MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **60** (2008) 385-394

ISSN 0340 - 6253

Combined Theory of Two-Electron Nonrelativistic and Quasirelativistic Multicenter Integrals over Integer and Noninteger n Slater Type Orbitals Using Auxiliary Functions Q_{ns}^{q} and G_{-ns}^{q}

I. I. Guseinov

Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey

(Received January 23, 2008)

Abstract:

Using complete orthonormal sets of ψ^{α} – exponential type orbitals ($\alpha = 1, 0, -1, -2, \ldots$) a large number of series expansion formulas for the two-electron nonrelativistic and quasirelativistic multicenter integrals over integer and noninteger n Slater type orbitals is obtained through the non- and quasi- relativistic basic functions. The non- and quasi-relativistic basic functions are determined by the linear combinations of auxiliary functions Q_{ns}^{q} and G_{-ns}^{q} introduced by the author. The coefficients of series expansion relations are expressed in terms of two-center overlap integrals over integer n Slater functions. The relationships obtained are valid for the arbitrary location, quantum numbers and screening constants of orbitals.

1. Introduction

One of the oldest mathematical and computational problems of molecular electron structure theory is the efficient and reliable evaluation of the notoriously difficult molecular multicenter integrals of exponentially decaying basis functions. Over the years, a large variety of different approaches have been tried out, but in spite of the heroic efforts of numerous researches, a completely satisfactory solution has not been found yet. A principal tool is reduction of a multicenter integral to so-called auxiliary functions, which are essentially special functions. The use of auxiliary functions was a particularly "hot" topic in the fifties of the last century, as documented in Refs. [1-4]. However, even today, there is a lot of work which all deal with auxiliary functions [5-8]. We have also worked quite extensively on the use of auxiliary functions in connection with the evaluation of multicenter integrals of exponentially decaying functions [9-20]. The aim of this work is to use auxiliary functions

$$Q_{ns}^{q}(p,pt)=\int_{1}^{\infty}\int_{-1}^{1}(\mu\nu)^{q}(\mu+\nu)^{n}(\mu-\nu)^{s}e^{-p\mu-pt\nu}d\mu d\nu \tag{1}$$

and

$$G_{-ns}^{q}(p_a;p,pt)=\int_{1}^{\infty}\int_{-1}^{1}\frac{(\mu\nu)^{q}(\mu-\nu)^{s}}{(\mu+\nu)^{n}}(1-e^{-p_a(\mu+\nu)}\sum_{k=0}^{n-1}\frac{[p_a(\mu+\nu)]^{k}}{k!})e^{-p\mu-pt\nu}d\mu d\nu \tag{2}$$

presented in previous papers [21-23] in evaluation of two-electron non- and quasi-relativistic (NQR) multicenter integrals of integer and noninteger n Slater type orbitals (ISTO and NISTO) arising in the study of electronic structure of atomic and molecular systems when the nonrelativistic and quasirelativistic theories are employed [24]. Here, $p_a>0$, $p>0$ and $-p\le pt\le p$. The indices n, s and q are all nonnegative integers. The auxiliary functions Q_{ns}^{q} and G_{-ns}^{q} were all calculated in Refs. [9, 14, 16, 22, 23] by the use of recurrence relations, analytical expressions and series expansion formulas for all values of parameters.

2. Use of expansion formulae for NISTO charge densities

The two-electron NQR multicenter integrals examined in the present work have the following form:

$$\begin{aligned}&I_{p_1^*p_1'^*,p_2^*p_2'^*}(\zeta_1\zeta_1',\zeta_2\zeta_2';\vec{R}_{ca},\vec{R}_{db},\vec{R}_{ab})\\&\quad=\int\int\chi_{p_1^*}^{*}(\zeta_1,\vec{r}_{a1})\chi_{p_1'^*}(\zeta_1',\vec{r}_{c1})O(r_{21})\chi_{p_2^*}(\zeta_2,\vec{r}_{b2})\chi_{p_2'^*}^{*}(\zeta_2',\vec{r}_{d2})dv_1dv_2\end{aligned} \tag{3}$$

$$\begin{aligned}&I^{i}_{p_1^*p_1'^*,p_2^*p_2'^*}(\zeta_1\zeta_1',\zeta_2\zeta_2';\vec{R}_{ca},\vec{R}_{db},\vec{R}_{ab})\\&\quad=\int\int\chi_{p_1^*}^{*}(\zeta_1,\vec{r}_{a1})\chi_{p_1'^*}(\zeta_1',\vec{r}_{c1})O^{i}(\vec{r}_{21})\chi_{p_2^*}(\zeta_2,\vec{r}_{b2})\chi_{p_2'^*}^{*}(\zeta_2',\vec{r}_{d2})dv_1dv_2\end{aligned} \tag{4}$$

$$\begin{aligned}&I^{ij}_{p_1^*p_1'^*,p_2^*p_2'^*}(\zeta_1\zeta_1',\zeta_2\zeta_2';\vec{R}_{ca},\vec{R}_{db},\vec{R}_{ab})\\&\quad=\int\int\chi_{p_1^*}^{*}(\zeta_1,\vec{r}_{a1})\chi_{p_1'^*}(\zeta_1',\vec{r}_{c1})O^{ij}(\vec{r}_{21})\chi_{p_2^*}(\zeta_2,\vec{r}_{b2})\chi_{p_2'^*}^{*}(\zeta_2',\vec{r}_{d2})dv_1dv_2\end{aligned} \tag{5}$$

$$\begin{aligned}&L^{ij}_{p_1^*p_1'^*,p_2^*p_2'^*}(\zeta_1\zeta_1',\zeta_2\zeta_2';\vec{R}_{ca},\vec{R}_{db},\vec{R}_{ab})\\&\quad=\int\int\chi_{p_1^*}^{*}(\zeta_1,\vec{r}_{a1})\chi_{p_1'^*}(\zeta_1',\vec{r}_{c1})R^{ij}(\vec{r}_{21})\chi_{p_2^*}(\zeta_2,\vec{r}_{b2})\chi_{p_2'^*}^{*}(\zeta_2',\vec{r}_{d2})dv_1dv_2\end{aligned}, \tag{6}$$

where $i,j=0,\pm1$, $\vec{r}_{21}=\vec{r}_1-\vec{r}_2; x_1^1=x_1, x_1^{-1}=y_1, x_1^0=z_1$ and $x_2^1=x_2, x_2^{-1}=y_2, x_2^0=z_2$ are the Cartesian coordinates of electrons; $p_k^*\equiv n_k^*l_km_k$ and $p_k'^*\equiv n_k'^*l_k'm_k'$; n_k^* *and* $n_k'^*$ are the noninteger and integer (for $n_k^*=n_k$ *and* $n_k^*=n_k'$) principal quantum numbers; the normalized complex or real NISTO are determined by

$$\chi_{n^*lm}(\zeta,\vec{r})=[\Gamma(2n^*+1)]^{-1/2}(2\zeta)^{n^*+\frac{1}{2}}r^{n^*-1}e^{-\zeta r}S_{lm}(\theta,\varphi). \tag{7}$$

The operators containing in Eqs. (3)-(6) are defined as [24]

$$O(r_{21}) = \frac{1}{r_{21}} \tag{8}$$

$$O^i(\vec{r}_{21}) = \frac{x_{21}^i}{r_{21}^3} \tag{9}$$

$$O^{ij}(\vec{r}_{21}) = \frac{3x_{21}^i x_{21}^j - \delta_{ij} r_{21}^2}{r_{21}^5} - \frac{4\pi}{3}\delta_{ij}\delta(\vec{r}_{21}) \tag{10}$$

$$R^{ij}(\vec{r}_{21}) = \frac{x_{21}^i x_{21}^j}{r_{21}^3} \tag{11}$$

Here, the operators (8) and (11) correspond to the classical relativistic correction to the interaction between the electrons. The correction is due to the retardation of the electromagnetic field produced by an electron. The operators (9) and (10) describe the spin-orbit and spin-spin magnetic moment interactions of the two-electrons, respectively.

In order to evaluate integrals (3)-(6), we use the expansion formulae of the electron charge densities established in previous paper [25] in the following form:

$$\chi_{p^*}(\zeta, \vec{r}_a)\chi^*_{p'^*}(\zeta', \vec{r}_c) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{p^* p'^* q}(\zeta\zeta' z; \vec{R}_{ca}, 0)\chi_q(z, \vec{r}_a), \tag{12}$$

where $\alpha = 1, 0, -1, -2, \ldots$, $q \equiv \mu\nu\sigma$ and $z = \zeta + \zeta'$. Then, we derive the expressions in terms of the charge density expansion coefficients and two-center basic integrals:

$$\begin{aligned} I_{p_1^* p_1'^*, p_2^* p_2'^*}(\zeta_1\zeta_1', \zeta_2\zeta_2', \vec{R}_{ca}, \vec{R}_{db}, \vec{R}_{ab}) = & \lim_{N_1 N_2 \to \infty} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W^{\alpha N_1}_{p_1^* p_1'^* q_1}(\zeta_1\zeta_1' z_1; \vec{R}_{ca}, 0) \\ & \times \sum_{\mu_2=1}^{N_2} \sum_{\nu_2=0}^{\mu_2-1} \sum_{\sigma_2=-\nu_2}^{\nu_2} W^{\alpha N_2}_{p_2^* p_2'^* q_2}(\zeta_2\zeta_2' z_2; \vec{R}_{db}, 0) K_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) \end{aligned} \tag{13}$$

$$\begin{aligned} I^i_{p_1^* p_1'^*, p_2^* p_2'^*}(\zeta_1\zeta_1', \zeta_2\zeta_2', \vec{R}_{ca}, \vec{R}_{db}, \vec{R}_{ab}) = & \lim_{N_1 N_2 \to \infty} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W^{\alpha N_1}_{p_1^* p_1'^* q_1}(\zeta_1\zeta_1' z_1; \vec{R}_{ca}, 0) \\ & \times \sum_{\mu_2=1}^{N_2} \sum_{\nu_2=0}^{\mu_2-1} \sum_{\sigma_2=-\nu_2}^{\nu_2} W^{\alpha N_2}_{p_2^* p_2'^* q_2}(\zeta_2\zeta_2' z_2; \vec{R}_{db}, 0) K^i_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) \end{aligned} \tag{14}$$

$$\begin{aligned} I^{ij}_{p_1^* p_1'^*, p_2^* p_2'^*}(\zeta_1\zeta_1', \zeta_2\zeta_2', \vec{R}_{ca}, \vec{R}_{db}, \vec{R}_{ab}) = & \lim_{N_1 N_2 \to \infty} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W^{\alpha N_1}_{p_1^* p_1'^* q_1}(\zeta_1\zeta_1' z_1; \vec{R}_{ca}, 0) \\ & \times \sum_{\mu_2=1}^{N_2} \sum_{\nu_2=0}^{\mu_2-1} \sum_{\sigma_2=-\nu_2}^{\nu_2} W^{\alpha N_2}_{p_2^* p_2'^* q_2}(\zeta_2\zeta_2' z_2; \vec{R}_{db}, 0) K^{ij}_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) \end{aligned} \tag{15}$$

$$L^{ij}_{p_1^* p_1'^*, p_2^* p_2'^*}(\zeta_1\zeta_1', \zeta_2\zeta_2'; \vec{R}_{ca}, \vec{R}_{db}, \vec{R}_{ab}) = \lim_{N_1 N_2 \to \infty} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W^{\alpha N_1}_{p_1^* p_1'^* q_1}(\zeta_1\zeta_1' z_1; \vec{R}_{ca}, 0)$$
$$\times \sum_{\mu_2=1}^{N_2} \sum_{\nu_2=0}^{\mu_2-1} \sum_{\sigma_2=-\nu_2}^{\nu_2} W^{\alpha N_2}_{p_2^* p_2'^* q_2}(\zeta_2\zeta_2' z_2; \vec{R}_{db}, 0) L^{ij}_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) \quad . \tag{16}$$

Here, $K_{q_1 q_2}(z_1 z_2, \vec{R}_{ab})$, $K^i_{q_1 q_2}(z_1 z_2, \vec{R}_{ab})$, $K^{ij}_{q_1 q_2}(z_1 z_2, \vec{R}_{ab})$ and $L^{ij}_{q_1 q_2}(z_1 z_2, \vec{R}_{ab})$ are the two-electron basic integrals defined as

$$K_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int J_{q_1}(z_1, \vec{r}_{a2}) \chi_{q_2}(z_2, \vec{r}_{b2}) dv_2 \tag{17}$$

$$K^i_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int J^i_{q_1}(z_1, \vec{r}_{a2}) \chi_{q_2}(z_2, \vec{r}_{b2}) dv_2 \tag{18}$$

$$K^{ij}_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int J^{ij}_{q_1}(z_1, \vec{r}_{a2}) \chi_{q_2}(z_2, \vec{r}_{b2}) dv_2 \tag{19}$$

$$L^{ij}_{q_1 q_2}(z_1 z_2, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int \Lambda^{ij}_{q_1}(z_1, \vec{r}_{a2}) \chi_{q_2}(z_2, \vec{r}_{b2}) dv_2 \ . \tag{20}$$

The quantities J_q, J^i_q, J^{ij}_q and Λ^{ij}_q occurring in these formulas are the one-electron basic integrals defined as

$$J_q(z, \vec{r}_{a2}) = \frac{1}{\sqrt{4\pi}} \int \chi^*_q(z, \vec{r}_{a1}) O(r_{21}) dv_1 \tag{21a}$$

$$= f^{00}_{\mu\nu,\nu\sigma}(z, \vec{r}_{a2}) \tag{21b}$$

$$J^i_q(z, \vec{r}_{a2}) = \frac{1}{\sqrt{4\pi}} \int \chi^*_q(z, \vec{r}_{a1}) O^i(\vec{r}_{21}) dv_1 \tag{22a}$$

$$= \sum_{m=-(\nu-1)}^{\nu-1} a^i_{\nu\sigma,m} f^{10}_{\mu\nu,\nu-1m}(z, \vec{r}_{a2}) - (2\nu+1) \left(\frac{x^i_{a2}}{r_{a2}} \right) f^{11}_{\mu\nu,\nu\sigma}(z, \vec{r}_{a2}) \tag{22b}$$

$$J^{ij}_q(z, \vec{r}_{a2}) = \frac{1}{\sqrt{4\pi}} \int \chi^*_q(z, \vec{r}_{a1}) O^{ij}(\vec{r}_{21}) dv_1 \tag{23a}$$

$$= \sum_{m=-(\nu-2)}^{\nu-2} a^{ij}_{\nu\sigma,m} f^{20}_{\mu\nu,\nu-2m}(z, \vec{r}_{a2}) - (2\nu+1)$$
$$\times \sum_{m=-(\nu-1)}^{\nu-1} \left[a^i_{\nu\sigma,m} \left(\frac{x^j_{a2}}{r_{a2}} \right) + a^j_{\nu\sigma,m} \left(\frac{x^i_{a2}}{r_{a2}} \right) \right] f^{21}_{\mu\nu,\nu-1m}(z, \vec{r}_{a2}) - (2\nu+1) \delta_{ij} f^{21}_{\mu\nu,\nu\sigma}(z, \vec{r}_{a2})$$
$$+ (2\nu+1)(2\nu+3) \left(\frac{x^i_{a2}}{r_{a2}} \right) \left(\frac{x^j_{a2}}{r_{a2}} \right) f^{22}_{\mu\nu,\nu\sigma}(z, \vec{r}_{a2}) - \frac{\sqrt{4\pi}}{3} \delta_{ij} \chi^*_{\mu\nu\sigma}(z, \vec{r}_{a2}) \tag{23b}$$

$$\Lambda_q^{ij}(z,\vec{r}_{a2}) = \frac{1}{\sqrt{4\pi}} \int \chi_q^*(z,\vec{r}_{a1}) R^{ij}(\vec{r}_{21}) dv_1 \,. \tag{24a}$$

$$\begin{aligned} &= \frac{1}{3} \sum_{lm,LM} (2L+1)(2l+1)^{1/2} C^{l|m|}(1j,\nu\sigma) A_{j\sigma}^m \\ &\times C^{L|M|}(1i,lm) A_{im}^M f_{\mu L,LM}^{00}(z,\vec{r}_{a2}) \end{aligned} \tag{24b}$$

See Ref. [21] for the exact definition of generalized Gaunt coefficients $C^{L|M|}$ and coefficients A^M. We notice that the charge densities expansion coefficients $W^{\alpha N}$ occurring in Eqs. (13)-(16) depend on overlap integrals for the calculation of which one can use the computer programs presented in previous papers [26, 27].

The relations (21)-(23) have been established in previous paper [28]. The quantities $f_{\mu\nu,\kappa m}^{tk}(z,\vec{r})$ are the one-electron basic functions which are determined by

$$f_{\mu\nu,\kappa m}^{tk}(z,\vec{r}) = f_{\mu\nu}^{tk}(z,r) \left(\frac{4\pi}{2\kappa+1} \right)^{1/2} S_{\kappa m}^*(\theta,\varphi) \tag{25}$$

$$f_{\mu\nu}^{tk}(z,r) = f_{\mu\nu,00}^{tk}(z,r) = \frac{N_{\mu\nu}^t(2z)}{(zr)^{\nu+t+!}} \left(1 - e^{-zr} \sum_{s=0}^{\mu+\nu+k} \gamma_s^{\nu k}(\mu)(zr)^s \right), \tag{26}$$

where $t = 0,1,2$, $0 \le k \le t, \kappa = \nu, \nu-1, \nu-2$ and

$$N_{\mu\nu}^t(2z) = 2^{\mu-t+1}(\mu+\nu+1)! \left[\frac{(2z)^{2t-1}}{(2\nu+1)(2\mu)!} \right]^{1/2} \tag{27}$$

$$\gamma_s^{\nu 0}(\mu) = \gamma_s^{\nu}(\mu) = \frac{1}{s!} - \frac{(\mu-\nu)!}{(\mu+\nu+1)!(s-2\nu-1)!} \tag{28}$$

$$\gamma_s^{\nu 1}(\mu) = \frac{1}{2\nu+1} \left[(2\nu+1-s)\gamma_s^{\nu}(\mu) + \gamma_{s-1}^{\nu}(\mu) \right] \tag{29}$$

$$\begin{aligned} \gamma_s^{\nu 2}(\mu) = \frac{1}{(2\nu+1)(2\nu+3)} &\left[(2\nu+1-s)(2\nu+3-s)\gamma_s^{\nu}(\mu) \right. \\ &\left. + (4\nu+5-2s)\gamma_{s-1}^{\nu}(\mu) + \gamma_{s-2}^{\nu}(\mu) \right] \end{aligned} \,. \tag{30}$$

The terms with negative factorials in Eq. (28) should be equated to zero and $\gamma_s^{\nu}(\mu) = 0$ for $s < 0$ and $s > \mu + \nu$.

Now we introduce the two-electron basic functions defined as

$$\mathrm{D}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}^{tk}(z_1 z_2, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int f_{\mu_1\nu_1,\nu\sigma}^{tk}(z_1,\vec{r}_{a2}) \chi_{\mu_2\nu_2\sigma_2}(z_2,\vec{r}_{b2}) dv_2 \,, \tag{31}$$

where the $f^{tk}_{\mu_1\nu_1,\nu\sigma}(z_1,\vec{r}_{a2})$ are one-electron basic functions determined by Eq. (25).

In order to express the two-electron basic integrals $K_{q_1q_2}(z_1z_2,\vec{R}_{ab})$, $K^i_{q_1q_2}(z_1z_2,\vec{R}_{ab})$, $K^{ij}_{q_1q_2}(z_1z_2,\vec{R}_{ab})$ and $L^{ij}_{q_1q_2}(z_1z_2,\vec{R}_{ab})$ in terms of basic functions, Eq. (31), we take into account Eqs. (21)-(24) in (17)-(20). Then, we obtain:

$$K_{q_1q_2}(z_1z_2,\vec{R}_{ab}) = D^{00}_{\mu_1\nu_1,\nu_1\sigma_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \tag{32}$$

$$K^i_{q_1q_2}(z_1z_2,\vec{R}_{ab}) = \sum_{m_1=-(\nu_1-1)}^{\nu_1-1} a^i_{\nu_1\sigma_1,m_1} D^{10}_{\mu_1\nu_1,\nu_1-1m_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) - (2\nu_1+1) D^{11,i}_{\mu_1\nu_1,\nu_1\sigma_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \tag{33}$$

$$\begin{aligned} K^{ij}_{q_1q_2}(z_1z_2,\vec{R}_{ab}) = & \sum_{m_1=-(\nu_1-2)}^{\nu_1-2} a^{ij}_{\nu_1\sigma_1,m_1} D^{20}_{\mu_1\nu_1,\nu_1-2m_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \\ & -(2\nu_1+1)\sum_{m_1=-(\nu_1-1)}^{\nu_1-1}\left[a^i_{\nu_1\sigma_1,m_1} D^{21,j}_{\mu_1\nu_1,\nu_1-1m_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) + a^j_{\nu_1\sigma_1,m_1} D^{21,i}_{\mu_1\nu_1,\nu_1-1m_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab})\right] \\ & -(2\nu_1+1)\delta_{ij} D^{21}_{\mu_1\nu_1,\nu_1\sigma_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) + (2\nu_1+1)(2\nu_1+3) D^{22,ij}_{\mu_1\nu_1,\nu_1\sigma_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \\ & -\frac{1}{3}\delta_{ij} S_{\mu_1\nu_1\sigma_1,\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \end{aligned} \tag{34}$$

$$\begin{aligned} L^{ij}_{q_1q_2}(z_1z_2,\vec{R}_{ab}) = & \frac{1}{3}\sum_{lm,LM}(2L+1)(2l+1)^{1/2} C^{l|m|}(1j,\nu\sigma) A^m_{j\sigma} \\ & \times C^{L|M|}(1i,lm) A^M_{im} D^{00}_{\mu L,LM;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \end{aligned}, \tag{35}$$

where

$$S_{\mu_1\nu_1\sigma_1,\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) = \int \chi^*_{\mu_1\nu_1\sigma_1}(z_1,\vec{r}_{a2})\chi_{\mu_2\nu_2\sigma_2}(z_2,\vec{r}_{b2})dv_2 \tag{36}$$

are the overlap integrals. It is easy to express the quantities $D^{11,i}$, $D^{21,i}$ and $D^{22,ij}$ occurring in Eqs. (33) and (34) in terms of two-electron basic functions $\mathrm{D}^{tk}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab})$:

$$D^{11,i}_{\mu_1\nu_1,\nu_1\sigma_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}}\int\left(\frac{x^i_{a2}}{r_{a2}}\right) f^{11}_{\mu_1\nu_1,\nu_1\sigma_1}(z_1,\vec{r}_{a2})\chi_{\mu_2\nu_2\sigma_2}(z_2,\vec{r}_{b2})dv_2 \tag{37a}$$

$$= \sum_{lm}\frac{(2l+1)}{[3(2\nu_1+1)]^{1/2}} C^{l|m|}(1i,\nu_1\sigma_1) A^m_{i\sigma_1} D^{11}_{\mu_1\nu_1,lm;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \tag{37b}$$

$$D^{21,i}_{\mu_1\nu_1,\nu_1-1m_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}}\int\left(\frac{x^i_{a2}}{r_{a2}}\right) f^{21}_{\mu_1\nu_1,\nu_1-1m_1}(z_1,\vec{r}_{a2})\chi_{\mu_2\nu_2\sigma_2}(z_2,\vec{r}_{b2})dV_2 \tag{38a}$$

$$= \sum_{lm}\frac{2l+1}{[3(2\nu_1-1)]^{1/2}} C^{l|m|}(1i,\nu_1-1m_1) A^m_{im_1} D^{21}_{\mu_1\nu_1,lm;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \tag{38b}$$

$$D^{22,ij}_{\mu_1\nu_1,\nu_1\sigma_1;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\int\left(\frac{x^i_{a2}}{r_{a2}}\right)\left(\frac{x^j_{a2}}{r_{a2}}\right)f^{22}_{\mu_1\nu_1,\nu_1\sigma_1}(z_1,\vec{r}_{a2})\chi_{\mu_2\nu_2\sigma_2}(z_2,\vec{r}_{b2})dv_2 \tag{39a}$$

$$=\frac{1}{3}\sum_{lm,LM}(2L+1)\left(\frac{2l+1}{2\nu_1+1}\right)^{1/2}C^{l|m|}(1j,\nu_1\sigma_1)A^m_{j\sigma_1} \times C^{L|M|}(1i,lm)A^M_{im}D^{22}_{\mu_1\nu_1,LM;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab}) \tag{39b}$$

3. Expressions for two-electron basic functions in terms of auxiliary functions Q^q_{ns} and G^q_{-ns}

Now we express the two-electron basic functions $D^{tk}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab})$ in terms of auxiliary functions Q^q_{ns} and G^q_{-ns}. For this purpose we use Eqs. (5) and (17) of Ref. [29] for the rotation of two-center overlap integrals over arbitrary atomic orbitals in molecular coordinate system:

$$D^{tk}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}(z_1z_2,\vec{R}_{ab})=\sum_{\lambda=0}^{\min(\nu,\nu_2)}T^{\lambda^*}_{\nu\sigma,\nu_2\sigma_2}(\theta_{ab},\varphi_{ab})D^{tk}_{\mu_1\nu_1,\nu\lambda;\mu_2\nu_2\lambda}(z_1z_2,R_{ab}). \tag{40}$$

Here, the quantities $D^{tk}_{\mu_1\nu_1,\nu\lambda;\mu_2\nu_2\lambda}(z_1z_2,R_{ab})$ are the two-center basic functions relative to lined-up coordinate systems:

$$D^{tk}_{\mu_1\nu_1,\nu\lambda;\mu_2\nu_2\lambda}(z_1z_2,R_{ab})=\frac{1}{\sqrt{4\pi}}\int f^{tk}_{\mu_1\nu_1,\nu\lambda}(z_1,\vec{r}_{a2})\chi_{\mu_2\nu_2\lambda}(z_2,\vec{r}_{b2})dv_2. \tag{41}$$

Transforming (41) from Cartesian to elliptical coordinates and integrating over azimuthal angle $\varphi_2=\varphi_{a2}=\varphi_{b2}$, we finally obtain for two-center basic functions in terms of auxiliary functions Q^q_{ns} and G^q_{-ns} the expressions

$$D^{tk}_{\mu_1\nu_1,\nu\lambda;\mu_2\nu_2\lambda}(z_1z_2,R)=A^t_{\mu_1\nu_1,\nu,\mu_2}(p_1,p_2)\sum_{\alpha\beta q}g^q_{\alpha\beta}(\nu\lambda,\nu_2\lambda)$$

$$\times\begin{cases} Q^q_{|\nu_1+\alpha+t|,\mu_2-\beta}(p_2,-p_2)-\sum_{s=0}^{\mu_1+\nu_1+k}\gamma^{\nu_1k}_s(\mu_1)p_1^sQ^q_{s+|\nu_1+\alpha+t|,\mu_2-\beta}(p_{12},p_{12}t_{12}) \ for\ \nu_1+\alpha+t\le 0 & (42a)\\ G^q_{-(\nu_1+\alpha+t),\mu_2-\beta}(p_1;p_{12},p_{12}t_{12})-\sum_{s=\nu_1+\alpha+t}^{\mu_1+\nu_1+k}\gamma^{\nu_1k}_s(\mu_1)p_1^sQ^q_{s-(\nu_1+\alpha+t),\mu_2-\beta}(p_{12},p_{12}t_{12}) \ for\ \nu_1+\alpha+t>0. & (42b)\end{cases}$$

Here, $R=R_{ab}$, $p_1=\frac{1}{2}z_1R$, $p_2=\frac{1}{2}z_2R$, $\eta=z_2/z_1$ and

$$A^{t}_{\mu_1\nu_1,\nu,\mu_2}(p_1,p_2)=\frac{2^{\mu_1+\mu_2-t+3}(\mu_1+\nu_1+1)!\,p_2^{\mu_2-t+2}}{[(2\nu_1+1)(2\nu+1)(2\mu_1)!(2\mu_2)!(p_1/p_2)]^{1/2}\,p_1^{\nu_1+1}}. \tag{43}$$

It is easy to derive for one-center basic functions the following relations:

$$D^{tk}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}(z_1z_2)=D^{tk}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}(z_1z_2,0)=\delta_{\nu\nu_2}\delta_{\sigma\sigma_2}B^{t}_{\mu_1\nu_1,\nu,\mu_2}(z_1,z_2)$$

$$\times\begin{cases}\dfrac{|\nu_1-\mu_2+t|!}{\eta^{|\nu_1-\mu_2+t|+1}}-\displaystyle\sum_{s=0}^{\mu_1+\nu_1+k}\gamma_s^{\nu_1 k}(\mu_1)\frac{(|\nu_1-\mu_2+t|+s)!}{(1+\eta)^{|\nu_1-\mu_2+t|+s+1}}\ \ for\ \nu_1-\mu_2+t\le 0 & (44a)\\ G_{-(\nu_1-\mu_2+t)}(\eta)-\displaystyle\sum_{s=\nu_1-\mu_2+t}^{\mu_1+\nu_1+k}\gamma_s^{\nu_1 k}(\mu_1)\frac{[s-(\nu_1-\mu_2+t)]!}{(1+\eta)^{s-(\nu_1-\mu_2+t)+1}}\ \ for\ \nu_1-\mu_2+t>0, & (44b)\end{cases}$$

where

$$B^{t}_{\mu_1\nu_1,\nu,\mu_2}(z_1,z_2)=\frac{2^{\mu_1+\mu_2+1}(\mu_1+\nu_1+1)!}{[(2\nu_1+1)(2\nu+1)(2\mu_1)!(2\mu_2)!]^{1/2}}\left(\frac{z_2}{z_1}\right)^{\mu_2+1/2}z_1^{t-2} \tag{45}$$

$$G_{-n}(\eta)=\int_0^\infty\frac{dx}{x^n}\left(1-e^{-x}\sum_{s=0}^{n-1}\frac{x^s}{s!}\right)e^{-\eta x}\qquad for\quad n\ge 1. \tag{46}$$

See Ref. [21] for the exact definition of coefficients $g^{q}_{\alpha\beta}(\nu\lambda,\nu_2\lambda)$. The functions $G_{-n}(\eta)$ can be determined by the use of the following relations:

$$G_{-1}(\eta)=\ln\frac{1+\eta}{\eta}\quad for\quad n=1 \tag{47}$$

$$G_{-n}(\eta)=\frac{(-\eta)^{n-1}}{(n-1)!}\left[G_{-1}(\eta)+\sum_{s=1}^{n-1}\frac{(-1)^s}{s\eta^s}\right]\quad for\quad n\ge 2. \tag{48}$$

Taking into account the formulae obtained for two-electron one- and two-center basic functions all of the two-electron nonrelativistic and quasirelativistic multicenter integrals over ISTO and NISTO, Eqs. (13)-(16), can be calculated with the help of auxiliary functions Q^{q}_{ns} and G^{q}_{-ns}. Thus, by the use of relationships for basic functions $f^{tk}_{\mu\nu,\kappa m}$ and $\mathrm{D}^{tk}_{\mu_1\nu_1,\nu\sigma;\mu_2\nu_2\sigma_2}$ obtained in Ref. [26] and in this study, respectively, all the one- and two-electron nonrelativistic and quasirelativistic multicenter integrals over integer and noninteger n STO can be evaluated using Cartesian coordinates of the nuclei and the arbitrary values of parameters of Slater orbitals. It should be noted that the relationships obtained for one-electron NQR multicenter integrals can also be used in evaluation of multicenter electronic attraction, electric field and electric field gradient integrals of integer and noninteger n STO arising in investigation of the electrostatic potential created by the electrons of a molecule and its derivatives with respect to the coordinates of nuclei.

References

1. C. C. J. Roothaan, *J. Chem. Phys.* **24** (1956) 947.
2. K. Ruedenberg, C. C. J. Roothaan, W. Jaunzemis, *J. Chem. Phys.* **24** (1956) 201.
3. F. J. Corbato, *J. Chem. Phys.* **24** (1956) 452.
4. T. C. Chen, *J. Chem. Phys.* **24** (1956) 1268.
5. M. P. Barnett, *Int. J. Quantum Chem.* **76** (2000) 464.
6. F. E. Harris, *Int. J. Quantum Chem.* **100** (2004) 142.
7. J. Fernandez, R. Lopez, I. Ema, G. Ramirez, J. F. Rico, *Int. J. Quantum Chem.* **106** (2006) 1986.
8. I. Ema, R. Lopez, J. Fernandez, G. Ramirez, J. F. Rico, *Int. J. Quantum Chem.* **108** (2008) 25.
9. I. I. Guseinov, *J. Chem. Phys.* **78** (1983) 2801.
10. I. I. Guseinov, R. F. Yassen, *J. Mol. Struc. (Theochem)* **339** (1995) 243.
11. I. I. Guseinov, A. Özmen, U. Atav, H. Yüksel, *Int. J. Quantum Chem.* **67** (1998) 199.
12. I. I. Guseinov, B. A. Mamedov, *J. Mol. Struc. (Thoechem)* **528** (2000) 245.
13. I. I. Guseinov, B. A. Mamedov, M. Kara, M. Orbay, *Pramana J. Phys.* **56** (2001) 691.
14. I. I. Guseinov, B. A. Mamedov, *Int. J. Quantum Chem.* **81** (2001) 117.
15. I. I. Guseinov, B.A. Mamedov, *J. Theor. Comput. Chem.*, **1** (2002) 17.
16. I. I. Guseinov, B. A. Mamedov, *Int. J. Quantum Chem.* **86** (2002) 440.
17. I. I. Guseinov, B. A. Mamedov, *J. Mol. Model.* **8** (2002) 272.
18. I. I. Guseinov, *J. Math. Chem.* **36** (2004) 83.
19. I. I. Guseinov, B. A. Mamedov, *J. Math. Chem.* **38** (2005) 21.
20. I. I. Guseinov, B. A. Mamedov, *Chem. Phys.* **312** (2005) 223.
21. I. I. Guseinov, *J. Phys. B* **3** (1970) 1399.
22. I. I. Guseinov, *J. Chem. Phys.* **67** (1977) 3837.
23. I. I. Guseinov, *J. Chem. Phys.* **69** (1978) 4990.
24. H. A. Bethe, E. E. Salpeter, *Quantum Mechanics of One- and Two- Electron Atoms*, Springer-Verlag, Berlin, 1957.

25. I. I. Guseinov, *J. Math. Chem.* **42** (2007) 415.

26. I. I. Guseinov, B. A. Mamedov, *MATCH Commun. Math. Comput. Chem.* **52** (2004) 47.

27. I. I. Guseinov, B. A. Mamedov, *Z. Naturforsch.* **62a** (2007) 467.

28. I. I. Guseinov, *J. Phys. A: Math. Gen.* **37** (2004) 957.

29. I. I. Guseinov, *Phys. Rev. A* **32** (1985) 1864.