

Evaluation of two-center Coulomb and hybrid integrals over complete orthonormal sets of Ψ^α -ETO using auxiliary functions

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Received: 6 March 2010 / Accepted: 7 June 2010 / Published online: 25 June 2010
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Abstract By the use of ellipsoidal coordinates, the two-center Coulomb and hybrid integrals over complete orthonormal sets of Ψ^α – exponential type orbitals arising in ab initio calculations of molecules are evaluated, where $\alpha = 1, 0, -1, -2, \dots$. These integrals are expressed through the auxiliary functions Q_{ns}^q and G_{-ns}^q . The comparison is made with some values of integrals for Slater type orbitals the computation results of which are in good agreement with those obtained in the literature. The relationships obtained are valid for the arbitrary quantum numbers, screening constants and location of orbitals. Closed form expressions for two-center Coulomb and hybrid integrals for 1s and 2s orbitals with $\alpha=1$ are also presented. As an example of application, the Hartree-Fock-Roothaan calculations for the ground state of H_2 molecule are carried out with $\alpha=1$ and $\alpha=0$.

Keywords Auxiliary functions · Coulomb integrals · Ψ^α – exponential type orbitals · Hybrid integrals

Introduction

It is well known that the electronic structure properties of molecular systems obtained from the linear combination of atomic orbitals (LCAO) or basis set expansion method strongly depend on the chosen basis functions [1, 2]. For the calculations of these properties it is desirable to use exponential type orbitals (ETO) as basis sets because they

describe correctly the asymptotic behavior of exact solutions of atomic or molecular Schrödinger equation both in the vicinity of the nuclei [3] and at large distances away from the nuclei [4]. However, the main problem for the use of ETO basis in molecular calculations arises in the evaluation of the multicenter integrals [5]. Various studies have focused on the developing efficient methods for the calculation of these integrals using ETO functions as basis sets (see Refs. [6–8] and references therein). The complete orthonormal sets of Ψ^α – ETO have a special significance in the theory and application of quantum mechanics to molecules [9–13]. The main advantage of Ψ^α – ETO functions is that they possess simple and compact one-range addition theorems which are very useful for the calculations of arbitrary multicenter integrals. We note that, one can calculate the multicenter molecular integrals over Slater type orbitals (STO) using their one-range addition theorems established with the help of complete orthonormal sets of Ψ^α – ETO [9, 11]. The Ψ^α – ETO functions can be usable as a basis set in their own right for molecular calculations [14]. Therefore, in the study of molecular electronic structure one needs efficient and reliable evaluation of molecular integrals over Ψ^α – ETO.

It is well known that the auxiliary functions method is one of the most important methods for the evaluation of multicenter molecular integrals over ETO [15–20]. Even today, there is a lot of work which all deal with auxiliary functions [21–24]. In a recent study [25], we have suggested the method for evaluation of one-electron molecular integrals with the help of auxiliary functions. In the present work, we derive the formulas for two-center Coulomb and hybrid integrals with Ψ^α – ETO using auxiliary functions Q_{ns}^q and G_{-ns}^q [26]. These integrals arise not only in their own right, but are also usable in the calculation of other multicenter electron-repulsion integrals.

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Definitions and basic formulas

The complete orthonormal sets of Ψ^α – ETO are defined as follows [9]:

$$\Psi_{nlm}^\alpha(\zeta, \vec{r}) = (2\zeta)^{3/2} N_{nl}^\alpha x^l e^{-x/2} L_{n+l+1-\alpha}^{2l+2-\alpha}(x) S_{lm}(\theta, \varphi), \quad (1)$$

where $\alpha = 1, 0, -1, -2, \dots, x=2\zeta r$ and

$$N_{nl}^\alpha = (-1)^\alpha \left[\frac{(n-l-1)!}{(2n)^\alpha [(n+l+1-\alpha)!]^3} \right]^{1/2}. \quad (2)$$

The functions $L_q^p(x)$ and $S_{lm}(\theta, \varphi)$ are the generalized Laguerre polynomials and the complex ($S_{lm} \equiv Y_{lm}$) or real spherical harmonics, respectively. The definition of phases in this work for the complex spherical harmonics ($Y_{lm}^* = Y_{l-m}$) differs from the Condon-Shortley phases [27] by sign factor $(-1)^m$.

The Ψ^α – ETO are orthonormal with respect to the weight function $(n/\zeta r)^\alpha$:

$$\int \Psi_{nlm}^{\alpha*}(\zeta, \vec{r}) \left(\frac{n}{\zeta r}\right)^\alpha \Psi_{n'l'm'}^\alpha(\zeta, \vec{r}) dV = \delta_{nn'} \delta_{ll'} \delta_{mm'}. \quad (3)$$

The products of Ψ^α – ETO in the same center are transformed to their linear combinations [10]:

$$\begin{aligned} \Psi_{nlm}^{\alpha*}(\zeta, \vec{r}) \Psi_{n'l'm'}^\alpha(\zeta', \vec{r}) \\ = \frac{(2z)^{3/2}}{\sqrt{4\pi}} \sum_{N=1}^{n+n'-1} \sum_{L=0}^{N-1} \sum_{M=-L}^L B_{nlm, n'l'm'}^{\alpha NLM}(\eta) \Psi_{NLM}^{\alpha*}(z, \vec{r}), \end{aligned} \quad (4)$$

where $\eta = \zeta/\zeta'$ and $z = \zeta + \zeta'$. The analytical relations for coefficients $B_{nlm, n'l'm'}^{\alpha NLM}$ are presented in [10].

It should be noted that the Coulomb-Sturmian and Lambda ETO introduced in Refs. [28–31] are the special cases of Ψ^α – ETO for $\alpha=1$ and $\alpha=0$, respectively. The STO can be represented by finite linear combinations of Ψ^α – ETO:

$$\chi_{nlm}(\zeta, \vec{r}) = \sum_{n'=l+1}^n \bar{\omega}_{n'l}^{\alpha l} \Psi_{n'lm}^\alpha(\zeta, \vec{r}), \quad (5)$$

where

$$\chi_{nlm}(\zeta, \vec{r}) = \left[(2\zeta)^{2n+1} / (2n)! \right]^{1/2} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \quad (6)$$

See Ref. [9] for the exact definition of coefficients $\bar{\omega}_{n'l}^{\alpha l}$. Using Eq. 5 we can express the molecular integrals with STO as finite linear combinations of integrals involving Ψ^α – ETO.

The two-center integrals examined in this work are defined as:

Coulomb integrals

$$C_{aa,bb}^\alpha = \int \Psi_{p_1}^{\alpha*}(\zeta_1, \vec{r}_{a1}) \Psi_{p_1}^\alpha(\zeta'_1, \vec{r}_{a1}) \frac{1}{r_{21}} \Psi_{p_2}^\alpha(\zeta_2, \vec{r}_{b2}) \Psi_{p_2}^{\alpha*}(\zeta'_2, \vec{r}_{b2}) dv_1 dv_2, \quad (7)$$

hybrid integrals

$$H_{aa,ab}^\alpha = \int \Psi_{p_1}^{\alpha*}(\zeta_1, \vec{r}_{a1}) \Psi_{p_1}^\alpha(\zeta'_1, \vec{r}_{a1}) \frac{1}{r_{21}} \Psi_{p_2}^\alpha(\zeta_2, \vec{r}_{a2}) \Psi_{p_2}^{\alpha*}(\zeta'_2, \vec{r}_{b2}) dv_1 dv_2, \quad (8)$$

where $p_i \equiv n_i l_i m_i$, $p'_i \equiv n'_i l'_i m'_i$ and $\vec{r}_{gi} = \vec{r}_i - \vec{R}_g$ ($i=1, 2$ and $g=a, b$).

In this work, we evaluate the integrals (7) and (8) using ellipsoidal coordinates. The final results are given in terms of the following auxiliary functions [26]:

$$Q_{ns}^q(p, t) = \int_1^\infty \int_{-1}^1 (\xi\eta)^q (\xi + \eta)^n (\xi - \eta)^s e^{-p\xi - p't\eta} d\xi d\eta \quad (9)$$

$$\begin{aligned} G_{-ns}^q(p_a, p, t) = \int_1^\infty \int_{-1}^1 \frac{(\xi\eta)^q (\xi - \eta)^s}{(\xi + \eta)^n} \left(1 - e^{-p_a(\xi + \eta)} \sum_{k=0}^{n-1} \frac{(p_a(\xi + \eta))^k}{k!} \right) \\ \times e^{-p\xi - p't\eta} d\xi d\eta, \end{aligned} \quad (10)$$

where $p_a > 0, p > 0$ and $-1 \leq t \leq 1$. The indices n, s , and q are all nonnegative integers. In Ref. [32, 33] the functions Q_{ns}^q and G_{-ns}^q were all calculated from the recurrence relations, analytical expressions and series expansion formulas which can be used for all values of parameters.

Table 1 Two-center Coulomb integrals with Ψ^α – ETO for $\alpha = 1$ ($\zeta = \zeta_1 = \zeta'_1 = \zeta_2 = \zeta'_2$ and $r = R_{ab}$)

$\langle n_1 s n'_1 s n_2 s n'_2 s \rangle$	Eq. 11
$\langle 1s1s 1s1s \rangle$	$\frac{e^{-2\zeta r} (-24 + 24e^{2\zeta r} - \zeta r (33 + 2\zeta r (9 + 2\zeta r)))}{24r}$
$\langle 1s1s 1s2s \rangle$	$\frac{e^{-2\zeta r} (48 - 48e^{2\zeta r} + \zeta r (81 + 2\zeta r (33 + 4\zeta r (4 + \zeta r))))}{96r}$
$\langle 1s1s 2s2s \rangle$	$\frac{e^{-2\zeta r} (-240 + 240e^{2\zeta r} - \zeta r (390 + \zeta r (300 + \zeta r (145 + 2\zeta r (25 + 6\zeta r))))}{240r}$
$\langle 1s2s 1s2s \rangle$	$\frac{e^{-2\zeta r} (-120 + 120e^{2\zeta r} - \zeta r (195 + 2\zeta r (75 + 4\zeta r (10 + \zeta r (5 + 2\zeta r))))}{480r}$
$\langle 1s2s 2s2s \rangle$	$\frac{e^{-2\zeta r} (960 - 960e^{2\zeta r} + \zeta r (1635 + 2\zeta r (675 + 2\zeta r (5 + 2\zeta r) (35 + 2\zeta r (-1 + 2\zeta r))))}{1920r}$
$\langle 2s2s 2s2s \rangle$	$\frac{e^{-2\zeta r} (-26880 + 26880e^{2\zeta r} - \zeta r (45675 + 2\zeta r (18795 + 2\zeta r (5005 + 8\zeta r (245 + \zeta r (70 + \zeta r (7 + 6\zeta r))))))}{26880r}$

Table 2 Two-center hybrid integrals with Ψ^α – ETO for $\alpha = 1$ ($\zeta = \zeta_1 = \zeta'_1 = \zeta_2 = \zeta'_2$ and $r = R_{ab}$)

$\langle n_1 s n'_1 s n_2 s n'_2 s \rangle$	Eq. 12
$\langle 1s1s 1s1s \rangle$	$\frac{e^{-3\zeta r}(-5-2\zeta r+e^{2\zeta r}(5+2\zeta r(1+8\zeta r)))}{16r}$
$\langle 1s1s 1s2s \rangle$	$\frac{e^{-3\zeta r}(-3(53+20\zeta r)+e^{2\zeta r}(159-8\zeta r(36+\zeta r(-21+16\zeta r))))}{192r}$
$\langle 1s1s 2s1s \rangle$	$\frac{e^{-3\zeta r}(45+24\zeta r(3+\zeta r)-e^{2\zeta r}(45+12\zeta r+64\zeta^3 r^3))}{192r}$
$\langle 1s1s 2s2s \rangle$	$\frac{e^{-3\zeta r}(75+3\zeta r(33+10\zeta r)+e^{2\zeta r}(-75+\zeta r(87+2\zeta r(27+8\zeta r(-2+\zeta r))))}{96r}$
$\langle 1s2s 1s1s \rangle$	$\frac{e^{-3\zeta r}(39+8\zeta r(4+\zeta r)+e^{2\zeta r}(-39+4\zeta r(9-8\zeta r)))}{64r}$
$\langle 1s2s 1s2s \rangle$	$\frac{e^{-3\zeta r}(339+6\zeta r(43+10\zeta r)+e^{2\zeta r}(-339+2\zeta r(219+2\zeta r(-51+16\zeta r))))}{192r}$
$\langle 1s2s 2s1s \rangle$	$\frac{e^{-3\zeta r}(e^{2\zeta r}(132-51\zeta r+32\zeta^3 r^3)-3(44+\zeta r(65+4\zeta r(9+2\zeta r))))}{192r}$
$\langle 1s2s 2s2s \rangle$	$\frac{e^{-3\zeta r}(-3(623+4\zeta r(200+\zeta r(99+20\zeta r)))+e^{2\zeta r}(1869+4\zeta r(-363+\zeta r(3-16\zeta r(-2+\zeta r))))}{768r}$
$\langle 2s2s 1s1s \rangle$	$\frac{e^{-3\zeta r}(-103-\zeta r(105+4\zeta r(11+2\zeta r))+e^{2\zeta r}(103+\zeta r(-77+64\zeta r)))}{64r}$
$\langle 2s2s 1s2s \rangle$	$\frac{e^{-3\zeta r}(-3(1287+4\zeta r(306+\zeta r(119+20\zeta r)))+e^{2\zeta r}(3861-4\zeta r(1041+\zeta r(-423+128\zeta r))))}{768r}$
$\langle 2s2s 2s1s \rangle$	$\frac{e^{-3\zeta r}(e^{2\zeta r}(-1779+756\zeta r-256\zeta^3 r^3)+3(593+8\zeta r(112+\zeta r(71+4\zeta r(6+\zeta r))))}{768r}$
$\langle 2s2s 2s2s \rangle$	$\frac{e^{-3\zeta r}(e^{2\zeta r}(-13491+4\zeta r(2349+2\zeta r(-93+32\zeta r(-2+\zeta r)))+3(4497+16\zeta r(376+\zeta r(215+2\zeta r(33+5\zeta r))))}{1536r}$

Evaluation of two-center Coulomb and hybrid integrals

The procedure for calculating two-center Coulomb and hybrid integrals is one and the same and therefore we can consider them together. We use Eq. 4 for the one-electron distribution in Eqs. 7 and 8. Then, the Coulomb and hybrid integrals are expressed through the expansion coefficients and the basic two-center Coulomb c^α and hybrid h^α integrals:

$$C_{aa,bb}^\alpha = \sum_{N_1=1}^{n_1+n'_1-1} \sum_{L_1=0}^{N_1-1} \sum_{M_1=-L_1}^{L_1} \sum_{N_2=1}^{n_2+n'_2-1} \sum_{L_2=0}^{N_2-1} \sum_{M_2=-L_2}^{L_2} B_{p_1 p'_1}^{\alpha q_1}(\eta_1) B_{p_2 p'_2}^{\alpha q_2}(\eta_2) c_{q_1 q_2}^\alpha(z_1, z_2; \vec{R}) \tag{11}$$

$$H_{aa,ab}^\alpha = \sum_{N_1=1}^{n_1+n'_1-1} \sum_{L_1=0}^{N_1-1} \sum_{M_1=-L_1}^{L_1} B_{p_1 p'_1}^{\alpha q_1}(\eta_1) h_{q_1 p_2 p'_2}^\alpha(z_1, \zeta_2, \zeta'_2; \vec{R}), \tag{12}$$

where $q_i \equiv N_i L_i M_i$, $\eta_i = \zeta_i / \zeta'_i$, $z_i = \zeta_i + \zeta'_i$, $\vec{R} = \vec{R}_a - \vec{R}_b$ and

$$c_{q_1 q_2}^\alpha(z_1, z_2; \vec{R}) = \frac{(4z_1 z_2)^{3/2}}{4\pi} \int \Psi_{q_1}^{\alpha*}(z_1, \vec{r}_{a1}) \frac{1}{r_{21}} \Psi_{q_2}^\alpha(z_2, \vec{r}_{b2}) dv_1 dv_2 \tag{13}$$

$$h_{q_1 p_2 p'_2}^\alpha(z_1, \zeta_2, \zeta'_2; \vec{R}) = \frac{(2z_1)^{3/2}}{\sqrt{4\pi}} \int \Psi_{q_1}^{\alpha*}(z_1, \vec{r}_{a1}) \frac{1}{r_{21}} \Psi_{p_2}^\alpha \times (\zeta_2, \vec{r}_{a2}) \Psi_{p'_2}^{\alpha*}(\zeta'_2, \vec{r}_{b2}) dv_1 dv_2. \tag{14}$$

The evaluation of these basic integrals can be carried out by means of integration over the coordinates of the first electron which represents the electrostatic potential energy of the second electron in the presence of first:

$$U_{nlm}^\alpha(\zeta, \vec{r}_{a2}) = \int \Psi_{nlm}^{\alpha*}(\zeta, \vec{r}_{a1}) \frac{1}{r_{21}} dv_1. \tag{15}$$

Table 3 The values of two-center Coulomb integrals over STO in lined-up coordinate systems

n_1	l_1	m_1	ζ_1	n'_1	l'_1	m'_1	ζ'_1	n_2	l_2	m_2	ζ_2	n'_2	l'_2	m'_2	ζ'_2	R	$C_{aa,bb}$	
																	Eqs. 5 and 11	Ref. [38]
1	0	0	5.2	1	0	0	5.2	2	0	0	4.1	2	0	0	4.1	0.2	0.1822892554E+01	0.1822892554E+01
1	0	0	5.2	2	1	0	3.1	2	0	0	4.1	3	2	0	2.5	0.2	-0.2360643021E-01	-0.2360643021E-01
2	1	1	4.0	1	0	0	5.2	2	1	1	3.1	2	0	0	4.1	0.2	0.2035688538E+00	0.2035688538E+00
1	0	0	5.2	1	0	0	5.2	2	1	-1	3.1	2	1	-1	3.1	8.5	0.1173928965E+00	0.1173928965E+00
2	1	0	3.1	2	1	0	3.1	4	2	2	0.5	4	2	2	0.5	8.5	0.8752847763E-01	0.8752847763E-01
3	2	-2	1.8	3	2	-2	1.8	2	0	0	4.1	2	0	0	4.1	8.5	0.1156689749E+00	0.1156689749E+00

Table 4 The values of two-center hybrid integrals over STO in lined-up coordinate systems

n_1	l_1	m_1	ζ_1	n'_1	l'_1	m'_1	ζ'_1	n_2	l_2	m_2	ζ_2	n'_2	l'_2	m'_2	ζ'_2	R	$H_{aa,ab}$	
																	Eqs. 5 and 12	Ref. [38]
1	0	0	5.2	1	0	0	5.2	1	0	0	5.2	2	0	0	4.1	0.2	0.1822833273E+01	0.1822833273E+01
1	0	0	5.2	2	1	0	3.1	2	1	1	4.0	3	2	1	3.0	0.2	0.6868282918E-01	0.6868282918E-01
2	1	0	3.1	2	1	1	4.0	2	1	0	3.1	3	1	1	1.5	2.5	0.5094919530E-02	0.5094919530E-02
4	3	0	3.5	2	1	0	3.1	1	0	0	5.2	2	0	0	4.1	2.5	0.1455277481E-03	0.1455277481E-03
2	1	1	4.0	2	1	1	4.0	1	0	0	5.2	3	2	0	2.5	8.5	0.6525699399E-06	0.6525699424E-06
2	1	0	3.1	2	1	0	3.1	4	3	0	3.5	3	2	0	2.5	8.5	0.1087085814E-04	0.1087085814E-04

Using Laplace expression of r_{21}^{-1} and orthogonality properties of spherical harmonics, it is easy to obtain for the potential (15) the following relation:

$$U_{nlm}^\alpha(\zeta, \vec{r}_{a2}) = N_{nl}^\alpha \sum_{i=0}^{n-l-1} (2\zeta)^{l+i+3/2} \gamma_{n+l+1-\alpha, i}^{2l+2-\alpha} \frac{4\pi(2l+i+2)!}{r_{a2}^{2l+i+3} \zeta^{2l+i+3} (2l+1)} S_{lm}^*(\theta_{a2}, \varphi_{a2}) \times \left(1 - e^{-\zeta r_{a2}} \sum_{s=0}^{2l+i+1} (\zeta r_{a2})^s \Upsilon_s^l(l+i+1) \right). \tag{16}$$

See Refs. [10, 34] for the exact definition of coefficients $\gamma_{q,i}^p$ and $\Upsilon_s^l(n)$, respectively.

Now we can move on to the integration of basic integrals with respect to the coordinates of the second electron.

Expressions for basic Coulomb and hybrid integrals in terms of auxiliary functions

For the evaluation of basic Coulomb and hybrid integrals we take into account Eq. 16 for potential function in Eqs. 13 and 14. Then, it is necessary to perform a rotation of basic Coulomb and hybrid integrals from the nonlined-up coordinate systems to the lined-up coordinate systems the polar axes of which are placed along the line joining the centers. It is easy to show that the following relations hold for the rotation of basic Coulomb and hybrid integrals:

$$c_{nlm, n'l'm'}^\alpha(\zeta, \zeta'; \vec{R}) = \sum_{\lambda=0}^{\min(l, l')} T_{lm, l'm'}^{\lambda*}(\theta, \varphi) c_{nl, n'l\lambda}^{\prime\alpha}(\zeta, \zeta'; R) \tag{17}$$

$$h_{nlm, n'l'm', n''l''m''}^\alpha(\zeta, \zeta', \zeta''; \vec{R}) = \sum_{L=|l-l'|}^{l+l'} \sum_{M=-L}^L \sum_{\lambda=0}^{\min(L, l'')} T_{LM, l''m''}^{\lambda*}(\theta, \varphi) (2L+1)^{1/2} C^{L|M|}(lm, l'm') A_{mm'}^M \times h_{nl, n'l, n''l'', L\lambda}^{\prime\alpha}(\zeta, \zeta', \zeta''; R). \tag{18}$$

See Refs. [26, 35] for the definition of generalized Gaunt coefficients $C^{L|M|}$ and A^M coefficients, and rotation coefficients T^λ , respectively. Now, we change from integration with respect to spherical coordinates to integration with respect to ellipsoidal coordinates. Then,

using expansion formulas for a product of two normalized associated Legendre functions in ellipsoidal coordinates established in Ref. [26], we obtain for the radial coefficients $c^{\prime\alpha}$ the following relations in terms of auxiliary functions:

$$c_{nl, n'l\lambda}^{\prime\alpha}(\zeta, \zeta'; R) = (-1)^{l-\lambda} N_{nl}^\alpha N_{n'l}^{\alpha'} \sum_{i, i', \mu, \nu, q} \frac{2^{l+l'+i+i'+7} p_b^{l+i'+3} (2l+i+2)!}{p_a^l (2l+1) R} \gamma_{n+l+1-\alpha, i}^{2l+2-\alpha} \gamma_{n'+l'+1-\alpha', i'}^{2l'+2-\alpha'} \times g_{\mu\nu}^q(l\lambda, l'\lambda) \left(G_{-(l+\mu), l'+l'+1-\nu}^q(p_a, p_b, -1) - \sum_{s=l+\mu}^{2l+i+1} p_a^s \Upsilon_s^l(l+i+1) Q_{s-l-\mu, l'+l'+1-\nu}^q(p, t) \right), \tag{19}$$

where $0 \leq i \leq n-l-1$, $0 \leq i' \leq n'-l'-1$, $-\lambda \leq \mu(2) \leq l$, $\lambda \leq \nu(2) \leq l'$, $0 \leq q \leq \mu + \nu$, $p_a = \zeta R/2$, $p_b = \zeta' R/2$, $p = p_a + p_b = (R/2)(\zeta + \zeta')$ and $t = (\zeta - \zeta')/(\zeta + \zeta')$.

Carrying through calculations for the h'^α analogous to those for c'^α we obtain for the basic two-center hybrid integrals the following formula:

$$\begin{aligned}
 h'_{nl,n'l',n''l'',L\lambda}(\zeta, \zeta', \zeta''; R) &= (-1)^{l''-\lambda} N_{nl}^\alpha N_{n'l'}^\alpha N_{n''l''}^\alpha \sum_{i,i',i'',\mu,\nu,q} \gamma_{n+l+1-\alpha,i}^{2l+2-\alpha} \gamma_{n'+l'+1-\alpha,i'}^{2l'+2-\alpha} \gamma_{n''+l''+1-\alpha,i''}^{2l''+2-\alpha} \\
 &\times \frac{2^{l+i+3} \zeta (2p'_a)^{l'+i+3/2} (2p_b)^{l''+i'+3/2} (2l+i+2)!}{(p_a)^{l+1} (2l+1)} g_{\mu\nu}^q(L\lambda, l''\lambda) \\
 &\times \begin{cases} G_{-(l+\mu-l'-i'), l''+i'+1-\nu}^q(p_a, p, t) - \sum_{s=l+\mu-l'-i'}^{2l+i+1} p_a^s \Upsilon_s^l(l+i+1) Q_{s+l'+i'-l-\mu, l''+i'+1-\nu}^q(p_{ab}, t_{ab}) & \text{for } l+\mu-l'-i' > 0 \\ Q_{l'+i'-l-\mu, l''+i'+1-\nu}^q(p, t) - \sum_{s=0}^{2l+i+1} p_a^s \Upsilon_s^l(l+i+1) Q_{s+l'+i'-l-\mu, l''+i'+1-\nu}^q(p_{ab}, t_{ab}) & \text{for } l+\mu-l'-i' \leq 0, \end{cases}
 \end{aligned}
 \tag{20}$$

where $0 \leq i \leq n-l-1$, $0 \leq i' \leq n'-l'-1$, $0 \leq i'' \leq n''-l''-1$, $-\lambda \leq \mu(2) \leq L$, $\lambda \leq \nu(2) \leq l''$, $0 \leq q \leq \mu + \nu$, $p_a = \zeta R/2$, $p'_a = \zeta' R/2$, $p_b = \zeta'' R/2$, $p = p'_a + p_b = (R/2)(\zeta' + \zeta'')$, $t = (\zeta' - \zeta'') / (\zeta' + \zeta'')$, $p_{ab} = p_a + p = (R/2)(\zeta + \zeta' + \zeta'')$ and $t_{ab} = (\zeta + \zeta' - \zeta'') / (\zeta + \zeta' + \zeta'')$.

The expressions for coefficients $g_{\mu\nu}^q$ occurring in Eqs. 19 and 20 in terms of binomial coefficients are given in Ref. [36].

Results and discussion

The algorithm for evaluating two-center Coulomb and hybrid integrals over $\Psi^\alpha - \text{ETO}$ based on the usage of ellipsoidal coordinates has been described. For this purpose, we use Eq. 4 for one-center expansion of $\Psi^\alpha - \text{ETO}$ and perform a rotation from molecular coordinate system to lined-up coordinate systems. Finally, two-center Coulomb and hybrid integrals are expressed in terms of auxiliary functions Q_{ns}^q and G_{-ns}^q that can be calculated efficiently and accurately for arbitrary values of parameters. We notice that all of the multicenter electron-repulsion integrals arising in the Hartree-Fock-Roothaan (HFR) equations for molecules can also be expressed in terms of basic two-center Coulomb and hybrid integrals using general expansion formulas for the charge density over $\Psi^\alpha - \text{ETO}$ obtained by one of the authors [37].

The algorithm of calculation of two-center Coulomb and hybrid integrals has been implemented in a computer program written in Mathematica 6.0 international mathematical software. The results of calculations in atomic units are given in Tables 1, 2, 3, 4 and 5. Closed form expressions for two-center Coulomb and hybrid integrals of 1s and 2s orbitals with $\Psi^\alpha - \text{ETO}$ for $\alpha=1$ are exemplified in Tables 1 and 2, respectively. The symbol $\langle n_1 s'_1 s | n_2 s'_2 s \rangle$ means $C^1_{n_1 00 n'_1 00, n_2 00 n'_2 00}$ and $H^1_{n_1 00 n'_1 00, n_2 00 n'_2 00}$.

In order to support the reliability of our procedure we present in Tables 3 and 4 the test values of two-center Coulomb and hybrid integrals over STO obtained from those with $\Psi^\alpha - \text{ETO}$ using Eq. 5. The STO integrals are shown without indices α . As can be seen from Tables 3 and 4, our results are in good agreement with values obtained in literature [38]. As an application of presented formulas, the HFR calculations have been carried out for ground state of H_2 molecule with Ψ^1 and $\Psi^0 - \text{ETO}$. We have used $\{1s, 2s, 2p\}$ basis set in these calculations. Optimized orbital exponents are $\{1.36, 1.18, 1.83\}$ and $\{1.35, 1.18, 1.84\}$ for $\alpha=1$ and $\alpha=0$, respectively. Our results and other works used STO with the same size of basis set [39, 40] are given in Table 5. We see from Table 5 that the use of $\Psi^\alpha - \text{ETO}$ gives good results for H_2 molecule. In future work, we plan to use the basis sets of $\Psi^\alpha - \text{ETO}$ in calculations of multielectronic-polyatomic molecules.

It should be noted that the algorithm presented in this study could be useful for the calculations of two-center Coulomb and hybrid integrals over $\Psi^\alpha - \text{ETO}$ for the determination of various properties of molecules when HFR and explicitly correlated approximations are employed. The main reason for developing efficient procedures for molecular integrals with $\Psi^\alpha - \text{ETO}$ is to use the $\Psi^\alpha - \text{ETO}$ as basis functions in molecular calculations. Furthermore, the formulas obtained in this study can also be used in calculations of multicenter multielectron integrals over STO. For this purpose one can

Table 5 Numerical results for ground state of H_2 molecule

Atomic Orbital	Energy
$\Psi^1 - \text{ETO}^a$	-1.1335068
$\Psi^0 - \text{ETO}^a$	-1.1335062
STO ^b	-1.1334978
STO ^c	-1.133494

^a: This work ^b: Ref [39] ^c: Ref [40]

use the one-range addition theorems of STO established with the help of complete orthonormal sets of Ψ^α – ETO [9, 11].

Acknowledgments One of us, ES, thanks TUBITAK-BIDEB for financial support for his PhD education.

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