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ORIGINAL PAPER

Use of binomial coefficients in fast and accurate calculation of Löwdin-α radial functions

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Abstract In the present paper, we introduce a new algorithm for the development of efficient numerical methods for the analytical solution of the Löwdin-α radial function. The final results are expressed through the binomial coefficients, which enable fast and accurate calculation of the Löwdin-α radial function. The comparisons of the obtained results with the literature have shown that the presented approach can be used for the fast calculation of multicenter multielectron integrals over Slater-type orbitals (STOs). The efficiency of the algorithm is discussed and its performance with several examples is demonstrated.

Keywords Slater-type orbitals · Löwdin-α function · Wave function · Multicenter integrals

1 Introduction

It is well-known that Löwdin-α radial functions play an important role in the study of the electronic structure of molecules. The different approaches of Löwdin-α function method for solving overlap integrals with Slater-type orbitals (STOs) are available in the literature [1–37]. The Löwdin-α radial functions are also central to the calculation of arbitrary multicenter integrals based on the series expansion formulas about a new center and one-range addition theorems for STOs [38–45], which necessitate one to accurately calculate the overlap integrals, especially for the large quantum numbers.

The calculation of the molecular integrals by the use of expansion formulas of STOs in terms of the Löwdin-α radial functions is reduced to the evaluation of $C_{l'}^{nl\lambda}(i, j)$ coefficients [2–17,46]. Therefore, the choice of reliable formulas for evaluation of

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$C_{l'}^{nl\lambda}(i,\,j)$ coefficients is of prime importance in the accurate calculations of the molecular integrals over STOs. The analytical formula to calculate $C_{l'}^{nl\lambda}(i,\,j)$ coefficients have been proposed in the article [23–33]. We have generalized Sharma's analytical formula [23–33] by using Jones's polynomial method [17] for calculating $C_{l'}^{nl\lambda}(i,\,j)$ coefficients. The formula is represented in terms of binomial coefficients, which make for faster and more accurate evaluation of the $C_{l'}^{nl\lambda}(i,\,j)$ coefficients.

2 Expressions for Löwdin-α radial functions and $C_{l'}^{nl\lambda}(i,\,j)$ coefficients in terms of binomial coefficients

The Slater-type orbitals are defined with respect to the Löwdin-α radial functions by [2–17]:

$$\chi_{nlm}(\zeta,\,\vec{r}) = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}\zeta^{n-1}}\left[\frac{(2l+1)(l+m)!}{4\pi(l-m)!}\right]^{1/2}\sum_{l'=m}^{\infty}\left[\frac{4\pi(l'+m)!}{(2l'+1)(l'-m)!}\right]^{1/2}(-1)^m \times\alpha_{l'}^{nlm}(\zeta a,\,\zeta r)S_{l'm}(\theta,\,\varphi), \tag{1}$$

where

$$\alpha_{l'}^{nlm}(\zeta a,\,\zeta r) = \frac{(2l'+1)(l'-m)}{2(l'+m)}\sum_{i=0}^{n+l+l'}\sum_{j=0}^{n+l'}C_{l'}^{nlm}(i,\,j)H_{ij}(\zeta a)^{i-l-l'-1}(\zeta r)^{j-l'-1}, \tag{2}$$

and

$$H_{ij} = \begin{cases} e^{-\zeta a}\left[(-1)^j e^{\zeta r} - e^{-\zeta r}\right], & r < a \\ e^{-\zeta r}\left[(-1)^i e^{\zeta a} - e^{-\zeta a}\right], & r > a \end{cases}. \tag{3}$$

See [17] for the exact definition of quantity a. Here, the complex and real spherical harmonics S_{lm} are determined by

$$S_{lm}(\theta,\,\varphi) = P_{l|m|}(\cos\theta)\Phi_m(\varphi), \tag{4}$$

where $P_{l|m|}$ are the normalized associated Legendre functions [47,48] and for complex spherical harmonics (SH)

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}, \tag{5}$$

for real spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\varphi & \text{for } m \geq 0 \\ \sin|m|\varphi & \text{for } m < 0\end{cases}. \tag{6}$$

It should be noted that our definition of phases for complex spherical harmonics ($Y^*_{lm} = Y_{l-m}$) differs from the Condon-Shortley phases [49] by the sign factor.

One of the efficient methods to calculate $C^{nlm}_{l'}(i, j)$ coefficients has been proposed by Sharma (see [23–33])

$$C^{nl\lambda}_{l'}(i, j) = \frac{(l-\frac{1}{2})!(l'-\frac{1}{2})!}{(l+\lambda)!(l'-\lambda)!} \sum_{K=0}^{\min\{[i/2],l+l'\}} \sum_{k=0}^{\min\{[j/2],l+l'-K\}} \times \frac{(n+l+2l'-2K-2k)!}{(i-2K)!(j-2k)!} b_{l+l'-K-kk}(l\lambda\backslash l'), \tag{7}$$

where

$$b_{Kk}(l\lambda\backslash l') = \frac{(l-\lambda)!(l+\lambda)!(l'-\lambda)!(l'+\lambda)!(l-K-\frac{1}{2})!(l'-k-\frac{1}{2})!}{(l+l'-K-k)!(l-\frac{1}{2})!K!(l'-\frac{1}{2})!k!} \times \sum_{s=0}^{l-\lambda} \frac{(-l+K+k+s-\frac{1}{2})!}{s!(l-\lambda-s)!(l'-l+s)!(-l+s-\frac{1}{2})!(l+\lambda-s)!}. \tag{8}$$

Another efficient method for calculating $C^{nl\lambda}_{l'}(i, j)$ coefficients has been proposed by Jones (see [17]) following

$$\begin{aligned} &\sum_{i=0}\sum_{j=0} C^{nlm}_{l'}(i, j) a^i r^j \\ &= \sum_{p=0}^{[(l+m)/2]} \sum_{q=0}^{l+m-2p} \sum_{v=0}^{l+m-2p-q} \sum_{p'=0}^{[(l'-m)/2]} \sum_{q'=0}^{l'-m-2p'} \sum_{v'=0}^{l'-m-2p'-q'} \sum_{k=0}^{t} \sum_{k'=0}^{t-k} \\ &\times \frac{a^x r^y (-1)^{v+q'+p+p'+l}(2l-2p)!(2l'-2p')!}{4^{l+l'+p-p'}(l-p)!p!p'!q!q'!v!v'!(l+m-2p-q-v)!} \\ &\times \frac{(n-l+2p+2q+2q')!}{(l'-p')!(l'-m-2p'-q'-v')!k'!(n-l+2p+2q+2q'-k-k')!}. \end{aligned} \tag{9}$$

Here $x = n + l + 2l' - 2p' - 2v' - 2v - k - k'$, $y = 2p' + 2v + 2v' + k'$ and $t = n - l + 2p + 2q + 2q'$.

We notice that the calculation results of Formulas (7) and (9) with respect to some values of i and j are not in complete agreement. It is clear from our tests that the Jones's polynomial method (Eq. 9) for arbitrary values of parameters i and j yield the correct results. By using Jones's polynomial method, we have generalized Sharma's analytical formula for arbitrary values of i and j. We can also express Sharma's analytical formula for the $C^{nlm}_{l'}(i, j)$ coefficients in terms of binomial coefficients. Thus,

Sharma's analytical formula for the $C_{l'}^{nlm}(i,j)$ coefficients becomes

$$C_{l'}^{nl\lambda}(i,j) = \begin{cases} (n+l+2l'-i-j)! \sum_{\mu=0}^{\min\{[i/2],l+l'\}} \sum_{\nu=0}^{\min\{[j/2],l+l'-\mu\}} F_{j-2\nu}(n+l+2l'-2\nu-i) & \\ \times F_{i-2\mu}(n+l+2l'-2\mu-2\nu) B_{\mu\nu}^{ll'\lambda} & \text{for } i+j \le n+l-\lambda+2l'. \\ 0 & \text{for } i+j > n+l-\lambda+2l' \end{cases} \tag{10}$$

In Eq. 10, the coefficients $B_{\mu\nu}^{ll'\lambda}$ are also rewritten in terms of binomial coefficients as

$$\begin{aligned} B_{\mu\nu}^{ll'\lambda} &= F_\mu\left(\mu+\nu-l'-\frac{1}{2}\right)(\nu-l'-1/2)!(l'-\nu-1/2)! \\ &\times \sum_{s=0}^{l-\lambda} F_s(l-\lambda) F_{l+\lambda-s}(l'+\lambda) F_{l+l'-\mu-\nu}\left(l'-\mu+s-\frac{1}{2}\right) \\ &\times F_\nu\left(s-l+\nu-\frac{1}{2}\right). \end{aligned} \tag{11}$$

Here the quantities $F_m(n)$ are determined by

$$F_m(n) = \begin{cases} \frac{n!}{m!(n-m)!} & \text{for } 0 \le m \le n \\ 0 & \text{for } m < 0 \text{ and } m > n \end{cases}. \tag{12}$$

For quicker calculations for the positive integer values of n, the binomial coefficients are stored in the memory of the computer. For the binomial coefficients, we use the following recurrence relation [50–52]

$$F_m(n) = \left(\frac{n+1}{m} - 1\right) F_{m-1}(n). \tag{13}$$

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

$$F(m,n) = \frac{n(n+1)}{2} + m + 1. \tag{14}$$

The clarifications of Eq. 14 are presented in Ref. [50]. In Eqs. 7, 8, and 11, the factorial $(p-1/2)!$ has the form [33]

$$(p-1/2)! = \begin{cases} (p-1/2)(p-3/2)\ldots 1/2 & \text{for a positive integer } p \\ 1/[(-1)^{-p}(-p-1/2)!] & \text{for a negative integer } p \end{cases}, \tag{15}$$

with $(-1/2)! \equiv 1$. Thus, the following relation holds [33]:

$$(p-1/2)!(-p-1/2)! = (-1)^p. \tag{16}$$

Table 1 The comparative results and times for basic nuclear attraction integrals over STOs obtained in the molecular coordinate system (in a.u.)

n	l	m	ζ	R	θ	φ	Eq. 17 use of formula (7)	CPU time	Eq. 17 use of formula (10)	CPU time
3	2	1	2.5	1.6	120	60	0.12120979305638946	0.016	0.12120979305638946	0
4	2	0	0.5	0.6	150	60	0.007999344866904986	0.047	0.007999344866904986	0.031
4	3	2	5.5	3.6	120	60	0.001728488688380815	0.031	0.001728488688380815	0.016
5	4	3	5.5	3.6	120	60	−0.002720616007064828	0.093	−0.002720616007064828	0.045
6	5	3	5.5	3.3	128	50	0.003618644296175013	0.188	0.003618644296175013	0.078
10	9	8	3.5	2.3	115	75	0.017759299209905245	1.482	0.017759299209905245	0.655
20	15	10	5.5	4.3	15	75	7.493536779050277E−6	20.842	7.493536779050277E−6	9.984
30	20	10	5.5	4.4	150	60	−0.0046397254746812563	103.615	−0.0046397254746812563	55.833

As can be seen from the Eqs. 10 and 11, the $C_{l'}^{nlm}(i,j)$ and $B_{\mu\nu}^{ll'\lambda}$ coefficients are expressed in terms of binomial coefficients. The new algorithm is conceptually easy and it offers computational time advantage over currently available algorithms. As an application of Eq. 10, we have solved the basic nuclear attraction integrals over STOs by using following formulae (see [46,53])

$$J_{nlm}(\zeta,\vec{R}) = 2^n\sqrt{\frac{2\pi}{\zeta(2n)!}}\sum_{i=0}^{n+1}\sum_{j=0}^{n} j!C_0^{nl0}(i,j) \times\left[\sum_{k=0}^{j}\frac{1}{(j-k)!}(R\zeta)^{i+j-l-k-1}\left((-1)^i-(-1)^{j-k-1}\right) -2e^{-\zeta R}(R\zeta)^{i-l-1}\right]S_{lm}(\theta,\varphi). \tag{17}$$

3 Numerical results and discussions

We have presented a simple and straightforward algorithm for evaluating the Löwdin-α radial functions in terms of binomial coefficients. The use of this approach allows us fast and efficient calculation of multicenter multielectron integrals over STOs. From the viewpoint of computational efficiency and accuracy of our and various other approximations, the basic nuclear attraction integral over STOs was evaluated by the Mathematica 6.0 International Mathematical Software on an AMD Athlon^{TM} 2 Duo-Core Processor TK-55 1.80 GHz computer. The comparative results of the calculations for the basic nuclear attraction integral over STOs are presented in Table 1. It can be seen from Table 1 that the results for the basic nuclear attraction integral over STOs using Eq. 10 show the CPU times to be remarkably less than the other results (Eq. 7). The usefulness of the new approach for $C_{l'}^{nlm}(i,j)$ coefficients is widely acknowledged and is valued for its simple and quickness of calculation. Overall, the present results provide an alternative analytic structure for discussing and designing multicenter multielectron integrals over STOs.

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