Computation of Overlap, Kinetic and Nuclear Attraction Integrals by a Novel Method

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Abstract

A new way of computing overlap, kinetic and nuclear attraction integrals over Slater functions by means of optimized Gaussian expansion is proposed. This article is concerned with the construction of the general algorithm for evaluating the three integrals. These integral formulae presented in the form of a series whose terms are the analytical function of inter-atomic distances. In the present method, unlike many other popular methods, the numerical integration procedure is unnecessary since it does not contain the incomplete gamma function. The present scheme has been programmed in standard Fortran-77 and tested for various orbitals. The result of the calculation are compared with the literature data.

1. Introduction

Due to rapid advances in computer technology, there has been an increasingly widespread use of numerical electronic structure calculations. On the other hand, while there exist a number of highly accurate, computationally efficient and user friendly computer packages, many molecules are so large that only a semiempirical treatment is feasible. 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. The ease of evaluating molecular integrals over Gaussian functions in contrast with Slater-type orbitals was originally reported by Boys [1] . With the advent of high-speed computers, considerable exploration work on the use of Gaussian functions

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for molecular calculations has been undertaken. Huzinaga [2] explored the same matter in greater detail and with much larger GTO basis set functions. In the same work, Huzinaga developed GTO expansions for approximate Hartree-Fock solutions of first-row atoms.

The method of least squares for Gaussian expansions has been employed by a variety of workers [3-6]. Boys and Shavitt [3] used a least-squares method whereby the exponential coefficients and the expansion coefficients were adjusted in blocks, but not simultaneously in a full matrix method, to arrive at a minimum error. Reeaves and Flecther [4] used linear least squares for determination of the expansion coefficients and adjusted the exponential variables by finite differencing method. Expansion of Clementi [7] STO SCF AOs for some first-row atoms with GTOs have been obtained by the method of least squares.

Under these circumstances, it is still important to obtain simpler and compact expression for evaluation of multi-center one-electron integrals permitting one to more easily to generate the associate computer-based solutions [8-11]. In the present work, a computer algorithm is proposed for computation of overlap, kinetic and nuclear attraction integrals over Gaussian basis set functions for the region of moderate overlap. Unlike many other popular methods, our method does not ascertain the incomplete gamma function which needs many numerical integration procedures.

2. Mathematical Analysis

In this section we give the analytical solutions for the molecular integrals needed in the SCF computation. In Cartesian coordinates a GTO centered at $\mathbf{A}$ is written as

$$\chi(\mathbf{A}, \alpha, l, m, n) = (x - A_x)^l (y - A_y)^m (z - A_z)^n \exp(-\alpha \mathbf{r_A^2})$$
$$= x_A^l y_A^m z_A^n \exp(-\alpha \mathbf{r_A^2}). \tag{2.1}$$

Here, x_A, y_A and z_A are the components of position vector $\mathbf{r_A}$ relative to $\mathbf{A}$, i.e., $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$; and l, m and n are quantum numbers. The normalization factor for the Gaussian function (2.1) is

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

where $(2l-1)!! = 1.3.5\ldots(2l-1)$.

In the following formulae all coordinate systems are parallel and right-handed. The GTO function has the following characteristic property: Suppose that there are two 1s GTOs, $\exp(-\alpha_1 r_A^2)$ and $\exp(-\alpha_2 r_B^2)$, centered at $\mathbf{A}$ and $\mathbf{B}$, respectively (Figure 1). Thus, we have

$$S = \chi(\mathbf{A}, \alpha_1, l_1, m_1, n_1)\chi(\mathbf{B}, \alpha_2, l_2, m_2, n_2)$$
$$= N_{\alpha_1} N_{\alpha_2} x_A^{l_1} x_B^{l_2} y_A^{m_1} y_B^{m_2} z_A^{n_1} z_B^{n_2} \exp(-\alpha_1 r_A^2) \exp(-\alpha_2 r_B^2). \tag{2.3}$$
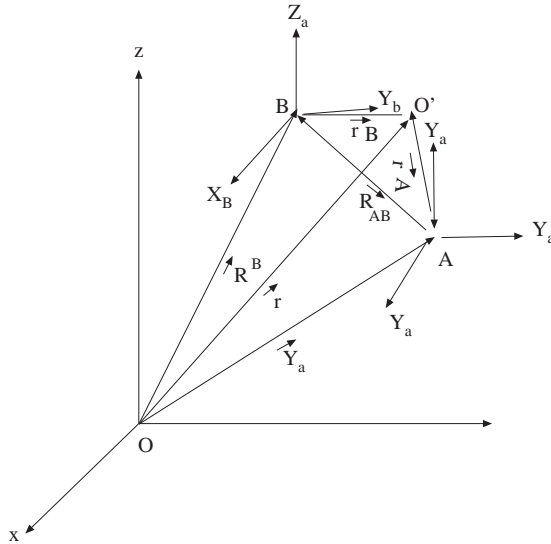
Figure 1. Coordinate system.

The following formula is the center of the new Gaussian function, the product of the Gaussians on **A** and **B**:

$$D_i = \frac{\alpha_1 \mathbf{A}_i + \alpha_2 \mathbf{B}_i}{\alpha_1 + \alpha_2}, (i = x, y, z).$$

Thus we have

$$N_{\alpha_1} N_{\alpha_2} x_A^{l_1} x_B^{l_2} y_A^{m_1} y_B^{m_2} z_A^{n_1} z_B^{n_2} \exp(-\alpha_D r_D^2) \exp(-\frac{\alpha_1 \alpha_2}{\alpha_D} r_{AB}^2), \qquad (2.4)$$

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

The Overlap Integral

The use of the formula (2.4) immediately gives the following expression for the overlap integral

$$O = \left\langle \chi(\mathbf{A}, \alpha_1, l_1, m_1, n_1) \chi(\mathbf{B}, \alpha_2, l_2, m_2, n_2) \right\rangle$$

$$= \int \int \int N_{\alpha_1} x_A^{l_1} y_A^{m_1} z_A^{n_1} exp(-\alpha_1 r_A^2) N_{\alpha_2} x_B^{l_2} y_B^{m_2} z_B^{n_2} exp(-\alpha_2 r_B^2) dx dy dz$$

$$= N_{\alpha_1} N_{\alpha_2} exp(-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} r_{AB}^2) O^x O^y O^z, \qquad (2.5)$$

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where

$$O^x = \int\limits_{-\infty}^{\infty} x_A^{l_1} x_B^{l_2} \exp(-\alpha_D x_D^2) dx. \qquad (2.6)$$

In defining the integrals over Gaussian functions (2.6), the following auxiliary functions are used:

$$(a+b)^n = \sum_{j=0}^{n} C_n^j a^{n-j} b^j, \quad n = 1, 2, 3 \ldots; \qquad (2.7)$$

$$C_n^j = \left(\begin{array}{c} n \\ j \end{array} \right) = \frac{n!}{j!(n-j)!}, (j = 0, 1, 2, \ldots \le n = 0, 1, 2, \ldots); \qquad (2.8)$$

$$\int\limits_{-\infty}^{\infty} x^n \exp(-px^2 + 2qx) dx = n! \exp(q^2/p) \sqrt{\frac{\pi}{p}} (\frac{q}{p})^n \sum_{k=0}^{\text{int}(n/2)} \frac{1}{(n-2k)!k!} (\frac{p}{4q^2})^k \qquad (2.9)$$

using the formulae (2.7), (2.8) and (2.9), we have

$$O^x = \sum_{k_1=0}^{l_1} \sum_{k_2=0}^{l_2} \left(\begin{array}{c} l_1 \\ k_1 \end{array} \right) \left(\begin{array}{c} l_2 \\ k_2 \end{array} \right) (X_D - X_A)^{l_1-k_1} (X_D - X_B)^{l_2-k_2} SART, \qquad (2.10)$$

where

$$SART = \begin{cases} \frac{(k_1+k_2-1)!!}{(2\alpha_D)^{k_1+k_2)/2}} \sqrt{\frac{\pi}{\alpha_D}} & \text{if } k_1 + k_2 \text{ is odd} \\ 0 & \text{if } k_1 + k_2 \text{ is even} \end{cases} \qquad (2.11)$$

The Kinetic Energy Integral
The kinetic energy integral is defined by

$$\begin{aligned} KI &= \left\langle \chi(\mathbf{A}, \alpha_1, l_1, m_1, n_1) \left| -\frac{1}{2}\nabla^2 \right| \chi(\mathbf{B}, \alpha_2, l_2, m_2, n_2) \right\rangle \\ &= N_{\alpha_1} N_{\alpha_2} [\alpha_2 \{2(l_2 + m_2 + n_2) + 3\} \langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2, m_2, n_2) \rangle \\ &- 2\alpha_2^2 \{\langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2+2, m_2, n_2) \rangle \\ &+ \langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2, m_2+2, n_2) \rangle \\ &+ \langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2, m_2, n_2+2) \rangle \} \\ &- \frac{1}{2} l_2(l_2-1) \langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2-2, m_2, n_2) \rangle \end{aligned}$$

$$- \frac{1}{2} m_2(m_2 - 1) \langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2, m_2 - 2, n_2) \rangle$$

$$- \frac{1}{2} n_2(n_2 - 1) \langle (\mathbf{A}, \alpha_1, l_1, m_1, n_1)(\mathbf{B}, \alpha_2, l_2, m_2, n_2 - 2) \rangle]. \tag{2.12}$$

The Nuclear Attraction Integrals

The two-center nuclear attraction integral is defined by

$$NI2 = \langle \chi(\mathbf{C}, \alpha_1, l_1, m_1, n_1) \left| \frac{1}{r_A} \right| \chi(\mathbf{C}, \alpha_2, l_2, m_2, n_2) \rangle, \tag{2.13}$$

where

$$\left| \frac{1}{r_A} \right| = \frac{4\pi}{R} \sum_{l=0}^{\infty} \sum_{m=1}^{l} (-1)^l (\frac{r_D}{R})^l \frac{Y_l^m(\theta_D, \varphi_D) Y_l^m(\theta_R, \varphi_R)}{2l+1} = \frac{1}{R} \sum_{l=0}^{\infty} (-1)^l (\frac{r_D}{R})^l$$

$$\left[P_l(\cos\theta_D) P_l(\cos\theta_R) + 2 \sum_{m=1}^{l} \frac{(l-m)!}{(l+m)!} P_l^m(\cos\theta_D) P_l^m(\cos\theta_R) \cos m(\varphi_D - \varphi_R) \right]. \tag{2.14}$$

Putting this expression back into Eqn. (2.13), we obtain

$$NI2 = N_{\alpha_1} N_{\alpha_2} \sum_{l=0}^{\infty} (-1)^l \frac{1}{R^{l+1}} I(r) I(\theta_R, \varphi_R, \theta_D, \varphi_D), \tag{2.15}$$

where

$$I(r) = \int_0^{\infty} r_D^{l_1+l_2+m_1+m_2+n_1+n_2+2+l} \exp(-(\alpha_1 + \alpha_2)r^2) dr_D$$

$$I(\theta_R, \varphi_R, \theta_D, \varphi_D) = I(\theta_D, \varphi_D, P_l) + 2 \sum_{m=1}^{l} \frac{(l-m)!}{(l+m)!} I(\theta_D, \varphi_D, P_l^m),$$

where

$$I(\theta_D, \varphi_D, P_l) = \left[\int_0^{2\pi} (\sin\varphi_D)^{m_1+m_2} (\cos\varphi_D)^{l_1+l_2} d\varphi_D \right.$$

$$\left. \cdot \int_0^{\pi} (\sin\theta_D)^{l_1+l_2+m_1+m_2+1} (\cos\theta_D)^{n_1+n_2} P_l(\cos\theta_D) d\theta_D \right] P_l(\cos\theta_R)$$

$$I(\theta_D, \varphi_D, P_l^m) = \left[\int\limits_0^{2\pi} (\sin\varphi_D)^{m_1+m_2}(\cos\varphi_D)^{l_1+l_2}\cos(m\varphi_D)d\varphi_D \right.$$

$$\left. \int\limits_0^{\pi} (\sin\theta_D)^{l_1+l_2+m_1+m_2+1}(\cos\theta_D)^{n_1+n_2}P_l^m(\cos\theta_D)d\theta_D \right] \cos(m\varphi_R)P_l^m(\cos\theta_R)$$

$$+ \left[\int\limits_0^{2\pi} (\sin\varphi_D)^{m_1+m_2}(\cos\varphi_D)^{l_1+l_2}\sin(m\varphi_D)d\varphi_D \right.$$

$$\left. \cdot \int\limits_0^{\pi} (\sin\theta_D)^{l_1+l_2+m_1+m_2+1}(\cos\theta_D)^{n_1+n_2}P_l^m(\cos\theta_D)d\theta_D \sin(m\varphi_R)P_l^m(\cos\theta_R) \right],$$

and where

$$P_l^m(x) = (1-x^2)^{m/2}2^{-l}\sum_{k=0}^{(l-m)/2}(-1)^k\frac{(2l-2k)!}{k!(l-m-2k)!(l-k)!}$$

$$R_{AC} = \sqrt{(X_C - X_A)^2 + (Y_C - Y_A)^2 + (Z_C - Z_A)^2}$$

$$\theta_R = arctan[(Z_C - Z_A)/R_{AC}]$$

$$\varphi_R = arctan[(Y_C - Y_A)/(X_C - X_A)]$$

The three-center nuclear attraction integral is defined by

$$NI3 = \left\langle \chi(\mathbf{A}, \alpha_1, l_1, m_1, n_1) \left| \frac{1}{r_C} \right| \chi(\mathbf{B}, \alpha_2, l_2, m_2, n_2) \right\rangle$$

$$= N_{\alpha_1}N_{\alpha_2}\exp(-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}R_{AB}^2)\sum_{k_1=0}^{l_1}\sum_{k_2=0}^{m_1}\sum_{k_3=0}^{n_1}\sum_{k_4=0}^{l_2}\sum_{k_5=0}^{m_2}\sum_{k_6=0}^{n_2}\left(\begin{array}{c}l_1\\k_1\end{array}\right)\left(\begin{array}{c}m_1\\k_2\end{array}\right)\left(\begin{array}{c}n_1\\k_3\end{array}\right)$$

$$\left(\begin{array}{c}l_2\\k_4\end{array}\right)\left(\begin{array}{c}m_2\\k_5\end{array}\right)\left(\begin{array}{c}n_2\\k_6\end{array}\right)X_{DA}^{l_1-k_1}Y_{DA}^{m_1-k_2}Z_{DA}^{n_1-k_3}X_{DB}^{l_2-k_4}Y_{DB}^{m_2-k_5}Z_{DB}^{n_2-k_6}I(r_D,\theta_D,\varphi_D),$$

$$(2.16)$$

where

$$I(r_D,\theta_D,\varphi_D) = \sum_{l=0}^{\infty}(-1)^l\frac{1}{R^{l+1}}\int\limits_0^{\infty}r_D^{l+k_1+k_2+k_3+k_4+k_5+k_6+2}\exp(-\alpha_D r_D^2)dr_D$$

$$\int\limits_0^{\pi}\int\limits_0^{2\pi}(\sin\theta_D)^{k_1+k_2+k_4+k_5+1}(\cos\theta_D)^{k_3+k_6}(\sin\varphi_D)^{k_2+k_5}(\cos\varphi_D)^{k_1+k_4}$$

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$$\left[P_l(\cos\theta_D)P_l(\cos\theta_R) + 2\sum_{m=1}^{l} \frac{(l-m)!}{(l+m)!} P_l^m(\cos\theta_D)P_l^m(\cos\theta_R)\cos m(\varphi_D - \varphi_R) \right] d\theta_D d\varphi_D.$$

Hear,

$$R = \sqrt{(X_{nuc} - X_D)^2 + (Y_{nuc} - Y_D)^2 + (Z_{nuc} + Z_D)^2}$$
$$\theta_R = \arctan[(Z_D - Z_{nuc})^2/R]$$
$$\varphi_R = \arctan[(Y_D - Y_{nuc})/(X_D - X_{nuc})]$$
$$J_{D\dot{I}} = J_D - J_{\dot{I}}, J = X, Y, Z; \dot{I} = A, B.$$

3. Computer Details

In this section we shall briefly outline the organization of the computer program [12-13]. All the numerical calculations were performed on a Pentium 200 processor. All the programs were written using the Fortran 77 language with double precision (about 11-12 digits accuracy). The computation is over all the possible combinations of Gaussian functions. 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 apperaring in the integral does not exceed $2(l+m+n \le 2)$. This restriction makes it possible to get an efficient program.

For the overlap integral,
i) in the Eqn.(2.5); l, m and n are integer quantum numbers and are zeros or positive. Thus, N_α is written as,

$$N_{\alpha,i} = \frac{2^{2i}}{(2i-1)!!}\sqrt{\frac{2\alpha}{\pi}}, i = l, m, n$$
$$N_\alpha = \sqrt{N_{\alpha,l}N_{\alpha,m}N_{\alpha,n}}.$$

ii) In Eqn.(2.11); in the term of SART, if X_A and X_B are zeros, $k_1 + k_2$ must be equal to $l_1 + l_2$.

To calculate the kinetic energy integral, it is enough to solve the overlap integrals. According to quantum number being linked to only subprogram, the integrals in the Eqn.(2.12) are separately calculated.

To calculate the nuclear attraction integrals, our task is to code the above formulae (Eqns.2.15 and 2.16) for the computer. For this purpose, we should solve the following integrals:
1) $I(r) = \int_0^\infty r^n \exp(-pr^2)dr; p = \alpha_1 + \alpha_2$
and is solved as,

$$\text{if } n \text{ is even } I(r) = \frac{(2n-1)!!}{2^{n+1}p^n}\sqrt{\frac{\pi}{p}}; |p > 0|$$

$$\text{if } n \text{ is odd } I(r) = \frac{n!}{2p^{n+1}}; |p > 0|;$$

2) $I(\varphi) = \int\limits_0^{2\pi} (\sin\varphi)^p(\cos\varphi)^q d\varphi$

If p and q are simultaneously even, the nonzero solutions of this integral can be possible.

This quantity is computed in our program using the following explicit expressions:

$$I(\varphi) = \int\limits_0^{2\pi} (\sin\varphi)^{2m}(\cos\varphi)^{2l}d\varphi = \frac{(2l-1)!!(2m-1)!!}{[(2l+2m)(2l+2m-2)\dots(2m+2)]}\frac{2\pi}{2^m m!}$$

3) $I(\theta) = \int\limits_0^\pi (\cos\theta)^p(\sin\theta)^q d\theta.$

With q always even $(q = 2n)$, this integral is solved for the following two condition of $p : (a)$ if p is even $(p = 2l)$,

$$I(\theta) = \int\limits_0^\pi (\cos\theta)^{2n}(\sin\theta)^{2l}d\theta = \frac{(2n-1)!!}{[(2n+2l)(2n+2l-2)\dots(2l+2)]}\frac{(2l-1)!!}{2^l l!}\pi;$$

(b) if p is odd $(p = 2l + 1)$,

$$I(\theta) = \int\limits_0^\pi (\cos\theta)^{2n}(\sin\theta)^{2l+1}d\theta = \frac{(2n-1)!!}{[(2n+2l+1)(2n+2l-1)\dots(2l+3)]}\frac{2^{2l+1}(l!)^2}{(2l+1)!}.$$

4) $\int\limits_0^\pi (\sin\theta)^l(\cos\theta)^m P_s^k(\cos\theta)d\theta = \frac{(2s-1)!!}{(s-k)!}$

$$\left[\int\limits_0^\pi (\sin\theta)^{l+k}(\cos\theta)^{m+s-k}d\theta + \sum_{j=1}^{}\int\limits_0^\pi (\sin\theta)^{l+k}(\cos\theta)^{s-k-2j}d\theta \prod_{p=1}^j \frac{(\alpha+p-1)(\beta+p-1)}{(\gamma+p-1)p}\right],$$

where $P_s^k(\cos\theta)$ is the associated Legendre polynomial, and

$$\alpha = \frac{k-s}{2}, \beta = \frac{k-s+1}{2}, \gamma = \frac{1}{2} - s.$$

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5)

$$\int\limits_0^{2\pi} (\cos\varphi)^l (\sin\varphi)^m \cos k\varphi d\varphi = 2^{k-1} \int\limits_0^{2\pi} (\cos\varphi)^{l+k} (\sin\varphi)^m d\varphi$$

$$+ \sum_{d=1}^{k/2} (-1)^d \frac{k}{d} \left(\begin{array}{c} k-(d+1) \\ d-1 \end{array} \right) 2^{k-(2d+1)} \int\limits_0^{2\pi} (\cos\varphi)^{l+k-2d} (\sin\varphi)^m d\varphi.$$

6)

$$\int\limits_0^{2\pi} (\cos\varphi)^l (\sin\varphi)^m \sin k\varphi d\varphi = \sum_{d=1}^{k/2} (-1)^d \left(\begin{array}{c} k-(d+1) \\ d \end{array} \right) 2^{k-(2d+1)}$$

$$\int\limits_0^{2\pi} (\cos\varphi)^{l+k-(2d+1)} (\sin\varphi)^{m+1} d\varphi.$$

Two- and three-center nuclear attraction integrals given in Eqns.(2.15 and 2.16) are easily calculated by means of the integrals given in (1)-(6).

4. Results and Discussion

The values of multi-center one electron integrals (overlap, kinetic and nuclear attraction) for 1s, 3p and 3d atomic orbitals are computed over the 1s Slater function by using the approximate GTO expansions. We choose various shells and subshells (1s, 3p and 3d) to verify the presented method. The results of the calculations are comparetivelly given with the literature data in Tables I and II. In these calculations, we used the values of d_i and α_i given by Taketa et. al [14]. The overlapping of the orbitals centered on A(0,0,0), B(R,0,0), C(0,R,0) and D(0,0,R) depend on R (Figure 2).
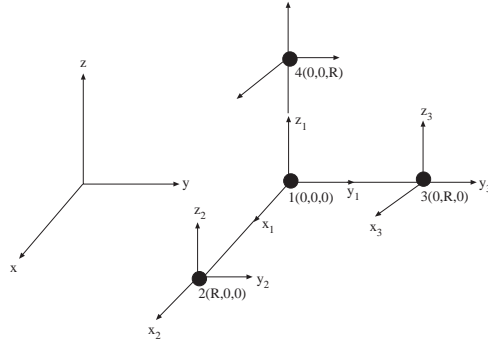

Figure 2. Used Model system.

Table 1. The Overlap and Kinetic Energy Integrals: 1s, 3pπ and 3dπ

	R	Present Work		Literature value[14]		Analytical[15]
		1S-4G	1S-8G	1S-4G	1S-8G	
Overlap for 1s	4	0.189074	0.1892667	0.189074	0.189267	0.1892616
	8	0.009785914	0.01021712	0.009786	0.010217	0.0111757
	12	0.000102757	0.00035429	0.000103	0.000354	0.000374797
	16	3.36864E-07	7.54556E-06	0.0000003	0.000008	1.15161E-05
Kinetic for 1s	4	-0.00257877	-0.003045098	-0.002579	-0.003048	-
	8	-0.002309783	-0.002049277	-0.00231	-0.002049	
	12	-6.45325E-05	-0.000111485	0.000065	-0.000111	
	16	-3.93411E-07	-3.33865E-06	-0.0000004	-0.000003	
Overlap for 3pπ	4	0.4931019	0.4931038	0.493102	0.493104	-
	8	0.08129859	0.08134646	0.081299	0.081346	
	12	0.007042267	0.007181212	0.007042	0.007181	
	16	0.000378117	0.00045748	0.000378	0.000457	
Kinetic for 3pπ	4	0.07198013	0.07197791	0.07198	0.071978	-
	8	0.00057553	0.000569408	0.000576	0.000569	
	12	-0.000701426	-0.000695286	-0.000701	-0.000695	
	16	-7.50065E-05	-7.29553E-05	-0.000075	-0.000073	
Overlap for 3dπ	4	-0.2763853	-0.2823668	-0.282754	-0.282409	-
	8	-0.1707508	-0.1691214	-0.171105	-0.16913	
	12	-0.01945192	-0.02079979	-0.019459	-0.0208	
	16	-0.000854101	-0.001480048	-0.000854	-0.001484	
Kinetic for 3dπ	4	-0.1739189	-0.1774697	-0.177519	-0.177497	-
	8	-0.0232008	-0.0226	-0.023193	-0.0226	
	12	0.001003907	0.000743542	0.001007	0.000744	
	16	0.00020677	0.000198189	0.000207	0.000198	

Table 2. The Two- and Three-center Nuclear Attraction (N.A.) Integrals: 1s, 3p and 3d.

	R	N	Two-center Nuclear attraction		Three-center Nuclear Attraction		Analytical for Two-center N.A.[15]
			1S-4G	1S-8G	1S-4G	1S-8G	
1s	4	2	-0.2500005	-0.2500001	-0.0419334	-0.0419585	-0.249587
		4	-0.2500005	-0.2500001	-0.0419334	-0.0419585	
		9	-0.2500005	-0.2500001	-0.0419334	-0.0419585	
	8	2	-0.1250003	-0.1250001	-0.0008895	-0.0011324	-0.1249999
		4	-0.1250003	-0.1250001	-0.0008895	-0.0011324	
		9	-0.1250003	-0.1250001	-0.0008895	-0.0011324	
	12	2	-0.0833335	-0.0833334	-7.655E-06	-2.623E-05	-0.0833333
		4	-0.0833335	-0.0833334	-7.655E-06	-2.623E-05	
		9	-0.0833335	-0.0833334	-7.655E-06	-2.623E-05	
	16	2	-0.0625001	-0.0625	-1.883E-08	-4.207E-07	-0.625
		4	-0.0625001	-0.0625	-1.883E-08	-4.207E-07	
		9	-0.0625001	-0.0625	-1.883E-08	-4.207E-07	
3p	8	2	-0.1332028	-0.1332032	-0.002768	-0.002768	–
		4	-0.1305002	-0.1304995	-0.002768	-0.002768	
		9	-0.1297164	-0.1296908	-0.002768	-0.002768	
	12	2	-0.0857638	-0.085764	-0.0001316	-0.000133	–
		4	-0.0854079	-0.0854079	-0.0001316	-0.000133	
		9	-0.0854566	-0.0854562	-0.0001316	-0.000133	
	16	2	-0.0635253	-0.0635254	-4.504E-06	-5.275E-06	–
		4	-0.0634409	-0.0634409	-4.504E-06	-5.275E-06	
		9	-0.0634518	-0.0634518	-4.504E-06	-5.275E-06	
3d	8	2	-0.1409152	-0.1445161	-0.0007119	-0.0007518	–
		4	-0.1339476	-0.1375069	-0.0007119	-0.0007518	
		9	-0.1340079	-0.1373775	-0.0007119	-0.0007518	
	12	2	-0.0867477	-0.0891108	-1.58E-05	-1.844E-05	–
		4	-0.0858302	-0.0881878	-1.58E-05	-1.844E-05	
		9	-0.0859485	-0.088304	-1.58E-05	-1.844E-05	
	16	2	-0.0631719	-0.0649344	-2.191E-07	-4.369E-07	–
		4	-0.0629542	-0.0647154	-2.191E-07	-4.369E-07	
		9	-0.0629753	-0.0647366	-2.191E-07	-4.369E-07	

1S-4G and 1S-8G representations in Tables I and II are the approximate values of integrals computed by using the 4-term and the 8-term GTO expansion of 1s STO, respectively. The 4-term observes rather poor approximate values while the 8-term expansion seems to yield values good enough for most purposes.

The calculated results for the various orbital for different N, M (1S-4G and 1S-8G) and R values show that the series contained in the integrals converge very rapidly in the region where overlapping is moderate or weak (Tables I and II). As seen from Table II, the accuracy of 12 significant figures is achieved for very good convergence of the present proposed method. We may conclude that the series converge very rapidly at N=2 or 4 in the present method. The series also converges at the various value of R depending on the main atomic orbital radius, as expected. In the same way, convergence analysis of the series provides us a method to find the starting point for the convergency of various atomic orbitals.

Summary

A general expansion is derived for multi-center nuclear attraction integrals in the form of a series giving sufficiently accurate values, each containing only two or three terms. With the method described in this manuscript one can obtain a sufficiently accurate and 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.

References

[1] S. F. Boys, *Proc. Soc. (London)* **A200**, 542 (1950).

[2] S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

[3] S.F. Boys and I. Shavitt, *Proc. Soc. (London)* **A254**, 437 (1960).

[4] C. M. Reeves and R. Fletcher, *J. Chem. Phys.* **42**, 4073 (1965).

[5] M. J. D. Powell, *Computer J.* **7**, 155 (1964).

[6] K. O-ohata, H. Taketa and S. Huzinaga, *J. Phys. Soc.* **Japan 21**, 2306 (1966).

[7] E. Clementi, *IBM J. Res. Develop. Suppl.* **9**, 2 (1965).

[8] H. Takewaki and T. Koga, *Chem. Phys. Letters*, **228**, 562 (1994).

[9] T. Koga, H. Takewaki and A. J. Thakkar, *J. Chem. Phys.*, **100**, 8140 (1994).

[10] C. F. Bunge, J. A. Barrientos, A. V. Bunge and J. A. Cogordan, *Phys. Rev.* **A46**, 3691 (1992).

[11] E. N. Maslen and M. G. Trefry, *Int. J. Quantum Chem.*, **37**, 51 (1990).

[12] G. Budak, PhD Thesis, Atatürk University, (1996) (unpublished).

[13] A. Karabulut, PhD Thesis, Atatürk University, (1996) (unpublished).

[14] H. Taketa, S. Huzinaga and K. O-ohata, *J. Phys. Soc.* **Japan 21**, 2313 (1966).

[15] P. Gombs, Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmecha- nik, Basel, p.266 (1950).

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