GENERAL FORM OF THE TOTAL ONE-ELECTRON HAMILTONIAN IN THE RESTRICTED OPEN SHELL HARTREE–FOCK METHOD

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The structure of the effective one-electron Hamiltonian $\hat{R}$ in the Hartree–Fock equation $\hat{R}\phi_i = \varepsilon_i\phi_i$ is discussed in many works. The most general definitions of $\hat{R}$, satisfying all necessary conditions imposed by the variational principle for the energy in open shell systems are derived by Dyadyusha and Kuprievich and by Hirao and Nakasutji. In this work it is shown that these definitions cannot be concordant with additional variational conditions imposed by Koopmans' theorem. A more general form of $\hat{R}$ is proposed which provides a combination of the variational conditions imposed on the Hartree–Fock orbitals by the variational principle and Koopmans' theorem.

INTRODUCTION

The principles of the Hartree–Fock method for systems with open electron shells, which satisfies the spin purity requirement for the wave function, had been established in the classical Roothaan work [1]. Later numerous reformulations and generalizations of this method were proposed (see monographs [2-4] and review [5]). The current formulation of this method called the restricted open-shell Hartree–Fock method (ROHF) is based on the representation of the total electronic energy in the form

$$E_{\text{ROHF}} = 2\sum_i f_i H_{ii} + \sum_i \sum_j f_i f_j (2a_{ij}J_{ij} - b_{ij}K_{ij}), \tag{1}$$

which involves only Coulomb J_{ij} and exchange K_{ij} integrals and does not involve three- and four-index electronic repulsion integrals $\langle ij|kl\rangle$. In Eq. (1) and further the i and j indices belong to occupied orbitals; f_i is the occupation number of the ϕ_i orbital ($f_i = 1$ for the closed shell orbitals, $0 < f_i < 1$ for the open shell orbitals, and $f_i = 0$ for the virtual orbitals); a_{ij} and b_{ij} are the coupling coefficients characterizing the state and electronic configuration the system under study [1].

The application of the variational principle to energy functional (1) under additional orthonormalization conditions of the orbitals $\langle\phi_i|\phi_j\rangle = \delta_{ij}$ yields the familiar Euler equations [6]

$$\hat{F}_i|\phi_i\rangle = \sum_j |\phi_j\rangle\theta_{ji}, \tag{2a}$$

$$\left\langle \varphi_i \middle| \hat{F}_i = \sum_j \left\langle \varphi_j \middle| \theta_{ij}, \right. \right. \tag{2b}$$

where $\theta_{ji} = \langle \phi_j | \hat{F}_i | \phi_i \rangle$ are the Langrangian multipliers meeting the condition

$$\theta_{ji} = \theta_{ij}^*, \tag{3}$$

or in a more detailed record, $\theta_{ji} = \langle \phi_j | \hat{F}_i | \phi_i \rangle = \langle \phi_i | \hat{F}_j | \phi_j \rangle^* = \langle \phi_j | \hat{F}_j | \phi_i \rangle$, and $\hat{F}_i$ is the Fock operator [6]

$$\hat{F}_i = f_i(\hat{h} + \sum_j f_j(2a_{ij}\hat{J}_j - b_{ij}\hat{K}_j)), \tag{4}$$

expressed in terms of Hermitian one-electron $\hat{h}$, Coulomb $\hat{J}_j$, and exchange $\hat{K}_j$ operators [1].

As it was shown by Roothaan for the first time, the system of coupled equations (2)-(3) can be presented in the form of the generalized Hartree–Fock equation

$$\hat{R} | \phi_i \rangle = \varepsilon_i | \phi_i \rangle, \tag{5}$$

where $\hat{R}$ is the total one-electron Hamiltonian, also called the unified coupling operator. The analytical expression for $\hat{R}$ was obtained by Roothaan for systems with one open shell.

The most general definitions of $\hat{R}$ applicable to any non-multiple (non-repeating) state of an arbitrary system with many open shells were derived independently by Dyadyusha and Kuprievich [7] and by Hirao and Nakasuji [8]. The definitions [7, 8] are not equal to each other (see below), nonetheless, they are completely equivalent from the standpoint of the variational principle expressed by Euler equations (2)-(3).

In this work it is shown that the definitions of $\hat{R}$ [7, 8] cannot be agreed with the additional variational conditions imposed by Koopmans' theorem (KT) [9]. A more general form of $\hat{R}$ is proposed which enables to unify the variational conditions imposed on the Hartree–Fock orbitals by the variational principle and KT.

VARIATIONAL PRINCIPLE AND THE HAMILTONIAN STRUCTURE IN THE ROHF METHOD (BRIEF REVIEW)

In order to simplify the following formulas we denote the closed, open, and virtual shell orbitals by the indices (k, l), (m, n), and (u, w) respectively, and the indices (i, j), as previously, correspond to all occupied orbitals. The respective orbital subspaces (shells) are denoted by the letters c (closed), o (open), and v (virtual), so that c = $\{\phi_k\}$, o = $\{\phi_m\}$, and v = $\{\phi_u\}$. For the designation of orbitals from any set the indices (p, q) are used.

The definitions of $\hat{R}$ derived in [7, 8] can be presented in the following form involving three different contributions:

$$\hat{R} = \hat{R}_{(1)} + \hat{R}_{(2)} + \hat{R}_{(3)}, \tag{6}$$

$$\hat{R}_{(1)} = \sum_i \tau_i[(I - \rho)\hat{F}_i\rho^i + \rho^i\hat{F}_i(I - \rho)], \tag{7}$$

$$\hat{R}_{(2)} = \sum_i \sum_j \lambda_{ij}\rho^j(\hat{F}_i - \hat{F}_j)\rho^i, \tag{8}$$

and the term $\hat{R}_{(3)}$, the analysis of which is the main purpose of our study and which is essentially different in the definitions [7, 8], is discussed below. In Eqs. (7)-(8)

$$\rho^i = | \phi_i \rangle\langle \phi_i |, \qquad \rho = \sum_i \rho^i = \sum_k \rho^k + \sum_m \rho^m, \tag{9}$$

$$I - \rho = \sum_u \rho^u, \tag{10}$$

$\hat{F}_i$ is Fock operator (4), τ_i and λ_{ij} ($\lambda_{ij} = -\lambda_{ji}$) are the *arbitrary non-zero* numbers. Note here that in the original definitions of $\hat{R}$ [7, 8] the number of arbitrary non-zero coefficients is different. The choice of coefficients in Eqs. (7)-(8) in general corresponds to the approach [8]. Note also that in [7, 8] the separation of the total Hamiltonian $\hat{R}$ into three components (6) was not given explicitly. The meaning of this separation becomes evident from the following.

The components $\hat{R}_{(1)}$ and $\hat{R}_{(2)}$ are the main contributions to $\hat{R}$, which were obtained from variational principle (2)-(3). The term $\hat{R}_{(3)}$ involves all the other (non-variational) contributions to $\hat{R}$. In the definition [7] this term has the form

$$\hat{R}_{(3)} = \sum_p \rho^p \hat{B} \rho^p, \tag{11}$$

where $\hat{B}$ is an *arbitrary non-zero* operator, and the summation in (11) is performed over all orbitals (occupied and virtual). In the definition [8] the component $\hat{R}_{(3)}$ takes another form

$$\hat{R}_{(3)} = \sum_i \rho^i \hat{F}_i \rho^i + \sum_u \sum_w \sum_i \rho^u \hat{F}_i \rho^w. \tag{12}$$

Before discussing definitions (11)-(12), let us clarify the relationship between the components $\hat{R}_{(1)}$ and $\hat{R}_{(2)}$ and initial Euler equations (2)-(3). This is necessary in order to make sure, firstly, the definitions of $\hat{R}$ [7, 8] are physically equivalent, and secondly, that definitions (11)-(12) of the component $\hat{R}_{(3)}$ indeed do not result from the variational principle. Eq. (2a) can be presented in the following equivalent forms:

$$\hat{F}_i \,|\, \phi_i \rangle = \sum_j |\, \phi_j \rangle \langle \phi_j \,|\, \hat{F}_i \,|\, \phi_i \rangle = \rho \hat{F}_i \,|\, \phi_i \rangle, \tag{13a}$$

$$(I - \rho)\hat{F}_i \,|\, \phi_i \rangle = 0, \tag{13b}$$

$$(I - \rho)\hat{F}_i \rho^i = 0. \tag{13c}$$

A similar consideration of Eq. (2b) gives

$$\rho^i \hat{F}_i (I - \rho) = 0. \tag{14}$$

From (13) and (14) it follows that Euler equations (2) express the variational conditions *between the occupied and virtual orbitals*. In accordance with these conditions, the matrix elements $\langle \phi_u \,|\, \hat{F}_i \,|\, \phi_i \rangle = \langle \phi_i \,|\, \hat{F}_i \,|\, \phi_u \rangle^*$ must become zero when the self-consistency is achieved. It is easy to see that conditions (13)-(14) are explicitly involved into the component $\hat{R}_{(1)}$ of the total one-electron Hamiltonian (6).

The Hermitian condition of Lagrangian multipliers (3) can be presented in equivalent forms

$$\langle \phi_j \,|\, \hat{F}_i - \hat{F}_j \,|\, \phi_i \rangle = 0, \tag{15a}$$

$$\rho^j (\hat{F}_i - \hat{F}_j) \rho^i = 0, \tag{15b}$$

from which it follows that Eq. (3) expresses the variational conditions *among the occupied orbitals*. These conditions are included in the component $\hat{R}_{(2)}$ of (8). From Eq. (15) it follows that the component $\hat{R}_{(2)}$ is non-trivial only in the open shell systems. For the closed-shell systems all Fock operators $\hat{F}_i$ are equal to each other, and hence, $\hat{R}_{(2)} \equiv 0$.

From Eqs. (13)-(15) it follows that the definition of the HF Hamiltonian $\hat{R}$ in form (6)-(8) includes *all necessary variational conditions* imposed by Euler equations (2)-(3). This definition derived for the first time by Dyadyusha and Kuprievich [7] and later and independently by Hirao and Nakasuji [8] has played a significant role in the development of the general formulation of the ROHF method and later of the MC SCF method [2]. Unfortunately, the work [7] remained unknown in the West for a long time, and therefore discussions on the general structure of the Hamiltonian in the ROHF

method lasted continuously until the publication of [8]. Detailed bibliography on this problem covering the period since 1960 to 1976 is given in the monograph [2].

A principally important point in the definition of the HF Hamiltonian in form (6)-(8) is that the variational conditions included in $\hat{R}$ are consistent with Brillouin's theorem [10]. With regard to the importance of this fact let us consider it in more detail by the example of high-spin half-filled open-shell systems. These systems (designated here by the letter X) are described in the ROHF method by a one-determinant wave function and are characterized by two Fock operators (4); $\hat{F}_c$ for the closed shell ($\hat{F}_k = \hat{F}_c$) and $\hat{F}_o$ for the open shell ($\hat{F}_m = \hat{F}_c$)

$$\hat{F}_c = \hat{h} + (2\hat{J}_c - \hat{K}_c) + f(2\hat{J}_o - \hat{K}_o), \tag{16a}$$

$$\hat{F}_o = f[\hat{h} + (2\hat{J}_c - \hat{K}_c) + f(2a\hat{J}_o - b\hat{K}_o)], \tag{16b}$$

where, in this case, $f = 1/2$, $a = 1$, $b = 2$ [1]. The substitution of (16) into equations (7) and (8) shows that when the convergence is achieved, i.e. at $\hat{R}_{pq} = \delta_{pq}\varepsilon_p$, the following equalities are satisfied (at arbitrary non-zero τ_i and λ_{ij} coefficients)

$$\langle \phi_k \mid \hat{F}_c \mid \phi_v \rangle = 0, \tag{17a}$$

$$\langle \phi_m \mid \hat{F}_o \mid \phi_v \rangle = 0, \tag{17b}$$

$$\langle \phi_k \mid \hat{F}_c \mid \phi_m \rangle = 0. \tag{17c}$$

These equalities also follow from Brillouin's theorem [10], in accordance with which the matrix elements $\langle \Psi_0 | \hat{H} | \Psi^* \rangle$ of the total many-electron Hamiltonian $\hat{H}$ on the wave functions of the ground Ψ_0 and singly excited states Ψ^* become zero if Ψ_0 both Ψ_0 and Ψ^* are formed using the Hartree-Fock orbitals $\{\phi_p\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_u\}$, which are optimal for the ground state of the system X. The relationship beyween equations (17) and Brillouin's theorem is discussed in in more detail [8]. Note also that the theorem [10] was primarily formulated for the closed shell systems for which a set of equations (17) is reduced to Eq. (17a) with the operator $\hat{F}_c$ (16) and $f = 0$.

DISADVANTAGES OF THE EXISTING DEFINITIONS OF $\hat{R}$

As noted above, variational conditions (2)-(3) are completely included in definition (6) of $\hat{R}$ in the form $\hat{R}_{(1)}$ and $\hat{R}_{(2)}$. From here it follows that the component $\hat{R}_{(3)}$ is not related to the variational principle and its appearance in definition (6) is due to other reasons. Let us discuss briefly the meaning of the component $\hat{R}_{(3)}$ and its definitions (11)-(12) obtained in [7, 8].

First of all, let us note that if $\hat{R}_{(3)} = 0$ in Eq. (6), then all eigenvalues of the HF Hamiltonian $\hat{R}$, i.e. orbital energies, vanish. The latter follows from that the operators $\hat{R}_{(1)}$ and $\hat{R}_{(2)}$ determine the matrix elements of the Hamiltonian $\hat{R}$ only between the orbitals from different shells. In the full matrix of the Hamiltonian $\hat{R}$ all these elements are off-diagonal, and hence, are zero in the self-consistent limit. From here it follows that all eigenvalues $\hat{R}$ are zero if $\hat{R}_{(3)} = 0$. Just in order to separate the orbitals with different orbital energies the additional *non-zero* component $\hat{R}_{(3)}$ was introduced. Omitting the argumentation [7, 8] underlying definitions (11)-(12) of $\hat{R}_{(3)}$, let us focus on the main consequencies following from these definitions.

From definition (11) obtained by Dyadyusha and Kuprievich [7] it follows that only the diagonal elements of the operator $\hat{R}_{(3)}$ are non-vanishing

$$(\hat{R}_{(3)})_{pq} = \delta_{pq}\hat{B}_{pq}, \tag{18}$$

where, let us recall, $\hat{B}$ is an *arbitrary non-zero* operator. From alternative definition (12) derived by Hirao and Nakasuji [8] it follows:

$$(\hat{R}_{(3)})_{ij} = \delta_{ij}(\hat{F}_i)_{ii}, \qquad (\hat{R}_{(3)})_{uw} = \sum_i (\hat{F}_i)_{uw}, \qquad (\hat{R}_{(3)})_{jw} = 0, \tag{19}$$

where the indices u and w enumerate the virtual orbitals. Thus, the definitions of $\hat{R}_{(3)}$ in forms (11)-(12) impose *strict restrictions* on the matrix elements of the total one-electron Hamiltonian $\hat{R}$ between the orbitals from the same shell, i.e. on the matrix elements of the kind $\langle\phi_k|\hat{R}|\phi_l\rangle$, $\langle\phi_m|\hat{R}|\phi_n\rangle$, and $\langle\phi_u|\hat{R}|\phi_w\rangle$.

Restrictions (18)-(19) following from (11)-(12) *are not dictated by any physical conditions* and this is the main disadvantage of the definitions of $\hat{R}$ [7, 8]. It should be emphasized here that in the cases when the desired results of the ROHF calculation are only the total energy and electron densities, the calculations performed by the methods [7, 8] are certainly correct. However, due to rigid restrictions (18)-(19), the definitions of $\hat{R}$ [7, 8] do not make it possible to eliminate the principal disadvantage of the ROHF method consisting in that the ROHF orbitals are defined only up to a unitary transformation in the respective shells, and the eigenvalues of $\hat{R}$ (orbital energies) are defined ambiguously (not uniquely), and hence, do not obey fundamental KT [9].

GENERAL VIEW OF THE COMPONENT $\hat{R}_{(3)}$ AND KOOPMANS' THEOREM

From the above it follows that the symmetric (Hermitian) matrix of total HF Hamiltonian $\hat{R}$ (6) defined in the molecular orbital basis has a specific block structure in which the elements of each block are determined by different components of $\hat{R}$

$$
\begin{array}{c}
 \quad \text{Closed (c)} \quad \text{Open (o)} \quad \text{Virtual (v)} \\
\begin{array}{c}c\\[1em]o\\[1em]v\end{array}
\left\|
\begin{array}{c:c:c}
\hat{R}_{(3)} & \hat{R}_{(2)} & \hat{R}_{(1)} \\ \hdashline
 & \hat{R}_{(3)} & \hat{R}_{(1)} \\ \hdashline
 & & \hat{R}_{(3)}
\end{array}
\right\|
\end{array}. \tag{20}
$$

The dimensions of the diagonal blocks in (20) are $N_c \times N_c$, $N_o \times N_o$, and $N_v \times N_v$, where N_c, N_o, and N_v are the numbers of orbitals in the open, closed, and virtual shells respectively. For the particular case of high-spin half-filled open shell systems (system X), this matrix takes the form [11, 12]

$$
\begin{array}{c}
 \quad \text{Closed (c)} \quad \text{Open (o)} \quad \text{Virtual (v)} \\
\begin{array}{c}c\\[1em]o\\[1em]v\end{array}
\left\|
\begin{array}{c:c:c}
\hat{R}_{(cc)} & 2(\hat{F}_c - \hat{F}_o) & \hat{F}_c \\ \hdashline
 & \hat{R}_{(oo)} & 2\hat{F}_o \\ \hdashline
 & & \hat{R}_{(vv)}
\end{array}
\right\|
\end{array}, \tag{21}
$$

where the explicit form of operators in the non-diagonal blocks is found by Eqs. (7)-(8) with the use of the following arbitrary coefficients: $\tau_k = \tau_c = 1$, $\tau_m = \tau_o = 2$, $\tau_k = \lambda_{co} = 2$ (the choice of these coefficients is explained in [12]). The explicit form of the operators in diagonal blocks of (21) is discussed below.

In systems with a larger number of open shells matrix (21) has a more complex structure. For example, for non-Roothaan d^N terms [13] appearing in atoms with the configuration d^N at $2 \le N \le 8$, the number of open shells is 5 (each d orbital is considered as a separate shell), and the Fock operators $\hat{F}_m$ [Eq. (4)] are not equal to each other for these shells

$(\hat{F}_{m1} \neq \hat{F}_{m2} \neq \ldots \neq \hat{F}_{m5})$. Nonetheless, the elements of all non-diagonal blocks are determined similarly, i.e. as matrix elements of the operators $\hat{R}_{(1)}$ and $\hat{R}_{(2)}$.

The elements of the diagonal blocks in (21) designated as $\hat{R}_{(ss)}$ ($s =$ c, o, v) are determined by the component $\hat{R}_{(3)}$. In accordance with the above mentioned, this component cannot be derived from the variational principle, and hence, can be arbitrary. The only restriction is that the Hermitian operator $\hat{R}_{(3)}$ must be totally symmetric [13], and its elements are determined only in respective diagonal blocks (21). Strict restrictions (18)-(19) are excessive and must be removed. With regard to this, the general expression for $\hat{R}_{(3)}$ in equation (6) can be presented in the form

$$\hat{R}_{(3)} = \sum_k \sum_l \rho^k \hat{R}_{(cc)} \rho^l + \sum_m \sum_n \rho^m \hat{R}_{(oo)} \rho^n + \sum_u \sum_w \rho^u \hat{R}_{(vv)} \rho^w = \sum_s \sum_{i_s} \sum_{j_s} \rho^{i_s} \hat{R}_{(ss)} \rho^{j_s}, \tag{22}$$

where i_s and j_s are the indices for the orbitals from the same electron shell s ($s =$ c, o, v), and $\hat{R}_{(ss)}$ are *arbitrary non-zero* Hermitian operators.

The principal distinction of definition (22) from previous (11)-(12) is that it does not impose any restrictions on diagonal operators $\hat{R}_{(ss)}$ (21). This enables their determination based on various physical conditions. As was shown for the first time in [12], the operators $\hat{R}_{(ss)}$ can be defined from the *additional variational conditions* imposed by KT [9]. The latter makes it possible to obtain the Hartree–Fock orbitals and orbital energies having a physical meaning [12, 14-17].

A detailed discussion of all conditions related to the KT formulation in the ROHF method is beyond the scope of this paper. It is worth noting here that at present in the literarure there are *mutually exclusive statements* about the validity of KT in the ROHF method. Thus, in [18, 19] and recent monographs [20, 21] it is insisted that KT in its exact (variational) meaning is not satisfied in the ROHF method. On the other hand, in [22-28] it is shown that KT is partially fulfilled in the ROHF method, at least for some ionization processes. A detailed analysis of the results of [18-28] and the exact formulation of additional variational conditions imposed by KT on the ROHF orbitals is given in [12, 14-16].

Let us consider these conditions by the example of the above systems X in which six different one-electron processes $X \rightarrow X_{p,\sigma}^{\pm}$, where σ is the spin of the removed or attached electron ($\sigma = \alpha$ or β) and p is the number of the corresponding orbital, are possible. When the β electron is removed from the closed shell ($X \rightarrow X_{k,\beta}^{+}$ process), the generally accepted formulation of KT has the form

$$\varepsilon_k = -I_k^{\beta}, \tag{23}$$

where I_k^{β} is the vertical ionization potential determined in Koopmans' approximation [9], i.e. as an energy difference between the ground state $E_{ROHF}(X)$ and the $X_{k,\beta}^{+}$ cation defined in the frozen orbital approximation

$$I_k^{\beta} = E_{frozen}(X_{k,\beta}^{+}) - E_{ROHF}(X), \tag{24}$$

$$E_{frozen}(X_{k,\beta}^{+}) = \langle \Psi(X_{k,\beta}^{+}) | \hat{H} | \Psi(X_{k,\beta}^{+}) \rangle, \tag{25}$$

where, in this case, $\Psi(X_{k,\beta}^{+})$ is the one-determinant wave function obtained from the ground state wave function $\Psi_{ROHF}(X)$ by removing the spin-orbital $\overline{\varphi}_k = (\phi_k, \beta)$.

The main difficulty in the formulation of KT in the ROHF method (in comparison with a similar problem in the *canonical* HF method for the closed shells [6]) is that the ROHF Hamiltonian $\hat{R}$ (equations (6) and (21)) and its eigenvalues ε_p are defined ambiguously (non-uniquely), while the respective orbitals $\{\phi_p\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$ are defined only up to a unitary transformation within the corresponding shells. Consequently, both ion energy (25) and ionization potential (24) depend on a particular choice of orbitals $\{\phi_p\}$, and hence are not physically defined values.

Fundamental Koopmans' condition [9] underlying KT is that the frozen orbitals $\{\phi_i\}$ optimal for X must also be optimal (the best in the variational meaning) for the considered $X_{k,\beta}^+$ ion. The latter means that energy (25) must have the minimum (stationary) value with respect to the choice of orbitals in the frozen orbital subspaces $\{\phi_k\}$, $\{\phi_m\}$, and $\{\phi_v\}$ obtained by the ROHF method for the system X under study.

It is easy to see that $X_{k,\beta}^+$ ion energy (25) depends on the choice of the orbitals $\{\phi_l\}$ belonging to the ionized electron shell c $(l \subset c)$ and does not depend on the choice of the orbitals $\{\phi_m\}$ and $\{\phi_v\}$ from the other two (non-ionized) shells. From here it follows that energy (25) must be stationary with respect to variation of the orbitals $\{\phi_l\}$ in the ionized shell c (at frozen orbitals $\{\phi_m\}$ and $\{\phi_v\}$). The latter condition can be expressed in the form of the variational condition imposed on the orbitals $\{\phi_l\}$ of the closed shell [12, 16],

$$\delta E_{\text{frozen}}(X_{k,\beta}^+)[\phi_l] = 0, \qquad (k, l \subset c). \tag{26}$$

This condition is additional to the conditions imposed on the molecular orbitals by variational principle (2)-(3).

As was shown for the first time in [12], condition (26) determines the operator $\hat{R}_{(cc)}$ in the diagonal block of matrix (21) and in the expression for the component $\hat{R}_{(3)}$ in (22)

$$\hat{R}_{(cc)} = 2(\hat{F}_c - \hat{F}_o). \tag{27}$$

The operators $\hat{R}_{(oo)}$ and $\hat{R}_{(vv)}$ are defined similarly, i.e. from the energy stationarity condition for the corresponding $X_{p,\sigma}^\pm$ ions appearing in the open and virtual shells [12, 15].

Variational condition (26) and its analogues for other electron shells represent the *exact (variational) formulation of KT in the* ROHF *method*. These conditions define operators $\hat{R}_{(ss)}$ (27) included in component $\hat{R}_{(3)}$ (22), and thus determine the special (*canonical*) form of ROHF Hamiltonian $\hat{R}$ (21) [12, 15]. The eigenvalues of this Hamiltonian *necessarily* satisfy Koopmans' relationhips $\varepsilon_i = -I_i$ and $\varepsilon_v = -A_v$ [12], where A_v is the vertical electron affinity. The eigenvectors of $\hat{R}$ (*canonical* ROHF *orbitals*) are simultaneously the natural orbitals in the limited configuration interaction method [14, 15] and Dyson's orbitals [16]. These features of the canonical ROHF solutions are completely similar to those in the *canonical* Hartree–Fock method for the closed-shell systems [6].

Concluding the discussion of the new definition of contribution $\hat{R}_{(3)}$ (22) to total Hartree-Fock Hamiltonian (6) let us note a number of points concerning the generality of this definition:

(*i*)   As shown above, a representation of $\hat{R}_{(3)}$ in form (22) eliminates the restrictions in the ROHF method on the account of additional variational conditions imposed by KT. Recall that these restrictions are caused by the previous definitions of $\hat{R}_{(3)}$ in form (11)-(12). It is worth noting that these restrictions are fully eliminated in the present approach only for high-spin half-filled open-shell systems described in the ROHF method by a one-determinant wave function (and designated in this work by the letter X). For more complex electronic systems, there arises a number of new restrictions discussed below.

(*ii*)   Both definition (22) of $\hat{R}_{(3)}$ and definition of total HF Hamiltonian $\hat{R}$ (6) do not contain spin variables, since the ROHF method [1,7,8] is based on the use of the same orbitals for electrons with different spins. For the systems X, definition (22) involves three operators $\hat{R}_{(ss)}$ ($s = $ c, o, v) whose the explicit form is defined by KT from variational condition (26) [12]. Within such a "spinless" approach, KT can be satisfied only for three (out of the six possible in the system X) one-electron processes $X \rightarrow X_{p,\sigma}^\pm$ ($p \in s$; $\sigma = \alpha$, β). This specific restriction of the approach [12] is lifted by using in Eq. (22) the spin-dependent operators $\hat{R}_{(ss)}^\alpha$ and $\hat{R}_{(ss)}^\beta$ [15,16]. The latter necessarily leads to the appearance of *two different*

sets of orbitals and orbital energies in the ROHF method (similar to that in the UHF method). The principal difference between the approach [15,16] and the UHF method is that the new (*canonical*) ROHF orbitals and orbital energies for α and β spins completely satisfy Brillouin's and Koopmans' theorems, and the total wave function is free of spin contamination.

(*iii*)   In the case of *orbitally degenerate* systems one faces new restrictions on the validity of KT in the ROHF method [29]. These restrictions are caused by the appearance of a number of states in the degenerate open-shell configuration γ^N (ground and/or ionized), some of which can have the same spin and spatial symmetry (repeated states). In these cases, the definition of $\hat{R}_{(3)}$ in form (22) remains in force, but resulting Koopmans' relationships of form (23) for ionization processes with a participation of orbitally degenerate states take a more complex form [29].

CONCLUSIONS

In this work it is shown that the general definition of the total one-electron Hamiltonian $\hat{R}$ in the ROHF method, which was derived by Dyadyusha and Kuprievich [7] and by Hirao and Nakasuji [8], cannot be agreed with the additional variational conditions imposed by KT [9]. The component $\hat{R}_{(3)}$ of total HF Hamiltonian $\hat{R}$ (6) not defined from the variational principle imposes excessively rigid restrictions on $\hat{R}$. The more general form of component $\hat{R}_{(3)}$ (22) free from this disadvantage is proposed. The new form of $\hat{R}_{(3)}$ makes it possible to include additional variational conditions imposed by KT into the general definition of $\hat{R}$ (6), and thus to eliminate the main disadvantage of the classical ROHF method [1], i.e. the nonphysical character of its one-electron characteristics (orbitals and orbital energies).

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