

Calculation of three-center nuclear attraction integral over Slater type orbitals in molecular coordinate system using Löwdin α -radial function and Guseinov's two-center charge density expansion formulae

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Abstract Using Löwdin α -radial function and the Guseinov's charge density expansion formulae, the calculation of the three-center nuclear attraction integrals over Slater type orbitals in molecular coordinate system is performed. The proposed algorithm is especially useful for computation of multicenter-multielectron integrals that arise in the Hartree-Fock-Roothaan approximation, which plays a significant role for the study of electronic structure and electron-nuclei interaction properties of atoms, molecules and solids. The algorithm described in the present work is valid for the arbitrary values of quantum numbers, screening constants and internuclear distances. The calculation results are in good agreement with those obtained using the alternative evaluation procedure.

Keywords Slater type orbitals · Three-center nuclear attraction integrals · Löwdin α function · Guseinov charge density expansion formula

1 Introduction

It is well known that the determination of multielectron properties for atoms and molecules requires more accurate solutions of Hartree-Fock-Roothaan (HFR) equations [1,2]. The matrix elements of nuclear attraction and electron-repulsion operators between the determinantal wave functions of molecules arising from HFR equations are expressed through the multicenter integrals with the same operators. The difficulties in solving the multicenter molecular integrals over Slater-type orbitals (STOs), in particular the three-center nuclear attraction integrals, have restricted their use in electronic structure calculations of molecules. Since the early years of quantum chemistry,

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the evaluation of molecular integrals over STOs has attracted attention continuously [3–22]. To our knowledge, many authors have addressed this problem and, although a lot of improvement has been made in the past years by the use of computers, an efficient program for the calculation of the three-center nuclear attraction integral over STOs are not yet available in the literature [21, 22]. In spite of all developments, the evaluation of the three-center nuclear attraction integral over STOs is still one of the main problems. The Löwdin α -radial function convoluted with the Guseinov's two-center charge density expansion formula is one of the most important ingredients for accurate and efficient implementation of electronic structure calculation methods regardless of HFR method [23, 24]. With this in mind, we have obtained the general analytical expression for the three-center nuclear attraction integrals in molecular coordinate system using convolution of the Löwdin α -radial function and the Guseinov's two-center charge density expansion formula with the arbitrary values of integral parameters [21–28].

2 Löwdin α -radial and Guseinov- charge density expansion functions

It is well known that the molecular integrals over STOs can be expressed in terms of $C_l^{nlm}(i, j)$ coefficients by using Löwdin α -radial functions [29, 30]. The main approach is to use the polynomial expression derived by Jones, in which $C_l^{nlm}(i, j)$ coefficients are written as the matrix form. Analytical expressions for $C_l^{nlm}(i, j)$ coefficients in terms of summation of products of factorials have been published in [29, 30]. By using Jones's polynomial method we can write the Sharma's analytical formula for the $C_l^{nlm}(i, j)$ coefficients in the following form [24–26]:

$$C_l^{nl\lambda}(i, j) = \begin{cases} \frac{(l-\frac{1}{2})!(l'-\frac{1}{2})!}{(l+\lambda)!(l'-\lambda)!} \sum_{K=0}^{\min\{[i/2], l+l'\}} \sum_{k=0}^{\min\{[j/2], l+l'-K\}} \frac{(n+l+2l'-2K-2k)!}{(i-2K)!(j-2k)!} \\ \times b_{l+l'-K-k}(l\lambda\lambda') & \text{for } i + j \leq n + l - \lambda + 2l' \\ 0 & \text{for } i + j > n + l - \lambda + 2l' \end{cases}, \quad (1)$$

where

$$b_{Kk}(l\lambda\lambda') = \frac{(l-\lambda)!(l+\lambda)!(l'-\lambda)!(l'+\lambda)!(l-K-\frac{1}{2})!(l'-k-\frac{1}{2})!}{(l+l'-K-k)!(l-\frac{1}{2})!K!(l'-\frac{1}{2})!k!} \\ \times \sum_{s=0}^{l-\lambda} \frac{(-l+K+k+s-\frac{1}{2})!}{s!(l-\lambda-s)!(l'-l+s)!(-l+s-\frac{1}{2})!(l+\lambda-s)!}. \quad (2)$$

The factorial $(p-1/2)!$ in Eqs. 1 and 2 has the form [31]

$$(p-1/2)! = \begin{cases} (p-1/2)(p-3/2)\dots 1/2 & \text{for a positive integer } p \\ 1/[-1]^{(-1)^{-p}}(-p-1/2)! & \text{for a negative integer } p \end{cases} \quad (3)$$

with $(-1/2)! \equiv 1$. Thus the following relation holds [31]:

$$(p - 1/2)!(-p - 1/2)! = (-1)^p. \tag{4}$$

We notice that Eq. 1 is valid for arbitrary values of parameters.

The Guseinov two-center charge density expansion formula over STOs is given [21] by

$$\begin{aligned} &\chi_{nlm}(\zeta, \vec{r}_a)\chi_{n'l'm'}^*(\zeta', \vec{r}_c) \\ &= \frac{1}{4\pi} \lim_{N \rightarrow \infty} \sum_{\mu=1}^N \sum_{\nu=0}^{\mu-1} \sum_{-\nu}^{\nu} W_{nlm,n'l'm',\mu\nu\sigma}^{\alpha N}(\zeta, \zeta', z; \vec{R}_{ca}, 0) \chi_{\mu\nu\sigma}(z, \vec{r}_a) \end{aligned} \tag{5}$$

where

$$\begin{aligned} &W_{nlm,n'l'm',\mu\nu\sigma}^{\alpha N}(\zeta, \zeta', z; \vec{R}_{ca}, 0) \\ &= \lim_{N' \rightarrow \infty} \sum_{\mu'=1}^{N'} \sum_{\nu'=0}^{\mu'-1} \sum_{\sigma'=-\nu'}^{\nu'} W_{nlm,\mu'\nu'\sigma',\mu\nu\sigma}^{\alpha N}(\zeta, \zeta', z; 0, 0) V_{n'l'm',\mu'\nu'\sigma'}^{\alpha N'}(\zeta', \zeta'; \vec{R}_{ca}) \end{aligned} \tag{6}$$

$$V_{nlm,n'l'm'}^{\alpha N}(\zeta, \zeta'; \vec{R}) = \sum_{n''=l'+1}^N \Omega_{n'n''}^{\alpha l'}(N) S_{nlm,n''-\alpha l'm'}(\zeta, \zeta'; \vec{R}). \tag{7}$$

Here $S_{nlm,n'l'm'}$ is the overlap integral and

$$\Omega_{n\kappa}^{\alpha l}(N) = \left[\frac{[2(k - \alpha)]!}{(2\kappa)!} \right]^{\frac{1}{2}} \sum_{n'=\max(n,\kappa)}^N (2n')^\alpha \omega_{n'n}^{\alpha l} \omega_{n'\kappa}^{\alpha l}, \tag{8}$$

$$\begin{aligned} \omega_{nn'}^{\alpha l} &= (-1)^{n'-l-1} \\ &\times \left[\frac{(n' + l + 1)!}{(2n)^\alpha (n' + l + 1 - \alpha)!} F_{n'+l+1-\alpha}(n + l + 1 - \alpha) \right. \\ &\quad \left. F_{n'-l-1}(n - l - 1) F_{n'-l-1}(2n') \right]^{1/2}. \end{aligned} \tag{9}$$

$$W_{nlm,n'l'm',\mu\nu\sigma}^{\alpha N}(\zeta, \zeta', z; 0, 0) = W_{nlm,n'l'm',k\nu\sigma}(\zeta, \zeta', z) V_{kv,\mu\nu}^{\alpha N} \tag{10}$$

$$V_{kv,\mu\nu}^{\alpha N} = \sum_{\mu'=\nu+1}^N \Omega_{\mu\mu'}^{\alpha \nu}(N) (k + \mu' - \alpha)! / [2k!(2\mu' - 2\alpha)!]^{1/2} \tag{11}$$

$$\begin{aligned} &W_{nlm,n'l'm',k\nu\sigma}(\zeta, \zeta', z) \\ &= \frac{z^{3/2}}{2^k} \left[\frac{2\nu + 1}{2} \frac{(2k)!}{(2n)!(2n')!} \right]^{1/2} \\ &\times (1 + t)^{n+\frac{1}{2}} (1 - t)^{n'+\frac{1}{2}} C^{|\sigma|}(lm, l'm') A_{mm'}^\sigma \delta_{k,n+n'-1}. \end{aligned} \tag{12}$$

The generalized Gaunt coefficients $C^{\nu|\sigma|}(lm, l'm')$, and $A_{mm'}^{\sigma}$ in Eq. 12 are determined by the following relationships [21]:

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

$$A_{mm'}^M = \begin{cases} \frac{1}{\sqrt{2}} \left(2 - |\eta_{mm'}^{m-m'}|\right)^{1/2} \delta_{M,\varepsilon|m-m'|} + \frac{1}{\sqrt{2}} \eta_{mm'}^{m+m'} \delta_{M,\varepsilon|m+m'|} & \text{for real STOs} \\ \delta_{M,m-m'} & \text{for complex STOs} \end{cases} \quad (14)$$

See [21] for the exact definition of quantities $\eta_{mm'}^{m\pm m'}$ and $\varepsilon = \varepsilon_{mm'}$

3 Analytical expression for three-center nuclear attraction integrals with STOs

The three-center nuclear attraction integrals over STOs are defined with respect to a molecular coordinate system by

$$I_{nlm,n'l'm'}(\zeta, \zeta', \vec{R}_{ca}, \vec{R}_{ab}) = \int \chi_{nlm}^*(\zeta, \vec{r}_a) \chi_{n'l'm'}(\zeta', \vec{r}_c) \frac{1}{r_b} d^3\vec{r}, \quad (15)$$

where $\vec{R}_{ab} = \vec{r}_a - \vec{r}_b$, $\vec{R}_{ca} = \vec{r}_c - \vec{r}_a$ and

$$\chi_{nlm}(\zeta, \vec{r}) = (2\zeta)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \quad (16)$$

Here, the complex and real spherical harmonics S_{lm} are determined by

$$S_{lm}(\theta, \varphi) = P_{l|m|}(\cos \theta) \Phi_m(\varphi), \quad (17)$$

where $P_{l|m|}$ are the normalized associated Legendre functions [32] and for complex spherical harmonics (SH)

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad (18)$$

for real spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1 + \delta_{m0})}} \begin{cases} \cos |m| \varphi & \text{for } m \geq 0 \\ \sin |m| \varphi & \text{for } m < 0 \end{cases}. \quad (19)$$

It should be noted that our definition of phases for complex spherical harmonics ($Y_{lm}^* = Y_{l-m}$) differs from the Condon-Shortley phases [33] by the sign factor.

By using Guseinov’s two-center charge density expansion formula, it is easy to obtain for the three-center nuclear attraction integral over STOs the following formula [22]:

$$I_{nlm,n'l'm'}(\zeta, \zeta'; \vec{R}_{ca}, \vec{R}_{ab}) = \lim_{N \rightarrow \infty} \sum_{\mu=1}^N \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W_{nlm,n'l'm',\mu\nu\sigma}^{\alpha N}(\zeta, \zeta', z; \vec{R}_{ca}, 0) J_{\mu\nu\sigma}(z, \vec{R}_{ab}), \quad (20)$$

where $\alpha = 1, 0, -1, -2, \dots$ and $z = \zeta + \zeta'$. In Eq. 20, $J_{\mu\nu\sigma}(z, \vec{R}_{ab})$ are the basic nuclear attraction integrals determined as

$$J_{nlm}(\zeta, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int \chi_{nlm}^*(\zeta, \vec{r}_a) \frac{1}{r_b} d^3\vec{r}. \quad (21)$$

As seen from Eq. 20, the choice of reliable formulas for the evaluation of overlap integrals $S_{nlm,n'l'm'}$ and basic nuclear attraction integrals $J_{\mu\nu\sigma}(z, \vec{R}_{ab})$ has the prime importance in accurately calculating the three-center nuclear attraction integrals over STOs in molecular coordinate system. Several useful procedures for evaluating the overlap integrals $S_{nlm,n'l'm'}$ and basic nuclear attraction integrals $J_{\mu\nu\sigma}(z, \vec{R}_{ab})$ can be found in literature [21–23].

In our recently published paper [23], an efficient and reliable accurate formula has been presented for the direct evaluation of basic nuclear attraction integrals by using Löwdin α -radial function:

$$J_{nlm}(\zeta, \vec{R}) = 2^n \left(\frac{2l+1}{2\zeta (2n)!} \right)^{1/2} \sum_{i=0}^{n+l} \sum_{j=0}^n j! C_0^{nl0}(i, j) \times \left[e^{-\zeta R} (R\zeta)^{i-l-1} \left((-1)^{i-j-1} - 1 \right) + \sum_{k=0}^j \frac{1}{(j-k)!} (R\zeta)^{i+j-l-k-1} \left((-1)^i - (-1)^{j-k-1} \right) \right] S_{lm}(\theta, \varphi). \quad (22)$$

As can be seen from Eqs. 6, 7 and 22 that the three-center nuclear attraction integrals over STOs in molecular coordinate system are expressed through the Guseinov’s two-center charge density expansion formula and Löwdin α -radial functions.

4 Numerical results and discussion

We proposed calculation algorithm for the three-center nuclear attraction integrals over STOs in molecular coordinate system. From the viewpoint of the computational efficiency and accuracy of our and various approximations, the three-center

Table 1 Comparison methods of computing three-center nuclear attraction integrals over STOs obtained in the molecular coordinate system for $N = 15$ (in a.u.)

n	l	m	ζ	n'	l'	m'	ζ'	R_{ca}	θ_{ca}	ϕ_{ca}	R_{ab}	θ_{ab}	ϕ_{ab}	Eq. 20		Refs. [22]
														$\alpha = 0$	$\alpha = 1$	
1	0	0	4.1	1	0	0	2.3	3.2	144	240	3.5	180	288	8.584046588E-4	8.583952977E-4	8.584046728E-4
1	0	0	9	1	0	0	3	2.3	90	240	2.3	90	180	7.644832112E-4	7.643097243E-4	7.645995858E-4
2	1	1	7.6	1	0	0	3.4	2.1	108	300	1.4	60	180	2.594160883E-3	2.597283035E-3	2.594160871E-3
2	1	1	8.5	2	1	0	5.3	1.7	36	60	2.2	30	108	1.674296990E-3	1.674285618E-3	1.674297177E-3
2	1	1	9.6	2	1	1	6.3	0.8	30	45	1.8	120	72	2.126040768E-2	2.1260403949E-2	2.111570172E-2
3	1	1	8.7	3	1	1	3.5	2.8	120	135	2.1	150	108	-1.30812045E-3	-1.309640295E-3	-1.31684047E-3

Table 2 Convergence of the series expansion relations for three-center nuclear attraction integrals over STOs as a function of summation limits for N

N	Eq. 20 for $I_{211,211} (6.1, 2.2, \vec{R}_{ca}, \vec{R}_{ab})$
8	0.6782940084566805
9	0.6783058641030268
10	0.6782948818257085
11	0.6782779936375349
12	0.6782630509422058
13	0.6782527281088085
14	0.6782470729731457
15	0.6782450448130202
16	0.6782453589897365
17	0.6782468905679029
18	0.6782488182752487
19	0.6782506302505485
20	0.6782520676635844
21	0.6782530503329973

$$R_{ca} = 0.1, \quad \theta_{ca} = 30,$$

$$\phi_{ca} = 60, \quad R_{ab} = 0.8,$$

$$\theta_{ab} = 120, \quad \phi_{ab} = 150,$$

$$\alpha = 0$$

Table 3 Convergence of the series expansion relations for three-center nuclear attraction integrals over STOs as a function of summation limits for N

N	Eq. 20 for $I_{100,100} (4.1, 2.3, \vec{R}_{ca}, \vec{R}_{ab})$
8	0.00085356557963337
9	0.00085802551708385
10	0.00085884731127713
11	0.00085853829707925
12	0.00085837189196420
13	0.00085837937153217
14	0.00085840576799912
15	0.00085840465880694
16	0.00085839883252226
17	0.00085840189335944
18	0.00085840566849512
19	0.00085840407453633
20	0.00085840099547699
21	0.00085840069305671

$$R_{ca} = 3.2, \quad \theta_{ca} = 144,$$

$$\phi_{ca} = 240, \quad R_{ab} = 3.5,$$

$$\theta_{ab} = 180, \quad \phi_{ab} = 288,$$

$$\alpha = 0$$

nuclear attraction integrals over STOs in molecular coordinate system were evaluated with Mathematica 6.0 international mathematical software. As seen from Eq. 20, the problem of the three-center nuclear attraction integrals over STOs in molecular coordinate system reduces to the calculation of Guseinov's two-center charge density expansion formula and Löwdin α -radial functions. The results of calculations for three-center nuclear attraction integrals are given in Tables 1, 2 and 3. As can be seen from the Table 1, we compared these numerical results with those obtained using the

alternative schemes in Ref. [22]. As will be clear from our tests, all the equations yield the expected results. We see from Tables 2 and 3 that our results show a good rate of convergence and numerical stability under a wide range of quantum numbers, orbital exponents and internuclear distances. The algorithms proposed in this work can be useful for the fast calculations of three-center nuclear attraction integrals. The computer time required for the calculation of three-center nuclear attraction integrals are not given in the tables due to the fact that the comparison cannot be made with the different computers used in the literature. For instance, for $I_{211,211} \left(6.1, 2.2, \vec{R}_{ca}, \vec{R}_{ab} \right)$ with sets $R_{ca} = 0.1, \theta_{ca} = 30, \phi_{ca} = 60, R_{ab} = 0.8, \theta_{ab} = 120, \phi_{ab} = 150, \alpha = 0, N = 15$, CPU time takes about 4.758 ms.

We notice that the algorithm presented in this work is of a completely general type and can be used to calculate the three-center nuclear attraction integrals with the arbitrary values of integer principal quantum numbers, screening constants and location of STOs appearing in the HFR equations for molecules.

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