ORIGINAL PAPER

Application of combined open shell Hartree–Fook–Roothaan theory to molecules using symmetrical one-range addition theorems of Slater type orbitals

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Abstract   We study the efficiency of symmetrical one-range addition theorems for Slater type orbitals which are used in the calculation of multicenter integrals arising in the combined open shell Hartree–Fook–Roothaan equations for molecules. As an example of application, the calculations are performed for the ground state of electronic configuration of molecules NH_3 and CH_2 that have the closed and open shells, respectively. The results of computer calculations for the orbital and total energies (in a.u.), and linear combination coefficients for symmetrical molecular orbitals are presented.

1 Introduction

The choice of reliable basis atomic orbitals is of prime importance in molecular quantum- mechanical calculations since the quality of molecular properties depends on the nature of these orbitals. During the past few years, a pragmatic preference has developed for Gausian type orbitals (GTO) basis functions. This is motivated by the practical requirement for easy and rapid evaluation of multicenter integrals over GTO. It should be noted that the GTO basis functions fail to satisfy two mathematical conditions for atomic electronic distributions, namely, the cusp condition at the origin [1] and exponential decay at long range [2]. The Slater type orbitals (STO) are viable

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alternative to GTO because they better suit these conditions than GTO. Therefore, it is desirable to use STO basis set in electronic structure calculations.

It is well known that the two-range addition theorem is widely used in calculation of multicenter integrals of STO [3]. Unfortunately, this theorem is not, in general, suitable for applications due to the problems which arise in calculation of multicenter integrals. Therefore, it is desirable to use the unsymmetrical or symmetrical one-range addition theorems for STO suggested by one of the authors in [4] in which the problems of evaluation of multicenter integrals do not arise. The expansion coefficients of unsymmetrical and symmetrical one-range addition theorems are the overlap integrals and STO, respectively [4]. The unsymmetrical one-range addition theorems and their applications have been discussed in our previous papers (see e.g., [5]). The purpose of this work is to make of use the symmetrical one-range addition theorems in calculations of multicenter integrals appearing in the combined Hartree–Fock–Roothaan (CHFR) equations (see [6]) and electronic structure of molecules NH_3 and CH_2 with closed and open shells, respectively.

2 Definitions and basic formulas

The multicenter integrals of CHFR equations examined in the present paper have the following form:
multicenter nuclear attraction integrals

$$I_{p_1 p_1'}^{ac,b}\left(\zeta_1 \zeta_1'\right) = \int \rho_{p_1 p_1'}^*\left(\zeta_1, \vec{r}_{a1}; \zeta_1', \vec{r}_{c1}\right) \frac{1}{r_{b1}} d^3 \vec{r}_1, \tag{1}$$

multicenter electron-repulsion integrals

$$I_{p_1 p_1', p_2 p_2'}^{ac,bd}\left(\zeta_1 \zeta_1', \zeta_2 \zeta_2'\right)$$
$$= \int\int \rho_{p_1 p_1'}^*\left(\zeta_1, \vec{r}_{a1}; \zeta_1', \vec{r}_{c1}\right) \frac{1}{r_{21}} \rho_{p_2 p_2'}\left(\zeta_2, \vec{r}_{b2}; \zeta_2', \vec{r}_{d2}\right) d^3 \vec{r}_1 d^3 \vec{r}_2, \tag{2}$$

where $p_i \equiv n_i l_i m_i$, $p_i' \equiv n_i' l_i' m_i'$, $p \equiv nlm$, $p' \equiv n'l'm'$ and

$$\rho_{pp'}\left(\zeta, \vec{r}_g; \zeta', \vec{r}_h\right) = \chi_p\left(\zeta, \vec{r}_g\right) \chi_{p'}^*\left(\zeta', \vec{r}_h\right). \tag{3}$$

The normalized real or complex STO occurring in Eqs. 1–3 are determined by

$$\chi_{nlm}\left(\zeta, \vec{r}\right) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \tag{4}$$

3 Use of symmetrical one-range addition theorems for STO and charge densities

In order to evaluate one- and two-electorn multicenter integrals (1) and (2), we use the following symmetrical one-range addition theorems for the STO and charge densities established in previous paper [4]:

$$\chi_p\left(\zeta, \vec{r}_a\right) = \lim_{N \to \infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} V_{pq}^{\alpha N*}\left(\zeta, \zeta; \vec{R}_{ab}\right) \chi_q\left(\zeta, \vec{r}_b\right) \tag{5}$$

$$\chi_p\left(\zeta, \vec{r}_a\right) \chi_{p'}^{*}\left(\zeta', \vec{r}_b\right)$$

$$= \frac{1}{\sqrt{4\pi}} \begin{cases} \lim_{N \to \infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W_{pp'q}^{\alpha N*}\left(\zeta, \zeta', z; \vec{R}_{ab}, 0\right) \chi_q\left(z, \vec{r}_a\right) & \text{for } b \not\equiv a \quad (6) \\[2mm] \sum_{\nu=|l-l'|}^{l+l'} \sum_{\sigma=-\nu}^{\nu} W_{pp'q}\left(\zeta, \zeta', z\right) \chi_q\left(z, \vec{r}_a\right), & \text{for } b \equiv a \quad (7) \end{cases}$$

where $k = n + n' - 1$, $u' \equiv \mu' - \alpha \nu \sigma$, $z = \zeta + \zeta'$, $t = \frac{\zeta - \zeta'}{\zeta + \zeta'}$, $\vec{R} = \vec{R}_{ab}$, $\vec{P} = \zeta \vec{R}$ and

$$W_{pp'q}(\zeta, \zeta', z)$$

$$= \frac{z^{3/2}}{2^k} \left[\frac{2\nu+1}{2} \frac{(2k)!}{(2n)!(2n')!} \right]^{1/2} (1+t)^{n+\frac{1}{2}} (1-t)^{n'+\frac{1}{2}} C^{\nu|\sigma|}(lm, l'm') A_{mm'}^{\sigma} \tag{8}$$

$$W_{pp'q}^{\alpha N}(\zeta, \zeta', z; \vec{R}, 0)$$

$$= \lim_{N' \to \infty} \sum_{\mu'=1}^{N'} \sum_{\nu'=0}^{\mu'-1} \sum_{\sigma'=-\nu'}^{\nu'} W_{pq'q}^{\alpha N}(\zeta, \zeta', z; 0, 0) V_{p'q'}^{\alpha N'}(\zeta', \zeta'; \vec{R}) \tag{9}$$

$$W_{pp'q}^{\alpha N}(\zeta, \zeta', z; 0, 0) = W_{pp'q}(\zeta, \zeta', z) \tag{10}$$

$$V_{pq}^{\alpha N}\left(\zeta, \zeta; \vec{R}\right) = \sum_{\mu'=\nu+1}^{N} \Omega_{\mu\mu'}^{\alpha \nu}(N) S_{pu'}\left(\zeta, \zeta; \vec{R}\right) \tag{11}$$

$$S_{pp'}\left(\zeta, \zeta; \vec{R}\right) = \int \chi_p^{*}\left(\zeta, \vec{r}_a\right) \chi_{p'}\left(\zeta, \vec{r}_b\right) d^3\vec{r} \tag{12}$$

$$= \frac{1}{\zeta^{\frac{3}{2}}} \sum_{\mu=1}^{n+n'+1} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} g_{pp'}^{\alpha q} \chi_q^{*}\left(\zeta, \vec{R}\right) \tag{13}$$

$$= e^{-P} \sum_{\mu=\nu+1}^{n+n'+1} \sum_{\nu=|l-l'|}^{l+l'} \sum_{\sigma=-\nu}^{\nu} P^{\mu-1} G_{pp'}^{\alpha q} \left(\frac{4\pi}{2\nu+1}\right)^{\frac{1}{2}} S_{\nu\sigma}(\Theta, \Phi). \tag{14}$$

The expressions for the coefficients $C^{\nu|\sigma|}$, $A_{mm'}^{\sigma}$, $\Omega_{\mu\mu'}^{\alpha\nu}(N)$, $g_{pp'}^{\alpha q}$ and $G_{pp'}^{\alpha q}$ occurring in these equations are given in [7–9].

With the help of symmetrical one-range addition theorems (5) and (5), it is easy to derive for the multicenter integrals the following formulas in terms of the charge

density expansion coefficients and one-and two-center basic integrals: nuclear attraction integrals

$$I_{p_1 p_1'}^{ac,b}(\zeta_1 \zeta_1') = \lim_{N_1 \to \infty} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W_{p_1 p_1' q_1}^{\alpha N_1}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0) J_{q_1}^{(1)}(z_1, \vec{R}_{ab}),$$

(15)

electron-repulsion integrals

$$I_{p_1 p_1', p_2 p_2'}^{ac,bd}(\zeta_1 \zeta_1', \zeta_2 \zeta_2')$$

$$= \lim_{\substack{N_1 \to \infty \\ N_2 \to \infty}} \sum_{\mu_1=1}^{N_1} \sum_{\nu_1=0}^{\mu_1-1} \sum_{\sigma_1=-\nu_1}^{\nu_1} W_{p_1 p_1' q_1}^{\alpha N_1}(\zeta_1, \zeta_1', z_1; \vec{R}_{ca}, 0)$$

$$\times \sum_{\mu_2=1}^{N_2} \sum_{\nu_2=0}^{\mu_2-1} \sum_{\sigma_2=-\nu_2}^{\nu_2} W_{p_2 p_2' q_2}^{\alpha N_2*}(\zeta_2, \zeta_2', z_2; \vec{R}_{db}, 0) J_{q_1 q_2}^{(2)}(z_1 z_2, \vec{R}_{ab}).$$

(16)

Here, the basic integrals $J_{q_1}^{(1)}$ and $J_{q_1 q_2}^{(2)}$ are defined by

$$J_{q_1}^{(1)}(z_1, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int \chi_{q_1}^*(z_1, \vec{r}_{a1}) \frac{1}{r_{b1}} d^3 \vec{r}_1$$

(17)

$$J_{q_1 q_2}^{(2)}(z_1 z_2, \vec{R}_{ab}) = \frac{1}{4\pi} \int \int \chi_{q_1}^*(z_1, \vec{r}_{a1}) \frac{1}{r_{21}} \chi_{q_2}(z_2, \vec{r}_{b2}) d^3 \vec{r}_1 d^3 \vec{r}_2.$$

(18)

The relations for integrals (17) and (18) are presented in [9].

All the multicenter integrals (15) and (16) arising in the CHFR equations can be calculated by the use of computer programs presented in our previous papers [10–14]. As an application, we have solved CHFR equations for the ground state of the molecules $CH_2(1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1, {}^3B_1)$ and $NH_3(1a_1^2 2a_1^2 1e_x^2 1e_y^2 3a_1^2, {}^1A_1)$ with C_{2v} and C_{3v} symmetry, respectively. The Slater determinants, symmetrical molecular orbitals, STO and coordinates of atoms are determined by for CH_2

$$U(4m_{s7}, 5m_{s8})$$

$$\equiv U(\ldots 4m_{s7}, 5m_{s8})$$

$$= \frac{1}{\sqrt{8!}} \hat{A}[u_{11/2}(x_1) u_{1-1/2}(x_2) u_{21/2}(x_3) u_{2-1/2}(x_4) u_{31/2}(x_5)$$

$$\times u_{3-1/2}(x_6) u_{4m_{s7}}(x_7) u_{5m_{s8}}(x_8)]$$

$u_{n\gamma}: u_{1a_1} \ u_{2a_1} \ u_{1b_2} \ u_{1b_1} \ u_{3a_1} \ u_{4a_1} \ u_{2b_2}$

$u_i \quad : u_1 \quad u_2 \quad u_3 \quad u_4 \quad u_5 \quad u_6 \quad u_7$

$\chi_{nlm}: \chi_{100}(H_1) \ \chi_{100}(H_2) \ \chi_{100}(C) \ \chi_{200}(C) \ \chi_{211}(C) \ \chi_{21-1}(C) \ \chi_{210}(C)$

$\chi_p \quad : \chi_1 \qquad \chi_2 \qquad \chi_3 \qquad \chi_4 \qquad \chi_5 \qquad \chi_6 \qquad \chi_7$

$R_{C-H} = 2.04468, \alpha_{HCH} = 132.4°, H_1(0, -1.87082, 0.82512), H_2(0, 1.87082, 0.82512), C(0, 0, 0)$ (see [15]), for NH_3

$$U \equiv U(\ldots 51/2, 5 - 1/2)$$
$$= \frac{1}{\sqrt{10!}} \hat{A}[u_{11/2}(x_1)u_{1-1/2}(x_2)u_{21/2}(x_3)u_{2-1/2}(x_4)u_{31/2}(x_5)u_{3-1/2}(x_6)$$
$$u_{41/2}(x_7)u_{4-1/2}(x_8)u_{51/2}(x_9)u_{5-1/2}(x_{10})].$$

$u_{n\gamma}$: u_{1a_1} u_{2a_1} u_{1e_x} u_{1e_y} u_{3a_1} u_{4a_1} u_{2e_x} u_{2e_y}

u_i : u_1 u_2 u_3 u_4 u_5 u_6 u_7 u_8

χ_{nlm} : $\chi_{100}(H_1)$ $\chi_{100}(H_2)$ $\chi_{100}(H_3)$ $\chi_{100}(N)$ $\chi_{200}(N)$ $\chi_{211}(N)$ $\chi_{21-1}(N)$ $\chi_{210}(N)$

χ_p : χ_1 χ_2 χ_3 χ_4 χ_5 χ_6 χ_7 χ_8

$R_{N-H} = 1.91099, \alpha_{HNH} = 123.4°, H_1(1.77059622, 0, -0.71896457), H_2(-0.885$
$29811, 1.5333813, -0.71996000), H_3(-0.88529811, -1.5333813, -0.71896457),$
$N(0, 0, 0)$ (see [15,17]). Here $x \equiv xyz\sigma, u_{im_s}(x) \equiv u_i(x, y, z)u_{m_s}(\sigma)$ and $u_i(x, y, z)$
are the molecular spin and spatial orbitals, respectively. The atomic orbital exponents
we take from [16].

The values of results of calculations for the determinantal and multideterminantal
wave functions, coupling-projection coefficients and solutions of CHFR equations for
ground state of electronic configurations are presented in Tables 1, 2, 3, and 4. The
symmetrized basis orbitals φ_p occurring in Tables 3 and 4 are determined through the
Slater type orbitals by the following relation:

$$\varphi_p = \sum_q \chi_q g_{qp}. \tag{19}$$

The molecular orbitals through the basic functions φ_p and χ_p are defined by

$$u_i = \sum_p \varphi_p D_{pi}, \tag{20}$$

Table 1 The independent determinantal and multideterminantal wave fuctions

CH_2		NH_3	
$U(\ldots 4m_{s7}, 5m_{s8})$	$\Psi_{M_S}^S$	$U(\ldots 51/2, 5 - 1/2)$	$\Psi_{M_S}^S$
	$^3B_1$:		$^1A_1$:
$U_1(41/2, 51/2)$	$\Psi_1^1 = U_1$	$U(51/2, 5 - 1/2)$	$\Psi_0^0 = U$
$U_2(41/2, 5 - 1/2)$	$\Psi_0^1 = \frac{1}{\sqrt{2}}(U_2 + U_3)$		
$U_3(4 - 1/2, 51/2)$	$\Psi_{-1}^1 = U_4$		
$U_4(4 - 1/2, 5 - 1/2)$	$^1B_1 : \Psi_0^0 = \frac{1}{\sqrt{2}}(U_2 - U_3)$		

Table 2 The values of coupling projection coefficients

ij	kl	CH$_2$		NH$_3$	
		A_{kl}^{ij}	B_{kl}^{ij}	A_{kl}^{ij}	B_{kl}^{ij}
11	11	1	1	1	1
	22	1	1	1	1
	33	1	1	1	1
	44	1/2	1/2	1	1
	55	1/2	1/2	1	1
22	22	1	1	1	1
	33	1	1	1	1
	44	1/2	1/2	1	1
	55	1/2	1/2	1	1
33	33	1	1	1	1
	44	1/2	1/2	1	1
	55	1/2	1/2	1	1
44	44	–	–	1	1
	55	1/4	1/2	1	1
55	55	–	–	1	1

$$u_i = \sum_p \chi_p C_{pi}. \tag{21}$$

The coefficients C_{pi} in Eq. 21 can be determined from coefficient D_{pi} by the use of relation

$$C = gD . \tag{22}$$

The coefficient g_{qp} have the form: for CH$_2$

$$g = \begin{pmatrix} 0.6617112 & 0 & 0 & 0 & 0 & 0.7633422 & 0 \\ 0.6617112 & 0 & 0 & 0 & 0 & -0.7633422 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}, \tag{23}$$

for NH$_3$

Table 3 The orbital energies and coefficients of symmetrized molecular orbitals for ground state term of CH$_2$ ($1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$, $^3B_1$)

$u_i = u_{n\gamma}$	$u_1 = u_{1a_1}$	$u_2 = u_{2a_1}$	$u_3 = u_{1b_2}$	$u_4 = u_{3a_1}$	$u_5 = u_{1b_1}$	$u_6 = u_{2b_2}$	$u_7 = u_{4a_1}$
ε_i	ε_{1a_1}	ε_{2a_1}	ε_{1b_2}	ε_{3a_1}	ε_{1b_1}	ε_{2b_2}	ε_{4a_1}
D_{pi}	−11.4047063	−0.8253460	−0.6172854	−0.2397862	−0.2223890	0.0000000	0.0000000
φ_p							
$\varphi_1 = \varphi(1a_1)$	−0.0776678	−0.5976618	0.0000000	0.0904706	0.0000000	0.0000000	−1.3953487
$\varphi_2 = \varphi(2a_1)$	0.9856522	0.1746182	0.0000000	0.0508269	0.0000000	0.0000000	−0.2358570
$\varphi_3 = \varphi(3a_1)$	0.0892915	−0.5015843	0.0000000	−0.2595444	0.0000000	0.0000000	1.3825888
$\varphi_4 = \varphi(4a_1)$	0.0280194	0.0086615	0.0000000	0.9556274	0.0000000	0.0000000	0.5037326
$\varphi_5 = \varphi(1b_1)$	0.0000000	0.0000000	0.0000000	0.0000000	1.0000000	0.0000000	0.0000000
$\varphi_6 = \varphi(1b_2)$	0.0000000	0.0000000	−0.4913582	0.0000000	0.0000000	1.3189581	0.0000000
$\varphi_7 = \varphi(2b_2)$	0.0000000	0.0000000	0.59130823	0.0000000	0.0000000	1.2772734	0.0000000

$E = -38.69129$
$E = -38.9221$ [15]

Table 4 The orbital energies and coefficients of symmetrized molecular orbitals for ground state term of $NH_3(1a_1^2 2a_1^2 1e_x^2 1e_y^2 3a_1^2, {}^1A_1)$

$\varphi_p u_{n\gamma}$	$u_1 = u_{1a_1}$	$u_2 = u_{2a_1}$	$u_3 = u_{1e_x}$	$u_4 = u_{1e_y}$	$u_5 = u_{3a_1}$	$u_6 = u_{4a_1}$	$u_7 = u_{2e_x}$	$u_8 = u_{2e_y}$
ε_i	$\varepsilon_1 = \varepsilon_{1a_1}$	$\varepsilon_2 = \varepsilon_{2a_1}$	$\varepsilon_3 = \varepsilon_{1e_x}$	$\varepsilon_4 = \varepsilon_{1e_y}$	$\varepsilon_5 = \varepsilon_{3a_1}$	$\varepsilon_6 = \varepsilon_{4a_1}$	$\varepsilon_7 = \varepsilon_{2e_x}$	$\varepsilon_8 = \varepsilon_{2e_y}$
D_{pi}	−15.5758157	−1.1147207	−0.5937045	−0.5936576	−0.3796265	0.5672155	0.6699893	0.6712819
$\varphi_1 = \varphi_{1a_1}$	0.0083968	0.3058983	0.0000000	0.0000000	0.2520405	1.5254106	0.0000000	0.0000000
$\varphi_2 = \varphi_{2a_1}$	−0.9964877	−0.2072792	0.0000000	0.0000000	0.0797376	0.1631053	0.0000000	0.0000000
$\varphi_3 = \varphi_{3a_1}$	−0.0185613	0.7526170	0.0000000	0.0000000	−0.4440911	−1.2978786	0.0000000	0.0000000
$\varphi_4 = \varphi_{1a_1}$	0.0035409	−0.1440419	0.0000000	0.0000000	−0.8955362	0.5629362	0.0000000	0.0000000
$\varphi_5 = \varphi_{1e_x}$	0.0000000	0.0000000	−0.5290813	0.0000000	0.0000000	0.0000000	1.1015463	0.0000000
$\varphi_6 = \varphi_{2e_x}$	0.0000000	0.0000000	0.5973157	0.0000000	0.0000000	0.0000000	1.0660888	0.0000000
$\varphi_7 = \varphi_{1e_y}$	0.0000000	0.0000000	0.0000000	−0.5293122	0.0000000	0.0000000	0.0000000	1.1011709
$\varphi_8 = \varphi_{2e_y}$	0.0000000	0.0000000	0.0000000	−0.5970923	0.0000000	0.0000000	0.0000000	−1.0659581

$E = -56.0056638$
$E = -56.1714$ [17]

Table 5 Comparison methods of computing multicenter nuclear attraction integrals over STO obtained in the molecular coordinate system with screening constants $\zeta_{H_1(1s)} = \zeta_{H_2(1s)} = \zeta_{H_3(1s)} = 1.1$ and $\zeta_{N(2s)} = \zeta_{N(2p_x)} = \zeta_{N(2p_y)} = \zeta_{N(2p_z)} = 0.4$ for NH$_3$

Integrals	Present work	Refs. [18,19]
$\left\langle H_1(1s) \left\| \frac{1}{r(H_2)} \right\| H_1(1s) \right\rangle$	0.3244017696	0.3244017696
$\left\langle N(2p_x) \left\| \frac{1}{r(H_1)} \right\| N(2p_x) \right\rangle$	0.2122267034	0.2122267034
$\left\langle N(2p_y) \left\| \frac{1}{r(H_2)} \right\| N(2p_y) \right\rangle$	0.2058341119	0.2058341119
$\left\langle N(2p_y) \left\| \frac{1}{r(N)} \right\| H_3(1s) \right\rangle$	−0.6608685440	−0.6608685440
$\left\langle N(2p_x) \left\| \frac{1}{r(N)} \right\| H_3(1s) \right\rangle$	−0.3815526318	−0.3815526318
$\left\langle N(2p_x) \left\| \frac{1}{r(H_3)} \right\| H_2(1s) \right\rangle$	−0.053302947	−0.0533340089
$\left\langle N(2p_z) \left\| \frac{1}{r(H_3)} \right\| H_2(1s) \right\rangle$	−0.0432881649	−0.0433133904
$\left\langle N(2p_y) \left\| \frac{1}{r(H_1)} \right\| H_2(1s) \right\rangle$	0.0201604598	0.0202072870
$\left\langle N(1s) \left\| \frac{1}{r(H_2)} \right\| H_1(1s) \right\rangle$	0.0218639703	0.0219055127

$$
g = \begin{pmatrix}
0.4751662 & 0 & 0 & 0 & -0.9354616 & 0 & 0.8101335 & 0 \\
0.4751662 & 0 & 0 & 0 & 0.4677308 & 0 & -0.8101335 & 0 \\
0.4751662 & 0 & 0 & 0 & 0.4677308 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0
\end{pmatrix}. \tag{24}
$$

We see from Tables 3 and 4 that, in the case of minimal basis set, the results of computer calculation obtained by the use of CHFR approach for the molecules CH$_2$ and NH$_3$ are satisfactory.

Numerical values of sample multicenter nuclear attraction integrals for NH$_3$ are given in Table 5. As can be seen from the Table 5, we compared our numerical results with those obtained using the alternative schemes in [18,19]. We see from Table 5 that the results presented show a good rate of convergence and numerical stability under a wide range of quantum numbers, orbital exponents and internuclear distances.

4 Conclusion

It this study, the results of calculations, obtained by the use of closed and open shell CHFR equations [6], are presented for ground states of NH$_3$ and CH$_2$ molecules. The multicenter integrals in these equations are calculated with the help of symmetrical one-range addition theorems for STO suggested by one of the authors. It can be concluded that this newly proposed approximation leads to reasonable used as method of electronic structure calculations.

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