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ORIGINAL PAPER

Use of auxiliary functions Q_{ns}^{q} and G_{-ns}^{q} in evaluation of multicenter integrals over integer and noninteger n-Slater type orbitals arising in Hartree–Fock–Roothaan equations for molecules

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Abstract With the help of expansion relations for the two-center Slater type orbitals (STOs) charge densities established by the author from the use of complete orthonormal sets of Ψ^{α}-exponential type orbitals (Ψ^{α}-ETOs), where $\alpha = 1, 0, -1, -2, \ldots$, a large number of series expansion formulas for the multicenter integrals of integer and noninteger n-STOs (ISTOs and NISTOs) occurring in Hartree–Fock–Roothaan (HFR) equations for molecules is derived through the auxiliary functions Q_{ns}^{q} and G_{-ns}^{q}, and one- and two-center basic integrals of ISTOs. The analytical relations for basic integrals are presented. As an example of application, the calculations have been performed for the ground state of electronic configuration of $CH_4((1a_1)^2(2a_1)^2(1t_{2x})^2(1t_{2y})^2(1t_{2z})^2, {}^1A_1)$ using combined HFR theory suggested by the author.

Keywords Slater type orbitals · Hartree–Fock–Roothaan equations · Multicenter integrals · Auxiliary functions · Noninteger principal quantum numbers

1 Introduction

It is well known that the auxiliary functions method is one of the most important methods for the evaluation of multicenter molecular integrals over STOs [1]. There is a long history, starting with Kotani et al. [2], Mulliken et al. [3], Barnett and Coulson [4], Roothaan [5], Ruedenberg [6], Löwdin [7], Harris and Mitchel [8] of systematic attempts to obtain accurate and fast evaluations of molecular integrals using auxiliary functions. Different approaches, now available for solving multicenter integrals with STOs, have introduced a rather large number of diverse auxiliary functions [9–18]. Unfortunately, they were not entirely successful. We have had considerable success

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in using the auxiliary function method. In our previous paper [19], all the multicenter electron-repulsion integrals between integer n STOs were expressed in terms of the following auxiliary functions:

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

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

where $p_a > 0$, $p > 0$ and $-p \le pt \le p$. The indices n, s, and q are all nonnegative integers. In [19–23] 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.

The aim of this work is with the help of expansion formulae for two-center STOs charge densities presented in previous paper [24] to establish the series expansion relations for the multicenter integrals of integer and noninteger n-STOs appearing in HFR equations for molecules in terms of auxiliary functions Q_{ns}^{q} and G_{-ns}^{q}. The multicenter integrals of HFR equations examined in the present work have the following form:

one-electron integrals

$$I_{p_1^{*}p_1^{\prime *}}^{ac,b}(\zeta_1\zeta_1') = \int \chi_{p_1^{*}}^{*}(\zeta_1,\vec{r}_{a1})\chi_{p_1^{\prime *}}(\zeta_1',\vec{r}_{c1})\frac{1}{r_{b1}}dv_1, \tag{3}$$

two-electron integrals

$$I_{p_1^{*}p_1^{\prime *},p_2^{*}p_2^{\prime *}}^{ac,bd}(\zeta_1\zeta_1',\zeta_2\zeta_2') = \int\int \chi_{p_1^{*}}^{*}(\zeta_1,\vec{r}_{a1})\chi_{p_1^{\prime *}}(\zeta_1',\vec{r}_{c1})\frac{1}{r_{21}}\chi_{p_2^{*}}(\zeta_2,\vec{r}_{b2})\chi_{p_2^{\prime *}}^{*}(\zeta_2',\vec{r}_{d2})dv_1dv_2, \tag{4}$$

where $p_i^{*} \equiv n_i^{*}l_im_i$ and $p_i^{\prime *} \equiv n_i^{\prime *}l_i'm_i'$. Here, n_i^{*} and $n_i^{\prime *}$ are the noninteger or integer (for $n_i^{*} = n_i$ and $n_i^{\prime *} = n_i$) principal quantum numbers. The normalized real or complex STOs containing in Eqs. (3) and (4) are determined by

$$\chi_{n^{*}lm}(\zeta,\vec{r}) = [\Gamma(2n^{*}+1)]^{-1/2}(2\zeta)^{n^{*}+1/2}r^{n^{*}-1}e^{-\zeta r}S_{lm}(\theta,\phi). \tag{5}$$

2 Multicenter integrals of integer and noninteger n-STOs, and their application

In order to evaluate one- and two-electron multicenter integrals (3) and (4), we use the following expansion formulae of the electron charge densities established in previous paper [24]:

$$\chi_{p^*}(\zeta,\vec{r}_a)\chi^*_{p'^*}(\zeta',\vec{r}_b) = \frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N^*}_{p^*p'^*q}(\zeta,\zeta',z;\vec{R}_{ba},0)\chi_q(z,\vec{r}_a) \tag{6}$$

$$\chi^*_{p}(\zeta,\vec{r}_a)\chi^*_{p'^*}(\zeta',\vec{r}_a) = \frac{1}{\sqrt{4\pi}}\sum_{\nu|l-l'|}^{l+l'}\sum_{\sigma=-\nu}^{\nu} W^*_{p^*p'^*q^*}(\zeta,\zeta',z)\chi_{q^*}(z,\vec{r}_a) \tag{7}$$

$$= \frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N^*}_{p^*p'^*q}(\zeta,\zeta',z,0,0) \times\chi_q(z,\vec{r}_a), \tag{8}$$

where $q=\mu\nu\sigma$, $z=\zeta+\zeta'$, $q^*=k^*\nu\sigma$ and $k^*=n^*+n'^*-1$. Then, we obtain for the multicenter molecular integrals the expressions in terms of the charge density expansion coefficients and basic integrals:

for three-center nuclear attraction integrals

$$I^{ac,b}_{p_1^*p_1'^*}(\zeta_1\zeta_1') = \lim_{N_1\to\infty}\sum_{\mu_1=1}^{N_1}\sum_{\nu_1=0}^{\mu_1-1}\sum_{\sigma_1=-\nu_1}^{\nu_1} W^{\alpha N_1}_{p_1^*p_1'^*q_1}(\zeta_1\zeta_1'z_1;\vec{R}_{ca},0)J^{(1)}_{q_1}(z_1,\vec{R}_{ab}), \tag{9}$$

for four-center electron-repulsion integrals

$$I^{ac,bd}_{p_1^*p_1'^*,p_2^*p_2'^*}(\zeta_1\zeta_1',\zeta_2\zeta_2') = \lim_{N_1N_2\to\infty}\sum_{\mu_1=1}^{N_1}\sum_{\nu_1=0}^{\mu_1-1}\sum_{\sigma_1=-\nu_1}^{\nu_1} W^{\alpha N_1}_{p_1^*p_1'^*q_1}(\zeta_1\zeta_1'z_1;\vec{R}_{ca},0) \times\sum_{\mu_2=1}^{N_2}\sum_{\nu_2=0}^{\mu_2-1}\sum_{\sigma_2=-\nu_2}^{\nu_2} W^{\alpha N_2^*}_{p_2^*p_2'^*q_2}(\zeta_2\zeta_2'z_2;\vec{R}_{db},0) \times J^{(2)}_{q_1q_2}(z_1z_2,\vec{R}_{ab}), \tag{10}$$

where $z_i=\zeta_i+\zeta_i'$ and $q_i\equiv\mu_i\nu_i\sigma_i$.

The basic integrals $J^{(1)}_{q_1}$ and $J^{(2)}_{q_1q_2}$ occurring in these equations are determined by the following relations:

for $R_{ab} \neq 0$

$$J^{(1)}_{\mu\nu\sigma}(z, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int \chi^*_{\mu\nu\sigma}(z, \vec{r}_{a1}) \frac{1}{r_{b1}} dv_1$$
$$= \sqrt{4\pi} \frac{2^{\mu+1}\,(\mu+\nu+1)!}{(2\nu+1)\,[(2\mu)!\,(2z)]^{1/2}\,(zR_{ab})^{\nu+1}}$$
$$\times \left[1 - e^{-zR_{ab}} \sum_{s=0}^{\mu+\nu} \gamma^{\nu}_{s}(\mu)(zR_{ab})^s\right] S^*_{\nu\sigma}(\theta_{ab}, \varphi_{ab}), \tag{11}$$

$$J^{(2)}_{\mu\nu\sigma,\mu'\nu'\sigma'}(z_1, z'_1; \vec{R}_{ab}) = \frac{1}{4\pi} \int\int \chi^*_{\mu\nu\sigma}(z, \vec{r}_{a1}) \frac{1}{r_{21}} \chi_{\mu'\nu'\sigma'}(z', \vec{r}_{b2}) dv_1 dv_2$$
$$= \frac{1}{\sqrt{4\pi}} \int J^{(1)}_{\mu\nu\sigma}(z, \vec{r}_{a2}) \chi_{\mu'\nu'\sigma'}(z', \vec{r}_{b2}) dv_2 \tag{12a}$$

$$J^{(2)}_{\mu\nu\sigma,\mu'\nu'\sigma'}\left(z_1, z'_1; \vec{R}_{ab}\right) = \sum_{\lambda=0}^{\min(\nu,\nu')} T^{\lambda^*}_{\nu\sigma,\nu'\sigma'}(\theta_{ab}, \varphi_{ab})$$
$$\times J^{(2)}_{\mu\nu\lambda,\mu'\nu'\lambda}\left(z_1, z'_1; R_{ab}\right) \tag{12b}$$

$$J^{(2)}_{\mu\nu\lambda,\mu'\nu'\lambda'}\left(z_1, z'_1; R_{ab}\right) = \frac{2^{\mu+\mu'+1}(\mu+\nu+1)!\,p'^{\mu+2}}{[(2\mu)!(2\mu')!]^{1/2}(2\nu+1)z'\sqrt{zz'}\,p^{\nu+1}} \sum_{\alpha\beta q} g^q_{\alpha\beta}(\nu\lambda, \nu'\lambda)$$
$$\times \begin{cases} Q^q_{|\nu+\alpha|,\mu'-\beta}(p'; -p') - \sum_{s=0}^{\mu+\nu} \gamma^{\nu}_{s}(\mu) p^s \\ \quad \times Q^q_{|\nu+\alpha|+s,\mu'-\beta}(p_{ab}, p_{ab}t_{ab}) \quad \text{for } \nu+\alpha \leq 0 \\ G^q_{-(\nu+\alpha),\mu'-\beta}(p, p', -p') - \sum_{s=\nu+\alpha}^{\mu+\nu} \gamma^{\nu}_{s}(\mu) p^s \\ \quad \times Q^q_{s-(\nu+\alpha),\mu'-\beta}(p_{ab}, p_{ab}t_{ab}) \quad \text{for } \nu+\alpha > 0, \end{cases} \tag{12c}$$

for $R_{ab} = 0$

$$J^{(1)}_{\mu\nu\sigma}(z) = J^{(1)}_{\mu\nu\sigma}(z, 0) = \frac{2^{\mu+1}\mu!}{[(2\mu)!\,(2z)]^{1/2}} \delta_{\nu 0}\delta_{\sigma 0}, \tag{13}$$

$$J^{(2)}_{\mu\nu\sigma,\mu'\nu'\sigma'}(z, z') = J^{(2)}_{\mu\nu\sigma,\mu'\nu'\sigma'}(z, z'; 0)$$
$$= \delta_{\nu\nu'}\delta_{\sigma\sigma'} \frac{2^{\mu+\mu'+1}}{z'\sqrt{zz'}\,x^{\nu+1}}$$

Table 1 The orbital energies and linear combination coefficients of molecular orbitals for the ground state of $CH_4((1a_1)^2(2a_1)^2(1t_{2x})^2(1t_{2y})^2(1t_{2z})^2, {}^1A_1)$

χ_q	ε_i				
	$\varepsilon_1 = \varepsilon_{1a_1}$	$\varepsilon_2 = \varepsilon_{2a_1}$	$\varepsilon_3 = \varepsilon_{1t_{2x}}$	$\varepsilon_4 = \varepsilon_{1t_{2y}}$	$\varepsilon_5 = \varepsilon_{1t_{2z}}$
	−11.3333598	−0.9797468	−0.5864467	−0.5859592	−0.58545131
χ_1 ($\zeta = 1.0$)	−0.00543313	0.13190068	−0.30281755	−0.30257895	−0.30261972
χ_2 ($\zeta = 1.0$)	−0.00544511	0.13257997	0.30271157	−0.30257895	0.30259181
χ_3 ($\zeta = 1.0$)	−0.00545713	0.13325322	−0.30286668	0.30251624	0.30265341
χ_4 ($\zeta = 1.0$)	−0.00546919	0.13392052	0.30288785	0.30284299	−0.30271974
χ_5 ($\zeta = 5.7$)	0.99525933	−0.20740065	0.00020663	−0.00012981	0.00013715
χ_6 ($\zeta = 1.625$)	0.02868325	0.68819366	0.00080625	0.00032697	−0.00019273
χ_7 ($\zeta = 1.625$)	−0.00001298	0.00002534	−0.59186252	0.00018987	0.00020024
χ_8 ($\zeta = 1.625$)	0.00002596	0.00005050	0.00079125	−0.59193954	−0.00072142
χ_9 ($\zeta = 1.625$)	0.00000004	0.00001084	−0.00043821	0.00033158	−0.59190321

Total energy: This work: −40.37829; Ref [30]: −40.04437; Ref [31]: −40.1823; Ref [32]: −39.63703

$$\times \left[\frac{2(\nu+1)F_{\mu-\nu-1}(\mu+\nu+1)}{(2\nu+1)F_{\mu+\nu+1}(2\mu)F_{\mu'-\nu}(2\mu')F_{\mu'-\nu}(\mu'+\nu)} \right]^{1/2}$$
$$\times \left[1 - \sum_{s=0}^{\mu+\nu} s!\gamma_s^{\nu}(\mu)F_s(\mu'-\nu+s)\frac{x^s}{(1+x)^{\mu'-\nu+s+1}} \right]. \quad (14)$$

Here, $\vec{R} = \vec{R}_{ab}$, $p = \frac{1}{2}zR$, $p' = \frac{1}{2}z'R$, $p_{ab} = p + p'$, $t_{ab} = \frac{p-p'}{p+p'}$ and $x = \frac{z}{z'} = \frac{p}{p'}$. See [24] for the exact definition ofcoefficients occurring in Eqs. 9 and 10. The relations for rotation coefficients $T^{\lambda}_{\nu\sigma,\nu'\sigma'}$ are given in [25]. We notice that the formulae (11), (13) and (14) were derived in our previous paper [26]. The auxiliary functions Q^q_{ns} and G^q_{-ns} appearing in Eq. 12 are defined by Eqs. 1 and 2, respectively.

As can be seen from the formulae obtained for all of the multicenter integrals over integer and noninteger n-STOs appearing in the HFR equations for molecules, namely, for one-, two- and three-center nuclear attraction integrals ($I^{aa,a}$, $I^{aa,b}$ and $I^{ac,b}$) and one-, two-, three and four-center electron-repulsion integrals ($I^{aa,aa}$, $I^{aa,bb}$, $I^{aa,ab}$, $I^{ab,ab}$, $I^{aa,bd}$, $I^{ac,ad}$ and $I^{ac,bd}$) can be evaluated with the help of Eqs. 9 and 10, respectively. It is desirable to use Eqs. 11, 12 and 13, 14 for the calculation of integrals $I^{ac,b}$, $I^{aa,b}$, $I^{ac,bd}$, $I^{aa,bd}$, $I^{aa,bb}$ and $I^{aa,a}$, $I^{ac,ab}$, $I^{ab,ab}$, $I^{aa,ab}$, $I^{aa,aa}$, respectively. The charge densities expansion coefficients $W^{\alpha N}$ which were expressed through the overlap integrals, and the auxiliary functions Q^q and G^q occurring in Eq. 12 can be calculated by the use of computer programs presented in our previous papers [27,28].

As an application of Eqs. 9 and 10 for the multicenter integrals, we have solved combined HFR equations [29] for the ground state of $CH_4((1a_1)^2(2a_1)^2(1t_{2x})^2(1t_{2y})^2(1t_{2z})^2, {}^1A_1)$ using integer n Slater type atomic orbitals as a minimal basis set. The results of computer calculations for orbital and total energies, and linear combination coefficients of molecular orbitals defined by

$$u_i = \sum_{q=1}^{9} \chi_q C_{qi} \quad (15)$$

are presented in Table 1. In this table, the published literature data are also given [30–32]. We have used for the atoms of CH_4 the following coordinates:

$$\begin{array}{lrrr} & X & Y & Z \\ H_1 & \frac{R}{\sqrt{3}} & \frac{R}{\sqrt{3}} & \frac{R}{\sqrt{3}} \\ H_2 & -\frac{R}{\sqrt{3}} & \frac{R}{\sqrt{3}} & -\frac{R}{\sqrt{3}} \\ H_3 & \frac{R}{\sqrt{3}} & -\frac{R}{\sqrt{3}} & -\frac{R}{\sqrt{3}} \\ H_4 & -\frac{R}{\sqrt{3}} & -\frac{R}{\sqrt{3}} & \frac{R}{\sqrt{3}} \\ C & 0 & 0 & 0, \end{array}$$

where $R = R_{CH} = 2.066499998$.

The Slater type orbitals χ_q occurring in Table 1 are denoted as

χ_{nlm} :	$\chi_{100}(H_1)$	$\chi_{100}(H_2)$	$\chi_{100}(H_3)$	$\chi_{100}(H_4)$	$\chi_{100}(C)$	$\chi_{200}(C)$	$\chi_{211}(C)$	$\chi_{21-1}(C)$	$\chi_{210}(C)$
χ_p :	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8	χ_9

We see from Table 1 that, in the case of minimal basis set, the results of computer calculation for the ground state of CH_4 are satisfactory. Work is in progress in our group for the analytical combined HFR calculations of small molecules using integer and noninteger n-Slater type orbitals as basis sets.

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