THE ROLE OF THE FERMI SURFACE IN ADSORBATE-METAL INTERACTIONS: AN ENERGY DECOMPOSITION ANALYSIS

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The interpretation of chemical bonding and reactivity has been greatly aided by the development of energy decomposition methods, which afford a quantification of concepts such as Pauli repulsion, electrostatic interaction, (frontier) orbital interaction.[1] The Kohn-Sham model of DFT uses molecular orbitals which are eminently suitable for this type of analysis. [2]

We will discuss the extension of energy decomposition methods to extended systems, in particular for chemisorption of a molecule on a metal slab. This introduces a new energy component, which we call the relief of the Pauli repulsion due to the existence of the Fermi level in the metal: antibonding levels that rise above the Fermi level can be depleted by electrons falling down into the Fermi sea. We will highlight the significance of this electronic structure feature of metallic systems as the key factor that gives them their singular reactivity properties, which are so much exploited in heterogeneous catalysis.[3]

More detailed insight into the electronic structure origin of differences between metals will emerge from this type of analysis: why a large barrier for H\textsubscript{2} dissociation on Cu, and no barrier on Pd? Why preference for adsorption on hollow sites for one metal, and on top for another metal? [4]