf{l}-\mathbf{1}_{\mu},\mathbf{t}-\mathbf{1}_{\mu})=N_{\mu}(\mathbf{t})D(2\zeta\mathbf{b},\mathbf{l},\mathbf{t}), \quad (30)$$

$$\sum_{t=0}^{l-1}H(t)=\sum_{t=1}^{l}H(t-1), \quad (31)$$

and

$$\sum_{t=1}^{l}tH(t)=\sum_{t=0}^{l}tH(t). \quad (32)$$

We note that the right-hand sides of Eqs. (26)–(29) do not include the sixfold summation appearing in $\mathcal{Q}_{\mathrm{EF}}$ [Eq. (24)].

B. Definition of basic integrals

In performing *ab initio* calculations of molecular systems by using the Cartesian Gaussian functions

$$\varphi_i(\mathbf{r})=\varphi(\mathbf{r}-\mathbf{R}_i;\mathbf{n}_i,\zeta_i), \quad (33)$$

one has to evaluate one-electron integrals (OEI's)

$$(\mathbf{n}_a|\mathscr{O}(\mathbf{r})|\mathbf{n}_b)=\int d\mathbf{r}\,\varphi_a(\mathbf{r})\mathscr{O}(\mathbf{r})\varphi_b(\mathbf{r}) \quad (34)$$

and two-electron integrals (TEI's)

$$(\mathbf{n}_a\mathbf{n}_b|\mathscr{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{n}_c\mathbf{n}_d)=\int d\mathbf{r}_1\int d\mathbf{r}_2\,\varphi_a(\mathbf{r}_1)\varphi_c(\mathbf{r}_2)\times\mathscr{O}(\mathbf{r}_1,\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\varphi_d(\mathbf{r}_2). \quad (35)$$

Here $\mathscr{O}(\mathbf{r})$ and $\mathscr{O}(\mathbf{r}_1,\mathbf{r}_2)$ are one- and two-electron operators, respectively, in the Hamiltonian $\mathscr{H}$ of the equation

$$\mathscr{H}\Psi=E\Psi, \quad (36)$$

which is either nonrelativistic, with two components for each electron, or relativistic with four components for each electron. When a molecule is in a uniform external field, the time-independent relativistic wave equation is given by using spatial operators $\mathbf{r}-\mathbf{R}$, $|\mathbf{r}-\mathbf{R}|^{-\lambda}$, $|\mathbf{r}_1-\mathbf{r}_2|^{-\lambda}$, and $\mathbf{p}(=-i\hbar\nabla=-i\hbar\partial/\partial\mathbf{r})$, as well as spin matrices. Therefore, the reduced relativistic equation to the nonrelativistic form includes products of the above spatial operators[18]; for instance, the spatial part of the operators for the orbital Zeeman interaction $\mathscr{L}_{\mu}$, the electron–electron orbital interaction $\mathscr{E}_{\mu\nu}$, and the electron spin–spin dipolar interaction $\mathscr{R}_{\mu\nu}$ become

$$\begin{aligned}\mathscr{L}_{\mu}&=\{(\mathbf{r}-\mathbf{R}_s)\times\nabla\}_{\mu}\\&=(\mathbf{r}-\mathbf{R}_s)_{\mu+}\frac{\partial}{\partial r_{\mu-}}-(\mathbf{r}-\mathbf{R}_s)_{\mu-}\frac{\partial}{\partial r_{\mu+}}, \quad (37)\end{aligned}$$

$$\mathscr{E}_{\mu\nu}=\frac{(\mathbf{r}_1-\mathbf{r}_2)_{\mu}}{|\mathbf{r}_1-\mathbf{r}_2|^3}\nabla_{2\nu}=\left(\frac{\partial}{\partial r_{2\mu}}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right)\frac{\partial}{\partial r_{2\nu}}, \quad (38)$$

and

$$\begin{aligned}\mathscr{R}_{\mu\nu}&=\frac{\delta_{\mu\nu}}{|\mathbf{r}_1-\mathbf{r}_2|^3}-3\frac{(\mathbf{r}_1-\mathbf{r}_2)_{\mu}(\mathbf{r}_1-\mathbf{r}_2)_{\nu}}{|\mathbf{r}_1-\mathbf{r}_2|^5}\\&=-\left\{\frac{\partial^2}{\partial r_{2\mu}\partial r_{2\nu}}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right\}, \quad (39)\end{aligned}$$

respectively, where $\mu+$ and $\mu-$ denote the next and the preceding component of μ, respectively, in a cyclic order of x, y, z. The Dirac delta function $\delta(\mathbf{r}-\mathbf{R})$ is also involved in the reduced relativistic Hamiltonian as a substitute for the operator $(4\pi)^{-1}(\nabla^2|\mathbf{r}-\mathbf{R}|^{-1})$, such as that for the Fermi contact hyperfine interaction. Another type of molecular in-

tegral important in *ab initio* calculations are the derivatives of the OEI's and TEI's:

$$\mathscr{Q}_d(\mathbf{l})(\mathrm{OEI}) = \left(\frac{\partial}{\partial R_x}\right)^{l_x}\left(\frac{\partial}{\partial R_y}\right)^{l_y}\left(\frac{\partial}{\partial R_z}\right)^{l_z} \times (\mathbf{n}_a|\mathscr{O}(\mathbf{r})|\mathbf{n}_b) \tag{40}$$

and

$$\mathscr{Q}_d(\mathbf{l})(\mathrm{TEI}) = \left(\frac{\partial}{\partial R_x}\right)^{l_x}\left(\frac{\partial}{\partial R_y}\right)^{l_y}\left(\frac{\partial}{\partial R_z}\right)^{l_z} \times (\mathbf{n}_a\mathbf{n}_b|\mathscr{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{n}_c\mathbf{n}_d) \tag{41}$$

with respect to the coordinates of the function center $\mathbf{R}$, which are necessary in the analytical derivative method.[15,16]

Before formulating these molecular integrals, we look over the mathematical relations concerning the above spatial operators. As is well known, the above multiplicative operators $\mathbf{r}-\mathbf{R}$, $\delta(\mathbf{r}-\mathbf{R})$, and $|\mathbf{r}-\mathbf{R}|^{-\lambda}$ can be expressed in terms of the unnormalized Cartesian Gaussian functions. The $|\mathbf{n}|$th order moment operator is the function with the angular momentum $|\mathbf{n}|$ and the zero orbital exponent

$$\begin{aligned}(r_x-R_x)^{n_x}(r_y-R_y)^{n_y}(r_z-R_z)^{n_z} &= \{\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta)\}_{\zeta=0} \\ &= \lim_{\zeta\to 0}\varphi(\mathbf{r}-\mathbf{R};\mathbf{n};\zeta),\end{aligned} \tag{42}$$

the Dirac delta function $\delta(\mathbf{r}-\mathbf{R})$ is given by the s-type function

$$\delta(\mathbf{r}-\mathbf{R}) = \lim_{\zeta\to\infty}\left(\frac{\zeta}{\pi}\right)^{3/2}\varphi(\mathbf{r}-\mathbf{R};\mathbf{0},\zeta), \tag{43}$$

and the operator $|\mathbf{r}-\mathbf{R}|^{-\lambda}$ can be expressed as an integral of the s-type function over the square root of its orbital exponent u^2, namely, the Laplace transform of the operator

$$\left(\frac{1}{|\mathbf{r}-\mathbf{R}|}\right)^{\lambda} = \int_0^\infty du\,\frac{2u^{\lambda-1}}{\Gamma(\lambda/2)}\varphi(\mathbf{r}-\mathbf{R};\mathbf{0},u^2), \tag{44}$$

where $\Gamma(\lambda/2)$ is the Gamma function, and for $\lambda=1$, $\Gamma(1/2)=\pi^{1/2}$. By virtue of Eq. (11), the differential operator $i\hbar\partial/\partial\mathbf{R}$ plays the same role as $\mathbf{p}(=-i\hbar\partial/\partial\mathbf{r})$ when it operates on the Cartesian Gaussian function

$$\begin{aligned}\mathbf{p}\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta) &= -i\hbar\frac{\partial}{\partial\mathbf{r}}\varphi(\mathbf{r}-\mathbf{R};\mathbf{n},\zeta) \\ &= i\hbar\frac{\partial}{\partial\mathbf{R}}\varphi(\mathbf{r}-\mathbf{R},\mathbf{n},\zeta),\end{aligned} \tag{45}$$

and hence $\mathbf{p}$ can be treated similar to the differential operators in $\mathscr{Q}_d(\mathbf{l})$. The Leibnitz relation for integration by part is also useful to treat the operator $\partial/\partial\mathbf{r}$ because of Eq. (13):

$$\begin{aligned}(\mathbf{n}_a|\left\{\frac{\partial}{\partial r_\mu}\cdot\mathscr{O}(\mathbf{r})\right\}|\mathbf{n}_b) &= -\int d\mathbf{r}\left\{\frac{\partial}{\partial r_\mu}\cdot\varphi_a\right\}\mathscr{O}(\mathbf{r})\varphi_b - \int d\mathbf{r}\,\varphi_a\mathscr{O}(\mathbf{r})\left\{\frac{\partial}{\partial r_\mu}\cdot\varphi_b\right\} \\ &= \left\{\frac{\partial}{\partial R_{a\mu}}+\frac{\partial}{\partial R_{b\mu}}\right\}(\mathbf{n}_a|\mathscr{O}(\mathbf{r})|\mathbf{n}_b).\end{aligned} \tag{46}$$

Combination of these mathematical relations reduces molecular integrals with the operators $\mathscr{T}_\mu$, $\mathscr{E}_{\mu\nu}$, and $\mathscr{R}_{\mu\nu}$ to

$$\begin{aligned}(\mathbf{n}_a|\mathscr{T}_\mu|\mathbf{n}_b) &= \lim_{\zeta_s\to 0}(\mathbf{n}_a|\left\{\varphi_s(\mathbf{r}-\mathbf{R}_s;\mathbf{1}_{s\mu+},\zeta_s)\frac{\partial}{\partial r_{\mu-}} - \varphi_s(\mathbf{r}-\mathbf{R}_s;\mathbf{1}_{s\mu-},\zeta_s)\frac{\partial}{\partial r_{\mu+}}\right\}|\mathbf{n}_b) \\ &= -\lim_{\zeta_s\to 0}\frac{\partial}{\partial R_{b\mu-}}(\mathbf{n}_a|\varphi_s(\mathbf{1}_{s\mu+})|\mathbf{n}_b) + \lim_{\zeta_s\to 0}\frac{\partial}{\partial R_{b\mu+}}(\mathbf{n}_a|\varphi_s(\mathbf{1}_{s\mu-})|\mathbf{n}_b),\end{aligned} \tag{47}$$

$$\begin{aligned}(\mathbf{n}_a\mathbf{n}_b|\mathscr{E}_{\mu\nu}|\mathbf{n}_c\mathbf{n}_d) &= -\int du_{12}\frac{2}{\pi^{1/2}}\left(\frac{\partial}{\partial R_{c\mu}}+\frac{\partial}{\partial R_{d\mu}}\right)\frac{\partial}{\partial R_{dv}}(\mathbf{n}_a\mathbf{n}_b|\varphi_{12}(\mathbf{r}_1-\mathbf{r}_2;\mathbf{0}_{12},u_{12}^2)|\mathbf{n}_c\mathbf{n}_d) \\ &= -\sum_{i=c,d}\int_0^\infty du_{12}\frac{2}{\pi^{1/2}}\frac{\partial}{\partial R_{i\mu}}\frac{\partial}{\partial R_{dv}}(\mathbf{n}_a\mathbf{n}_b|\varphi_{12}(\mathbf{0}_{12})|\mathbf{n}_c\mathbf{n}_d),\end{aligned} \tag{48}$$

and

$$\begin{aligned}(\mathbf{n}_a\mathbf{n}_b|\mathscr{R}_{\mu\nu}|\mathbf{n}_c\mathbf{n}_d) &= -\int_0^\infty du_{12}\frac{2}{\pi^{1/2}}\left(\frac{\partial}{\partial R_{c\mu}}+\frac{\partial}{\partial R_{d\mu}}\right)\left(\frac{\partial}{\partial R_{cv}}+\frac{\partial}{\partial R_{dv}}\right)(\mathbf{n}_a\mathbf{n}_b|\varphi_{12}(\mathbf{r}_1-\mathbf{r}_2;\mathbf{0}_{12},u_{12}^2)|\mathbf{n}_c\mathbf{n}_d) \\ &= -\sum_{i,j=c,d}\int_0^\infty du_{12}\frac{2}{\pi^{1/2}}\frac{\partial}{\partial R_{i\mu}}\frac{\partial}{\partial R_{jv}}(\mathbf{n}_a\mathbf{n}_b|\varphi_{12}(\mathbf{0}_{12})|\mathbf{n}_c\mathbf{n}_d),\end{aligned} \tag{49}$$

respectively. These expressions for $(\mathbf{n}_a|\mathscr{T}_\mu|\mathbf{n}_b)$, $(\mathbf{n}_a\mathbf{n}_b|\mathscr{G}_{\mu\nu}|\mathbf{n}_c\mathbf{n}_d)$, and $(\mathbf{n}_a\mathbf{n}_b|\mathscr{R}_{\mu\nu}|\mathbf{n}_c\mathbf{n}_d)$ as well as the above mathematical relations of the operators allow us to express molecular integrals as a linear combination of the basic one- or two-electron integrals:

$$(\mathrm{OEI}) = \sum_i c_i (\mathrm{BOEI})_i, \tag{50}$$

$$(\mathrm{TEI}) = \sum_i c_i (\mathrm{BTEI})_i. \tag{51}$$

The definitions of the basic one-electron integrals (BOEI's) and basic two-electron integrals (BTEI's) will follow.

We define the basic one-electron integrals (BOEI's) as

$$(\{\mathbf{n}\}:\{\mathbf{l}\}) = \mathscr{Q}_A \mathscr{Q}_I \mathscr{Q}_D(\{\mathbf{l}\}) \int d\mathbf{r}\, \mathscr{G}(\{\mathbf{n}\}). \tag{52}$$

Here $\mathscr{G}(\{\mathbf{n}\})$ is a product of N unnormalized Cartesian Gaussian functions

$$\mathscr{G}(\{\mathbf{n}\}) = \prod_{i=1}^{N} \varphi(\mathbf{r}-\mathbf{R}_i;\mathbf{n}_i,\zeta_i), \tag{53}$$

which includes not only the basis functions but also those originating from the one-electron operator $\mathscr{O}(\mathbf{r})$, and $\mathscr{Q}_D(\{\mathbf{l}\})$ is a product of differential operators with respect to *all* the function centers $\mathbf{R}_i$'s in the product $\mathscr{G}(\{\mathbf{n}\})$,

$$\mathscr{Q}_D(\{\mathbf{l}\}) = \prod_{i=1}^{N} \left(\frac{\partial}{\partial R_{ix}}\right)^{l_{ix}} \left(\frac{\partial}{\partial R_{iy}}\right)^{l_{iy}} \left(\frac{\partial}{\partial R_{iz}}\right)^{l_{iz}}, \tag{54}$$

where unnecessary differentiations are to be suppressed by setting the derivative index $\mathbf{l}_i$ identically to $\mathbf{0} = (0,0,0)$. The $\{\mathbf{n}\}$ and $\{\mathbf{l}\}$ denote collectively the angular momentum indices $\mathbf{n}_i$'s in Eq. (53) and the derivative indices $\mathbf{l}_i$'s in Eq. (54), respectively. The operator $\mathscr{Q}_I$ in Eq. (52) means integrations over u's in Eq. (44),

$$\mathscr{Q}_I = \prod_v \left\{ \int du_v \frac{2u_v^{\lambda-1}}{\Gamma(\lambda/2)} \right\}, \tag{55}$$

and $\mathscr{Q}_A$ means other necessary operations, such as to put an orbital exponent to zero in the moment operator [Eq. (42)]. When the operators $\mathscr{Q}_I$ and $\mathscr{Q}_A$ are unnecessary in some molecular integrals, they are to be considered as $\mathscr{Q}_I = 1$ and $\mathscr{Q}_A = 1$. Since the $\mathscr{Q}_I$ and $\mathscr{Q}_A$ operate on different parameters in $\mathscr{G}(\{\mathbf{n}\})$, they commute ($\mathscr{Q}_A\mathscr{Q}_I = \mathscr{Q}_I\mathscr{Q}_A$). For convenience of later discussions, we designate the integrals of $\mathscr{G}(\{\mathbf{n}\})$ over the electron coordinate as

$$[\{\mathbf{n}\}] = \int d\mathbf{r}\, \mathscr{G}(\{\mathbf{n}\}), \tag{56}$$

their derivatives as

$$[\{\mathbf{n}\}:\{\mathbf{l}\}] = \mathscr{Q}_D(\{\mathbf{l}\})[\{\mathbf{n}\}], \tag{57}$$

and refer to them as overlap OEI's (OOEI's) and derivatives of OOEI's (DOOEI's), respectively.

Similarly we define the basic two-electron integrals (BTEI's) as

$$(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}) = \mathscr{Q}_A\mathscr{Q}_I[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}], \tag{58}$$

where

$$\mathscr{Q}_A = \mathscr{Q}_{A,12}\mathscr{Q}_A^{(1)}\mathscr{Q}_A^{(2)}, \tag{59}$$

$$\mathscr{Q}_I = \mathscr{Q}_{I,12}\mathscr{Q}_I^{(1)}\mathscr{Q}_I^{(2)}, \tag{60}$$

the square-bracketted integral $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\},:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]$ in Eq. (58) is the derivative of the overlap TEI (DOTEI)

$$[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}] = \mathscr{Q}_D^{(1)}(\{\mathbf{l}^{(1)}\})\mathscr{Q}_D^{(2)}(\{\mathbf{l}^{(2)}\})[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}], \tag{61}$$

and $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$ in Eq. (61) is the overlap TEI (OTEI)

$$[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}] = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \mathscr{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}). \tag{62}$$

The superscripts 1 and 2 in Eqs. (58)–(62) refer to the first and the second electron, respectively, and $\mathscr{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$ denotes the product of $\mathscr{G}^{(1)}(\{\mathbf{n}^{(1)}\})$, $\mathscr{G}^{(2)}(\{\mathbf{n}^{(2)}\})$, and the Cartesian Gaussian function $\varphi(\mathbf{r}_1-\mathbf{r}_2;\mathbf{n}_{12},\zeta_{12})$ in the two-electron operator, such as $|\mathbf{r}_1-\mathbf{r}_2|^{-\lambda}$ and $\delta(\mathbf{r}_1-\mathbf{r}_2)$:

$$\mathscr{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}) = \mathscr{G}^{(1)}(\{\mathbf{n}^{(1)}\})\mathscr{G}^{(2)}(\{\mathbf{n}^{(2)}\})\varphi(\mathbf{r}_1-\mathbf{r}_2;\mathbf{n}_{12},\zeta_{12}). \tag{63}$$

$\mathscr{Q}_{I,12}$ in Eq. (60) indicates integration over $u_{12}(=\zeta_{12}^{1/2})$, when it is necessary such as for $\mathscr{G}_{\mu\nu}$ and $\mathscr{R}_{\mu\nu}$:

$$\mathscr{Q}_{I,12} = \int du_{12} \frac{2u_{12}^{\lambda-1}}{\Gamma(\lambda/2)}, \tag{64}$$

and $\mathscr{Q}_{A,12}$ in Eq. (59) indicates other necessary operations with respect to ζ_{12}.

By the use of these notations for the integrals, the molecular integrals $(\mathbf{n}_a|\mathscr{T}_\mu|\mathbf{n}_b)$ and $(\mathbf{n}_a\mathbf{n}_b|\mathscr{G}_{\mu\nu}|\mathbf{n}_c\mathbf{n}_d)$, for instance, become

$$(\mathbf{n}_a|\mathscr{T}_\mu|\mathbf{n}_b) = -\mathscr{Q}_A[\mathbf{n}_a,\mathbf{n}_b,\mathbf{1}_{s\mu+}:\mathbf{0}_a,\mathbf{1}_{b\mu-},\mathbf{0}_s] + \mathscr{Q}_A[\mathbf{n}_a,\mathbf{n}_b,\mathbf{1}_{s\mu-}:\mathbf{0}_a,\mathbf{1}_{b\mu+},\mathbf{0}_s] \tag{65}$$

and

$$(\mathbf{n}_a\mathbf{n}_b|\mathscr{G}_{\mu\nu}|\mathbf{n}_c\mathbf{n}_d) = -\mathscr{Q}_{I,12}[\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{1}_{c\mu},\mathbf{1}_{d\nu}] - \mathscr{Q}_{I,12}[\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c,\mathbf{1}_{d\mu}+\mathbf{1}_{d\nu}], \tag{66}$$

respectively, with

$$\mathscr{Q}_A = \lim_{\zeta_s\to 0}, \tag{67}$$

$$\mathscr{Q}_{I,12} = \int_0^\infty du_{12} \frac{2}{\pi^{1/2}}. \tag{68}$$

It is noteworthy that the present formulation of integrals is suited for the derivative integrals necessary in the analytical derivative method, since they can be specified by just giving the appropriate values for the derivative indices I's in the basic integrals. Also note that molecular integrals with any arbitrarily defined spatial operators, even if the operators are not of the reduced form of the relativistic Hamiltonian, can be dealt with so far as the molecular integrals can be expressed in terms of the basic integrals. One of the examples is the molecular integral with the spherically symmetric operator $\mathscr{O}_{\mathrm{ECP}}$ of the effective core potential (ECP)

proposed by Kahn, Baybutt, and Truhlar.[14] The operator located at $\mathbf{R}_c$ takes the form

$$\mathcal{O}_{\mathrm{ECP}} = \frac{N_c}{|\mathbf{r}-\mathbf{R}_c|} + \sum_k d_k |\mathbf{r}-\mathbf{R}_c|^{n_k-2} \times \exp[-\eta_k(\mathbf{r}-\mathbf{R}_c)^2], \tag{69}$$

where N_c, d_k, η_k, and n_k are the prefixed constants, and n_k takes one of the values 0, 1, and 2. The second term of the $\mathcal{O}_{\mathrm{ECP}}$ with $n_k = 0$, for instance, can be reduced to

$$\sigma = |\mathbf{r}-\mathbf{R}_c|^{-2}\exp[-\eta_k(\mathbf{r}-\mathbf{R}_c)^2] = \int_0^\infty du\, 2u\varphi(\mathbf{r}-\mathbf{R}_c;\mathbf{0}_c,\eta_k+u^2), \tag{70}$$

and thereby the molecular integral with this operator becomes

$$(\mathbf{n}_a|\sigma|\mathbf{n}_b) = \int d\mathbf{r}\,\varphi_a(\mathbf{r})\sigma\varphi_b(\mathbf{r}) = \int_0^\infty du\, 2u[\mathbf{n}_a,\mathbf{n}_b,\mathbf{0}_c:\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c]. \tag{71}$$

The present formulation is also applicable to molecular integrals including the kernel of the Fourier transform, because the product of the Cartesian Gaussian function and the kernel becomes a sum of Cartesian Gaussian functions having a complex function center [Eq. (14)]. The molecular integrals then become reducible to the form of Eq. (50) or (51). The details will be given in a later section.

As far as the molecular integrals are reducible to the form of Eq. (50) or (51), the recurrence relations for the molecular integrals can be readily obtained by using the recurrence relations of the basic integrals as will be exemplified in later sections. Reduction of molecular integrals to sums of the basic integrals affords the key to get the recurrence relations for the target molecular integrals. Now it may be instructive to work out some other molecular integrals. The overlap integrals

$$(\mathbf{n}_a\|\mathbf{n}_b) = \int d\mathbf{r}\,\varphi(\mathbf{r}-\mathbf{R}_a;\mathbf{n}_a,\zeta_a)\varphi(\mathbf{r}-\mathbf{R}_b;\mathbf{n}_b,\zeta_b), \tag{72}$$

the nuclear attraction integrals

$$(\mathbf{n}_a|\mathscr{A}|\mathbf{n}_b) = \int d\mathbf{r}\,\varphi(\mathbf{r}-\mathbf{R}_a;\mathbf{n}_a,\zeta_a) \times \frac{1}{|\mathbf{r}-\mathbf{R}_c|}\varphi(\mathbf{r}-\mathbf{R}_b;\mathbf{n}_b,\zeta_b), \tag{73}$$

and the electron repulsion integrals

$$(\mathbf{n}_a\mathbf{n}_b,\mathbf{n}_c\mathbf{n}_d) = \int d\mathbf{r}_1 \int d\mathbf{r}_2\,\varphi(\mathbf{r}_1-\mathbf{R}_a;\mathbf{n}_a,\zeta_a) \times\varphi(\mathbf{r}_1-\mathbf{R}_b;\mathbf{n}_b,\zeta_b)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \times\varphi(\mathbf{r}_2-\mathbf{R}_c;\mathbf{n}_c,\zeta_c)\varphi(\mathbf{r}_2-\mathbf{R}_d;\mathbf{n}_d,\zeta_d) \tag{74}$$

are found to be

$$(\mathbf{n}_a\|\mathbf{n}_b) = [\mathbf{n}_a,\mathbf{n}_b:\mathbf{0}_a,\mathbf{0}_b], \tag{75}$$

$$(\mathbf{n}_a|\mathscr{A}|\mathbf{n}_b) = \int_0^\infty du\,\frac{2}{\pi^{1/2}}[\mathbf{n}_a,\mathbf{n}_b,\mathbf{0}_c:\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c], \tag{76}$$

and

$$(\mathbf{n}_a\mathbf{n}_b,\mathbf{n}_c\mathbf{n}_d) = \int_0^\infty du_{12}\,\frac{2}{\pi^{1/2}}[\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c,\mathbf{0}_d], \tag{77}$$

respectively. As their derivatives, the kinetic energy integrals

$$(\mathbf{n}_a|\mathscr{T}|\mathbf{n}_b) = \int d\mathbf{r}\,\varphi(\mathbf{r}-\mathbf{R}_a;\mathbf{n}_a,\zeta_a) \times(-\tfrac{1}{2}\nabla^2)\varphi(\mathbf{r}-\mathbf{R}_b;\mathbf{n}_b,\zeta_b), \tag{78}$$

the electric field gradient integrals

$$(\mathbf{n}_a|\mathscr{A}_{\mu\nu}|\mathbf{n}_b) = \int d\mathbf{r}\,\varphi(\mathbf{r}-\mathbf{R}_a;\mathbf{n}_a,\zeta_a) \times\left\{\frac{\partial^2}{\partial R_{c\mu}\partial R_{c\nu}}\frac{1}{|\mathbf{r}-\mathbf{R}_c|}\right\}\varphi(\mathbf{r}-\mathbf{R}_b;\mathbf{n}_b,\zeta_b), \tag{79}$$

and the derivatives of the electron repulsion integrals with respect to the function centers

$$(\mathbf{n}_a\mathbf{n}_b,\mathbf{n}_c\mathbf{n}_d:\mathbf{l}_a\mathbf{l}_b,\mathbf{l}_c\mathbf{l}_d) = \left\{\prod_{i=a,b,c,d}\left(\frac{\partial}{\partial R_{ix}}\right)^{l_{ix}}\left(\frac{\partial}{\partial R_{iy}}\right)^{l_{iy}}\left(\frac{\partial}{\partial R_{iz}}\right)^{l_{iz}}\right\} \times(\mathbf{n}_a\mathbf{n}_b,\mathbf{n}_c\mathbf{n}_d) \tag{80}$$

can be written

$$(\mathbf{n}_a|\mathscr{T}|\mathbf{n}_b) = \frac{1}{2}\sum_{\nu=x,y,z}[\mathbf{n}_a,\mathbf{n}_b:\mathbf{1}_{a\nu},\mathbf{1}_{b\nu}], \tag{81}$$

$$(\mathbf{n}_a|\mathscr{A}_{\mu\nu}|\mathbf{n}_b) = \int du\,\frac{2}{\pi^{1/2}} \times[\mathbf{n}_a,\mathbf{n}_b,\mathbf{0}_c:\mathbf{0}_a,\mathbf{0}_b,\mathbf{1}_{c\mu}+\mathbf{1}_{c\nu}], \tag{82}$$

and

$$(\mathbf{n}_a\mathbf{n}_b,\mathbf{n}_c\mathbf{n}_d:\mathbf{l}_a\mathbf{l}_b,\mathbf{l}_c\mathbf{l}_d) = \int du_{12}\,\frac{2}{\pi^{1/2}}[\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{l}_a,\mathbf{l}_b,\mathbf{l}_c,\mathbf{l}_d], \tag{83}$$

respectively.

C. Recurrence formulas for basic two-electron integrals

One can reduce the basic two-electron integrals (BTEI's) to the basic one-electron integrals (BOEI's), noting the following relation for the DOTEI's and the DOOEI's:

$$[\{\mathbf{n}^{(1)}\}:\{\mathbf{l}^{(1)}\}] = \mathscr{Q}_A[\mathbf{0}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{0}^{(2)}\}], \tag{84}$$

$$\mathscr{Q}_A = \left\{\prod_{i=1}^{N^{(2)}}\lim_{\zeta_i^{(2)}\to 0}\right\}\lim_{\zeta_{12}\to\infty}\left(\frac{\zeta_{12}}{\pi}\right)^{3/2} \tag{85}$$

obtained from the mathematical property of the Dirac delta function $\delta(\mathbf{r}_1-\mathbf{r}_2)$ and the s-type unnormalized Cartesian Gaussian function with a zero orbital exponent (which is unity)

$$\int d\mathbf{r}\, H(\mathbf{r}) = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, H(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2) \times \prod_{i=1}^{N^{(2)}} \{\varphi(\mathbf{r}_2-\mathbf{R}_i^{(2)};\mathbf{0}_i^{(2)},\zeta_i^{(2)})\}_{\zeta_i^{(2)}=0}. \tag{86}$$

Now the recurrence formulas for the BTEI's will be derived in this section, and the reduction to those for one-electron integrals will be given in the Appendix.

There are two kinds of Cartesian Gaussian functions in the $\mathcal{G}^{(k)}(\{\mathbf{n}^{(k)}\})$ $(k=1,2)$: one is those with constant orbital exponents, and the other with *integration exponents* over which the integrations are to be carried out [Eq. (44)]. We collect the former kind of functions in the first $G^{(k)}$ functions of $\mathcal{G}^{(k)}(\{\mathbf{n}^{(k)}\})$, and the latter kind in the remaining $(N^{(k)}-G^{(k)})$ functions:

$$\mathcal{G}^{(k)}(\{\mathbf{n}^{(k)}\}) = \left\{\prod_{g=1}^{G^{(k)}} \varphi(\mathbf{r}_k-\mathbf{R}_g^{(k)};\mathbf{n}_g^{(k)},\zeta_g^{(k)})\right\} \times \left\{\prod_{u=G^{(k)}+1}^{N^{(k)}} \varphi(\mathbf{r}_k-\mathbf{R}_u^{(k)};\mathbf{n}_u^{(k)},\zeta_u^{(k)})\right\}. \tag{87}$$

The subscripts g and h refer to the former kind of functions, the subscripts u and v to the latter ones, and the subscripts i and j to either of them. Since the notations $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$, $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$, and $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]$ are lengthy to write down, we abbreviate them as $\mathcal{G}$, [ ], and [:], respectively. When some of the angular momentum indices and the derivative indices are different from those in $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$, $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$, and $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]$, only the distinct indices will be given, and thus $\mathcal{G}(\mathbf{n}_{12}+\mathbf{1}_\mu,\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$, for instance, will be designated as $\mathcal{G}(\mathbf{n}_{12}+\mathbf{1}_\mu)$.

First, in order to derive a recurrence relation for the OTEI's $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$, we differentiate $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$ with respect to the μ component of the first electron coordinate $r_{1\mu}$. Equations (5), (8), and (9) allow us to write the derivative as

$$\frac{\partial}{\partial r_{1\mu}}\mathcal{G} = -2\zeta_{12}\mathcal{G}(\mathbf{n}_{12}+\mathbf{1}_\mu) + N_\mu(\mathbf{n}_{12})\mathcal{G}(\mathbf{n}_{12}-\mathbf{1}_\mu) - \left\{\sum_{i=1}^{N^{(1)}} 2\zeta_i^{(1)}(\mathbf{r}_1-\mathbf{R}_i^{(1)})_\mu\right\}\mathcal{G} + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})\mathcal{G}(\mathbf{n}_i^{(1)}-\mathbf{1}_\mu). \tag{88}$$

Introducing the parameters $Z^{(k)}$ and $\mathbf{R}_Z^{(k)}$ $(k=1,2)$,

$$Z^{(k)} = \sum_{i=1}^{N^{(k)}} \zeta_i^{(k)}, \tag{89}$$

$$\mathbf{R}_Z^{(k)} = \frac{1}{Z^{(k)}}\sum_{i=1}^{N^{(k)}} \zeta_i^{(k)}\mathbf{R}_i^{(k)}, \tag{90}$$

we rewrite the factor in the third term of Eq. (88) as

$$-\left\{\sum_{i=1}^{N^{(1)}} 2\zeta_i^{(1)}(\mathbf{r}_1-\mathbf{R}_i^{(1)})_\mu\right\} = -2Z^{(1)}(\mathbf{r}_1-\mathbf{R}_Z^{(1)})_\mu = -2Z^{(1)}(\mathbf{r}_1-\mathbf{R}_j^{(1)})_\mu + 2Z^{(1)}(\mathbf{R}_Z^{(1)}-\mathbf{R}_j^{(1)})_\mu, \tag{91}$$

and then finally obtain

$$\frac{\partial}{\partial r_{1\mu}}\mathcal{G} = -2\zeta_{12}\mathcal{G}(\mathbf{n}_{12}+\mathbf{1}_\mu) + N_\mu(\mathbf{n}_{12})\mathcal{G}(\mathbf{n}_{12}-\mathbf{1}_\mu) - 2Z^{(1)}\mathcal{G}(\mathbf{n}_j^{(1)}+\mathbf{1}_\mu) + 2Z^{(1)}(\mathbf{R}_Z^{(1)}-\mathbf{R}_j^{(1)})_\mu\mathcal{G} + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})\mathcal{G}(\mathbf{n}_i^{(1)}-\mathbf{1}_\mu). \tag{92}$$

The left-hand side of Eq. (92) vanishes by integration over $r_{1\mu}$ due to Eq. (13). Therefore, integration of both sides over $\mathbf{r}_1$ and $\mathbf{r}_2$ gives

$$[\mathbf{n}_{12}+\mathbf{1}_\mu] = \frac{1}{2\zeta_{12}}N_\mu(\mathbf{n}_{12})[\mathbf{n}_{12}-\mathbf{1}_\mu] - \frac{Z^{(1)}}{\zeta_{12}}[\mathbf{n}_j^{(1)}+\mathbf{1}_\mu] + \frac{Z^{(1)}}{\zeta_{12}}(\mathbf{R}_Z^{(1)}-\mathbf{R}_j^{(1)})_\mu[\ ] + \frac{1}{2\zeta_{12}}\sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})[\mathbf{n}_i^{(1)}-\mathbf{1}_\mu]. \tag{93}$$

Another formula for $[\mathbf{n}_{12}+\mathbf{1}_\mu,\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$ is obtainable by differentiating $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$ with respect to the *second* electron coordinate $r_{2\mu}$ and then integrating over $\mathbf{r}_1$ and $\mathbf{r}_2$;

$$[\mathbf{n}_{12}+\mathbf{1}_\mu] = \frac{1}{2\zeta_{12}}N_\mu(\mathbf{n}_{12})[\mathbf{n}_{12}-\mathbf{1}_\mu] + \frac{Z^{(2)}}{\zeta_{12}}[\mathbf{n}_k^{(2)}+\mathbf{1}_\mu] - \frac{Z^{(2)}}{\zeta_{12}}(\mathbf{R}_Z^{(2)}-\mathbf{R}_k^{(2)})_\mu[\ ] - \frac{1}{2\zeta_{12}}\sum_{i=1}^{N^{(2)}} N_\mu(\mathbf{n}_i^{(2)})[\mathbf{n}_i^{(2)}-\mathbf{1}_\mu]. \tag{94}$$

The OTEI $[\mathbf{n}_k^{(2)}+\mathbf{1}_\mu]$ in Eq. (94) can be expressed in terms of $[\mathbf{n}_{12}+\mathbf{1}_\mu]$, $[\mathbf{n}_j^{(1)}+\mathbf{1}_\mu]$, and [ ], because the factor $(\mathbf{r}_2-\mathbf{R}_k^{(2)})_\mu$ in its integrand can be decomposed into

$$(\mathbf{r}_2-\mathbf{R}_k^{(2)})_\mu = -(\mathbf{r}_1-\mathbf{r}_2)_\mu + (\mathbf{r}_1-\mathbf{R}_j^{(1)})_\mu + (\mathbf{R}_j^{(1)}-\mathbf{R}_k^{(2)})_\mu. \tag{95}$$

Substituting Eq. (95) into Eq. (94) and then subtracting Eq. (93) multiplied by $(1+Z^{(2)}/\zeta_{12})$, we obtain the recurrence formula for $[\mathbf{n}_j^{(1)}+\mathbf{1}_\mu]$,

$$[\mathbf{n}_j^{(1)}+\mathbf{1}_\mu] = \{(\mathbf{R}_Z^{(1)}-\mathbf{R}_j^{(1)})_\mu + \Theta(\mathbf{W}-\mathbf{R}_Z^{(1)})_\mu\}[\ ] + \frac{1-\Theta}{2Z^{(1)}} \times \left\{N_\mu(\mathbf{n}_{12})[\mathbf{n}_{12}-\mathbf{1}_\mu] + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})[\mathbf{n}_i^{(1)}-\mathbf{1}_\mu]\right\} + \frac{\Theta}{2Z}\sum_{k=1,2}\sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)})[\mathbf{n}_i^{(k)}-\mathbf{1}_\mu], \tag{96}$$

where the parameters Z, $\mathbf{W}$, and Θ are defined by

$$Z = Z^{(1)} + Z^{(2)}, \tag{97}$$

$$\mathbf{W} = \frac{Z^{(1)}\mathbf{R}_Z^{(1)} + Z^{(2)}\mathbf{R}_Z^{(2)}}{Z}, \tag{98}$$

and

$$\Theta = \frac{\zeta_{12}}{\rho_Z + \zeta_{12}}, \tag{99}$$

respectively, with

$$\rho_Z = \frac{Z^{(1)}Z^{(2)}}{Z}. \tag{100}$$

Equation (96) is a generalization of the recurrence formula for one-electron three-center overlap integrals introduced in our previous paper[13] to that for the two-electron $(N^{(1)} + N^{(2)})$-center overlap integrals.

Operation of $\mathcal{Q}_D^{(k)}$ $(\{\mathbf{l}^{(k)}\})$ $(k = 1,2)$ on both sides of Eq. (96) gives the recurrence formulas for the DOTEI's. Noting that the coefficient in the first term of Eq. (96) is linear with respect to $\mathbf{R}$ and those of the remianing terms are independent of $\mathbf{R}$, we readily find the formula for the DOTEI's

$$\begin{aligned}
&[\mathbf{n}_j^{(1)} + \mathbf{1}_\mu :] \\
&= \{(\mathbf{R}_Z^{(1)} - \mathbf{R}_j^{(1)})_\mu + \Theta(\mathbf{W} - \mathbf{R}_Z^{(1)})_\mu\}[:] + \frac{1-\Theta}{2Z^{(1)}} \\
&\times \left\{ N_\mu(\mathbf{n}_{12})[\mathbf{n}_{12} - \mathbf{1}_\mu :] + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})[\mathbf{n}_i^{(1)} - \mathbf{1}_\mu :] \right\} \\
&+ \frac{1-\Theta}{Z^{(1)}} \sum_{i=1}^{N^{(1)}} \zeta_i^{(1)} \\
&\times \{N_\mu(\mathbf{l}_i^{(1)}) \times [:\mathbf{l}_i^{(1)} - \mathbf{1}_\mu] - N_\mu(\mathbf{l}_j^{(1)})\ [:\mathbf{l}_j^{(1)} - \mathbf{1}_\mu]\} \\
&+ S_j^{(1)} + S_j^{(2)},
\end{aligned} \tag{101}$$

where $S_j^{(k)}$ represents

$$\begin{aligned}
S_j^{(k)} &= \frac{\Theta}{2Z} \sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)})[\mathbf{n}_i^{(k)} - \mathbf{1}_\mu :] \\
&+ \frac{\Theta}{Z} \sum_{i=1}^{N^{(k)}} \zeta_i^{(k)} \\
&\times \{N_\mu(\mathbf{l}_i^{(k)})[:\mathbf{l}_i^{(k)} - \mathbf{1}_\mu] \\
&- N_\mu(\mathbf{l}_j^{(1)})[:\mathbf{l}_j^{(1)} - \mathbf{1}_\mu]\}.
\end{aligned} \tag{102}$$

The recurrence formulas with respect to other indices can also be derived by the use of the above equations; operation of $\mathcal{Q}_D^{(k)}$ on Eq. (93) and subsequent substitution of Eqs. (101) and (102) yield the recurrence formula with respect to $\mathbf{n}_{12}$,

$$\begin{aligned}
[\mathbf{n}_{12} + \mathbf{1}_\mu :] &= \frac{1-\Theta}{2}\left(\frac{1}{Z^{(1)}} + \frac{1}{Z^{(2)}}\right) N_\mu(\mathbf{n}_{12}) \\
&\times [\mathbf{n}_{12} - \mathbf{1}_\mu :] + T^{(1)} - T^{(2)},
\end{aligned} \tag{103}$$

where $T^{(k)}$ denotes

$$\begin{aligned}
T^{(k)} &= (1-\Theta)(\mathbf{R}_Z^{(k)})_\mu [:] \\
&+ \frac{1-\Theta}{2Z^{(k)}} \sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)})[\mathbf{n}_i^{(k)} - \mathbf{1}_\mu :] \\
&+ \frac{1-\Theta}{Z^{(k)}} \sum_{i=1}^{N^{(k)}} \zeta_i^{(k)} N_\mu(\mathbf{l}_i^{(k)})[:\mathbf{l}_i^{(k)} - \mathbf{1}_\mu].
\end{aligned} \tag{104}$$

The formula with respect to the derivative index $\mathbf{l}_j^{(1)}$ can be obtained by differentiating $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$ with respect to $R_{j\mu}^{(1)}$, substituting Eq. (12), and finally operating $\mathcal{Q}_D^{(k)}$:

$$[:\mathbf{l}_j^{(1)} + \mathbf{1}_\mu] = 2\zeta_j^{(1)}[\mathbf{n}_j^{(1)} + \mathbf{1}_\mu :] - N_\mu(\mathbf{n}_j^{(1)})[\mathbf{n}_j^{(1)} - \mathbf{1}_\mu :]. \tag{105}$$

Substitution of Eq. (101) into the first term of Eq. (105) gives a formula involving lower angular momentum and derivative indices. In order to use these recurrence formulas we need an *initial* DOTEI $[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}]$, namely, the DOTEI over s-type Cartesian Gaussian functions, which readily reduces to

$$\begin{aligned}
&[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}] \\
&= \mathcal{S}^{(1)}\mathcal{S}^{(2)}(1-\Theta)^{3/2}\exp[-\Theta\rho_Z(\mathbf{R}_Z^{(1)} - \mathbf{R}_Z^{(2)})^2]
\end{aligned} \tag{106}$$

by employing the expression for $\mathcal{G}^{(k)}(\{\mathbf{0}^{(k)}\})$,

$$\begin{aligned}
&\mathcal{G}^{(k)}(\{\mathbf{0}^{(k)}\}) \\
&= \left(\frac{\pi}{Z^{(k)}}\right)^{-3/2} \mathcal{S}^{(k)} \exp[-Z^{(k)}(\mathbf{r}_k - \mathbf{R}_Z^{(k)})^2],
\end{aligned} \tag{107}$$

where $\mathcal{S}^{(k)}$ is the one-electron overlap integral over $N^{(k)}$ s-type Cartesian Gaussian functions:

$$\begin{aligned}
\mathcal{S}^{(k)} &= \left(\frac{\pi}{Z^{(k)}}\right)^{3/2} \prod_{\substack{i,j=1 \\ (i<j)}}^{N^{(k)}} \\
&\times \exp\left[-\frac{\zeta_i^{(k)}\zeta_j^{(k)}}{Z^{(k)}}(\mathbf{R}_i^{(k)} - \mathbf{R}_j^{(k)})^2\right].
\end{aligned} \tag{108}$$

For the BTEI's *without* the integration over u's in Eq. (44), namely, $\mathcal{Q}_I = 1$, the operation of $\mathcal{Q}_A\mathcal{Q}_I\,(= \mathcal{Q}_A)$ on the above formulas (101), (103), and (105) readily gives the recurrence formulas for the BTEI's. In contrast, for the BTEI's *with* the integrations, namely, $\mathcal{Q}_I \neq 1$, these formulas are not suited for the operation of $\mathcal{Q}_A\mathcal{Q}_I$, since the integration exponents appear in their coefficients through the parameters Θ, $Z^{(k)}$, Z, $\mathbf{R}_Z^{(k)}$, and $\mathbf{W}$. So we rewrite the above recurrence formulas by the use of the following decompositions of these parameters:

$$\begin{aligned}
\frac{1-\Theta}{Z^{(k)}} &= \frac{1-\Theta}{\zeta_G^{(k)}} \cdot \frac{\zeta_G^{(k)}}{Z^{(k)}} \\
&= \frac{1-\Theta}{\zeta_G^{(k)}} - \frac{1}{\zeta_G^{(k)}} \sum_{u=G^{(k)}+1}^{N^{(k)}} \eta_u^{(k)},
\end{aligned} \tag{109}$$

$$\frac{\Theta}{Z} = \frac{\Theta}{\zeta_G} - \frac{1}{\zeta_G} \sum_{k=1,2} \sum_{u=G^{(k)}+1}^{N^{(k)}} \xi_u^{(k)}, \tag{110}$$

$$\begin{aligned}
&(1-\Theta)\mathbf{R}_Z^{(k)} \\
&= (1-\Theta)\mathbf{R}_G^{(k)} - \sum_{u=G^{(k)}+1}^{N^{(k)}} \eta_u^{(k)}(\mathbf{R}_G^{(k)} - \mathbf{R}_u^{(k)}),
\end{aligned} \tag{111}$$

and

$$\Theta\mathbf{W} = \Theta\mathbf{W}_G - \sum_{k=1,2} \sum_{u=G^{(k)}+1}^{N^{(k)}} \xi_u^{(k)}(\mathbf{W}_G - \mathbf{R}_u^{(k)}). \tag{112}$$

Here $\zeta_G^{(k)}$, ζ_G, $\mathbf{R}_G^{(k)}$, and $\mathbf{W}_G$ are expressible in terms of the constant parameters $\zeta_g^{(k)}$ and $\mathbf{R}_g^{(k)}$:

$$\zeta_G^{(k)} = \sum_{g=1}^{G^{(k)}} \zeta_g^{(k)}, \tag{113}$$

$$\zeta_G = \zeta_G^{(1)} + \zeta_G^{(2)}, \tag{114}$$

$$\mathbf{R}_G^{(k)} = \frac{1}{\zeta_G^{(k)}} \sum_{g=1}^{G^{(k)}} \zeta_g^{(k)} \mathbf{R}_g^{(k)}, \tag{115}$$

and

$$\mathbf{W}_G = \frac{1}{\zeta_G} (\zeta_G^{(1)} \mathbf{R}_G^{(1)} + \zeta_G^{(2)} \mathbf{R}_G^{(2)}), \tag{116}$$

respectively, and $\eta_u^{(k)}$ and $\xi_u^{(k)}$, which include the integration exponents, are defined by

$$\eta_u^{(k)} = (1-\Theta) \frac{\zeta_u^{(k)}}{Z^{(k)}}, \tag{117}$$

$$\xi_u^{(k)} = \Theta \frac{\zeta_u^{(k)}}{Z}, \tag{118}$$

respectively. For the convenience of reducing $[:\mathbf{l}_j^{(1)} + \mathbf{1}_\mu]$, we also introduce the parameters $\eta_{uv}^{(k)}$ and $\xi_{uv}^{(k')}$ defined by

$$\eta_{uv}^{(k)} = (1-\Theta) \frac{\zeta_u^{(k)} \zeta_v^{(k)}}{Z^{(k)}}, \tag{119}$$

$$\xi_{uv}^{(k')} = \Theta \frac{\zeta_u^{(k)} \zeta_v^{(k')}}{Z} \quad (k,k' = 1,2). \tag{120}$$

Equations (109)–(112) allow the recurrence formulas to be reduced to those having constant coefficients and DOTEI's multiplied by any one of the above parameters Θ, $\eta_u^{(k)}$, $\xi_u^{(k)}$, $\eta_{uv}^{(k)}$, and $\xi_{uv}^{(k')}$. Now we introduce an *auxiliary* DOTEI (ADOTEI) defined by the DOTEI and the parameters Θ, $\eta_u^{(k)}$, $\xi_u^{(k)}$, $\eta_{uv}^{(k)}$, and $\xi_{uv}^{(k')}$:

$$[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}] = [\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}] P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}), \tag{121}$$

where

$$P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}) = \Theta^{m_{12}} \left\{ \prod_{u=G^{(1)}+1}^{N^{(1)}} \mathscr{F}_u^{(1)} \right\} \left\{ \prod_{v=G^{(2)}+1}^{N^{(2)}} \mathscr{F}_v^{(2)} \right\} \times \left\{ \prod_{u=G^{(1)}+1}^{N^{(1)}} \prod_{v=G^{(2)}+1}^{N^{(2)}} (\xi_{uv}^{(12)})^{M_{uv}} \right\} \tag{122}$$

and

$$\mathscr{F}_u^{(k)} = (\eta_u^{(k)})^{m_{uu}^{(k)}} (\xi_u^{(k)})^{M_{uu}} \times \prod_{\substack{v=G^{(k)}+1 \\ (v>u)}}^{N^{(k)}} \{(\eta_{uv}^{(k)})^{m_{uv}^{(k)}} (\xi_{uv}^{(kk)})^{M_{uv}}\}. \tag{123}$$

The indices $\mathbf{m}^{(k)}$ $(k=1,2)$ and $\mathbf{M}$ in Eq. (121) are $U^{(k)} \times U^{(k)}$ and $(U^{(1)}+U^{(2)}) \times (U^{(1)}+U^{(2)})$ $(U^{(k)} = N^{(k)} - G^{(k)})$ matrices, respectively, and denote collectively the elements $m_{uv}^{(k)}$'s $(u,v = G^{(k)}+1,\ldots,N^{(k)})$ and M_{uv}'s $(u,v = G^{(1)}+1,\ldots,N^{(1)},G^{(2)}+1,\ldots,N^{(2)})$ in their diagonal and *upper* half off-diagonal parts. The indices m_{12}, $\mathbf{m}^{(k)}$, and $\mathbf{M}$ termed *integration indices* take values of nonnegative integers, and when they all vanish the ADOTEI's become the corresponding DOTEI's, because $P(0_{12},\mathbf{0}^{(1)},\mathbf{0}^{(2)},\mathbf{0}) = 1$. With no integration exponent, say, in the $\mathscr{G}^{(1)}(\{\mathbf{n}^{(1)}\})$, the indices $\mathbf{m}^{(1)}$ become redundant, but, for clarity they will be retained with $\mathbf{m}^{(1)} = \mathbf{0}$ rather than be omitted.

Substitution of Eqs. (109)–(112) into Eq. (101) and multiplication by $P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})$ lead to the recurrence formula for the ADOTEI's with respect to the angular momentum index $\mathbf{n}_j^{(1)}$,

$$\begin{aligned}[\mathbf{n}_j^{(1)} + \mathbf{1}_\mu::] &= (\mathbf{R}_G^{(1)} - \mathbf{R}_j^{(1)})_\mu [::] - \sum_{u=G^{(1)}+1}^{N^{(1)}} (\mathbf{R}_G^{(1)} - \mathbf{R}_u^{(1)})_\mu [::m_{uu}^{(1)} + 1] + (\mathbf{W}_G - \mathbf{R}_G^{(1)})_\mu [::m_{12} + 1] \\ &+ \frac{1}{2\zeta_G^{(1)}} \left\{ N_\mu(\mathbf{n}_{12}) \langle \mathbf{n}_{12} - \mathbf{1}_\mu::\rangle^{(1)} + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)}) \langle \mathbf{n}_i^{(1)} - \mathbf{1}_\mu::\rangle^{(1)} \right\} \\ &+ \frac{1}{\zeta_G^{(1)}} \sum_{g=1}^{G^{(1)}} \zeta_g^{(1)} \{ N_\mu(\mathbf{l}_g^{(1)}) \langle :\mathbf{l}_g^{(1)} - \mathbf{1}_\mu:\rangle^{(1)} - N_\mu(\mathbf{l}_j^{(1)}) \langle :\mathbf{l}_j^{(1)} - \mathbf{1}_\mu:\rangle^{(1)} \} \\ &+ \sum_{u=G^{(1)}+1}^{N^{(1)}} \{ N_\mu(\mathbf{l}_u^{(1)}) [:\mathbf{l}_u^{(1)} - \mathbf{1}_\mu:m_{uu}^{(1)} + 1] - N_\mu(\mathbf{l}_j^{(1)}) [:\mathbf{l}_j^{(1)} - \mathbf{1}_\mu:m_{uu}^{(1)} + 1] \} + S_{Aj}^{(1)} + S_{Aj}^{(2)}, \end{aligned} \tag{124}$$

where only the indices different from those in the integrals $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}]$ are explicitly given. The bracketted integrals $\langle::\rangle^{(k)}$ in Eq. (124) are defined by

$$\langle::\rangle^{(k)} = [::] - [::m_{12}+1] - \sum_{u=G^{(k)}+1}^{N^{(k)}} [::m_{uu}^{(k)} + 1], \tag{125}$$

and $S_{Aj}^{(k)}$ is expressed as

$$\begin{aligned} S_{Aj}^{(k)} &= - \sum_{u=G^{(k)}+1}^{N^{(k)}} (\mathbf{W}_G - \mathbf{R}_u^{(k)})_\mu [::M_{uu}+1] + \frac{1}{2\zeta_G} \sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)}) \ll \mathbf{n}_i^{(k)} - \mathbf{1}_\mu::\gg \\ &+ \frac{1}{\zeta_G} \sum_{g=1}^{G^{(k)}} \zeta_g^{(k)} \{ N_\mu(\mathbf{l}_g^{(k)}) \ll :\mathbf{l}_g^{(k)} - \mathbf{1}_\mu:\gg - N_\mu(\mathbf{l}_j^{(1)}) \ll :\mathbf{l}_j^{(1)} - \mathbf{1}_\mu:\gg \} \\ &+ \sum_{u=G^{(k)}+1}^{N^{(k)}} \{ N_\mu(\mathbf{l}_u^{(k)}) [:\mathbf{l}_u^{(k)} - \mathbf{1}_\mu:M_{uu}+1] - N_\mu(\mathbf{l}_j^{(1)}) [:\mathbf{l}_j^{(1)} - \mathbf{1}_\mu:M_{uu}+1] \}, \end{aligned} \tag{126}$$

where the doubly bracketted integrals $\ll:\!:\gg$ are

$$\ll:\!:\gg = [::m_{12}+1] - \sum_{k=1,2}\sum_{u=G^{(k)}+1}^{N^{(k)}} [::M_{uu}+1]. \tag{127}$$

The recurrence formula with respect to $\mathbf{n}_{12}$ [Eq. (103)] reduces to

$$[\mathbf{n}_{12}+\mathbf{1}_\mu::] = \sum_{k=1,2}\frac{1}{2\zeta_G^{(k)}} N_\mu(\mathbf{n}_{12})\langle \mathbf{n}_{12}-\mathbf{1}_\mu::\rangle^{(k)} + T_A^{(1)} - T_A^{(2)}, \tag{128}$$

where $T_A^{(k)}$ denotes

$$\begin{aligned} T_A^{(k)} = (\mathbf{R}_G^{(k)})_\mu \langle::\rangle^{(k)} &+ \sum_{u=G^{(k)}+1}^{N^{(k)}} (\mathbf{R}_u^{(k)})_\mu [::m_{uu}^{(k)}+1] + \frac{1}{2\zeta_G^{(k)}}\sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)})\langle \mathbf{n}_i^{(k)}-\mathbf{1}_\mu::\rangle^{(k)} \\ &+ \frac{1}{\zeta_G^{(k)}}\sum_{g=1}^{G^{(k)}} \zeta_g^{(k)} N_\mu(\mathbf{l}_g^{(k)})\langle:\mathbf{l}_g^{(k)}-\mathbf{1}_\mu:\rangle^{(k)} + \sum_{u=G^{(k)}+1}^{N^{(k)}} N_\mu(\mathbf{l}_u^{(k)})[:\mathbf{l}_u^{(k)}-\mathbf{1}_\mu:m_{uu}^{(k)}+1]. \end{aligned} \tag{129}$$

For the recurrence formula with respect to the derivative indices $\mathbf{l}_j^{(1)}$'s we have to consider two cases, namely, $j=g$ and $j=u$. When $j=g$, the orbital exponent $\zeta_j^{(1)}$ is not the integration exponent, and therefore multiplication of Eq. (105) by $P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})$ readily yields the recurrence formula

$$[:\mathbf{l}_g^{(1)}+\mathbf{1}_\mu:] = 2\zeta_g^{(1)}[\mathbf{n}_g^{(1)}+\mathbf{1}_\mu::] - N_\mu(\mathbf{n}_g^{(1)})[\mathbf{n}_g^{(1)}-\mathbf{1}_\mu::], \tag{130}$$

and substitution of Eq. (124) into the first term of Eq. (130) gives a formula involving lower angular momentum and derivative indices. When $j=u$, namely, the exponent $\zeta_u^{(1)}$ is the integration exponent, the integral $2\zeta_u^{(1)}[\mathbf{n}_u^{(1)}+\mathbf{1}_\mu:]$ multiplied by the factor $P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})$ is *not* the ADOTEI. Accordingly, we have to rewrite Eq. (105) by the use of Eq. (101) as well as Eqs. (109)–(112) in order to express the formula in terms of the ADOTEI's. Utilizing the following relation:

$$(1-\Theta)\zeta_u^{(1)}\left(1-\frac{\zeta_u^{(1)}}{Z^{(1)}}\right) + \Theta\zeta_u^{(1)}\left(1-\frac{\zeta_u^{(1)}}{Z}\right) = \zeta_G^{(1)}(\eta_u^{(1)}+\xi_u^{(1)}) + \sum_{\substack{v=G^{(1)}+1 \\ (v\neq u)}}^{N^{(1)}} (\eta_{uv}^{(1)}+\xi_{uv}^{(11)}) + \sum_{v=G^{(2)}+1}^{N^{(2)}} \xi_{uv}^{(12)}, \tag{131}$$

we finally arrive at the following recurrence formula:

$$\begin{aligned} [:\mathbf{l}_u^{(1)}+\mathbf{1}_\mu:] = {} & 2\zeta_G^{(1)}(\mathbf{R}_G^{(1)}-\mathbf{R}_u^{(1)})_\mu[::m_{uu}^{(1)}+1] + 2\zeta_G(\mathbf{W}_G-\mathbf{R}_u^{(1)})_\mu[::M_{uu}+1] \\ & + N_\mu(\mathbf{n}_{12})[\mathbf{n}_{12}-\mathbf{1}_\mu::m_{uu}^{(1)}+1] + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})[\mathbf{n}_i^{(1)}-\mathbf{1}_\mu::m_{uu}^{(1)}+1] \\ & + 2\sum_{g=1}^{G^{(1)}} \zeta_g^{(1)} N_\mu(\mathbf{l}_g^{(1)})[:\mathbf{l}_g^{(1)}-\mathbf{1}_\mu:m_{uu}^{(1)}+1] - 2\zeta_G^{(1)} N_\mu(\mathbf{l}_u^{(1)})[:\mathbf{l}_u^{(1)}-\mathbf{1}_\mu:m_{uu}^{(1)}+1] \\ & + U_u^{(1)} + U_u^{(2)} - N_\mu(\mathbf{n}_u^{(1)})[\mathbf{n}_u^{(1)}-\mathbf{1}_\mu::] + 2\sum_{v=G^{(1)}+1}^{N^{(1)}} (\mathbf{R}_v^{(1)}-\mathbf{R}_u^{(1)})_\mu[::m_{uv}^{(1)}+1] \\ & + 2\sum_{v=G^{(1)}+1}^{N^{(1)}} \{N_\mu(\mathbf{l}_v^{(1)})[:\mathbf{l}_v^{(1)}-\mathbf{1}_\mu:m_{uv}^{(1)}+1] - N_\mu(\mathbf{l}_u^{(1)})[:\mathbf{l}_u^{(1)}-\mathbf{1}_\mu:m_{uv}^{(1)}+1]\}, \end{aligned} \tag{132}$$

where $U_u^{(k)}$ is defined by

$$\begin{aligned} U_u^{(k)} = {} & \sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)})[\mathbf{n}_i^{(k)}-\mathbf{1}_\mu::M_{uu}+1] + 2\sum_{g=1}^{G^{(k)}} \zeta_g^{(k)} N_\mu(\mathbf{l}_g^{(k)})[:\mathbf{l}_g^{(k)}-\mathbf{1}_\mu:M_{uu}+1] \\ & - 2\zeta_G^{(k)} N_\mu(\mathbf{l}_u^{(1)})[:\mathbf{l}_u^{(1)}-\mathbf{1}_\mu:M_{uu}+1] + 2\sum_{v=G^{(k)}+1}^{N^{(k)}} (\mathbf{R}_v^{(k)}-\mathbf{R}_u^{(1)})_\mu[::M_{uv}+1] \\ & + 2\sum_{v=G^{(k)}+1}^{N^{(k)}} \{N_\mu(\mathbf{l}_v^{(k)})[:\mathbf{l}_v^{(k)}-\mathbf{1}_\mu:M_{uv}+1] - N_\mu(\mathbf{l}_u^{(1)})[:\mathbf{l}_u^{(1)}-\mathbf{1}_\mu:M_{uv}+1]\}. \end{aligned} \tag{133}$$

It is to be noted that the off-diagonal indices $m_{uv}^{(k)}$ and M_{uv} now appear in the last two terms of Eqs. (132) and (133), and they are to be read as $m_{vu}^{(k)}$ and M_{vu}, respectively, for $u>v$.

Substitution of Eqs. (109)–(112) into Eqs. (106) and (108) leads to the expression for the initial ADOTEI's

$$[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}]$$
$$= \mathcal{S}_G^{(1)}\mathcal{S}_G^{(2)}\left\{\frac{\zeta_G^{(1)}}{Z^{(1)}}\frac{\zeta_G^{(2)}}{Z^{(2)}}(1-\Theta)\right\}^{3/2}\mathscr{E}(\Theta,\rho_G(\mathbf{R}_G^{(1)}-\mathbf{R}_G^{(2)})^2,m_{12})$$
$$\times\left\{\prod_{u=G^{(1)}+1}^{N^{(1)}}\mathscr{F}_{u,0}^{(1)}\right\}\left\{\prod_{v=G^{(2)}+1}^{N^{(2)}}\mathscr{F}_{v,0}^{(2)}\right\}\left\{\prod_{u=G^{(1)}+1}^{N^{(1)}}\prod_{v=G^{(2)}+1}^{N^{(2)}}\mathscr{E}(\xi_{uv}^{(12)},(\mathbf{R}_u^{(1)}-\mathbf{R}_v^{(2)})^2,M_{uv})\right\}. \quad (134)$$

Here the factor $\mathcal{S}_G^{(k)}$ is the one-electron overlap integral over the first $G^{(k)}$ s-type Cartesian Gaussian functions in $\mathcal{G}^{(k)}$ $(\{\mathbf{0}^{(k)}\})$:

$$\mathcal{S}_G^{(k)} = \left(\frac{\pi}{\zeta_G^{(k)}}\right)^{3/2}\prod_{\substack{g,h=1\\(g<h)}}^{G^{(k)}} \times\exp\left[-\frac{\zeta_g^{(k)}\zeta_h^{(k)}}{\zeta_G^{(k)}}(\mathbf{R}_g^{(k)}-\mathbf{R}_h^{(k)})^2\right], \quad (135)$$

the function $\mathscr{E}(w,a,m)$ stands for

$$\mathscr{E}(w,a,m) = w^m\exp[-aw], \quad (136)$$

$\mathscr{F}_{u,0}^{(k)}$ can be expressed in terms of $\mathscr{E}(w,a,m)$ as

$$\mathscr{F}_{u,0}^{(k)} = \mathscr{E}(\eta_u^{(k)},\zeta_G^{(k)}(\mathbf{R}_G^{(k)}-\mathbf{R}_u^{(k)})^2,m_{uu}^{(k)})$$
$$\times\mathscr{E}(\xi_u^{(k)},\zeta_G(\mathbf{W}_G-\mathbf{R}_u^{(k)})^2,M_{uu})$$
$$\times\prod_{\substack{v=G^{(k)}+1\\(v>u)}}^{N^{(k)}}\{\mathscr{E}(\eta_{uv}^{(k)},(\mathbf{R}_u^{(k)}-\mathbf{R}_v^{(k)})^2,m_{uv}^{(k)})$$
$$\times\mathscr{E}(\xi_{uv}^{(kk)},(\mathbf{R}_u^{(k)}-\mathbf{R}_v^{(k)})^2,M_{uv})\}, \quad (137)$$

and ρ_G is defined by

$$\rho_G = \frac{\zeta_G^{(1)}\zeta_G^{(2)}}{\zeta_G^{(1)}+\zeta_G^{(2)}}. \quad (138)$$

It is to be noted that the initial ADOTEI's consist only of the function $\mathscr{E}(w,a,m)$ except for the factor $\mathcal{S}_G^{(1)}\mathcal{S}_G^{(2)}\{(\zeta_G^{(1)}/Z^{(1)})(\zeta_G^{(2)}/Z^{(2)})(1-\Theta)\}^{3/2}$ independent of the integration indices.

With the definitions of the BTEI's [Eq. (58)] and the ADOTEI's [Eq. (121)], we define auxiliary BTEI's (ABTEI's) as

$$(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})$$
$$= \mathcal{Q}_A\mathcal{Q}_I[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}]. \quad (139)$$

The recurrence formulas for the ABTEI's can be readily found by operating $\mathcal{Q}_A$ and $\mathcal{Q}_I$ on Eqs. (124), (128), (130), and (132), since the coefficients are now independent of the integration exponents. For $\mathcal{Q}_A = 1$, the resulting formulas take the same mathematical forms except that all the square brackets are replaced by parentheses.

We add how to get recurrence formulas with respect to the indices $\mathbf{n}_j^{(2)}$ and $\mathbf{l}_j^{(2)}$ of the jth function in the *second* factor $\mathcal{G}^{(2)}(\{\mathbf{n}^{(2)}\})$ of $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$ [Eq. (63)]. If one considers an interchange of the electron coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ in $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$, one may notice that the product $\mathcal{G}^{(2)}(\{\mathbf{n}^{(2)}\})$ becomes equivalent to $\mathcal{G}^{(1)}(\{\mathbf{n}^{(1)}\})$ in the original $\mathcal{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$, and the interchanged two-electron function $\varphi(\mathbf{r}_2-\mathbf{r}_1;\mathbf{n}_{12},\zeta_{12})$ takes the opposite sign to the original one $\varphi(\mathbf{r}_1-\mathbf{r}_2;\mathbf{n}_{12},\zeta_{12})$ when the angular momentum $|\mathbf{n}_{12}|$ is odd. The latter property means that the interchanged two-electron function $\varphi(\mathbf{r}_2-\mathbf{r}_1;\mathbf{n}_{12}\pm\mathbf{1}_\mu,\zeta_{12})$ having a higher or lower angular momentum by one always takes the opposite sign to $\varphi(\mathbf{r}_2-\mathbf{r}_1;\mathbf{n}_{12},\zeta_{12})$. Thus one has the following prescription: (1) interchange the superscripts 1 and 2 in the recurrence formulas given above, and (2) invert the signs of terms having the angular momentum index $\mathbf{n}_{12}+\mathbf{1}_\mu$ or $\mathbf{n}_{12}-\mathbf{1}_\mu$.

As an illustration of the present formulation, we give the recurrence formulas for the derivatives of the electron repulsion integrals (ERI's). Since the integrals include integration over u_{12} [Eq. (83)], we must resort to the formulas for the auxiliary integrals. With no integration exponent in $\mathcal{G}^{(k)}(\{\mathbf{n}^{(k)}\})$ $(k=1,2)$, the integration indices $\mathbf{m}^{(k)}$ and $\mathbf{M}$ are zero, namely, the factor P in ADOTEI's is $P=P(m,0,0,0)$, and all the terms involving summation over u or v in the recurrence formulas are missing. The auxiliary integrals reduce to

$$(\mathbf{n}_a\mathbf{n}_b,\mathbf{n}_c\mathbf{n}_d:\mathbf{l}_a\mathbf{l}_b,\mathbf{l}_c\mathbf{l}_d)^{(m)}$$
$$= (\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{l}_a,\mathbf{l}_b,\mathbf{l}_c,\mathbf{l}_d:m,0,0,0)$$
$$= \int_0^\infty du_{12}\frac{2}{\pi^{1/2}}$$
$$\times[\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{l}_a,\mathbf{l}_b,\mathbf{l}_c,\mathbf{l}_d:m,0,0,0] \quad (140)$$

according to Eqs. (83) and (139), and the recurrence formulas are found to take the forms

$$(\mathbf{n}_a+\mathbf{1}_\mu::) = (\mathbf{R}_G^{(1)}-\mathbf{R}_a)_\mu(::) + (\mathbf{W}_G-\mathbf{R}_G^{(1)})_\mu(::m+1) + \frac{1}{2\zeta_G^{(1)}}\sum_{i=a,b}N_\mu(\mathbf{n}_i)$$
$$\times\left\{(\mathbf{n}_i-\mathbf{1}_\mu::) - \frac{\rho_G}{\zeta_G^{(1)}}(\mathbf{n}_i-\mathbf{1}_\mu::m+1)\right\} + \frac{1}{2\zeta_G}\sum_{i=c,d}N_\mu(\mathbf{n}_i)(\mathbf{n}_i-\mathbf{1}_\mu::m+1)+A, \quad (141)$$

$$(:\mathbf{l}_a+\mathbf{1}_\mu:) = 2\zeta_a(\mathbf{n}_a+\mathbf{1}_\mu::) - N_\mu(\mathbf{n}_a)(\mathbf{n}_a-\mathbf{1}_\mu::) \quad (142)$$

from Eqs. (124) and (130), respectively, where A represents

$$A = -\frac{\zeta_b}{\zeta_G^{(1)}} N_\mu(\mathbf{l}_a)\left\{(:\mathbf{l}_a-\mathbf{1}_\mu:)+\frac{\zeta_a}{\zeta_b}\frac{\rho_G}{\zeta_G^{(1)}}(:\mathbf{l}_a-\mathbf{1}_\mu:m+1)\right\}+\frac{\zeta_b}{\zeta_G^{(1)}} N_\mu(\mathbf{l}_b)\left\{(:\mathbf{l}_b-\mathbf{1}_\mu:)-\frac{\rho_G}{\zeta_G^{(1)}}(:\mathbf{l}_b-\mathbf{1}_\mu:m+1)\right\}$$
$$+\frac{\zeta_c}{\zeta_G} N_\mu(\mathbf{l}_c)(:\mathbf{l}_c-\mathbf{1}_\mu:m+1)+\frac{\zeta_d}{\zeta_G} N_\mu(\mathbf{l}_d)(:\mathbf{l}_d-\mathbf{1}_\mu:m+1), \tag{143}$$

which vanishes when all the derivative indices $\mathbf{l}_i$ $(i=a,b,c,d)$ are $\mathbf{0}=(0,0,0)$. The recursive calculations begin with the integrals obtained from Eqs. (134) and (140):

$$(\mathbf{0}_a\mathbf{0}_b,\mathbf{0}_c\mathbf{0}_d:\mathbf{0}_a\mathbf{0}_b,\mathbf{0}_c\mathbf{0}_d)^{(m)}$$
$$=\frac{2}{\pi^{1/2}}\mathscr{S}_G^{(1)}\mathscr{S}_G^{(2)}\int_0^\infty du_{12}\left\{\frac{\zeta_G^{(1)}\zeta_G^{(2)}}{Z^{(1)}Z^{(2)}}(1-\Theta)\right\}^{3/2}$$
$$\times\mathscr{E}(\Theta,T,m)$$
$$=2\left(\frac{\rho_G}{\pi}\right)^{1/2}\mathscr{S}_G^{(1)}\mathscr{S}_G^{(2)}F_m(T), \tag{144}$$

where $Z^{(k)}$ $(k=1,2)$ is actually $\zeta_G^{(k)}$ in this case, and T denotes

$$T=\rho_G(\mathbf{R}_G^{(1)}-\mathbf{R}_G^{(2)})^2. \tag{145}$$

$F_m(T)$ reduces to

$$F_m(T)=\int_0^1 dt\, t^{2m}\exp[-Tt^2], \tag{146}$$

after the following transformation of the variable:

$$t^2=\frac{u_{12}^2}{\rho_G+u_{12}^2}, \tag{147}$$

and its evaluation is simple.[4,13,19,20] The above formulas are generalizations of those for the ERI's given in our previous paper[13] and those for the first and the second derivatives of ERI's given by Schlegel, Binkley, and Pople.[12]

Since the molecular integrals $(\mathbf{n}_a\mathbf{n}_b|\mathscr{E}_{\lambda\nu}|\mathbf{n}_c\mathbf{n}_d)$ and $(\mathbf{n}_a\mathbf{n}_b|\mathscr{R}_{\lambda\nu}|\mathbf{n}_c\mathbf{n}_d)$ take forms of linear combinations of the derivatives of ERI's [Eqs. (66) and (49)], the recurrence formulas readily follow from Eqs. (141)–(143) with appropriate derivative indices, such as $(\mathbf{l}_a,\mathbf{l}_b,\mathbf{l}_c,\mathbf{l}_d)=(\mathbf{0},\mathbf{0},\mathbf{1}_\lambda,\mathbf{1}_\nu)$ and $(\mathbf{0},\mathbf{0},\mathbf{0},\mathbf{1}_\lambda+\mathbf{1}_\nu)$ for $(\mathbf{n}_a\mathbf{n}_b|\mathscr{E}_{\lambda\nu}|\mathbf{n}_c\mathbf{n}_d)$. The recurrence formulas thus obtained take the same mathematical form with Eq. (141) for the first four terms, and the remaining terms in $(\mathbf{n}_a+\mathbf{1}_\mu,\mathbf{n}_b|\mathscr{E}_{\lambda\nu}|\mathbf{n}_c\mathbf{n}_d)$ and $(\mathbf{n}_a+\mathbf{1}_\mu,\mathbf{n}_b|\mathscr{R}_{\lambda\nu}|\mathbf{n}_c\mathbf{n}_d)$ become

$$A(\mathscr{E}_{\lambda\nu})=-\frac{\zeta_c+\zeta_d}{\zeta_G}\delta_{\mu\lambda}\langle d\nu\rangle-\frac{\zeta_d}{\zeta_G}\delta_{\mu\nu}\{\langle c\lambda\rangle+\langle d\lambda\rangle\} \tag{148}$$

and

$$A(\mathscr{R}_{\lambda\nu})=-\frac{\zeta_c+\zeta_d}{\zeta_G}[\delta_{\mu\lambda}\{\langle c\nu\rangle+\langle d\nu\rangle\}$$
$$+\delta_{\mu\nu}\{\langle c\lambda\rangle+\langle d\lambda\rangle\}], \tag{149}$$

respectively, with

$$\langle c\lambda\rangle=(\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{1}_{c\lambda},\mathbf{0}_d:m+1,0,0,0), \tag{150}$$

$$\langle d\lambda\rangle=(\mathbf{0}_{12},\mathbf{n}_a,\mathbf{n}_b,\mathbf{n}_c,\mathbf{n}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c,\mathbf{1}_{d\lambda}:m+1,0,0,0). \tag{151}$$

D. Exponential-factor-including basic integrals

Now to formulate molecular integrals including the exponential factor $\exp[i\mathbf{k}\cdot\mathbf{r}]$ in their integrands, we introduce exponential factor (EF)-including basic one-electron integrals (EF-BOEI's) and EF-including basic two-electron integrals (EF-BTEI's) as well as their auxiliary integrals.

We define *auxiliary* EF-including BOEI's (AEF-BOEI) $(\mathbf{k};\mathbf{q}|\{\mathbf{n}\}:\{\mathbf{l}\})$ as BOEI's whose integrand $\mathscr{G}(\{\mathbf{n}\})$ is multiplied by the factor $F(\mathbf{k};\mathbf{q})\exp[i\,\mathbf{k}\cdot\mathbf{r}]$,

$$(\mathbf{k};\mathbf{q}|\{\mathbf{n}\}:\{\mathbf{l}\})=\mathscr{Q}_A\mathscr{Q}_I[\mathbf{k};\mathbf{q}|\{\mathbf{n}\}:\{\mathbf{l}\}], \tag{152}$$

$$[\mathbf{k};\mathbf{q}|\{\mathbf{n}\}:\{\mathbf{l}\}]=F(\mathbf{k};\mathbf{q})\mathscr{Q}_D(\{\mathbf{l}\})\int d\mathbf{r}\,\mathscr{G}(\{\mathbf{n}\})$$
$$\times\exp[i\,\mathbf{k}\cdot\mathbf{r}], \tag{153}$$

$$F(\mathbf{k};\mathbf{q})=(ik_x)^{q_x}(ik_y)^{q_y}(ik_z)^{q_z}, \tag{154}$$

where the square-bracketted integral [Eq. (153)] is the auxiliary EF-including DOOEI (AEF-DOOEI), and $\mathbf{q}$ consists of nonnegative integers q_μ $(\mu=x,y,z)$ referred to as the *linear momentum index*. The true EF-BOEI's and EF-DOOEI's are, of course, those having the linear momentum index $\mathbf{q}$ being $\mathbf{0}=(0,0,0)$, since in this case the factor reduces to just $\exp[i\,\mathbf{k}\cdot\mathbf{r}]$.

Similarly we define EF-including two-electron integrals whose integrand $\mathscr{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$ is multiplied by the factor $F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})\exp[i\mathbf{k}^{(1)}\cdot\mathbf{r}_1+i\,\mathbf{k}^{(2)}\cdot\mathbf{r}_2]$:

$$(\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\})=\mathscr{Q}_A\mathscr{Q}_I$$
$$\times[\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}], \tag{155}$$

$$[\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]$$
$$=F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})\mathscr{Q}_D^{(1)}(\{\mathbf{l}^{(1)}\})\mathscr{Q}_D^{(2)}(\{\mathbf{l}^{(2)}\})$$
$$\times\int d\mathbf{r}_1\int d\mathbf{r}_2\,\mathscr{G}(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\})$$
$$\times\exp[i\,\mathbf{k}^{(1)}\cdot\mathbf{r}_1+i\,\mathbf{k}^{(2)}\cdot\mathbf{r}_2]. \tag{156}$$

Multiplication of Eq. (156) by $P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})$ gives the auxiliary EF-including *auxiliary* DOTEI (AEF-*A* DOTEI)

$$[\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},$$
$$\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}]$$
$$=[\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]$$
$$\times P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}). \tag{157}$$

As has been noted, the product of the Cartesian Gaussian function and $\exp[i\,\mathbf{k}\cdot\mathbf{r}]$ can be reduced to a linear combination of Cartesian Gaussian functions [Eqs. (14) and

(20)]. Therefore, the recurrence formulas given in the previous section can be utilized after substituting Eq. (20) into the EF-including integrals having $\mathbf{n}_{12}+\mathbf{1}_\mu$, $\mathbf{n}_j^{(k)}+\mathbf{1}_\mu$, or $\mathbf{l}_j^{(k)}+\mathbf{1}_\mu$ $(k=1,2)$. Although Eq. (20) includes sixfold summation [Eq. (24)], the reduction is not complicated by virtue of the four relations [Eqs. (26)–(29)]. The recurrence formula with respect to the angular momentum indices, for instance, becomes

$$\begin{aligned}[;|\mathbf{n}_j^{(1)}+\mathbf{1}_\mu:] &= \{(\mathbf{R}_Z^{(1)}-\mathbf{R}_j^{(1)})_\mu+\Theta(\mathbf{W}-\mathbf{R}_Z^{(1)})_\mu\}[;|:] + \frac{1-\Theta}{2Z^{(1)}}\Big\{N_\mu(\mathbf{n}_{12})[;|\mathbf{n}_{12}-\mathbf{1}_\mu:] \\ &\quad + \sum_{i=1}^{N^{(1)}} N_\mu(\mathbf{n}_i^{(1)})[;|\mathbf{n}_i^{(1)}-\mathbf{1}_\mu:]\Big\} + \frac{1-\Theta}{Z^{(1)}}\sum_{i=1}^{N^{(1)}}\zeta_i^{(1)}\{N_\mu(\mathbf{l}_i^{(1)})[;|:\mathbf{l}_i^{(1)}-\mathbf{1}_\mu] \\ &\quad - N_\mu(\mathbf{l}_j^{(1)})[;|:\mathbf{l}_j^{(1)}-\mathbf{1}_\mu]\} \\ &\quad + S_{\mathrm{EF}j}^{(1)} + S_{\mathrm{EF}j}^{(2)} + \langle[;|\mathbf{n}_j^{(1)}+\mathbf{1}_\mu:]\rangle, \end{aligned} \tag{158}$$

where $\mathbf{k}^{(k)}$ and $\mathbf{q}^{(k)}$ $(k=1,2)$ in the AEF-DOTEI's have been omitted for simplicity, and $S_{\mathrm{EF}j}^{(k)}$ is defined by

$$S_{\mathrm{EF}j}^{(k)} = \frac{\Theta}{2Z}\sum_{i=1}^{N^{(k)}} N_\mu(\mathbf{n}_i^{(k)})[;|\mathbf{n}_i^{(k)}-\mathbf{1}_\mu:] + \frac{\Theta}{Z}\sum_{i=1}^{N^{(k)}}\zeta_i^{(k)}\{N_\mu(\mathbf{l}_i^{(k)})[;|:\mathbf{l}_i^{(k)}-\mathbf{1}_\mu] - N_\mu(\mathbf{l}_j^{(1)})[;|:\mathbf{l}_j^{(1)}-\mathbf{1}_\mu]\}. \tag{159}$$

The last term $\langle[:|\mathbf{n}_j^{(1)}+\mathbf{1}_\mu:]\rangle$ results from the decomposition of the complex parameters $\mathbf{R}_Z^{(1)\dagger}$ and $\mathbf{W}^\dagger$ into the real parameters and $i\,\mathbf{k}^{(k)}(k=1,2)$, and involves terms whose linear momentum indices $\mathbf{q}^{(1)}$ and $\mathbf{q}^{(2)}$ are increased by one:

$$\langle[;|\mathbf{n}_j^{(1)}+\mathbf{1}_\mu:]\rangle = \frac{1-\Theta}{2Z^{(1)}}[;\mathbf{q}^{(1)}+\mathbf{1}_\mu|:] + \frac{\Theta}{2Z}\sum_{k=1,2}[;\mathbf{q}^{(k)}+\mathbf{1}_\mu|:]. \tag{160}$$

As can be seen from these formulas, the expression for $[;|\mathbf{n}_j^{(1)}+\mathbf{1}_\mu:]$ takes the same form with that for $[\mathbf{n}_j^{(1)}+\mathbf{1}_\mu:]$ [Eq. (101)] except for the last term. Remaining recurrence formulas reduced from Eqs. (103), (105), (124), (128), (130), and (132) also take the same forms with those for the corresponding ones except for the additional terms resulting from the decomposition of the complex parameters. In the following we give only these additional terms:

$$\langle[;|\mathbf{n}_{12}+\mathbf{1}_\mu:]\rangle = \frac{1-\Theta}{2Z^{(1)}}[;\mathbf{q}^{(1)}+\mathbf{1}_\mu|:] - \frac{1-\Theta}{2Z^{(2)}}[;\mathbf{q}^{(2)}+\mathbf{1}_\mu|:], \tag{161}$$

$$\langle[;|:\mathbf{l}_j^{(1)}+\mathbf{1}_\mu]\rangle = 0, \tag{162}$$

$$\langle[;|\mathbf{n}_j^{(1)}+\mathbf{1}_\mu::]\rangle = \frac{1}{2\zeta_G^{(1)}}\langle;\mathbf{q}^{(1)}+\mathbf{1}_\mu|::\rangle^{(1)} + \frac{1}{2\zeta_G}\sum_{k=1,2}\ll;\mathbf{q}^{(k)}+\mathbf{1}_\mu|::\gg, \tag{163}$$

$$\langle[;|\mathbf{n}_{12}+\mathbf{1}_\mu::]\rangle = \frac{1}{2\zeta_G^{(1)}}\langle;\mathbf{q}^{(1)}+\mathbf{1}_\mu|::\rangle^{(1)} - \frac{1}{2\zeta_G^{(2)}}\langle;\mathbf{q}^{(2)}+\mathbf{1}_\mu|::\rangle^{(2)}, \tag{164}$$

$$\langle[;|:\mathbf{l}_g^{(1)}+\mathbf{1}_\mu:]\rangle = 0, \tag{165}$$

$$\langle[;|:\mathbf{l}_u^{(1)}+\mathbf{1}_\mu:]\rangle = \frac{1}{2\zeta_G^{(1)}}[;\mathbf{q}^{(1)}+\mathbf{1}_\mu|::m_{uu}^{(1)}+1] + \sum_{k=1,2}[;\mathbf{q}^{(k)}+\mathbf{1}_\mu|::M_{uu}+1], \tag{166}$$

where $\langle;|::\rangle^{(k)}(k=1,2)$ and $\ll;|::\gg$ are defined similarly to $\langle::\rangle^{(k)}$ and $\ll::\gg$ [Eqs. (125) and (127)]:

$$\langle;|::\rangle^{(k)} = [;|::] - [;|::m_{12}+1] - \sum_{u=G^{(k)}+1}^{N^{(k)}}[;|::m_{uu}^{(k)}+1], \tag{167}$$

$$\ll;|::\gg = [;|::m_{12}+1] - \sum_{k=1,2}\sum_{u=G^{(k)}+1}^{N^{(k)}}[;|::m_{uu}^{(k)}+1]. \tag{168}$$

The expressions for the AEF-DOTEI's and the AEF-*A* DOTEI's over *s*-type functions reduce via Eqs. (106) and (134) to

$$\begin{aligned}&[\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}] \\ &\quad = F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}]^\dagger \\ &\quad = F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}]\exp[T_{\mathrm{EF}}]\end{aligned} \tag{169}$$

and

$$\begin{aligned}&[\mathbf{k}^{(1)},\mathbf{k}^{(2)};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}] \\ &\quad = F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}]^\dagger \\ &\quad = F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})[\mathbf{0}_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}]\exp[T_{\mathrm{EF}}],\end{aligned} \tag{170}$$

respectively, where the daggers in Eqs. (169) and (170) indicate that the parameters $\mathbf{R}_Z^{(k)}$, $\mathbf{R}_G^{(k)}$, $\mathscr{S}^{(k)}$, $\mathscr{S}_G^{(k)}(k=1,2)$, and $\mathbf{W}_G$ have been replaced by the following daggered ones:

$$\mathbf{R}_Z^{(k)\dagger} = \mathbf{R}_Z^{(k)} + \frac{i\mathbf{k}^{(k)}}{2Z^{(k)}}, \tag{171}$$

$$\mathbf{R}_G^{(k)\dagger} = \mathbf{R}_G^{(k)} + \frac{i\mathbf{k}^{(k)}}{2\zeta_G^{(k)}}, \tag{172}$$

$$\mathscr{S}^{(k)\dagger} = \mathscr{S}^{(k)} \exp\left[i\mathbf{k}^{(k)}\left(\mathbf{R}_Z^{(k)} + \frac{i\mathbf{k}^{(k)}}{4Z^{(k)}}\right)\right], \tag{173}$$

$$\mathscr{S}_G^{(k)\dagger} = \mathscr{S}_G^{(k)} \exp\left[i\mathbf{k}^{(k)}\left(\mathbf{R}_G^{(k)} + \frac{i\mathbf{k}^{(k)}}{4\zeta_G^{(k)}}\right)\right], \tag{174}$$

$$\mathbf{W}_G^{\dagger} = \mathbf{W}_G + \frac{i\mathbf{k}^{(1)} + i\mathbf{k}^{(2)}}{2\zeta_G}. \tag{175}$$

The last expressions of Eqs. (169) and (170) do not involve the daggered parameters while they include the exponential factor $\exp[T_{\mathrm{EF}}]$, where

$$T_{\mathrm{EF}} = (1-\Theta)\sum_{k=1,2} i\mathbf{k}^{(k)}\left(\mathbf{R}_Z^{(k)} + \frac{i\mathbf{k}^{(k)}}{4Z^{(k)}}\right) + \Theta(i\mathbf{k}^{(1)} + i\mathbf{k}^{(2)})\left(\mathbf{W} + \frac{i\mathbf{k}^{(1)} + i\mathbf{k}^{(2)}}{4Z}\right), \tag{176}$$

which can be rewritten by the use of Eqs. (109)–(112) as

$$T_{\mathrm{EF}} = \sum_{k=1,2} i\mathbf{k}^{(k)}\left\{(1-\Theta)\frac{\zeta_G^{(k)}}{Z^{(k)}}\left(\mathbf{R}_G^{(k)} + \frac{i\mathbf{k}^{(k)}}{4\zeta_G^{(k)}}\right) + \sum_{u=G^{(k)}+1}^{N^{(k)}} \eta_u^{(k)}\mathbf{R}_u^{(k)}\right\} + (i\mathbf{k}^{(1)} + i\mathbf{k}^{(2)})\left\{\Theta\left(\mathbf{W}_G + \frac{i\mathbf{k}^{(1)} + i\mathbf{k}^{(2)}}{4\zeta_G}\right) + \sum_{k=1,2}\sum_{u=G^{(k)}+1}^{N^{(k)}} \xi_u^{(k)}\mathbf{R}_u^{(k)}\right\}. \tag{177}$$

Let us illustrate the EF-including integrals. Theoretical analysis of the van der Waals forces based on the linear response theory[21] requires the following two-electron integrals:

$$(\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}) = \pi^3 \int d\mathbf{k}\,\frac{1}{|\mathbf{k}|}\exp[i\mathbf{k}\cdot\mathbf{V}][\mathbf{k};\mathbf{0}^{(1)},\mathbf{0}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}], \tag{178}$$

where $\mathbf{V}$ is a prefixed coordinate, and $[\mathbf{k};\mathbf{0}^{(1)},\mathbf{0}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$ is the EF-including integrals defined by

$$[\mathbf{k};\mathbf{0}^{(1)},\mathbf{0}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}] = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \exp[-i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)] \times \mathscr{G}^{(1)}(\{\mathbf{n}^{(1)}\})\mathscr{G}^{(2)}(\{\mathbf{n}^{(2)}\}). \tag{179}$$

One may notice that the integral $[\mathbf{k};\mathbf{0}^{(1)},\mathbf{0}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$ is closely related to the momentum–space represen-tation of the two-electron density described by $\mathscr{G}^{(1)}(\{\mathbf{n}^{(1)}\})\mathscr{G}^{(2)}(\{\mathbf{n}^{(2)}\})$. The integral $[\mathbf{k};\mathbf{0}^{(1)},\mathbf{0}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$ can be expressed in terms of the AEF-DOTEI's as

$$[\mathbf{k};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}] = \lim_{\zeta_{12}\to 0}[-\mathbf{k},\mathbf{k};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\mathbf{0}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}] \tag{180}$$

with $\mathbf{q}^{(k)} = \mathbf{0}(k=1,2)$, so that Eqs. (158) and (180) yield the recurrence formula for the integrals $[k;\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}]$,

$$[\mathbf{k};|\mathbf{n}_j^{(1)} + \mathbf{1}_\mu] = (\mathbf{R}_Z^{(1)} - \mathbf{R}_j^{(1)})_\mu[\mathbf{k};|] + \sum_{i=1}^{N^{(1)}}\frac{N_\mu(\mathbf{n}_i^{(1)})}{2Z^{(1)}} \times [\mathbf{k};|\mathbf{n}_i^{(1)} - \mathbf{1}_\mu] + \frac{1}{2Z^{(1)}}[\mathbf{k};\mathbf{q}^{(1)} + \mathbf{1}_\mu|]. \tag{181}$$

If one introduces the auxiliary molecular integrals defined by

$$(\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\mathbf{q}^{(1)},\mathbf{q}^{(2)}) = \pi^3 \int d\mathbf{k}\,\frac{1}{|\mathbf{k}|}\exp[i\mathbf{k}\cdot\mathbf{V}][\mathbf{k};\mathbf{q}^{(1)},\mathbf{q}^{(2)}|\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}], \tag{182}$$

the recurrence formula for the auxiliary molecular integrals becomes

$$(\mathbf{n}_j^{(1)} + \mathbf{1}_\mu:) = (\mathbf{R}_Z^{(1)} - \mathbf{R}_j^{(1)})_\mu(:) + \sum_{i=1}^{N^{(1)}}\frac{N_\mu(\mathbf{n}_i^{(1)})}{2Z^{(1)}} \times (\mathbf{n}_i^{(1)} - \mathbf{1}_\mu:) + \frac{1}{2Z^{(1)}}(:\mathbf{q}^{(1)} + \mathbf{1}_\mu), \tag{183}$$

where only different indices from those in $(\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\mathbf{q}^{(1)},\mathbf{q}^{(2)})$ are given. Equations (169), (176), (180), and (182) provide us with the expression for the initial integrals

$$(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{q}^{(1)},\mathbf{q}^{(2)}) = \pi^3\mathscr{S}^{(1)}\mathscr{S}^{(2)}\mathscr{K}(|\mathbf{q}^{(1)}|) \times \int d\mathbf{k}\,\frac{1}{|\mathbf{k}|}(ik_x)^{q_x}(ik_y)^{q_y}(ik_z)^{q_z}\exp[i\mathbf{k}\cdot\mathbf{Q}] \times \exp\left[-\frac{\mathbf{k}^2}{4\rho_Z}\right], \tag{184}$$

where ρ_Z has been defined by Eq. (100), $|\mathbf{q}^{(1)}|$ is the sum of $q_x^{(1)}$, $q_y^{(1)}$, and $q_z^{(1)}$, and other parameters $\mathscr{K}(|\mathbf{q}^{(1)}|)$, q_μ, and $\mathbf{Q}$ denote

$$\mathscr{K}(|\mathbf{q}^{(1)}|) = \begin{cases} 1 & (|\mathbf{q}^{(1)}| = \text{even}) \\ -1 & (|\mathbf{q}^{(1)}| = \text{odd}) \end{cases}, \tag{185}$$

$$q_\mu = q_\mu^{(1)} + q_\mu^{(2)}, \tag{186}$$

and

$$\mathbf{Q} = \mathbf{V} - \mathbf{R}_Z^{(1)} + \mathbf{R}_Z^{(2)}, \tag{187}$$

respectively.

As can be seen from Eq. (184), the initial integrals satisfy the following differential relation with respect to $\mathbf{Q}$:

$$\begin{aligned}(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{q}^{(1)},\mathbf{q}^{(2)}) &= \mathscr{K}(|\mathbf{q}^{(1)}|)\left[\frac{\partial}{\partial Q_x}\right]^{q_x}\left[\frac{\partial}{\partial Q_y}\right]^{q_y}\left[\frac{\partial}{\partial Q_z}\right]^{q_z} \\ &\times(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{0}^{(1)},\mathbf{0}^{(2)}).\end{aligned} \tag{188}$$

As a consequence, we have to evaluate $(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{0}^{(1)},\mathbf{0}^{(1)})$, which can be expressed as[21]

$$(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{0}^{(1)},\mathbf{0}^{(2)}) = B(\mathbf{Q}^2)F_0(T), \tag{189}$$

where $F_m(T)$ has been defined by Eq. (146), and

$$B(\mathbf{Q}^2) = 8\pi^4\rho_Z\mathscr{S}^{(1)}\mathscr{S}^{(2)}\exp[-\rho_Z\mathbf{Q}^2], \tag{190}$$

$$T = -\rho_Z\mathbf{Q}^2. \tag{191}$$

Then $(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{1}_\mu^{(1)},\mathbf{0}^{(2)})$ and $(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{1}_\mu^{(1)},\mathbf{1}_\nu^{(2)})$, for instance, become

$$\begin{aligned}&(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{1}_\mu^{(1)},\mathbf{0}^{(2)}) \\ &\quad = 2\rho_Z Q_\mu B(\mathbf{Q}^2)\{F_0(T) - F_1(T)\}\end{aligned} \tag{192}$$

and

$$\begin{aligned}&(\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\mathbf{1}_\mu^{(1)},\mathbf{1}_\nu^{(2)}) \\ &\quad = 2\rho_Z\delta_{\mu\nu}B(\mathbf{Q}^2)\{F_0(T) - F_1(T)\} \\ &\qquad - 4\rho_Z^2 Q_\mu Q_\nu B(\mathbf{Q}^2)\{F_0(T) - 2F_1(T) + F_2(T)\},\end{aligned} \tag{193}$$

respectively.

We note that the recurrence formulas and the expressions for the initial integrals provide us with a simple scheme to obtain nonrecursive but explicit expressions for molecular integrals over higher angular momentum functions. Thus the formulas, such as Eqs. (183), (189), (192), and (193), can reproduce the explicit expressions over all possible combinations of s and p functions tabulated according to Boys' scheme[2] by Ishida.[21]

III. DISCUSSION

The auxiliary basic two-electron integrals (ABTEI's) with $\mathscr{Q}_A = 1$,

$$\begin{aligned}&(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}) \\ &\quad = \mathscr{Q}_1[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}],\end{aligned} \tag{194}$$

which will be discussed in this section, are closely related to important two-electron integrals, such as the electron repulsion integrals and their derivatives. The effect of $\mathscr{Q}_A(\neq 1)$ on the recurrence formulas is trivial, as in Eq. (84). The recurrence formulas for ADOTEI's given in the previous sections will be referred to as those for the ABTEI's, because for $\mathscr{Q}_A = 1$ they take the same mathematical forms.

First we consider the range of the values of the integration indices m_{12}, $\mathbf{m}^{(k)}$, and $\mathbf{M}$ in the initial ABTEI's $(0_{12},\{\mathbf{0}^{(1)}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{0}^{(1)}\}.\{\mathbf{0}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})$ necessary to start the recursive calculations to get the target integrals $(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}:0_{12},\mathbf{0}^{(1)},\mathbf{0}^{(2)},\mathbf{0})$. The lower bound of these indices is zero, and their upper bound remains to be found. From the recurrence formulas (124), (128), (130), and (132), one notes that the sum of all the indices $\mathbf{n}_{12}$, $\mathbf{n}_i^{(k)}$, $\mathbf{l}_i^{(k)}$, m_{12}, $\mathbf{m}^{(k)}$, and $\mathbf{M}$ in each ABTEI in the right-hand side is not greater than the sum on the left-hand side. Repeated use of this relation gives a relation between the sums of the initial integrals and the target integrals. The sums of the diagonal and the off-diagonal integration indices in the initial integrals designated as M_{dia} and M_{off}, respectively,

$$M_{\text{dia}} = m_{12} + \sum_{k=1,2}\sum_{u=G^{(k)}+1}^{N^{(k)}}(m_{uu}^{(k)} + M_{uu}), \tag{195}$$

$$\begin{aligned}M_{\text{off}} &= \sum_{k=1,2}\sum_{\substack{u,v=G^{(k)}+1 \\ (u<v)}}^{N^{(k)}}(m_{uv}^{(k)} + M_{uv}) \\ &\quad + \sum_{u=G^{(1)}+1}^{N^{(1)}}\sum_{v=G^{(2)}+1}^{N^{(2)}}M_{uv},\end{aligned} \tag{196}$$

satisfy the following inequalities:

$$0 \leqslant M_{\text{dia}} + M_{\text{off}} \leqslant |\mathbf{n}_{12}| + \sum_{k=1,2}\sum_{i=1}^{N^{(k)}}(|\mathbf{n}_i^{(k)}| + |\mathbf{l}_i^{(k)}|), \tag{197}$$

$$0 \leqslant M_{\text{off}} \leqslant \sum_{k=1,2}\sum_{u=G^{(k)}+1}^{N^{(k)}}|\mathbf{l}_u^{(k)}|, \tag{198}$$

where $|\mathbf{l}|$ is the sum of l_x, l_y, and l_z, and the latter inequality obtains because the off-diagonal indices are involved only in the recurrence formula for $(:\mathbf{l}_u^{(k)} + \mathbf{1}_\mu:)$. In the case of the derivatives of the electron repulsion integrals [Eq. (140)], for instance, the inequality (197) becomes

$$0 \leqslant m \leqslant \sum_{i=a,b,c,d}(|\mathbf{n}_i| + |\mathbf{l}_i|). \tag{199}$$

Since the auxiliary BTEI's are mathematical artifacts introduced to reduce the expressions to recursive forms, they are less directly related to the physical situation than the corresponding true integrals. This means that it is not guaranteed that the auxiliary integrals take finite values. Of course, their finiteness is essential for the present recursive formulation, and hence we investigate the condition of the ABTEI's being finite when the corresponding true BTEI's are finite. The recurrence formulas given in the previous sections are linear with respect to the ABTEI's, so that they do not induce divergence (if they are not linear, say, including divisions by the ABTEI's, they would diverge when the integrals happen to vanish). Therefore the divergence of ABTEI's would originate from the divergence of the initial ABTEI's, which differ from the corresponding true ones only for the nonzero value of m in $\mathscr{E}(w,a,m)$ [Eq. (134)].

Thus we have only to investigate the relation between $\mathscr{E}(w,a,m)$ $(m>0)$ and $\mathscr{E}(w,a,0)$.

When m is one of the indices m_{12} and the diagonal ones $m_{uu}^{(k)}$ and M_{uu}, the parameter w in $\mathscr{E}(w,a,m)$ stands for one of the factors Θ, $\eta_u^{(k)}$, and $\xi_u^{(k)}$, respectively. For the possible values of the integration exponents ζ_{12} and $\zeta_u^{(k)}$ $(0\leqslant\zeta_{12},\zeta_u^{(k)}\leqslant\infty)$ any one of these parameters takes a value between zero and one $(0\leqslant\Theta,\eta_u^{(k)},\xi_u^{(k)}\leqslant 1)$, as can be seen from Eqs. (99), (117), and (118). For $0\leqslant w\leqslant 1$, $\mathscr{E}(w,a,m)$ satisfies the following inequality:

$$0\leqslant\mathscr{E}(w,a,m)=w^m\mathscr{E}(w,a,0)\leqslant\mathscr{E}(w,a,0)$$
$$(a\geqslant 0,0\leqslant w\leqslant 1,m>0)\,. \tag{200}$$

Application of this inequality to the integrands of the initial ABTEI's yields the following relation:

$$0\leqslant(::m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})\leqslant(::0_{12},\mathbf{m}_{\rm off}^{(1)},\mathbf{m}_{\rm off}^{(2)},\mathbf{M}_{\rm off})\,, \tag{201}$$

where the subscript off indicates that only the off-diagonal part of the indices have nonzero values. For $\mathbf{m}_{\rm off}^{(k)}=\mathbf{0}$ and $\mathbf{M}_{\rm off}=\mathbf{0}$, corresponding to a large class of molecular integrals, Eq. (201) shows that the auxiliary integrals are finite.

When m in $\mathscr{E}(w,a,m)$ is one of the off-diagonal indices $m_{uv}^{(k)}$ and M_{uv}, w denotes one of the factors $\eta_{uv}^{(k)}$ and $\xi_{uv}^{(kk')}$, respectively, and takes, at maximum, positive infinity for the possible values of ζ_{12} and $\zeta_u^{(k)}$'s. Because of the exponential factor in $\mathscr{E}(w,a,m)$, however, the following relation holds as far as $a=(\mathbf{R}_u^{(k)}-\mathbf{R}_v^{(k')})^2$ is not zero:

$$\mathscr{E}(w,a,m)=w^m\mathscr{E}(w,a,0)$$
$$=w^m\exp[-aw]\to 0\quad(a>0,w\to\infty,m\geqslant 0)\,. \tag{202}$$

Therefore, for a large value of w the contribution of $\mathscr{E}(w,a,m)$ to the integrals can be ignored, which means that we can find a finite positive value $V_{\max}$ which satisfies the relation

$$0\leqslant(::0_{12},\mathbf{m}_{\rm off}^{(1)},\mathbf{m}_{\rm off}^{(2)},\mathbf{M}_{\rm off})\leqslant V_{\max}(::0_{12},\mathbf{0}^{(1)},\mathbf{0}^{(2)},\mathbf{0})\,. \tag{203}$$

From Eqs. (201) and (203), one sees that the auxiliary integrals are finite as far as $a>0$, namely, the centers $\mathbf{R}_u^{(k)}$ and $\mathbf{R}_v^{(k')}$ of functions having integration exponents are different from each other. Note that even if $a=0$, namely $\mathbf{R}_u^{(k)}=\mathbf{R}_v^{(k')}$, corresponding to the same function center, the integrals having the sum of the derivative indices $\mathbf{l}_u^{(k)},\mathbf{l}_v^{(k')}\cdots$ less than 2:

$$\sum_{\substack{k,u\\(\text{same function center})}}|\mathbf{l}_u^{(k)}|<2 \tag{204}$$

can be evaluated by using the recurrence formula for $(:\mathbf{1}_u^{(k)}+\mathbf{1}_\mu:)$, since in this case the terms with positive off-diagonal indices in the formula drop out by virtue of $(\mathbf{R}_u^{(k)}-\mathbf{R}_v^{(k')})_\mu=0$ and $N_\mu(\mathbf{l}_u^{(k)})=0$.

The same discussion is applicable to the finiteness of the AEF-ABTEI's as far as the integrations over the integration exponents $\zeta_u^{(k)}$'s and ζ_{12} are concerned, since the AEF-ABTEI's [Eq. (170)] are just ABTEI's multiplied by the factor $F(\mathbf{k}^{(1)};\mathbf{q}^{(1)})F(\mathbf{k}^{(2)};\mathbf{q}^{(2)})\exp(T_{\rm EF})$, which is common to both the auxiliary and true integrals.

Once the initial ABTEI's are found to be finite, they can be evaluated, namely, integrated over u's in $\mathscr{Q}_I$ straightforwardly. Although in some cases convenient expressions for actual evaluations can be found, such as $F_m(T)$ [Eq. (146)] for the electron repulsion integrals and their derivatives, in general the integrations are to be replaced by the quadrature sums

$$\mathscr{Q}_I H(\zeta_u)\sim\mathscr{Q}_Q H(\zeta_{u\alpha})=\sum_\alpha\frac{2\zeta_{u\alpha}^{(\lambda-1)/2}}{\Gamma(\lambda/2)}W_\alpha H(\zeta_{u\alpha})\,, \tag{205}$$

where α refers to the quadrature node, $\zeta_{u\alpha}$ is the integration exponent at the quadrature node, and W_α is the weight factor. Numerical calculation based on the quadrature formulas is a classical mathematical problem, so we just refer to the famous books by Stroud and Secrest,[22] and Krylov.[23]

With the quadrature, we have two computational procedures for the calculation of the target integrals. The first one is, as above, to use the quadrature only for the initial integrals, and then to proceed recursively by using the recurrence formulas for the ABTEI's. The second one is to use the quadrature directly to the target integrals

$$(\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\})$$
$$\sim\mathscr{Q}_Q[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]_\alpha\,, \tag{206}$$

where $\mathscr{Q}_Q$ denotes the product of the quadrature sums as in Eq. (205), and the integrals $[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]_\alpha$ can be evaluated recursively by using the recurrence formulas for the DOTEI's [Eqs. (101), (103), and (105)] rather than those for the auxiliary ones. The second procedure can be made efficient by taking advantage of the fact that the DOTEI's can be factored as the product of three Cartesian components

$$[\mathbf{n}_{12},\{\mathbf{n}^{(1)}\},\{\mathbf{n}^{(2)}\}:\{\mathbf{l}^{(1)}\},\{\mathbf{l}^{(2)}\}]$$
$$=\prod_{\mu=x,y,z}[n_{12\mu},\{n_\mu^{(1)}\},\{n_\mu^{(2)}\}:\{l_\mu^{(1)}\},\{l_\mu^{(2)}\}]\,, \tag{207}$$

and the linearity of the recurrence formulas allows us to write the recurrence formula for each Cartesian component. Details can be found in the work by King, Dupuis, and Rys[8] for calculations of the electron repulsion integrals. Note that the efficiency of the second procedure relies on the smallness of the number of quadrature nodes, because for each node each of the three Cartesian components of the DOTEI's has to be calculated.

It would be noteworthy that even for the basic integrals with *divergent* operators the recurrence relations remain valid. This is because the divergence appears after the integration of the ADOTEI's over u's in $\mathscr{Q}_I$, while the recurrence relations already hold before the integration. By virtue of this property, we need not worry about the appearance of divergent operators in reducing molecular integrals to sums of the basic integrals [Eqs. (50) and (51)]. In actual calculations, of course, one must employ sums of the recurrence formulas for the basic integrals and of the initial integrals rather than sums of the *values* evaluated from these expressions. This caution would not be trivial when the quadrature is employed with a finite numerical accuracy on a computer, because the more accurate quadrature does not always give

the more accurate value in the "sum-of-values" scheme. Let us give an illustration. The first expression for $\mathscr{R}_{\mu\nu}$ in Eq. (39),

$$\mathscr{R}_{\mu\nu}=\sigma_1+\sigma_2=\frac{\delta_{\mu\nu}}{|\mathbf{r}_1-\mathbf{r}_2|^3}-3\frac{(\mathbf{r}_1-\mathbf{r}_2)_\mu(\mathbf{r}_1-\mathbf{r}_2)_\nu}{|\mathbf{r}_1-\mathbf{r}_2|^5} \tag{208}$$

consists of divergent operators, and the divergence can be seen in the expressions for the initial integrals

$$(\mathbf{0}_a\mathbf{0}_b|\sigma_1|\mathbf{0}_c\mathbf{0}_d)^{(m)} = V\delta_{\mu\nu}\int_0^1 dt\left\{\frac{1}{1-t^2}\right\}t^{2(m+1)}\exp[-Tt^2], \tag{209}$$

$$\begin{aligned}(\mathbf{0}_a\mathbf{0}_b|\sigma_2|\mathbf{0}_c\mathbf{0}_d)^{(m)} &= V\delta_{\mu\nu}\int_0^1 dt\left\{\frac{-t^2}{1-t^2}\right\}t^{2(m+1)}\exp[-Tt^2] \\ &\quad -2\rho_G V(\mathbf{R}_G^{(1)}-\mathbf{R}_G^{(2)})_\mu(\mathbf{R}_G^{(1)}-\mathbf{R}_G^{(2)})_\nu \\ &\quad \times\int_0^1 dt\,t^{2(m+2)}\exp[-Tt^2],\end{aligned} \tag{210}$$

$$V=4\rho_G\left(\frac{\rho_G}{\pi}\right)^{1/2}\mathscr{S}_G^{(1)}\mathscr{S}_G^{(2)}, \tag{211}$$

obtained from the expressions for σ_1 and σ_2,

$$\sigma_1=\delta_{\mu\nu}\int_0^\infty du_{12}\frac{2u_{12}^2}{\Gamma(3/2)}\varphi(\mathbf{r}_1-\mathbf{r}_2;\mathbf{0}_{12},u_{12}^2), \tag{212}$$

$$\sigma_2=-3\int_0^\infty du_{12}\frac{2u_{12}^4}{\Gamma(5/2)}\varphi(\mathbf{r}_1-\mathbf{r}_2;\mathbf{1}_\mu+\mathbf{1}_\nu,u_{12}^2), \tag{213}$$

as well as from Eqs. (128), (134), and the transformation of the variable u_{12} to t [Eq. (147)]. As $t\to 1$, the factors in braces in Eqs. (209) and (210) become positive and negative infinity, respectively, while the other factors in the integrands remain positive finite, so that these integrals diverge. When one employs a less accurate quadrature, with few quadrature nodes near $t=1$, the sum-of-values scheme might give reasonable values for the initial integrals. However, with a more accurate quadrature having many nodes near $t=1$ as well as in other regions within $0\leqslant t\leqslant 1$, the scheme will fail to give more accurate values owing to the divergent factors. On the contrary, the "sum-of-expressions" scheme works well because the divergent factors become identically unity in the summed expression. In this particular case of $\mathscr{R}_{\mu\nu}$, the initial integrals can be calculated by using the recurrence formulas for $(:\mathbf{l}_g+\mathbf{1}_\mu:)$ [Eq. (142)] and the initial integrals for the electron repulsion integrals [Eq. (144)]. Thus in this sum-of-expressions scheme, no divergence difficulty arises.

In general, any numerical calculations based on recurrence relations are advised to check whether recursively calculated values become less accurate due to the amplification of the original errors of the initial value. If the recurrence relation is used a large number of times, and/or if quite accurate final values are required, it would be safe to check the stability of the recurrence relation mathematically.[24] In the usual *ab initio* calculations, however, the recurrence relations for the molecular integrals are used a moderate number of times, for instance, eight times for the electron repulsion integral $(d_{xy}d_{xy},d_{xy}d_{xy})^{(m)}$, and a relative error of 10^{-10} for the final value appears to be achieved in double-precision computation. Therefore, in these calculations it would be sufficient to check the evaluated values rather than the stability of the relation. In the calculation of the electron repulsion integrals over *s*, *p*, and *d* functions with initial integrals having a relative error of 10^{-15},[13] we have encountered no problem. Although about the same accuracy is expected for other molecular integrals, it is recommended to check the accumulated error in the following cases: (1) the recursive calculations are initiated with less accurate values of initial integrals and/or (2) much higher angular momentum functions are employed in the molecular integrals, which requires much more than ten times of the utilization of the recurrence relations.

Finally a comment is in order on a relation among the derivative indices $\mathbf{l}_i^{(k)}$ in the basic and the auxiliary basic integrals. The translational invariance of these integrals allows us to find the relation, for instance, for the ABTEI's:

$$\sum_{i=1}^{N^{(1)}}(:\mathbf{l}_i^{(1)}+\mathbf{1}_\mu:)+\sum_{i=1}^{N^{(2)}}(:\mathbf{l}_i^{(2)}+\mathbf{1}_\mu:)=0. \tag{214}$$

This relation is of use in reducing the number of terms in the recurrence formulas, as is shown in the reduction of the formulas for the kinetic energy integrals in the Appendix.

IV. CONCLUDING REMARKS

In this paper we have introduced basic one- and two-electron integrals, and have shown how general one- and two-electron molecular integrals over Cartesian Gaussian functions can be expressed in terms of the basic integrals, how the recurrence relations satisfied by the basic integrals can be derived, and how these relations can be reduced to recurrence formulas for the target molecular integrals. The present formulation of molecular integrals is applicable (1) to the integrals with any spatial operators in the nonrelativistic form of the relativistic Hamiltonian, (2) to those including the kernel $\exp[i\mathbf{k}\cdot\mathbf{r}]$ of the Fourier transform in their integrands, (3) to those with any arbitrarily defined spatial operators as far as they can be expressed in terms of the basic integrals, and (4) to any order of their derivatives with respect to the function centers. This formulation allows an efficient recursive computation of molecular integrals. The present method is, therefore, expected to be of general use for a further extension of *ab initio* theoretical studies of molecular systems.

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APPENDIX

Recurrence formulas for basic one-electron integrals

By the use of Eq. (84), the recurrence formulas for the derivatives of the overlap one-electron integrals (DOOEI's) can be reduced from Eqs. (101) and (105) to

$$[\mathbf{n}_j+\mathbf{1}_\mu:] = (\mathbf{R}_Z-\mathbf{R}_j)_\mu[:] + \frac{1}{2Z}\sum_{i=1}^{N} N_\mu(\mathbf{n}_i)[\mathbf{n}_i-\mathbf{1}_\mu:] + \sum_{i=1}^{N}\frac{\zeta_i}{Z}\{N_\mu(\mathbf{l}_i)[:\mathbf{l}_i-\mathbf{1}_\mu] - N_\mu(\mathbf{l}_j)[:\mathbf{l}_j-\mathbf{1}_\mu]\} \tag{A1}$$

and

$$[:\mathbf{l}_j+\mathbf{1}_\mu] = 2\zeta_j[\mathbf{n}_j+\mathbf{1}_\mu:] - N_\mu(\mathbf{n}_j)[\mathbf{n}_j-\mathbf{1}_\mu:], \tag{A2}$$

respectively, where the superscript 1 is omitted for simplicity. The omission will be made for other formulas in this section as far as no confusion would take place. The DOOEI's over s-type Cartesian Gaussian functions become

$$[\{\mathbf{0}\}:\{\mathbf{0}\}] = \mathscr{S} \tag{A3}$$

by the use of Eq. (106) and the following relation:

$$\frac{\zeta_{12}}{\pi}\cdot\frac{\pi}{Z^{(1)}}\cdot\frac{\pi}{Z^{(2)}}\cdot(1-\Theta) = \frac{\pi}{Z^{(1)}Z^{(2)}/\zeta_{12}+(Z^{(1)}+Z^{(2)})} \to \frac{\pi}{Z^{(1)}} \quad (\zeta_{12}\to\infty,\zeta_i^{(2)}\to 0). \tag{A4}$$

With no integration exponent ($\mathscr{Q}_I = 1$), such as in the kinetic energy integrals, the above formulas can be readily reduced to those for the BOEI's. In contrast, for $\mathscr{Q}_I \neq 1$ we have to use the auxiliary integrals. Formally the auxiliary DOOEI's (ADOOEI's) are obtained from the corresponding two-electron integrals and $\mathscr{Q}_A$ defined by Eq. (85) as

$$[\{\mathbf{n}\}:\{\mathbf{l}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}] = \mathscr{Q}_A[\mathbf{0}_{12},\{\mathbf{n}\},\{\mathbf{0}^{(2)}\}:\{\mathbf{l}\},\{\mathbf{0}^{(2)}\}:m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}] = [\{\mathbf{n}\}:\{\mathbf{l}\}]\times\{\mathscr{Q}_A P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M})\}. \tag{A5}$$

Here, however, all of the integration indices except for M are not necessary in the case of one-electron integrals. This is because at positive infinity of ζ_{12}, the factor Θ becomes identically unity, and the factors $\eta_u^{(k)}$ and $\eta_{uv}^{(k)}$ ($k=1,2$) identically vanish, therefore the index m_{12} (the power of Θ) can be set always to zero, and the indices $m_{uu}^{(k)}$ (the power of $\eta_u^{(k)}$) and $m_{uv}^{(k)}$ (the power of $\eta_{uv}^{(k)}$) are to be taken into account only when $m_{uu}^{(k)} = m_{uv}^{(k)} = 0$. Thus we have

$$\mathscr{Q}_A P(m_{12},\mathbf{m}^{(1)},\mathbf{m}^{(2)},\mathbf{M}) = \begin{cases} P(0,\mathbf{0}^{(1)},\mathbf{0}^{(2)},\mathbf{M}) & (\mathbf{m}^{(k)}=\mathbf{0}) \\ 0 & (\mathbf{m}^{(k)}\neq\mathbf{0}) \end{cases}. \tag{A6}$$

Then $[\{\mathbf{n}\}:\{\mathbf{l}\}:0_{12},\mathbf{0}^{(1)},\mathbf{0}^{(2)},\mathbf{M}]$ of Eq. (A5) denoted as $[\{\mathbf{n}\}:\{\mathbf{l}\}:\mathbf{M}]$ becomes

$$[\{\mathbf{n}\}:\{\mathbf{l}\}:\mathbf{M}] = [\{\mathbf{n}\}:\{\mathbf{l}\}]\prod_{u=G+1}^{N}\left\{\left(\frac{\zeta_u}{Z}\right)^{M_{uu}}\prod_{\substack{v=G+1\\(v>u)}}^{N}\left(\frac{\zeta_u\zeta_v}{Z}\right)^{M_{uv}}\right\}. \tag{A7}$$

With the aid of Eq. (A6), Eq. (124) can be rewritten

$$[\mathbf{n}_j+\mathbf{1}_\mu::] = (\mathbf{R}_G-\mathbf{R}_j)_\mu[::] - \sum_{u=G+1}^{N}(\mathbf{R}_G-\mathbf{R}_u)_\mu[::M_{uu}+1] + \frac{1}{2\zeta_G}\sum_{i=1}^{N}N_\mu(\mathbf{n}_i)\ll\mathbf{n}_i-\mathbf{1}_\mu::\gg + \sum_{g=1}^{G}\frac{\zeta_g}{\zeta_G}\{N_\mu(\mathbf{l}_g)\ll:\mathbf{l}_g-\mathbf{1}_\mu:\gg - N_\mu(\mathbf{l}_j)\ll:\mathbf{l}_j-\mathbf{1}_\mu:\gg\} + \sum_{u=G+1}^{N}\{N_\mu(\mathbf{l}_u)[:\mathbf{l}_u-\mathbf{1}_\mu:M_{uu}+1] - N_\mu(\mathbf{l}_j)[:\mathbf{l}_j-\mathbf{1}_\mu:M_{uu}+1]\}, \tag{A8}$$

where the doubly bracketted integrals denote

$$\ll::\gg = [::] - \sum_{u=G+1}^{N}[::M_{uu}+1]. \tag{A9}$$

In combination with Eq. (A8), Eq. (130) is found to reduce to

$$[:\mathbf{l}_g+\mathbf{1}_\mu:] = 2\zeta_g(\mathbf{R}_G-\mathbf{R}_g)_\mu[::] - 2\zeta_g\sum_{u=G+1}^{N}(\mathbf{R}_G-\mathbf{R}_u)_\mu[::M_{uu}+1] + \frac{\zeta_g}{\zeta_G}\sum_{i=1}^{N}N_\mu(\mathbf{n}_i)\ll\mathbf{n}_i-\mathbf{1}_\mu::\gg - N_\mu(\mathbf{n}_g)[\mathbf{n}_g-\mathbf{1}_\mu::] + 2\zeta_g\sum_{h=1}^{G}\frac{\zeta_h}{\zeta_G}\{N_\mu(\mathbf{l}_h)\ll:\mathbf{l}_h-\mathbf{1}_\mu:\gg - N_\mu(\mathbf{l}_g)[:\mathbf{l}_g-\mathbf{1}_\mu:]\} + 2\zeta_g\sum_{u=G+1}^{N}N_\mu(\mathbf{l}_u)[:\mathbf{l}_u-\mathbf{1}_\mu:M_{uu}+1]. \tag{A10}$$

The recurrence formula with respect to $\mathbf{l}_u$ finally takes the form

$$[:\mathbf{l}_u+\mathbf{1}_\mu:]=2\zeta_G(\mathbf{R}_G-\mathbf{R}_u)_\mu[::M_{uu}+1]+\sum_{i=1}^{N}N_\mu(\mathbf{n}_i)[\mathbf{n}_i-\mathbf{1}_\mu::M_{uu}+1]-N_\mu(\mathbf{n}_u)[\mathbf{n}_u-\mathbf{1}_\mu::]$$
$$+2\sum_{g=1}^{G}\zeta_g N_\mu(\mathbf{l}_g)[:\mathbf{1}_g-\mathbf{1}_\mu:M_{uu}+1]-2\zeta_G N_\mu(\mathbf{l}_u)[:\mathbf{l}_u-\mathbf{1}_\mu:M_{uu}+1]$$
$$+2\sum_{v=G+1}^{N}(\mathbf{R}_v-\mathbf{R}_u)_\mu[::M_{uv}+1]$$
$$+2\sum_{v=G+1}^{N}\{N_\mu(\mathbf{l}_v)[:\mathbf{l}_v-\mathbf{1}_\mu:M_{uv}+1]-N_\mu(\mathbf{l}_u)[:\mathbf{l}_u-\mathbf{1}_\mu:M_{uv}+1]\}, \tag{A11}$$

where the off-diagonal indices M_{uv} are involved in the last two terms. The integrals over s-type Cartesian Gaussian functions become

$$[\{\mathbf{0}\}:\{\mathbf{0}\}:\mathbf{M}]$$
$$=\mathscr{S}_G\left(\frac{\zeta_G}{Z}\right)^{3/2}\prod_{u=G+1}^{N}\left\{\mathscr{E}\left(\frac{\zeta_u}{Z},\zeta_G(\mathbf{R}_G-\mathbf{R}_u)^2,M_{uu}\right)\right.$$
$$\left.\times\prod_{\substack{v=G+1\\(v>u)}}^{N}\mathscr{E}\left(\frac{\zeta_u\zeta_v}{Z},(\mathbf{R}_u-\mathbf{R}_v)^2,M_{uv}\right)\right\}. \tag{A12}$$

The definition of the auxiliary basic one-electron integrals (ABOEI's) is

$$(\{\mathbf{n}\}:\{\mathbf{l}\}:\mathbf{M})=\mathscr{Q}_A\mathscr{Q}_I[\{\mathbf{n}\}:\{\mathbf{l}\}:\mathbf{M}]. \tag{A13}$$

The range of the integration index $\mathbf{M}$ in the initial integrals $(\{\mathbf{0}\}:\{\mathbf{0}\}:\mathbf{M})$ necessary to calculate the target integrals $(\{\mathbf{n}\}:\{\mathbf{l}\}:\mathbf{0})$ is

$$0\leqslant\sum_{u=G+1}^{N}M_{uu}+\sum_{\substack{u,v=G+1\\(u<v)}}^{N}M_{uv}\leqslant\sum_{i=1}^{N}(|\mathbf{n}_i|+|\mathbf{l}_i|), \tag{A14}$$

$$0\leqslant\sum_{\substack{u,v=G+1\\(u<v)}}^{N}M_{uv}\leqslant\sum_{u=G+1}^{N}|\mathbf{l}_u|. \tag{A15}$$

As in the two-electron integrals [cf. Eq. (214)], the translational invariance of the integrals leads to the relation for the derivative indices, such as

$$\sum_{i=1}^{N}(:\mathbf{l}_i+\mathbf{1}_\mu)=0 \tag{A16}$$

for the BOEI's.

The recurrence formulas for the AEF-DOOEI's and AEF-ADOOEI's take the same forms with those for DOOEI's [Eqs. (A1) and (A2)] and ADOOEI's [Eqs. (A8), (A10), and (A11)], respectively, except for the additional terms. The additional terms in these recurrence formulas are

$$\langle[;|\mathbf{n}_j+\mathbf{1}_\mu:]\rangle=\frac{1}{2Z}[;\mathbf{q}+\mathbf{1}_\mu|:], \tag{A17}$$

$$\langle[;|:\mathbf{l}_j+\mathbf{1}_\mu]\rangle=0, \tag{A18}$$

$$\langle[;|\mathbf{n}_j+\mathbf{1}_\mu::]\rangle=\frac{1}{2\zeta_G}[;\mathbf{q}+\mathbf{1}_\mu|::]$$
$$-\frac{1}{2\zeta_G}\sum_{u=G+1}^{N}[;\mathbf{q}+\mathbf{1}_\mu|::M_{uu}+1], \tag{A19}$$

$$\langle[;|:\mathbf{l}_g+\mathbf{1}_\mu:]\rangle=\frac{\zeta_g}{\zeta_G}[:\mathbf{q}+\mathbf{1}_\mu|::]$$
$$-\frac{\zeta_g}{\zeta_G}\sum_{u=G+1}^{N}[;\mathbf{q}+\mathbf{1}_\mu|::M_{uu}+1], \tag{A20}$$

$$\langle[;|:\mathbf{l}_u+\mathbf{1}_\mu:]\rangle=[;\mathbf{q}+\mathbf{1}_\mu|::M_{uu}+1]. \tag{A21}$$

The initial integrals for the AEF-DOOEI's and AEF-ADOOEI's are

$$[\mathbf{k};\mathbf{q}|\{\mathbf{0}\}:\{\mathbf{0}\}]=F(\mathbf{k};\mathbf{q})\ [\{\mathbf{0}\}:\{\mathbf{0}\}]^\dagger$$
$$=F(\mathbf{k};\mathbf{q})\ [\{\mathbf{0}\}:\{\mathbf{0}\}]\exp\left[i\mathbf{k}\left(\mathbf{R}_Z+\frac{i\,\mathbf{k}}{4Z}\right)\right], \tag{A22}$$

$$[\mathbf{k};\mathbf{q}|\{\mathbf{0}\}:\{\mathbf{0}\}:\mathbf{M}]$$
$$=F(\mathbf{k};\mathbf{q})\ [\{\mathbf{0}\}:\{\mathbf{0}\}:\mathbf{M}]^\dagger$$
$$=F(\mathbf{k};\mathbf{q})\ [\{\mathbf{0}\}:\{\mathbf{0}\}:\mathbf{M}]$$
$$\times\exp\left[i\mathbf{k}\frac{\zeta_G}{Z}\left(\mathbf{R}_G+\frac{i\,\mathbf{k}}{4\zeta_G}\right)\right]+i\,\mathbf{k}\sum_{u=G+1}^{N}\frac{\zeta_u}{Z}\mathbf{R}_u, \tag{A23}$$

where the daggered integrals are defined by Eqs. (A3) and (A12) with $\mathscr{S}^\dagger$ [Eq. (175)], $\mathscr{S}_G^\dagger$ [Eq. (176)], $\mathbf{R}_G^\dagger$ [Eq. (174)] instead of $\mathscr{S}$, $\mathscr{S}_G$, and $\mathbf{R}_G$, respectively.

The recurrence formula for the kinetic energy integrals, for instance,

$$(\mathbf{n}_a|\mathscr{T}|\mathbf{n}_b)=\frac{1}{2}\sum_{v=x,y,z}[\mathbf{n}_a,\mathbf{n}_b:\mathbf{1}_{av},\mathbf{1}_{bv}] \tag{A24}$$

can be readily obtained by noting that the summand in Eq. (A24) satisfies the following recurrence relation:

$$[\mathbf{n}_a+\mathbf{1}_\mu:]$$
$$=(\mathbf{R}_G-\mathbf{R}_a)_\mu[:]+\frac{1}{2\zeta_G}\sum_{i=a,b}N_\mu(\mathbf{n}_i)[\mathbf{n}_i-\mathbf{1}_\mu:]$$
$$+\frac{\zeta_b}{\zeta_G}\{N_\mu(\mathbf{1}_{bv})[:\mathbf{1}_{bv}-\mathbf{1}_\mu]$$
$$-N_\mu(\mathbf{1}_{av})[:\mathbf{1}_{av}-\mathbf{1}_\mu]\}. \tag{A25}$$

Owing to the translational invariance [Eq. (A16)], the last term in Eq. (A25) can be rewritten as a sum of the overlap integrals:

$$\frac{\zeta_b}{\zeta_G}\{N_\mu(\mathbf{1}_{b\nu})[:\mathbf{1}_{b\nu}-\mathbf{1}_\mu]-N_\mu(\mathbf{1}_{a\nu})[:\mathbf{1}_{a\nu}-\mathbf{1}_\mu]\}$$
$$=2\delta_{\mu\nu}\frac{\zeta_b}{\zeta_G}[\mathbf{n}_a,\mathbf{n}_b:\mathbf{1}_{a\mu},\mathbf{0}_b]$$
$$=2\delta_{\mu\nu}\frac{\zeta_b}{\zeta_G}\{2\zeta_a[\mathbf{n}_a+\mathbf{1}_\mu,\mathbf{n}_b:\mathbf{0}_a,\mathbf{0}_b]-N_\mu(\mathbf{n}_a)[\mathbf{n}_a-\mathbf{1}_\mu,\mathbf{n}_b:\mathbf{0}_a,\mathbf{0}_b]\}. \quad \text{(A26)}$$

Then one can finally obtain the formula given in our previous paper.[13]

The molecular integral necessary for the calculation of the diamagnetic contribution to the nuclear spin–spin coupling constant[25] involves two integration exponents. The operator $\mathscr{D}_{\lambda\nu}$ for the molecular integral is

$$\mathscr{D}_{\lambda\nu}=\frac{(\mathbf{r}-\mathbf{R}_c)_\lambda(\mathbf{r}-\mathbf{R}_d)_\nu}{|\mathbf{r}-\mathbf{R}_c|^3|\mathbf{r}-\mathbf{R}_d|^3}$$
$$=\mathscr{Q}_I\frac{\partial^2}{\partial R_{c\lambda}\partial R_{d\nu}}\varphi(\mathbf{r}-\mathbf{R}_c;\mathbf{0}_c,u_c^2)\times\varphi(\mathbf{r}-\mathbf{R}_d;\mathbf{0}_d,u_d^2), \quad \text{(A27)}$$

with

$$\mathscr{Q}_I=\int_0^\infty du_c\int_0^\infty du_d\frac{4}{\pi}, \quad \text{(A28)}$$

and the auxiliary molecular integral becomes

$$(\mathbf{n}_a|\mathscr{D}_{\lambda\nu}|\mathbf{n}_b)^{(\mathbf{M})}=(\mathbf{n}_a,\mathbf{n}_b,\mathbf{0}_c,\mathbf{0}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{1}_{c\lambda},\mathbf{1}_{d\nu}:\mathbf{M})$$
$$=\mathscr{Q}_I[\mathbf{n}_a,\mathbf{n}_b,\mathbf{0}_c,\mathbf{0}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{1}_{c\lambda},\mathbf{1}_{d\nu}:\mathbf{M}], \quad \text{(A29)}$$

where $\mathbf{M}$ is a 2×2 matrix

$$\mathbf{M}=\begin{bmatrix}M_{cc} & M_{cd}\\ 0 & M_{dd}\end{bmatrix}. \quad \text{(A30)}$$

Equation (A8) provides us with the recurrence formula for the molecular integrals with respect to the angular momentum $\mathbf{n}_a$,

$$(\mathbf{n}_a+\mathbf{1}_\mu::)=(\mathbf{R}_G-\mathbf{R}_a)_\mu(::)-(\mathbf{R}_G-\mathbf{R}_c)_\mu(::M_{cc}+1)-(\mathbf{R}_G-\mathbf{R}_d)_\mu(::M_{dd}+1)$$
$$+\frac{1}{2\zeta_G}\sum_{i=a,b}N_\mu(\mathbf{n}_i)\ll\mathbf{n}_i-\mathbf{1}_\mu::\gg+\delta_{\mu\lambda}(:\mathbf{1}_{c\lambda}-\mathbf{1}_\mu:M_{cc}+1)+\delta_{\mu\nu}(:\mathbf{1}_{d\nu}-\mathbf{1}_\mu:M_{dd}+1) \quad \text{(A31)}$$

with

$$\ll::\gg=(::)-(::M_{cc}+1)-(::M_{dd}+1). \quad \text{(A32)}$$

The initial integral is

$$(\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c,\mathbf{0}_d:\mathbf{0}_a,\mathbf{0}_b,\mathbf{0}_c,\mathbf{0}_d:\mathbf{M})$$
$$=\frac{4}{\pi}\mathscr{S}_G\int_0^\infty du_c\int_0^\infty du_d\left(\frac{\zeta_G}{Z}\right)^{3/2}\times\mathscr{E}\left(\frac{u_c^2}{Z},\zeta_G(\mathbf{R}_G-\mathbf{R}_c)^2,M_{cc}\right)\times\mathscr{E}\left(\frac{u_d^2}{Z},\zeta_G(\mathbf{R}_G-\mathbf{R}_d)^2,M_{dd}\right)\times\mathscr{E}\left(\frac{u_c^2u_d^2}{Z},(\mathbf{R}_c-\mathbf{R}_d)^2,M_{cd}\right), \quad \text{(A33)}$$

and can be evaluated by quadrature.[25] According to Eq. (A11), the values of the derivative indices can be increased. For the increase from $(\mathbf{l}_c,\mathbf{l}_d)=(\mathbf{0}_c,\mathbf{0}_d)$ to $(\mathbf{1}_{c\lambda},\mathbf{0}_d)$, e.g.,

$$(:\mathbf{1}_{c\lambda},\mathbf{0}_d:)=2\zeta_G(\mathbf{R}_G-\mathbf{R}_c)_\lambda(:\mathbf{0}_c,\mathbf{0}_d:M_{cc}+1)+2(\mathbf{R}_d-\mathbf{R}_c)_\lambda(:\mathbf{0}_c,\mathbf{0}_d:M_{cd}+1)+\sum_{i=a,b}N_\lambda(\mathbf{n}_i)(\mathbf{n}_i-\mathbf{1}_\lambda:\mathbf{0}_c,\mathbf{0}_d:M_{cc}+1). \quad \text{(A34)}$$

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