Journal of Mathematical Chemistry Vol. 38, No. 4, November 2005 (© 2005)
DOI: 10.1007/s10910-005-6912-4

Reply to "comment on 'calculation of two-center nuclear attraction integrals over integer and noninteger n-slater-type orbitals in nonlined-up coordinate systems" '

Telhat Özdoğan

Department of Physics, Faculty of Education, Ondokuz Mayis University, 05189 Amasya, Turkey
E-mail: telhatoz@omu.edu.tr

Received 8 December 2004; revised 27 May 2005

The comments of Guseinov on our recent paper (T. Özdoğan, S. Gümüş and M. Kara, J. Math. Chem. 33 (2003) 181) are critically analyzed. It is proved that the expansion formula for the product of two normalized associated Legendre functions and the expressions for two-center nuclear attraction integrals over Slater type orbitals have been obtained independently, by the use of basic mathematical rules.

KEY WORDS: Slater-type orbital, nuclear attraction integral, Legendre function

AMS subject classification: 81-08, 81-V55, 81V45

1. Introduction

The aim of this report is to prove that the formulae presented in our previous paper [1] for the expansion formula for the product of two normalized associated Legendre functions and expressions for two-center nuclear attraction integrals over Slater type orbitals (STOs) are obtained independently, not by changing the summation indices of papers cited in Ref. [2].

2. Independent proof of the expansion formula for the product of two normalized associated legendre functions with different centers

During the calculation of arbitrary multicenter multielectron molecular integrals over STOs using ellipsoidal coordinates method, one shall require a formula for the product of two normalized associated Legendre functions centered on points a and b,

$$T^{l\lambda,l'\lambda}(\theta_a,\theta_b) = \mathrm{P}_{l\lambda}(\cos\theta_a)\,\mathrm{P}_{l'\lambda}(\cos\theta_b)\,. \tag{1}$$

The analytical expression for the normalized associated Legendre functions have been defined by Yasui and Saika [3] in terms of factorials. By the use of well-known properties of the binomial coefficients, we re-expressed the following relation for the normalized associated Legendre functions as [4]

$$\mathrm{P}_{lm}\left(\cos\theta\right) = (-1)^{(|m|-m)/2}\sum_{k} C_{lm}^{k}\left(\sin\theta\right)^{2k+m}\left(\cos\theta\right)^{l-(2k+m)}, \tag{2}$$

where $1/2\left(|m|-m\right)\leqslant k\leqslant E\left((l-m)/2\right)$ and

$$E\left(\tfrac{n}{2}\right) = \tfrac{n}{2}-\tfrac{1}{4}\left(1-(-1)^{n}\right), \tag{3}$$

and

$$C_{lm}^{k} = \frac{(-1)^{k}}{2^{2k+m}}\left[\frac{2l+1}{2}\,F_{l-k}\left(l+m\right)F_{k+m}\left(l-k\right)F_{2k}\left(l-m\right)F_{k}\left(2k\right)\right]^{1/2}. \tag{4}$$

For obtaining the relation for the product of two normalized associated Legendre functions, we need the relations between spherical polar coordinates and ellipsoidal coordinates centered at atoms A and B separated by a distance R, as given below:

$$r_a = \frac{R}{2}\left(\mu+\nu\right),\quad \cos\theta_a = \frac{1+\mu\nu}{\mu+\nu},\quad \sin\theta_a = \frac{\left[\left(\mu^2-1\right)\left(1-\nu^2\right)\right]^{1/2}}{\mu+\nu}, \tag{5a}$$

$$r_b = \frac{R}{2}\left(\mu-\nu\right),\quad \cos\theta_b = \frac{1-\mu\nu}{\mu-\nu},\quad \sin\theta_b = \frac{\left[\left(\mu^2-1\right)\left(1-\nu^2\right)\right]^{1/2}}{\mu-\nu}, \tag{5b}$$

Substituting equations (2)–(5) in equation (1), we have the following relation for the product of two normalized associated Legendre functions in ellipsoidal coordinates

$$\begin{aligned}T^{l\lambda,l'\lambda}\left(\mu,\nu\right) &= \mathrm{P}_{l\lambda}\left(\tfrac{1+\mu\nu}{\mu+\nu}\right)\mathrm{P}_{l'\lambda}\left(\tfrac{1-\mu\nu}{\mu-\nu}\right)\\ &= \sum_{k\,k'} C_{l\,\lambda}^{k}C_{l'\,\lambda}^{k'}\frac{\left[\left(\mu^2-1\right)\left(1-\nu^2\right)\right]^{k+k'+\lambda}}{\left(\mu+\nu\right)^{l}\left(\mu-\nu\right)^{l'}}\left(1+\mu\nu\right)^{l-(2k+\lambda)}\\ &\quad\times\left(1-\mu\nu\right)^{l'-(2k'+\lambda)}.\end{aligned} \tag{6}$$

Using the identity

$$\left(\mu^2-1\right)\left(1-\nu^2\right) = \left(\mu+\nu\right)^2-\left(1+\mu\nu\right)^2 \tag{7}$$

and well-known binomial expansion

$$\left(\mu+\nu\right)^{N} = \sum_{m=0}^{N} F_m\left(N\right)\,\mu^{N-m}\,\nu^{m}, \tag{8}$$

we obtain

$$\begin{aligned}\left[\left(\mu^2-1\right)\left(1-\nu^2\right)\right]^{k+k'+\lambda} &= \left[(\mu+\nu)^2-(1+\mu\nu)^2\right]^{k+k'+\lambda} \\ &= \sum_{u=0}^{k+k'+\lambda} (-1)^u\, F_u\left(k+k'+\lambda\right)(\mu+\nu)^{2\left(k+k'+\lambda\right)-2u} \\ &\quad\times(1+\mu\nu)^{2u}\,. \end{aligned} \tag{9}$$

Substituting equation (9) in equation (6) we find

$$\begin{aligned} T^{l\lambda,l'\lambda}(\mu,\nu) &= \sum_{k\,k'} C^{k}_{l\,\lambda} C^{k'}_{l'\,\lambda} \sum_{u=0}^{k+k'+\lambda} (-1)^u F_u\left(k+k'+\lambda\right) \\ &\quad\times\frac{(1+\mu\nu)^{l-(2k+\lambda)+2u}\,(1-\mu\nu)^{l'-\left(2k'+\lambda\right)}}{(\mu+\nu)^{l-2(k+k'+\lambda)+2u}\,(\mu-\nu)^{l'}}. \end{aligned} \tag{10}$$

Next, using the well-known relation [5]

$$(\mu+\nu)^N\,(\mu-\nu)^{N'} = \sum_{m=0}^{N+N'} F_m\left(N,N'\right)\mu^{N+N'-m}\nu^m \tag{11}$$

in equation (10), we obtain

$$\begin{aligned} &(1+\mu\nu)^{l-(2k+\lambda)+2u}\,(1-\mu\nu)^{l'-\left(2k'+\lambda\right)} \\ &= \sum_{s=0}^{l+l'-2\left(k+k'+\lambda\right)+2u} F_s\left(l-2k-\lambda+2u,\, l'-2k'-\lambda\right)(\mu\nu)^s. \end{aligned} \tag{12}$$

Substituting equation (12) in equation (10), the expansion formula for the product of two normalized associated Legendre funcitons is obtained as

$$T^{l\lambda,l'\lambda}(\mu,\nu) = \sum_{k,k'}\sum_{u,s} a^{kk'}_{us}\left(l\lambda,l'\lambda\right)\frac{(\mu\nu)^s}{(\mu+\nu)^{l-2(k+k'+\lambda)+2u}\,(\mu-\nu)^{l'}} \tag{13}$$

where the expansion coefficients are

$$a^{kk'}_{us}\left(l\lambda,l'\lambda\right) = C^{k}_{l\lambda}C^{k'}_{l'\lambda}\,(-1)^u\,F_u\left(k+k'+\lambda\right)F_s\left(l-2k-\lambda+2u,\, l'-2k'-\lambda\right), \tag{14}$$

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

$$\begin{aligned} &0 \leqslant k \le E\left(\tfrac{l-\lambda}{2}\right), && 0\leqslant k' \leqslant E\left(\tfrac{l'-\lambda}{2}\right), \\ &0\leqslant u \leqslant \left(k+k'+\lambda\right), && 0\le s\le \left(l+l'\right)-2\left(k+k'+\lambda\right)+2u. \end{aligned} \tag{15}$$

In equations (11), (12) and (14), the coefficient $F_m\left(N, N'\right)$ is defined in Ref. [5]. Meanwhile, similar expressions for the product of two normalized normalized associated Legendre functions in ellipsoidal coordinates can be found elsewhere (see: equation (A.12) of Ref. [5] and equation (10) of [6]). Our formula includes binomials, which have very useful recurrence relations and therefore enable one to calculate multicenter integrals with enough speed and accuracy.

Using expansion formula for the product of two normalized associated Legendre functions (equation (13)) in equations (2) and (3) of our paper [1], it is easy to have analytic relations for two center nuclear attraction integrals. Meanwhile, it should be noted that nuclear attraction integrals given by equation (1) of the comment of Guseinov [2] is not the aim of our recent paper [1]. But, it is worthwhile to express that nuclear attraction integrals of this type have been analyzed more recently by our group [7].

It is seen from the proofs presented above that the formulae presented in Refs. [1,8] have been obtained independently, not by changing the summation indices of papers cited in comment.

References

[1] T. Özdoğan, S. Gümüş and M. Kara, J. Math. Chem. 33 (2003) 181.
[2] I.I. Guseinov, J. Math. Chem. 36 (2004) 123.
[3] J. Yasui and A. Saika, J. Chem. Phys. 76 (1982) 468.
[4] T. Özdoğan, M. Orbay, Czech. J. Phys. 52 (2002) 1297.
[5] J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory* (Mc-Graw Hill, 1970).
[6] I.I. Guseinov, J. Phys. B., 3 (1970) 1399.
[7] S. Gümüş, T. Özdoğan, *Commun. Theor. Phys*. 39 (2003) 701.
[8] T. Özdoğan and M. Orbay, Int. J. Quantum Chem. 87 (2002) 15.