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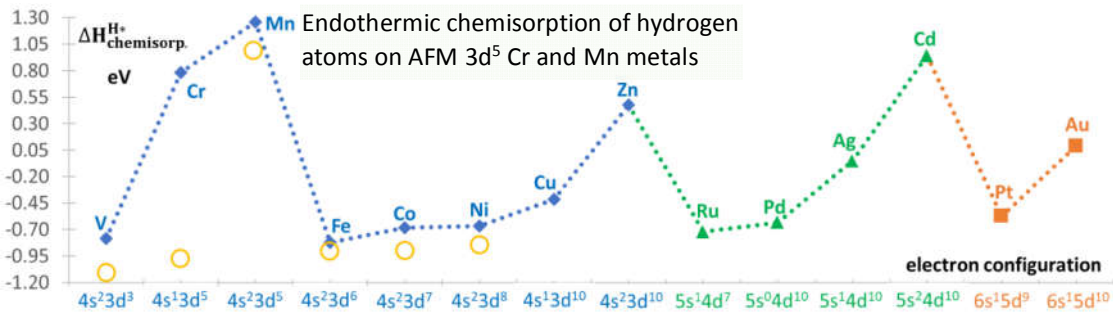
### The Trend of Chemisorption of Hydrogen and Oxygen Atoms on Pure Transition Metals: Magnetism justifies Unexpected Behavior of Mn and Cr

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<b>Abstract:</b>	<p>The spin of the electron is decisive to understand electronic interactions in heterogeneous catalysis, mainly because the stabilizing Quantum Spin Exchange Interactions (QSEI) are always a significant contribution to the energy of magnetic catalysts and reactants during catalytic events. Cooperative QSEI in compositions with multi-atomic open-shell configurations (QSEI-OS) maximize the influence of the spin dependent potentials, determining the electronic properties of magnetic materials and shaping their reactivity. Because of the intra- and inter- atomic QSEI-OS, high-spin (3d<sup>5</sup>) antiferromagnetic (AFM) metals like Cr and Mn can be more inert (or "noble") than Au itself towards the formation of covalent bonds with hydrogen atoms. AFM QSEI-OS lead to a relative higher destabilization of the unoccupied (spin-)orbitals (Mott upper band) in Cr and Mn compared with other metals. In oxygen adsorption, QSEI-OS lead to the reduction of the electronic repulsions in occupied 3d<sup>5</sup> orbitals with a concomitant decrease of the chemisorption enthalpy of the oxygen atoms. Since hydrogen and oxygen atoms are the most important intermediates in relevant catalytic processes like oxygen reduction reaction and water splitting, the effect of QSEI-OS needs to be properly incorporated as a critical factor to understand the activity of catalysts based on magnetic metals.</p>
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### Highlights:

- Stabilizing Quantum Spin Exchange Interactions (QSEI) are always a significant contribution to the energy of magnetic catalysts and reactants during catalytic events.
- Cooperative QSEI in compositions with multi-atomic open-shell configurations (QSEI-OS) maximize the influence of the spin dependent potentials, determining the electronic properties of magnetic materials and shaping their reactivity.
- Because of the intra- and inter- atomic QSEI-OS, high-spin (3d5) antiferromagnetic (AFM) metals like Cr and Mn can be more inert (or “noble”) than Au itself towards the formation of covalent bonds with hydrogen atoms.
- On the other hand, compositions with dominant ferromagnetic interactions become typically activated by the spin-polarization in relation with more optimal (milder) chemisorption enthalpies and electronic mobility.
- Cooperative QSEI in open-shell configurations influence the structure and reduce the adsorption energies of reactants.
- The effect of QSEI-OS needs to be properly incorporated as a critical factor to understand the activity of catalysts based on magnetic metals.
- The design of catalysts via orbital engineering should boost the application of quantum concepts in catalysis and create the specific field of spintro-catalysis.



## The Trend of Chemisorption of Hydrogen and Oxygen Atoms on Pure Transition Metals: Magnetism justifies Unexpected Behaviour of Mn and Cr

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**Keywords:** *heterogeneous catalysis; quantum spin exchange interactions; spin-dependent catalysis, strongly correlated electrons; magnetic ordering*

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**Abstract:** The spin of the electron is decisive to understand electronic interactions in heterogeneous catalysis, mainly because the stabilizing Quantum Spin Exchange Interactions (QSEI) are always a significant contribution to the energy of magnetic catalysts and reactants during catalytic events. Cooperative QSEI in compositions with multi-atomic open-shell configurations (QSEI-OS) maximize the influence of the spin dependent potentials, determining the electronic properties of magnetic materials and shaping their reactivity. Because of the intra- and inter- atomic QSEI-OS, high-spin ( $3d^5$ ) antiferromagnetic (AFM) metals like Cr and Mn can be more inert (or “noble”) than Au itself towards the formation of covalent bonds with hydrogen atoms. AFM QSEI-OS lead to a relative higher destabilization of the unoccupied (spin-)orbitals (Mott upper band) in Cr and Mn compared with other metals. In oxygen adsorption, QSEI-OS lead to the reduction of the electronic repulsions in occupied  $3d^5$  orbitals with a concomitant decrease of the chemisorption enthalpy of the oxygen atoms. Since hydrogen and oxygen atoms are the most important intermediates in relevant catalytic processes like oxygen reduction reaction and water splitting, the effect of QSEI-OS needs to be properly incorporated as a critical factor to understand the activity of catalysts based on magnetic metals.

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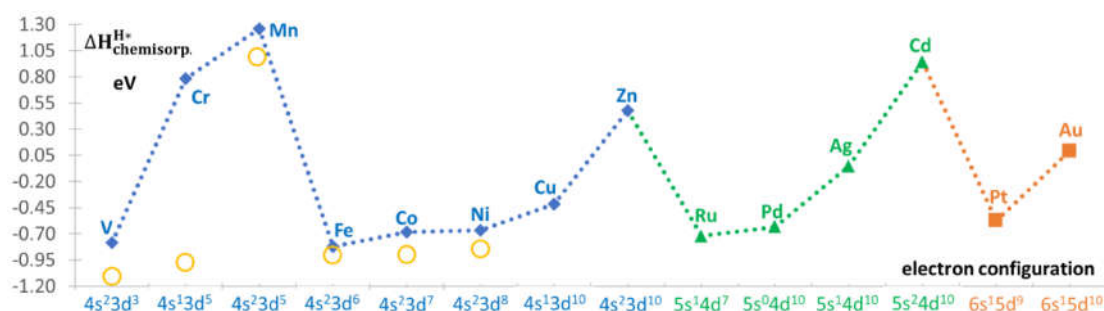
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**Introduction.** The interaction between electrons in atomic systems are governed by quantum mechanics and not all the factors contributing to the energetics of the processes (like in catalytic events, for instance) have a classical correspondence. The quantum spin exchange interactions (QSEI) are the most significant correlation mechanisms without a straightforward classical meaning. Electrons with the same spin substantially mitigate their mutual charge repulsion because they can avoid to occupy near regions in space via a quantum spin exchange mechanism (i.e., exchanging orbitals in a correlated movement).<sup>1,2</sup> Two electrons with the same spin experience an additional stabilization energy with the associated integral terms  $QSEI_{ab}^{\alpha\alpha(\beta\beta)} = -\left\langle \varphi_a^{\alpha(\beta)}(\vec{x}_2)\varphi_b^{\alpha(\beta)}(\vec{x}_1) \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \varphi_a^{\alpha(\beta)}(\vec{x}_1)\varphi_b^{\alpha(\beta)}(\vec{x}_2) \right\rangle < 0$ ,<sup>1</sup> when an anti-symmetric wave function (a single Slater determinant most frequently) is introduced as solution to the effective Hamiltonian of the system ( $\hat{H}_{e-}^{\text{H-F}}$  in the Hartree-Fock method or in the  $\hat{H}_{e-}^{\text{Kohn-Sham}}$  in density functional theory (DFT)).<sup>1,3</sup> Overall the stabilizing QSEI energy, consequence of the imposition of a wavefunction that satisfies the Pauli principle, means that the quantum reality introduces the possibility that two indistinguishable electrons with the same spin can interchange their orbitals, position and momentum. This mechanism reduces their mutual Coulomb repulsion. Cooperative intra- and inter- atomic QSEI-OS stabilize open-shell orbital configurations becoming even very influential in their physical properties. It is imperative to properly describe cooperative QSEI-OS in order to understand general trends in heterogeneous catalysis across the periodic table. The electronic energy of a structure, a catalyst for instance, should be accurately discussed from the point of view of the quantum electronic potentials:  $V_{N+e-}^{\text{cat.}}$  (*Coulomb*), changes in the Coulomb attraction between nuclei and electrons, and  $V_{e-e-}^{\text{cat.}}$ , changes in the electronic repulsions. Three factors contribute to  $V_{e-e-}^{\text{cat.}}$ : the classical Coulomb repulsions,  $V_{e-e-}^{\text{cat.}}$  (*Coulomb*), QSEI (as previously introduced) and the Correlation energy  $E(\text{Correlation})$ , due to higher order mechanics for the lessening of the electronic repulsions. Modern computational approaches already approximate the  $E(\text{Correlation})$  in methods like Density functional Theory (DFT).<sup>3</sup> QSEI-OS, however, are an even more important factor, particularly when differentiating between closed-shell and open-shell systems. As we observe in our theoretical study, the QSEI associated with the open-shell orbital configurations for the magnetic 3d-metals V, Cr, Mn, Fe, Co and Ni, represents, respectively, the 2.4%, 12.1%, 18.8%, 13.5%, 9.9% and 2.6% of the electronic energy associated

to the 3d electron (we obtained these values comparing the total energy with fictitious closed-shells calculations).

**Antiferromagnetic (AFM) Cr and Mn metals show the weakest bonds in the chemisorption of hydrogen atoms.** Fig. 1 shows the variations in the calculated chemisorption enthalpy of

hydrogen atoms ( $\Delta H_{chemisorp}^{H^*}$  versus  $H_2$  gas) on several transition metals, for similar close-packed surfaces at 0.5 monolayer (ML) coverage. Our calculated  $H^*$  binding energies are in excellent agreement with the available values reported by Greeley and Mavrikakis.<sup>4</sup> Our calculations point out that closed-shell metals Zn and Cd and the open-shell AFM  $3d^5$ -metals Cr and Mn show the highest  $\Delta H_{chemisorp}^{H^*}$  values, corresponding to the most endothermic chemisorptions. These values are more endothermic than the value calculated for Au, commonly believed the most “noble” among transition metals.



**Figure 1.** Calculated chemisorption enthalpies for hydrogen atoms ( $\Delta H_{chemisorp}^{H^*}$ ) versus gaseous  $H_2$  on equivalent close-pack surfaces of V, Cr, Fe (BCC (1 1 0) surface);  $\alpha$ -Mn (100); Co, Zn, Ru and Cd (HCP (1 1 1) surface); Ni, Cu, Pd, Ag, Pt and Au (FCC (1 1 1) surface) at 0.5 ML. The circles indicate calculated  $\Delta H_{chemisorp}^{H^*}$  on fictitious closed-shell configurations, the crystal structure is the same as for the open-shell calculations.

A hydrogen atom [ $1s^1$ ] has a single valence electron in the 1s-orbital. The stabilizing Coulomb attraction by the proton is not too strong,  $V_{N+e^-}^{Coulomb}(H \cdot)$ , compared to that of most radical adsorbates ( $CH_x$ ,  $NH_x$ ,  $OH_x$ ,  $SH_x$  etc.). The critical factor in hydrogen chemisorption lies in the ability of the orbital configuration of the metal to stabilize a covalent bond with the electron in the  $H^*$  [ $1s^1$ ].

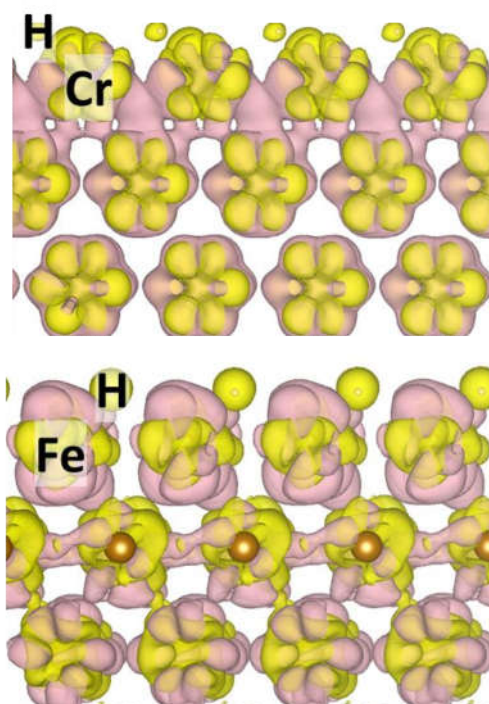
In the chemisorption of H\* on Au, the increasing electronic repulsions ( $\Delta V_{e-e}^{Au+H^*}$ ) slightly dominate over the nuclear attractions ( $\Delta V_{N+e}^{Au+H^*}$ ). This occurs because the 5d-shell is fully occupied for Au-[5d<sup>10</sup>6s<sup>1</sup>], making  $\Delta H_{\text{chemisorp.}}^{\text{H}^*} \approx 0.1$  eV endothermic. The formation of anti-bonding orbitals between Au and the adsorbate destabilizes the chemisorption. Notice that for Pt-[5d<sup>9</sup>6s<sup>1</sup>]

5  $\Delta H_{\text{chemisorp.}}^{\text{H}^*} \approx -0.6$  eV is exothermic, because the 5d-band is not initially fully occupied. Thus, we could infer that Pt is less “noble” than Au. Consistently, Zn-[3d<sup>10</sup>4s<sup>2</sup>] and Cd-[4d<sup>10</sup>5s<sup>2</sup>] show  $\Delta H_{\text{chemisorp.}}^{\text{H}^*}$  values more endothermic than Au, see Fig. 1, since their valence *d* and *s* orbitals are completely occupied.

Analogously, the AFM Cr and Mn metals result to be “noble” from the point of view of the endothermicity of  $\Delta H_{\text{chemisorp.}}^{\text{H}^*}$ , as shown again in Fig. 1. The contribution of the cooperative QSEI due to the open-shell configuration of the metals, QSEI-OS, justify the limited H\* chemisorption enthalpy. The high-spin configuration [ $3d_{\alpha}^5 3d_{\beta}^0$ ] of Cr and Mn metals gets stabilized by the dominant intra-atomic diminution of the repulsion between electrons with the same spin in the compact 3d-orbitals, and by optimum inter-atomic nuclei attractions because of the AFM connections. Neglecting  $\text{QSEI}_{\text{shell}}^{\text{open}}$ , forcing for example hypothetical closed-shell configurations on magnetic metals, leads to unphysical results, particularly catastrophic for the structures with metals in high-spin [ $3d_{\alpha}^5 3d_{\beta}^0$ ] and [ $3d_{\alpha}^3 3d_{\beta}^0$ ] configurations. The bonding energy of Cr-H\* increases of ~200% going from endothermic, in the correct open-shell calculations, to exothermic in the imaginary close-shell calculations, see Fig. 1. QSEI-OS are even more crucial to understand the behavior of Mn. The actual unexpected AFM crystal structure of  $\alpha$ -Mn arises from complex magnetic interactions.<sup>5</sup> The relatively smaller increase of  $\Delta H_{\text{chemisorp.}}^{\text{H}^*}$  from the value of a fictitious closed-shell  $\alpha$ -Mn is certainly the result of these magnetic interactions in the by crystal structure.  $\Delta H_{\text{chemisorp.}}^{\text{H}^*}$  of H\* on an unrealistic non-magnetic Mn surface retaining the same crystal structure as Cr (BCC) becomes so exothermic that fell off-chart in Fig. 1.

25 The effect of QSEI-OS on ferromagnetic Fe, Co and Ni metals also show non-negligible 1.5%, 29.5% and 24.5 % increments of  $\Delta H_{\text{chemisorp.}}^{\text{H}^*}$ , with respect to imaginary closed-orbital configurations. If we compare the difference in the electronic density between AFM Cr and a hypothetical FM orbital configuration both with the same BCC structure, we observe that dominant AFM orderings favors electronic localization,<sup>6</sup> as clearly demonstrated by the yellow orbital lobes

in Fig. 2, top. Fe shows more delocalized stabilization of electronic density in the 3d-orbitals (red lobes) via FM ordering rather than AFM ordering (yellow lobes), Fig. 2 bottom. Thus, the AFM ordering results less stable. The overall magnetization slightly diminishes in FM Fe upon the formation of the covalent bonds with H\* (with respect to the clean surface), indicating that some stabilizing  $QSEI_{shells}^{open}$  are lost weakening the chemisorption.

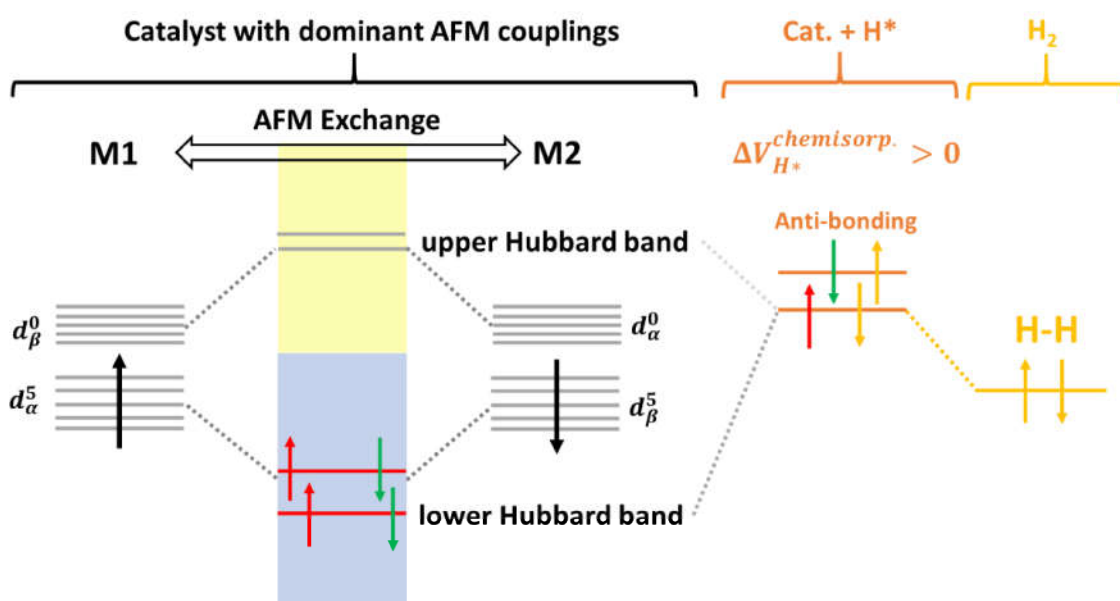


**Figure 2.** Top: difference in the electronic density between orbital configurations for Cr: AFM (yellow iso-surfaces) versus hypothetical FM (red iso-surfaces). Bottom: difference in the electronic density between orbital configurations for Fe: FM (red iso-surfaces) versus hypothetical AFM (yellow iso-surfaces). All structures are BCC. Plots done with VESTA.<sup>7</sup>

**Lower and Upper Hubbard bands in AFM Cr and Mn.** The antiparallel spin orientation between metal centers in the dominant AFM structure of Cr and Mn allows electron pairs to localize in crystals. In the outstanding analysis of the orbital origins of magnetism by Landrum and Dronskowski,<sup>6</sup> the authors observed a reduction of the density of states (DOS) around the Fermi level for Cr and Mn metals. In the high-spin configurations  $[3d_{\alpha}^5 3d_{\beta}^0]$ , the strong intra-

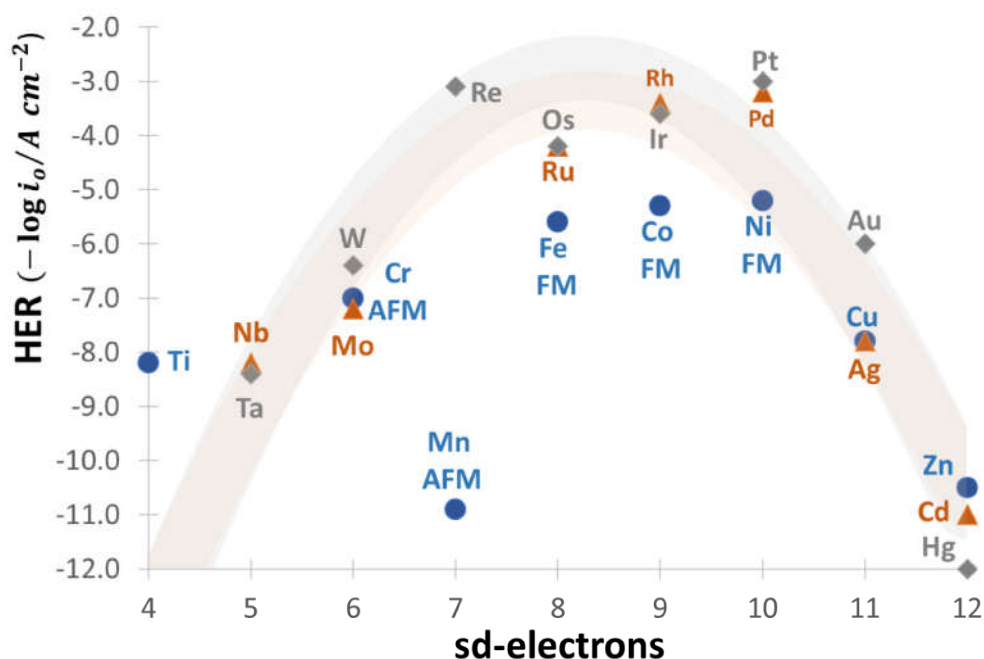


atomic QSEI-OS stabilize the magnetically oriented electrons and the inter-atomic nuclear attractions favor the AFM ordering. Hence, *QSEI-OS* and  $V_{N+e-}^{cat.}$  (*Coulomb*) cause an additional energy splitting between the occupied high-spin  $3d_{\alpha}^5$ -orbitals and the empty  $3d_{\beta}^0$ , also called lower Hubbard band (with a marked bonding character) and upper Hubbard band (with a marked anti-bonding character), respectively.<sup>6,8</sup> Fig. 3 explains that the dominant endothermicity ( $\Delta H_{chemisorp.}^{H^*} > 0$ ) seen for the chemisorption of  $H^*$  onto AFM Cr and Mn metals is due to the increase of the electronic repulsions, between the lower Hubbard band and the incoming  $H_2$ .



**Figure 3.** Left: representation of AFM Cr or Mn structures with high-spin  $3d^5$  configuration. The antiparallel spin orientation between metals centers enhance the formation of the lower and upper Hubbard bands (for clarity purposes, the number of electrons does not reflect the total amount of  $d$  electrons). Right: occupied energy levels of a gaseous  $H_2$  molecule. Center: partial filling of the anti-bonding upper Hubbard energy levels upon  $H^*$  chemisorption.

Fig. 4 shows a set of experimental data extrapolated from literature in good agreement with our calculations: AFM Mn, Zn and Cd are the least active metals for the hydrogen evolution reaction (HER).<sup>9,10,11,12</sup> Overall the agreement between chemisorption enthalpies, Fig. 1, and HER activity, Fig. 4, is very remarkable bearing in mind that only a single surface have been considered in the calculations.



**Figure 4.** Experimental current during hydrogen evolution reaction (HER) on transition metals.<sup>9,10,11,12</sup> versus the number of *sd*-electrons.

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Antiferromagnetic high-spin  $3d^5$  and  $3d^3$  configurations in octahedral fields have orbital shells that are magnetically fully occupied. Because of the strong intra- and inter- atomic cooperative QSEI-OS, we expect that the catalytic behavior of such configurations towards reactants with a low electronegativity (like  $H^*$ , for instance) resembles the suboptimal behavior of  $d^{10}$  noble metals in catalysis.<sup>13,14,15</sup> Previous conclusion is also in agreement with adsorption energies for the  $NH_3$  molecule on the surface of 3d metals, reported by Bhattacharjee et al..<sup>16</sup> Although these authors proposed an updated theoretical model to explain the results, we will present a different theoretical model based on QSEI-OS.

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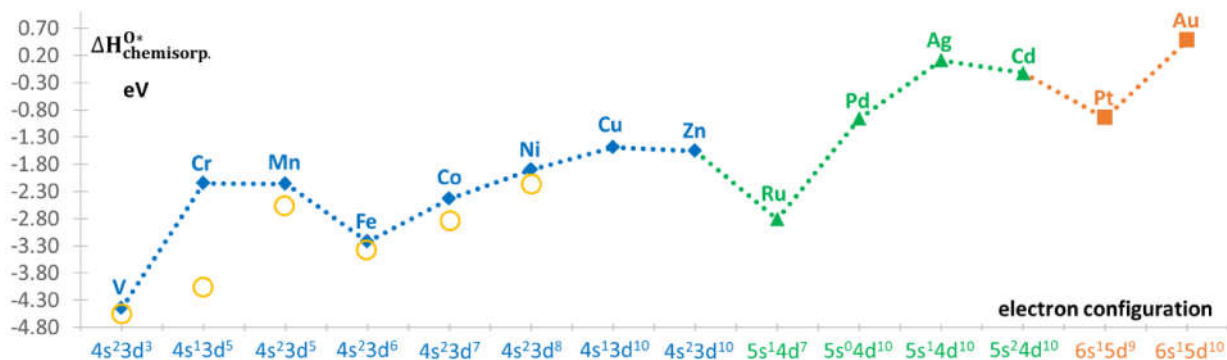
The influence of the indirect spin potentials decreases for the FM Fe, Co and Ni metals, even though their contribution is still diminishing significantly the exothermicity of chemisorption on these metals. These conclusions are in agreement with the results published by Escaño and coworkers for the comparison of actual FM alloys versus fictitious non-magnetic configurations.<sup>17</sup> Recently, admirable experiments have also proved the direct enhancement of the activity of magnetic catalysts for water splitting reaction by the exposition of the process to an exogenous

magnetic field.<sup>18</sup> All these insights point to the fact that engineering orbital magnetism to enhance catalytic activity of abundant 3d-metals via QSEI-OS and electron-spin delocalization<sup>13,14,15</sup> may receive a considerable attention in the next decade.

5 **The chemisorption of oxygen atoms is weaker on Au than on other metals.** The semi-occupied [2p<sup>4</sup>] valence orbitals of oxygen atoms are degenerate and more electrophilic than the hydrogen [1s<sup>1</sup>]. This due to stronger nucleus-electron  $V_{N+e-}^{Coulomb}(O^*)$  interactions. The *d*-orbitals of the metals effectively lose more electron density towards the oxygen atoms upon their chemisorption, since all the 2 sp-shell tries to fulfill the octet rule by forming adsorbed O<sup>2-</sup> ions (O\*).

10 Stronger atomic O\* chemisorption occurs for the most electron-donating metals, starting from the lowest occupations of the *sd*-shell,  $s^2d^1$ ,  $s^2d^2$ ,  $s^1d^3$  and  $s^2d^3$ . The endothermicity of  $\Delta H_{chemisorp}^{O^*}$  grows with the occupation of the *sd*-shell, albeit this increment is not linear as Fig. 5 shows. Due to the larger radial extension of the 5*d*-orbitals,<sup>19</sup> ultimately Au has the lowest  $\Delta H_{chemisorp}^{O^*}$  value in the subgroup we investigated. In other words, Au, with a 6s<sup>1</sup>5d<sup>10</sup>-shell, has the higher relative

15 stability against oxidation among investigated pure metals.

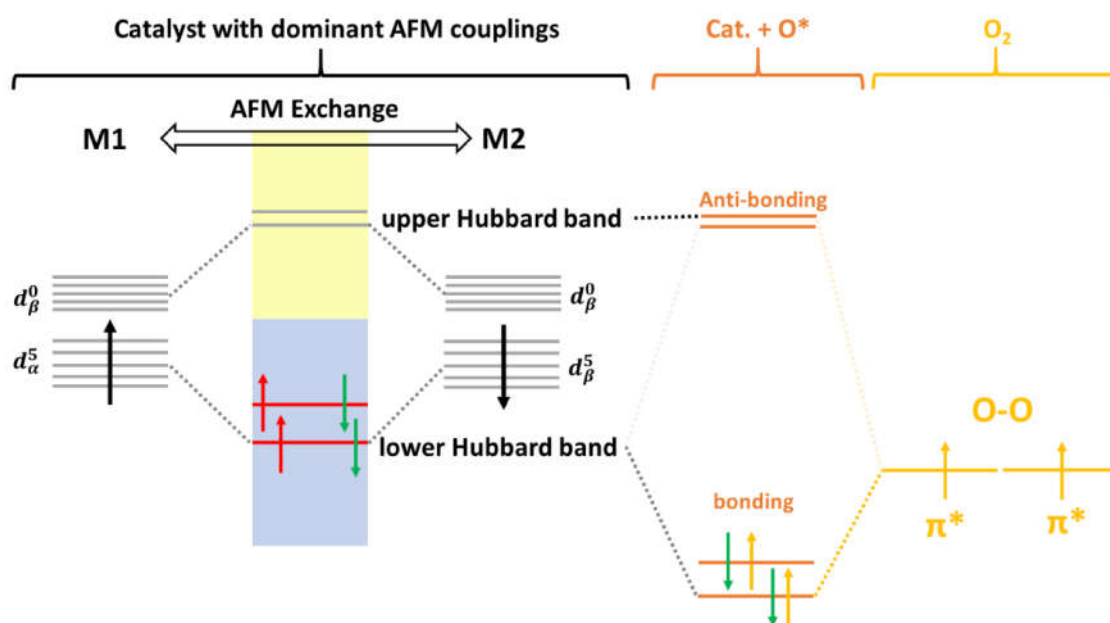


20 **Figure 5.** Calculated chemisorption enthalpies for hydrogen atoms ( $\Delta H_{chemisorp}^{O^*}$ ) versus gaseous H<sub>2</sub> on equivalent close-pack surfaces of V, Cr, Fe (BCC (1 1 0) surface),  $\alpha$ -Mn (100), Co, Zn, Ru and Cd (HCP (1 1 1) surface), Ni, Cu, Pd, Ag, Pt and Au (FCC (1 1 1) surface) at 0.5 ML. The circles indicate calculated  $\Delta H_{chemisorp}^{O^*}$  on fictitious closed-shell configurations.

As expected,  $\Delta H_{chemisorp}^{O^*}$  values are again smaller for the magnetic 3*d*-metals because of QSEI-OS, the chemisorption of O\* onto these magnetic metals is more exothermic. The relative

decrement is again lower for the AFM orderings than for the FM configurations; Fe and Co show a more exothermic chemisorption of  $O^*$  than Cr and Mn. This time Cr and Mn are less “noble” than Au. Unlike hydrogen, the interaction of incoming  $O_2$  with the bonding lower Hubbard band this time leads to a partial oxidation of the latter and a great diminution of the electronic repulsions in the more compact  $3d$ -orbitals, with a concomitant gain of Coulomb attractions between the catalyst and  $O^*$  ( $V_{N+e^-}^{Coulomb}(Cat.+O^*)$ ). Fig. 6 summarizes this behavior. Nonetheless, the stabilizing QSEI-OS, particularly in the AFM lower Hubbard band, always tend to moderate the exothermicity of  $O^*$  binding.

We hope that previous explanations also make likewise understandable why for instance, nickel-chromium alloys (chromium is quite soluble in nickel) have excellent resistance to high temperature oxidation and corrosion.



**Figure 6.** Left: AFM Cr and Mn structures with high-spin  $3d^5$  configurations causing the formation of the lower and upper Hubbard bands. Right: highest occupied orbitals of gaseous  $O_2$  molecule. Center: participation of the lower Hubbard band in the exothermic  $O^*$  chemisorption.

**Specific QSEI corrections for metals with open-shells to the adsorption enthalpies.** We try to compare trends between heterogenous closed-shell and open-shell catalysts by introducing an

effective spin-dependent enthalpic contribution,  $\Delta J_{adsorption}^{QSEI_{shells}^{open}}(\mathbf{f}_d) \cdot \vec{S}_{cat.}(\mathbf{f}_d)$  (with  $\Delta J_{adsorption}^{QSEI_{shells}^{open}} > 0$ , and  $\Delta H_{adsorption}^{open-shell} < 0$  indicating exothermic chemisorption), similar to the effective Heisenberg exchange energy term used in magnetism.<sup>6</sup>  $\vec{S}_{cat.}(\mathbf{f}_d)$  is the magnetic moment accumulated in the bonds of the catalyst<sup>20</sup> and  $\mathbf{f}_d$  refers to the orbital filling.<sup>15</sup> The fitting factor  $\Delta J_{adsorption}^{QSEI_{shells}^{open}}(\mathbf{f}_d) \cdot \vec{S}_{cat.}(\mathbf{f}_d)$  refers to the reduction of the adsorption energies of the intermediates because of stabilizing QSEI<sub>shells</sub><sup>open</sup> in the catalyst, Eq. 1:

$$\text{Eq. 1) } \Delta H_{adsorption}^{open-shell} = \Delta H_{adsorption}^{closed-shell} + \Delta J_{adsorption}^{QSEI_{shells}^{open}} \cdot \vec{S}_{cat.}$$

In agreement with the Sabatier's principle, the increased endothermicity in the chemisorption of a low electronegative reactant like H\* on catalysts with dominant AFM interactions like Mn and Cr may be so pronounced that the activation barrier for hydrogen evolution increases. On the other hand, FM (Fe, Co and Ni for pure metals) compositions become typically activated by the spin-polarization in relation with more optimal (milder) chemisorption enthalpies and electronic mobility. Previous statements and Eq. 1 are being particularly useful to rationalize oxygen electro-catalysis,<sup>14,21,22</sup> relevant in clean energy technologies. The statements presented here are necessarily general and have broad applicability since there are multiple crucial reactions in heterogenous catalysis where the most active compositions are magnetic, like CO hydrogenation towards hydrocarbons,<sup>23,24</sup> ammonia synthesis,<sup>25</sup> oxidation of organic molecules,<sup>26</sup> hydrodesulfurization,<sup>27</sup> etc.<sup>28</sup>

## Conclusions.

Just as the research in spin-electronics (spintronics) gave rise to a separated field from electronics over the years, the design of catalysts via orbital engineering should boost the application of quantum concepts in catalysis and create the specific field of *spinthro-catalysis*.<sup>29,30,14</sup> The study of spin-dependent interactions in catalysis should not be seen as an antagonist of previously reported successful models for non-magnetic structures, like d-band model,<sup>31,32,33,34</sup> rather much it should be used as a complementary tool demanded by the of highly-correlated magnetic materials. The analysis of cooperative QSEI-OS is fundamental to understand the multippeak catalytic activity

trends versus the orbital occupation observed for strongly correlated magnetic catalysts, since the incorporation of QSEI-OS into the models explains all the interesting sudden variations and divergences due to the spin in catalysts based on 3d-metals.<sup>13,14,15</sup> At this point, it makes sense, to emphasize that nature uses spin-potentials to developed the most efficient energy catalysts from abundant magnetic elements.<sup>21</sup>

Cooperative QSEI in open-shell configurations influence the structure and reduce the adsorption energies of reactants. In particular, fully AFM high-spin  $[3d_{\alpha}^5 3d_{\beta}^0]$  configurations, like Cr and Mn metals and, to a lesser degree, AFM high-spin  $[3d_{\alpha}^3 3d_{\beta}^0]$  configurations, become less reactive and more “noble”-like.

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We have no conflict of interest to declare