

## Extended-Hückel parameters for third-row transition metals

### Part 1: VOIP parameters

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A parameter set for valence orbital ionization potentials (VOIP's) of  $5d$  transition metals has been derived from their atomic spectra. The set, which can be used for Extended-Hückel calculations, includes relativistic effects on orbital energies. It is thus helpful for quantum-chemical explanations of chemical differences between complexes of  $4d$  and  $5d$  transition metals.

**Key words:** Extended-Hückel parameters — Third-row transition metals

### 1. Introduction

For quantum-chemical descriptions of medium-sized systems which contain several "heavy" atoms the Extended-Hückel method [1] is so far the only method suitable for comprehensive studies on related series of species [2]. The advantage of this method is the fact that the calculational effort for, e.g., a tungsten complex is not greater than that for a corresponding chromium complex.

The calculation of charges for atoms of highly polar species (like transition metal complexes) very often results in unphysically high values if the original formulation (with constant Coulomb integrals  $H_{ii}$ ) is used. This deficiency has been removed by the introduction of charge iteration, especially in the form of the "self-consistent charge and configuration" (SCCC) formalism [3] where the Coulomb integrals are calculated as population dependent linear combinations of several VOIP's ("valence orbital ionization potentials"). For instance, a valence  $d$  shell  $H_{ii}$  can be described by a linear combination of  $d$  electron ionization

potentials, which are connected to the electron configurations  $d^n$ ,  $d^{n-1}s^1$ , and  $d^{n-1}p^1$  according to

$$-H_{dd} = (1 - p_s - p_p) * \text{VOIP}(d^n) + p_s * \text{VOIP}(d^{n-1}s^1) + p_p * \text{VOIP}(d^{n-1}p^1)$$

( $p_s$  and  $p_p$  are the populations of the  $s$  and  $p$  AO's, respectively).

Each VOIP is assumed to have a quadratic charge dependence:

$$\text{VOIP}_i = A_i * q^2 + B_i * q + C_i.$$

While the parametrisation (i.e. numerical values for  $A_i$ ,  $B_i$ , and  $C_i$ ) for light elements (with  $Z \leq 35$  where  $Z$  is atomic number) is well documented in the literature [4], rather drastic approximations have often been used for the VOIP's of the heavier transition metals [5]. Parameter sets derived for the second-row transition metals [6, 7] are based on less extensive experimental material [8], compared with their lighter homologs. For third-row transition metals, so far no complete set of VOIP parameters has been published in the literature.

For these elements, the data in published atomic spectra [8] are not sufficiently complete to allow for a reliable calculation of average energies of the configurations as defined by Slater [9] and a subsequent estimation of VOIP parameters. On the other hand, the atomic spectra strongly suggest that it is not justified to equate the parameters for  $5d$  elements to those of the homologous  $4d$  elements as proposed [5] by Beach and Gray.

As equivalences and differences of  $4d$  and  $5d$  homologs become more and more interesting in the field of transition metal chemistry, there is a growing need for a corresponding quantum chemical background. Thus, it appeared to be useful to develop a consistent set of VOIP parameters for the third-row transition elements. In a following paper, the choice of basis sets will be discussed [10].

## 2. Results and discussion

According to Viste and Gray [11], the VOIP for a specific electron in a specific configuration of the neutral atom is given by the equation

$$\text{VOIP} = \text{IP} + E_2 - E_1.$$

Here, IP is the first ionization potential,  $E_1$  the average energy of the given configuration relative to the electronic ground state of the neutral atom (as defined by Slater [9]), and  $E_2$  the corresponding energy relative to the electronic ground state of the ionized atom.

If the energies of all terms belonging to one specific configuration are not known, values of  $E_1$  and  $E_2$  cannot be calculated in the usual way. It is, however, possible to compare the particular energies of states belonging to a specific configuration observed [8] for an element of the second transition metal period (in the sequel marked by "(2)") with the energies of the homologous element of the third period (marked by "(3)"). From these energies of specific terms  $^{2S+1}L_J$  (relative to the

corresponding electronic ground states) characteristic energy differences  $\Delta$  can be derived, according to

$$\Delta(^{2S+1}L_J) = E((3), ^{2S+1}L_J) - E((2), ^{2S+1}L_J).$$

As an example, this is illustrated for the  $d^5s^1$  configurations of Mo and W, using the values compiled in Table 1. The energy difference  $D_1$  (describing configuration energies for neutral atoms) is the average of all given  $\Delta$  values. Correspondingly,  $D_2$  values are obtained for pairs of ionized atoms with charges  $q = +1$ .

Energy differences obtained by this procedure are compiled in Table 2; as data for the atomic spectrum of  $\text{Ir}^+$  are not available in [8], no values for the couple Rh/Ir are given. Now, most of the VOIP's for third-row metals can be calculated using the values  $D_1$  and  $D_2$  (from Table 2),  $IP(2)$  and  $IP(3)$  (from [8]), and the VOIP(2) (from [6]) according to

$$\text{VOIP}(3) = \text{VOIP}(2) + IP(3) - IP(2) + D_2 - D_1.$$

For example, the VOIP of a  $6s$  electron of W in the  $d^5s^1$  configuration is obtained as follows:

$$\begin{aligned} \text{VOIP}(2) = \text{VOIP}(\text{Mo}): & \quad 55.0 * 10^3 \text{ cm}^{-1} \quad (\text{from [6]}) \\ IP(2) = IP(\text{Mo}): & \quad 57.3 * 10^3 \text{ cm}^{-1} \quad (\text{from [8]}) \\ IP(3) = IP(\text{W}): & \quad 64.4 * 10^3 \text{ cm}^{-1} \quad (\text{from [8]}) \\ D_2(d^5): & \quad 2.9 * 10^3 \text{ cm}^{-1} \quad (\text{from Table 2}) \\ D_1(d^5s^1): & \quad 2.3 * 10^3 \text{ cm}^{-1} \quad (\text{from Table 2}) \end{aligned}$$

$$\text{VOIP}(3) = 55.0 + 64.4 - 57.3 + 2.9 - 2.3 = 62.7 * 10^3 \text{ cm}^{-1}.$$

**Table 1.** Energies for  $d^5s^1$  configurations of Mo and W relative to the electronic ground states [8] and corresponding energy differences  $\Delta$  [ $10^3 \text{ cm}^{-1}$ ]

Term	$J$	$E(\text{W})$	$E(\text{Mo})$	$\Delta$
$^7S$	3	2.951	0.000	2.95
$^5G$	2	18.117	16.641	1.48
	3	18.974	16.693	2.28
	4	19.256	16.748	2.51
	5	19.535	16.785	2.75
$^5S$	2	18.288	10.768	7.52
$^5P$	3	19.828	18.229	1.60
	2	20.983	18.357	2.62
	1	20.428	18.480	1.95
$^5D$	4	22.477	20.158	2.32
$^5F$	5	22.853	25.906	-3.05
				$D_1 = 2.3$

**Table 2.** Averaged energy differences  $D_1$  (neutral atoms) and  $D_2$  (singly charged atoms) [ $10^3 \text{ cm}^{-1}$ ] for homologous  $4d$  and  $5d$  elements (see text)

Elements	Neutral atoms configuration	$D_1$	Singly charged atoms configuration	$D_2$
Zr/Hf	$d^3s^1$	10.6	$d^3$	18.0
	$d^2s^2$	1.1	$d^2s^1$	6.2
	$d^2s^1p^1$	1.6	$d^2p^1$	11.5
Nb/Ta	$d^5$	0.5	$d^4$	14.7
	$d^4s^1$	10.7	$d^3s^1$	-1.9
	$d^4p^1$	18.8		
	$d^3s^2$	1.0		
Mo/W	$d^3s^1p^1$	3.4		
	$d^6$	-1.8	$d^5$	2.9
	$d^5s^1$	2.3	$d^4s^1$	-11.6
	$d^5p^1$	0.6	$d^4p^1$	-3.6
	$d^4s^2$	-11.3		
Tc/Re	$d^4s^1p^1$	-8.7		
	$d^6s^1$	14.5	$d^5s^1$	0.0
	$d^6p^1$	15.0	$d^5p^1$	6.0
	$d^5s^2$	0.0		
Ru/Os	$d^5s^1p^1$	3.3		
	$d^7s^1$	4.9	$d^6s^1$	-9.2
	$d^6s^2$	-7.4	$d^6p^1$	-2.1
	$d^6s^1p^1$	-1.2		
Pd/Pt	$d^{10}$	6.1	$d^9$	0.0
	$d^9s^1$	-2.4	$d^8s^1$	-15.4
	$d^9p^1$	-5.0	$d^8p^1$	-11.0
	$d^8s^2$	-24.3		
Ag/Au	$d^{10}s^1$	0.0	$d^{10}$	0.0
	$d^{10}p^1$	7.8	$d^9s^1$	-19.9
	$d^9s^2$	-21.1	$d^9p^1$	-21.8
	$d^9s^1p^1$	-13.5		
Cd/Hg	$d^{10}s^2$	0.0	$d^{10}s^1$	0.0
	$d^{10}s^1p^1$	9.7	$d^{10}p^1$	10.7

**Table 3.** VOIP's for neutral  $5d$  atoms ("raw data", see text) [ $10^3 \text{ cm}^{-1}$ ]

VOIP <sup>a</sup>	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1		59.7	54.1				68.5		
2	41.8	48.6	55.8	61.1	75.8		86.8	95.9	
3			75.3	86.0			100.5	99.5	
4	58.0	65.8	62.7				67.5	73.6	
5	61.5	66.1	68.4	68.8	75.2		83.2	84.9	82.9
6	76.9		87.5	86.0	91.9			88.9	96.1
7		35.9	41.2				41.2	35.5	
8									
9	41.4	41.9	44.2	41.9	43.7			46.1	39.2

<sup>a</sup> The type of electron being ionised, and the configurations, are as follows for the nine VOIP curves (1)  $d$ ,  $d^n$ ; (2)  $d$ ,  $d^{n-1}s^1$ ; (3)  $d$ ,  $d^{n-1}p^1$ ; (4)  $s$ ,  $d^{n-1}s^1$ ; (5)  $s$ ,  $d^{n-2}s^2$ ; (6)  $s$ ,  $d^{n-1}s^1p^1$ ; (7)  $p$ ,  $d^{n-1}p^1$ ; (8)  $p$ ,  $d^{n-2}p^2$ ; (9)  $p$ ,  $d^{n-1}s^1p^1$

The VOIP's calculated by this procedure are compiled in Table 3. Subsequently, these values were (if possible) subjected to least-squares-fits using a quadratic polynomial

$$\text{VOIP}_E(q=0) = a_0 + a_1 * n_E + a_2 * n_E^2,$$

where  $n_E$  is the number of valence electrons belonging to the corresponding neutral element  $E$  (e.g.  $n_E = 6$  for  $E = \text{W}$ ), in order to compensate for errors and to interpolate missing values. In cases where this procedure was not possible (because of too few values for a specific VOIP curve), it was supposed that the coefficients  $a_2$  are equal for second-row and third-row transition metals. In the parameter set for  $4d$  transition metals [6], the parameters for  $5p$  VOIP's of the  $d^{n-2}p^2$  configuration should be replaced by those of the  $d^{n-2}s^1p^1$  configuration as the former are based on only two experimental values for the whole  $4d$  transition metal period, resulting in a somewhat dubious  $Z$ -dependence. Hence, for the  $5d$  metals, VOIP curve 8 was equated to VOIP curve 9. Finally, the VOIP values for the neutral  $5d$  transition elements compiled in Table 4 were obtained.

The problem of charge dependence of the VOIP's has still to be answered. As experimental data on the atomic spectra of doubly and triply charged  $5d$  transition metal atoms are even less complete than those of neutral and singly charged species, further assumptions are necessary. Exemplary differential ionization energies given by Jørgensen [12] suggest that for the second and third transition metal series the VOIP curves differ essentially only in the ionization potentials and not in the charge dependence. It can thus be supposed that the  $A$  and  $B$  values from [6] can be used to calculate VOIP's of the homologous  $5d$  metals. For Ag/Au and Cd/Hg, these parameters had to be extrapolated from the values of [6]; they are given in Table 5.

From the values of Table 4, basic features of third-row transition metal valence orbital energies become obvious: The  $6s$  levels are strongly stabilized relative to the  $5s$  levels of the corresponding second row transition metals, while the  $5d$  levels are somewhat destabilized compared to the  $4d$  levels of the lighter homologs. These features have been observed before [13] and were attributed to relativistic effects. The present "empirical" parameter set should therefore be

**Table 4.** VOIP parameters ( $C$  values) for third-row transition metals [ $10^3 \text{ cm}^{-1}$ ]

VOIP <sup>a</sup>	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1	54.1	55.6	57.5	59.8	62.5	65.6	69.1	73.1	77.4
2	38.7	47.2	55.6	64.2	72.7	81.3	90.0	98.9	107.4
3	68.3	73.6	78.7	83.7	88.6	93.3	98.0	102.6	107.0
4	60.8	63.0	65.1	66.8	68.2	69.4	70.3	70.8	71.2
5	59.3	63.6	67.6	71.3	74.7	77.9	80.7	83.2	85.4
6	80.0	82.3	84.4	86.3	88.0	89.5	90.9	92.0	93.0
7	36.7	37.2	37.7	37.9	37.7	37.1	36.1	34.7	32.9
8=9	42.7	42.8	42.9	43.2	43.5	43.9	44.3	44.8	45.4

<sup>a</sup> See footnote in Table 3

**Table 5.** VOIP parameters (*A* and *B* values) for Ag/Au and Cd/Hg [ $10^3 \text{ cm}^{-1}$ ]

VOIP <sup>a</sup>	Ag/Au		Cd/Hg	
	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
1	8.0	89.0	11.65	83.65
2	3.6	102.7	4.0	106.5
3	5.25	97.15	5.9	101.3
4	3.45	69.95	3.75	72.75
5	0.9	76.1	3.55	73.15
6	0.9	73.5	3.55	76.95
7	4.75	55.45	5.95	55.85
8=9	4.75	59.25	5.95	63.05

<sup>a</sup> See footnote in Table 3

checked against “theoretical” parameters used in the iterative version of the relativistically parameterized Extended-Hückel model [14], which were obtained from atomic calculations with the relativistic  $X\alpha$  method.

According to the classification in a recent review by Pyykkö [15], the present parameter set can be used for “quasi-relativistic” calculations, i.e. calculations, in which two of the relativistic effects (namely the relativistic contractions of the *s* and *p* AO’s (atomic orbitals) and the self-consistent expansion of the *d* AO’s connected to corresponding stabilizations and destabilizations of the ionization energies) described in [13] are contained. The third relativistic effect (spin-orbit coupling) is neglected.

The parameter set described in the present paper has been tested with respect to two particular classes of species, namely oxothiometalates of the type  $[\text{MO}_{4-n}\text{S}_n]^{2-}$  ( $\text{M} = \text{Mo}, \text{W}; n = 0-4$ ) [16], and thiometalato complexes, in which the former ions function as ligands to other (mainly transition) metal ions [17]. The results suggested that these VOIP parameters will be useful for other calculations.

Generally, the trends in valence orbital ionization energies mentioned above are expected to have profound consequences on chemical bonding in third-row transition metal complexes. This is due to the fact that, in contrast to complexes of lighter homologs, the *d* and *s* valence orbital energies (i.e.  $H_{5d,5d}$  and  $H_{6s,6s}$ ) are practically equal, so there should be appreciable *6s* mixing in the MO’s (molecular orbitals) with strong metal-ligand interaction, somewhat reducing the predominant influence of *5d* AO’s. As a result,  $\sigma$ -bonding is supposed to be stronger and  $\pi$ -bonding weaker, than in the analogous second-row transition metal complexes (cf. [16, 18]).

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