ΔSCF and Transition Operator (TO) Calculations in the Theoretical Determination of Vertical Ionization Energies in Transition Metal Compounds

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The interrelation between theoretically determined vertical ionization potentials in transition metal compounds based on the ΔSCF approximation ($I^{\Delta\mathrm{SCF}}_{v,j}$) and based on the "transition operator (TO)" method ($I^{\mathrm{TO}}_{v,j}$) has been investigated. Numerical results in the outer valence region have been obtained by means of semiempirical INDO calculations. The difference between the calculated ionization energies ($I^{\Delta\mathrm{SCF}}_{v,j}$ and $I^{\mathrm{TO}}_{v,j}$) is enlarged with increasing atomic numbers of the transition metal center due to noncompensating terms in third order of perturbation. The necessary conditions for the imbalance of both theoretical procedures are large two-electron interaction integrals and highly populated transition metal hole-states. Both requirements are enhanced by going from the left side of the 3d series to the extreme right. For d^4–d^6 complexes a simplified expression for $I^{\Delta\mathrm{SCF}}_{v,j}$ has been derived containing only one third order element.

1. Introduction

For the theoretical investigation of photoelectron (PE) spectra of 3d transition metal compounds the validity of Koopmans' theorem (1) can not be assumed [1]. Large electronic rearrangements in the case of ionization processes of strongly localized metal 3d electrons often cause changes between the MO sequence predicted in the electronic ground state (N electron system) and the ordering of the ionization energies [2, 3].

$$I^{K}_{v,j} = -\varepsilon_j = E_j(N-1)_{\mathrm{HF,\,unrel}} - E(N)_{\mathrm{HF}}. \tag{1}$$

$I^{K}_{v,j}$ in (1) is the j'th vertical ionization potential derived under the validity of Koopman's theorem, $E(N)_{\mathrm{HF}}$ is the Hartree-Fock (HF) energy of the N electron system while $E_j(N-1)_{\mathrm{HF,\,unrel}}$ is the energy of the j'th cationic system calculated with the unrelaxed orbital wave functions of the ground state. $E(N)_{\mathrm{HF}}$ is defined in (2) by means of the canonical molecular orbital energies ε_i and by means of two-electron Coulomb-exchange integrals $V_{il[il]}$.

$$E(N)_{\mathrm{HF}} = \sum_i \varepsilon_i - \tfrac{1}{2} \sum_i \sum_l V_{il[il]}, \quad i, l \in \{\mathrm{occ}\}, \tag{2}$$

$$V_{il[il]} = V_{ilil} - V_{illi} = \left\langle i(1)\,l(2) \middle| \frac{1}{r_{12}} \middle| (1 - P_{12})\, i(1)\,l(2) \right\rangle. \tag{3}$$

P_{12} in (3) is the convenient permutational operator.

On the level of the HF approximation there are two procedures beyond Koopmans' theorem taking into account the relaxation contribution of the whole electronic rearrangement (relaxation and correlation): the ΔSCF procedure [4] and the "transition operator (TO) method" [5, 6].

In the ΔSCF framework separate HF SCF calculations have to be performed for each cationic hole-state and $I^{\Delta\mathrm{SCF}}_{v,j}$ is defined in (4).

$$I^{\Delta\mathrm{SCF}}_{v,j} = E_j(N-1)_{\mathrm{HF}} - E(N)_{\mathrm{HF}}. \tag{4}$$

An alternative to the ΔSCF procedure is the TO algorithm using fractional occupation numbers in the HF scheme [7]. Formally the TO method is an operator (Fock-operator) analog to Slater's transition state model [8] developed in the X_α framework. The basis equations of the TO approach are defined in (5)–(8).

$$F^{\mathrm{TO}}_j = h_1 + \sum_{i \neq j} \langle i \| i \rangle + \tfrac{1}{2} \langle j \| j \rangle = F(N) - \tfrac{1}{2} \langle j \| j \rangle, \tag{5}$$

$$\langle i \| i \rangle = \left\langle i(2) \middle| \frac{1}{r_{12}} \middle| (1 - P_{12})\, i(2) \right\rangle, \tag{6}$$

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$$F_j^{\mathrm{TO}} i(1) = \varepsilon_i^{\mathrm{TO}} i(1)\,, \tag{7}$$

$$I_{v,j}^{\mathrm{TO}} = -\,\varepsilon_j^{\mathrm{TO}}\,. \tag{8}$$

F_j^{TO} is the transition Fock operator for the j'th spin orbital, $F(N)$ is the ordinary Fockian for the N electron system, h_1 represents the one-electron contribution to F_j^{TO} and $\langle i \| i \rangle$ is the Hartree-Fock Coulomb-exchange operator for the i'th orbital. Equation (5) clearly indicates that F_j^{TO} corresponds to a hypothetical transition state for the j'th ionization process as the occupation number of the j'th orbital is between the occupation numbers of the electronic ground state ($n_j = 1$) and the cationic hole-state ($n_j = 0$). The associated orbital energy, $\varepsilon_j^{\mathrm{TO}}$, is related to the j'th vertical ionization potential (Eq. (8)) by means of a Koopmans' analog equation.

In the case of molecules without transition metal center, the approximate identity (9) has been verified, the ΔSCF and the TO formalism guide to almost identical ionization energies [5, 6, 9].

$$\text{molecules without 3d center:} \qquad I_{v,j}^{\Delta\mathrm{SCF}} \approx I_{v,j}^{\mathrm{TO}}\,. \tag{9}$$

In contrast to (9) recent INDO investigations [10] on transition metal compounds have shown the unequality (10) which means that calculated ionization potentials based on the TO approach are smaller than the corresponding ΔSCF values. This unequality

$$\text{3d complexes:} \qquad I_{v,j}^{\mathrm{TO}} < I_{v,j}^{\Delta\mathrm{SCF}} \tag{10}$$

has been demonstrated in bis(π-allyl)nickel [11], in iron tetracarbonyl carbene complexes [12], in bisdiene iron monocarbonyl derivatives [13], in binuclear iron metallocenes [14] as well as in various transition metal tricarbonyl complexes containing Cr, Mn or Fe as 3d center [15, 16]. The calculated deviations between $I_{v,j}^{\mathrm{TO}}$ and $I_{v,j}^{\Delta\mathrm{SCF}}$ are large if the MO's are strongly localized at the transition metal center, with reduced 3d amplitudes in the orbital wave function the identity (9) is asymptotically reached. A representative selection of ΔSCF and TO calculations based on the INDO-Hamiltonian of [10] is summarized in Table 1. It is seen that both values can differ up to 1.5 eV. The origin for this behaviour as well as the factors influencing the unequality (10) are analyzed in the present work.

Table 1. Comparison between calculated ionization potentials within an INDO-Hamiltonian based on the ΔSCF approximation ($I_{v,j}^{\Delta\mathrm{SCF}}$) and based on the transition operator formalism ($I_{v,j}^{\mathrm{TO}}$); for comparison also the experimental ionization energies are given ($I_{v,j}^{\mathrm{exp}}$). All values in eV. Additionally the orbital energies, ε_j, the irreducible representation, the MO-type and the metal 3d character of the orbitals are displayed (TMM = trimethylenemethane).

Nr.	Compound	Γ_j	ε_j	MO-Type	% 3d	$I_{v,j}^{\Delta\mathrm{SCF}}$	$\Delta I_j^{\Delta\mathrm{SCF}}$	$I_{v,j}^{\mathrm{TO}}$	ΔI_j^{TO}	$\Delta I_j^{\mathrm{TO}} - \Delta I_j^{\Delta\mathrm{SCF}}$	$I_{v,j}^{\mathrm{exp}}$	Ref.
I	$\mathrm{Cr(CO)_3(C_6H_6)}$	17 a_1	− 10.08	Cr $3d_{z^2}$	75.5	8.25	1.83	7.50	2.58	0.75	7.42	[15]
		17 e	− 9.90	Cr $3d_{x^2-y^2}/3d_{xy}$	58.4	8.57	1.33	8.13	1.77	0.44	7.42	
		16 e	− 12.42	$L(\pi)$, Cr $3d_{xz}/3d_{yz}$	12.9	11.75	0.67	11.64	0.78	0.11	10.70	
II	$\mathrm{Mn(CO)_3(C_5H_5)}$	33 a′	− 10.48	Mn $3d_{z^2}$	70.4	8.42	2.08	7.53	2.95	0.87	8.20	[15]
		34 a′	− 10.32	Mn $3d_{x^2-y^2}/3d_{xy}$	50.6	8.55	1.77	7.74	2.58	0.81	8.20	
		18 a″	− 10.33			8.55	1.78	7.74	2.59	0.81		
		31 a′	− 13.33	$L(\pi)$, Mn $3d_{z^2}$	14.5	12.82	0.51	12.74	0.59	0.08	13.00	
III	$\mathrm{Fe(CO)_3TMM}$	14 e	− 11.87	Fe $3d_{x^2-y^2}/3d_{xy}$	90.0	8.85	2.02	7.61	3.26	1.24	8.62	[15]
		17 a_1	− 10.34	Fe $3d_{z^2}$, $L(\pi)$	41.5	8.64	1.70	7.82	2.52	0.82	8.62	
		15 e	− 10.47	$L(\pi)$, Fe $3d_{xz}/3d_{yz}$	28.3	9.64	0.83	9.17	1.30	0.47	9.26	
IV	$\mathrm{Fe(CO)_3(C_4H_4)}$	16 a″	− 11.33	Fe $3d_{x^2-y^2}/3d_{xy}$	77.4	8.60	2.73	7.03	4.30	1.57	8.45	[15]
		29 a′	− 11.34			8.75	2.59	7.40	3.94	1.35		
		30 a′	− 10.44	Fe $3d_{z^2}$	59.0	8.18	2.26	7.07	3.37	1.11	8.45	
V	$\mathrm{Ni(C_3H_5)_2}$	12 a_g	− 12.44	Ni $3d_{z^2}$	96.1	9.19	3.25	7.70	4.74	1.49		[11]
		11 a_g	− 12.51	Ni $3d_{x^2-y^2}$	92.9	9.35	3.16	7.91	4.60	1.44	8.18	
		5 b_g	− 12.48	Ni $3d_{xy}$	95.7	9.25	3.23	7.89	4.59	1.36	8.58	
		13 a_g	− 11.15	Ni $3d_{yz}$, $L(\pi)$	66.6	8.81	2.34	7.55	3.60	1.26		
		7 a_u	− 9.12	$L(\pi)$	0.0	7.55	1.57	7.50	1.62	0.05	7.76	
		11 b_u	− 11.42	$L(\pi)$	0.0	11.16	0.26	10.96	0.46	0.20	10.38	

The relation between $I_{v,j}^{\Delta\mathrm{SCF}}$ and $I_{v,j}^{\mathrm{TO}}$ has been studied in large detail by Born, Kurtz and Öhrn [9] by means of finite order perturbation theory. The equations of [9] are used as theoretical framework for this investigation. Thematically related work to the finite order perturbational approach [9] has been done by Pickup and Goscinski [17] (ΔSCF analysis only) and by Goscinski and coworkers [5, 6] (opposition ΔSCF/TO).

In Ref. [11] and [15] we have shown that the Cr complex I is a d^6 system, II—IV are also formal d^6 species due to predominant metal to ligand charge transfer while V can be classified as d^8 compound; the associated cationic hole-states therefore are d^5 (I—IV) and d^7 (V) systems.

2. Basis Equations

Born, Kurz and Öhrn [9] have derived an expression for $I_{v,j}^{\Delta\mathrm{SCF}}$ that is valid up to third order in perturbation starting from the definition (11) for the j'th vertical ionization potential.

$$
\begin{aligned}
I_{v,j}^{\Delta\mathrm{SCF}} &= E_j(N-1)_{\mathrm{HF}} - E(N)_{\mathrm{HF}} \\
&= \Big[\sum_{i\neq j} \tilde{\varepsilon}_i - \tfrac{1}{2}\sum_i \sum_{l\neq j} \tilde{V}_{il[il]}\Big] \\
&\quad - \Big[\sum_i \varepsilon_i - \tfrac{1}{2}\sum_i \sum_l V_{il[il]}\Big]. \qquad (11)
\end{aligned}
$$

The tilde in the first paranthesis corresponds to orbital energies and electron-electron interaction integrals associated to the $(N-1)$ system. The indices i, j, k, l are associated to orbitals occupied in the N electron HF ground state, a and b are used for the virtual Fermi sea while p and q correspond to the full MO space. The Fock operators determining $E(N)_{\mathrm{HF}}$ and $E_j(N-1)_{\mathrm{HF}}$ are given in (12) and (13).

$$
F(N) = h_1 + \sum_i \langle i \| i \rangle, \qquad (12)
$$

$$
\begin{aligned}
F_j(N-1) &= h_1 + \sum_{i\neq j} \langle \tilde{i} \| \tilde{i} \rangle \\
&= F(N) - \langle j \| j \rangle \\
&\quad + \sum_{i\neq j} [\langle \tilde{i} \| \tilde{i} \rangle - \langle i \| i \rangle]. \qquad (13)
\end{aligned}
$$

$F_j(N-1)$ thus can be decomposed into the Fockian of the unperturbed reference system $F(N)$ and into two perturbational operators F_{P1} and F_{P2}. Making use of Rayleigh-Schrödinger

$$
F_j(N-1) = F(N) + F_{P1} + F_{P2}, \qquad (14)
$$

$$
F_{P1} = -\langle i \| i \rangle, \qquad (15)
$$

$$
F_{P2} = \sum_{i\neq j} [\langle \tilde{i} \| \tilde{i} \rangle - \langle i \| i \rangle]. \qquad (16)
$$

(RS) expansions for the tilde quantities $\tilde{\varepsilon}_i$ and $\tilde{i}$ (in $\tilde{V}_{il[il]}$), (17) and (18), Born, Kurtz and Öhrn obtained (19) for $I_{v,j}^{\Delta\mathrm{SCF}}$.

$$
\tilde{\varepsilon}_i = \varepsilon_i + \varepsilon_i^{(1)} + \varepsilon_i^{(2)} + \cdots, \qquad (17)
$$

$$
\tilde{i} = i + i^{(1)} + i^{(2)} + \cdots, \qquad (18)
$$

$$
\begin{aligned}
I_{v,j}^{\Delta\mathrm{SCF}} = &-\varepsilon_j + \sum_l \sum_b \frac{V_{jl[jb]}^2}{\varepsilon_l - \varepsilon_b} + \sum_i \sum_l \sum_a \sum_b \frac{V_{jl[jb]} V_{ib[al]} V_{ji[ja]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_i - \varepsilon_a)} \\
&+ \sum_i \sum_l \sum_a \sum_b \frac{V_{jl[jb]} V_{il[ab]} V_{ji[ja]}}{(\varepsilon_i - \varepsilon_a)(\varepsilon_l + \varepsilon_i - \varepsilon_a - \varepsilon_b)} + \sum_i \sum_l \sum_a \sum_b \frac{V_{il[ab]} V_{ja[ji]} V_{jb[jl]}}{(\varepsilon_i - \varepsilon_a)(\varepsilon_l + \varepsilon_i - \varepsilon_a - \varepsilon_b)} \\
&- \sum_l \sum_a \sum_b \frac{V_{aj[bj]} V_{bj[lj]} V_{lj[aj]}}{(\varepsilon_l - \varepsilon_a)(\varepsilon_l - \varepsilon_b)} + \sum_i \sum_l \sum_b \frac{V_{ij[bj]} V_{bj[lj]} V_{lj[ij]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_j - \varepsilon_b)}. \qquad (19)
\end{aligned}
$$

Remembering the descent of the various increments of (19) from the wellknown Goldstone graphs [18] of diagrammatic perturbation theory [19, 20] (19) can be simplified furthermore. In Fig. 1 we have collected the Goldstone diagrams of a full many body ansatz together with the relaxational contributions contained in the diagrams; the nomenclature corresponds to [19]. The relaxational increments are obtained from the diagonal elements of the many body diagrams (index j) due to separation of definite hole-lines.

The expression with the twofold summation (l, b) is derived from the (2h1p) second order diagram. The first increment with four indices is related to D6 when a single hole-line has been removed. The next two increments are derived from D4 and D5; the diagonal elements of the many body diagrams are identical [19] and the same is found for the relaxational contributions (this is explicitely seen if the $V_{ij[kl]}$ integrals are rearranged). The last two expressions are associated to C6 and D6 (separation of two hole-lines). Cederbaum has shown

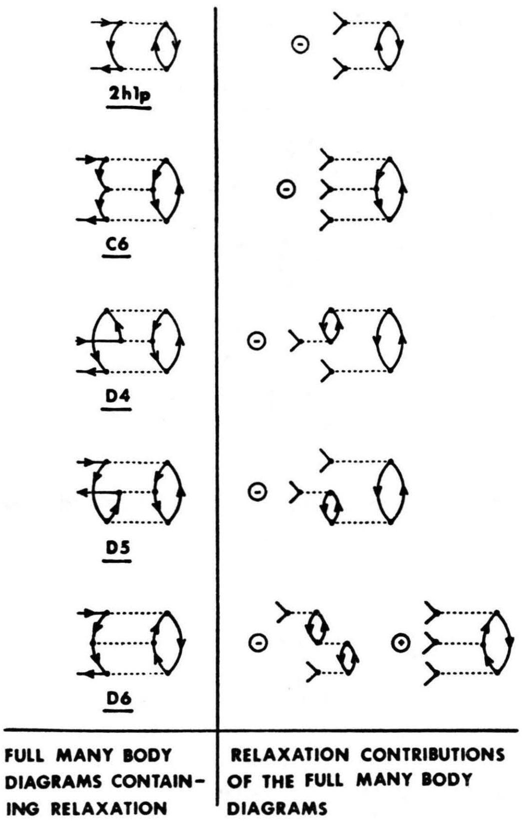

Fig. 1. Second and third order many body diagrams (left) that are leading to relaxational contributions (right).

that C6 and D6 are antigraphs compensating each other [19].

In the case of cationic hole-states with d^4-d^6 configuration this compensation nearly holds for the last two relaxational increments in transition metal compounds. For this electron configuration the (2p1h) and (1p2h) summation are of comparable importance to the net perturbational summation.

$$[\chi^{(3)}_{\mathrm{C6|D6}}]_{jj,\mathrm{rel}} = -\sum_l \sum_a \sum_b \frac{V_{aj[bj]} V_{bj[lj]} V_{lj[aj]}}{(\varepsilon_l - \varepsilon_a)(\varepsilon_l - \varepsilon_b)} + \sum_i \sum_l \sum_b \frac{V_{ij[bj]} V_{bj[lj]} V_{lj[ij]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_i - \varepsilon_b)} . \tag{20}$$

In the first sum of (20) those contributions are predominant where the particle-indices a and b are equivalent while $i = l$ result in the most important contributions of the second sum.

$$\begin{aligned}[\chi^{(3)}_{\mathrm{C6|D6}}]_{jj,\mathrm{rel}} &= -\sum_l \sum_b \frac{V_{bj[bj]} V_{bj[lj]} V_{lj[bj]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_l - \varepsilon_b)} + \sum_l \sum_b \frac{V_{lj[bj]} V_{bj[lj]} V_{lj[lj]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_l - \varepsilon_b)} \\ &= \sum_l \sum_b \frac{V_{bj[lj]} V_{lj[bj]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_l - \varepsilon_b)} \cdot [V_{bj[bj]} - V_{lj[lj]}] .\end{aligned} \tag{21}$$

With the assumption (22), which holds if the electron-electron interaction between the j'th hole-state and strongly localized occupied and virtual orbitals l and b are comparable, the anticipated compensation is fulfilled.

$$\bar{V}_{bj[bj]} \approx \bar{V}_{lj[lj]} , \quad \bar{V} \to \text{averaging} . \tag{22}$$

$I^{\Delta\mathrm{SCF}}_{v,j}$ for the studied transition metal complexes therefore is given by the approximate relation (23) where besides ε_j only one second order and two third order contributions are encountered; the simplification due to (21) however depends on transition metal under investigation.

$$\begin{aligned} I^{\Delta\mathrm{SCF}}_{v,j} \approx -\varepsilon_j &+ \sum_l \sum_b \frac{V^2_{jl[jb]}}{\varepsilon_l - \varepsilon_b} \\ &+ \sum_i \sum_l \sum_a \sum_b \frac{V_{jl[jb]} V_{ib[al]} V_{ji[ja]}}{(\varepsilon_l - \varepsilon_b)(\varepsilon_i - \varepsilon_a)} \\ &+ 2 \sum_i \sum_l \sum_a \sum_b \frac{V_{jl[jb]} V_{il[ab]} V_{ji[ja]}}{(\varepsilon_i - \varepsilon_a)(\varepsilon_l + \varepsilon_i - \varepsilon_a - \varepsilon_b)} .\end{aligned} \tag{23}$$

In the last expression of (23) the factor 2 and $(\varepsilon_i - \varepsilon_a)$ in the $(\varepsilon_l + \varepsilon_i - \varepsilon_a - \varepsilon_b)$ contribution to the energy denominator nearly compensate each other; so we arrive to the simple expression (24):

$$\begin{aligned} I^{\Delta\mathrm{SCF}}_{v,j} \approx -\varepsilon_j &+ \sum_l \sum_b \frac{V^2_{jl[jb]}}{\varepsilon_l - \varepsilon_b} \\ &+ 2 \sum_i \sum_l \sum_a \sum_b \frac{V_{jl[jb]} V_{ib[al]} V_{ji[ja]}}{(\varepsilon_l - \varepsilon_a)(\varepsilon_i - \varepsilon_b)} \\ &\text{(for } d^4 - d^6 \text{ systems)} .\end{aligned} \tag{24}$$

It is clear seen that the second order contribution to the approximate $I^{\Delta\mathrm{SCF}}_{v,j}$ expression has a lowering effect in comparison to $-\varepsilon_j$ while the third order increment guides to a renormalization of the second order correction, a result that is in line with an effective approximation to the self-energy part within Green's function calculations in transition metal compounds [21–23].

To derive an expression for $I^{\mathrm{TO}}_{v,j}$ by means of finite order perturbation theory [9] two different expansions for $F(N)$ and $F_j(N-1)$ (25) and (26)) are necessary.

$$F(N) = F_j^{\mathrm{TO}} + \tfrac{1}{2}\langle j \| j\rangle + \sum_{i \neq j} [\langle \tilde{i} \| \tilde{i}\rangle - \langle i \| i\rangle], \quad (25)$$

$$F_j(N-1) = F_j^{\mathrm{TO}} - \tfrac{1}{2}\langle j \| j\rangle + \sum_{i \neq j} [\langle \tilde{i} \| \tilde{i}\rangle - \langle i \| i\rangle]. \quad (26)$$

It is seen that the last expression in (25) and (26) is equivalent to F_{P2} (Equation (16)). F_{P1} $(=\frac{1}{2}\langle j \| j\rangle)$ enters both perturbational approaches with a different sign.

Following [9] $I_{v,j}^{\mathrm{TO}}$ is related to the ΔSCF approach by means of (27).

$$I_{v,j}^{\Delta\mathrm{SCF}} = E_j(N-1)_{\mathrm{TO}} - E(N)_{\mathrm{TO}} = -\varepsilon_j^{\mathrm{TO}} - \frac{1}{4}\sum_i \sum_{\substack{p \\ p \neq j}} \sum_{\substack{q \\ q \neq j}} \frac{V_{pj[qj]}\, V_{qj[ij]}\, V_{ij[pj]}}{(\varepsilon_p - \varepsilon_i)(\varepsilon_q - \varepsilon_i)} + \frac{1}{4}\sum_i \sum_p \frac{V_{pj[ij]}\, V_{ij[ij]}\, V_{ij[pj]}}{(\varepsilon_i - \varepsilon_p)^2}. \quad (27)$$

The indices TO in $E_j\,(N-1)_{\mathrm{TO}}$ and $E\,(N)_{\mathrm{TO}}$ in (27) remember to electronic energies based on the TO related Fockians defined in (25) and (26). The equality (unequality) of $I_{v,j}^{\Delta\mathrm{SCF}}$ and $I_{v,j}^{\mathrm{TO}}$ $(= -\varepsilon_j^{\mathrm{TO}})$ now depends on the perfect (imperfect) compensation of the two summations in (27).

To analyze this behaviour the threefold summation in (27) is devided into three partial summations schematically displayed in (28)–(30). In (28) p and q are restricted to hole-indices, in the second class p or q corresponds to the hole-summation while in (30) both indices are restricted to the unoccupied orbitals.

1. summation: $$-\frac{1}{4}\sum_i \sum_k \sum_l \frac{c}{(\varepsilon_k - \varepsilon_i)(\varepsilon_l - \varepsilon_i)}, \quad (28)$$

2. summation: $$-\frac{1}{4}\sum_i \sum_l \sum_a \frac{c'}{(\varepsilon_l - \varepsilon_i)(\varepsilon_a - \varepsilon_i)} - \frac{1}{4}\sum_i \sum_a \sum_l \frac{c''}{(\varepsilon_a - \varepsilon_i)(\varepsilon_l - \varepsilon_i)}, \quad (29)$$

3. summation: $$-\frac{1}{4}\sum_i \sum_a \sum_b \frac{c'''}{(\varepsilon_a - \varepsilon_i)(\varepsilon_b - \varepsilon_i)}, \quad (30)$$

c, c', c'' = constant nominators.

Inspection of the energy denominators in (28) and (29) clearly shows that both summations do not guide to a net contribution of the perturbational sum due to the fact that on the average always one increment with a plus sign is compensated by a corresponding increment with a minus sign in the hole-summation. The only contribution to (27) is therefore due to the 2p1h summation (30).

In the twofold summation $\left(\sum_i \sum_p\right)$ of (27) always a positive energy denominator as a result of the quadratic expression $(\varepsilon_i - \varepsilon_p)^2$ is encountered where p runs through the occupied and empty Fermi sea. Equation (27) therefore can be simplified to (31).

$$I_{v,j}^{\Delta\mathrm{SCF}} = E_j(N-1)_{\mathrm{TO}} - E(N)_{\mathrm{TO}} = I_{v,j}^{\mathrm{TO}} - \frac{1}{4}\sum_i \sum_a \sum_b \frac{V_{aj[bj]}\, V_{bj[ij]}\, V_{ij[aj]}}{(\varepsilon_a - \varepsilon_i)(\varepsilon_b - \varepsilon_i)} + \frac{1}{4}\sum_i \sum_{\substack{p \\ p \neq j}} \frac{V_{pj[ij]}\, V_{ij[ij]}\, V_{ij[pj]}}{(\varepsilon_i - \varepsilon_p)^2}. \quad (31)$$

The basis integrals V_{ijkl} entering (31) are given by the ZDO adapted four-index transformation (32); this is the suitable choice for the INDO results presented in Table 1.

$$V_{ijkl} = \sum_\mu \sum_\nu c_{i\mu}\, c_{k\mu}\, c_{j\nu}\, c_{l\nu}\, \gamma_{\mu\nu} + V^{\mathrm{INDO}}, \quad (32)$$

$$\gamma_{\mu\nu} = \left\langle \mu(1)\,\mu(1) \left| \frac{1}{r_{12}} \right| \nu(2)\,\nu(2) \right\rangle. \quad (33)$$

V^{INDO} contains all one-center exchange integrals and is defined in [24]. The $c_{i\mu}$'s are the LCAO coefficients connecting the μ'th atomic orbital with the i'th molecular orbital.

3. Discussion

On the basis of (31) and (32) it is now easy to compare ionization potentials derived in the ΔSCF framework and TO eigenvalues. The numeric values of the two summations are influenced by two factors, the magnitude of the two-electron integrals V_{ijkl} and by the energy denominators. Equation (32) shows that the V_{ijkl} integrals are enhanced if the basis integrals $\gamma_{\mu\nu}^{AA}$ and $\gamma_{\mu\nu}^{AB}$ (A, B atomic sides) are enlarged and if the MO wave functions show pronounced localization properties. For occupied MO's of predominant metal character often 3d contributions exceeding 80% are calculated; the orbitals are predominantly atomic quantities. This condition is not completely fulfilled in the virtual MO set

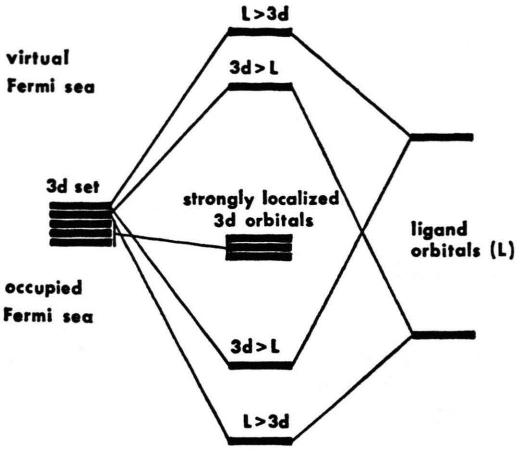

Fig. 2. Schematical interaction diagram for the valence orbitals in transition metal complexes. Two types of occupied 3d orbitals are displayed; stabilized ones due to metal to ligand charge transfer and strongly localized ones where the interaction with ligand orbitals is small as a result of a negligible mutual overlap.

with significant transition metal amplitudes. The destabilization is always the result of a strong metal-ligand interaction (see Fig. 2) and therefore these MO's contain metal 3d contributions not exceeding 50–60%. Within the 3d series increasing integrals $\gamma_{\mu\nu}^{AA}$, $\gamma_{\mu\nu}^{AB}$ are found with enlarged atomic numbers [21, 25]. If the two summations in (31) do not compensate each other, the differences between $I_{v,j}^{\Delta\mathrm{SCF}}$ and $I_{v,j}^{\mathrm{TO}}$ should be more pronounced on the right side of the periodic system in comparison to the left one. The inspection of the particle- and hole-indices in (31) displays, that this effect is enhanced by the energy denominators. In the threefold summation there are always energy differences between occupied and virtual orbitals that enter the perturbational summation. In transition metal compounds $(\varepsilon_a - \varepsilon_i)$ within the used INDO model is at least 6 eV. The indices (i, a, b) in this summation clearly show that the contributions are most efficient if there are a maximum number of unoccupied orbitals with pronounced 3d character. The twofold particle-summation here allows the accumulation of significant third order perturbational contributions. In the second expression i is restricted to molecular hole-states while p runs through both MO sets. The most important contributions to the net sum therefore are given by those increments where p belongs to the hole-set leading to small energy denominators $(\varepsilon_i - \varepsilon_l)$. Due to the small energy gaps within the twofold summation this term should always dominate the 2p1h summation in the 3d complexes listed in Table 1. The two summations enter (31) with different signs. Δ_j defined in (35) therefore is a parameter for the deviation of $I_{v,j}^{\Delta\mathrm{SCF}}$ and $I_{v,j}^{\mathrm{TO}}$.

$$I_{v,j}^{\Delta\mathrm{SCF}} = I_{v,j}^{\mathrm{TO}} + \Delta_j\,, \tag{34}$$

$$\Delta_j = -\frac{1}{4}\sum_i\sum_a\sum_b \frac{V_{aj[bj]}\,V_{bj[ij]}\,V_{i[aj]}}{(\varepsilon_a-\varepsilon_i)(\varepsilon_b-\varepsilon_i)} + \frac{1}{4}\sum_i\sum_{\substack{p\\(p\neq i)}} \frac{V_{pj[ij]}\,V_{ij[ij]}\,V_{ij[pj]}}{(\varepsilon_i-\varepsilon_p)^2}\,. \tag{35}$$

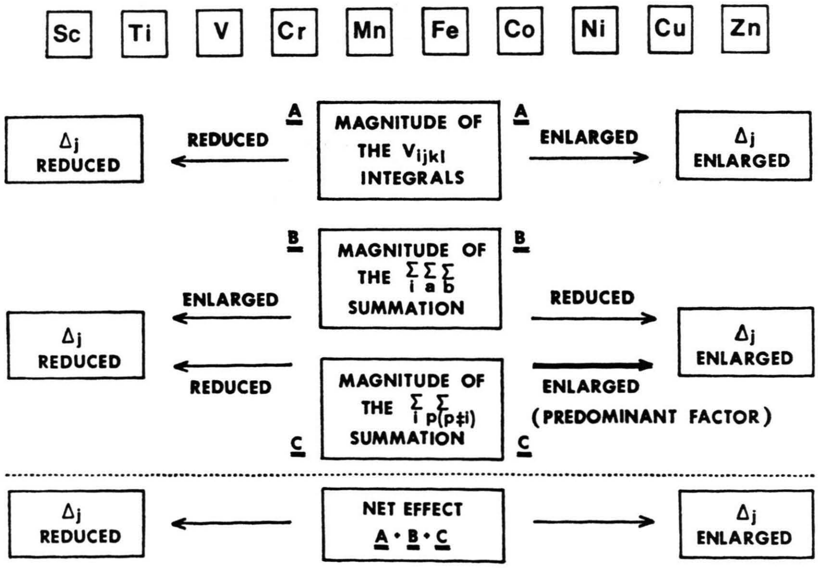

Fig. 3. Schematical representation of the factors favouring significant Δ_j values in the 3d series.

Δ_j is enlarged due to the latter summation in the case of 3d complexes with large 3d occupation numbers where the i summation and the occupied subspace of the p set are leading to large positive Δ_j increments. Hence more pronounced differences between $I_{v,j}^{\Delta\text{SCF}}$ and $I_{v,j}^{\text{TO}}$ must be expected in transition metal compounds with 3d centers located in the right of the periodic system (e.g. Co, Ni, Cu). A schematical representation of the three Δ_j determining factors (values of the two-electron integrals, magnitude and sign of the threefold and twofold summation as function of the 3d occupation) is given in Figure 3.

The INDO results collected in Table 1 demonstrate the validity of the foregoing deduction. In the Cr complex *I* the smallest deviations between both relaxational methods (ΔSCF and TO) are encountered. With increasing atomic numbers enlarged differences between $I_{v,j}^{\Delta\text{SCF}}$ and $I_{v,j}^{\text{TO}}$ are calculated.

In the case of molecules not containing a transition metal center Δ_j differs only slightly from zero leading to the equality (9). On one side this can be traced back to the smaller two-electron integrals in (35). On the other side also the energy denominator influence is reduced as in most molecules there is no chance for the $\sum_i \sum_p$ accumulation due to (nearly) degenerate orbitals with large interaction integrals. This condition is only observed in transition metal complexes with a large number of closely spaced localized orbitals.

4. Conclusions

The origin of the unequality between theoretically determined vertical ionization potentials on the basis of ΔSCF calculations and the "transition operator (TO)" formalism in 3d complexes has been analyzed. Starting point of this analysis are elements that have been obtained by finite order perturbation theory. In third order of perturbation differences between ΔSCF and TO have been derived. In the case of relatively small electron-electron interaction integrals and in the absence of closely spaced molecular hole-states the various contributions leading to Δ_j nearly compensate each other. With enlarged two-electron integrals and 3d occupations the compensation becomes less efficient leading to the unequality (10).

The differences between both procedures are due to the perturbational operator $F_{\text{P1}}^{\text{TO}}$ (Eq. (36)) of the j'th transition state orbital.

$$F_{\text{P1}}^{\text{TO}} = \pm \tfrac{1}{2} \langle j \| j \rangle_{\text{TO}} \,. \tag{36}$$

The plus sign enters a perturbational expansion for the (N) electron system, the minus sign enters the ($N-1$) hole-state expansion leading to nonvanishing third order components in $F_{\text{P1}}^{\text{TO}}$. This LCAO result is in line with theoretical findings derived in the "transition state (TS)" model where also third order components have been diagnozed that result in different numerical values for $\varepsilon_j^{\text{TS}}$ and $E_j(N-1)_{\text{HF}} - E(N)_{\text{HF}}$ [8]. Necessary condition for significant differences between $I_{v,j}^{\Delta\text{SCF}}$ and $I_{v,j}^{\text{TO}}$ is the extremely slow convergence of the relaxational contributions to the self-energy expansion (37). In 3d complexes significant third order contributions to the $M(\omega)$ expansion as function of the 3d center and the available hole- and particle-states have been verified in several publications [21, 26].

$$\begin{aligned} M(\omega)_{\text{rel}} &= M(\omega)_{\text{rel}}^{(2)} + M(\omega)_{\text{rel}}^{(3)} \\ &\quad + \cdots + M(\omega)_{\text{rel}}^{(\infty)}, \end{aligned} \tag{37}$$

$$M(\omega)_{\text{rel}}^{(n)} = \text{relaxation contribution to the self-energy matrix } M(\omega) \text{ of order } n.$$

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