On the Quantum Chemical Origin for the Nonvalidity of Koopmans' Theorem in Transitionmetal Compounds

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The quantum chemical origin for the nonvalidity of Koopmans' theorem in transitionmetal compounds of the 3d series is analyzed by means of the Green's function formalism applied in the framework of a semiempirical INDO Hamiltonian. In the case of ferrocene (**1**), cyclobutadiene iron tricarbonyl (**2**) and irontetracarbonyl dihydride (**3**) the self-energy part of a geometric approximation has been partitioned into relaxation and correlation (pair removal, pair relaxation) increments. The breakdown of Koopmans' theorem for strongly localized MOs with large Fe 3d amplitudes is predominantly the result of electronic relaxation lowering the calculated ionization potentials. On the other hand the variation of the pair correlation energy in the cationic hole-state is by no means negligible and acts into the opposite direction as the relaxation increment. These significant pair relaxation contributions explain the wellknown failtures of the ΔSCF approach in combination with large scale *ab initio* bases. The loss of ground state pair correlation in the outer valence region is small in comparison to relaxation and pair relaxation. The magnitude of the aforementioned reorganization increments has been studied as a function of the localization properties of the MOs and as a function of the one-electron energies of the available particle- and hole-states. The computational findings derived with the INDO model are compared with recent *ab initio* studies.

Key words: Electronic reorganization in 3d complexes – Breakdown of Koopmans' theorem – Green's function formalism – Semiempirical MO calculations.

1. Introduction

The comparison of measured ionization potentials with calculated ionization energies has shown that orbital reorganization effects are of significant importance in transitionmetal species [1, 2]. Often the sequence of the ionic states derived under the assumption of the validity of Koopmans' theorem [3] $(I_{v,j}^K = -\varepsilon_j)$ is changed upon the inclusion of electronic reorganization. The classification of the deviations from $I_{v,j}^K$ causes some trouble in the literature [4]; in the following we want to use the term reorganization energy as head notation which is divided into relaxation and correlation increments. This classification allows us to link computational procedures beyond the Hartree–Fock (HF) picture with the wellknown ΔSCF approximation [5] which has been used extensively for the interpretation of photoelectron (PE) spectra of organometallics.

In the recent ΔSCF studies, where only the relaxation energy of the total electronic reorganization is considered, it has been shown that there exists a strong correspondence between the localization properties of the orbital wavefunction (localized metal orbital vs. delocalized ligand function) and the deviations from $I_{v,j}^K$ [1, 2]. Classical examples for transitionmetal compounds that have been studied on the ΔSCF level are ferrocene [6, 7] and bis(π-allyl)nickel [8, 9]. The severe shortcomings of the ΔSCF approach have been verified in the latter compound. As a result of the neglected correlation contributions the calculated first ionization potential (IP) was by about 2.5 eV smaller than the measured vertical IP [9]. ΔSCF calculations on $Ni(CO)_4$ within a near Hartree–Fock basis led to a discrepancy of 3–4 eV between theory and experiment $(I_{v,j}^{exp} = 8.98 \text{ eV}, I_{v,j}^{\Delta SCF} = 4.90 \text{ eV}$ for the ionization out of the triply degenerate $9t_2$ MO) [10]. To include the important correlation effects in the theoretical approach many-body models beyond the Hartree–Fock approximation have to be employed.

In the case of small and medium size molecules CI [11] and Green's function [12] calculations with large scale *ab initio* Hamiltonians have been performed. In the case of extended transitionmetal compounds the Green's function formalism has been successfully applied in the inner [13] and outer [14–16] valence region in combination with semiempirical MO models based on the ZDO approximation (CNDO [17] and INDO [18] Hamiltonian). In various publications we have demonstrated that the INDO operator of Ref. 18 allows the calculation of IPs in the outer valence region of transitionmetal compounds with high accuracy. We have used second order approximations for the self-energy part [14, 15] as well as extensions to higher order contributions by means of a geometric approximation [16].

In the present publication we would like to present results of Green's function calculations on some iron complexes where the net reorganization energies are decomposed into relaxation and correlation increments in order to understand the quantum chemical origin leading to the breakdown of Koopmans' theorem

in transitionmetal compounds of the 3d series. The representative iron complexes are displayed below.
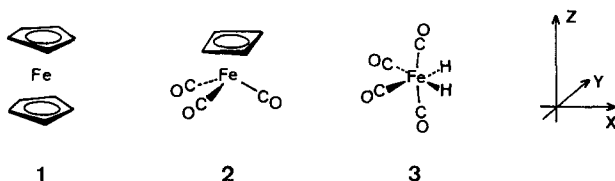
Ferrocene (**1**), cyclobutadiene iron tricarbonyl (**2**) and irontetracarbonyl dihydride (**3**) can be considered as d^6 complexes if it is assumed that the Cp(Cp = cyclopentadienyl) ligand in (**1**) acts as $Cp^{\ominus}$, cyclobutadiene in (**2**) as dianionic ligand forming a 6π system while the H atoms in (**3**) are of hydride type. Thus all transition metal complexes are characterized by three occupied MOs of predominant Fe $3d$ character (hole-states) and two virtual MOs with large Fe $3d$ amplitudes (particle-states). A detailed analysis of the electronic structure of (**1**)–(**3**) is not given in the present contribution.

In the following section the basis equations of the Green's function formalism are shortly reviewed. The self-energy operator is decomposed into the aforementioned relaxation and correlation increments. To our knowledge this separation into correlation and relaxation elements for the determination of vertical IPs has not been performed in the organometallic field (see however Ref. 19). Only sparse informations are available in the case of atoms and small molecules. Born, Kurtz and Öhrn have analyzed the magnitude of relaxation and correlation in H_2O [20], Reitz and Kutzelnigg performed a separation into various types of reorganization energies in coupled cluster calculations applied to Ne and H_2O [21]. In Sect. 3 the interrelation between the semiempirical parametrization and the absolute values of the calculated reorganization energies is discussed. In the next section the ground state properties of (**1**), (**2**) and (**3**) are shortly reviewed. In Chap. 5 the results of the partitioning scheme within the Green's function formalism are presented. In 6 the quantum chemical origin leading to the breakdown of Koopmans' theorem in transitionmetal compounds is analyzed.

2. Basis Equations

The theoretical background of the Green's function approach has been clarified in several thorough contributions [22–24]. Therefore only the most important aspects are given below. The vertical ionization potentials in the Green's function formalism are related to the zeros of the inverse Dyson equation (1) [25]

$$G(\omega)^{-1} = \omega I - \varepsilon - \Sigma(\omega). \tag{1}$$

G symbolizes the Green's function, ω is the energy coordinate that has to be determined, I is the unit-matrix of proper size and ε represents the diagonal matrix of the canonical HF orbitals. In analogy to recent investigations [16] we make use of a model potential for the self-energy part $\Sigma(\omega)$ that has been derived

by Cederbaum [26] on the basis of a geometric approximation which is related to the original suggestions of Kelly [27]. Within this framework $\Sigma(\omega)$ is given by the second order contribution $\Sigma^{(2)}(\omega)$ and a single third order renormalization contribution D4 (see below); the nomenclature corresponds to Ref. 26

$$\Sigma_{jj}(\omega_j)^{\text{eff}} = \Sigma_{jj}^{(2)}(\omega_j) + (D4)_{jj}. \tag{2}$$

In Eq. (3) the jth vertical ionization potential is related to the jth one-electron energy ε_j (Koopmans' theorem) and to the diagonal elements of the self-energy operator (Rayleigh–Schrödinger approximation)

$$-I_{v,j}^{G} = \varepsilon_j + \Sigma_{jj}^{(2)}(\varepsilon_j) + (D4)_{jj}. \tag{3}$$

The self-energy elements in second and third order of perturbation can be fragmented into simple relaxation and correlation increments if a diagonal approximation to $\Sigma(\omega)$ is employed. Pickup and Goscinski [28] have performed this fragmentation for $\Sigma_{jj}^{(2)}(\varepsilon_j)$ on the basis of Sinanoğlu's treatment of first-order pair correlation energies [29]. According to Ref. 28 $\Sigma_{jj}^{(2)}(\varepsilon_j)$ can be decomposed into three increments. $R_{jj}^{(2)}$ is the second order contribution to the electronic relaxation (HF contribution) in the jth cationic hole-state. $C_{\text{REM},jj}^{(2)}$ takes into account the loss of pair correlation upon removal of the jth spin orbital, e.g. the ground state correlation energy which disappears due to the transition from the N electron system to the $(N-1)$ hole-state. The third element is called pair relaxation energy, $C_{\text{REL},jj}^{(2)}$, and represents the many-body response in the $(N-1)$ system to the electronic relaxation (HF contribution). $C_{\text{REL},jj}^{(2)}$ thus is a measure for the modification of the remaining correlated pairs in the various cationic

2. ORDER   3. ORDER

PARTICLE   HOLE
DIAGRAM   DIAGRAMS
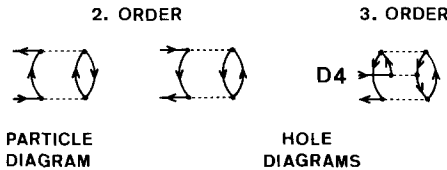
states. The explicit formulas for $R_{jj}^{(2)}$, $C_{\text{REM},jj}^{(2)}$ and $C_{\text{REL},jj}^{(2)}$ are given in Eqs. (4)–(6). i and l represent MO indices of the occupied Fermi-sea while the indices a and b are restricted to the particle-states. The four-index integral V_{ijkl} in the canonical MO basis $\{\varphi_i, \varphi_j, \varphi_k, \varphi_l\}$ is defined in Eq. (7)

$$R_{jj}^{(2)} = \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{V_{jaji}^2 + (V_{jaji} - V_{jaij})^2}{\varepsilon_a - \varepsilon_i} \tag{4}$$

$$C_{\text{REM},jj}^{(2)} = \frac{1}{2} \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} \sum_{b}^{\text{vir}} \frac{V_{jiab}^2 + V_{jiba}^2 + (V_{jiab} - V_{jiba})^2}{\varepsilon_j - \varepsilon_i - \varepsilon_a - \varepsilon_b} \tag{5}$$

$$C_{\text{REL},jj}^{(2)} = \frac{1}{2} \sum_{i \neq j}^{\text{occ}} \sum_{l \neq i}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{V_{jail}^2 + V_{jali}^2 + (V_{jail} - V_{jali})^2}{\varepsilon_j + \varepsilon_a - \varepsilon_i - \varepsilon_l}$$
$$- \sum_{i \neq j}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{V_{jaij}^2}{\varepsilon_a - \varepsilon_i} \tag{6}$$

$$V_{ijkl} = \langle \varphi_i(1)\varphi_j(2) \Big| \frac{1}{r_{12}} \Big| \varphi_k(1)\varphi_2(2) \rangle. \tag{7}$$

A similar partitioning scheme can be employed also in the case of the third order $D4$ hole-diagram [20, 30]. The third order relaxation increment of $(D4)_{jj}$ is given in Eq. (8)

$$R_{D4,jj}^{(3)} = \sum_i^{occ} \sum_l^{occ} \sum_a^{vir} \sum_b^{vir} \frac{V_{jajl}[V_{liab}(4V_{jijb}-2V_{jibj})+V_{liba}(V_{jibj}-2V_{jijb})]}{(\varepsilon_a-\varepsilon_l)(\varepsilon_i+\varepsilon_l-\varepsilon_a-\varepsilon_b)}$$

$$+ \sum_i^{occ} \sum_l^{occ} \sum_a^{vir} \sum_b^{vir} \frac{V_{jalj}[V_{liab}(V_{jibj}-2V_{jijb})+V_{liba}(V_{jijb}-2V_{jibj})]}{(\varepsilon_a-\varepsilon_l)(\varepsilon_i+\varepsilon_l-\varepsilon_a-\varepsilon_b)}. \tag{8}$$

The correlation increment of the $(D4)_{jj}$ element belongs to the pair relaxation type (associated to the $(N-1)$ system). This follows from the fact that $D4$ is a member of the hole-diagrams [20, 22]. The explicit formula for $(D4)_{jj}$ can be found in the literature [24]. Within the chosen potential for $\Sigma(\omega)$ $I_{v,j}^G$ is determined by means of Eq. (9)

$$-I_{v,j}^G = \varepsilon_j + R_{jj}^{(2)} + C_{REM,jj}^{(2)} + C_{REL,jj}^{(2)} + R_{D4,jj}^{(3)} + C_{D4/REL,jj}^{(3)}. \tag{9}$$

It is seen that ε_j is corrected due to second $(R_{jj}^{(2)})$ and third $(R_{D4,jj}^{(3)})$ order relaxation increments. These HF contributions cause many-body responses (e.g. modification of the pair correlation in the $(N-1)$ state) that are characterized by $C_{REL,jj}^{(2)}$ and $C_{D4/REL,jj}^{(3)}$. $C_{REM,jj}^{(2)}$ at least is a measure for the loss of ground state pair correlation due to the ejection of the jth electron. The correlation energy contained in $(D4)_{jj}$ is calculated by the difference of the full $(D4)_{jj}$ formula and Eq. (8).

3. The Parameter Dependence of the Calculated Reorganization Energies

The INDO operator used in the present investigation is an effective Hamiltonian where experimental two-electron integrals are employed in the various formulas (see Ref. 18). The most important consequences of this "dressing" are the renormalization of the two-electron part of the molecular Hamiltonian and of the one-particle energies. The interrelation between the magnitude of two-electron interactions and the importance of many-body effects in CI, coupled cluster and Green's function approaches has been studied in various publications [31–34].

To demonstrate the difference between effective semiempirical MO models and *ab initio* results we have compared relaxation energies (ΔSCF approach) for strongly localized Fe $3d$ MOs in the case of ferrocene (**1**). In Table 1 we have summarized the theoretically determined relaxation energies for ionization events out of the MOs $4e_{2g}$ $(3d_{x^2-y^2}/3d_{xy})$ and $8a_{1g}(3d_{z^2})$ based on the present INDO operator and based on two *ab initio* calculations with different AO basis

Table 1. Calculated relaxation energies ΔI^{REL} in the ΔSCF framework for the ferrocene MOs $4e_{2g}$ $(3d_{x^2-y^2}/3d_{xy})$ and $8a_{1g}$ $(3d_{z^2})$ within the present INDO Hamiltonian, the near minimal basis *ab initio* results of Coutiére, Demuynck, and Veillard (CDV) and the double zeta basis results of Bagus, Wahlgren and Almlöf (BWA). All values in eV

MO	INDO	*ab initio* CDV	*ab initio* BWA
$4e_{2g}$	2.74	6.10	6.14
$8a_{1g}$	2.90	6.50	6.83

sets. In the calculation of Coutiére *et al.* [6] 293 Gauss functions have been contracted to 85 functions $(293 \rightarrow 85)$ which corresponds to a minimal basis except the split $3d$ set. The basis of Bagus *et al.* [7] is characterized by the contraction $284 \rightarrow 188$. The comparison between the three computational procedures clearly displays that the differences between the two *ab initio* bases are only of minor importance while the semiempirical INDO based relaxation energies are dramatically reduced. This reduction is expected on the basis of the previous experience and has its origin in the smoothed two-electron integrals. On the other side an almost constant ratio $\Delta I^{REL}(8a_{1g})/\Delta I^{REL}(4e_{2g})$ is observed that is independent of the nature of the employed model operator (1.06, 1.07 and 1.11). This comparison demonstrates the parameter dependence of the calculated reorganization energies and is comparable with thematically related studies on semiempirical Hamiltonians [31–34]. It should be mentioned that the experimental PE spectrum of ferrocene [35, 36] is fairly reproduced either by the INDO model [37] or by the two *ab initio* approaches [6, 7].

4. Ground State Properties

To simplify the discussion in the following sections we have summarized the one-electron energies in the outer valence region for (1)–(3) as derived in the INDO framework. The ε_i spectrum together with the MO type and the localization properties of the orbital wavefunctions are shown in Table 2–Table 4. The INDO calculations on the iron complexes were performed with geometrical parameters obtained from X-ray or electron diffraction studies ((1)[38], (2)[39] and (3)[40]).

In ferrocene (1) two MOs with predominant Fe $3d$ amplitudes are found: $8a_{1g}$ $(3d_{z^2})$ at -10.75 eV and $4e_{2g}$ $(3d_{x^2-y^2}/3d_{xy})$ at -11.22 eV. The Fe contribution in any case exceeds 90%. Nonvanishing Fe $3d$ amplitudes are also predicted in the MOs $4e_{1g}$ and $3e_{1g}$ which correspond to ligand π and ligand σ linear combinations. The INDO results of Table 2 suggest that the outer valence orbitals of (1) can be divided into two classes: the strongly localized Fe $3d$ orbitals $8a_{1g}$ and $4e_{2g}$ on one side and the remaining delocalized ligand functions on the other side.

Table 2. Valence orbitals of ferrocene (**1**) according to the semiempirical INDO approach. The orbital energies, ε_i, are given in eV. The composition (%), the type as well as the irreducible representation (Γ_i) of the MO wavefunction are indicated. Cp = cyclopentadienyl ligand

MO	Γ_i	MO-Type	ε_i	% Fe	% Cp π	% Cp σ
28/29	$4e_{1u}$	Cp(π)	-9.91	0.3	99.1	0.6
27	$8a_{1g}$	$3d_{z^2}$	-10.75	93.4	2.7	3.9
25/26	$4e_{1g}$	Cp(π), $3d_{xz}/3d_{yz}$	-10.94	25.3	58.0	16.7
23/24	$4e_{2g}$	$3d_{x^2-y^2}/3d_{xy}$	-11.22	90.1	6.1	3.8
22	$6a_{2u}$	Cp(π)	-11.62	0.3	99.2	0.5
20/21	$5e_{1u}$	Cp(σ)	-13.37		0.2	99.8
18/19	$3e_{2u}$	Cp(σ)	-14.03			100.0
16/17	$3e_{1g}$	Cp(σ)	-14.04	14.5	5.1	80.4
14/15	$3e_{2g}$	Cp(σ)	-14.29	2.6		97.4
13	$7a_{1g}$	Cp(π)	-16.17	4.2	93.8	2.0

Table 3. Valence orbitals of cyclobutadiene iron tricarbonyl (**2**) according to the INDO Hamiltonian. See legend Table 2

MO	Γ_i	MO-Type	ε_i	% Fe	% C_4H_4 π	% C_4H_4 σ	% CO
29	$31a'$	$1e_g(\pi)$, $2e$ Fe(CO)$_3$	-9.94	35.2	50.2	0.9	13.8
28	$17a''$	$1e_g(\pi)$, $2e$ Fe(CO)$_3$	-9.95	34.4	50.7	0.9	13.9
27	$30a'$	$1a$ Fe(CO)$_3$,$1a_{2u}(\pi)$	-10.44	59.2	19.0	0.8	21.2
26	$29a'$	$1e$ Fe(CO)$_3$	-11.33	79.3	6.8	4.5	9.4
25	$16a''$	$1e$ Fe(CO)$_3$	-11.34	77.4	7.3	3.4	11.9
24	$28a'$	$1a_{2u}(\pi)$, $1a$ Fe(CO)$_3$	-13.04	28.6	54.6	1.1	15.7
23	$27a'$	$3e_u$(walsh)	-13.30	4.6	0.5	72.7	22.2
22	$15a''$	$3e_u$(walsh)	-13.30	4.6	2.6	72.7	20.1

$1e$ Fe(CO)$_3$: $3d_{x^2-y^2}/3d_{xy}$
$1a$ Fe(CO)$_3$: $3d_{z^2}$ (predominant Fe $3d$ amplitude)
$2e$ Fe(CO)$_3$: $3d_{xz}/3d_{yz}$

Table 4. Valence orbitals of irontetracarbonyl dihydride (**4**) according to the INDO Hamiltonian. See legend Table 2

MO	Γ_i	MO-Type	ε_i	% Fe	% H	% CO
25	$19a_1$	FeH(σ)	-11.54	24.9	37.9	37.1
24	$10b_2$	$3d_{xz}$	-11.59	74.2		25.8
23	$3a_2$	$3d_{yz}$	-12.13	89.5		10.5
22	$18a_1$	$3d_{x^2-y^2}$	-12.20	90.4	0.3	9.3
21	$10b_1$	FeH(σ)	-12.51	23.2	43.2	33.6

This simple splitting pattern is not conserved in the case of the tricarbonyl complex (2); here a stronger coupling between the $3d$ set of the transitionmetal center and ligand π functions is encountered. Therefore MOs of the complex are calculated where comparable contributions from the formal fragments $(Fe(CO)_3$ and $C_4H_4)$ are found. Predominant Fe $3d$ amplitudes are predicted for the MO pair $29a'/16a''$ where the Fe $3d$ character exceeds 75%. These two MOs are derived from the degenerate $1e$ combination of the $Fe(CO)_3$ fragment which contains significant $3d_{x^2-y^2}/3d_{xy}$ contributions [41]. A remarkable metal ligand coupling is predicted for the MOs $31a'/17a''$ (35% Fe $3d$ character) and $30a'/28a'$. The latter linear combinations are the antibonding and bonding components of the interaction between $3d_{z^2}$ of the iron center and the lowest π orbital of the cyclic ligand. In the out-of-phase combination at -10.44 eV a predominance of the Fe character is diagnosed (59%) while this value is reduced to 29% in the stabilized counterpart where the $1a_{2u}(\pi)$ amplitude is of major importance (54.6%).

The five highest occupied MOs of (3) are collected in Table 4. MO $19a_1$ and MO $10b_1$ at -11.54 eV and -12.51 eV, respectively, correspond to the FeH σ combinations. The Fe $3d$ contributions to the orbital wavefunctions are comparable in the two MOs (24.9% and 23.2%). The remaining orbitals – $10b_2$, $3a_2$ and $18a_1$ – are strongly localized at the iron center and are primarily of $3d_{xz}$, $3d_{yz}$ and $3d_{x^2-y^2}$ type. In $10b_2$ the strongest coupling to the carbonyl ligands is found; the Fe $3d$ amplitude is reduced to 74.2%. In the other two MOs Fe $3d$ contributions of about 90% are predicted.

5. The Partitioning of the Self-Energy Operator into Relaxation and Correlation Increments

The reorganization increments discussed in Sect. 2 $(R_{jj}^{(2)}, C_{\text{REM},jj}^{(2)}, C_{\text{REL},jj}^{(2)}, R_{D4,jj}^{(3)}$ and $C_{D4/\text{REL},jj}^{(3)})$ for the outer valence orbitals of (1), (2) and (3) are summarized in the Tables 5–7. A schematic display of the various correction elements is shown in Figs. 1 and 2. In the case of ferrocene 17 hole-states and 8 particle-functions have been considered in the expansion of the self-energy operator. In the tricarbonyl complex (2) the corresponding dimensions are 14 to 10 while in the dihydride complex (3) 12 hole- and 10 particle-states have been taken into account.

The computational results clearly indicate that there are common findings for all transitionmetal complexes. Thus it is seen that the second order pair removal component, $C_{\text{REM},jj}^{(2)}$, is small in comparison to the other second order quantities. The absolute values are often smaller than 0.5 eV. Of course $C_{\text{REM},jj}^{(2)}$ leads to an increase of the calculated ionization energy (in comparison to $I_{v,j}^{K}$). The origin of this behaviour is recognized in the denominator of Eq. (5). In the following we want to analyze the predominant reorganization increments in larger detail.

In the case of ferrocene (Table 5) large relaxation energies are observed for the strongly localized MOs $8a_{1g}$ and $4e_{2g}$. $R_{jj}^{(2)}$ of $8a_{1g}$ amounts to 8.72 eV, in the

Table 5. Decomposition of the calculated Koopmans' defects of ferrocene into the various relaxation and correlation increments. All values in eV.

MO	Γ_j	$I^K_{v,j}$	$R^{(2)}_{jj}$	$C^{(2)}_{\text{REL},jj}$	$C^{(2)}_{\text{REM},jj}$	$R^{(3)}_{D4,jj}$	$C^{(3)}_{D4/\text{REL},jj}$	Σ^{eff}_{jj}	$I^G_{v,j}$
23/24	$4e_{2g}$	11.22	7.97	−4.19	−0.14	−0.95	0.01	2.70	8.52
27	$8a_{1g}$	10.75	8.72	−4.60	−0.01	−1.16	0.01	2.96	7.79
28/29	$4e_{1u}$	9.91	0.13	0.51	−0.25	−0.02	−0.03	0.34	9.57
25/26	$4e_{1g}$	10.94	0.92	0.19	−0.37	−0.10	−0.05	0.59	10.35
22	$6a_{2u}$	11.62	0.12	0.64	−0.11	−0.02	−0.04	0.59	11.03
20/21	$5e_{1u}$	13.37	0.09	0.62	−0.02	−0.01	−0.06	0.62	12.75
16/17	$3e_{1g}$	14.04	0.45	0.57	−0.16	−0.05	−0.08	0.73	13.31
18/19	$3e_{2u}$	14.03	0.10	0.68	−0.02	−0.01	−0.09	0.66	13.37
14/15	$3e_{2g}$	14.29	0.14	0.79	−0.01	−0.02	−0.11	0.79	13.50
13	$7a_{1g}$	16.17	0.19	1.58	−0.06	−0.04	−0.19	1.48	14.69

Table 6. Decomposition of the calculated Koopmans' defects of cyclobutadiene iron tricarbonyl into the various relaxation and correlation increments. All values in eV.

MO	Γ_j	$I^K_{v,j}$	$R^{(2)}_{jj}$	$C^{(2)}_{\text{REL},jj}$	$C^{(2)}_{\text{REM},jj}$	$R^{(3)}_{D4,jj}$	$C^{(3)}_{D4/\text{REL},jj}$	Σ^{eff}_{jj}	$I^G_{v,j}$
27	$30a'$	10.44	4.70	−1.36	−0.23	−0.83	−0.25	2.03	8.41
26	$29a'$	11.33	8.20	−3.68	−0.24	−1.41	−0.14	2.73	8.60
25	$16a''$	11.34	7.74	−3.49	−0.31	−1.30	−0.10	2.55	8.79
29	$31a'$	9.94	2.09	−0.52	−0.57	−0.29	−0.07	0.64	9.30
28	$17a''$	9.95	2.04	−0.53	−0.58	−0.23	−0.03	0.67	9.28
24	$28a'$	13.04	1.72	−0.73	+0.14	−0.23	−0.48	1.60	11.44
23	$27a'$	13.30	1.42	−0.30	−0.07	−0.10	−0.11	0.84	12.46
22	$15a''$	13.30	1.40	−0.23	−0.07	−0.10	−0.14	0.76	12.54

Table 7. Decomposition of the calculated Koopmans' defects of irontetracarbonyl dihydride into the various relaxation and correlation increments. All values in eV

MO	Γ_i	$I_{v,i}^K$	$R_{ii}^{(2)}$	$C_{REL,ii}^{(2)}$	$C_{REM,ii}^{(2)}$	$R_{D4/ii}^{(3)}$	$C_{D4/REL,ii}^{(3)}$	Σ_{ii}^{eff}	$I_{v,i}^G$
22	$18a_1$	12.20	7.62	−3.60	−0.13	−1.04	−0.01	2.84	9.36
24	$10b_2$	11.59	5.27	−2.06	−0.19	−0.70	−0.08	2.23	9.36
23	$3a_2$	12.13	7.31	−3.55	−0.17	−0.97	0.03	2.65	9.48
25	$19a_1$	11.54	1.45	−0.01	−0.40	−0.18	−0.05	0.81	10.73
21	$10b_1$	12.51	1.36	0.04	−0.39	−0.16	−0.04	0.80	11.71
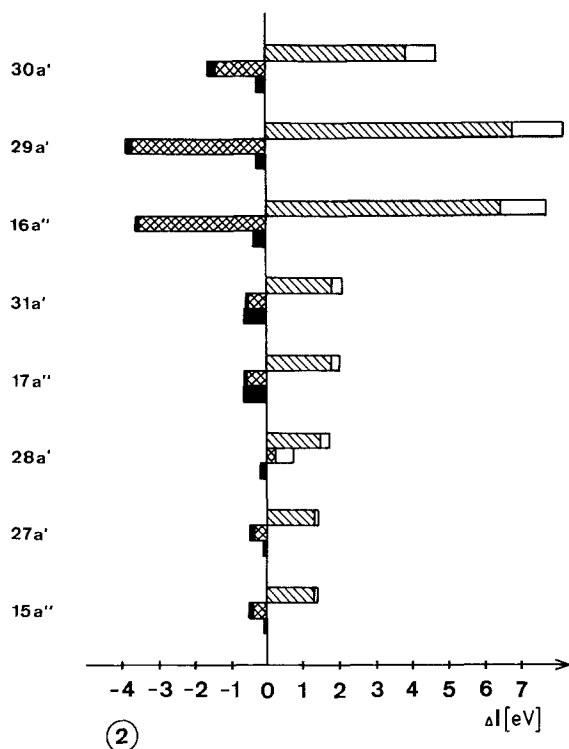
Fig. 1. Decomposition of the net Koopmans' defects in cyclobutadiene iron tricarbonyl (**2**) into relaxation and correlation increments. The first histogram in each group corresponds to the relaxation increments ($R_{jj}^{(2)}$, and $R_{D4,jj}^{(3)}$). The top of the beam measures $R_{jj}^{(2)}$, the third order increment is symbolized by the blank area. The renormalized relaxation energy therefore is given by the hatched area. The third (black) histogram corresponds to the single pair removal parameter $C_{REM,jj}^{(2)}$. The second member shows the pair relaxation components $C_{REL,jj}^{(2)}$ and $C_{D4/REL,jj}^{(3)}$. If both increments have different signs and act into different directions with respect to $I_{v,j}^{K}$ the third order contribution is represented by a blank field while the renormalized pair relaxation correction is given by the hatched area. If both increments have the same sign the renormalized contribution is given by the sum of the (hatched) second order and the (black) third order corrections

case of the degenerate $4e_{2g}$ combination a value of 7.97 eV is predicted. $R_{jj}^{(2)}$ causes a dramatical reduction of the calculated ionization energies (see denominator of Eq. (4)). On the other side it is seen that these large relaxation effects in the cationic hole-state are accompanied by a strong modification of the pair relaxation in the $(N-1)$ system. $C_{REL,jj}^{(2)}$ leads to an increase of the calculated IPs. In the case of $8a_{1g}$ and $4e_{2g}$ -4.60 eV and -4.19 eV are calculated. For strongly localized complex MOs thus an approximate ratio between $R_{jj}^{(2)}$ and $C_{REL,jj}^{(2)}$ of $-2:1$ is found. The third order increments of $8a_{1g}$ and $4e_{2g}$ are predominantly determined by the relaxation parameter while the correlation term is only of minor significance. The combined effects of all reorganization
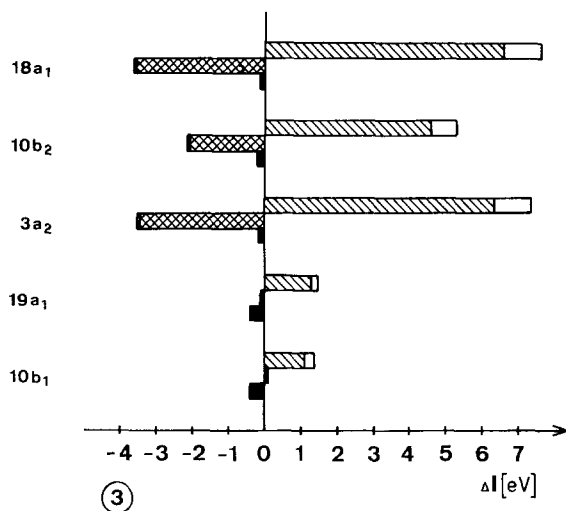
Fig. 2. Decomposition of the net Koopmans' defects in irontetracarbonyl dihydride (**3**) into relaxation and correlation increments. See legend Fig. 1

elements create net deviations from $I_{v,j}^K$ (Koopmans' defects) of 2.96 eV ($8a_{1g}$) and 2.70 eV ($4e_{2g}$).

The Koopmans' defects of the remaining ferrocene orbitals are small in comparison to $8a_{1g}/4e_{2g}$. The net defects for most of the ligand functions are smaller than 1 eV. It is seen that $R_{jj}^{(2)}$ and $C_{\mathrm{REL},jj}^{(2)}$ act into the same direction in the case of the delocalized Cp functions while both increments partially compensate each other in the localized Fe $3d$ MOs. The results summarized in Table 5 also demonstrate the variation of the relative importance of relaxation and correlation with increasing one-electron energies. For π and σ combinations in the high energy limit of the outer valence region Koopmans' defects are predicted that are the result of electronic correlation. This is best rationalized within the $7a_{1g}$ combination where $I_{v,j}^K$ is lowered by 1.48 eV. The relaxation contributions to this value amount only to 0.15 eV while the combined correlation parameters are added to 1.33 eV.

The calculated defect increments of the strongly localized MOs $29a'$ and $16a''$ of (**2**) (Table 6, Fig. 1) are in line with the expectations extrapolated from the ferrocene analysis. The second order relaxation terms fluctuate about 8 eV, the associated pair relaxation elements amount to $-3.68/-3.49$ eV. In the case of the MO pair $30a'$ and $28a'$ (antibonding and bonding metal ligand combination) $R_{jj}^{(2)}$ parameters of 4.70 eV ($30a'$) and 1.72 eV ($28a'$) are extracted from the Green's function approach. The INDO results of Table 6 indicate that the net defects within this MO pair are the result of opposite combinations of $R_{jj}^{(2)}$ and $C_{\mathrm{REL},ii}^{(2)}$. In the antibonding combination both effects act into different directions

while they sum up in the bonding MO:

$$
\begin{array}{llll}
 & R_{jj}^{(2)} & C_{\mathrm{REL},jj}^{(2)} & \\
30a': & 4.70 & -1.36 & = 3.34\ \mathrm{eV} \\
28a': & 1.72 & +0.73 & = 2.45\ \mathrm{eV}
\end{array}
$$

Significant relaxation energies are also found for the complex MOs $31a'$ and $17a''$. The relaxation terms of about 2 eV are reduced to 1 eV due to pair removal and pair relaxation.

Large relaxation and pair relaxation elements (second order) are predicted for the strongly localized MOs ($3a_2$, $18a_1$) of (**3**). $R_{jj}^{(2)}$ values of $7.31/7.62$ eV and $C_{\mathrm{REL},jj}^{(2)}$ increments of $-3.55/-3.60$ eV are encountered. In the $10b_2$ combination (75% Fe $3d$ character) reduced second order defect components (5.27 eV and -2.06 eV for relaxation and pair relaxation) are predicted by the computational approach. In the case of the two FeH σ linear combinations $C_{\mathrm{REL},jj}^{(2)}$ terms are found that differ only insignificantly from zero. This indicates that the FeH orbitals belong to a MO type where the pair relaxation increments change their sign from an increasing contribution in the limit of strongly localized complex MOs to a decreasing effect for sufficiently delocalized ligand functions (with respect to $I_{v,j}^{K}$ as internal standard).
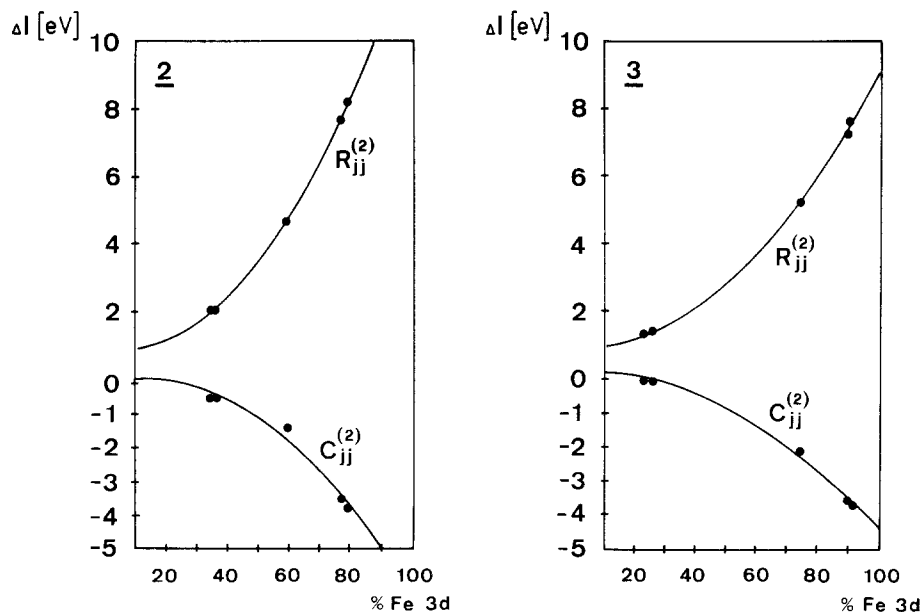

Fig. 3. Second order relaxation ($R_{jj}^{(2)}$) and second order pair relaxation ($C_{\mathrm{REL},jj}^{(2)}$ in the text, $C_{jj}^{(2)}$ in the figure) elements as a function of the Fe $3d$ amplitude in the jth hole-state in cyclobutadiene iron tricarbonyl (left) and irontetracarbonyl dihydride (right)

The strong interrelation between the calculated $R_{jj}^{(2)}$ and $C_{\text{REL},jj}^{(2)}$ increments and the localization properties of the orbital wave function is displayed in Fig. 3 where both quantities are plotted as a function of the Fe $3d$ character for the jth hole-state for the iron complexes (**2**) and (**3**).

The partitioning scheme into relaxation and correlation increments allows the formulation of the following general rules concerning the breakdown of Koopmans' theorem in transitionmetal compounds:

(a) In the investigated model systems and in the framework of the semiempirical INDO Hamiltonian it has been shown that the loss of ground state pair correlation (pair removal) does not lead to pronounced corrections to the calculated ionization energies in the outer valence region. The IPs are enhanced by about 0.5 eV (in comparison to $I_{v,j}^{K}$).

(b) In the case of ionization processes out of strongly localized metal $3d$ MOs deviations from $I_{v,j}^{K}$ are encountered that are prevailingly called forth due to electronic relaxation. With increasing localization of the orbital wave function $R_{jj}^{(2)}$ becomes the leading term of Eq. (9). As a result of the relaxation (HF contribution) in the $(N-1)$ system a lowering of the calculated IP with respect to $I_{v,j}^{K}$ is encountered. It can be expected that purely relaxational approaches (e.g. ΔSCF procedure [5], transition operator method (TOM) [42, 43]) are most successful in this domain (extreme outer valence region, strongly localized complex MOs, $3d$ functions on top of ligand MOs).

(c) With increasing relaxation in the cationic hole-state, however, enlarged pair relaxation contributions have been diagnosed; this increment is the many-body response to the electronic relaxation.

(d) The magnitude of the pair relaxation corrections spans a wide range. For strongly localized valence orbitals in the lower energy region correlation increments are encountered that act into the opposite direction as $R_{jj}^{(2)}$ and raise the value of the calculated IP. For complex MOs with metal amplitudes between 80–90% a ratio between the increments of the second order hole-diagram of $-2:1$ is observed. With increasing delocalization this value is enlarged due to the stronger reduction of the pair relaxation parameter. In the framework of the present INDO Hamiltonian $C_{\text{REL},jj}^{(2)}$ oscillations around zero are found for complex orbitals with metal $3d$ contributions between 25–30%. If the metal amplitude in the MO is reduced furthermore $C_{\text{REL},jj}^{(2)}$ changes the sign and acts into the same direction as $R_{jj}^{(2)}$, the calculated ionization energies are reduced. With increasing one-particle energies (absolute values) enlarged $C_{\text{REL},jj}^{(2)}$ elements are observed. The reduction of IPs of ligand σ orbitals at the higher energy side has its origin in the magnitude of the pair relaxation terms.

(e) In the present study only the $D4$ contribution to the total ensemble of third order elements has been considered. The leading term of $D4$ is a relaxation parameter renormalizing the second order components of the self-energy expansion. The correlation increment of $D4$ is only of minor importance. With decreasing localization $R_{D4,jj}^{(3)}$ is reduced dramatically, renormalization effects are thus most important in the case of complex orbitals with large $3d$ amplitudes.

6. Theoretical Analysis

To understand the origin that leads to the breakdown of Koopmans' theorem in transitionmetal compounds one has to analyze the magnitude of $R_{jj}^{(2)}$, $C_{\text{REM},jj}^{(2)}$, $C_{\text{REL},jj}^{(2)}$, $R_{\text{D4},jj}^{(3)}$ and $C_{\text{D4/REL},jj}^{(3)}$ as a function of the one-electron energies ε_j and as a function of the localization properties of the orbital wavefunction. Additionally one has to investigate the possibility of the remaining available hole- and particle-states in the molecule to contribute to the one-electron excitations leading to relaxation and correlation.

It has been demonstrated in the last section that the second order pair removal increments (Eq. (5)) are small in comparison to the other second order quantities. Eq. (5) shows that the numerator of $C_{\text{REM},jj}^{(2)}$ is in any case positive due to the quadratic V_{ijkl} expressions; the sign of this increment therefore is determined by the energy denominator. The one-electron energies of the jth hole-state and the other ε_i values of the occupied Fermi-sea are added to a remarkable negative number which is often enlarged by means of the particle-state energies ε_a and ε_b. These large denominators allow only small corrections due to $C_{\text{REM},jj}^{(2)}$. Eq. (10) defines the sign of the second order pair removal corrections

$$C_{\text{REM},jj}^{(2)} < 0. \tag{10}$$

The most important element of Eq. (9) is the second order relaxation correction $R_{jj}^{(2)}$ (Eq. (4)). $R_{jj}^{(2)}$ is strongly dependent on the magnitude of the V_{jaji} and V_{jaij} integrals but is independent from the one-electron energy ε_j of the jth hole-state. This result differs significantly from conclusions derived in an older investigation [2]. The calculated relaxation energies are not a function of the relative energy separation between ε_j and the remaining one-electron energies ε_i and ε_a, respectively. $R_{jj}^{(2)}$ is given by a double sum with one hole- and one particle-index. With increasing localization of the j'th cationic hole-state the interaction of the jth hole-density $\langle \varphi_j(1)\varphi_j(1)|$ with the transition density $|\varphi_a(2)\varphi_i(2)\rangle$ is enlarged. Obviously the V_{jaji} integrals are maximized if the MOs φ_i (occupied) and φ_a (virtual) are also localized at the transitionmetal center (in analogy to φ_j). Thus the most pronounced relaxation increments must be found in those transition-metal complexes where simultaneously localized hole- and particle-states are available, a condition that is fulfilled in $d^5 - d^7$ species. With a decreasing number of $3d$ electrons the i-summation in (4) is reduced while in the case of $d^8 - d^{10}$ complexes the efficiency of the particle summation is diminished. In a recent publication we have verified that deviations from $I_{v,j}^K$ are enlarged in the series $Cr \rightarrow Mn \rightarrow Fe$ [44]. In auxiliary group VIII elements (Fe $\rightarrow$ Co $\rightarrow$ Ni) Koopmans' defects are calculated that are nearly constant [16]. These constant defects are the result of two opposite mechanisms. On one side the localization of the orbital wavefunction is continuously increased in the series Fe $\rightarrow$ Co $\rightarrow$ Ni; additionally the one-center Coulomb integrals ($3d$ AOs) are enlarged (e.g. Fe = 15.37 eV, Co = 16.04 eV, Ni = 16.71 eV [18]). The combined effects of stronger localization and enlarged AO basis integrals leads to enhanced V_{jaji} parameters. On the other side the number of available localized particle-states φ_i is reduced. If both effects nearly compensate each other constant $R_{jj}^{(2)}$ and $C_{\text{REL},jj}^{(2)}$ elements must

be expected. To extrapolate these findings to the complete $3d$ series small relaxation effects should be found on the left side (Sc, Ti, V) [45] but also on the extreme right (Cu, Zn). In any case $R_{jj}^{(2)}$ satisfies the inequality relation (11)

$$R_{jj}^{(2)} > 0. \tag{11}$$

To analyze the characteristic properties of $C_{REL,jj}^{(2)}$ we have decomposed the pair relaxation energy into two different summations (Eq. (6)). Due to the quadratic form of the V_{ijkl} integrals the sign of $C_{REL,jj}^{(2)}$ is determined by the predominance of one of the two summations as well as by the corresponding energy denominators. In the triple sum two hole-indices (i, l) and one particle-index (a) are involved in the perturbational expansion. In the double sum one hole- and one particle-index are encountered; the second contribution is therefore similar to the $R_{jj}^{(2)}$ element. The first summation is a function of the one-electron energy ε_j, the second one is independent from the energy of the jth orbital. If the jth MO is strongly delocalized the two-electron integrals in both summations are of comparable size. $C_{REL,jj}^{(2)}$ is therefore prevailingly determined by the first summation as the small increments of the threefold summation exceed the contributions of the double sum. With increasing influence on $C_{REL,jj}^{(2)}$ due to the first summations (delocalized ligand MOs) pair relaxation increments are calculated that depend on the one-electron energy ε_j. Deviations from $I_{v,j}^K$ are therefore enhanced with enlarged ε_j values.

This ε_j dependence is demonstrated in a simple numerical example. In the case of model (A) the orbital energy of the ionized MO is assumed to be -10 eV while in example (B) ε_j is set equal to -20 eV. For the remaining occupied MOs φ_i, φ_l one-electron energies of -15 eV are accepted while an averaged particle-state energy of 5 eV is employed

$$\mathbf{A} \quad \frac{C}{-10+5+15+15} = \frac{C}{25} \tag{12}$$

$$\mathbf{B} \quad \frac{C}{-20+5+15+15} = \frac{C}{15} \tag{13}$$

$C = $ constant numerator.

In the first example (A) the $C_{REL,jj}^{(2)}$ influence is reduced due to the larger energy denominator (in comparison to (B)). In contrast to the pair removal energy, $C_{REM,jj}^{(2)}$ it is possible in $C_{REL,jj}^{(2)}$ that the orbital energies $(\varepsilon_i, \varepsilon_l)$ of the remaining hole-states φ_i, φ_l $(i, l \neq j)$ largely compensate ε_j leading to significant $C_{REL,jj}^{(2)}$ corrections. In the limit of strongly delocalized MOs with V_{ijkl} integrals of the long-range type the triple sum in Eq. (6) is predominant and acts into the same direction as $R_{jj}^{(2)}$

delocalized MOs: $C_{REL,jj}^{(2)} > 0.$ \tag{14}

The breakdown of Koopmans' theorem in small and medium size molecules in the high energy domain of the outer valence region has its origin in this correlation fragment [46].

With increasing localization of the jth MO at the transitionmetal center the influence of the twofold summation in Eq. (8) is enlarged as the interaction between the local charge distributions $\langle\varphi_j(1)\varphi_i(1)|$ and $|\varphi_j(2)\varphi_a(2)\rangle$ allows an efficient magnification of the V_{jaij} integrals. The V_{jaij} elements now belong to short-range integrals and exceed the magnitude of the triple summation (V_{jail}, V_{jali}). In the theory of metals this situation (short-range forces) is called low-density limit while the aforementioned long-range behaviour is similar to the high-density limit [47]. In the case of strong localization $C_{REL,jj}^{(2)}$ acts against $R_{jj}^{(2)}$ and raises the theoretically calculated IPs (Eq. (15))

$$\text{localized MOs: } C_{REL,jj}^{(2)} < 0. \tag{15}$$

In the ΔSCF approximation for ionization processes of transitionmetals these significant correlation corrections are neglected and the calculated IPs are too small if the AO basis reaches the HF limit. Most of the ΔSCF *ab initio* calculations on organometallic systems however are far from this limit. The pair relaxation corrections therefore pretend only a latent contribution as the neglect of $C_{REL,jj}^{(2)}$ and the deviations from the HF limit in minimal basis approaches often compensate each other. Two sparse examples where the neglect of the pair relaxation leads to calculated IPs that are too small have been mentioned in the introduction [9, 10].

The correction elements $R_{jj}^{(2)}$ and $C_{REL,jj}^{(2)}$ of Eq. (4) and Eq. (6) allow a quantum chemical classification of the nature of the reorganization processes accompanying the ionization events. Principally two types of reorganizational rearrangements can be discriminated: intraatomic and interatomic, delocalized scattering processes. Inspection of Eqs. (4) and (6) clearly demonstrates that ionization events out of localized complex MOs are accompanied by local intraatomic reorganizations via the ensemble of occupied and virtual "$3d$ orbitals". The influence of the organic ligands is determined by means of $3d$ particle-states which are characterized by a remarkable metal ligand coupling. In the case of the iron complexes (1)–(3) Fe amplitudes in the $3d$ acceptor states between 40–50% are encountered. The predominant intraatomic nature of electronic reorganization has been demonstrated by Rohmer, Demuynck and Veillard [9] in ΔSCF calculations on bis(π-allyl)nickel.

7. Conclusion

The net reorganization energies in Green's function calculations on some iron complexes have been decomposed into relaxation terms (HF contribution) and into correlation parameters taking into account the loss of ground state pair correlation due to the ionization process (pair removal) as well as the variation of the pair correlation in the cationic hole-state (pair relaxation). In the case of strongly localized $3d$ orbitals the main contribution to the self-energy expansion is due to electronic relaxation. On the other hand a significant amount of this relaxation energy is compensated by pair relaxation contributions. The increments of $R_{jj}^{(2)}$ and $C_{REL,jj}^{(2)}$ are largest if a comparable number of localized hole- and particle-states are available in the transitionmetal complex. The largest

deviations from Koopmans' theorem therefore must be expected in d^5/d^6 complexes (Mn^{2+}, Mn^{3+}, Fe^{2+}, Co^{3+}). With a decreasing atomic number of the $3d$ element (Sc, Ti, V) the capability of the occupied $3d$ set in the elementary excitations is reduced while on the right side of the $3d$ series (Cu, Zn) the scattering capability of the virtual $3d$ set is diminished.

The computational results in the present contribution are based on a semi-empirical INDO Hamiltonian. The theoretical consequences of the specific parametrization scheme for the magnitude of the calculated reorganization energies have been mentioned. The V_{ijkl} integrals entering the perturbational expansion are reduced in comparison to an *ab initio* Hamiltonian. The INDO based relaxation and correlation corrections are smaller than reorganization energies derived by means of *ab initio* calculations; deviations from the exact self-energy part are less pronounced in comparison to first principle MO calculations. Simplified MO models in combination with the Green's function procedure therefore should be a suitable tool to calculate ionization energies of medium size and larger organometallics where *ab initio* bases near the HF limit are beyond computational capabilities.

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