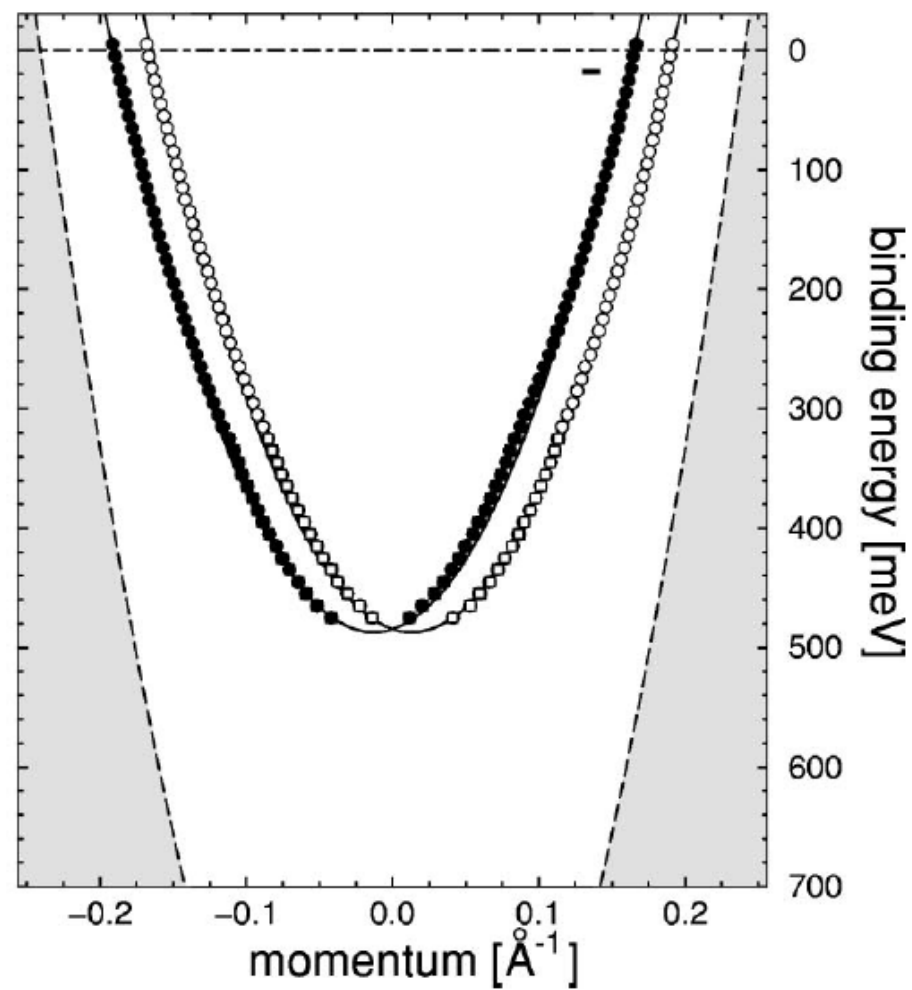
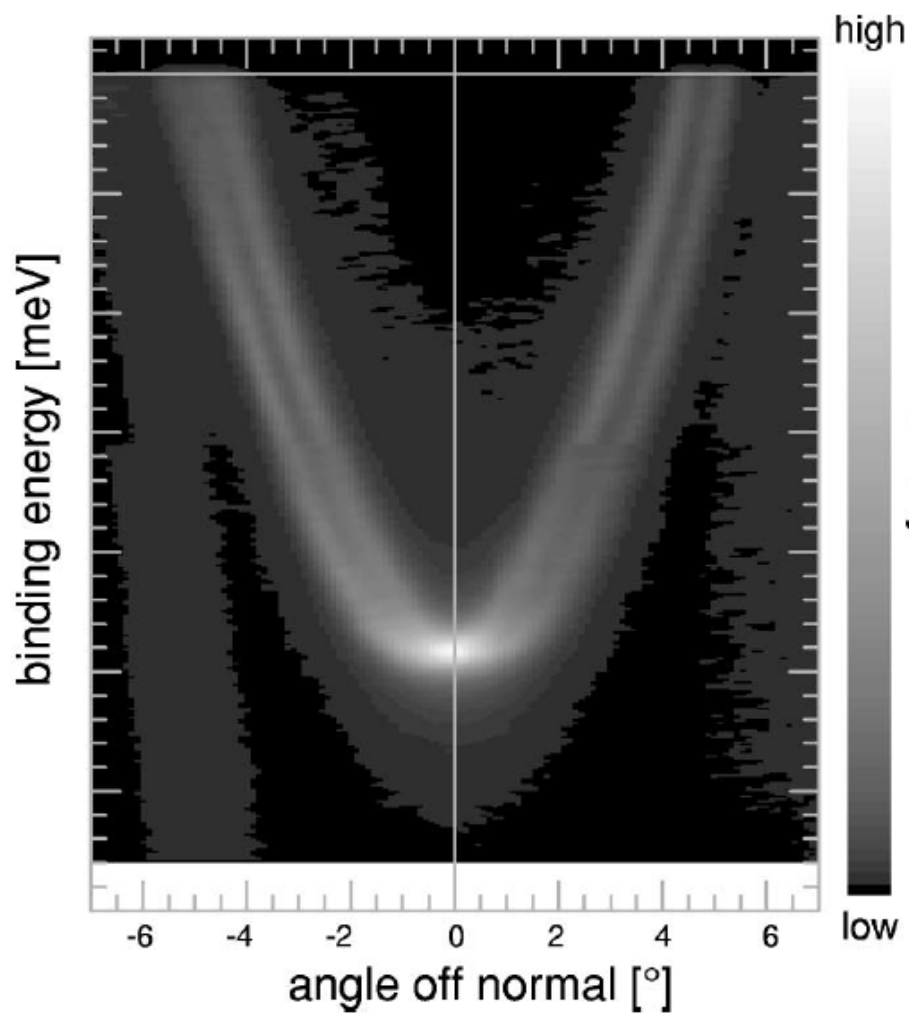




# Au(111) surface state



relativistic correction to Schrödinger equation:

PRL **77**, 3419 (1996)

$$H_{\text{SOC}} = (\hbar/4mc^2) (\nabla V \times \vec{p}) \cdot \vec{\sigma}$$

$V$ : external potential,  $p$ : momentum,  $\sigma$ : Pauli spin operator

approximately proportional to:  $\vec{L} \cdot \vec{S}$  **SOC**

→ spin degenerate levels may be spin split by SOC

but: forbidden for systems inversion symmetry

crystal surface breaks this symmetry!

Au(111):

Fermi surfaces and (one half of) the surface Brillouin zone.

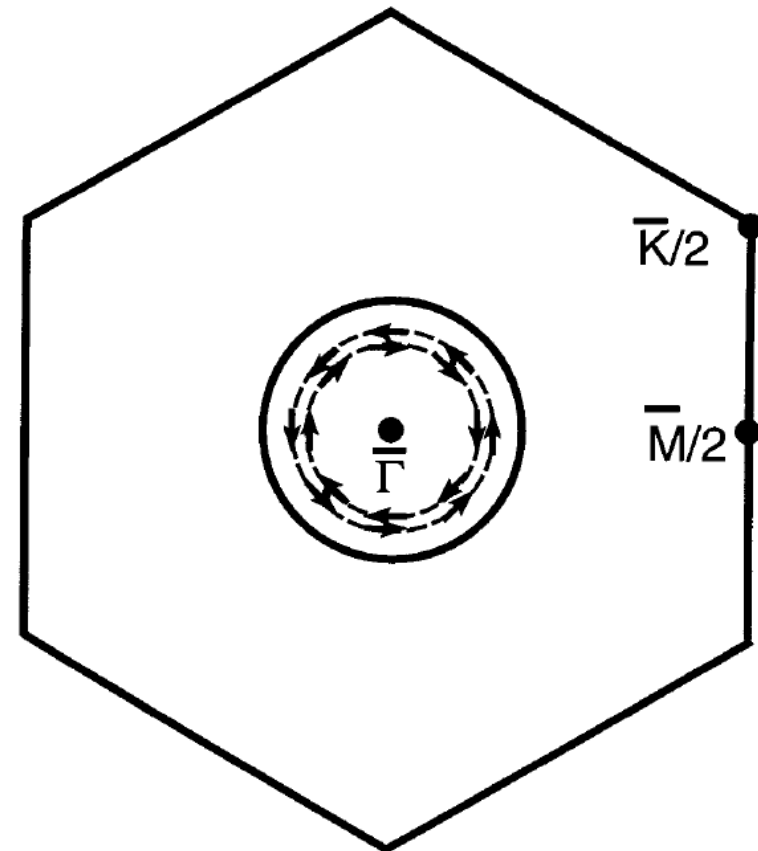
Arrows and dashed lines indicate spin orientations

Solid line represents the bulk Fermi surface neck.

All spins are in the plane of the surface.

At the surface:  $k_F = -0.153, 0.177 \text{ \AA}^{-1}$ ,  $M = 1.26 \text{ \AA}^{-1}$ .

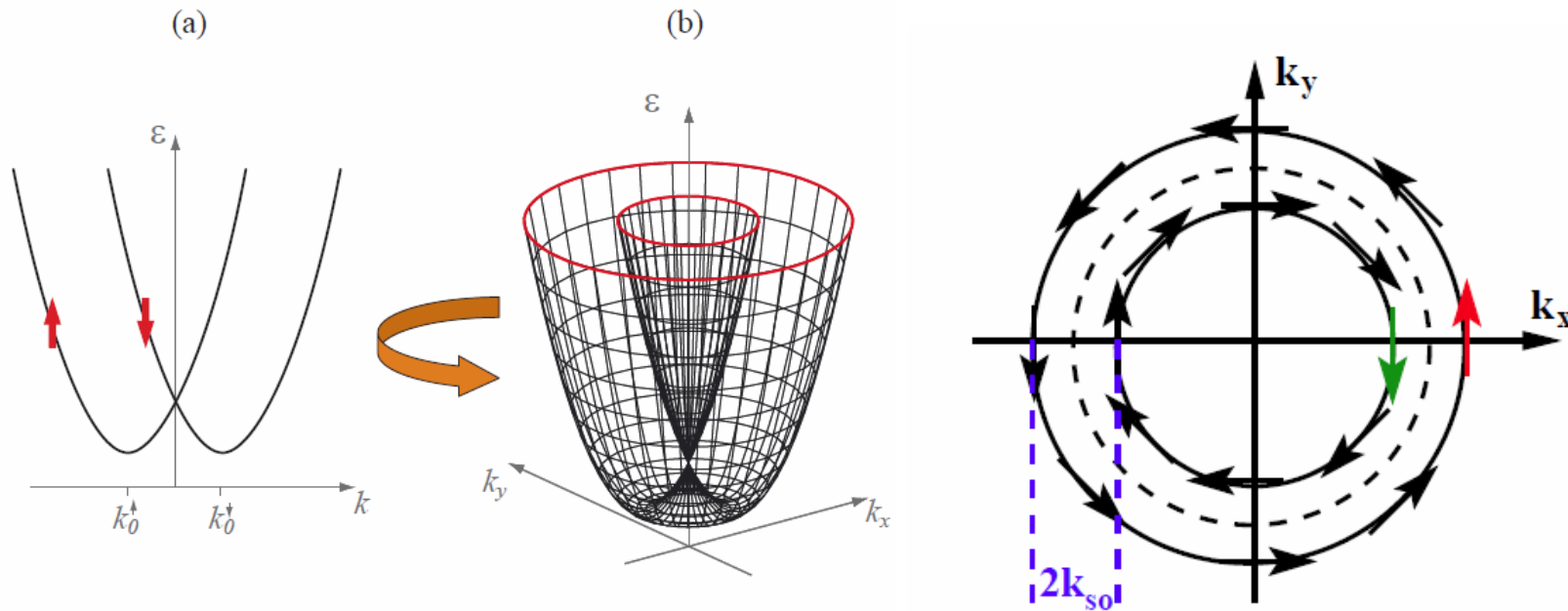
In the bulk:  $k_F = -0.216 \text{ \AA}^{-1}$ .



# SIA: Rashba-Effekt

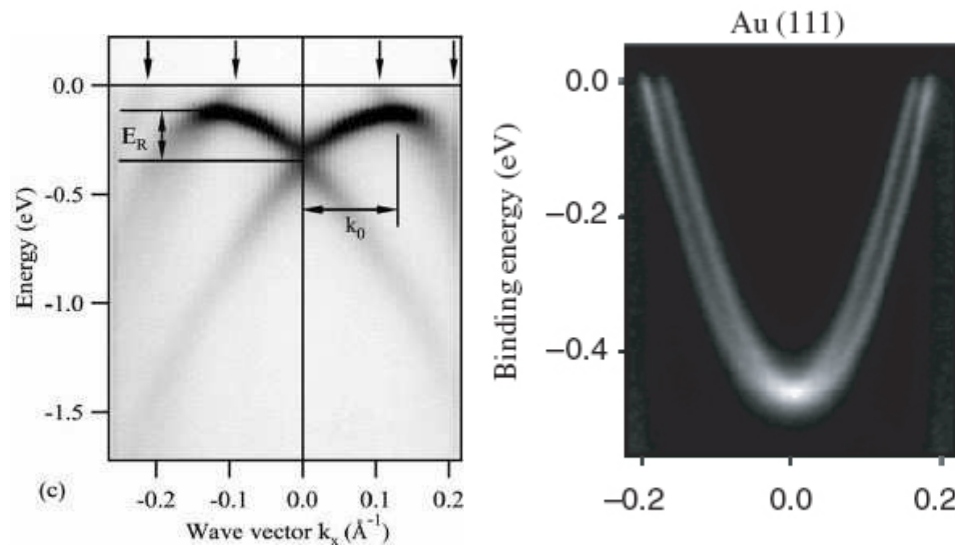
$$E_{\uparrow,\downarrow}(k_x) = \frac{\hbar^2 k_x^2}{2m^*} \pm \alpha_R k_x$$

„k-lineare Terme“

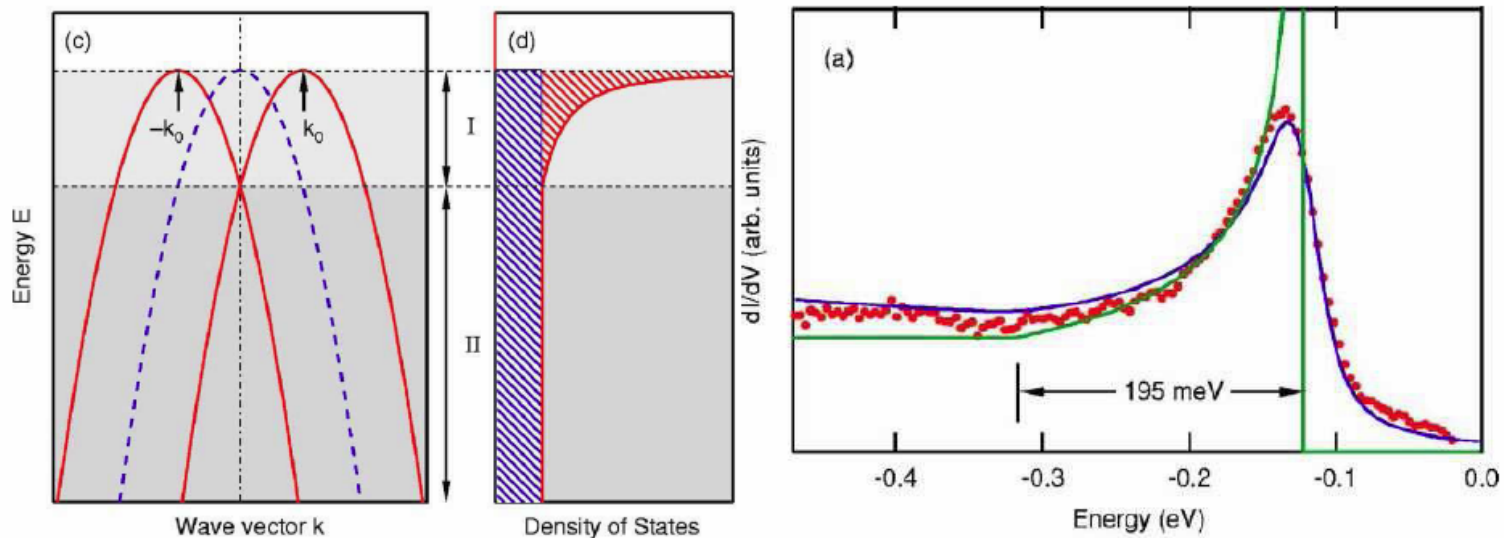


# Rashba-Effekt im Experiment

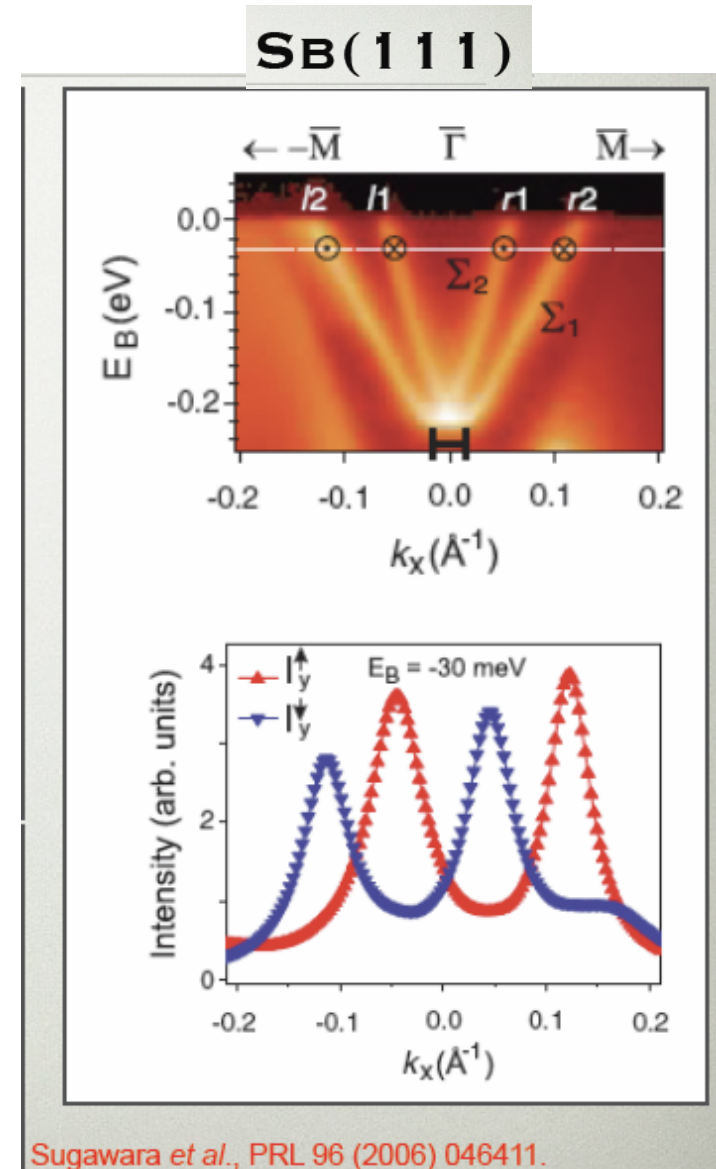
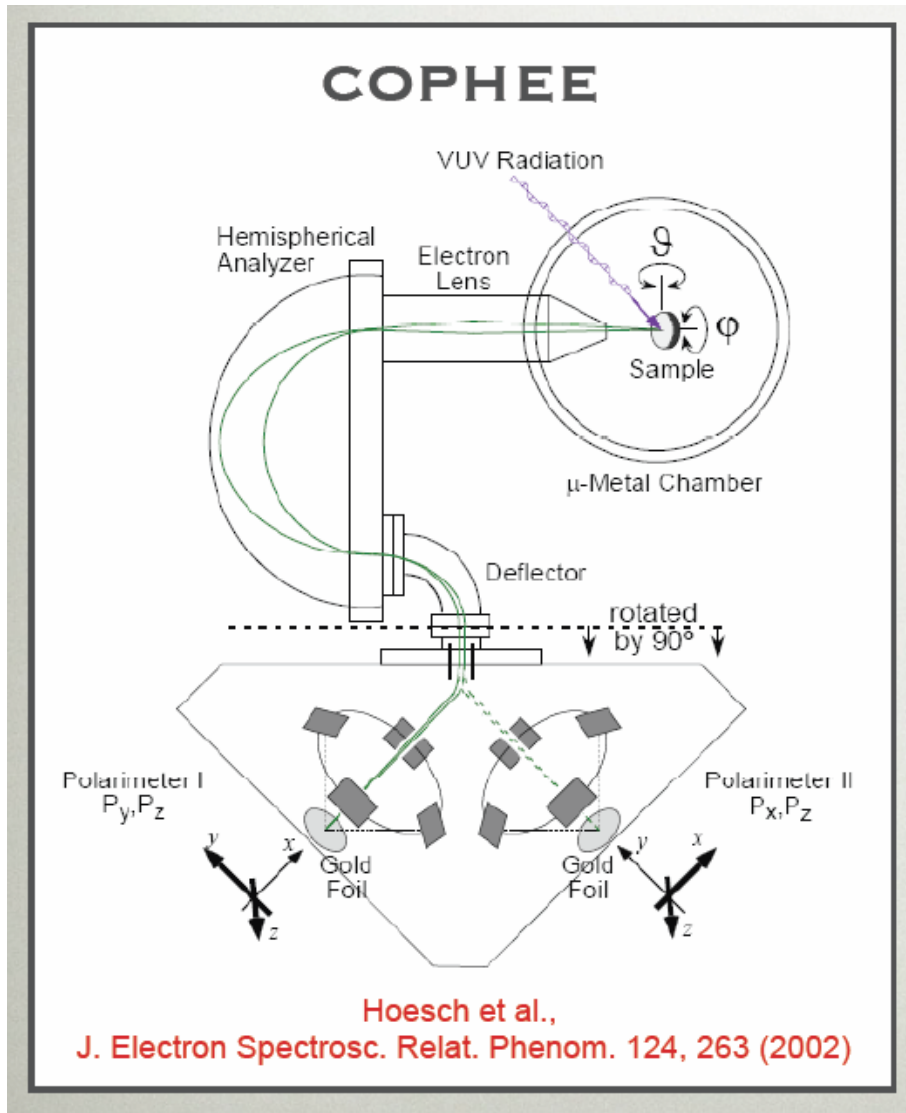
Winkelaufgelöste  
Photoelektronenspektroskopie  
(ARPES)



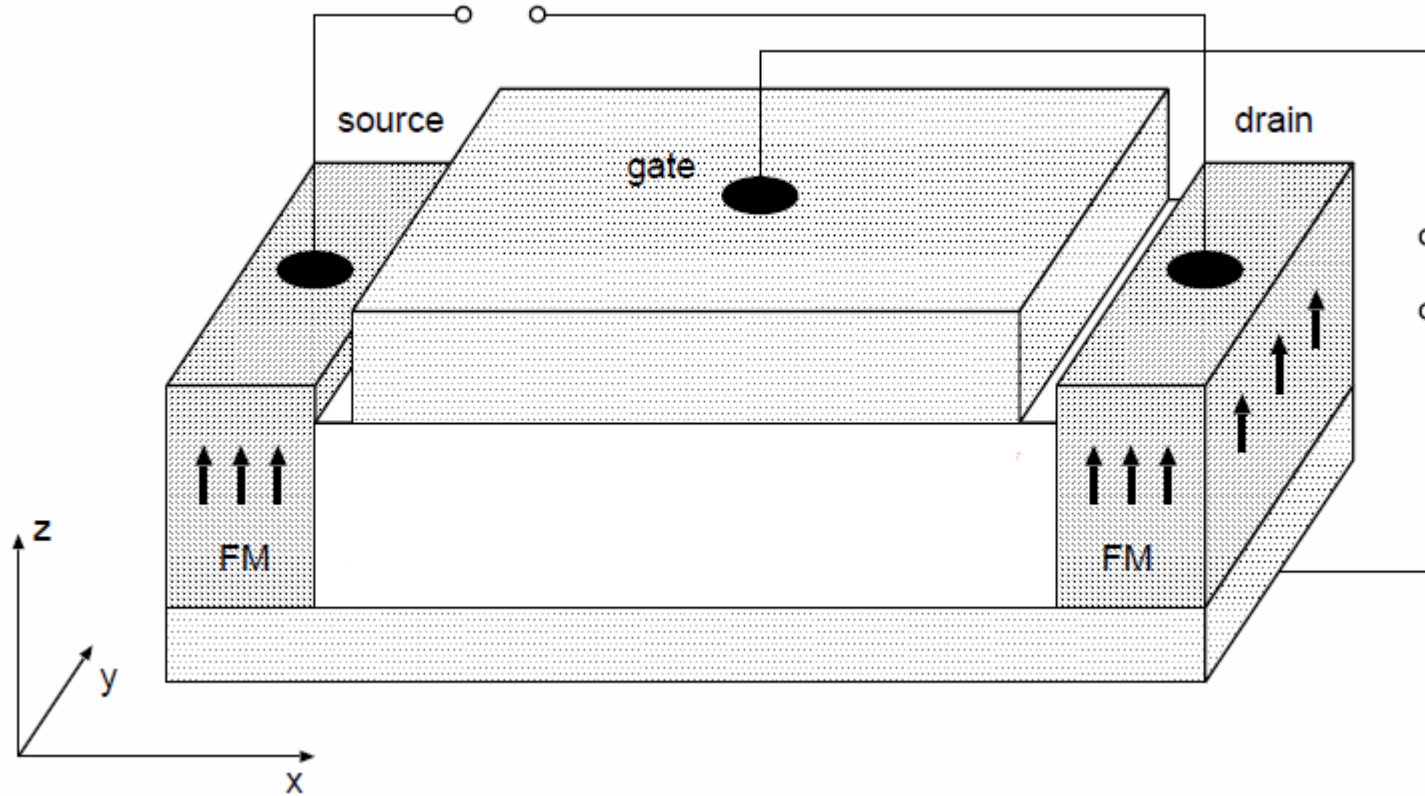
STM



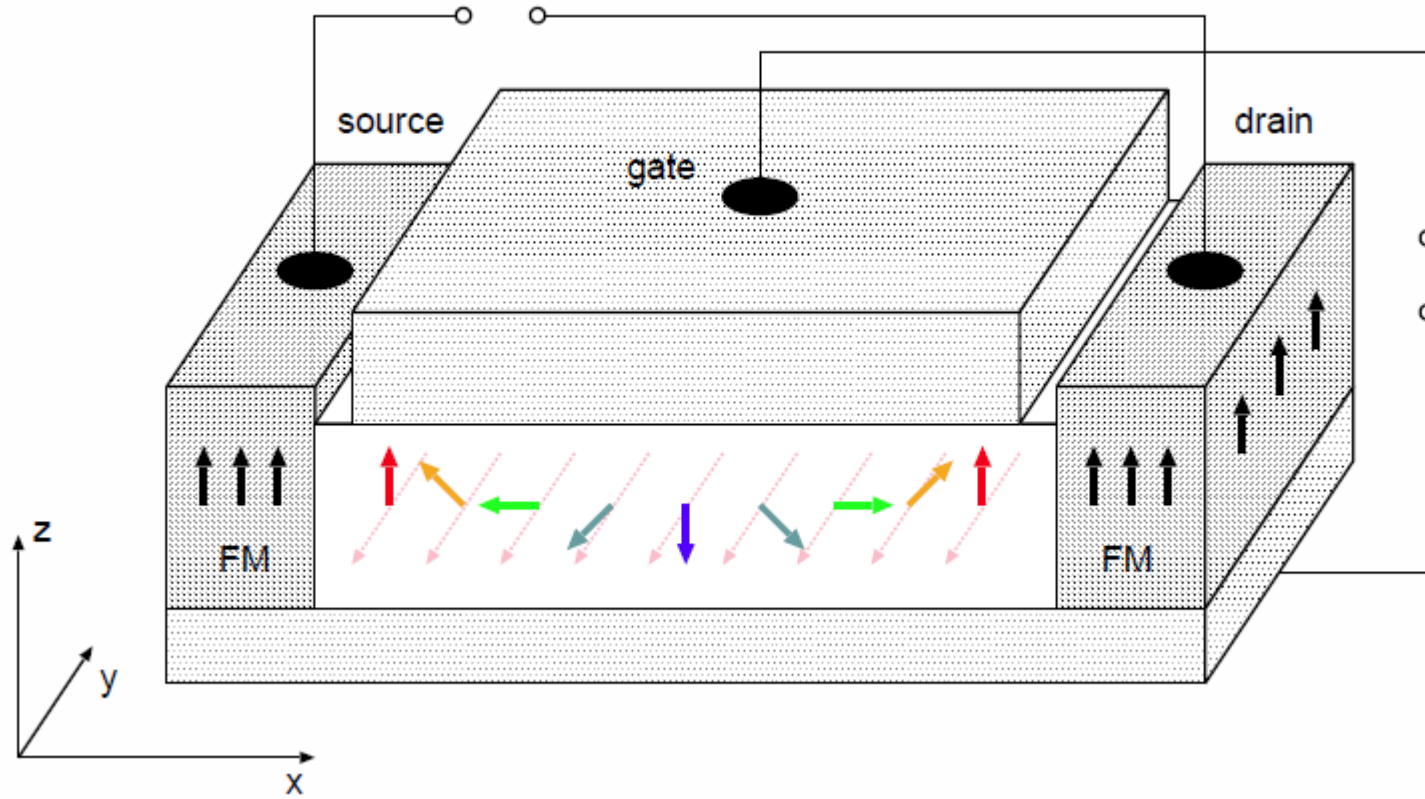
# ARPES incl. Spin-Erwartungswert



# Spin-FET



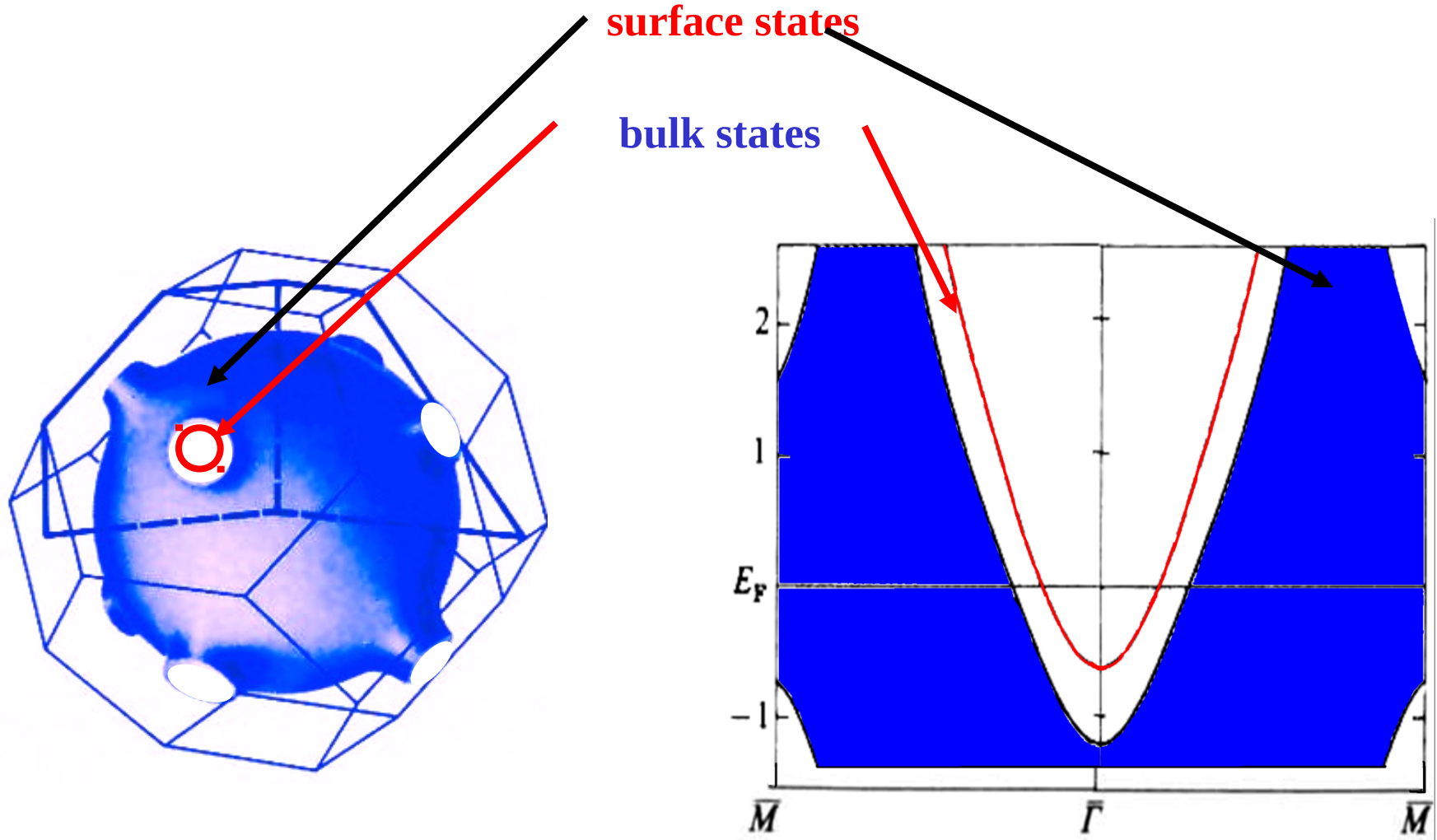
# Spin-FET



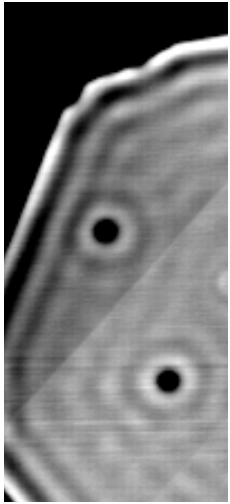


# Oberflächenzustand auf (111)-Flächen von Edelmetallen:

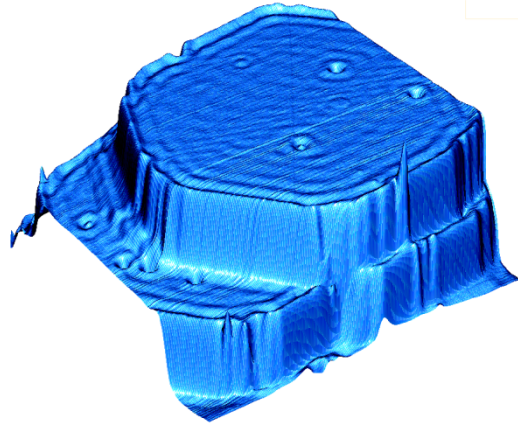
- isotrop
- parabolisch
- „free-electron like“



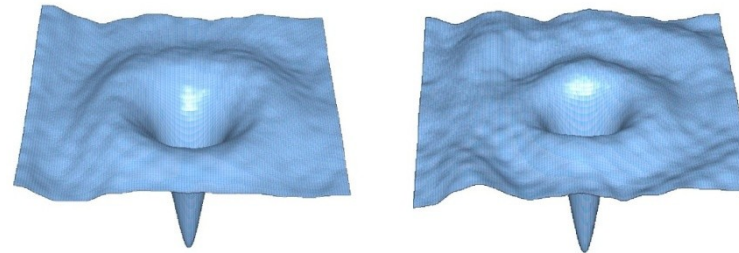
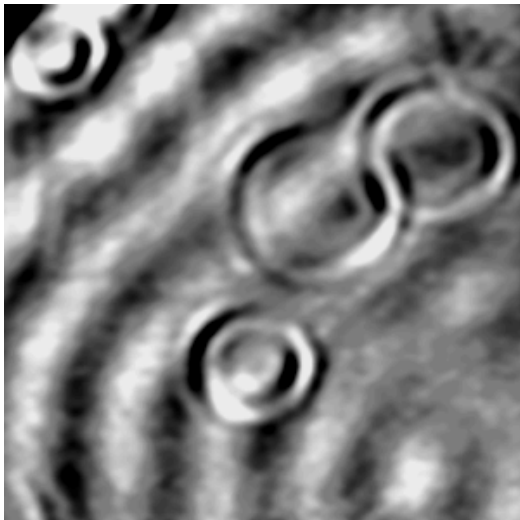
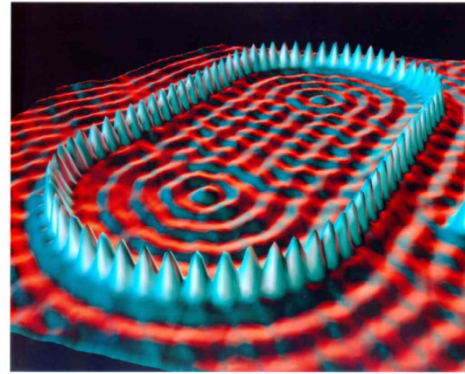
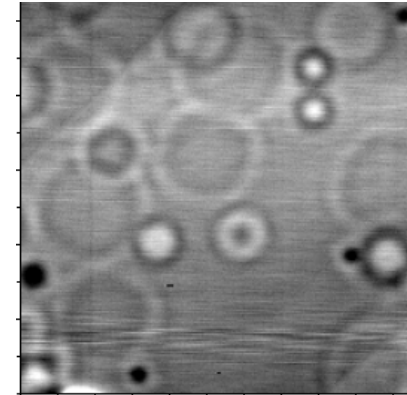
# Stehwellenmuster



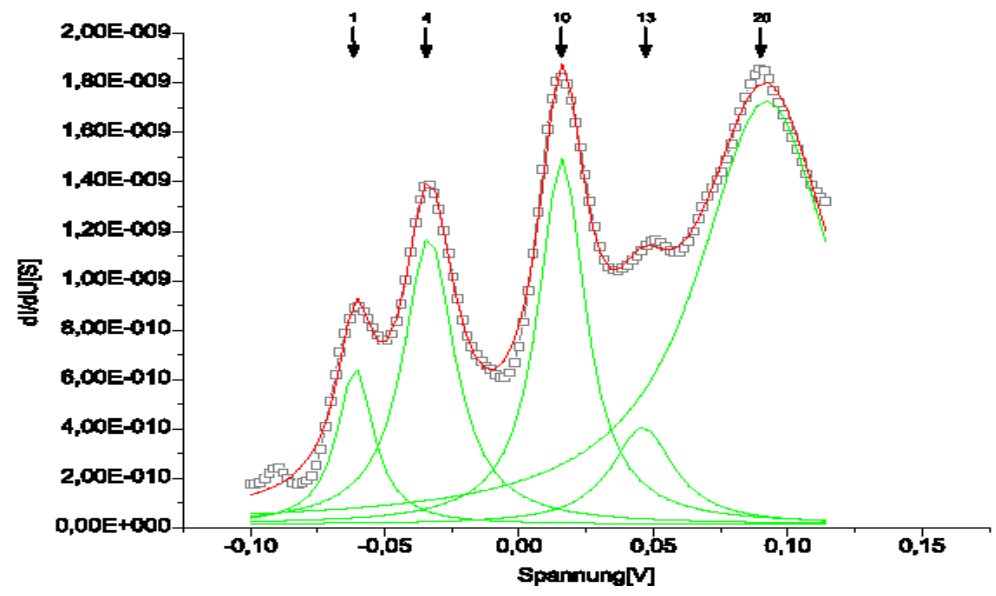
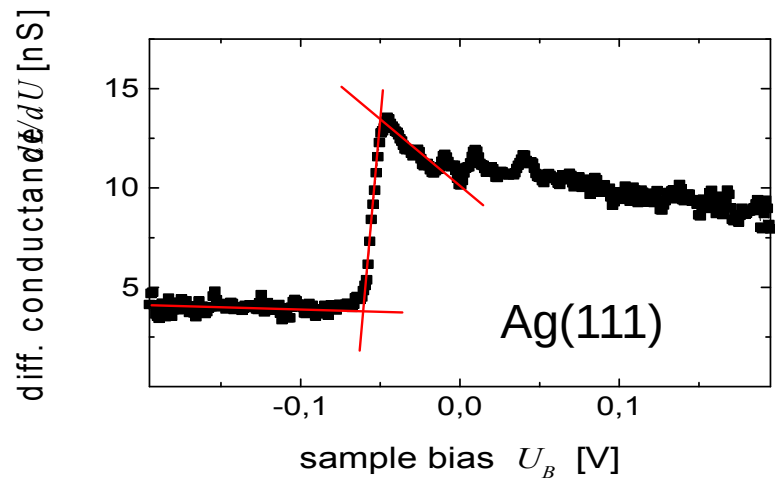
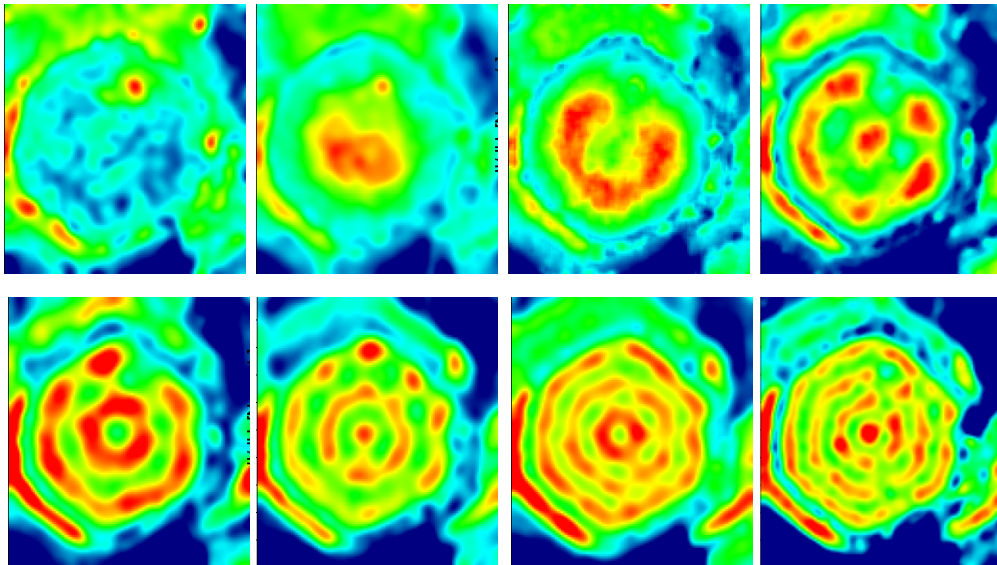
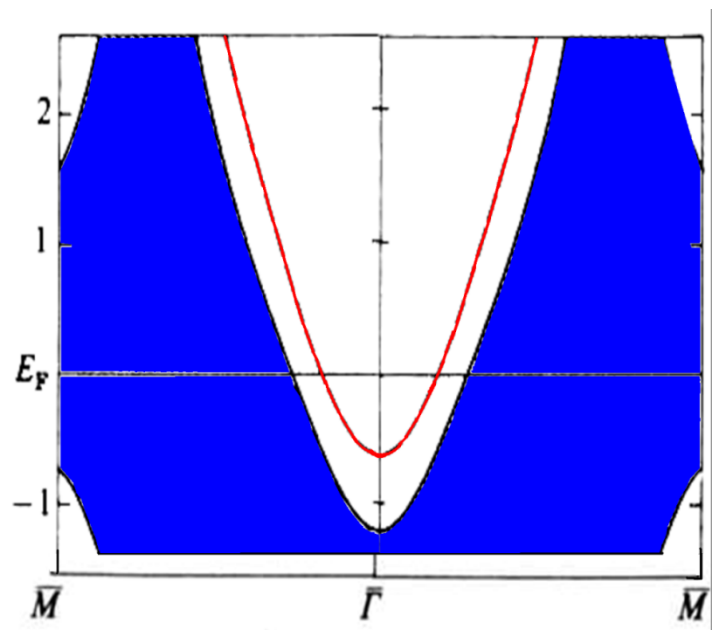
Cu(111)

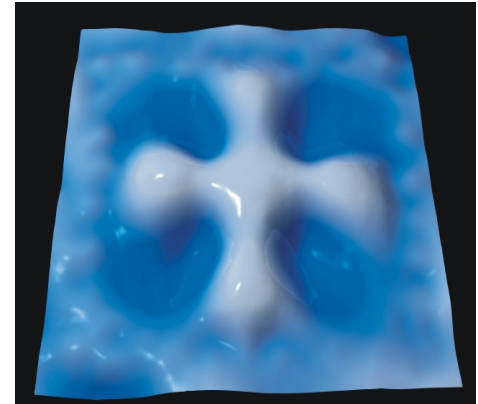
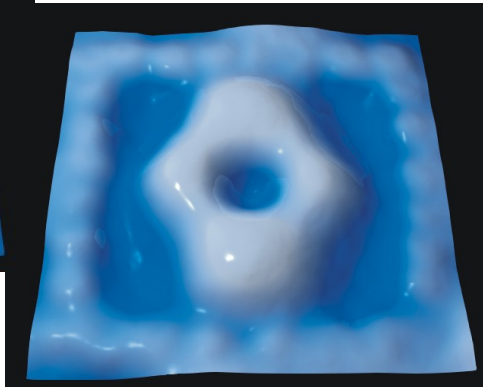
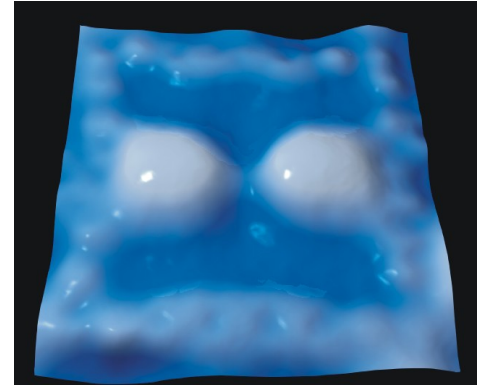
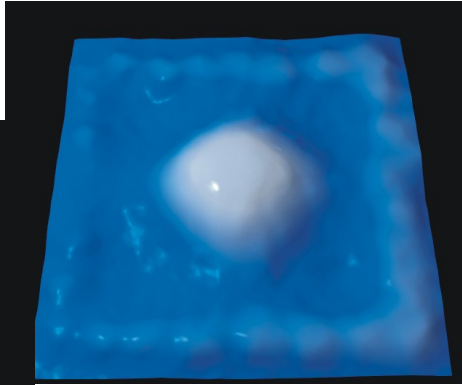
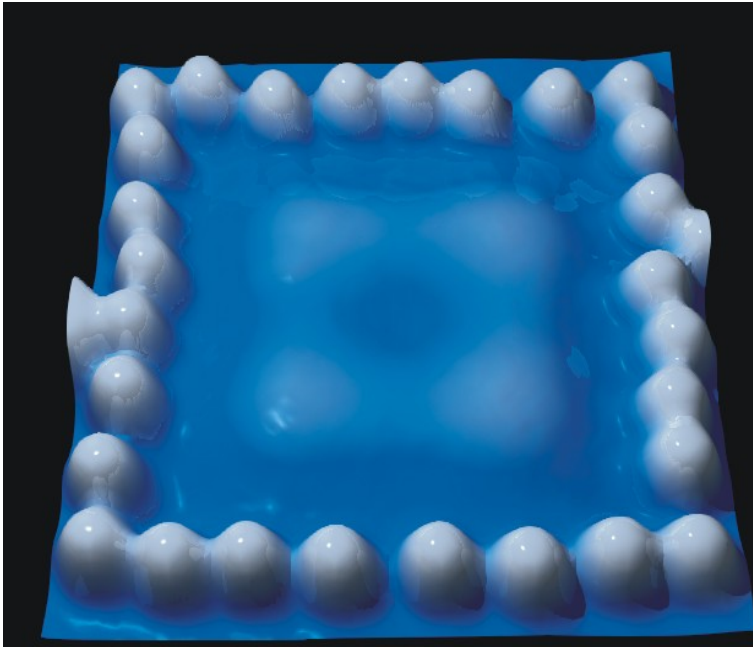


Cu(100)

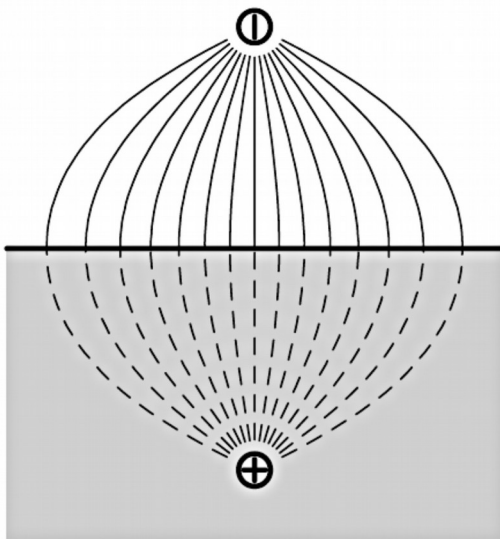


Änderung der Probenspannung  
(Dispersion)

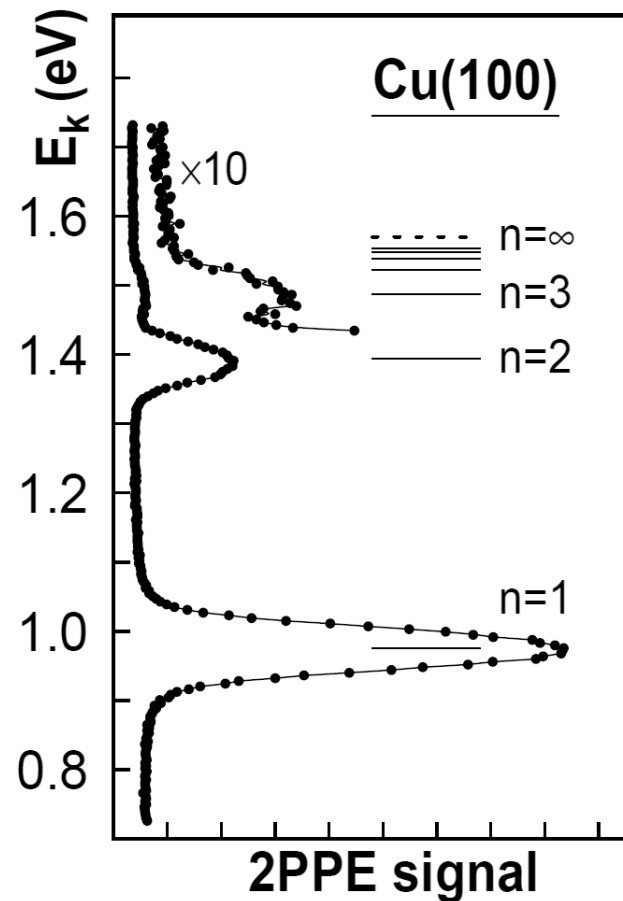
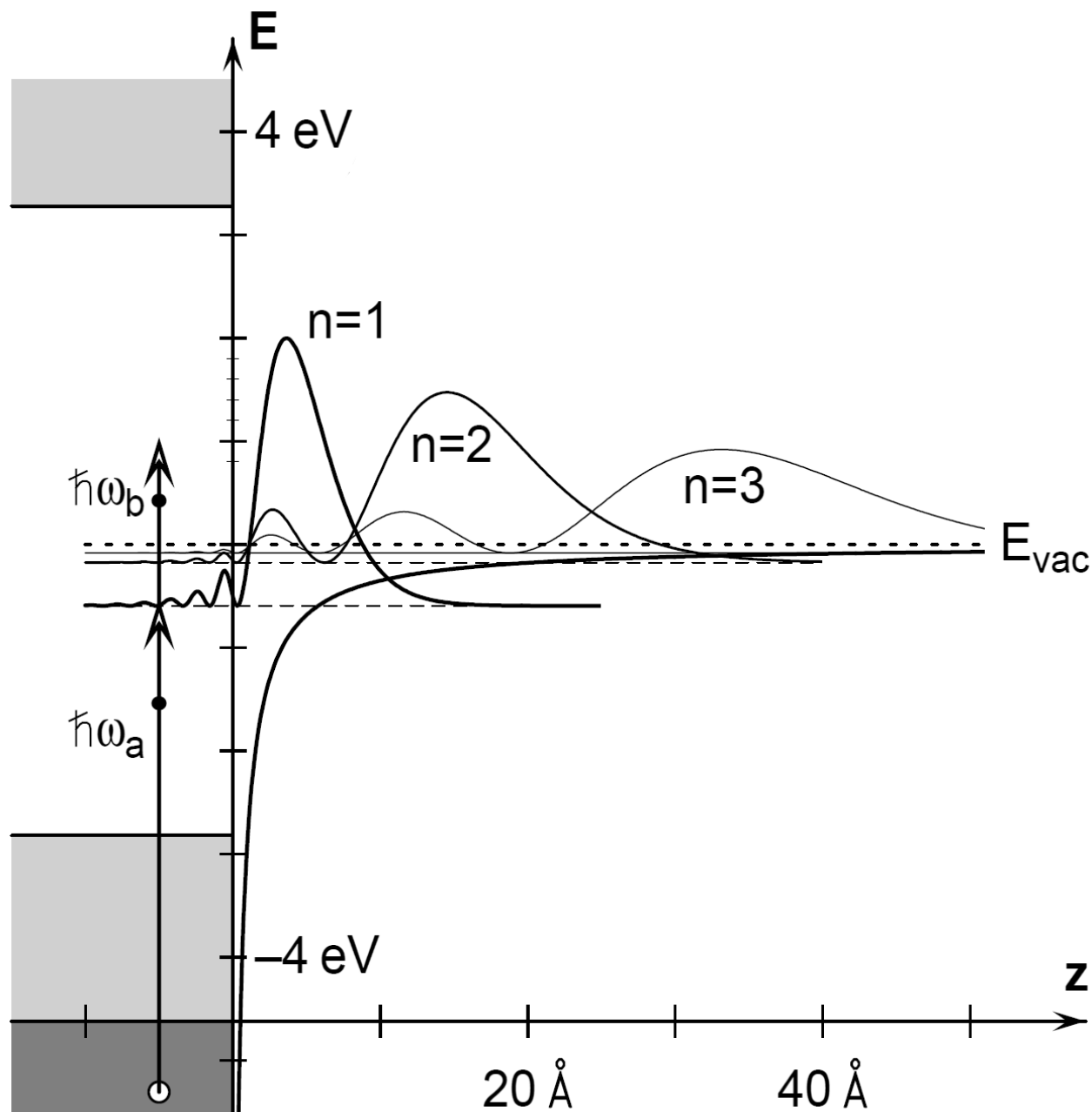




# Bildpotentialzustände



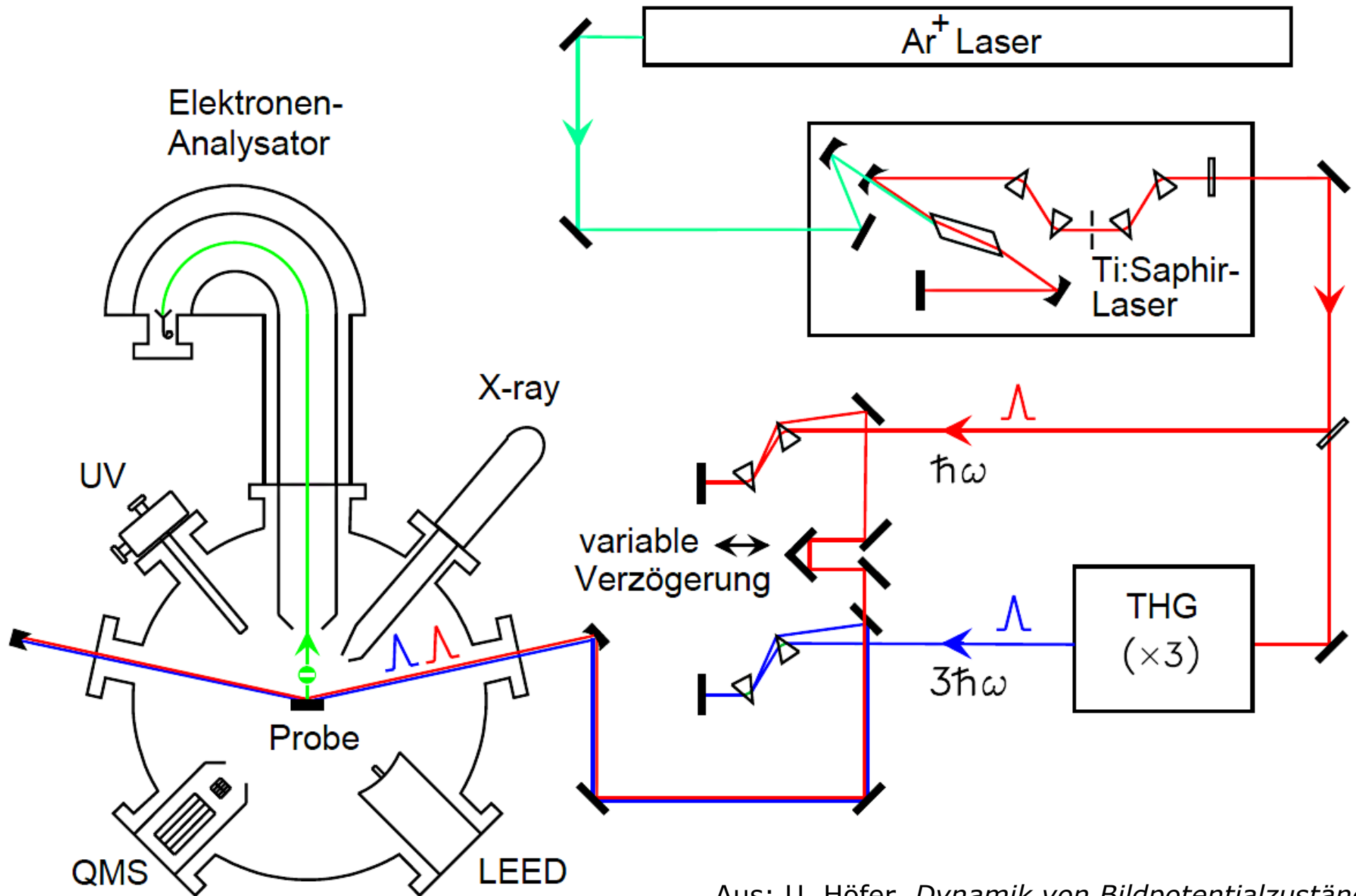
$$E_n = E_{\text{vac}} - \frac{0.85 \text{ eV}}{(n + a)^2}, \quad n = 1, 2, \dots$$

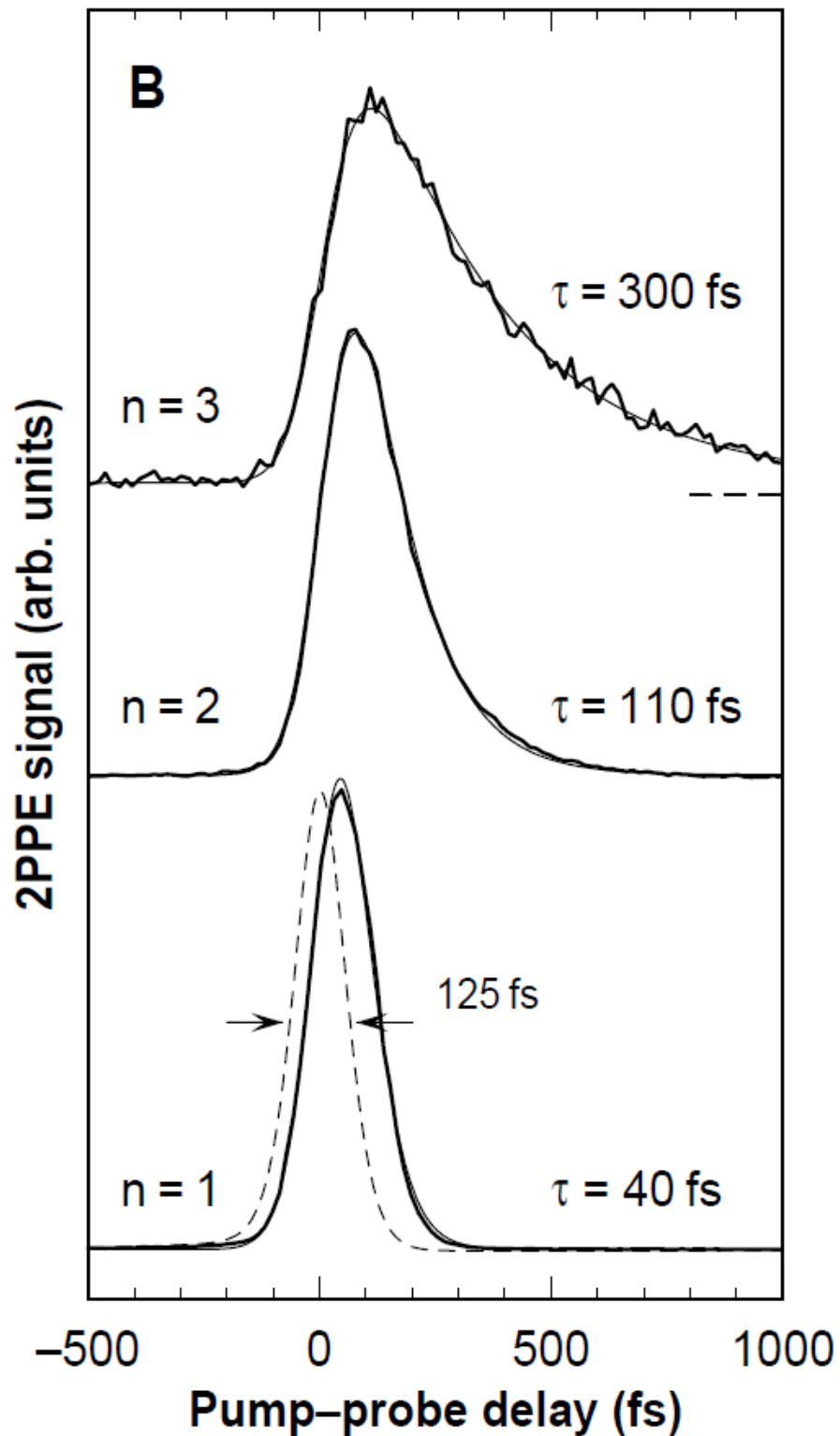


Photoelektronen-Spektrum  
 Aufgrund sequentieller  
 Anregung mit Photonen der  
 Energien  $h\nu_a$  und  $h\nu_b$



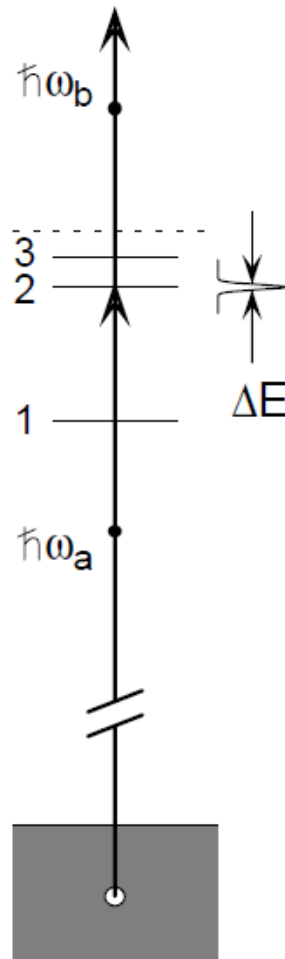
# Zweiphotonenphotoemission (2PPE)





Cu(100)

$E_B > 80$  meV



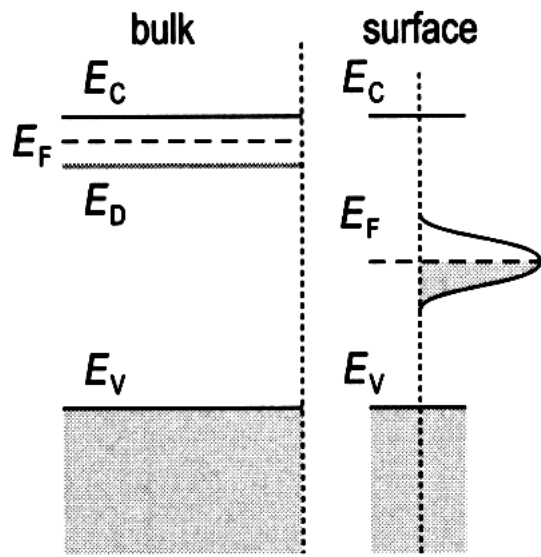
Zeitabhängigkeit des 2PPE-Signals  
der niedrigsten drei Bildpotentialzustände  
von Cu(100).

Gestrichelte Linie: Kreuzkorrelation der  
Pump- und Probeimpulse ohne  
resonante Zwischenzustände.

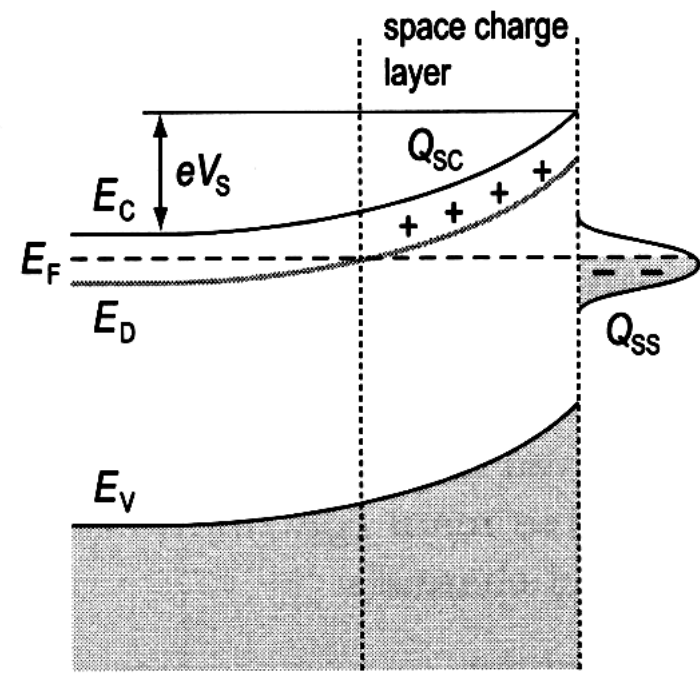
Die geringe spektrale Breite  $\Delta E$  der  
Pumpimpulse auf der Energieskala der  
Bildpotentialzustände verdeutlicht das  
Anregungsschema rechts.



**n-type semiconductor**

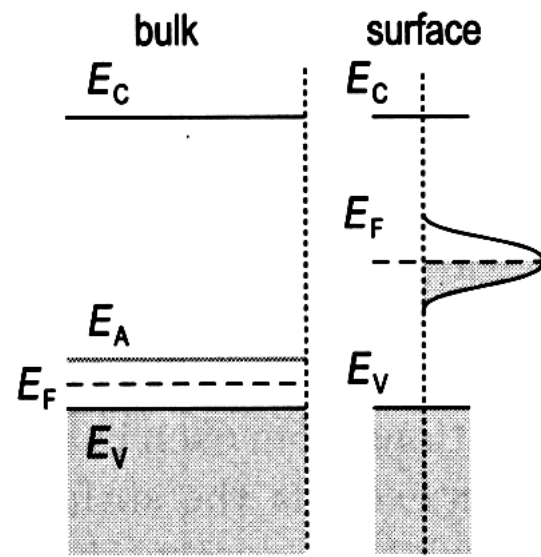


**a**

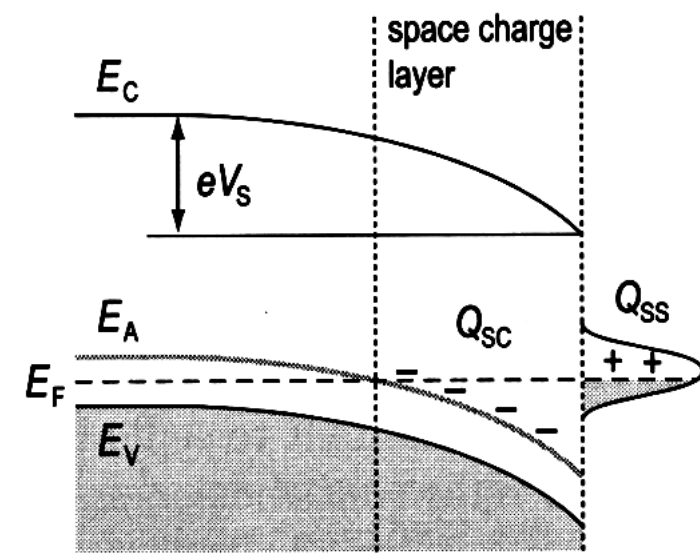


**b**

**p-type semiconductor**

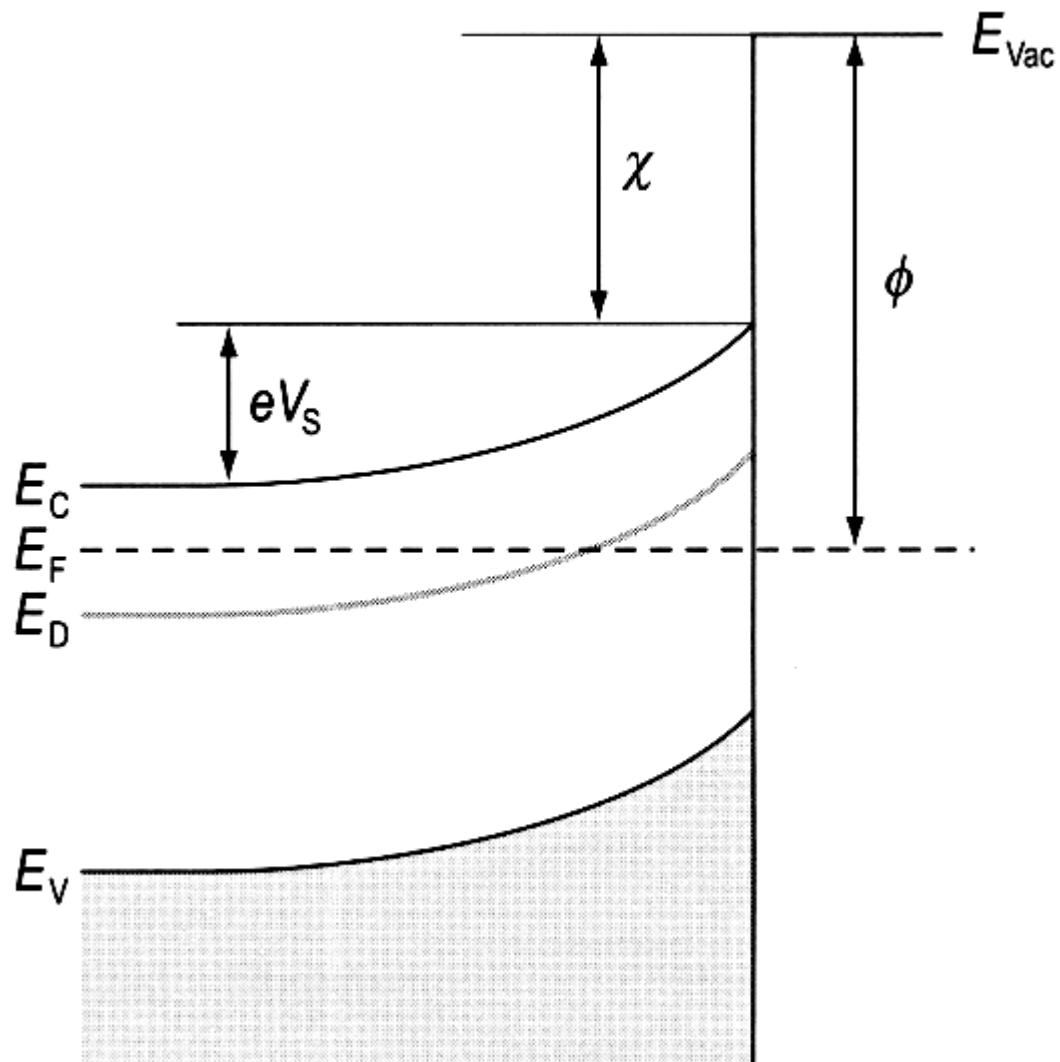


**c**



**d**

**Fig. 11.16.** Schematic illustration of band bending near the surface of **a**, **(b)** *n*-type and **c**, **(d)** *p*-type semiconductors. **(a)** and **(c)** illustrate the disequilibrium between the bulk and the surface. **(b)** and **(d)** show band bending at equilibrium.  $E_C$  and  $E_V$  are the conduction- and valence-band edges,  $E_F$  the Fermi energy,  $E_D$  and  $E_A$  the energy of the bulk donor and acceptor levels.  $Q_{SS} = -Q_{SC}$  are the charges accumulated at the surface and in the space charge layer.  $eV_s = ev(z=0)$  denotes the band bending



**Fig. 11.21.** Schematic band diagram for a semiconductor surface.  $\phi$  is the work function,  $\chi$  the electron affinity,  $eV_{\text{S}}$  the band bending,  $E_{\text{V}}$  the valence band maximum,  $E_{\text{C}}$  the conduction band minimum, and  $E_{\text{F}}$  the Fermi level

# Adsorption

# Ni(110) 2x1 CO

- Ni ist wichtiger Katalysator, z. B.:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

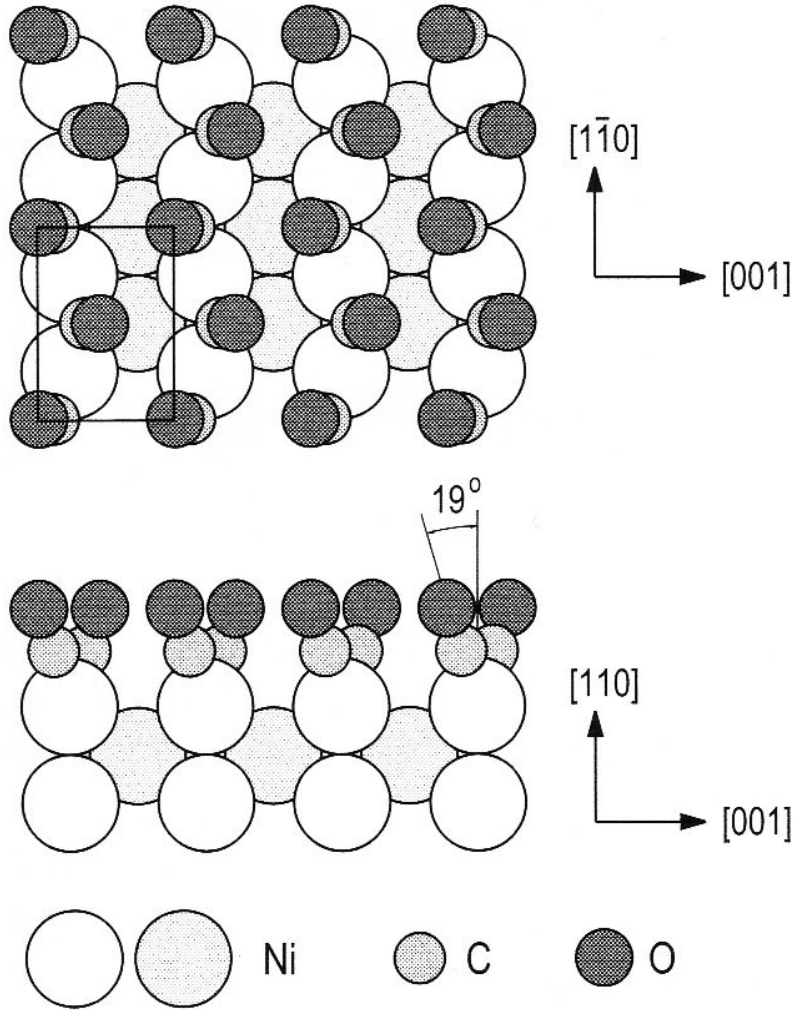


Fig. 9.17

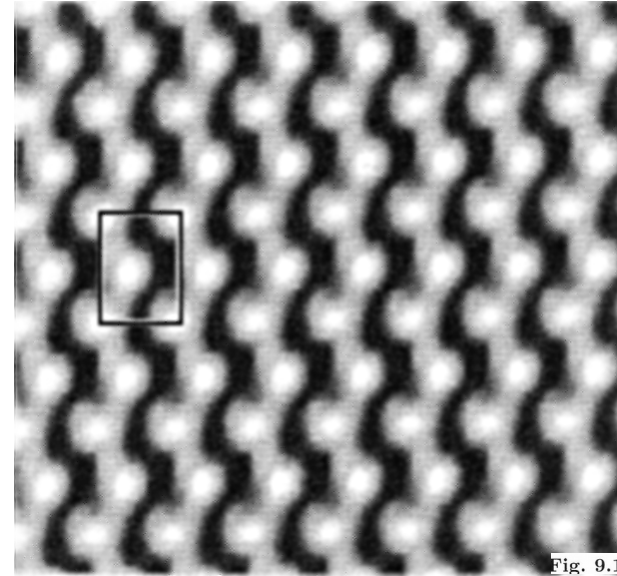


Fig. 9.18

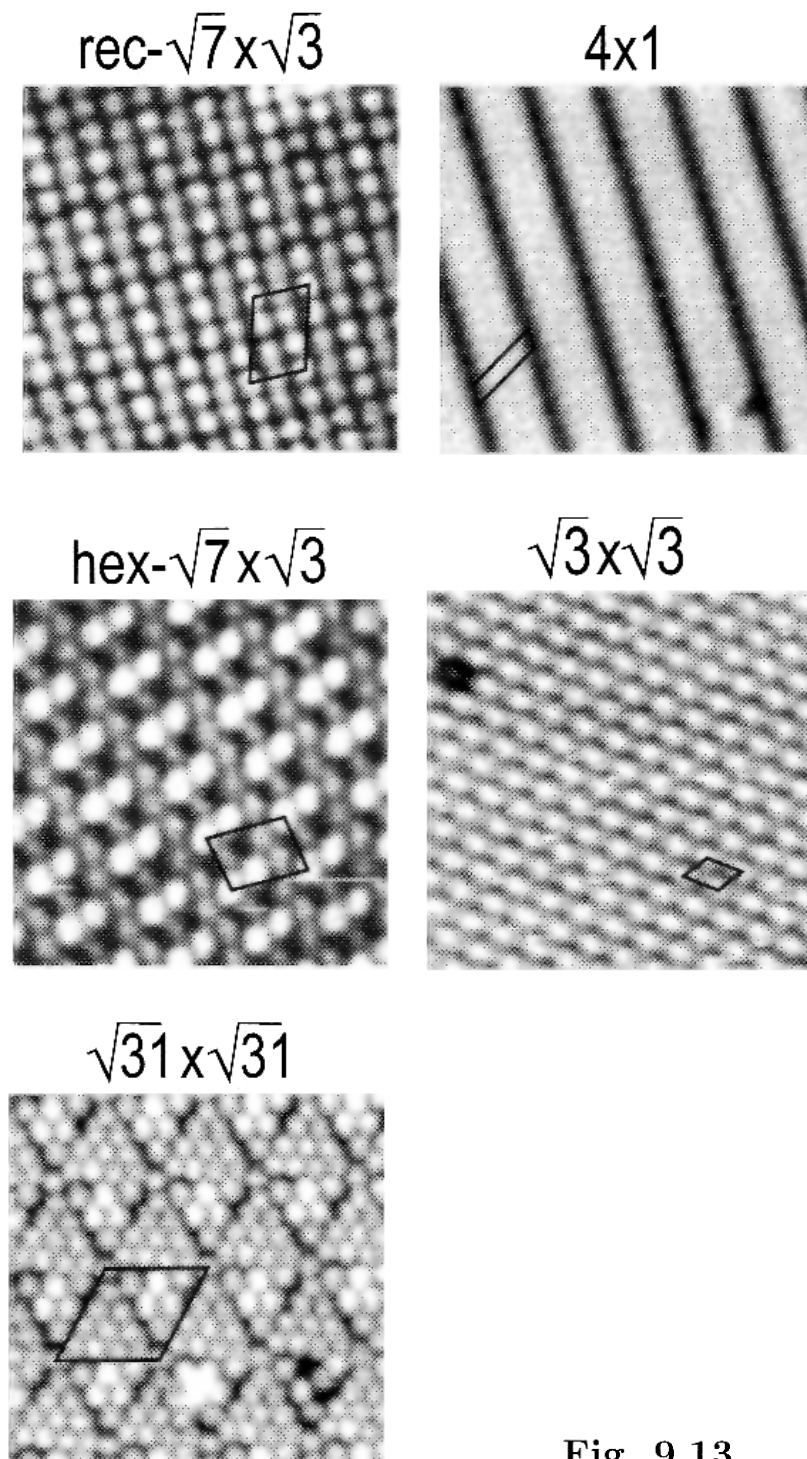
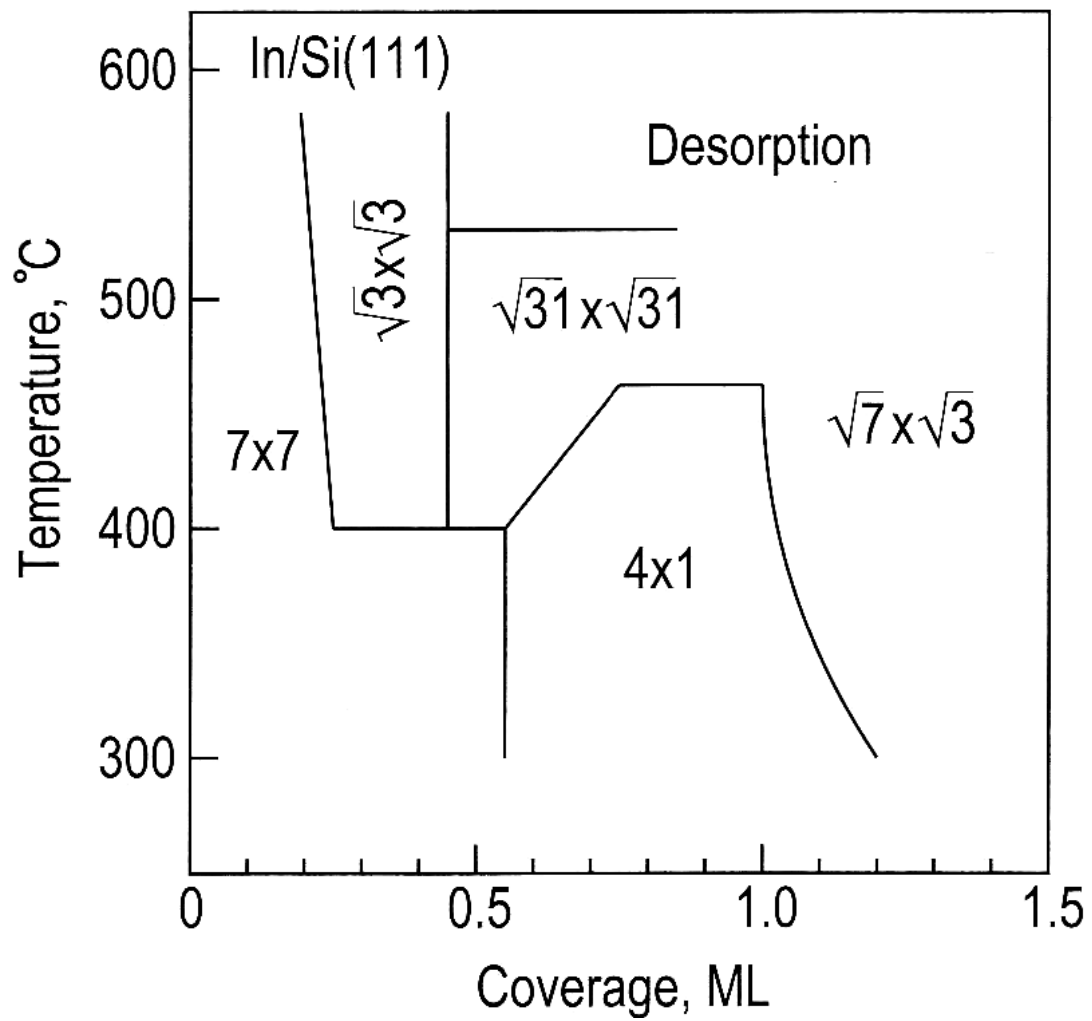
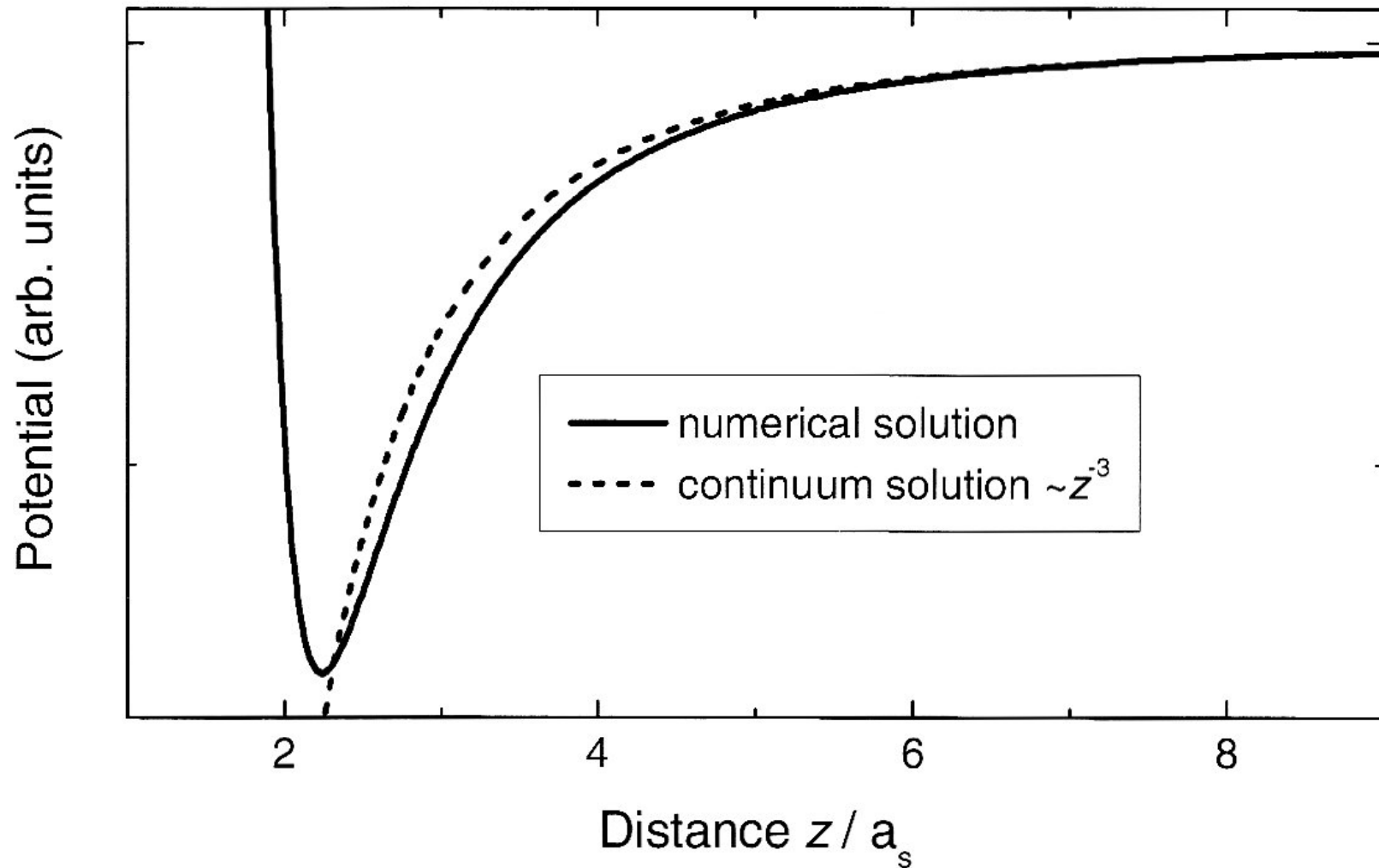


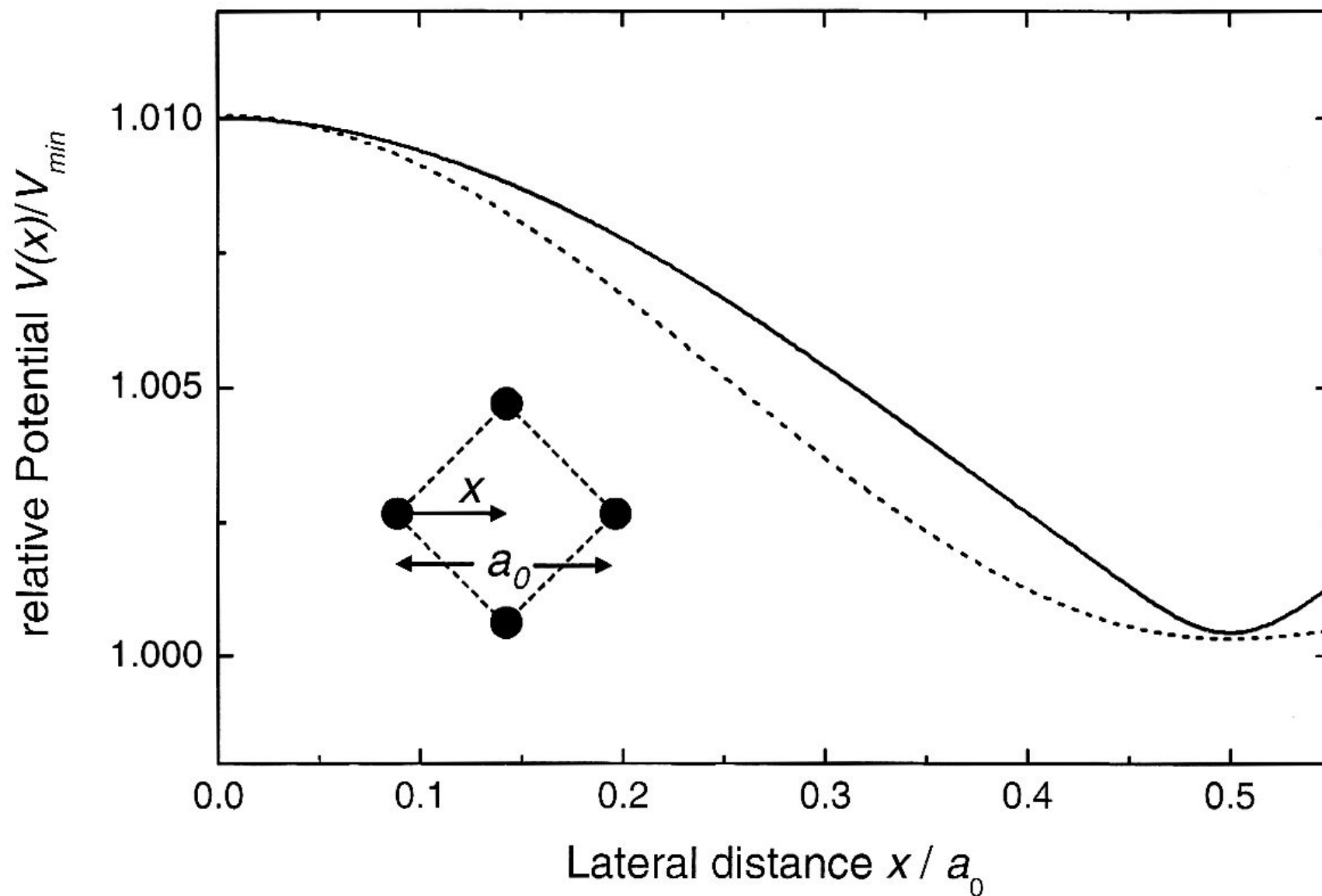
Fig. 9.13

# Van der Waals Bindung: Abstandsabhängigkeit



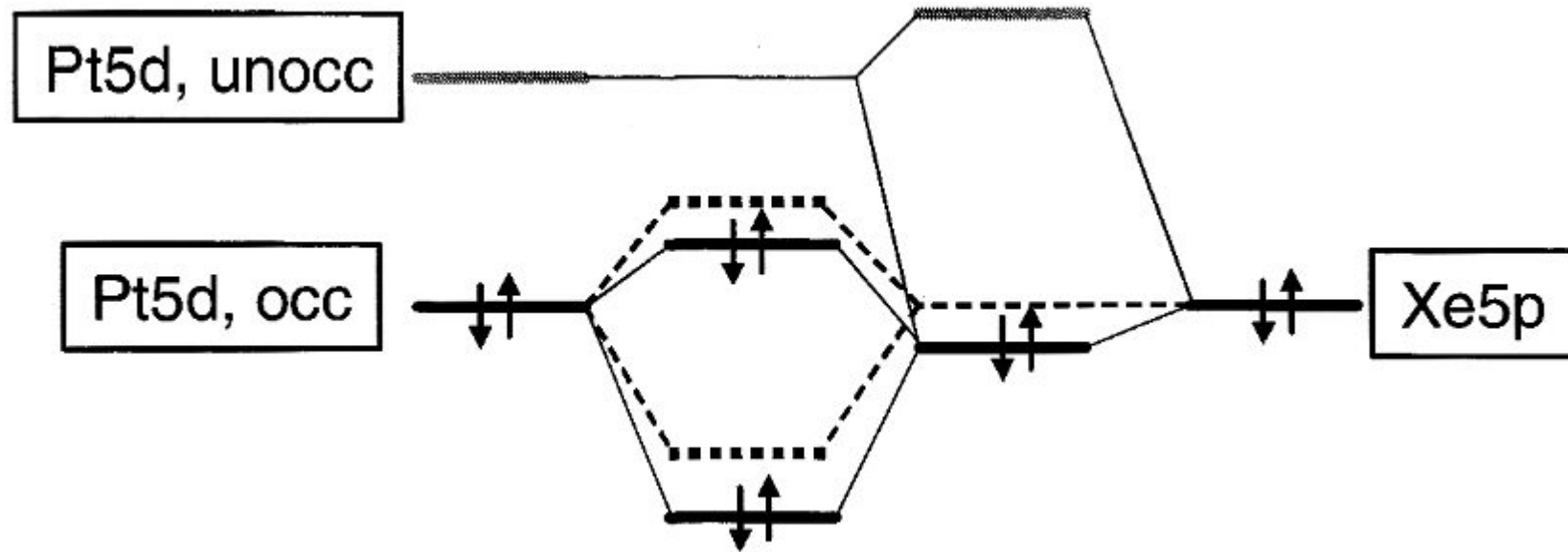
**Fig. 6.1.** Van-der-Waals bonding to a surface of an fcc-crystal. The parameters are chosen to represent Xe on Pt(100). The distance  $z$  is in units of the surface lattice constant  $a_s$ . Solid line is the numerical solution for a pair-wise Lennard-Jones Potential. The dashed line is the continuum solution for the attractive part (6.3).

# Van der Waals Bindung: Variation über Einheitszelle



**Fig. 6.2.** Relative corrugation of the minimum in the physisorption potential (solid line). The potential deviates significantly from a simple cosine-function (dotted line).

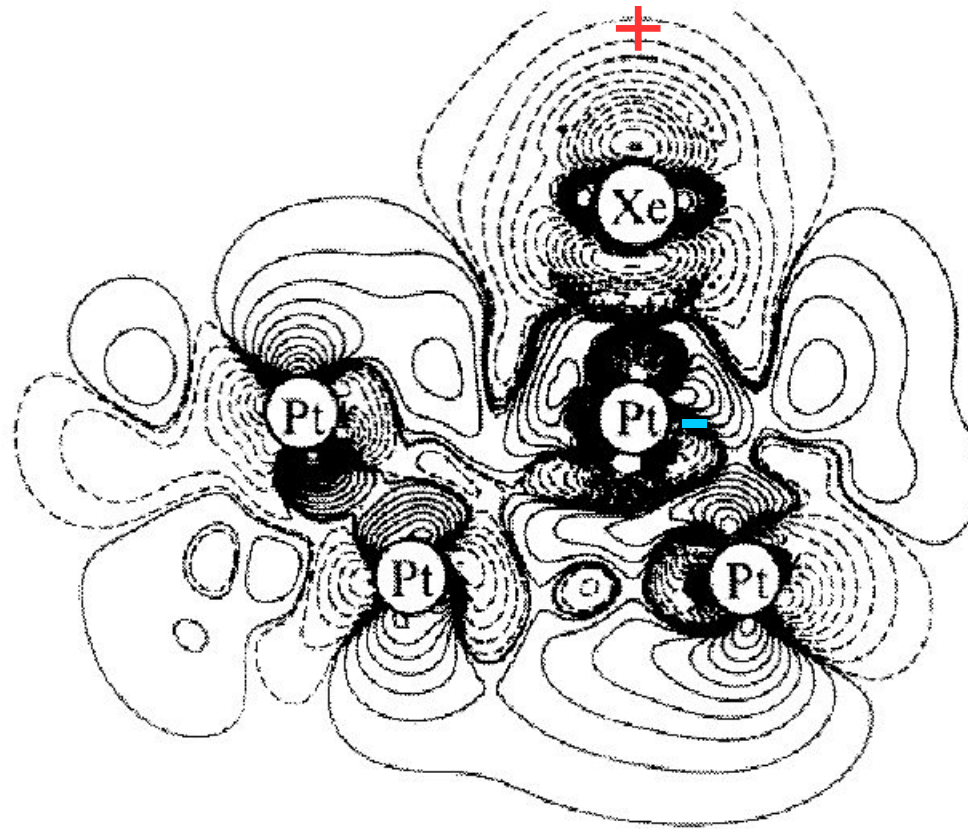
# Xe auf Pt: Chemische Effekte bei kleinen Abständen



**Fig. 6.3.** Schematic picture of the bonding of rare-gas atoms on a transition metal for the example of Xe on Pt: The coupling of the occupied Xe5p-states with the occupied Pt5d-states leads to occupied bonding and anti-bonding states (dashed lines) and thereby to Pauli-repulsion. Mixing with the unoccupied Pt5d states (*polarization states*) leads to a considerable charge transfer and to an overall downshift of the electron states, and thereby to a weak chemical bonding.



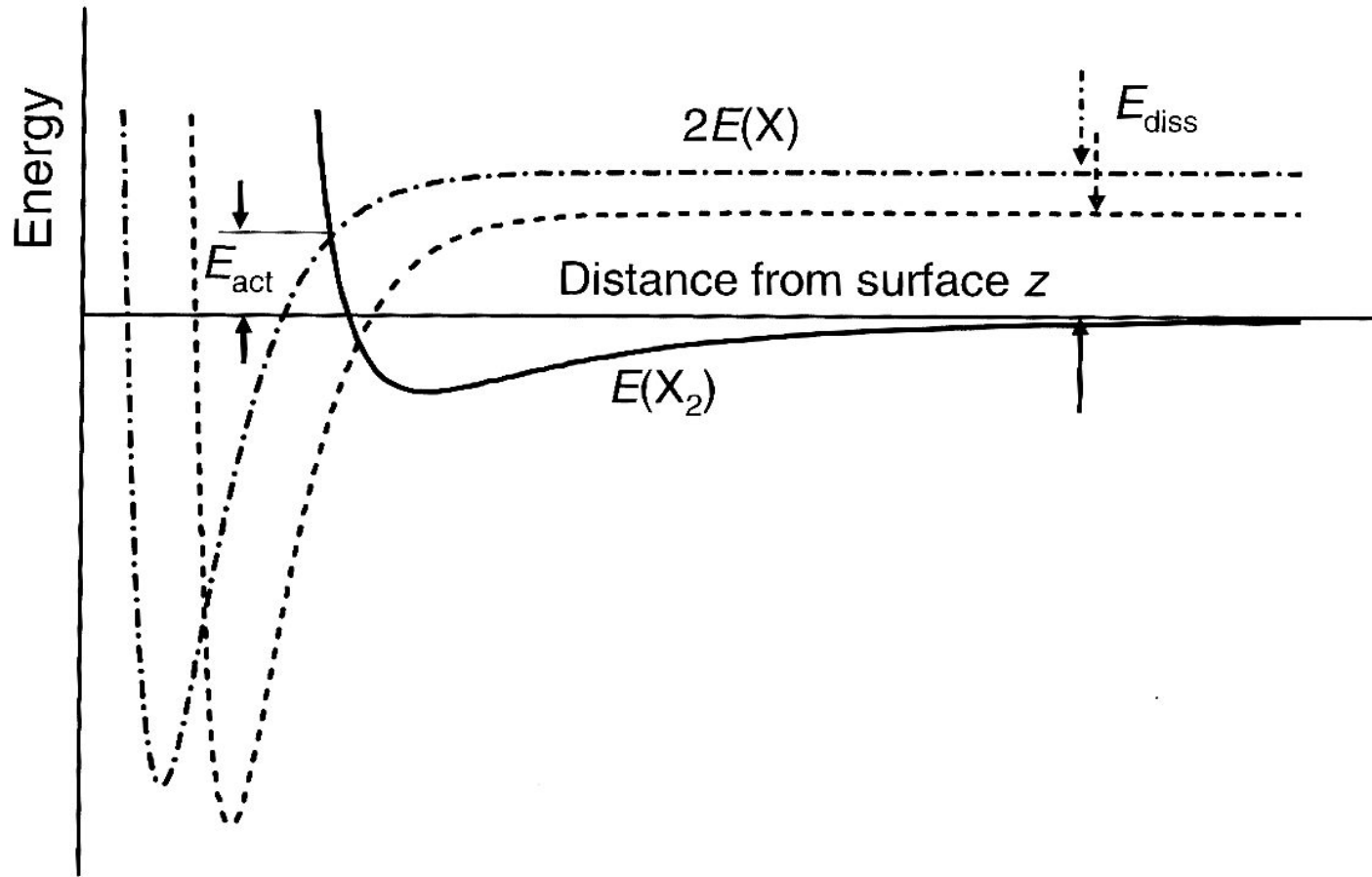
# Xe auf Pt: Ladungstransfer



**Fig. 6.4.**

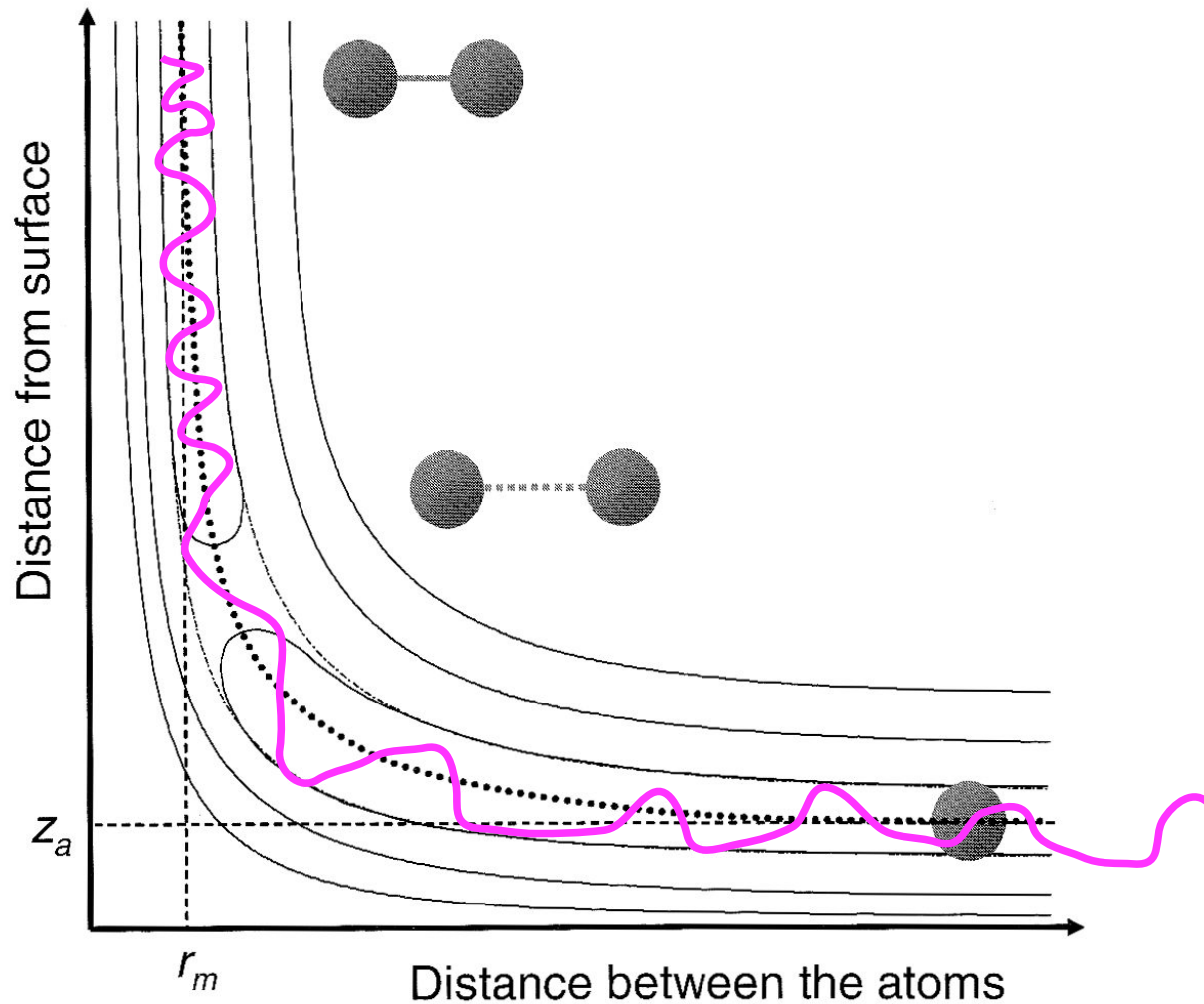
charge density difference  
 $\rho(\mathbf{r}) = \rho(\text{XePt}_{22}) - \rho(\text{Xe}) - \rho(\text{Pt}_{22})$  along the intersection AB shown on the left. Dashed and solid contour lines indicate charge deficit and surplus, respectively. Note the net charge transfer into the substrate!

# Adsorption: dissoziativ vs. molekular



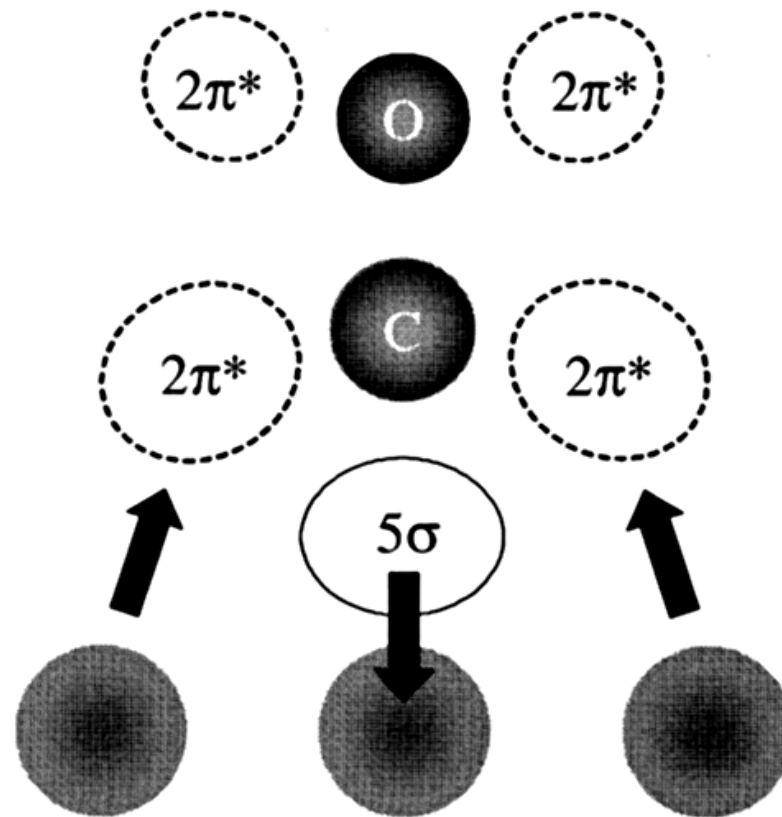
**Fig. 6.5.** Grossly simplified illustration of the energetics of the adsorption process for diatomic molecules: The solid line represents the physisorption potential or the potential of whatever bond the molecule may establish as a whole with the surface. The dashed and dash-dotted lines show two possible cases for the energy of the dissociated molecule. Depending on the energy of dissociation in the gas phase, the equilibrium bond distance and the adsorption energy for the atoms, there may be a barrier for dissociation or not.

# Adsorption: VIELE Parameter; Reaktionskoordinate



**Fig. 6.6.** Schematic drawing of the contour lines of the atom potential for a molecule approaching a flat surface ("elbow plot"). For large distances, the potential has a minimum at the gas-phase equilibrium bond distance. As the molecule draws closer to the surface, the bond distance increases. Eventually the potential is independent of the atom-atom distance. The molecule may or may not encounter an activation barrier along the path (solid and thin dash-dotted contour lines).

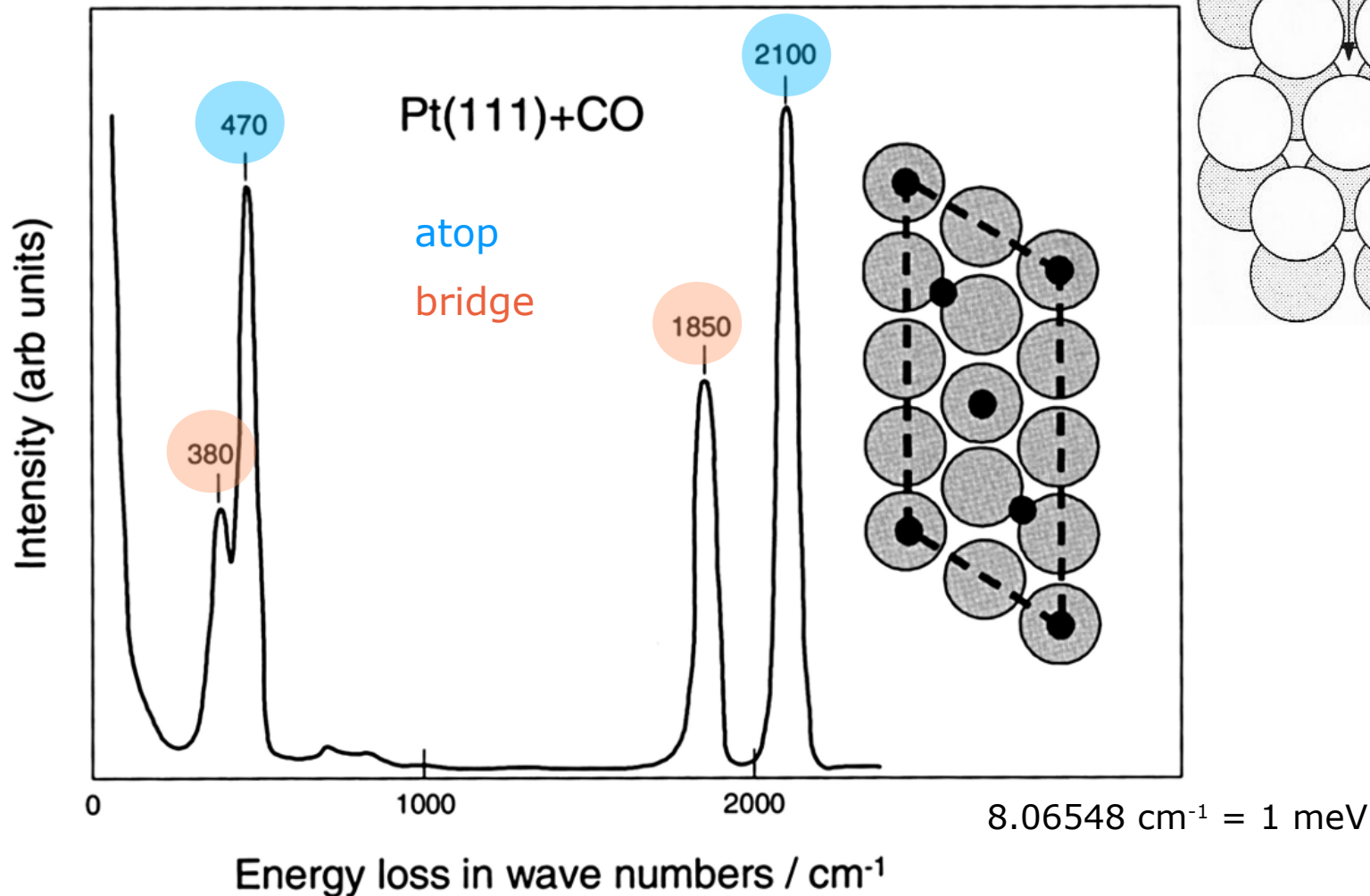
CO !



**Fig. 6.26.** Orbital scheme of the CO-molecule. As the largest weight of the  $5\sigma$ -orbital is on the backside of the carbon atom, CO bonds with the carbon atom pointing towards the surface.

# EELS von c(4x2) CO auf Pt(111)

$E_0 = 2 \text{ eV}$



**Fig. 6.27.** Electron energy loss spectrum of 2 eV electrons backscattered in specular reflection from a CO-covered Pt(111) surface [6.29]. The energy loss is given in spectroscopic units ( $8.065 \text{ cm}^{-1} = 1 \text{ meV}$ ). The mode pair  $2100 \text{ cm}^{-1}/470 \text{ cm}^{-1}$  belongs to CO in the a-top site, the pair at  $1850 \text{ cm}^{-1}/380 \text{ cm}^{-1}$  to CO in the two-fold bridge site. The spectrum corresponds to half a monolayer coverage for which the system realizes a c(4x2) structure (see insert).

# Newns-Anderson Model

$$\mathcal{H}_{\text{bulk}} = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}}$$

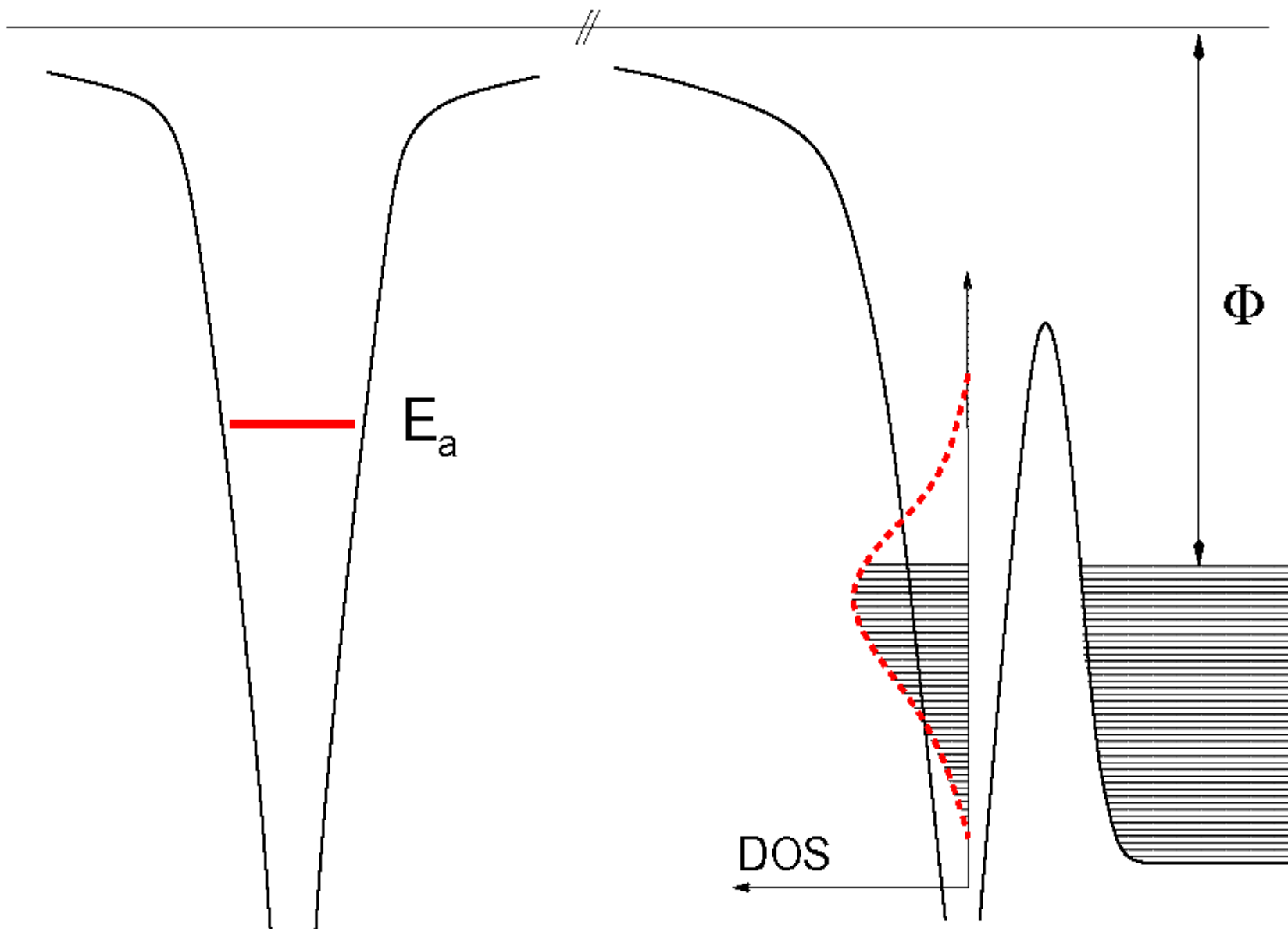
$$\mathcal{H}_{\text{ad}} = \varepsilon_a c_a^{\dagger} c_a + \sum_{\mathbf{q}} V_{a\mathbf{q}} c_a^{\dagger} a_{\mathbf{q}} + \text{H.c.}$$

$$n_a(E) = \frac{1}{\pi} \frac{\Delta(E)}{[E - \varepsilon_a - \Lambda(E)]^2 + \Delta(E)^2}$$

$$\Delta(E) = \pi \sum_{\mathbf{q}} |V_{a\mathbf{q}}|^2 \delta(E - \varepsilon_{\mathbf{q}})$$

$$\Lambda(E) = \frac{1}{\pi} \int dE' \frac{\Delta(E')}{E - E'}$$

# Newns-Anderson Model: Shift & Broadening



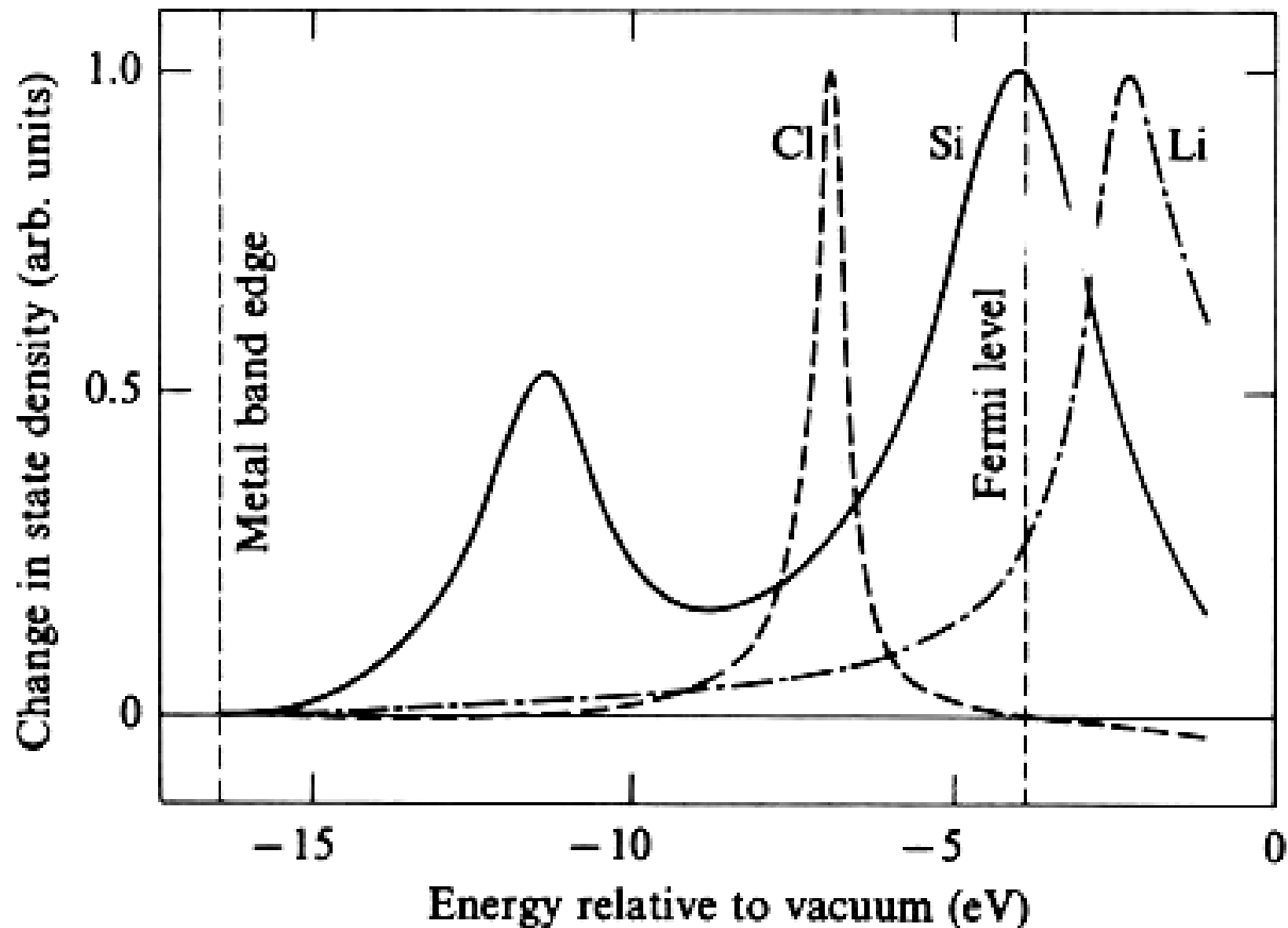
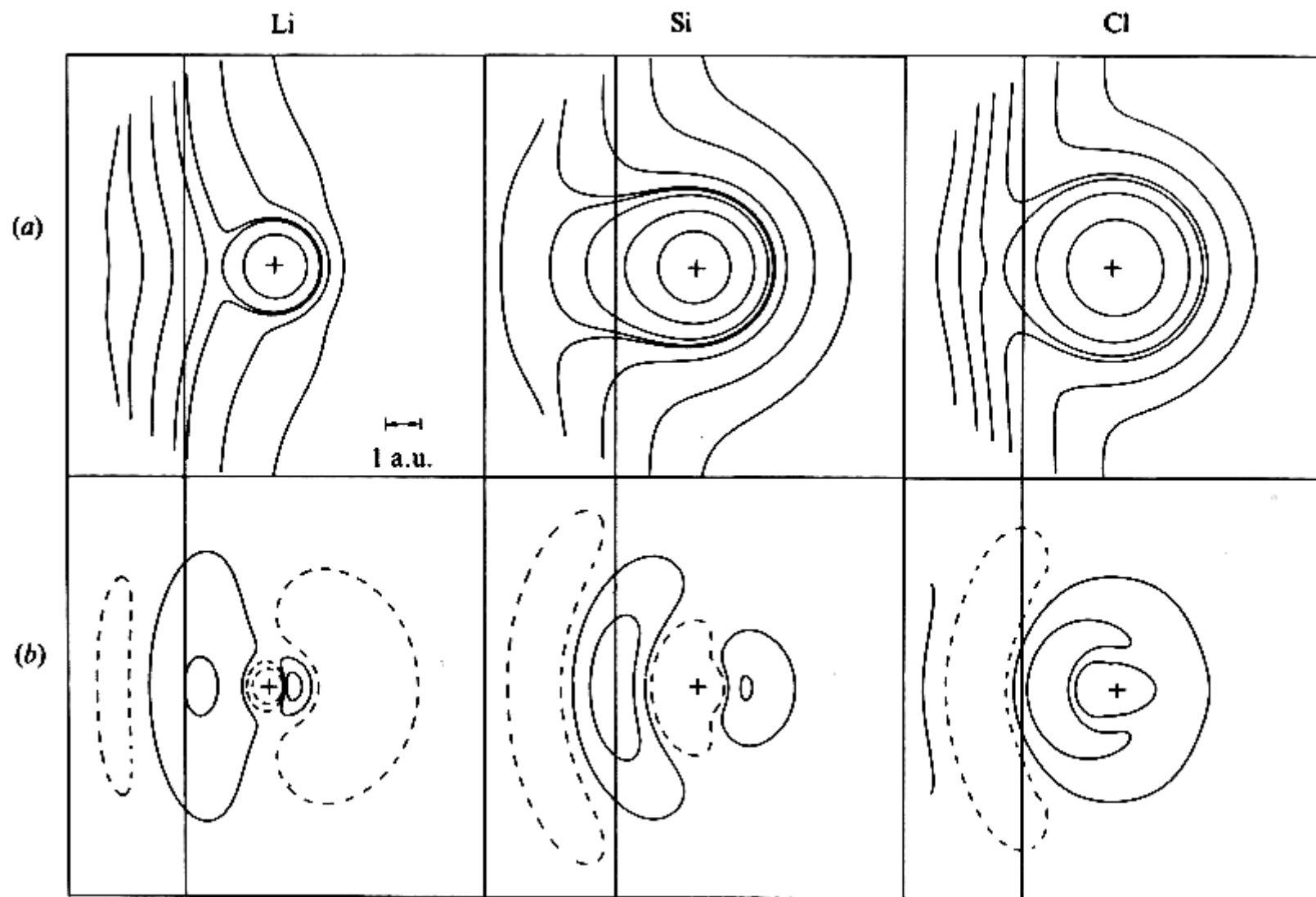


Fig. 9.10. Change in density of states due to chemisorption for Cl, Si and Li atoms adsorbed on jellium ( $r_s = 2$ ). The silicon curve exhibits both 3s-derived and 3p-derived resonances (Lang & Williams, 1978).





**Fig. 9.11.** Contours of constant charge density for Cl, Si and Li atoms adsorbed on a jellium substrate: (a) total charge; (b) induced charge. Solid (dashed) curves denote a surplus (depletion) of electrons (Lang & Williams, 1978).