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Efficient recursive computation of molecular integrals over Cartesian Gaussian functions

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Recurrence expressions are derived for various types of molecular integrals over Cartesian Gaussian functions by the use of the recurrence formula for three-center overlap integrals. A number of characteristics inherent in the recursive formalism allow an efficient scheme to be developed for molecular integral computations. With respect to electron repulsion integrals and their derivatives, the present scheme with a significant saving of computer time is found superior to other currently available methods. A long innermost loop incorporated in the present scheme facilitates a fast computation on a vector processing computer.

I. INTRODUCTION

Computation of molecular integrals is still a problem of paramount importance in theoretical studies of molecular systems by *ab initio* calculations. As the system gets larger, computation of electron repulsion integrals (ERI's) becomes one of the most laborious and time-consuming steps in the process. Improvement of the computational methods of molecular integrals, especially of ERI's would be indispensable to a further development in computational studies of large molecular systems, such as transition metal compounds and biologically important molecular systems.

One apparent method for reducing the computer time is to take advantage of molecular symmetry,[1] if it is available. However, one cannot resort to molecular symmetry, for instance, in calculations of potential energy hypersurfaces, because the energies at nonsymmetric molecular geometries have to be calculated. Although recent developments of computers such as a vector processing machine would somewhat relieve the difficulty of the time consuming procedure, it is desirable to develop a fast computational algorithm. The purpose of this work is to describe a new formulation of molecular integrals leading to an efficient method of computing them.

Since Boys[2] proposed to use Gaussian functions as basic functions in theoretical studies of atoms and molecules, they have been utilized widely, and several modifications for the angular part of the function have been introduced. Here we are concerned with molecular integrals over Cartesian Gaussian functions in most common use. For other modifications, we only refer to excellent reviews by Saunders.[3]

Boys[2] gave formulas for molecular integrals over s functions and suggested to differentiate these formulas with respect to the nuclear coordinates to obtain those over higher angular momentum functions. Taketa, Huzinaga, and Ohata[4] gave general expressions for one- and two-electron molecular integrals. Since then, several improvements have been embodied for saving of computation time. McMurchie and Davidson[5] (MD) proposed to use the Hermite Gaussian functions as the intermediaries for the calculation of molecular integrals over Cartesian Gaussian functions, and showed that the computation can be carried out efficiently by using the differential relation of the Hermite Gaussian functions.

If one confines oneself to ERI's there are now in use several powerful methods.[3(b)] Pople and Hehre[6] (PH) developed a method using a local coordinate system defined by four centers of functions in an ERI. The method requires only one fifth of the computation time required by the MD method in the calculation of hydrogen peroxide.[5] However, it is not applied to ERI's including higher angular momentum functions than p, and the calculated ERI's are, in some cases, subject to a round-off error.[3(b)] Dupuis, Rys, and King (DRK) proposed to use a numerical quadrature method,[7,8] and to take advantage of a recurrence relation[9] of two-dimensional integrals. The computer time[5] required by their method is about five times longer than that by the PH method. Saunders[10] introduced a compromised method between the MD and DRK methods, and van der Velde[11] modified the summation procedure in the ERI expression. Hegarty and van der Velde[12] analyzed the number of arithmetic operations in these methods as well as in the MD method, and found that the Saunders method requires the least number of arithmetic operations. In view of the trivial differences among these methods, however, they adopted the MD method for their implementation on a vector processing computer.

In the analytical "force method" [13,14] the derivatives of ERI's and one-electron integrals with respect to the nuclear coordinates come into play. Since the derivatives of ERI's can be expressed as a linear combination of ERI's including higher and lower angular momentum functions, they are usually calculated by the method for the ERI computation. Recently Schlegel[15] devised a method of calculation where the first derivative of the total energy is calculated directly, while Schlegel, Binkley, and Pople[16] applied a numerical quadrature method for the calculation of the first and the second derivatives of ERI's without employing higher angular momentum functions.

In this paper we develop a new procedure for evaluating ERI's as well as one-electron integrals, i.e., overlap integrals, kinetic energy integrals, moment integrals, nuclear attraction integrals, electric field and electric field gradient integrals, angular momentum integrals, and spin-orbit interaction integrals. The formulation is based on the recurrence formula for three-center overlap integrals. The derived expressions are in recursive form with respect to the angular

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momenta of functions in the integral. In effect, they can be given as a linear combination of integrals (and auxiliary integrals for some of the molecular integrals) over lower angular momentum functions. A number of potential merits for efficient computation of various types of molecular integrals inhabit in the present recursive formulation. Thus a new computational scheme based on this method is reported in the present paper. It has been programmed and tested in comparison with other methods. With respect to the computation of ERI's and their first derivatives, the proposed method is found to be uniformly superior to other methods presently in use and particularly suited for a vector processing computer.[17]

In the next section the recurrence formulation of ERI's is described. In Sec. III the characteristics of this formulation are discussed from the computational viewpoint. Section IV outlines a strategy for the ERI computation. Computer times are compared with those of the PH and the DRK methods in Sec. V, and concluding remarks are drawn in the last section. Expressions for the one-electron integrals are collected in the Appendix.

II. A RECURRENCE FORMULA FOR ELECTRON REPULSION INTEGRALS OVER CARTESIAN GAUSSIAN FUNCTIONS

A. Cartesian Gaussian functions

We write the unnormalized Cartesian Gaussian function with origin at $\mathbf{R}$ as

$$\varphi(\mathbf{r};\zeta,\mathbf{n},\mathbf{R}) = (x-R_x)^{n_x}(y-R_y)^{n_y}(z-R_z)^{n_z} \times \exp[-\zeta(\mathbf{r}-\mathbf{R})^2] , \quad (1)$$

where $\mathbf{r} = (x,y,z)$ represents the coordinates of the electron, ζ is the orbital exponent, and $\mathbf{n}$ denotes a set of nonnegative integers n_x, n_y, and n_z:

$$\mathbf{n} = (n_x, n_y, n_z) . \quad (2)$$

The normalization constant of the function is then given by

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

Letting λ be defined as the sum of n_x, n_y, and n_z, one notes that it is closely related to the total angular momentum quantum number. λ and $\mathbf{n}$ will be hereafter termed the angular momentum and the angular momentum index, respectively. The functions with λ equal to 0,1,2,..., are referred to as s,p,d,..., respectively. A set of $(\lambda+1)(\lambda+2)/2$ functions at $\mathbf{R}$ associated with the same angular momentum λ and orbital exponent ζ constitute a *shell*, and the functions in the shell are *components* of the shell. The single component of the s shell with the angular momentum index $\mathbf{0} = (0,0,0)$ is usually designated s. The components of the p shell have the angular momentum indices $\mathbf{1}_i (i = x,y,z)$, where $\mathbf{1}_i$ is defined by

$$\mathbf{1}_i = (\delta_{ix},\delta_{iy},\delta_{iz}) \quad (4)$$

with Kronecker's deltas. These components will be designated p_x, p_y, and p_z. The components of the d shell with the angular momentum indices $\mathbf{1}_i + \mathbf{1}_j (i,j = x,y,z)$ will be designated $d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}$, and d_{yz}. In later discussions all the components in a shell are assumed to be exhausted as the basic functions, and to be treated together in the computation of molecular integrals.

First we give the basic equations for Cartesian Gaussian functions that will be utilized in the following derivations of molecular integrals. The Cartesian Gaussian functions satisfy the differential relation

$$\frac{\partial}{\partial R_i}\varphi(\mathbf{r};\zeta,\mathbf{n},\mathbf{R}) = 2\zeta\varphi(\mathbf{r};\zeta,\mathbf{n}+\mathbf{1}_i,\mathbf{R}) - N_i(\mathbf{n})\varphi(\mathbf{r};\zeta,\mathbf{n}-\mathbf{1}_i,\mathbf{R}) \quad (i = x,y,z) , \quad (5)$$

where $N_i(\mathbf{n})$, standing for n_i, is meant to take the value of the i component of the angular momentum index $\mathbf{n}$, and thus $N_i(\mathbf{1}_j)$ plays the same role as the Kronecker's delta δ_{ij}. It follows readily that

$$N_i(\mathbf{n}+\mathbf{n}') = N_i(\mathbf{n}) + N_i(\mathbf{n}') . \quad (6)$$

In the Cartesian Gaussian function the nuclear coordinate R_i always appears in the form of $r_i - R_i$. Therefore, differentiation with respect to R_i can be replaced by that with respect to r_i:

$$\frac{\partial}{\partial R_i}\varphi(\mathbf{r};\zeta,\mathbf{n},\mathbf{R}) = -\frac{\partial}{\partial r_i}\varphi(\mathbf{r};\zeta,\mathbf{n},\mathbf{R}) . \quad (7)$$

B. Three-center overlap integrals

Three-center overlap integrals over unnormalized Cartesian Gaussian functions are of the form:

$$(\mathbf{a}|\mathbf{c}|\mathbf{b}) = \int d\mathbf{r}\,\varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})\varphi(\mathbf{r};\zeta_c,\mathbf{c},\mathbf{C})\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B}) . \quad (8)$$

According to Eq. (5), the integral $(\mathbf{a}+\mathbf{1}_i|\mathbf{c}|\mathbf{b})$ can be decomposed as

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{c}|\mathbf{b}) = \frac{1}{2\zeta_a}\frac{\partial}{\partial A_i}(\mathbf{a}|\mathbf{c}|\mathbf{b}) + \frac{1}{2\zeta_a}N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i|\mathbf{c}|\mathbf{b}) . \quad (9)$$

Here the integral $(\mathbf{a}|\mathbf{c}|\mathbf{b})$ can be factored as

$$(\mathbf{a}|\mathbf{c}|\mathbf{b}) = \kappa_{abc}\, I_x(n_{ax},n_{bx},n_{cx})\, I_y(n_{ay},n_{by},n_{cy}) \times I_z(n_{az},n_{bz},n_{cz}) , \quad (10)$$

where

$$\kappa_{abc} = \exp[-\xi(\mathbf{A}-\mathbf{B})^2]\exp\left[-\frac{\zeta\zeta_c}{\zeta+\zeta_c}(\mathbf{P}-\mathbf{C})^2\right] \quad (11)$$

$$= \exp\left[(\zeta_a+\zeta_b+\zeta_c)\left(\mathbf{G}^2 - \frac{\zeta_a\mathbf{A}^2+\zeta_b\mathbf{B}^2+\zeta_c\mathbf{C}^2}{\zeta_a+\zeta_b+\zeta_c}\right)\right] . \quad (12)$$

$$\xi = \frac{\zeta_a\zeta_b}{\zeta_a+\zeta_b} , \quad (13)$$

$$\zeta = \zeta_a + \zeta_b , \quad (14)$$

$$\mathbf{P} = \frac{\zeta_a\mathbf{A}+\zeta_b\mathbf{B}}{\zeta_a+\zeta_b} , \quad (15)$$

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$$\mathbf{G}=\frac{\zeta\mathbf{P}+\zeta_c\mathbf{C}}{\zeta+\zeta_c}=\frac{\zeta_a\mathbf{A}+\zeta_b\mathbf{B}+\zeta_c\mathbf{C}}{\zeta_a+\zeta_b+\zeta_c}, \tag{16}$$

and

$$I_i(n_{ai},n_{bi},n_{ci})=\left(\frac{\pi}{\zeta_a+\zeta_b+\zeta_c}\right)^{1/2}$$
$$\times\sum_{k_{ai}=0}^{n_{ai}}\sum_{k_{bi}=0}^{n_{bi}}\sum_{\substack{k_{ci}=0\\(k_{ai}+k_{bi}+k_{ci}=\text{even})}}^{n_{ci}}\binom{n_{ai}}{k_{ai}}\binom{n_{bi}}{k_{bi}}\binom{n_{ci}}{k_{ci}}$$
$$\times(G_i-A_i)^{n_{ai}-k_{ai}}(G_i-B_i)^{n_{bi}-k_{bi}}(G_i-C_i)^{n_{ci}-k_{ci}}$$
$$\times\frac{(k_{ai}+k_{bi}+k_{ci}-1)!!}{\{2(\zeta+\zeta_c)\}^{k_{ai}+k_{bi}+k_{ci}}}. \tag{17}$$

Differentiating κ_{abc} and $I_i(n_{ai},n_{bi},n_{ci})$ with respect to A_i, we have

$$\frac{1}{2\zeta_a}\frac{\partial}{\partial A_i}\kappa_{abc}=(G_i-A_i)\,\kappa_{abc} \tag{18}$$

and

$$\frac{1}{2\zeta_a}\frac{\partial}{\partial A_i}I_i(n_{ai},n_{bi},n_{ci})$$
$$=n_{ai}\left\{\frac{1}{2(\zeta+\zeta_c)}-\frac{1}{2\zeta_a}\right\}I_i(n_{ai}-1,n_{bi},n_{ci})$$
$$+n_{bi}\frac{1}{2(\zeta+\zeta_c)}I_i(n_{ai},n_{bi}-1,n_{ci})$$
$$+n_{ci}\frac{1}{2(\zeta+\zeta_c)}I_i(n_{ai},n_{bi},n_{ci}-1), \tag{19}$$

respectively. Substitution of Eqs. (18) and (19) into Eq. (9) gives finally

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{c}|\mathbf{b})=(G_i-A_i)(\mathbf{a}|\mathbf{c}|\mathbf{b})+\frac{1}{2(\zeta+\zeta_c)}$$
$$\times N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i|\mathbf{c}|\mathbf{b})+\frac{1}{2(\zeta+\zeta_c)}N_i(\mathbf{b})(\mathbf{a}|\mathbf{c}|\mathbf{b}-\mathbf{1}_i)$$
$$+\frac{1}{2(\zeta+\zeta_c)}N_i(\mathbf{c})(\mathbf{a}|\mathbf{c}-\mathbf{1}_i|\mathbf{b}). \tag{20}$$

The recurrence formula for $(\mathbf{a}|\mathbf{c}+\mathbf{1}_i|\mathbf{b})$, which will be used later, can be obtained similarly in the same functional form with Eq. (20) except that the coefficient G_i-A_i for the first term is replaced by G_i-C_i. The integral over s functions is given by

$$(\mathbf{0}_A|\mathbf{0}_C|\mathbf{0}_B)=\left(\frac{\pi}{\zeta_a+\zeta_b+\zeta_c}\right)^{3/2}\kappa_{abc}$$
$$=\left(\frac{\zeta}{\zeta+\zeta_c}\right)^{3/2}(\mathbf{0}_A\|\mathbf{0}_B)\exp\left[-\frac{\zeta\zeta_c}{\zeta+\zeta_c}(\mathbf{P}-\mathbf{C})^2\right], \tag{21}$$

where $(\mathbf{0}_A\|\mathbf{0}_B)$ is the overlap integral between two s functions centered at $\mathbf{A}$ and $\mathbf{B}$:

$$(\mathbf{0}_A\|\mathbf{0}_B)=(\pi/\zeta)^{3/2}\exp[-\xi(\mathbf{A}-\mathbf{B})^2]. \tag{22}$$

C. Electron repulsion integrals

For the electron repulsion integrals (ERI's) over unnormalized Cartesian Gaussian functions

$$(\mathbf{ab},\mathbf{cd})=\int d\mathbf{r}_1\int d\mathbf{r}_2[\varphi(\mathbf{r}_1;\zeta_a,\mathbf{a},\mathbf{A})\varphi(\mathbf{r}_1;\zeta_b,\mathbf{b},\mathbf{B})]$$
$$\times|\mathbf{r}_1-\mathbf{r}_2|^{-1}[\varphi(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{C})\varphi(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{D})], \tag{23}$$

we may substitute the identity

$$|\mathbf{r}_1-\mathbf{r}_2|^{-1}=\frac{2}{\pi^{1/2}}\int_0^\infty du\,\exp[-(\mathbf{r}_1-\mathbf{r}_2)^2u^2], \tag{24}$$

to obtain

$$(\mathbf{ab},\mathbf{cd})=\frac{2}{\pi^{1/2}}\int_0^\infty du(\mathbf{ab}|u|\mathbf{cd}), \tag{25}$$

where

$$(\mathbf{ab}|u|\mathbf{cd})=\int d\mathbf{r}_2\,\varphi(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{C})\varphi(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{D})(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b}) \tag{26}$$

and

$$(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b})=\int d\mathbf{r}_1\,\varphi(\mathbf{r}_1;\zeta_a,\mathbf{a},\mathbf{A})\varphi(\mathbf{r}_1;\zeta_b,\mathbf{b},\mathbf{B})$$
$$\times\exp[-u^2(\mathbf{r}_1-\mathbf{r}_2)^2]. \tag{27}$$

Since the exponential function in Eq. (27) corresponds to an s-type Cartesian Gaussian function with the orbital exponent u^2 centered at $\mathbf{r}_2$, $(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b})$ is just a three-center overlap integral. Using Eq. (20), we obtain

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{0}_{r_2}|\mathbf{b})=(P_i-A_i)(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b})+\frac{1}{2\zeta}N_i(\mathbf{a})$$
$$\times\left(1-\frac{\rho}{\zeta}\frac{u^2}{\rho+u^2}\right)(\mathbf{a}-\mathbf{1}_i|\mathbf{0}_{r_2}|\mathbf{b})+\frac{1}{2\zeta}N_i(\mathbf{b})$$
$$\times\left(1-\frac{\rho}{\zeta}\frac{u^2}{\rho+u^2}\right)(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b}-\mathbf{1}_i)+\frac{1}{\zeta+\eta}\frac{u^2}{\rho+u^2}$$
$$\cdot\eta(r_{2i}-P_i)(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b})-\frac{1}{\zeta+\eta}\frac{u^2}{\rho+u^2}\cdot u^2(\mathbf{a}|\mathbf{1}_{ir_2}|\mathbf{b}), \tag{28}$$

where we have made use of the relations

$$(\mathbf{a}|\mathbf{1}_{ir_2}|\mathbf{b})=-\frac{\zeta}{\zeta+u^2}(r_{2i}-P_i)(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b})$$
$$+\frac{1}{2(\zeta+u^2)}N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i|\mathbf{0}_{r_2}|\mathbf{b})$$
$$+\frac{1}{2(\zeta+u^2)}N_i(\mathbf{b})(\mathbf{a}|\mathbf{0}_{r_2}|\mathbf{b}-\mathbf{1}_i), \tag{29}$$

and

$$\frac{1}{\zeta+u^2}=\frac{1}{\zeta}\left(1-\frac{\rho}{\zeta}\frac{u^2}{\rho+u^2}\right)-\frac{1}{\zeta+\eta}\frac{u^2}{\zeta+u^2}\frac{u^2}{\rho+u^2} \tag{30}$$

with the parameters η and ρ defined by

$$\eta=\zeta_c+\zeta_d, \tag{31}$$

$$\rho=\frac{\zeta\eta}{\zeta+\eta}. \tag{32}$$

The integration over $\mathbf{r}_2$ of the last term of Eq. (28) multiplied by $\varphi(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{C})$ and $\varphi(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{D})$ can be rewritten as

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$$-\frac{1}{\zeta+\eta}\frac{u^2}{\rho+u^2}\int d\mathbf{r}_2\,\varphi(\mathbf{r}_2;\zeta_c,\mathbf{c},\mathbf{C})\varphi(\mathbf{r}_2;\zeta_d,\mathbf{d},\mathbf{D})u^2$$
$$\times(\mathbf{a}|\mathbf{1}_{ir_2}|\mathbf{b})=\frac{1}{\zeta+\eta}\frac{u^2}{\rho+u^2}\int d\mathbf{r}_1\,\varphi(\mathbf{r}_1;\zeta_a,\mathbf{a},\mathbf{A})$$
$$\times\varphi(\mathbf{r}_1;\zeta_b,\mathbf{b},\mathbf{B})u^2(\mathbf{c}|\mathbf{1}_{ir_1}|\mathbf{d})\,. \tag{33}$$

Multiplying the recurrence formula for $(\mathbf{c}|\mathbf{1}_{ir_1}|\mathbf{d})$ by $\eta+u^2$ we find

$$u^2(\mathbf{c}|\mathbf{1}_{ir_1}|\mathbf{d})=-\eta(r_{1i}-Q_i)(\mathbf{c}|\mathbf{0}_{r_1}|\mathbf{d})+\tfrac{1}{2}N_i(\mathbf{c})$$
$$\times(\mathbf{c}-\mathbf{1}_i|\mathbf{0}_{r_1}|\mathbf{d})+\tfrac{1}{2}N_i(\mathbf{d})(\mathbf{c}|\mathbf{0}_{r_1}|\mathbf{d}-\mathbf{1}_i)-\eta(\mathbf{c}|\mathbf{1}_{ir_1}|\mathbf{d})\,, \tag{34}$$

where

$$\mathbf{Q}=\frac{1}{\eta}(\zeta_c\mathbf{C}+\zeta_d\mathbf{D})\,. \tag{35}$$

Referring to Eq. (26), and using Eqs. (28), (33), and (34), we arrive at

$$[(\mathbf{a}+\mathbf{1}_i)\mathbf{b}|u|\mathbf{cd}]=(P_i-A_i)(\mathbf{ab}|u|\mathbf{cd})+(W_i-P_i)\frac{u^2}{\rho+u^2}(\mathbf{ab}|u|\mathbf{cd})$$
$$+\frac{1}{2\zeta}N_i(\mathbf{a})\left(1-\frac{\rho}{\zeta}\frac{u^2}{\rho+u^2}\right)[(\mathbf{a}-\mathbf{1}_i)\mathbf{b}|u|\mathbf{cd}]+\frac{1}{2\zeta}N_i(\mathbf{b})\left(1-\frac{\rho}{\zeta}\frac{u^2}{\rho+u^2}\right)[\mathbf{a}(\mathbf{b}-\mathbf{1}_i)|u|\mathbf{cd}]$$
$$+\frac{1}{2(\zeta+\eta)}N_i(\mathbf{c})\frac{u^2}{\rho+u^2}[\mathbf{ab}|u|(\mathbf{c}-\mathbf{1}_i)\mathbf{d}]+\frac{1}{2(\zeta+\eta)}N_i(\mathbf{d})\frac{u^2}{\rho+u^2}[\mathbf{ab}|u|\mathbf{c}(\mathbf{d}-\mathbf{1}_i)]\,, \tag{36}$$

where

$$\mathbf{W}=\frac{\zeta\mathbf{P}+\eta\mathbf{Q}}{\zeta+\eta}\,. \tag{37}$$

Let us introduce an auxiliary electron repulsion integral $(\mathbf{ab},\mathbf{cd})^{(m)}$, which plays a central role in further manipulation of ERI's:

$$(\mathbf{ab},\mathbf{cd})^{(m)}=\frac{2}{\pi^{1/2}}\int_0^\infty du\left(\frac{u^2}{\rho+u^2}\right)^m(\mathbf{ab}|u|\mathbf{cd})\,, \tag{38}$$

where m is a nonnegative integer. Note that the integral $(\mathbf{ab},\mathbf{cd})^{(0)}$ is a true ERI $(\mathbf{ab},\mathbf{cd})$. Equations (36) and (38) allow us to obtain

$$[(\mathbf{a}+\mathbf{1}_i)\mathbf{b},\mathbf{cd}]^{(m)}=(P_i-A_i)(\mathbf{ab},\mathbf{cd})^{(m)}+(W_i-P_i)(\mathbf{ab},\mathbf{cd})^{(m+1)}$$
$$+\frac{1}{2\zeta}N_i(\mathbf{a})\left\{[(\mathbf{a}-\mathbf{1}_i)\mathbf{b},\mathbf{cd}]^{(m)}-\frac{\rho}{\zeta}[(\mathbf{a}-\mathbf{1}_i)\mathbf{b},\mathbf{cd}]^{(m+1)}\right\}$$
$$+\frac{1}{2\zeta}N_i(\mathbf{b})\left\{[\mathbf{a}(\mathbf{b}-\mathbf{1}_i),\mathbf{cd}]^{(m)}-\frac{\rho}{\zeta}[\mathbf{a}(\mathbf{b}-\mathbf{1}_i),\mathbf{cd}]^{(m+1)}\right\}$$
$$+\frac{1}{2(\zeta+\eta)}N_i(\mathbf{c})[\mathbf{ab},(\mathbf{c}-\mathbf{1}_i)\mathbf{d}]^{(m+1)}+\frac{1}{2(\zeta+\eta)}N_i(\mathbf{d})[\mathbf{ab},\mathbf{c}(\mathbf{d}-\mathbf{1}_i)]^{(m+1)}\quad(i=x,y,z)\,. \tag{39}$$

Use of the above recurrence formula requires the explicit expression for the auxiliary integral over s functions. With the help of Eqs. (21) and (26), we get

$$(\mathbf{0}_A\mathbf{0}_B,\mathbf{0}_C\mathbf{0}_D)^{(m)}=(\mathbf{0}_A\|\mathbf{0}_B)(\mathbf{0}_C\|\mathbf{0}_D)\frac{2}{\pi^{1/2}}$$
$$\times\int_0^\infty du\left(\frac{u^2}{\rho+u^2}\right)^m\left(\frac{\rho}{\rho+u^2}\right)^{3/2}$$
$$\times\exp\left[-\frac{\rho u^2}{\rho+u^2}(\mathbf{P}-\mathbf{Q})^2\right]. \tag{40}$$

Integration over u can be carried out by transforming variable from u to t:

$$t^2=\frac{u^2}{\rho+u^2}\,, \tag{41}$$
$$du=\rho^{1/2}(1-t^2)^{-3/2}\,dt\,, \tag{42}$$
$$\left(\frac{\rho}{\rho+u^2}\right)^{3/2}=(1-t^2)^{3/2}\,, \tag{43}$$

to obtain

$$(\mathbf{0}_A\mathbf{0}_B,\mathbf{0}_C\mathbf{0}_D)^{(m)}$$
$$=2\left(\frac{\rho}{\pi}\right)^{1/2}(\mathbf{0}_A\|\mathbf{0}_B)(\mathbf{0}_C\|\mathbf{0}_D)F_m(T)$$
$$=(\zeta+\eta)^{-1/2}K(\zeta_a,\zeta_b,\mathbf{A},\mathbf{B})K(\zeta_c,\zeta_d,\mathbf{C},\mathbf{D})F_m(T)\,, \tag{44}$$

where

$$F_m(T)=\int_0^1 dt\,t^{2m}\exp[-Tt^2]\,, \tag{45}$$
$$T=\rho(\mathbf{P}-\mathbf{Q})^2\,, \tag{46}$$

and

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TABLE I. Recurrence expressions[a] for the electron repulsion integrals over s and p Cartesian Gaussian functions.

$$(ss,ss)^{(0)} = (\zeta+\eta)^{-1/2} K(\zeta_a,\zeta_b,\mathbf{A},\mathbf{B}) K(\zeta_c,\zeta_d,\mathbf{C},\mathbf{D}) F_0(T)$$

$$(p_i s,ss)^{(0)} = (P_i - A_i)(ss,ss)^{(0)} + (W_i - P_i)(ss,ss)^{(1)}$$

$$(p_i s,p_k s)^{(0)} = (Q_k - C_k)(p_i s,ss)^{(0)} + (W_k - Q_k)(p_i s,ss)^{(1)} + \frac{\delta_{ik}}{2(\zeta+\eta)}(ss,ss)^{(1)}$$

$$(p_i p_j,ss)^{(0)} = (P_j - B_j)(p_i s,ss)^{(0)} + (W_j - P_j)(p_i s,ss)^{(1)} + \frac{\delta_{ij}}{2\zeta}\{(ss,ss)^{(0)} - \frac{\rho}{\zeta}(ss,ss)^{(1)}\}$$

$$(p_i p_j,p_k s)^{(0)} = (Q_k - C_k)(p_i p_j,ss)^{(0)} + (W_k - Q_k)(p_i p_j,ss)^{(1)} + \frac{1}{2(\zeta+\eta)}\{\delta_{ik}(sp_j,ss)^{(1)} + \delta_{jk}(p_i s,ss)^{(1)}\}$$

$$(p_i p_j,p_k p_l)^{(0)} = (Q_l - D_l)(p_i p_j,p_k s)^{(0)} + (W_l - Q_l)(p_i p_j,p_k s)^{(1)} + \frac{1}{2(\zeta+\eta)}\{\delta_{il}(sp_j,p_k s)^{(1)} + \delta_{jl}(p_i s,p_k s)^{(1)}\} + \frac{\delta_{kl}}{2\eta}\{(p_i p_j,ss)^{(0)} - \frac{\rho}{\eta}(p_i p_j,ss)^{(1)}\}$$

$$(i,j,k,l = x,y,z)$$

[a] For the definition of the variables, see the text.

$$K(\zeta,\zeta',\mathbf{R},\mathbf{R}') = 2^{1/2}\frac{\pi^{5/4}}{\zeta+\zeta'}\exp\left[-\frac{\zeta\zeta'}{\zeta+\zeta'}(\mathbf{R}-\mathbf{R}')^2\right]. \tag{47}$$

Explicit forms of the recurrence formulas over s and p functions are given in Table I, where s, p_i, and d_{ij} are used instead of $\mathbf{0}$, $\mathbf{1}_i$, and $\mathbf{1}_i + \mathbf{1}_j$, respectively.

It may be instructive to add a mathematical relation between a true ERI $(\mathbf{ab},\mathbf{cd})$ and the corresponding auxiliary ERI's $(\mathbf{ab},\mathbf{cd})^{(m)}$, although the relation is not necessary for the calculation of ERI's. As has been shown by Taketa, Ohata, and Huzinaga[4] the true integral is reduced to a linear combination of $F_k(T)$'s multiplied by appropriate coefficients X_k's:

$$(\mathbf{ab},\mathbf{cd}) = \sum_k X_k F_k(T). \tag{48}$$

The corresponding auxiliary integrals can be expressed in terms of the same coefficients as

$$(\mathbf{ab},\mathbf{cd})^{(m)} = \sum_k X_k F_{k+m}(T), \tag{49}$$

which can be readily proved by Eqs. (36) and (38).

Recursive forms of one-electron integrals, derived from three-center overlap integrals, are described in the Appendix.

III. DISCUSSION

The recurrence formula, as given by Eq. (39), involves true and auxiliary ERI's as intermediary integrals. Efficient use of these intermediary integrals can be made in calculating target ERI's, if all the components of each shell are adopted as basic functions. As an illustration, let us consider the ERI's $(p_i p_j, ss)$ $(i,j = x,y,z)$. Calculation of the nine integrals resulting from all possible combinations of i and j requires the intermediary integrals $(p_i s, ss)^{(m)}$ $(i = x,y,z$ and $m = 0,1)$ and $(ss,ss)^{(m)}$ $(m = 0,1,2)$. All of these intermediary integrals except $(ss,ss)^{(2)}$ can be used three times, because for each of three j values the integral can be expressed as

$$(p_i p_j, ss) = (P_j - B_j)(p_i s,ss)^{(0)} + (W_j - P_j)(p_i s,ss)^{(1)} + \frac{\delta_{ij}}{2\zeta}\left\{(ss,ss)^{(0)} - \frac{\rho}{\zeta}(ss,ss)^{(1)}\right\}. \tag{50}$$

Furthermore the intermediary integrals $(p_i s, ss)^{(m)}$ can also be calculated efficiently from the three intermediary integrals $(ss,ss)^{(m)}$ $(m = 0,1,2)$.

The present algorithm would be most efficient for a basis set consisting of constrained functions, namely, a basis set in which a common set of orbital exponents is employed for functions with different angular momenta. When p functions in the above example are sp-constrained, the intermediary integrals $(p_i s, ss)^{(0)}$ and $(ss,ss)^{(0)}$ also become target ERI's. Hence, the extra integrals to be calculated are $(sp_j, ss)^{(0)}$ $(j = x,y,z)$.

The coefficients, such as $(P_i - A_i)$, $(2\zeta)^{-1}$, and $\rho\zeta^{-1}$, in the recurrence formula do not depend on the angular momenta of functions in the integrals. The independence is an advantage of this method in comparison with the usual method based on the overlap distributions.[3] The overlap distribution is defined as a product of two Gaussian functions, and can be reduced to a linear combination of Gaussian functions multiplied by appropriate coefficients. These coefficients depend on the angular momentum indices, namely, not only on the angular momenta but also on their components. Therefore, the number of the coefficients increases as the sum of the angular momenta of the functions increases. By this increase, the calculation of ERI's becomes more time consuming, and the coding of an efficient program more difficult. The present scheme, with a program structure involving a long innermost loop, alleviates this problem as will be detailed in the next section.

The differential relation (5) allows the derivatives of ERI's to be written as a linear conbination of ERI's. The first derivative, for instance, becomes

$$\frac{\partial}{\partial A_i}(\mathbf{ab},\mathbf{cd})^{(m)} = 2\zeta_a[(\mathbf{a}+\mathbf{1}_i)\mathbf{b},\mathbf{cd}]^{(m)} - N_i(\mathbf{a})[(\mathbf{a}-\mathbf{1}_i)\mathbf{b},\mathbf{cd}]^{(m)}. \tag{51}$$

The second term on the right-hand side of Eq. (51) can be calculated as an intermediary for the first term using the recurrence formula. Thus it is noted that the number of arithmetic operations is largely determined by that of the operations for the integral over the highest angular momentum functions.

A brief additional comment may be in order here. Substitution of Eq. (39) into the first term of Eq. (51) gives an expression for the derivative which does not include higher angular momentum functions. This expression corresponds to that given by Schlegel, Binkley, and Pople[16]; however ours is for ERI's, whereas theirs is for two-dimensional integrals.

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SCHEME I.

```
(First step)
    DO ICS = 1,n_CS    loops for the contracted shells
    DO JCS = 1,ICS
    DO IPS = 1,m_ICS   loops for the primitive shells
    DO JPS = 1,m_JCS
    The calculation of the parameters P, ζ, and K(ζ,ζ',R,R')
    for each pair of primitive shells
    CONTINUE

(Second Step)
    DO IPPS = 1,N_PPS   a loop for the first pair of primitive shells
    DO JPPS = 1, IPPS   a loop for the second pair of primitive shells
    The evaluation of ERI's
    CONTINUE
```

The expressions for the one-electron integrals in the present formalism bear all the desirable characteristics of those for ERI's described above. Accordingly, fast computation can be expected also for one-electron integrals.

IV. STRATEGY OF ERI COMPUTATION

In usual *ab initio* calculations contracted Gaussian functions are used as the basis set. The contracted function, χ, takes the form:

$$\chi(\mathbf{r};\mathbf{n},\mathbf{R}) = \sum_{k=1}^{m_c} d_k\, \mathfrak{N}(\zeta_k,\mathbf{n})\varphi(\mathbf{r};\zeta_k,\mathbf{n},\mathbf{R}) , \qquad (52)$$

where d_k is the contraction coefficient. In this section we term φ a *primitive* function in order to distinguish it from a contracted one.

The overall structure of the program is composed of two main steps. The first step is to calculate the parameters $\mathbf{P}$, ζ, and $K(\zeta,\zeta',\mathbf{R},\mathbf{R}')$ and the second step is to evaluate ERI's using the recurrence formula. Since the parameters do not require a large area for their storage as has been discussed previously, they can be calculated in a bunch for all possible combinations of primitive shells rather than separately for each primitive component. The first step includes four loops, as shown in Scheme I, where n_{cs} is the number of contracted shells in the basis set, and the m_{ics} and m_{jcs} are the number of primitive shells in the *ICS* th and *JCS* th contracted shells, respectively. The second step is composed of two loops. The N_{PPS} in the scheme is the number of the sets of parameters generated in the first step. The feature of this program structure is that the inner loop in the second step is iterated, at most, N_{PPS} times. If a hundred primitive shells are included in the basis set, the number becomes 5500, which would be sufficiently large for a vector processing computer.

As can be seen from Eq. (39) or Table I, ERI's having the same combination of four angular momenta irrespective of function centers, such as all (ss, ss)'s or (ps, ss)'s require the same explicit form of the recurrence formula. Then the second step in Scheme I may be executed only once for each of these assemblies because the programs for this algorithm become simpler at a little sacrifice of the largeness of N_{PPS} for a vector processing computer. In implementing the above procedure the parameters originating from the same combination of two angular momenta are to be collected by reordering the shells in the basis set according to their angular momenta beforehand. For derivatives of ERI's, reduction of the computer time taking advantage of the translational invariance can be immediately accomplished by subgrouping the collected parameters according to the centers of the functions.

By means of the recurrence formula for the ERI's the angular momentum of one of the four functions is reduced. The function with the lowest angular momentum should be chosen first, since then the factor $N_i(\mathbf{n})$ will become zero at an early stage of the reduction, and thus the total number of necessary intermediary integrals will become least.

In the present program the functions $F_n(T)$ are evaluated using two formulas depending on the value T. For values from zero to a certain threshold value T_F, we employ the seven-term Taylor expansion:

$$F_n(T) = \sum_{k=0}^{6} F_{n+k}(T^*)(T^*-T)^k/k!, \qquad (53)$$

where $F_{n+k}(T^*)$ has been evaluated by the Shavitt method[18] for T^* at intervals of 0.05 and tabulated. Another formula, used for T greater than T_F, is an asymptotic formula of $F_n(T)$, where the upper limit of the integration range is replaced by positive infinity:

$$F_n(T) \sim \int_0^\infty t^{2n}\exp(-Tt^2)\,dt = \frac{(2n-1)!!}{2(2T)^n}\left(\frac{\pi}{T}\right)^{1/2}. \qquad (54)$$

The relative error Δ of the expansion by Eq. (53) can be estimated using Lagrange's remainder

$$\Delta = \frac{|T^*-T|^7}{7!} \times \left[\frac{F_{n+7}\{T^*+\theta(T-T^*)\}}{F_n(T)}\right] \quad (0<\theta<1); \qquad (55)$$

it is roughly 1.2×10^{-15} by assuming that $|T^*-T|$ takes the maximum value, i.e., 0.025 and the factor in the square brackets of Eq. (55) to be unity. A more precise estimate was made for the ranges of n and T between 0 and 16 and between 0 and 80, respectively. The maximum relative error was found to be 0.9×10^{-15}, which corresponds to $F_{16}(0.025)$. A relative error of about 10^{-15} seems to be sufficiently small for usual *ab initio* calculations. Therefore the value of the threshold T_F was determined so that the asymptotic formula may have a relative error of less than 10^{-15} as is given in Table II.

McMurchie and Davidson[5] gave an efficient computational method for $F_n(T)$, where seven formulas are used,

TABLE II. Values of T_F used in the evaluation of $F_n(T)$.

n	T_F	n	T_F	n	T_F
0	33	6	51	12	66
1	37	7	54	13	68
2	41	8	56	14	70
3	43	9	58	15	72
4	46	10	61	16	74
5	49	11	63		

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TABLE III. CPU time[a] for ERI computation (in seconds).

Molecule	Basis set	PH[b]	Present[c]	Ratio	DRK[d]	Present	Ratio
H_2O_2	3-21G[e]	0.40	0.27	1.5	1.5	0.29	5.2
C_2H_4O	3-21G	2.7	1.7	1.6	10.6	2.0	5.3
C_2H_4O	4-31G[f]	4.5	4.0	1.1	23.3	5.5	4.2
H_2O_2	MIDI-1[g]	1.0	0.53	1.9	3.5	0.55	6.4
C_2H_4O	MIDI-1	6.4	3.3	1.9	23.0	3.9	5.9
C_2H_4O	MIDI-4[g]	9.9	7.0	1.4	41.0	8.9	4.6
H_2O_2	3-21G + d[h]				4.0	1.5	2.7
C_2H_4O	3-21G + d				25.8	8.7	3.0
H_2O_2	MIDI-1 + d				7.3	2.1	3.5
C_2H_4O	MIDI-1 + d				45.9	12.9	3.6

[a] The CPU time only for the arithmetic operations measured on FACOM M-382, a scalar computer.
[b] The Pople and Hehre method (Ref. 20).
[c] The threshold values of T_v and T_F are 10^{-8} a.u. and 15, respectively.
[d] The Dupuis, Rys, and King method (Ref 21).
[e] Reference 22.
[f] Reference 23.
[g] Reference 24.
[h] A primitive d function ($\zeta = 0.8$) is added on each carbon and/or oxygen atom.

and Harris[19] proposed another method using three formulas. The present method of evaluating $F_n(T)$ would be slower on a scalar computer than theirs. On a vector processing computer, however, it would become faster, since a program with a fewer number of branches to use one of these formulas in an inner loop can be more efficiently vectorized.

The computer time can be reduced further by omitting ERI's over primitive functions that make a small contribution to ERI's over the contracted functions. In the present program, the omission is actually carried out in the calculation of the parameters. For the product V of the contraction coefficients, the normalization constants, and the factor K,

$$V = d_{at} \cdot \mathfrak{N}(\zeta_a,\mathbf{a}) \cdot d_{bt} \cdot \mathfrak{N}(\zeta_b,\mathbf{b}) \cdot K(\zeta_a,\zeta_b,\mathbf{A},\mathbf{B}) \quad (56)$$

smaller than a given threshold T_V the corresponding parameters are omitted, and hence the corresponding ERI's are not calculated. We take T_V to be 10^{-15} a.u., because the maximum relative error 10^{-15} allowed for $F_n(T)$ would result in this order of error.

V. COMPARISON WITH OTHER METHODS

Execution times on a scalar computer FACOM M-382 and on a vector processing computer FACOM VP-100 are compared with those required by the Pople and Hehre (PH) method in GAUSSIAN 80[20] and the Dupuis, Rys, and King (DRK) method in GAMESS.[21] The basis sets used are of valence-double zeta quality, i.e., 3-21G,[22] 4-31G,[23] MIDI-1,[24] and MIDI-4,[24] where the former two sets contain sp-constrained functions while the latter two sets do not. The CPU time is for the evaluation without utilizing molecular symmetry, and does not include I/O operations. All programs are written in FORTRAN, and are compiled at the highest level of optimization with the intention of reducing inefficiencies in program codes. Incidentally the optimization is found to reduce the computer times to about 60% (PH), about 40% (DRK), and about 50% (ours) of those for the unoptimized versions. The speeds of M-382 and VP-100 are 23 MIPS (mega instructions per second) and 250 MFLOPS (mega floating operations per second), respectively, although they have the same speed for scalar operations.

Table III lists the CPU times of ERI calculations for ethylene oxide and hydrogen peroxide on the scalar computer. For the basis sets with sp-constrained functions, i.e., the 3-21G and 4-31G sets, the present method is from 1.1 to 1.6 times faster than the PH method, with the accuracy of the present method intentionally reduced almost to that (about eight decimal characters) of the PH method by setting the thresholds T_F and T_V at 15 and 10^{-8}, respectively. For the basis sets without sp-constrained functions, i.e., the MIDI-1 and MIDI-4 sets, the CPU time ratio is somewhat enhanced, but this may not be a fair comparison, since the program of the PH method treats all p functions as sp-constrained ones, and thus calculates unnecessary ERI's for these basis sets. The CPU time ratio of the DRK method to the present method ranges between 4.2 and 6.4 in the calculation of ERI's with the above basis sets. For the 3-21G and MIDI-1 basis sets augmented by a primitive d function on each carbon and/or oxygen atom, the CPU time ratio ranges between 2.7 and 3.6. The decrease in the ratio is a reflection of the efficiency of the DRK method for higher angular momentum functions.[9]

From Table IV we observe that the present method is from 4.1 to 6.7 times faster than the DRK method for the first derivative of ERI's on the scalar computer. We expect that the present method is also faster than the method proposed by Schlegel, Binkley, and Pople[16] since their method requires almost the same number of arithmetic operations with that required by the DRK method for the calculation of the first derivative of (dd,dd).

The computer times on the vector processing computer are presented in Table V for the calculation of ERI's for ethylene oxide, together with the maximum number of iterations N_{PPS} in the second step of Scheme I. The calculation of

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TABLE IV. CPU time[a] for the computation of the first derivative of ERI's (in seconds).

Molecule	Basis set	DRK[b]	Present	Ratio
H_2O_2	3-21G[c]	5.3	1.3	4.1
C_2H_4O	3-21G	47.6	9.0	5.3
C_2H_4O	4-31G[d]	102.3	22.7	4.5
H_2O_2	MIDI-1[e]	10.8	1.7	6.4
C_2H_4O	MIDI-1	82.2	12.2	6.7
C_2H_4O	MIDI-4[e]	153.8	27.6	5.6

[a] The CPU time only for the arithmetic operations measured on FACOM M-382, a scalar computer.
[b] The Dupuis, Rys, and King method (Ref. 21).
[c] Reference 22.
[d] Reference 23.
[e] Reference 24.

ERI's is accomplished from 4.1 to 5.4 faster than on the scalar computer. The CPU time for integrals involving smaller N_{PPS} such as (pp, pp) in the table does not give a good estimate for large molecular systems having N_{PPS} much larger than a hundred. If we count the CPU time excluding (pp, pp), the CPU time ratio becomes $5.2 \sim 6.1$ as given in parentheses in the last row of Table V. In these calculations the programs have not been rewritten for the vector processing computer, and hence revision of the programs would further reduce the CPU time. In any event, the results are indicative of the efficiency of the long innermost loop in the second step in Scheme I.

VI. CONCLUDING REMARKS

In this paper we have shown how the recurrence formula for three-center overlap integrals can be efficiently utilized in developing recursive formulation of ERI's and one-electron integrals over Cartesian Gaussian functions. The method proposed for the evaluation of a wide variety of molecular integrals, when implemented on a computer, exhibits the following outstanding characteristics: (1) an efficient use of intermediary integrals; (2) an efficient treatment of constrained functions; (3) a smaller storage for coefficients in the recurrence formulas due to their independence on the angular momenta of functions; and (4) a large number of iterations in the innermost loop.

Computer times have been compared with various methods for the calculation of ERI's and their first derivative with respect to the nuclear coordinates. The comparison shows that the above characteristics of the present method offer a definite advantage over the PH and the DRK methods in current use. The characteristic (4) is particularly suited for a vector processing computer, and indeed the CPU time on a vector processing machine is reduced to about one fifth of that on a scalar computer. The method should thus prove useful in molecular integral calculations over Cartesian Gaussian functions.

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APPENDIX

Two-center overlap integrals

The two-center overlap integral over unnormalized Cartesian Gaussian functions

TABLE V. CPU time[a] for the computation of ERI's for ethylene oxide on a scalar (S)[b] and a vector (V)[c] processing computers (in milliseconds).

	3-21G			MIDI-1			MIDI-4		
	N_{PPS}[d]	S	V	N_{PPS}[d]	S	V	N_{PPS}[d]	S	V
(ss, ss)	179	105	18	397	550	79	578	1184	150
(ss, sp)	179	370	54	397	1185	168	578	2802	340
(ss, pp)	179	184	28	397	360	63	578	843	120
(sp, sp)	177	385	80	258	775	147	412	1880	304
(sp, pp)	177	690	146	258	780	213	412	1672	450
(pp, pp)	45	295	160	45	199	122	75	449	250
Others[e]		17	9		23	14		34	15
Sum[f]		2046	495		3872	806		8864	1629
		(1751)	(335)		(3673)	(684)		(8415)	(1379)
Ratio (S/V)[g]		4.1			4.8			5.4	
		(5.2)			(5.4)			(6.1)	

[a] The CPU time only for the arithmetic operations.
[b] FACOM M-382.
[c] FACOM VP-100.
[d] The maximum number of iterations in the innermost loop of the second step in Scheme I.
[e] Most part of the CPU time is spent for the calculation of the parameters generated in the first step in Scheme I.
[f] The number in parentheses is the sum of the CPU time excluding that for (pp, pp).
[g] The number in parentheses is the ratio of the sums excluding the CPU time for (pp, pp).

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$$(\mathbf{a}\|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B}) \tag{A1}$$

corresponds to the three-center overlap integral where one of the three functions is unity, namely, an s function having the orbital exponent of zero. Using Eq. (20), the two-center overlap integrals reduces to

$$(\mathbf{a}+\mathbf{1}_i\|\mathbf{b}) = (P_i - A_i)(\mathbf{a}\|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i\|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{b})(\mathbf{a}\|\mathbf{b}-\mathbf{1}_i)\,. \tag{A2}$$

The integral over s functions has been given by Eq. (22).

Moment integrals

The moment integrals around $\mathbf{C}$ can be written in the form:

$$(\mathbf{a}|\mathfrak{M}(\boldsymbol{\mu})|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})\mathfrak{M}(\boldsymbol{\mu})\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B})\,, \tag{A3}$$

where

$$\mathfrak{M}(\boldsymbol{\mu}) = (x-C_x)^{\mu_x}(y-C_y)^{\mu_y}(z-C_z)^{\mu_z}\,, \tag{A4}$$

and

$$\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)\,. \tag{A5}$$

By expressing the operator $\mathfrak{M}(\boldsymbol{\mu})$ in terms of a Cartesian Gaussian function as

$$\mathfrak{M}(\boldsymbol{\mu}) = \{\varphi(\mathbf{r};\zeta_c, \boldsymbol{\mu},\mathbf{C})\}_{\zeta_c=0}\,, \tag{A6}$$

the moment integral is deduced from Eq. (20) as

$$(\mathbf{a}+\mathbf{1}_i|\mathfrak{M}(\boldsymbol{\mu})|\mathbf{b}) = (P_i - A_i)(\mathbf{a}|\mathfrak{M}(\boldsymbol{\mu})|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i|\mathfrak{M}(\boldsymbol{\mu})|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{b}) \times (\mathbf{a}|\mathfrak{M}(\boldsymbol{\mu})|\mathbf{b}-\mathbf{1}_i) + \frac{1}{2\zeta} N_i(\boldsymbol{\mu})(\mathbf{a}|\mathfrak{M}(\boldsymbol{\mu}-\mathbf{1}_i)|\mathbf{b})\,. \tag{A7}$$

The moment integrals over s functions are given by

$$(\mathbf{0}_A|\mathfrak{M}(\boldsymbol{\mu}+\mathbf{1}_i)|\mathbf{0}_B) = (P_i - C_i)(\mathbf{0}_A|\mathfrak{M}(\boldsymbol{\mu})|\mathbf{0}_B) + \frac{1}{2\zeta} N_i(\boldsymbol{\mu})(\mathbf{0}_A|\mathfrak{M}(\boldsymbol{\mu}-\mathbf{1}_i)|\mathbf{0}_B)\,, \tag{A8}$$

and $(\mathbf{0}_A|\mathfrak{M}(\mathbf{0})|\mathbf{0}_B)$ becomes a two-center overlap integral over s functions [Eq. (22)].

Kinetic energy integrals

The kinetic energy integral has the form:

$$(\mathbf{a}|\mathscr{T}|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})(-\tfrac{1}{2}\nabla^2)\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B})\,, \tag{A9}$$

where

$$\nabla^2 = \sum_{\nu=x,y,z} \frac{\partial^2}{\partial r_\nu^2}\,. \tag{A10}$$

Using Eqs. (5) and (7), and the identity

$$\int d\mathbf{r}\, \varphi_i \nabla^2 \varphi_j = -\int d\mathbf{r}(\nabla\varphi_i)\cdot(\nabla\varphi_j)\,, \tag{A11}$$

the kinetic energy integral reduces to a linear combination of the two-center overlap integrals. Then with the aid of Eq. (A2), we find

$$(\mathbf{a}+\mathbf{1}_i|\mathscr{T}|\mathbf{b}) = (P_i - A_i)(\mathbf{a}|\mathscr{T}|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i|\mathscr{T}|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{b})(\mathbf{a}|\mathscr{T}|\mathbf{b}-\mathbf{1}_i) + 2\xi\left\{(\mathbf{a}+\mathbf{1}_i\|\mathbf{b}) - \frac{1}{2\zeta_a} N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i\|\mathbf{b})\right\}. \tag{A12}$$

The iteration begins with the kinetic energy integral over s functions:

$$(\mathbf{0}_A|\mathscr{T}|\mathbf{0}_B) = \xi\{3 - 2\xi(\mathbf{A}-\mathbf{B})^2\}(\mathbf{0}_A\|\mathbf{0}_B)\,. \tag{A13}$$

Nuclear attraction integrals

The nuclear attraction integral for a nucleus located at $\mathbf{C}$,

$$(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A}) \frac{1}{|\mathbf{r}-\mathbf{C}|} \varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B}) \tag{A14}$$

reduces to

$$(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b}) = \frac{2}{\pi^{1/2}} \int_0^\infty du\, (\mathbf{a}|\mathbf{0}_C|\mathbf{b})\,, \tag{A15}$$

where

$$(\mathbf{a}|\mathbf{0}_C|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})\varphi(\mathbf{r};;\zeta_b,\mathbf{b},\mathbf{B}) \times \exp[-u^2(\mathbf{r}-\mathbf{C})^2]\,, \tag{A16}$$

and we have used Eq. (24). The exponential function in Eq. (A16) corresponds to an s-type Cartesian Gaussian function having the exponent u^2 and centered at $\mathbf{C}$, so the integral is a three-center overlap integral. Using Eq. (20), we get

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{0}_C|\mathbf{b}) = (P_i - A_i)(\mathbf{a}|\mathbf{0}_C|\mathbf{b}) - (P_i - C_i)\frac{u^2}{\zeta+u^2}(\mathbf{a}|\mathbf{0}_C|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{a})\left(1 - \frac{u^2}{\zeta+u^2}\right)(\mathbf{a}-\mathbf{1}_i|\mathbf{0}_C|\mathbf{b}) + \frac{1}{2\zeta} N_i(\mathbf{b})\left(1 - \frac{u^2}{\zeta+u^2}\right)(\mathbf{a}|\mathbf{0}_C|\mathbf{b}-\mathbf{1}_i)\,. \tag{A17}$$

Now if we define an auxiliary nuclear attraction integral as

$$(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m)} = \frac{2}{\pi^{1/2}} \int_0^\infty du \left(\frac{u^2}{\zeta+u^2}\right)^m (\mathbf{a}|\mathbf{0}_C|\mathbf{b}) \tag{A18}$$

with a nonnegative integer m, it satisfies the recurrence formula

$$(\mathbf{a}+\mathbf{1}_i|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m)} = (P_i - A_i)(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m)} - (P_i - C_i)(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m+1)} + \frac{1}{2\zeta} N_i(\mathbf{a})$$

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$$\times\{(\mathbf{a}-\mathbf{1}_i|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m)}-(\mathbf{a}-\mathbf{1}_i|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m+1)}\}+\frac{1}{2\zeta}N_i(\mathbf{b})\{(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b}-\mathbf{1}_i)^{(m)}-(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b}-\mathbf{1}_i)^{(m+1)}\}. \tag{A19}$$

The auxiliary integral over s functions is found to be

$$\begin{aligned}(\mathbf{0}_A|\mathscr{A}(\mathbf{0})|\mathbf{0}_B)^{(m)}&=\frac{2}{\pi^{1/2}}\int_0^\infty du\left(\frac{u^2}{\zeta+u^2}\right)^m\left(\frac{\zeta}{\zeta+u^2}\right)^{3/2}(\mathbf{0}_A\|\mathbf{0}_B)\\&\quad\times\exp\left[-\zeta(\mathbf{P}-\mathbf{C})^2\frac{u^2}{\zeta+u^2}\right]\\&=2\left(\frac{\zeta}{\pi}\right)^{1/2}(\mathbf{0}_A\|\mathbf{0}_B)\,F_m(U),\end{aligned} \tag{A20}$$

where

$$U=\zeta(\mathbf{P}-\mathbf{C})^2. \tag{A21}$$

Electric field and electric field gradient integrals

The operators for electric fields and electric field gradients are obtained by differentiating the nuclear attraction operator:

$$\mathscr{A}(\boldsymbol{\mu})=\left(\frac{\partial}{\partial C_x}\right)^{\mu_x}\left(\frac{\partial}{\partial C_y}\right)^{\mu_y}\left(\frac{\partial}{\partial C_z}\right)^{\mu_z}\frac{1}{|\mathbf{r}-\mathbf{C}|}, \tag{A22}$$

$$\boldsymbol{\mu}=(\mu_x,\mu_y,\mu_z).$$

The operator with $\boldsymbol{\mu}=\mathbf{1}_i$ or $\mathbf{1}_i+\mathbf{1}_j$ $(i,j=x,y,z)$ corresponds to that of the electric field or the electric field gradient, respectively. These integrals are obtained by differentiating the nuclear attraction integrals:

$$(\mathbf{a}|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b})^{(m)}=\left(\frac{\partial}{\partial C_x}\right)^{\mu_x}\left(\frac{\partial}{\partial C_y}\right)^{\mu_y}\left(\frac{\partial}{\partial C_z}\right)^{\mu_z}(\mathbf{a}|\mathscr{A}(\mathbf{0})|\mathbf{b})^{(m)}. \tag{A23}$$

Differentiation of Eq. (A19) yields finally

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b})^{(m)}&=(P_i-A_i)(\mathbf{a}|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b})^{(m)}-(P_i-C_i)(\mathbf{a}|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b})^{(m+1)}\\&\quad+\frac{1}{2\zeta}N_i(\mathbf{a})\{(\mathbf{a}-\mathbf{1}_i|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b})^{(m)}-(\mathbf{a}-\mathbf{1}_i|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b})^{(m+1)}\}\\&\quad+\frac{1}{2\zeta}N_i(\mathbf{b})\{(\mathbf{a}|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b}-\mathbf{1}_i)^{(m)}-(\mathbf{a}|\mathscr{A}(\boldsymbol{\mu})|\mathbf{b}-\mathbf{1}_i)^{(m+1)}\}+N_i(\boldsymbol{\mu})(\mathbf{a}|\mathscr{A}(\boldsymbol{\mu}-\mathbf{1}_i)|\mathbf{b})^{(m+1)}.\end{aligned} \tag{A24}$$

The electric field and electric field gradient integrals over s functions are obtained from Eqs. (A20) and (A23) as

$$(\mathbf{0}_A|\mathscr{A}(\mathbf{1}_i)|\mathbf{0}_B)^{(m)}=2\zeta(P_i-C_i)(\mathbf{0}_A|\mathscr{A}(\mathbf{0})|\mathbf{0}_B)^{(m+1)}, \tag{A25}$$

and

$$\begin{aligned}(\mathbf{0}_A|\mathscr{A}(\mathbf{1}_i+\mathbf{1}_j)|\mathbf{0}_B)^{(m)}&=-2\zeta\delta_{ij}(\mathbf{0}_A|\mathscr{A}(\mathbf{0})|\mathbf{0}_B)^{(m+1)}\\&\quad+4\zeta^2(P_i-C_i)(P_j-C_j)(\mathbf{0}_A|\mathscr{A}(\mathbf{0})|\mathbf{0}_B)^{(m+2)},\end{aligned} \tag{A26}$$

TABLE VI. Recurrence expressions[a] for overlap integrals over s, p, and d Cartesian Gaussian functions.

$$(s\|s)=\left(\frac{\pi}{\zeta}\right)^{3/2}\exp\{-\xi(\mathbf{A}-\mathbf{B})^2\}$$

$$(p_i\|s)=(P_i-A_i)(s\|s)$$

$$(p_i\|p_j)=(P_j-B_j)(p_i\|s)+\frac{\delta_{ij}}{2\zeta}(s\|s)$$

$$(d_{ij}\|s)=(P_j-A_j)(p_i\|s)+\frac{\delta_{ij}}{2\zeta}(s\|s)$$

$$(d_{ij}\|p_k)=(P_k-B_k)(d_{ij}\|s)+\frac{\delta_{ik}}{2\zeta}(p_j\|s)+\frac{\delta_{jk}}{2\zeta}(p_i\|s)$$

$$(d_{ij}\|d_{kl})=(P_l-B_l)(d_{ij}\|p_k)+\frac{\delta_{il}}{2\zeta}(p_j\|p_k)+\frac{\delta_{jl}}{2\zeta}(p_i\|p_k)+\frac{\delta_{kl}}{2\zeta}(d_{ij}\|s)$$

$$(i,j,k,l=x,y,z)$$

[a] For the definition of the variables, see the text.

respectively.

Angular momentum integrals

The matrix element of the orbital angular momentum around $\mathbf{C}$ requires an integral

TABLE VII. Recurrence expressions[a] for the first moment integrals over s, p, and d Cartesian Gaussian functions.

$$(s|\mathfrak{M}_\mu|s)=(P_\mu-C_\mu)\left(\frac{\pi}{\zeta}\right)^{3/2}\exp\{-\xi(\mathbf{A}-\mathbf{B})^2\}=(P_\mu-C_\mu)(s\|s)$$

$$(p_i|\mathfrak{M}_\mu|s)=(P_i-A_i)(s|\mathfrak{M}_\mu|s)+\frac{\delta_{\mu i}}{2\zeta}(s\|s)$$

$$(p_i|\mathfrak{M}_\mu|p_j)=(P_j-B_j)(p_i|\mathfrak{M}_\mu|s)+\frac{\delta_{ij}}{2\zeta}(s|\mathfrak{M}_\mu|s)+\frac{\delta_{\mu j}}{2\zeta}(p_i\|s)$$

$$(d_{ij}|\mathfrak{M}_\mu|s)=(P_j-A_j)(p_i|\mathfrak{M}_\mu|s)+\frac{\delta_{ij}}{2\zeta}(s|\mathfrak{M}_\mu|s)+\frac{\delta_{\mu j}}{2\zeta}(p_i\|s)$$

$$(d_{ij}|\mathfrak{M}_\mu|p_k)=(P_k-B_k)(d_{ij}|\mathfrak{M}_\mu|s)+\frac{\delta_{ik}}{2\zeta}(p_j|\mathfrak{M}_\mu|s)+\frac{\delta_{jk}}{2\zeta}(p_i|\mathfrak{M}_\mu|s)+\frac{\delta_{\mu k}}{2\zeta}(d_{ij}\|s)$$

$$(d_{ij}|\mathfrak{M}_\mu|d_{kl})=(P_l-B_l)(d_{ij}|\mathfrak{M}_\mu|p_k)+\frac{\delta_{il}}{2\zeta}(p_j|\mathfrak{M}_\mu|p_k)+\frac{\delta_{jl}}{2\zeta}(p_i|\mathfrak{M}_\mu|p_k)+\frac{\delta_{kl}}{2\zeta}(d_{ij}|\mathfrak{M}_\mu|s)+\frac{\delta_{\mu l}}{2\zeta}(d_{ij}\|p_k)$$

$$\mathfrak{M}_\mu=\mathfrak{M}(\mathbf{1}_\mu)$$

$$(i,j,k,l,\mu=x,y,z)$$

[a] For the definition of the variables, see the text.

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TABLE VIII. Recurrence expressions[a] for the kinetic energy integrals over s, p, and d Cartesian Gaussian functions.

$$(s|\mathscr{T}|s) = \xi\{3 - 2\xi(\mathbf{A}-\mathbf{B})^2\}(s\|s)$$

$$(p_i|\mathscr{T}|s) = (P_i - A_i)(s|\mathscr{T}|s) + 2\xi(p_i\|s)$$

$$(p_i|\mathscr{T}|p_j) = (P_j - B_j)(p_i|\mathscr{T}|s) + \frac{\delta_{ij}}{2\zeta}(s|\mathscr{T}|s) + 2\xi(p_i\|p_j)$$

$$(d_{ij}|\mathscr{T}|s) = (P_j - A_j)(p_i|\mathscr{T}|s) + \frac{\delta_{ij}}{2\zeta}(s|\mathscr{T}|s) + 2\xi\left\{(d_{ij}\|s) - \frac{\delta_{ij}}{2\zeta_a}(s\|s)\right\}$$

$$(d_{ij}|\mathscr{T}|p_k) = (P_k - B_k)(d_{ij}|\mathscr{T}|s) + \frac{\delta_{ik}}{2\zeta}(p_j|\mathscr{T}|s) + \frac{\delta_{jk}}{2\zeta}(p_i|\mathscr{T}|s) + 2\xi(d_{ij}\|p_k)$$

$$(d_{ij}|\mathscr{T}|d_{kl}) = (P_l - B_l)(d_{ij}|\mathscr{T}|p_k) + \frac{\delta_{il}}{2\zeta}(p_j|\mathscr{T}|p_k) + \frac{\delta_{jl}}{2\zeta}(p_i|\mathscr{T}|p_k) + \frac{\delta_{kl}}{2\zeta}(d_{ij}|\mathscr{T}|s) + 2\xi\left\{(d_{ij}\|d_{kl}) - \frac{\delta_{kl}}{2\zeta_b}(d_{ij}\|s)\right\}$$

$$(i, j, k, l = x, y, z)$$

[a] For the definition of the variables, see the text.

TABLE IX. Recurrence expressions[a] for the nuclear attraction integrals over s, p, and d Cartesian Gaussian functions.

$$(s|\mathscr{A}_0|s)^{(0)} = \frac{2\pi}{\zeta}\exp\{-\xi(\mathbf{A}-\mathbf{B})^2\}F_0(U) = 2\left(\frac{\zeta}{\pi}\right)^{1/2}(s\|s)F_0(U)$$

$$(p_i|\mathscr{A}_0|s)^{(0)} = (P_i - A_i)(s|\mathscr{A}_0|s)^{(0)} - (P_i - C_i)(s|\mathscr{A}_0|s)^{(1)}$$

$$(p_i|\mathscr{A}_0|p_j)^{(0)} = (P_j - B_j)(p_i|\mathscr{A}_0|s)^{(0)} - (P_j - C_j)(p_i|\mathscr{A}_0|s)^{(1)} + \frac{\delta_{ij}}{2\zeta}\{(s|\mathscr{A}_0|s)^{(0)} - (s|\mathscr{A}_0|s)^{(1)}\}$$

$$(d_{ij}|\mathscr{A}_0|s)^{(0)} = (P_j - A_j)(p_i|\mathscr{A}_0|s)^{(0)} - (P_j - C_j)(p_i|\mathscr{A}_0|s)^{(1)} + \frac{\delta_{ij}}{2\zeta}\{(s|\mathscr{A}_0|s)^{(0)} - (s|\mathscr{A}_0|s)^{(1)}\}$$

$$(d_{ij}|\mathscr{A}_0|p_k)^{(0)} = (P_k - B_k)(d_{ij}|\mathscr{A}_0|s)^{(0)} - (P_k - C_k)(d_{ij}|\mathscr{A}_0|s)^{(1)} + \frac{\delta_{ik}}{2\zeta}\{(p_j|\mathscr{A}_0|s)^{(0)} - (p_j|\mathscr{A}_0|s)^{(1)}\} + \frac{\delta_{jk}}{2\zeta}\{(p_i|\mathscr{A}_0|s)^{(0)} - (p_i|\mathscr{A}_0|s)^{(1)}\}$$

$$(d_{ij}|\mathscr{A}_0|d_{kl})^{(0)} = (P_l - B_l)(d_{ij}|\mathscr{A}_0|p_k)^{(0)} - (P_l - C_l)(d_{ij}|\mathscr{A}_0|p_k)^{(1)} + \frac{\delta_{il}}{2\zeta}\{(p_j|\mathscr{A}_0|p_k)^{(0)} - (p_j|\mathscr{A}_0|p_k)^{(1)}\} + \frac{\delta_{jl}}{2\zeta}\{(p_i|\mathscr{A}_0|p_k)^{(0)} - (p_i|\mathscr{A}_0|p_k)^{(1)}\} + \frac{\delta_{kl}}{2\zeta}\{(d_{ij}|\mathscr{A}_0|s)^{(0)} - (d_{ij}|\mathscr{A}_0|s)^{(1)}\}$$

$$\mathscr{A}_0 = \mathscr{A}(0) \quad (i, j, k, l = x, y, z)$$

[a] For the definition of the variables, see the text.

TABLE X. Recurrence expressions[a] for the electric field integrals over s, p, and d Cartesian Gaussian functions.

$$(s|\mathscr{A}_\mu|s)^{(0)} = 2\zeta(P_\mu - C_\mu)(s|\mathscr{A}_0|s)^{(1)}$$

$$(p_i|\mathscr{A}_\mu|s)^{(0)} = (P_i - A_i)(s|\mathscr{A}_\mu|s)^{(0)} - (P_i - C_i)(s|\mathscr{A}_\mu|s)^{(1)} + \delta_{\mu i}(s|\mathscr{A}_0|s)^{(1)}$$

$$(p_i|\mathscr{A}_\mu|p_j)^{(0)} = (P_j - B_j)(p_i|\mathscr{A}_\mu|s)^{(0)} - (P_j - C_j)(p_i|\mathscr{A}_\mu|s)^{(1)} + \frac{\delta_{ij}}{2\zeta}\{(s|\mathscr{A}_\mu|s)^{(0)} - (s|\mathscr{A}_\mu|s)^{(1)}\} + \delta_{\mu j}(p_i|\mathscr{A}_0|s)^{(1)}$$

$$(d_{ij}|\mathscr{A}_\mu|s)^{(0)} = (P_j - A_j)(p_i|\mathscr{A}_\mu|s)^{(0)} - (P_j - C_j)(p_i|\mathscr{A}_\mu|s)^{(1)} + \frac{\delta_{ij}}{2\zeta}\{(s|\mathscr{A}_\mu|s)^{(0)} - (s|\mathscr{A}_\mu|s)^{(1)}\} + \delta_{\mu j}(p_i|\mathscr{A}_0|s)^{(1)}$$

$$(d_{ij}|\mathscr{A}_\mu|p_k)^{(0)} = (P_k - B_k)(d_{ij}|\mathscr{A}_\mu|s)^{(0)} - (P_k - C_k)(d_{ij}|\mathscr{A}_\mu|s)^{(1)} + \frac{\delta_{ik}}{2\zeta}\{(p_j|\mathscr{A}_\mu|s)^{(0)} - (p_j|\mathscr{A}_\mu|s)^{(1)}\} + \delta_{\mu k}(d'_{ij}|\mathscr{A}_0|s)^{(1)} + \frac{\delta_{jk}}{2\zeta}\{(p_i|\mathscr{A}_\mu|s)^{(0)} - (p_i|\mathscr{A}_\mu|s)^{(1)}\}$$

$$(d_{ij}|\mathscr{A}_\mu|d_{kl})^{(0)} = (P_l - B_l)(d_{ij}|\mathscr{A}_\mu|p_k)^{(0)} - (P_l - C_l)(d_{ij}|\mathscr{A}_\mu|p_k)^{(1)} + \frac{\delta_{il}}{2\zeta}\{(p_j|\mathscr{A}_\mu|p_k)^{(0)} - (p_j|\mathscr{A}_\mu|p_k)^{(1)}\} + \delta_{\mu l}(d_{ij}|\mathscr{A}_0|p_k)^{(1)} + \frac{\delta_{jl}}{2\zeta}\{(p_i|\mathscr{A}_\mu|p_k)^{(0)} - (p_i|\mathscr{A}_\mu|p_k)^{(1)}\} + \frac{\delta_{kl}}{2\zeta}\{(d_{ij}|\mathscr{A}_\mu|s)^{(0)} - (d_{ij}|\mathscr{A}_\mu|s)^{(1)}\}$$

$$\mathscr{A}_0 = \mathscr{A}(0) \quad \mathscr{A}_\mu = \mathscr{A}(1_\mu) \quad (i, j, k, l, \mu = x, y, z)$$

[a] For the definition of the variables, see the text.

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$$(\mathbf{a}|\mathscr{L}_\mu|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})\mathscr{L}_\mu\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B}) , \qquad (A27)$$

where

$$\mathscr{L}_\mu = \{(\mathbf{r}-\mathbf{C})\times\nabla\}_\mu \quad (\mu = x,y,z) . \qquad (A28)$$

Using Eq. (7), the z component of the integral, for instance, becomes

$$(\mathbf{a}|\mathscr{L}_z|\mathbf{b}) = -\int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A}) \times\left\{(x-C_x)\frac{\partial}{\partial B_y} - (y-C_y)\frac{\partial}{\partial B_x}\right\}\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B}) . \qquad (A29)$$

Then Eq. (5) allows the angular momentum integral to be written as a linear combination of the first moment integrals. Through the use of Eq. (A7) we have

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|\mathscr{L}_\mu|\mathbf{b}) &= (P_i - A_i)(\mathbf{a}|\mathscr{L}_\mu|\mathbf{b}) \\ &+ \frac{1}{2\zeta}N_i(\mathbf{a})(\mathbf{a}-\mathbf{1}_i|\mathscr{L}_\mu|\mathbf{b}) + \frac{1}{2\zeta}N_i(\mathbf{b})(\mathbf{a}|\mathscr{L}_\mu|\mathbf{b}-\mathbf{1}_i) \\ &+ \frac{\zeta_b}{\zeta}\{\mathbf{1}_i\times(\mathbf{B}-\mathbf{C})\}_\mu(\mathbf{a}\|\mathbf{b}) \\ &+ \frac{1}{2\zeta}\sum_{k=x,y,z}N_k(\mathbf{b})\{\mathbf{1}_i\times\mathbf{1}_k\}_\mu(\mathbf{a}\|\mathbf{b}-\mathbf{1}_k) , \end{aligned} \qquad (A30)$$

starting with the integral over s functions:

$$(\mathbf{0}_A|\mathscr{L}_\mu|\mathbf{0}_B) = 2\xi\{(\mathbf{A}-\mathbf{C})\times(\mathbf{B}-\mathbf{C})\}_\mu(\mathbf{0}_A\|\mathbf{0}_B) . \qquad (A31)$$

Spin-orbit interaction integrals

The matrix element of the orbital part of the spin-orbit interaction requires an integral

$$(\mathbf{a}|\mathscr{S}_\mu|\mathbf{b}) = \int d\mathbf{r}\, \varphi(\mathbf{r};\zeta_a,\mathbf{a},\mathbf{A})\mathscr{S}_\mu\varphi(\mathbf{r};\zeta_b,\mathbf{b},\mathbf{B}) , \qquad (A32)$$

where

$$\mathscr{S}_\mu = \left(\frac{\mathbf{r}-\mathbf{C}}{|\mathbf{r}-\mathbf{C}|^3}\times\nabla\right)_\mu \quad (\mu = x,y,z) . \qquad (A33)$$

Equations (5) and (7) reduce the integral to a linear combination of electric field integrals, which can be expressed by the auxiliary nuclear attraction integrals. The expression becomes finally

$$\begin{aligned}&(\mathbf{a}+\mathbf{1}_i|\mathscr{S}_\mu|\mathbf{b})^{(m)} \\ &= (P_i - A_i)(\mathbf{a}|\mathscr{S}_\mu|\mathbf{b})^{(m)} - (P_i - C_i)(\mathbf{a}|\mathscr{S}_\mu|\mathbf{b})^{(m+1)} \\ &+ \frac{1}{2\zeta}N_i(\mathbf{a})\{(\mathbf{a}-\mathbf{1}_i|\mathscr{S}_\mu|\mathbf{b})^{(m)} - (\mathbf{a}-\mathbf{1}_i|\mathscr{S}_\mu|\mathbf{b})^{(m+1)}\} \\ &+ \frac{1}{2\zeta}N_i(\mathbf{b})\{(\mathbf{a}|\mathscr{S}_\mu|\mathbf{b}-\mathbf{1}_i)^{(m)} - (\mathbf{a}|\mathscr{S}_\mu|\mathbf{b}-\mathbf{1}_i)^{(m+1)}\} \\ &+ 2\zeta_b\{\mathbf{1}_i\times(\mathbf{B}-\mathbf{C})\}_\mu(\mathbf{a}|\mathscr{A}(0)|\mathbf{b})^{(m+1)} \\ &+ \sum_{k=x,y,z}N_k(\mathbf{b})\{\mathbf{1}_i\times\mathbf{1}_k\}_\mu(\mathbf{a}|\mathscr{A}(0)|\mathbf{b}-\mathbf{1}_k)^{(m+1)} , \end{aligned} \qquad (A34)$$

and the integral over s functions is given by

$$\begin{aligned}&(\mathbf{0}_A|\mathscr{S}_\mu|\mathbf{0}_B)^{(m)} \\ &= 4\zeta_a\zeta_b\{(\mathbf{A}-\mathbf{C})\times(\mathbf{B}-\mathbf{C})\}_\mu(\mathbf{0}_A|\mathscr{A}(0)|\mathbf{0}_B)^{(m+1)} . \end{aligned} \qquad (A35)$$

The expressions for two-center overlap integrals, first moment integrals, kinetic energy integrals, nuclear attraction integrals, and electric field integrals including up to d functions are assembled in Tables VI, VII, VIII, IX, and X, respectively.

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