# Calculation of multicentre nuclear attraction integrals over Slater-type orbitals using unsymmetrical one-range addition theorems

Israfil I. Guseinov[a)], N. Seckin Gorgun[b)], and Nimet Zaim[b)]

[a)] *Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey*
[b)] *Department of Physics, Faculty of Arts and Sciences, Trakya University, Edirne, Turkey*

(Received 25 May 2009; revised manuscript received 27 July 2009)

Using the unsymmetrical one-range addition theorems introduced by one of the authors with the help of complete orthonormal sets of $\Psi^{\alpha}$-exponential type orbitals ($\alpha = 1, 0, -1, -2, ...$), this paper presents the sets of series expansion relations for multicentre nuclear attraction integrals over Slater-type orbitals arising in Hartree–Fock–Roothaan equations for molecules. The final results are expressed through multicentre charge density expansion coefficients and basic integrals. The convergence of the series is tested by calculating concrete cases for arbitrary values of parameters of orbitals.

**Keywords:** Slater-type orbitals, nuclear attraction integrals, Hartree–Fock–Roothaan equations, unsymmetrical one-range addition theorems

**PACC:** 3115, 3120A

## 1. Introduction

It is well known that the vast majority of all the molecular electronic structure calculations are nowadays performed on the basis of the Hartree–Fock–Roothaan (HFR) equations.[1,2] These equations contain the so-called one- and two-electron multicentre integrals whose numerical values are needed in the subsequent iterative solution of the HFR equations. The efficient and reliable evaluation of these integrals has been a major bottleneck since the early days of computational quantum chemistry. The only truly demanding one-electron integral is the so-called three-centre nuclear attraction integral, whose evaluation is much more difficult than the evaluation of the one-electron two-centre integrals. Compared with one-electron integrals, the computation of the two-electron integrals is usually more difficult by some orders of magnitude. Even today and in spite of the recent progress in mathematical techniques and in computer hard- and software, this integral problem of computational quantum chemistry is not yet solved in a completely satisfactory way.[3]

The computational problems which have to be overcome depend strongly on the basis functions being used. The Gaussian basis functions, as proposed by Boys,[4] are used on a large scale in molecular calculations. These functions have many obvious disadvantages. In particular, they are nonphysical in the sense that they are not able to describe correctly the asymptotic behaviour of exact molecular wave functions either in the vicinity of the nuclei[5] or at large distances away from the nuclei.[6] The only, but nevertheless decisive, advantage of Gaussian functions is that their molecular multicentre integrals can be computed comparatively easily. So, it would be desirable to use the physically better motivated exponentially decaying basis functions in electronic structure calculations. The multicentre integrals can be computed both efficiently and reliably if the integrals are calculated by the use of addition theorems for Slater-type orbitals (STO)[7] established with the help of complete orthonormal sets of $\Psi^{\alpha}$-exponential type orbitals ($\Psi^{\alpha}$-ETO, $\alpha = 1, 0, -1, -2, ...$).[8]

In the context of atomic and molecular electronic structure calculations, two fundamentally different types of addition theorems occur in the literature. The addition theorems of the first type all have the typical two-range form of the Laplace expansion of the Coulomb potential. There is a second class of addition theorems, namely, unsymmetrical and symmetrical one-range addition theorems,[7] which can be constructed by expanding a function located at a cen-

© 2010 Chinese Physical Society and IOP Publishing Ltd

tre $a$ in terms of a complete orthonormal set located at a centre $b$. The use of unsymmetrical and symmetrical one-range addition theorems in molecular *ab initio* calculations would be highly desirable since they are capable of producing much better approximations than the two-range addition theorems. The aim of this work is to calculate the multicentre nuclear attraction integrals appearing in the HFR equations for molecules using unsymmetrical one-range addition theorems of STO.

## 2. Definition

The multicentre nuclear attraction integrals examined in this work are defined as

$$I^{ac,b}_{p_1p'_1}(\zeta_1,\zeta'_1) = \int \chi^*_{p_1}(\zeta_1,\boldsymbol{r}_{a1})\chi_{p'_1}(\zeta'_1,\boldsymbol{r}_{c1})\frac{1}{r_{b1}}\mathrm{d}v_1, \quad (1)$$

where $p_1 \equiv n_1l_1m_1$, $p'_1 \equiv n'_1l'_1m'_1$ and

$$\chi_{nlm}(\zeta,\boldsymbol{r}) = [(2n)!]^{-1/2}(2\zeta)^{n+1/2}r^{n-1}\mathrm{e}^{-\zeta r}S_{lm}(\theta,\varphi). \quad (2)$$

Here, $S_{lm}(\theta,\varphi)$ are the complex (for $S_{lm} \equiv \mathrm{Y}_{lm}$) or real spherical harmonics determined by

$$S_{lm}(\theta,\varphi) = \mathrm{P}_{l|m|}(\cos\theta)\Phi_m(\varphi), \quad (3)$$

where $\mathrm{P}_{l|m|}$ are the normalized associated Legendre functions[9] and for complex spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}m\varphi}, \quad (4)$$

for real spherical harmonics

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

It is easy to show that equations (3) and (5) for the real spherical functions are obtained with the help of $\mathrm{Y}^*_{lm}(\theta,\varphi) = \mathrm{Y}_{l-m}(\theta,\varphi)$ (see Ref. [10]). Therefore, our definition of phases for complex spherical harmonics ($\mathrm{Y}^*_{lm} = \mathrm{Y}_{l-m}$) differs from the Condon–Shortley phases[11] by the sign factor $(-1)^m$.

## 3. Use of unsymmetrical one-range addition theorems

With the evaluation of integral (1) we use the following relation for the unsymmetrical one-range addition theorems established in a previous paper[12] for the charge density of STO: for three-centre cases

$$\chi^*_{p_1}(\zeta_1,\boldsymbol{r}_{a1})\chi_{p'_1}(\zeta'_1,\boldsymbol{r}_{c1}) = \frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;\boldsymbol{R}_{ca},\boldsymbol{R}_{ab})\chi^*_p(z,\boldsymbol{r}_{b1}), \quad (6a)$$

$$\chi^*_{p_1}(\zeta_1,\boldsymbol{r}_{a1})\chi_{p'_1}(\zeta'_1,\boldsymbol{r}_{c1}) = \frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;\boldsymbol{R}_{cb},\boldsymbol{R}_{ab})\chi^*_p(z,\boldsymbol{r}_{b1}), \quad (6b)$$

for two-centre cases

$$\chi^*_{p_1}(\zeta_1,\boldsymbol{r}_{a1})\chi_{p'_1}(\zeta'_1,\boldsymbol{r}_{c1}) = \frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;\boldsymbol{R}_{ca},0)\chi^*_p(z,\boldsymbol{r}_{a1}) \quad (7a)$$

$$\chi^*_{p_1}(\zeta_1,\boldsymbol{r}_{a1})\chi_{p'_1}(\zeta'_1,\boldsymbol{r}_{b1}) = \frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;0,\boldsymbol{R}_{ab})\chi^*_p(z,\boldsymbol{r}_{b1}), \quad (7b)$$

for one-centre case

$$\chi^*_{p_1}(\zeta_1,\boldsymbol{r}_1)\chi_{p'_1}(\zeta'_1,\boldsymbol{r}_1) = \frac{1}{\sqrt{4\pi}}\sum_{\nu=|l_1-l'_1|}^{l_1+l'_1}\sum_{\sigma=-\nu}^{\nu}W_{p_1p'_1q}(\zeta_1,\zeta'_1,z)\chi^*_q(z,\boldsymbol{r}_1), \quad (8)$$

where $p \equiv nlm$, $q \equiv \mu\nu\sigma$, $\mu = n_1 + n'_1 - 1$ and $z = \zeta_1 + \zeta'_1$; the index $N$ is a positive integer number. See Ref. [12] for the exact definition of multicentre charge density expansion coefficients $W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;\boldsymbol{R}_{ca},\boldsymbol{R}_{ab})$, $W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;\boldsymbol{R}_{ca},0)$, $W^{\alpha N}_{p_1p'_1p}(\zeta_1,\zeta'_1,z;0,\boldsymbol{R}_{ab})$ and $W_{p_1p'_1p}(\zeta_1,\zeta'_1,z)$ occurring in these equations. It should be

noted that equations (6a), (6b), (7a) and (7b) are obtained by making use of unsymmetrical one-range addition theorems presented in Ref. [7].

Taking into account Eqs. (6a), (6b), (7a), (7b) and (8) in Eq. (1) we obtain for the multicentre nuclear attraction integrals the following formulae: for three-centre integrals

$$I_{p_1p_1'}^{ac,b}(\zeta_1,\zeta_1') = \lim_{N\to\infty}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} W_{p_1p_1'p}^{\alpha N}(\zeta_1,\zeta_1',z;\boldsymbol{R}_{ca},0)J_p(z,\boldsymbol{R}_{ab}), \tag{9a}$$

$$I_{p_1p_1'}^{ac,b}(\zeta_1,\zeta_1') = \left(\frac{2}{z}\right)^{1/2}\lim_{N\to\infty}\sum_{n=1}^{N} W_{p_1p_1'k}^{\alpha N}(\zeta_1,\zeta_1',z;\boldsymbol{R}_{ca},\boldsymbol{R}_{ab})\,2^n n!\left[(2n)!\right]^{-1/2}, \tag{9b}$$

$$I_{p_1p_1'}^{ac,b}(\zeta_1,\zeta_1') = \left(\frac{2}{z}\right)^{1/2}\lim_{N\to\infty}\sum_{n=1}^{N} W_{p_1p_1'k}^{\alpha N}(\zeta_1,\zeta_1',z;\boldsymbol{R}_{cb},\boldsymbol{R}_{ab})\,2^n n!\left[(2n)!\right]^{-1/2}, \tag{9c}$$

for two-centre integrals

$$I_{p_1p_1'}^{aa,b}(\zeta_1,\zeta_1') = \sum_{\nu=\left|l_1-l_1'\right|}^{l_1+l_1'}\sum_{\sigma=-\nu}^{\nu} W_{p_1p_1'q}(\zeta_1,\zeta_1',z)J_q(z,\boldsymbol{R}_{ab}), \tag{10a}$$

$$I_{p_1p_1'}^{ab,b}(\zeta_1,\zeta_1') = \left(\frac{2}{z}\right)^{1/2}\lim_{N\to\infty}\sum_{n=1}^{N} W_{p_1p_1'k}^{\alpha N}(\zeta_1,\zeta_1',z;0,\boldsymbol{R}_{ab})2^n n!\left[(2n)!\right]^{-1/2}, \tag{10b}$$

for one-centre integrals

$$I_{p_1p_1'}(\zeta_1,\zeta_1') \equiv I_{p_1p_1'}^{aa,a}(\zeta_1,\zeta_1') = \delta_{l_1l_1'}\delta_{m_1m_1'}\frac{(n_1+n_1'-1)!}{\left[(2n_1)!\,(2n_1')!\right]^{1/2}}x_1^{n_1+1/2}x_1'^{\,n_1'+1/2}z, \tag{11}$$

where $k \equiv n00$, $x_1 = 2\zeta_1/z$, $x_1' = 2\zeta_1'/z$ and $z = \zeta_1 + \zeta_1'$. In Eqs. (9a) and (10a), the quantities $J_p(z,\boldsymbol{R}_{ab})$ are the basic nuclear attraction integrals over STO defined as

$$J_{nlm}(z,\boldsymbol{R}_{ab}) = \frac{1}{\sqrt{4\pi}}\int \chi_{nlm}^{*}(z,\boldsymbol{r}_{a1})\frac{1}{r_{b1}}\,\mathrm{d}v_1. \tag{12}$$

It is easy to show that the basic nuclear attraction integrals (12) are determined by the following relations:

$$J_{nlm}(z,\boldsymbol{R}_{ab}) = 2^n\sqrt{\frac{2}{F_n(2n)z}}\delta_{l0}\delta_{m0} \quad \text{for} \quad \boldsymbol{R}_{ab}=0, \tag{13a}$$

$$J_{nlm}(z,\boldsymbol{R}_{ab}) = 2^n\sqrt{\frac{2}{F_n(2n)z}}F_n(n+l+1)(l+1)! \times\frac{1}{x^{l+1}}\left[1-\mathrm{e}^{-x}\sum_{k=0}^{n+l}\gamma_k(n,l)\frac{x^k}{k!}\right]\frac{\sqrt{4\pi}}{2l+1}S_{lm}^{*}(\Theta_{ab},\Phi_{ab}) \quad \text{for} \quad \boldsymbol{R}_{ab}\neq 0, \tag{13b}$$

where $F_m(n) = (n!)/(m!(n-m)!)$, $x = zR_{ab}$ and

$$\gamma_k(n,l) = 1 - \frac{F_{2l+1}(k)}{F_{n-l}(n+l+1)}. \tag{14}$$

It should be noted that equation (13b) is unsuited for numerical computations for small values of $x$, because the function $J_{nlm}(z,\boldsymbol{R}_{ab})$ becomes numerically unstable for $x \to 0$. In this case, the infinite-form expression can be obtained from the following series expansion:[9]

$$\mathrm{e}^{-x} = \sum_{k=0}^{\infty}\frac{(-x)^k}{k!}. \tag{15}$$

Taking into account Eq. (15) in Eq. (13b) we obtain the following series expansion formula:[10]

$$J_{nlm}(z,\boldsymbol{R}_{ab}) = 2^n\sqrt{\frac{2}{F_n(2n)z}}F_n(n+l+1)(l+1)!$$

$$\times \left[ \frac{1}{l!} \sum_{k=0}^{\infty} \frac{(-x)^k}{k!(l+1+k)} - \mathrm{e}^{-x} \sum_{k=l+1}^{n+l} \gamma_k(n,l) \frac{x^{k-(l+1)}}{k!} \right] \frac{\sqrt{4\pi}}{2l+1} S^*_{lm}(\Theta_{ab}, \Phi_{ab}). \tag{16}$$

For the derivation of Eq. (16) we have taken into account the relation

$$\frac{1}{x^n} \left( 1 - \mathrm{e}^{-x} \sum_{k=0}^{n-1} \frac{x^k}{k!} \right) = \frac{1}{(n-1)!} \sum_{k=0}^{\infty} \frac{(-x)^k}{k!(n+k)}. \tag{17}$$

# 4. Numerical results and discussion

The applicability of unsymmetrical one-range addition theorems is tested by calculating the multicentre nuclear attraction integrals determined by Eqs. (9a), (9b), (9c), (10a), (10b) and (11). On the basis of these formulae we constructed the program which is performed in the Mathematica 6.0 language packages.

The results of calculations in atomic units for three-centre nuclear attraction integrals (9a) using basic integrals, equations (13a) and (13b), are presented in Tables 1, 2 and 3. The numerical results for three-centre nuclear attraction integrals (9a) for arbitrary values of screening constants, quantum numbers and location of orbitals are placed in Table 1. This table shows a good rate agreement for $\alpha = 1$ and $\alpha = 0$. The convergence properties of the series expansion relation for the three-centre nuclear attraction integral $I^{ac,b}_{100,100}(4.3, 3.1)$ are shown in Table 2 and Figs. 1, 2.

The convergence of the series shown in Figs. 1 and 2 is described by $10^2 \Delta f_L = I^{ac,b}_{100,100}(4.3, 3.1)_L - I^{ac,b}_{100,100}(4.3, 3.1)_{L=14}$ and $10^3 \Delta f_M = I^{ac,b}_{100,100}(4.3, 3.1)_M - I^{ac,b}_{100,100}(4.3, 3.1)_{M=14}$, respectively. In these table and figures, the partial summations corresponding to progressively increasing upper summation limits in Eq. (9a) are denoted by $N$, $L$, and $M$. As can be seen from Figs. 1 and 2, equation (9a) displays the most rapid convergence to the numerical results with six digits which are stable as a function of summation limits for $L = 9$, and $M = 7$, respectively. Therefore, the convergence of the series with respect to $l$ and $m$ is rapid. So, one can include only a few terms in the summations over indices $l$ and $m$ arising in Eq. (9a). Table 2 shows that the accuracy of calculations is satisfactory for the different values of summation index $N$. The dependence of three-centre nuclear attraction integrals on the internuclear distances for $\alpha = 1$, $\alpha = 0$ and $N = 15$ are shown in Table 3. The convergence in this case is also satisfactory. We notice that a greater accuracy is attainable by using more terms in series expansion relations obtained in this work.

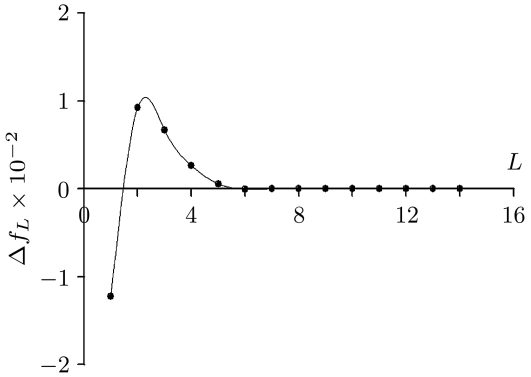



**Fig. 1.** Convergence of the series expansion relation (9a) for the three-centre nuclear attraction integral $I^{ac,b}_{100,100}(4.3, 3.1)$ as a function of summation limit $L$ ($0 \le l \le L$ and $-l \le m \le l$) for $R_{ca} = 0.6$, $\theta_{ca} = 2\pi/3$, $\varphi_{ca} = \pi$, $R_{ab} = 0.7$, $\theta_{ab} = \pi/6$, $\varphi_{ab} = \pi/4$, $N = 15$ and $\alpha = 1$.

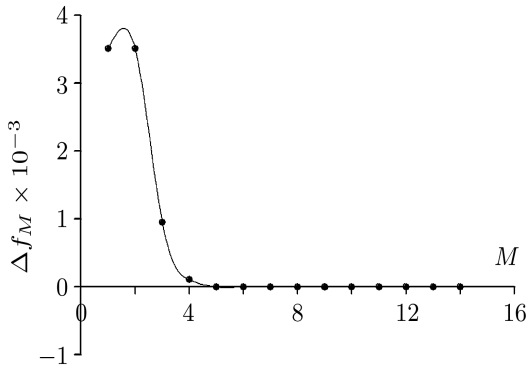



**Fig. 2.** Convergence of the series expansion relation (9a) for the three-centre nuclear attraction integral $I^{ac,b}_{100,100}(4.3, 3.1)$ as a function of summation limit $M$ ($0 \le l \le N-1$ and $-M \le m \le M$) for $R_{ca} = 0.6$, $\theta_{ca} = 2\pi/3$, $\varphi_{ca} = \pi$, $R_{ab} = 0.7$, $\theta_{ab} = \pi/6$, $\varphi_{ab} = \pi/4$, $N = 15$ and $\alpha = 1$.

**Table 1.** Comparison of methods of computing three-centre nuclear attraction integrals with STO using series expansion relations for $N = 15$.

| $n_1$ | $l_1$ | $m_1$ | $\zeta_1$ | $n'_1$ | $l'_1$ | $m'_1$ | $\zeta'_1$ | $R_{ca}$ | $\theta_{ca}$ | $\varphi_{ca}$ | $R_{ab}$ | $\theta_{ab}$ | $\varphi_{ab}$ | Eq. (9a) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | $\alpha = 1$ | $\alpha = 0$ |
| 1 | 0 | 0 | 4.3 | 1 | 0 | 0 | 3.1 | 0.6 | 120 | 180 | 0.7 | 30 | 45 | 0.8665624076078977 | 0.8666894509976633 |
| 2 | 0 | 0 | 3.7 | 1 | 0 | 0 | 5.4 | 0.1 | 120 | 90 | 1.2 | 60 | 36 | 0.5445177524181889 | 0.5445398854228105 |
| 2 | 1 | 1 | 9.6 | 2 | 1 | 1 | 6.3 | 0.8 | 30 | 45 | 1.8 | 120 | 72 | 0.0214596651207774 | 0.0214596514070074 |
| 3 | 1 | 1 | 8.7 | 3 | 1 | 1 | 3.5 | 2.8 | 120 | 135 | 2.1 | 150 | 108 | –0.0013125604912938 | –0.0013110646092757 |

**Table 2.** Convergence of the series expansion relation (9a) for the three-centre nuclear attraction integral $I^{ac,b}_{100,100}(4.3, 3.1)$ as a function of summation limit $N$ for $R_{ca} = 0.6$, $\theta_{ca} = 2\pi/3$, $\varphi_{ca} = \pi$, $R_{ab} = 0.7$, $\theta_{ab} = \pi/6$, $\varphi_{ab} = \pi/4$.

| $N$ | $\alpha = 1$ |
|---|---|
| 8 | 0.8688913684407814 |
| 9 | 0.8683541427516125 |
| 10 | 0.8677757313706731 |
| 11 | 0.8672936528887564 |
| 12 | 0.8669816173992039 |
| 13 | 0.8667985739159082 |
| 14 | 0.8666716359201255 |
| 15 | 0.8665624076078977 |

**Table 3.** Convergence of the series expansion relation (9a) for the three-centre nuclear attraction integral $I^{ac,b}_{100,100}(4.3, 3.1)$ as a function of $R_{ab}$ (with $\theta_{ab} = \pi/6$, $\varphi_{ab} = \pi/4$ ) for $R_{ca} = 0.6$, $\theta_{ca} = 2\pi/3$, $\varphi_{ca} = \pi$ and $N = 15$.

| $R_{ab}$ | $\alpha = 1$ | $\alpha = 0$ |
|---|---|---|
| 0.7 | 0.8665624076078977 | 0.8666894509976633 |
| 3.0 | 0.1830014181441383 | 0.1830014190979357 |
| 5.0 | 0.1071799599052002 | 0.1071799599049620 |
| 7.0 | 0.0757714455834380 | 0.0757714455834270 |
| 9.0 | 0.0585974573897790 | 0.0585974573897624 |
| 11.0 | 0.0477696126540140 | 0.0477696126539971 |
| 13.0 | 0.0403190908230971 | 0.0403190908230815 |
| 15.0 | 0.0348789973797444 | 0.0348789973797303 |

As can be seen from our tests, the series expansion formulae obtained with the help of unsymmetrical one-range addition theorems for STO are useful tools for evaluation of the multicentre nuclear attraction integrals with arbitrary values of quantum numbers, orbital parameters and internuclear distances.

# References


[1] Roothaan C C J 1951 *Rev. Mod. Phys.* **23** 69

[2] Roothaan C C J 1960 *Rev. Mod. Phys.* **32** 179

[3] Levine I N 2000 *Quantum Chemistry* 5th ed. (NJ: Prentice Hall)

[4] Boys S F 1955 *Proc. Roy. Soc. Lond.* A **200** 542

[5] Kato T 1957 *Commun. Pure Appl. Math.* **10** 151

[6] Agmon S 1982 *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-Body Schrödinger Operators* (Princeton: Princeton University Press)

[7] Guseinov I I 2008 *J. Theor. Comput. Chem.* **7** 257

[8] Guseinov I I 2002 *Int. J. Quantum Chem.* **90** 114

[9] Gradshteyn I S and Ryzhik I M 1980 *Tables of Integrals, Sums, Series and Products* 4th ed. (New York: Academic Press)

[10] Guseinov I I 1970 *J. Phys.* B **3** 1399

[11] Condon E U and Shortley G H 1970 *Theory of Atomic Spectra* (Cambridge: Cambridge University Press)

[12] Guseinov I I 2007 *J. Math. Chem.* **42** 415