

Chemisorption

František Máca

VIII.

NEVF 514 Surface Physics

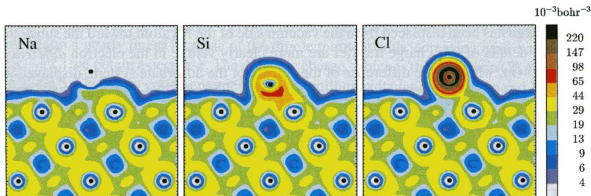
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Chemisorption

The knowledge of chemisorption phenomena requires the determination of

- ▶ the geometrical structure of the system (*adsorption site, bond length, ...*),
- ▶ the adsorption binding and diffusion activation energy,
- ▶ the charge transfer,
- ▶ the electronic structure of the adsorbate and substrate,
- ▶ vibration frequencies, ...

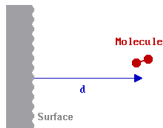


Electron density (valence only) for three different adatoms on an Al(111) substrate. From Bormet et al., 1994.

Potential energy curves and energetics of adsorption

A single molecule approaching a clean surface

Simple model: The energy of the system E is a function only of the distance d of an adsorbate from a surface i.e. $E = E(d)$

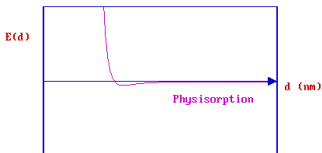


We neglect

- ▶ the angular orientation of the molecule
- ▶ changes in the internal bond angles and bond lengths of the molecule
- ▶ the position of the molecule parallel to the surface plane

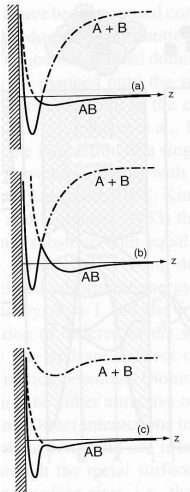
Physisorption (e.g. Ar / metals)

In the case of pure physisorption , the only attraction between the adsorbing species and the surface arises from weak, **van der Waals** forces.



There is no barrier to prevent the molecule from approaching the surface, i.e. the process is not activated and the kinetics of physisorption are very fast.

Molecular chemisorption



Three different state configurations: a) dissociative chemisorption, b) dissociative chemisorption with a physisorbed precursor, c) molecular chemisorption.

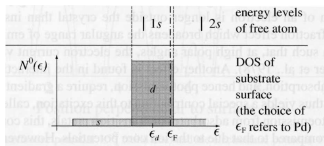
From Lennard-Jones, 1932.

If chemical bond formation between the adsorbate and substrate can also occur, the **$E(d)$** curve is dominated by a much deeper chemisorption minimum at shorter values of **d** .

The depth of the chemisorption well is a measure of the strength of binding to the surface.

Molecule - initially being completely isolated from the surface (very large **d**) - can also be dissociated in isolated atoms.

Adsorbate - substrate interaction



H on transition metal surface (Pd).

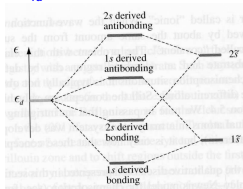
Interaction with broad s-band: $\epsilon_i \rightarrow \tilde{\epsilon}_i$ energy level shifting and broadening

- ▶ a shift caused by charge transfer at the adatom
- ▶ a shift (surface \longleftrightarrow bulk, selfinteraction)

Interaction with narrow d-band: splitting

bonding: $\psi_b \approx \phi_{H1s} + \phi_{Pd4d}$

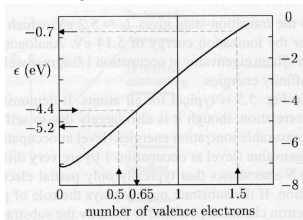
antibonding: $\psi_a \approx \phi_{H1s} - \phi_{Pd4d}$



A selfconsistent treatment is crucial for calculation of adsorbate-substrate interaction!!

Left: the d -band-center energy of the clean surface. Right: the *renormalized energy levels* of the free atom (i.e. after interaction with the s -band, but before interaction with the d -band). Middle: the resulting bonding and antibonding H $1s$ - and H $2s$ -derived levels on adsorption.

Energy level and its occupation



Kohn-Sham energy level (DFT-LDA) of the 3s-state of Na as function of the number of valence electron: $f_{3s} = 0$ is the Na^+ ion, $f_{3s} = 1$ the neutral atom, and $f_{3s} = 2$ the Na^- ion. For $f_{3s} = 0.5$ the eigenvalue gives the ionization energy (≈ 5.2 eV). Fermi level of Al(001) is 4.4 eV, the electron affinity ≈ 0.7 eV. [From Horn and Scheffler, 2000.](#)

Ionization energy:

$I_k \equiv$ total energy difference of the neutral atom and the positive charged ion

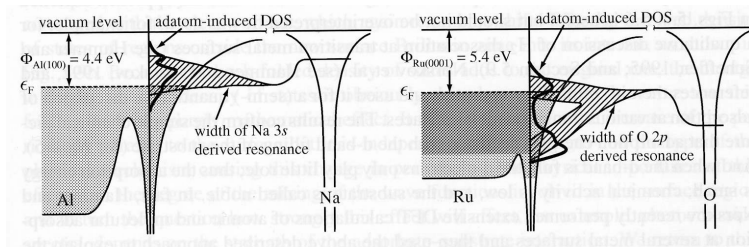
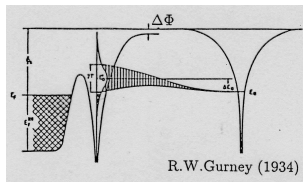
$$I_k = E^{N-1} - E^N = \int_N^{N-1} \frac{dE^{N'}}{dN'} dN' = - \int_0^1 \epsilon_k(f_k) df_k \approx -\epsilon_k(f_k = 0.5)$$

Afinity energy:

total energy difference of the negatively charged ion and the neutral atom

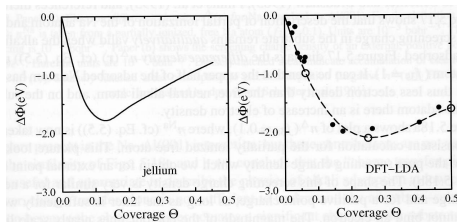
- ▶ electron-electron correlation is very important
- ▶ Kohn-Sham eigenvalue \neq measurable ionization energy
- ▶ selfinteraction (artefact LDA) is important in small systems (atom, cluster)
- ▶ E_F is fixed by the substrate (an electron reservoir)

Atomic energy level and its occupation



The adsorbate-induced change in the density of states as a function of distance. Left: Na on Al(001). Right: O on Ru(0001)

Work function and screening



Change in work function with increasing coverage. Left: Results of Lang (1971) using a jellium on jellium model with parameters corresponding to Na on Al(001). Right: DFT-LDA calculations (open circles) for periodic Na adlayers on Al(001). Experimental results from Porteus (1974) and Paul (1987).

Langmuir-Gurney model (1932-4)

- ▶ positively charged adatom induces a negative screening charge density in the substrate surface
 \Rightarrow an adsorbate-induced dipole moment $\mu \Rightarrow$ reduction in the work function Φ with the increase of the coverage Θ

$$\Delta\Phi_{ads} = \Theta \cdot \mu(\Theta)$$

- ▶ increasing coverage \rightarrow adsorbate-adsorbate distance decreases i.e. electrostatic repulsion increases to weaken the repulsion the depolarisation takes place

Classical electrostatics: point charge at a distance d

at small distances ($\lesssim 3 \text{ \AA}$) breaks down

metallic screening is still important

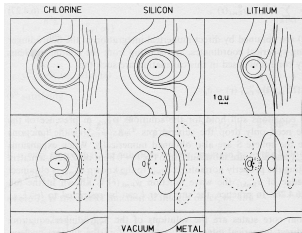
Atomic chemisorption on jellium surface

Model: Semiinfinite jellium + an adatom at a distance d from the edge of the positive background.

Solving the Schrödinger equation at the surface

$$\begin{aligned} \text{density} &\longleftrightarrow \text{potential} & E &= E[\rho^-(\vec{r})] \\ &[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\rho^-, \vec{r}_{||}, z)]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \\ E &= \sum_{i \text{ occ}} \epsilon_i ; & \rho^-(\vec{r}) &= \sum_{i \text{ occ}} |\psi_i(\vec{r})|^2 \end{aligned}$$

- ▶ the perturbing potential ($V_{\text{eff}} - V_{\text{eff}}^0$) is short-ranged due to metallic screening.



Contours of constant charge density for Cl, Si, and Li atoms on a jellium substrate ($r_s = 2$ a.u.) Upper row: total charge density. Center row: variation of charge density. Solid (dashed) curves denote a surfeit (depletion) of electron. Bottom row: bare metal electron density profile. From Wilke and Scheffler, 1996.

Calculation scheme - Green function formalism

- ▶ Step 1: Calculate Green's function \mathbf{G}_0 of a reference system
- ▶ Step 2: Solve Dyson's equation

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0 \Delta \mathbf{V}[\rho] \mathbf{G}$$

with $\Delta \mathbf{V}$ localized within a bounded region

Green function primer

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

$$\hat{H} = \hat{H}_0 + \Delta V$$

$$\hat{G}(E - \hat{H}) = (E - \hat{H})\hat{G} = \hat{1}$$

$$\hat{H}_0 \longrightarrow \hat{G}_0 \quad \hat{H} \longrightarrow \hat{G}$$

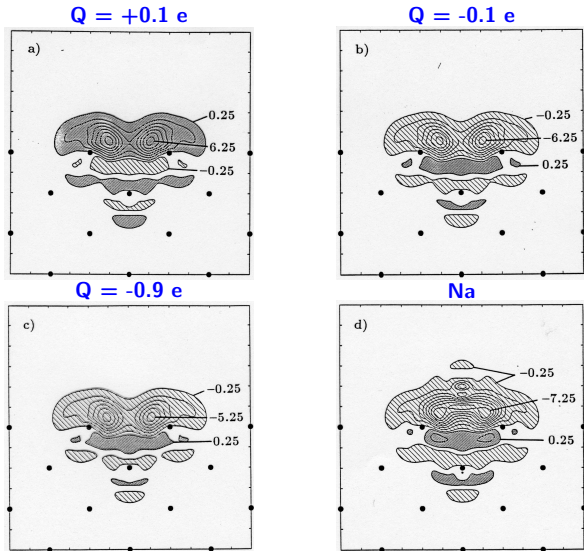
$$G^+(\vec{r}, \vec{r}'; E) = \sum_n \frac{\psi_n(\vec{r})\psi_n^*(\vec{r}')}{E + i\delta - E_n}$$

$$n(\vec{r}; E) = -\frac{1}{\pi} \text{Im} G^+(\vec{r}, \vec{r}; E)$$

$$\rho(\vec{r}) = \int_{-\infty}^{E_F} n(\vec{r}; E) dE$$

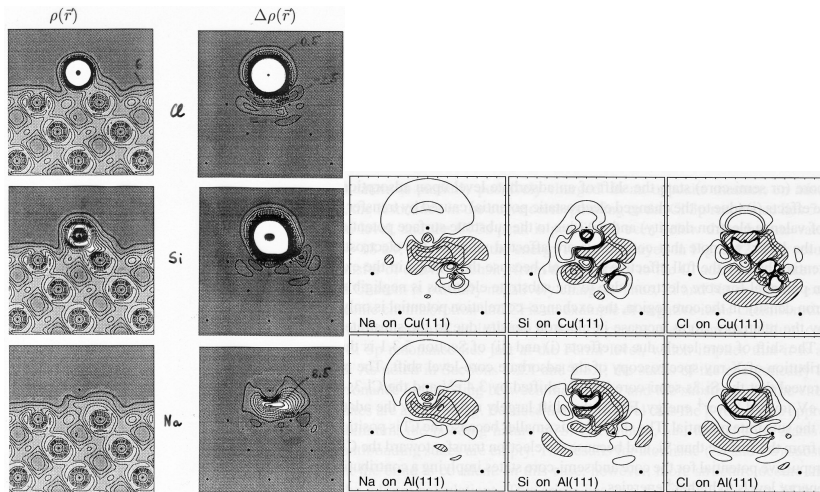
$$\left(\frac{\hbar^2}{2m}\Delta - V(\vec{r}) + E\right)G^+(\vec{r}, \vec{r}'; E) = \delta(\vec{r} - \vec{r}')$$

Charge transfer between the adatom and the substrate



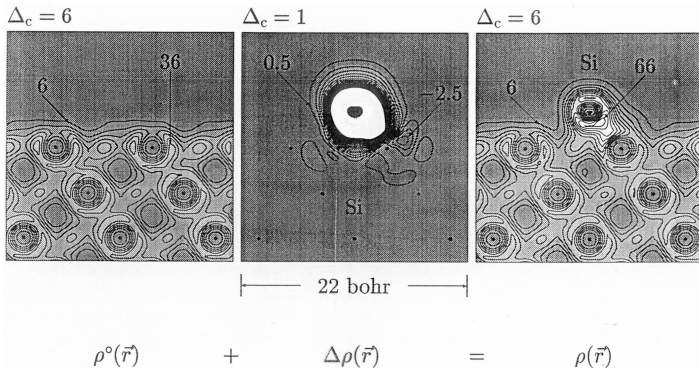
The charge density change induced by a point charge Q in the distance of 1.88 bohr above the surface [Scheffler, *Physica B*, 1991].

Chemisorbed atoms on metallic surfaces

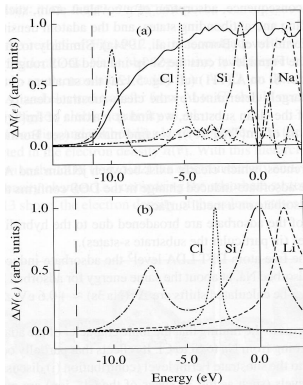


Electron valence density and electron difference density for three different adatoms on an Al or Cu substrates. From Yang et al., 1994 and Bormet et al., 1994.

Covalent binding of Si on Al(111)



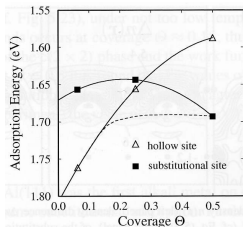
Adsorption of isolated adatoms



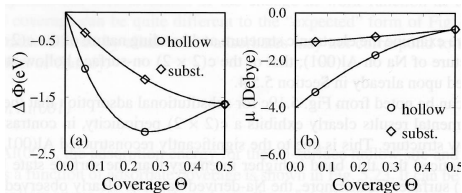
a) Adsorbate-induced change of the density of states for three different adatoms on the Al(111) substrate and b) on jellium with an electron density corresponding to Al. The dashed line indicates the bottom of the band of the substrate.
From Bormet, 1994 (top) and Lang and Williams, 1978 (bottom).

- Na, Cl - excellent agreement with the induced DOS on jellium
- Si - interaction with substrate splits the Si 3p induced resonance into occupied bonding and empty antibonding states

Na on Al(001)



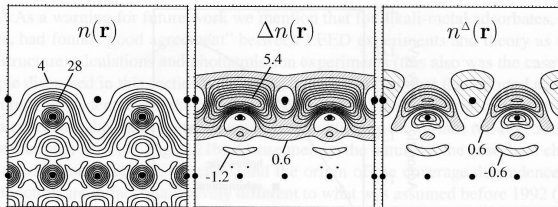
Adsorption energy versus coverage for Na on Al(001) in the on-surface hollow site and in the surface substitutional site. From Stampfl and Scheffler, 1995.



Change in work function $\Delta\Phi$ and surface dipole moment μ as a function of coverage for Na in the substitutional (diamonds) and on-surface hollow sites (circles) for Na on Al(001). From Stampfl and Scheffler, 1995.

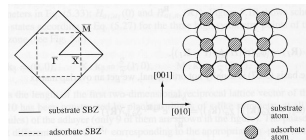
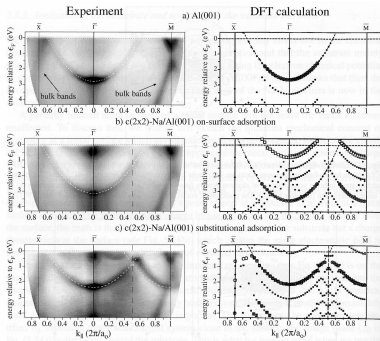
$$\Delta n(\mathbf{r}) = n(\mathbf{r}) - n^0(\mathbf{r}),$$

$$n^\Delta(\mathbf{r}) = n(\mathbf{r}) - n^0(\mathbf{r}) - n^{Na, f_{3s}}(\mathbf{r})$$

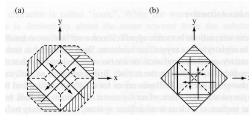


Total valence electron density $n(\mathbf{r})$ (left panel), density difference $\Delta n(\mathbf{r})$ (middle panel) and the difference density $n^\Delta(\mathbf{r})$ for $f_{3s} = 1$ (right panel), of the substitutional geometry of the Na/Al(001) adsorbate system at $\Theta = 0.5$. From Stampfl, 1998.

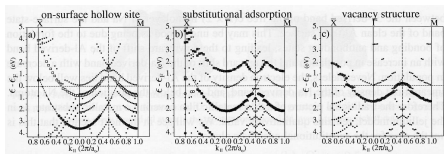
Surface band structure



The surface Brillouin zones and real-space lattice of a $c(2 \times 2)$ adlayer on an $fcc(001)$ surface.



The relation between the surface Brillouin zone (full line) and the projection of the bulk Brillouin zone of an fcc substrate onto the 001 surface (broken line).



Surface band structure of $c(2 \times 2)$ Na on $Al(001)$ for a) on-surface adsorption, b) substitutional adsorption, c) the vacancy structure. Squares and circles represent Na- and Al-derived bands, respectively. [From Stampfl, 1998.](#)

Chemical reactions on metal surfaces

dissociation, oxidation, poisoning, promoters, catalysis

Reactivity = ability to break bonds of an approaching molecule and to adsorb the fragments

MODEL for **dissociation of H_2** (simplest chemical reaction)

A molecular beam (molecules in well defined states) is sent toward the surface

The probability of dissociation is given by

- ▶ energetical "path" \iff energy minimization principle
- ▶ statistical average over many trajectories

\iff different boundary conditions

\implies active sites at the surface, reflectivity of the surface, ...

Proper treatment of the dynamics is crucial for the realistic description!

Classical dynamics (Newton's eqs.) but the forces acting on the atoms from DFT:
ab initio molecular dynamics Carr & Parrinello (1985)

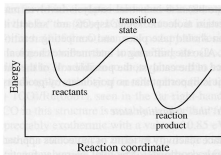
$H_2 \rightarrow$ surface (surface atoms don't move)

two H atoms in 6-dim configuration space (rotation, translation)

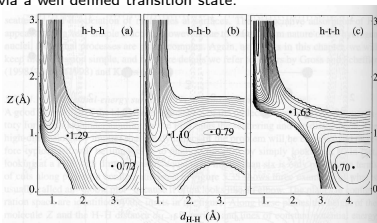
\implies **12 dimensional configuration space**

Energetics of a chemical reaction is complex and difficult to calculate!

Transition state



Energetics of a chemical reaction in which reactants (their energy is of the left minimum) reach the reaction product (energy of the right minimum) via a well defined transition state.



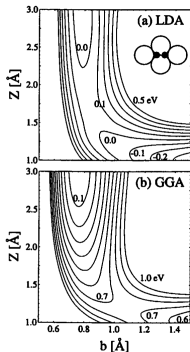
Cut through the six-dimensional potential energy surface (**PES**) of an H_2 molecule above of $\text{Ag}(001)$. We display plots where Z is the height of the H_2 center of mass over the surface, and $d_{\text{H-H}}$ is the distance between the two hydrogen atoms. From Wilke and Scheffler, 1996.

Potential energy surface:

- ▶ high dimensional surface → complicated
- ▶ no statistical treatment, no dynamics of the atoms
- ▶ ? selfinteraction in LDA (small system!)

FIRST STEPS TOWARDS REALISTIC DESCRIPTION

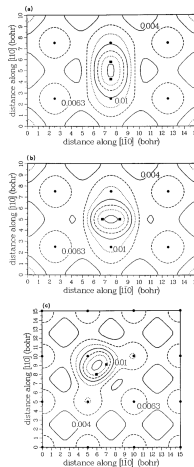
Dissociative chemisorption



←
Activation energy barrier for dissociation calculated in GGA is in better agreement with experiment as LDA results (too small!!!)



The bridge-to-bridge orientation is energetically favored (three Rh atoms are involved).



Charge contour plots in electrons/ a_0^3 in a plane 2.98 a_0 above the outer Rh nuclei (heavy dots) for three different $H_2/Rh(001)$ orientations with the H nuclei at 3.98 a_0 (heavy squares). (a) A top-to-top molecular orientation, (b) hollow-to-hollow bonding, and (c) bridge-to-bridge case. From Feibelman (1991).

Non bonding interactions

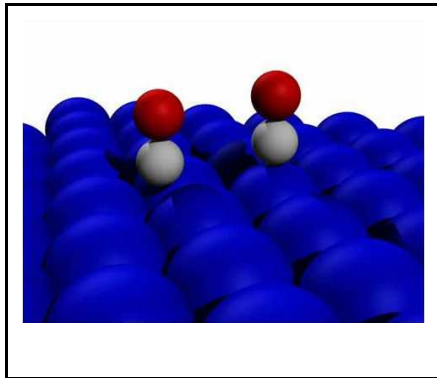
Types

- ▶ Hydrogen-Bonded systems
- ▶ Charge-Transfer systems
- ▶ Dipole-Interacting systems
- ▶ Weak Interactions (VdW, ...)

There are systems where special care is recommended.

Failure of present-day xc-functionals

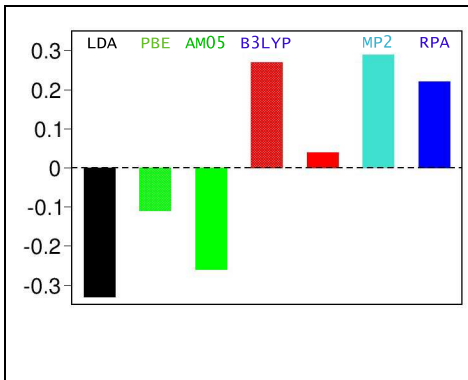
CO adsorption on transition metal surfaces:



LDA and GGA functionals dramatically fail to predict the correct adsorption site. For low coverage the theory predicts **the hollow site** but the experimentally CO adsorbs **on top** (e.g. CO on Cu(111) the LDA error is ≥ 0.4 eV, and the GGA error is ≥ 0.2 eV).

Hybrid functionals and RPA corrections

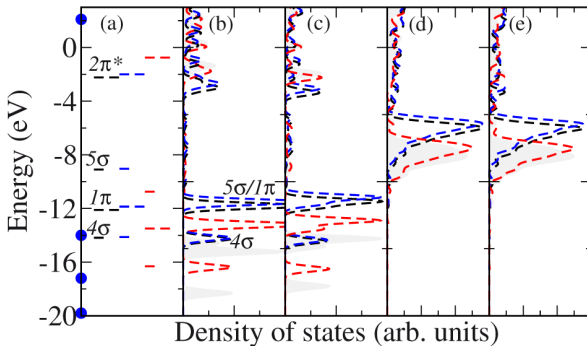
CO adsorption on the Cu(111) surface:



$E^{\text{fcc}} - E^{\text{top}}$ in eV. Wrong preference for the hollow site in LDA and GGA (PBE, AM05) corrected by hybrid functionals and RPA.

CO on the Cu(111) surface

Orbital-energy levels and DOS of CO molecule on Cu(111)



LDA (black dash lines), PBE (blue dashed lines), PBE0 (red dashed lines)

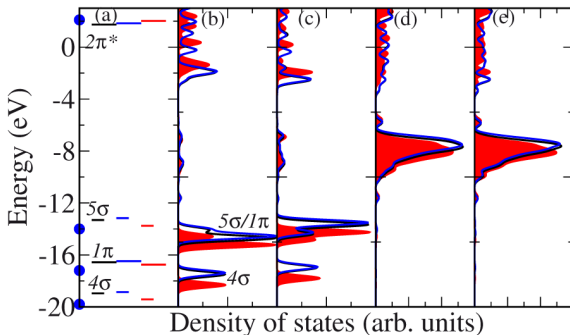
(a) Free CO molecule: experimental orbital energy levels are marked by blue circles.

(b,c) CO/Cu₁₆: DOS projected on the CO orbitals on the top site and on the hollow site.

(d,e) CO/Cu₁₆: DOS projected on the Cu orbitals on the top site and on the hollow site.

CO on the Cu(111) surface

Orbital-energy levels and DOS of CO molecule on Cu(111) calculated with G_0W_0 - self-energy included



LDA (black solid line), PBE (blue solid line), PBE0 (red solid line)

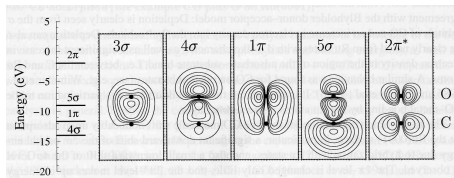
(a) Free CO molecule: experimental orbital energy levels are marked by blue circles.

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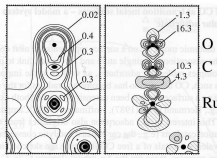
(d,e) CO/Cu₁₆: DOS projected on the Cu orbitals on the top site and on the hollow site.

Self-interaction error is reduced substantially already in the ground-state calculation (G_0W_0).

Adsorption of CO at transition metal surface



Electron density of the valence molecular orbitals of a free CO molecule and their DFT-GGA Kohn-Sham eigenvalues (far left) with respect to the vacuum level. The small black dots indicate the position of the C and O atoms, respectively.



first-principle calculations support donor-acceptor Blyholder model, the bonding is more complicated

Valence electron density (left) and *difference density* $n^{\Delta}(\mathbf{r})$ for the adsorption of CO in the top site on Ru(0001). Units are bohr^{-3} in the left panel and $10^{-3} \text{ bohr}^{-3}$ in the right panel.

Concept of frontier orbitals: HOMO LUMO

strongest interaction occurs for an overlap between occupied and unoccupied orbitals

- ▶ electron transfer from **Highest Occupied Molecular Orbital** (5σ)
- ▶ electron transfer into **Lowest Unoccupied Molecular Orbital** ($2\pi^*$)

Catalytic oxidation of CO

simple prototype system of a surface heterogeneous catalytic reaction

- ▶ molecular adsorption **or** dissociative adsorption
- ▶ surface diffusion, surface reaction
- ▶ desorption of products

CO on Ru(0001) - example high-dimensional PES

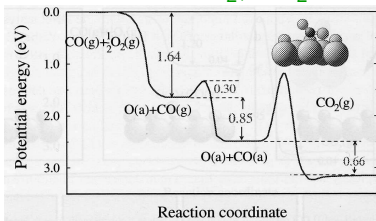
1) $\text{CO} + \text{O}/\text{Ru}(0001)$ (Eley-Rideal mechanism)

1ML O adsorbed on Ru, CO can not adsorb

2) $\text{CO} + \text{O}/\text{Ru}(0001)$ (Langmuir-Hinshelwood mechanism)

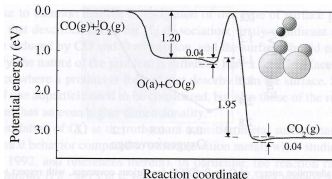
vacancies in the $(1 \times 1)\text{O}$ adlayer on Ru:

CO adsorbs, reacts $\text{CO} + \text{O} \rightarrow \text{CO}_2$, CO_2 desorbs

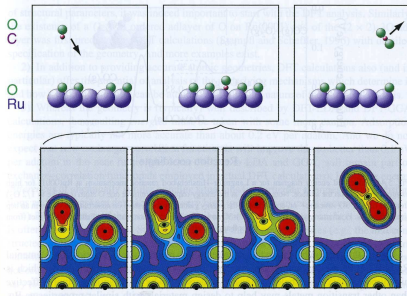


Calculated energy diagram for a Langmuir-Hinshelwood reaction mechanism at Ru(0001) for high oxygen coverages on the surface. The transition state is indicated in the inset. [From Stampf and Scheffler, 1999.](#)

Co oxidation at Ru(0001)



Energy diagram for a scattering reaction of gas-phase CO (Eley-Rideal mechanism) with an adsorbed O atom of the 1 ML phase on Rh(0001). The geometry of the transition state is indicated in the inset.



Snapshots of the Langmuir-Hinshelwood reaction (top panel) of CO oxidation at Ru(0001). The bottom panels display the electron density distribution along a reaction path close to the transition states. The units are bohr^{-3} .

Scheffler and Stampfl in Handbook of Surface Science, Vol. 2: Electronic Structure, Elsevier, 2000.

Surface - a DFT laboratory

- ▶ Density-functional theory is an important tool for analyzing surface geometries.
- ▶ DFT calculations offer the potential of analysis the underlying mechanisms which determine if and how a certain geometry can be attained and what the nature of the chemical bond is.
- ▶ Geometry is (typically) well described by DFT-LDA/GGA calculations, the resulting energies must be taken with some more caution. Adsorption energies are typically not more accurate than ≈ 0.2 eV/atom.
- ▶ Energy differences of chemically similar bonding situations (in particular energies of small distortions and phonons) are described with very well (possibly even meV) accuracy.
- ▶ The correlation between local-coordination and bond-strength, as noted for molecules by Pauling, appears to be fulfilled for adsorbates. The energy per atom scales roughly proportional to the square root of the coordination.
- ▶ A metal surface attempts to reach charge neutrality on a rather short length scale. In fact, typically a perturbation is even slightly over-screened on the length scale of the nearest-neighbor distance and then the induced electron density is slowly decaying in an oscillatory manner.

Scheffler and Stampfl in Handbook of Surface Science, Vol. 2: Electronic Structure, Elsevier, 2000.