

On the Ordering of Orbital Energies in the ROHF Method: Koopmans' Theorem versus Aufbau Principle

B.N. Plakhutin, A.V. Novikov, N.E. Polygalova and T.E. Prokhorov

Abstract The restricted open-shell Hartree-Fock (ROHF) method in its different formulations is a standard tool used by quantum chemists for studying open-shell systems. This work presents a discussion of specific difficulties which arise in the ROHF method in those cases where the orbital energies violate the Aufbau principle (AP). The AP violations are often treated in the literature as a deficiency of both a ROHF method leading to these violations and of the respective computational results. We summarize examples of different AP violations and analyze them from the viewpoint of both Koopmans' theorem (KT) and experimental ionization potentials. We show that the main source of AP violations is a specific ordering of the ROHF orbital energies based on the orbital occupancies. In those cases, where the orbital energies obey KT, the violations of the AP reflect the physical reality. To overcome computational difficulties which arise in the iterative SCF procedure, we describe a simple and effective *orbital-energy scaling technique* which enables one to perform ROHF computations of systems violating the Aufbau principle.

Keywords Aufbau principle • Koopmans' theorem • ROHF method • Endofullerene N@C₆₀ • Atom Mn

1 Introduction

In the iterative procedure of solving the Hartree-Fock (HF) equation for the closed-shell systems [1], the orbital energies ε_i are usually ordered by their values,

Electronic supplementary material The online version of this chapter (doi:[10.1007/978-3-319-50255-7_2](https://doi.org/10.1007/978-3-319-50255-7_2)) contains supplementary material, which is available to authorized users.

B.N. Plakhutin (✉) · A.V. Novikov · N.E. Polygalova · T.E. Prokhorov
Laboratory of Quantum Chemistry, Boreskov Institute of Catalysis,
Russian Academy of Sciences, Novosibirsk 630090, Russian Federation
e-mail: Plakhutin@catalysis.ru

$\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \dots$, and electrons fill the lowest energy orbitals. At convergence, the closed-shell and virtual orbital energies, ε_k and ε_v , respectively, obey the condition

$$\varepsilon_k < \varepsilon_v \quad (1)$$

which is usually called the Aufbau principle (AP). The HF orbital energies (1) also satisfy the physically meaningful relationships following from Koopmans' theorem [2]

$$\varepsilon_k = -I_k \quad (2)$$

$$\varepsilon_v = -A_v \quad (3)$$

where I_k and A_v are the vertical ionization potential (IP) and electron affinity (EA), respectively, defined in the “frozen” orbital approximation (see below). A fulfillment of Koopmans' relationships (2)–(3) shows that the orbital energies ε_k and ε_v are well-defined quantities, and this substantiates the use of the AP (1) for ordering of the orbitals in the closed-shell HF method.

In the restricted open-shell HF (ROHF) method [3] and in its different reformulations and generalizations [4–11], the full orbital space $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$ is separated into three orbital subspaces, closed-shell $\{\phi_k\}$, open-shell $\{\phi_m\}$, and virtual $\{\phi_v\}$, characterized by the respective orbital occupancies f_i ,

$$f_k = 1; 0 < f_m < 1; f_v = 0 \quad (4)$$

The ROHF orbitals are usually ordered by their occupancies, i.e., the open-shell orbitals lie above the closed-shell (doubly occupied) orbitals and below the virtual ones. Within each of these subspaces, the orbitals are ordered by the values of the orbital energies. Based on this specific orbital ordering, it is often assumed that the ROHF orbital energies ε_i must obey the Aufbau principle, which in this case takes the form

$$\varepsilon_k < \varepsilon_m < \varepsilon_v \quad (5)$$

In practice, the ordering of the ROHF orbital energies derived for the ground state of different open-shell systems usually obeys the AP (5), however, a number of cases is known where the orbital energies violate the condition (5). The point is that the latter cases are sometimes treated as a deficiency of both a ROHF method leading to this violation and of the respective computational results [12, 13]. In the clear form this point of view was presented in Ref. [13]: “*The Aufbau principle states that electrons will fill the lowest energy orbitals first for the ground state. Computational results that predict otherwise must be view skeptically*”.

This work presents a discussion of the Aufbau principle (5) and of its violations in the ROHF method. We summarize examples of different AP violations derived with different versions of the ROHF method and analyze them from the viewpoint of both Koopmans' theorem (KT) and experimental IPs. The main result of our

treatment is that in those cases, where the orbital energies obey KT, the violations of the AP reflect the physical reality. To overcome computational difficulties which arise in the iterative SCF procedure, we describe a simple and effective *orbital-energy scaling technique* which enables one to perform ROHF computations of systems violating the Aufbau principle.

The paper is organized as follows. Section 2 presents a brief review of the present state of the art of the ROHF method and of its special (*canonical*) form [14–17], in which the orbital energies obey Koopmans’ theorem. In Sect. 3 we discuss different kinds of AP violations in the ROHF method. A description of the *orbital-energy scaling technique* is presented in Supplementary materials.

2 Theory

2.1 Total One-Electron Hamiltonian in the ROHF Method

The present-day formulation of the ROHF method is based on the familiar representation for the total electronic energy [3]:

$$E_{ROHF}(X) = 2 \sum_i f_i h_{ii} + \sum_i \sum_j f_i f_j (2a_{ij}J_{ij} - b_{ij}K_{ij}) \quad (6)$$

that involves only the Coulomb J_{ij} and exchange K_{ij} integrals and does not involve the 3- and 4-indexed electron repulsion integrals $\langle ij | kl \rangle$. In Eq. (6) and below, f_i is the occupation number (4), a_{ij} and b_{ij} are coupling coefficients characterizing the state and configuration of an open-shell system X under consideration [3]. Application of the variational principle to the energy functional (6) gives the generalized Hartree-Fock equation [3]:

$$\hat{R}|\phi_i\rangle = \varepsilon_i|\phi_i\rangle \quad (7)$$

where $\hat{R}$ is the total one-electron ROHF Hamiltonian. The most general definitions of $\hat{R}$ valid for an arbitrary unique state (non-repeating term symbol) arising from an arbitrary many-open-shell electronic configuration were derived by Dyadyusha and Kuprievich [4], and, later and independently, by Hirao and Nakatsuji [5]. The definitions [4, 5] are completely equivalent from the viewpoint of the variational principle [18], however, they are not equal to each other, and this point deserves discussion. The definitions [4, 5] can be presented in the following form:

$$\hat{R} = \hat{R}_{(1)} + \hat{R}_{(2)} + \hat{R}_{(3)} \quad (8)$$

where

$$\hat{R}_{(1)} = \sum_i \omega_i [(I - \rho) \hat{F}_i \rho^i + \rho^i \hat{F}_i (I - \rho)] \quad (9)$$

$$\hat{R}_{(2)} = \sum_i \sum_j \lambda_{ij} \rho^j (\hat{F}_i - \hat{F}_j) \rho^i \quad (10)$$

The term $\hat{R}_{(3)}$ which differs in the two definitions [4, 5] is discussed just below. In Eqs. (9)–(10): $\rho^i = |\phi_i\rangle\langle\phi_i|$, $\rho = \sum_{(k)} \rho^k + \sum_{(m)} \rho^m$, and $(I - \rho) = \sum_{(v)} \rho^v$ are the projectors; ω_i and λ_{ij} are arbitrary nonzero numbers ($\lambda_{ij} = -\lambda_{ji}$); and $\hat{F}_i$ is the Fock operator for the orbital ϕ_i [1],

$$\hat{F}_i = f_i [\hat{h} + \sum_j f_j (2a_{ij} \hat{J}_j - b_{ij} \hat{K}_j)] \quad (11)$$

The term $\hat{R}_{(1)}$ (9) expresses the variational conditions between occupied and virtual orbitals, while $\hat{R}_{(2)}$ (10) represents the variational conditions among occupied orbitals [4, 5]. All of these conditions are satisfied at convergence (see also below). For closed-shell systems, $\hat{R}_{(2)} \equiv 0$, since the Fock operators (11) for the closed-shell orbitals are all the same. The term $\hat{R}_{(3)}$ derived by Dyadyusha and Kuprievich [4] takes the form

$$\hat{R}_{(3)} = \sum_i \rho^i \hat{Q} \rho^i \quad (12)$$

where $\hat{Q}$ is an arbitrary nonvanishing Hermitian operator. The term $\hat{R}_{(3)}$ derived by Hirao and Nakatsuji [5] takes another form

$$\hat{R}_{(3)} = \sum_i \rho^i \hat{F}_i \rho^i + \sum_u \sum_w \sum_i \rho^u \hat{F}_i \rho^w \quad (13)$$

where the indices u and w refer to the virtual orbitals. To clarify the definitions (12) and (13), we present the matrix of the total ROHF Hamiltonian (8), $\hat{R}_{ij}$, defined in the molecular orbital basis $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$. For simplicity, we express this symmetric (Hermitian) matrix in terms of matrix elements of operators $\hat{R}_{(1)}$, $\hat{R}_{(2)}$, and $\hat{R}_{(3)}$,

$$\begin{array}{c} \begin{array}{c} c \\ o \\ v \end{array} \left| \begin{array}{ccc} c & o & v \\ \hline \hat{R}_{(3)} & \hat{R}_{(2)} & \hat{R}_{(1)} \\ \hline & \hat{R}_{(3)} & \hat{R}_{(1)} \\ \hline & & \hat{R}_{(3)} \end{array} \right| \end{array} \quad (14)$$

where the letters c , o , and v designate the closed-shell (c), open-shell (o), and virtual (v) orbital subspaces, respectively, i.e., $c = \{\phi_k\}$, $o = \{\phi_m\}$, and $v = \{\phi_v\}$

At convergence, matrix elements of operators $\hat{R}_{(1)}$ and $\hat{R}_{(2)}$ vanish,

$$\begin{aligned}\hat{R}_{kv} &= (\hat{R}_{(1)})_{kv} = 0 \\ \hat{R}_{mv} &= (\hat{R}_{(1)})_{mv} = 0 \\ \hat{R}_{km} &= (\hat{R}_{(2)})_{km} = 0\end{aligned}\tag{15}$$

and this provides a fulfillment of all the conditions imposed by the variational principle in the case of open-shell systems [3–5].

From the conditions (15) it follows that operator $\hat{R}_{(3)}$ standing in diagonal blocks of (14) cannot be defined from the variational principle [4, 5]. It is noteworthy that operator $\hat{R}_{(3)}$ should be nonvanishing, otherwise all eigenvalues of $\hat{R}$ (8) which are equal to eigenvalues of $\hat{R}_{(3)}$ will be equal to zero, and hence, all eigenvectors of $\hat{R}$ will be degenerate.

This arbitrariness in the choice of $\hat{R}_{(3)}$ reveals the way to take into account the additional conditions necessary to also satisfy Koopmans' theorem. As first shown by Plakhutin et al. [14], a proper form of the operator $\hat{R}_{(3)}$ whose eigenvalues obey Koopmans' relationships of the kind (2) and (3) can be derived from Kramers' variational condition underlying Koopmans' theorem [2]. A detailed discussion of Kramers' condition and of the approach [14] based on this condition is presented in Sect. 2.3.

Here we point out that the original definitions of $\hat{R}_{(3)}$ given by Eqs. (12) or (13) are not quite satisfactory [11, 19]. Offdiagonal matrix elements of $\hat{R}_{(3)}$ inside of the diagonal blocks $\hat{R}_{cc}$ and $\hat{R}_{oo}$ of the matrix (14) were postulated [4, 5] to be equal to zero, and this presents a rigid restriction which does not follow from the variational principle. A general form of $\hat{R}_{(3)}$ following from the treatment [4, 5] is as follows [19]:

$$\hat{R}_{(3)} = \sum_k \sum_l \rho^k \hat{R}_{(cc)} \rho^l + \sum_m \sum_n \rho^m \hat{R}_{(oo)} \rho^n + \sum_u \sum_w \rho^u \hat{R}_{(vv)} \rho^w = \sum_s \sum_{i_s} \sum_{j_s} \rho^{i_s} \hat{R}_{(ss)} \rho^{j_s}\tag{16}$$

where i_s and j_s are the numbers of orbitals from the orbital subspace s ($s = c, o, v$), and $\hat{R}_{(ss)}$ are *arbitrary nonvanishing* Hermitian operators.

2.2 High-Spin Half-Filled Open-Shell (HSHFOS) Systems

Here we consider in more detail the particular case of open-shell systems which is represented by high-spin half-filled open-shell (HSHFOS) systems. Within a one configuration approximation underlying the ROHF method, the HSHFOS systems are described by a one determinant wave function (similar to that in the unrestricted

HF (UHF) method [20]) and are characterized by the following values of Roothaan's open-shell coefficients f , a , and b [3],

$$f_m = f = 1/2, a_{mn} = a = 1, b_{mn} = b = 2 \quad (17)$$

The set of the Fock operators (11) characterizing HSHFOS systems is reduced to the two operators, $\hat{F}_c$ and $\hat{F}_o$, which are specific for the closed-shell and open-shell orbitals, respectively,

$$\begin{aligned} \hat{F}_c &= \hat{h} + (2\hat{J}_c - \hat{K}_c) + f(2\hat{J}_o - \hat{K}_o) \\ \hat{F}_o &= f[\hat{h} + (2\hat{J}_c - \hat{K}_c) + f(2a\hat{J}_o - b\hat{K}_o)] \end{aligned} \quad (18)$$

If arbitrary coefficients ω_i and λ_{ij} in Eqs. (9) and (10) are chosen in the form $\omega_k = \omega_c = 1$, $\omega_m = \omega_o = 2$, and $\lambda_{km} = \lambda_{co} = 2$, the operators (9) and (10) take the form $\hat{R}_{(1)} = \hat{R}_{cv} = \hat{F}_c$, $\hat{R}_{(1)} = \hat{R}_{ov} = 2\hat{F}_o$, and $\hat{R}_{(2)} = 2(\hat{F}_c - \hat{F}_o)$, respectively, and the symmetric ROHF Hamiltonian matrix (14) for HSHFOS systems takes the familiar form

$$\begin{array}{c|ccc} & c & o & v \\ \hline c & \hat{R}_{(cc)} & 2(\hat{F}_c - \hat{F}_o) & \hat{F}_c \\ \hline o & & \hat{R}_{(oo)} & 2\hat{F}_o \\ \hline v & & & \hat{R}_{(vv)} \end{array} \quad (19)$$

The diagonal operators $\hat{R}_{(ss)}$ ($s = c, o$, or v) in Eq. (19) are different in different versions of the ROHF method [3, 6–10]. As shown by Montgomery [21], the diagonal operators $\hat{R}_{(ss)}$ in the methods [3, 6–10] can be expressed in the same form

$$\hat{R}_{(ss)} = 2\{A_{(ss)}\hat{F}_o + B_{(ss)}(\hat{F}_c - \hat{F}_o)\} \quad (20)$$

where $A_{(ss)}$ and $B_{(ss)}$ are some coefficients (for details, see the manual [21] to the GAMESS suite of programs [22]). The values of these coefficients derived by Montgomery are presented in Table 1. For completeness, Table 1 also presents the

Table 1 Coefficients $A_{(ss)}$ and $B_{(ss)}$ of Eq. (20) for high-spin half-filled open-shell systems

$A_{(cc)}$	$B_{(cc)}$	$A_{(oo)}$	$B_{(oo)}$	$A_{(vv)}$	$B_{(vv)}$	ROHF Hamiltonian	
-1/2	3/2	1/2	1/2	3/2	-1/2	Roothaan	Ref. [3]
1/2	1/2	1	0	–	–	Roothaan and Bagus	Ref. [23]
1/3	2/3	1/3	1/3	2/3	1/3	McWeeny and Dierksen	Ref. [6]
1/2	1/2	1	0	1	0	Davidson	Ref. [7]
1/2	1/2	1	0	0	1	Binkley, Pople and Dobosh	Ref. [8]
1/2	1/2	1/2	1/2	1/2	1/2	Guest and Saunders	Ref. [9]
1/2	1/2	1	0	1/2	1/2	Faegri and Manne	Ref. [10]
1/2	1/2	1/2	0	1/2	1/2	Euler equations	Ref. [1]

$A_{(ss)}$ and $B_{(ss)}$ coefficients specific for the atomic ROHF method developed by Roothaan and Bagus [23] and similar coefficients characterizing the ROHF method based on direct solving the Euler equations [1] (for details, see Ref. [14]).

2.3 Koopmans' Theorem in the Closed-Shell HF and ROHF Methods

In all of the ROHF methods [3–11] treated above, the orbital energies do not obey Koopmans' theorem (KT) [2] (a fulfillment of KT was not presupposed in the derivations [3–11]). For the first time, the special (*canonical*) form of the ROHF method for HSHFOS systems, in which the orbital energies ε_k , ε_m , and ε_v satisfy the KT relationships of the kind (2) and (3) has been developed in Ref. [14]. The further elaboration and extension of the approach [14] has been given in Refs. [15–17]. Here we analyze the variational conditions underlying KT in both closed-shell HF and ROHF methods mainly following Refs. [14–17].

Before treating the validity of KT in the ROHF method, we recall that the formulation of KT in the closed-shell HF method in the form of the relationships (2) and (3) does not reveal the main (variational) essence of this theorem [14, 24]. This point deserves discussion. The validity of Koopmans' relationships (2)–(3) is due to the use in the closed-shell HF equation [1]

$$\hat{F}|\phi_i\rangle = \varepsilon_i|\phi_i\rangle \quad (21)$$

of the specific form of the one-electron effective Hamiltonian

$$\hat{F} = \hat{h} + (2\hat{J}_c - \hat{K}_c) \quad (22)$$

This form of the HF Hamiltonian derived by Fock [1] and called the *Fock operator* is the particular form of the total one-electron Hamiltonian $\hat{R}$ (8). Different particular forms of $\hat{R}$ for the closed-shell systems generate the same orbital subspaces $\{\phi_k\}$ and $\{\phi_v\}$ and the same energy $E_{HF}(X)$, however, only eigenvalues of the Fock operator (22) obey the KT relationships (2) and (3). It is why the form of the one-electron Hamiltonian in the closed-shell HF method given by Eq. (22) is called *canonical*.

To gain a better understanding of the difference between $\hat{F}$ (22) and other possible forms of the closed-shell HF Hamiltonian, we consider the expressions for I_k (2) and A_v (3) defined in Ref. [2] in the “frozen” orbital approximation (FOA):

$$I_k = E_{frozen}(X_k^+) - E_{HF}(X) \quad (23)$$

$$A_v = E_{HF}(X) - E_{frozen}(X_v^-) \quad (24)$$

$$E_{frozen}(X_j^\pm) = \langle \Psi(X_j^\pm) | \hat{H} | \Psi(X_j^\pm) \rangle, \quad (25)$$

where $E_{HF}(X)$ is the HF energy of a closed-shell system X under consideration; $X_j^\pm$ is an ion having a hole or an extra electron in the orbital ϕ_j ; $\Psi(X_j^\pm) = \Psi_{frozen}(X_j^\pm)$ is a one-determinant wave function of $X_j^\pm$ formed using the same (“frozen”) HF orbitals $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_v\}$ optimal for X ; and $\hat{H}$ is the total many-electron Hamiltonian. The energy of ions $X_j^\pm$ (25) is defined in the FOA, i.e., in a non-variational manner, and hence, depends on the choice of “frozen” orbitals $\{\phi_k\}$ and $\{\phi_v\}$ defined up to a unitary transformation in the respective orbital subspaces.

The fundamental result underlying KT is that the orbitals $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_v\}$ derived as eigenvectors of the *canonical* HF Hamiltonian $\hat{F}$ (22) for the initial (non-ionized) system X provide also the minimal (stationary) value of $E_{frozen}(X_j^\pm)$ with respect to the choice of “frozen” orbitals $\{\phi_k\}$ and $\{\phi_v\}$. This crucial result providing the variational meaning of KT in the closed-shell HF method [1] has been proved by Kramers [25].

It follows from here that the *canonical* HF orbitals $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_v\} = \{\phi^{(c)}\} \oplus \{\phi^{(v)}\}$ for a closed-shell system X obey three variational conditions. The first of them is the variational principle for the total energy

$$\delta E_{HF}(X)[\{\phi_i\}] = 0 \quad (26)$$

while two other ones represent the Kramers’ condition [25] which is imposed upon the orbitals of the respective (ionized) electronic shell in both cation X_k^+ and anion X_u^- . These two particular forms of Kramers’ condition [25] can be presented as follows [14, 17]:

$$\delta E_{frozen}(X_k^+)[\{\phi^{(c)}\}] = 0 \quad (\phi_k \in \{\phi^{(c)}\}) \quad (27)$$

$$\delta E_{frozen}(X_u^-)[\{\phi^{(v)}\}] = 0 \quad (\phi_u \in \{\phi^{(v)}\}) \quad (28)$$

where the orbitals of non-ionized electronic shells, i.e., the virtual orbitals $\{\phi^{(v)}\}$ in X_k^+ and closed-shell orbitals $\{\phi^{(c)}\}$ in X_u^- , remain “frozen” in the respective variational procedures (27) and (28).

In line with the above treatment (see Eq. (15) and the respective text), the variational principle (26) defines only the operator $\hat{R}_{(cv)}$ standing in the off-diagonal block of the closed-shell HF Hamiltonian matrix. The diagonal operators $\hat{R}_{(cc)}$ and $\hat{R}_{(vv)}$ cannot be defined from the variational principle, however, they can be defined from the conditions (27) and (28), respectively [14, 16]. It is easy to show that $\hat{R}_{(cv)}$ derived from the condition (26) takes the form $\hat{R}_{(cv)} = \omega \hat{F}$, where ω is an arbitrary nonzero coefficient, while $\hat{R}_{(cc)}$ and $\hat{R}_{(vv)}$ derived from the conditions (27) and (28) take the form $\hat{R}_{(cc)} = \hat{R}_{(vv)} = \hat{F}$. It follows from here that Kramers’ conditions (27)–(28) are

satisfied in the canonical closed-shell HF method [1], and this provides a physical meaning of the KT relationships (2) and (3).

The variational conditions (27)–(28) can be extended to open-shell systems in order to derive a special (*canonical*) form of the ROHF Hamiltonian [14], whose eigenvalues (orbital energies) obey KT. For the first time, this extension has been given in Refs. [14, 16] for the particular case of HSHFOS systems. A generalization of the approach [14, 16] to open-shell systems with arbitrary orbital occupancies and arbitrary total spin S including orbitally degenerate systems, such as atoms with configuration p^N , will be published elsewhere [26].

In HSHFOS systems under study, the full orbital space $\{\phi_i\}$ is divided into three subspaces, $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\} = c \oplus o \oplus v$ characterized by different orbital occupancies (4), and hence, there are six different one-electron processes $X \rightarrow X_{j,\sigma}^\pm$ which lead to formation of six ions: $X_{k,\alpha}^+$, $X_{k,\beta}^+$, $X_{m,\alpha}^+$, $X_{m,\beta}^+$, $X_{v,\alpha}^-$, and $X_{v,\beta}^-$, where $\sigma = \alpha$ or β is the spin of a removed (attached) electron. The full set of the variational conditions imposed upon the canonical ROHF orbitals in HSHFOS systems involves the variational principle for the total energy

$$\delta E_{ROHF}(X)[\{\phi_i\}] = 0 \quad (29)$$

and six conditions, each of which is imposed upon the energy of the respective ion defined in the FOA. These six conditions can be presented in the form [14, 17]:

$$\delta E_{frozen}(X_{j,\sigma}^\pm)[\{\phi^{(s)}\}] = 0, \quad (j \in s) \quad (30)$$

where $s = c, o, \text{ or } v$, and, $\sigma = \alpha \text{ or } \beta$

In line with the above treatment (see Eq. (15) and the respective text), the variational principle (29) defines only the operators $\hat{R}_{(co)}$, $\hat{R}_{(cv)}$, and $\hat{R}_{(ov)}$ standing in the off-diagonal blocks of the matrix (19). The fundamental meaning of the conditions (30) is that each of them defines the respective diagonal operator $\hat{R}_{(ss)}^\sigma$ in Eq. (19), whose eigenvalues obey Koopmans' theorem. An explicit form of operators $\hat{R}_{(ss)}^\sigma$ is presented below.

As proved in Refs. [14, 16], if the ROHF orbitals $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$ used to evaluate the energies $\delta E_{frozen}(X_{j,\sigma}^\pm)$ in Eq. (30) obey the variational principle (29), the eigenvalues of each of the operators $\hat{R}_{(ss)}^\sigma$ derived from the respective condition (30) obey the following Koopmans' relationship:

$$\begin{aligned} \hat{R}_{(cc)}^\alpha: \quad \varepsilon_k^\alpha &= -I_k^\alpha \\ \hat{R}_{(oo)}^\alpha: \quad \varepsilon_m^\alpha &= -I_m^\alpha \\ \hat{R}_{(vv)}^\alpha: \quad \varepsilon_v^\alpha &= -A_v^\alpha \end{aligned} \quad (31)$$

and

$$\begin{aligned}
\hat{R}_{(cc)}^\beta: \quad \epsilon_k^\beta &= -I_k^\beta \\
\hat{R}_{(oo)}^\beta: \quad \epsilon_m^\beta &= -A_m^\beta \\
\hat{R}_{(vv)}^\beta: \quad \epsilon_v^\beta &= -A_v^\beta
\end{aligned} \tag{32}$$

It follows from (31)–(32) that the conditions (30) define two different operators, $\hat{R}_{(ss)}^\alpha$ and $\hat{R}_{(ss)}^\beta$, for each orbital subspace s . These two operators provide a fulfillment of KT for two respective one-electron processes which are possible in the electronic shell s . From here it follows that the conditions (29)–(30) define *two different ROHF Hamiltonians*, which we denote $\hat{R}^I$ and $\hat{R}^{II}$ [17].

The matrices of these two Hamiltonians take the same form (19) and differ from each other only in diagonal blocks. The triples of diagonal operators $\hat{R}_{(ss)}^\sigma$ ($s = c = o, v$) entering each of the Hamiltonians $\hat{R}^I$ and $\hat{R}^{II}$ can be different [14, 16, 17], for example,

$$\hat{R}^I = (\hat{R}_{(cc)}^\beta, \hat{R}_{(oo)}^\alpha, \hat{R}_{(vv)}^\alpha) \tag{33a}$$

$$\hat{R}^{II} = (\hat{R}_{(cc)}^\alpha, \hat{R}_{(oo)}^\beta, \hat{R}_{(vv)}^\beta) \tag{33b}$$

or

$$\hat{R}^I = (\hat{R}_{(cc)}^\alpha, \hat{R}_{(oo)}^\alpha, \hat{R}_{(vv)}^\alpha) \tag{34a}$$

$$\hat{R}^{II} = (\hat{R}_{(cc)}^\beta, \hat{R}_{(oo)}^\beta, \hat{R}_{(vv)}^\beta) \tag{34b}$$

(See also Table 2). This specific ambiguity of $\hat{R}^I$ and $\hat{R}^{II}$ follows from that the three diagonal operators of a ROHF Hamiltonian are, by definition, independent of each other [see also Eq. (16)]. Below we will specify the diagonal blocks of $\hat{R}^I$ and $\hat{R}^{II}$ by referring to the respective definitions (33a), (33b) or (34a), (34b). In the particular

Table 2 Coefficients $A_{(ss)}^\sigma$ and $B_{(ss)}^\sigma$ of Eq. (37) characterizing a one-electron process $X \rightarrow X_{j,\sigma}^\pm$ ($j \in s$) in HSHFOS systems with the total electronic spin S

$A_{(cc)}^\sigma$	$B_{(cc)}^\sigma$	$A_{(oo)}^\sigma$	$B_{(oo)}^\sigma$	$A_{(vv)}^\sigma$	$B_{(vv)}^\sigma$	Canonical ROHF Hamiltonian	
$X \rightarrow X_{k,\beta}^+$		$X \rightarrow X_{m,\alpha}^+$		$X \rightarrow X_{v,\alpha}^-$			
0	1	1	0	1	0	Plakhutin, Gorelik and Breslavskaya	Ref. [14]
$X \rightarrow X_{k,\alpha}^+$		$X \rightarrow X_{m,\beta}^-$		$X \rightarrow X_{v,\beta}^-$			
$\frac{2S+1}{2S}$	$\frac{-1}{2S}$	0	1	$\frac{-1}{2S}$	$\frac{2S+1}{2S}$	Davidson and Plakhutin	Ref. [16]

case, where the triples of diagonal operators $\hat{R}_{(ss)}^\sigma$ are chosen in the form (34a), (34b), the ROHF Hamiltonians $\hat{R}^I$ and $\hat{R}^{II}$ can be designated $\hat{R}^\alpha$ and $\hat{R}^\beta$, respectively [17].

The eigenvectors and eigenvalues of $\hat{R}^I$ and $\hat{R}^{II}$ represent *two sets of the canonical ROHF orbitals and orbital energies* [14, 16]. These characteristics can be derived by solving two different and independent (uncoupled) HF equations [16, 17],

$$\hat{R}^I |\phi_i^I\rangle = \varepsilon_i^I |\phi_i^I\rangle \quad (35)$$

$$\hat{R}^{II} |\phi_i^{II}\rangle = \varepsilon_i^{II} |\phi_i^{II}\rangle \quad (36)$$

A detailed discussion of the structure of solutions of Eqs. (35)–(36) is presented in Ref. [17]. Here we note that each of these equations can be solved using the usual iterative procedure. In this work, Eqs. (35) and (36) are solved using the general ROHF algorithm for HSHFOS systems implemented in the GAMESS program [21, 22] and the *orbital-energy scaling technique* described in Supplementary materials. When treating the AP violations in different open-shell systems (see Sect. 3) we present either both sets of the orbital energies derived by Eqs. (35)–(36) or only one of them derived by Eq. (35) with the use of the diagonal operator $\hat{R}^I$ (33a) [14].

As shown in Refs. [14, 16], the diagonal operators $\hat{R}_{(ss)}^\sigma$ (31)–(32) derived from the variational conditions (30) can be expressed in the above form (20)

$$\hat{R}_{(ss)}^\sigma = 2\{A_{(ss)}^\sigma \hat{F}_o + B_{(ss)}^\sigma (\hat{F}_c - \hat{F}_o)\} \quad (37)$$

where $A_{(ss)}^\sigma$ and $B_{(ss)}^\sigma$ are characteristic coefficients of the *canonical* ROHF method. It is worth noting that despite of a formal analogy between the definitions (37) and (20), there is a principal difference between them. The operators $\hat{R}_{(ss)}^\sigma$ (37) are derived from the physically meaningful conditions (30), each of which provides a fulfillment of KT for the respective one-electron process $X \rightarrow X_{j,\sigma}^\pm$ (31)–(32), while the operators $\hat{R}_{(ss)}$ (20) and their eigenvalues have not a physical meaning. The numerical values of $A_{(ss)}^\sigma$ and $B_{(ss)}^\sigma$ (37) are presented in Table 2.

2.4 CI-Based Formulation of Koopmans' Theorem in the ROHF Method

Canonical ROHF orbitals and orbital energies derived from the extended set of the variational conditions [Eqs. (29) and (30)] can also be derived by an alternative method [15] based on a limited configuration interaction (CI) approach. This allows one to give an alternative (CI-based) formulation of KT in the ROHF method [17].

In this section we present only those formulas of the method [15, 17] which will be used in the treatment below, and refer the reader to the original work for details.

The essence of the approach [15] is that a system X under study is treated within a ROHF method, while ions $X_{j,\sigma}^{\pm}$ are treated within the ORMAS-CI (Occupation Restricted Multiple Active Space-CI) method [27]. The starting orbitals in the CI treatment are ROHF orbitals $\{\phi_i\}$ which are optimal for X and are derived by *any* ROHF method. The approach [15, 17] compares the CI energy of ion $X_{j,\sigma}^{\pm}$ derived with the ORMAS-CI method, $E_{CI}(X_{j,\sigma}^{\pm})$, and the energy $E_{frozen}(X_{j,\sigma}^{\pm})$ evaluated using the “frozen” ROHF orbitals $\{\phi_i\}$.

It has been shown [15] that the minimal (stationary) value of $E_{frozen}(X_{j,\sigma}^{\pm})$, as the latter is defined by the condition (30), is equal to the energy $E_{CI}(X_{j,\sigma}^{\pm})$,

$$E_{frozen}(X_{j,\sigma}^{\pm})_{\min} = E_{CI}(X_{j,\sigma}^{\pm}) \quad (38)$$

Based on this result, it has been proved that the *canonical* ROHF orbital energies $\epsilon_j^{\sigma}(X)$ for a system X under study obeying the KT relationships (31) and (32), and the energies $E_{CI}(X_{j,\sigma}^{\pm})$ are connected by the fundamental relationship [15, 17]

$$\epsilon_j^{\sigma}(X) = \pm \{ -E_{CI}(X_{j,\sigma}^{\pm}) + E_{ROHF}(X) \} \quad (39)$$

where the two upper or the two lower signs must be taken together.

In the present work, the relationship (39) will be used for independent verification of the results derived with the canonical ROHF method in those cases where the orbital energies obeying KT (31)–(32) violate the Aufbau principle (5).

3 Violations of the Aufbau Principle

The well-known deficiency of the ROHF method [3–11] is that the orbital energies are defined ambiguously [3]. This ambiguity can lead and, in some cases, does lead to violations of the AP (5) [17]. Moreover, an ambiguity of the ROHF orbital energies is sometimes treated as a single source of AP violations (see, for example, Ref. [13]). In this section we discuss violations of the AP which arise in ROHF calculations of two open-shell systems, endofullerene $N@C_{60}(I_h)$ and atom Mn. The AP violations in these two systems have been revealed many years ago (see below), however, as pointed out in Refs. [15, 28], these violations cannot be treated as well-substantiated, since the ROHF orbital energies derived for these systems generally do not obey KT. In this work we perform a detailed study of the discussed AP violations using two different ROHF approaches presented in Sects. 2.3 and 2.4.

3.1 Atom N and Endofullerene N@C₆₀ (*I_h*)

The geometry and electronic structure of endofullerene N@C₆₀ (*I_h*) has been studied by different experimental and theoretical methods (for review and bibliography, see Ref. [29]). By now, the main features of the electronic structure of N@C₆₀ are well established. The ground state of this molecule is ⁴A_u arising from the electronic configuration [... 6h_u¹⁰ 7t_{1u}³]. The three-fold degenerate open-shell orbitals 7t_{1u} are practically pure atomic 2p_N orbitals, and so the encapsulated nitrogen keeps its atomic electronic configuration [... 2p³]. The highest in energy closed-shell orbitals 6h_u of N@C₆₀ are essentially the orbitals of the cage C₆₀ (*I_h*).

Together with this, the quantum chemical data for N@C₆₀ derived in previous years with different quantum chemical methods were essentially different (for discussion and bibliography, see Refs. [28–30]). Of particular interest is the ROHF results [30] derived using the quantum chemical program Turbomole [31]. From computations [30] it follows that the orbital energy $\varepsilon(7t_{1u})$ and a number of closed-shell orbital energies ε_k including $\varepsilon(6h_u)$ for N@C₆₀ obey the relationship $\varepsilon(6h_u) > \varepsilon_k$, and thus, violate the AP (5). It was assumed in Ref. [30] that the ROHF orbital energies derived with program Turbomole [31] obey KT, and hence, the discussed AP violation is well-substantiated. However, these two related assumptions [30] deserve discussion.

To clarify the AP violation in N@C₆₀ following from computations [30], this work presents the orbital energies $\varepsilon(7t_{1u})$ and $\varepsilon(6h_u)$ for N@C₆₀ derived with different ROHF methods. (The other orbital energies for N@C₆₀ are not presented explicitly since those values are of little interest in a treatment below). To gain a better understanding of the source of the discussed AP violation [30], we also present the ROHF orbital energies for the free nitrogen atom N. All computations were performed with the GAMESS program using the coefficients $A_{(ss)}$ and $B_{(ss)}$ from Table 1 and similar coefficients $A_{(ss)}^\sigma$ and $B_{(ss)}^\sigma$ from Table 2. In the iterative SCF procedure for N@C₆₀ these coefficients were scaled as described in Supplementary materials. Computations of N@C₆₀ (and, for comparison, of C₆₀) were performed using the geometry of the cage C₆₀ taken from Ref. [30]: $R_{CC} = 1.4507$ Å (C–C bond in regular pentagons) and $R_{CC} = 1.3906$ Å (a shorter C–C bond in hexagons). Icosahedral symmetry was retained in all calculations.

The results of calculations for atom N and endofullerene N@C₆₀ are presented in Table 3. To compare the full orbital energy spectra for N@C₆₀ derived with different ROHF methods, Fig. 1 presents a schematic representation of these spectra and compares them with the respective data for two constituents of N@C₆₀ (*I_h*), i.e., for fullerene C₆₀ (*I_h*) and atom N.

An inspection of the data presented in Table 3 allows one to make a number of conclusions. First, we note that the open-shell orbital energies $\varepsilon(2p)$ for atom N and the orbital energies $\varepsilon(7t_{1u})$ for N@C₆₀ derived with different ROHF methods vary over wide limits. Both these variations and a similar one for the closed-shell orbital energy $\varepsilon(2s)$ in atom N are caused by ambiguity of the orbital energies in the

Table 3 ROHF orbital energies (eV) for atom N ($^4S, 1s^2 2s^2 2p^3$), and endohedral N@C₆₀($^4A_u, \dots, 6h_u^{10} 7t_u^3$), derived with the use of different versions of the ROHF method, and experimental IPs for atom N. Basis set 6-31G (5*d*). Open-shell orbital energies are marked in bold

	McWeeny and Diercksen (Ref. [6])	Roothaan (Ref. [3])	Euler equations (Ref. [1])	Faegri and Manne (Ref. [10])	Roothaan and Bagus (Ref. [23])	Canonical ROHF ^a (Ref. [14])	IPs and cation states (experim.) (Ref. [32])
N							
3 <i>s</i>	+26.352	+23.685	+26.886	+26.886	–	+25.285	
3 <i>p</i>	+24.448	+20.860	+25.166	+25.166	–	+23.013	
2 <i>p</i>	–3.218	–4.827	–7.696	–15.392	–15.392	–15.392	14.534 (3P)
2 <i>s</i>	–23.798	–14.439	–25.667	–25.667	–25.667	–20.055	20.33 (5S)
1 <i>s</i>	–425.084	–423.179	–425.467	–425.467	–425.467	–424.319	
<i>E</i> _{total} (a.u.)	–54.382051						
N@C ₆₀ (<i>I</i> _{<i>h</i>}) ^b							
7 <i>t</i> _{1u} (2 <i>p</i> _N)	–3.436			–15.701		–15.701	
6 <i>h</i> _{<i>u</i>}	–7.596			–7.595		–7.595	
<i>E</i> _{total} (a.u.)	–2326.196557			–2326.196557		–2326.196557	

^aFor brevity, we here present only one set of the canonical ROHF orbital energies derived by the method [14], i.e., ϵ_i^{β} , ϵ_i^{α} , and ϵ_i^{α} (for details, see Eq. (33a) and Table 2). The orbital energies ϵ_{2s}^{β} and ϵ_{2p}^{α} are related via KT to the IPs I_{2s}^{β} and I_{2p}^{α} , respectively, presented in the last column

^bFor comparison, we also present the orbital energy $\epsilon(6h_u)$ and experimental IP $I(6h_u)$ for molecule C₆₀ (*I*_{*h*}): $\epsilon(6h_u) = -7.593$, $I(6h_u) = 7.61$ [33]

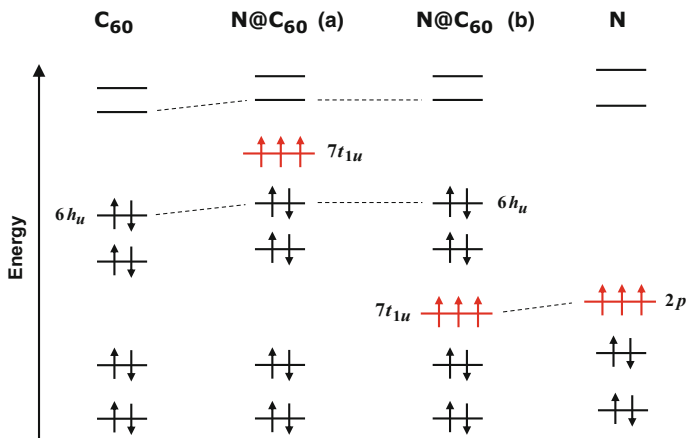


Fig. 1 Schematic representation of the spectra of ROHF orbital energies for fullerene $C_{60}(I_h)$, atom N, and endofullerene $N@C_{60}(I_h)$. The orbital energies for $N@C_{60}$ presented in the panel (a) were derived using the ROHF method [6]. The orbital energies for $N@C_{60}$ presented in the panel (b) and the orbital energies for atom N were derived using the canonical ROHF method [14]. (For details, see Table 3 and the respective text)

ROHF method [3]. Second, we point out that the open-shell orbital energies $\varepsilon(2p)$ for atom N and $\varepsilon(7t_{1u})$ for $N@C_{60}$ derived with the same ROHF method are close to each other. The latter agrees with the well-established result that the open-shell orbitals $7t_{1u}$ in $N@C_{60}$ are practically pure atomic $2p_N$ orbitals (for discussion and bibliography, see Ref. [30]).

The closest agreement between computed orbital energies for atom N and the respective experimental IPs is achieved in the canonical ROHF method [14]. This result is expected since the orbital energies [14] obey Koopmans' theorem. Of particular interest is that the orbital energy $\varepsilon(2p) = -15.392$ eV for atom N derived with the methods [10, 23] is equal to the respective energy derived with the canonical ROHF method [14]. This equality follows from that the diagonal operators $\hat{R}_{(oo)}$ in methods [10, 23] (and also in methods [7, 8]) are equal to the diagonal operator $\hat{R}_{(oo)}^\alpha$ in the canonical ROHF method [14] (for details, see Tables 1 and 2), and hence, the eigenvalues $\varepsilon(2p)$ derived with the methods [7, 8, 10, 23] are equal to each other and are equal to the orbital energy $\varepsilon(2p)$ in the method [14]. It follows from here that the open-shell orbital energies ε_m for HSHFOS systems, such as $N@C_{60}$ or atom Mn, derived by the methods [7, 8, 10, 23] satisfy the KT relationship $\varepsilon_m = -I_m^\alpha$ (31), although a fulfillment of KT was not presupposed in the derivations [7, 8, 10, 23].

As compared to this, the closed-shell orbital energy $\varepsilon(2s)$ for atom N derived by the methods [4–10, 23] is not equal to the respective canonical ROHF orbital energy [14], and hence, the closed-shell orbital energies in the methods [4–10, 23] do not obey KT. This conclusion clarifies the assumption [30] that the ROHF orbital energies for $N@C_{60}$ derived with program Turbomole [31] obey KT.

The ROHF method used in computations [30] is the method [10] developed by Faegri and Manne and implemented in program Turbomole. The latter means that the assumption [30] is correct only partially.

From Table 3 it follows, that the canonical ROHF orbital energies $\varepsilon(6h_u)$ and $\varepsilon(7t_{1u})$ in N@C₆₀ obey the relationship $\varepsilon(6h_u) > \varepsilon(7t_{1u})$ and hence, violate the AP (5). This result based on Koopmans' theorem confirms the prediction [30]. Unfortunately, this result cannot be verified by direct comparison of these orbital energies with the respective experimental IPs. To our best knowledge, the observed IPs $I(7t_{1u})$ and $I(6h_u)$ for N@C₆₀ are unavailable in the literature. However, taking into account that the canonical ROHF method [14] obeying KT gives good estimates for both open-shell and highest closed-shell orbital energies in atom N, we believe that the AP violation in N@C₆₀, following from the canonical ROHF calculations, can be considered as well-substantiated.

To complete this treatment, we should comment the form of the orbital energy spectrum for N@C₆₀ presented in the panel (b) of Fig. 1. This spectrum shows that the open-shell energy level $\varepsilon(7t_{1u})$ lies below a number of closed-shell energy levels. If all the canonical ROHF orbital energies in N@C₆₀ are ordered by their values ($\varepsilon_1 < \varepsilon_2 < \varepsilon_3 \dots$, i.e., are presented in the form shown in the panel (b) of Fig. 1, the highest occupied five-fold degenerate orbitals $6h_u$ and open-shell orbitals $7t_{1u}$ take the numbers $k = 181, 182, \dots, 185$, and $m = 143, 144, 145$, respectively. It follows from here that the canonical open-shell ROHF orbitals $7t_{1u}$ in N@C₆₀ lie on the energy scale below the *forty* closed-shell orbitals.

3.2 Atom Mn

Violations of the Aufbau principle (5) in ROHF computations of 3d transition-metal atoms have been revealed several decades ago [34, 35]. As follows from the numerical HF computation [35] of atom Mn in its ground state ($^6S, \dots 4s^2 3d^5$), performed using Roothaan and Bagus' atomic ROHF method [23], the highest closed-shell orbital energy ε_{4s} and open-shell orbital energy ε_{3d} are equal to -0.2479 and -0.6388 (a.u.), respectively. These orbital energies satisfy the relationship $\varepsilon_{4s} > \varepsilon_{3d}$, and hence, violate the AP (5). The same violation follows from the data [34]. It should be noted, however, that this AP violation cannot be treated as well-substantiated. As follows from Tables 1 and 2, only the open-shell orbital energy ε_{3d} for atom Mn derived with the method [23] obeys KT.

This work presents a detailed treatment of the discussed AP violation in atom Mn. Table 4 presents orbital energies for atom Mn derived with different ROHF methods including the canonical ROHF method. These data are compared with both experimental IPs and orbital energies derived by the fundamental relationship (39).

Before discussing the data of Table 4 we note that the AO basis set for atom Mn [36, 37] used in this work gives the ROHF energy close to the HF limit [35], and so, all the orbital energies in Table 4 can be immediately compared with each other.

Table 4 ROHF orbital energies and experimental IPs for atom Mn (6S , $\dots$ $4s^2 3d^5$), and CI energies of ions $Mn^{\pm 1}$. Basis set (23s, 15p, 11d) from Refs. [36, 37]. Energy values in a.u. Violations of the Aufbau principle (5) are marked in bold

	Roothaan (Ref. [31])	McWeeny and Diercksen (Ref. [6])	Numerical HF (Ref. [35])	Canonical ROHF (Refs. [14, 16]) ^a		$\pm\{-E_{CI}(Mn_{i,\sigma}^{\pm 1}) + E_{ROHF}(Mn)\}^{b,c}$ (Refs. [15 and 17])		IPs and cation states (Ref. [32])
				I (α)	II (β)	$\sigma = \alpha$	$\sigma = \beta$	
Virtual						Mn^{-1}	Mn^{-1}	
4p	+0.2424	+0.2841	-	+0.2678	+0.3249	+0.2678	+0.3249	5p
5s	+0.0765	+0.0824	-	+0.0802	+0.0876	+0.0802	+0.0876	5s
Open						Mn^{+1}	Mn^{+1}	
3d					+0.3578		+0.3578	5d
Closed	-0.1406	-0.0937	-0.6388	-0.6388		Mn^{+1}	-0.6388	5d
4s	-0.2153	-0.2424	-0.2479		-0.2316	Mn^{+1}	Mn^{-1}	0.5231 (5d)
3p	-1.9903	-2.3981	-2.4795	-0.2707			-0.2316	7s
3s	-3.4162	-3.7500	-3.8166	-2.8210	-2.2351	5d	-2.2351	7s
				-4.0964	-3.6165	5p	-2.6165	7p
2p	-24.6824	-24.7908	-24.8126	-24.9047	-24.7473	5s	-24.7473	7p
2s	-28.9777	-29.0874	-29.1095	-29.2022	-29.0435	5p	-29.0435	7s
1s	-240.5325	-240.5337	-240.5340	-240.5350	-240.5332	5s	-240.5350	5s
E_{total}	-1149.866 215	-1149.866 251	-1149.866 215	-1149.866 215				

^aThe two sets of the orbital energies, I (α) and II (β), were derived by Eqs. (35) and (36), in which the diagonal parts of $\hat{R}^I$ and $\hat{R}^{II}$ are formed as shown in Eqs. (34a) and (34b), respectively
^bFor details, see Eq. (39) and the respective text
^cThe CI energies of $Mn^{\pm 1}$ were derived with the method ORMAS-CI [27]. The ROHF orbitals used to construct the CI matrices for $Mn^{\pm 1}$ were taken from the ROHF computation of the neutral atom Mn performed with McWeeny and Diercksen's method [6]

The details of a computational procedure used in computations of atom Mn are analogous to those used in computations of N@C₆₀.

From Table 4 it follows that the canonical ROHF method [14, 16] generates two different sets of orbitals and orbital energies, and so, there is some similarity between one-electron characteristics derived with the canonical ROHF [14, 16] and UHF [20] methods (see also below). The orbital energies ϵ_{3d} and ϵ_{4s} of Ref. [35] violating the Aufbau principle (5) split in the canonical ROHF method into two respective pairs of orbital energies, $(\epsilon_{3d}^\alpha \text{ and } \epsilon_{3d}^\beta)$ and $(\epsilon_{4s}^\alpha \text{ and } \epsilon_{4s}^\beta)$ where $\epsilon_{3d}^\beta > \epsilon_{4s}^\beta > \epsilon_{4s}^\alpha > \epsilon_{3d}^\alpha$. At first we consider three latter orbital energies which can be compared with the respective IPs presented in Table 4. It is easy to see that although the agreement between IPs estimated via KT and observed IPs in these three cases is just qualitative, the order of orbital energies $\epsilon_{4s}^\beta > \epsilon_{4s}^\alpha > \epsilon_{3d}^\alpha$ derived with the canonical ROHF method [14, 16] corresponds to that following from the experimental data.

Taking this into account we conclude that a fulfillment of the relationship $\epsilon_{4s}^\alpha > \epsilon_{3d}^\alpha$, which is the counterpart of the relationship $\epsilon_{4s} > \epsilon_{3d}$ [34, 35], is well-substantiated, and a violation of the AP (5) in atom Mn represented by these relationships *reflects the physical reality*.

Table 4 also reveals the second violation of the Aufbau principle in the spectrum of the canonical ROHF orbital energies [14, 16]. The open-shell orbital energy ϵ_{3d}^β and the respective virtual ones, ϵ_{5s}^β and ϵ_{4p}^β , obey the relationship $\epsilon_m^\beta > \epsilon_v^\beta$, and thus, violate the AP (5). This second violation deserves discussion. The orbital energies ϵ_{3d}^β , ϵ_{5s}^β and ϵ_{4p}^β are related via KT (31)–(32) to the vertical electron affinities (EAs). To our best knowledge, the respective experimental EAs for atom Mn are unavailable in the literature. On the other hand, the KT estimates of EAs derived within the Hartree-Fock approach usually do not agree with experimental EAs even qualitatively, and this presents a fundamental drawback, which is inherent to all Hartree-Fock methods based on a one configuration approximation (see, for example, Ref. [16]). In this situation, we should prove that the second AP violation in atom Mn taking the form $\epsilon_m^\beta > \epsilon_v^\beta$ is not the result of a deficiency of the canonical ROHF method [14, 16].

For this purpose, Table 4 presents the ROHF orbital energies derived using the fundamental relationship (39) [15, 17]. The orbital energies (39) are, by definition, **independent** of the ROHF method used, in the sense that the energy $E_{ROHF}(X)$ entering the definition (39) is the same in all ROHF methods, while the CI energies of ions $X_{j,\sigma}^\pm$ can be derived using the ROHF orbitals $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$, which are derived for a system X under study by any ROHF method.

A comparison between the orbital energies (39) and all other sets of orbital energies for atom Mn presented in Table 4 shows that the orbital energies (39) are equal in all cases to the canonical ROHF orbital energies. It allows one to conclude that the violation of the AP (5) for atom Mn, represented by the relationship $\epsilon_m^\beta > \epsilon_v^\beta$, is not caused by any deficiency of the canonical ROHF method [14–17] and thus is well-substantiated.

3.3 Discussion

The above treatment of different AP violations allows one to consider in more detail the sources of these violations. At first, we recall that in the previous (non-canonical) ROHF methods [3–11], the orbital energies are defined ambiguously [3]. Due to this ambiguity, the orbital energies can violate the Aufbau principle (5). Moreover, AP violations predicted by different ROHF methods *for the same system* can be essentially different, i.e., either $\varepsilon_k > \varepsilon_m < \varepsilon_v$ or $\varepsilon_k < \varepsilon_m > \varepsilon_v$ (for more details, see Ref. [17]). It is obvious that such violations do not reflect any reality and, in accordance with Glaesemann and Schmidt [13], must be viewed skeptically.

In the canonical ROHF method [14–17], the orbital energies obey the physically meaningful KT relationships (31)–(32). These orbital energies are obtained either as the eigenvalues of the canonical ROHF Hamiltonians (35)–(36) [14, 16] or by Eq. (39), which is the essence of the alternative (CI-based) formulation of Koopmans’ theorem [15, 17]. The violations of the Aufbau principle (5) following from the canonical ROHF computations are well-substantiated.

To clarify the source of the latter violations, we compare the canonical ROHF orbital energies ε_i^σ ($\sigma = \alpha, \beta$) for atom Mn presented in Table 4 with the respective UHF orbital energies derived in Ref. [15] (we denote the UHF orbital energies ω_i^σ). For brevity, we here consider only the orbital energies with $\sigma = \alpha$, since a treatment of the case $\sigma = \beta$ is quite similar. A comparison between ε_i^α of Table 4 and ω_i^α of Ref. [15] derived using the same AO basis set [36, 37] shows that the respective orbital energies are approximately equal to each other in all cases, i.e., $\varepsilon_i^\alpha \approx \omega_i^\alpha$.

The full set of the ROHF orbital energies, $\{\varepsilon_i^\alpha\}$, is divided into three different subsets, $\{\varepsilon_i^\alpha\} = \{\varepsilon_k^\alpha\} \oplus \{\varepsilon_m^\alpha\} \oplus \{\varepsilon_v^\alpha\}$, while the UHF orbital energies $\{\omega_i^\alpha\}$ are divided into two subsets, $\{\omega_i^\alpha\} = \{\omega_j^\alpha\} \oplus \{\omega_v^\alpha\}$, where, in this case, the index j refers to the occupied UHF orbitals. For the particular case of atom Mn, these two different divisions result in that the ROHF open-shell orbital energy ε_{3d}^α forms a separate subset $\{\varepsilon_m^\alpha\}$, while the UHF open-shell orbital energy ω_{3d}^α belongs to the subset $\{\omega_j^\alpha\}$.

Since in the UHF method all the orbital energies are ordered by their values, the orbital energies ω_{3d}^α and ω_{4s}^α belonging to the same subset obey the Aufbau principle, i.e., $\omega_{3d}^\alpha < \omega_{4s}^\alpha$. In the ROHF method, the respective orbital energies ε_{3d}^α and ε_{4s}^α belong to *different* subsets. Since the ordering of orbital energies in the ROHF method is performed separately in each subset [see Eq. (4)], the orbital energies ε_{3d}^α and ε_{4s}^α violate the AP (5), (see also Table 4). A similar explanation can be done for other AP violations displayed in Tables 3 and 4.

Based on these considerations, we conclude that the single source of violations of the AP (5) in the canonical ROHF method [14–17] is the specific separation of the occupied ROHF orbitals into the closed-shell and open-shell orbital subspaces, characterized by different orbital occupancies (4). This separation follows from the classic Roothaan’s equations [3], in line with which the variational conditions imposed upon the open-shell and closed-shell orbitals are different.

It should be noted here that violations of the Aufbau principle appearing in the canonical ROHF method [14–17] lead to well-known difficulties in a computational procedure (see also Supplementary materials to this paper), and thus, can be considered as a deficiency of the method [14–17] itself. In this respect, the UHF method [20], which is free of AP violations, seems more preferable than the method [14–17]. However, this small preference of the UHF method becomes negligible if we compare the methods [14–17, 21] in more detail.

The canonical ROHF solutions (orbitals, orbital energies, and total wave function) obey the full set of the variational and symmetrical conditions, which are imposed upon a Hartree-Fock (HF, ROHF, UHF) solution by two fundamental theorems, KT [2] and Brillouin's theorem [38] (for discussion, see Ref. [17]). In contrast to this, a fulfillment of the theorems [2, 38] in the UHF method [20] is *purely formal* [15, 17], since UHF wave functions for both a system X under study and its ionized $X_{j,\sigma}^{\pm}$ and excited $X_j \rightarrow \nu$ states generally suffer from spin contamination. The latter means that UHF wave functions do not correspond to well-defined quantum states, as is required by both Koopmans' and Brillouin's theorems.

It is worth noting that two discussed methods become completely equivalent *from the physical viewpoint* if the UHF method is presented in its special (*canonical*) form developed in Ref. [17], in which all the deficiencies of the original UHF method [20] were eliminated.

Acknowledgements We thank Prof. Ernest R. Davidson for many valuable discussions. This work was conducted within the framework of budget project No. 0303-2016-0001 for Boreskov Institute of Catalysis and was supported by the Russian Foundation for Basic Research under Grant No. RFBR 15-03-00830.

References

1. Fock VA (1930) *Zs f Phys* 61:126
2. Koopmans TA (1934) *Physica (Amsterdam)* 1:104
3. Roothaan CCJ (1960) *Rev Mod Phys* 32:179
4. Dyadyusha GG, Kuprievich VA (1965) *Theor Exp Chem* 1:262
5. Hirao K, Nakatsuji H (1973) *J Chem Phys* 59:1457
6. McWeeny R, Diercksen G (1968) *J Chem Phys* 49:4852
7. Davidson ER (1973) *Chem Phys Lett* 21:565
8. Binkley JS, Pople JA, Dobosh PA (1974) *Mol Phys* 28:1423
9. Guest MF, Saunders VR (1974) *Mol Phys* 28:819
10. Faegri K, Manne R (1976) *Mol Phys* 31:1037
11. Bouscasse L, Jaffé HH (1979) *J Chem Phys* 71:4969
12. Tsuchimochi T, Scuseria GE (2010) *J Chem Phys* 133:141102
13. Glaesemann KR, Schmidt MW (2010) *J Phys Chem A* 114:8772
14. Plakhutin BN, Gorelik EV, Breslavskaya NN (2006) *J Chem Phys* 125:204110
15. Plakhutin BN, Davidson ER (2009) *J Phys Chem A* 113:12386
16. Davidson ER, Plakhutin BN (2010) *J Chem Phys* 132:184110
17. Plakhutin BN, Davidson ER (2014) *J Chem Phys* 140:014102

18. Carbó R, Riera JM (1978) A general SCF theory. Lecture notes in chemistry, vol 5. Springer, Berlin
19. Plakhutin BN (2014) J Struct Chem 55:1001
20. Pople JA, Nesbet RK (1954) J Chem Phys 22:571
21. <http://www.msg.ameslab.gov/GAMESS/GAMESS.html>
22. Schmidt MW, Baldridge KK, Boatz JA et al (1993) J Comput Chem 14:1347
23. Roothaan CCJ, Bagus PS (1963) Methods Comput Phys 2:47
24. Huzinaga S (1983) *Metod Molekulayrnyh Orbitalей (Method of Molecular Orbitals)*. Mir, Moscow (translated from Japanese to Russian)
25. As pointed out by Koopmans in his Nobel prize lecture: <http://www.nobelprize.org/economics/laureates/1975/koopmans-autobio.html>, the proof of this result has been given by Kramers
26. Plakhutin BN (2012) Book of abstracts. In: XVII international workshop on quantum systems in chemistry and physics, Turku, Finland, 2012. Åbo Akademi University, p 23
27. Ivanic J (2003) J Chem Phys 119:9364; *ibid* (2003) 119:9377
28. Plakhutin BN, Breslavskaya NN, Gorelik EV, Arbuznikov AV (2005) J Molec Struct: THEOCHEM 727:149
29. Yang S, Wang CR (eds) (2014) Endohedral fullerenes. From fundamentals to applications. World Scientific, Singapore
30. Greer JC (2000) Chem Phys Lett 326:567
31. Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C (1989) Chem Phys Lett 162:165
32. Grigor'ev IS, Meilikhov EZ (eds) (1991) Fizicheskie velichiny (Physical quantities), Handbook, (Energo-Atom-Izdat, Moscow) (in Russian)
33. Zimmerman JA, Eyrer JR, Bach SBH, McElvany SW (1991) J Chem Phys 94:3556
34. Clementi E, Roetti C (1974) At Data Nucl Data Tables 14:177
35. Froese Fisher C (1977) The Hartree-Fock method for atoms: a numerical approach. Wiley, New York
36. Partridge H (1989) J Chem Phys 90:1043
37. <http://www.emsl.pnl.gov/forms/basisform.html>
38. Brillouin LN (1934) J Phys Radium 5:413

Quantum Systems in Physics, Chemistry, and Biology

Advances in Concepts and Applications

Tadger, A.; Pavlov, R.; Maruani, J.; Brändas, E.J.;

Delgado-Barrio, G. (Eds.)

2017, XXXIX, 449 p. 123 illus., 74 illus. in color.,

Hardcover

ISBN: 978-3-319-50254-0