Turk J Chem
25 (2001) , 405 – 418.

Calculation of Multi-Center Integrals for the Region of Moderate and Weak Overlap

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Received 12.10.1998

In this study a general formula was established for multi-center integrals over Gaussian basis sets using the two-center expansion of nuclear attraction and electron repulsion potentials. The terms of the formula are the analytical functions of interatomic distances.

Three kinds of integrals contained in these formulae can be evaluated analytically. In the presented method, unlike many other popular methods, the numerical integrations procedure is unnecessary since it does not contain the incomplete gamma function. A computer program was written and tested for various orbitals. The calculations show that the series converge very rapidly.

Introduction

The evaluation of multi-center integrals, which is still a important problems in the quantum mechanical treatment of many-atomic systems has been continuously considered over the last 50 years.

Currently used `ab initio methods,` even over Gaussian basis sets, which are prefered to Slater basis sets since the evaluation of the integrals is relatively simple, are expensive and applicable only to small molecules. An appreciable difficulty appearing in such methods is the fact that the expression for the multi-center integrals quite often used in these methods are greatly complicated and consume enormous amounts of computer time[1].

In view of the rapid progress of computer capability, it is very desirable to have a reliable assessment of the usefulness of a Gaussian-type orbital (GTO) as a basis function for large-scale molecular calculation. The advent of high-speed computers has encouraged researchers to launch a major programming effort on quantum-mechanical calculations of polyatomic systems, considerable exploratory work on the use of Gaussian functions for molecular calculations has been undertaken.

Under these circumstances, it is still important to obtain simpler and compact expressions for the evaluation of multi-center two-electron integrals permitting one to more easily generate the associated

computer-based solutions. In recent years, many-centered two-electron integrals have been calculated by many authors[2−5].

In the present work, a general formula is derived for the evaluation of multi-center nuclear attraction and electron repulsion integrals over Gaussian basis functions for the case of moderate overlap. Unlike many other popular methods, the presented method does not contain the incomplete gamma function, which needs many numerical integration procedures.

Definitions and Formulae

The contracted Cartesian Gaussian function ϕ_A on a center A is defined as

$$\phi_A(\vec{r}) = \sum_{k=1}^{M} D_k \chi_k(A, \alpha_k, \ell, m, n) \tag{1}$$

where the D_k are known as contraction coefficients and M is known as the degree of contraction of ϕ_A and

$$\chi_k(A, \alpha_k, \ell, m, n) = N_\alpha (x - X_A)^\ell (y - Y_A)^m (z - Z_A)^n e^{-\alpha(\vec{r} - \vec{R_A})^2} \tag{2}$$

is the normalized primitive Cartesian Gaussian function with exponent α_k. The normalization factor in eq. (2) is given by

$$N_\alpha = \left(\frac{2^{2(\ell+m+n)} \alpha^{\ell+m+n}}{(2\ell-1)!!(2m-1)!!(2n-1)!!} \left(\sqrt{\frac{2\alpha}{\pi}}\right)^3\right)^{1/2} \tag{3a}$$

A multi-center integral over a contracted Gaussian function given by equation (1) can be calculated as a linear combination of the multi-center integrals over the primitive Gaussian functions given by equation (2).

All the coordinate systems on various centers are considered parallel and right handed in all the following formulas.

The overlap and kinetic energy integral formulae are similar to the formulae given by Taketa et al.[6]. But for easy evaluation algorithms, normalization factor and overlap integrals are written as follows:

$$N_\alpha = [I(2(\ell + m + n + 1), 2\alpha) IA(2m, 2\ell) IB(2(m + \ell) + 1, 2n)]^{-1/2} \tag{3b}$$

$$\langle \chi(A, \alpha_1, \ell_1, m_1, n_1) \, | \chi(B, \alpha_2, \ell_2, m_2, n_2) \rangle = N_{\alpha_1} N_{\alpha_2} e^{-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} {R_{AB}}^2}$$

$$\sum_{k_1=0}^{\ell_1} \sum_{k_2=0}^{\ell_2} \sum_{k_3=0}^{m_1} \sum_{k_4=0}^{m_2} \sum_{k_5=0}^{n_1} \sum_{k_6=0}^{n_2} X_{DA}^{l_1-k_1} X_{DB}^{l_2-k_2} Y_{DA}^{m_1-k_3} Y_{DB}^{m_2-k_4} Z_{DA}^{n_1-k_5} Z_{DB}^{n_2-k_6}$$

$$C_{k_1}^{\ell_1} C_{k_2}^{\ell_2} C_{k_3}^{m_1} C_{k_4}^{m_2} C_{k_5}^{n_1} C_{k_6}^{n_2} I(k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + 2, \alpha_1 + \alpha_2)$$

$$IA(k_3 + k_4, k_1 + k_2) IB(k_1 + k_2 + k_3 + k_4 + 1, k_5 + k_6) \tag{4}$$

$$C_i^j = \frac{i!}{j!(i-j)!}$$
$$\overrightarrow{R}_{AB} = \overrightarrow{R}_A - \overrightarrow{R}_B$$

$$I(N,\alpha) = \int_0^\infty r^N \exp(-\alpha r^2) dr \tag{4a}$$

$$IB(M,N) = \int_0^\pi (\sin\theta)^M (\cos\theta)^N d\theta \tag{4b}$$

$$IA(M,N) = \int_0^{2\pi} (\sin\varphi)^M (\cos\varphi)^N d\varphi \tag{4c}$$

where $X_{DA} = \frac{\alpha_1 X_A + \alpha_2 X_B}{\alpha_1+\alpha_2} - X_A$, $X_{DB} = \frac{\alpha_1 X_A + \alpha_2 X_B}{\alpha_1+\alpha_2} - X_B$ and Y_{DA}, Y_{DB}, Z_{DA}, Z_{DB} are similarly defined for the y- and z-coordinates.

Two-center Nuclear Attraction Integral

The two-center nuclear attraction integral is defined as

$$NC2 = \langle \chi(C,\alpha_1,\ell_1,m_1,n_1) \left| \frac{1}{\overrightarrow{r_A}} \right| \chi(C,\alpha_2,\ell_2,m_2,n_2) \rangle \tag{5}$$

Here $\left|\frac{1}{\overrightarrow{r_A}}\right|$ can be evaluated by using the two-center expansion[7] as follows:

$$\begin{aligned} \frac{1}{|\overrightarrow{r_A}|} &= \frac{1}{R} \sum_{s=0}^{\infty} (-1)^s \left(\frac{r}{R}\right)^s [P_s(\cos\theta)\ P_s(\cos\theta_R) \\ &+ 2 \sum_{t=-s}^{s} \frac{(s-t)!}{(s+t)!} P_s^t(\cos\theta) P_s^t(\cos\theta_R)\ \cos t(\varphi - \varphi_R)] \end{aligned} \tag{6}$$

where $\overrightarrow{r_A}$ is the position vector of the electron from the nuclear center A; R is the distance from A to another nuclear center C; (r, θ, φ) and (R, φ_R, θ_R) are the spherical polar coordinates of electron and A centered about C, respectively. It is clear that R, θ_R and φ_R can be written in terms of the coordinates of C and A as follows:

$$R = \sqrt{(X_A - X_C)^2 + (Y_A - Y_C)^2 + (Z_A - Z_C)^2} \tag{7}$$

$$\theta_R = \arccos \frac{Z_C - Z_A}{R} \tag{8}$$

$$\varphi_R = \arctan \frac{Z_C - Z_A}{X_C - X_A} \tag{9}$$

In eq. (6), $P_\ell^m(\cos\theta)$ are the well known associated Legendre functions.

It is easy to obtain the integral values over the variables of electron of eq. (5) by introducing eq. (6) into eq. (5) and referring to the spherical polar coordinates with the nucleus C as the origin:

$$NC2 = N_{\alpha_1} N_{\alpha_2} \sum_{s=0}^{\infty} (-1)^s \frac{I_s(J, \alpha_1 + \alpha_2)}{R^{s+1}} I_s(L, \theta_R, \varphi_R) \tag{10}$$

where

$$\begin{aligned} I_s(L, \theta_R, \varphi_R) &= IA_s(m_1 + m_2, \ell_1 + \ell_2) IB_s(\ell_1 + \ell_2 + m_1 + m_2 + 1, n_1 + n_2) P_s(\cos\theta_R) \\ &+ 2 \sum_{t=1}^{s} \frac{(s-t)!}{(s+t)!} IP_{s,t}(\ell_1 + \ell_2 + m_1 + m_2 + 1, n_1 + n_2) P_s^t(\cos\theta_R) \\ &[IC_t(n_1 + n_2, \ell_1 + \ell_2) \cos t\varphi_R + IS_t(m_1 + m_2, \ell_1 + \ell_2) \sin t\varphi_R] \end{aligned} \tag{11}$$

L stands for a set of $(\ell_1, m_1, n_1, \ell_2, m_2, n_2)$ numbers and

$$J = \ell_1 + \ell_2 + m_1 + m_2 + n_1 + n_2 + 2$$

$$I_\ell(J, \alpha) = \int_0^\infty r^{J+\ell} e^{-\alpha r^2} dr$$

$$IP_\ell(M, N) = \int_0^\pi \sin^M\theta \cos^N\theta P_\ell(\cos\theta) d\theta$$

$$IP_{\ell,m}(M, N) = \int_0^\pi \sin^M\theta \cos^N\theta P_\ell^m(\cos\theta) d\theta$$

$$IS_m(M, N) = \int_0^{2\pi} \sin^M\varphi \cos^N\varphi \sin m\varphi d\varphi$$

$$IC_m(M, N) = \int_0^{2\pi} \sin^M\varphi \cos^N\varphi \cos m\varphi d\varphi$$

The analytical solution of these integrals is possible (see appendix).

Three-center Nuclear Attraction Integral

The three-center nuclear attraction integral is defined as

$$NC3 = \langle \chi(C, \alpha_1, \ell_1, m_1, n_1) \left| \frac{1}{\vec{r_A}} \right| \chi(B, \alpha_2, \ell_2, m_2, n_2) \rangle \tag{12}$$

We obtained the resultant formula by using the expressions of χ's and $\left|\frac{1}{\vec{r_A}}\right|$ given by eqs. (2) and (6), respectively.

$$\begin{aligned} NC3 = N_{\alpha_1} N_{\alpha_2} e^{-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2} R_{CB}^2} \sum_{k_1k_2k_3k_4k_5k_6} C_{\ell_1}^{k_1} C_{m_1}^{k_2} C_{n_1}^{k_3} C_{\ell_2}^{k_4} C_{m_2}^{k_5} C_{n_2}^{k_6} X_{DA}^{\ell_1-k_1} Y_{DA}^{m_1-k_2} Z_{DA}^{n_1-k_3} \\ X_{DB}^{\ell_2-k_4} Y_{DB}^{m_2-k_5} Z_{DB}^{n_2-k_6} \sum_{s=0}^{\infty} (-1)^s \tfrac{1}{R_{DA}^{s+1}} I_s(k, \alpha_1+\alpha_2) I_s(LK, \theta_{DA}, \varphi_{DA}) \end{aligned} \tag{13}$$

where

$$k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$$

$$\begin{aligned} I_s(LK, \theta_{DA}, \varphi_{DA}) = IA_s(k_2+k_5, k_1+k_4) IB_s(k_1+k_4+k_2+k_5+1, k_3+k_6) P_s(\cos\theta_{DA}) \\ +2 \sum_{t=1}^{s} \tfrac{(s-t)!}{(s+t)!} IP_{s,t}(k_1+k_2+k_4+k_5+1, k_3+k_6) P_s^t(\cos\theta_{DA}) \\ [IC_t(k_3+k_6, k_1+k_4)\cos t\varphi_{DA} + IS_t(k_2+k_5, k_1+k_4)\sin t\varphi_{DA}] \end{aligned} \tag{14}$$

LK stands for a set of $(k_1, k_2, k_3, k_4, k_5, k_6)$ numbers. Where

$$X_D = \frac{\alpha_1 X_C + \alpha_2 X_B}{\alpha_1 + \alpha_2}$$

and Y_D and Z_D are similarly defined,

$$\begin{aligned} \vec{R_{CB}} &= \vec{R_C} - \vec{R_B} \\ \vec{R_{DA}} &= \vec{R_D} - \vec{R_A} \\ \vec{R_{AB}} &= \vec{R_B} - \vec{R_A} \end{aligned}$$

$$\theta_{DA} = \arccos \frac{Z_D - Z_A}{R_{DA}}$$

$$\varphi_{DA} = \arctan \frac{Y_D - Y_A}{X_D - X_A}$$

The summations in eq. (14) are over the following ranges:

$$k_1 = 0 - \ell_1; k_2 = 0 - m_1; k_3 = 0 - n_1; k_4 = 0 - \ell_2; k_5 = 0 - m_2; k_6 = 0 - n_2$$

Two-center Two-electron Repulsion Integral

A two-center two-electrons repulsion integral can be defined as

$$ER2 = \langle \chi(A,\alpha_1,\ell_1,m_1,n_1)\chi(A,\alpha_2,\ell_2,m_2,n_2) \left|\tfrac{1}{\vec{r}_{12}}\right| \chi(B,\alpha_3,\ell_3,m_3,n_3)\chi(B,\alpha_4,\ell_4,m_4,n_4)\rangle \tag{15}$$

For the evaluation of $ER2$, we used the two-center expansion of $\left|\frac{1}{\vec{r}_{12}}\right|$ as given in[8]

$$\begin{aligned}\tfrac{1}{r_{12}} = \sum_{s_1=0}^{\infty}\sum_{s_2=0}^{\infty}\tfrac{r_1^{s_1}r_2^{s_2}}{R_{AB}^{s1+s_2+1}}\,[F(s_1,s_2,0)\;P_{s_1}^0(\cos\theta_1)P_{s_2}^0(\cos\theta_2)\\ +2\sum_{t=1}^{S_{\min}}(-1)^t\sqrt{\tfrac{(s_1-t)!(s_2-t)!}{(s_1+t)!(s_2+t)!}}F(s_1,s_2,t)P_{s_1}^t(\cos\theta_1)P_{s_2}^t(\cos\theta_2)\;\cos t(\varphi_1-\varphi_2)]\end{aligned} \tag{16}$$

where

$$F(s_1,s_2,t) = (-1)^{s_2}\frac{(s_1+s_2)!}{((s_1+t)!(s_1-t)!(s_2+t)!(s_2-t)!)^{1/2}} \tag{17}$$

$(r_1\theta_1\varphi_1)$ and $(r_2\theta_2\varphi_2)$ the spherical polar coordinates of 1 and 2 electrons centered about nuclei A and B, respectively. Introducing eq. (16) into eq. (15) and referring to spherical polar coordinates with the nuclei A and B as the origin for each electrons integrating over the coordinates of the electrons simultaneously, we have

$$ER2 = N_1N_2N_3N_4\sum_{s_1=0}^{\infty}\sum_{s_2=0}^{\infty}\frac{I_{s_1}(J_1,\alpha_1+\alpha_2)I_{s_2}(J_2,\alpha_3+\alpha_4)}{R_{AB}^{s_1+s_2+1}}I_{s_1s_2}(L_1,L_2) \tag{18}$$

where

$$\begin{aligned}I_{s_1s_2}(L_1,L_2) = IA_{s_1}(m_1+m_2,\ell_1+\ell_2)\\ IA_{s_2}(m_3+m_4,\ell_3+\ell_4)IP_{s_1}(\ell_1+\ell_2+m_1+m_2+1,n_1+n_2)\\ IP_{s_2}(\ell_3+\ell_4+m_3+m_4+1,n_3+n_4)P_s^t(\cos\theta_R)F(s_1,s_2,0)\\ +2\sum_{t=1}^{S_{\min}}(-1)^t\sqrt{\tfrac{(s_1-t)!(s_2-t)!}{(s_1+t)!(s_2+t)!}}(F(s_1,s_2,t)IP_{s_1t}(\ell_1+\ell_2+m_1+m_2+1,n_1+n_2)\\ IP_{s_2t}(\ell_3+\ell_4+m_3+m_4+1,n_3+n_4)\,[IC_t(m_1+m_2,\ell_1+\ell_2)\\ IC_t(m_3+m_4,\ell_3+\ell_4)+IS_t(m_1+m_2,\ell_1+\ell_2)\;IS_t(m_3+m_4,\ell_3+\ell_4)]\end{aligned} \tag{19}$$

$$J_1 = \ell_1+\ell_2+m_1+m_2+n_1+n_2+2; J_2 = \ell_3+\ell_4+m_3+m_4+n_3+n_4+2.$$

Three-center Two-electron Repulsion Integral

Due to the definition of the three-center two-electron repulsion integral

$$\begin{array}{c} ER3 = \langle \chi(A,\alpha_1,\ell_1,m_1,n_1)\chi(A,\alpha_2,\ell_2,m_2,n_2) \left|\frac{1}{\vec{r}_{12}}\right| \\ \chi(B,\alpha_3,\ell_3,m_3,n_3)\chi(C,\alpha_4,\ell_4,m_4,n_4)\rangle \end{array} \tag{20}$$

and using the similar procedure given in subsection 3.3, we obtain

$$\begin{array}{c} ER3 = N_1N_2N_3N_4 e^{-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}R_{AB}^2} e^{-\frac{\alpha_3\alpha_4}{\alpha_3+\alpha_4}R_{CB}^2} \sum_{s_1=0}^{\infty}\sum_{s_2=0}^{\infty}\sum_{k_1k_2k_3k_4k_5k_6} \\ C_{\ell_3}^{k_1}C_{\ell_4}^{k_2}C_{m_3}^{k_3}C_{m_4}^{k_4}C_{n_3}^{k_5}C_{n_4}^{k_6} X_{DB}^{\ell_3-k_1}X_{DC}^{\ell_4-k_2}Y_{DB}^{m_3-k_3}Y_{DC}^{m_4-k_4}Z_{DB}^{n_3-k_5}Z_{DC}^{n_4-k_6} \\ \frac{I_{s_1}(J_1,\alpha_1+\alpha_2)I_{s_2}(K_2,\alpha_3+\alpha_4)}{R_{DA}^{s_1+s_2+1}} I_{s_1s_2}(L_1,LK_1) \end{array} \tag{21}$$

where

$$\begin{array}{c} I_{s_1s_2}(L_1,LK_1) = IA(m_1+m_2,\ell_1+\ell_2)IA(k_3+k_4,k_1+k_2) \\ IP_{s_1}(\ell_1+\ell_2+m_1+m_2+1,n_1+n_2)IP_{s_2}(k_1+k_2+k_3+k_4+1,k_5+k_6)(F(s_1,s_2,0) \\ \\ +2\sum_{t=1}^{S_{\min}}(-1)^t\sqrt{\frac{(s_1-t)!(s_2-t)!}{(s_1+t)!(s_2+t)!}}(F(s_1,s_2,t)IP_{s_1t}(\ell_1+\ell_2+m_1+m_2+1,n_1+n_2) \\ IP_{s_2k}(k_1+k_2+k_3+k_4+1,k_5+k_6)\,[IC_m(m_1+m_2,\ell_1+\ell_2)\;IC_m(k_3+k_4,k_1+k_2) \\ IS_m(m_1+m_2,\ell_1+\ell_2)\;IS_m(k_3+k_4,k_1+k_2)] \end{array} \tag{22}$$

$$K_2 = k_1+k_2+k_3+k_4+k_5+k_6+2$$

$$X_D = \frac{\alpha_3X_B+\alpha_4X_C}{\alpha_3+\alpha_4}$$

Y_D and Z_D are also similarly defined,

$$\begin{array}{c} \vec{R_{DB}} = \vec{R_D} - \vec{R_B} \\ \vec{R_{DC}} = \vec{R_D} - \vec{R_C} \end{array}$$

$$\begin{array}{c} \vec{R_{DA}} = \vec{R_D} - \vec{R_A} \\ \vec{R_{CB}} = \vec{R_C} - \vec{R_B} \end{array}$$

The summations in eq. (16b) are over the following ranges:

$$k_1 = 0-\ell_3; k_2 = 0-\ell_4; k_3 = 0-m_3; k_4 = 0-m_4; k_5 = 0-n_3; k_6 = 0-n_4$$

Four-center Two-electron Repulsion Integral

The definition of the four-center two-electrons repulsion integral is as follows:

$$ER4 = \langle \chi(A,\alpha_1,\ell_1,m_1,n_1)\chi(B,\alpha_2,\ell_2,m_2,n_2) \left|\frac{1}{\vec{r_{12}}}\right| \chi(C,\alpha_3,\ell_3,m_3,n_3)\chi(D,\alpha_4,\ell_4,m_4,n_4)\rangle \tag{23}$$

Using a procedure similar to that given in subsection 2.3, we obtain

$$ER4 = N_1N_2N_3N_4 e^{(-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}R_{AB}^2+\frac{\alpha_3\alpha_4}{\alpha_3+\alpha_4}R_{CD}^2)} \sum_{s_1=0}^{\infty}\sum_{s_2=0}^{\infty}\sum_{k_1k_2k_3\ldots k_{12}}$$

$$C_{m_1}^{k_1}C_{\ell_1}^{k_2}C_{n_1}^{k_3}C_{m_2}^{k_4}C_{\ell_2}^{k_5}C_{n_2}^{k_6}C_{m_3}^{k_7}C_{\ell_3}^{k_8}C_{n_3}^{k_9}C_{m_4}^{k_{10}}C_{\ell_4}^{k_{11}}C_{n_4}^{k_{12}}$$

$$X_{FA}^{m_1-k_1}Y_{FA}^{\ell_1-k_2}Z_{FA}^{n_1-k_3}X_{FB}^{m_2-k_4}Y_{FB}^{\ell_2-k_5}Z_{FB}^{n_2-k_6}X_{PC}^{m_3-k_7}Y_{PC}^{\ell_3-k_8}Z_{PC}^{n_3-k_9}X_{PD}^{m_4-k_{10}}Y_{PD}^{\ell_4-k_{11}}Z_{PD}^{n_4-k_{12}}$$

$$\frac{I_{s_1}(K_1,\alpha_1+\alpha_2)I_{s_2}(K_2,\alpha_3+\alpha_4)}{R_{FP}^{s_1+s_2+1}} I_{s_1s_2}(LK_1,LK_2) \tag{24}$$

where

$$I_{s_1s_2}(LK_1,LK_2) = IA(k_1+k_4,k_2+k_5)IA(k_7+k_{10},k_8+k_{11})$$

$$IP_{s_1}(k_1+k_2+k_4+k_5+1,k_3+k_6)IP_{s_2}(k_7+k_8+k_{10}+k_{11}+1,k_9+k_{12})(F(s_1,s_2,0)$$

$$+2\sum_{t=1}^{S_{\min}}(-1)^t\sqrt{\frac{(s_1-t)!(s_2-t)!}{(s_1+t)!(s_2+t)!}}(F(s_1,s_2,t)IP_{s_1t}(k_1+k_2+k_4+k_5+1,k_3+k_6)$$

$$IP_{s_2t}(k_7+k_8+k_{10}+k_{11}+1,k_9+k_{12})\,[IC_t(k_1+k_4,k_2+k_5)\;IC_t(k_7+k_{10},k_8+k_{11})$$

$$IS_t(k_1+k_4,k_2+k_5)\;IS_t(k_7+k_{10},k_8+k_{11})] \tag{25}$$

$$K_1 = k_1+k_2+k_3+k_4+k_5+k_6+2, K_2 = k_7+k_8+k_9+k_{10}+k_{11}+k_{12}+2$$

The summations in eq. (24) are over the following ranges:

$$k_1 = 0 \div m_1; k_2 = 0 \div \ell_2; k_3 = 0 \div n_1; k_4 = 0 \div m_2; k_5 = 0 \div \ell_2; k_6 = 0 \div n_2;$$
$$k_7 = 0 \div m_3; k_8 = 0 \div \ell_3; k_9 = 0 \div n_3; k_{10} = 0 \div m_4; k_{11} = 0 \div \ell_4; k_{12} = 0 \div n_4.$$

$$X_F = \frac{\alpha_1X_A+\alpha_2X_B}{\alpha_1+\alpha_2}$$

Y_F and Z_F are similarly defined,

$$X_P = \frac{\alpha_3X_C+\alpha_4X_D}{\alpha_3+\alpha_4}$$

Y_P and Z_P are similarly defined,

$$\vec{R_{AB}} = \vec{R_A} - \vec{R_B}$$
$$\vec{R_{CB}} = \vec{R_C} - \vec{R_B}$$
$$\vec{R_{FP}} = \vec{R_F} - \vec{R_P}$$

Results and Discussion

Analytical evaluations of the integrals $I_s(J,\alpha)$, $IA(M,N)$, $IB(M,N)$ are described in the appendix. The latter two integrals are independent of exponent α_k and therefore they can be coded for all possible values of M,N and reach the computer main memory in the form of an array with two indices for any contracted functions combination. For instance, the overlap integral over contracted Gaussian functions $\phi_A(\overrightarrow{r})$ and $\phi_B(\overrightarrow{r})$ centered at points A and B, respectively, can be coded on the basis of the formula:

$$\langle\phi_A(\overrightarrow{r}) \mid \phi_B(\overrightarrow{r})\rangle = \left\langle \sum_{p=1}^{M_1} d_p\chi_p(A,\alpha_p,\ell_1,m_1,n_1) \mid \sum_{q=1}^{M_2} d_q\chi_q(B,\alpha_q,\ell_2,m_2,n_2) \right\rangle$$

$$= (IA(2m_1,2\ell_1)IA(2m_2,2\ell_2)IB(2(m_1+\ell_1)+1,2n_1)IB(2(m_2+\ell_2)+1,2n_2))^{-1/2}$$

$$\sum_{k_1=0}^{\ell_1}\sum_{k_2=0}^{\ell_2}\sum_{k_3=0}^{m_1}\sum_{k_4=0}^{m_2}\sum_{k_5=0}^{n_1}\sum_{k_6=0}^{n_2} C_{k_1}^{\ell_1}C_{k_2}^{\ell_2}C_{k_3}^{m_1}C_{k_4}^{m_2}C_{k_5}^{n_1}C_{k_6}^{n_2} IA(k_3+k_4,k_1+k_2)$$

$$IB(k_1+k_2+k_3+k_4+1,k_5+k_6)\sum_{q=1}^{M_q}\sum_{p=1}^{M_p}[I(2(\ell_1+m_1+n_1+1)\alpha_q) \tag{26}$$

$$I(2(\ell_2+m_2+n_2+1)\alpha_p)\,]^{-1/2}\, I((k_1+k_2+k_3+k_4+k_5+k_6+2),\alpha_q+\alpha_p)$$

$$X_{DA}^{\ell_1-k_1}X_{DB}^{\ell_2-k_2}Y_{DA}^{m_1-k_3}Y_{DB}^{m_2-k_4}Z_{DA}^{n_1-k_5}Z_{DB}^{n_2-k_6}\exp(-\tfrac{\alpha_p\alpha_q}{\alpha_q+\alpha_p}R_{AB}^2)d_pd_q$$

All multi-center integrals can be computed in a similar way by using the values of $IA(M,N)$, $IB(M,N)$ over and over again when they have been calculated once.

For the $I_s(J,\alpha_p+\alpha_q)$ integrals, we can also use tree indices array form depending on the evaluable computer memory capacity and speed of computations. Then each primitive Gaussian function must have definite numeration in the data input and any integral $I_s(J,\alpha_p+\alpha_q)$ may have indices $(J+s,n_p,n_q)$, where n_q and n_p are the data input numeration of primitive Gaussian function χ_q and χ_p, respectively.

To evaluate the effect of the concerned number of the terms in the series in electron-electron repulsion and nuclear attraction integrals and contraction coefficients on calculation sensitivity and calculation time of the computer, test calculations are made for the systems containing four-centered orbitals. In these calculations, we used the values of d_K and α_k given by Taketa[6]. The overlapping of the orbitals centered on A(0,0,0), B(R,0,0), C(0,R,0) and D(0,0,R) depends on R. The calculated results for the various orbitals for the different M and S values show that the convergence of the series contained in the integrals is fast in the region where the overlapping is moderate or weak. As an example, the results of 1*s* type (1s Slater-type function ($\frac{1}{\pi}\exp(-r)$) by using the approximate GTO expansions[6]) orbitals for N=2, 9 and M=4, 8 are given in Table 1. Analytical values of two-center integrals are also given in Tables 1 and 2 for comparison. As seen from the table, there was a difference about 10^{-5} in the calculated values for N=2 and N=9 in R=2 (corresponding to an overlapping equal to 0.5864529) state but there was no difference for R=4 (corresponding to an overlapping equal to 0.189261). The latter one is also in good agreement with the analytical value. An important aspect of this situation is that the effect of the M values on the sensitivities of the integral values is small (the differences for M=4 and for M=8 are not greater than 10^{-7}). In addition,

the results of $3p$ and $3d$ types by using the approximate GTO expansion orbitals for N=2, 9 and M=4, 8 are given in Tables 3 and 4. A similar tendency is also obtained for all the concerned orbitals. But the series converges at the different values of R depending on the main atomic orbital radius, as expected.

Table 1. Many-center nuclear attraction integrals for 1s type orbitals (All the values are in atomic units)

R	N	NC2		NC3	
		4G	8G	4G	8G*
	2	-.50000100	-.50000300	-.26001350	-.26001980
2	9	-.49999530	-.49999310	-.26001280	-.26001830
	Anal.[10]	-.47252660		-	
	2	-.2500005	-.2500001	-.041933360	-.04195849
4	9	-.2500005	-.2500001	-.041933360	-.04195849
	Anal.	-.2495870		-	
	2	-.1250003	-.1250001	-.0008894574	-.00113242
8	9	-.1250003	-.1250001	-.0008894574	-.00113242
	Anal.	-.1249999		-	
	2	-.08333351	-.08333337	-.000007655	-.000026234
12	9	-.08333351	-.08333337	-.000007655	-.000026234
	Anal.	-.08333333		-	
	2	-.06250013	-.06250004	-.000000019	-.00000042
16	9	-.06250013	-.06250004	-.000000019	-.00000042
	Anal.	-.06250000		-	

* STO-4G and -8G are a minimal basis having one STO, approximated by four and eight Gaussian functions.

Table 2. Many-center two-electron integrals for 1s type orbitals

R	N	ER2		ER3		ER4*	
		4G	8G	4G	8G	4G	8G
	2	.5000020	.4999989	.2600139	.2600198	.1221766	.1221239
2	9	.4999983	.4999945	.2600128	.2600183	.1221680	.1221138
	Anal.	.4259743		-		-	
	2	.2500010	.2499994	.04193343	.04195834	.00305804	.00310594
4	9	.2500010	.2499994	.04193343	.04195833	.00305804	.00310594
	Anal.	.2475539		-		-	
	2	.12500050	.12499970	.00088946	.00113242	.00000027	.00000091
8	9	.12500050	.12499970	.00088946	.00113242	.00000027	.00000091
	Anal.	.12499800		-		-	
	2	.08333366	.08333308	.00000766	.00002623	.00000000	.00000000
12	9	.08333366	.08333308	.00000766	.00002623	.00000000	.00000000
	Anal.	.08333333		-		-	
	2	.06250025	.06249986	.00000002	.00000042	.00000000	.00000000
16	9	.06250025	.06349986	.00000002	.00000042	.00000000	.00000000
	Anal.	.06250000		-		-	

Table 3. Many-center two-electron integrals for 3p type orbitals

R	N	ER2		ER3		ER4	
		4G	8G	4G	8G	4G	8G
16	2	.058802190	.058802270	.00000438527	.00000513633	.000000000005	.000000000019
	7	.058743730	.058744210	.00000437687	.00000512139	.000000000004	.000000000014
	9	.059032600	.059037270	.00000437203	.00000512057	.000000000004	.000000000014
24	2	.04050455	.040504680	.00000000168	.00000000685	.00000000000	.00000000000
	7	.04045714	.040457250	.00000000168	.00000000684	.00000000000	.00000000000
	9	.04045749	.040457610	.00000000168	.00000000684	.00000000000	.00000000000
28	2	.034973550	.034973620	.00000000016	.0000000002	.00000000000	.00000000000
	7	.034949580	.034950980	.00000000016	.0000000002	.00000000000	.00000000000
	9	.034949520	.034949650	.00000000016	.0000000002	.00000000000	.00000000000

Table 4. Many-center two-electron integrals for 3d type orbitals

R	N	ER2		ER3		ER4	
		4G	8G	4G	8G	4G	8G
16	2	.050601230	.053672150	.00000091585	.00000192612	.00000000	.00000000
	7	.051248000	.054319120	.00000091309	.00000192023	.00000000	.00000000
	9	.051555770	.054658180	.00000091303	.00000192023	.00000000	.00000000
24	2	.036226260	.038407280	.000000000031	.000000002126	.00000000	.00000000
	7	.036210510	.038389760	.000000000031	.000000002125	.00000000	.00000000
	9	.036211890	.038391250	.000000000031	.000000002125	.00000000	.00000000
28	2	.031678620	.033574240	.00000000000	.000000000064	.00000000	.00000000
	9	.031664300	.033559090	.00000000000	.000000000064	.00000000	.00000000
	9	.031664410	.033559150	.00000000000	.000000000064	.00000000	.00000000

In the same way, convergence analysis of the series allows us to find the starting point of the convergence for different orbitals.

As a result, a general formula is derived for the evaluation of the multi-center nuclear attraction and electron repulsion integrals in the form of the series giving sufficiently accurate values, each containing only two or three terms.

Besides the sufficient accuracy, the presented formulae can provide a fast algorithm for the calculation of non-valence intra- and inter-molecular interaction energies in polyatomic systems, in which the computation time is not unreasonable in relation to the information obtained. Undoubtedly, this method of approach is very attractive for the calculations of the overlap, nuclear attraction and electron repulsion integrals of the 2-4 centered system containing similar atoms.

References

1. Paper Symposium on Computational Methods in Quantum Chemistry, Solid-State Theory and Molecular Biology in Honor of Enrico Clementi, **Int. J. Quantum Chem., 42**, 523-1632(1992).
2. E. F. Valeev, F Schaefer, **J. Chem. Phys., 113 (10)**, 3390 (2000).
3. V. Magnasco, A. Rapallo, **Int. J. Quantum Chem., 79 (2)**, 91 (2000).
4. V. Magnasco, M. Casanova, A. Rapallo, **Chem. Phys. Letters, 289 (1-2)**, 81 (1998).

5. J. F. Rico, R. Lopez, I. Ema, G. Ramirez, **Comp. Phys. Com., 105 (2-3)**, 216 (1997).
6. H. Taketa, S. Huzinaga, K. O-ohata, **J. Phys. Soc. Japan, 21**, 11 (1966).
7. V. I. Smirnov, **Kurs Vis. Mat., Moscow, Nauka, 3, 2** (1969) (Russian).
8. A. T. Amos, Gripsin R.J., **Theoretical Chemistry: Advances and Perspectives, 2**, 1 (1976).
9. I. J. Gradsteyn and I. M. Rijik, **Integral, series, addition and derivation tables**, (1952) (Russian).
10. P. Gombas, **Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik**, Basel, p.266 (1950).

Appendix

1- According to reference [9], the integral $I_e(j,\alpha)$ is given by

$$I_S(j,\alpha)=\frac{(j+l-1)!!}{2(2\alpha)^{\frac{j+S}{2}}}\sqrt{\frac{\pi}{\alpha}} \text{ for } l+j=2n \tag{A1}$$

and

$$_S(j,\alpha)=\frac{(\frac{j+l-1}{2})!}{2\alpha^{\frac{j+l+1}{2}}} \text{ for } l+j=2n+1 \tag{A2}$$

2- $IA(M,N)$ integral equals zero, unless both M and N are even, so

$$IA(2m,2n)=\frac{(2m-1)!!(2n-1)!!}{(2m+2n)(2m+2n-2)\dots(2m+2)}\frac{2\pi}{2^m m!} \tag{A3}$$

3- $IB(M,N)$ integral equals zero, unless N is even and given by

$$IB(2m,2n)=\frac{(2n-1)!!(2m-1)!!}{(2m+2n)(2m+2n-2)\dots(2m+2)}\frac{\pi}{2^m m!} \text{ for } M=2m \tag{A4}$$

and

$$IB(2m,2n)=\frac{(2n-1)!!}{(2m+2n+1)(2m+2n-1)\dots(2m+3)}\frac{2^{2m+1}(m!)^2}{(2m+1)!} \text{ for } M=2m+1 \tag{A5}$$

4-

$$\begin{aligned} IP_{l,m}(M,N)&=\tfrac{(2l-1)!!}{(l-m)!}(IB(M+m,N+l-m)+\\ &+\sum_{j=1}\prod_{k=1}^{j}\tfrac{(\alpha+k-1)(\beta+k+1)}{(\gamma+k-1)^k}IB(M+m,l-m-2j)) \end{aligned} \tag{A6}$$

In this equation the summation is restricted with the non-negative values of $n-m-2j$. Where

$$\alpha=\frac{m-l}{2};\beta=\frac{m-l+1}{2};\gamma=\frac{1}{2}-l \tag{A7}$$

5-

$$IP_l(M,N)=IP_{l,0}(M,N) \text{ for } m=0 \tag{A8}$$

6-

$$IS_m(M,N) = 2^{m-1}IA(M+1,N+m-1) - C^1_{m-2}2^{m-3}IA(M+1,N+m-3)$$
$$+C^2_{m-3}2^{m-5}IA(M+1,N+m-5)\cdots(-1)^d C^d_{m-(d+1)}2^{m-(2d+1)}IA(M+1,N+m-(2d+1) \tag{A9}$$

The series can be expanded to $d > (m+(d+1))$ at which the binomial coefficients are equal to zero.

7-

$$IC_m(M,N) = 2^{m-1}IA(M,N+m) - \tfrac{m}{1}2^{m-3}IA(M,N+m-2)$$
$$+\tfrac{m}{2}C^1_{m-3}2^{m-5}IA(M,N+m-4)\cdots(-1)^d\tfrac{m}{d}C^{d-1}_{m-(d+1)}2^{m-(2d+1)}IA(M,N+m-2d) \tag{A10}$$