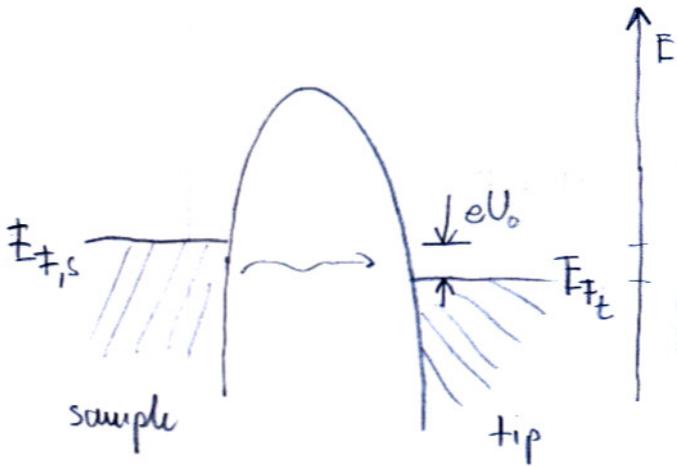


We already know, that this picture can not be entirely correct, as we neglect the image potential. Therefore we have

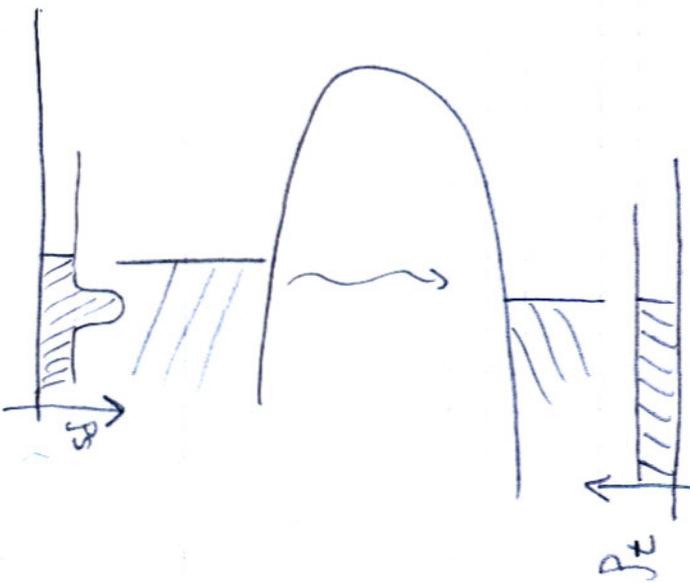
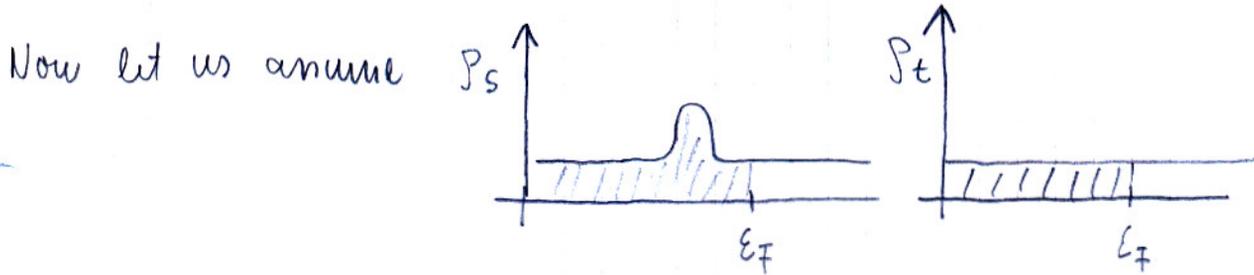


and

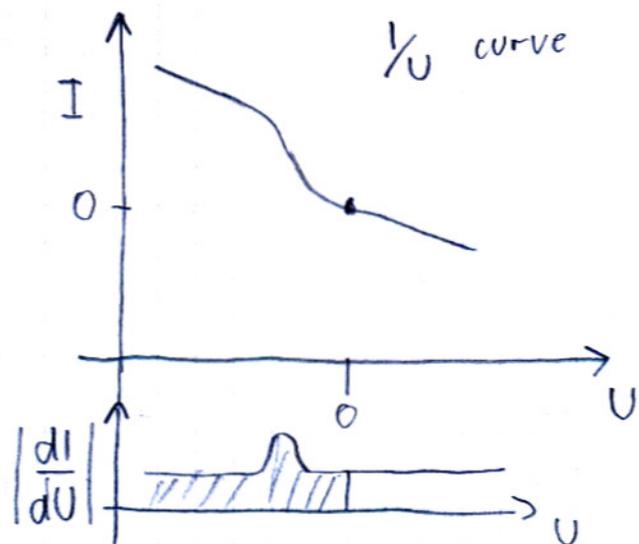
$$I \sim \int_0^{eU} \rho_S(\vec{r}_t, E) \rho_T(E - eU) dE$$

The tunneling current is determined by the local density of states of the sample at the tip position. In simple theory this is just the product of the sample density of states at the sample position times a transmission coefficient describing the tunneling probability

$$\rho_S(\vec{r}_t, E) = \rho_{S_0}(E) \cdot T(E, U)$$



What happens when we change U ?



In other words: $\frac{dI}{dU}|_{U_0} \sim \rho_{s_0}(eU_0)$; the $\frac{dI}{dU}$ -curve is proportional to the local density of states at the sample surface. This makes STS a very important tool for surface electronic structure investigations. Unlike photoemission, STS can probe both, occupied and unoccupied states.

Now we are in the position to understand measuring image potential states by STS. In Fig. 3.25 on the left we see the energy diagram for $\text{Ni}(001)$. (a) shows the field free image potential states, (b) suggest that they shift down somewhat by surface corrugation. In (c) it is shown that the applied field E adds to the image potential as eEz and therefore shifts the image potential states apart. Upon reducing the tunneling voltage the tunneling edge of the tip (i.e. the tip Fermi level) moves through the image potential states. Whenever the tunneling edge hits an image potential state, the conductance greatly increases and a peak in the $\frac{dI}{dU}$ curve appears.

3.3 Shockley and Tamm surface states

The electronic states in the crystal are described by the Bloch theorem.

They are wavefunctions of the form

$$\psi(\vec{r}) = e^{i\vec{k}\vec{r}} u(\vec{r}) \quad \text{with} \quad u(\vec{r}) = u(\vec{r} + \vec{R}),$$

i.e. plane waves multiplied by a lattice periodic function.

As shown in Fig. 3.26 (a), the introduction of the surface necessarily breaks the full periodicity of the wavefunction. The surface can be modeled in a simple approximation through a potential step at $z=0$ such that $V(z) = V_0$ $z > 0$. Any wavefunction bound to the crystal

must decay exponentially into the vacuum, i.e. for $z > 0$ we have $\psi(\vec{r}) = \psi_0 e^{-\kappa_v z}$ with κ_v being the damping constant into the vacuum determined by the height of the potential step:

$$k_v \sim \sqrt{\frac{2mV_0}{\hbar^2}}$$

We therefore have to match the Bloch wave function valid for $z < 0$ at $z = 0$ to $\psi(\vec{r}) = e^{-kz}$ for $z > 0$.

Besides this almost obvious modification introduced by the surface, there is one more interesting one. The fact, that the wavevectors \vec{k} of the Bloch functions are real was imposed by the periodic boundary conditions of the form $\psi(x+L, y, z) = \psi(x, y, z)$. However, through the introduction of the surface this restriction is not more justified and we are forced to allow complex wave vectors of the form

$$\vec{k} \approx \vec{k} + i\vec{\kappa}$$

This gives rise to solutions

$$\psi(\vec{r}) = e^{i\vec{k}\vec{r}} u(\vec{r}) \cdot e^{-\vec{\kappa}\vec{r}}$$

inside the crystal. Certainly arbitrary values of $\vec{\kappa}$ can be allowed, otherwise ψ might increase without bound. $\vec{\kappa}$ must be of the form $\vec{\kappa} = (0, 0, \kappa_z)$ such that the wave function decays into the crystal. The matching condition to the exponentially decaying wave function into the vacuum (continuous and derivatives continuous)

forces these states to be in the bulk energy gap, at least in the 1D case. Such a surface state wave function is sketched in Fig. 3.26. Note that surface state wave functions are ordinary Bloch functions in the direction parallel to the surface. Surface state wave functions have a substantial amount of their electron density at or at above the surface. Often these surface states display a nearly free electron dispersion relation.

Typical examples for such surface states are those of noble metals (see below). Surface states, that may be well described in the

nearly free electron picture are called Shockley surface states.

Surface states derived from more localized electrons are called Tamm surface states. Typical examples are the dangling bond

of semiconductor surfaces.

In order to understand the relation of surface states and bulk states better, we introduce the concept of the projected bulk band structure. For a given direction k_{\parallel} parallel to the surface, we project all energy values of all wavevector $\vec{k} = (k_{\parallel}, k_{\perp})$ to a fixed value k_{\parallel} onto the surface. The areas shaded in Fig. 3.27 have states with that energy for some k_{\perp} , those not shaded have no states with that energy for some k_{\perp} . The non shaded areas are the band gaps of the projected bulk band structure. The material projected in Fig. 3.27

is a metal. (Why?) The surface states appear now in the band gap of the projected bulk band structure, but may move for larger values of k_{\parallel} into the projected bulk band structure. Then they are called surface resonances, bulk states with a specifically high amplitude at the surface. Compare Fig. 3.28. Fig 3.29 displays a compilation of experimental data measured for the Cu(111) surface state. Grey shaded is the projected bulk band structure, the calculations are shown by the dashed line and the symbols are experimental results. Fig. 3.30 exemplifies how

the STM data was recorded. The left panel shows the variation of $\frac{dI}{dU}$ at various voltages U in the direction normal to the step.

Characteristic oscillations in the periodicity of these oscillations are visible. As surface state electrons move parallel to the surface, they are scattered at defects. The right panel shows for a small voltage a topographic image of Cu(111). Fringes at steps and point defects are visible.

Electrons in surface states moving normal to the step with a wave vector $k_{\parallel} = \frac{2\pi}{\lambda}$ create standing waves at steps with a periodicity $\frac{\lambda}{2}$.

Measuring the wavelength of the standing wave pattern at a given tunneling voltage (and thus energy) allows us to establish

$E(k_{||})$ as shown in the inset of Fig. 3.30. It is $E = \frac{\hbar^2 k_{||}^2}{2m^*} + E_0, m^* \approx 0.4m_0$

As surface states are located in the band gap of the bulk bands, electrons in surface states have negligible overlap with states of the same energy in the bulk. Therefore, the holes created by photoemission or tunneling in an occupied surface state band has a relatively long lifetime and the photoemission line is relatively sharp. Therefore surface state spectroscopy served in the past as a benchmark for spectrometer resolution. The current spectrometer generation reaches an instrumental resolution ≈ 1 meV and is eventually good enough to resolve the natural line width of Shockley

surface states. The improvement in resolution is shown in Fig 3.31. In STS the measured local density of states (LDOS) has a very sharp rise when the voltage increases to allow tunneling out of the surface state. The sharpness of this rise is a direct measure for the line width of the surface states.

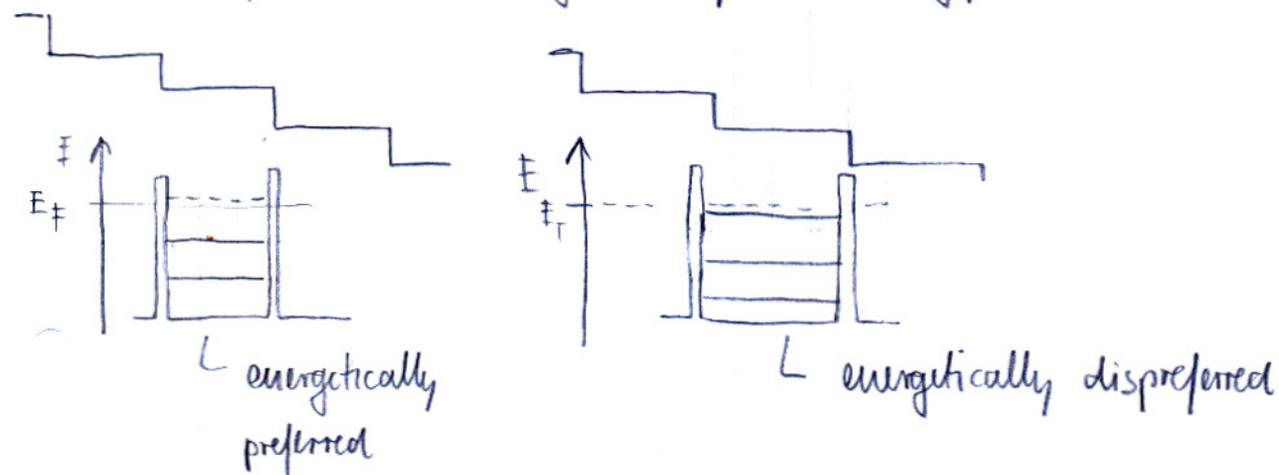
Surface states have a number of remarkable consequences for the stability of nanostructures. To give an example we analyse their effect on the interaction of adatoms. As you can see in Fig. 3.30 adatoms scatter electrons

in surface states visible by the circular ring pattern. A second adatom nearby a first causing a ring pattern will experience slight variations of its potential energy, depending on whether it sits on a maximum or a minimum of the scattered surface state charge density. A quantitative theory shows that the pair interaction energy E as a function of the adatom distance d is

$$E \sim \frac{-1}{(k_F d)^2} \cdot \sin(2k_F \cdot d + 2S_F)$$

$2k_F$ corresponding to $\lambda_F/2$ enters here, because the charge density oscillations are dominated by electrons close to the Fermi edge. S_F is a scattering induced phase factor. Fig. 3.33 shows a corresponding

experiment. At 15 K Cu adatoms are just mobile and able to sense slight differences in potential energy. Therefore they seek minimum energy positions and minimum energy separations on the surface. Freeing the equilibrated adatom shows a quasi regular pattern of adatom distances. Preferred separations are found and from them the pair potential $E(d)$ is obtained. It shows the expected decay with the distance and clear oscillations with a periodicity of $\frac{\lambda_F}{2}$. Meanwhile, besides adatom-adatom interaction a number of situations were identified, in which quantisation effects or Friedel oscillations of surface electrons are relevant. For instance, vicinal surfaces with regular step spacings lead to a quantization of the surface state electrons. Energetically, step distances are preferred with no state at the Fermi edge, thus lowering the system energy.



Another example is the observation, that the decay rate of adatom slows down for successively decreasing diameters differing by $\frac{\lambda_F}{2}$.

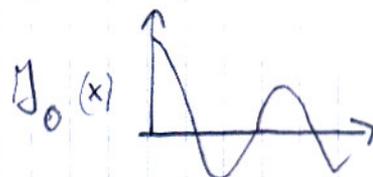
A beautiful experiment demonstrating quantization of the free surface state electron gas in a confined geometry is shown in Fig 3.34. A 60 atom quantum corral has been constructed by atomic manipulation on Cu (111). We can model the situation as a free electron gas in a radially symmetric potential, for simplicity of infinite height.

The solutions of the Schrödinger equation are

$$\psi_{nl}(r, \varphi) \sim Y_l^m(k_{nl} \cdot r) \cdot e^{i l \varphi}$$

with $k_{nl} = \frac{z_{nl}}{r_0}$ where $z_{nl} = n$ th zero of $J_l(z)$
 $r_0 =$ radius of corral
 $J_l =$ Bessel function

and Eigen energies $E_{nl} = \frac{\hbar^2 k_{nl}^2}{2m^*}$

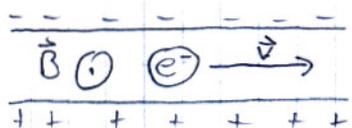


The radially symmetric appearance of the standing waves and the maxima in the center show, that states with $l=0$ dominate. The $\frac{dI}{dU}$ spectrum is very well reproduced by this simple model.

Finally we come to a surface specific spin-orbit splitting of the surface states. Let us remember first the origin of spin-orbit splitting in the hydrogen atom. In the system of rest of the electron, the proton performs an orbit around the electron. This current creates a magnetic field at the electrons position

which interacts with the spin magnetic moment of the electron. The energy of the electron will thus differ, depending whether the spin is parallel or antiparallel to the \vec{B} -field.

A similar situation is present at the surface. Consider our capacitor model of the dipole layer. In the rest system of the electron moving between the capacitor plates, the e^- sees current running above and underneath it through the plates.



Therefore it experiences a magnetic field \vec{B} in the plane of the capacitor. The spin moment of the electron will interact with this field and depending on the spin being \parallel or antiparallel with