

# Calculation of two-center nuclear attraction integrals over integer and noninteger $n$ -Slater type orbitals in nonlined-up coordinate systems

T. Özdoğan \*, S. Gümüş and M. Kara

Department of Physics, Faculty of Education, Ondokuz Mayıs University, Amasya, Turkey

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Two-center nuclear attraction integrals over Slater type orbitals with integer and noninteger principal quantum numbers in nonlined up coordinate systems have been calculated by means of formulas in our previous work (T. Özdoğan and M. Orbay, *Int. J. Quant. Chem.* 87 (2002) 15). The computer results for integer case are in best agreement with the prior literature. On the other hand, the results for noninteger case are not compared with the literature due to the scarcity of the literature, but also compared with the limit of integer case and good agreements are obtained. The proposed algorithm for the calculation of two-center nuclear attraction integrals over Slater type orbitals with noninteger principal quantum numbers in nonlined-up coordinate systems permits to avoid the interpolation procedure used to overcome the difficulty introduced by the presence of noninteger principal quantum numbers. Finally, numerical aspects of the presented formulae are analyzed under wide range of quantum numbers, orbital exponents and internuclear distances.

**KEY WORDS:** Slater type orbitals, noninteger principal quantum numbers, nuclear attraction integrals, rotation coefficients

## 1. Introduction

Most electronic structure calculations are carried out in an algebraic framework where the Schrödinger equation, or some approximation thereof, is projected onto a finite space constructed from a basis of suitable one-particle functions. Slater type orbitals (STOs) [1] and Gaussian type orbitals (GTOs) [2] are the most common basis functions.

An STO is defined by

$$\chi_{nlm}(\zeta, \vec{r}) = \frac{(2\zeta)^{n+1/2}}{\sqrt{\Gamma(2n+1)}} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi), \quad (1)$$

where  $\zeta$  is orbital exponent,  $\Gamma(n)$  is gamma function [3], and the functions  $S_{lm}(\theta, \varphi)$  are complex or real spherical harmonics [4].

However, there are extensive literatures on the evaluation of multicenter integrals over STOs with integer principal quantum numbers (integer  $n$ -STOs), it is well-known

\* Corresponding author. E-mail: telhatoz@omu.edu.tr

that STOs with noninteger principal quantum numbers (noninteger  $n$ -STOs) provide a more flexible basis for molecular calculations than integer  $n$ -STOs [5–22]. Also it was demonstrated unequivocally that noninteger  $n$ -STOs are more accurate than are integer  $n$ -STOs and particularly so when  $d$ -orbitals are involved. For the detailed discussion of the use of noninteger  $n$ -STOs in molecular calculations the study of Bishop [12] is advised for reading and wide range of literatures.

Some work was done on multicenter integrals involving noninteger  $n$ -STOs by Geller [10,11], Silverstone [12], Allouche [14], Taylor [15], Mekelleche and Baba-Ahmed [16–19] with cumbersome algebra. The aim of this work is to calculate two-center nuclear attraction integrals over integer and noninteger  $n$ -STOs in nonlined-up coordinate systems efficiently since this integral constitute the basic building block in the calculation of other multicenter integrals when the series expansion formulas for translation of STOs are used [23].

Atomic units (a.u.) are used from this point onwards.

## 2. Two-center nuclear attraction integrals over integer and noninteger $n$ -STOs

Two-center nuclear attraction integrals examined in the present work (in nonlined-up coordinate systems) have the following form:

$$U_{nlm,n'l'm'}^{(A)}(\zeta, \zeta'; \vec{R}, \theta, \varphi) = \int \chi_{nlm}^*(\zeta, \vec{r}_a) \frac{1}{r_a} \chi_{n'l'm'}(\zeta', \vec{r}_b) dV, \quad (2)$$

$$U_{nlm,n'l'm'}^{(B)}(\zeta, \zeta'; \vec{R}, \theta, \varphi) = \int \chi_{nlm}^*(\zeta, \vec{r}_a) \frac{1}{r_b} \chi_{n'l'm'}(\zeta', \vec{r}_b) dV, \quad (3)$$

where  $(R, \theta, \varphi)$  are the spherical-polar coordinates of radius vector  $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$ ,  $\chi_{nlm}(\zeta, \vec{r}_a)$  and  $\chi_{n'l'm'}(\zeta', \vec{r}_b)$  are normalized complex or real STOs centered on the nuclei  $a$  and  $b$ , respectively.

For the calculation of nuclear attraction integrals in nonlined-up coordinate systems it is need to rotate two-center nuclear attraction integrals from lined-up coordinate systems to nonlined-up coordinate systems:

$$U_{nlm,n'l'm'}^{(A,B)}(\zeta, \zeta'; \vec{R}, \theta, \varphi) = \sum_{\lambda=0}^{\min(l,l')} T_{lm,l'm'}^{\lambda}(\theta, \varphi) U_{nl\lambda,n'l'\lambda}^{(A,B)}(\zeta, \zeta'; \vec{R}), \quad (4)$$

where  $U_{nl\lambda,n'l'\lambda}^{(A,B)}$  are two-center nuclear attraction integrals in lined-up coordinate systems and  $T_{lm,l'm'}^{\lambda}$  are rotation coefficients for two-center one electron integrals defined by

$$T_{lm,l'm'}^{\lambda}(\theta, \varphi) = \frac{2}{(1 + \delta_{\lambda 0})[(1 + \delta_{m 0})(1 + \delta_{m' 0})]^{1/2}} \times \sum_{i=\pm}^{(2)} \sum_{L=|l-l'|}^{l+l'}^{(2)} (\varepsilon_{m 0})^{\delta_{i,\varepsilon_{mm'}}} C_{i\gamma,\gamma',i\gamma+\gamma'}^{l'l'L} C_{\lambda,-\lambda,0}^{l'lL} \times \left[ \frac{2\pi (1 + \delta_{M_i 0})}{2L + 1} \right]^{1/2} S_{LM_i}(\theta, \varphi) \quad (5)$$

in which  $C_{mm'M}^{l'lL}$  are Clebsch–Gordan coefficients,  $\gamma = |m|$ ,  $\gamma' = |m'|$  and  $M_i = \varepsilon_{mm'} |i\gamma + \gamma'|$  and  $\varepsilon_{mm'} = \text{sign}(m) \cdot \text{sign}(m')$ . In equation (5), the symbol  $\sum^{(2)}$  indicates that the summation is to be performed in steps of two. For  $\gamma = \gamma'$  and  $\varepsilon_{mm'} = -1$ , terms with a negative value of index  $i$  ( $i = -1$ ) contained in equation (5) should be equated to zero [24].

We have presented recently an algorithm for the evaluation of nuclear attraction integrals over integer and noninteger  $n$ -STOs in lined-up coordinate system, by the use of ellipsoidal coordinates method, as follows [25,26].

(a) Nuclear attraction integrals over integer  $n$ -STOs:

$$\begin{aligned}
 &U_{nl\lambda,n'l'\lambda}^{(A)}(\zeta, \zeta'; \vec{R}) \\
 &= \frac{2}{R} N_{nn'}(p, t) (-1)^{l'-\lambda} \sum_{k,k'} \sum_{u,s} a_{us}^{kk'}(l\lambda, l'\lambda) \\
 &\quad \times \sum_{h=0}^{\gamma-1} F_h(n-l+2k+2k'+2\lambda-2u-1, n'-l') A_i(p) B_j(pt), \quad (6)
 \end{aligned}$$

$$\begin{aligned}
 &U_{nl\lambda,n'l'\lambda}^{(B)}(\zeta, \zeta'; \vec{R}) \\
 &= \frac{2}{R} N_{nn'}(p, t) (-1)^{l'-\lambda} \sum_{k,k'} \sum_{u,s} a_{us}^{kk'}(l\lambda, l'\lambda) \\
 &\quad \times \sum_{h=0}^{\gamma-1} F_h(n-l+2k+2k'+2\lambda-2u, n'-l'-1) A_i(p) B_j(pt); \quad (7)
 \end{aligned}$$

(b) Nuclear attraction integrals over noninteger  $n$ -STOs:

$$\begin{aligned}
 &U_{nl\lambda,n'l'\lambda}^{(A)}(\zeta, \zeta'; \vec{R}) \\
 &= \frac{2}{R} N_{nn'}(p, t) (-1)^{l'-\lambda} \sum_{k,k'} \sum_{u,s} a_{us}^{kk'}(l\lambda, l'\lambda) \\
 &\quad \times \sum_{h=0}^{\infty} f_h(n-l+2k+2k'+2\lambda-2u-1, n'-l') A_i(p) B_j(pt), \quad (8)
 \end{aligned}$$

$$\begin{aligned}
 &U_{nl\lambda,n'l'\lambda}^{(B)}(\zeta, \zeta'; \vec{R}) \\
 &= \frac{2}{R} N_{nn'}(p, t) (-1)^{l'-\lambda} \sum_{k,k'} \sum_{u,s} a_{us}^{kk'}(l\lambda, l'\lambda) \\
 &\quad \times \sum_{h=0}^{\infty} f_h(n-l+2k+2k'+2\lambda-2u, n'-l'-1) A_i(p) B_j(pt). \quad (9)
 \end{aligned}$$

The parameters contained in equations (6)–(9) are:

$$p = \frac{R(\zeta + \zeta')}{2}; \quad t = \frac{\zeta - \zeta'}{\zeta + \zeta'}, \quad (10a)$$

$$N_{nn'}(p, t) = \frac{[p(1+t)]^{n+1/2}[p(1-t)]^{n'+1/2}}{\sqrt{\Gamma(2n+1)\Gamma(2n'+1)}}, \quad (10b)$$

$$i = (n + n') - (l + l') + 2(k + k' + \lambda) - 2u + s - h - 1, \quad j = h + s, \quad (10c)$$

$$\gamma = (n + n') - (l + l') + 2(k + k' + \lambda) - 2u, \quad (10d)$$

and the ranges of the indices  $k, k', u$  and  $s$  are as follows:

$$0 \leq k \leq E\left(\frac{l - \lambda}{2}\right), \quad 0 \leq k' \leq E\left(\frac{l' - \lambda}{2}\right), \quad (11a)$$

$$0 \leq u \leq (k + k' + \lambda), \quad 0 \leq s \leq (l + l') - 2(k + k' + \lambda) + 2u, \quad (11b)$$

with

$$E\left(\frac{n}{2}\right) = \frac{n}{2} - \frac{1}{4}(1 - (-1)^n). \quad (12)$$

The functions  $a_{us}^{kk'}(l\lambda, l'\lambda)$  contained in equations (6)–(9) are the expansion coefficients for the product of two normalized associated Legendre functions arising in the evaluation of multicenter integrals (see appendix for derivation of expansion coefficients  $a_{us}^{kk'}(l\lambda, l'\lambda)$ ):

$$a_{us}^{kk'}(l\lambda, l'\lambda) = (-1)^u F_u(k + k' + \lambda) F_s(l - 2k - \lambda + 2u, l' - 2k' - \lambda) C_{l\lambda}^k C_{l'\lambda}^{k'} \quad (13)$$

with

$$F_m(N, N') = \sum_{i,j=0}^m (-1)^{N'-j} F_i(N) F_j(N'); \quad F_m(n) = \frac{n!}{m!(n-m)!}, \quad (14)$$

$$C_{lm}^k = \frac{(-1)^k}{2^{2k+m}} \left[ \frac{2l+1}{2} F_{l-k}(l+m) F_{k+m}(l-k) F_{2k}(l-m) F_k(2k) \right]^{1/2}. \quad (15)$$

The function  $F_m(N, N')$  is defined for integer  $N$  and  $N'$ . In the case of noninteger  $N$  and  $N'$ , this function takes the form  $f_m(N, N')$  defined by

$$f_m(N, N') = \sum_{\sigma=0}^{\infty} (-1)^\sigma f_{m-\sigma}(N) f_\sigma(N'), \quad (16)$$

in which

$$f_m(N) = \frac{(-1)^m \Gamma(m-N)}{m! \Gamma(-N)}. \quad (17)$$

The auxiliary functions  $A_k(p)$  and  $B_k(pt)$  involved in equations (6)–(9) are the well-known Mulliken's integrals [27] and the numerical implementation of these functions can be found in [28,29].

### 3. Computational results and discussions

On the basis of formulae presented in this work and in [25,26] we have constructed computer programs in Turbo Pascal 7.0 programming language for the evaluation of two-center nuclear attraction integrals over integer and noninteger  $n$ -STOs in nonlined-up coordinate system by rotating integrals in lined-up coordinate systems. The efficiency of computer results depends deeply on the accurate calculation of the auxiliary functions  $A_k$ ,  $B_k$  and  $f_m(N, N')$ . In our previous paper [28], we have analyzed the best running range for the auxiliary functions  $A_k$  and  $B_k$ . The auxiliary functions  $A_k$ ,  $B_k$  and  $F_m(N, N')$ , and rotation coefficients  $T_{lm,l'm'}^\lambda(\theta, \varphi)$  are stored in the memory of the computer during compilation of the programs and get back from the memory during calculations. This is very memory consuming but very time gaining. The convergence limit for nuclear attraction integrals over noninteger  $n$ -STOs in lined-up coordinate systems is determined for 18-decimal digit accuracy, with typically at most 20–40 terms in infinite sums, in the whole calculations.

Numerical results for two-center nuclear attraction integrals over integer  $n$ -STOs in nonlined-up coordinate systems are given in table 1. Our computer results for this case are in best agreement with [30,31], at least for 13-decimal digit accuracy. The computer results for two-center nuclear attraction integrals over noninteger  $n$ -STOs are listed in table 2 with no comparison due to the scarcity of the literature. But also we have tested the results for limit of noninteger case with integer case, and good agreement have been obtained. To the best of our knowledge, the results presented in this work for two-center nuclear attraction integrals over noninteger  $n$ -STOs in nonlined-up coordinate systems will be the first in the literature.

The numerical performance of the formulas for two-center nuclear attraction integrals over noninteger  $n$ -STOs have been analyzed. As can be seen from figure 1 the infinite sums in equations (8) and (9) converge rapidly by decreasing internuclear dis-

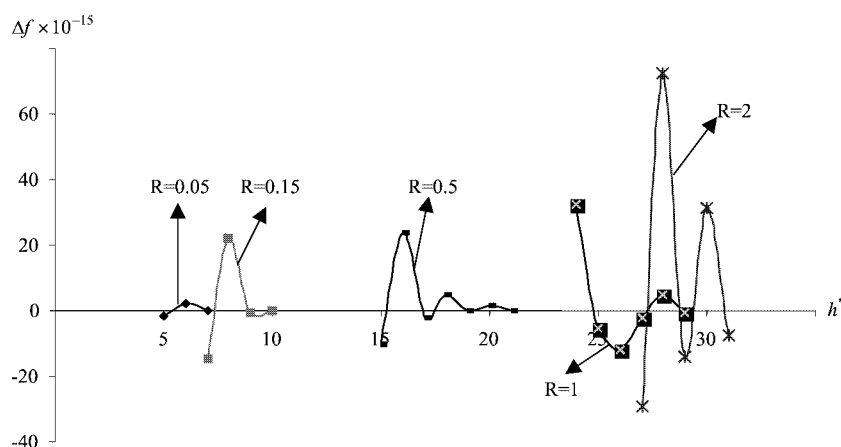


Figure 1. Convergence of infinite series (8) versus internuclear distances.  $h$  denotes the upper limit of summation indices in equation (8).

Table 1  
Comparative values for two-center nuclear attraction integrals over integer  $n$ -STOs (in a.u.).

$n$	$l$	$m$	$n'$	$l'$	$m'$	$\zeta$	$\zeta'$	$R$	$\theta$	$\varphi$	$U(A)$	$U(B)$
2	1	1	3	2	0	6	4	0.2	120	45	-3.01210886262645E-01	-2.07878011190490E-01
4	3	2	2	1	1	6.5	3.5	7.5	45	60	-6.13094833488931E-10	-1.72374065526525E-10
8	7	4	7	6	6	5	5	15	30	120	-1.49147476663654E-20	-1.70454259044180E-20
12	11	11	13	12	12	0.5	9.5	4	60	210	1.60267358965124E-12	4.48156811654186E-12
15	8	7	17	10	9	7	3	2	135	150	2.16991567571567E-03	1.26475881962798E-03
17	4	4	18	3	2	8	2	1.5	150	240	-6.16622891350373E-06	-2.87124703297172E-06
20	15	14	20	15	14	0.6	0.4	2.4	30	60	9.97142854301042E-03	9.94426376972577E-03
24	20	15	25	20	14	0.8	0.2	3.5	22.5	135	-4.53754361226039E-09	-5.13120878758356E-09
28	25	14	26	24	12	5.5	4.5	6	15	90	-8.52181751519504E-03	6.22347686836766E-03
30	8	7	30	9	8	8.5	1.5	8	60	30	1.29866257807686E-06	2.09576395022971E-07
35	10	10	36	10	9	0.7	0.3	3	40	150	1.24562949320417E-07	8.62148805018620E-08
40	8	7	40	7	7	0.04	0.06	40	30	60	3.88278832012582E-05	4.14600646894658E-05

Table 2  
Computer results for two-center nuclear attraction integrals over noninteger  $n$ -STOs (in a.u.).

$n$	$l$	$m$	$n'$	$l'$	$m'$	$\zeta$	$\zeta'$	$R$	$\theta$	$\varphi$	$U(A)$	$U(B)$
1.8	1	0	2.1	1	1	7	3	3	45	150	-3.91965065923110E-03	-9.68096569343648E-04
3.4	2	2	3.6	2	1	5.5	4.5	2	120	240	6.42901996397275E-02	5.31988152171202E-02
5.7	4	3	6.4	4	4	8	2	1.4	60	45	2.87974317001977E-03	1.04052159615994E-03
8.5	7	6	8.8	6	6	9	1	0.4	22.5	60	-1.67984037750840E-07	1.68657820669978E-06
10.3	9	8	9.7	8	7	8.5	1.5	1.8	150	30	-1.76442519777183E-04	1.4570277270606E-04
12.1	6	3	13.5	7	5	7.5	2.5	2.4	75	120	-9.17355319118306E-04	-6.54377661806302E-04
14.9	4	4	15.2	7	7	5	5	5	30	45	-1.34860551259631E-03	-1.14680752793084E-03
16.6	10	10	16.8	12	11	0.75	0.25	6	60	150	7.22012310014807E-05	6.19658242700741E-05
17.4	4	3	18.8	5	3	0.07	0.03	15	120	240	6.61299163366883E-06	6.09359822645633E-06
20.5	3	2	21.3	4	3	5.3	4.7	2.5	60	30	7.33621082311529E-02	6.12740242765154E-02
22.7	5	5	25.8	6	4	3.2	6.8	0.5	30	120	-2.33680027843102E-05	-5.45419844885583E-05
27.4	6	5	26.3	6	6	6.2	3.8	0.15	80	70	4.42278770054648E-06	7.39827301897260E-06

tances. It should be noted that the convergence of these infinite series becomes somewhat slower as the values of  $t$  increase.

Another important aspect of the formulae presented in this work is that two-center nuclear attraction integrals over integer and noninteger  $n$ -STOs is calculated easily in the case of near or equal values of orbital and magnetic quantum numbers, and also in the case of high values of principal quantum numbers.

Analyzing two-center nuclear attraction integrals it is observed that two-center one-electron integrals have the following useful relation which enable us to calculate these integrals for larger values of internuclear distances or small values of orbital exponents that computer may give inaccurate results:

$$U_{nlm,n'l'm'}(\xi, \xi'; \vec{R}, \theta, \varphi) = U_{nlm,n'l'm'}\left(\frac{\xi}{2}, \frac{\xi'}{2}; 2\vec{R}, \theta, \varphi\right). \quad (\text{A.17})$$

The proposed algorithm for the calculation of two-center nuclear attraction integrals over integer and noninteger  $n$ -STOs permits to avoid the interpolation procedure used to overcome the difficulty introduced by the presence of noninteger principal quantum numbers.

Consequently, the formulae presented in this work show good rate of convergence and great numerical stability under wide range of quantum numbers, orbital exponents and internuclear distances. Work is in progress for the evaluation of the multicenter molecular integrals over integer and noninteger  $n$ -STOs based on the computer results for the formulae presented in this work.

### Appendix. Derivation of expansion coefficients $a_{us}^{kk'}(l\lambda, l'\lambda)$

When dealing with the evaluation of multicenter integrals, the product of two normalized associated Legendre functions is encountered. In this section, we will give the derivation of expansion coefficients  $a_{us}^{kk'}(l\lambda, l'\lambda)$  of the product of two normalized associated Legendre functions.

Following definition for normalized associated Legendre functions and interconversions between spherical and elliptical coordinates, one can easily write

$$T^{l\lambda, l'\lambda}(\mu, \nu) = \sum_{k, k'} \sum_{u, s} a_{us}^{kk'}(l\lambda, l'\lambda) \frac{(\mu\nu)^s}{(\mu + \nu)^{l-2(k+k'+\lambda)+2u} (\mu - \nu)^{l'}}. \quad (\text{A.1})$$

Here, the expansion coefficients are  $a_{us}^{kk'}(l\lambda, l'\lambda)$ :

$$a_{us}^{kk'}(l\lambda, l'\lambda) = C_{l\lambda}^k C_{l'\lambda}^{k'} (-1)^u F_u(k + k' + \lambda) F_s(l - 2k - \lambda + 2u, l' - 2k' - \lambda), \quad (\text{A.2})$$

in which  $F_m(n, n')$  are expansion coefficients in

$$(\mu + \nu)^n (\mu - \nu)^{n'} = \sum_{m=0}^{n+n'} F_m(n, n') \mu^{n+n'-m} \nu^m, \quad (\text{A.3})$$

as defined in equation (14). The ranges of the summation indices  $k$ ,  $k'$ ,  $u$  and  $s$  are given by equation (11).

The expansion formula given by equation (A.1) can be used in the evaluation of multicenter multielectron integrals over STOs, and now we are studying on this project, expecting to attain higher accuracy and speed in the case of near values of orbital and magnetic quantum numbers.

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