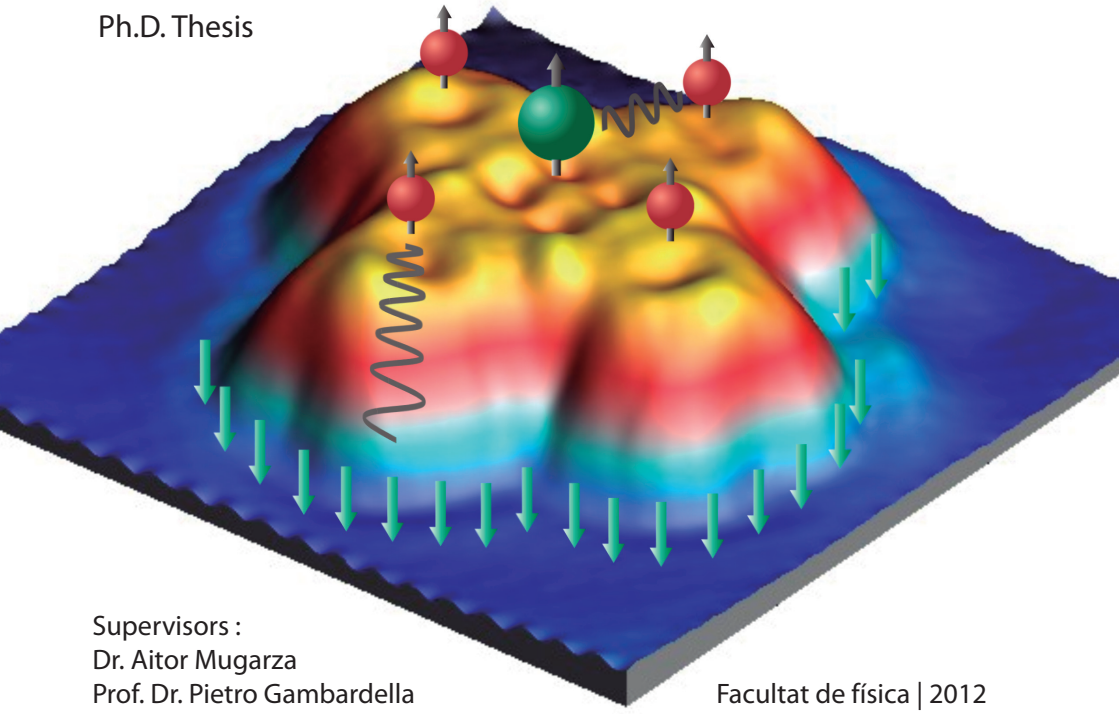
Electronic structure of metal phthalocyanines on Ag (100)

Cornelius Krull

Ph.D. Thesis



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Appendix B

B Adsorption of molecules on surface

One of the central questions of this thesis is the influence adsorption on a substrate has on organic molecules. While this is a complex topic especially for larger molecules, and each systems is different, some general remarks can be made. Here we will introduce the basic concepts focussing on the adsorption of organic molecules on metal surfaces.

B.1. Chemisorption and Physisorption

Adsorption is a process where atoms and molecules from the gas or liquid phase bind on the surface of a solid surface. This binding involves some type of interaction between the adsorbate and the supporting substrate. Based on the strength and type of the interaction one roughly divides between chemisorption and physisorption. A physisorbed particle has typically less than ~0.3eV of binding energy, and the interaction is based on van der Waals forces. As a consequence the electronic structure of the adsorbate is generally similar to that of the gas-phase. In the latter the interaction is a strong chemical binding, like covalent, metallic, ionic. This binding involves orbital overlap and charge transfer between surface and adsorbate, and hence strong changes in the electronic structure, bond lengths and bond angles occur regularly. Theoretical description of these systems is complex and the complete system, that is the substrate and adsorbate, has to be considered as a whole.

Theoretical descriptions of adsorbate-substrate interaction are undertaken at two different levels. First the accurate, but computational demanding many electron description. These calculations can be done using wave function based methods [251], which are limited by computational power to roughly 100 electrons. Therefore usually the framework of Density Functional Theory (DFT) [252, 253, 61, 254, 62] is used. Here the ground state electron density and total energy are calculated using a set of one electron-Schrödinger equations rather than the many electron one. Several choices have to be made which basis set is used, and how the exchange correlation is approximated. Typical choices are the Linear Density Approximation (LDA) [63], and the Generalized Gradient Approximation (GGA). As a general tendency dispersive *i.e.* van der Waals (vdW) forces are not well represented using these functionals. Recent developments have implemented GGA+vdW functionals, so that intermolecular interaction and physisorption can be described more accurately. DFT has become an important tool to determine the adsorption geometries, binding strengths and hybridization of substrate and adsorbate orbitals

The second level of description is represented by model Hamiltonians including only a limited number of electrons. The focus lies in understanding the physics involved, when atoms and molecules interact with a metal surface. The models are instructive and we be presented in the next section.

B.2. Weak and strong chemisorption

One of the most important model describing the electronic structure of adsorbates on metal surfaces, is the Newns-Anderson model [255]. It was developed in 1969 as an extension of the Anderson model. The simple form of this model considers an adsorbates with a single valence state $|a\rangle$ with energy E_a coupled to a metal surface with many $|k\rangle$ one-electron states with energy E_k forming a conduction band, and the hybridization between between the states via a coupling matrix $V_{a\vec{k}}$. The Hamiltonian can then be written:

$$H_N = \underbrace{\sum_{\vec{k}} E_k n_{\vec{k}}}_{\text{conduction band}} + \underbrace{E_a n_a}_{\text{adsorbate}} + \underbrace{\frac{1}{\sqrt{N}} \sum_{\vec{k}} \left[V_{a\vec{k}} c^\dagger_{\vec{k}} c_a + V^*_{a\vec{k}} c^\dagger_a c_{\vec{k}} \right]}_{\text{hybridization}} \tag{B.1}$$

Where $n_{\vec{k}} = c^{\dagger}_{\vec{k}} c_{\vec{k}}$ is the electron number operator, while $c^{\dagger}_{\vec{k}}$, $c_{\vec{k}}$ refer to the respective creation and annihilation operators.

The infinitely many metal states form a band, making it difficult to track them with the coupling switched on. It is however possible and instructive to follow the projection on the density of states of the adsorbate:

$$n_a(E) = \sum_m |\langle m\,|a\rangle|^2\, \delta(E - E_m) \tag{B.2}$$

by introducing the self energy $q(E)$ in a Greens's function treatment Equation B.2 can be evaluated [256] :

$$q(E) = \Lambda(E) + i\Delta(E) \tag{B.3}$$

$$\Delta(E) = \pi \sum_k \left|V_{a\vec{k}}\right|^2 \delta(E - E_k) \tag{B.4}$$

$$\Lambda(E) \propto \frac{1}{\pi} \int \frac{\Delta(E')}{E - E'} dE' \tag{B.5}$$

$$n_a(E) = \frac{1}{\pi} \frac{\Delta(E)}{(E - E_a - \Lambda(E))^2 + \Delta(E)^2} \tag{B.6}$$

$\Delta(E)$ can be regarded as a local projection of the metal states around the adsorbate.

The electronic structure of the substrate comes into play now. In a metal crystal the large number of atomic states are treated as one or several bands of states. The interaction with the adsorbate will take place mainly through the bands close to E_F. For all transition metal these can have either s or d character, the s band is broad and half filled, while the d states create a more localized narrower band (see Figure B.1). Depending on the different elements and the occupancy of the d state in position in energy varies.

These considerations lead to two easily solvable cases for Equation B.6. If we consider only the interaction with a half filled s band, the DOS only varies slightly around E_F. We can thus approximate $\Delta(E)$ to be independent from energy. For$\Delta(E) = \Delta$, Equation B.5 becomes zero and Equation B.6 describes a Lorentzian peak around E_a, with a width of Δ.

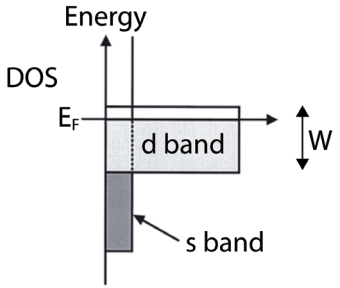

Figure B.1.: Schematics of the density of states of a transition metal: the board s band and the narrow d band around E_F are shown.

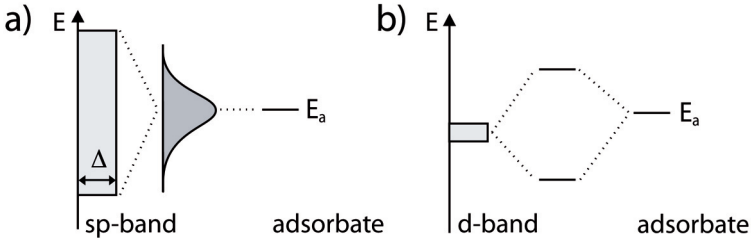

Figure B.2.: Local density of state in the Newns-Anderson model, for the two limiting cases of a) a broad energy independent $\Delta(E)$ as in sp bands and b) for a narrow d- band.

The adsorbate level is broadened by the finite lifetime of an electron in the adsorbate state. This is called weak chemisorption (see Figure B.2a).

In the other case, the interaction with a narrow d band, the width of the band is smaller than the coupling matrix elements $V_{a\vec{k}}$, which effectively reduces the system to a two level problem. The solution to which is the formation of a sharp bonding and an antibonding state, above and below the two states (see Figure B.2b). This kind of interaction is called strong chemisorption.

B.3. The role of the d-band: Atomic adsorption

In real transition metal systems the hybridization of the adsorbate states will be a combination of these two limiting cases. A good, and well studied, model system is the ordered p(2x2) adsorption of O atoms on a Pt (111) surface[257]. The main interaction between adsorbate and surface takes

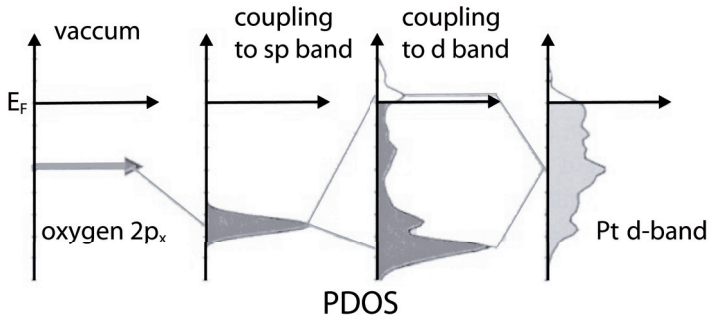

Figure B.3.: The change in electronic structure of oxygen atom upon adsorption on metal surfaces. The interaction with the sp band of the metal broadens the gas phase atomic states and shifts them down. Then these resonances interact with the narrow d band forming covalent bonding and antibonding states below and above the initial adsorbate and metal states. The coupling to the metal d electrons can roughly be viewed as a two-level coupling. The projected DOS are from the self-consistent calculations [256].

place through the valance states of both. In Figure B.3 the schematics of the effect of the adsorption on the DOS are demonstrated. The oxygens $2p_x$ valence state lie below E_F, so all them are completely filled. One can think of the hybridization between the O state and the Pt as a two step process. The coupling to the broad sp band, broadens the adsorbate state and shifts it down in energy. When the coupling to the narrow d band is considered the adsorbate state and the d-band form a bonding and antibonding state above and below the original states. The resulting strength of the bonding has two contributions, one from the s band and an additional one from the d bands. The impact of the d band hybridization depends on the filling, width, and band center E_d of the band. These parameters are intertwined as shown in Figure B.4a. We will focus on the position of the band E_d to reveal the underlying dependencies .

The effect of E_d on bond strength becomes clear, if one moves left in periodic table from Cu, Ag or Au. The position of the d band shifts upward in energy (see Figure B.4b). This means that the anti bonding states created by the hybridization with the adsorbates will shift up, cross E_F and becomes unoccupied, effectively strengthening the bond . If the d band is, however, further down the antibonding states will be (partially) below E_F and therefore occupied, weakening the bond strength. Another effect is important when determining the bond strength. The Pauli principle

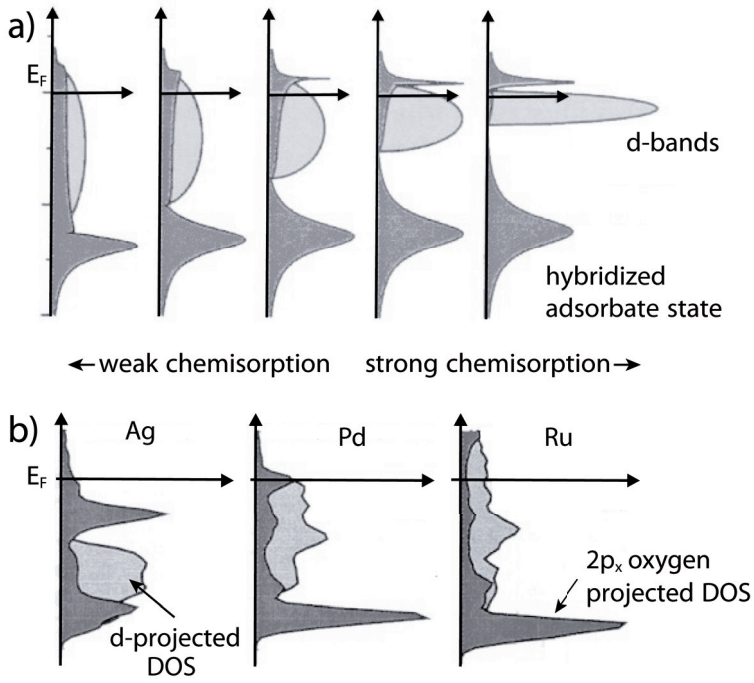

Figure B.4.: Strong to weak chemisorption: a) Schematics of the DOS projected onto an adsorbate state interacting with the d bands illustrating the effect of the d band width, position, and position. Strong chemisorption occurs when the antibonding state is strongly pronounced above E_F. The strength of the adsorbate–surface coupling matrix element V is kept fixed as the center of the d bands E_d is shifted up towards E_F and the width W of the d bands is decreased to keep the number of electrons in the bands constant. The light shaded areas refer to the d band before adsorption. Adapted from [257]. b) Calculated LDOS for atomic O on various metal surface, projected onto the oxygen 2px state (dark-shaded area) for atomic oxygen 1.3Å above close-packed surfaces of late transition metals. The light-shaded show the corresponding metal d-band projected DOS before the adsorption of oxygen. From [256].

states that no two electrons can occupy the same state. This leads to another contribution that weakens the bond strength. The adsorbate and the substrate orbitals have to be orthogonal to each other. This depends on the metal, the adsorption geometry and the adsorbate. To put an example this effect is very strong for Au as it is 5d transition metal. The 5d orbitals extend further than e.g. 3d, creating a huge overlap between orbitals of the substrate and the adsorbate. The Pauli repulsion energy will thus be higher for 5d metal than for 3d, as can be seen by the fact that Au has a very noble, inert surface.

B.4. Molecular adsorption

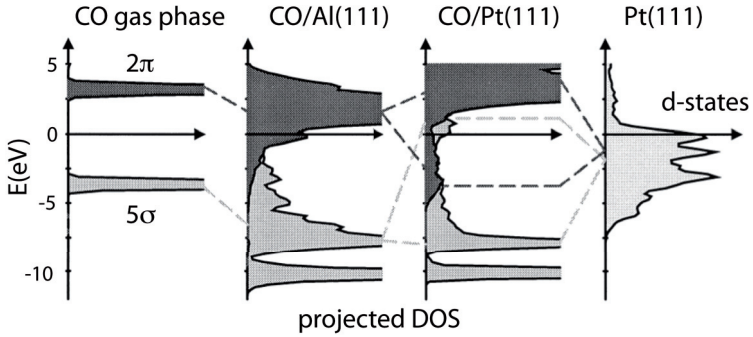

Figure B.5.: Molecular adsorption of CO: Calculated LDOS projected onto the 5σ and $2\pi^*$ orbitals of gas phase CO, and CO adsorbed on a Al(111) or a Pt(111) surface. The gas phase molecular states broaden into resonances and shift down in energy on the simple Al(111) metal surface (intermixing with the 4σ state causes the additional peak in the 5σ resonance). On the transition metal surface the CO resonances further hybridizes with d states, creating a bonding and an antibonding state for both the 5σ and the 2π molecular orbitals. Also shown is the DOS from the d bands in the Pt(111) surface. Adapted from [258].

The adsorption of molecules is only slightly more complex. Usually more than one adsorbate state interacts with substrate. A good example for small molecules is CO, which has been suggested to couple mainly through the filled 5σ and the doubly degenerate empty $2\pi^*$ states [257]. We consider this molecule in the same framework as atomic adsorbates. Figure B.5 shows the resulting hybridization of the molecular states for

CO adsorbed on a simple metal Al(111) and a transition metal Pt(111). For Al(111) the interaction is mainly with the s bands and again the molecular levels are broadened and shifted down. For the transition metal additionally the interaction with the d bands gives rise to bonding and antibonding states below and above the two original states. This splitting of the two adsorbate levels can be treated independently, because due to the different symmetries the 5σ and $2\pi^*$ interact with different d orbitals. Several observations can be made from the DOS of CO on Pt(111).

The contribution of the 5σ orbital to the bonding is small, because only a few antibonding states lie above the Fermi level. Adding the Pauli repulsion makes this interaction repulsive (Van Santen, R. A., and Neurock, M., Catal. Rev.—Sci. Eng. 37, 557 (1995)).

On the other hand the $2\pi^*$ orbital gives rise to a strong attractive interaction. This is because the $2\pi^*$ state was above E_F before the adsorption, and the new hybridized bonding state lies completely below the Fermi level. Note this mechanism is very solid and even for noble metals an attractive $2\pi-$ d interaction occurs.

This model does include a charge transfer from the substrate to the molecule, the 5σ state, which was completely filled in the gas state is now partially above E_F, in contrast the $2\pi^*$ state has shifted down and is now partially occupied. This picture is reaffirmed by the commonly used model by Blyholder [259] for the CO–metal bond: the CO 5σ to donates an electron to the metal and a receives a back-donation from the metal to the CO $2\pi^*$.

All these considerations are valid even for larger molecules, however several additional aspects are important to point out. The complexity of the interaction between molecule and substrate does not always leave the molecule in its gas form and conformational changes can occur [260]. On the other hand reconstruction of the surtface near molecular adsorption sites has been reported [261, 262, 263]. Naturally these changes affect the electronic structure of the molecule. Therefore to determine the resulting electronic structure one has to consider the whole system: Molecule and substrate, which is quite a formidable task for larger molecules.

B.5. Van der Waals forces

The other type of adsorption mentioned before was physisorption. This involves a different kind of interaction between the surface and the adsor-

bate: van der Waals forces. These kind of interaction is especially common for non-polar gases and liquids, and is responsible of the adsorption of closed shell molecules like CH_4or N_2. Furthermore many self assembled monolayer structures are based on the interplay between the molecule-substrate forces and molecule-molecule van der Waals interaction. The term vdW summarizes three types of interactions: Firstly the attraction of parallel aligned dipoles [264], secondly polar molecules temporarily induce image dipoles in the surface charge distribution which causes an attractive interaction for aligned dipoles. And lastly the London forces arising form electron fluctuations in molecules. These fluctuations create temporary dipole moments, which average out in short time interval. Nevertheless such time-varying dipoles induce image dipoles in the surface, resulting in a net attractive force. These forces are present even for completely non-polar molecules.

The attractive van-der-Waals energy for an adsorbate on a surface depends on the adsorbate-surface distance R [264]:

$$E_{att} = -c_1 R^{-3} \tag{B.7}$$

c_1 is a product of two dipole moments, the adsorbate's and the image dipole inducing in the substrate. Naturally the polarizability of the molecule influences its dipole moment.

If the molecule is very close to the surface, the Pauli repulsion between overlapping filled orbitals becomes important, giving rise to repulsive forces [264]:

$$E_{rep} \approx n(R) = c_2 e^{-c_3 R} \tag{B.8}$$

where n(R) is the charge density of the surface that decays exponentially into the vacuum, and c_2 and c_3 are constants. The van-der-Waals interaction energy E_{vdW} is hence given by

$$E_{vdW} = c_2 e^{-c_3 R} - c_1 R^3 \tag{B.9}$$

The physisorption potential is thus characterized by a minimum a few Ångström from the surface. Usually E_{vdW} for noble gases and small gaseous molecules is in the order 0.01–0.1 eV, mainly depending on the polarizability of the adsorbate. Larger molecules however have a large contact area to the surface and the single van der Waals contributions add up and may lead to a strong overall bonding.

For interactions between molecules, on the other hand, the situation is different. The field E of a dipole which induces a dipole moment in an adjacent molecule, decays as R^{-3}. The overall interaction energy decays like $E_{att} \propto -R^{-6}$ [265].

Nomenclature

E_F	Fermi level
DFT	Density Functional Theory
GGA	Generalized Gradient Approximation
HOMO	Highest Occupied Molecular Orbital
LDA	Local Density Approximation
LDOS	Local Density Of States
LEED	Low Energy Electron Diffraction
LUMO	Lowest Unoccupied Molecular Orbital
MePc	Metal Phthalocyanines
MO	Molecular Orbital
N_a	aza-Nitrogens
N_p	pyrole-Nitrogen
NDR	Neagtive Differential Resistance
NRG	Numerical Renormalization Group
Pc	Phthalocyanine
PDOS	Projected Density of States
STM	Scanning Tunneling Microscopy
STS	Scanning Tunneling Spectroscopy
TM	Transition Metal
UHV	Ultra High Vacuum (p< 10^{-9} mBar)
vdW	van der Waals

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1. C. Krull, A. Mugarza, and P. Gambardella. "**Controlling the Kondo interaction of Fe adatoms on Ag(100) through organic molecules**". in preparation

2. C. Krull, A. Mugarza, and P. Gambardella. "**Evolution of the electronic structure for CuPc on Ag(100) as a function of coverage: from clusters to multilayers** ". in preparation

3. C. Krull, R. Robles, A. Mugarza, and P. Gambardella. '**Atom by atom doping in metal-organic molecules: manipulating charge and spin**". to be submitted

4. A. Mugarza, R. Robles, C. Krull, R. Korytar, N. Lorente, S. Stepanow, and P. Gambardella. "**Electronic and magnetic properties of molecule-metal interfaces: transition metal phthalocyanines adsorbed on Ag(100)**". *Physical Review B*, 85(15):155437, April 2012. doi:10.1103/PhysRevB.85.155437.

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