

Application of combined Hartree–Fock–Roothaan theory to molecules with arbitrary number of closed and open shells

I. I. Guseinov

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Abstract In this study, the applicability of the combined Hartree–Fock–Roothaan (CHFR) theory of atomic-molecular and nuclear systems (Guseinov, J Math Chem 42:177, 2007) to the molecules is demonstrated using minimal basis set of Slater type orbitals (STO). As an example of application of CHFR theory, the calculations have been performed for the ground state of electronic configuration of methylene molecule CH_2 which has two open shells. The results of computer calculations for the orbital, kinetic and total energies, linear combination coefficients of symmetrized molecular orbitals and virial ratios are presented.

Keywords Electronic configurations · Open shells · Slater type orbitals · Combined Hartree–Fock–Roothaan theory

1 Introduction

The quantum mechanical calculation of a molecule can be achieved via the usual Hartree–Fock–Roothaan (HFR) equations, involving the linear combination coefficients of molecular orbitals [1]. These equations are reduced to the separate descriptions of the closed and open shells electrons. Because of these separate descriptions, the Roothaan’s Hartree–Fock (HF) theory and its extensions by others [2–10] are, in general, applicable only to a state of single open shell electronic configuration. In a recent paper [11], we have eliminated these insufficiencies arising in the Roothaan’s HF theory and have suggested a combined open shell Hartree–Fock theory of atomic-molecular and nuclear systems which includes the arbitrary number of open shell cases. The aim of the present paper is to perform, as an application of CHFR theory, the calculations

I. I. Guseinov (✉)
Faculty of Arts and Sciences, Department of Physics, Onsekiz Mart University, Çanakkale, Turkey
e-mail: isguseinov@yahoo.com

for the ground state of two open shell electronic configuration of molecule CH_2 and to compare with the results obtained in the literature [12].

2 Theory

The main points of the CHF theory of atomic-molecular and nuclear systems in the case of molecules are as follows. For the arbitrary number of closed and open shell electronic configurations the CHF equations have the form [11]:

$$\hat{F}^i u_i = \varepsilon_i u_i, \quad (1)$$

where \hat{F}^i is the Fock operator determined by

$$\hat{F}^i = f_i \hat{h} + \hat{G}^i, \quad (2)$$

$$\hat{h} = -\frac{1}{2} \nabla^2 - \sum_a \frac{Z_a}{r_a}, \quad (3)$$

$$\hat{G}^i = \sum_{jkl} (2\hat{A}_{kl}^{ij} \hat{J}_{kl} - \hat{B}_{kl}^{ij} \hat{K}_{kl}). \quad (4)$$

Here, the occupied orbitals are described by the indices i, j, k and l . \hat{J}_{kl} , \hat{K}_{kl} and \hat{A}_{kl}^{ij} , \hat{B}_{kl}^{ij} are the Coulomb, exchange and coupling-projection operators, respectively. They are defined as follows:

$$\hat{J}_{kl}(\vec{r}_1)\varphi(\vec{r}_1) = \left(\int u_k^*(\vec{r}_2) \frac{1}{r_{21}} u_l(\vec{r}_2) dv_2 \right) \varphi(\vec{r}_1), \quad (5)$$

$$\hat{K}_{kl}(\vec{r}_1)\varphi(\vec{r}_1) = \left(\int u_k^*(\vec{r}_2) \frac{1}{r_{21}} \varphi(\vec{r}_2) dv_2 \right) u_l(\vec{r}_1), \quad (6)$$

$$\hat{A}_{kl}^{ij} u_i = A_{kl}^{ij} u_j, \quad (7)$$

$$\hat{B}_{kl}^{ij} u_i = B_{kl}^{ij} u_j. \quad (8)$$

The molecular orbitals u_i occurring in these equations obey the following orthonormality constraint:

$$\int u_i^* u_j dv = \delta_{ij}. \quad (9)$$

According to the CHF theory the coefficients A_{kl}^{ij} and B_{kl}^{ij} for molecules are determined by comparing the following relations:

Postulated energy (see Eq. 4 of [11])

$$E(2S+1\Gamma) = 2 \sum_i^n f_i h_i + \sum_{ij,kl}^n (2A_{kl}^{ij} J_{kl}^{ij} - B_{kl}^{ij} K_{kl}^{ij}), \tag{10}$$

expectation value of energy (see Eq. 7 of [11])

$$E(2S+1\Gamma) = \frac{1}{\Gamma_d(2S+1)} \sum_{M_\Gamma M_S} \int \Psi_{M_\Gamma M_S}^{\Gamma S*} \hat{H} \Psi_{M_\Gamma M_S}^{\Gamma S} d\tau, \tag{11}$$

where f_i is the fractional occupancy of shell i and

$$\hat{H} = \sum_{\mu=1}^N \left(-\frac{1}{2} \nabla_\mu^2 - \sum_a \frac{Z_a}{r_{a\mu}} \right) + \sum_{\mu=1}^{N-1} \sum_{\nu=\mu+1}^N \frac{1}{r_{\mu\nu}}, \tag{12}$$

$$h_i = \int u_i^*(\vec{r}_1) \hat{h} u_i(\vec{r}_1) dv_1, \tag{13}$$

$$J_{kl}^{ij} = \iint u_i^*(\vec{r}_1) u_k^*(\vec{r}_2) \frac{1}{r_{21}} u_j(\vec{r}_1) u_l(\vec{r}_2) dv_1 dv_2, \tag{14}$$

$$K_{kl}^{ij} = \iint u_i^*(\vec{r}_1) u_k^*(\vec{r}_2) \frac{1}{r_{21}} u_l(\vec{r}_1) u_j(\vec{r}_2) dv_1 dv_2. \tag{15}$$

The quantities $\Psi_{M_\Gamma M_S}^{\Gamma S}$ occurring in Eq. 11 are the multideterminantal wave functions which can be constructed by the use of Slater’s or modified Slater’s determinantal method (see Sect. 4 of [11]).

For the cases of closed–closed and closed–open shells interactions, the coefficients A_{kl}^{ij} and B_{kl}^{ij} can also be determined from the relations:

$$A_{kl}^{ij} = B_{kl}^{ij} = f_i f_k \delta_{ij} \delta_{kl}. \tag{16}$$

We notice that the coupling-projection coefficients appearing in Eqs. 8–10 have the following symmetry properties:

$$A_{kl}^{ij} = A_{ij}^{kl}, \quad A_{kl}^{ij} = A_{lk}^{ji}, \tag{17}$$

$$B_{kl}^{ij} = B_{ij}^{kl}, \quad B_{kl}^{ij} = B_{lk}^{ji}. \tag{18}$$

The coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} obtained from the CHF theory are taking into account in the CHFR equations defined as follows [11]:

$$\sum_q (\hat{F}_{pq}^i - \varepsilon_i S_{pq}) C_{qi} = 0, \tag{19}$$

where C_{qi} are the linear combination coefficients of nonsymmetrized molecular orbitals

$$u_i = \sum_q \chi_q C_{qi}, \quad (20)$$

and

$$\hat{F}_{pq}^i = f_i h_{pq} + \hat{G}_{pq}^i, \quad (21)$$

$$S_{pq} = \int \chi_p^* \chi_q dv, \quad (22)$$

$$h_{pq} = \int \chi_p^* \hat{h} \chi_q dv_1, \quad (23)$$

$$\hat{G}_{pq}^i = \sum_{j,rs} \left(2\hat{a}_{rs}^{ij} I_{rs}^{pq} - \hat{b}_{rs}^{ij} K_{rs}^{pq} \right). \quad (24)$$

The coupling-projection operators \hat{a}^{ij} and \hat{b}^{ij} appearing in Eq. 24 are defined as

$$\hat{a}^{ij} C_{qi} = a^{ij} C_{qj}, \quad (25)$$

$$\hat{b}^{ij} C_{qi} = b^{ij} C_{qj}, \quad (26)$$

where

$$\hat{a}^{ij} = C \hat{A}^{ij} C^+, \quad (27)$$

$$\hat{b}^{ij} = C \hat{B}^{ij} C^+. \quad (28)$$

The Coulomb and exchange integrals occurring in Eq. 24 are determined as

$$I_{rs}^{pq} = \iint \chi_p^*(x_1) \chi_r^*(x_2) \frac{1}{r_{21}} \chi_q(x_1) \chi_s(x_2) dv_1 dv_2, \quad (29)$$

$$K_{rs}^{pq} = \iint \chi_p^*(x_1) \chi_r^*(x_2) \frac{1}{r_{21}} \chi_s(x_1) \chi_q(x_2) dv_1 dv_2 = I_{rq}^{ps}. \quad (30)$$

The orthonormality constraint for the expansion coefficients is defined by

$$C^+ S C = I, \quad (31)$$

where S is the matrix of overlap integrals.

We note that the numerical and analytical calculations of CHF and CHFR equations determined by Eqs. 1 and 19, respectively, can be performed for the arbitrary states of electronic configurations which have any number of closed and open shells.

3 Numerical results and discussion

In order to calculate the CHF and CHFR equations one has to perform the following steps:

- (1) Find the independent determinantal wave functions U_i using modified Slater's determinantal method.
- (2) Determine the multideterminantal wave functions $\Psi_{M_\Gamma M_S}^{\Gamma S}$ in terms of independent determinants U_i .
- (3) Obtain the values of coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} using Eqs. 10 and 11.
- (4) Construct the CHF operator and the CHFR matrix operator.
- (5) Solve the CHF and CHFR equations self-consistently for the one-electron orbitals u_i and linear combination coefficients C_{qi} , respectively.

To perform these steps concrete, we have solved CHFR equations for the ground state of molecule CH_2 .

The general form of orthonormal Slater determinants of the electronic configuration $1a_1^2 2a_1^2 1b_2^2 1b_1^1 3a_1^1$ of CH_2 molecule may be written as

$$U(4m_{s7}, 5m_{s8}) = \frac{1}{\sqrt{8!}} \hat{A}[u_{11/2}(x_1)u_{1-1/2}(x_2)u_{21/2}(x_3)u_{2-1/2}(x_4)u_{31/2}(x_5)u_{3-1/2}(x_6)u_{4m_{s7}}(x_7)u_{5m_{s8}}(x_8)], \quad (32)$$

where $u_{im_s}(x) = u_i(x, y, z)u_{m_s}(\sigma)$ are the molecular spin orbitals; the spatial orbitals $u_i(x, y, z)$ occupied by electrons are the basis functions of the irreducible representation of the symmetry group C_{2v} . The molecular orbitals $u_{n\gamma}$ and Slater type orbitals χ_p are denoted as

$$\begin{array}{l} u_{n\gamma} : u_{1a_1} \quad u_{2a_1} \quad u_{1b_2} \quad u_{1b_1} \quad u_{3a_1} \\ u_i : u_1 \quad u_2 \quad u_3 \quad u_4 \quad u_5 \end{array}$$

$$\begin{array}{l} \chi_{nlm} : \chi_{100}(H_1) \quad \chi_{100}(H_2) \quad \chi_{100}(C) \quad \chi_{200}(C) \quad \chi_{211}(C) \quad \chi_{21-1}(C) \quad \chi_{210}(C) \\ \chi_p : \quad \chi_1 \quad \quad \chi_2 \quad \quad \chi_3 \quad \quad \chi_4 \quad \quad \chi_5 \quad \quad \chi_6 \quad \quad \chi_7 \end{array}$$

The geometric parameters of CH_2 have been taken from [12]:

$$\begin{aligned} R_{C-H} &= 2.04468, \quad \alpha_{HCH} \\ &= 132.4^\circ, \quad H_1(0, -1.87082, 0.82512), \quad H_2(0, 1.87082, 0.82512), \quad C(0, 0, 0). \end{aligned}$$

The atomic orbital exponents we take from [13].

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 configuration $(1a_1^2 2a_1^2 1b_2^2 1b_1^1 3a_1^1, {}^3B_1)$ are presented in

Table 1 The independent determinantal wave functions

m_{s7}	m_{s8}	M_S	$U(4m_{s7}, 5m_{s8})$
1/2	1/2	1	$U_1(41/2, 51/2)$
	-1/2	0	$U_2(41/2, 5-1/2)$
-1/2	1/2	0	$U_3(4-1/2, 51/2)$
	-1/2	-1	$U_4(4-1/2, 5-1/2)$

Table 2 Terms and their multideterminantal wave functions

Terms	$\Psi_{M_S}^S$
$3B_1$	$\Psi_1^1 = U_1$ $\Psi_0^1 = \frac{1}{\sqrt{2}}(U_2 + U_3)$ $\Psi_{-1}^1 = U_4$
$1B_1$	$\Psi_0^0 = \frac{1}{\sqrt{2}}(U_2 - U_3)$

Table 3 The values of coupling-projection coefficients

ij	kl	$A_{kl}^{ij} = A_{ij}^{kl}$	$B_{kl}^{ij} = B_{ij}^{kl}$
1 1	1 1	1	1
	2 2	1	1
	3 3	1	1
	4 4	1/2	1/2
	5 5	1/2	1/2
2 2	2 2	1	1
	3 3	1	1
	4 4	1/2	1/2
	5 5	1/2	1/2
3 3	3 3	1	1
	4 4	1/2	1/2
	5 5	1/2	1/2
4 4	5 5	1/4	1/2

Table 4 The orbital energies and linear combination coefficients of symmetrized molecular orbitals ($u_i = \sum_p \varphi_p D_{pi}$) for ground state term 3B_1

$u_i = u_{ny}$	$u_1 = u_{1a_1}$	$u_2 = u_{2a_1}$	$u_3 = u_{1b_2}$	$u_4 = u_{1b_1}$	$u_5 = u_{3a_1}$	$u_6 = u_{4a_1}$	$u_7 = u_{2b_2}$
ε_i	ε_{1a_1}	ε_{2a_1}	ε_{1b_2}	ε_{1b_1}	ε_{3a_1}	ε_{4a_1}	ε_{2b_2}
D_{pi}	-11.24682	-0.78709	-0.27728	-0.15800	-0.01828	0.00000	0.00000
φ_p							
$\varphi_1 = \varphi(1a_1)$	0.07781	0.60064	0.00000	0.00000	-0.06778	-1.39535	0.00000
$\varphi_2 = \varphi(2a_1)$	-0.98562	-0.17245	0.00000	0.00000	-0.05835	-0.23586	0.00000
$\varphi_3 = \varphi(3a_1)$	-0.08951	0.49145	0.00000	0.00000	0.27819	1.38259	0.00000
$\varphi_4 = \varphi(4a_1)$	-0.02707	0.02739	0.00000	0.00000	-0.95530	0.50373	0.00000
$\varphi_5 = \varphi(1b_1)$	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000	0.00000
$\varphi_6 = \varphi(1b_2)$	0.00000	0.00000	0.49193	0.00000	0.00000	0.00000	1.31897
$\varphi_7 = \varphi(2b_2)$	0.00000	0.00000	-0.59131	0.00000	0.00001	0.00000	1.27727

$$E = -38.97519$$

$$E = -38.9221 [12]$$

Tables 1–4. The symmetrized basis orbitals φ_p occurring in Table 4 are determined through the Slater type orbitals by the following relation:

$$\varphi_p = \sum_q \chi_q g_{qp}, \quad (33)$$

where

$$g = \begin{pmatrix} 0,66171 & 0 & 0 & 0 & 0 & 0,76334 & 0 \\ 0,66171 & 0 & 0 & 0 & 0 & -0,76334 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}. \quad (34)$$

$$D = g^{-1}C \quad (35)$$

We see from Table 4 that, in the case of minimal basis set, the results of computer calculation obtained by the use of CHFR approach for the molecule CH_2 having two open shells are satisfactory. Work is in progress in our group for the CHFR calculations of small molecules with the arbitrary number of closed and open shells.

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