Commun. Fac. Sci. Univ. Ank. Series A2-A3
V. 49(1). pp.1-7. (2005)

CALCULATIONS OF TWO-CENTER ONE-ELECTRON INTEGRALS

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(Received Feb.22, 2005; Accepted March 24, 2005)

ABSTRACT

Two-center kinetic energy and nuclear attraction integrals are defined in terms of overlap integrals and incomplete gamma functions. A new analytical expression is obtained for nuclear attraction integral $V^{(C)}$ where the nuclear attraction operator is not located at the same center with the basis functions. The recursive relations and generalized binomial coefficients are used for the evaluation of these integrals. Computer results are in good agreements with values given in the literature.

KEYWORDS: Slater-type orbitals; nuclear attraction and kinetic energy integrals

1. INTRODUCTION

In *ab-initio* molecular calculations one has to calculate multicenter integrals. If one uses Gaussian type orbitals (GTOs), calculation of these integrals is relatively easier. However the behavior of GTOs, especially for the extreme values of radial distances, is quite different from the exact atomic orbitals. Slater type orbitals (STOs) supply a better approximation to the exact atomic orbitals, but calculation of these integrals over STOs is never easy. Furthermore, in some special cases there is not a consensus in the literature on how to calculate these integrals. Most of the multicenter integrals can be defined in terms of overlap integrals. Therefore it is rather important to calculate overlap integrals quickly and accurately for higher angular momentum quantum numbers when the distance between the centers is too small or too large, or the difference between the screening constants is small. Several studies on the calculation of overlap integrals and two-center one-electron integrals with STOs can be found in the literature [1-7]. Recently, Mekelleche and Baba-Ahmed[8] have also derived an analytical expression using sigma-functions for the overlap, kinetic energy and nuclear attraction integrals in ellipsoidal coordinates. Overlap integrals have been expressed in terms of generalized binomial

coefficients and well-known auxiliary functions A_k and B_k by Guseinov *et al.*[9]. In molecular calculation, one encounters two types of two-center nuclear attraction integrals: First, the nucleus may be located at the same center with one of the STOs. In this case nuclear attraction integral can easily be defined in terms of overlap integrals. In the second type, the nucleus is located at a center which different from the center of STOs. In the latter case, nuclear attraction integral cannot be defined in terms of overlap integrals.

In this study we have expressed a new analytical expression for the $V^{(C)}$ nuclear attraction integrals in terms of incomplete gamma functions and generalized binomial coefficients. We have calculated kinetic energy and nuclear-attraction integrals by expressing in terms of overlap integrals.

2. TWO-CENTER INTEGRALS

Two-center overlap integrals are given the following form

$$S_{n\ell m,n'\ell'm'}(\zeta,\zeta';\vec{R}) = \int \chi_{n\ell m}(\zeta,\vec{r}_a)^* \chi_{n'\ell'm'}(\zeta',\vec{r}_b)dV . \tag{1}$$

χ 's are normalized complex STO's and their general form is

$$\chi_{n\ell m}(\zeta,\vec{r}) = \left[(2\zeta)^{2n+1}/(2n)!\right]^{1/2} r^{n-1}e^{-\zeta r}Y_{\ell m}(\theta,\varphi), \tag{2}$$

where ζ is the screening constant and n,ℓ,m are the quantum numbers. $Y_{\ell m}(\theta,\varphi)$ are well-known complex spherical harmonics

$$Y_{\ell m}(\theta,\varphi) = \frac{1}{\sqrt{2\pi}} P_{\ell m}(\cos\theta)e^{im\varphi}, \tag{3}$$

where $P_{\ell m}(\cos\theta)$ is normalized associated Legendre polynomials. Substituation of Eq.(2) in Eq.(1), two center overlap integrals in elliptical coordinates are expressed as following

$$S_{n\ell\lambda}^{n'\ell'\lambda}(\zeta,\zeta';R) = N_{nn'} \sum_{\alpha=-\lambda}^{\ell} {}^{(2)} \sum_{\beta=\lambda}^{\ell'} {}^{(2)} \sum_{q=0}^{\alpha+\beta} g_{\alpha\beta}^{q}(\ell\lambda,\ell'\lambda)$$

$$\times \sum_{i=0}^{n+n'-\alpha-\beta} F_i(n-\alpha,n'-\beta)A_{q+n+n'-\alpha-\beta-i}(p)B_{q+i}(pt), \tag{4}$$

where $N_{nn'} = \left[(2\zeta)^{2n+1}(2\zeta')^{2n'+1}/(2n)!(2n')!\right]^{1/2}$, $p = \frac{R}{2}(\zeta+\zeta')$, $t = \frac{\zeta-\zeta'}{\zeta+\zeta'}$, $\lambda = |m| = |m'|$. $g_{\alpha\beta}^{q}(\ell\lambda,\ell'\lambda)$ are expansion coefficients given by

Guseinov[5]. $F_m(k,s)$ are the generalized binomial coefficients and given as follows in terms of binomial coefficients

$$F_m(N,N') = \sum_{\sigma=\frac{1}{2}\{|m-N|+(m-N)\}}^{\min(m,N')} (-1)^\sigma F_{m-\sigma}(N) F_\sigma(N') \tag{5}$$

The functions A_k and B_k are well-known the auxiliary functions given by

$$A_k(p) = \int_1^\infty \mu^n e^{-p\mu} d\mu, \qquad B_k(pt) = \int_{-1}^{+1} \nu^n e^{-pt\nu} d\nu. \tag{6}$$

The kinetic energy and nuclear attraction integrals are defined by

$$T_{n\ell m,n'\ell'm'}(\zeta,\zeta';\vec{R}) = -\frac{1}{2}\int \chi_{n\ell m}(\zeta,\vec{r}_a)^* (\Delta) \chi_{n'\ell'm'}(\zeta',\vec{r}_b) dV \tag{7}$$

$$V^{(a)}_{n\ell m,n'\ell'm'}(\zeta,\zeta';\vec{R}) = \int \chi_{n\ell m}(\zeta,\vec{r}_a)^* \left(\frac{-Z_a}{\vec{r}_a}\right) \chi_{n'\ell'm'}(\zeta',\vec{r}_b) dV, \tag{8a}$$

$$V^{(b)}_{n\ell m,n'\ell'm'}(\zeta,\zeta';\vec{R}) = \int \chi_{n\ell m}(\zeta,\vec{r}_a)^* \left(\frac{-Z_b}{\vec{r}_b}\right) \chi_{n'\ell'm'}(\zeta',\vec{r}_b) dV, \tag{8b}$$

$$V^{(C)}_{n\ell m,n'\ell'm'}(\zeta,\zeta';\vec{R}) = \int \chi_{n\ell m}(\zeta,\vec{r}_a)^* \left(\frac{-Z_b}{r_b}\right) \chi_{n'\ell'm'}(\zeta',\vec{r}_a)\, dV, \tag{8c}$$

where Z_a and Z_b denote the nuclear charge of the *a* and *b* nuclei, respectively. Substituation of Eq.(2) in Eq.(7)-Eq.(8b), kinetic energy and nuclear attraction integrals can be expressed in terms of overlap integrals

$$T^{n'\ell'\lambda}_{n\ell\lambda}(\zeta,\zeta';\vec{R}) = \frac{-\zeta'^2}{2} S^{n'\ell'\lambda}_{n\ell\lambda}(\zeta,\zeta';\vec{R}) + \frac{2\zeta'^2 n'}{\sqrt{(2n')(2n'-1)}} S^{(n'-1)\ell'\lambda}_{n\ell\lambda}(\zeta,\zeta';\vec{R})$$

$$+ \frac{2\zeta'^2\left[\ell'(\ell'+1) - n'(n'-1)\right]}{\sqrt{2n'(2n'-1)(2n'-2)(2n'-3)}} S^{(n'-2)\ell'\lambda}_{n\ell\lambda}(\zeta,\zeta';\vec{R}) \tag{9}$$

,

$$V^{(A)}_{n\ell\lambda,n'\ell'\lambda}(\zeta,\zeta';\vec{R}) = -Z_a \frac{2\zeta}{\sqrt{2n(2n-1)}} S^{n'\ell'\lambda}_{(n-1)\ell\lambda}(\zeta,\zeta';\vec{R}), \tag{10}$$

$$V^{(B)}_{n\ell\lambda,n'\ell'\lambda}(\zeta,\zeta';\vec{R}) = -Z_b \frac{2\zeta}{\sqrt{2n(2n-1)}} S^{(n'-1)\ell'\lambda}_{n\ell\lambda}(\zeta,\zeta';\vec{R}). \tag{11}$$

In Eq.(8c), if r_b is the distance from center a which is located on the x axis, $\frac{1}{r_b}$ can be expanded in terms of spherical harmonics

$$\frac{1}{r_b}=\sum_{k=0}^{\infty}\sum_{s=-k}^{k}\frac{4\pi}{2k+1}Y_{ks}(\theta_a,\phi_a)\,Y^{*}_{ks}(\pi/2,0)\,\frac{r_<^k}{r_>^{k+1}}\,. \tag{12}$$

Where $Y_{ks}(\pi/2,0)$ complex spherical harmonics can be defined in terms of binomial coefficients as

$$Y_{ks}(\pi/2,0)=\begin{cases}\dfrac{1}{\sqrt{2\pi}}\dfrac{(-1)^{\frac{k-s}{2}}}{2^k}\left\{\dfrac{2k+1}{2}\dfrac{1}{F_s(k)F_s(k+s)}\right\}^{1/2}\left(F_{\frac{k+s}{2}}(k+s)\,F_{\frac{k-s}{2}}(\frac{k+s}{2})\right), & \text{for even } k-s\\ 0, & \text{for odd } k-s\end{cases} \tag{13}$$

Substituation of Eq.(12) into Eq.(8c), we can obtain

$$V^{(C)}_{n\ell m,n'\ell'm'}(\zeta,\zeta';R)=-Z_b\,\frac{(2\zeta)^{n+1/2}\,(2\zeta')^{n'+1/2}}{\sqrt{(2n)!(2n')!}}\sum_{L=\max(|\ell-\ell'|,|m-m'|)}^{\ell+\ell'}{}^{(2)}\,(-1)^{(L-M)/2}\,\frac{1}{2^L}$$

$$\times\,C^{L}(\ell m,\ell' m')\left\{\frac{1}{F_M(L)\,F_M(L+M)}\right\}^{1/2}\left\{F_{\frac{L+M}{2}}(L+M)F_{\frac{L-M}{2}}\left(\frac{L+M}{2}\right)\right\}$$

$$\times\left\{\frac{1}{R^{L+1}}\frac{1}{(\zeta+\zeta')^{n+n'+L+1}}\,\gamma\left(n+n'+L+1,R(\zeta+\zeta')\right)\right.$$

$$\left.+\;R^{L}\frac{1}{(\zeta+\zeta')^{n+n'-L}}\,\Gamma\left(n+n'-L,R(\zeta+\zeta')\right)\right\} \tag{14}$$

where $M=m-m'$, $|\ell-\ell'|\le L\le\ell+\ell'$ and $C^{L}(\ell m,\ell' m')$ are called Gaunt coefficients[10]. $\gamma(a,x)$ and $\Gamma(a,x)$ are well-known incomplete gamma functions, and they are given in terms of finite series by[11]

$$\gamma(a,x)=\int_0^x t^{a-1}e^{-t}dt=(a-1)!\left(1-e^{-x}\sum_{i=0}^{a-1}\frac{x^i}{i!}\right) \qquad (15a)$$

$$\Gamma(a,x)=\int_x^\infty t^{a-1}e^{-t}dt=(a-1)!e^{-x}\sum_{j=0}^{a-1}\frac{x^j}{j!} \quad a=1,2,.... \qquad (15b)$$

Recurrence relations of incomplete gamma functions can be derived as following

$$\gamma(a,x)=-\left[x^{a-1}e^{-x}-\delta_{a,1}\right]+(a-1)\gamma(a-1,x), \qquad \gamma(1,x)=1-e^{-x} \qquad (16)$$

$$\Gamma(a,x)=x^{a-1}e^{-x}+(a-1)\Gamma(a-1,x), \quad \Gamma(1,x)=e^{-x} \qquad (17)$$

3. RESULTS AND DISCUSSIONS

In this study we have used the algorithm defined by Guseinov *et al.*[9] for the calculation of kinetic energy and nuclear attraction integrals. This algorithm is quite useful even at large values when the distance between the centers is too small or too large, or the difference between the screening constants is small. In order to simplify the evaluation of nuclear attraction integral $V^{(C)}$, we have assumed without any loss of generalization, that center *a* is located at the origin and the center *b* is located on the *x* axis. We have used the recursive relations of incomplete gamma function defined in Eq.(16-17) to calculate of these integrals. The recursive relations mentioned above are very stable and the use of these relations speed up the calculations considerably. Calculations are performed using Force 2.0 Fortran on PC Pentium IV at 2GHz provided with 512MB of RAM. Also Double-precision arithmetic is used in all calculations. The results obtained by the method described in this study for the kinetic energy and nuclear attraction integrals are given in Table 1, Table 2, Table 3 and Table 4 with 15 significant figures in the floating notation where –E means 10^{-E}, respectively. Obtained results are in good agreement with the literature.

Table 1. Kinetic energy integral

Eq.(9)	R	This Work	Ref.[8]
<320(6.5197)|320(2.0387)>	3.75803	0.506937527831541-02	0 .50693752782488-02
<321(6.5197)|321(2.0387)>	3.75803	0.244136900700645-03	0.24413690069512-03
<322(6.5197)|322(2.0387)>	3.75803	-0.355439766714982-03	-0.35543976671098-03
<210(.1)|210(0.4)>	0.5	6.49347080011743-03	
<522(0.5)|432(0.8)>	2	3.69305628904252-4	
<954(2)|864(3.5)>	6	4.20642333356047-2	
<12109(5)|1099(1.5)>	0.5	3.87643471267154-2	
<14128(1)|1288(1.5)>	3	1.73046474973549-2	

Table 2. Nuclear attraction integral

Eq.(10)	R	Z_a	This Work	Ref.[8]
<320(6.5197)|320(2.0387)>	3.75803	35	-0.486277949158865+0	-0.486277949158857+0
<321(6.5197)|321(2.0387)>	3.75803	35	0.265448562634649+0	0.265448562634643+0
<322(6.5197)|322(2.0387)>	3.75803	35	-0.413875309079840-1	-0.413875309079738-1
<200(0.1)|200(0.2)>	0.5	1	-0.58468787157391-3	
<430(4)|320(2.5)>	5	5	-0.222260283461752-3	
<642(0.5)|522(8)>	10	2	-0.206371306754453-5	
<1055(1.5)|855(10)>	0.5	2	-0.979517979405703-6	

Table 3. Nuclear attraction integral

Eq.(11)	R	Z_b	This Work	Ref.[8]
<320(6.5197)|320(2.0387)>	3.75803.	35	-0.865697113601657-1	-0.865697113601649-1
<321(6.5197)|321(2.0387)>	3.75803	35	0.397046469000436-1	0.397046469000443-1
<322(6.5197)|322(2.0387)>	3.75803	35	-0.539466601538607-2	-0.539466601538536-2
<211(3.7)|211(2.5)>	2.5	2	-0.337967020037566-1	
<420(10.5)|430(8.4)>	0.5	6	0.260824990589433+0	
<531(3.7)|321(3)>	10	6	0.434633116616420-7	
<1086(6)|1386(1.5)>	1	8	-0.151335134197928-1	

Table 4. Nuclear attraction integral values

Eq.(14)	R	Z_b	This Work	Ref.[12]
<200(0.4)|200(0.4)>	1.911	1	-0.196585166190231-2	-0.1965851657-2
<210(0.4)|210(0.4)>	1.911	1	-0.186656337806799-2	-0.1866563373-2
<321(2)|321(1.5)>	3	2	0.581335891840337-2	
<654(3)|854(3.4)>	2.5	2	-0.725721529264715-2	
<1286(41186(1.5)>	5	5	-0.763739957303281-2	

ÖZET: İki-merkez kinetik ve potansiyel enerji integralleri overlap integralleri ve incomplete gamma fonksiyonları cinsinden tanımlandı. Baz fonksiyonlarıyla aynı merkezde olmayan potansiyel enerji operartörü V(c) için yeni bir analitik ifade elde edildi. Bu integrallerin kesaplanmasında rikörsif bağıntılar ve genelleştirilmiş binom katsayıları kullanıldı. Sonuçlarımız literatürdeki sonuçlarla uyumludur.

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