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Evaluation of two-center overlap integrals using slater type orbitals in terms of bessel type orbitals

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Using the definition of STOs in terms of BTOs, we have presented analytical formula for two-center overlap integrals. The obtained formula contains generalized binomial coefficients and Mulliken integrals A_k and B_k. Taking into account the recent advances on the efficient calculation of Mulliken integrals (Harris, *Int. J. Quantum Chem.,* 100 (2004) 142), we have obtained many more satisfactory results for two-center overlap integrals, for arbitrary quantum numbers, scaling parameters, and location of atomic orbitals.

KEY WORDS: Slater type orbital, Bessel type orbital, two-center overlap integral

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1. Introduction

The *ab initio* calculations using the LCAO–MO approach, where molecular orbitals are built from a linear combination of atomic orbitals, strongly depend on the choice of the basis functions for the reliability of the electronic distributions they provide. A good atomic orbital basis should satisfy two pragmatic conditions for analytical solutions of the appropriate Schrödinger equation, namely the cusp at the origin [1] and exponential decay at infinity [2]. Among the basis functions used in the literature, the Slater type orbitals (STOs) satisfy the aforementioned requirements [3,4]. Unfortunately, the notorious problems arise in the evaluation of multicenter integrals when STOs used. Due to the advance in applied mathematics and computer science, there are a progressive interest in the use of STOs in multicenter integrals, (see [3,4] and quoted therein). Since the calculations of multicenter integrals over STOs is extremely difficult, STOs are expressed as linear combinations of Bessel type orbitals

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(BTOs) [5] then and all the multicenter integrals can be calculated more easily (see [6] detailed discussion of BTOs).

Among the multicenter integrals, two-center overlap integral constitutes the basic building block of many more complicated multicenter integrals since the expectation value of one-electron operators can be expressed as linear combination of two-center overlap integrals, and also since two-electron integrals can be calculated by taking quadrature of two-center overlap integrals. At the same time, these type integrals also contribute to the total energy of the molecule which is required to a precision sufficient for small fraction changes to be evaluated. In practice, an error in the range of 10^{-8}–10^{-10} in integrals will deteriorate the energy by an amount of 10^{-3} atomic units (a.u.) [4].

Recently, we have presented analytical, series and recurrence relations for the evaluation of multicenter integrals over STOs [7]. In this work, we are dealing with the evaluation of two-center overlap integrals using STOs as linear combinations of BTOs, which seems to be quite promising for use in *ab initio* calculations.

2. General definitions and basic formulas

In the most real case, a STO is defined as follow:

$$\chi_{nlm}(\alpha, \vec{r}) = N_n(\alpha)\, r^{n-1} e^{-\alpha r} S_{lm}(\theta, \varphi), \tag{1}$$

where α is scaling parameter and $N_n(\alpha)$ is the normalization coefficient given by

$$N_n(\alpha) = \frac{(2\alpha)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} \tag{2}$$

and $S_{lm}(\theta, \varphi)$ denotes the real spherical harmonic [8]:

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

in which $P_{l|m|}$ is the normalized associated Legendre function and the $\Phi_m(\varphi)$ is defined by

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{mo})}} \begin{cases} \cos m\varphi & \text{for } m \geqslant 0, \\ \sin |m|\, \varphi & \text{for } m < 0. \end{cases} \tag{4}$$

Using the expansion formula for unnormalized STOs in terms of BTOs [5], we re-express normalized STOs as finite linear combination of BTOs as

$$\chi_{nlm}(\alpha, \vec{r}) = \Omega_n(\alpha) \sum_{p=\hat{p}}^{n-l} K_{nl}^{p} B_{p,l}^{m}(\alpha, \vec{r}), \tag{5}$$

where

$$\Omega_n(\alpha) = \alpha^{1-n} N_n(\alpha), \tag{6a}$$

$$K_{nl}^{p} = \frac{(-1)^{n-l-p}(n-l)!(l+p)!2^{l+p}}{(2p-n-l)!(2n-2l-2p)!!}, \tag{6b}$$

and

$$\hat{p} = \begin{cases} (n-l)/2 & \text{if } n-l \text{ even}, \\ (n-l+1)/2 & \text{if } n-l \text{ odd}. \end{cases} \tag{7}$$

In equation (5), a BTO is defined as follow [5]:

$$\mathrm{B}_{nl}^{m}(\alpha, \vec{r}) = \frac{(\alpha r)^l}{2^{n+l}(n+l)!} \hat{k}_{n-\frac{1}{2}}(\alpha r) S_{lm}(\theta, \varphi), \tag{8}$$

where $\hat{k}_{n-\frac{1}{2}}$ is reduced Bessel function defined by

$$\hat{k}_{n-\frac{1}{2}}(z) = z^{-1} e^{-z} \sum_{j=1}^{n} \frac{(2n-j-1)!}{(j-1)!(n-j)!} 2^{j-n} z^j. \tag{9}$$

3. Two-center overlap integrals over STOs

Two-center overlap integrals examined in the present work have the following form:

$$S_{nlm,n'l'm'}\left(\alpha, \beta; \vec{R}\right) = \int \chi_{nlm}^{*}(\alpha, \vec{r}_a)\, \chi_{n'l'm'}(\beta, \vec{r}_b)\, dV, \tag{10}$$

where $\chi_{nlm}(\alpha, \vec{r}_a)$ and $\chi_{n'l'm'}(\beta, \vec{r}_b)$ are STOs located on centers a and b, and $\vec{R}$ is the radius vector given by $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_b - \vec{r}_a$.

Substituting equation (5) into equation (10), we obtain the following relation for two-center overlap integrals over STOs

$$S_{nlm,n'l'm'}\left(\alpha, \beta; \vec{R}\right) = \Omega_{nn'}(\alpha, \beta) \sum_{p,q} K_{pq}^{nl,n'l'} I_{plm,ql'm'}\left(\alpha, \beta; \vec{R}\right), \tag{11}$$

where

$$\Omega_{nn'}(\alpha, \beta) = \Omega_n(\alpha)\, \Omega_{n'}(\beta), \tag{12a}$$

$$K_{pq}^{nl,n'l'} = K_p^{nl} K_q^{n'l'}. \tag{12b}$$

In equation (11), $I_{plm,ql'm'}$ is the integral of the form:

$$I_{plm,ql'm'}\left(\alpha,\beta;\vec{R}\right)=\int B_{pl}^{m}\left(\alpha,\vec{r}_a\right)B_{ql'}^{m'}\left(\beta,\vec{r}_b\right)dV, \tag{13}$$

and called two-center overlap integrals between two BTOs. In the literature, this type of integrals are calculated by one center expansion method (reduction theorem) [9] and Fourier transform convolution theorem [10]. It is known that Fourier transform convolution theorem injure from some possible instability problems [11] and we think that one center expansion method may also injure from possible instability problems due to the fact that this method contains approximations.

To overcome the possible instability problems occurring in the calculation of two-center overlap integrals, using rotation coefficients for two-center overlap integrals [12], we express the integral in equation (11) as

$$I_{plm,ql'm'}\left(\alpha,\beta;\vec{R}\right)=\sum_{\lambda=0}^{\min(l,l')}T_{lm,l'm'}^{\lambda}\left(\theta,\varphi\right)I_{pl\lambda,ql'\lambda}\left(\alpha,\beta;R\right), \tag{14}$$

where $T_{lm,l'm'}^{\lambda}\left(\theta,\varphi\right)$ is rotation coefficients for two-center overlap integrals and

$$I_{pl\lambda,ql'\lambda}\left(\alpha,\beta;\vec{R}\right)=\int B_{pl}^{\lambda}\left(\alpha,\vec{r}_a\right)B_{ql'}^{\lambda}\left(\beta,\vec{r}_b\right)dV. \tag{15}$$

Using the definition of the reduced Bessel functions given by equation (9) into equation (15), we express the overlap integral of two BTOs by the following formula:

$$\begin{aligned}I_{pl\lambda,ql'\lambda}\left(\alpha,\beta;R\right)&=\gamma_{pq}^{ll'}\sum_{i,j}^{p,q}\eta_{pi}\eta_{qj}\alpha^{l+i-1}\beta^{l'+j-1}\\&\quad\times\int r_a^{l+i-1}r_b^{l'+j-1}\mathrm{e}^{-\alpha r_a-\beta r_b}P_{l\lambda}\left(\cos\theta_a\right)P_{l'\lambda}\left(\cos\theta_b\right)dV,\end{aligned} \tag{16}$$

where

$$\gamma_{pq}^{ll'}=\left[(p+l)!!\left(q+l'\right)!!\right]^{-1}, \tag{17}$$

and

$$\eta_{p\kappa}=\frac{F_{\kappa-1}\left(2p-\kappa-1\right)}{F_{p-\kappa}\left(2p-2\kappa\right)\left(p-\kappa\right)!}2^{\kappa-p}. \tag{18}$$

Here $F_m\left(n\right)$ is usual binomial coefficient defined by

$$F_m\left(n\right)=\frac{n!}{m!\left(n-m\right)!}. \tag{19}$$

As can be seen equation (16), it is necessary to have an equation for the expansion of the product of two normalized associated Legendre functions centered on a and b:

$$T^{l\lambda,l'\lambda}(\theta_a,\theta_b)=\mathrm{P}_{l\lambda}(\cos\theta_a)\,\mathrm{P}_{l'\lambda}(\cos\theta_b)\,. \tag{20}$$

Recently [7a], we have presented the expansion formula for the product of two normalized associated Legendre functions in ellipsoidal coordinate system (μ,ν,φ) as

$$T^{l\lambda,l'\lambda}(\mu,\nu)=\sum_{k,k'}\sum_{u,s}a_{us}^{kk'}\left(l\lambda,l'\lambda\right)\frac{(\mu\nu)^s}{(\mu+\nu)^{l-2(k+k'+\lambda)+2u}(\mu-\nu)^{l'}}\,, \tag{21}$$

where the expansion coefficients are

$$\begin{aligned}a_{us}^{kk'}\left(l\lambda,l'\lambda\right)=&C_{l\lambda}^{k}C_{l'\lambda}^{k'}(-1)^u\,F_u\left(k+k'+\lambda\right)\\&\times F_s\left(l-2k-\lambda+2u,l'-2k'-\lambda\right),\end{aligned} \tag{22}$$

and

$$C_{lm}^{k}=\frac{(-1)^k}{2^{2k+m}}\left[\frac{2l+1}{2}F_{l-k}(l+m)\,F_{k+m}(l-k)\,F_{2k}(l-m)\,F_k(2k)\right]^{1/2} \tag{23}$$

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

$$\begin{aligned}&0\leqslant k\leqslant E\left(\tfrac{l-\lambda}{2}\right),\qquad 0\leqslant k'\leqslant E\left(\frac{l'-\lambda}{2}\right),\\&0\leqslant u\leqslant\left(k+k'+\lambda\right),\quad 0\leqslant s\leqslant\left(l+l'\right)-2\left(k+k'+\lambda\right)+2u.\end{aligned} \tag{24}$$

In equation (22), $F_m\left(N,N'\right)$ is called generalized binomial coefficients [12, 13] and recently we have re-expressed this quantity in terms of usual binomial coefficients as [14]

$$F_m\left(N,N'\right)=\sum_{i,j=0}^{m}(-1)^{N'-j}\,F_i(N)\,F_j\left(N'\right)\delta_{m,i+j}. \tag{25}$$

Consequently, using equation (21) and ellipsoidal form of the radial part included in equation (16), two-center overlap integrals between two BTOs take the form:

$$\begin{aligned}I_{pl\lambda,ql'\lambda}(\alpha,\beta;R)=&\gamma_{pq}^{ll'}\sum_{i,j}^{p,q}\eta_{pi}\eta_{qj}\alpha^{l+i-1}\beta^{l'+j-1}\left[\frac{R}{2}\right]^{l+l'+i+j+1}\\&\times\sum_{kk',us}a_{us}^{kk'}\left(l\lambda,l'\lambda\right)Q_{i+2(k+k'+\lambda-u),j}^{s}(p,t),\end{aligned} \tag{26}$$

where

$$Q^{s}_{n,n'}(p,t) = \sum_{m=0}^{n+n'} F_m\left(n,n'\right) A_{n+n'+s-m}(p)\, B_{m+s}(pt) \tag{27}$$

and A_k and B_k are the well-known Mulliken integrals [15], and p and t parameters are given by

$$p = \frac{R}{2}(\alpha+\beta), \qquad t = \frac{\alpha-\beta}{\alpha+\beta}. \tag{28}$$

It is advised for readers of interest to see [12b] for $Q^{s}_{n,n'}(p,t)$ and their useful recurrence relations.

4. Computational details

The expression we derived for two-center overlap integrals contains generalized binomial coefficients $F_m\left(N,N'\right)$ and Mulliken integrals A_k and B_k. To speed up the calculations, we store the generalized binomial coefficients and Mulliken integrals into the memory of the computer during the compilation of the program and we get them from the memory during the calculations. This process is very memory consuming but also very time gaining.

In storing the generalized binomial coefficients to the memory of the computer, we use the position of a certain $F_m\left(N,N'\right)$ is determined by the relation [16]:

$$\begin{aligned} F^{NN'm} = \tfrac{1}{8}\Big\{ N\left(2N^2-11N+14\right) + 2\Big[N'\left(2N+N'-6\right) \\ +\beta^{N1}+\beta^{NN'}-5\Big] + 3\beta^{N0}\Big\} + \tfrac{1}{2}\left(2-\delta_{NN'}\right)m + \delta_{NN'} \end{aligned} \tag{29}$$

in which $\delta_{NN'}$ is kronecker delta function and

$$\beta^{NN'} = \tfrac{1}{2}\left[1-(-1)^{N+N'}\right]. \tag{30}$$

The symmetry properties of $F_m\left(N,N'\right)$ have been taken into account in storing this quantity.

Other quantities arising in the expression for two-center overlap integrals are Mulliken integrals A_k and B_k. These integrals have the following form:

$$A_k(p) = \int_1^{\infty} x^k e^{-px} dx, \tag{31}$$

$$B_k(pt) = \int_{-1}^{+1} x^k e^{-ptx} dx. \tag{32}$$

As can be seen from equations (26) and (27), in case of higher quantum numbers one has to calculate these integrals accurately since these integrals converge very slowly. The $A_k(p)$ integral are only needed for $p > 0$ and are easily and stably calculated by upward recurrence relation well-known in literature [17]:

$$A_k(p) = \frac{k}{p} A_{k-1}(p) + A_0(p) \tag{33}$$

with starting point

$$A_0(p) = \frac{e^{-p}}{p}. \tag{34}$$

The integral $B_k(pt)$ can not be calculated easily as in $A_k(p)$, since this integral is not convergent for all k and pt values. In literature, the following recurrence relation is known for integral $B_k(pt)$:

$$B_k(pt) = \frac{1}{pt}\left[kB_{k-1}(pt) + (-1)^n e^{pt} - e^{-pt}\right]. \tag{35}$$

On the other hand, it is well-known that upward recurrence relation is stable only for $k < |pt|$ and downward recurrence relation is stable only for $k > |pt|$. Corbato presented a procedure for the calculation of integral $B_k(pt)$, stable for all k and pt values, using modified spherical Bessel functions [18]. However, this method requires more computational effort than the use of upward or downward recurrence relations. Recently, Harris has pointed out that the main problem in the calculation of integral $B_k(pt)$ is to be able to calculate efficiently the starting value for recurrence relation (35) and presented an algorithm for the efficient calculation of integral $B_k(pt)$ using incomplete gamma functions [19]. A detailed discussion of expansions for incomplete gamma functions can be found in [20].

5. Computation results and discussion

We have presented an algorithm for the evaluation of two-center overlap integrals over STOs, using the definition of STOs in terms of BTOs. The presented formula contains two-center overlap integrals between two BTOs for which include generalized binomial coefficients $F_m(N, N')$, expansion coefficients for the product of two normalized associated Legendre functions $a_{us}^{kk'}(l\lambda, l'\lambda)$ and Mulliken integrals A_k and B_k.

Based on equation (11), we have constructed a computer program in Mathematica 4.0 [21] for the calculation of two-center overlap integrals over STOs. In constructing computer program, the two-center overlap integrals between two BTOs and Mulliken integrals have been stored in the memory of the computer for reducing computational time. As can be seen from equation (11), for any

quantum sets, overlap integrals between two BTOs can be stored in the memory of the computer in two dimensional array. Since this operation would take more computational time, we have derived a memory formula for reducing two dimensional array to the one dimensional array as follow:

$$I_{pq}^{(n)} = pn - (n - q) - \frac{p\,(p-1)}{2}. \tag{36}$$

Using computer program constructed for equation (11), we have calculated two-center overlap integrals over STOs for various quantum sets. The comparative values of two-center overlap integrals over STOs have been listed in table 1. It is seen from table 1 that our computer results are in agreement with the literature [7b, 22, 23] for wide range of quantum numbers, scaling parameters and internuclear distances. Also, we notice that the presented algorithm does not suffer from possible instability problems and can be used in molecular orbital calculations when Hartree–Fock–Roothaan approximation is employed. We think that the main cause of the stability of the algorithm presented here depends on the use of the expansion formula for the product of two normalized associated Legendre functions. It should be noted that such algorithms have been presented in literature [12, 13]. It is advised for readers to read [12d] on the interconversion among the formulae in the literature and more recent developments on the evaluation of multicenter integrals based on the use of expansion formula [24].

Works are in progress in our laboratory and some preliminary results on two-center two-electron integrals over STOs will be reported in short.

In the whole calculations, double precision floating point arithmetic is used.

Table 1
Comparative values of two-center overlap integrals over STOs (in a.u).

n	l	m	n'	l'	m'	α	β	R	θ	φ	This work [eq. (11)]	Literature
2	1	0	2	1	0	7.5	2.5	6.0	60	120	−2.01912763169777E-05	−2.01912763169782E-05[a]
3	2	0	3	2	0	7.5	2.5	5.0	60	120	−6.80340033108123E-05	−6.80340033108473E-05[b]
4	3	3	4	3	2	3.0	2.0	20	30	60	3.75545611854733E-02	3.75545611854747E-02[a]
7	3	2	4	3	2	8.5	1.5	30	0	0	1.76861050691297E-18	1.76861050692265E-18[a]
7	6	4	5	4	4	6.0	4.0	0.8	0	0	2.658829482343624E-01	–
8	7	−6	7	5	5	2.5	1.5	2.4	150	240	−4.44987258245886E-02	–
13	12	11	13	12	11	4.0	4.0	2.5	0	0	−4.01371353396521E-01	−4.01371353397628E-01[a]
15	8	4	12	8	6	5.0	5.0	1.0	67.5	22.5	2.54324132559121E-03	2.5432413255908E-03[c]
17	8	4	8	7	4	5.5	4.5	10	0	0	−1.00623367111237E-06[c]	−1.00623367113747E-06[c]
20	8	2	10	8	1	5.0	5.0	5.0	60	45	7.93865462132564E-04	7.938654621681[b]
25	12	9	24	10	7	7.5	2.5	3.0	45	60	1.1603598984785E-05	–

[a]Ref. [22]; [b]Ref. [7c]; [c]Ref. [23].

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