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

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Recently published formulas for the calculation of two-center nuclear attraction integrals (T. Özdoğan, S. Gümüş and M. Kara, J. Math. Chem. 33 (2003) 181) are critically analyzed. It is shown that the analytical relations presented in this work are not original and they can easily be derived by means of a simple algebra from the formulas for overlap integrals, their rotation coefficients and expansion of the product of two normalized associated Legendre functions in elliptical coordinates published in our papers (I.I. Guseinov, J. Phys. B 3 (1970) 1399; Phys. Rev. A 32 (1985) 1864; J. Mol. Struct.: Theochem 336 (1995) 17).

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1. Introduction

The evaluation of two-center nuclear attraction integrals over integer and noninteger n-slater-type orbitals (STOs) is of fundamental importance in the study of molecular systems. 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 translation formulas given by the present author for the expansion of STOs about a new center. It should be noted that two-center integrals of nuclear attraction of types $\langle a\,|(1/r_a)|\,b\rangle$ and $\langle a\,|(1/r_b)|\,b\rangle$ can be expressed by overlap integrals [1]. Recently, Özdoğan et al. [2] published the formulas for the calculation of two-center nuclear attraction integrals of these types. In this Comment we demonstrate that the results published by these authors in two-center nuclear attraction integrals are not original

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and can be easily derived from the formulas for overlap integrals published in our papers.

2. Theory

It is well known that the two-center nuclear attraction integrals over normalized complex or real STOs in the molecular coordinate system (nonlined-up coordinate systems) are defined by the following formulas [1]:

$$U_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=\int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\frac{1}{r_b}\chi_{n'l'm'}(\zeta',\vec{r}_a)\mathrm{d}V, \tag{1}$$

$$U^{(A)}_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=\int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\frac{1}{r_a}\chi_{n'l'm'}(\zeta',\vec{r}_b)\mathrm{d}V, \tag{2}$$

$$U^{(B)}_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=\int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\frac{1}{r_b}\chi_{n'l'm'}(\zeta',\vec{r}_b)\mathrm{d}V, \tag{3}$$

where (R,θ,φ) are the spherical coordinates of radius vector $\vec{R}\equiv\vec{R}_{ab}=\vec{r}_a-\vec{r}_b$ and

$$\chi_{nlm}(\zeta,\vec{r})=R_n(\zeta,r)S_{lm}(\theta,\varphi), \tag{4}$$

$$R_n(\zeta,r)=(2\zeta)^{n+1/2}[\Gamma(2n+1)]^{-1/2}r^{n-1}\mathrm{e}^{-\zeta r}. \tag{5}$$

Here, n is the integer or noninteger principal quantum number and $\Gamma(n)$ is the gamma function.

Taking into account the relation

$$\frac{1}{r}R_n(\zeta,r)=2\zeta\left[\frac{\Gamma(2n-1)}{\Gamma(2n+1)}\right]^{1/2}R_{n-1}(\zeta,r), \tag{6}$$

it is easy to show that the nuclear attraction integrals (2) and (3) are expressed through the two-center overlap integrals:

$$U^{(A)}_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=2\zeta\left[\frac{\Gamma(2n-1)}{\Gamma(2n+1)}\right]^{1/2}S_{n-1lm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi), \tag{7}$$

$$U^{(B)}_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=2\zeta'\left[\frac{\Gamma(2n'-1)}{\Gamma(2n'+1)}\right]^{1/2}S_{nlm,n'-1l'm'}(\zeta,\zeta';R,\theta,\varphi), \tag{8}$$

where overlap integrals are defined by

$$S_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=\int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm'}(\zeta',\vec{r}_b)\,\mathrm{d}V. \tag{9}$$

Using equation (7) for $n\to n+1$ and $n'\to n'-1$ in equation (8) we can express the $U^{(B)}$-integral through the $U^{(A)}$-integral:

$$U^{(B)}_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)$$
$$=\frac{\zeta'}{\zeta}\left[\frac{\Gamma(2n+3)\Gamma(2n'-1)}{\Gamma(2n+1)\Gamma(2n'+1)}\right]^{1/2}U^{(A)}_{n+1lm,n'-1l'm'}(\zeta,\zeta';R,\theta,\varphi), \tag{10}$$

and, conversely,

$$U^{(A)}_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)$$
$$=\frac{\zeta}{\zeta'}\left[\frac{\Gamma(2n-1)\Gamma(2n'+3)}{\Gamma(2n+1)\Gamma(2n'+1)}\right]^{1/2}U^{(B)}_{n-1lm,n'+1l'm'}(\zeta,\zeta';R,\theta,\varphi). \tag{11}$$

Hence, we have only two kinds of independent two-center nuclear attraction integrals, namely, equation (1) and one of equations (2) and (3) which is reduced to the two-center overlap integrals.

The authors of [2–4] published the formulas for the evaluation of overlap integrals (9), and nuclear attraction integrals (2) and (3) which, by the use of equations (7) and (8), can be expressed through the overlap integrals. In [5] we proved that the published in [3,4] results for two-center overlap integrals in lined-up coordinate systems and expansion of the product of two normalized associated Legendre functions in elliptical coordinates can easily be derived from our papers [6–8] by changing the summation indices and application of a simple algebra. In this Comment we show that the presented in [2] formulas for the calculation of two-center nuclear attraction integrals in nonlined-up coordinate systems based on the results of [3,4] can also be derived from the formulas of our articles [5–9].

For the evaluation of integral (9) relative to nolined-up coordinate system in [7] (see also [9]) we established the following relation for the rotation of two-center overlap integrals with integer and noninteger n-STOs:

$$S_{nlm,n'l'm'}(\zeta,\zeta';R,\theta,\varphi)=\sum_{\lambda=0}^{\min(l,l')}T^{\lambda*}_{lm,l'm'}(\theta,\varphi)S_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R,0,0). \tag{12}$$

Here $S_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R,0,0)$ and $T^{\lambda}_{lm,l'm'}(\theta,\varphi)$ are the two-center overlap integrals in lined-up coordinate systems and the rotation coefficients, respectively:

$$S_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R,0,0)=(-1)^{l'-\lambda}N_{nn'}(p,t)\sum_{\alpha\beta q}g^{q}_{\alpha\beta}(l\lambda,l'\lambda)Q^{q}_{n-\alpha,n'-\beta}(p,t), \tag{13}$$

$$T^{\lambda}_{lm,l'm'}(\theta,\varphi)=\frac{2}{(1+\delta_{\lambda0})\left[(1+\delta_{m0})(1+\delta_{m'0})\right]^{1/2}}\sum_{i=-1}^{1}{}^{(2)}\sum_{L=|l-l'|}^{l+l'}{}^{(2)}(\varepsilon_{m0})^{\delta_{i,\varepsilon_{mm'}}}$$
$$\times C^{ll'L}_{i\gamma,\gamma',i\gamma+\gamma'}C^{ll'L}_{\lambda,-\lambda,0}\left[\frac{2\pi\left(1+\delta_{M_i0}\right)}{2L+1}\right]^{1/2}S_{LM_i}(\theta,\varphi), \tag{14}$$

where $\gamma = |m|$, $\gamma' = |m'|$ and $M_i = \varepsilon_{mm'} |i\gamma + \gamma'|$. In equation (14) the symbol $\sum^{(2)}$ indicates that the summation is to be performed in steps of two. For $\gamma = \gamma'$ and $\varepsilon_{mm'} = -1$ terms with a negative value of index I ($i = -1$) contained in equation (14) should be equated to zero. We notice that the symbol $\varepsilon_{mm'}$ in equation (14) may have the values ± 1 and is determined by the product of the signs m and m' (the sign of zero is regarded as positive). The quantities C in equation (14) is the Clebsch–Cordan coefficients in the case of our phases ($Y^*_{lm} = Y_{l-m}$, see [9]).

$$Q^q_{n,n'}(p,t) = \int_1^\infty \int_{-1}^1 (\mu\nu)^q (\mu+\nu)^n (\mu-\nu)^{n'} \mathrm{e}^{-p\mu - pt\nu}\, \mathrm{d}\mu\, \mathrm{d}\nu$$

$$= \sum_{m=0} F_m(n,n') A_{n+n'+q-m}(p) B_{q+m}(pt), \tag{15}$$

where $p = \frac{R}{2}(\zeta + \zeta')$, $t = \frac{\zeta - \zeta'}{\zeta + \zeta'}$, $0 \leqslant m \leqslant n + n'$ for integer n, $0 \leqslant m \leqslant \infty$ for noninteger n and $F_m(n,n')$ is the generalized binomial coefficient defined by

$$F_m(n,n') = \sum_{\sigma=0}^{\infty} (-1)^\sigma F_{m-\sigma}(n) F_\sigma(n'), \tag{16}$$

$$F_m(n) = \begin{cases} n!/[m!(n-m)!] & \text{for integer } n \\ \frac{(-1)^m \Gamma(m-n)}{m!\Gamma(-n)} & \text{for noninteger } n. \end{cases} \tag{17}$$

The terms with negative factorials in equation (16) do not contribute to the summation.

By changing the summation indices we obtained in [5] an alternative expansion to equation (13) based on the formulas for the expansion of the product of two normalized associated Legendre functions in elliptical coordinates established in [6]:

$$S_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R,0,0) = (-1)^{l'-\lambda} N_{nn'}(p,t) \sum_{kk'us} a^{kk'}_{us}(l\lambda, l'\lambda)$$

$$\times \sum_h F_h(n-l+2k+2k'+2\lambda-2u, n'-l')$$

$$\times A_{i'}(p) B_j(pt), \tag{18}$$

where $i' = i+1$, $i = \gamma + s - h - 1$, $\gamma = (n+n') - (l+l') + 2(k+k'+\lambda) - 2u$, $0 \leqslant h \leqslant \gamma$ for integer n, $0 \leqslant h \leqslant \infty$ for noninteger n and $j = s + h$. See [5] for the exact definition of other quantities and indices in equations (12)–(18).

Now we are in a position to obtain the formulas published by Özdoğan, et al. [2] from the above mentioned relationships. Substituting equations (12) and (18) into equations (7) and (8) one gets equations (4)–(9) of [2]. It should

be noted that all of the formulas presented in [3] and [4] for the calculation of two-center overlap, and nuclear attraction integrals in lined-up coordinate systems can also be derived, as shown in [5], from the equations (7), (8) and (18).

Thus, the formulas published in [2–4] for the calculation of two-center overlap and nuclear attraction integrals over integer and noninteger n-STOs in nonlined-up and lined-up coordinate systems are derived from the use of established in our papers formulas for two-center overlap integrals [5–9]. We notice that, by means of relations for nuclear attraction integrals (1) and overlap integrals (9) presented in our papers we have had considerable success in the calculation of multicenter molecular integrals using translation formulas for STOs the expansion coefficients of which are expressed in terms of overlap integrals (See, e.g. [10, 11]).

References

[1] C.C.J. Roothaan, J. Chem. Phys. 19 (1951) 1445.
[2] T. Özdoğan, S. Gümüş and M. Kara, J. Math. Chem. 33 (2003) 181.
[3] T. Özdoğan and M. Orbay, Int. J. Quant. Chem. 87 (2002) 15.
[4] T. Özdoğan, M. Orbay and S. Gümüş, Commun. Theor. Phys. 37 (2002) 711.
[5] I.I. Guseinov, Int. J. Quant. Chem. 91 (2003) 62.
[6] I.I. Guseinov, J. Phys. B 3 (1970) 1399.
[7] I.I. Guseinov, Phys. Rev. A 32 (1985) 1864.
[8] I.I. Guseinov and J. Mol. Struct. (Theochem) 336 (1995) 17.
[9] I.I. Guseinov and B.A. Mamedov, J. Mol. Struct. (Theochem) 465 (1999) 1.
[10] I.I. Guseinov, J. Mol. Struct. (Theochem) 593 (2002) 65; 625 (2003) 221; J. Chem. Phys. 119 (2003) 4614; J. Mol. Mod. 9 (2003) 115; 9 (2003) 190.
[11] I.I. Guseinov and B.A. Mamedov, J. Comput. Phys. 174 (2001) 428; J. Math. Chem. 32 (2002) 309; Int. J. Quant. Chem. 86 (2002) 440; 93 (2003) 9; J. Theor. Comput. Chem. 1 (2002) 17; Theor. Chem. Acc. 108 (2002) 21; J. Mol. Mod. 8 (2002) 272.