JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 21, No. 11, NOVEMBER, 1966

Gaussian-Expansion Methods for Molecular Integrals

Hiroshi TAKETA, Sigeru HUZINAGA and Kiyosi O-OHATA
General Education Department, Kyushu University
Otsubomachi, Fukuoka

(Received June 30, 1966)

The Gaussian-expansion method for the evaluation of molecular integrals is described. The molecular integrals over the Slater-type functions are chosen as numerical examples, but the method can be applied to integrals over any other functions as long as the functions can duly be expressed in terms of Gaussian-type functions. A fairly detailed description is presented of the mathematical analysis with the purpose of facilitating the computer coding.

§ Introduction

The title of the present paper bears a close resemblance to that of a recent paper by Shavitt and Karplus,[1] "Gaussian-Transform Method for Molecular Integrals." In order to express the 1*s* Slater-type function, Shavitt and Karplus used the integral transform,

$$e^{-\zeta r}=\frac{\zeta}{2\sqrt{\pi}}\int_0^\infty s^{-\frac{3}{2}}e^{-\frac{\zeta^2}{4s}}e^{-sr^2}ds\,. \qquad (1)$$

In the present paper we use an approximate finite-set Gaussian expansion,

$$e^{-\zeta r}\cong\sum_i c_i e^{-\alpha_i r^2}\,. \qquad (2)$$

This idea is not at all new. In fact, Foster and Boys[2] reported briefly such an attempt.

The transform (1) is an obvious mathematical sophistication of the finite expansion (2) in that the transform (1) can be regarded as an exact infinite-set expansion. However, there is no guarantee that a mathematical sophistication infallibly brings in overall excellence or convenience. A simple-minded approach could be quite useful and good enough for certain purposes. As we will describe later there are several reasons to invoke approximate finite-set Gaussian expansions such as (2) for the evaluation of multicenter molecular integrals.

Let us consider the general electron repulsion integral

$$\iint A(1)B(1)(1/r_{12})C(2)D(2)dr_1dr_2 \,, \qquad (3)$$

where A, B, C, D represent certain functions or orbitals on generally different centers and 1 and 2 designate electron coordinates. If one adopts the Slater-type orbitals (STO's) for the calculation on polyatomic molecules, one has to evaluate a number of integrals of the type of (3), in which A, B, C, D represent STO's. In 1950 Boys[3] pointed out that if A, B, C, D in (3) are Gaussian-type orbitals (GTO's) the evaluation of the integral presents no grave difficulty. Shavitt and Karplus made full use of Boys' finding through the integral transform (1), but their undertaking is said to be strictly STO-oriented. In their method STO's play the role of basis functions for molecular calculations and GTO's are used as only mathematical tools in evaluating difficult molecular integrals such as (1) in which A, B, C, D represent STO's.

Our basic attitude in the present paper may be regarded as GTO-oriented but only in a broad sense. One of us (S. H.)[4] demonstrated, through direct energy calculation of atomic systems, that the Gaussian-type functions are not hopelessly poor in representing both Slater-type and Hartree-Fock-type atomic orbitals, if one is willing to use several Gaussian-type functions. The project has been pushed further extensively by using the least squares curve-fitting method, and some encouraging results are presented in the preceding paper.[5] For example, suppose the function $A(1)$ in (3) is either $2p$ STO's or $3p$ STO's. To represent it, we adopt a finite-set GTO expansion, say,

$$\sum_{i=1}^{N} c_{Ai}N_i(\alpha_i)(x-x_A)e^{-\alpha_i(r_i-r_A)^2} \,, \qquad (4)$$

where $N_i(\alpha_i)$ is a normalization factor and c_A the expansion coefficient. Here, it is imperative to have a good approximate expansion without using too many terms. In the preceding paper, it is shown that by using eight terms of $x\exp(-\alpha r^2)$ type functions we can obtain decent expansions for both $2p$ and $3p$ Slater-type orbitals. In the present paper it will be shown that those expansions actually yield fairly accurate values for various molecular integrals over $2p$ and $3p$ STO's. The implication is that we may evaluate various multicenter molecular integrals over $3p$ STO's with no more cost than over $2p$ STO's. This is one of the advantages of using the finite-set expansions over using rather inflexible integral transform (1). A similar situation holds also for $1s$, $2s$ and $3s$ STO's for which we use only the lowest s-type GTO, $\exp(-\alpha r^2)$. Going back to our example, we may also suppose that the function $A(1)$ is a Hartree-Fock-Roothaan $2p$ or $3p$ orbital for a certain atom. It seems quite possible that we can obtain fairly good approximate GTO expansions for them using about the same number of terms as required for expanding $2p$ or $3p$ STO.

So far we are concerned with obtaining "approximate" expansions of some functions in terms of GTO's. However, we may mold a linear combination of several GTO's which is a basis function for molecular calculations in its own right. For example, an approximate GTO expansion of a certain atomic Hartree-Fock orbital may, under a new light, be regarded not as an "approximate" function but as an independent basis function which has a reasonable "resemblance" to the Hartree-Fock orbital. Furthermore, we can split such a linear combination of several GTO's into, say, two parts which, after properly renormalized, are regarded as two newly molded basis functions for molecular calculations. A new name, the combined Gaussian-type orbitals (CGTO's), may be coined for these more or less artificially molded linear combinations of GTO's. It is worth-while to note that the scaling procedure applied to the GTO expansion of STO[5] can be applied also to this CGTO basis function. There is no such convenience of scaling in the original Hartree-Fock-Roothaan expansion that is a linear combinatoin of Slater-type orbitals.

In the following section we shall describe the mathematical analysis. The Gaussian-transform method as described by Shavitt and Karplus[1] is undoubtedly a very powerful and promising approach to the evaluation of multicenter integrals. However, the whole set-up is rather formidable and its complete computer programming is far from an easy task. By contrast, mathematical simplicity in the expansion method would encourage even a novice to start coding a multicenter molecular integral program. In the third section presented is a brief description of the programs actually coded. Numerical results and concluding discussions are presented in the last section and additional advantages of the Gaussian-expansion method over the Gaussian-transform method are mentioned.

§ 2. Mathematical Analysis

The following mathematical analysis is essentially due to Wright.[6] Considerable supplementations are added and a few alterations are made in order to make the presentation more readable and ready for actual program coding.

1. *Preliminary*

In the Cartesian coordinates a GTO centered at A is written as

$$x(\boldsymbol{A}, \alpha, l, m, n)=x_A{}^l y_A{}^m z_A{}^n \exp(-\alpha r_A{}^2)\,. \tag{2.1}$$

Here x_A, y_A and z_A are the components of a position vector $\boldsymbol{r}_A$ relative to $\boldsymbol{A}$, $\boldsymbol{r}_A=\boldsymbol{r}-\boldsymbol{A}$, and l, m and n are "quantum numbers" and are zeros or positive integers. The normalization constant is omitted for convenience. The normalized GTO is obtained by multiplying the normalization constant N:

$$N(\alpha, l, m, n)=\left\{\frac{2^{2(l+m+n)+3/2}\alpha^{l+m+n+3/2}}{(2l-1)!!\,(2m-1)!!\,(2n-1)!!\,\pi^{3/2}}\right\}^{\frac{1}{2}}, \tag{2.2}$$

where $(2l-1)!!=1\cdot3\cdot5\cdot\cdots\cdot(2l-1)$.

The GTO function has the following characteristic property: Suppose that there are two 1*s* GTO's, $\exp(-\alpha_1 r_A{}^2)$ and $\exp(-\alpha_2 r_B{}^2)$, centered at $\boldsymbol{A}$ and $\boldsymbol{B}$ respectively. The product of these GTO's yields again a GTO centered at $\boldsymbol{P}=(\alpha_1\boldsymbol{A}+\alpha_2\boldsymbol{B})/(\alpha_1+\alpha_2)$, namely.

$$\exp(-\alpha_1 r_A{}^2)\exp(-\alpha_2 r_B{}^2)=\exp(-\alpha_1\alpha_2\overline{AB}^2/\gamma)\exp(-\gamma r_P{}^2)\,, \tag{2.3}$$

where $\gamma=\alpha_1+\alpha_2$.

When the GTO's are not 1*s* orbitals, extra factors such as $x_A{}^{l_1}x_B{}^{l_2}$ appear in their product. For later analysis we rewrite these factors in terms of x_P, the coordinate relative to $\boldsymbol{P}$. We note that $\boldsymbol{r}_A=\boldsymbol{r}-\boldsymbol{A}=(\boldsymbol{r}-\boldsymbol{P})+(\boldsymbol{P}-\boldsymbol{A})=\boldsymbol{r}_P+(\boldsymbol{P}-\boldsymbol{A})$, hence $x_A=x_P+\overline{PA}_x$ and $x_B=x_P+\overline{PB}_x$. Therefore

$$x_A{}^{l_1}x_B{}^{l_2}=(x_P+\overline{PA}_x)^{l_1}(x_P+\overline{PB}_x)^{l_2}=\sum_j f_j(l_1, l_2, \overline{PA}_x, \overline{PB}_x)x^j\,, \tag{2.4}$$

$f_j(l, m, a, b)$ means the coefficient of x^j in the expansion of $(x+a)^l(x+b)^m$. Thus we have

$$\begin{aligned}\chi(\boldsymbol{A}, \alpha_1, l_1, m_1, n_1)&\chi(\boldsymbol{B}, \alpha_2, l_2, m_2, n_2)\\ &=\exp(-\alpha_1\alpha_2\overline{AB}^2/\gamma)\sum_i f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x)x_P{}^i\exp(-\gamma x_P{}^2)\\ &\times\sum_j f_j(m_1, m_2, \overline{PA}_y, \overline{PB}_y)y_P{}^j\exp(-\gamma y_P{}^2)\sum_k f_k(n_1, n_2, \overline{PA}_z, \overline{PB}_z)z_p{}^k\exp(-\gamma z_P{}^2)\,.\end{aligned} \tag{2.5}$$

This characteristic property of GTO's makes it rather easy to calculate various molecular integrals with the aid of the following mathematical formulae.

$$\int_0^\infty x^{2n}\exp(-\alpha x^2)dx=\frac{(2n-1)!!}{2^{n+1}}\sqrt{\frac{\pi}{\alpha^{2n+1}}}\,. \tag{2.6}$$

$$\int_{-\infty}^\infty e^{ixy}x^n\exp(-ax^2)dx=i^n\left(\frac{\pi}{a}\right)^{\frac{1}{2}}\left(\frac{1}{2\sqrt{a}}\right)^n H_n\left(\frac{y}{2\sqrt{a}}\right)\exp\left(-\frac{y^2}{4a}\right). \tag{2.7}$$

Here $H_n(z)$ is the Hermitian function and is defined as

$$H_n(z)=(-)^n\exp(z^2)\frac{d^n}{dz^n}\exp(-z^2)=n!\sum_{i=0}^{[n/2]}\frac{(-)^i(2z)^{n-2i}}{i!(n-2i)!}\,, \tag{2.8}$$

where $[x]$ means "largest integer less than or equal to x". This formula is given by Wright[6] without proof, but can be proved by the method of mathematical induction if we differentiate the above expression with respect to y.

$$\frac{1}{r}=\frac{1}{2\pi^2}\int\frac{d\boldsymbol{k}}{k^2}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,. \tag{2.9}$$

This is a well-known formula and one can refer to various text books[8] for its explanation.

$$\exp(-\delta k^2)=2\delta k^2\int_0^1 S^{-3}\exp\left(-\frac{\delta}{S^2}k^2\right)ds\ . \tag{2.10}$$

This is derived from an identity $e^{-a}=a\int_1^\infty e^{-ax}dx$ by letting $a=\delta k^2$ and $x=1/s^2$.

$$F_\nu(t)=\int_0^1 u^{2\nu}\exp(-tu^2)du\ . \tag{2.11}$$

This is the definition of an auxiliary function F_ν, and the relating formulae can be found in Shavitt's paper.[9]

2. Overlap integral

The use of the formulae (2.5) and (2.6) immediately gives the following expression for the overlap integral:

$$\begin{aligned}&\int\chi(\boldsymbol{A},\alpha_1,l_1,m_1,n_1)\chi(\boldsymbol{B},\alpha_2,l_2,m_2,n_2)dxdydz\\ &\quad=\left(\frac{\pi}{\gamma}\right)^{3/2}\exp(-\alpha_1\alpha_2\overline{AB}^2/\gamma)\sum_{i=0}^{[(l_1+l_2)/2]}f_{2i}(l_1,l_2,\overline{PA}_x,\overline{PB}_x)\frac{(2i-1)!!}{(2\gamma)^i}\\ &\quad\times\sum_{j=0}^{[(m_1+m_2)/2]}f_{2j}(m_1,m_2,\overline{PA}_y,\overline{PB}_y)\frac{(2j-1)!!}{(2\gamma)^j}\cdot\sum_{k=0}^{[(n_1+n_2)/2]}f_{2k}(n_1,n_2,\overline{PA}_z,\overline{PB}_z)\frac{(2k-1)!!}{(2\gamma)k}\ .\end{aligned}\tag{2.12}$$

3. Kinetic energy integral

The kinetic energy integral is defind by

$$\mathrm{KE}=\int\chi(\boldsymbol{A},\alpha_1,l_1,m_1,n_1)(-\Delta/2)\chi(\boldsymbol{B},\alpha_2,l_2,m_2,n_2)d\boldsymbol{r}\ . \tag{2.13}$$

If we denote the overlap integral between $\chi(\boldsymbol{A},\alpha_1,l_1,m_1,n_1)$ and $\chi(\boldsymbol{B},\alpha_2,l_2,m_2,n_2)$ as $S(l_2,m_2,n_2)$, we have

$$\begin{aligned}KE=&\alpha_2\{2(l_2+m_2+n_2)+3\}S(l_2,m_2,n_2)\\ &-2\alpha_2^2\{S(l_2+2,m_2,n_2)+S(l_2,m_2+2,n_2)+S(l_2,m_2,n_2+2)\}\\ &-\frac{1}{2}\{l_2(l_2-1)S(l_2-2,m_2,n_2)+m_2(m_2-1)S(l_2,m_2-2,n_2)+n_2(n_2,1)S(l_2,m_2,n_2-2)\}\ .\end{aligned}\tag{2.14}$$

4. Nuclear attraction integral

The nuclear attraction integral is defined by

$$\mathrm{NAI}=\int\chi(\boldsymbol{A},\alpha_1,l_1,m_1,n_1)\frac{1}{r_C}\chi(\boldsymbol{B},\alpha_2,l_2,m_2,n_2)d\boldsymbol{r}\ , \tag{2.15}$$

where r_c is the distance between $\boldsymbol{r}$ and $\boldsymbol{C}$; $r_c=|\boldsymbol{r}-\boldsymbol{C}|=|\boldsymbol{r}_c|$. The product of two wave function is again rewritten in terms of the coordinates relative to $\boldsymbol{P}$. We note that $\boldsymbol{r}_c=\boldsymbol{r}-\boldsymbol{C}=\boldsymbol{r}-\boldsymbol{P}+(\boldsymbol{P}-\boldsymbol{C})=\boldsymbol{r}_P+\boldsymbol{p}$ and use the formula (2.9), then $1/r_c$ can be rewritten as

$$\frac{1}{r_C}=\frac{1}{2\pi^2}\int\frac{d\boldsymbol{k}}{k^2}e^{i\boldsymbol{k}\cdot\boldsymbol{r}_C}=\frac{1}{2\pi^2}\int\frac{d\boldsymbol{k}}{k^2}e^{i\boldsymbol{k}\cdot\boldsymbol{p}}\,e^{i\boldsymbol{k}\cdot\boldsymbol{r}_P}\ .$$

Then we have

$$\begin{aligned}\mathrm{NAI}=&\frac{1}{2\pi^2}\exp(-\alpha_1\alpha_2\overline{AB}^2/\gamma)\sum_{i,j,k}f_i(l_1,l_2,\overline{PA}_x,\overline{PB}_x)\\ &\times\cdot f_j(m_1,m_2,\overline{PA}_y,\overline{PB}_y)\cdot f_k(n_1,n_2,\overline{PA}_z,\overline{PB}_z)\cdot\int\frac{d\boldsymbol{k}}{k^2}e^{i\boldsymbol{k}\cdot\boldsymbol{p}}\int dxe^{ik_x\cdot x}x^i\exp(-\gamma x^2)\\ &\times\int dye^{ik_y\cdot y}y^j\exp(-\gamma y^2)\int dze^{ik_z\cdot z}z^k\exp(-\gamma z^2)\ ,\end{aligned}\tag{2.16}$$

where $\gamma=\alpha_1+\alpha_2$. Integrations over x, y, and z can be carried out by formula (2.7). Thus, the integral part in the right-side of the above equation becomes, letting $\epsilon=1/4\gamma$,

$$I=\int\frac{d\boldsymbol{k}}{k^2}e^{i\boldsymbol{k}\cdot\boldsymbol{p}}\,i^i\left(\frac{\pi}{\gamma}\right)^{\frac{1}{2}}\left(\frac{1}{2\sqrt{\gamma}}\right)^i H_i\left(\frac{k_x}{2\sqrt{\gamma}}\right)\cdot i^j\left(\frac{\pi}{\gamma}\right)^{\frac{1}{2}}\left(\frac{1}{2\sqrt{\gamma}}\right)^j H_j\left(\frac{k_y}{2\sqrt{\gamma}}\right)$$
$$\times i^k\left(\frac{\pi}{\gamma}\right)^{\frac{1}{2}}\left(\frac{1}{2\sqrt{\gamma}}\right)^k H_k\left(\frac{k_z}{2\sqrt{\gamma}}\right)\exp(-\epsilon k^2)\,.$$

Using the formulae (2.8), (2.10) and (2.7), we have

$$I=\frac{4\pi^3}{\gamma}(-)^i i!\sum_{r=0}^{[i/2]}\frac{\epsilon^r}{r!}\sum_{u=0}^{[(i-2r)/2]}\frac{(-)^u p_x{}^{i-2r-2u}\epsilon^u}{u!(i-2r-2u)!}$$
$$\times(-)^j j!\sum_s\frac{\epsilon^s}{s!}\sum_v\frac{(-)^v p_y{}^{j-2s-2v}\epsilon^v}{v!(j-2s-2v)!}\cdot(-)^k k!\sum_t\frac{\epsilon^t}{t!}\sum_w\frac{(-)^w p_z{}^{k-2t-2w}\epsilon^w}{w!(k-2t-2w)!}$$
$$\times\int_0^1 dS\cdot S^{2\{i+j+k-2(r+s+t)-(u+v+w)\}}\exp\left(-\frac{p^2}{4\epsilon}S^2\right).$$

Putting this expression back into eq. (2.16), we obtain

$$\mathrm{NAI}=\frac{2\pi}{\gamma}\exp(-\alpha_1\alpha_2\overline{AB}^2/\gamma)\cdot\sum_{i,r,u}A_{i,r,u}(l_1,l_2,A_x,B_x,C_x,\gamma)$$
$$\times\sum_{j,s,v}A_{j,s,v}(m_1,m_2,A_y,B_y,C_y,\gamma)\sum_{k,t,w}A_{k,t,w}(n_1,n_2,A_z,B_z,C_z,\gamma)F_\nu\left(\frac{\overline{CP}^2}{4\epsilon}\right), \tag{2.17}$$

where $\nu=i+j+k-2(r+s+t)-(u+v+w)$, and

$$A_{i,r,u}(l_1,l_2,A_x,B_x,C_x\,\gamma)=(-)^i f_i(l_1,l_2,\overline{PA}_x,\overline{PB}_x)\cdot\frac{(-)^u i!\,\overline{CP}_x{}^{i-2r-2u}(1/4\gamma)^{r+u}}{r!u!(i-2r-2u)!}\,. \tag{2.18}$$

In eq. (2.17) the summations with respect to indices i, r and u extend form 0 to l_1+l_2, $[i/2]$ and $[(i-2r)/2]$, respectively. The ranges of (j, s, v) or (k, t, w) can be easily found in the same way.

5. *Electron repulsion integral*

The definition of the electron repulsion integral is

$$\mathrm{ERI}=\iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 x_{A1}^{l_1}y_{A1}^{m_1}z_{A1}^{n_1}\exp(-\alpha_1 r_{A1}^2)x_{B1}^{l_2}y_{B1}^{m_2}z_{B1}^{n_2}\exp(-\alpha_2 r_{B1}^2)$$
$$\times\left(\frac{1}{r_{12}}\right)x_{C2}^{l_3}y_{C2}^{m_3}z_{C2}^{n_3}\exp(-\alpha_3 r_{C2}^2)x_{D2}^{l_4}y_{D2}^{m_4}z_{D2}^{n_4}\exp(-\alpha_4 r_{D2}^2)\,. \tag{2.19}$$

Here r_{12} denotes the distance between the two electrons ($r_{12}=|\boldsymbol{r}_{12}|=|\boldsymbol{r}_2-\boldsymbol{r}_1|$), where $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the position vectors of each electrons. The manipulation of this integral closely parallels that of the nuclear attraction integral. From the characteristic property of Gaussian functions we can reduce the above integral to the following form.

$$\mathrm{ERI}=\exp\{-(\alpha_1\alpha_2\overline{AB}^2/\gamma_1)-(\alpha_3\alpha_4\overline{CD}^2/\gamma_2)\}$$
$$\times\sum_{i_1}f_{i_1}(l_1,l_2,\overline{PA}_x,\overline{PB}_x)\sum_{j_1}f_{j_1}(m_1,m_2,\overline{PA}_y,\overline{PB}_y)\sum_{k_1}f_{k_1}(n_1,n_2,\overline{PA}_z,\overline{PB}_z)$$
$$\times\sum_{i_2}f_{i_2}(l_3,l_4,\overline{QC}_x,\overline{QD}_x)\sum_{j_2}f_{j_2}(m_3,m_4,\overline{QC}_y,\overline{QD}_y)\sum_{k_2}f_{k_2}(n_3,n_4,\overline{QC}_z,\overline{QD}_z)$$
$$\times\iint d\boldsymbol{r}_{P1}d\boldsymbol{r}_{Q2}x_{P1}^{i_1}y_{P1}^{j_1}z_{P1}^{k_1}\exp(-\gamma_1 r_{P1}^2)x_{Q2}^{i_2}y_{Q2}^{j_2}z_{Q2}^{k_2}\exp(-\gamma_2 r_{Q2}^2)\,, \tag{2.20}$$

where $\gamma_1=\alpha_1+\alpha_2$ and $\gamma_2=\alpha_3+\alpha_4$. $\boldsymbol{Q}$ is defined as $\boldsymbol{Q}=(\alpha_3\boldsymbol{C}+\alpha_4\boldsymbol{D})/(\alpha_3+\alpha_4)$, and $\boldsymbol{r}_{P1}=\boldsymbol{r}_1-\boldsymbol{P}$ and $\boldsymbol{r}_{Q2}=\boldsymbol{r}_2-\boldsymbol{Q}$. Further we shall denote $\boldsymbol{Q}-\boldsymbol{P}$ as $\boldsymbol{p}$. Formula (2.9) can be expressed as

$$\frac{1}{r_{12}}=\frac{1}{2\pi^2}\int\frac{d\boldsymbol{k}}{k^2}\exp(i\boldsymbol{k}\cdot\boldsymbol{r}_{12})=\frac{1}{2\pi^2}\int\frac{d\boldsymbol{k}}{k^2}\exp\{i\boldsymbol{k}\cdot(\boldsymbol{p}-\boldsymbol{r}_{P1}+\boldsymbol{r}_{Q2})\}\ ,$$

where $\boldsymbol{r}_{12}=\boldsymbol{p}-\boldsymbol{r}_{P1}+\boldsymbol{r}_{Q2}$. Thus, the integral part in the right side of eq. (2.20) becomes after some manipulations,

$$\begin{aligned}
I'&=\iint d\boldsymbol{r}_{P1}d\boldsymbol{r}_{Q2}x_{P1}^{i_1}y_{P1}^{j_1}z_{P1}^{k_1}\exp(-\gamma_1 r_{P1}^2)\frac{1}{r_{12}}x_{Q2}^{i_2}y_{Q2}^{j_2}z_{Q2}^{k_2}\exp(-\gamma_2 r_{Q2}^2)\\
&=\pi\delta\left(\frac{1}{\gamma_1\gamma_2}\right)^{3/2}\int_0^1 dS\\
&\times\left(\frac{1}{2\gamma_1}\right)^{i_1}\left(\frac{1}{2\gamma_2}\right)^{i_2}i_1!i_2!\sum_{r_1=0}^{[i_1/2]}\sum_{r_2=0}^{[i_2/2]}\frac{(-)^{r_1+r_2}\gamma_1{}^{r_1}\gamma_2{}^{r_2}}{r_1!(i_1-2r_1)!r_2!(i_2-2r_2)!}\\
&\qquad\int dk_x\,k_x{}^{i_1+i_2-2(r_1+r_2)}\,e^{ik_xp_x}\exp\left(-\frac{\delta}{S^2}k_x\right)\\
&\times\left(\frac{1}{2\gamma_1}\right)^{j_1}\left(\frac{1}{2\gamma_2}\right)^{j_2}j_1!j_2!\sum_{s_1}\sum_{s_2}\frac{(-)^{s_1+s_2}\gamma_1{}^{s_1}\gamma_2{}^{s_2}}{s_1!(j_1-2s_1)!s_2!(j_2-2s_2)!}\\
&\qquad\int dk_y\,k_y{}^{j_1+j_2-2(s_1+s_2)}\,e^{ik_yp_y}\exp\left(-\frac{\delta}{S^2}k_y\right)\\
&\times\left(\frac{1}{2\gamma_1}\right)^{k_1}\left(\frac{1}{2\gamma_2}\right)^{k_2}k_1!k_2!\sum_{t_1}\sum_{t_2}\frac{(-)^{t_1+t_2}\gamma_1{}^{t_1}\gamma_2{}^{t_2}}{t_1!(k_1-2t_1)!k_2!(k_2-2t_2)!}\\
&\qquad\int dk_z\,k_z{}^{k_1+k_2-2(t_1+t_2)}\,e^{ik_zp_z}\exp\left(-\frac{\delta}{S^2}k_z\right)\ ,
\end{aligned}$$

where $\delta=(1/4\gamma_1)+(1/4\gamma_2)$. The integration over k_x in this expression can be carried out as follows by using the formula (2.7) again.

$$\begin{aligned}
&\int dk_x\,e^{ik_xp_x}\,k_x{}^{i_1+i_2-2(r_1+r_2)}\exp\left(-\frac{\delta}{S^2}k_x{}^2\right)\\
&=i^{i_1+i_2-2(r_1+r_2)}\left(\frac{\pi}{\delta}\right)^{\frac{1}{2}}S\left(\frac{S}{2\sqrt{\delta}}\right)^{i_1+i_2-2(r_1+r_2)}H_{i_1+i_2-2(r_1+r_2)}\left(\frac{P_x}{2\sqrt{\delta}}S\right)\exp\left(-\frac{P_x{}^2}{4\delta}S^2\right)\\
&=i^{i_1+i_2}(-)^{r_1+r_2}\left(\frac{\pi}{\delta}\right)^{\frac{1}{2}}S\left(\frac{1}{2\delta}\right)^{i_1+i_2-2(r_1+r_2)}\exp\left(\frac{P_x{}^2}{4\delta}S^2\right)\\
&\times\{i_1+i_2-2(r_1+r_2)\}!\sum_u\frac{(-)^u p_x{}^{i_1+i_2-2(r_1+r_2)-2u}\delta^u}{u!\{i_1+i_2-2(r_1+r_2)-2u\}!}S^{2\{i_1+i_2-2(r_1+r_2)-u\}}\ .
\end{aligned}\tag{2.21}$$

The integration over k_y and k_z can be carried out by exactly the same manner, and we obtain

$$\begin{aligned}
\mathrm{ERI}&=\frac{2\pi^2}{\gamma_1\gamma_2}\left(\frac{\pi}{\gamma_1+\gamma_2}\right)^{\frac{1}{2}}\exp\left\{-\frac{\alpha_1\alpha_2\overline{AB}^2}{\gamma_1}-\frac{\alpha_3\alpha_4\overline{CD}^2}{\gamma_2}\right\}\\
&\times\sum_{i_1,i_2,r_1,r_2,u}B_{i1,i2,r1,r2,u}(l_1,l_2,A_x,B_x,P_x,\gamma_1|l_3,l_4,C_x,D_x\ ,Q_x,\gamma_2)\\
&\times\sum_{j_1,j_2,s_1,s_2,v}B_{j1,j2,s1,s2,v}(m_1,m_2,A_y,B_y,P_y,\gamma_1|m_3,m_4,C_y,D_y,Q_y,\gamma_2)\\
&\times\sum_{k_1,k_2,t_1,t_2,w}B_{k1,k2,t1,t2,w}(n_1,n_2,A_z,B_z,P_z,\gamma_1|n_3,n_4,C_z,D_z,Q_z,\gamma_2)F_\nu(\overline{PQ}^2/4\delta)\ .
\end{aligned}$$

where $\nu=i_1+i_2+j_1+j_2+k_1+k_2-2(r_1+r_2+s_1+s_2+t_1+t_2)-u-v-w$, and

$$\begin{aligned}
&B_{i1,i2,r1,r2,u}(l_1,l_2,A_x,B_x,P_x,\gamma_1|l_3,l_4,C_x,D_x,Q_x,\gamma_2)\\
&=(-)^{i_2}f_{i1}(l_1,l_2,\overline{PA}_x,\overline{PB}_x)f_{i2}(l_3,l_4,\overline{QC}_x,\overline{QD}_x)\\
&\quad\times\frac{i_1!\ i_2!}{(4\gamma_1)^{i_1}(4\gamma_2)^{i_2}\delta^{i_1+i_2}}\cdot\frac{(4\gamma_1)^{r_1}(4\gamma_2)^{r_2}\delta^{r_1+r_2}}{r_1!r_2!(i_1-2r_1)!(i_2-2r_2)!}\\
&\quad\times[i_1+i_2-2(r_1+r_2)]!\,\frac{(-)^u p_x{}^{i_1+i_2-2(r_1+r_2)-2u}\delta^u}{u!\{i_1+i_2-2(r_1+r_2)-2u\}!}\ .
\end{aligned}\tag{2.22}$$

In eq. (2.21) the summations with respect to the indices i_1, i_2, r_1, r_2 and u extend from 0 to l_1+l_2, l_3+l_4, $[i_1/2]$, $[i_2/2]$ and $[(i_1+i_2)/2-r_1-r_2]$, respectively. The ranges of (j_1, j_2, s_1, s_2, v) or (k_1, k_2, t_1, t_2, w) may be found in the same way.

§ 3. Computer Program

Our next task is to code the above formulae for the computer. It is not very hard to code these formulae quite generally, but our coding is limited to the cases in which the sum of the "quantum numbers" of a GTO appearing in the integral does not exceeds 2. ($l+m+n \leqq 2$ in eq. (2.1)). This restriction makes it possible to get an efficient program.

In our program a subroutine for $f_j(l_1, l_2, a, b)$ is prepared in which the explicit formulae of f_j are coded for all possible values of l_1 and l_2 according to the definition (2.4). Once we have the subroutine of f_j, it is straightforward to code the programs for the overlap integral and the kinetic energy integral. The formulae for the nuclear attraction integral and the electron repulsion integral contain the auxiliary function F_ν given by eq. (2.11). The necessary formulae for computing $F_\nu(t)$ can be found in Shavitt's paper.[9]

The central task is to carry out the multiple sum appeared in the nuclear attraction integral or the electron repulsion integral. For nuclear attraction integral, the summation in question is

$$W=\sum_{i,r,u} A_{i,r,u}(l_1, l_2, A_x, B_x, C_x, \gamma) \sum_{j,s,v} A_{j,s,v}(m_1, m_2, A_y, B_y, C_y, \gamma) \\ \times \sum_{k,t,w} A_{k,t,w}(n_1, n_2, A_z, B_z, C_z, \gamma) F_\nu(\gamma p^2) ,$$

where $\nu=i+j+k-2(r+s+t)-u-v-w$. We rewrite this as

$$W=\sum_I G_I(l_1, l_2, A_x, B_x, C_x, \gamma) \sum_J G_J(m_1, m_2, A_y, B_y, C_y, \gamma) \\ \times \sum_K G_I(n_1, n_2, A_z, B_z, C_z, \gamma) F_{I+J+K}(\gamma p^2)=\sum_\nu \{ \sum_{I,J,K}^{(I+J+K=\nu)} G_I G_J G_K \} F_\nu , \tag{3.1}$$

where the notation $(I+J+K=\nu)$ means that the summation must be taken over the values of indices satisfying the condition $I+J+K=\nu$, and G_I is defined as

$$G_I(l_1, l_2, A_x, B_x, C_x, \gamma)=\sum_i \sum_r \sum_u^{(i-2r-u=I)} (-)^i f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \cdot \frac{(-)^u i! p_x{}^{i-2r-2u} \epsilon^{r+u}}{r! u! (i-2r-2u)!} , \tag{3.2}$$

where the summation must be taken over the values of indices satisfying the condition $i-2r-u=I$. The simplest way to calculate the values of G_I's is perhaps to write down the explicit formulae, *i.e.*

$$\begin{array}{ll} l_1+l_2=0: & G_0=1 , \\ l_1+l_2=1: & G_0=f_0 , \\ & G_1=-p . \\ l_1+l_2=2: & G_0=f_0+f_1/2\gamma , \\ & G_1=-f_1 p-f_1/2\gamma , \\ & G_2=p^2 . \\ l_1+l_2=3: & G_0=f_0+f_2/2\gamma , \\ & G_1=-f_1 p-f_2/2\gamma-3p/2\gamma , \\ & G_2=f_2 p^2+3p/2\gamma , \\ & G_3=-p^3 . \\ l_1+l_2=4: & G_0=f_0+f_2/2\gamma+3/4\gamma^2 , \\ & G_1=-f_1 p-f_2/2\gamma-3pf_3/\gamma-3/2\gamma^2 , \\ & G_2=f_2 p^2+3pf_3/2\gamma+3p^2/\gamma+3/4\gamma^2 , \\ & G_3=-f_3 p^3-3p^2/\gamma , \\ & G_4=p^4 . \end{array}$$

The method of carrying out the multiple sum in the electron repulsion integral is similar to that for the nuclear attraction integral, but a little more complicated. We rewrite this summation as

$$W'=\sum\sum\sum B_{i_1,i_2,r_1,r_2,u}\,B_{j_1,j_2,s_1,s_2,v}\,B_{k_1,k_2,t_1,t_2,w}\,F_\nu$$
$$=\sum_{I,J,K}C_IC_JC_KF_{I+J+K}=\sum_\nu\{\sum_{I,J,K}^{(I+J+K=\nu)}C_IC_JC_K\}F_\nu\;, \tag{3.3}$$

where

$$C_I=\sum_{i_1}^{(i_1+i_2-2(r_1+r_2)-u=I)}\sum_{i_2}\sum_{r_1}\sum_{r_2}\sum_{u}f_{i_1}\frac{i_1!}{(4\gamma_1)^{i_1}}\cdot\frac{(4\gamma_1)^{r_1}}{r_1!(i_1-2r_1)!}\cdot f_{i_2}\frac{(-)^{i_2}i_2!}{(4\gamma_2)^{i_2}}\cdot\frac{(4\gamma_2)^{r_2}}{r_2!(i_2-2r_2)!}$$
$$\times\frac{\{i_1+i_2-2(r_1+r_2)\}!(-)^u p_x{}^{i_1+i_2-2(r_1+r_2)-2u}}{u!\{i_1+i_2-2(r_1+r_2)-2u\}!\,\delta^{i_1+i_2-2(r_1+r_2)-u}}$$
$$=\sum\sum\sum_{L,M,u}^{(L+M-u=I)}H_L(l_1,l_2,\overline{PA}_x,\overline{PB}_x,\gamma_1)\cdot(-)^M H_M(l_3,l_4,\overline{QC}_x,\overline{QD}_x,\gamma_2)$$
$$\times\frac{(L+M)!(-)^u p_x{}^{(L+M)-2u}}{u!\{(L+M)-2u\}!\,\delta^{L+M-u}}\;. \tag{3.4}$$

and

$$H_L(l_1,l_2,a,b,\gamma)=\sum_i^{(i-2r=L)}\sum_r\frac{i!f_i(l_1,l_2,a,b,\gamma)}{r!(i-2r)!(4\gamma)^{i-2r}}\;. \tag{3.5}$$

This quantity is computed, in our program, by using the following explicit expressions.

$l_1=0,\ l_2=0$: $H_0=1$.
$l_1=1,\ l_2=0$: $H_0=a$,
$H_1=1/4\gamma$.
$l_1=1,\ l_2=1$: $H_0=ab+1/2\gamma$,
$H_1=(a+b)/4\gamma$,
$H_2=(1/4\gamma)^2$.
$l_1=2,\ l_2=0$: $H_0=a^2+1/2\gamma$,
$H_1=a/2\gamma$,
$H_2=(1/4\gamma)^2$.
$l_1=2,\ l_2=1$: $H_0=a^2b+(2a+b)/2\gamma$,
$H_1=(2ab+a^2)/4\gamma+6(1/4\gamma)^2$,
$H_2=(2a+b)(1/4\gamma)^2$,
$H_3=(1/4\gamma)^3$.
$l_1=2,\ l_2=2$: $H_0=(ab)^2+(a^2+4ab+b^2)/2\gamma+12(1/4\gamma)^2$,
$H_1=ab(a+b)/2\gamma+12(a+b)(1/4\gamma)^2$,
$H_2=(a^2+4ab+b^2)(1/4\gamma)^2+12(1/4\gamma)^3$,
$H_3=2(a+b)(1/4\gamma)^3$,
$H_4=(1/4\gamma)^4$.

To calculate C_I's we first prepare the storage locations for C_I's, and calculate the value of the summands one by one for all possible values of L, M, and $u\,(0\leq L\leq l_1+l_2,\ 0\leq M\leq l_3+l_4,\ u\leq[(L+M)/2])$. The value of a summand found is accumulated into the storage location C_{L+M-u}.

So far we have described the calculation of individual integrals. We shall now go over to the construction of the whole program. We first notice that the wave function concerned is not a single GTO but a combined GTO (CGTO), *i.e.* a linear combination of several GTO's, all of which have common "quantum numbers". A molecular integral over these wave functions can be calculated as a linear combination of the molecular integrals over the individual GTO's.

The same factors f_j can be used in the cases of the overlap integral, the kinetic energy integral and the nuclear attraction integral. For this reason, in our program "One electron integral", the overlap integral, the kinetic energy integral and the nuclear attraction integrals over the individual GTO's are simultaneously calculated and accumulated into the respective storage location to calculate these integrals over CGTO's. While in the program "Two electron integral", $H_L(l_1, l_2, a, b, \gamma)$ are calculated directly as explained before without using f_j.

A CGTO is specified by l, m, n (quantum numbers), n_k (number of GTO's included in the CGTO), $\alpha_1, \alpha_2, \cdots, \alpha_{nk}$ (exponent parameters of GTO's), $c_1, c_2, \cdots, c_{nk}$ (coefficients of the linear combination), and of course the position of the center of CGTO. All necessary CGTO's and all necessary coordinates are numbered and stored. Then we can select a wave function by two integers numbering the CGTO and the position of the center.

§ 4. Results and Discussions

In Table I presented are the computed values of the two-center one-electron integrals over the 1s Slater-type function $(1/\sqrt{\pi})\exp(-r)$ by using the approximate GTO expansions described in details in the preceding paper.[5] The column "4, 6, 8, 10, A" has the following meaning: Numbers in the row following a numeral, say 8, are the approximate values of integrals computed by using the 8-term GTO expansion of 1s STO, the parameters of which are specified in Table 2 of the preceding paper.[5] The row headed by A gives the accurate values of integrals for the purpose of comparison. One observes that the 4-term expansion naturally gives rather poor approximate values while the 10-term expansion seems to yield values good enough for most purposes.

Table I. One electron integrals: 1s−1s.

R_{ab} (a.u.)	4.0	8.0	12.0	16.0
$(1s_a\|1s_b)$				
4	0.189074	0·009786	0.000103	0.3×10^{-6}
6	0.189215	0.009747	0.000207	0.000002
8	0.189267	0.010217	0.000354	0.000008
10	0.189261	0.010169	0.000396	0.000014
A	0.189262	0.010176	0.000375	0.000012
$\left(1s_a\|-\frac{1}{2}\Delta\|1s_b\right)$				
4	−0.002579	−0.002310	−0.000065	-0.4×10^{-6}
6	−0.003138	−0.002142	−0.000097	−0.000002
8	−0.003048	−0.002049	−0.000111	−0.000003
10	−0.003048	−0.002078	−0.000105	−0.000004
A	−0.003053	−0.002069	−0.000107	−0.000004
$(1s_a\|1/r_a\|1s_b)$				
4	0.091748	0.002208	0.000017	0.4×10^{-7}
6	0.091518	0.002851	0.000041	0.3×10^{-6}
8	0.091584	0.003042	0.000072	0.000001
10	0.091581	0.003012	0.000087	0.000002
A	0.091578	0.003019	0.000080	0.000002

Table II contains the result of the similar pilot calculations for the two-center one-electron integrals over the 2$p\pi$ STO $(1/\sqrt{\pi})x\exp(-r)$, Table III over the 3$p\pi$ STO $(2/15\pi)^{\frac{1}{2}}xr\exp(-r)$ and Table IV over the 3dyz STO $(\sqrt{2/\pi}/81)yz\exp(-r)$. The Cartesian coordinate system used here has the z-axis along the line connecting the two centers a and b. The format of these three tables is almost identical with that of Table I and may need no further explanation.

Table II. One electron integrals: 2$p\pi$−2$p\pi$.

R_{ab} (a.u.)	4.0	8.0	12.0	16.0
$(2p\pi_a\|2p\pi_b)$				
4	0.286986	0.023067	0.001041	0.000026
6	0.286949	0.023079	0.001065	0.000028
8	0.286945	0.023073	0.001146	0.000039
A	0.286945	0.023057	0.001142	0.000044
$\left(2p\pi_a\|-\frac{1}{2}\Delta\|2p\pi_b\right)$				
4	0.045850	−0.001318	−0.000207	−0.000009
6	0.045798	−0.001328	−0.000205	−0.000009
8	0.045784	−0.001358	−0.000197	−0.000011
A	0.045789	−0.001353	−0.000196	−0.000010
$(2p\pi_a\|1/r_a\|2p\pi_b)$				
4	0.094649	0.005099	0.000168	0.000003
6	0.094634	0.005098	0.000172	0.000004
8	0.094629	0.005089	0.000188	0.000005
A	0.094631	0.005088	0.000187	0.000005

Table I, II, III and IV present part of the results of our preliminary molecular integral calculation with the purpose of checking of the Gaussian-expansion method in the case of the one-electron molecular integrals. For the two-electron molecular integrals we shall show the results for the integrals for which the reference values are readily available in the papers of Karplus and Shavitt.[1,10] In Table V three families of ap-

Table III. One electron integrals: $3p\pi - 3p\pi$.

R_{ab} (a.u.)	4.0	8.0	12.0	16.0
$(3p\pi_a \vert 3p\pi_b)$				
4	0.493102	0.081299	0.007042	0.000378
6	0.493104	0.081346	0.007178	0.000445
8	0.493104	0.081346	0.007181	0.000457
A	0.493104	0.081346	0.007175	0.000440
$\left(3p\pi_a \vert -\frac{1}{2}\Delta \vert 3p\pi_b)\right)$				
4	0.071980	0.000576	−0.000701	−0.000075
6	0.071978	0.000567	−0.000694	−0.000074
8	0.071978	0.000569	−0.000695	−0.000073
A	0.071978	0.000568	−0.000694	−0.000074
$(3p\pi_a \vert 1/r_a \vert 3p\pi_b)$				
4	0.136026	0.016364	0.001080	0.000045
6	0.136024	0.016369	0.001100	0.000055
8	0.136024	0.016370	0.001100	0.000057
A	0.136024	0.016369	0.001100	0.000054

Table IV. One electron integrals: $3d_{yz} - 3d_{yz}$.

R_{ab} (a.u.)	4.0	8.0	12.0	16.0
$(3d_{yza} \vert 3d_{yzb})$				
4	−0.282754	−0.171105	−0.019459	−0.000854
6	−0.282409	−0.169100	−0.020951	−0.001364
8	−0.282409	−0.169130	−0.020800	−0.001480
A	−0.282410	−0.169147	−0.020801	−0.001487
$\left(3d_{yza} \vert -\frac{1}{2}\Delta \vert 3d_{yzb}\right)$				
4	−0.177519	−0.023193	0.001007	0.000207
6	−0.177495	−0.022534	0.000702	0.000214
8	−0.177497	−0.022600	0.000744	0.000198
A	−0.177487	−0.022618	0.000748	0.000198
$(3d_{yza} \vert 1/r_a \vert 3d_{yzb})$				
4	−0.106282	−0.036084	−0.003000	−0.000101
6	−0.106232	−0.035709	−0.003244	−0.000164
8	−0.106232	−0.035725	−0.003218	−0.000181
A	−0.106231	−0.035730	−0.003218	−0.000182

Table V. Pi-electron repulsion integrals for the benzene molecule (a.u.).

Integral	Accurate values	4-term	6-term	8-term	Errors × 10^6		
					4	6	8
11 12	0.121755	0.121785	0.121760	0.121755	+30	+ 5	0
11 13	0.013891	0.013899	0.013902	0.013888	+ 8	+11	− 3
11 14	0.005796	0.005807	0.005808	0.005802	+11	+12	+ 6
11 23	0.068193	0.068204	0.068194	0.068194	+11	+ 1	+ 1
11 24	0.010001	0.010005	0.010008	0.010002	+ 4	+ 7	+ 1
11 25	0.005416	0.005421	0.005424	0.005420	+ 5	+ 8	+ 4
11 26	0.016131	0.016129	0.016135	0.016129	− 2	+ 4	− 2
11 34	0.051664	0.051672	0.051665	0.051664	+ 8	+ 1	0
11 35	0.008846	0.008847	0.008850	0.008845	+ 1	+ 4	− 1
12 12	0.034091	0.034105	0.034092	0.034090	+14	+ 1	− 1
13 13	0.000633	0.000633	0.000634	0.000633	0	+ 1	0
14 14	0.000124	0.000124	0.000124	0.000124	0	0	0
12 13	0.004112	0.004113	0.004113	0.004111	+ 1	+ 1	− 1
12 14	0.001535	0.001538	0.001538	0.001536	+ 3	+ 3	+ 1
12 15	0.003174	0.003176	0.003176	0.003173	+ 2	+ 2	− 1
12 16	0.023927	0.023936	0.023928	0.023927	+ 9	+ 1	0
13 14	0.000252	0.000252	0.000253	0.000252	0	+ 1	0
13 15	0.000481	0.000481	0.000481	0.000480	0	0	− 1
12 34	0.015663	0.015668	0.015663	0.015663	+ 5	0	0
12 35	0.002517	0.002517	0.002518	0.002516	0	+ 1	− 1
12 36	0.001465	0.001466	0.001467	0.001466	+ 1	+ 2	+ 1
12 45	0.013740	0.013744	0.013740	0.013740	+ 4	0	0
13 24	0.000578	0.000578	0.000578	0.000578	0	0	0
13 25	0.000255	0.000255	0.000255	0.000255	0	0	0
13 46	0.000437	0.000437	0.000437	0.000437	0	0	0
14 25	0.000122	0.000123	0.000123	0.000122	+ 1	+ 1	0

Table VI. Two-electron integrals for a methane molecule:

Atom	x	y	z	Orbital	Symbol	Exponent
C	0.0	0.0	0.0	$1s(C)$	c	5.70
H_1	0.0	0.0	−2.0	$2p(C)$	x, y, z	1.625
H_2	1.88561808	0.0	0.666666667	$1s(H)$	h	1.000
H_3	−0.94280904	1.63299316	0.666666667			
H_4	−0.94280904	−1.63299316	0.666666667			

Integral	4-term	6-term	8-term	10-term	Comparison value
$(h_1 h_2; h_3 h_4)$	0.0306538	0.0306826	0.0306814	0.0306827	0.0306825[a]
$(h_1 h_2; h_1 h_3)$	0.0356602	0.0356951	0.0356930	0.0356947	0.0356937[b]
$(h_1 h_1; h_2 h_3)$	0.0956640	0.0957073	0.0957053	0.0957075	0.0957056[a]
$(c\ h_1; h_3 h_4)$	0.0125312	0.0126835	0.0127382	0.0127439	0.0127407[a]
$(c\ h_1; c\ h_2)$	0.0110484	0.0111416	0.0111836	0.0111903	0.0111949[c]
$(c\ c\ ; h_1 h_2)$	0.1664934	0.1665295	0.1665273	0.1665312	0.1665363[c]
$(c\ h_1; x\ h_2)$	0.0194777	0.0197179	0.0198054		0.0198090[a]
$(c\ h_1; z\ h_2)$	0.0058439	0.0058706	0.0058844		0.0058852[a]

a. Pitzer. b. Shavitt and Karplus ($20\times20\times24$). c. Shavitt and Karplus ($24\times24\times28$).

proximate values of the π-electron repulsion integrals for the benzene molecule are shown. These values should be compared with Table I in the Short Note by Karplus and Shavitt.[10] The three families of values result from the 4-term, 6-term and 8-term GTO expansions of the $2p\pi$ Slater-type orbital with the orbital exponent 1.59. The C-C distance is 2.6320755 a.u. These parameter values are the same as those used by Karplus and Shavitt.[10] The performances of the 6- and 8-term expansions are gratifying and even the 4-term expansion gives approximate values quite satisfying when compared to the values given by Sklar's or Mulliken's approximation which are listed in Table I of Karplus and Shavitt.[10]

In Table VI an attempt is made to present several values of many-center integrals for a methane molecule which are to be compared with the values shown in Table I in a recent paper by Shavitt and Karplus.[1]

In the Gaussian-expansion method, we must carry out a fourfold summation to evaluate a two-electron integral. This means that we need to compute N^4 basic summands, N being the number of Gaussian-type functions in the expansion. (For simplicity we assume that all four expansions have the same N.) This is unavoidable as long as the present finite-set method is adopted. However, the Gaussian-transform method of Shavitt and Karplus also contains a three-fold summation: We must perform a three-dimensional numerical integration. Thus, the numbers of summations to be compared are N^4 in the present paper and $u\times v\times w$ in the paper of Shavitt and Karplus.[1] The Gaussian-transform method seems to have had a serious trouble getting a convergent result for $(ch_1;\ h_3h_4)$. It does not seem to settle down in the final value even if $u\times v\times w$ soars up to $28\times28\times28\simeq2.2\times10^4$. Convergence studies in the present Gaussian-expansion method are not very exhaustive but there are indications that the asymmetric integral such as $(ch_1; h_3h_4)$ is less troublesome to be evaluated in the present method. Since the individual summand of the present method is simpler than the corresponding integrand in the Gaussian-transform method, the overall performance of the expansion method could be much more economical than the sophisticated Gaussian-transform method if we are not pursueing a very accurate evaluation of the molecular integral as such.

So far the discussion has been rather STO-oriented but of course we need not confine ourselves to this realm. For instance, our basis functions that are combinations of several GTO's may bear close resemblances to Hartree-Fock orbitals of certain atom. In the present integral program it does not matter what the combined Gaussian-type orbitals actually represent.

The computer we have been using is the OKITAC 5090H which has 8K core and needs 250μs for a floating point multiplication and 330μs for a floating point division. The program is coded in ALGOL. It is not easy to make a definite statement about the computation time but we feel it safe to state that the present Gaussian-expansion method is at least as economical and useful as the Gaussian-transform method of Shavitt and Karplus[1] for *ab initio* calculation of the electronic structures of poly-atomic molecular systems.

Acknowledgments

The authors wish to express their sincere thanks to the staff at the Kyushu University computation center who provided them every convenience during the use of the OKITAC 7090H computer at the center. This work is partially supported by the Grant-in-Aid from the Ministry of Education.

The authors also wish to present this paper as a tribute to Professor Masao Kotani in commemoration of his 60th birthday. It is a real pleasure to acknowledge professor Kotani's continuing guidance given to them through long years.

References

1) I. Shavitt and M. Karplus: J. chem. Phys. **43** (1965) 398.
2) J. M. Foster and S. F. Boys: Rev. mod. Phys. **32** (1960) 303, 305.
3) S. F. Boys: Proc. Roy. Soc. **A200** (1950) 542.
4) S. Huzinaga: J. chem. Phys. **42** (1965) 1293.
5) K. O-ohata, H. Taketa and S. Huzinaga: J. Phys. Soc. Japan **21** (1966) 2306.
6) J. P. Wright: Quarterly Progress Report Solid State and Molecular Theory Group MIT, October 1963, p. 35.
7) M. Krauss: J. Res. Nat. Bur. Stand. (U.S.A) **68B** (1964) 35.
8) H. A. Bethe and E. E. Salpeter: *Handbuch der Physik* **35** (Springer, 1957) 266.
9) I. Shavitt: *Methods in Computational Physics* (Academic Press Inc., New York., 1963) vol. 2, p. 1.
10) M. Karplus and I. Shavitt: J. chem. Phys. **38** (1963) 1256.