

Coupling coefficients “symmetry dilemma” in the restricted open-shell Hartree–Fock method

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Two opposite conclusions are known on the symmetry of the vector coupling coefficients (VCCs), a_{mn} and b_{mn} , in the restricted open-shell Hartree–Fock (ROHF) method. The first one states that the VCCs are symmetric for all spectroscopic terms, i.e., $a_{mn} = a_{nm}$ and $b_{mn} = b_{nm}$. An opposing statement is that the “non-Roothaan” terms, arising from the degenerate open-shell electronic configuration γ^N , can be characterized by non-symmetric VCCs matrices only: $\|a_{mn}\| \neq \|a_{nm}\|$, $\|b_{mn}\| \neq \|b_{nm}\|$. This article presents a detailed analysis of the VCCs symmetry problem. A general approach to the VCCs determination has been developed leading to non-symmetric VCCs for γ^N systems with $\dim \gamma \geq 3$. The main purpose of this work is to eliminate the contradiction arising in the ROHF theory when the latter is applied to highly symmetric open-shell molecules and atoms.

1. Introduction

In the restricted open-shell Hartree–Fock (ROHF) method [1–5], one starts from the following expression for energy functional:

$$E_{\text{ROHF}} = 2 \sum_i f_i H_{ii} + \sum_i \sum_j f_i f_j (2a_{ij} J_{ij} - b_{ij} K_{ij}), \quad (1.1)$$

where a_{ij} and b_{ij} are non-variable coefficients, characterizing the state under consideration, usually called the “vector coupling coefficients” (VCCs) [6]; f_i is the fractional occupation number of one-electron orbital ϕ_i ; H_{ii} , J_{ij} and K_{ij} are the usual core, Coulomb and exchange integrals, respectively.

Application of the variational principle to the expression (1.1) with the additional orthonormality conditions

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (1.2)$$

leads to the Euler equations [2]

$$F_i |\phi_i\rangle = \sum_j |\phi_j\rangle \theta_{ji}, \quad (1.3a)$$

$$\theta_{ji} = \theta_{ij}^*, \quad (1.3b)$$

where θ_{ji} is the Lagrangian multiplier, and F_i is the Fock operator [4,5]

$$F_i = f_i \left(h + \sum_j f_j (2a_{ij} J_j - b_{ij} K_j) \right) \quad (1.4)$$

expressed in terms of the Hermitian one-electron h , Coulomb J_j and exchange K_j operators [1].

In this paper we consider the particular case of equations (1.1) and (1.4), corresponding to a state of the degenerate open-shell electronic configuration γ^N ($\gamma = p, d, \dots$ for atoms, and $\gamma = e, t, g, h$ for non-linear molecules). For this case, equation (1.1) can be written as

$$E_{\text{ROHF}} = E(2^{S+1}\Gamma, \gamma^N) = E_r + f^2 \sum_m \sum_n (2a_{mn} J_{mn} - b_{mn} K_{mn}), \quad (1.5)$$

where $2^{S+1}\Gamma$ is the state under consideration; $f = N/(2 \dim \gamma)$; $\dim \gamma$ is the dimension of the irreducible representation γ , and the term E_r (E_{rest}) is the same for all states of a configuration γ^N [1]:

$$\begin{aligned} E_r = & 2 \sum_k H_{kk} + \sum_k \sum_l (2J_{kl} - K_{kl}) \\ & + 2f \left(\sum_m H_{mm} + \sum_k \sum_m (2J_{km} - K_{km}) \right) \end{aligned} \quad (1.6)$$

(m, n are the indices for the open-shell orbitals; k, l are for the closed-shell ones, and i, j are for orbitals of either set).

The expression (1.4) for the open-shell Fock operator reads

$$F_m = f \left(h + 2J_c - K_c + f \sum_n (2a_{mn} J_n - b_{mn} K_n) \right), \quad (1.7)$$

where $J_c = \sum_k J_k$ and $K_c = \sum_k K_k$.

The coefficients a_{mn} and b_{mn} , entering equations (1.5) and (1.7), are supposed [5–8] to form the symmetric matrices

$$a_{mn} = a_{nm}, \quad b_{mn} = b_{nm}. \quad (1.8)$$

This supposition is based on the expression for energy functional (1.5). Since the Coulomb and exchange integrals are symmetric ($J_{mn} = J_{nm}$ and $K_{mn} = K_{nm}$), the coefficients a_{mn} and b_{mn} in equation (1.5) can be derived in symmetric form as well [5].

On the other hand, two expressions under consideration, equations (1.5) and (1.7), are essentially different from the viewpoint of the coupling coefficients symmetry. In contrast to equation (1.5), the expression for the Fock operator (equation (1.7)) is

asymmetric with respect to the repositioning of the coefficients a_{mn} and a_{nm} , and also for b_{mn} and b_{nm} .

Such a VCCs asymmetry of the Fock operators was found to be responsible for the somewhat paradoxical results [9,10]. According to the latter works, several states arising from the atomic configurations d^N and $p^M d^N$ ($N = 1-9$, $M = 1-5$), can be characterized by non-symmetric VCCs matrices only:

$$\|a_{mn}\| \neq \|a_{nm}\|, \quad \|b_{mn}\| \neq \|b_{nm}\|. \quad (1.9)$$

This conclusion follows from the analysis of the symmetry restrictions, to which the coefficients of both equations (1.5) and (1.7) must satisfy in the cases under consideration [9,10]. For d^N atoms, this conclusion was confirmed by the results of the ROHF calculations. By comparing the two sets of the ROHF results derived with non-symmetric VCCs of [9] and previously published symmetric VCCs [11], respectively, with the reference results derived by the Roothaan–Bagus atomic “expansion method” [12] we unambiguously show the validity of non-symmetric VCCs only [9] (see also the discussion below).

In [13–15] we found that the VCCs asymmetry (equation (1.9)) arises for the most highly symmetric open-shell systems with configuration γ^N . For systems with $\dim \gamma \leq 3$, such as the structures of cubic symmetry ($T_d, 0, 0_h$) with electronic configuration t^N ($N = 1-5$), the use of both symmetric and non-symmetric VCCs leads to identical ROHF results [13]. For more complex γ^N systems with $\dim \gamma > 3$, examples of which are the icosahedral symmetry structures (I, I_h) with configurations g^N ($\dim g = 4$) or h^N ($\dim h = 5$), the situation is similar to that as for d^N atoms. For several (${}^{2S+1}\Gamma, g^N$) and (${}^{2S+1}\Gamma, h^N$) states, only non-symmetric VCCs are found to satisfy all necessary symmetry restrictions [14,15].

The latter result explains the difficulties which arise in the ROHF calculations on open-shell fullerenes and their metal complexes of icosahedral symmetry. According to [16,17], many open-shell states of such structures cannot be calculated by the existing ROHF method (based on the use of symmetric VCCs only).

However, before using the non-symmetric VCCs in routine calculations, one should overcome the contradiction arising in the ROHF theory while introducing the VCCs. As follows from [5,8], the use of non-symmetric VCCs, in itself, comes into conflict with the Euler equations (1.3). The Fock operators of equation (1.7) constructed with non-symmetric VCCs cannot be derived straightforwardly from the initial energy functional of equation (1.1).

This paper presents the detailed analysis of the VCCs symmetry problem. Section 2 gives a review of the ROHF theory for highly symmetric open-shell γ^N systems. In section 3 we show the necessity for the VCCs of equations (1.5), (1.7) to be symmetric and discuss in more detail the arising contradiction.

In sections 4 and 5 we reanalyze the symmetry restrictions that the γ^N state VCCs, a_{mn} and b_{mn} , must satisfy, and derive the complete set of equations for determining the VCCs. For several γ^N states with $\dim \gamma \geq 3$, new equations give the

non-symmetric VCCs only. A testing of the theory developed is given in section 6 in the example of d^N atoms. Finally, in section 7, we prove the equivalency of the Fock operators constructed with different VCCs sets (both symmetric and non-symmetric) that can be derived from new symmetry restrictions.

2. Brief review

Expression (1.1) for the Hartree–Fock open-shell state energy is valid in the most but not all cases. A more general expression has the form [4,5]

$$E = \sum_i \sum_j \left(\omega_{ij} H_{ij} + \sum_k \sum_l \beta_{ij,kl} \langle ij|kl \rangle \right), \quad (2.1)$$

where

$$\langle ij|kl \rangle = \int \phi_i^*(1) \phi_j(1) \frac{1}{r_{12}} \phi_k^*(2) \phi_l(2) dV_1 dV_2 \quad (2.2)$$

and $\omega_{ij}, \beta_{ij,kl}$ are coefficients, characterizing the state under consideration. (In equations (2.1) and (2.2), the indices i, j, k, l refer to all occupied orbitals.)

Expression (2.1) stems from the general definition of the ROHF state energy [1], which can be written as follows:

$$E(^{2S+1}\Gamma) = \frac{1}{\dim \Gamma} \sum_{\Gamma_r} \langle \Psi(S, M_S, \Gamma, \Gamma_r) | \hat{H} | \Psi(S, M_S, \Gamma, \Gamma_r) \rangle, \quad (2.3)$$

where $\Psi(S, M_S, \Gamma, \Gamma_r)$ is the multielectron wave function of the correct spin (S, M_S) and spatial (Γ, Γ_r) symmetry; Γ_r is the row of the degenerate irreducible representation Γ . In the case of an atom, the Γ and Γ_r characteristics are substituted by quantum numbers L and M_L (total angular momentum and its projection), respectively.

Expression (2.3) corresponds to the Roothaan's definition of state energy as "the average expectation value for all the degenerate total wave functions of the state under consideration" [1]. (An additional averaging over M_S in equation (2.3) is not necessary.)

Equation (2.1) gives a general expression for energy, valid in both monoconfigurational (Hartree–Fock) and multiconfigurational approaches [4,5]. In the former, expression (2.1) is not used in practice since for most open-shell systems it can be presented in more simple form of equation (1.1). Such a representation of energy leads to the essential simplification of the ROHF variational equations [2,4] and makes the practical computations much easier [5,8]. The methods for reducing equation (2.1) to equation (1.1) are discussed below.

The optimum orbitals $\{\phi_i\}$ which minimize the energy of equation (1.1) can be found by the direct solving of the Euler equation (1.3) [18,19]. In an equivalent but more general approach developed in [1–5], the orbitals to be found are the eigenfunctions of the Hartree–Fock equation

$$R|\phi_i\rangle = \varepsilon_i|\phi_i\rangle, \quad (2.4)$$

where R is the unified SCF coupling operator. For the first time, an equation of type (2.4) was derived by Roothaan [1] for the states, where energy can be expressed by equation (1.5) with

$$a_{mn} = a, \quad b_{mn} = b. \quad (2.5)$$

General expressions for the Hermitian R operator, corresponding to the energy functional (1.1), were derived in [2–6]. Hereinafter, we use the expression for the operator R derived in [3,4]:

$$R = \sum_i \left((I - \rho) F_i \rho^i + \rho^i F_i (I - \rho) + \rho^i F_i \rho^i \right) + \sum_i \sum_j \lambda_{ij} \rho^j (F_i - F_j) \rho^i, \quad (2.6)$$

where $\lambda_{ji} = -\lambda_{ij}$ are arbitrary non-zero numbers, F_i is the Fock operator of equation (1.4), and

$$\rho^i = |\phi_i\rangle\langle\phi_i|, \quad \rho = \sum_i \rho^i \quad (2.7)$$

are the projection operators.

When solving the Euler equation (1.3), or the equivalent Hartree–Fock equation (2.4), one faces the known difficulty [1–3]. The Lagrangian multipliers in equation (1.3) must be Hermitian, i.e., $\theta_{ji} - \theta_{ij}^* = 0$. The latter constraints can be expressed in the form [2,3]

$$\langle\phi_j|F_i - F_j|\phi_i\rangle = 0, \quad (2.8)$$

i.e., in the form of the variational conditions among the occupied orbitals. These conditions are non-trivial only for open-shell systems with $F_i \neq F_j$, whereas for closed-shell systems, equations (2.8), (1.3b) assert identically. Inasmuch as equation (1.3a) expresses the variational conditions between occupied and virtual orbitals, two Euler equations (1.3a,b) represent the complete set of variational conditions [2,3].

As shown in [3], the latter set of conditions is equivalent to that following from the generalized Brillouin theorem [20]. If the optimum orbitals $\{\phi_i\}$ are obtained, which satisfy the Euler equation (1.3), the off-diagonal Hamiltonian matrix elements over the wave functions of the ground and one-electron excited states vanish.

In the one operator approach (equations (2.4), (2.6)), the constraints discussed are incorporated into the expression for the R operator. In the self-consistent limit ($R_{ij} = \delta_{ij}\varepsilon_i$) the orbitals of equation (2.4) represent the solution of equations (1.3a,b) as well.

2.1. Coupling coefficients for configuration γ^N with $\dim \gamma \leq 3$

From a physical point of view, the VCCs a_{ij} and b_{ij} entering equation (1.1) and subsequent variational equations (1.3), (1.4), (2.4), are some parameters of the theory, i.e., some coefficients not defined by basic equations. In general, these coefficients can correspond either to a separate spectroscopic term [1,8], or to some average

energy functionals [17,18,21]. In some approximations, such as the "half-electron method" [22], these quantities have well-defined values independent of the system under consideration.

A usual approach for determining the state VCCs

$$a_{ij} = a_{ij}({}^{2S+1}\Gamma), \quad b_{ij} = b_{ij}({}^{2S+1}\Gamma) \quad (2.9)$$

is to somehow represent the initial expression for state energy (equation (2.3)) in the form of equation (1.1).

Such a representation can be derived either by direct methods (see section 5) or through the mediation of equation (2.1). For γ^N systems under study, all terms in equation (2.1) describing the closed-shell electronic subsystem and the interaction between the closed-shell and open-shell manifolds, are expressed by equation (1.6) [1]. The difficulty in reducing equation (2.1) to equation (1.5) arises from the non-vanishing four-indexed integrals, $\langle m\underline{m}|n\underline{n}\rangle$, over the degenerate open-shell $\{\gamma\}$ orbitals.

Representation of the latter terms by equation (1.5) is easily obtained for γ^N systems with $\dim \gamma \leq 3$, such as the p^N atoms, or molecular systems with configurations e^N and t^N . For such system, the representation (1.5) immediately follows from equation (2.1) if one uses the degenerate orbitals of the "standard" representation [23].

Degenerate open-shell orbitals $\{\phi_m\}$, $m = 1, 2, \dots, \dim \gamma$, are the eigenfunctions of the R operator (equation (2.4)), and are determined within the accuracy up to a unitary transformation U :

$$\{\phi_m\} = \{\phi_m\}^\circ \times U, \quad (2.10)$$

where $\{\phi_m\}^\circ$ are the orbitals of the standard representation γ . The latter orbitals can be obtained from arbitrary $\{\phi_m\}$ ones by the action of the $\varepsilon^{(\gamma)}$ projection operators [23]. The advantage of using the $\{\phi_m\}^\circ$ orbitals is that the majority of the $\langle m\underline{m}|n\underline{n}\rangle$ integrals over the $\{\phi_m\}^\circ$ orbitals are equal to zero.

In particular, for systems of tetragonal symmetry (D_{4h}, C_{4v}, D_{2d}) with configuration e^N , or of cubic symmetry (T_d, O_h) with configuration t^N , all the $\langle m\underline{m}|n\underline{n}\rangle$ integrals over the real $\{e_m\}^\circ$ or $\{t_m\}^\circ$ orbitals, apart from the Coulomb and exchange, vanish [24]:

$$\langle m\underline{m}|n\underline{n}\rangle = \delta_{m\underline{m}}\delta_{n\underline{n}}J_{mn} + (\delta_{m\underline{n}}\delta_{\underline{m}n} + \delta_{mn}\delta_{\underline{m}\underline{n}})(1 - \delta_{\underline{m}m})K_{\underline{m}m} \quad (2.11)$$

($m, \underline{m}, n, \underline{n} = 1, 2, \dots, \dim \gamma$), i.e., there are only three non-zero integrals: $J_{mm} = J_{nn}$, J_{mn} and K_{mn} ($m \neq n$). Substitution of equation (2.11) into equation (2.1) gives the desired representation (1.5) with the coefficients

$$\begin{aligned} a_{mn} &= \beta_{mm,nn}/(2f^2), \\ b_{mn} &= (2\delta_{mn}\beta_{mm,mm} - (\beta_{mn,nm} + \beta_{mn,mn}))/f^2. \end{aligned} \quad (2.12)$$

As indicated above, such an approach is valid only for γ^N systems with $\dim \gamma \leq 3$. For more complex electronic configurations, such as d^N of an atom, or

g^N ($\dim g = 4$) and h^N ($\dim h = 5$) of icosahedral symmetry systems (I, I_h), the representation (2.11) is no longer valid. Some three and four indexed integrals over the $\{\phi_m\}^\circ$ orbitals remain non-zeroth [14,15,25].

The known methods for determining the VCCs of equation (1.5) [5–8,17,18,21,24] are also valid for γ^N states with $\dim \gamma \leq 3$ only. For systems with $\dim \gamma > 3$, these methods give the VCCs only for states that appear isolated by spin multiplicity, or for some averaged energy functionals [17,18,21].

A general approach to determining the VCCs of equation (1.5) [26] valid for any state of arbitrary configuration γ^N (except for the multiple (double) terms) is presented in section 5.

2.2. “Non-Roothaan” states

The VCCs a_{mn} and b_{mn} defined by equation (2.12) correspond to the *definite* choice of the degenerate orbitals, i.e., to the $\{\phi_m\}^\circ$ ones of equation (2.10). In section 5 one shows that the representation (1.5) can also be derived for an *arbitrary* choice of the $\{\phi_m\}$ orbitals. The essential point is that the VCCs a_{mn} and b_{mn} of equation (1.5) depend on the $\{\phi_m\}$ orbital basis used [24,27].

The latter dependence can be symbolically written as

$$a_{mn} = a_{mn}(U), \quad b_{mn} = b_{mn}(U). \quad (2.13)$$

In the iterative SCF procedure, the matrix U defined by equation (2.10) is an arbitrary one. Inasmuch as the state VCCs a_{mn} and b_{mn} enter variational equations (1.3), (1.4), (2.4), one must use some special measures to maintain the symmetry of the state under study in the iterative procedure [24,27]. A usual approach to account for the VCCs “phase dependence” (equation (2.13)) is to fix the $\{\phi_m\}^\circ$ basis in the iterative procedure [9,13].

The VCCs phase dependence (2.13) takes place for most but not all states of a configuration γ^N . Such a dependence does not arise for γ^N states characterized by the two coupling coefficients of equation (2.5) [1]:

$$a_{mn} = a, \quad b_{mn} = b.$$

For all other γ^N states, for which equation (2.5) does not assert, one uses the VCCs matrices, a_{mn} and b_{mn} , defined over the degenerate $\{\gamma\}$ orbitals. In such cases, the VCCs to be found are dependent on the choice of the degenerate $\{\gamma\}$ orbitals.

Hereinafter, we shall refer to the states of a configuration γ^N characterized by the VCCs of equation (2.5), as to *Roothaan states*. All other γ^N ones characterized by the phase-dependent VCCs matrices of equation (2.13), will be referred to as *non-Roothaan states*.

Such a division of the γ^N states is a natural one in the ROHF theory [9,24] (see also section 6.1). As an example of such a division, one can consider the states of the configuration t_{1u}^4 in the O_h point symmetry group:

$$t_{1u}^4(O_h) \rightarrow {}^3T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}. \quad (2.14)$$

These states are divided into two groups, (${}^3T_{1g}, {}^1A_{1g}$) and (${}^1T_{2g}, {}^1E_g$), respectively. The states of the first group are characterized by the Roothaan's VCCs [24]

$$\begin{aligned} a({}^1A_{1g}) &= 3/4, & b({}^1A_{1g}) &= 0; \\ a({}^3T_{1g}) &= 15/16, & b({}^3T_{1g}) &= 9/8. \end{aligned} \quad (2.15)$$

Two other states are non-Roothaan ones and are characterized by the VCCs matrices, $\|a_{mn}\|$ and $\|b_{mn}\|$, depending on the choice of the degenerate $\{t_{1u}\}$ orbitals [24].

If one uses the $\{t_{1u}\}^\circ$ orbitals of the standard representation, $\{t_{1u,x}, t_{1u,y}, t_{1u,z}\}$ [23], the VCCs matrices for the ${}^1T_{2g}$ and 1E_g states under consideration can be expressed in the form

$$a_{mn} = \delta_{mn}a' + (1 - \delta_{mn})a'', \quad b_{mn} = b \quad (2.16)$$

with three independent coefficients, a' , a'' and b [24]:

$$\begin{aligned} {}^1T_{2g}: & \quad a' = 9/16, \quad a'' = 15/16, \quad b = 3/8; \\ {}^1E_g: & \quad a' = 21/16, \quad a'' = 12/16, \quad b = 9/8. \end{aligned} \quad (2.17)$$

The origin of the coefficients in equations (2.15)–(2.17), and the interrelations between them are shown in figure 1.

Figure 1 shows the relationship between the VCCs for the t^N states of cubic symmetry systems and for the corresponding (parent) atomic p^N states. As follows from figure 1, the non-Roothaan states of configuration t^4 are those which originate

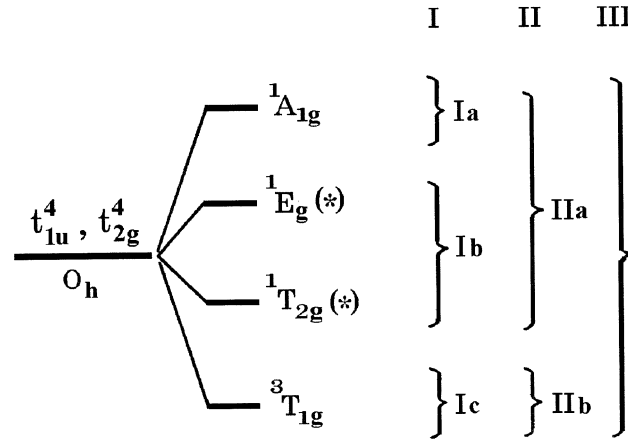


Figure 1. Methods of averaging the energy over the states of the configuration t^4 in the point group O_h , leading to energy expression of the Roothaan type (equation (2.5)): (I) Over the states arising from one parent atomic state of the configuration p^4 ; the a and b coefficients in the E_{Ia} , E_{Ib} and E_{Ic} functionals coincide with the corresponding coefficients [1] for the 1S , 1D and 3P atomic states, respectively; non-Roothaan states are marked by asterics. (II) Over the states of one multiplicity; corresponding $a(E_s)$ and $b(E_s)$ coefficients are given in equation (2.21). (III) Average energy of the configuration, E_{av} ; the $a(E_{av})$ and $b(E_{av})$ coefficients are given in equation (2.22).

from the one parent atomic state (${}^1D, p^4$) due to the Bethe's splitting [28]. The latter correspondence can be expressed as

$$2E({}^1E_g, t^4) + 3E({}^1T_{2g}, t^4) = 5E({}^1D, p^4) \quad (2.18)$$

or, in form of the relations between the states VCCs [24],

$$\begin{aligned} 2a_{mn}({}^1E_g, t^4) + 3a_{mn}({}^1T_{2g}, t^4) &= 5a({}^1D, p^4), \\ 2b_{mn}({}^1E_g, t^4) + 3b_{mn}({}^1T_{2g}, t^4) &= 5b({}^1D, p^4). \end{aligned} \quad (2.19)$$

These relations are valid for any choice of the degenerate $\{t_{1u}\}$ orbitals.

The a_{mn} and b_{mn} coefficients discussed also satisfy some other relations inherent in the states of a configuration γ^N (see figure 1). The first relation can be derived from the expression for the average multiplet energy, E_S , i.e., the average energy of the states of one multiplicity

$$E_S = \sum_{\Gamma} (E({}^{2S+1}\Gamma) \times \dim \Gamma) / \sum_{\Gamma} \dim \Gamma. \quad (2.20)$$

As shown in [24], the average multiplet energy E_S of a configuration γ^N can be represented by equation (1.5) with the two coupling coefficients of the Roothaan's type:

$$\begin{aligned} a(E_S, \gamma^N) &= (N^2(N-1) + fN(N-4) + 4fS(S+1)) / (N(N^2 - 4f^2)), \\ b(E_S, \gamma^N) &= (4f(N-1) + N(N-4) + 4S(S+1)) / (N^2 - 4f^2), \end{aligned} \quad (2.21)$$

where $f = N/(2 \dim \gamma)$. For the above configurations t_{1u}^4 and p^4 , the coefficients of equation (2.21) are as follows: $a(E_0) = 27/32$, $b(E_0) = 9/16$, and $a(E_1) = 15/16$, $b(E_1) = 9/8$.

The well-known representability of the average energy E_{av} of a configuration γ^N by the Roothaan's VCCs [25,29]

$$a(E_{av}, \gamma^N) = b(E_{av}, \gamma^N) = (N-1)/(N-f) \quad (2.22)$$

follows from equations (2.20), (2.21), if one averages the latter expressions over all possible values of the spin number S [24].

All the above coupling coefficients, corresponding either to a separate $({}^{2S+1}\Gamma, \gamma^N)$ state, or to the average values of equations (2.19), (2.21) and (2.22), satisfy the fundamental condition [24]

$$f^2 \left(- \sum_m b_{mm} + 2 \sum_m \sum_n a_{mn} \right) = N(N-1)/2 \quad (2.23)$$

following from two-particle density normalization for a γ^N system.

In section 5 we show the latter condition is the one of the set of conditions ensuring the consistency between the two representations for γ^N state energy given by equations (1.5) and (2.3).

2.3. Non-totally symmetric Fock operators

For a γ^N state described by the Roothaan one-open-shell SCF theory [1], i.e., characterized by the VCCs of equation (2.5), all the Fock operators F_m of equation (1.7) are equal to each other ($F_m = F_0$) and are totally symmetric. The latter follows from that the Hermitian J_0 and K_0 operators,

$$J_0 = \sum_n J_n, \quad K_0 = \sum_n K_n, \quad (2.24)$$

are totally symmetric [1], i.e., their eigenfunctions belong to the irreducible representations of the symmetry group under consideration.

As follows from the definition of a totally symmetric operator, its matrix over the degenerate $\{\phi_m\}$ orbitals is a diagonal one with diagonal elements equal to each other. In the case of J_0 and K_0 operators, the condition of equality of the diagonal elements, $(J_0)_{mm} = (J_0)_{\underline{m}\underline{m}}$ and $(K_0)_{mm} = (K_0)_{\underline{m}\underline{m}}$, $m \neq \underline{m}$, is expressed as

$$\sum_n J_{mn} = \sum_n J_{\underline{m}n}, \quad \sum_n K_{mn} = \sum_n K_{\underline{m}n} \quad (m \neq \underline{m}). \quad (2.25a)$$

Corresponding off-diagonal matrix elements, $(J_0)_{m\underline{m}}$ and $(K_0)_{m\underline{m}}$, are equal to zero, i.e.,

$$\sum_n \langle m\underline{m} | nn \rangle = 0, \quad \sum_n \langle mn | n\underline{m} \rangle = 0 \quad (m \neq \underline{m}). \quad (2.25b)$$

The latter relations will be used below.

If the state VCCs, a_{mn} and b_{mn} , are not equal to each other in the sense of equation (2.5), the open-shell Fock operators F_m (equation (1.7)) are *non-totally symmetric*. It follows herefrom, that non-Roothaan states of a configuration γ^N can be described by non-totally symmetric Fock operators only.

There is nothing wrong with it from the purely theoretical point of view, since the Fock operators play some auxiliary part in the ROHF theory (see also section 7). The totally symmetric operator is the one-electron Hamiltonian R of equation (2.4). From a practical point of view, however, there arise some inconveniences since those F_m operators are non-invariant under arbitrary unitary transformation within an open-shell orbital set.

Such a non-invariance was discussed by Hirao [4], who proposed to use the *totally symmetric* Fock F_1 and projection ρ^1 operators, i.e., the operators averaged over the separate orbitals sets. As shown in [4], the Euler equations (1.3), as well as the Hartree–Fock equation (2.4), can also be expressed in terms of the F_1 and ρ^1 operators (see [4, equation (3.8)]).

As a matter of a fact, the approach [4] does not eliminate all the difficulties arising in the ROHF calculations on highly symmetric structures [16,17]. For the γ^N

systems under consideration, there are two sets of orbitals, closed-shell and open-shell, spanned by the projection operators

$$\rho^c = \sum_k |\phi_k\rangle\langle\phi_k|, \quad \rho^0 = \sum_m |\phi_m\rangle\langle\phi_m| \quad (2.26)$$

and $\rho = \rho^c + \rho^0$. The totally symmetric shell-averaged Fock operators F_1 of [4] can be expressed as

$$F_c = h + 2J_c - K_c + f(2J_0 - K_0), \quad (2.27a)$$

$$F_0 = f(h + 2J_c - K_c + f(2a_0J_0 - b_0K_0)), \quad (2.27b)$$

where a_0 and b_0 are some coefficients. In this meaning, the latter correspond to one of the Roothaan's VCCs sets given by equations (2.15), (2.21) and (2.22).

Thus, for the γ^N systems under consideration, this approach [4] is equivalent to the Roothaan's one-open-shell ROHF theory [1]. As a consequence, the non-Roothaan states characterized by the VCCs matrices of a general form (equations (2.13), (2.16)) are not covered by the method [4].

Such a limitation does not arise in the ROHF theory if one uses the non-totally symmetric Fock operators. To eliminate the non-invariance of the latter under transformation of the degenerate orbitals, one can either use the fixed $\{\phi_m\}^\circ$ orbitals basis [9,13], or introduce the explicit form for the VCCs phase dependence of equation (2.13) into the SCF iterative procedure [26].

The other side of this problem is to satisfy all conditions following from the requirement for the R operator of equation (2.4) to be totally symmetric. These conditions are discussed in section 4.

3. The VCCs asymmetry problem

The most serious difficulty arising in the ROHF theory is connected with the asymmetry of the VCCs, a_{mn} and b_{mn} , for the states of the degenerate open-shell configuration γ^N . As pointed out in the introduction, there are two opposite conclusions for this problem (see equations (1.8), (1.9), and corresponding text).

This section presents a simple proof of the supposition [5,8] that the VCCs of equations (1.1), (1.4) are to be symmetric for all spectroscopic terms:

$$a_{ij} = a_{ji}, \quad b_{ij} = b_{ji}. \quad (3.1)$$

In the next subsection, we discuss the origin of the VCCs asymmetry and formulate the main points of the arising contradiction.

The supposition [5,8], itself, has a fundamental basis. The expression for energy (equation (1.1)), underlying the ROHF theory [1–5], is symmetric with respect to the repositioning of the coupling coefficients, a_{ij} and a_{ji} , and also for b_{ij} and b_{ji} . Therefore, all other expressions derived from the energy functional, must also be

symmetric in this sense. The latter means that the VCCs a_{ij} and b_{ij} , themselves, can always be symmetric.

The principal question raised is where can the VCCs asymmetry come from? As shown in [9], the source of the VCCs asymmetry is the expression for the Fock operator of equation (1.4), which does not possess the necessary symmetry with respect to the VCCs repositioning.

Taking the latter into account, the authors of [30] have reanalyzed the variational procedure (equations (1.1)–(1.4)), leading to the expression for the Fock operator. For the first variation of the energy, the well-known expression [2] was derived:

$$\delta E_{\text{ROHF}} = 2 \sum_i (\langle \delta i | \Phi_i | i \rangle + \langle i | \Phi_i | \delta i \rangle), \quad (3.2)$$

where Φ_i is the “new” Fock operator defined by the expression [30]

$$\Phi_i = f_i \left(h + \sum_j f_j (2A_{ij}J_j - B_{ij}K_j) \right) \quad (3.3)$$

with the coefficients

$$A_{ij} = (a_{ij} + a_{ji})/2, \quad B_{ij} = (b_{ij} + b_{ji})/2. \quad (3.4)$$

The Euler equation (1.3), in which the Fock operators F_i of equation (1.4) are substituted by the new ones of equation (3.3), follow from equation (3.2) if one takes into account the additional orthonormality conditions of equation (1.2).

Equations (3.3), (3.4) are the basic ones considered when discussing the VCCs symmetry problem. By definition, the coefficients A_{ij} and B_{ij} are symmetric:

$$A_{ij} = A_{ji}, \quad B_{ij} = B_{ji}. \quad (3.5)$$

It follows herefrom that the usual expression for the Fock operator (equation (1.4)) is valid if the restrictions of equation (3.1) hold, in accordance with [5,8].

To clarify the latter statement, one can substitute the a_{ij} and b_{ij} coefficients entering the expression for energy (equation (1.1)) by their symmetric (A_{ij} and B_{ij}) and antisymmetric

$$A'_{ij} = (a_{ij} - a_{ji})/2, \quad B'_{ij} = (b_{ij} - b_{ji})/2 \quad (3.6)$$

combinations. Substitution of equations (3.4), (3.6) into equation (1.1) gives

$$E_{\text{ROHF}} = 2 \sum_i f_i H_{ii} + \sum_i \sum_j f_i f_j (2A_{ij}J_{ij} - B_{ij}K_{ij}). \quad (3.7)$$

In terms of the symmetric coefficients A_{ij} and B_{ij} , the expression for the Fock operator derivative of the energy functional (3.7) is nothing but equation (3.3). If one further renames the coefficients A_{ij} and B_{ij} in equations (3.3), (3.5) and (3.7) as a_{ij} and b_{ij} , the initial equations (1.1) and (1.4) are obtained, added by the rigid VCCs symmetry restrictions of equation (3.1).

3.1. Comments to the contradiction arisen

The above proof of the VCCs symmetry is a simple one and would not deserve attention if the consequences were not so serious. Equation (3.1) first presented without proof in [5,8] is in grave contradiction with the results [9,10,13–15] mentioned in the introduction. Here we briefly recall the latter results and formulate the main points of this contradiction.

According to [9,14], the *non-Roothaan* states arising from the electronic configurations γ^N with $\dim \gamma > 3$ (such as the d^N of an atom, or g^N and h^N of icosahedral symmetry systems) cannot be calculated with symmetric VCCs. The correct ROHF calculation on such states is possible with non-symmetric VCCs only [9,14]. As for the corresponding Roothaan states, they can be calculated with both symmetric and non-symmetric VCCs. For more simple systems with $\dim \gamma \leq 3$, the symmetric and non-symmetric VCCs are found to be equivalent for all γ^N states [13,26].

Taking into account both the above proof of the VCCs symmetry and the results mentioned, one can formulate the main points of the arising contradiction:

- (1) The operators of equations (1.4), (1.7) are the true Fock operators derivative of energy functional (equation (1.1)), if the VCCs a_{mn} and b_{mn} are symmetric.
- (2) The use of expression (equation (1.7)) with non-symmetric VCCs, as proposed in [9], actually means that one uses some “pseudo-Fock” operators instead of the true ones. Those pseudo-Fock operators cannot be derived straightforwardly from the given expression for energy (equation (1.1)).
- (3) The equivalency of symmetric and non-symmetric VCCs for the Roothaan γ^N states found in calculations [9,13] means the following: the optimum orbitals $\{\phi_i\}$ derived from variational equations (1.3), (2.4) by using the pseudo-Fock operators are identical to those derived by using the true Fock operators. Moreover, the unified coupling operator R of equation (2.4) constructed from either set of the Fock operators is the same.
- (4) For the non-Roothaan γ^N states with $\dim \gamma > 3$, the use of only non-symmetric VCCs makes it possible to maintain the symmetry of the state under study in the Euler and Hartree–Fock equations [9,14].

The purpose of present article is to give a theoretical substantiation of the results (3) and (4), first found by numerical calculations. Following this purpose, in the next sections we use the expression for the Fock operator given by equation (1.7) with no prior suppositions as to the VCCs symmetry restrictions. The above rigid constraints of equations (1.8), (3.1) are discussed in a corresponding place after a deriving the alternative VCCs symmetry restrictions.

4. Totally symmetric unified coupling operator

As pointed out in section 2.3, the requirement for the unified SCF coupling operator R of equation (2.4) to be totally symmetric has to be satisfied independently

Table 1
General structure of the totally symmetric operator R matrix over the degenerate non-self-consistent orbitals of the symmetry γ .

	Open-shell orbitals				Virtual orbitals ^{a,b}			
	1	2	...	n_γ	$M+1$	$M+2$...	$M+n_\gamma$
1	R_{00}			0	R_{0v}			0
2		R_{00}				R_{0v}		
...			
n_γ	0			R_{00}	0			R_{0v}
$M+1$	R_{v0}			0	R_{vv}			0
$M+2$		R_{v0}				R_{vv}		
...			
$M+n_\gamma$	0			R_{v0}	0			R_{vv}

^a $(M+1)$ is the number of the first virtual orbital of the symmetry γ ; $n_\gamma = \dim \gamma$.

^b Diagonal structure of the off-diagonal matrix blocks is obtained if the corresponding orbitals of the two sets, ϕ_m and ϕ_{M+m} ($m = 1, 2, \dots, n_\gamma$), belong to the one row γ_m of the irreducible representation γ .

of the Fock operators symmetry. In this section we analyze the restrictions on the γ^N state VCCs, a_{mn} and b_{mn} , which arise from the requirement for the Hermitian R operator to be totally symmetric [26].

Table 1 shows the general structure of the R operator matrix over the degenerate orbitals of symmetry γ . To simplify the presentation of the matrix, only the open-shell and virtual orbitals are shown in table 1.

In the first place, we consider the diagonal matrix block $\|R_{mm}\|$ over the open-shell orbitals $\{\phi_m\}$. As pointed out in section 2.3, such a matrix must be the diagonal one with diagonal elements equal to each other. These two conditions can be expressed as

$$R_{mm} = R_{\underline{m}\underline{m}} \quad (m \neq \underline{m}), \quad (4.1)$$

$$R_{m\underline{m}} = R_{\underline{m}m}^* = 0 \quad (m \neq \underline{m}). \quad (4.2)$$

Using the expression for the R operator (equation (2.6)), the R_{mm} element takes the form

$$\begin{aligned} R_{mm} &= \langle \phi_m | R | \phi_m \rangle = \langle \phi_m | F_m | \phi_m \rangle \\ &= f \left(H_{mm} + \sum_k (2J_{km} - K_{km}) + f \sum_n (2a_{mn} J_{mn} - b_{mn} K_{mn}) \right), \quad (4.3) \end{aligned}$$

where the open-shell Fock operators F_m are defined by equation (1.7). Substituting equation (4.3) into equation (4.1) and taking into account the equalities

$$H_{mm} = H_{\underline{m}\underline{m}}, \quad \sum_k (2J_{km} - K_{km}) = \sum_k (2J_{k\underline{m}} - K_{k\underline{m}}), \quad (4.4)$$

valid for all degenerate $m \neq \underline{m}$ [1], equation (4.1) can be expressed in the form of the restrictions on the VCCs to be found:

$$\sum_n (2a_{mn}J_{mn} - b_{mn}K_{mn}) = \sum_n (2a_{\underline{m}n}J_{\underline{m}n} - b_{\underline{m}n}K_{\underline{m}n}) \quad (m \neq \underline{m}). \quad (4.5)$$

This equation was first derived in [9] using a somewhat different approach.

The second symmetry condition (equation (4.2)) takes the form

$$R_{m\underline{m}} = \lambda_{m\underline{m}} \langle \underline{m} | F_m - F_{\underline{m}} | m \rangle = 0 \quad (m \neq \underline{m}), \quad (4.2a)$$

where $\lambda_{m\underline{m}} \neq 0$ (see equation (2.6)). This condition is nothing but the Euler equation (2.8) expressing the variational conditions among the open-shell orbitals.

For a system with *non-degenerate* open-shell orbitals, the constraints of equations (2.8), (4.2a) are satisfied after self-consistence is achieved [2,3]. In the case of degenerate $\{\phi_m\}$ orbitals, equation (4.2a) must assert identically, i.e., for arbitrary *non-self-consistent* orbitals.

Off-diagonal matrix element $\langle \underline{m} | F_m | m \rangle$ of equation (4.2a) is equal to

$$\begin{aligned} \langle \underline{m} | F_m | m \rangle = f & \left[\sum_k (2\langle \underline{m}m | kk \rangle - \langle \underline{m}k | km \rangle) \right. \\ & \left. + f \sum_n (2a_{mn}\langle \underline{m}m | nn \rangle - b_{mn}\langle \underline{m}n | nm \rangle) \right]. \end{aligned} \quad (4.6)$$

The first sum in equation (4.6) is equal to zero since the operators J_c and K_c are totally symmetric (see also equation (2.25b)). Substituting the expressions for the $\langle \underline{m} | F_m | m \rangle$ and $\langle \underline{m} | F_{\underline{m}} | m \rangle$ elements into equation (4.2a) one derives the second restriction on the VCCs a_{mn} and b_{mn} :

$$\sum_n (2a_{mn}\langle \underline{m}m | nn \rangle - b_{mn}\langle \underline{m}n | nm \rangle) = \sum_n (2a_{\underline{m}n}\langle \underline{m}m | nn \rangle - b_{\underline{m}n}\langle \underline{m}n | nm \rangle) \quad (m \neq \underline{m}). \quad (4.7)$$

The constraints of equation (4.2a) need further consideration. If the operator F_m is totally symmetric, its matrix elements $\langle \underline{m} | F_m | m \rangle$ with $m \neq \underline{m}$ vanish. Since $\langle \underline{m} | F_m | m \rangle = \theta_{\underline{m}m}$, where $\theta_{\underline{m}m}$ are the Lagrangian multipliers of equation (1.3), one obtains

$$\langle \underline{m} | F_m | m \rangle = \theta_{\underline{m}m} = 0. \quad (4.8)$$

Substitution of equation (4.6) into equation (4.8) gives more rigid symmetry restrictions on the VCCs a_{mn} and b_{mn} than those of equation (4.7):

$$\sum_n (2a_{mn}\langle \underline{m}m|nn\rangle - b_{mn}\langle \underline{m}n|nm\rangle) = 0 \quad (m \neq \underline{m}). \quad (4.9)$$

In the case of non-Roothaan states, the Fock operators F_m are non-totally symmetric (see section 2.3). However, the symmetry restrictions of equations (4.8) and (4.9) are valid in this case as well.

Equation (4.8) expresses the fundamental condition [1] that the Lagrangian multipliers $\theta_{\underline{m}m}$ of equations (1.3) between the orbitals of different symmetry must be equal to zero. Therefore, equations (4.8) and (4.9) hold in the case of non-totally symmetric Fock operators as well. A proof of the latter statement is given below.

Off-diagonal matrix blocks

Similar treatment can be given to the off-diagonal matrix blocks, $\|R_{vm}\|$ and $\|R_{mv}\|$, where the index v ($v = M + 1, M + 2, \dots, M + n_\gamma$) enumerates the virtual orbitals. The latter are supposed to be transformed according to the footnote "b" of table 1. (The one-to-one correspondence between the orbitals of the two sets under consideration is necessary for theoretical analysis only. It does not assume the virtual orbitals transformation in the ROHF calculation.)

Since the operator R is totally symmetric, the following relationships must assert identically:

$$R_{M+m,m} = R_{M+\underline{m},\underline{m}} = R_{m,M+m}^* = R_{\underline{m},M+\underline{m}}^* \quad (m \neq \underline{m}), \quad (4.10)$$

$$R_{M+m,\underline{m}} = R_{M+\underline{m},m} = R_{\underline{m},M+m}^* = R_{m,M+\underline{m}}^* = 0 \quad (m \neq \underline{m}). \quad (4.11)$$

The diagonal element of the matrix block $\|R_{vm}\|$ takes the form

$$\begin{aligned} R_{M+m,m} &= \langle (M+m)|F_m|m\rangle \\ &= f \left[H_{M+m,m} + \sum_k (2\langle (M+m)m|kk\rangle - \langle (M+m)k|km\rangle) \right. \\ &\quad \left. + f \sum_n (2a_{mn}\langle (M+m)m|nn\rangle - b_{mn}\langle (M+m)n|nm\rangle) \right]. \quad (4.12) \end{aligned}$$

According to the Wigner–Eckart theorem [31], the integrals of type $\langle (M+m) \cdot \underline{m}|n\underline{n}\rangle$ are proportional to the integrals $\langle m\underline{m}|n\underline{n}\rangle$:

$$\langle (M+m)\underline{m}|n\underline{n}\rangle = C_\gamma \langle m\underline{m}|n\underline{n}\rangle, \quad (4.13)$$

where the coefficient C_γ is the same for all integrals $\langle m\underline{m}|n\underline{n}\rangle$.

(One can present the simple example where the latter statement is evident. In case of an atom, the orbitals m and $(M+m)$ have the same angular part, so the C_γ coefficient is independent of the angular parts of the degenerate orbitals $m, \underline{m}, n, \underline{n}$.)

Taking into account equations (4.13) and (4.4), one finds that the symmetry conditions of equation (4.10) give the same restrictions on the VCCs a_{mn} and b_{mn} , as the above conditions of equation (4.1) do. These restrictions are expressed by equation (4.5).

The off-diagonal matrix element of equation (4.11) is equal to

$$\begin{aligned} R_{M+\underline{m},m} &= \langle (M + \underline{m}) | F_m | m \rangle \\ &= f \left[\sum_k (2 \langle (M + \underline{m})m | kk \rangle - \langle (M + \underline{m})k | km \rangle) \right. \\ &\quad \left. + f \sum_n (2a_{mn} \langle (M + \underline{m})m | nn \rangle - b_{mn} \langle (M + \underline{m})n | nm \rangle) \right]. \end{aligned} \quad (4.14)$$

Since equation (4.13), the first sum in equation (4.14) vanishes and, therefore, the second one is also equal to zero. By using equation (4.13) with the second sum, one derives the above presented symmetry restrictions of equation (4.9).

Similar consideration can be given to the off-diagonal matrix blocks, $\|R_{mk}\|$ and $\|R_{km}\|$, not presented in table 1, between the open-shell and closed-shell orbitals. No new restrictions on the γ^N state VCCs can be derived from such a consideration [26].

Thus, the requirement for the R operator of equation (2.6) to be totally symmetric imposes the two conditions on the non-variable VCCs a_{mn} and b_{mn} , expressed by equations (4.5) and (4.9). To represent the latter in the form of *purely symmetry restrictions*, one should eliminate from equations (4.5), (4.9) the variable characteristics, i.e., the one-electron orbitals to be found.

5. General equations for γ^N state VCCs

According to the above derivation, equations (4.5) and (4.9) are the restrictions on the VCCs a_{mn} and b_{mn} to the extent that they enter the expression for the Fock operator (equation (1.7)). Since no suppositions have been made on the VCCs symmetry, the restrictions (4.5) and (4.9) are valid for both the true Fock and “pseudo-Fock” operators (see section 3.1).

Additional restrictions on the VCCs a_{mn} and b_{mn} arise from the requirement for the γ^N state energy of equation (1.5) to be related to the basic definition of equation (2.3).

A straightforward approach for deriving the latter restrictions [26] is based on the use of the representations for open-shell energy and electron repulsion integrals over degenerate orbitals in terms of the *reduced matrix elements* [32,33]. For an atom with configuration l^N ($l = p, d, \dots$), the latter elements are the Slater–Condon parameters, $F^k(l, l)$ [25]. For molecular γ^N systems under study ($\gamma = e, t, g, h$), corresponding elements are the molecular invariants, $H^k(\gamma, \gamma)$, defined in [14,26].

For completeness, the following presentation of our approach for determining the γ^N state VCCs is given in example of d^N atoms which provide a way for indepen-

dent checking [9]. An extension of this approach to molecular γ^N systems is given in [26,34].

The ROHF energy of transition-metal atoms can be expressed in terms of the Slater–Condon parameters, $F^k(\mathbf{d}, \mathbf{d})$ [25]:

$$E(2S+1L, \mathbf{d}^N) = E_r + \sum_k c^{(k)} \times F^k(\mathbf{d}, \mathbf{d}), \quad (5.1)$$

where E_r is defined by equation (1.6); $c^{(k)}$ are fundamental constants, characterizing the \mathbf{d}^N state (L, S -multiplet) under consideration, and $k = 0, 2, 4$.

Two representations for transition-metal atom energy, i.e., equations (5.1) and (2.3), are equivalent, as they both correspond to the Hartree–Fock (monoconfigurational) approximation for the multielectron wave function [25,33]. If one supposes that this energy can also be represented in the desired form of equation (1.5), the VCCs a_{mn} and b_{mn} to be found should satisfy the condition

$$f^2 \sum_m \sum_n (2a_{mn}J_{mn} - b_{mn}K_{mn}) = \sum_k c^{(k)} \times F^k(\mathbf{d}, \mathbf{d}), \quad (5.2)$$

where, in this case, the indices m, n enumerate the degenerate open-shell $\{\mathbf{d}\}$ orbitals.

As shown above, the γ^N state VCCs should also satisfy the two restrictions given by equations (4.5) and (4.9). These three equations, i.e., equations (4.5), (4.9), (5.2), give the complete set of equations for determining the VCCs a_{mn} and b_{mn} [26].

For representing equations (4.5), (4.9), (5.2) in the form of purely symmetry restrictions on the VCCs to be found, one should express all electron repulsion integrals, $\langle m\underline{m}|n\underline{n}\rangle$, over the degenerate $\{\mathbf{d}\}$ orbitals in terms of the reduced matrix elements [25]:

$$\langle m\underline{m}|n\underline{n}\rangle = \sum_k \alpha^{(k)}(m, \underline{m}, n, \underline{n}) \times F^k(\mathbf{d}, \mathbf{d}), \quad (5.3)$$

where $\alpha^{(k)}(m, \underline{m}, n, \underline{n})$ with $k = 0, 2, 4$ are the coefficients specific for the integral and the basis of $\{\mathbf{d}\}$ orbitals under consideration [25]. In the particular case of the Coulomb and exchange integrals, equation (5.3) takes a usual form

$$J_{mn} = \sum_k p_{mn}^{(k)} \times F^k(\mathbf{d}, \mathbf{d}), \quad K_{mn} = \sum_k q_{mn}^{(k)} \times F^k(\mathbf{d}, \mathbf{d}), \quad (5.4)$$

where $p_{mn}^{(k)} = \alpha^{(k)}(m, m, n, n)$ and $q_{mn}^{(k)} = \alpha^{(k)}(m, n, n, m)$. The values of these coefficients, corresponding to $k = 2$ and $k = 4$, are given in [25] for complex $\{\mathbf{d}\}$ orbitals and in [35] for real ones. The remaining coefficients, $p_{mn}^{(0)}$ and $q_{mn}^{(0)}$, have the same values for any choice of $\{\mathbf{d}\}$ orbitals [25,35]:

$$p_{mn}^{(0)} = 1, \quad q_{mn}^{(0)} = \delta_{mn}. \quad (5.5)$$

Most of the integrals in equation (5.3), defined over the {d} orbitals of either set [25,35], apart from the Coulomb and exchange vanish. For example, in the case of real {d} orbitals

$$\{\phi_m\} = \{d(z^2), d(xz), d(yz), d(x^2 - y^2), d(xy)\} = \{\sigma, \pi, \pi', \delta, \delta'\}, \quad (5.6)$$

one has the following non-vanishing 3 and 4 indexed integrals [35]:

$$\begin{aligned} \langle \sigma\delta | \pi'\pi' \rangle &= -\langle \sigma\delta | \pi\pi \rangle = -\langle \sigma\delta' | \pi\pi' \rangle = 2\sqrt{3}B, \\ \langle \sigma\pi | \pi\delta \rangle &= -\langle \sigma\pi' | \pi'\delta \rangle = \langle \sigma\pi | \pi'\delta' \rangle = \langle \sigma\pi' | \pi\delta' \rangle = \sqrt{3}B, \\ \langle \pi\delta | \pi'\delta' \rangle &= -\langle \pi\delta' | \pi'\delta \rangle = 3B, \end{aligned} \quad (5.7)$$

where $B = (9F^2 - 5F^4)/441$ is the Racah parameter [36]. In the case of complex {d} orbitals, all three indexed integrals of type $\langle \underline{m}m | nn \rangle$ and $\langle \underline{m}n | nm \rangle$, $m \neq \underline{m}$, entering equation (4.9), vanish [25].

The desired form of the purely symmetry restrictions on the VCCs to be found is obtained from equations (4.5), (4.9), (5.2), by substituting the representations of equations (5.3), (5.4). The following equalization of the terms, containing the F^0 , F^2 and F^4 parameters, respectively, on the left and right hand sides of every equation gives the desired form.

In the case of equation (5.2), such a procedure gives 3 linear non-uniform equations:

$$f^2 \sum_m \sum_n (2a_{mn}p_{mn}^{(k)} - b_{mn}q_{mn}^{(k)}) = c^{(k)}, \quad (5.8)$$

where $k = 0, 2$ and 4 , respectively, for determining the unknown VCCs a_{mn} and b_{mn} in terms of the known symmetry coefficients $p_{mn}^{(k)}$, $q_{mn}^{(k)}$ and $c^{(k)}$.

A similar substitution of equation (5.4) into equation (4.5) gives uniform equations

$$\sum_n (2a_{mn}p_{mn}^{(k)} - b_{mn}q_{mn}^{(k)}) = \sum_n (2a_{\underline{m}n}p_{\underline{m}n}^{(k)} - b_{\underline{m}n}q_{\underline{m}n}^{(k)}), \quad (5.9)$$

where $m \neq \underline{m}$ and $k = 0, 2, 4$. Since the number of independent pairs of indices (m, \underline{m}) is equal to 4 (e.g., $m = 1$ and $\underline{m} = 2, 3, 4, 5$), the number of independent equations (5.9) is equal to 12.

Substitution of equation (5.3) into equation (4.9) gives

$$\sum_n (2a_{mn}\alpha^{(k)}(\underline{m}, m, n, n) - b_{mn}\alpha^{(k)}(\underline{m}, n, n, m)) = 0 \quad (m \neq \underline{m}). \quad (5.10)$$

In this case the number of independent pairs of indices (m, \underline{m}) is equal to $20 = 5 \times 4$, since the pairs (m, \underline{m}) and (\underline{m}, m) are non-equivalent.

In the particular case of real {d} orbitals (equation (5.6)), the number of equations (5.10) reduces to 2. Those non-vanishing equations correspond to the following pairs of the indices (m, \underline{m}) :

$$(m = \sigma, \underline{m} = \delta): \quad 4(a_{\sigma\pi} - a_{\sigma\pi'}) + (b_{\sigma\pi} - b_{\sigma\pi'}) = 0 \quad (5.11a)$$

and

$$(m = \delta, \underline{m} = \sigma): \quad 4(a_{\delta\pi} - a_{\delta\pi'}) + (b_{\delta\pi} - b_{\delta\pi'}) = 0 \quad (5.11b)$$

(see also equation (5.7)). In the case of the complex {d} orbitals [25], equations (5.10) do not impose any restrictions on the VCCs to be found.

Thus, the ($^{2S+1}L, d^N$) state VCCs a_{mn} and b_{mn} entering equations (1.5) and (1.7) have to satisfy the set of symmetry restrictions given by equations (5.8)–(5.10). These restrictions express the *necessary* physical requirements and so are valid in all cases, i.e., regardless of using any other restrictions such as those of equation (1.8).

Comments on equations (5.8)–(5.10)

The details in solving equations (5.8)–(5.10) are given in the next section for both the real and complex {d} orbitals. Here we point out some general aspects of these equations.

1. For both the {d} orbitals bases [25,35], the number of equations (5.8)–(5.10) is less than the number of unknowns, a_{mn} and b_{mn} , equal to $50 = 2 \times (5 \times 5)$. This means that there is the arbitrariness in the choice of the d^N state VCCs.

According to [6,24], such an arbitrariness is inherent in the ROHF theory for all γ^N systems. The simple criterion on the validity of the so-defined VCCs is as follows [13]: if the set of equations for determining the VCCs is the complete one, i.e., involves all the necessary restrictions on the VCCs to be found, the remaining arbitrariness in the choice of the VCCs has no effect on the results of the ROHF calculations.

2. As follows from equations (5.8)–(5.10), the VCCs a_{mn} and b_{mn} to be found depend on the choice of {d} orbitals. (The coefficients $\alpha^{(k)}(m, \underline{m}, n, \underline{n})$ of equation (5.3) are specific ones for each {d} orbitals basis.) Such a dependence is the particular case of general "VCCs phase dependence" expressed by equation (2.13).

3. For any choice of {d} orbitals, the VCCs a_{mn} and b_{mn} defined by equations (5.8)–(5.10) satisfy the fundamental condition of equation (2.23). For d^N states under study, equation (2.23) immediately follows from equations (5.5) and (5.8) with $k = 0$, since $c^{(0)} = N(N - 1)/2$ [25].

6. Non-symmetric VCCs for transition-metal atoms

This section presents the different solutions of equations (5.8)–(5.10) and the results of the ROHF calculations on d^N atoms performed with the VCCs found. For solving equations (5.8)–(5.10) we use the special code designed *in integers* [26]. Such a method of solving is possible, as all the coefficients, $c^{(k)}$, $p_{mn}^{(k)}$ and $q_{mn}^{(k)}$, entering equations (5.8)–(5.10) are the rational numbers [25,35]. With this method one obtains the exact solution, i.e., without truncation errors. In the problem under study, the latter is essential as it permits one to avoid any ambiguity when recognizing the solution, i.e., either the VCCs a_{mn} and b_{mn} are symmetric or non-symmetric.

6.1. Basis of real $\{d\}$ orbitals

In the case of real $\{d\}$ orbitals (equation (5.6)), one can derive the solution of equations (5.8)–(5.10) in the symmetric form of equation (1.8):

$$a_{mn} = a_{nm}, \quad b_{mn} = b_{nm},$$

for only several states of the configuration d^N . The analysis of equations (5.8) and (5.9) added by the restrictions of equation (1.8) shows that the unified set of equations (5.8), (5.9), (1.8) is compatible if and only if the coefficients $c^{(k)}$ characterizing the $({}^{2S+1}L, d^N)$ state under study satisfy the condition

$$c^{(2)} = c^{(4)}. \quad (6.1)$$

This result stems from a numerical solving as follows. Taking into account equation (1.8), one has 30 independent unknowns, a_{mn} and b_{mn} , and 15 equations (5.8), (5.9) for their determination. Let us resolve 12 homogeneous equations (5.9) with respect to some 12 unknowns. Substitution of this solution into equations (5.8) shows that the left-hand sides of the two equations (5.8), corresponding to $k = 2$ and $k = 4$, appear to be identical to each other.

The latter result also holds if one first resolves equations (5.9) with respect to 12 arbitrary unknowns, and then imposes the symmetry restrictions of equation (1.8).

In other words, if *symmetric* VCCs a_{mn} and b_{mn} satisfy equations (5.9), they also satisfy the equation

$$\sum_m \sum_n (2a_{mn}p_{mn}^{(2)} - b_{mn}q_{mn}^{(2)}) = \sum_m \sum_n (2a_{mn}p_{mn}^{(4)} - b_{mn}q_{mn}^{(4)}). \quad (6.2)$$

In turn, equation (6.2) together with equation (5.8) leads to the above condition (6.1).

Thus, with symmetric VCCs of equation (1.8) one can calculate only those $({}^{2S+1}L, d^N)$ states for which $c^{(2)} = c^{(4)}$. A list of such states and the structure of symmetric VCCs matrices are presented below.

To gain a better understanding of the crucial restriction (equation (6.1)), we consider the states of a configuration d^N described by the Roothaan one-open-shell SCF theory [1], i.e., characterized by the two coupling coefficients of equation (2.5):

$$a_{mn} = a, \quad b_{mn} = b.$$

Using the same values of the $p_{mn}^{(k)}$ and $q_{mn}^{(k)}$ coefficients [35], one derives from equations (5.8) and (2.5) the following relations [9]:

$$\begin{aligned} c^{(0)} &= f^2(50a - 5b), \\ c^{(2)} &= -630f^2b/441, \\ c^{(4)} &= -630f^2b/441. \end{aligned} \quad (6.3)$$

It follows herefrom that the d^N states described by the Roothaan's ROHF theory [1] are those ones for which $c^{(2)} = c^{(4)}$. The corresponding values of the state VCCs are obtained from equation (6.3):

$$a = (2c^{(0)} - 7c^{(2)})/(100f^2), \quad b = -7c^{(2)}/(10f^2). \quad (6.4)$$

It is easy to show that the VCCs of equation (6.4) also satisfy homogeneous equations (5.9). The latter follows from the known properties of the coefficients $p_{mn}^{(k)}$ and $q_{mn}^{(k)}$ [25,35]:

$$\sum_n p_{mn}^{(k)} = \sum_n p_{\underline{m}n}^{(k)}, \quad \sum_n q_{mn}^{(k)} = \sum_n q_{\underline{m}n}^{(k)} \quad (m \neq \underline{m}). \quad (6.5)$$

(Relations (6.5) also follow from above equation (2.25a).) In a similar way one finds that the VCCs of equation (6.4) satisfy equation (5.10) (the latter immediately follows from equation (2.25b)). Thus, the VCCs of equation (6.4) represent the particular solution of equations (5.8)–(5.10) for the states where $c^{(2)} = c^{(4)}$.

In line with the above terminology (see section 2), the $({}^{2S+1}L, d^N)$ multiplets with $c^{(2)} = c^{(4)}$ are the *Roothaan states*, since they can be calculated with the VCCs of type $(a_{mn} = a, b_{mn} = b)$. Table 2 gives a list of such states along with the corresponding values of the a and b coefficients.

As shown above, for the states with $c^{(2)} = c^{(4)}$ one can also derive more general solutions, i.e., symmetric VCCs matrices, a_{mn} and b_{mn} . Since the number of the VCCs

Table 2
Coupling coefficients a and b of equation (6.4) for the states of atomic configurations d^N described by the Roothaan one-open-shell SCF theory [1].

Configuration, state	a	b	$c^{(2)} = c^{(4)}$ [25]*
$d^1 \quad {}^2D$	0	0	0
$d^2 \quad {}^1S$	0	-5	126/441
$d^4 \quad {}^3D$	15/16	30/16	-189/441
$d^5 \quad {}^6S$	1	2	-315/441
$d^6 \quad {}^5D$	35/36	50/36	-315/441
$d^8 \quad {}^1S$	15/16	10/16	-252/441
$d^9 \quad {}^2D$	80/81	80/81	-504/441

*The values of the $c^{(2)}$ and $c^{(4)}$ coefficients used in the present article differ from those given by Slater, $c_{av}^{(2)}$ and $c_{av}^{(4)}$ [25], as the latter correspond to the following expression for a state energy

$$E({}^{2S+1}L, d^N) = E_{av} + c_{av}^{(2)} F^2 + c_{av}^{(4)} F^4,$$

where E_{av} is the average energy of the configuration d^N [25],

$$E_{av} = E_r + N(N-1)(F^0/2 - 7(F^2 + F^4)/441),$$

and E_r is defined by equation (1.6). Comparison of these expressions with equation (5.1) gives $c^{(0)} = N(N-1)/2$, $c^{(2)} = c_{av}^{(2)} - 7N(N-1)/441$, and $c^{(4)} = c_{av}^{(4)} - 7N(N-1)/441$.

Table 3

General structure of the matrix b_{mn} for the states of the configuration d^N over the basis of *real* $\{d\}$ orbitals* ($a_{mn} = a = c^{(0)}/(50f^2) + \beta/10$).

	$\sigma = d(z^2)$	$\pi = d(xz)$	$\pi' = d(yz)$	$\delta = d(x^2 - y^2)$	$\delta' = d(xy)$
σ	β	R	R	$R + 3Q$	$R + 3Q$
π	$R - 3Q$	β	$R + 3Q$	$R + 3Q$	$R + 3Q$
π'	$R - 3Q$	$R + 3Q$	β	$R + 3Q$	$R + 3Q$
δ	$-2R + 6Q + 3\omega$	$3R - 2\omega$	$3R - 2\omega$	β	ω
δ'	$-2R + 6Q + 3\omega_0$	$3R - 2\omega_0$	$3R - 2\omega_0$	ω_0	β

* $R = 7(5c^{(2)} - 12c^{(4)})/(50f^2) - 4\beta/10$,
 $Q = 7(-5c^{(2)} + 5c^{(4)})/(50f^2)$,
 and β, ω and ω_0 are the arbitrary numbers.

to be found is greater than the total number of equations (5.8), (5.9), (5.11), there is an infinite number of such solutions. Moreover, one can also derive non-symmetric VCCs of type (equation (1.9)), if the symmetry restrictions of equation (1.8) are neglected (see below).

A principally distinct situation takes place if the coefficients $c^{(2)}$ and $c^{(4)}$ for the $(2S+1L, d^N)$ state under study are not equal to each other:

$$c^{(2)} \neq c^{(4)}. \tag{6.6}$$

For such “non-Roothaan” states, the set of equations (5.8), (5.9) added by the rigid VCCs symmetry restrictions of equation (1.8) is incompatible, despite the great difference in the number of unknowns and equations. For such states, the set of equations (5.8)–(5.10) has **only non-symmetric solutions** of type (equation (1.9)).

Table 3 presents a general solution for equations (5.8)–(5.10) over the real $\{d\}$ orbitals. The three types of solutions mentioned above, indicated by equations (1.8), (1.9) and (6.4), are the particular cases of this general one. Let us make some necessary comments on the data tabulated.

The general solution of equations (5.8), (5.9) contains $35 = 50 - 15$ arbitrary parameters. To present this solution in a practically convenient form, we put all coefficients a_{mn} equal to each other

$$a_{mn} = a, \tag{6.7}$$

where a is some quantity to be determined. Besides, we constrained the b_{mn} coefficients by the additional “natural” restrictions

$$\begin{aligned} b_{\sigma\pi} = b_{\sigma\pi'}; & \quad b_{\sigma\delta} = b_{\sigma\delta'}; & \quad b_{\pi\pi'} = b_{\pi\delta} = b_{\pi\delta'}; \\ b_{\delta\pi} = b_{\delta\pi'}; & \quad b_{\delta'\pi} = b_{\delta'\pi'}; & \quad b_{\pi'\pi} = b_{\pi'\delta} = b_{\pi'\delta'}. \end{aligned} \tag{6.8}$$

(Relations (6.8) follow in a natural way from equations (5.8), (5.9), as the unknowns ($b_{\sigma\pi}$ and $b_{\sigma\pi'}$), ($b_{\sigma\delta}$ and $b_{\sigma\delta'}$), \dots , enter each of equations (5.8) and (5.9) with equal coefficients.) Due to relations (6.7), (6.8), the necessary symmetry restrictions of equations (5.11a,b) are satisfied automatically.

Equations (6.7) and (6.8) give 24 and 8 additional relations, respectively, therefore the solution of the set of equations (5.8), (5.9), (6.7), (6.8) contains 3 arbitrary parameters, denoted in table 3 as ω , ω_0 and β .

As follows from table 3, matrix $\|b_{mn}\|$ is in general a non-symmetric one for all the $(2S+1L, d^N)$ states. In quantum chemical calculations one can use *any* numerical values of the a and b_{mn} coefficients of table 3, according to the choice of arbitrary parameters (see below).

The symmetric form of the matrix $\|b_{mn}\|$ can be obtained only for the Roothaan d^N states discriminated by the condition $c^{(2)} = c^{(4)}$. Putting the arbitrary numbers $\omega = \omega_0 = R$, one obtains

$$\begin{aligned} a_{mn} &= c^{(0)}/(50f^2) + \beta/10, \\ b_{mn} &= \delta_{mn}\beta - (1 - \delta_{mn})(49c^{(2)}/(50f^2) + 4\beta/10). \end{aligned} \quad (6.9)$$

If one put further $\beta = R = -7c^{(2)}/(10f^2)$, the coupling coefficients are obtained in the standard Roothaan's form of equation (6.4).

For the non-Roothaan states with $c^{(2)} \neq c^{(4)}$, the solution of equations (5.8), (5.9), (5.11) cannot be derived in the symmetric form of equation (1.8) for any choice of arbitrary parameters. This principal conclusion immediately follows from equations (5.8), (5.9) and is not caused by using any additional relations between unknowns.

Table 4 presents the results of non-empirical SCF calculations on transition-metal atoms performed by two different ROHF methods, i.e., by the unified coupling operator (UCO) method [1–5] and by the Roothaan–Bagus atomic “expansion method” [12]. The first column of table 4 presents our results [9,26] derived by the ROHF–UCO method using the VCCs of tables 2 and 3.

Comments on the ROHF–UCO calculations

All calculations were performed by the MONSTERGAUSS program [39] modified in some points as described in [9]. In the first place, we have checked that the results of the ROHF calculations do not depend on the arbitrariness in the choice of the VCCs of table 3. It has been made by the variation of arbitrary numbers β , ω and ω_0 .

Additional calculations were carried out for checking the restrictions of equations (5.11a,b) that were not taken into account in [9]. For this purpose, we varied the values of the VCCs entering equation (5.11) without changing the other VCCs. (In the course of this variation, the additional relations (6.7) and (6.8) were lifted.)

For eliminating the VCCs phase dependence (see section 2.2), all calculations were carried out over real {d} orbitals of the fixed representation. Degenerate open-shell {d} orbitals were transformed *at each iteration* to the form of equation (5.6).

The data presented in table 4 can be summarized as follows:

1. The identity of the ROHF–UCO results for d^N atoms derived with using different VCCs sets means the physical equivalency of *all the solutions* of equations (5.8)–(5.10).

Table 4
Energy of the first row transition atoms (in a.u.), calculated by two different ROHF methods
(Gaussian basis set (14s9p5d)/[8s4p2d] from [37]).

Atom, configuration, state ^a	Unified SCF coupling operator method [1–5]		Roothaan–Bagus “expansion method” [12]	
	[9,26] ^b	[11] ^c	[37]	[38]
	Sc d ¹ ² D	–759.705047	–759.705047	–759.7050
Ti d ² ³ F	–848.367900	(–848.349942)	–848.3685	–848.367900
V d ³ ⁴ F	–942.837196	(–942.817440)	–942.8372	–942.837196
<i>E</i> (<i>S</i> = 3/2)	–942.817440 ^d	–	–	–942.817440
⁴ P	–942.771401	–	–	–942.771402
² G	–942.770986	–	–	–942.770986
² H, ² P	–942.749087	–	–	–942.749088
² F	–942.683500	–	–	–
Cr d ⁴ ⁵ D	–1043.249620	–1043.249620	–1043.2497	–1043.249620
Mn d ⁵ ⁶ S	–1149.787155	–1149.787155	–1149.7872	–1149.787155
Fe d ⁶ ⁵ D	–1262.350361	–1262.350361	–1262.3504	–1262.350360
Co d ⁷ ⁴ F	–1381.289383	(–1381.263774)	–1381.2895	–1381.289382
Ni d ⁸ ³ F	–1506.720591	(–1506.693632)	–1506.7206	–1506.720590
Cu d ⁹ ² D	–1638.786455	–1638.786455	–1638.7867	–1638.786455
d ¹⁰ s ¹ ² S	–1638.801243	–1638.801243	–1638.8015	–1638.801243

^aBy fat font we mark the “non-Roothaan” states, for which $c^{(2)} \neq c^{(4)}$ [25].

^bCalculations performed using the VCCs from tables 2 and 3. For the Roothaan states, both symmetric and non-symmetric VCCs were used corresponding to the different values of arbitrary numbers β , ω and ω_0 . Non-Roothaan states were calculated by the use of non-symmetric VCCs only (symmetric VCCs do not exist).

^cCalculations performed with symmetric VCCs, derived by Peterson for both the Roothaan and **non-Roothaan** states (see [11, pp. 67–69]). Similar VCCs have been earlier derived by Guest and Saunders [18].

^dAverage energy of the d³ states with $S = 3/2$ (see discussion in [9]).

- Of prime importance is the equivalency of symmetric and non-symmetric VCCs (in those cases where symmetric VCCs exist). The cause of such an equivalency is discussed in section 7.
- The non-Roothaan d^{*N*} states discriminated by the condition $c^{(2)} \neq c^{(4)}$, can be calculated with non-symmetric VCCs only. This result explains the discrepancy between the previously published data [11,37] (see table 4).

6.2. Basis of complex {d} orbitals

Essentially distinct results are obtained if one uses the complex {d} orbitals

$$\{\phi_m\} = \{d_0, d_{+1}, d_{-1}, d_{+2}, d_{-2}\}. \quad (6.10)$$

Recall that the difference between the VCCs over the real and complex {d} orbitals arises due to the difference in corresponding coefficients $p_{mn}^{(k)}$ and $q_{mn}^{(k)}$ of equation (5.4) [25,35].

Table 5
General structure of the matrix b_{mn} for the states of the configuration d^N over the basis of complex $\{d\}$ orbitals* ($a_{mn} = a = c^{(0)}/(50f^2) + \beta/10$).

	0	+1	-1	+2	-2
0	β	R	R	$R + 3Q$	$R + 3Q$
+1	$4R - 6\tau$	β	$2Q + \beta/2 + \tau$	$R + 2Q$	$-R + 4\tau$
-1	$4R - 6\tau$	$2Q + \beta/2 + \tau$	β	$-R + 4\tau$	$R + 2Q$
+2	$R + 3Q$	$R + 2Q$	$Q + \beta - 2\nu$	β	$R + \nu$
-2	$R + 3Q$	$Q + \beta - 2\nu$	$R + 2Q$	$R + \nu$	β

* $R = 7(5c^{(2)} - 12c^{(4)})/(50f^2) - 4\beta/10$,
 $Q = 7(-5c^{(2)} + 5c^{(4)})/(50f^2)$,
and β , τ and ν are the arbitrary numbers.

In the case of complex $\{d\}$ orbitals, one can derive a solution for equations (5.8) and (5.9) in symmetric form *for all states* for which the Slater–Condon representation of a state energy (equation (5.1)) is valid. In contrast with the case of real $\{d\}$ orbitals, symmetric VCCs a_{mn} and b_{mn} derived from equation (5.9) over complex $\{d\}$ orbitals, do not satisfy equation (6.2) identically. Instead of the latter equation, one obtains two equations (5.8), corresponding to $k = 2$ and $k = 4$, with non-equal left-hand sides.

Table 5 presents a general solution [26] for equations (5.8), (5.9) over complex $\{d\}$ orbitals. (Recall that in this case equation (5.10) does not impose any restrictions on the VCCs to be found.) In order to present this solution in a practically convenient form (with three arbitrary parameters as in table 3), we use the same restrictions on the a_{mn} coefficients as above: $a_{mn} = a$ (see equation (6.7)), and corresponding "natural" relations between the b_{mn} coefficients:

$$b_{0,1} = b_{0,-1}; \quad b_{0,2} = b_{0,-2}. \quad (6.11)$$

To exclude the remaining arbitrariness, the following additional relations are used:

$$\begin{aligned} b_{1,0} &= b_{-1,0}; & b_{1,-1} &= b_{-1,1}; \\ b_{1,-2} &= b_{-1,2}; & b_{2,-1} &= b_{-2,1}; \\ b_{2,-2} &= b_{-2,2}; & b_{1,2} &= b_{-1,-2} = b_{2,1} = b_{-2,-1}; \\ b_{2,0} &= b_{-2,0} = b_{0,2}. \end{aligned} \quad (6.12)$$

Relations (6.12) reduce the number of unknowns, b_{mn} , and simultaneously reduce the number of independent equations (5.9) to 8 [26]. The net result is that the solution of equations (5.8), (5.9) added by the additional relations of equations (6.7), (6.11), (6.12) has three arbitrary parameters denoted in table 5 as β , τ and ν .

In line with the above discussion, in the ROHF calculations one can use any numerical values of the a and b_{mn} coefficients of table 5, according to the choice of arbitrary parameters. If one chooses the latter as

$$\tau = R/2, \quad \nu = (-R + Q + \beta)/2 \quad (6.13)$$

(see table 5), the VCCs are obtained in symmetric form for all non-multiple (non-double) states of a configuration d^N .

As in the previous case of real $\{d\}$ orbitals, the specific Roothaan’s form of the VCCs given by equation (6.4) can be derived for the states with $c^{(2)} = c^{(4)}$ if one put further $\beta = R = -7c^{(2)}/(10f^2)$.

7. Equivalency of auxiliary Fock operators

As pointed out in section 3, the expression for the Fock operator of equation (1.7) with non-symmetric VCCs defines some “pseudo-Fock” operators that cannot be derived straightforwardly from expression for energy. However, as follows from the results of the ROHF calculations on the Roothaan d^N states (see table 4), the use of both the true and “pseudo-Fock” operators leads to the same ROHF results.

Such an equivalency of different Fock operators demonstrates a general character of equations (5.8)–(5.10) that define the VCCs and thus define the “pseudo-Fock” operators themselves. This equivalency also shows the rigid VCCs symmetry restrictions of equation (1.8) to be unnecessary.

However, the question of equivalency of the true and pseudo Fock operators needs a more rigorous treatment. This section presents the proof of the following statement:

The expression for the Fock operator (equation (1.7)), in which the coefficients a_{mn} and b_{mn} are determined by equations (5.8)–(5.10), defines a whole class of the Fock-like operators equivalent from the viewpoint of the Euler and Hartree–Fock equations. In other words, the basic ROHF variational equations (1.3), (2.4) expressed in terms of both the true and pseudo Fock operators give the same optimum orbitals.

To simplify the following treatment, we designate the symmetric VCCs as A_{mn} and B_{mn} . The above designations, a_{mn} and b_{mn} , are used for non-symmetric VCCs only. Both the VCCs sets, $\{A_{mn}, B_{mn}\}$ and $\{a_{mn}, b_{mn}\}$, are supposed to be derived from equations (5.8)–(5.10) or, what is the same, from initial equations (4.5), (4.9), (5.2).

In general, non-symmetric VCCs a_{mn} and b_{mn} **cannot be symmetrized**, i.e., their symmetric combinations, $(a_{mn} + a_{nm})/2$ and $(b_{mn} + b_{nm})/2$, do not represent the solution of equations (5.8)–(5.10) (see, e.g., table 3). Because of this,

$$A_{mn} \neq (a_{mn} + a_{nm})/2, \quad B_{mn} \neq (b_{mn} + b_{nm})/2. \quad (7.1)$$

Using the two VCCs sets, $\{A_{mn}, B_{mn}\}$ and $\{a_{mn}, b_{mn}\}$, one can construct the two corresponding sets of the Fock operators by equation (1.7). The operators constructed with symmetric VCCs $F_m\{A_{mn}, B_{mn}\}$, are nothing but the true Fock operators Φ_m defined by equation (3.3)

$$F_m\{A_{mn}, B_{mn}\} = \Phi_m. \quad (7.2a)$$

The "pseudo-Fock" operators, $F_m\{a_{mn}, b_{mn}\}$, constructed with non-symmetric VCCs have no counterparts among the Φ_m operators. To distinguish the operators of the two sets, the $F_m\{a_{mn}, b_{mn}\}$ operators are designated as merely F_m :

$$F_m\{a_{mn}, b_{mn}\} = F_m. \quad (7.2b)$$

In general, the operators Φ_m and F_m corresponding to the same one-electron orbital Φ_m are not equal to each other:

$$\Phi_m \neq F_m \quad (m = 1, 2, \dots, \dim \gamma). \quad (7.3)$$

In particular, if one uses the Roothaan's VCCs of equation (6.4), all the Φ_m operators are equal to each other, $\Phi_m = \Phi_0$, and are totally symmetric. By contrast, the F_m operators of equation (7.2b) are always non-totally symmetric (see section 2.3) and are not equal to each other.

We wish to prove that the two unified coupling operators of equation (2.6), $R\{\Phi\}$ and $R\{F\}$, constructed by using the two above sets of Fock operators (equations (7.2), (7.3)) are *identical*, i.e.,

$$R\{\Phi\} \equiv R\{F\}. \quad (7.4)$$

(By writing identity (7.4) one assumes that the set of trial orbitals, $\{\phi_i\}$, used for constructing the Φ_m and F_m operators is the same in both cases.) Here we do not consider the closed-shell Fock operator F_c of equation (2.27a) as the latter is independent of the state VCCs.

Taking into account the structure of the R operator matrix (see table 1), the proof of equation (7.4) reduces to the proof of identity of the diagonal elements in corresponding matrix blocks:

$$\langle m | R\{\Phi\} | m \rangle \equiv \langle m | R\{F\} | m \rangle, \quad (7.5)$$

$$\langle (M+m) | R\{\Phi\} | m \rangle \equiv \langle (M+m) | R\{F\} | m \rangle. \quad (7.6)$$

(Diagonal elements of type $\langle (M+m) | R\{F\} | (M+m) \rangle$ defined over virtual orbitals vanish; see equation (2.6).)

Due to expressions (4.3) and (4.4), equation (7.5) takes the form

$$\sum_n (2A_{mn}J_{mn} - B_{mn}K_{mn}) = \sum_n (2a_{mn}J_{mn} - b_{mn}K_{mn}). \quad (7.7)$$

Since both symmetric $\{A_{mn}, B_{mn}\}$ and non-symmetric $\{a_{mn}, b_{mn}\}$ VCCs satisfy equations (5.2) and (4.5), the left- and right-hand sides of equation (7.7) do not depend on the index m and are equal to the same quantity

$$\sum_k c^{(k)} \times F^k(\mathbf{d}, \mathbf{d}) / (f^2 \dim \gamma) \quad (7.8)$$

and therefore are equal to each other. The proof of equation (7.6) can be derived in a similar way if one takes into account equations (4.9), (4.13) and (4.14).

Thus, two unified coupling operators, $R\{\Phi\}$ and $R\{F\}$, appear to be identical to each other despite the auxiliary Fock operators, Φ_m and F_m , are essentially distinct. It is this result that has been found in the ROHF–UCO calculations [9,10,13] on different γ^N systems.

According to [2,3], the occupied orbitals $\{\phi_i\}$ found by solving the Hartree–Fock equation (2.4) represent the solution of the Euler equations (1.3) as well. Taking into account the identity of the operators $R\{\Phi\}$ and $R\{F\}$, one concludes that in the self-consistent limit ($R_{ij} = \delta_{ij}\varepsilon_i$) both sets of the Fock operators, $\{\Phi_m\}$ and $\{F_m\}$, satisfy the Euler equations (1.3a,b) with the *same* set of $\{\phi_i\}$ orbitals.

Concluding remarks

The above equivalency of the true Fock and “pseudo-Fock” operators has the apparent origin. Although the two operators, Φ_m and F_m , corresponding to the same one-electron orbital ϕ_m are not equal to each other, their matrices, $\|\Phi_m\|$ and $\|F_m\|$, have one identical row and column with the number “ m ”, i.e.,

$$\langle m|\Phi_m|j\rangle = \langle m|F_m|j\rangle, \quad \langle j|\Phi_m|m\rangle = \langle j|F_m|m\rangle, \quad (7.9)$$

where the index j runs over all one-electron orbitals (both occupied and virtual). This result immediately follows from the above derivation of equations (4.5) and (4.9).

In other words, if the open-shell Fock operator is defined by equation (1.7), in which the coefficients a_{mn} and b_{mn} are defined by equations (5.8)–(5.10), the matrix elements of equation (7.9) are the only ones that are defined unambiguously. All other matrix elements depend on the choice of the VCCs (e.g., symmetric or non-symmetric), i.e., are defined in an ambiguous manner.

Such a non-uniqueness of the Fock operator matrix is dictated actually by variational equations. The Fock operator F_m is defined by how it operates on the given orbital ϕ_m , so the elements of equation (7.9) are the only ones necessary for solving the Euler equation (1.3) or for constructing the matrix of one-electron Hamiltonian R by equation (2.6). All other matrix elements are *immaterial*.

8. Summary

The present study was initiated by the works [11,16,17] where it was shown that the existing ROHF theory cannot be directly applied to some open-shell states of highly symmetric systems, such as fullerenes with electronic configurations g^N and h^N , and d^N atoms. To eliminate this limitation of the theory, we have reanalysed the symmetry restrictions to which the γ^N state VCCs, a_{mn} and b_{mn} , must satisfy in a general case ($\gamma = p, d, \dots$ for atoms, and $\gamma = e, t, g, h$ for non-linear molecules).

The final expressions for determining the VCCs are given by equations (5.8)–(5.10). The most important result following from these equations is that some γ^N states can be calculated with non-symmetric VCCs only. A testing of the theory developed

in an appropriate sample of d^N atoms showed it does overcome the limitation [11] under study (see table 4).

However, the new VCCs symmetry restrictions of equations (5.9), (5.10) come into conflict with the known ones of equation (1.8) which are more rigid. The main problem is that the Fock operators of equation (1.7) constructed with non-symmetric VCCs cannot be derived straightforwardly from the energy functional of equation (1.5) (for details, see section 3).

We have shown that in contrast to the Fock operators, the total one-electron Hamiltonian R of equation (2.4) is independent of the VCCs symmetry. In particular, for those γ^N states for which both symmetric and non-symmetric VCCs exist, the use of either VCCs set leads to the same operator R , i.e., gives the same Hartree–Fock orbitals. The latter proves the validity of the approach developed.

An extension of this approach to molecular γ^N systems is given in [26]. In the next article [34] we present the VCCs values for open-shell fullerenes of icosahedral symmetry discussed in [16,17] along with the results of corresponding non-empirical calculations.

However, not all the questions are answered in our approach regarding the VCCs asymmetry. The Fock operators with non-symmetric VCCs are introduced in the form of a postulate and this is why we call the problem under study the VCCs *symmetry dilemma*.

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References

- [1] C.C.J. Roothaan, Rev. Mod. Phys. 32 (1960) 179.
- [2] S. Huzinaga, J. Chem. Phys. 51 (1969) 3971.
- [3] K. Hirao and H. Nakatsuji, J. Chem. Phys. 59 (1973) 1457.
- [4] K. Hirao, J. Chem. Phys. 60 (1974) 3215.
- [5] R. Carbo and J.M. Riera, *A General SCF Theory*, Lecture Notes in Chemistry, Vol. 5 (Springer, Berlin, 1978).
- [6] W.D. Edwards and M.C. Zerner, Theoret. Chim. Acta 72 (1987) 347.
- [7] L. Domingo and J.I. Burgos, Studies Phys. Theor. Chem. 62 (1989) 103.
- [8] J.B. Rose and V. McKoy, J. Chem. Phys. 55 (1971) 5435.
- [9] B.N. Plakhutin, G.M. Zhidomirov and A.V. Arbuznikov, Int. J. Quantum Chem. 41 (1992) 311.
- [10] B.N. Plakhutin, A.V. Arbuznikov and A.B. Trofimov, Int. J. Quantum Chem. 45 (1993) 363.

- [11] R. Poirier, R. Kari and I.G. Csizmadia, *Physical Sciences Data*, Vol. 24 (Elsevier, Amsterdam, 1985).
- [12] C.C.J. Roothaan and P.S. Bagus, *Methods Comput. Phys.* 2 (1963) 47.
- [13] B.N. Plakhutin and A.V. Arbuznikov, *Chem. Phys. Lett.* 232 (1995) 247.
- [14] B.N. Plakhutin, *Chem. Phys. Lett.* 227 (1994) 396.
B.N. Plakhutin, *J. Struct. Chem.* 39 (1998) 3.
- [15] B.N. Plakhutin, J.M. Oliva and R. Carbo, in: *Proc. 35th Sanibel Symp.* (FL, USA, 1995), p. 202.
B.N. Plakhutin, J.M. Oliva and R. Carbo, to be submitted.
- [16] A.H.H. Chang, W.C. Ermler and R.M. Pitzer, *J. Phys. Chem.* 95 (1991) 9288.
- [17] G.T. Klimko and M.M. Mestechkin, *Int. J. Quantum Chem.* 37 (1990) 753.
G.T. Klimko, M.M. Mestechkin and G.E. Whyman, *Struct. Chem.* 2 (1991) 489.
- [18] M.F. Guest and V.R. Saunders, *Mol. Phys.* 28 (1974) 819.
- [19] J. Hinze and E. Yutsever, *J. Chem. Phys.* 70 (1979) 3188.
- [20] B. Levy and G. Berthier, *Int. J. Quantum Chem.* 2 (1968) 307.
- [21] R.M. Pitzer, OSU-TCG, Report No. 101 (unpublished).
- [22] M.J.S. Dewar, J.A. Hashmall and G.J. Venier, *J. Amer. Chem. Soc.* 90 (1968) 1953.
F.O. Ellison and F.M. Matheu, *Chem. Phys. Lett.* 10 (1972) 322.
B.N. Plakhutin and G.M. Zhidomirov, *Russian J. Phys. Chem.* 62 (1988) 1724.
- [23] I.G. Kaplan, *Symmetry of Many-Electron Systems* (Academic Press, New York, 1975).
- [24] B.N. Plakhutin, G.T. Klimko, M.M. Mestechkin and G.M. Zhidomirov, *Theor. Exp. Chem.* 23 (1987) 129.
G.T. Klimko, M.M. Mestechkin, B.N. Plakhutin, G.M. Zhidomirov and R.A. Evarestov, *Int. J. Quantum Chem.* 37 (1990) 35.
- [25] J.C. Slater, *Quantum Theory of Atomic Structure*, Vols. I and II (McGraw-Hill, New York, 1960).
- [26] B.N. Plakhutin, D.Sc. thesis, Moscow State University (1995).
- [27] B.N. Plakhutin and G.M. Zhidomirov, *J. Struct. Chem.* 27(2) (1986) 3.
- [28] H.A. Bethe, *Ann. Phys.* 3 (1929) 133.
- [29] R. McWeeny and B.T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic Press, London, 1969).
- [30] A.V. Arbuznikov and B.N. Plakhutin, *Dokl. Ross. Akad. Nauk* 324 (1992) 349 (in Russian).
- [31] E. Wigner, *Z. Phys.* 43 (1927) 624.
C. Eckart, *Rev. Mod. Phys.* 2 (1930) 305.
G.F. Koster, *Phys. Rev.* 109 (1958) 227.
- [32] E.P. Wigner, in: *Quantum Theory of Angular Momentum*, eds. L.C. Biedenharn and H. van Dam (Academic Press, New York, 1965), pp. 87–133.
- [33] C.C.J. Roothaan and J.H. Detrich, *Phys. Rev. A* 27 (1983) 29.
- [34] B.N. Plakhutin, in preparation.
- [35] C.J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1961).
- [36] G. Racah, *Phys. Rev.* 63 (1942) 438.
- [37] A.J.H. Wachters, *J. Chem. Phys.* 52 (1970) 1033.
- [38] B.N. Plakhutin and A.B. Trofimov, *J. Struct. Chem.* 33(6) (1992) 21.
- [39] M. Peterson and R. Poirier, MONSTERGAUSS-92, Department of Chemistry, University of Toronto and Memorial University of Newfoundland, St. John's, NF, Canada.