

Use of unsymmetrical one-range addition theorems of Slater type orbitals in molecular electronic structure determination

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Abstract In this work, the applicability of the unsymmetrical one-range addition theorems obtained from the use of complete orthonormal sets of Ψ^α -exponential type orbitals (Ψ^α -ETOs, where $\alpha = 1, 0, -1, -2, \dots$) to the study of electronic structure of molecules is demonstrated using minimal basis sets of Slater type orbitals (STOs). As an example of application of unsymmetrical one-range addition expansion method to evaluate the multicenter electronic integrals, the calculation has been performed for the ground state of BH_3 molecule. The results of computer calculations for the orbital and total energies, and linear combination coefficients of symmetrized molecular orbitals are presented.

Keywords Slater type orbitals · Hartree–Fock–Roothaan equations · Multicenter integrals · One-range addition theorems

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 Gaussian type orbitals (GTOs) basis functions. This is motivated

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by the practical requirement for easy and rapid evaluation of multicenter integrals. Unfortunately, the GTOs 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, 3]. The Slater type orbitals would be desirable for basis sets because they satisfy these conditions.

It is well known that the unsymmetrical one-range expansion method is one of the most important methods for the evaluation of multicenter integrals over STOs [4]. This method is based on the expansion of STOs in terms of STOs at a displaced center obtained from the use of complete orthonormal sets of Ψ^α -ETOs suggested by one of the authors in Ref. [5]. The expansion coefficients of this approach are the overlap integrals over STOs which can be expressed through the basic overlap integrals introduced in a previous paper [6]. Thus, the basic overlap integrals constitute the basic building block of many more complicated multicenter molecular integrals occurring in the quantum-mechanical calculations of the electronic structure of molecules. By making use of unsymmetrical one-range addition theorems approach, all of the molecular integrals appearing in the combined Hartree–Fock–Roothaan (HFR) approximation [7] can be expressed through the basic overlap integrals over STOs. The basic overlap integrals algorithm is especially useful for the computation of multicenter integrals.

The purpose of this work is to use the basic overlap integrals arising in the application of the unsymmetrical one-range addition theorems for the evaluation of multicenter integrals which appear in the combined HFR equations for the linear combination coefficients of symmetrized molecular orbitals

$$u_i = \sum_p \varphi_p D_{pi}. \quad (1)$$

Here $\varphi_1, \varphi_2, \dots$ are the symmetrized basis functions constructed from the Slater type orbitals χ_1, χ_2, \dots by the following relation:

$$\varphi_p = \sum_q \chi_q g_{qp}. \quad (2)$$

The matrix elements g_{qp} in Eq. 2 can be determined with the help of symmetry group of molecule [8]. It should be noted that the symmetrized basis functions and symmetrized molecular orbitals are different kinds of basis functions of irreducible representation of the molecular symmetry group. Using Eqs. 1–2 and the formula

$$u_i = \sum_q \chi_q C_{qi} \quad (3)$$

for the unsymmetrized molecular orbitals, it is easy to establish the following matrix relation between coefficients C_{qi} and D_{pi} :

$$C = gD. \quad (4)$$

2 Expressions for unsymmetrical one-range addition theorems in terms of basic overlap integrals

For the calculation of multicenter integrals occurring in the combined HFR equations for molecule [7] we shall use the following relation for the unsymmetrical one-range addition theorems [5]:

$$\chi_{nlm}(\zeta, \vec{r}_{a1}) = \lim_{N \rightarrow \infty} \sum_{n'=1}^N \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} V_{nlm, n'l'm'}^{\alpha N}(\zeta, \zeta'; \vec{R}) \chi_{n'l'm'}(\zeta', \vec{r}_{b1}), \quad (5)$$

where $\zeta > 0$, $\zeta' > 0$, $\alpha = 1, 0, -1, -2, \dots$, $\vec{R} = \vec{R}_{ab}$ and

$$V_{nlm, n'l'm'}^{\alpha N}(\zeta, \zeta'; \vec{R}) = \sum_{n''=l'+1}^N \Omega_{n'n''}^{\alpha l'}(N) S_{nlm, n''-\alpha l'm'}(\zeta, \zeta'; \vec{R}) \quad (6)$$

$$\Omega_{nk}^{\alpha l}(N) = \left[\frac{[2(k-\alpha)]!}{(2k)!} \right]^{1/2} \sum_{n'=\max(n,k)}^N (2n')^\alpha \omega_{n'n}^{\alpha l} \omega_{n'k}^{\alpha l} \quad (7)$$

$$\omega_{nn'}^{\alpha l} = (-1)^{n'-l-1} \left[\frac{(n'+l+1)!}{(2n)^\alpha (n'+l+1-\alpha)!} F_{n'+l+1-\alpha}(n+l+1-\alpha) \times F_{n'-l-1}(n-l-1) F_{n'-l-1}(2n') \right]^{1/2}. \quad (8)$$

Here, $F_k(n) = n!/k!(n-k)!$ is the binomial coefficient. The quantities $S_{nlm, n''-\alpha l'm'}(\zeta, \zeta'; \vec{R}) = S_{nlm, n''-\alpha l'm'}(p, t; \theta, \phi)$ occurring in Eq. 6 are the overlap integrals defined as

$$S_{nlm, n'l'm'}(p, t; \theta, \phi) = \int \chi_{nlm}^*(\zeta, \vec{r}_a) \chi_{n'l'm'}(\zeta', \vec{r}_b) dV, \quad (9)$$

where $p = \frac{1}{2}(\zeta + \zeta')R$, $t = (\zeta - \zeta')/(\zeta + \zeta')$ and (R, θ, ϕ) are the spherical-polar coordinates of radius vector $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$; $\chi_{nlm}(\zeta, \vec{r}_a)$ and $\chi_{n'l'm'}(\zeta', \vec{r}_b)$ are normalized STOs centered on the nuclei a and b , respectively,

$$\chi_{nlm}(\zeta, \vec{r}) = (2\zeta)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \phi). \quad (10)$$

Here, the functions S_{lm} are complex or real spherical harmonics defined by

$$S_{lm}(\theta, \varphi) = P_{l|m|}(\cos \theta) \Phi_m(\varphi), \quad (11)$$

where $P_{l|m}$ are the normalized associated Legendre functions and for complex spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \tag{12}$$

for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1 + \delta_{m0})}} \begin{cases} \cos |m|\phi & \text{for } m \geq 0 \\ \sin |m|\phi & \text{for } m < 0 \end{cases}. \tag{13}$$

For the evaluation of integrals (9), we use Eqs. 5 and 17 of Ref. [9] for the rotation of two-center overlap integrals in the following form

$$S_{nlm,n'l'm'}(p, t; \vec{R}) = \sum_{\lambda=0}^{\min(l,l')} T_{lm,l'm'}^{*\lambda}(\theta, \varphi) S_{nl\lambda,n'l'\lambda}(p, t; R). \tag{14}$$

Here, the $S_{nl\lambda,n'l'\lambda}(\zeta, \zeta'; R)$ are the overlap integrals relative to lined-up coordinate systems:

$$S_{nl\lambda,n'l'\lambda}(p, t) = \int \chi_{nl\lambda}^*(\zeta, \vec{r}_a) \chi_{n'l'\lambda}(\zeta', \vec{r}_b) dV, \tag{15}$$

where $\lambda = |m| = |m'|$.

In Ref. [6], we have shown that the overlap integrals occurring on the right side of Eq. 14 are expressed through the basic overlap integrals $S_{n00,n'00}(p, t)$ by the formula

$$\begin{aligned} S_{nl\lambda,n'l'\lambda}(p, t) &= \sum_{\alpha=-\lambda}^l (2) \sum_{\beta=\lambda}^{l'} (2) \sum_{q=0}^{\alpha+\beta} \frac{g_{\alpha\beta}^q(l\lambda, l'\lambda)}{2^{2q-1}} \sum_{k=0}^q (-1)^k p^{\alpha+\beta-2q} F_k(q) \\ &\times [F_{2(n-\alpha+2q-2k)}(2n) F_{2(n'-\beta+2k)}(2n') [2(\alpha - 2q + 2k)]! \\ &\times [2(\beta - 2k)]!]^{-1/2} (1+t)^{\alpha-2q+2k} (1-t)^{\beta-2k} \\ &\times S_{n-\alpha+2q-2k00,n'-\beta+2k00}(p, t). \end{aligned} \tag{16}$$

The basic overlap integrals $S_{n00,n'00}(p, t)$ can be calculated with the help of recurrence relations (see Eqs. 10–15 of Ref. [6]).

All of the multicenter integrals over STOs appearing in the combined HFR equations for molecules can be evaluated with the help of basic overlap integrals using computer programs presented in our previous papers [10–15].

As an application of unsymmetrical one-range addition theorems and basic overlap integrals methods, we have solved combined HFR equations for the ground state of $BH_3((1a_1)^2 (2a_1)^2 (1e_x)^2 (1e_y)^2, {}^1A_1)$ using Slater type atomic orbitals as a minimal basis set. In the case of BH_3 , by the use of properties of symmetry group D_3 [8], it is

easy to establish the following relation for matrix g appearing in Eq. 2:

$$g = \begin{pmatrix} 0.51700126 & 0 & 0 & 0 & 0 & 0 & 0.87214513 & 0 \\ 0.51700126 & 0 & 0 & 0 & -0.75529984 & 0 & -0.43607256 & 0 \\ 0.51700126 & 0 & 0 & 0 & 0.75529984 & 0 & -0.43607256 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (17)$$

The results of computer calculations for orbital and total energies, and linear combination coefficients of symmetrized molecular orbitals defined by Eq. 1, where $1 \leq p \leq 8$, are presented in Table 1. The data for the screening constants of STOs were taken from Ref. [16]. The results obtained using minimal basis set of STOs agree well with published data [17, 18]. We have used for the atoms of BH_3 the following coordinates:

$$\begin{array}{ccc} & X & Y & Z \\ H_1 & 0 & R & 0 \\ H_2 & -\frac{\sqrt{3}}{2}R & -\frac{R}{2} & 0 \\ H_3 & \frac{\sqrt{3}}{2}R & -\frac{R}{2} & 0 \\ B & 0 & 0 & 0, \end{array}$$

where $R = R_{BH} = 2.26014098$.

The Slater type orbitals χ_q , symmetrized functions φ_p and symmetrized molecular orbitals u_i are denoted as

χ_{nlm}	$\chi_{100}(H_1)$	$\chi_{100}(H_2)$	$\chi_{100}(H_3)$	$\chi_{100}(B)$	$\chi_{200}(B)$	$\chi_{211}(B)$	$\chi_{21-1}(B)$	$\chi_{210}(B)$
χ_q	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8
$\varphi_{n\gamma m_\gamma}$	φ_{1a_1}	φ_{2a_1}	φ_{3a_1}	φ_{1a_2}	φ_{1e_x}	φ_{1e_y}	φ_{2e_x}	φ_{2e_y}
φ_p	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$u_{n\gamma m_\gamma}$	u_{1a_1}	u_{2a_1}	u_{1e_x}	u_{1e_y}	u_{1a_2}	u_{2e_x}	u_{2e_y}	u_{3a_1}
u_i	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8

It should be noted that the similar table can also be obtained for the linear combination coefficients C_{qi} occurring in the case of molecular orbitals of BH_3 , Eq. 3, when unsymmetrized χ -STO basis set is employed. For this purpose we should use in Eq. 4 the values of matrix g and D (Eq. 17 and Table 1).

We see from Table 1 that, in the case of minimal basis set, the results of computer calculation for the ground state of BH_3 are satisfactory. Work is in progress in our group for the analytical combined HFR calculations of small molecules using Slater type orbitals as basis sets.

Table 1 The orbital energies and linear combination coefficients of symmetrized molecular orbitals for the ground state of $BH_3((1a_1)^2(2a_1)^2(1e_x)^2(1e_y)^2, ^1A_1)$

φ_p	$\varepsilon_1 = \varepsilon_{1a_1}$	$\varepsilon_2 = \varepsilon_{2a_1}$	$\varepsilon_3 = \varepsilon_{1e_x}$	$\varepsilon_4 = \varepsilon_{1e_y}$	$\varepsilon_5 = \varepsilon_{1a_2}$	$\varepsilon_6 = \varepsilon_{3a_1}$	$\varepsilon_7 = \varepsilon_{2e_x}$	$\varepsilon_8 = \varepsilon_{2e_y}$
$\varphi_1 = \varphi_{1a_1}$	0.00715993	-0.46983423	0.00000000	0.00000000	0.00000000	-1.65402800	0.00000000	0.00000000
$\varphi_2 = \varphi_{2a_1}$	-0.99670499	0.18782755	0.00000000	0.00000000	0.00000000	-0.16559120	0.00000000	0.00000000
$\varphi_3 = \varphi_{3a_1}$	-0.01919680	-0.59633593	0.00000000	0.00000000	0.00000000	1.64208636	0.00000000	0.00000000
$\varphi_4 = \varphi_{1a_2}$	0.00000000	0.00000000	0.00000000	0.00000000	1.00000000	0.00000000	0.00000000	0.00000000
$\varphi_5 = \varphi_{1e_x}$	0.00000000	0.00000000	-0.51032510	0.00000000	0.00000000	0.00000000	-1.35729900	0.00000000
$\varphi_6 = \varphi_{2e_x}$	0.00000000	0.00000000	-0.56646435	0.00000000	0.00000000	0.00000000	1.33484475	0.00000000
$\varphi_7 = \varphi_{1e_y}$	0.00000000	0.00000000	0.00000000	0.51029281	0.00000000	0.00000000	0.00000000	1.35731092
$\varphi_8 = \varphi_{2e_y}$	0.00000000	0.00000000	0.00000000	0.56649613	0.00000000	0.00000000	0.00000000	-1.33483101
Total energy:	This work	Ref. [17]	Ref. [18]	Ref. [18]				
	-26.362082	-26.3742	-26.523979	-26.523979				

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