

RIGID AND RELAXED DIAGONAL ORBITAL  
HARDNESSES OF THE VALENCE SHELL  
OF TRANSITION METAL IONS  
FROM  $X\alpha$  CALCULATIONS\*

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Valence shell diagonal hardnesses (electron repulsion) parameters are reported for the first- and second-row transition metal ions, determined via finite differences from the  $X\alpha$  eigenvalues for alternative configurations and charges. Both *rigid* (unrelaxed orbitals) and orbitally *relaxed* hardnesses have been calculated. The relaxed parameters provide a convenient basis for generating a realistic hardness tensor of catalytic systems involving transition metals at the *atoms-in-molecules* (AIM) oxidation state and configurations, thus facilitating the *charge-sensitivity-analysis* of chemisorption systems both at the AIM and orbital resolutions. The observed trends in the orbital relaxation effects are briefly discussed.

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## Introduction

The molecular charge-sensitivity-analysis (CSA) [1–14], based upon the concepts of global and regional (rigid and relaxed) chemical potentials, hardnesses, softnesses, the Fukui function parameters, and the related energy derivatives, has recently been advocated as an attractive theoretical framework for applications in the theory of chemisorption and catalysis [11, 13]. This approach has already been successfully applied both qualitatively and quantitatively to selected rules of chemistry [1, 2, 4, 5, 7, 9,] and trends in the chemical reactivity [4, 7, 9–17]. Most of the reported applications to large molecular systems adopt the atoms-in-molecules (AIM) resolution, although the orbitally resolved CSA has also been developed at various levels of sophistication [13, 18–22]. Future wider applications of this method would require the realistic AIM (global or orbital) data for alternative oxidation states and orbital configurations, sufficient to generate the canonical AIM chemical potentials and hardness tensor corresponding to the actual valence state of the AIM in the system under consideration, as revealed by the standard SCF MO calculations. Of particular importance is also the inclusion of the orbital relaxation in the derivatives involving electron population variables. The attempts to include such effects in atomic systems, via finite differences and the virial theorem (Fock) scaling, respectively, have recently been reported [20, 23] for selected atoms.

Applications of the CSA to model catalytic systems involving clusters of metallic and oxide catalysts would require the detailed knowledge of the valence shell orbital hardnesses for alternative states of transition metal ions, preferably the data including the changes in the orbital exponents due to a removal or addition of electrons from/to the metal atom/ion. One possible source of such parameters, used in the semiempirical AIM CSA [7], are the experimental values of the electron affinity and ionization potential data [14, 24], but they hardly cover the full range of the atomic valence states required for an adequate interpolation; alternatively such data can be calculated theoretically, e. g., using the Hartree–Fock (HF) or the SCF calculations [10–13, 17, 19, 21], the hyper-HF [20, 25], Kohn–Sham [Local Density Approximation (LDA)] [14, 15], and the  $X\alpha$  [20, 22] theories. The latter method [26, 27] is especially attractive for this purpose since the first derivatives of the energy,  $E = E(n)$ , with respect to the canonical orbital occupation numbers,  $n = (n_1, n_2, \dots)$ , both variational (orbitally relaxed) and partial (orbitally unrelaxed), give the respective one-electron eigenvalues,  $e = (e_1, e_2, \dots)$ :

$$(\delta E / \delta n_i)_{n^0} = (\partial E / \partial n_i)_{n^0} = e_i(n^0); \quad (1)$$

here  $n^0$  specifies the atom electron configuration. This feature allows one to determine the approximate estimates of the relaxed hardness (electron repulsion) derivatives:

$$\eta_{ij}^{\text{rel}}(n^0) = (\delta^2 E / \delta n_i \delta n_j)_{n^0} = (\delta e_i / \delta n_j)_{n^0} = (\delta e_j / \delta n_i)_{n^0}, \quad (2)$$

via finite differences from the known  $X\alpha$  eigenvalues. The corresponding partial second derivatives determine the orbitally unrelaxed (rigid) hardnesses:

$$\eta_{ij}^{\text{unrel}}(n^0) = (\partial^2 E / \partial n_i \partial n_j)_{n^0} = (\partial e_i / \partial n_j)_{n^0} = (\partial e_j / \partial n_i)_{n^0} \neq \eta_{ij}^{\text{rel}}(n^0). \quad (3)$$

It is the main purpose of the present work to report the relaxed and unrelaxed diagonal ( $\eta_{ii}$ ) hardnesses of transition metal ions (first- and second-row) from  $X\alpha$  calculations. The reported results have been generated for future applications of the CSA to catalytic systems.

### Calculations and results

The unrelaxed hardnesses, calculated directly within the standard  $X\alpha$  program, have been obtained from the usual expression [26]:

$$\eta_{ii}^{\text{unrel}}(n^{\circ}) \equiv J_i^{\text{unrel}}(n^{\circ}) = F_{ii}^0 - 2\alpha \left(\frac{3}{8\pi}\right)^{1/3} \int \varrho_i^2(r) \left[ \sum_j n_j^{\circ} \varrho_j(r) \right]^{-2/3} dr, \quad (4)$$

where the familiar Slater integral  $F_{ii}^0$  accounts for the Coulomb contribution to the hardness while the second integral represents the local approximation of the exchange part; here  $\varrho_i(r)$  stands for the orbital probability density and  $\alpha$  is the method adjustable parameter scaling the exchange interactions [14, 26].

The following simplest finite-difference estimate of the relaxed diagonal hardness has been adopted in the present study:

$$\eta_{ii}^{\text{rel}}(n^{\circ}) \equiv J_i^{\text{rel}}(n^{\circ}) \approx \frac{1}{\Delta n} [e_i(n^{\circ}) - e_i(n_i)], \quad (5)$$

where  $\Delta n = 1/2$  and the shifted occupancy vector  $n_i = (n_1^{\circ}, n_2^{\circ}, \dots, n_i^{\circ} - \Delta n, \dots)$  involves a removal of  $\Delta n$  electrons from the  $i$ -th orbital only relative to  $n^{\circ}$ .

The results for the first- and second-row transition metals are listed in Table I. In Fig. 1 we examine the resulting trends in the magnitude of the orbital relaxation effects, measured by the  $J_i^{\text{rel}}/J_i^{\text{unrel}}$  ratio, for the oxidation states and configurations considered in Table I.

The experimental approximations of the orbital hardnesses for a given oxidation state  $q$  can be generated via the familiar Pariser [28] finite difference formula:

$$\eta_{ii}^{\text{exp}}(q) \approx I_i(q) - I_i(q-1), \quad (6)$$

for the relevant electron configurations; here  $I_i$  is the corresponding orbital ionization potential ( $I_i(q-1) = A_i(q)$  is the corresponding orbital electron affinity). The so-called Valence State Ionization Energies (VSIE) developed for the Self Consistent Charge and Configuration Molecular Orbital Theory [29], via an interpolation of the average atomic spectroscopic data, can be used to approximate the valence orbital ionization potentials (electron affinities).

In Table II we compare the  $X\alpha$  relaxed orbital hardnesses with the corresponding experimental estimates from Eq. (6) and the VSIE, for the first-row transition metals. A graphical representation of this comparison is shown in Fig. 2.

TABLE I  
The X $\alpha$  valence shell hardnesses  
of transition metal ions (in eV).

element	$n_i^0$		$i$	$J_i^{\text{unrel}}$	$J_i^{\text{rel}}$
	3d	4s			
Ti <sup>0</sup>	2	2	3d	15.780	10.808
	2	2	4s	6.410	5.735
Ti <sup>+1</sup>	2	1	3d	16.450	12.759
	2	1	4s	6.860	6.395
Ti <sup>+2</sup>	2	0	3d	17.230	14.416
Ti <sup>+3</sup>	1	0	3d	19.330	17.134
V <sup>0</sup>	3	2	3d	17.560	11.463
	3	2	4s	6.730	6.024
V <sup>+1</sup>	3	1	3d	18.100	13.404
	3	1	4s	7.230	6.729
V <sup>+2</sup>	3	0	3d	18.760	15.047
V <sup>+3</sup>	2	0	3d	20.760	20.052
Cr <sup>0</sup>	5	1	3d	17.200	9.922
	5	1	4s	6.460	5.726
Cr <sup>+1</sup>	5	0	3d	17.940	12.154
Cr <sup>+2</sup>	4	0	3d	20.230	15.673
Cr <sup>+3</sup>	3	0	3d	22.170	18.419
Cr <sup>+4</sup>	2	0	3d	23.860	20.713
Cr <sup>+5</sup>	1	0	3d	25.390	22.779
Mn <sup>0</sup>	5	2	3d	20.780	12.666
	5	2	4s	7.310	6.541
Mn <sup>+1</sup>	5	1	3d	21.170	14.652
	5	1	4s	7.870	7.341
Mn <sup>+2</sup>	5	0	3d	21.680	16.304
Mn <sup>+3</sup>	4	0	3d	23.560	19.059
Mn <sup>+4</sup>	3	0	3d	25.230	21.396
Fe <sup>0</sup>	6	2	3d	22.290	13.253
	6	2	4s	7.570	6.778
Fe <sup>+1</sup>	6	1	3d	22.630	15.256
	6	1	4s	8.160	7.592

TABLE I (cont.)

element	$n_i^0$		$i$	$J_i^{\text{unrel}}$	$J_i^{\text{rel}}$
	3d	4s			
Fe <sup>+2</sup>	6	0	3d	23.090	16.919
Fe <sup>+3</sup>	5	0	3d	24.940	19.695
Co <sup>0</sup>	7	2	3d	23.750	13.805
	7	2	4s	7.820	6.746
Co <sup>+1</sup>	7	1	3d	24.060	15.846
	7	1	4s	8.450	7.896
Co <sup>+2</sup>	7	0	3d	24.490	17.532
Co <sup>+3</sup>	6	0	3d	26.300	20.319
Cu <sup>0</sup>	10	1	3d	24.830	12.880
	10	1	4s	7.570	6.860
Cu <sup>+1</sup>	9	0	3d	25.250	15.211
Cu <sup>+2</sup>	8	0	3d	27.220	18.710
Ni <sup>0</sup>	8	2	3d	25.180	14.345
	8	2	4s	8.060	7.227
Ni <sup>+1</sup>	8	1	3d	25.470	16.421
	8	1	4s	8.720	8.160
Ni <sup>+2</sup>	8	0	3d	25.870	18.125
Ni <sup>+3</sup>	7	0	3d	27.650	23.610
Zn <sup>0</sup>	10	2	3d	27.970	15.379
	10	2	4s	8.530	7.643
Zn <sup>+1</sup>	10	1	3d	28.230	17.080
	10	1	4s	9.250	8.663
Zn <sup>+2</sup>	10	0	3d	28.580	19.296
Y <sup>0</sup>	4d	5s			
	1	2	4d	9.260	7.333
	1	2	5s	5.610	4.986
Y <sup>+1</sup>	1	1	4d	10.070	8.812
	1	1	5s	5.980	5.569
Y <sup>+2</sup>	1	0	4d	10.800	9.967
Zr <sup>0</sup>	2	2	4d	10.780	8.055
	2	2	5s	5.970	5.305

TABLE I (cont.)

element	$n_i^0$		$i$	$J_i^{\text{unrel}}$	$J_i^{\text{rel}}$
	4d	5s			
Zr <sup>+1</sup>	2	1	4d	11.350	9.465
	2	1	5s	6.380	5.909
Zr <sup>+2</sup>	2	0	4d	11.930	10.600
Zr <sup>+3</sup>	1	0	4d	12.990	10.650
Nb <sup>0</sup>	4	1	4d	11.190	7.829
	4	1	5s	5.880	3.770
Nb <sup>+1</sup>	4	0	4d	11.790	9.372
Nb <sup>+2</sup>	3	0	4d	12.990	11.213
Nb <sup>+3</sup>	2	0	4d	13.980	12.618
Nb <sup>+4</sup>	1	0	4d	14.830	13.769
Mo <sup>0</sup>	5	1	4d	12.390	8.502
	5	1	5s	6.090	5.440
Mo <sup>+1</sup>	5	0	4d	12.890	10.021
Mo <sup>+2</sup>	4	0	4d	14.000	11.810
Mo <sup>+3</sup>	3	0	4d	14.940	13.200
Mo <sup>+4</sup>	2	0	4d	15.760	14.356
Mo <sup>+5</sup>	1	0	4d	16.500	15.360
Tc <sup>0</sup>	6	1	4d	13.500	9.122
	6	1	5s	6.270	5.653
Tc <sup>+1</sup>	6	0	4d	13.920	10.640
Tc <sup>+2</sup>	5	0	4d	14.970	12.393
Tc <sup>+3</sup>	4	0	4d	15.870	13.774
Tc <sup>+4</sup>	3	0	4d	16.670	15.944
Tc <sup>+5</sup>	2	0	4d	17.390	16.856

TABLE I (cont.)

element	$n_i^0$		$i$	$J_i^{\text{unrel}}$	$J_i^{\text{rel}}$
	4d	5s			
Ru <sup>0</sup>	7	2	4d	14.550	9.705
Ru <sup>+1</sup>	7	1	4d	14.910	11.237
Ru <sup>+2</sup>	7	0	4d	15.920	12.965
Ru <sup>+3</sup>	6	0	4d	16.790	14.337
Ru <sup>+4</sup>	5	0	4d	17.570	15.496
Ru <sup>+5</sup>	4	0	4d	18.280	16.516
Ru <sup>+6</sup>	3	0	4d	18.930	17.437
Rh <sup>0</sup>	8	1	4d	15.550	10.258
	8	1	5s	6.580	6.006
Rh <sup>+1</sup>	8	0	4d	15.870	11.815
Rh <sup>+2</sup>	7	0	4d	16.840	13.525
Rh <sup>+3</sup>	6	0	4d	17.680	14.893
Rh <sup>+4</sup>	5	0	4d	18.450	16.054
Rh <sup>+5</sup>	4	0	4d	19.140	17.080
Pd <sup>0</sup>	10	0	4d	15.680	10.002
Pd <sup>+1</sup>	9	0	4d	16.800	12.379
Pd <sup>+2</sup>	8	0	4d	17.770	14.074
Pd <sup>+3</sup>	7	0	4d	18.560	15.440
Pd <sup>+4</sup>	6	0	4d	19.310	16.606
Ag <sup>0</sup>	10	1	4d	17.460	11.300
	10	1	5s	6.830	6.290
Ag <sup>+1</sup>	10	0	4d	17.710	12.930
Ag <sup>+2</sup>	9	0	4d	18.620	14.617

TABLE II

A comparison between the  $X\alpha$  relaxed orbital hardnesses and the finite difference estimates (Pariser formula) from the VSIE (eV) for the first-row transition metals\*.

Metal	Oxidation State	3d		4s	
		VSIE	$X\alpha$	VSIE	$X\alpha$
Ti	0	9.31	10.81	6.10	5.74
	1	11.94	12.76	6.34	6.40
	2	9.52	14.42	10.08	.
	3	18.18	17.13	11.64	.
V	0	11.63	11.46	6.74	6.02
	1	12.52	13.40	6.61	6.73
	2	9.70	15.05	9.89	.
Cr	3	18.22	20.05	12.01	.
	0	11.11	9.92	6.04	5.73
	1	8.27	12.15	8.13	.
	2	14.75	15.67	10.13	.
	3	18.41	18.42	12.12	.
Mn	4	22.07	20.71	14.12	.
	5	25.72	22.78	16.12	.
	0	16.40	12.67	6.94	6.54
	1	10.54	14.65	7.18	7.34
	2	10.16	16.30	10.37	.
Fe	3	18.76	19.06	12.27	.
	4	22.25	21.40	14.14	.
	0	12.78	13.25	8.15	6.78
	1	10.80	15.26	7.46	7.59
Co	2	10.44	16.92	10.65	.
	3	19.24	19.70	12.47	.
	0	13.33	13.81	8.43	6.75
Ni	1	11.07	15.85	7.75	7.90
	2	10.76	17.53	10.96	.
	3	19.89	20.32	12.76	.
Cu	0	13.85	14.35	8.64	7.23
	1	11.35	16.42	8.05	8.16
	2	11.11	18.13	11.29	.
Zn	3	20.64	23.61	13.12	.
	1	9.71	15.21	9.78	.
Zn	2	18.76	18.71	11.67	.
	1	.	8.64	8.66	.
	2	11.91	19.30	12.06	.

\*See Table I for the specification of the electronic configurations. The VSIE of the 4s orbital at the higher oxidation states have been calculated from the interpolation formulae [29] for the  $d^{n-1}s$  configurations.

## Discussion

It follows from Fig. 1 that the magnitude of the *s*-type relaxed hardness, relative to the corresponding rigid hardness value,  $x_{nl}(q) \equiv J_{nl}^{\text{rel}}(q)/J_{nl}^{\text{unrel}}(q)$ , is predicted to remain approximately constant ( $\sim 90\%$ ) within the  $X\alpha$  model, for all transition metals considered in the present study. This ratio is slightly higher ( $\sim 93\%$ ) for the positive ions ( $q = 1$ ) due to a "harder" orbital electron distribution for a less screened nucleus. The unexpectedly low  $x_{5s}$  value for Nb is probably an artefact of a very approximate nature of the numerical differentiation of Eq. (5). It also follows from Fig. 1 that the relaxational lowering of the hardness value in the *d*-type orbitals is much higher than that observed for *s*-type orbitals, ranging from 20–45% for neutral atoms.

A reference to Fig. 1 also shows that the  $x_{nd}$  ratios from the  $X\alpha$  calculations exhibit a slightly decreasing trend across a given row of transition metals. A comparison of the  $x_{nd}$  values for the elements in the same group of the periodic table also reveals that in most cases  $x_{3d}(q) < x_{4d}(q)$ ; also, for a given element,  $x_{nd}(q) < x_{nd}(q + 1)$ . The observed deviations from these general characteristics can certainly be attributed partly to the changing configurations, leading to variations in the nuclear charge shielding; they are also partly the artefacts of the finite difference procedure adopted in this work. Since a higher  $x_{nl}$  value reflects a lower orbital relaxation lowering of the hardness, i.e. a "harder", less polarizable electron distribution, we conclude that the  $X\alpha$  model predicts a slight relative hardening of the *nd* electrons across a given row of transition metals, and a relative softening of the  $\rho_{nd}$  when going from the first to the second row of transition metals. Such a relative hardening of the electron distribution is also observed when going to higher oxidation states, as one would expect intuitively on the basis of simple nuclear screening considerations.

However, as can be seen in Table II, the  $\eta_{ii}$  values from the VSIE are often lower for  $q = 1, 2$  than those for  $q = 0$ , particularly for *d* orbitals. These deviations are represented in Fig. 2 by the cluster of points deviating most from the otherwise satisfactory correlation between the hardnesses from the  $X\alpha$  and VSIE sources. In general the agreement for *s* orbitals is better than that observed for *d* orbitals. It should be stressed that both estimates use different  $\Delta n$  in the finite difference procedure:  $\Delta n = 1/2$  in Eq. (5) (one numerical differentiation) and  $\Delta n = \pm 1$  in Eq. (6) (two numerical differentiations), and different configuration averaging.

The full AIM modeling of the hardness tensor would also require the corresponding collection of the off-diagonal hardnesses  $\eta_{ij}^{\text{rel}}$  for the valence shell orbitals and different oxidation states. Such parameters can in principle be generated using a similar finite difference approach based upon either the  $X\alpha$  calculations or experimental spectroscopic data for atomic systems. Alternatively one can transform the known molecular orbital (MO) hardness tensor, already reflecting the actual valence states of constituent atoms, to the AIM representation [13, 18]. The latter approach is strongly recommended when the CSA follows the standard SCF MO calculations for molecular systems.

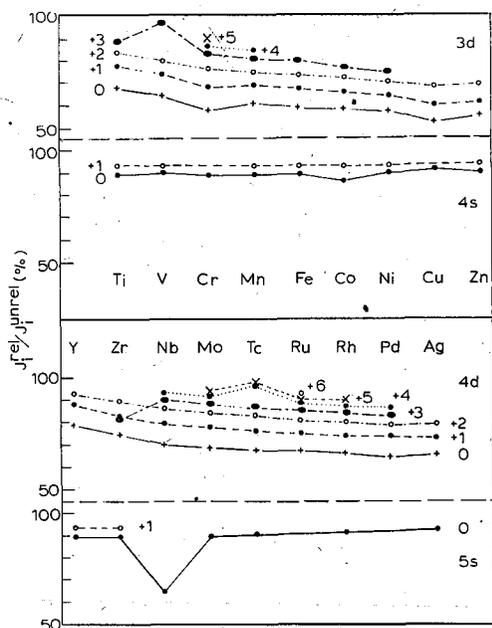


Fig. 1. Plots of the  $x_i = J_i^{\text{rel}}/J_i^{\text{unrel}}$  ratios (in %) from the data of Table I for the valence shell  $d$  and  $s$  orbitals of transition metal atoms and ions; see Table I for specifications of the relevant electron configurations.

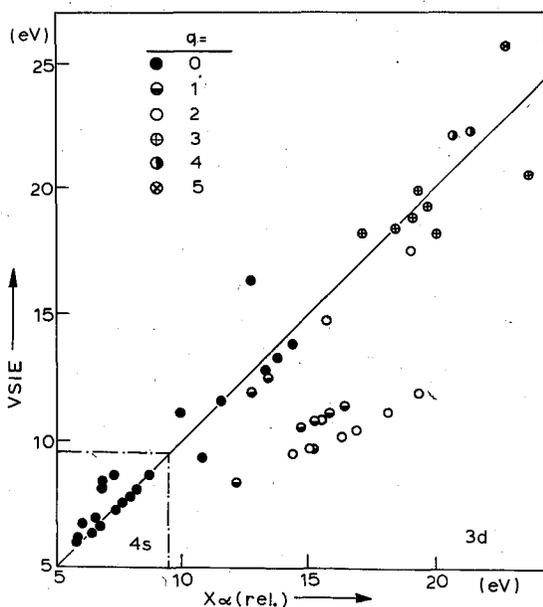


Fig. 2. A graphical comparison between the relaxed orbital hardnesses from the  $X\alpha$  calculations (Table I) and the VSIE hardness estimates (Table II), for the first-row transition metals.

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