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# Calculation of Two-center Nuclear Attraction Integrals over Slater Type Orbitals in Molecular Coordinate System

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A closed analytical relation is derived for the two-center nuclear attraction integrals over Slater type orbitals (STOs) in terms of binomial coefficients. This formula can be used in highly accurate calculations of the nuclear attraction integrals. The relationships obtained are valid for arbitrary values of quantum numbers and screening constants of STOs and location of nuclei.

**Keywords** Slater type orbitals, nuclear attraction integrals, overlap integrals, molecular integrals

## Introduction

Molecular integrals over STOs arising in the Hartree-Fock-Roothaan (HFR) equations play a central role in the quantum theory of the electronic structure of atoms and molecules.[1] It is important for practical reasons to be able to quickly and accurately calculate these multicenter integrals. Currently calculations of these integrals are performed mainly with the help of Gaussian type orbitals (GTOs).[2,3] It is well known that GTOs are mathematically simpler than STOs, but less accurate. GTOs basis of various size showed that a STOs can obtain comparable accuracy.[4,5] Thus, in these areas, and if relatively small basis sets are necessary, for HFR calculations, GTOs should be replaced by STOs which have more physical basis functions. However, the difficulties in the calculation of multicenter integrals have restricted the use of STOs in molecular quantum mechanics.

We notice that, in some areas of research, the calculations of two-center nuclear attraction integrals over STOs must be exact.[6-9] Also, these integrals are central to the calculation of three-center nuclear attraction integrals based on the series expansion formulas for STOs about a new center.[10-12] In our previous paper,[13] the three-center nuclear attraction integrals have been expressed in terms of two-center nuclear attractions integrals. Therefore two-center nuclear attraction integrals represent a fundamental class of molecular integrals in calculation of multicenter nuclear attraction integrals appearing in HFR equation for molecules. In this paper, we present a new approach for the exact calculation of two-center nuclear attraction integrals.

## General definition

Two-center nuclear attraction integrals over STOs with respect to the molecular coordinate system have the following form:

$$I_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\frac{1}{r_b}\chi_{n'l'm'}(\zeta',\vec{r}_b)\mathrm{d}V \quad (1)$$

and

$$J_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\frac{1}{r_b}\chi_{n'l'm'}(\zeta',\vec{r}_a)\mathrm{d}V \quad (2)$$

where $\vec{R}\equiv\vec{R}_{ab}=\vec{r}_a-\vec{r}_b$ and $\chi_{nlm}$ are the normalized complex or real STOs determined by

$$\chi_{nlm}(\zeta,\vec{r})=R_n(\zeta,r)S_{lm}(\theta,\varphi) \quad (3)$$

$$R_n(\zeta,r)=(2\zeta)^{n+\frac{1}{2}}\left[(2n)!\right]^{-\frac{1}{2}}r^{n-1}e^{-\zeta r} \quad (4)$$

Here $S_{lm}$ are the complex ($S_{lm}\equiv Y_{lm}$) or real spherical harmonics determined by the relation

$$S_{lm}(\theta,\varphi)=P_{l|m|}(\cos\theta)\Phi_m(\varphi) \quad (5)$$

where $P_{l|m|}$ are normalized associated Legendre functions[14] and for complex spherical harmonics

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi} \quad (6)$$

for real spherical harmonics

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$$\Phi_m(\varphi)=\frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\varphi & \text{for} \quad m\geqslant 0\\ \sin|m|\varphi & \text{for} \quad m<0\end{cases} \tag{7}$$

## Use of overlap integrals

It is easy to show that the nuclear attraction integrals (1) can be expressed through the overlap integrals by the following formula:[15]

$$I_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\frac{2\zeta'}{[2n'(2n'-1)]^{1/2}}S_{nlm,n'-1l'm'}(\zeta,\zeta';\vec{R}) \tag{8}$$

where

$$S_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\int\chi^{*}_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm'}(\zeta',\vec{r}_b)\mathrm{d}V \tag{9}$$

are the overlap integrals. Therefore, the nuclear attraction integrals (1) are expressed through the overlap integrals for which in Ref. 16 the analytical relations were obtained. Thus, in this study we confine ourselves to the calculation of integrals (2).

By the use of the one-center charge density expansion formulas,[17] the two-center nuclear attraction integrals Eq. (2) can be expressed in terms of basic integrals $J_{nlm}(\zeta,\vec{R})$ by the following formula:

$$J_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\sum_{\nu=|l-l'|}^{l+l'}\sum_{\sigma=-\nu}^{\nu}W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta';z)J_{\mu\nu\sigma}(z,\vec{R}) \tag{10}$$

$$J_{nlm}(\zeta,\vec{R})=\frac{1}{\sqrt{4\pi}}\int\chi^{*}_{nlm}(\zeta,\vec{r}_a)\frac{1}{\vec{r}_b}\mathrm{d}V \tag{11}$$

Here
$z=\zeta+\zeta'$, $\mu=n+n'-1$ and $W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta';z)$ are the charge density coefficients defined as

$$W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta';z)\equiv W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta',z;0,0)$$
$$=\frac{z\sqrt{z}}{2^{\mu}}\frac{F_{n'}(\mu)}{n}\left[\frac{2l+1}{2}\frac{F_n(2n)}{F_n(2n)F_{n'}(2n')}\right]^{1/2}$$
$$\times(1+t)^{n+\frac{1}{2}}(1-t)^{n'+\frac{1}{2}}C^{\nu|\sigma|}(lm,l'm')A^{\sigma}_{mm'}\delta_{\mu,n+n'-1} \tag{12}$$

where

$$C^{L|M|}(lm,l'm')=\begin{cases}C^{L}(lm,l'm') & \text{for} \quad |M|=|m-m'|\\ C^{L}(lm,l'-m') & \text{for} \quad |M|=|m+m'|\end{cases} \tag{13}$$

$$A^{M}_{mm'}=\begin{cases}\frac{1}{\sqrt{2}}(2-|\eta^{m-m'}_{mm'}|)^{1/2}\delta_{M,\varepsilon|m-m'|}+\\ \frac{1}{\sqrt{2}}\eta^{m+m'}_{mm'}\delta_{M,\varepsilon|m+m'|} & \text{for real STO's}\\ \delta_{M,m-m'} & \text{for complex STO's}\end{cases} \tag{14}$$

Here, the quantities $C^{L}(lm,l'm')$ are the Gaunt coefficients.[18-24] See Ref. 19 for the exact definition of quantities $\eta^{m\pm m'}_{mm'}$ and $\varepsilon=\varepsilon_{mm'}$.

Now we can move on to the calculation of basic integrals. It is easy to show that the basic integrals, Eq. (11), can also be obtained from overlap integrals using the relation:

$$J_{nlm}(\zeta,\vec{R})=\frac{1}{\sqrt{4\pi}}\lim_{\zeta'\to 0}\frac{\sqrt{4\pi}}{(2\zeta')^{1/2}}\times\int\chi^{*}_{nlm}(\zeta,\vec{r}_a)\chi_{000}(\zeta',\vec{r}_b)\mathrm{d}V \tag{15}$$

From Eq. (15) we obtain:

$$J_{nlm}(\zeta,\vec{R})=\lim_{\zeta'\to 0}\frac{1}{(2\zeta')^{1/2}}S_{nlm,000}(\zeta,\zeta';\vec{R}) \tag{16}$$

Here $S_{nlm,000}$ are the overlap integrals over STOs with respect to molecular coordinate system determined by Eq. (9).

In a previous paper,[16] by use of Talman's formulas for overlap integrals in the lined-up coordinate systems and Guseinov's transformation technique we presented a new expression for computing the two-center overlap integrals over STOs with respect to the molecular coordinate system. From these formulas, it is easy to obtain for the overlap integrals $S_{nlm,000}$ the following relation:

$$S_{nlm,000}(\zeta,\zeta';\vec{R})=T^{0}_{lm,00}(\theta,\varphi)S_{nl0,000}(\zeta,\zeta';R) \tag{17}$$

where $S_{nl0,000}(\zeta,\zeta';R)$ are the overlap integrals in lined up coordinate systems defined in Ref. 25 as:

$$S_{nl0,000}(\zeta,\zeta';R)=\frac{(2\zeta)^{n+1/2}(2\zeta')^{1/2}}{\sqrt{(2n)!}}\sum_{\lambda,L}C(0l0,\lambda L)Q_{\lambda L} \tag{18}$$

The expressions for the rotation coefficients $T^{\lambda}$ are given in Ref. 26. From the general expressions $T^{\lambda}$, it is easy to obtain for the coefficients $T^{0}_{lm,00}(\theta,\varphi)$ the following relation:

$$T^{0}_{lm,00}(\theta,\varphi)=\sqrt{\frac{4\pi}{2l+1}}S_{lm}(\theta,\varphi) \tag{19}$$

The coefficients $C(0l0,\lambda L)$ and $Q_{\lambda L}$ in Eq. (18) are determined by relationships:

$$C(0l0,\lambda L)=(-1)^{l-\lambda}[(2l+1)]^{1/2} \times(2L+1)F_{\lambda}(l)\begin{bmatrix}\lambda & 0 & L\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}\lambda & 0 & L\\ 0 & 0 & 0\end{bmatrix} \tag{20}$$

$$Q_{\lambda L}=\sum_{k=0}^{[L/2]}\sum_{p=0}^{L-2k}\begin{bmatrix}D_{Lkp}R^{l-\lambda+L-2k-2p-1}J\\ \times(n'+\lambda+2k-L,n-l,p)\end{bmatrix} \tag{21}$$

The quantities $\begin{bmatrix}l_1 & l_2 & l_3\\ 0 & 0 & 0\end{bmatrix}$ in Eq. (20) are the $3-j$ coefficients which are expressed in terms of binomial coefficients (see Ref. 16).

In Eq. (21) coefficients $D$ and $J$ have the form

$$D_{Lkp}=\frac{(-1)^{k}}{2^{2L-2k}}F_{k}(L)F_{L}(2L-2k)F_{p}(L-2k) \tag{22}$$

$$J(M,N,p)=R^{M+N+2p+2}\sum_{\mu=0}^{M+N}B_{MN\mu}A_{\mu+p}(u)B_{M+N-\mu+p}(u) \tag{23}$$

where $u=\zeta R/2$ and

$$B_{MN\mu}=\frac{1}{2^{M+N+1}}\sum_{i}(-1)^{N-\mu+i}F_{i}(M)F_{\mu-i}(N) \tag{24}$$

Here $F_m(n)=n!/[(m!(n-m)!]$ are the binomial coefficients and $A_k$ and $B_k$ are the well known auxiliary functions which are given in Ref. 27.

As can seen from Eqs. (18), (21) and (23) that the two-center nuclear attraction integrals over STOs in the elliptical coordinate system are expressed through the molecular auxiliary functions defined by:[28]

$$A_{k}(u)=\int_{0}^{\infty}\mu^{k}e^{-u\mu}\mathrm{d}\mu \tag{25}$$

$$B_{k}(u)=\int_{-1}^{1}\nu^{k}e^{-u\nu}\mathrm{d}\nu \tag{26}$$

For the calculation of the functions $A_k$ and $B_k$ useful algorithm and efficient computer programs have been established in our work.[29] Therefore, the work is especially useful for demonstration of the accuracy of machine computations for nuclear attraction integrals through the elliptic coordinate system, which are expressed in terms of $A_k$ and $B_k$ auxiliary functions.

## Numerical results and discussion

As can be seen from Eqs. (10) and (16), the two-center nuclear attraction integrals are expressed in terms of overlap integrals. The results of calculations in atomic units for the two-center nuclear attraction integrals in molecular coordinate system on a PENTIUM III 800 MHz (using Turbo Pascal language) are represented in Table 2. We see from the Table, our results are satisfactory with the values obtained in Ref. 13 from other analytical expression. The calculation in this work is based on the reformulation of two-center nuclear attraction integrals as the summation of products of binomial coefficients. For quick calculations, the binomial coefficients are stored in the memory of the computer. For the binomial coefficients we use the following recurrence relation:

$$F_{m}(n)=F_{m}(n-1)+F_{m-1}(n-1) \tag{27}$$

where $F_0(n)=1$ and $F_m(n)=0$ for $m<0$, $m>n$. By using the recursive relation for binomial coefficients, we can avoid the calculation of factorials of integer. By utilizing this formula, not only can we keep at each step of a calculation an integer but we also can maintain the maximum number in the computation of a binomial that binomial itself. In order to put these coefficients into or to get them back from the memory, the positions of certain coefficients $F_m(n)$ are determined by the following relation:

$$F(n,m)=n(n+1)/2+m+1 \tag{28}$$

The examples of generation for the positions of coefficients are shown in Table 1.

**Table 1** Generation of positions for binomial coefficients for $0\leqslant n\leqslant 4$

| *n* | *m* | *F*(*n*,*m*) | *n* | *m* | *F*(*n*,*m*) |
|---|---|---|---|---|---|
| 0 | 0 | 1 | 3 | 2 | 9 |
| 1 | 0 | 2 | 3 | 3 | 10 |
| 1 | 1 | 3 | 4 | 0 | 11 |
| 2 | 0 | 4 | 4 | 1 | 12 |
| 2 | 1 | 5 | 4 | 2 | 13 |
| 2 | 2 | 6 | 4 | 3 | 14 |
| 3 | 0 | 7 | 4 | 4 | 15 |
| 3 | 1 | 8 | | | |

**Table 2** Values of two-center nuclear attraction integrals over STOs in molecular coordinate system (a.u.)

| $n$ | $l$ | $m$ | $\zeta$ | $n'$ | $l'$ | $m'$ | $\zeta'$ | $R$ | $\theta$ | $\varphi$ | Eq. (10) | Ref. 13 | CPU (msec) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 0 | 7.6 | 2 | 1 | 1 | 1.5 | 2.3 | 45 | 180 | 2.00987043387478E−03 | 2.00987043387524E−03 | — |
| 2 | 1 | 1 | 6.7 | 2 | 1 | 1 | 4.1 | 0.2 | 135 | 20 | 2.27254384427713E−00 | 2.27254384427714E−00 | — |
| 3 | 1 | 0 | 8.6 | 2 | 1 | 1 | 7.4 | 4 | 54 | 40 | −5.42130987268004E−04 | −5.42130987268124E−04 | — |
| 3 | 2 | 0 | 10.8 | 3 | 1 | 1 | 3.7 | 5.4 | 54 | 40 | 7.81819078634517E−04 | 7.81819078633329E−04 | — |
| 3 | 2 | 1 | 13.8 | 3 | 2 | 1 | 7.3 | 3.5 | 18 | 80 | 2.01752673993300E−01 | 2.01752673993300E−01 | 0.2 |
| 3 | 2 | 2 | 1.3 | 3 | 2 | 1 | 6.7 | 0.8 | 72 | 100 | −9.22910317271328E−04 | −9.22910317271328E−04 | 0.28 |
| 3 | 2 | 2 | 14.1 | 3 | 2 | −2 | 9.6 | 1.8 | 90 | 120 | 1.34137985116218E−04 | 1.34137985116187E−04 | 0.34 |
| 3 | 2 | 2 | 12.4 | 3 | 2 | 2 | 10.6 | 6.1 | 0 | 0 | 1.60316721578661E−01 | 1.60316721578661E−01 | 0.11 |
| 4 | 2 | 1 | 6.1 | 2 | 1 | 0 | 10.6 | 8.6 | 36 | 140 | 3.70472929702988E−04 | 3.70472929703281E−04 | 0.36 |
| 4 | 2 | 2 | 8.6 | 2 | 1 | 1 | 12.2 | 10.8 | 108 | 160 | 5.35136519862680E−04 | 5.35136519862794E−04 | 0.38 |
| 4 | 2 | −2 | 4.8 | 3 | 2 | 1 | 3.1 | 9.1 | 126 | 180 | −8.82285738243633E−25 | −8.82285738243633E−25 | 0.41 |
| 4 | 3 | 2 | 7.4 | 3 | 2 | 2 | 5.3 | 5.9 | 144 | 200 | −5.46603780760789E−03 | −5.46603780760856E−03 | 0.45 |
| 4 | 3 | 2 | 8.7 | 4 | 3 | 2 | 7.5 | 4.5 | 162 | 220 | 2.16776797962649E−01 | 2.16776797962649E−01 | 0.51 |

It should be noted that the algorithm presented in this paper could be used to calculate the three-center nuclear attraction integrals for the arbitrary values of parameters using translation formulas for STOs.

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