Supplementary Information

Electronic-Structure-Based Chemical Descriptors: (In)dependence on Self-Interaction and Hartree-Fock Exchange

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Computational Details

Periodic bulk calculations based on the Kohn-Sham formalism of Density Functional Theory (*DFT*) were carried out using the VASP program package.[1] In this work we considered one functional from each rung of the Jacob 's ladder. Among many possibilities we selected functionals that were shown to be the best suited for the description of geometric, energetic, and elastic properties of bulk transition metals according to a recent systematic study.[2] Namely, we used the Vosko-Wilk-Nusair (*VWN*)[3] *xc* within the Local Spin Density Approximation (*LSDA*), the Perdew-Burke-Ernzerhof (*PBE*)[4] within the Generalized Gradient Approximation (*GGA*), the Tao−Perdew−Staroverov−Scuseria (*TPSS*) meta-GGA,[5] and the Heyd−Scuseria−Ernzerhof (HSE06) hybrid functional.[6] Optimized bulk structures are taken from the literature[2,7] and we refer there for further computational details. Here single-point calculations were carried out using Projector Augmented Wave (*PAW*) method[8] to represent atomic cores, and an optimized cutoff of 415 eV was chosen for the plane wave basis set.

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The convergence criterion of the self-consistency process was set to 10^{-6} eV. Monkhorst-Pack **k**-point grids[9] were increased with respect to previous calculations to 11×11×11 (3×3×3 in the case of Mn unit cell with 58 atoms). 20 bands were explicitly calculated per bulk atom, ensuring a suited description of the number of occupied and virtual states, yet 40 bands were needed for La. A tetrahedron method with Blöchl corrections was used to gain the Density Of States (*DOS*), with a smearing of 0.05 eV. The *d*-band analysis has been carried out on the Projected DOS (*PDOS*). The DOS has been evaluated on nearly 10.000 energy points, ensuring an energy resolution better than 0.01 eV. The *d*-band center, ε_d, has been obtained calculating the gravimetric center of *d*-states, integrating PDOS from the *d*-band onset energy level, ε_I, until the upper edge energy, ε_f, i.e. the energy that would yield full occupation of the *d*-PDOS. The *d*-band center is here referred to the Fermi energy, ε_F, used as zero energy reference. The band width *W* has been obtained from the subtraction of ε_i from ε_f. Finally, transition metal function, ε_u, has been determined equaling it to the highest peak energy position of the Hilbert transform of the *d*-PDOS. For few metals two peaks are competing as a function of the employed *xc* functional. In these cases the highest energy peak has been consistently used. Further details are provided in the literature.[10]

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Table S1 List of calculated *d*-band centers, ε_d, in eV, for all transition metal bulks, gained using different *xc* functionals.

Metal	VWN	PBE	TPSS	HSE06
Sc	4.53	4.18	4.13	3.50
Ti	3.18	2.96	3.17	2.90
V	3.99	3.88	4.06	4.46
Cr	-0.46	-0.48	-0.48	-0.42
Mn	0.77	0.69	0.90	-0.22
Fe	0.52	0.53	0.47	-0.43
Co	-0.26	-0.33	-0.32	-1.54
Ni	-0.64	-0.64	-0.75	-2.02
Cu	-2.91	-2.86	-3.08	-4.06
Zn	-7.58	-7.69	-7.83	-9.49
Y	4.41	4.78	4.14	4.48
Zr	3.27	3.18	3.27	3.12
Nb	1.23	1.23	1.25	1.45
Mo	-0.48	-0.41	-0.39	-0.02
Tc	-0.72	-0.65	-0.65	-0.75
Ru	-1.86	-1.73	-1.79	-2.13
Rh	-2.25	-2.19	-2.23	-2.60
Pd	-2.45	-2.42	-2.45	-2.79
Ag	-4.44	-4.39	-4.56	-5.55
Cd	-9.05	-9.16	-8.93	-10.49
La	7.86	7.71	8.50	7.14
Hf	3.16	3.07	3.09	3.29
Ta	3.16	2.97	2.91	3.30
W	2.03	1.94	1.90	2.32
Re	1.10	1.02	1.00	1.42
Os	-0.75	-0.80	-0.79	-1.01
Ir	-1.55	-1.52	-1.44	-1.80
Pt	-2.77	-2.73	-2.87	-3.29
Au	-3.88	-3.83	-4.08	-4.78
Hg	-5.34	-5.26	-6.18	-6.68

Table S2 List of calculated *d*-band widths, *W*, in eV, for all transition metal bulks gained using different *xc* functionals.

Metal	VWN	PBE	TPSS	HSE06
Sc	21.98	20.91	19.75	14.02
Ti	21.38	20.14	20.75	19.44
V	23.62	23.79	24.04	25.82
Cr	8.82	8.51	8.85	10.28
Mn	22.02	21.46	23.30	26.59
Fe	20.81	20.29	20.85	22.22
Co	21.21	21.00	21.54	23.57
Ni	20.99	20.99	21.11	22.47
Cu	7.32	7.23	7.52	7.83
Zn	9.18	9.15	9.83	11.14
Y	17.12	19.78	15.06	15.72
Zr	17.37	16.74	16.89	16.40
Nb	9.62	9.55	9.55	10.87
Mo	9.10	9.65	9.95	11.46
Tc	11.10	11.08	11.65	13.82
Ru	10.30	11.48	11.56	13.68
Rh	10.06	10.71	10.77	12.88
Pd	6.03	5.98	5.84	6.11
Ag	6.86	6.92	6.92	7.64
Cd	9.69	9.76	9.96	11.54
La	27.23	26.81	29.66	25.23
Hf	16.90	15.97	15.86	16.17
Ta	18.76	18.34	17.35	18.99
W	25.99	25.32	24.87	29.65
Re	24.37	23.76	23.36	27.68
Os	22.65	22.43	23.09	25.44
Ir	23.16	22.94	22.94	25.32
Pt	10.07	10.11	10.52	11.93
Au	7.95	7.85	8.11	8.97
Hg	5.87	5.90	6.98	7.37

Table S3 List of calculated upper *d*-band edges, ε_u, in eV, for all transition metal bulks, gained using different *xc* functionals.

Metal	VWN	PBE	TPSS	HSE06
Sc	3.88	3.93	4.10	4.81
Ti	3.49	3.48	3.65	4.24
V	2.82	2.83	2.92	3.91
Cr	1.47	1.50	1.51	2.67
Mn	1.53	1.52	1.96	2.28
Fe	1.73	2.04	2.03	3.83
Co	1.27	1.30	1.36	1.97
Ni	0.14	0.14	0.29	1.11
Cu	-1.59	-1.57	-1.65	-2.64
Zn	-6.88	-6.82	-7.20	-8.98
Y	5.92	5.96	6.18	6.58
Zr	5.14	5.16	5.32	5.82
Nb	4.03	4.06	4.13	4.94
Mo	2.3	2.35	2.47	3.21
Tc	3.26	3.26	3.35	4.09
Ru	1.78	1.78	1.81	2.30
Rh	0.86	0.87	0.87	1.01
Pd	0.22	0.21	0.21	0.08
Ag	-2.96	-3.05	-3.05	-4.02
Cd	-8.11	-8.21	-8.28	-10.04
La	6.16	6.13	6.45	6.74
Hf	6.69	6.73	6.78	7.44
Ta	4.95	5.05	5.13	5.92
W	3.12	3.18	3.20	4.04
Re	4.34	4.35	4.36	5.21
Os	2.41	2.41	2.47	3.02
Ir	1.29	1.29	1.27	1.73
Pt	0.34	0.34	0.39	0.55
Au	-1.73	-1.77	-1.81	-2.72
Hg	-4.80	-4.85	-5.33	-6.31