Atomic Force Microscope (AFM)*

The AFM was developed from the STM in 1986 by Binnig, Quate, and Gerber. The principle of operation is amazingly simple: A fine tip is in mechanical contact with the sample and by scanning the tip a map of the topography can be obtained. Of course, this is only the most simple picture of the operation.

The general concept of operation is depicted in the slide. The interatomic forces between the tip and the sample surface atoms cause the cantilever to deflect. The cantilever displacement is measured by a deflection sensor, for example by the reflection of a laser beam from the rear of the cantilever. Typically, sensors can detect deflections as small as 10^{-2} Å. Measuring the deflection of the cantilever while the tip is scanned over the sample allows the surface topography to be mapped. A great advantage is that AFM also works for non-conducting surfaces.

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* For some reason, the German name of the AFM is „Rasterkraftmikroskop" instead of „Atomkraftmikroskop".

The force vs. distance curve between tip and cantilever is depicted in the [slide].
When the tip-to-sample separation is relatively large, the cantilever is weakly attracted to the sample. With decreasing distance, the attraction increases until the separation becomes so small that the electron clouds of the tip and the sample overlap and Pauli repulsion starts. The net force goes to zero at a distance on the order of the length of a chemical bond (a few Å) and at closer distances the repulsion dominates.

The AFM can be operated either in <u>contact mode</u> or in <u>non-contact mode</u>. In contact mode, the tip is in soft physical contact with the sample and is subjected to repulsive forces. These forces cause the cantilever to bend, following the changes in surface topography. In non-contact mode, the tip is further away and senses attractive forces. Here, the cantilever is put to vibration close to its resonance frequency.
Changes in the attractive potential lead to detuning of the resonance frequency. This can be determined very accurately and used as the feedback signal
[slide]

A recent development is the Q-Plus sensor [slide]. Here, a tuning fork as found in a quartz watch is used as the oscillator. With such instruments, atomic resolution is routinely achieved.

Photoelectron spectroscopy (PES)

Photoelectron spectroscopy (PES) is the most commonly used analytical technique to probe the electronic structure of occupied states at the surface and near-surface region. It is based on the photoelectric effect in which the electron, initially in a state with binding energy E_b absorbs a photon of energy $\hbar\omega$ and leaves the solid with kinetic energy

$$\boxed{E_{kin} = \hbar\omega - E_b - \phi},$$

where $\phi = E_{vac} - E_F$ is the work function of the material [slide], schematics: [slide]

Depending on the energy (wavelength) of the photons used for electron excitation, photoelectron spectroscopy is divided into:

X-ray photoelectron spectroscopy (XPS), pioneered by Siegbahn ([slide]), where x-ray radiation is used ($\hbar\omega$ = 100 eV - 10 keV). As a consequence, XPS probes the deep core levels.

Ultraviolet photoelectron spectroscopy (UPS), when the photons are in the ultraviolet spectral range 10-50 eV. As a result, UPS is used for studying valence and conduction bands. It should be noted that this division is not very sharp. For example, the same detector can be used and the transition between core and valence levels is a gradual one.

value of m_l. In most cases, linear combinations of orbitals with different values of m_l are a more useful basis set. The $\boxed{\text{slide}}$ gives an overview of the different orbital shapes. Finally, m_s is the spin of the electron and can be $\pm \frac{1}{2}$. The full energy scheme is shown on the $\boxed{\text{slide}}$. According to <u>Pauli's exclusion principle</u>, each electron has to have its own, unique set of the four quantum numbers. Finally, the angular momentum given by l creates a magnetic field. The spin of the electron can then align in this field, leading to an energetic splitting of the energy level (part of the <u>fine structure</u>) caused by this <u>spin orbit coupling</u>.

In photoemission, the energy levels (and consequently the peaks in the electron spectrum) are labelled as this:

$$\underbrace{Ir}_{\text{element}}\ \overset{n}{5}\ \overset{l}{d}\ \underset{j=l+s}{3/2}$$

The binding energy E_b of the electrons in the different orbitals is element-specific (see $\boxed{\text{slide}}$)

Refresher: Atomic levels

Remember that the eigenfunctions of a bound electron are defined by <u>four quantum numbers</u> n, l, m_l, and m_s.

n is the <u>principle quantum number</u> and denotes the <u>shell</u> in which the electron is sitting,

$n = 1, 2, 3, \ldots$

l is the <u>azimuthal quantum number</u> (or the <u>angular momentum</u>) and describes the <u>subshell</u> or the shape of the <u>electron orbital</u>. The value of l ranges from 0 to $n-1$. Traditionally, l is indicated using letters ($s=0$, $p=1$, $d=2$, $f=3$, ...). In the absence of external fields (electric or magnetic), the energy of the electron is almost completely given by n and l. The subsequent filling of these orbitals according to their energy determines the arrangement of elements in the <u>periodic system of the elements</u> $\boxed{\text{slide}}$. The third quantum number m_l is the <u>magnetic quantum number</u>, which is the projection of l along a given direction (you can think of it as the direction of the orbital). m_l ranges from $-l$ to l.

Note that you will very rarely see a drawing of an orbital with a specific

Some experimental details: The photons are provided either by <u>laboratory sources</u> or from a <u>synchrotron</u>. The synchrotron radiation has many advantages: variable photon energy (from UV to x-ray), high intensity, polarized light. Access to these sources is, however, limited. Lab sources are specifically designed for a wavelength regime (which is in fact the main reason to distinguish between UPS and XPS)

X-ray tubes use a high voltage to accelerate electrons onto a metal surface from which then x-ray photons are emitted. UV-sources are gas discharge lamps where gas atoms (often rare gases) are exited by collisions and emit UV-photons. As the escape depth of electrons from solids is rather limited (remember the universal curve) the samples under consideration have to have very clean surfaces. Therefore, samples are analyzed under ultra-high vacuum (UHV) conditions and have well-prepared surfaces. Finally, the electrons are detected using a <u>spectrometer</u> capable of measuring the kinetic energy of the incoming electrons. Basically, the electrons fly through an electric field where they are deflected

depending on their kinetic energy. Several types of spectrometers exist, today the most widely used one is the <u>hemispherical</u> photoelectron spectrometer $\boxed{\text{slide}}$. The most modern spectrometers are able to detect the electrons sorted in energy and emission angle on a position sensitive detector.

The photoemission process can be described in a three-step model: $\boxed{\text{slide}}$. In the first step, the electrons are excited by the photon into unoccupied bands, i.e. above the Fermi energy. Of course, if the energy of the photon is high enough, they can also be excited above the vacuum level. Of course, this does not imply that the electron is already in vacuum, it is still inside the sample (and could well be very far away from a surface). The electron now travels to the surface. On the way, some electrons are scattered and loose energy. To finally escape from the solid, the kinetic energy has to be large enough to overcome the <u>work function ϕ</u>.

Let us now look at some examples. The slide shows a survey spectrum, i.e. a scan over a wide energy range, of the oxidized surface of InAs. The composition of the sample can be inferred from the peaks observed. With Core, this can even be done quantitatively. In addition to the clearly visible photoemission peaks, signals from Auger processes as well as a background of secondary electrons is visible. This capability for chemical analysis has led to the wide spread use of XPS in materials science and mineralogy. Zooming in on the peaks reveals the spin-orbit splitting. With very high resolution, one can observe an additional substructure, caused by the chemical shift slide. Here, the position of the core levels is sensitive to the chemical binding pattern. Chemical binding involves mostly valence electrons. For the case of covalent bonds, valence electrons are shared between two nuclei. The electrons prefer to accumulate at the more electronegative partner. This reduces the electron density seen by the core electrons of the other partner (the valence electrons have a large probability density also close to the nucleus)

Consequently, the positive charge of the nucleus is not screened as effectively as before, therefore the binding energy of the core electrons increases.

The limitation to clean surfaces can be overcome by the use of hard x-rays that generate photoelectrons with high kinetic energies, able to travel inside the solid for quite some distance. This is then called <u>HAXPES (hard x-ray PES)</u>. Recently, spectrometers capable of resolving small energy differences of the high energy photoelectrons became available, leading to an increased interest in this technique.

UPS reveals the band structure of the valence electrons which form broad bands due to their delocalization $\boxed{\text{slide}}$. With high resolution spectrometers, the shape of the Fermi distribution can be accurately <u>determined</u>.

The full power of UPS is obtained, when the <u>angular resolved</u> mode of measuring is used: ARPES (angular resolved PES). By measuring the kinetic energy E_{kin} as well as the azimuthal and polar angle of electron

emission, the wave vector of the free electron can be determined (slide).
The rough angle is set by the angle of the sample with respect to the analyzer, the measurement is done by using the position sensitive detector. Of course, we are not very much interested in the properties of the free electron in vacuum, but in the properties of the electron in the solid. Here we can use the respective conservation laws. For the energy, we already know $E_{kin} = h\nu - E_B - \phi$. For the momentum $\vec{p}$ (or equivalently the wave vector $\vec{k}$), only the component parallel to the surface is conserved as the surface breaks the translational symmetry of the system. Therefore, in ARPES you measure the <u>projection</u> of the wave function on a given surface. Things become particularly easy for two dimensional systems, see the example for graphene (slide). ARPES thus produces pictures very similar to the schematic band structure diagrams found in text books.
The methods we have considered up to now are limited to the occupied part of the band structure. However, knowledge of the unoccupied part is also needed. This

is experimentally more demanding. One suitable method is <u>inverse photoemission spectroscopy (IPES)</u>. As the name implies, this is the reversed process of photoelectron emission: Electrons are shot on the sample and may be captured in unoccupied states [slide]. This is the an excited, metastable state of the system which can decay to a state closer to E_{Fermi} by emission of a photon. The conservation of energy in this case is written as:

$$\hbar\omega = E_{kin} + e\phi + E_b$$

Note that the binding energy of an unoccupied state is negative. IPES faces several experimental difficulties. First, the cross section of the process is low. Second, it is much more difficult to detect energy-resolved photons than electrons. A second method is <u>two-photon photoemission (2PPE)</u> [slide]. Here, an electron is excited into a state below the vacuum level. From this metastable state it can decay to a state with lower energy on the timescale of femto-seconds. When it is hit by another photon before this decay, it can be transferred above the vacuum-level and detected. To achieve this, high photon-fluxes are necessary. Consequently, lasers are used. By putting in a delay between the two pulses, the dynamics of the excited state can be explored (lifetime). This is called a <u>pump-probe</u> experiment.

X-ray adsorption spectroscopy (XAS)

Up to now, we only looked at the photoelectrons excited by the x-ray photons. However, much can also be learned by looking at the adsorption of the x-rays itself. The basis is again the photoelectric effect. We already know that an x-ray can only be adsorbed by an atom when its energy is greater than or equal to the binding energy of an electron. We have already introduced the law of Lambert-Beer, which reads:

$$\underbrace{I}_{\text{transmitted intensity}} = \underbrace{I_0}_{\text{incident intensity}} e^{-\underbrace{\mu}_{\text{absorption coefficient}} \underbrace{t}_{\text{thickness}}}$$

At most x-ray energies, the adsorption coefficient μ is a smooth function of energy and can be written as:

$$\mu \approx \frac{\underbrace{\rho}_{\text{density}} \underbrace{Z^4}_{\text{atomic number}}}{\underbrace{A}_{\text{atomic mass}} \underbrace{E^3}_{\text{x-ray energy}}}$$

Looking at real curves of $\mu(E)$ reveals a more complex behaviour [slide]. When the incident x-ray has an energy equal to that of the binding energy of a core electron, there is a sharp rise in absorption: an <u>absorption edge</u> corresponding to the promotion of this core electron to the continuum. For some reasons, the edges belonging to $n=1, 2, 3 \ldots$ are named K, L, M.

In x-ray absorption fine structure (XAFS), one looks at $\mu(E)$ near and at energies just above these absorption edges.

In order to detect the absorption of the photon, one looks at the decay of the associated excited state of the atom. There are two basic processes at work here: The first one is <u>x-ray fluorescence</u> [slide] in which a higher energy core-level electron fills the deeper core-hole, ejecting an x-ray of well-defined energy (to conserve energy). The fluorescence energies emitted in this way are characteristic of the atom and can be used to identify the atoms in a system and to quantify their concentrations. The second process for de-excitation is the Auger-effect, in which an electron drops from a higher level and now transfers its energy to a third electron which is emitted from the atom. Although this might seem a rather complicated process, for lower energy x-ray absorption (< 2 keV) it is actually the dominating one. Experimentally there are different methods to measure the absorption [slide]. First, rather straightforward, determine the beam intensity before and after the sample <u>(transmission mode)</u>. Second, record the fluorescence <u>(fluorescence yield)</u>. Third, measure all electrons that leave the sample by recording the current needed to refill electrons (total yield). Finally, record the photo electrons above a certain treshhold <u>(partial yield)</u>.

As an example, the slide shows a typical XAFS spectrum for FeO. Depending on how close to the edge you look, the technique is further divided into X-ray absorption near-edge spectroscopy (XANES) and extended XAFS (EXAFS). The sharp rise in $\mu(E)$ due to the Fe 1s electron level (at 7112 eV) is clearly visible in the spectra, as are the oscillations in $\mu(E)$ that are the XAFS. Let us first look at the oscillations in the EXAFS-regime. They are caused by interference effects between neighboring atoms: The excited electron is scattered at the neighboring atoms which leads to accumulation or depletion of charge density, which in turn influences the absorption probability of the photon. By going through the full theory, the number, distance, and chemical species of the neighbors can be determined. Very close to the edge (XANES-regime), the excited electron is not always brought to an energy above the vacuum level, but resides in metastable states close to it. This enhances the probability of absorption. In consequence, one can derive information on the chemical environment from this part of the spectrum. By using polarized light, one can also learn something about the direction of chemical bonds.

Synchrotron light sources

Already several times during this lecture, we looked at experiments performed at synchrotron light sources (x-ray diffraction, x-ray photoelectron spectroscopy). This chapter now introduces this experimental method in more detail. The main characteristics of synchrotron radiation are:

- extremely high intensity (brilliance)
- broad energy range
- very good collimation
- polarization
- pulsed emission

In short, a „tunable light source with fantastic properties"

The principle of light generation is photon emission from accelerated charge, where the most simple example is the dipole antenna [slide]. A charge oscillating on a straight wire induces electromagnetic radiation. The maximum intensity occurs perpendicular to the acceleration of the charge. This general effect does also occur for a charge on a circular orbit (constant acceleration towards the center of orbit). [slide] In a synchrotron, electrons with a speed close to the speed of light are used, which makes a relativistic description necessary. Basically, the high energy electrons emit very intense radiation, focused in a sharp forward cone.

The generation of synchrotron radiation is occurs in four steps [slide]. Electric fields are use to accelerate the electrons, and magnetic fields are used to define the electron path. First, electrons are created in an electron gun. In the next step, the electrons are accelerated in a linear accelerator. The main part is the <u>booster synchrotron</u> where the electrons go up to their final energies. In this ring-shape device, the electrons pass the accellerating E-field many times. To keep them on the desired orbit, the magnetic field has to be ramped up in synchronicity with the increase in energy (hence synchrotron). Finally, the electrons are transferred to the <u>storage ring</u>, where their velocity is constant. The energy loss due to emission of radiation is compensated by fields. The emitted light is extracted from the ring to a large number of <u>beamlines</u>.
Historically, however, the interest in synchrotrons came from <u>particle physics</u> where high energy particles were needed for collision experiments. In this context, synchrotron radiation was an undesired side effect as it leads to loss of energy. Solid state physicist, however, realized the high potential of synchrotron radiation and started to build beamlines at facilities focused on particle physics (parasitic use).

This changed when the first machines specifically designed to produce synchrotron radiation were put into use (~ 1980s), the <u>second generation synchrotrons</u>. During the use of these machines devices specifically designed for the excitation of synchrotron light were invented, the <u>wiggler</u> and the <u>undulator</u> (called <u>insertion devices</u>) Synchrotrons especially designed to incorporate a large number of insertion devices form the <u>third generation</u> [slide] Let us now look at bending magnets, wigglers, and undulators in more detail.

Due to the relativistic behavior of the electrons, the core of the emitted light is very narrow [slide] Consequently, one electron gives out a very short pulse of light for an observer sitting tangentially to the storage ring. The frequency (energy) spectrum is therefore very broad (it is the Fourier transform of the time domain) and contains rather high frequencies [slide]. Before we proceed, it is important to mention that several quantities can be used to describe synchrotron radiation:

$$\text{Total flux} = \frac{\text{Photons}}{\text{time}}$$

$$\text{Spectral flux} = \frac{\text{Total flux}}{0.1\,\%\ \text{bandwidth}}$$

$$\text{Brightness} = \frac{\text{Total flux}}{\text{solid angle} \cdot 0.1\,\%\ \text{bandwidth}}$$

$$\text{Brilliance} = \frac{\text{Total flux}}{\text{solid angle} \cdot \text{source area} \cdot 0.1\,\%\ \text{bandwidth}}$$

The brilliance is the figure of merit for third generation synchrotrons. High total flux and small solid angle give a lot of photons on your sample, a lot of photons per wavelength interval allows you to select a highly monochromatized beam, and a small source ensures a high spatial coherence, useful for diffraction studies. The next slide shows the brightness normalized to the electron current for bending magnets used for electrons of different energies and compares the flux with other sources.

For the insertion devices, the principle is to introduce alternating magnetic fields to the straight sections of the storage ring [slide]. Hence, the electrons perform a wiggling or undulating motion, always emitting photons where the trajectory is curved [slide] The special property of undulators is that the cones resulting from neighboring oscillation periods overlap and constructive interference occurs, resulting in a line spectrum of emission [slide]. The period of the magnets can be varied mechanically, thus allowing the use of different wavelengths.

The next [slides] compare the different devices and show the historical evolution of brightness.

X-ray optics

In most of the cases, the generated radiation is not directly suitable for the experiment. It has to be monochromatized and focused.