Koopmans' Theorem in the Restricted Open-Shell Hartree−Fock Method. 1. A Variational Approach[†]

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A general formulation of Koopmans' theorem is derived for high-spin half-filled open shells in the restricted open-shell Hartree−Fock (ROHF) method based on a variational treatment of *both* the initial (nonionized) open-shell system under study, e.g., X, and the corresponding high-spin ions X_k^+, X_m^+, and X_v^- having a hole or an extra electron in the closed, open, and virtual shell, respectively. The ions are treated within a FCI-RAS (full CI in the restricted active space) method with a use of arbitrary ROHF orbitals optimal for the initial system. We show that the desired *canonical* ROHF orbitals and orbital energies satisfying Koopmans' theorem, first defined within the canonical ROHF treatment [Plakhutin; et al. *J. Chem. Phys.* **2006**, *125*, 204110], generally appear as the natural CI orbitals and the eigenvalues of CI matrices for the respective ions $X^\pm$. A comparison is performed between the results derived with the present CI approach and the canonical ROHF method for the specific case where the canonical orbital energies satisfying Koopmans' theorem do not satisfy the Aufbau principle.

I. Introduction

In applications of Koopmans' theorem[1] (KT) to closed-shell systems within the Hartree−Fock method this theorem is commonly formulated in the particular form

$$I_k = -\varepsilon_k \tag{1}$$

where I_k is Koopmans' approximation to the *k*th ionization potential, and ε_k is the respective eigenvalue of the Hartree−Fock (HF) equation,

$$\hat{F}\,|\theta_k\rangle = \varepsilon_k\,|\theta_k\rangle \tag{2}$$

As is known, the eq 1 represents Koopmans' theorem[1] in the particular case when the orbital energies ε_k are eigenvalues of the special (*canonical*) form for the Hartree−Fock Hamiltonian,

$$\hat{F} = \hat{h} + \sum_k (2\hat{J}_k - \hat{K}_k) \tag{3}$$

For other possible forms of the HF Hamiltonian[2−4] the eq 1 is generally not valid and, because of this, one must appeal to the general (*variational*) formulation of Koopmans' theorem in the HF method[1] which is discussed below.

The Hartree−Fock method for closed-shell systems is commonly used in the canonical form (2) and (3), and this makes the formulation of KT by eq 1 sufficient for applications. As compared to this, the restricted open-shell Hartree−Fock (ROHF) method has been worked out and implemented in various quantum chemical programs in significantly different forms (for a review and bibliography, see ref 5). The orbital energies derived with different (noncanonical) ROHF Hamiltonians vary over wide limits and generally cannot be correlated with the respective ionization potentials or electron affinities. The orbitals from these ROHF calculations differ from each other by an arbitrary unitary transformation within the closed, open, and virtual sets.

The canonical form for the ROHF Hamiltonian has been first derived by Plakhutin et al.[5] for the systems X possessing high-spin half-filled open electronic shells. By derivation, the eigenvalues of the canonical Hamiltonian[5] obey the three KT relationships corresponding to the three (of the six) one-electron ionization processes possible in such systems:

(A) a removal of a β electron from the *k*th closed-shell orbital,

$$\varepsilon_k = -I_k^\beta \tag{4a}$$

(B) a removal of an α electron from the *m*th open-shell orbital,

$$\varepsilon_m = -I_m^\alpha \tag{4b}$$

(C) an attachment of an α electron to the *v*th virtual orbital,

$$\varepsilon_v = -A_v^\alpha \tag{4c}$$

where

$$\begin{aligned} I_i &= E(X_i^+) - E_{\mathrm{ROHF}}(X) \qquad (i = k, m) \\ A_v &= E_{\mathrm{ROHF}}(X) - E(X_v^-) \end{aligned} \tag{5}$$

are the vertical ionization potentials (IPs) and electron affinities (EAs), respectively, defined in the approximation of "frozen" orbitals. The term "frozen" here means that the energies of ions, $E(X_i^+)$ and $E(X_v^-)$, are defined as the expectation value of the total many-electron Hamiltonian $\hat{H}$ with a one-determinantal wave function for the ion formed with the same (*canonical*) ROHF orbitals optimal for the parent system *X*. Below we shall denote these energies as $E_{\mathrm{frozen}}(X_i^+)$ and $E_{\mathrm{frozen}}(X_v^-)$, respectively.

For a better understanding of the essense of KT relationships (4), we should discriminate between two different conceptions: Koopmans' theorem and Koopmans' approximation. Koopmans' theorem in its exact meaning[1] is a rigorous mathematical

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theorem which states that the energy difference $\Delta E_k = E_{\text{frozen}}(X_k^+) - E_{\text{HF}}(X)$ is equal to the *canonical* HF orbital energy for the initial closed-shell system: $\Delta E_k = -\varepsilon_k$. The essense of Koopmans' approximation is that the same energy difference ΔE_k is equated to the experimental IP: $\Delta E_k = I_k$. The latter is an obvious approximation. The KT relationships (4a)−(4c) take a rigorous form if and only if the right-hand sides of (4) have the meaning of the respective energy differences ΔE_i (5) but not of the experimental IPs and EAs.[5] In the treatment below we also shall deal with Koopmans' theorem in its exact (narrow) meaning, i.e., with a rigorous mathematical theorem.

By derivation, the relationships (4) correspond to well-defined spin states of both X and $X^{1\pm}$ in (5):

$$\begin{aligned} S(X_{k,\beta}^+) &= S(X) + 1/2 \\ S(X_{m,\alpha}^+) &= S(X) - 1/2 \\ S(X_{v,\alpha}^-) &= S(X) + 1/2 \end{aligned} \tag{6}$$

where S (X) is the total spin of a high-spin open-shell system X with one or more half-filled orbitals. An analogous but more complex treatment for the other three ionization processes—removal of an α electron from the closed shell, addition of a β electron to the open shell, and addition of a β electron to the virtual shell—will be the subject of another paper.

The present work presents a more detailed study of the validity of KT in the ROHF method. We give a general (*variational*) formulation of KT which is valid in an arbitrary ROHF treatment and reduces to the particular formulation (4) within the canonical ROHF method.[5]

A starting point of our study is the fundamental Koopmans' idea[1] to relate a HF treatment of closed-shell systems to a treatment of the respective ionized systems (cations) within a limited *variational* approach. Koopmans considered the family of single determinant wave functions for the ion which could be formed using orbitals that were linear combinations of the occupied orbitals of the neutral. He then asked for the best ion wave function of this *one-determinantal* form.

An approach equivalent to Koopmans' is to define the energy and total wave functions of cations as eigenvalues and eigenfunctions of the CI matrix $\langle \Psi_k^+ | \hat{H} | \Psi_l^+ \rangle$ where Ψ_k^+ is a one-determinant wave function for cation X_k^+ having a hole in an orbital ϕ_k (k = 1, 2, ..., N_c). The orbitals $\{\phi_k\}$ used for constructing determinants $|\Psi_k^+\rangle \equiv |\Psi_k^+\{\phi\}\rangle$ are *arbitrary* unitary transforms of the occupied HF orbitals optimal for the parent closed-shell system X. The ionization potential I_z can be estimated as $I_z = E_{\text{CI}}(X_z^+) - E_{\text{HF}}(X)$, where $E_{\text{CI}}(X_z^+)$ is the zth eigenvalue (z = 1, 2, ..., N_c) of the CI matrix above representing the CI energy of cation X_z^+. It is easy to show that this set of configurations is closed under a unitary transformation of the occupied orbitals of X, so the CI wave functions and energies are unchanged by this transform.

Using the present CI terminology, the three main statements forming the famous Koopmans' theorem[1] can be formulated as follows: (i) the multideterminantal CI wave function of cation X_z^+ can be represented by a single Slater determinant $|\Psi_z^+\{\theta\}\rangle$, where the new orbitals $\{\theta_k\}$ are *natural CI orbitals*, i.e., eigenvectors of the CI one-body density matrix for cation X_z^+; (ii) the new orbitals $\{\theta_k\}$ are identical to the *canonical* closed-shell HF orbitals optimal for the parent system *X*.

These two fundamental results represent the first part of KT.[1] From these results it follows that the CI energy of cation X_z^+, $E_{\text{CI}}(X_z^+)$, is equal to the monodeterminantal energy, $\langle \Psi_z^+\{\theta\} | \hat{H} | \Psi_z^+\{\theta\} \rangle$, defined in a nonvariational manner, i.e., in the approximation of "frozen" orbitals,

$$E_{\text{CI}}(X_z^+) = \langle \Psi_z^+\{\theta\} | \hat{H} | \Psi_z^+\{\theta\} \rangle = E_{\text{frozen}}(X_z^+) \tag{7}$$

On the basis of the results (i) and (ii), Koopmans has proved the third fundamental result[1] that can be presented in the form

$$\begin{aligned} I_z &= E_{\text{CI}}(X_z^+) - E_{\text{HF}}(X) \\ &= E_{\text{frozen}}(X_z^+) - E_{\text{HF}}(X) \\ &= -\varepsilon_z \end{aligned} \tag{8}$$

where ε_z is the eigenvalue of the *canonical* HF equation (2) for the parent system X. The last of the relationships (8) is nothing but the relationship (1) above usually called "Koopmans' theorem". However, this relationship does not reveal the fundamental (*variational*) character of KT expressed by the first two of the relationships (8). The CI approach minimizes the right-hand side of the first relationship while Koopmans minimized the right-hand side of the second relationship in his derivation.

The approach to analysis of KT outlined above but in a simpler form has been earlier discussed by Newton.[6] For the case of ions formed from closed-shell systems, Newton has proved the validity of the relationship (7) above, but he did not reveal the fundamental relation between canonical closed-shell orbitals for X and natural CI orbitals for ions. Newton's analysis[6] of KT has been later extended by Stepanov et al.[7] to open-shell systems within an unrestricted Hartree−Fock method (UHF).

On the basis of ideas like these,[6,7] Sauer et al.[8] tried to give a similar (CI-based) formulation of KT in the ROHF method. This attempt, however, has led to the conclusion that KT *is not valid* in the ROHF method. Below we shall discuss how the generalization of KT to the open shell case made by Sauer et al.[8] differs from the generalization we have made in this paper. Moreover, as an alternative to KT in the ROHF method, Sauer et al. have formulated the so-called "Simplified Koopmans' theorem",[8,9] according to which IPs and EAs (5) might be compared not with eigenvalues of some special (canonical) ROHF Hamiltonian, but with slightly modified *diagonal elements* of Roothaan's Hamiltonian.[10]

In the present work, we perform a more detailed analysis of the validity of KT in the ROHF method. Following Koopmans' variational idea,[1] we combine a ROHF treatment of the parent open-shell system X with a FCI-RAS (full CI in the restricted active space) treatment of ionized systems $X^\pm$. We analyze the CI equations for the three ionization processes (4) and show the results are the same as those derived with the canonical ROHF method.[5] This enables us to give a general (*variational*) formulation of KT which is valid in different ROHF treatments with arbitrary (noncanonical) choices for the orbitals.

We also present two illustrative calculations based on these equations. In the process of doing these calculations with the GAMESS program,[11] we found some specific problems which may arise in canonical ROHF calculations in the case where the orbital energies satisfying KT (4) do not satisfy the *Aufbau principle*.

II. Koopmans' Theorem and the ROHF Method

A starting point of a ROHF method is the familiar expression for the total electronic energy:[10]

$$E_{\text{ROHF}}(X) = 2\sum_i f_i H_{ii} + \sum_i \sum_j f_i f_j (2a_{ij} J_{ij} - b_{ij} K_{ij}) \tag{9}$$

where the indices i, j numerate the occupied orbitals; f_i is the occupation number for the orbital ϕ_i ($f_i = 1$ for the closed-shell orbitals, and $0 < f_i < 1$ for the open-shell orbitals); a_{ij} and b_{ij} are coupling coefficients specific for the open-shell system X under consideration.[10] Application of the variational principle to the energy functional (9) yields the generalized Hartree−Fock equation,

$$\hat{R}\,|\phi_i\rangle = \varepsilon_i[\hat{R}]\,|\phi_i\rangle \tag{10}$$

where $\hat{R}$ represents the family of ROHF Hamiltonians that provide a fulfillment of the variational conditions. The explicit form of these conditions and different definitions for $\hat{R}$ have been summarized in ref 5.

The eigenvalues of the Hartree−Fock equation (10), $\varepsilon_i[\hat{R}]$, generally cannot be correlated with the respective IPs or EAs via KT (4). Such a correlation is possible if, and only if, the ROHF Hamiltonian and its eigenvalues and eigenvectors are *canonical*,

$$\hat{R}_{\rm can}|\theta_i\rangle = \varepsilon_i[\hat{R}_{\rm can}]\,|\theta_i\rangle \tag{11}$$

that is, they satisfy a number of conditions following from Koopmans' theorem.[1] Here we analyze these conditions for the particular case of high-spin half-filled open-shell systems characterized by Roothaan open-shell coefficients[10]

$$f = 1/2 \qquad a = 1 \qquad b = 2 \tag{12}$$

For this case, the widely used choices for the ROHF Hamiltonian $\hat{R}$ (10) can be presented in the common form of the symmetric (Hermitian) matrix $\langle\phi_i|\hat{R}|\phi_j\rangle$ defined in the basis of arbitrary molecular orbitals:[5]

$$\begin{array}{r|ccc|}
 & \text{Closed-shell} & \text{Open-shell} & \text{Virtual} \\
\text{Closed-shell} & \hat{R}^{(cc)} & 2(\hat{F}_c - \hat{F}_o) & \hat{F}_c \\
\text{Open-shell} & \hat{F}^{\beta} & \hat{R}^{(oo)} & 2\hat{F}_o \\
\text{Virtual} & (\hat{F}^{\alpha} + \hat{F}^{\beta})/2 & \hat{F}^{\alpha} & \hat{R}^{(vv)}
\end{array} \tag{13}$$

where

$$\begin{aligned}
\hat{F}_{\rm c} &= \hat{h} + (2\hat{J}_{\rm c} - \hat{K}_c) + f(2\hat{J}_{\rm o} - \hat{K}_{\rm o}) \\
\hat{F}_{\rm o} &= f[\hat{h} + (2\hat{J}_{\rm c} - \hat{K}_c) + f(2a\hat{J}_{\rm o} - b\hat{K}_{\rm o})]
\end{aligned} \tag{14}$$

are the ROHF Fock operators[10,12] for the closed-shell and open-shell orbitals, respectively. For comparison, the lower triangle of the matrix (13) is expressed in terms of the Fock operators $\hat{F}^{\alpha}$ and $\hat{F}^{\beta}$ defined in the UHF method,[13]

$$\begin{aligned}
\hat{F}^{\alpha} &= \hat{h} + (\hat{J}^{\alpha} + \hat{J}^{\beta}) - \hat{K}^{\alpha} \\
\hat{F}^{\beta} &= \hat{h} + (\hat{J}^{\alpha} + \hat{J}^{\beta}) - \hat{K}^{\beta}
\end{aligned} \tag{15}$$

For the case under consideration (12), the ROHF and UHF Fock operators defined on the *same ROHF orbitals* are connected by the relationships: $\hat{F}^{\alpha} = 2\hat{F}_{\rm o}$ and $\hat{F}^{\beta} = 2(\hat{F}_{\rm c} - \hat{F}_{\rm o}) = \hat{h} + (2\hat{J}_{\rm c} - \hat{K}_{\rm c}) + \hat{J}_{\rm o}$, so that the ROHF Hamiltonian matrix (13) is symmetric.[12]

In the self-consistent limit, the off-diagonal blocks in (13) vanish and this provides a fulfillment of the variational conditions. For the systems (12) under study, various definitions for the Hamiltonian (10) differ between the diagonal blocks only. The definitions of the diagonal blocks in (13) derived by different authors can be presented in the common form[5,11]

$$\begin{aligned}
\hat{R}^{(\rm ss)} &= 2\{A_{(\rm ss)}\hat{F}_{\rm o} + B_{(\rm ss)}(\hat{F}_{\rm c} - \hat{F}_{\rm o})\} \\
&= A_{(\rm ss)}\hat{F}^{\alpha} + B_{(\rm ss)}\hat{F}^{\beta}
\end{aligned} \tag{16}$$

where $A_{(\rm ss)}$ and $B_{(\rm ss)}$ are the coefficients characterizing different ROHF treatments, and s = c, o, v for the closed, open, and virtual shell, respectively. A list of coefficients (16) for some choices of $\hat{R}$ in commonly used programs is presented in ref 5.

For the special case $\hat{R} = \hat{R}_{\rm can}$ (11), the diagonal blocks take the form

$$\hat{R}^{(\rm cc)}_{\rm can} = 2(\hat{F}_{\rm c} - \hat{F}_{\rm o}) = \hat{F}^{\beta} \tag{17a}$$

$$\hat{R}^{(\rm oo)}_{\rm can} = 2\hat{F}_{\rm o} = \hat{F}^{\alpha} \tag{17b}$$

$$\hat{R}^{(\rm vv)}_{\rm can} = 2\hat{F}_{\rm o} = \hat{F}^{\alpha} \tag{17c}$$

derived by Plakhutin et al.[5] from the respective KT conditions (4a)−(4c) above. Comparing with (16), we see that the canonical choice is $A_{(\rm cc)} = 0$, $B_{(\rm cc)} = 1$; $A_{(\rm oo)} = 1$, $B_{(\rm oo)} = 0$; $A_{(\rm vv)} = 1$, $B_{(\rm vv)} = 0$.

As is known,[5] the exact choice for the diagonal blocks in (14) does not affect the total energy $E_{\rm ROHF}(X)$ of eq 9. The choice (17) is of special meaning in the sense[2,5] that it provides a consistent definition of the expectation value for the energy of the *ionic* systems $X^{1\pm}$ in the approximation of "frozen" orbitals in the sense of Koopmans' theorem (4) and (5). To understand this better, we analyze below the wave functions and density matrices for the ionized systems $X^{1\pm}$ in the respective three cases (4a)−(4c).

III. Canonical ROHF Method and Limited CI

Following the variational spirit of the Koopmans' approach,[1] we first consider the family of Slater determinants, $|\Psi^+_{k,\beta}\rangle$, formed by removing a β electron from a closed-shell orbital ϕ_k ($k = 1, 2, ..., N_{\rm c}$) of the open-shell system X under study,

$$\begin{aligned}
|\Psi^+_{k,\beta}\rangle = \det|\phi_1\overline{\phi}_1 \ldots \phi_{k-1}\overline{\phi}_{k-1}\phi_k \quad \phi_{k+1}\overline{\phi}_{k+1} \ldots \phi_{N_{\rm c}}\overline{\phi}_{N_{\rm c}} \\
\phi_{N_{\rm c}+1} \ldots \phi_{N_{\rm c}+N_{\rm o}}|
\end{aligned} \tag{18}$$

where both the closed-shell $\{\phi_k\}$ and open-shell $\{\phi_m\}$ orbitals ($m = N_{\rm c} + 1, N_{\rm c} + 2, ..., N_{\rm c} + N_{\rm o}$) are derived for the parent system X with the use of an *arbitrary* (noncanonical) Hamiltonian $\hat{R}$ (10).

Let us further define the configuration interaction (CI) matrix $T^{(\rm cc)}_{kl}$ as

$$T^{(\rm cc)}_{kl} = \langle\Psi^+_{k,\beta}|\,\hat{H}\,|\Psi^+_{l,\beta}\rangle \tag{19}$$

where $k, l = 1, 2, ..., N_{\rm c}$. The diagonal element of this matrix, $T^{(\rm cc)}_{kk}$, represents the expectation value of the energy of cation $X^+_{k,\beta}$ in the approximation of "frozen" orbitals. However, since the orbitals $\{\phi_k\}$ and $\{\phi_m\}$ used to form the determinants (18) are *arbitrary* transforms of the orbitals optimal for X, neither the wave function (18) nor the diagonal element of (19) are defined unambiguously. To derive the true value of $E_{\rm frozen}(X^+_{k,\beta})$ and to give the proper definition of the wave function for cation $X^+_{k,\beta}$, we consider the structure of matrix (19) in more detail. After some algebra, the diagonal element of (19) can be presented in the form

$$\begin{aligned}
T^{(\rm cc)}_{kk} &= E_{\rm ROHF}(X) - \{H_{kk} + \sum_l (2J_{kl} - K_{kl}) + \sum_m J_{km}\} \\
&= E_{\rm ROHF}({\rm X}) - (\hat{R}^{(\rm cc)}_{\rm can})_{kk}
\end{aligned} \tag{20}$$

where all matrix elements are defined in the basis of noncanonical orbitals $\{\phi_j\} = \{\phi_k\} \oplus \{\phi_m\}$ (10), and the operator $\hat{R}^{(\rm cc)}_{\rm can}$ is defined by eq 17a. The explicit form of the off-diagonal matrix elements (19) can be found via Slater rules:

$$\begin{aligned} T^{(\mathrm{cc})}_{lk} &= -\{H_{kl} + 2\sum_i [ii|kl] - \sum_i [ki|il] + \sum_m [mm|kl]\} \\ &= -\{H_{kl} + 2(\hat{J}_{\mathrm{c}})_{kl} - (\hat{K}_{\mathrm{c}})_{kl} + (\hat{J}_{\mathrm{o}})_{kl}\} \\ &= -(\hat{R}^{(\mathrm{cc})}_{\mathrm{can}})_{kl} \qquad (k \neq l) \end{aligned} \tag{21}$$

where index *i* runs over the closed-shell orbitals of the parent (nonionized) system X, and the notation $[ab|cd]$ means

$$[ab|cd] = \int \phi^*_a(1)\, \phi_b(1) \frac{1}{r_{12}} \phi^*_c(2)\, \phi_d(2)\, \mathrm{d}v_1\, \mathrm{d}v_2 \tag{22}$$

Taken together, (21) and (21) give us the important relationship between the CI matrix (19) and the diagonal block (17a) of the canonical ROHF Hamiltonian matrix,

$$T^{(\mathrm{cc})}_{lk} = T^{(\mathrm{cc})*}_{kl} = -(\hat{R}^{(\mathrm{cc})}_{\mathrm{can}})_{kl} + \delta_{kl}E_{\mathrm{ROHF}}(\mathrm{X}) \tag{23}$$

Before discussing this relationship corresponding to ionization from the closed shell, we consider two similar relationships corresponding to ionization of an α electron from the open shell (4b) and attachment of an α electron to the virtual shell (4c) with formation of ions $\mathrm{X}^+_{m,\alpha}$ ($m \in$ open shell) and $\mathrm{X}^-_{v,\alpha}$ ($v \in$ virtual shell), respectively. Following the approach described above, we consider two respective sets of Slater determinants,

$$|\Psi^+_{m,\alpha}\rangle = \det|\phi_1\bar{\phi}_1 \ldots \phi_{N_{\mathrm{c}}}\bar{\phi}_{N_{\mathrm{c}}} \quad \phi_{N_{\mathrm{c}}+1} \ldots \phi_{N_{\mathrm{c}}+m-1} \\ \phi_{N_{\mathrm{c}}+m+1} \ldots \phi_{N_{\mathrm{c}}+N_{\mathrm{o}}}| \tag{24}$$

and

$$|\Psi^-_{v,\alpha}\rangle = \det|\phi_1\bar{\phi}_1 \ldots \phi_{N_{\mathrm{c}}}\bar{\phi}_{N_{\mathrm{c}}} \quad \phi_{N_{\mathrm{c}}+1}\phi_{N_{\mathrm{c}}+2} \ldots \phi_{N_{\mathrm{c}}+N_{\mathrm{o}}}\phi_{N_{\mathrm{c}}+N_{\mathrm{o}}+v}| \tag{25}$$

representing configuration state functions (CSF) for ions $\mathrm{X}^+_{m,\alpha}$ and $\mathrm{X}^-_{v,\alpha}$ to be used in a restricted CI. By analogy with the case (19), we define two respective CI matrices,

$$T^{(\mathrm{oo})}_{mn} = \langle\Psi^+_{m,\alpha}\,|\,\hat{H}\,|\,\Psi^+_{n,\alpha}\rangle \tag{26}$$

where m, $n \in$ open shell, and

$$T^{(\mathrm{vv})}_{uv} = \langle\Psi^-_{u,\alpha}|\,\hat{H}\,|\Psi^-_{v,\alpha}\rangle \tag{27}$$

u, $v \in$ virtual shell. Using the same technique, one easily obtains the desired relationships between CI matrices (26) and (27) and the respective diagonal blocks (17b)-(17c) of the canonical ROHF Hamiltonian matrix,

$$T^{(\mathrm{oo})}_{nm} = (-1)^{n-m+1}(\hat{R}^{(\mathrm{oo})}_{\mathrm{can}})_{mn} + \delta_{mn}E_{\mathrm{ROHF}}(\mathrm{X}) \qquad (m \le n) \tag{28}$$

$$T^{(\mathrm{vv})}_{uv} = (\hat{R}^{(\mathrm{vv})}_{\mathrm{can}})_{uv} + \delta_{uv}E_{\mathrm{ROHF}}(\mathrm{X}) \tag{29}$$

which are counterparts of the relationship (23) for the respective ionization and attachment processes.

The relationship (28) needs some additional comments. As compared to the relationships (23) and (29), the two matrices entering (28), i.e., $T^{(\mathrm{oo})}_{nm}$ and $(\hat{R}^{(\mathrm{oo})}_{\mathrm{can}})_{mn}$, do not commute, and hence, do not possess the same set of eigenfunctions. It should be noted, however, that these two matrices can be made commutative if a factor of $(-1)^m$ is inserted in the definition of $\Psi^+_{m,\alpha}$ (24): $\tilde{\Psi}^+_{m,\alpha} = (-1)^m\Psi^+_{m,\alpha}$. This yields the new CI matrix $\tilde{T}^{(\mathrm{oo})}_{mn} = \langle\tilde{\Psi}^+_{m,\alpha}|\hat{H}|\tilde{\Psi}^+_{n,\alpha}\rangle \equiv (-1)^{n-m}T^{(oo)}_{mn}$, $(m \le n)$, which commutes with matrix $(\hat{R}^{(oo)}_{can})_{mn}$,

$$\tilde{T}^{(\mathrm{oo})}_{nm} = -(\hat{R}^{(\mathrm{oo})}_{\mathrm{can}})_{mn} + \delta_{mn}E_{\mathrm{ROHF}}(\mathrm{X}) \qquad (m \le n) \tag{30}$$

In the treatment below we shall deal, however, with the original CI matrix (26) and the respective relationship (28). This will allow us to perform a direct comparison between results of a theoretical treatment and results of CI calculations, as existing quantum chemical programs deal with the wave functions and CI matrices of the form (23)−(25).

IV. Variational Formulation of KT in the ROHF Method

The three above relationships (eqs 23, 28, and 29) establish a fundamental connection between diagonal blocks of the canonical ROHF Hamiltonian matrix for the initial system X and CI matrices for ions $\mathrm{X}^+_{k,\beta}$, $\mathrm{X}^+_{m,\alpha}$, and $\mathrm{X}^-_{v,\alpha}$ defined in the respective subspaces. By derivation, these relationships are fulfilled for an *arbitrary* choice of the orbitals used for constructing CI and canonical ROHF Hamiltonian matrices. In the treatment below we shall assume, however, that the $\{\phi_j\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$ orbitals are *optimal* for the initial open-shell system X and are derived with the use of an *arbitrary* (generally noncanonical) ROHF Hamiltonian (10). For this choice of $\{\phi_j\}$, the Hamiltonian matrix (13) takes a block-diagonal form.

As pointed out above, the wave function $\Psi^+_{k,\beta}$ (18) for cation $X^+_{k,\beta}$ and the expectation value for the energy of this cation, $\langle\Psi^+_{k,\beta}|\hat{H}|\Psi^+_{k,\beta}\rangle$, defined in the approximation of "frozen" orbitals $\{\phi_j\}$ are defined ambiguously. The same problem arises in the case of ions $\mathrm{X}^+_{m,\alpha}$ (24) and $X^-_{v,\alpha}$ (25). On the basis of eqs 23, 28, and 29, we give a general variational definition of both the energy and wave functions of ions that appear in the particular formulation of KT (4) and (5). Just as for the closed shell case, this derivation makes implicit use of the fact that the three CI spaces defined above are closed under the allowed unitary transforms on the three subsets of orbitals. Hence the CI results are independent of the choice of orbitals.

A. KT and the CI Energy of Ions. We start the treatment with the analysis of the relationship (23) corresponding to ionization from the closed shell. As follows from (23), the matrices $T^{(\mathrm{cc})}$ and $\hat{R}^{(\mathrm{cc})}_{\mathrm{can}}{}^*$ commute, and hence, the eigenvalues of these matrices, $\varepsilon_z[T^{(\mathrm{cc})}]$ and $\varepsilon_z[\hat{R}^{(\mathrm{cc})}_{\mathrm{can}}]$, where $z = 1, 2, \ldots, N_{\mathrm{c}}$, are connected by the relationship

$$\varepsilon_z[T^{(\mathrm{cc})}] = -\varepsilon_z[\hat{R}^{(\mathrm{cc})}_{\mathrm{can}}] + E_{\mathrm{ROHF}}(\mathrm{X}) \tag{31}$$

This relationship is a CI analog of Koopmans' relationship for the closed-shell systems (see eq 22 in ref 1). By definition, a zth eigenvalue of the matrix $T^{(\mathrm{cc})}$ is equal to the CI energy of cation $\mathrm{X}^+_{z,\beta}$:

$$\varepsilon_z[T^{(\mathrm{cc})}] \equiv E_{\mathrm{CI}}(X^+_{z,\beta}) \tag{32}$$

while the eigenvalues of the matrix $\hat{R}^{(\mathrm{cc})}_{\mathrm{can}}$ satisfy KT in the particular form (4a), i.e., $\varepsilon_z[\hat{R}^{(\mathrm{cc})}_{\mathrm{can}}] = -I^{\beta}_z$. Combining the latter relationship with eqs 5 and 32, we obtain the new formulation of KT in the ROHF method for the case of ionization from the closed shell,

$$\begin{aligned} I^{\beta}_z &= -\varepsilon_z[\hat{R}^{(\mathrm{cc})}_{\mathrm{can}}] \\ &= E_{\mathrm{CI}}(\mathrm{X}^+_{z,\beta}) - E_{\mathrm{ROHF}}(\mathrm{X}) \end{aligned} \tag{33}$$

which can be compared with the particular formulation[5] given by eqs 4a and 5 above,

$$\begin{aligned} I_z^{\beta} &= -\varepsilon_z[\hat{R}_{\mathrm{can}}^{(\mathrm{cc})}] \\ &= E_{\mathrm{frozen}}(X_{z,\beta}^{+}) - E_{\mathrm{ROH}F}(\mathrm{X}) \end{aligned}$$

Before discussing the key result (33), we consider two other ionization processes (4b)−(4c) and two respective relationships (28) and (29). Equation 29 is similar to (23) in the sense that the matrices entering (29) commute. Taking this into account, we immediately obtain the new formulation of KT for attachment of an α electron to the virtual shell:

$$\begin{aligned} A_z^{\alpha} &= -\varepsilon_z[\hat{R}_{\mathrm{can}}^{(\mathrm{vv})}] \\ &= E_{\mathrm{ROHF}}(\mathrm{X}) - E_{\mathrm{CI}}(\mathrm{X}_{z,\alpha}^{-}) \\ &= E_{\mathrm{ROHF}}(\mathrm{X}) - E_{\mathrm{frozen}}(\mathrm{X}_{z,\alpha}^{-}) \end{aligned} \tag{34}$$

where, in this case, $z \in$ virtual shell.

For the ionization from the open shell (4b), the respective relationship (28) is more complex, as the matrices $T^{(\mathrm{oo})}$ and $\hat{R}_{\mathrm{can}}^{(\mathrm{oo})*}$ entering (28) do not commute. However, it is easy to prove that the eigenvalues of these matrices obey the relationship similar to (31):

$$\varepsilon_z[T^{(\mathrm{oo})}] = -\varepsilon_z[\hat{R}_{\mathrm{can}}^{(\mathrm{oo})}] + E_{\mathrm{ROHF}}(\mathrm{X}) \tag{35}$$

(see also below), and hence,

$$\begin{aligned} I_z^{\alpha} &= -\varepsilon_z[\hat{R}_{\mathrm{can}}^{(\mathrm{oo})}] \\ &= E_{\mathrm{CI}}(\mathrm{X}_{z,a}^{+}) - E_{\mathrm{ROHF}}(\mathrm{X}) \\ &= E_{\mathrm{frozen}}(\mathrm{X}_{z,a}^{+}) - E_{\mathrm{ROHF}}(\mathrm{X}) \end{aligned} \tag{36}$$

where, in this case, $z \in$ open shell.

In complete analogy to eq 8, when there is no open shell, eqs 33, 34, and 36 give us the new (variational) formulation of KT in the ROHF method. According to this formulation, *both* the energy of the initial open-shell system X and the energy of ions $\mathrm{X}^{\pm}$ appearing in Koopmans' theorem are defined in a *variational* manner, i.e., by the ROHF and limited CI methods, respectively.

It also follows from eqs 33, 34, and 36 that in all three cases under consideration the CI energy of ions, $E_{\mathrm{CI}}(\mathrm{X}^{\pm})$, is equal to the energy $E_{\mathrm{frozen}}(\mathrm{X}^{\pm})$ first defined within the canonical ROHF method[5] in the approximation of "frozen" orbitals, i.e., in a *nonvariational* manner. This result is nontrivial (see, for comparison, ref 8) and needs a detailed explanation.

B. Reduction of the CI Wave Function to Monodeterminantal Form. To clarify the origin of the discussed equality $E_{\mathrm{CI}}(\mathrm{X}^{\pm}) = E_{\mathrm{frozen}}(X^{\pm})$, we have to prove that the multideterminantal CI wave function of an ion, say $\Phi^{(z)}(\mathrm{X}^{\pm})$, defined as an eigenfunction of the respective CI matrix, is equal (within the sign) to the one-determinant ROHF wave function $\Psi_z^{+}(\mathrm{X}^{\pm})$ defined in ref 5 in a *nonvariational* manner (i.e., in the "frozen" orbital approximation) on the basis of *canonical* orbitals optimal for X. We here present the desired proof for the most complex case, i.e., for ionization from the open shell, for which the matrices $T^{(\mathrm{oo})}$ and $\hat{R}_{\mathrm{can}}^{(\mathrm{oo})*}$ do not commute (28).

Let $\Phi^{(z)}$ be a zth eigenvector of the CI matrix $T_{mn}^{(\mathrm{oo})}$ (26):

$$|\Phi^{(z)}\rangle = \sum_n U_n^{(z)} |\Psi_{n,\alpha}^{+}\rangle \tag{37}$$

$$\sum_n T_{mn}^{(\mathrm{oo})} U_n^{(z)} = U_m^{(z)} \varepsilon_z[T^{(\mathrm{oo})}] \tag{38}$$

where $U_n^{(z)}$ are the coefficients of the CI expansion over determinants $|\Psi_{n,\alpha}^{+}\rangle$ (24). The determinants are defined on the basis of arbitrary (noncanonical) orbitals $\{\phi_j\} = \{\phi_k\} \oplus \{\phi_m\}$ optimal for X. Let θ_z be a zth eigenvector of the diagonal open-shell block $\hat{R}_{\mathrm{can}}^{(\mathrm{oo})}$ (17b) defined on the same basis $\{\phi_j\}$,

$$|\theta_z\rangle = \sum_n X_n^{(z)} |\phi_n\rangle \tag{39}$$

$$\sum_n (\hat{R}_{\mathrm{can}}^{(\mathrm{oo})})_{mn} X_n^{(z)} = X_m^{(z)} \varepsilon_z[\hat{R}_{\mathrm{can}}^{(\mathrm{oo})}] \tag{40}$$

where $X_n^{(z)}$ are the coefficients of the expansion of the canonical orbital θ_z over initial orbitals $\{\phi_m\}$.

On the basis of the relationship (28), one may prove that the eigenvalues (38) and (40) are connected by eq 35, i.e., $\varepsilon_z[T^{(\mathrm{oo})}] = -\varepsilon_z[\hat{R}_{\mathrm{can}}^{(\mathrm{oo})}] + E_{\mathrm{ROHF}}(\mathrm{X})$, while the respective expansion coefficients $U_n^{(z)}$ and $X_n^{(z)}$ satisfy the relationship

$$U_n^{(z)} = (-1)^n X_n^{(z)*} \tag{41}$$

and hence,

$$|\theta_z\rangle = \sum_n X_n^{(z)} |\phi_n\rangle = \sum_n (-1)^n U_n^{(z)*} |\phi_n\rangle \tag{42}$$

(We here note that in the similar case of ionization from the closed shell (23) the respective coefficients are connected by the relationship $U_n^{(z)} = X_n^{(z)*}$, while in the case of attachment of an electron to the virtual shell (29) they are equal to each other, i.e., $U_n^{(z)} = X_n^{(z)}$).

Now let us consider the one-body density matrix, $\rho^{(z)}(1, 1')$, corresponding to the CI wave function (37),

$$\rho^{(z)}(1, 1') = N \int_{\sigma(1)=\sigma(1')} \Phi^{(z)}(1,2,\ldots,N)\, \Phi^{(z)}(1',2,\ldots,N)^{*} \,\mathrm{d}\sigma_1\, \mathrm{d}v_2 d\sigma_2 \ldots \mathrm{d}v_N\, \mathrm{d}\sigma_N \tag{43}$$

where $N = (2N_c + N_{\mathrm{o}} - 1)$ is the total number of electrons in cation $\mathrm{X}_{z,\alpha}^{+}$, and σ_1 means the spin function of the first electron. Taking into account the definitions of $\Phi^{(z)}$ (37) and $\Psi_{n,\alpha}^{+}$ (24), the density matrix (43) takes the form

$$\rho^{(z)}(1, 1') = 2\sum_k \phi_k(1)\, \phi_k(1')^{*} + \sum_m \phi_m(1)\, \phi_m(1')^{*} - \sum_m \sum_n (-1)^{m+n+1} U_m^{(z)}\, U_n^{(z)*} \phi_n(1)\, \phi_m(1')^{*} \tag{44}$$

Substitution of eq 42 into eq 44 gives us the diagonal form for the CI density matrix

$$\rho^{(z)}(1, 1') = 2\sum_k \phi_k(1)\, \phi_k(1')^{*} + \sum_m \theta_m(1)\, \theta_m(1')^{*} - \theta_z(1)\, \theta_z(1')^{*} \tag{45}$$

where $m, z \in$ open shell.

The result (45) is principally important. At first, we note that the eigenvectors of the CI density matrix (45), i.e., the *natural CI orbitals* $\{\theta_m\}$ for cation $\mathrm{X}_{z,\alpha}^{+}$ coincide with the respective open-shell eigenvectors of the *canonical* ROHF Hamiltonian (11) for the initial system X. Second, the CI density matrix (45) is equal to the ROHF density matrix corresponding to the one-determinant wave function

$$|\Psi_{z,\alpha}^{+}\rangle = \det|\phi_1\bar{\phi}_1 \ldots \phi_{N_{\mathrm{c}}}\bar{\phi}_{N_{\mathrm{c}}} \quad \theta_{N_{\mathrm{c}}+1} \ldots \theta_{N_{\mathrm{c}}+z-1} \; \theta_{N_{\mathrm{c}}+z+1} \ldots \theta_{N_{\mathrm{c}}+N_{\mathrm{o}}}| \tag{46}$$

This immediately proves the desired result that the wave function (46) used in the canonical ROHF method[5] is equal to the CI wave function $\Phi^{(z)}$ (37), and hence, the respective energies $E_{\mathrm{frozen}}(\mathrm{X}_{z,a}^{+})$ and $E_{\mathrm{CI}}(\mathrm{X}_{z,a}^{+})$ of eq 36 are equal to each other.

A similar analysis has been performed for removal of a β electron from the closed shell and for attachment of an α electron to the virtual shell. We present the results of this analysis, i.e., the diagonal form of the CI density matrix (43) for cation $X^+_{z,\beta}$ having a hole in the closed shell,

$$\rho^{(z)}(1,1') = 2\sum_k \theta_k(1)\,\theta_k(1')^* - \theta_z(1)\,\theta_z(1')^* + \sum_m \phi_m(1)\,\phi_m(1')^* \quad (47)$$

(k, $z \in$ closed shell), and for anion $X^-_{z,\alpha}$ having an extra electron in the virtual shell,

$$\rho^{(z)}(1,1') = 2\sum_k \phi_k(1)\,\phi_k(1')^* + \sum_m \phi_m(1)\,\phi_m(1')^* + \theta_z(1)\,\theta_z(1')^* \quad (48)$$

where $z \in$ virtual shell.

These formulas conclude the new (variational) formulation of KT in the ROHF method. By derivation, this formulation is applicable to high-spin half-filled open-shell systems (12) and is valid within an arbitrary ROHF method. A detailed discussion of this formulation and some applications are given below.

To conclude this treatment, we note that the representability of the FCI-RAS wave functions for ions by a single determinant following from eqs 46−48 was expected for the particular case of ionization from the closed shell (47), as this result follows from both Koopmans' treatment[1] and a general Coleman's theorem.[14] According to Coleman, a full CI wave function for $(M - 1)$ electrons in M orbitals can be represented by a single determinant in the basis of natural CI orbitals.

C. Comparison with Previous Approaches. On the basis of the treatment above, we now can revert to a discussion of the Sauer et al. attempt[8] to give a variational (CI-based) formulation of KT in the ROHF method. At first, we recall that the Sauer et al.[8] treatment is based on the approaches of Newton[6] and Stepanov et al.[7] developed within the closed-shell HF and UHF methods, respectively. According to these references,[6,7] the CI wave function of cation X^+_i, formed by removing an electron from the initial system X, can be represented by a linear combination of determinants Ψ^+_j

$$|\Phi^+_i\rangle = \sum_j U^{(i)}_j |\Psi^+_j\rangle \quad (49)$$

where all determinants Ψ^+_j are defined in the basis of Hartree−Fock orbitals optimal for X and each of determinants corresponds to a hole in the respective orbital ϕ_j. In the UHF case,[7] all determinants Ψ^+_j in (49) correspond to a hole in the same occupied subspace of X, i.e., in either α ($\Psi^+_j \equiv \Psi^+_{j,\alpha}$) or β ($\Psi^+_j \equiv \Psi^+_{j,\beta}$) subspace. Using the ROHF notations, the active CI spaces in these two UHF cases can be presented in the form

$$\Psi^+_{j,\alpha} \in \{\Psi^+_{k,\alpha}\} \oplus \{\Psi^+_{m,\alpha}\} \quad (50a)$$

$$\Psi^+_{j,\beta} \in \{\Psi^+_{k,\beta}\} \quad (50b)$$

where, as above, $k = 1, 2, ..., N_c$ and $m = N_c + 1, ..., N_c + N_o$. In the closed-shell case,[6] both conditions (50a) and (50b) take the same form: $\Psi^+_j \in \{\Psi^+_k\}$. It is easy to prove[7] that the CI matrix for cation, $\langle\Psi^+_i|\hat{H}|\Psi^+_j\rangle$, and the respective Fock matrix for the initial system X are connected by the relationship $\langle\Psi^+_{i,\sigma}|\hat{H}|\Psi^+_{j,\sigma}\rangle = -\langle\phi_j|\hat{F}^\sigma|\phi_i\rangle + \delta_{ij}E_{UHF}(X)$, where $\sigma = \alpha$ or β.

In the closed-shell case,[6] the latter relationship takes a similar form with $E_{\mathrm{UHF}}(\mathrm{X}) = E_{\mathrm{HF}}(\mathrm{X})$ and $\hat{F}^\sigma = \hat{F}$, where $\hat{F}$ is defined by eq 3. From here one immediately obtains the relationship (8) above, i.e., $E_{\mathrm{CI}}(\mathrm{X}^+_z) - E_{\mathrm{HF}}(\mathrm{X}) = -\varepsilon_z$, that proves a variational character of Koopmans' theorem in the closed-shell HF method. As compared to this, the eigenvalues of the UHF Fock operators, $\varepsilon_{z,\sigma}$, satisfying Koopmans' theorem $E_{\mathrm{CI}}(\mathrm{X}^+_{z,\sigma}) - E_{\mathrm{UHF}}(\mathrm{X}) = -\varepsilon_{z,\sigma}$, cannot in general be equated to the experimental IPs via Koopmans' approximation $\varepsilon_{z,\sigma} = -I^\sigma_z$. A proof of this statement and a detailed analysis of the validity of KT in the UHF method will be given in another paper.

With some changes, the same CI approach was used by Stepanov et al.[7] and, later, by Sauer et al.[8] to give a variational formulation of KT in the ROHF method. A distinctive feature of the approach[7,8] is that the active CI space within the ROHF treatment is also defined by eq 50a, i.e., *the same as in the UHF treatment*.[7,8]

The latter statement needs some explanation. As pointed out in refs 7 and 8, in the ROHF case each of the functions Ψ^+_j in (50) can be the symmetry-adapted (spin-projected) combination of determinants, i.e., the ROHF functions Ψ^+_j (50) are defined in refs 7 and 8 as configuration state functions (CSF). In the discussion below this specializing does not play a significant role. The principally important point is that the active CI space for cation $X^+_{i,\alpha}$ (50a), defined in refs 7 and 8, involves determinants from *two different subspaces*, i.e., corresponding to a hole in both closed and open shells.

Before discussing the approach of refs 7 and 8, we present, for comparison, the respective active CI spaces used in the present work:

$$\Psi^+_{j,\alpha} \in \{\Psi^+_{m,\alpha}\} \quad (51a)$$

$$\Psi^+_{j,\beta} \in \{\Psi^+_{k,\beta}\} \quad (51b)$$

(see also eqs 18 and 24 above).

The problem with (50a) is that the respective CI matrix $\langle\Psi^+_{i,\alpha}|\hat{H}|\Psi^+_{j,\alpha}\rangle$, where $\Psi^+_{j,\alpha} \in \{\Psi^+_{k,\alpha}\} \oplus \{\Psi^+_{m,\alpha}\}$, does not commute with any ROHF Hamiltonian matrix (14), and hence, the eigenvalues of the so-defined CI matrix have no relation to Koopmans' theorem. It should be pointed out that the problem of (non)commutation of two these matrices has not been even mentioned by Stepanov et al.,[7] and so, their treatment actually proves neither validity nor invalidity of KT in the ROHF method.

This problem was later discussed in more detail by Sauer et al.[8] They regarded the CI in the spin-projected active space (50a), in which ROHF determinants $\Psi^+_{j,\alpha}$ are replaced by the respective CSFs, as the natural extension of Koopmans' approach to ROHF method. Their analysis has shown, however, that the eigenvalues of the CI matrix defined in the spin-projected space (50a) cannot be related to eigenvalues of any ROHF Hamiltonian. On the basis of this finding, they concluded that *Koopmans' theorem relating the CI energy to an orbital energy did not hold in the ROHF method*.

A comparison between the latter conclusion and the results of our treatment above reveals the source of the wrong conclusion.[8] For the case of a removal of an α *electron*, within a ROHF treatment, one should separate two different processes—ionization from the open shell which is described by the active CI space (51a), and ionization from the closed shell—because these spaces are not mixed by the allowed unitary transforms of the ROHF orbitals. A treatment of the latter case, i.e., of a removal of an α electron from the closed shell, is more complex and will be given in another paper.

D. Canonical ROHF Orbitals from FCI-RAS Calculations. In the next section we shall perform a detailed comparison between canonical ROHF orbitals and orbital energies derived by the method of ref 5, from the one side, and the respective characteristics derived by the present FCI-RAS method, i.e., natural CI orbitals and eigenvalues of CI matrices, from the other side. Before presenting the respective results, we should describe in more detail the procedure used for deriving canonical ROHF orbitals from FCI-RAS calculations.

As follows from eqs 45, 47, and 48 defining the diagonal form of the CI one-body density matrix (43) for ionic systems $X^{1\pm}$, the occupation numbers of natural CI orbitals $\{\theta_z\}$ are always equal to 0, 1, or 2. This means that the natural CI orbitals derived by diagonalization of the density matrix (43) are separated onto the three sets. Within each of these sets the natural orbitals are degenerate and are arbitrary within a unitary transformation. As noted above, these natural orbitals can be chosen to be the canonical ROHF orbitals for the parent system X. If this choice is made, then all of the CI wave functions considered here are *simultaneously* reduced to the form of a single Slater determinant.

In practice, a standard eigenvalue program will produce *arbitrary* mixtures of vectors within each degenerate subspace. Hence, the output vectors from a CI density matrix diagonalization are not equal in general to the desired canonical ROHF orbitals. To overcome this difficulty, we introduce the new difference density as follows:

$$q^{(z)}(1, 1') = \rho(1, 1') - \rho^{(z)}(1, 1') \tag{52}$$

where $\rho^{(z)}(1, 1')$ is the CI density matrix for ionic systems Xz $1\pm$ defined by eq 43 and $\rho(1, 1')$ is the ROHF one-body density matrix for the parent system X

$$\rho(1, 1') = 2\sum_k \phi_k(1)\,\phi_k(1')^* + \sum_m \phi_m(1)\,\phi_m(1')^* \tag{53}$$

For the three particular cases discussed in sections III and IV, the CI density matrix $\rho^{(z)}(1, 1')$ takes the diagonal form given by eqs 45, 47, and 48, respectively. For all these cases, the difference density (52) can be presented in the form

$$q^{(z)}(1, 1') = \pm\theta_z(1)\,\theta_z(1')^* \tag{54}$$

where the upper and lower signs correspond to cations and anions, respectively, and θ_z is the natural CI orbital for the respective ion $X_z^{1\pm}$.

It follows from (54) that a diagonalization of the difference density (52) yields a single eigenvector θ_z which, by derivation, represents a zth canonical ROHF orbital for the parent system X. To derive a full set of canonical ROHF orbitals, we should perform this procedure for all possible z, i.e. $(N_c + N_o + N_v)$ times. On the basis of orbitals defined in this way the CI wave functions for all ionized systems discussed in section III are represented by single Slater determinants.

V. Illustrative Calculations (ROHF and CI)

A. Koopmans' Theorem and the Aufbau Principle. As shown in ref 5, the canonical ROHF orbital energies satisfying KT (4a)−(4c) usually differ significantly from the respective values derived with other ROHF treatments (see, for example, Tables 1 and 2 in ref 5). Of particular interest here are the cases where the sequence of orbital energies satisfying KT does not obey the familiar *Aufbau principle*. Our experience has shown that such cases occur frequently in the canonical ROHF method.

Although violations of the Aufbau principle appear in calculations with different ROHF treatments, such violations within the canonical ROHF treatment are based on Koopmans' theorem, that is, have physical meaning, and hence, can be verified experimentally. Below we will show, for example, that violations of the Aufbau principle found from canonical ROHF calculations for manganese atoms agree with existing experimental data.

Violations of the Aufbau principle create some known difficulties in practical calculations. To perform such calculations within the canonical ROHF method,[5] a special algorithm is required. For the particular case of high-spin half-filled open-shell systems (12), such calculations can be performed (at least, in principle) with the use of a general ROHF algorithm designed by Montgomery in the GAMESS program.[11] However, because of a specific error in this algorithm, results of calculations for the systems not satisfying the Aufbau principle appear incorrectly labeled on the output (see also below).

The FCI-RAS approach developed in this work allows one to derive canonical orbital energies satisfying KT within an arbitrary ROHF treatment [via the relationships (32)−(35)]. This can be used for deriving the canonical MOs and orbital energies with programs where canonical orbitals are not available.

B. ROHF Calculations. This and the next subsections present results of ROHF and CI calculations performed with the aim to illustrate the approach developed in section IV. At first, we should note that in the course of these calculations an unexpected discrepancy in the computer output from the GAMESS package[11] has been revealed between the results derived by CI calculations and those derived with the canonical ROHF method.[5]

Taking this into account, we present here results of ROHF and CI calculations for a simple model system consisting of the HNO molecule in a highly excited state with total spin $S = 2$ (state $^5A''$) using the small basis set 6-31G. The choice of this model as an illustration is caused exclusively by its small size. All calculations have been performed at the same geometry of the model system ($R_{\mathrm{H-N}} = 1.062$ Å, $R_{\mathrm{N-O}} = 1.211$ Å, $\angle\mathrm{H{-}N{-}O} = 108.5°$), which has been taken as the same[15] as for the actual closed-shell ground state of HNO. All calculations have been performed with the GAMESS program.[11] These results are merely intended to illustrate the method and do not correspond to any actual energies of the HNO molecule.

For the high-spin half-filled open-shell systems (12) to which the model under study belongs, the canonical choice for the diagonal blocks of the ROHF Hamiltonian matrix (13) is presented by eq 17 above. For comparison, we also used the ROHF approach developed by Guest and Saunders[16] characterized by the coefficients[11]

$$A_{(ss)} = B_{(ss)} = 1/2 \qquad (s = c, o, v) \tag{55}$$

The results of calculations performed with the coefficients (17) and (55) are presented in Table 1 (see the columns entitled as "original sequence" and "Guest and Saunders's method", respectively). It is easy to see that although the total energy of HNO is the same in both calculations, the electronic configurations as reported in the output appear to be different:

$$\Gamma_c = 6a' \qquad \Gamma_o = 2a' + 2a'' \tag{56}$$

for the coefficients (17), and

$$\Gamma_c = 5a' + a'' \qquad \Gamma_o = 3a' + a'' \tag{57}$$

for the coefficients (55), and this presents an unexpected issue.

A similar discrepancy has been revealed in calculations of other systems. This discrepancy becomes particularly complex in the case of systems with multiple open and closed shells belonging to the symmetry point group C_1. For this

TABLE 1: ROHF Canonical and Noncanonical Orbital Energies ε_j for the Model Open-Shell System HNO (State $^5A''$), and CI Energies of Ions $HNO_z^{1\pm}$

	ROHF[a,b]								CI[a]			
MO	original sequence[c]		intermediate data[d]		canonical orbital energies[e]		Guest and Saunders' method[f]		z[g]	$E_{CI}(HNO_z^{1\pm})$[h]		ΔE_z[i]
Virtual										$q = -1$[j]		
20	+1.7068		+1.7068		+1.7068		+1.7362		10	−127.660701	(^{6}A″)	+1.7068
19	+1.2052		+1.2052		+1.2052		+1.2403		9	−128.162274		+1.2052
18	+1.1008		+1.1008		+1.1008		+1.1660		8	−128.266644		+1.1008
17	+1.0790	(a″)	+1.0790	(a″)	+1.0790	(a″)	+1.1074	(a″)	7	−128.288451	(^{6}A′)	+1.0790
16	+1.0578		+1.0578		+1.0578		+1.0915		6	−128.309632		+1.0578
15	+0.9743		+0.9743		+0.9743		+1.0432		5	−128.393195		+0.9743
14	+0.8250		+0.8250		+0.8250		+0.8650		4	−128.542485		+0.8250
13	+0.7622	(a″)	+0.7622	(a″)	+0.7622	(a″)	+0.8303	(a″)	3	−128.605266		+0.7622
12	+0.7447		+0.7447		+0.7447		+0.8237		2	−128.622791		+0.7447
11	+0.3505		+0.3505		+0.3505		+0.3993		1	−129.016994		+0.3505
Open-shell										$q = +1$		
10	−0.1388		−0.1388		−0.1388		+0.1102		1	−129.228656	(^{4}A″)	−0.1388
9	−0.5762	(a″)	−0.5762	(a″)	−0.5762	(a″)	−0.2194	(a″)	2	−128.791258	(^{4}A′)	−0.5762
8	−0.6601	(a″)	**−0.6753**		**−0.6753**		−0.2592		3	−128.692152		**−0.6753**
7	−0.6753		**−0.9166**		**−0.9166**		−0.5000		4	−128.450831		**−0.9166**
Closed-shell										$q = +1$		
6	−0.7196		**−0.6601 × 2**	**(a″)**	**−0.6601**	**(a″)**	−0.7426	(a″)	1	−128.707387	(^{4}A′)	**−0.6601**
5	−0.9107		**−0.7196 × 2**		**−0.7196**		−0.7897		2	−128.647918	(^{4}A″)	**−0.7196**
4	−0.9166		**−0.9107 × 2**		**−0.9107**		−1.0293		3	−128.456735		**−0.9107**
3	−1.5481		−1.5481 × 2		−1.5481		−1.6399		4	−127.819369		−1.5481
2	−15.7117		−15.7117 × 2		−15.7117		−15.7494		5	−113.655756		−15.7117
1	−20.7512		−20.7512 × 2		−20.7512		−20.7750		6	−108.616284		−20.7512
E_{total}	−129.367477		−129.367477		−129.367477		−129.367477					

[a] Basis set 6-31G. Energy values in Hartrees. All calculations have been performed at the same geometry[15] of HNO ($R_{H-N} = 1.062$ Å, $R_{N-O} = 1.211$ Å, ∠ H−N−O = 108.5°). [b] To simplify this table, only the a″ (π) molecular orbitals are marked explicitly. All other MOs have the symmetry a′(σ). Violations of the Aufbau principle are marked in bold. [c] Calculation with the coefficients $A_{(ss)}$ and $B_{(ss)}$ of eqs 17a−17c. The results of this calculation (MOs and orbital energies) were incorrectly rearranged at the last iteration of the SCF procedure (see the text for details). This caused the open and closed shells to be mis-identified on the output. [d] Calculation with the coefficients $A_{(ss)}$ and $B_{(ss)}$ of eqs 17b, 17c, and 58. [e] Orbital energies satisfying Koopmans' theorem (4a)−(4c). These energies and the respective orbitals are eigenvalues and eigenvectors of the canonical ROHF Hamiltonian (17). [f] Calculation with the coefficients $A_{(ss)}$ and $B_{(ss)}$ of eq 55. [g] z is the number of the CI eigenvalue. [h] Eigenvalues of CI matrices (19), (26), and (27). All matrices have been constructed with the orbitals $\{\phi_j\}$ derived with Guest and Saunders' ROHF method[16] for neutral HNO (state ^{5}A″). [i] $\Delta E_z = \pm\{E_{ROHF}(HNO) - E_{CI}(HNO_z^{1\pm})\}$, where $E_{ROHF}(HNO) = -129.367477$. [j] q is the charge of the ion.

case, all MOs have the same spatial symmetry and, because of this, an immediate ascertainment of the difference between two sets of MOs derived with coefficients (17) and (55) is difficult.

To clarify this discrepancy, we have carried out an additional ROHF calculation of the HNO model with the use of the same coefficients (17b) and (17c) for the open and virtual shells, respectively, and of the new (*intermediate*) coefficients for the closed shell,

$$\tilde{A}_{(cc)} = 0 \qquad \tilde{B}_{(cc)} = 2 \tag{58}$$

This change in the ROHF Hamiltonian must merely result in doubling the closed-shell orbital energies,[5]

$$\tilde{\varepsilon}_k = 2\varepsilon_k \qquad \tilde{\varepsilon}_m = \varepsilon_m \qquad \tilde{\varepsilon}_v = \varepsilon_v \tag{59}$$

without changing the orbitals.

In reality, the use of the specific "orbital-energy-scaling" (58) and (59) leads in this particular case to another order of the closed-shell and open-shell orbitals: compare the orbital energies ε_j in column "original sequence" of Table 1 with the values $\tilde{\varepsilon}_j$ in column "intermediate data". According to the latter data, the desired canonical orbital energies, $\varepsilon_j[\hat{R}_{can}]$, i.e., the eigenvalues of the canonical ROHF Hamiltonian (17), are as follows: $\varepsilon_k[\hat{R}_{can}] = \tilde{\varepsilon}_k/2$, $\varepsilon_m[\hat{R}_{can}] = \tilde{\varepsilon}_m$, and $\varepsilon_v[\hat{R}_{can}] = \tilde{\varepsilon}_v$ (see also the column "canonical orbital energies"). The principal difference between the two sets of orbital energies, ε_j and $\varepsilon_j[\hat{R}_{can}]$, is that the latter do not obey the Aufbau principle.

On the basis of this treatment, we may assume that the wrong data in the column "original sequence" are caused by the specific error in the ROHF algorithm implemented in Gamess.[11] The essense of the error is as follows: after convergence of the SCF procedure was achieved, the program makes a final diagonalization of the ROHF Hamiltonian *just to print out* self-consistent MOs and orbital energies. At this stage, molecular orbitals are rearranged according to the Aufbau principle $\varepsilon_k < \varepsilon_m < \varepsilon_v$. For those systems for which this principle is not fulfilled, the rearranged MO sequence appears incorrect, although the other results of calculation (such as the total energy and the density matrix) derived at the previous stage are correct. This is the case for the HNO model system.

C. CI calculations. To illustrate the use of eqs 33−35, we have derived canonical orbitals and orbitals energies for the same system HNO (state ^{5}A″) via a construction of the CI matrices (19), (26), and (27) and of the respective one-body density matrices (42) for ions $HNO^{1\pm}$. All calculations have been performed with the ORMAS-CI (orbitally restricted multiple active space-CI) method developed and implemented in program GAMESS by Ivanic.[11,17] All CI matrices were constructed on the *noncanonical* ROHF orbitals derived by Guest and Saunders' method.[16]

TABLE 2: ROHF and UHF Orbital Energies εj for Atom Mn (State ^{6}S, Configuration 3d^{5}4s^2) and Experimental IPs[a]

	ROHF				UHF		
	canonical orbital energies[b]	McWeeny and Diercksen' method[c]	Guest and Saunders' method[d]	numerical ROHF (Roothaan's atomic theory)[e]	α spin[f]	β spin	experimental IP[g]
Virtual					Virtual	Virtual	
4p	+0.2678	+0.2841	+0.2922		+0.2626	+0.3200	
(3d)						+0.2095	
5s	+0.0802	+0.0824	+0.0835		+0.0788	+0.0886	
Open-shell							
3d	**−0.6388**	−0.0937	−0.1406	**−0.63885**			0.5231
Closed-shell					Occupied	Occupied	
4s	**−0.2316**	−0.2424	−0.2479	**−0.24787**	−0.2734	−0.2260	0.2732[h]
(3d)					−0.6409		(0.5231)
3p	−2.2351	−2.3981	−2.4795	−2.47953	−2.7275	−2.2319	
3s	−3.6165	−3.7500	−3.8166	−3.81665	−4.0215	−3.6123	
2p	−24.7473	−24.7908	−24.8126	−24.81260	−24.8773	−24.7488	
2s	−29.0435	−29.0874	−29.1095	−29.10948	−29.1762	−29.0434	
1s	−240.5332	−240.5337	−240.5340	−240.53400	−240.5338	−240.5349	
E_{total}	−1149.866215	−1149.866215	−1149.866215	−1149.866251	−1149.869792		

[a] Basis set (23s,15p,11d) from refs 19 and 20. Energy values in Hartrees. Violations of the Aufbau principle are marked in bold. [b] Orbital energies satisfying Koopmans' theorem (4) and (33)−(35). These energies have been derived by two independent methods: canonical ROHF method[5] and limited CI (see the text for details). [c] Reference 18. [d] Reference 16. [e] Reference 21. These orbital energies have been derived with the Froese Fisher' program.[22] [f] $\langle\hat{S}^2\rangle = 8.771$. [g] Reference 23. [h] Experimental value $I_{4s} = 0.2732$ corresponds to the high-spin state ^{7}S of Mn$^+$ (3d^5 4s^1), i.e., corresponds to a removal of a β electron ($I_{4s} = I^{\beta}_{4s}$).

The results are presented in the three last columns of Table 1. We present the total CI energies of ions HNO$^{1\pm}$ and the energy differences,

$$\Delta E_z = \pm\{E_{\text{ROHF}}(\text{HNO}) - E_{\text{CI}}(\text{HNO}^{1\pm})\} \tag{60}$$

where the upper and lower signs correspond to cations and anions, respectively, and the index z numerates eigenvalues of the respective CI matrix. In the course of these calculations, we also derived three respective sets of natural CI orbitals representing the canonical ROHF orbitals for the closed, open, and virtual shells of the parent system HNO. As follows from Table 1, the energy differences ΔE_z (60) appear in all cases equal to the respective *canonical ROHF orbital energies* for the neutral HNO, $\varepsilon_j[\hat{R}_{\text{can}}]$, and this is in complete agreement with eqs 33−35.

For comparison, the same CI calculations have been performed with the use of ROHF orbitals derived by both Roothaan's method[10] and McWeeny and Diercksen's method,[18] for which the coefficients $A_{(\text{ss})}$ and $B_{(\text{ss})}$ of eq 16 differ significantly[5] from those in eqs 17 and 55. As expected, the results appeared identical to those of Table 1, because in the case under study the CI total energies and natural orbitals are independent of the choice of ROHF orbitals.

D. Manganese Atom. As a more physical example, we present here canonical orbital energies for a real (nonartificial) open-shell system in its ground state, for which the orbital energies satisfying Koopmans' theorem do not satisfy the Aufbau principle. In Table 2 we compare the orbital energies for the free atom Mn in its ground ^{6}S state (configuration 3d^{5}4s^2) derived with different ROHF treatments and experimental IPs. As is well-known, experiment shows that ionization from the closed 4s shell is easier than from the half-filled 3d orbitals. For completeness, we also present the respective UHF orbital energies.

To derive the canonical orbitals and orbital energies for the neutral Mn with the canonical ROHF method,[5] we exploited the technique described above [eqs 58 and 59 where, in this case, $\tilde{B}_{(\text{cc})} \geq 3$] to obtain correct results from GAMESS. The same canonical orbitals and orbital energies have been derived with a FCI-RAS method. The respective CI matrices (19), (26), and (27) of the dimension 10 × 10, 5 × 5, and 118 × 118, respectively, were constructed using the orbitals derived by Guest and Saunders method.[16]

The AO basis set[19,20] for atom Mn used in this work gives an ROHF energy close to the ROHF limit (see Table 2), and so, all the orbital energies in Table 2 can be immediately compared with each other. The essential differences in orbital energies derived with different ROHF treatments are caused by different forms of the respective Hamiltonians. For a better understanding of these differences, we present the coefficients[5] $A_{(\text{ss})}$ and $B_{(\text{ss})}$ of eq 16 characterizing the respective ROHF Hamiltonians:

	$A_{(cc)}$	$B_{(cc)}$	$A_{(oo)}$	$B_{(oo)}$	$A_{(vv)}$	$B_{(vv)}$
Canonical ROHF method[5]	0	1	1	0	1	0
McWeeny and Diercksen' method[18]	1/3	2/3	1/3	1/3	2/3	1/3
Guest and Saunders' method[16]	1/2	1/2	1/2	1/2	1/2	1/2
Roothaan atomic theory[21]	1/2	1/2	1	0	–	–

(61)

This shows that among the closed-shell orbital energies presented in Table 2 only the *canonical* ones satisfy KT. The open-shell energy ε_{3d} satisfying KT is correctly reproduced also in the ROHF atomic method.[21]

As follows from Table 2, the *canonical* ROHF orbital energies for atom Mn satisfying KT violate the Aufbau principle since the closed 4s orbital energy lies above the open 3d energy. The case of atom Mn provides us with a possibility to verify this violation by experimental data. A qualitative agreement between the canonical orbital energies $\varepsilon_{3d} = -0.6388$ and $\varepsilon_{4s} = -0.2316$ and the respective vertical IPs,[23] 0.5231 and 0.2732, following from Table 2 is of principal importance. This shows that the canonical ROHF orbital energies have physical meaning and that the violations of the Aufbau principle reflect the physical reality.

A comparison between the canonical ROHF and UHF data shows that in this specific case where the closed-shell and open-shell orbitals are fully separated by symmetry, the UHF orbital energies $\varepsilon_{3d}^{\alpha} = -0.6409$ and $\varepsilon_{4s}^{\beta} = -0.2260$ appear close to the respective ROHF energies (−0.6388 and −0.2316) and give approximately the same KT estimates for the vertical IPs. It should be emphasized, however, that this is not a general case.

The validity of Koopmans' theorem in the UHF method

$$\begin{aligned} \varepsilon_k^{\alpha} &= -I_k^{\alpha} \\ \varepsilon_k^{\beta} &= -I_k^{\beta} \\ \varepsilon_m^{\alpha} &= -I_m^{\alpha} \end{aligned} \tag{62}$$

where, as above, $k = 1, 2, ..., N_c$ and $m = N_c + 1, ..., N_c + N_o$, follows from the formal treatment of KT in the UHF method within both the limited CI[7] and the "frozen" orbital approximation. This validity needs a detailed reanalysis which will be given in another paper. Here we can state that the first of the three KT relationships (62) is wrong in the general case while the validity of the two last relationships in (62) needs a detailed analysis in each particular case.

VI. Conclusion

Koopmans' theorem for ROHF is closely related to the results of limited CI calculations using configurations differing by one orbital from the ROHF wave function. Using this concept, we have derived the relationship between the *canonical* ROHF orbital energies[5] satisfying Koopmans' theorem for the initial open-shell system X, $\varepsilon_z(\mathrm{X})$, and the limited CI energies for ions, $E_{\mathrm{CI}}(\mathrm{X}z\,\pm)$, in three cases: ionization of a β electron from the closed shell (4a), ionization of an α electron from the open shell (4b), and addition of an α electron to the virtual shell (4c). In all of these cases, the relationship takes the same form:

$$\varepsilon_z(\mathrm{X}) = \pm\{-E_{\mathrm{CI}}(\mathrm{X}_z^{\pm}) + E_{\mathrm{ROHF}}(\mathrm{X})\} \tag{63}$$

where the upper and lower signs correspond to cations and anions, respectively (see also eqs 29, 33, 34, and the last column in Table 1).

This key relationship proves that the energy of ions first defined within the canonical ROHF method[5] in a *nonvariational* manner, i.e., in the approximation of "frozen" orbitals, really corresponds to the limited CI energy. This result also explains the well-known "paradox"[24] according to which the estimates of IPs via Koopmans' theorem[24,25] in most cases agree better with experimental vertical IPs than the respective estimates derived by Δ*S*CF (ΔROHF) method.

On the basis of the CI approach developed, we also have shown that the *canonical* ROHF orbitals $\{\theta_z\}$ for the closed, open, and virtual shells of the initial system X generally appear as the *natural CI orbitals* for the respective ions. The multideterminantal CI wave functions for all of these ions constructed on the canonical ROHF orbitals $\{\theta_z\}$ are *simultaneously* reduced to the form of single Slater determinants.

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