

Local microscopies

Local microscopies or scanning probe microscopies SPM relies on five elements:

- small, local probe
- close proximity of probe and object
- stable positioning of probe with respect to the object
- distance dependent interaction of probe with object
- scanning of probe over object

Scanning Tunneling Microscope (STM)

The scanning tunneling microscope (STM) was developed in the early 1980s by G. Binnig and H. Rohrer, who were awarded the Nobel Prize in Physics in 1986 for the invention (shared with E. Ruska) slide

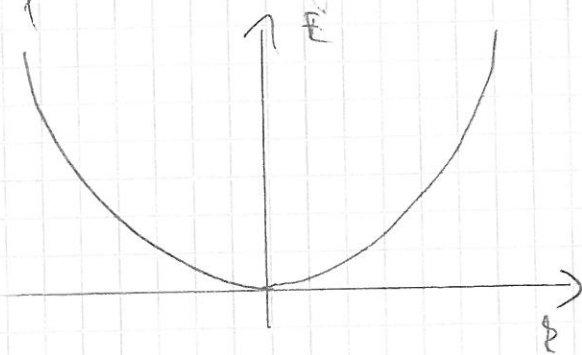
In this instrument, the small, local probe is a fine, metallic needle which is raster-scanned over the surface slide. The distance dependent interaction is the quantum-mechanical tunnel current between the tip and the conducting surface slide. Due to the exponential dependence, the current is a strongly varying function of distance. It changes by one order of magnitude when the distance between tip and sample is changed by $\approx 1 \text{ \AA}$.

Refresher: Electronic structure of solids

In the most simple picture, the electrons inside a solid are sorted into bands of increasing energy, where each band can only contain a certain number of electrons. slide. The electric behavior (metal, insulator, semiconductor) is then a consequence of the size and arrangement of the bands (occurrence of band gaps).

To go beyond this oversimplified description, one has to take the wave vector \vec{k} of the electrons into account (or their crystal momentum ($\vec{p}_{\text{crystal}} = \hbar \vec{k}$)). Consider for example a free electron. Here, the equation $E = \frac{\hbar^2 k^2}{2m}$ is obeyed;

i.e. a quadratic dispersion relation.



We now consider the solid as a box that we fill with electrons, starting at the lowest energy. Due to the Pauli exclusion principle, we cannot put all electrons at the lowest energy, so we subsequently fill up the parabola, putting each electron in

a separate state. Due to the shape of the dispersion relation, the density of states varies with energy $[D(E)]$ (in the solid state physics lecture you learned how to compute $D(E)$ from $E(\vec{k})$). For the case of free electrons, $D(E)$ has the form

$$D(E) = \frac{\overset{\text{volume}}{V}}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$$

When we put a certain number of electrons in our box, the states are occupied up to a characteristic energy, the Fermi energy,

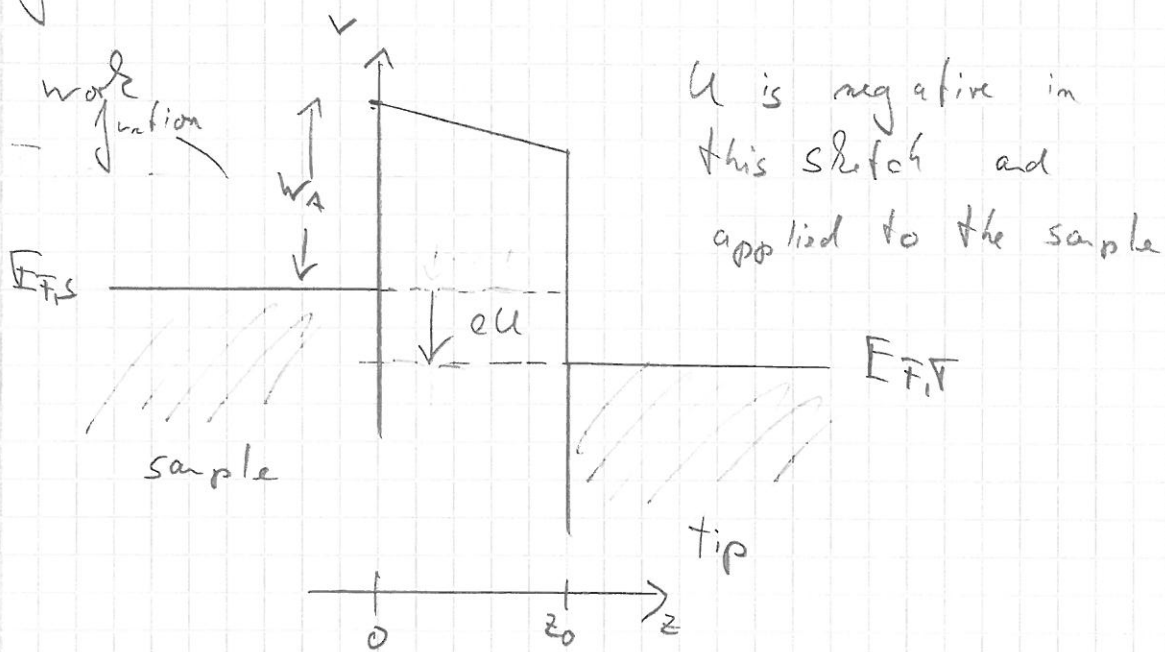
Real materials have a more complicated $E(\vec{k})$. For crystals, the translational symmetry has the consequence, that we do not have to consider all possible values for \vec{k} , but only those in the unit cell of reciprocal space, the Brillouin zone. A simple real example

is Aluminium, which is a quasi-free-electron material slide. Indeed, if you look closely, you will recognize the features of the free electron gas in $E(\vec{k})$ and $D(E)$. Note that Aluminium is a metal (no gap at E_F).

A more complicated example is the band structure and density of states of copper slide.

In general, the band structure governs important electronic and optical properties of the material, we will therefore discuss several experimental methods to determine $E(\vec{k})$ and $D(E)$.

In the following we will discuss the tunneling process in STM in more detail. Consider first a 1D-situation:



The wave function ψ_n of a plane wave at $E_n \approx E_{FS}$ is exponentially damped into the barrier:

$$\psi_n(z) = \psi_n(0) e^{-Kz}$$

If a small negative sample bias is applied, the electrons of the sample state n may tunnel into an unoccupied tip state. The probability w_n to find the electron at $z = z_0$ is:

$$w_n \sim |\psi_n(z)|^2 = |\psi_n(0)|^2 \cdot e^{-2Kz_0}$$

In a tunneling experiment, the tunneling current consists of all electrons of states within the interval $[E_{FS} + eU, E_{FS}]$ that are transmitted through the barrier. Thus:

$$I \sim \sum_{E_n \in [E_{FS} + eU, E_{FS}]} |\psi_n(0)|^2 e^{-2Kz_0}$$

If U is sufficiently small, the density of states does not vary significantly, and the sum may be expressed through the local density of states at a location z and energy $E_{F,S}$:

$$S_S(z, E_{F,S}) = \frac{1}{\varepsilon} \sum_{E_n \in [E_{F,S} + \varepsilon, E_{F,S}]} |\psi_n(z)|^2$$

$$(\varepsilon \text{ very small}) = \frac{1}{\varepsilon} \sum_{E_n \in [E_{F,S} + \varepsilon, E_{F,S}]} |\psi_n(0)|^2 e^{-2\kappa z}$$

(Note that for a full description we will also allow that the density of states can vary locally.) The sample local density of states is the number of states available for electrons per unit energy and volume at a given energy and distance (in this 1D-example, volume must be replaced by length).

Using S_S we may rewrite:

$$I \sim eU \cdot S_S(0, E_{F,S}) e^{-2\kappa z_0}$$

$$= eU \cdot S_S(z_0, E_{F,S})$$

The tunnelling current is thus proportional to the sample LDOS at the tip position.

A full $2+1$ dimensional calculation by Tersoff and Hamann for the case of small tunneling voltages gives an analogous result:

$$\nabla \sim \rho_s(\vec{r}_T, E_{FS}) \cdot U \cdot e^{2kR}$$

Here R is the tip radius and \vec{r}_T the position of the tip center of curvature. To obtain this result one also has to put in assumptions on the electronic structure of the tip.

Here, the tip is treated as an s-wave (i.e. spherical symmetry).

Most often, the tip-sample distance is controlled in order to keep the tunneling current constant (constant current mode).

In constant current mode the STM tip center of curvature follows a contour of constant sample LDOS

The essence of the Tersoff-Hamann approximation is visualized on the slide for the 1×1 - 2×1 and 3×1 reconstruction.

Although the structureless tip is a good starting point, frequently the corrugation of the tip motion is much stronger than expected from the Tersoff-Hamann model. This takes place if the tip atom has a more localized orbital (p_z, d_{z^2}).

With such a tip, atomic resolution on clean p(1x1) metal surfaces is obtained

[Slide]

The scanning and distance regulation is done by piezo-electric elements slide, which allow a positioning of the tip on the nm-scale using voltages on the order of several V. In the most often used mode of operation, the tunneling current is kept constant by a feedback loop acting on the tunneling distance (constant current mode). The instrument can achieve atomic resolution. A major breakthrough of the STM was the unambiguous verification of the real space structure of the Si(7x7) reconstruction proposed from diffraction experiments slide. In some (rare) cases, also chemical contrast can be achieved slide. The shape of the tip is crucial. Only for an atomically sharp tip, the real structure of a surface can be determined slide. However, this is easier than you might think now: Due to the exponential decay of the tunneling current, there has only to be an atom protruding a little bit more than the rest ("one atom is always the last").

As the tunneling current in STM is proportional to the local density of states one can also use this instrument to measure the electronic structure of the sample on a local scale.

This mode of operation is called scanning tunneling spectroscopy (STS). Basically, the tip is positioned at a given point of the surface and the voltage is changed while the tip-sample distance is kept fixed. Technically, the current signal is often measured using lock-in amplifiers, which gives the derivative of $I(U)$ as a output. Again, for a structureless s-wave tip we obtain:

$$\frac{dI}{dU} \Big|_U \sim \rho_s(\vec{r}_T, E_F + eU)$$

The signal that is determined is thus proportional to the density of states. In addition to measure $\rho(E)$ at one point, one can also measure the spatial distribution of $\rho(E_n)$ at a fixed energy E_n (dI/dU -maps).

In the following we discuss three examples for tunneling spectroscopy.

(i) Quantum corrals: By restricting electrons in the attractive potential of the tip over the surface, it is possible to create artificial surface structures (pioneered by Eigler).

1 slide

On the slide you see a circular structure of adatoms (the quantum corral), which scatter the surface state electrons (i.e. electrons confined to the surface). Due to the shape of the corral, a circular potential well is formed. For such a system, the eigenstates of the electrons are of the form: spherical Bessel function

$$\psi_{m,l}(r, \phi) = J_l(k_{m,l} \cdot r) \cdot e^{i l \phi}$$

$$k_{m,l} = z_{m,l}$$

with $z_{m,l} = n$ -th zero of $J_l(z)$
 $r_0 =$ radius of the corral

The eigenvalues are:

$$E_{m,l} = \frac{\hbar^2 k_{m,l}^2}{2m^*}$$

slide

↑ effective mass

The eigenfunctions with $l=0$ have a maximum in the center of the corral. Performing point spectroscopy then yields essentially the eigenvalues of the $l=0$ solutions.

ii) Spin polarized STM uses a magnetic tip. Ideally, the tip is magnetized either parallel or antiparallel to the surface domains. As sketched in the slide, for the same distance between tip and sample, the tunneling resistance will generally be lower for parallel

tip/sample domain geometry. This alone can not simply be used for imaging, since in constant current mode the difference in resistance will be compensated by a tiny little height difference not distinguishable from topographic height changes. Rather, a dI/dV - map is taken for a suitable voltage (giving optimal contrast) together with the topographic image. The dI/dV image has excellent magnetic contrast as shown in the slide

iii) If we place a molecule in between tip and sample usually the tunneling will not be strongly altered as long as the electrons tunnel elastically through the molecule. If however the electron energy is large enough that the electrons are able to excite the molecule into a vibration, a new inelastic tunneling channel opens. This appears like a suddenly increased occupied state DOS. The vibrations are in consequence very well visible in the second derivative d^2I/dV^2 .

The slide gives an example and demonstrates that the energy resolution of STM is sufficient to identify isotope effects for acetylene (H_2C_2 $H-C \equiv C-H$) on $Cu(100)$.