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Citation: *J. Chem. Phys.* **132**, 184110 (2010); doi: 10.1063/1.3418615

View online: <http://dx.doi.org/10.1063/1.3418615>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v132/i18>

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# Koopmans's theorem in the restricted open-shell Hartree–Fock method.

## II. The second canonical set for orbitals and orbital energies

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(Received 3 January 2010; accepted 8 April 2010; published online 14 May 2010)

A treatment of the validity of Koopmans's theorem (KT) in the restricted open-shell Hartree–Fock (ROHF) method can be separated into two essentially different cases. The first of them involves the one-electron processes  $X \rightarrow X_j^\pm$  in which the spin state of an ion  $X_j^\pm$  having a hole or an extra electron in the closed, open or virtual orbital  $\phi_j$  is correctly described by a one-determinant wave function. This case was analyzed using different methods by Plakhutin *et al.* [J. Chem. Phys. **125**, 204110 (2006)] and by Plakhutin and Davidson [J. Phys. Chem. A **113**, 12386 (2009)]. In the present work we analyze more complex processes where the state of an ion cannot be described by a single determinant. An example of such processes is the removal of an *alpha* electron from the closed shell of a high-spin half-filled open-shell system  $X$ . For this case we give a slightly generalized formulation of KT in both the “frozen” orbital approximation (i.e., within the *canonical* ROHF method) and the limited configuration interaction approach for ionized systems. We also show that a simultaneous treatment of KT for all one-electron ionization processes possible leads to the necessity of introducing in the canonical ROHF method *two different sets of orbitals* and *two respective sets of orbital energies*. The theory developed is compared with the previous formulations of KT in the restricted (ROHF) and unrestricted Hartree–Fock methods, and in the unrestricted density functional theory. The practical applicability of the theory is verified by comparing the KT estimates of the vertical ionization potentials in molecules  $O_2$  and  $NO_2$  with the respective experimental data. © 2010 American Institute of Physics. [doi:10.1063/1.3418615]

### I. INTRODUCTION

The validity of Koopmans's theorem<sup>1</sup> (KT) in the restricted open-shell Hartree–Fock (ROHF) method has been proved using different methods in our previous papers<sup>2,3</sup> for the three one-electron ionization processes **A1**, **B1**, and **C1** possible in a high-spin open-shell system  $X$  with one or more half-filled orbitals:

**A1**: a removal of a *beta* electron from the  $k$ th closed-shell orbital ( $X \rightarrow X_{k,\beta}^+$ ),

$$\varepsilon_k = -I_k^\beta, \quad (1a)$$

**B1**: a removal of an *alpha* electron from the  $m$ th open-shell orbital ( $X \rightarrow X_{m,\alpha}^+$ ),

$$\varepsilon_m = -I_m^\alpha, \quad (1b)$$

**C1**: an attachment of an *alpha* electron to the  $v$ th virtual orbital ( $X \rightarrow X_{v,\alpha}^-$ ),

$$\varepsilon_v = -A_v^\alpha, \quad (1c)$$

where  $\varepsilon_i$  are *canonical* ROHF orbital energies defined as eigenvalues of the special (canonical) ROHF Hamiltonian,  $\hat{R}_{\text{can}}$ ,

$$\hat{R}_{\text{can}}|\theta_i\rangle = \varepsilon_i|\theta_i\rangle, \quad (2)$$

derived by Plakhutin *et al.*<sup>2</sup> for open-shell systems  $X$  under study.

The  $I_j^\sigma$  and  $A_j^\sigma$  values ( $\sigma = \alpha$  or  $\beta$ ) in Eqs. (1a)–(1c) are Koopmans's approximations to the  $j$ th vertical ionization potential (IP) and electron affinity (EA), respectively,

$$I_j^\sigma = E(X_{j,\sigma}^+) - E_{\text{ROHF}}(X) \quad (j = k \text{ or } j = m), \quad (3)$$

$$A_j^\sigma = E_{\text{ROHF}}(X) - E(X_{j,\sigma}^-) \quad (j = v),$$

where  $E_{\text{ROHF}}(X)$  is the ROHF energy of the initial (nonionized) system  $X$  and  $E(X_{j,\sigma}^\pm)$  is the energy of an ion  $X_{j,\sigma}^\pm$ .

For the first time, the validity of Koopmans's relationships (1a)–(1c) has been proven in Ref. 2 for the case when  $E(X_{j,\sigma}^\pm)$  is defined within the approximation of “frozen” orbitals,

$$E(X_{j,\sigma}^\pm) = E_{\text{frozen}}(X_{j,\sigma}^\pm) = \langle \Psi_{j,\sigma}^\pm | \hat{H} | \Psi_{j,\sigma}^\pm \rangle, \quad (4)$$

where  $\Psi_{j,\sigma}^\pm$  is a one-determinant wave function for an ion  $X_{j,\sigma}^\pm$  formed with the same (frozen) canonical ROHF orbitals  $\{\theta_j\}$  of Eq. (2) optimal for the parent system  $X$ .

The principally important aspect of the proof<sup>2</sup> is that both the energy differences  $\Delta E_{j,\sigma} = E_{\text{frozen}}(X_{j,\sigma}^\pm) - E_{\text{ROHF}}(X)$  representing IPs or EAs (3) in the respective subspace ( $j \in$  closed shell,  $j \in$  open shell, or  $j \in$  virtual shell) and the special (canonical) orbitals  $\{\theta_j\}$  of the same subspace are

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defined from the additional variational condition  $\delta\Delta E_{j,\sigma}=0$  providing a stationarity of  $\Delta E_{j,\sigma}$  with respect to a variation of the orbitals  $\{\theta_j\}$  within the respective subspace. This condition was introduced by Plakhutin *et al.* within the canonical ROHF method<sup>2</sup> in addition to the usual condition,  $\delta E_{\text{ROHF}}=0$ , which provides the stationarity of the total energy  $E_{\text{ROHF}}(X)$  with respect to a variation in the orbitals  $\{\theta_j\}$  within the full orbital space  $\{\theta_j\}=\{\theta_k\}\oplus\{\theta_m\}\oplus\{\theta_v\}$ .

It is worth emphasizing here that the formulation<sup>2</sup> of KT in the ROHF method given by Eqs. (1a)–(1c) and (2), where  $I_j^\sigma$  and  $A_j^\sigma$  are defined in approximations (3) and (4) is in complete accordance with the original formulation of KT given by Koopmans<sup>1</sup> within the closed-shell self-consistent field (SCF). We also note here that the one-determinant wave functions  $\Psi_{j,\sigma}^\pm$  in the cases (1a)–(1c) describe correctly the spin states of ions  $X_{j,\sigma}^\pm$ ,

$$S(X_{k,\beta}^+) = S + 1/2, \quad S(X_{m,\alpha}^+) = S - 1/2, \quad S(X_{v,\alpha}^-) = S + 1/2, \quad (5)$$

where  $S \equiv S(X)$  is the total spin of a high-spin open-shell system  $X$  with one or more half-filled orbitals.

An alternative proof of the validity of Koopmans's relationships (1a)–(1c) has been given by Plakhutin and Davidson<sup>3</sup> using an elaboration of the method suggested by Newton<sup>4</sup> and Hillier and Saunders.<sup>5</sup> This proof showed that the energy of an ion  $E(X_{j,\sigma}^\pm) = E_{\text{frozen}}(X_{j,\sigma}^\pm)$  defined in Ref. 2 in the frozen orbital approximation is actually equal to the energy defined in a limited configuration interaction (CI),

$$E(X_{j,\sigma}^\pm) = E_{\text{frozen}}(X_{j,\sigma}^\pm) = E_{\text{CI}}(X_{j,\sigma}^\pm), \quad (6)$$

where  $E_{\text{CI}}(X_{j,\sigma}^\pm)$  is a  $j$ th eigenvalue of the CI matrix  $\langle \Psi_{p,\sigma}^\pm | \hat{H} | \Psi_{q,\sigma}^\pm \rangle$ . In this case, the one-determinant wave functions  $\Psi_{p,\sigma}^\pm$  and  $\Psi_{q,\sigma}^\pm$  are formed with *arbitrary* (possibly non-canonical) ROHF orbitals optimal for  $X$ , and the active CI space involves all the orbitals and electrons of the respective ionized shell ( $p, q \in$  closed shell,  $p, q \in$  open shell, or  $p, q \in$  virtual shell). Combining Eqs. (1a)–(1c), (3), (4), and (6), we have derived a CI-based formulation of KT in a ROHF method,<sup>3</sup>

$$I_j^\sigma = E_{\text{CI}}(X_{j,\sigma}^+) - E_{\text{ROHF}}(X) \\ = E_{\text{frozen}}(X_{j,\sigma}^+) - E_{\text{ROHF}}(X) = -\varepsilon_j, \quad (7)$$

and a similar form for the EA  $A_j^\sigma$ . The last two of relationship (7) represent the usual (particular) formulation of KT [Eqs. (1a)–(1c)], which is valid only within the canonical ROHF method,<sup>2</sup> while the first one represents a more general formulation of KT valid in arbitrary (noncanonical) ROHF treatments.<sup>3</sup>

The three one-electron ionization processes of Eqs. (1a)–(1c) do not exhaust all possible cases in a ROHF method. One can consider also three alternative processes, which we call as **A2**, **B2**, and **C2**, i.e.

**A2**: a removal of an alpha electron from the  $k$ th closed-shell orbital,

$$X \rightarrow X_{k,\alpha}^+, \quad (8a)$$

**B2**: an attachment of a *beta* electron to the  $m$ th open-shell orbital,

$$X \rightarrow X_{m,\beta}^-, \quad (8b)$$

**C2**: an attachment of a beta electron to the  $v$ th virtual orbital,

$$X \rightarrow X_{v,\beta}^-. \quad (8c)$$

An analysis of the validity of KT in these three cases is of interest in two respects. The first one is that the treatment of these cases in parallel with a treatment of cases (1a)–(1c) leads to the necessity of introducing in the canonical ROHF method<sup>2</sup> *two different sets of orbitals* and *two respective sets of orbital energies*. For the first time such a duality of the canonical ROHF method was discussed by Plakhutin and Gorelik<sup>6</sup> for the particular case of alternative processes **B1** and **B2**. In the present work we present a general treatment of cases (8a)–(8c) in comparison with the treatment<sup>2,3</sup> for cases (1a)–(1c) and the treatment<sup>6</sup> for case (8b) and give a detailed analysis of the duality of the canonical ROHF method.

The second specific problem arising in the treatment of KT for processes (8a)–(8c) is that the one-determinant wave functions for ions (8a) and (8c),  $\Psi_{k,\alpha}^+$  and  $\Psi_{v,\beta}^-$ , defined using the frozen orbitals optimal for the parent system  $X$ , are not eigenfunctions of the operator  $\hat{S}^2$  and, hence, do not describe properly the spin states of the respective ions. This essentially complicates a treatment of the validity of KT. The same problem arises within unrestricted Hartree-Fock (UHF) and density functional theory (UDFT) methods in the limit case of small spin polarization when the low-lying spin-up orbital energies approximate to doubly occupied ROHF levels.

As shown by Gritsenko and Baerends,<sup>7,8</sup> within unrestricted methods it is not possible to give a rigorous formulation of KT for process **A2** [Eq. (8a)]. This conclusion is in contrast to the well-known *formal* validity of KT within a UHF method first proved by Stepanov *et al.*<sup>9</sup> For two ionization processes in the closed shell, **A1** [Eq. (1a)] and **A2** [Eq. (8a)], taken here as an example, the KT relationships<sup>9</sup> take the form

$$I_k^\beta = -\varepsilon_k^\beta, \quad (9)$$

$$I_k^\alpha = -\varepsilon_k^\alpha,$$

where  $\varepsilon_k^\alpha$  and  $\varepsilon_k^\beta$  are the lowest eigenvalues of the UHF Fock operators  $\hat{F}^\alpha$  and  $\hat{F}^\beta$  corresponding to ROHF closed-shell orbital energies  $\varepsilon_k$  ( $k=1, 2, \dots, N_c$ ). As an alternative to Eq. (9), Gritsenko and Baerends<sup>7,8</sup> offered the following *approximate* analogs of KT for the same processes **A1** and **A2** within a UDFT approach,

$$I_k^\beta \approx -\varepsilon_k^\beta, \quad (10)$$

$$I_k^\alpha \approx -\{(2S+1)\varepsilon_k^\alpha - \varepsilon_k^\beta\}/(2S),$$

where  $S \equiv S(X)$  is the total spin of the initial (nonionized) system  $X$ , and in this case,  $I_k^\beta$  and  $I_k^\alpha$  are the *experimental* IPs,<sup>7</sup> and the first of the relationships (10) takes the form  $I_{N_c}^\beta = \varepsilon_{N_c}^\beta$  (exact equality) for the highest occupied beta level.<sup>7</sup> Below we shall discuss the approaches<sup>7-9</sup> and compare the

formulations of KT (9) and (10) with those developed in the present work.

The analysis of this problem at a ROHF level performed by Sauer *et al.*<sup>10,11</sup> has led to the conclusion that *KT is generally not valid in the ROHF method*, since some of the IPs and EAs defined by Eq. (3) cannot be equated to eigenvalues of some special (canonical) ROHF Hamiltonian. The source of this wrong conclusion<sup>10</sup> was discussed in our previous paper<sup>3</sup> with respect to process **B1**. Below we shall discuss how the approach of Sauer *et al.*<sup>10,11</sup> to more complex cases **A2** and **C2** differs from the approach developed in the present paper.

In this work we give the formulation of KT in the ROHF method for the ionization processes (8a)–(8c). We derive the new form for the canonical ROHF Hamiltonian  $\hat{Q}_{\text{can}}$ ,

$$\hat{Q}_{\text{can}} |\xi_i\rangle = \varepsilon_i [\hat{Q}_{\text{can}}] |\xi_i\rangle, \quad (11)$$

the eigenvalues  $\varepsilon_i [\hat{Q}_{\text{can}}]$  of which obey KT for processes (8a)–(8c),

$$\mathbf{A2:} \quad \varepsilon_k [\hat{Q}_{\text{can}}] = -I_k^\alpha, \quad (12a)$$

$$\mathbf{B2:} \quad \varepsilon_m [\hat{Q}_{\text{can}}] = -A_m^\beta, \quad (12b)$$

$$\mathbf{C2:} \quad \varepsilon_v [\hat{Q}_{\text{can}}] = -A_v^\alpha, \quad (12c)$$

while the respective eigenvectors  $\{\xi_i\} = \{\xi_k\} \oplus \{\xi_m\} \oplus \{\xi_v\}$  of  $\hat{Q}_{\text{can}}$  represent the *second canonical set of ROHF orbitals* for the parent system  $X$ .

By derivation, Koopmans's relationships (12a)–(12c) are based on the definition of IPs and EAs in frozen orbital approximation (4), i.e., the wave functions for ions (8a)–(8c) are defined on the same canonical orbitals  $\{\xi_i\}$  of Eq. (11) optimal for  $X$ . The essential point of our treatment is that the wave functions of all ions in Eqs. (8a)–(8c) are eigenfunctions of the operator  $\hat{S}^2$  and correctly describe the ion states,

$$S(X_{k,\alpha}^+) = S(X_{m,\beta}^-) = S(X_{v,\beta}^-) = S - 1/2. \quad (13)$$

The wave functions for ions  $X_{m,\beta}^-$  [Eq. (8b)] are represented by a single Slater determinant, while the wave functions for ions  $X_{k,\alpha}^+$  [Eq. (8a)] and  $X_{v,\beta}^-$  [Eq. (8c)] appear in our treatment as well-defined combinations of determinants with fixed (nonvariational) coefficients determined by spin projection.

To complete this treatment we also give a general (CI-based) formulation of KT for processes (8a)–(8c), which is based on the limited CI treatment for ions. We prove that the energy of ions (8a)–(8c) defined in Eqs. (12a)–(12c) in the frozen orbital approximation is actually equal to the energy defined in a limited CI. The new formulation of KT is valid in an arbitrary ROHF treatment and reduces to the particular formulation, Eqs. (12a)–(12c), within the canonical ROHF method.

## II. DUALITY OF THE CANONICAL ROHF METHOD

### A. Brief review

In order to simplify the following treatment we here present a brief summary of the basic definitions and formulas used in the treatment<sup>2,3</sup> of KT in the ROHF method. For a high-spin half-filled open-shell system  $X$ , which is a parent system in processes (1a)–(1c) and (8a)–(8c) and is characterized by Roothaan coupling coefficients<sup>12</sup>

$$f = 1/2, \quad a = 1, \quad b = 2, \quad (14)$$

the widely used choices for the total one-electron ROHF Hamiltonian  $\hat{R}$ ,

$$\hat{R}|\phi_i\rangle = \varepsilon_i [\hat{R}] |\phi_i\rangle, \quad (15)$$

can be presented in the common form of the symmetric (Hermitian) matrix  $\langle \eta_i | \hat{R} | \eta_j \rangle$  defined in the basis of *non-self-consistent* molecular orbitals  $\{\eta_i\}$ ,<sup>2</sup>

$$\begin{array}{c|ccc} & \text{Closed-shell} & \text{Open-shell} & \text{Virtual} \\ \hline \text{Closed-shell} & \hat{R}^{(cc)} & 2(\hat{F}_c - \hat{F}_o) & \hat{F}_c \\ \text{Open-shell} & \hat{F}^\beta & \hat{R}^{(oo)} & 2\hat{F}_o \\ \text{Virtual} & (\hat{F}^\alpha + \hat{F}^\beta)/2 & \hat{F}^\alpha & \hat{R}^{(vv)} \end{array}, \quad (16)$$

where

$$\hat{F}_c = \hat{h} + (2\hat{J}_c - \hat{K}_c) + f(2\hat{J}_o - \hat{K}_o), \quad (17)$$

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

are the ROHF Fock operators<sup>12,13</sup> for the closed-shell and open-shell orbitals, respectively. For comparison, the lower triangle of the matrix (16) is expressed in terms of the Fock operators  $\hat{F}^\alpha$  and  $\hat{F}^\beta$  defined in the UHF method,<sup>14</sup>

$$\hat{F}^\alpha = \hat{h} + (\hat{J}^\alpha + \hat{J}^\beta) - \hat{K}^\alpha, \quad (18)$$

$$\hat{F}^\beta = \hat{h} + (\hat{J}^\alpha + \hat{J}^\beta) - \hat{K}^\beta.$$

For the open-shell systems under consideration, Eq. (14), the ROHF and UHF Fock operators defined on the *same ROHF orbitals* are connected by the relationships  $\hat{F}^\alpha = 2\hat{F}_o$  and  $\hat{F}^\beta = 2(\hat{F}_c - \hat{F}_o) = \hat{h} + (2\hat{J}_c - \hat{K}_c) + \hat{J}_o$  so that the ROHF Hamiltonian matrix, Eq. (16), is symmetric.

In the self-consistent limit ( $\eta_i = \phi_i$ ), the off-diagonal blocks in Eq. (16) vanish, and this provides a fulfillment of the three variational conditions  $(\hat{F}_c)_{kv} = 0$ ,  $(2\hat{F}_o)_{mv} = 0$ , and  $2(\hat{F}_c - \hat{F}_o)_{km} = 0$ , which follow from both the usual variational condition in the ROHF method,  $\delta E_{\text{ROHF}} = 0$  (Ref. 12), and Brillouin's theorem.<sup>15</sup>

For the systems (14) under study, various definitions for ROHF Hamiltonians (15) and (16) differ between the diagonal blocks only.<sup>2</sup> The self-consistent orbitals  $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$  derived with different ROHF Hamiltonians (15) and (16) differ from each other by an arbitrary unitary

transformation within the closed  $\{\phi_k\}$ , open  $\{\phi_m\}$ , and virtual  $\{\phi_v\}$  sets. Below we shall refer to the orbitals  $\{\phi_i\}$  of Eq. (15) as to *arbitrary ROHF orbitals* optimal for  $X$ .

The special (canonical) ROHF orbitals  $\{\theta_i\} = \{\theta_k\} \oplus \{\theta_m\} \oplus \{\theta_v\}$  are obtained as eigenfunctions of the special ROHF Hamiltonian  $\hat{R} = \hat{R}_{\text{can}}$  of Eq. (2), which corresponds to the following choice for the diagonal blocks in Eq. (16):<sup>2</sup>

$$\mathbf{A1:} \quad \hat{R}_{\text{can}}^{(cc)} = 2(\hat{F}_c - \hat{F}_o) = \hat{F}^\beta, \quad (19a)$$

$$\mathbf{B1:} \quad \hat{R}_{\text{can}}^{(oo)} = 2\hat{F}_o = \hat{F}^\alpha, \quad (19b)$$

$$\mathbf{C1:} \quad \hat{R}_{\text{can}}^{(vv)} = 2\hat{F}_o = \hat{F}^\alpha. \quad (19c)$$

These three definitions have been derived by Plakhutin *et al.*<sup>2</sup> from the condition that the three respective Koopmans's relationships (1a)–(1c) above are to be satisfied in the “frozen” orbital approximation (4). The details of the computational procedure realizing the canonical ROHF method [Eqs. (14)–(16) and (19a)–(19c)] are presented in Sec. VI.

In the treatment below we extend the approach<sup>2,3</sup> to processes (8a)–(8c). At first we define the *second canonical form* for the diagonal blocks  $\hat{R}^{(ss)}$  of Eq. (16), where  $s=c, o,$  and  $v$  for the closed, open, and virtual shell, respectively, in order to satisfy the respective Koopmans's relationships (12a)–(12c). Following the notations of Eqs. (11) and (19a)–(19c), we shall designate the new blocks as  $\hat{Q}_{\text{can}}^{(cc)}$ ,  $\hat{Q}_{\text{can}}^{(oo)}$ , and  $\hat{Q}_{\text{can}}^{(vv)}$ , respectively.

## B. The second canonical set of orbitals and orbital energies for the open shell

We start the treatment with case **B2** of Eq. (8b) corresponding to attachment of a beta electron to the high-spin half-filled open shell,  $X \rightarrow X_{m,\beta}^-$ . The one-determinant wave function for anion  $X_{m,\beta}^-$  defined in the basis of *noncanonical* ROHF orbitals  $\{\phi_i\} = \{\phi_k\} \oplus \{\phi_m\}$  of Eq. (15) optimal for the initial (nonionized) system  $X$  takes the form

$$|\Psi_{m,\beta}^-\rangle = \det[\phi_1 \bar{\phi}_1 \dots \phi_{N_c} \bar{\phi}_{N_c} \phi_{N_c+1} \bar{\phi}_{N_c+2} \dots \phi_{N_c+m-1} \bar{\phi}_{N_c+m} \bar{\phi}_{N_c+m} \phi_{N_c+m+1} \bar{\phi}_{N_c+m+2} \dots \phi_{N_c+N_o}], \quad (20)$$

where  $N_c$  and  $N_o$  are the numbers of closed-shell and open-shell orbitals, respectively, in the initial system  $X$ . By definition, this wave function is an eigenfunction of the operator  $\hat{S}^2$ , and hence as shown previously,<sup>6</sup> a treatment of case **B2** is completely analogous to the treatment of cases **A1**, **B1**, and **C1** of Eqs. (1a)–(1c) within the canonical ROHF method.<sup>2</sup>

A starting point of the approach<sup>2,6</sup> to process **B2** is the particular form of KT for this case given by Eq. (12b) above, i.e.,  $\varepsilon_m[\hat{Q}_{\text{can}}] = -A_m^\beta$ , where  $A_m^\beta$  is defined in the frozen orbital approximation,  $A_m^\beta = E_{\text{ROHF}}(X) - \langle \Psi_{m,\beta}^- | \hat{H} | \Psi_{m,\beta}^- \rangle$ , with the use of the canonical ROHF orbitals  $\{\xi_i\}$  optimal for  $X$ . So, to prove the validity of Eq. (12b), we have to define the canonical ROHF Hamiltonian  $\hat{Q}_{\text{can}}$  (11), the eigenvectors  $\{\xi_i\}$  of which give the value of  $A_m^\beta$  satisfying Eq. (12b). Since both  $\langle \Psi_{m,\beta}^- | \hat{H} | \Psi_{m,\beta}^- \rangle$  and  $E_{\text{ROHF}}(X)$  are independent of the choice of closed-shell orbitals optimal for  $X$ , we actually have to

define the diagonal open-shell block  $\hat{Q}_{\text{can}}^{(oo)}$  only. The exact choice of this block unambiguously defines canonical orbitals  $\{\xi_m\}$  and orbital energies  $\varepsilon_m[\hat{Q}_{\text{can}}]$  for the open shell. Following this approach one obtains the following definition of  $\hat{Q}_{\text{can}}^{(oo)}$ :

$$\mathbf{B2:} \quad \hat{Q}_{\text{can}}^{(oo)} = 2(\hat{F}_c - \hat{F}_o) = \hat{F}^\beta, \quad (21)$$

first derived by Plakhutin and Gorelik.<sup>6</sup> It is easy to verify that the open-shell eigenvalues  $\varepsilon_m[\hat{Q}_{\text{can}}]$  of the *full* ROHF Hamiltonian  $\langle \eta_i | \hat{R} | \eta_j \rangle$ , Eq. (16), in which  $\hat{R}^{(oo)} = \hat{Q}_{\text{can}}^{(oo)}$  and the other diagonal blocks are arbitrary, do satisfy Koopmans's relationship (12b), i.e.,

$$\varepsilon_m[\hat{Q}_{\text{can}}] = -A_m^\beta.$$

The same eigenvalues  $\varepsilon_m[\hat{Q}_{\text{can}}]$  can be obtained by a diagonalization of the diagonal open-shell block  $\langle \phi_m | \hat{Q}_{\text{can}}^{(oo)} | \phi_n \rangle$  of matrix (16) defined in the basis of *self-consistent noncanonical* orbitals  $\{\phi_i\}$  of Eq. (15) optimal for  $X$ .

The eigenvectors  $\{\xi_m\}$  of ROHF Hamiltonian (16), in which  $\hat{R}^{(oo)} = \hat{Q}_{\text{can}}^{(oo)}$ , represent the second set of *canonical open-shell* ROHF orbitals.<sup>6</sup> The difference between two canonical sets of ROHF orbitals and orbital energies will be discussed below.

## C. Variational formulation of KT for process B2

Definition (21) enables us to give a more general (variational) formulation of KT (12b) similar to formulation (7) for cases **A1**, **B1**, and **C1**. Following the approach used in Ref. 3, we define the CI matrix  $T_{mn}^{(oo)}$  as

$$T_{mn}^{(oo)} = \langle \Psi_{m,\beta}^- | \hat{H} | \Psi_{n,\beta}^- \rangle, \quad (22)$$

where  $m, n = 1, 2, \dots, N_o$  and  $\Psi_{m,\beta}^-$  is defined by Eq. (20). Following the procedure<sup>3</sup> we obtain the following relationship between matrices (21) and (22):

$$T_{mn}^{(oo)} = (-1)^{n-m} (\hat{Q}_{\text{can}}^{(oo)})_{mn} + \delta_{mn} E_{\text{ROHF}}(X), \quad (23)$$

where both  $T_{nm}^{(oo)}$  and  $(\hat{Q}_{\text{can}}^{(oo)})_{mn}$  matrices are defined in the same noncanonical basis  $\{\phi_i\}$ , Eq. (15), optimal for  $X$ . It is easy to show<sup>3</sup> that although these matrices do not commute, their eigenvalues obey the relationship

$$\varepsilon_z[T^{(oo)}] = \varepsilon_z[\hat{Q}_{\text{can}}^{(oo)}] + E_{\text{ROHF}}(X), \quad (24)$$

where  $z = 1, 2, \dots, N_o$ . By definition, a  $z$ th eigenvalue of the matrix  $T^{(oo)}$  is equal to the CI energy of anion  $X_{z,\beta}^-$ ,

$$\varepsilon_z[T^{(oo)}] \equiv E_{\text{CI}}(X_{z,\beta}^-), \quad (25)$$

while the eigenvalues of the matrix  $\hat{Q}_{\text{can}}^{(oo)}$  satisfy KT in the particular form (12b), i.e.,  $\varepsilon_z[\hat{Q}_{\text{can}}^{(oo)}] = -A_z^\beta$ . Combining the latter relationship with Eqs. (4), (5), and (25), we obtain the general formulation of KT in the ROHF method for process **B2**,

$$A_z^\beta = E_{\text{ROHF}}(X) - E_{\text{CI}}(X_{z,\beta}^-) \\ = E_{\text{ROHF}}(X) - E_{\text{frozen}}(X_{z,\beta}^-) = -\varepsilon_z[\hat{Q}_{\text{can}}^{(oo)}]. \quad (26)$$

To complete this treatment, we note that the multideterminantal CI wave function  $|\Phi_{z,\beta}^- \rangle$  corresponding to anion  $X_{z,\beta}^-$  and derived as a  $z$ th eigenfunction of the matrix  $T^{(oo)}$ ,

$$|\Phi_{z,\beta}^- \rangle = \sum_n U_n^{(z)} |\Psi_{n,\beta}^- \rangle, \quad (27)$$

$$\sum_n T_{mn}^{(oo)} U_n^{(z)} = U_m^{(z)} \varepsilon_z [T^{(oo)}], \quad (28)$$

where  $U_n^{(z)}$  are the coefficients of the CI expansion over determinants  $|\Psi_{n,\beta}^- \rangle$  of Eq. (20) and all determinants (20) are defined with noncanonical ROHF orbitals  $\{\phi_i\}$  optimal for  $X$ , is reduced to a single Slater determinant defined in the basis of canonical open-shell ROHF orbitals  $\{\xi_m\}$ ,

$$|\Phi_{z,\beta}^- \rangle = \det |\phi_1 \bar{\phi}_1 \dots \phi_{N_c} \bar{\phi}_{N_c} \xi_1 \bar{\xi}_1 \dots \xi_{z-1} \bar{\xi}_{z-1} \xi_z \bar{\xi}_z \xi_{z+1} \bar{\xi}_{z+1} \dots \xi_{N_o} \bar{\xi}_{N_o}|, \quad (29)$$

where  $z=1, 2, \dots, N_o$ . We do not present here the proof of equivalency of Eqs. (27) and (29) since this proof is completely analogous to that given in Ref. 3 for case **B1**.

### III. THE IONIZATION PROCESSES A2 and C2

A treatment of KT in a ROHF method for processes **A2**, Eq. (8a), and **C2**, Eq. (8c), is more complex than that for processes **A1**, **B1**, and **C1** of Eqs. (1a)–(1c) and **B2** of Eq. (8b). The main problem comes from the fact that the one-determinant wave functions for the respective ions,  $X_{k,\alpha}^+$  and  $X_{v,\beta}^-$ , are not eigenfunctions of the operator  $\hat{S}^2$ . This makes the original Koopmans's idea<sup>1</sup> and previous approaches<sup>2,3,5</sup> to a treatment of KT in a ROHF method inapplicable. In this section we give a slightly generalized formulation of KT in a ROHF method based on the symmetry-adapted (multideterminantal) form for the wave functions of ions  $X_{k,\alpha}^+$  and  $X_{v,\beta}^-$ .

#### A. The pure spin symmetry ROHF wave function for ion $X_{k,\alpha}^+$

We start the treatment with the case  $X \rightarrow X_{k,\alpha}^+$ , Eq. (8a), corresponding to a removal of an alpha electron from the closed shell of the parent system  $X$ . The one-determinant wave function for ion  $X_{k,\alpha}^+$  formed with the frozen noncanonical ROHF orbitals  $\{\phi_i\}$ , Eq. (15), optimal for  $X$  takes the form

$$|\Psi_{k,\alpha}^+ \rangle = \det |\phi_1 \bar{\phi}_1 \dots \phi_{k-1} \bar{\phi}_{k-1} \quad \bar{\phi}_k \phi_{k+1} \bar{\phi}_{k+1} \dots \phi_{N_c} \bar{\phi}_{N_c} \\ \phi_{N_c+1} \phi_{N_c+2} \dots \phi_{N_c+N_o}|, \quad (30)$$

where the missing spin-orbital  $\phi_k$  corresponds to a hole in the closed shell. This wave function is not an eigenfunction of the operator  $\hat{S}^2$ , but is characterized by the spin projection  $M(X_{k,\alpha}^+) = M - 1/2$ , where  $M = N_o/2$  is the  $\langle \hat{S}_z \rangle$  projection of the total spin for the parent (nonionized) system  $X$ . To emphasize that  $\Psi_{k,\alpha}^+$  is an eigenfunction of the operator  $\hat{S}_z$ , we shall designate  $\Psi_{k,\alpha}^+$  also as  $\Psi_{k,\alpha}^+(M - 1/2)$ .

Determinant (30) can be decomposed into wave functions of pure spin symmetry,

$$\Psi_{k,\alpha}^+(M - 1/2) = \{\sqrt{2S} \times \Phi_{k,\alpha}^+(S - 1/2) + \Phi_{k,\alpha}^+(S + 1/2)\} / \sqrt{2S + 1}, \quad (31)$$

where  $S = N_o/2$  is the total spin of the parent system  $X$ , and all wave functions in Eq. (31) are characterized by the same spin projection ( $M - 1/2$ ) and are defined on the frozen noncanonical orbitals  $\{\phi_i\}$  optimal for  $X$ . The wave functions in the right-hand side of Eq. (31) are the well-defined combinations of Slater determinants with fixed coefficients,

$$\Phi_{k,\alpha}^+(S + 1/2) = \frac{1}{\sqrt{2S + 1}} \left\{ \Psi_{k,\alpha}^+ + \sum_{m=1}^{N_o} Y(k, \bar{m}) \right\}, \quad (32)$$

$$\Phi_{k,\alpha}^+(S - 1/2) = \frac{1}{\sqrt{2S(2S + 1)}} \left\{ 2S \times \Psi_{k,\alpha}^+ - \sum_{m=1}^{N_o} Y(k, \bar{m}) \right\}, \quad (33)$$

where  $Y(k, \bar{m})$  are determinants of the form

$$Y(k, \bar{m}) = \det |\phi_1 \bar{\phi}_1 \dots \phi_{k-1} \bar{\phi}_{k-1} \phi_k \quad \phi_{k+1} \bar{\phi}_{k+1} \dots \phi_{N_c} \bar{\phi}_{N_c} \\ \phi_{N_c+1} \dots \phi_{N_c+m-1} \bar{\phi}_{N_c+m} \phi_{N_c+m+1} \dots \phi_{N_c+N_o}|, \quad (34)$$

which differs from that for  $\Psi_{k,\alpha}^+$  (30) in two spin-orbitals,  $\bar{\phi}_k \rightarrow \phi_k$  and  $\phi_{N_c+m} \rightarrow \bar{\phi}_{N_c+m}$  ( $m=1, 2, \dots, N_o$ ). Each of determinants (30) and (34) corresponds to the same electronic configuration

$$(\phi_1 \phi_2 \dots \phi_{N_c})^{2N_c-1} (\phi_{N_c+1})^1 (\phi_{N_c+2})^1 \dots (\phi_{N_c+N_o})^1, \quad (35)$$

i.e., each corresponds to a hole in the closed shell. Wave function (32) is generated by the spin step-down operator  $\hat{S}_-$  acting on the one-determinant wave function  $\Psi_{k,\beta}^+$  for ion  $X_{k,\beta}^+$ , Eq. (1a), which corresponds to  $S(X_{k,\beta}^+) = M(X_{k,\beta}^+) = S + 1/2$  [see also Eq. (5)]. The proof that wave function (33) is an eigenfunction of the operator  $\hat{S}^2$  with  $\langle \hat{S}^2 \rangle = (S - 1/2)(S + 1/2)$  is straightforward.

#### B. Energy of cation $X_{k,\alpha}^+$ with spin $S(X_{k,\alpha}^+) = S(X) - 1/2$

Wave function (33) corresponding to  $S(X_{k,\alpha}^+) = M(X_{k,\alpha}^+) = S - 1/2$  is the desired approximation to the wave function of cation  $X_{k,\alpha}^+$  formed by removing an alpha electron from the closed shell of  $X$ . The average value of the total many-electron Hamiltonian  $\hat{H}$  with this wave function,

$$\langle \Phi_{k,\alpha}^+(S - 1/2, M - 1/2) | \hat{H} | \Phi_{k,\alpha}^+(S - 1/2, M - 1/2) \rangle, \quad (36)$$

represents the expectation value of the energy of cation ( $X_{k,\alpha}^+, S - 1/2$ ) in the approximation of frozen orbitals. However, since the closed-shell orbitals  $\{\phi_k\}$  used to form wave function (33) are arbitrary transforms of the orbitals optimal for  $X$ , the expectation value of the energy (36) is defined ambiguously and does not represent the well-defined quantity  $E_{\text{frozen}}(X_{k,\alpha}^+, S - 1/2)$  appearing in the definition of the vertical IP, Eqs. (3) and (4). The value (36) is equal to  $E_{\text{frozen}}(X_{k,\alpha}^+, S - 1/2)$  if and only if the wave function  $\Phi_{k,\alpha}^+(S$

$-1/2$ ) is defined on canonical closed-shell ROHF orbitals  $\{\xi_k\}$ .

Our task is, first, to reveal the explicit dependence of matrix element (36) on the choice of the closed-shell orbitals  $\{\phi_k\}$  and, second, to formulate the conditions to which the canonical closed-shell orbitals  $\{\xi_k\}$  must satisfy. Matrix element (36) is a diagonal element of the CI matrix,

$$T_{kl}^{(cc)} = \langle \Phi_{k,\alpha}^+(S-1/2) | \hat{H} | \Phi_{l,\alpha}^+(S-1/2) \rangle, \quad (37)$$

where  $k, l = 1, 2, \dots, N_c$ . To work out matrix elements (37), we express them using Eq. (31) in terms of two similar elements in the basis of determinants  $\Psi_{k,\alpha}^+(M-1/2)$  of Eq. (30) and wave functions  $\Phi_{k,\alpha}^+(S+1/2)$  of Eq. (32), respectively,

$$\begin{aligned} & \langle \Phi_{k,\alpha}^+(S-1/2) | \hat{H} | \Phi_{l,\alpha}^+(S-1/2) \rangle \\ &= \{ (2S+1) \times \langle \Psi_{k,\alpha}^+ | \hat{H} | \Psi_{l,\alpha}^+ \rangle \\ & \quad - \langle \Phi_{k,\alpha}^+(S+1/2) | \hat{H} | \Phi_{l,\alpha}^+(S+1/2) \rangle \} / (2S). \end{aligned} \quad (38)$$

Since  $\hat{H}$  commutes with spin, the matrix elements formed using the wave functions of Eq. (32) will be the same as those using the one-determinant wave functions  $\Psi_{k,\beta}^+ \equiv \Psi_{k,\beta}^+(S+1/2, M+1/2)$ . Therefore,

$$\begin{aligned} & \langle \Phi_{k,\alpha}^+(S+1/2, M-1/2) | \hat{H} | \Phi_{l,\alpha}^+(S+1/2, M-1/2) \rangle \\ &= \langle \Psi_{k,\beta}^+(S+1/2, M+1/2) | \hat{H} | \Psi_{l,\beta}^+(S+1/2, M+1/2) \rangle \\ &= -2 \langle \phi_l | (\hat{F}_c - \hat{F}_o) | \phi_k \rangle + \delta_{kl} E_{\text{ROHF}}(X), \end{aligned} \quad (39)$$

where the last of two relationships, Eq. (39), is given according to Ref. 3. Similarly,

$$\begin{aligned} & \langle \Psi_{k,\alpha}^+(M-1/2) | \hat{H} | \Psi_{l,\alpha}^+(M-1/2) \rangle \\ &= -2 \langle \phi_l | \hat{F}_o | \phi_k \rangle + \delta_{kl} E_{\text{ROHF}}(X). \end{aligned} \quad (40)$$

A substitution of Eqs. (38)–(40) into Eq. (37) yields

$$T_{kl}^{(cc)} = - \langle \phi_l | \hat{W} | \phi_k \rangle + \delta_{kl} E_{\text{ROHF}}(X), \quad (41)$$

where

$$\begin{aligned} \hat{W} &= [2(2S+1)\hat{F}_o - 2(\hat{F}_c - \hat{F}_o)] / (2S) \\ &= [(2S+1)\hat{F}^\alpha - \hat{F}^\beta] / (2S). \end{aligned} \quad (42)$$

In Eq. (42),  $S = N_o/2$  is the total spin of the parent (nonionized) system  $X$ , and both the ROHF and UHF Fock operators defined by Eqs. (17) and (18) are defined in the basis of the same noncanonical ROHF orbitals  $\{\phi_k\} \oplus \{\phi_m\}$  of Eq. (15) optimal for  $X$ .

From Eq. (41) it follows that matrix element (36) representing the expectation value of the energy of cation  $X_{k,\alpha}^+$  in the frozen orbital approximation takes the desired form

$$\begin{aligned} & \langle \Phi_{k,\alpha}^+(S-1/2) | \hat{H} | \Phi_{k,\alpha}^+(S-1/2) \rangle \\ &= - \langle \phi_k | \hat{W} | \phi_k \rangle + E_{\text{ROHF}}(X), \end{aligned} \quad (43)$$

in which the dependence of Eq. (36) on the choice of unitary undefined closed-shell orbitals  $\{\phi_k\}$  is expressed explicitly. [We note here that neither the energy  $E_{\text{ROHF}}(X)$  nor the op-

erator  $\hat{W}$  itself defined in Eq. (42) depends on the choice of orbitals  $\{\phi_j\} = \{\phi_k\} \oplus \{\phi_m\}$  optimal for  $X$ ].

To present Eq. (43) in the unique form independent of the choice of  $\{\phi_k\}$ , we define the new (canonical) closed-shell orbitals  $\{\xi_k\}$  as eigenfunctions of the operator  $\hat{W}$ ,

$$|\xi_z\rangle = \sum_l X_l^{(z)} |\phi_l\rangle, \quad (44)$$

$$\sum_l \langle \phi_k | \hat{W} | \phi_l \rangle X_l^{(z)} = X_k^{(z)} \varepsilon_z[\hat{W}], \quad (45)$$

where  $X_l^{(z)}$  are the coefficients of the expansion of the canonical orbital  $\xi_z$  over initial orbitals  $\{\phi_k\}$ , and  $k, l, z = 1, 2, \dots, N_c$ . The diagonal element in the right-hand side of Eq. (43) becomes equal to the eigenvalue of the operator  $\hat{W}$ , i.e.,  $\langle \xi_z | \hat{W} | \xi_z \rangle = \varepsilon_z[\hat{W}]$ , and hence, the expectation value of the energy of cation  $X_{z,\alpha}^+$  with spin  $S(X_{z,\alpha}^+) = S - 1/2$  in the frozen orbital approximation takes the sought-for form

$$\begin{aligned} E_{\text{frozen}}(X_{z,\alpha}^+, S-1/2) &= \langle \Phi_{z,\alpha}^+(S-1/2) | \hat{H} | \Phi_{z,\alpha}^+(S-1/2) \rangle \\ &= - \varepsilon_z[\hat{W}] + E_{\text{ROHF}}(X). \end{aligned} \quad (46)$$

It follows from Eq. (46) that the energy  $E_{\text{frozen}}(X_{z,\alpha}^+, S-1/2)$  defined using the canonical choice (44) for the closed-shell orbitals is a well-defined (variationally stationary) quantity.

### C. KT for process A2

It is easy to see that the energy of cation  $X_{z,\alpha}^+$  with spin  $S(X_{z,\alpha}^+) = S - 1/2$  defined in Eq. (46) in the frozen orbital approximation is also equal to the energy defined in the limited CI, (37). By definition of the CI matrix  $T_{kl}^{(cc)}$ , Eq. (37), its eigenvalues are equal to the CI energy of the respective cations  $X_{z,\alpha}^+$

$$\varepsilon_z[T^{(cc)}] = E_{\text{CI}}(X_{z,\alpha}^+, S-1/2). \quad (47)$$

From Eq. (41) it follows that the matrices  $T_{kl}^{(cc)}$  and  $\hat{W}_{kl}$  commute, and hence,

$$\varepsilon_z[T^{(cc)}] = - \varepsilon_z[\hat{W}] + E_{\text{ROHF}}(X). \quad (48)$$

Summarizing Eqs. (46)–(48), we obtain the important result

$$E_{\text{CI}}(X_{z,\alpha}^+, S-1/2) = E_{\text{frozen}}(X_{z,\alpha}^+, S-1/2). \quad (49)$$

So, if we define the diagonal closed-shell block of ROHF Hamiltonian (16) in the form

$$\hat{Q}_{\text{can}}^{(cc)} = \hat{W}, \quad (50)$$

where  $\hat{W}$  is defined in Eq. (42), we obtain the exact formulation of KT in a ROHF method for case A2,

$$\begin{aligned} I_z^\alpha &= E_{\text{frozen}}(X_{z,\alpha}^+, S-1/2) - E_{\text{ROHF}}(X) \\ &= E_{\text{CI}}(X_{z,\alpha}^+, S-1/2) - E_{\text{ROHF}}(X) \\ &= - \varepsilon_z[\hat{Q}_{\text{can}}], \end{aligned} \quad (51)$$

where  $z = 1, 2, \dots, N_c$  and  $\varepsilon_z[\hat{Q}_{\text{can}}]$  is the eigenvalue of both the diagonal block  $\langle \phi_k | \hat{Q}_{\text{can}}^{(cc)} | \phi_l \rangle$  defined in the basis of *self-consistent* closed-shell orbitals  $\{\phi_k\}$  optimal for  $X$  and full

ROHF Hamiltonian (16) with  $\hat{R}^{(cc)} = \hat{Q}_{\text{can}}^{(cc)}$  defined in the basis of arbitrary (*non-self-consistent*) orbitals  $\{\eta_i\} = \{\eta_k\} \oplus \{\eta_m\} \oplus \{\eta_v\}$ . A discussion of formulation (51) and a comparison of Eq. (51) with the previously reported formulations<sup>7-11</sup> of KT in ROHF, UHF, and UDFT methods will be given below.

#### D. KT for process C2

A treatment of this case corresponding to attachment of a beta electron to a virtual orbital with formation of anion  $X_{v,\beta}^-$  with  $S(X_{v,\beta}^-) = S - 1/2$  is completely analogous to the treatment above of process A2. We here present just the definition of the second canonical form for the virtual diagonal block  $\hat{R}^{(vv)} = \hat{Q}_{\text{can}}^{(vv)}$  of full ROHF Hamiltonian (16),

$$\begin{aligned} \hat{Q}_{\text{can}}^{(vv)} &= [-2\hat{F}_o + 2(2S+1)(\hat{F}_c - \hat{F}_o)]/(2S) \\ &= [-\hat{F}^\alpha + (2S+1)\hat{F}^\beta]/(2S), \end{aligned} \quad (52)$$

and the exact formulation of KT for process C2,

$$\begin{aligned} A_z^\beta &= E_{\text{ROHF}}(X) - E_{\text{frozen}}(X_{z,\beta}^-, S - 1/2) \\ &= E_{\text{ROHF}}(X) - E_{\text{CI}}(X_{z,\beta}^-, S - 1/2) \\ &= -\varepsilon_z[\hat{Q}_{\text{can}}], \end{aligned} \quad (53)$$

where, in this case,  $z \in$  virtual shell. These formulas are based on the ROHF wave function for anion  $X_{v,\beta}^-$  possessing the true spin and spatial symmetry

$$\Phi_{v,\beta}^-(S - 1/2) = \frac{1}{\sqrt{2S(2S+1)}} \left\{ 2S \times \Psi_{v,\beta}^- - \sum_{m=1}^{N_o} Y(\bar{m}, v) \right\}, \quad (54)$$

where  $\Psi_{v,\beta}^-$  is the one-determinant wave function for anion  $X_{v,\beta}^-$  and

$$Y(\bar{m}, v) = \det |\phi_1 \bar{\phi}_1 \dots \phi_{N_c} \bar{\phi}_{N_c} \phi_{N_c+1} \phi_{N_c+2} \dots \phi_{N_c+m-1} \bar{\phi}_{N_c+m} \phi_{N_c+m+1} \dots \phi_{N_c+N_o} \phi_{N_c+N_o+v}|. \quad (55)$$

The full set of ROHF wave functions, Eq. (54), with  $v = 1, 2, \dots, N_v$  also forms the basis of configuration state functions (CSFs) in the CI procedure.

#### IV. ACTIVE CI SPACE IN KOOPMANS' THEOREM

The CI-based formulation of KT in the ROHF method given above for cases A2 [Eq. (51)], B2 [Eq. (26)], and C2 [Eq. (53)] needs a more detailed discussion in the part concerning the choice of the active CI space. In case B2 [and also in cases A1, B1, and C1 of Eqs. (1a)–(1c)], the one-determinant wave function  $\Psi_{j,\sigma}^\pm$  for the respective ion  $X_{j,\sigma}^\pm$  is an eigenfunction of  $\hat{S}^2$ . Because of this, the whole active CI space in each of these cases involves all determinants  $\Psi_{j,\sigma}^\pm$  that can be formed within the respective ionized shell,

$$\begin{aligned} \mathbf{A1}: & \{\Psi_{k,\beta}^+\}, \\ \mathbf{B1}: & \{\Psi_{m,\alpha}^+\}, \\ \mathbf{C1}: & \{\Psi_{v,\alpha}^-\}, \\ \mathbf{B2}: & \{\Psi_{m,\beta}^-\}. \end{aligned} \quad (56)$$

Each of the CI spaces, Eq. (56), corresponds to a full CI in the restricted active space method<sup>3</sup> and is invariant under unitary transformation of the orbitals  $\{\phi_j\} = \{\phi_k\} \oplus \{\phi_m\} \oplus \{\phi_v\}$  of Eq. (15) within the respective ionized shell. [We recall that these orbitals are optimal for the initial [nonionized] system  $X$  with  $S(X) = S$ .] The remaining orbitals and electrons from nonionized shells are inactive in the CI procedure.

In case A2, the active CI space is given by the set of CSFs of Eq. (33),

$$\mathbf{A2}: \{\Phi_{k,\alpha}^+(S - 1/2)\}, \quad (57)$$

formed from determinants  $\Psi_{k,\alpha}^+$  (30), and  $Y(k, \bar{m})$  of (34). The number of CSFs (57) is equal to  $N_c$ , while the total number of determinants (30) and (34) is equal to  $N_c(N_o + 1)$ . Because of this, there arises the question of whether the results derived within the CI space (57) are invariant under separate unitary transformation of molecular orbitals within the closed or open shell.

At first we note that the whole CI space of dimension  $N_c(N_o + 1)$  for cation  $X_{k,\alpha}^+$  formed by determinants  $\Psi_{k,\alpha}^+$ , Eq. (30), and  $Y(k, \bar{m})$ , Eq. (34), is separated onto the three subspaces

$$\begin{aligned} \{\Psi_{k,\alpha}^+\} \oplus \{Y(k, \bar{m})\} &= \{\Phi_{k,\alpha}^+(S + 1/2)\} \oplus \{\Phi_{k,\alpha}^+(S - 1/2)\} \\ &\oplus \{Y_k^+(S - 1/2)\}, \end{aligned} \quad (58)$$

having the dimension  $N_c$ ,  $N_c$ , and  $N_c(N_o - 1)$ , respectively. The first two subspaces are defined by Eqs. (32) and (33), while the third one also corresponding to the spin number  $(S - 1/2)$  is formed by some combinations of determinants (34) orthogonal both to each other and to CSFs (32) and (33). We call this third subspace  $\{Y_k^+(S - 1/2)\}$ . By construction, this subspace is nonvanishing for the case  $N_o = 2S > 1$  only. For the simplest nonvanishing case  $N_o = 2$ , the CSFs from the subspace  $\{Y_k^+(S - 1/2)\}$  take the form

$$Y_k^+(S - 1/2) = [Y(k, \bar{1}) - Y(k, \bar{2})]/\sqrt{2}, \quad (59)$$

where the determinants  $Y(k, \bar{m})$  are defined by Eq. (34) and  $k = 1, 2, \dots, N_c$ .

A separation of the subspace  $\{\Phi_{k,\alpha}^+(S + 1/2)\}$  from the whole CI space (58) is dictated by the spin symmetry, while the separation of the  $(S - 1/2)$  CSFs into

$$\{\Phi_{k,\alpha}^+(S - 1/2)\} \oplus \{Y_k^+(S - 1/2)\} \quad (60)$$

is just the desired separation which is required by Eq. (33) defining the ROHF (monoconfigurational) wave function for cation  $X_{k,\alpha}^+$  with  $S(X_{k,\alpha}^+) = S - 1/2$ . In general, the CSFs from two subspaces (60) interact with each other, and because of this, the CI wave functions derived in the active space (58)



are divided in two (not three) sets corresponding to the spin numbers  $(S+1/2)$  and  $(S-1/2)$ .

The important point is that both the whole  $(S-1/2)$  CI subspace (60) and its subspace  $\{Y_k^+(S-1/2)\}$  are *not invariant* under arbitrary unitary transforms of either closed-shell  $\{\phi_k\}$  or open-shell  $\{\phi_m\}$  orbitals optimal for the parent system  $X$ . As compared to this, the active CI subspace  $\{\Phi_{k,\alpha}^+(S-1/2)\}$  for cation  $X_{k,\alpha}^+$  with  $S(X_{k,\alpha}^+) = M(X_{k,\alpha}^+)S-1/2$  defined by Eq. (57) is closed under unitary transforms within the closed or open shell. A discussion of these points is presented in the next subsection.

### A. Invariant CI subspaces

It is easy to understand that the source of a noninvariance of the subspace  $\{Y_k^+(S-1/2)\}$  with respect to arbitrary unitary transforms of closed-shell or open-shell orbitals is that the active CI space (58) formed by determinants (30) and (34) is not full. Since all these determinants correspond to the same electronic configuration (35),

$$(\phi_1 \phi_2 \dots \phi_{N_c})^{2N_c-1} (\phi_{N_{c+1}})^1 (\phi_{N_{c+2}})^1 \dots (\phi_{N_{c+N_o}})^1,$$

the obvious way to provide the invariance of the  $(S-1/2)$  CI space is to consider a wider electronic configuration

$$(\phi_1 \phi_2 \dots \phi_{N_c})^{2N_c-1} (\phi_{N_{c+1}} \phi_{N_{c+2}} \dots \phi_{N_{c+N_o}})^{N_o}, \quad (61)$$

also corresponding to a hole in the closed shell.

The full set of determinants with spin projection  $(S-1/2)$  corresponding to configuration (61) consists of the same determinants  $\Psi_{k,\alpha}^+$ , Eq. (30), and  $Y(k, \bar{m})$ , Eq. (34), specific for configuration (35) and also involves new determinants  $W(k, \bar{m}, n)$

$$W(k, \bar{m}, n) = \det | (g_k) \phi_{N_{c+1}} \dots \phi_{N_{c+m-1}} \overline{\phi_{N_{c+m}}} \overline{\phi_{N_{c+m}}} \phi_{N_{c+m+1}} \dots \phi_{N_{c+n-1}} \quad \phi_{N_{c+n+1}} \dots \phi_{N_{c+N_o}} |, \quad (62)$$

which differ from determinants  $Y(k, \bar{m})$  (34) in the one spin-orbital,  $\phi_{N_{c+n}} \rightarrow \overline{\phi_{N_{c+m}}}$ , so that the open-shell orbital  $\phi_{N_{c+m}}$  in Eq. (62) is doubly occupied while the orbital  $\phi_{N_{c+n}}$  is empty, and  $(g_k)$  designates a list of spin-orbitals from the ionized closed shell

$$(g_k) = \phi_1 \overline{\phi_1} \dots \phi_{k-1} \overline{\phi_{k-1}} \phi_k \quad \phi_{k+1} \overline{\phi_{k+1}} \dots \phi_{N_c} \overline{\phi_{N_c}},$$

which is as the same as in determinants  $Y(k, \bar{m})$ , Eq. (34). The total number of determinants of Eq. (62) is equal to  $N_c N_o (N_o - 1)$ .

The set of determinants corresponding to configuration (61), i.e.,  $\{\Psi_{k,\alpha}^+\} \oplus \{Y(k, \bar{m})\} \oplus \{W(k, \bar{m}, n)\}$ , can be separated into three groups of CSFs

$$\{\Phi_{k,\alpha}^+(S+1/2)\} \oplus \{\Phi_{k,\alpha}^+(S-1/2)\} \oplus \{\Lambda_k^+(S-1/2)\}, \quad (63)$$

where the first two groups are as the same as in Eq. (58), while the third one involves both CSFs  $Y_k^+(S-1/2)$  defined by Eq. (59) and all determinants of Eq. (62), i.e.,

$$\{\Lambda_k^+(S-1/2)\} = \{Y_k^+(S-1/2)\} \oplus \{W(k, \bar{m}, n)\}. \quad (64)$$

As compared to the previous CI space (58) corresponding to configuration (35), both the extended CI space (63) corresponding to the configuration (61) and each of its three subspaces are closed under arbitrary unitary transforms of the orbitals within the closed or open shell. We do not present here a proof of this statement since the proof itself is quite simple but requires a presentation of many ponderous formulas. We here present, just as an illustration, the main point of this proof for the simplest case where the subspace  $\{\Lambda_k^+(S-1/2)\}$  is nonvanishing, i.e., for the case  $N_o=2$ .

For the particular case  $N_o=2$ , the  $\{\Lambda_k^+(S-1/2)\}$  subspace (64) involves  $2 \times N_c$  determinants  $W(k, \bar{m}, n)$ , Eq. (62),

$$W(k, \bar{1}, 2) = \det | (g_k) \phi_{N_{c+1}} \overline{\phi_{N_{c+1}}} |, \quad (65a)$$

$$W(k, \bar{2}, 1) = \det | (g_k) \phi_{N_{c+2}} \overline{\phi_{N_{c+2}}} |,$$

and  $N_c$  configuration state functions (59) from the subspace  $\{Y_k^+(S-1/2)\}$ ,

$$Y_k^+(S-1/2) = \{Y(k, \bar{1}) - Y(k, \bar{2})\} / \sqrt{2} \\ = [\det | (g_k) \overline{\phi_{N_{c+1}}} \phi_{N_{c+2}} | \\ - \det | (g_k) \phi_{N_{c+1}} \overline{\phi_{N_{c+2}}} |] / \sqrt{2}, \quad (65b)$$

where  $k=1, 2, \dots, N_c$ . It is easy to see that for each value of the index  $k$ , the set of CSFs (65) forming the subspace  $\{\Lambda_k^+(S-1/2)\}$  is full in the sense that an arbitrary unitary transform of open-shell orbitals  $\{\phi_m\} \equiv \{\phi_{N_{c+1}}, \phi_{N_{c+2}}\}$  is equivalent to a related unitary transformation among CSFs (65). This means that the results of CI calculations (i.e., eigenvalues of the CI matrix and natural CI orbitals) performed in the basis of CSFs (65) are invariant under arbitrary unitary transform of open-shell orbitals  $\{\phi_m\}$  optimal for the initial system  $X$ .

In the same manner one can show that each of the three CSF groups in Eqs. (65a) and (65b), consisting of  $N_c$  members (CSFs) each, is full in the sense that an arbitrary unitary transform of *closed-shell* orbitals  $\{\phi_k\}$  is equivalent to a related unitary transformation among CSFs of the same group in Eqs. (65a) and (65b).

With some complications, the same approach can be used to prove the invariance of the subspace  $\{\Phi_{k,\alpha}^+(S-1/2)\}$  representing the active CI space for the ionization process **A2**, Eq. (57). At first we note that the set of CSFs  $\Phi_{k,\alpha}^+(S-1/2)$  is full in the sense that an arbitrary unitary transform of closed-shell orbitals  $\{\phi_k\}$  is equivalent to a related unitary transform among CSFs  $\Phi_{k,\alpha}^+(S-1/2)$ . To prove the invariance of Eq. (57) with respect to transformation of open-shell orbitals, we revert to decomposition (31),

$$\Psi_{k,\alpha}^+ = \{\sqrt{2S} \times \Phi_{k,\alpha}^+(S-1/2) + \Phi_{k,\alpha}^+(S+1/2)\} / \sqrt{2S+1},$$

where the determinant  $\Psi_{k,\alpha}^+$  is defined in Eq. (30). It immediately follows from Eq. (30) that  $\Psi_{k,\alpha}^+$  and hence, the right-hand side of Eq. (31) are invariant under arbitrary unitary transform of open-shell orbitals  $\{\phi_m\}$ . The same is true for determinants  $\Psi_{k,\beta}^+$  representing ROHF wave functions for

cations  $X_{k,\beta}^+$  with  $S(X_{k,\beta}^+) = M(X_{k,\beta}^+) = S + 1/2$ . Since the wave function  $\Phi_{k,\alpha}^+(S+1/2, M-1/2)$  in Eq. (31) is obtained by acting the spin-down operator  $\hat{S}_-$  on the determinant  $\Psi_{k,\beta}^+$ , we conclude that the wave function  $\Phi_{k,\alpha}^+(S+1/2)$ , and hence,  $\Phi_{k,\alpha}^+(S-1/2)$  are invariant under arbitrary unitary transform of open-shell orbitals  $\{\phi_m\}$ .

In conclusion, the space of functions  $\{\Phi_{k,\alpha}^+(S-1/2)\}$  considered in CI (57) is closed under all allowed transforms.

## V. COMPARISON WITH PREVIOUS APPROACHES

On the basis of the exact formulation of KT in a ROHF method given by Eqs. (1a)–(1c), (7), (26), (51), (53), (56), and (57), we can revert to a discussion of previous formulations<sup>7–11</sup> of KT within UHF, ROHF, and UDFT methods.

### A. CI-based approach within the UHF method

A formal validity of KT in the UHF method for ionization processes (1a), (8a), and (1b),

$$\mathbf{A1:} \quad \varepsilon_k^\beta = -I_k^\beta, \quad (66a)$$

$$\mathbf{A2:} \quad \varepsilon_k^\alpha = -I_k^\alpha, \quad (66b)$$

$$\mathbf{B1:} \quad \varepsilon_m^\alpha = -I_m^\alpha, \quad (66c)$$

where, as above,  $k=1, 2, \dots, N_c$  and  $m=N_c+1, \dots, N_c+N_o$  has been first proven by Stepanov *et al.*<sup>9</sup> within the limited CI. The active CI spaces<sup>9</sup> were defined as

$$\mathbf{A1:} \quad \{\Psi_{k,\beta}^+\}, \quad (67)$$

$$\mathbf{A2} \oplus \mathbf{B1:} \quad \{\Psi_{k,\alpha}^+\} \oplus \{\Psi_{m,\alpha}^+\},$$

where, in this case, all determinants (67) are defined on the UHF orbitals  $\{\phi_k^\alpha\} \oplus \{\phi_m^\alpha\}$  and  $\{\phi_k^\beta\}$  optimal for the initial system  $X$ .

A treatment of KT for two processes, **A2** and **B1**, using the united CI space (67) is natural within the UHF method since the two subsets of occupied UHF-alpha orbitals,  $\{\phi_k^\alpha\}$  and  $\{\phi_m^\alpha\}$ , actually belong to the same orbital set. Moreover, as shown in Ref. 9, the CI matrices defined in the basis sets  $\{\Psi_{k,\beta}^+\}$  and  $\{\Psi_{k,\alpha}^+\} \oplus \{\Psi_{m,\alpha}^+\}$  commute with the matrices of UHF Fock operators  $\hat{F}^\beta$  and  $\hat{F}^\alpha$ , Eq. (18), respectively. From here, one immediately obtains the KT relationships (66a)–(66c) in the form  $E_{\text{CI}}(X_{k,\beta}^+) = -\varepsilon_k^\beta + E_{\text{UHF}}(X)$  and  $E_{\text{CI}}(X_{j,\alpha}^+) = -\varepsilon_j^\alpha + E_{\text{UHF}}(X)$ , respectively, where  $j=k$  or  $m$ .

However, it is easy to show that within the *monoconfigurational* UHF method, the CI-based treatment (67) leads to physically incorrect results in specific case **A2**. To illustrate this, we consider the simple case of an open-shell system  $X$  having the electronic configuration  $(\phi_{A_1})^2 (\phi_{A_2})^1$ , where the subscripts  $A_1$  and  $A_2$  denote the spatial symmetry of orbitals. In the UHF method, this configuration takes the form  $(\phi_{A_1}^\alpha)^1 (\phi_{A_1}^\beta)^1 (\phi_{A_2}^\alpha)^1$ . The CI matrix for cations  $X_{j,\alpha}^+$  ( $j=A_1, A_2$ ) defined in the basis (67) takes a diagonal form with diagonal elements equal to  $E_{\text{CI}}(X_{A_1,\alpha}^+)$  and  $E_{\text{CI}}(X_{A_2,\alpha}^+)$ . The CI wave functions of cations are described by determinants

$$\Psi_{A_1,\alpha}^+ = \Psi_{k,\alpha}^+ = \det|\overline{\phi_{A_1}^\beta} \phi_{A_2}^\alpha|, \quad (68)$$

$$\Psi_{A_2,\alpha}^+ = \Psi_{m,\alpha}^+ = \det|\phi_{A_1}^\alpha \overline{\phi_{A_1}^\beta}|. \quad (69)$$

In the limit case of small spin polarization,  $\phi_{A_1}^\alpha \approx \phi_{A_1}^\beta$ , and so determinant (69) approximates to the ROHF closed-shell determinant with  $S(X_{A_2,\alpha}^+) = 0$ , while determinant (68) corresponding to ionization from the closed shell (case **A2**) is a superposition of the ROHF wave functions with  $S(X_{A_1,\alpha}^+) = 0$  and  $S(X_{A_1,\alpha}^+) = 1$  with equal coefficients [see also Eq. (31)].

It follows herefrom that although the Eq. (66b), which states the validity of KT in the UHF method for process **A2**, has been derived within a *formally correct* CI treatment (67), in reality relationship (66b) is *ill-defined* from the physical viewpoint.

### B. CI-based approach within a ROHF method

In order to overcome the above discussed drawback of the CI approach (67) to analysis of process **A2**, Sauer and Jung<sup>10</sup> suggested to modify the united CI space (67) constructed *on the ROHF orbitals* by replacing the determinants  $\{\Psi_{k,\alpha}^+\}$  with the symmetry-adapted combinations of determinants corresponding to  $S(X_{k,\alpha}^+) = 0$ . Although an explicit form of these combinations was not presented in Ref. 10, the active CI spaces for processes (66a)–(66c) can be presented in the form

$$\mathbf{A1:} \quad \{\Psi_{k,\beta}^+\}, \quad (70)$$

$$\mathbf{A2} \oplus \mathbf{B1:} \quad \{\Phi_{k,\alpha}^+(S-1/2)\} \oplus \{\Psi_{m,\alpha}^+\},$$

where  $\{\Phi_{k,\alpha}^+(S-1/2)\}$  are the CSFs defined above Eq. (57) and, in this case,  $S \equiv S(X) = 1/2$  (only such open-shell systems were discussed in Ref. 10).

The problem with Eq. (70) is that the CI matrix defined in the united space of CSFs  $\{\Phi_{k,\alpha}^+(S-1/2)\}$  and  $\{\Psi_{m,\alpha}^+\}$  does not commute with any ROHF Hamiltonian matrix (16). This means that the CI matrix so defined cannot be made diagonal by any allowed unitary transforms among the ROHF orbitals  $\{\phi_k\}$  and  $\{\phi_m\}$ , and hence, the eigenvalues of this CI matrix have no relation to KT. Based on this finding, Sauer and Jung<sup>10</sup> concluded that *KT relating the CI energy of an ion to an orbital energy of a neutral did not hold in the ROHF method*.

Actually the allowed separate unitary transforms of the open and closed-shell orbitals cannot mix CI wave functions from the sets **A2** and **B1**, so a CI considering them simultaneously goes beyond a treatment of KT in the ROHF method.

### C. Approximate analogs of KT in ROHF and UDFT methods

As an alternative to a rigorous KT in a ROHF method, Sauer *et al.*<sup>10,11</sup> formulated the so-called “simplified KT” (SKT), according to which the IPs and EAs defined in the frozen orbital approximation might be equated not to eigenvalues of some special (canonical) ROHF Hamiltonian but to slightly modified diagonal elements of Roothaan’s Hamil-

tonian. A similar approach was earlier discussed by Dodds and McWeeny.<sup>16</sup> For processes **A1**, **A2**, and **B1**, the SKT relationships<sup>11</sup> were derived in the form  $I_k^\beta \approx -\tilde{\varepsilon}_k + (1/2) \times \langle \tilde{\phi}_k | \hat{K}_o | \tilde{\phi}_k \rangle$ ,  $I_k^\alpha \approx -\tilde{\varepsilon}_k + (1/2) \langle \tilde{\phi}_k | 5\hat{K}_o | \tilde{\phi}_k \rangle$ , and  $I_m^\alpha \approx -\tilde{\varepsilon}_m + (1/2) \langle \tilde{\phi}_m | \hat{K}_o | \tilde{\phi}_m \rangle$ , respectively, where  $\{\tilde{\varepsilon}_i\}$  and  $\{\tilde{\phi}_i\}$  are the eigenvalues and eigenvectors of Roothaan's ROHF Hamiltonian<sup>12,13</sup> for the initial system  $X$  with  $S(X) = S = 1/2$ .

For a better understanding of SKT relationships,<sup>11</sup> we here present them in a simpler (but equivalent) form in which the right-hand sides of SKT relationships<sup>11</sup> are expressed in terms of diagonal matrix elements of the UHF Fock operators  $\hat{F}^\alpha$  and  $\hat{F}^\beta$ , Eq. (18),

$$\mathbf{A1:} \quad I_k^\beta \approx -\langle \tilde{\phi}_k | \hat{F}^\beta | \tilde{\phi}_k \rangle, \quad (71a)$$

$$\mathbf{A2:} \quad I_k^\alpha \approx -\langle \tilde{\phi}_k | 2\hat{F}^\alpha - \hat{F}^\beta | \tilde{\phi}_k \rangle, \quad (S = 1/2). \quad (71b)$$

$$\mathbf{B1:} \quad I_m^\alpha \approx -\langle \tilde{\phi}_m | \hat{F}^\alpha | \tilde{\phi}_m \rangle, \quad (71c)$$

where IPs  $I_j^\sigma$  and operators  $\hat{F}^\sigma (\sigma = \alpha, \beta)$  are defined by Eqs. (3) and (18) above using the same ROHF orbitals<sup>11</sup>  $\{\tilde{\phi}_k\} \oplus \{\tilde{\phi}_m\}$ . [We also note here that operators  $\hat{F}^\sigma$  themselves in Eqs. (71a)–(71c) do not depend on the choice of ROHF orbitals  $\{\tilde{\phi}_i\}$  optimal for  $X$ .]

At first we notice that both the left- and right-hand sides of SKT relationships (71a)–(71c) depend on the choice of ROHF orbitals optimal for  $X$ . The specific choice of these orbitals used in Ref. 11,  $\{\tilde{\phi}_i\} = \{\tilde{\phi}_k\} \oplus \{\tilde{\phi}_m\}$ , does not provide a variationally stationary value for the energy difference  $\Delta E_{j,\sigma} = E_{\text{frozen}}(X_{j,\sigma}^+) - E_{\text{ROHF}}(X)$ , and hence, the latter cannot be equated to Koopmans's approximation for  $I_j^\sigma$  given by Eqs. (3) and (4) above. Without loss of generality, one can consider the orbitals  $\{\tilde{\phi}_i\}$  in Eqs. (71a)–(71c) just as *arbitrarily* defined self-consistent ROHF orbitals, Eq. (15), optimal for  $X$ .

Taken in the form of Eqs. (71a)–(71c), the SKT relationships<sup>11</sup> can be compared with the formulations of KT in the UHF method, Eqs. (66a) and (66b), and with the approximate analogs of KT for the same cases **A1**, **A2**, and **B1** derived by Gritsenko and Baerends<sup>7,8</sup> within a UDFT approach,

$$\mathbf{A1:} \quad I_k^\beta \approx -\varepsilon_k^\beta, \quad (72a)$$

$$\mathbf{A2:} \quad I_k^\alpha \approx -\{(2S+1)\varepsilon_k^\alpha - \varepsilon_k^\beta\}/(2S), \quad (72b)$$

$$\mathbf{B1:} \quad I_m^\alpha \approx -\varepsilon_m^\alpha. \quad (72c)$$

where  $S \equiv S(X)$  is the total spin of the initial (nonionized) system  $X$ . The SKT relationships (71a)–(71c) become the analogs of KT in a UDFT method, Eqs. (72a)–(72c), in the particular case  $S = 1/2$  if we assume that the closed-shell ROHF orbitals  $\{\tilde{\phi}_k\}$  in Eqs. (71a)–(71c), where  $k = 1, 2, \dots, N_c$  are the lowest eigenvectors of both operators  $\hat{F}^\alpha$  and  $\hat{F}^\beta$ , and the open-shell ROHF orbitals  $\{\tilde{\phi}_m\}$  where  $m = N_c + 1, N_c + 2, \dots, (N_c + N_o)$  are the eigenvectors of  $\hat{F}^\alpha$ . (We note that in this case, the operators  $\hat{F}^\alpha$  and  $\hat{F}^\beta$  do not

necessarily commute). This assumption is close to that actually used in Ref. 7 when deriving Eq. (72b).

For case **A2**, both the SKT relationship (71b) and the analog of KT in a UDFT method (72b) are based (either explicitly<sup>11</sup> or implicitly<sup>7</sup>) on the symmetry-adapted (multideterminantal) ROHF wave function for cation  $X_{k,\alpha}^+$  with  $S(X_{k,\alpha}^+) = S - 1/2$  presented by Eq. (33) above. This key point of KT relationships (71a)–(71c) and (72a)–(72c) overcomes the main drawback of the previous formulation of KT in UHF method (66b) discussed above; however, neither of the KT formulations (71a)–(71c) and (72a)–(72c) corresponds to Koopmans's approximation<sup>1</sup> for IP.

To complete this comparison, we note that although the IP values derived within two different theoretical approaches, i.e., within the DFT method and within the wave function (ROHF and UHF) approach, have different meanings, an immediate comparison between the respective KT relationships, i.e., between Eqs. (72a)–(72c) and those of Eqs. (1a)–(1c), (51), (66a)–(66c), and (71a)–(71c), is possible. We note that within the Kohn–Sham DFT method, only one KT relationship corresponding to a removal of an electron from the highest occupied molecular orbital (HOMO) has a fundamental basis.<sup>17</sup> For cases (72a)–(72c) under consideration, the respective KT relationship takes the form<sup>17,18</sup>

$$\mathbf{B1:} \quad I_{N_c+N_o}^\alpha = -\varepsilon_{N_c+N_o}^\alpha \quad (73)$$

(exact equality), where  $(N_c + N_o)$  is the index of the  $\alpha$ -HOMO and  $I_{N_c+N_o}^\alpha$  is the experimental IP, which is assumed to correspond to formation of the first  $(S - 1/2)$  state of an ion. We also note here that according to Gritsenko and Baerends,<sup>7</sup> relationship (72a) also takes the form of the exact equality in the case of  $\beta$ -HOMO, i.e., for ionization to form the lowest  $(S + 1/2)$  state of the ion,

$$\mathbf{A1:} \quad I_{N_c}^\beta = -\varepsilon_{N_c}^\beta. \quad (74)$$

All other KT relationships, Eqs. (72a)–(72c), are only approximate and are not justified by any rigorous theorem. Our treatment has shown that the analogs of KT in UDFT methods (72a)–(72c) are also analogs of simplified KT relationships (71a)–(71c).

## VI. ILLUSTRATIVE CALCULATIONS

To illustrate the theory developed in the present work for ionization processes **A2** and **C2** and in our previous works<sup>2,3,6</sup> for processes **A1**, **B1**, **C1**, and **B2**, we present canonical ROHF orbital energies satisfying KT for molecules  $O_2$  and  $NO_2$  and compare them with experimental vertical IPs. Before presenting these results we briefly describe the details of calculations and the procedure of a verification of the generalized KT formulated above for processes **A2** and **C2**.

### A. Computational details

All calculations by the canonical ROHF method<sup>2</sup> were performed with the program GAMESS (Refs. 19 and 20) using the special ROHF algorithm designed by Montgomery<sup>20</sup> for the high-spin half-filled open-shell systems. The additional

data required for performing calculations by the method<sup>2</sup> are the special (canonical) values of the coefficients  $A_{(ss)}$  and  $B_{(ss)}$  that are used in the Montgomery's algorithm<sup>20</sup> as input data to define the diagonal blocks of total ROHF Hamiltonian (16),

$$\begin{aligned}\hat{R}^{(ss)} &= 2\{A_{(ss)}\hat{F}_o + B_{(ss)}(\hat{F}_c - \hat{F}_o)\} \\ &= A_{(ss)}\hat{F}^\alpha + B_{(ss)}\hat{F}^\beta\end{aligned}\quad (75)$$

[the respective off-diagonal blocks, which are the same in different ROHF treatments, are defined in Eq. (16)]. The canonical values of  $A_{(ss)}$  and  $B_{(ss)}$  for cases **A1**, **B1**, and **C1** have been defined in Ref. 2 (these values are also presented in the latest version of GAMESS manual<sup>20</sup>). The respective coefficients for alternative cases **A2**, **B2**, and **C2** are obtained from definitions (50), (21), and (52) of the respective canonical diagonal blocks,

$$\mathbf{A2}: A_{(cc)} = (2S + 1)/(2S), \quad B_{(cc)} = -1/(2S), \quad (76a)$$

$$\mathbf{B2}: A_{(oo)} = 0, \quad B_{(oo)} = 1, \quad (76b)$$

$$\mathbf{C2}: A_{(vv)} = -1/(2S), \quad B_{(vv)} = (2S + 1)/(2S), \quad (76c)$$

where, as above,  $S$  is the total spin of the initial (nonionized) system  $X$  and the coefficients, Eq. (76b), were first derived in Ref. 6.

To obtain the two sets of canonical ROHF orbitals and orbital energies corresponding to the two alternative cases,  $\{\mathbf{A1}, \mathbf{B1}, \mathbf{C1}\}$  and  $\{\mathbf{A2}, \mathbf{B2}, \mathbf{C2}\}$ , one should perform *two independent* ROHF calculations using two respective sets of coefficients  $A_{(ss)}$  and  $B_{(ss)}$ . It is worth noting here that the alternative processes in different electronic shells, i.e., (**A1** and **A2**), (**B1** and **B2**), and (**C1** and **C2**), can be combined within the same ROHF computation in an arbitrary manner. For example, the same two sets of canonical orbitals and orbital energies can be derived from another pair of the ROHF calculations,  $\{\mathbf{A1}, \mathbf{B2}, \mathbf{C1}\}$  and  $\{\mathbf{A2}, \mathbf{B1}, \mathbf{C2}\}$ , as well as from two other pairs,  $[\{\mathbf{A1}, \mathbf{B1}, \mathbf{C2}\}]$  and  $[\{\mathbf{A2}, \mathbf{B2}, \mathbf{C1}\}]$  and  $[\{\mathbf{A1}, \mathbf{B2}, \mathbf{C2}\}]$  and  $[\{\mathbf{A2}, \mathbf{B1}, \mathbf{C1}\}]$ , by the respective choice of the input coefficients  $A_{(ss)}$  and  $B_{(ss)}$ . In all these computations, the output orbitals of the first computation can be used as input data for the following computation, which, in this case, will merely produce different unitary transforms of the *self-consistent canonical* ROHF orbitals,  $\{\theta_j\} \leftrightarrow \{\xi_j\}$ , within the respective electronic shells [see also Eqs. (2) and (11)]. We also note here that because of the specific drawback in the Montgomery's algorithm,<sup>20</sup> which appears in the case of open-shell systems violating the Aufbau principle (for more details, see Ref. 3), such a freedom in performing canonical ROHF calculations presents a good opportunity for verification of the results. The other details of the canonical ROHF calculations including the use of the specific “*orbital-energy-scaling*” technique were described in Refs. 2 and 3.

To perform a verification of generalized KT (51) for process **A2**, we compared the closed-shell eigenvalues of canonical ROHF Hamiltonians (76a)–(76c),  $\varepsilon_k[\hat{Q}_{\text{can}}]$ , for a test system  $X$  (see below) and the respective energy differences  $\Delta E_{k,\alpha} = E_{\text{CI}}(X_{k,\alpha}^+, S - 1/2) - E_{\text{ROHF}}(X)$  for ions  $X_{k,\alpha}^+$ . The CI

calculations were performed in the active CI space  $\{\Phi_{k,\alpha}^+(S - 1/2)\}$  of Eq. (57). To generate this specific space, we exploited two different algorithms implemented in programs MELD (Ref. 21) and GAMESS.<sup>19,20</sup> In the latter case, we used the occupation restricted multiple active space–CI (ORMAS–CI) algorithm developed by Ivanic<sup>22</sup> with some additional possibilities implemented in this algorithm by Ivanic and Schmidt according to our request.

As found in testing calculations of the model open-shell system HNO with  $S=2$  (see Ref. 3), the eigenvalues  $\varepsilon_k[\hat{Q}_{\text{can}}]$  and the energy differences  $\Delta E_{k,\alpha}$  representing the vertical IPs  $I_k^\alpha$  derived with two different methods are in complete agreement with fundamental KT relationship (51).

## B. Molecule O<sub>2</sub>

In Table I we compare the two canonical sets of ROHF orbital energies for molecule O<sub>2</sub> with experimental vertical IPs.<sup>23,24</sup> All calculations were performed with using the basis set aug-cc-pVTZ (19s6p3d2f)/[5s4p3d2f] of Ref. 25 implemented in GAMESS and  $R_{\text{O-O}} = 1.20752 \text{ \AA}$  (Ref. 23). For easier understanding of our data, the orbital energies in Table I are arranged in the UHF-like form so that the first column of orbital energies corresponds to attachment or to detachment of an alpha electron, i.e., to ionization processes **A2**, **B1**, and **C1**, while the second column corresponds to processes **A1**, **B2**, and **C2** with participation of a beta electron.

At first we note that the number of the peaks in the experimental (e,2e) spectra<sup>24</sup> of O<sub>2</sub> is greater than the number of theoretical peaks corresponding to KT states. The latter states calculated using the canonical ROHF method [Eqs. (19a)–(19c) and (76a)–(76c)] exactly correspond to the active CI space  $\{\Phi_{k,\alpha}^+(S - 1/2)\}$  of Eq. (57), while the additional (shake-up) peaks at 17.5 eV ( $A^2\Pi_u^-$ ) and 40.9 eV ( $^2\Sigma_g^-$ ) can be associated with the states formed within the wider active CI space  $\{\Phi_{k,\alpha}^+(S - 1/2)\} \oplus \{Y_k^+(S - 1/2)\} \oplus \{W(k, \bar{m}, n)\}$  of Eqs. (63) and (64).

In the present work we did not compare the experimental shake-up peaks with the CI states from spaces (63) and (64) since such a comparison needs a detailed analysis, which goes beyond the scope of this work. In whole, as follows from Table I, the agreement between observed IPs and their estimates via KT is qualitative and, in general, appears to possess the same accuracy level as in the closed-shell SCF.

## C. Molecule NO<sub>2</sub>

In Table II we present the similar data for molecule NO<sub>2</sub> where we have added for comparison the respective UHF orbital energies and theoretical estimates of IPs via a  $\Delta\text{SCF}$  method,

$$I_m^\alpha(\Delta\text{SCF}) = E_{\text{ROHF}}(X_{m,\alpha}^+, S - 1/2) - E_{\text{ROHF}}(X), \quad (77)$$

$$I_k^\beta(\Delta\text{SCF}) = E_{\text{ROHF}}(X_{k,\beta}^+, S + 1/2) - E_{\text{ROHF}}(X),$$

where, in this case,  $X = \text{NO}_2$  and  $S = 1/2$ . All calculations have been performed with the experimental geometry<sup>26</sup> of NO<sub>2</sub> ( $R_{\text{O-N}} = 1.1934 \text{ \AA}$ ,  $\angle \text{O-N-O} = 134.1^\circ$ ) and the same basis set aug-cc-pVTZ.<sup>25</sup>

At first we notice that neither the UHF nor the  $\Delta\text{SCF}$

TABLE I. Canonical ROHF orbital energies  $\varepsilon_j$  and experimental vertical IPs (in eV) for molecule  $O_2$  (state  ${}^3\Sigma_g^-$ ).

MO	Canonical ROHF		Experiment	
	$\varepsilon_v = -A_v^\alpha, \varepsilon_m = -I_m^\alpha, \varepsilon_k = -I_k^\alpha$	$\varepsilon_v = -A_v^\beta, \varepsilon_m = -A_m^\beta, \varepsilon_k = -I_k^\beta$	Reference 23	Reference 24
Virtual				
$2\pi_g$	+5.426			
$2\pi_u$		+4.109	+4.381	
$4\sigma_g$		+3.845	+4.041	
$3\sigma_u$		+2.689	+2.781	
Open-shell				
$1\pi_g$		+2.961		
$1\pi_g$	-14.493		12.071 ( $1\pi_g$ )	12.30 ( ${}^2\Pi_g$ )
Closed-shell				
$1\pi_u$		-16.055	16.092 ( $1\pi_u$ )	16.7 ( ${}^4\Pi_u$ )
$3\sigma_g$		-19.097	18.159 ( $3\sigma_g$ )	18.2 ( ${}^4\Sigma_g^-$ )
$3\sigma_g$	-21.810			20.3 ( ${}^2\Sigma_g^-$ )
$1\pi_u$	-25.541			17.5 (A ${}^2\Pi_u$ ); 23.7 ( ${}^2\Pi_u(3)$ )
$2\sigma_u$		-27.489	24.549 ( $2\sigma_u$ )	24.5 (C ${}^4\Sigma_u^-$ )
$2\sigma_u$	-34.853			27.4 (C ${}^2\Sigma_u^-$ )
$2\sigma_g$		-43.473	39.6 ( $2\sigma_g$ )	38.9 ( ${}^4\Sigma_g^-$ )
$2\sigma_g$	-47.966			40.9 ( ${}^2\Sigma_g^-$ ); 48.4 ( ${}^2\Sigma_g^-(2)$ )
$1\sigma_u$	$1\sigma_u$	-565.310	-563.610	
$1\sigma_g$	$1\sigma_g$	-565.318	-563.645	
$E_{\text{total}}$ (hartree)		-149.654 711	-149.654 711	

methods correctly predict the nature of the *first* IP at 11.25 eV (see the values in Table II marked in bold). Both UHF and  $\Delta$ SCF methods predict that the first IP corresponds to a removal of a beta electron from the closed-shell orbital  $4b_2$  with formation of ion  ${}^3B_2$ , while the experiment<sup>27</sup> shows the easiest ionization of an alpha electron from the open-shell orbital  $6a_1$  ( ${}^1A_1$ ). Similar incorrect estimates of the first IP by both UHF and  $\Delta$ SCF methods have been found by the present authors for some other systems such as CN (state  ${}^2\Sigma^+$ ) and  $ClO_2$  (state  ${}^2B_1$ ). As in the previous case of  $O_2$ , the agreement between experimental IPs and their estimates via KT (within the canonical ROHF method) is qualitative.

In contrast to this, the KT estimates of the EA for both  $O_2$  and  $NO_2$ ,  $A_{1\pi_g}^\beta(O_2) = -2.961$  eV and  $A_{6a_1}^\beta(NO_2) = -0.942$  eV, have nothing in common with the observed values,  $A_{1\pi_g}^\beta(O_2) = 0.440$  eV (Ref. 28) and  $A_{6a_1}^\beta(NO_2) = 2.273$  eV (Ref. 29). Although an immediate comparison between these two sets of EAs is not possible since the experimental values are adiabatic, i.e., they correspond to the relaxed geometry of both  $O_2^-$  (state  ${}^2\Pi_{g,\sigma}$ ,  $R_{O-O} = 1.35$  Å) (Ref. 23) and  $NO_2^-$  (state  ${}^1A_1$ ,  $R_{O-N} = 1.25$  Å,  $\angle O-N-O = 117.5^\circ$ ),<sup>29</sup> we should not expect that the respective vertical EAs will differ essentially from the adiabatic ones.

This drawback of the theory in predicting EAs is not, of course, unexpected. We just emphasize here that this drawback by no means is the consequence of KT itself, which is a rigorous mathematical theorem. The problem comes from the monoconfigurational approximation [Eqs. (3), (4), and (6)] underlying the definition of IPs and EAs. As is known, in the case of EA, the neglect of correlation and orbital relaxation inherent to the definition [Eqs. (3), (4), and (6)] leads to large errors even for closed-shell systems.

## VII. CONCLUSION

We have shown that KT can be formulated in the ROHF method for all six one-electron processes  $X \rightarrow X_{j,\sigma}^\pm$  [Eqs. (1a)–(1c) and (8a)–(8c)], possible in a high-spin half-filled open-shell system  $X$  under study.

For four of these processes in which the spin state of an ion is correctly described by a one-determinant wave function {these cases are called above as **A1**, **B1**, **C1** [Eqs. (1a)–(1c)] and **B2** [Eq. (8b)]}, the formulation of KT given in our previous works<sup>2,3,6</sup> within two different approaches is analogous to that given by Koopmans for closed-shell systems. For more complex cases, **A2** and **C2** [Eqs. (8a) and (8c)], we have given a slightly generalized formulation of KT based on the description of an ion by a multideterminantal ROHF wave function of the true spin and spatial symmetry [Eqs. (33) and (54)].

We have also shown that a simultaneous treatment of KT for two alternative one-electron processes possible in each electronic shell (e.g., for processes **A1** and **A2** in the closed shell, **B1** and **B2** in the open shell, etc.) leads to the necessity of introducing in the canonical ROHF method<sup>2</sup> *two different sets* of orbitals and orbital energies within each shell. The details of the computational procedure for deriving both sets of canonical ROHF orbitals and orbital energies with the program GAMESS are described in Sec. VI.

A comparison between the present CI-based formulation of KT in the ROHF method and the previous formulations of KT in the ROHF and UHF methods<sup>9–11</sup> has shown that the source of the wrong conclusion<sup>10</sup> according to which KT is not valid in the ROHF method is that the respective active CI spaces for the four processes (**A2**, **B1**, **B2**, and **C2**) com-

TABLE II. Canonical ROHF and UHF orbital energies  $\varepsilon_j$  for molecule  $\text{NO}_2$ ,  $\Delta\text{SCF}$  energies of cations  $\text{NO}_2^+$ , and experimental vertical IPs (in eV) for molecule  $\text{NO}_2$  (state  ${}^2A_1$ ). Bold font marks both the experimental value and the theoretical estimates of the first IP.

MO	Canonical ROHF		UHF <sup>a</sup>		$\Delta\text{SCF}$	Experiment
	$\varepsilon_v = -A_v^\alpha$ , $\varepsilon_m = -I_m^\alpha$ , $\varepsilon_k = -I_k^\alpha$	$\varepsilon_v = -A_v^\beta$ , $\varepsilon_m = -A_m^\beta$ , $\varepsilon_k = -I_k^\beta$	Alpha spin	Beta spin	$\Delta E$ <sup>b</sup>	Reference <i>27</i>
Virtual			Virtual	Virtual		
	$7a_1$	+2.248		+2.517		
	$7a_1$	+2.054	+2.052			
	$2b_1$	+1.869	+1.859			
	$6a_1$			+0.392		
Open-shell			Occupied	Occupied		
	$6a_1$	+0.942				
	$6a_1$	<b>-13.796</b>			12.023	<b>11.25</b> ( ${}^1A_1$ )
Closed-shell						
	$4b_2$	-13.853		<b>-13.570</b>	<b>11.315</b>	13.02 ( ${}^3B_2$ ) (11.25)
( $6a_1$ )	$1a_2$	-14.251	-13.761	-14.370	12.813	13.60 ( ${}^3A_2$ ) 14.07 ( ${}^1A_2$ )
	$1a_2$	-14.784	-14.455			14.52 ( ${}^1B_2$ )
	$4b_2$	-17.753	-16.297			18.00 ( ${}^3A_1$ ) 17.45 ( ${}^3B_1$ )
	$5a_1$	-19.666		-19.524	18.339	
	$1b_1$	-20.450		-20.403	19.184	
	$3b_2$	-20.645		-20.632		
	$1b_1$	-21.307	-20.879			17.77 ( ${}^1B_1$ )
	$3b_2$	-23.514	-21.957			
	$5a_1$	-23.957	-22.799			21.2 ( ${}^1A_1$ )
	$4a_1$	-29.035	-24.235	-26.485	-24.148	
	$2b_2$	-41.811	-39.792	-40.850	-39.721	
	$3a_1$	-46.837	-44.668	-45.762	-44.597	
	$2a_1$	-432.850	-431.707	-432.167	-431.541	
	$1a_1$	-563.234	-562.693	-563.022	-562.633	
	$1b_2$	-563.234	-562.693	-563.022	-562.633	
$E_{\text{total}}$ (hartree)	-204.104 171	-204.104 171	-204.113 290			

<sup>a</sup> $\langle S^2 \rangle = 0.771$ .<sup>b</sup> $\Delta E = E_{\text{ROHF}}(\text{NO}_2^+) - E_{\text{ROHF}}(\text{NO}_2)$ ; see also Eq. (77).

bined in Ref. 10 into two pairs,  $\mathbf{A2} \oplus \mathbf{B1}$  and  $\mathbf{B2} \oplus \mathbf{C2}$ , were defined incorrectly [see Eq. (70)]. Within the discussed CI-based approach, each of these four processes must be treated separately [Eqs. (56) and (57)]. For the same reason, the formally correct CI-based formulation of KT in the UHF method<sup>9</sup> for processes  $\mathbf{A2} \oplus \mathbf{B1}$  [Eq. (67)] and  $\mathbf{B2} \oplus \mathbf{C2}$  is actually ill-defined from the physical viewpoint.

## ACKNOWLEDGMENTS

We thank Professor J. Ivanic and Professor M. Schmidt for implementation in the ORMAS-CI algorithm in GAMESS some additional possibilities requested by us. We also thank Dr. E. V. Gorelik for stimulating discussions and help in performing calculations. The helpful comments of the referees of this paper are also highly appreciated. This work was partially supported by the Russian Foundation for Basic Research (Grant No. 09-03-00113) and by the Chemistry and Material Science Section of the Russian Academy of Sciences (Grant No. 2009/5.1.9).

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