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).

In this instrument, the small, local probe is a fine, metallic needle which is raster-scanned over the surface. The distance dependent interaction is the quantum-mechanical tunnel current between the tip and the conducting surface. 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 1 Å.
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. The electronic 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 \( k \) of the electrons into account (or their crystal momentum \( \mathbf{p} = h \mathbf{k} \)). Consider, for example, a free electron. Here, the equation \( E = \frac{p^2}{2m} \) is obeyed.

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 pack all electrons at the lowest energy, so we subsequently fill up the parabolic potential each electron in
Due to the shape of the dispersion relation, the density of states varies with the energy \( D(E) \). In the solid state physics lecture, you learned how to compute \( D(E) \) from \( E(k^2) \).

For the case of free electrons, \( D(E) \) has the form:

\[
D(E) = \frac{1}{V} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}
\]

\[\text{Graph of } D(E) = \frac{1}{V} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \]

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 \( E(k) \). For crystals, the translational symmetry has the consequence, that we do not have to consider all possible values for \( k \), 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. Indeed, if you look closely, you will recognize a good use of the free electron gas in \( E(k^2) \) 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.

In general, the band structure governs important electronic and optical properties of the material. We will therefore discuss several experimental methods to determine $E(k)$ and $\sigma/E$.
In the following we will discuss the tunneling process in STM in more detail. Consider first a 1D situation:

\[ E_{FS} \rightarrow U \rightarrow E_{F_T} \]

\[ E_{FS} \rightarrow \text{Sample} \rightarrow \text{Tip} \]

The wave function \( \Psi_h(x) \) of a plane wave at \( x = E_{FS} \) is exponentially damped into the barrier:

\[ \Psi_h(x) = \Psi_h(0) e^{-k_2x} \]

If a small negative sample bias is applied, the electrons of the sample state in many tunnel into an unoccupied tip state. The probability \( p \) to find the electron at \( x = x_0 \) is:

\[ \rho = \frac{1}{2} \frac{|\Psi_h(x)|^2}{|\Psi_h(0)|^2} e^{-2k_2x_0} \]

In a tunneling experiment, the tunneling current consists of all electrons of Slater orbitals in the interval \( [E_{FS} + U, E_{FS}] \) that are transmitted through the barrier.

\[ I \propto \sum_{E_m \in [E_{FS} + U, E_{FS}]} \left( \frac{|\Psi_h(0)|^2}{|\Psi_h(0)|^2} e^{-2k_2x_0} \right) \]
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 \( E \).

\[
S_z(2, E_{qs}) = \sum_{E_n \in [E_{qs} + \epsilon, E_{qs}]} \left( \frac{1}{\Omega} \right)^2 |Y_m(z)|^2
\]

\[
(\text{very small}) = \sum_{E_n \in [E_{qs} + \epsilon, E_{qs}]} \left( \frac{1}{\Omega} \right)^2 e^{-2k^2}
\]

(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 case, volume must be replaced by length).

Using \( S_z \), we may rewrite:

\[
E_n \in U. S_z(0, E_{qs}) \propto \omega_{BZ}
\]

\[
= eU \cdot S_z(r_0, E_{qs})
\]

The 

the sample LOOS at the VP.

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

\[ E = E_s \left( \frac{\rho}{\rho_T}, E_{Fs} \right) - U_{\epsilon, p} \]

The \( R \) is the tip radius and \( \rho \) is 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
dip probe of curvature follows a contour
of constant sample LDOS

The essence of the Tersoff-Hamann approximation
is visualized on the slide for the 6H-(110)-2m
and 3x1 reconstruction.

Although the structureless dip is a good
starting point, deviation from the corrugation of
the dip motion is much stronger than
expected from the Tersoff-Hamann model. This
does place all the dip arm has a more
localized orbital (Pz, d_z^2). With such a
dip, atomic resolution on chalcogen metal surfaces
is observed.
The scanning and distance regulation is done by piezo-electric elements \[ \text{[slide]} \], which allows a positioning of the tip on the nanometer 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\((3\times1)\) reconstruction proposed from diffraction experiments \[ \text{[slide]} \]. In some (rare) cases, also chemical contrast can be achieved \[ \text{[slide]} \]. The shape of the tip is crucial. Only for an atomically sharp tip, the real structure of a surface can be determined \[ \text{[slide]} \]. However, this is easier than you might think now: Due to the exponential decay of the tunneling current, the hole only to be an atom, not melting 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 fixed point on 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 $I(V)$ as an output.

Again, for a structureless sharp tip, we obtain:

$$\frac{dI}{dU} \sim I_{c} (R_{T}, E_{F}, |\mathbf{E}|)$$

The signal that is determined is then proportional to the density of states in addition to measure $I(E)$ at one point, one can also measure the spatial distribution of $I_{c} (E_{F}, |\mathbf{E}|)$ at a fixed energy $E_{F}$ (adioint maps).

In the following, we discuss three examples for tunneling spectroscopy:

1) Quantum Corrals: By oscillating adatoms in the attractive potential of the tip over the surface, it is possible to create artificial surface structures (pioneered by Eigler).
On the slide you see a circular structure of solutions (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 eigenvalues of the electrons are of the form:

\[ E_{nl} = \frac{n^2 \pi^2 \hbar^2}{2m^* r_0^2} \]

The eigenvalues are:

\[ E_{nl} = \frac{n^2 \pi^2 \hbar^2}{2m^* r_0^2} \]

with \( n = 1, 2, 3, \ldots \)

\[ r_0 = \text{radius of the corral} \]

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

ii) Spin polarized SPM, 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.

ii) 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 sample 2DOS.
The vibrations are in consequence very small
visible in the second derivative $d^2I/dV^2$.

The slide gives an example and demonstrates
that the energy resolution of SPM is sufficient
to identify isotope effects for acetylene
($H_2C\equiv CH\equiv C\equiv C\equiv H$) on Cu (100).