

Combined open shell Hartree–Fock theory of atomic–molecular and nuclear systems

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In this study, the combined Hartree–Fock (HF) and Hartree–Fock–Roothaan equations are derived for multideterminantal single configuration states with any number of open shells of atoms, molecules and nuclei. It is shown that the postulated orbital-dependent energy and Fock operators are invariant to the unitary transformation of orbitals. This new methodology is based entirely on the spin-restricted HF theory. As an application of combined open shell theory of atomic–molecular and nuclear systems presented in this paper, we have solved Hartree–Fock–Roothaan equations for the ground state of electronic configuration $C(1s^2 2s^2 2p^2)$ using Slater type orbitals as a basis.

KEY WORDS: Hartree–Fock theory, open-shell systems, multideterminantal states

1. Introduction

The main application of Hartree–Fock (HF) method was, in atomic and molecular physics, the study of Coulomb systems (atoms, ions and molecules) with a purely Coulombic Hamiltonian of electrons interacting with static nuclei. In nuclear physics, the use of HF method to compute the ground state of nuclei is more recent and we refer, for example, to papers [1–5] and the references therein. Roothaan’s open shell HF theory [6] is commonly used to evaluate the various properties of certain states of atoms, molecules and nuclei (see, e.g., [7–15]). This approach does not seem to have been extended to arbitrary open-shell states. In Roothaan’s treatment, which is an extension of HF theory for closed shell systems [16], and in the extensions to open-shell states by others [17–23], there are well-known complicating features, which do not occur in the closed-shell equations. In [24], we eliminated these difficulties and derived HF and Hartree–Fock–Roothaan (HFR) equations applicable to any multideterminantal state of a single configuration of atomic and molecular systems that has arbitrary open-shells. The aim of this report is to derive the combined HF and HFR equations of atomic–molecular and nuclear systems applicable to any

multideterminantal state of a single configuration that has any number of open shells of any symmetry.

2. Definitions and basic formulas

In the present paper, we use the combined Hamiltonian of the atomic–molecular and nuclear systems of N particles (electrons or nucleons) in the following form:

$$\hat{H}^\omega = \sum_{\mu=1}^N \left(-\frac{1}{2m^{\omega-1}} \nabla_\mu^2 - \delta_{\omega 1} \sum_a \frac{Z_a}{r_{a\mu}} \right) + \sum_{\mu=1}^{N-1} \sum_{\nu=\mu+1}^N f^\omega(x_{\mu\nu}), \quad (1)$$

where $f^\omega(x_{\mu\nu})$ are the repulsion or attraction interaction potentials for electrons ($\omega = 1$) and nucleons ($\omega = 2$), respectively; m is the mass of nucleon. Thus we deal in both cases with fermions, i.e., particles which obey the Pauli exclusion principle. This means that the particles of atomic–molecular and nuclear systems will be described by antisymmetric wave functions–Slater determinants. The general form of Slater determinants for an N – particle open shell system may be written as [25]

$$\begin{aligned} & U(u_{n_{N-k+1}}(x_{N-k+1}) \dots u_{n_N}(x_N)) \\ & \equiv U(u_{n_1}(x_1)u_{n_2}(x_2) \dots u_{n_{N-k}}(x_{N-k})u_{n_{N-k+1}}(x_{N-k+1}) \dots u_{n_N}(x_N)) \\ & = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{n_1}(x_1) & u_{n_2}(x_1) & \dots & u_{n_{N-k}}(x_1) & u_{n_{N-k+1}}(x_1) & \dots & u_{n_N}(x_1) \\ u_{n_1}(x_2) & u_{n_2}(x_2) & \dots & u_{n_{N-k}}(x_2) & u_{n_{N-k+1}}(x_2) & \dots & u_{n_N}(x_2) \\ \cdot & \cdot & \dots & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot & \cdot & \dots & \cdot \\ u_{n_1}(x_N) & u_{n_2}(x_N) & \dots & u_{n_{N-k}}(x_N) & u_{n_{N-k+1}}(x_N) & \dots & u_{n_N}(x_N) \end{vmatrix}, \end{aligned} \quad (2)$$

where $n \equiv im_i^{\omega-1}m_s$ and $x \equiv xyz\kappa^{\omega-1}\sigma$. Here, $u_n(x) \equiv u_i(xyz)v_{m_i}^{\omega-1}(\kappa)u_{m_s}(\sigma)$ is the isospin–spin orbital; $u_i(xyz)$, $v_{m_i}(\kappa)$, and $u_{m_s}(\sigma)$ are the spatial, isospin and spin wave functions, respectively. The spin orbital $u_n(x) \equiv u_i(xyz)u_{m_s}(\sigma)$ for atoms and molecules is the special case of isospin–spin orbital for $\omega = 1$. The $(u_{n_1}, u_{n_2}, \dots, u_{n_{N-k}})$ and $(u_{n_{N-k+1}}, \dots, u_{n_N})$ occurring in equation (2) are the sets of orthonormal isospin–spin orbitals for closed and open shells, respectively, where $0 \leq k \leq N$. All of the orthonormal and independent Slater determinants for a given configuration can be obtained from equation (2). The first $N - k$ orthonormal and independent isospin–spin orbitals in these determinants are the same (closed shells), and all other k isospin–spin orbitals are different (open shells). The orbitals and Slater determinants form the orthonormal sets:

$$\int u_i^* u_s \, dv = \delta_{is}, \tag{3a}$$

$$\sum_k v_{m_t}^*(\kappa) v_{m'_t}(\kappa) = \delta_{m_t m'_t}, \tag{3b}$$

$$\sum_\sigma u_{m_s}^*(\sigma) u_{m'_s}(\sigma) = \delta_{m_s m'_s}, \tag{3c}$$

$$\int U^* U' \, d\tau = \delta_{UU'}. \tag{3d}$$

3. Combined orbital-dependent energy expression

The postulated energy expectation value for a single configuration multi-determinantal state of combined atomic–molecular and nuclear systems with a given space, spin and isospin symmetry can be written in the following form:

$$E^\omega = \omega \left[2 \sum_i^n f_i h_i + \sum_{ijkl}^n \left(2\omega A_{kl}^{ij} J_{kl}^{ij} - B_{kl}^{ij} K_{kl}^{ij} \right) \right]. \tag{4}$$

Here $n = n_c + n_o$ is the number of occupied orbitals belonging to closed (n_c) and open (n_o) shells, $1 \leq i, j, k, l \leq n$ and $\omega = 1, 2$. For $\omega = 1$ and for $\omega = 2$ equation (4) denotes the energy expectation value of atomic–molecular and nuclear systems, respectively; f_i is the fractional occupancy of shell i , which is determined by

$$f_i = \frac{N_i}{N_{0i}}, \tag{5}$$

where N_{0i} and N_i are number of states and particles in shell i , respectively. It should be noted that the orbital occupation numbers can also be determined by the use of MCSCF or CASSCF approaches, which are well suited for open-shell problems and routine these days (see, e.g., [7]). In MCSCF and CASSCF orbital optimizations, the orbital occupation numbers are the result of calculations and not some arbitrary numbers selected before the calculation is performed.

In equation (4), the coefficients A_{kl}^{ij} and B_{kl}^{ij} are the coupling-projection constants. For closed–closed and closed–open shell interaction energies ($1 \leq i, j \leq n_c, 1 \leq k, l \leq n$ and $1 \leq i, j \leq n, 1 \leq k, l \leq n_c$) the coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} are determined by

$$A_{kl}^{ij} = B_{kl}^{ij} = f_i f_k \delta_{ij} \delta_{kl}. \tag{6}$$

In the case of open–open shell interaction energies ($n_c + 1 \leq i, j \leq n$ and $n_c + 1 \leq k, l \leq n$) the values of coefficients A_{kl}^{ij} and B_{kl}^{ij} depend on the state under study. We notice that the possibility of writing the combined energy of

atomic–molecular and nuclear systems in form (4) is based on the assumption that the energy E^ω is the average expectation value for all the degenerate total orthonormal sets of multideterminantal wave functions $\Psi_{M_\Gamma}^\Gamma$ for state with the irreducible representation Γ :

$$E_\Gamma^\omega = \frac{1}{N_\Gamma} \sum_{M_\Gamma} \int \Psi_{M_\Gamma}^{\Gamma*} \hat{H} \Psi_{M_\Gamma}^\Gamma d\tau, \quad (7)$$

where

$$\Psi_{M_\Gamma}^\Gamma = \begin{cases} \Psi_{M_L M_T M_S}^{LTS} \\ \Psi_{M_L M_S}^{LS} \\ \Psi_{M_\Lambda M_S}^{\Lambda S} \\ \Psi_{M_\Gamma M_S}^{\Gamma S} \end{cases},$$

$$N_\Gamma = \begin{cases} (2L+1)(2T+1)(2S+1) & \text{for Nuclei,} \\ (2L+1)(2S+1) & \text{for Atoms,} \\ (2-\delta_{\Lambda 0})(2S+1) & \text{for Linear Molecules,} \\ \Gamma_d(2S+1) & \text{for Nonlinear Molecules.} \end{cases} \quad (8)$$

Here, the quantities L , T , and S are the total orbital, isospin and spin quantum numbers, respectively.

In equation (4), h_i , J_{kl}^{ij} and K_{kl}^{ij} are defined by

$$h_i = \int u_i^*(\vec{r}_1) \hat{h} u_i(\vec{r}_1) dv_1, \quad (9)$$

$$J_{kl}^{ij} = \int u_i^*(\vec{r}_1) \hat{J}_{kl}(\vec{r}_1) u_j(\vec{r}_1) dv_1 = \int u_k^*(\vec{r}_2) \hat{J}_{ij}(\vec{r}_2) u_l(\vec{r}_2) dv_2, \quad (10)$$

$$K_{kl}^{ij} = \int u_i^*(\vec{r}_1) \hat{K}_{kl}(\vec{r}_1) u_j(\vec{r}_1) dv_1 = \int u_k^*(\vec{r}_2) \hat{K}_{ij}(\vec{r}_2) u_l(\vec{r}_2) dv_2, \quad (11)$$

where

$$\hat{h} = -\frac{1}{2m^{\omega-1}} \nabla_1^2 - \delta_{\omega 1} \sum_a \frac{Z_a}{r_{a1}}, \quad (12)$$

$$\hat{J}_{kl}(\vec{r}_1) \varphi(\vec{r}_1) = \left(\int u_k^*(\vec{r}_2) f(x_{21}) u_l(\vec{r}_2) dv_2 \right) \varphi(\vec{r}_1), \quad (13)$$

$$\hat{K}_{kl}(\vec{r}_1) \varphi(\vec{r}_1) = \left(\int u_k^*(\vec{r}_2) f(x_{21}) \varphi(\vec{r}_2) dv_2 \right) u_l(\vec{r}_1). \quad (14)$$

Here, \hat{K}_{kl} is the exchange operator (see [24] for the definition of symmetrical properties of square n^2 -dimensional supermatrices A , B , J and K).

In the single-determinantal closed shell case, one has $f_i = f_k = 1$ and $A_{kl}^{ij} = B_{kl}^{ij} = \delta_{ij}\delta_{kl}$. Then, the formula for E^ω , equation (4), can be rewritten using integrals h_i , J_{kk}^{ii} , and K_{kk}^{ii} ,

$$E^\omega = \omega \left[2 \sum_i^n h_i + \sum_{ik}^n (2\omega J_{kk}^{ii} - K_{kk}^{ii}) \right], \tag{15}$$

where J_{kk}^{ii} and K_{kk}^{ii} are the ordinary 2-indexed integrals of Roothaan’s closed shell HF theory [16].

4. Use of modified Slater’s determinantal method in evaluation of coupling-projection coefficients

For the evaluation of coupling-projection coefficients occurring in the combined energy expression, equation (4), we have to find independent Slater determinants and orthonormal multideterminantal wave functions of terms. For this purpose, we use the determinantal method presented in [26,27]. However, by the use of Slater’s determinantal method it is not only difficult, in general, to find independent Slater determinants but also to simplify the construction of multideterminantal wave functions for open-shell systems. In this section, we have modified Slater’s determinantal method for the evaluation of independent Slater determinants, which are useful for the construction of multideterminantal wave functions and for the evaluation of coupling-projection coefficients.

We have now to consider the problem of determining which of the independent Slater determinants occur in a given configuration. According to Guseinov [25], we can write down the N individual sets comprising each complete set, which occurs in the configuration. The number and nature of the closed shells is without effect on the values of quantum numbers in the open-shell spin-orbitals. We denote here a set of quantum numbers for open-shell spin-orbitals by n_i (where $i = 1, 2, \dots, k$), namely,

$$n_i \equiv 1, 2, \dots, N_i, \tag{16}$$

where N_i is the number of spin-orbitals in the open shell i .

In order to obtain from equation (2), all of the independent Slater determinants for a given electronic or nucleonic configuration we modified the Slater’s determinantal method for the states of the same open-shell by taking into account in equation (2) only those values of n_i in the following form:

$$n_1 < n_2 < \dots < n_k. \tag{17}$$

We refer to the Slater rule based on the inequality (17) as modified Slater’s determinantal method for the evaluation of independent determinantal wave

functions. It should be noted that in the case of different open-shells the sets of quantum numbers in equation (2) are independent. Therefore, it is easy to obtain the independent determinantal wave functions for these systems by the use of modified determinantal method.

Now we can move on, as an example, to an application of modified determinantal method for the determination of Slater determinants for atoms. Having made a list of the complete sets, which belong to an atomic electronic configuration we may classify them by values of $\sum m_l = M_L$ and $\sum m_s = M_S$. To make the argument concrete, let us consider the configuration $C(1s^2 2s^2 2p^2)$, in which two electrons occur outside closed shells. The complete sets for these electrons classified by M_L, M_S values and the independent determinants obtained from equation (2) by modified determinantal method are shown in table 1.

It is easy to find from table 1 the terms and the orthonormal sets of multideterminantal wave functions $\Psi_{M_L M_S}^{LS}$, which are eigenfunctions of operators $\hat{L}^2, \hat{L}_Z, \hat{S}^2$ and \hat{S}_z . The results are given in table 2.

For the calculation of coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} for open shell electrons we have to take into account table 2 for wave functions $\Psi_{M_L M_S}^{LS}$ in equation (7) and to compare the results with equation (4). The obtained results

Table 1
The independent determinantal wave functions for the electronic configuration $C(1s^2 2s^2 2p^2)$.

$n_5 : m_{l_5} m_{s_5}$	$n_6 : m_{l_6} m_{s_6}$	M_L	M_S	$U(21m_{l_5}m_{s_5} 21m_{l_6}m_{s_6})$	
1 : $1\frac{1}{2}$	2 : $1-\frac{1}{2}$	2	0	$U_1(211\frac{1}{2})$	$211 - \frac{1}{2}$
	3 : $0\frac{1}{2}$	1	1	$U_2(211\frac{1}{2})$	$210\frac{1}{2}$
	4 : $0-\frac{1}{2}$	1	0	$U_3(211\frac{1}{2})$	$210-\frac{1}{2}$
	5 : $-1\frac{1}{2}$	0	1	$U_5(211\frac{1}{2})$	$21 - 1\frac{1}{2}$
	6 : $-1-\frac{1}{2}$	0	0	$U_6(211\frac{1}{2})$	$21 - 1-\frac{1}{2}$
2 : $1-\frac{1}{2}$	3 : $0\frac{1}{2}$	1	0	$U_4(211-\frac{1}{2})$	$210\frac{1}{2}$
	4 : $0-\frac{1}{2}$	1	-1	$U_9(211-\frac{1}{2})$	$210-\frac{1}{2}$
	5 : $-1\frac{1}{2}$	0	0	$U_7(211-\frac{1}{2})$	$21 - 1\frac{1}{2}$
	6 : $-1-\frac{1}{2}$	0	-1	$U_{10}(211-\frac{1}{2})$	$21 - 1-\frac{1}{2}$
3 : $0\frac{1}{2}$	4 : $0-\frac{1}{2}$	0	0	$U_8(210\frac{1}{2})$	$210-\frac{1}{2}$
	5 : $-1\frac{1}{2}$	-1	1	$U_{11}(210\frac{1}{2})$	$21 - 1\frac{1}{2}$
	6 : $-1-\frac{1}{2}$	-1	0	$U_{12}(210\frac{1}{2})$	$21 - 1-\frac{1}{2}$
4 : $0-\frac{1}{2}$	5 : $-1\frac{1}{2}$	-1	0	$U_{13}(210-\frac{1}{2})$	$21 - 1\frac{1}{2}$
	6 : $-1-\frac{1}{2}$	-1	-1	$U_{14}(210-\frac{1}{2})$	$21 - 1-\frac{1}{2}$
5 : $-1\frac{1}{2}$	6 : $-1-\frac{1}{2}$	-2	0	$U_{15}(21 - 1\frac{1}{2})$	$21 - 1-\frac{1}{2}$

Table 2
The terms of electronic configuration $C(1s^2 2s^2 2p^2)$ and their multideterminantal wave functions.

Terms	$\Psi_{M_L M_S}^{LS}$		
1S	$\Psi_{00}^{00} = \frac{1}{\sqrt{3}}(U_6 - U_7 - U_8)$		
1D	$\Psi_{20}^{20} = U_1$	$\Psi_{10}^{20} = \frac{1}{\sqrt{2}}(U_3 - U_4)$	$\Psi_{00}^{20} = \frac{1}{\sqrt{6}}(U_6 - U_7 + 2U_8)$
	$\Psi_{-10}^{20} = \frac{1}{\sqrt{2}}(U_{12} - U_{13})$	$\Psi_{-20}^{20} = U_{15}$	
3P	$\Psi_{11}^{11} = U_2$	$\Psi_{10}^{11} = \frac{1}{\sqrt{2}}(U_3 + U_4)$	$\Psi_{1-1}^{11} = U_9$
	$\Psi_{01}^{11} = U_5$	$\Psi_{00}^{11} = \frac{1}{\sqrt{2}}(U_6 + U_7)$	$\Psi_{0-1}^{11} = U_{10}$
	$\Psi_{-11}^{11} = U_{11}$	$\Psi_{-10}^{11} = \frac{1}{\sqrt{2}}(U_{12} + U_{13})$	$\Psi_{-1-1}^{11} = U_{14}$

Table 3
The values of coupling-projection coefficients A_{kl}^{ij} and B_{kl}^{ij} for electronic configuration $C(1s^2 2s^2 2p^2)$.

Closed–closed and closed–open shells equations (5) and (6)		Open–open shells equations (4) and (7)	
$A_{11}^{11} = 1$	$B_{11}^{11} = 1$	$A_{44}^{33} = A_{33}^{44} = \frac{1}{12}$	$B_{44}^{33} = B_{33}^{44} = \frac{1}{6}$
$A_{22}^{11} = A_{11}^{22} = 1$	$B_{22}^{11} = B_{11}^{22} = 1$	$A_{55}^{33} = A_{33}^{55} = \frac{1}{12}$	$B_{55}^{33} = B_{33}^{55} = \frac{1}{6}$
$A_{33}^{11} = A_{11}^{33} = \frac{1}{3}$	$B_{33}^{11} = B_{11}^{33} = \frac{1}{3}$	$A_{55}^{44} = A_{44}^{55} = \frac{1}{12}$	$B_{55}^{44} = B_{44}^{55} = \frac{1}{6}$
$A_{44}^{11} = A_{11}^{44} = \frac{1}{3}$	$B_{44}^{11} = B_{11}^{44} = \frac{1}{3}$		
$A_{55}^{11} = A_{11}^{55} = \frac{1}{3}$	$B_{55}^{11} = B_{11}^{55} = \frac{1}{3}$		
$A_{22}^{22} = 1$	$B_{22}^{22} = 1$		
$A_{33}^{22} = A_{22}^{33} = \frac{1}{3}$	$B_{33}^{22} = B_{22}^{33} = \frac{1}{3}$		
$A_{44}^{22} = A_{22}^{44} = \frac{1}{3}$	$B_{44}^{22} = B_{22}^{44} = \frac{1}{3}$		
$A_{55}^{22} = A_{22}^{55} = \frac{1}{3}$	$B_{55}^{22} = B_{22}^{55} = \frac{1}{3}$		

for $C(1s^2 2s^2 2p^2)$ are presented in table 3, where

$$nlm: 100 \ 200 \ 211 \ 210 \ 21 - 1$$

$$i: 1 \ 2 \ 3 \ 4 \ 5$$

and $n_c = 2, n_0 = 3, n = n_c + n_0 = 5, f_1 = f_2 = 1, f_3 = f_4 = f_5 = 2/6$.

5. Hartree–Fock and Hartree–Fock–Roothaan equations

The formula (4) for E^ω seems to be completely general, for a single configuration with any number of open shells. The use of symmetrical and Hermitian properties of the $A_{kl}^{ij}, B_{kl}^{ij}, \hat{J}_{kl}$ and \hat{K}_{kl} (see equations (11)–(14) of Ref. [24]) simplifies the derivation of combined HF equations.

We now apply the variational principle to the total energy, equation (4), in order to obtain the combined HF equations for the spatial orbitals u_i of atoms, molecules and nuclei. This derivation closely parallels the derivation of HF equations in [24] for the atomic and molecular systems. If we take into account the subsidiary conditions (3a) by the method of the Lagrangian undetermined multipliers, denote the Lagrangian multiplier by $-2\omega\varepsilon_{si}$ and make use of the symmetrical and Hermitian properties of A_{kl}^{ij} , B_{kl}^{ij} , \hat{h} , \hat{J}_{kl} and \hat{K}_{kl} , then the variation of energy E^ω , equation (4), gives the following equations for the orbitals;

$$\hat{F}^i u_i = \sum_s u_s \varepsilon_{si}, \quad (18)$$

where ε is a Hermitian matrix of Lagrangian multipliers and \hat{F}^i is the Fock operator defined by

$$\hat{F}^i = f_i \hat{h} + \hat{G}^i. \quad (19)$$

Here, the total particle interaction operator \hat{G}^i is determined by

$$\hat{G}^i = \sum_{j,kl}^n \left(2\omega \hat{A}_{kl}^{ij} \hat{J}_{kl} - \hat{B}_{kl}^{ij} \hat{K}_{kl} \right). \quad (20)$$

The quantities \hat{A}_{kl}^{ij} and \hat{B}_{kl}^{ij} occurring in equation (20) are the coupling-projection operators, defined by

$$\hat{A}_{kl}^{ij} u_i = A_{kl}^{ij} u_j, \quad (21)$$

$$\hat{B}_{kl}^{ij} u_i = B_{kl}^{ij} u_j. \quad (22)$$

The operator \hat{F}^i , which is defined in terms of the orbitals u_i , is easily shown to be invariant when orbitals are subjected to the unitary transformation by means of a unitary matrix Q [24]:

$$u_i(\vec{r}) = \sum_{i'} u'_{i'}(\vec{r}) Q_{i'i}^+, \quad u'_{i'}(\vec{r}) = \sum_i u_i(\vec{r}) Q_{ii'}. \quad (23)$$

It is easy to show that the energy expression, equation (4), is also invariant to such changes of the orbitals.

Accordingly, the orbitals $u'_{i'}$ satisfy

$$\hat{F}^{i'} u_{i'} = \sum_{s'} u'_{s'} \varepsilon'_{s'i'}, \quad (24)$$

where

$$\varepsilon' = Q^+ \varepsilon Q. \quad (25)$$

Equation (25) shows that the Fock operator can be diagonalized using the unitary combinations of the original orbitals. Since the matrix ε is Hermitian, there exists a unitary matrix Q so that $\varepsilon' = Q^+ \varepsilon Q$ is a diagonal matrix with real diagonal elements. It is therefore, no loss of generality if we assume that our set of orbitals satisfies the simpler equations

$$\hat{F}^i u_i = \varepsilon_i u_i, \tag{26}$$

where the operator \hat{F}^i is defined by equation (19).

It should be noted that the orbital-dependent Fock operators and total energy in Roothaan’s open shell HF theory defined by Roothaan [6]

$$E = 2 \sum_k H_k + \sum_{kl} (2J_{kl} - K_{kl}) + f \left[2 \sum_m H_m + f \sum_{mn} (2aJ_{mn} - bK_{mn}) + 2 \sum_{km} (2J_{km} - K_{km}) \right] \tag{27}$$

are not invariant to the unitary transformation of orbitals and, therefore, the Fock operators of Roothaan’s approach can not be diagonalized.

The combined HF equations for closed-shell atomic–molecular and nuclear systems can be obtained from equation (26) using equation (6) for $f_i = f_k = 1$:

$$\hat{F} u_i = \varepsilon_i u_i, \tag{28}$$

where

$$\hat{F} = \hat{h} + \hat{G}, \tag{29}$$

$$\hat{G} = \sum_k^n (2\omega \hat{J}_{kk} - \hat{K}_{kk}). \tag{30}$$

Using equations (4), (19), (20) and (26) we can express the total energy in terms of the orbital energies ε_i and the one-particle integrals h_i : for open-shell systems

$$E^\omega = \omega \sum_i^n (f_i h_i + \varepsilon_i), \tag{31}$$

for closed-shell systems

$$E^\omega = \omega \sum_i^n (h_i + \varepsilon_i). \tag{32}$$

It is well known that the orbitals u_i , occurring in the atomic–molecular and nuclear structure theories, usually are defined as linear combinations of arbitrary basic atomic or nuclear orbitals (LCAO or LCNO) [16]:

$$u_i = \sum_q \chi_q C_{qi}. \quad (33)$$

In order to obtain the HFR equations for the coefficients C_{qi} we have to minimize the expression (4) by varying the coefficients C_{qi} within the limits permitted by the requirement that the orbitals (33) form an orthonormal set, as expressed by equation (3a). We restrict ourselves here to writing down the results for the combined open shell HFR equations of atomic–molecular and nuclear systems:

$$\sum_q (\hat{F}_{pq}^i - \varepsilon_i S_{pq}) C_{qi} = 0, \quad (34)$$

where

$$S_{pq} = \int \chi_p^* \chi_q \, dv, \quad (35)$$

$$\hat{F}_{pq}^i = f_i h_{pq} + \hat{G}_{pq}^i, \quad (36)$$

$$h_{pq} = \int \chi_p^* \left(-\frac{1}{2m\omega-1} \nabla_1^2 - \delta_{\omega 1} \sum_a \frac{Z_a}{r_{a1}} \right) \chi_q \, dv_1, \quad (37)$$

$$\hat{G}_{pq}^i = \sum_{j,rs} \left(2\omega \hat{a}_{rs}^{ij} I_{rs}^{pq} - \hat{b}_{rs}^{ij} K_{rs}^{pq} \right). \quad (38)$$

Here, the \hat{a}_{rs}^{ij} and \hat{b}_{rs}^{ij} are the coupling-projection operators of HFR equations determined through the matrix elements of the square n -dimensional density matrices \hat{a}^{ij} and \hat{b}^{ij} by the following formulas:

$$\hat{a}^{ij} = C \hat{A}^{ij} C^+, \quad (39)$$

$$\hat{b}^{ij} = C \hat{B}^{ij} C^+, \quad (40)$$

where the operators \hat{a}^{ij} and \hat{b}^{ij} are defined by

$$\hat{a}^{ij} C_{qi} = a^{ij} C_{qj}, \quad (41)$$

$$\hat{b}^{ij} C_{qi} = b^{ij} C_{qj}. \quad (42)$$

The quantities I_{rs}^{pq} and K_{rs}^{pq} occurring in equation (38) are defined by

$$I_{rs}^{pq} = \iint \chi_p^*(x_1) \chi_r^*(x_2) f(x_{21}) \chi_q(x_1) \chi_s(x_2) \, dv_1 \, dv_2, \quad (43)$$

$$K_{rs}^{pq} = \iint \chi_p^*(x_1) \chi_r^*(x_2) f(x_{21}) \chi_s(x_1) \chi_q(x_2) \, dv_1 \, dv_2. \quad (44)$$

Taking into account equation (6) for $f_i = f_k = 1$ in equation (33) it is easy to obtain for the combined closed shell HFR equations the following formulas:

$$\sum_q (F_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0, \tag{45}$$

where

$$F_{pq} = h_{pq} + G_{pq}, \tag{46}$$

$$G_{pq} = \sum_{rs} \rho_{rs}^* (2\omega I_{rs}^{pq} - K_{rs}^{pq}), \tag{47}$$

$$\rho = CC^+. \tag{48}$$

We see from tables 1–3 that the modified determinantal method can be of considerable importance in the simplification and calculation of independent Slater determinants, multideterminantal wave functions and coupling-projection coefficients for open-shell systems. As an application of modified determinantal method, we have solved combined HFR equations for the ground state of an $C(1s^2 2s^2 2p^2)$ atom using Slater-type atomic orbitals as a basis. The results of computer calculations for the linear-combination coefficients, orbital energies, total energy and virial coefficient are given in table 4 (the data for the screening constants of Slater atomic orbitals were taken from Clementi and Raimondi [28]. The results given in this table agree well with published data [28,29].

It should be noted that the modified determinantal method presented in this paper can also be used to obtain the coupling-projection coefficients for open-shell nuclei and molecules. Work is in progress in our group for the computation of structure of atomic–molecular and nuclear systems with multideterminantal state of a single configuration that has arbitrary open-shells.

Table 4
Numerical linear combination coefficients of Slater atomic orbitals ($u_i = \sum_{q=1}^5 \chi_q C_{qi}$) for the ground state of $C(1s^2 2s^2 2p^2, ^3P)$ and orbital energies (in a.u.).

χ_q	ζ_q	$\varepsilon_1 = \varepsilon_{1s}$ -11.301550	$\varepsilon_2 = \varepsilon_{2s}$ -0.6774946	$\varepsilon_3 = \varepsilon_{2p_x}$ -0.1338743	$\varepsilon_4 = \varepsilon_{2p_z}$ -0.1338743	$\varepsilon_5 = \varepsilon_{2p_y}$ -0.1338743
$\chi_1 = C(1s)$	5.6727	0.997438	-0.235078	0.000000	0.000000	0.000000
$\chi_2 = C(2s)$	1.6083	0.011438	1.024702	0.000000	0.000000	0.000000
$\chi_3 = C(2p_x)$	1.5679	0.000000	0.000000	1.000000	0.000000	0.000000
$\chi_4 = C(2p_z)$	1.5679	0.000000	0.000000	0.000000	1.000000	0.000000
$\chi_5 = C(2p_y)$	1.5679	0.000000	0.000000	0.000000	0.000000	1.000000
Total energy		Kinetic energy		Virial ratio		
-37.622389		37.622691		-1.999992		
-37.622389 ([28])						
-37.579018 ([29])						

6. Conclusion

It is well known that in the Roothaan's HF theory the orbital-dependent energy functional, equation (27), and Fock operators are not invariant to unitary transformation of orbitals [24]. Therefore, Roothaan's Fock operators are not diagonalized. In this study, the new formulas are introduced for the combined total energy, equation (4), and Fock operators (equation (19)) of open shell atomic–molecular and nuclear systems, which are invariant with respect to unitary transformation of orbitals. The variational principle is applied to the energy functional and the new forms of HF and HFR equations are derived for spatial orbitals u_i and coefficients C_{qi} . For this purpose, we have minimized the postulated energy functional with respect to the orbitals u_i and coefficients C_{qi} , subject to the orthonormality constraints the Lagrangian multipliers of which are designated with $-2\omega\varepsilon_{si}$. We conclude that the Lagrangian multipliers form a Hermitian matrix, $\varepsilon_{si} = \varepsilon_{is}^*$, and the resulting equations have the off-diagonal coefficients ε_{si} .

It is shown that the operator \hat{F}^i is invariant with respect to the unitary transformation of orbitals. We may therefore diagonalize the matrix ε , so that all the orbitals u_i and coefficients C_{qi} satisfy the HF and HFR equations, respectively, $\hat{F}^i u_i = \varepsilon_i u_i$ and $\sum_q (\hat{F}_{pq}^i - \varepsilon_i S_{pq}) C_{qi} = 0$. Thus, in this paper we have established the combined HF and HFR equations for open shell atomic–molecular and nuclear systems.

We notice that in the case of integer and noninteger n -STOs, the multicenter integrals occurring in the combined HFR approach for atomic and molecular systems ($\omega = 1$) can be calculated by the use of expansion and one-range addition theorems for STOs, Ψ^α -ETOs and Coulomb–Yukawa like central and non-central interaction potentials established by Guseinov [30].

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