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

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Abstract

The application of the Löwdin α-radial function and Guseinov one-center charge density expansion formulas in the accurate evaluation of two center nuclear attraction integrals over Slater type orbitals (STOs) is considered. Extensive numerical tests and comparisons with some already existing methods show that this approach for the calculation of two-center nuclear attraction integrals is more efficient and competitive. The convoluation process is time consuming with minimal computational effort for arbitrary principal quantum numbers, screening constant and location of STOs.

I. Introduction

The evaluation of two-center nuclear attraction integrals over STOs contained in the Hartree- Fock Roothaan (HFR) equations plays a decisive role in calculating the various molecular parameters [1-4]. These integrals arise not only in their own right, but are also central to the calculation of the multicenter electron-repulsion and three-center nuclear attraction integrals based on the one-range addition theorems given in Refs. [3, 4]. Two-center nucleer attraction's applications require a much shorter time for the evaluation of

molecular integrals over STOs [5-7]. Therefore, precise evaluation of the two-center nuclear attraction integrals is of practical and fundamental importance.

The aim of this work is to obtain an analytical formula using the Löwdin α-radial function and Guseinov one-center charge density expansion formulas which is valid for any values of principal quantum numbers. Finally, simple examples are presented to compare the effectiveness of the described method with the established in the literature formulas for the two-center nuclear attraction integrals over STOs. We notice that the method can also be utilized in the efficient calculation of multicenter molecular integrals over STOs.

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

The two-center nuclear attraction integrals over STOs in molecular coordinate system is defined as

$$J_{nlm,n'l'm'}\left(\zeta,\zeta',\vec{R}\right)=\int\chi^{*}_{nlm}\left(\zeta,\vec{r}_a\right)\chi_{n'l'm'}\left(\zeta',\vec{r}_a\right)\frac{1}{r_b}dV\,, \tag{1}$$

where $\vec{R}\equiv\vec{R}_{ab}=\vec{r}_a-\vec{r}_b$ and

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

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

$$S_{lm}(\theta,\varphi)=P_{l|m|}(\cos\theta)\Phi_m(\varphi)\,, \tag{3}$$

where $P_{l|m|}$ are the normalized associated Legendre functions [9-10] and

for complex spherical harmonics (SH)

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi}\,, \tag{4}$$

for real spherical harmonics

$$\Phi_m(\varphi)=\frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\varphi & for\quad m\geq 0\\ \sin|m|\varphi & for\quad m<0\end{cases}\,. \tag{5}$$

It should be noted that our definition of phases for complex spherical harmonics $\left(Y^{*}_{lm}=Y_{l-m}\right)$ differs from the Condon-Shortley phases [11] by the sign factor.

It is well known that the molecular integrals over STOs can be expressed in terms of $C_l^{nlm}\left(i,j\right)$ coefficients by using Löwdin α-radial functions [12-15]. Main approach is to use the polynomial expression derived by Jones, in which $C_l^{nlm}\left(i,j\right)$ 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 [12-15]. By using Jones's polynomial method we can write Sharma's analytical formula for the $C_l^{nlm}(i,j)$ coefficients in the following form [1, 8]:

$$C_{l'}^{nl\lambda}(i,j)=\begin{cases}\dfrac{(l-\frac{1}{2})!(l'-\frac{1}{2})!}{(l+\lambda)!(l'-\lambda)!}\sum\limits_{K=0}^{\min\{[i/2],l+l'\}}\sum\limits_{k=0}^{\min\{[j/2],l+l'-K\}}\dfrac{(n+l+2l'-2K-2k)!}{(i-2K)!(j-2k)!} & \\ \times b_{l+l'-K-k,k}(l\lambda\backslash l') & for\quad i+j\le n+l-\lambda+2l' \\ 0 & for\quad i+j>n+l-\lambda+2l'\end{cases}, \quad (6)$$

where

$$b_{Kk}(l\lambda\backslash l')=\frac{(l-\lambda)!(l+\lambda)!(l'-\lambda)!(l'+\lambda)!(l-K-\frac{1}{2})!(l'-k-\frac{1}{2})!}{(l+l'-K-k)!(l-\frac{1}{2})!K!(l'-\frac{1}{2})!k!}$$
$$\times\sum_{s=0}^{l-\lambda}\frac{(-l+K+k+s-\frac{1}{2})!}{s!(l-\lambda-s)!(l'-l+s)!(-l+s-\frac{1}{2})!(l+\lambda-s)!}. \quad (7)$$

In Eqs.(6) and (7) the factorial $(p-1/2)!$ has the form [16]

$$(p-1/2)!=\begin{cases}(p-1/2)(p-3/2)...1/2 & \text{for a positive integer } p\\ 1/[(-1)^{-p}(-p-1/2)!] & \text{for a negative integer } p\end{cases}, \quad (8)$$

with $(-1/2)!\equiv 1$. Thus the following relation holds [16]:

$(p-1/2)!(-p-1/2)!=(-1)^p$.

We notice that Eq.(6) is valid for arbitrary values of parameters.

3. Analytical expression for two-center nuclear attraction integrals with STO

For the calculation of two-center nuclear attraction integrals we use in Eq.(1) the one-center charge density expansion formula [17-18]. Then we obtain

$$J_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\sum_{\nu=|l-l'|}^{l+l'}\sum_{\sigma=-\nu}^{\nu}W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta';z)J_{\mu\nu\sigma}(z,\vec{R}), \quad (9)$$

where $J_{nlm}(\zeta,\vec{R})$ are the basic two-center nuclear attraction integrals

$$J_{nlm}(\zeta,\vec{R})=\frac{1}{\sqrt{4\pi}}\int\chi_{nlm}^{*}(\zeta,\vec{r}_a)\frac{1}{\vec{r}_b}dV \quad (10)$$

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

$$W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta',z)$$
$$=\frac{z\sqrt{z}}{2^{\mu}}\frac{F_{n'}(\mu)}{n}\left[\frac{2l+1}{2}\frac{F_{\mu}(2\mu)}{F_n(2n)F_{n'}(2n')}\right]^{1/2}(1+t)^{n+\frac{1}{2}}(1-t)^{n'+\frac{1}{2}}C^{\nu|\sigma|}(lm,l'm')A^{\sigma}_{mm'}\delta_{\mu,n+n'-1} \quad . \tag{11}$$

The generalized Gaunt coefficients $C^{\nu|\sigma|}(lm,l'm')$, and $A^{\sigma}_{mm'}$ in Eq.(11) are determined by the following relationships [19-25]:

$$C^{L|M|}(lm,\ l'm')=\begin{cases}C^{L}(lm,\ l'm') & for \quad |M|=|m-m'|\\ C^{L}(lm,\ l'-m') & for \quad |M|=|m+m'|\end{cases}, \tag{12}$$

$$A^{M}_{mm'}=\begin{cases}\frac{1}{\sqrt{2}}(2-|\eta^{m-m'}_{mm'}|)^{1/2}\ \delta_{M,\ \varepsilon|m-m'|}+\frac{1}{\sqrt{2}}\eta^{m+m'}_{mm'}\delta_{M,\ \varepsilon|m+m'|} & for\ \ real\ \ STO's\\ \delta_{M,\ m-m'} & for\ \ complex\ \ STO's\end{cases} \tag{13}$$

See Ref.[20] for the exact definition of quantities $\eta^{m\pm m'}_{mm'}$ *and* $\varepsilon=\varepsilon_{mm'}$

It is easy to show that the basic two-center nuclear attraction integrals, Eq.(10), can be expressed through the overlap integrals by the following formula:

$$J_{nlm}(\zeta,\vec{R})=\lim_{\zeta'\to 0}\frac{1}{(2\zeta')^{1/2}}S_{nlm,000}(\zeta,\zeta';\vec{R}) \quad . \tag{14}$$

Here $S_{nlm,n'l'm'}$ are the overlap integrals over normalized STOs with respect to molecular coordinate system determined by

$$S_{nlm,000}(\zeta,\zeta';\vec{R})=T^{0}_{lm,00}(\theta,\varphi)S_{nl0,000}(\zeta,\zeta';R) \quad , \tag{15}$$

where $T^{\lambda}_{lm,l'm'}(\theta,\varphi)$ are the rotation coefficients for overlap integrals [26-28].

Now we can move on to the calculation of $S_{nlm,000}(\zeta,\zeta';\vec{R})$ overlap integrals. To evaluate the $S_{nlm,000}(\zeta,\zeta';\vec{R})$, we use the Löwdin α method [2] in lined-up coordinate systems and Guseinov's transformational relation for overlap integral [26-28]. We then find the following formula for the two-center nuclear attraction integrals over STOs in molecular coordinate systems:

$$J_{nlm}(\zeta,\vec{R})=2^{n}\left(\frac{2l+1}{2\zeta(2n)!}\right)^{1/2}\sum_{i=0}^{n+l}\sum_{j=0}^{n}j!C^{nl0}_{0}(i,j)\Big[e^{-\zeta R}(R\zeta)^{i-l-1}\left((-1)^{i-j-1}-1\right)$$
$$+\sum_{k=0}^{j}\frac{1}{(j-k)!}(R\zeta)^{i+j-l-k-1}\left((-1)^{i}-(-1)^{j-k-1}\right)\Big]S_{lm}(\theta,\varphi). \tag{16}$$

As can be seen from Eq.(16) that the two-center nuclear attraction integrals over STOs in molecular coordinate system are expressed through the Guseinov's one-center charge density expansion and Löwdin α-radial coefficients.

4. Numerical Results and Discussion

We have developed an efficient algorithm for the the two-center nuclear attraction integrals over STOs in molecular coordinate system based on the Löwdin α function and Guseinov's one-center charge density expansion formula. On the basis of Eqs. (9) and (16) we constructed a program for the computation of two-center nuclear attraction integrals over STOs using Mathematica 6.0 international mathematical software. The examples of the computer calculation for two-center nuclear attraction integrals over STOs are shown in Tables 1 and 2. The results obtained were compared with the values of formulas given in Ref.[6]. As can be seen from Tables 1 and 2 that the complete agreement was obtained by taking arbitrary principal quantum numbers, screening constant and location of STOs.

It can be seen that the proposed algorithm allows us to compute the two-center nuclear attraction integrals more rapidly.The use of the present form of the formulas (Eqs.(9) and 16)) shows its simplicity. We have thus attained our goal in demostrating formulas.

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Table 1. The comparative values of basic two-center nuclear attraction integrals over STOs obtained in the molecular coordinate system (in a.u.)

n	l	m	z	R	θ	φ	Eq.(18) in Ref.[6]	Eq.(16)
3	2	2	7.6	3.2	60	180	2.22371798577297694026986783861E-3	2.22371798577297694026986783861E-3
4	2	2	0.6	3.2	60	180	2.43081975920290114442383044968E-1	2.43081975920290114442383044968E-1
4	3	2	0.6	3.2	60	60	-7.09459665998389282000162602935E-2	-7.09459665998389282000162602935E-2
10	9	9	2.5	2.2	120	60	3.55938243244452979270275575288E-3	3.55938243244452979270275575288E-3
20	10	10	2.5	1.6	120	60	-6.05980750086911557365421070224E-8	-6.05980750086911557365421070224E-8
30	25	20	2.5	3.6	30	60	-1.91151209734662849623208734621E-12	-1.91151209734662849623208734621E-12
30	30	25	4.4	1.2	30	180	3.24527211751076793001885989347E-19	3.24527211751076793001885989347E-19
40	35	30	2.2	3.2	30	30	-4.44842070077606460519226602335E-24	-4.44842070077606460519226602335E-24
50	45	40	4.4	3.3	30	180	8.58637054115549083912054687410E-23	8.58637054115549083912054687410E-23

Table 2. The comparative values of two-center nuclear attraction integrals over STOs obtained in the molecular coordinate system (in a.u.)

n	l	m	ζ	n'	l'	m'	ζ'	R	θ	φ	Eq.(9)	Eq.(17) in Ref.[6]
4	3	2	15.9	5	3	3	10.7	15.5	40	30	-4.65385676682644716066781161577E-6	4.65385676682644716066781161577E-6
6	4	4	14.8	6	5	5	20.8	25.1	60	180	1.98425009417673468563768377009E-4	1.98425009417673468563768377009E-4
8	7	7	21.4	7	6	6	20.8	53.2	70	210	5.16357446188276991882482982749E-5	5.16357446188276991882482982749E-5
10	9	-7	12.5	10	8	-8	10.2	100.7	80	240	-1.58615189629609754713294029539E-6	-1.58615189629609754713294029539E-6
15	13	13	31.5	14	13	13	23.8	0.7	0	0	9.64834293778154204781872124590E-1	9.64834293778154204781872124590E-1
25	24	24	15.5	25	24	24	10.4	15.5	36	36	2.34470131643286749402692732246E-2	2.34470131643286749402692732246E-2
40	20	20	9.2	40	20	20	9.2	8.5	54	144	1.16227304275567798418354633847E-1	1.16227304275567798418354633847E-1
50	21	20	12.9	50	21	20	7.9	38	126	324	1.30238004549548995645605277911E-3	1.30238004549548995645605277911E-3
50	31	-20	13.3	50	31	20	12.9	33	126	320	-2.17756640842333665954736933893E-42	-2.17756640842333665954736933893E-42
60	55	30	20.3	60	55	-30	18.2	40	100	250	$-1.10051736619488303220578904930\times10^{-65}$	$-1.10051736619488303220578904930\times10^{-65}$
70	35	-30	25	70	35	-30	25	40	150	150	2.49776401464309016394451765020E-2	2.49776401464309016394451765020E-2
75	55	50	33.3	75	55	50	32.2	42.3	100	80	2.31538153039637015071282197913E-2	2.31538153039637015071282197913E-2
80	55	50	31	80	55	50	30	44.4	300	200	2.20439483559014846889943556561E-2	2.20439483559014846889943556561E-2
90	60	30	52.5	90	60	30	55.5	55	252	340	1.69546653946454486710440817619E-2	1.69546653946454486710440817619E-2
100	60	40	70.3	100	60	40	66.6	68.8	320	288	1.35055392578515364072009107675E-2	1.35055392578515364072009107675E-2

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