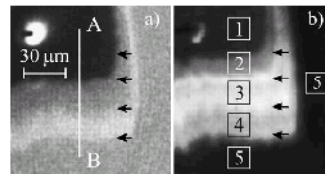
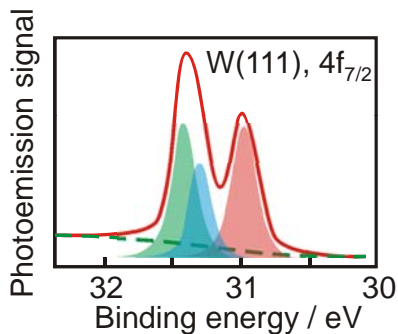


Frontiers of Experimental Condensed Matter Physics

Part B: Excitations Part 2

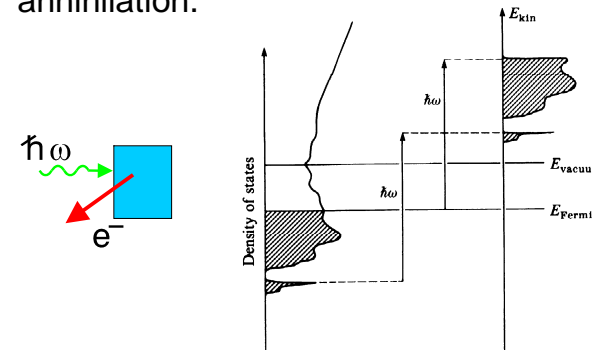
- Photoemission and electron spectroscopy
 - Photoemission processes
 - Auger and inelastic events
 - X rays: XPS
 - Core-level spectroscopy.
 - Core shifts, final state effects
 - Surface core-level shifts.
 - Ultraviolet spectroscopy: UPS
 - Kinematics, determination of band-structures
 - Surfaces and surface states.



1

The photoemission process

- removes electrons from the solid by providing the energy of escape from a photon annihilation.



- The power of the technique lies in the ability to probe all occupied states.

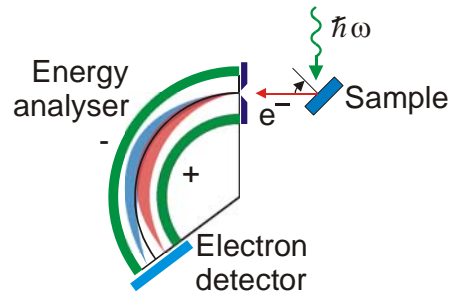
Inverse photoemission

- provides complementary information about the un-occupied states.
- In both cases the experiment and its interpretation are non-trivial.

2

Experimental aspects

Three aspects of experiment:



➤ Photon source:

- UV (20-200eV): He discharge, Synchrotron (especially for higher energies).
- X-rays (~1 keV): electron impact sources, Synchrotron (especially for variable energy studies).

➤ Sample.

- necessarily in a vacuum chamber (and usually at ultra-high-vacuum, UHV)

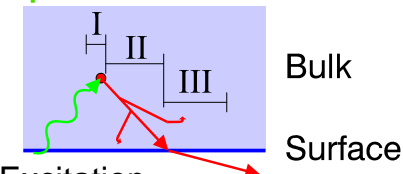
➤ Electron energy-analyser (typically 0 - 1 keV):

- electrostatic deflection type (eg. concentric cylinders/hemispheres), disperses energy across exit plane.
- position detection gives the e^- energy

3

Photoemission process

Three stage process:



- I Excitation
- II Transport to surface
- III Emission

➤ **Excitation:** Energy conservation gives

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

Maximum energy for $E_b = E_F$

Minimum energy, zero. $\hbar\omega = \phi + E_b$.

At UV energies, and above, the excitation process is a vertical transition in the band structure from an occupied to an un-occupied state.

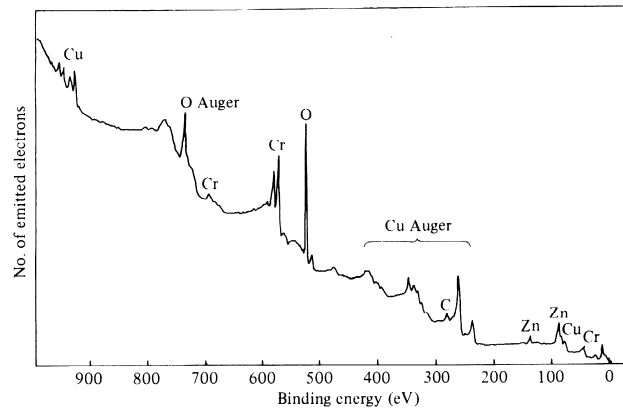
➤ **Transport:** inelastic scattering leads to a background of secondary electrons. The short mean free path, $\lambda \sim 10\text{\AA}$, implies a degree of surface sensitivity.

➤ **Emission:** Surface "breaks" the bulk periodicity. We have a 2-D periodic system, with conservation of the 2-D crystal momentum $K_{||}$.

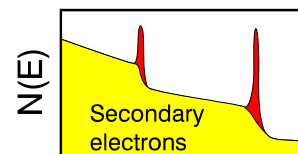
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Photoemission using x-rays

X-ray Photoelectron Spectroscopy (XPS).



- Sharp core levels whose energy is characteristic of the elemental composition.
 - Note non have the δ -function shape expected from our one-electron, tight-binding description
 - Peak shape and peak shift give information on the electronic environment, as we will see.
- Background has a characteristic stepped structure as the threshold for each new “source” of secondary electrons is passed.

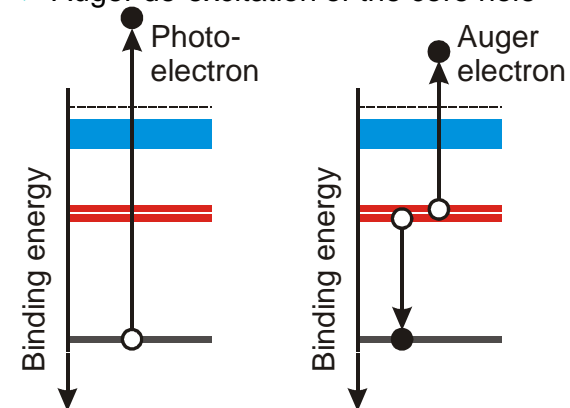


Electron energy 5

Origin of features

Peaks: Two processes dominate:

- Direct photoemission creating a core hole
- Auger de-excitation of the core hole



Note:

- Energy of the photo-electron depends on the incident photon; however, the energy of the Auger electron is purely a property of the solid.
- Any process that creates a core hole will give rise to Auger electrons. Auger spectroscopy (i.e. using the energy of Auger electrons as a tool) generally uses high-energy electrons to create the core hole. Hence techniques such as Scanning Auger Microscopy (SAM).

Energy of features

■ Beyond the naïve view....

- No change in the final state orbitals except to the one-electron orbital that is ejected is naïve...

$$E_{kin} = \hbar\omega - E_b.$$

Koopman's binding energy

- In fact, the other electrons will be able to adjust to their new environment (specifically the unscreened core). A better expression for the energy is

$$E_{kin} = \hbar\omega - (E_f^{N-1} - E_i^N)$$

E_f and E_i both -ve

- "Relaxation" of the remaining electrons tends to lower the final state energy (i.e. E_f^{N-1} is more negative), the photo-electron energy is greater (**binding energy appears lower**).
- Excitations of the remaining electrons can also occur. They are known as "shake up" processes. The energy to cause the excitation necessarily comes from the photoelectron energy, its energy is reduced, so a feature appears at lower electron energy (**satellite appears at greater binding energy**).

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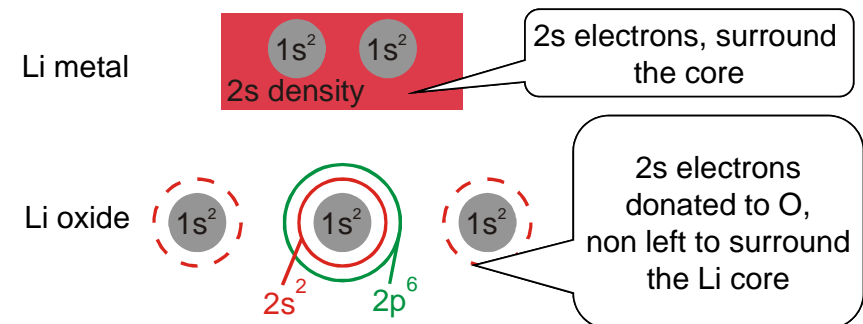
Chemical shifts

■ Relaxation shifts

- Small energy shifts of the photoelectrons creates the opportunity to use as a spectroscopy.
- The local electronic environment determines the "binding energy", hence the phrase "chemical shifts".

■ Example: illustration of the principles .

- Energy of the 1s peak in photoemission from Lithium metal compared with Li_2O .
 - atomic Lithium has electronic structure ($1s^2 2s$)
 - atomic Oxygen has structure ($1s^2 2s 2p^4$)

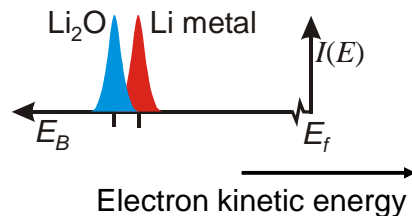


Hufner "Photoelectron Spectroscopy", ch 2 (Springer 1996)

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Chemical shifts II

- Metal case: As the 1s, core electron is ejected, the valence electrons relax in response to the unscreened nuclear charge.
 - lowering of the final state energy and a greater kinetic energy of the outgoing electron: a “lower binding energy”
- Oxide case: There is no nearby charge to relax and the nuclear charge remains unscreened.
 - the final state has a higher energy, the electron a lower kinetic energy and the peak position appears at a “higher binding energy”.



Equivalent core approximation

- Energy shifts are not easy to calculate, but can be estimated from other experimentally accessible data (eg. ionisation energies)
- Sometimes reasonable approximations can be made and, remarkably, the measured energies sometimes be related to heats of chemical reactions. The argument is subtle....

Equivalent core approximation

- We note that the core state to be ionised has a small size. The absence of an electron from the core can, therefore, be approximated by adding one charge to the nucleus.
- In the case of the 1s energy of a Li atom, the argument is as follows:
 - * = core state ionised
- Equate the energy of $Li^*(1s\ 2s) \Leftrightarrow Be^+(1s^2\ 2s)$
 - + = valence state ionised
- Removing one electron from each gives
 - $Li^{++}(1s\) \equiv Li^{*+}(1s\) \Leftrightarrow Be^{++}(1s^2\)$
 - and we know (from measurements of the ionisation energies of Be) that it takes +18.2eV.

- Thus, the **final state** of the photoemission system is 18.2eV below that of Li⁺⁺ .
- Ionisation energies for Li show it takes 81eV to remove two electrons. Thus, the **initial state** is 81eV below that of Li⁺⁺ .
- The photoelectron should therefore appear at a “binding energy” of (81 - 18.2) eV = 62.8 eV. In fact direct measurement gives 64.8 eV, which gives a measure of the (modest) accuracy of the equivalent core approximation.

■ Core shifts and reaction energies

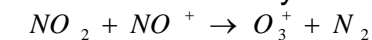
- An unusual, but interesting example: Suppose we wish to compare the chemical shift in core photoemission from nitrogen in N₂ with that for NO₂. i.e. we want the energy difference between $\Delta E_B = [E(N_2^*) - E(N_2)] - [E(N^*O_2) - E(NO_2)]$ rewriting $E(NO_2) + E(N_2^*) = E(N^*O_2) + E(N_2) + \Delta E_B$ (A)
- Making the equivalent core approximation we can say $N^* \leftrightarrow O^+$ and deduce the equality $E(N^*O_2) + E(NO^+) = E(O_3^+) + E(N_2^*)$ (B)

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- Adding (A) and (B) enables us to eliminate the two final state energies

$$E(NO_2) + E(NO^+) = E(O_3^+) + E(N_2) + \Delta E_B$$

Note the similarity to the chemical reaction



- The energy difference in the reaction can be obtained from thermodynamic data, giving $\Delta E_B = 3.3$ eV . The measured result is 3.0 eV.

■ Spin and exchange splitting

- So far we have ignored the spin of the core state.
- The simplest case is a hole in the an s-core, which will have a spin 1/2.
- There will be a sizeable exchange interaction with any open-shell electrons (and we would expect the two spins to want to align, giving a lower binding energy).

■ Classic example, which illustrates chemical shifts and the spin of the core hole is:

- Photoemission from the O core in O₂ and H₂O mixtures.

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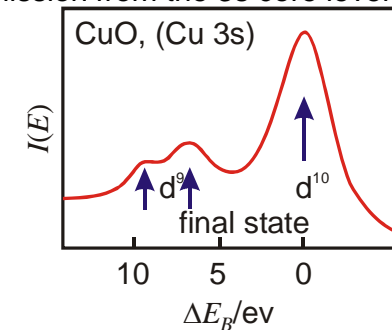
Core polarisation

- The data shows, for the 1s core of O:
-
- In H_2O , the O peak is a single peak at lower binding energy
- In O_2 , the O peak is a doublet at higher binding energy
- To explain we need to know
- O is O^{2-} ($2p^6$ full shell) in H_2O
 - O is O° ($2p^4$ open shell) in O_2
- First, the doublet structure in the O_2 spectrum
- The spin 1/2 of the core hole combines with the net spin, 1, of the $2p^4$ electrons. This gives 2 peaks: spin 3/2 (4 m -configurations) and spin 1/2 (2 m -configurations). Note, the 2:1 ratio of intensities.
 - The aligned spins gives a more strongly bound *final* state and, hence, higher electron energy (lower E_B).
- Second, the chemical shift between O_2 and H_2O .
- In H_2O there are more p electrons on the O site and hence more effective screening of the core hole, which also leads to a more strongly bound *final* state and, hence, higher electron energy (lower E_B).

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A word on satellites

- **Example:** another classic case. This example is taken from transition metal oxides, CuO , and we observe photoemission from the 3s core level of Cu



- The *initial* state configuration is $\text{Cu}^{2+}\text{O}^{2-}$ which leaves the Cu with a $3d^9$ configuration. How then do we interpret the spectrum:
- The main line, a singlet, corresponds to a closed d-shell (spin 0). Evidently the core hole, makes it favourable for an electron from a nearby O atom to hop onto the Cu^* atom. This must be the **ground state** of the *final* state, since it corresponds to the highest kinetic energy (lowest E_B).
 - The satellite is an excitation with the electron kicked back onto the oxygen atom. The d^9 (spin 1/2) shell then gives an exchange-split doublet with the spin 1/2 core.

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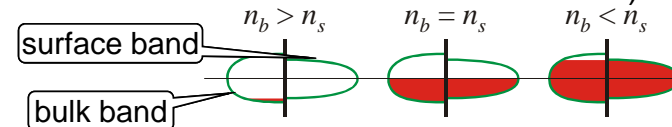
Surface core-level shifts

Shifts due to coordination:

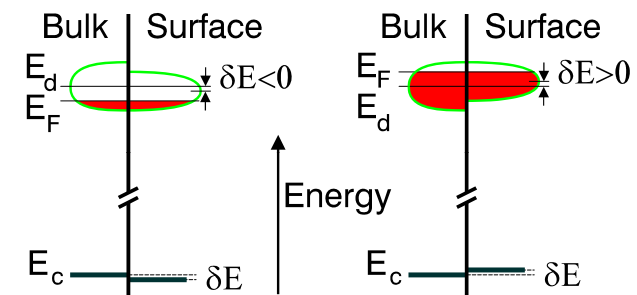
- Earlier we saw how shifts arose as a consequence of the charge state of an atom in the solid, and we attributed the main effect to the energy of the final state.
- The initial state energy is also affected by the charge state and a good example arises in the case where the coordination number (number of bonds to nearest neighbours) changes.
- Such an effect happens at every surface, since the surface atoms have $\sim 1/2$ the number of nearest neighbours. Hence we might expect surface atoms to experience a core-shift. Hence the notion of “surface, core-level shifts”
- We need the following concepts (Part B1)
 - Bandwidth increases with coordination);
 - Bands broaden (approximately) symmetrically about the atomic level;
 - The conduction electrons in a metal ensure all atoms are neutral (common Fermi level).

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- Consider bulk and surface bands arising from the same atomic level (eg. 3d), but with different numbers of electrons in the band (i.e. as we move across the transition metal series).



- Note that the number of surface and bulk electrons is only equal when the band is exactly half full.
- To maintain charge neutrality, the surface bands move up, or down. The effect is largely electrostatic and all bands shift “rigidly”.

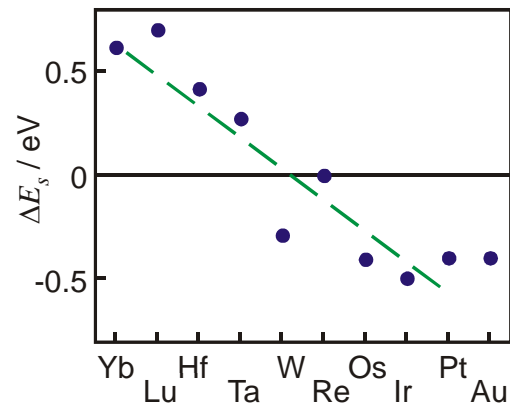


- Left fig. $N_d < 5$. We have to push all levels of the surface atom down.
- Right fig. $N_d > 5$. We have to push all levels of the surface atom up.

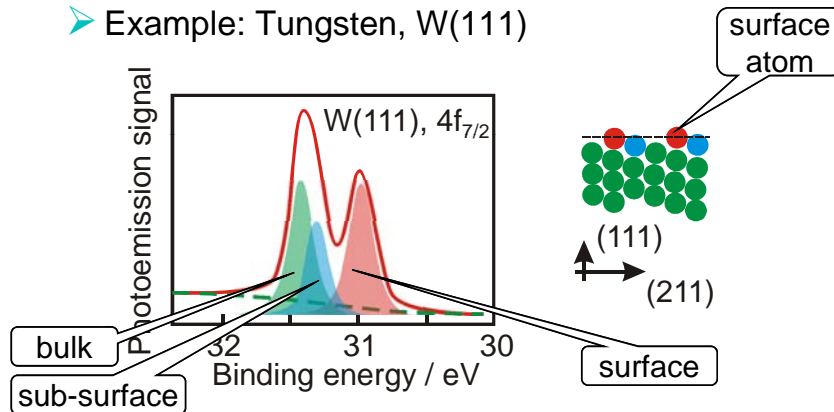
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Valence states

- Experiment gives the expected trend. Eg. across the 5d transition series, the measured surface shift is:



- Example: Tungsten, W(111)



Hufner "Photoelectron spectroscopy" ch. 8

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■ Ultra-violet Photoemission Spectroscopy (UPS).

- Studies of the valence band, with its low binding energies, is usually performed using photons of a correspondingly low energy – in the ultra-violet regime.
- The power of the technique lies in giving experimental access to the band structure.

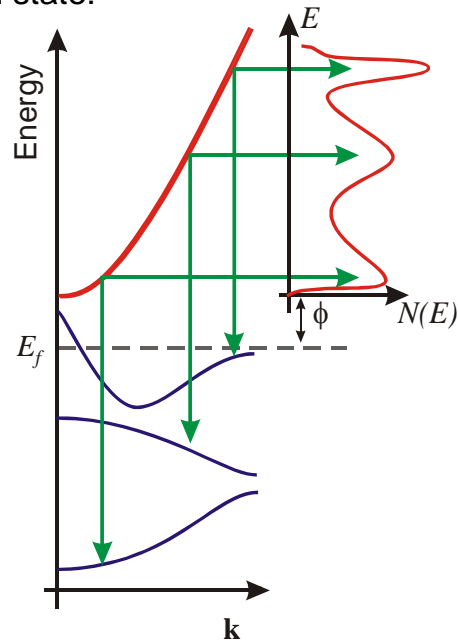
■ Principle (Angle Resolved UPS)

- Measurement of the energy and momentum of the photoelectron defines $E(k)$ for the initial state.
- There are several difficulties.
 - We measure the energy difference between an initial state and a final state. i.e., like in XPS, the photoelectron does not just provide information on the initial state.
 - In passing through the surface we lose some information on the momentum \mathbf{k} , since only the parallel component of \mathbf{k} is conserved.
 - To relate internal and external energies we need to know the work function of the surface.

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Energies

- The process is a vertical transition from initial to final state:



- Four equations define the kinematics

$$E_{final} - E_{initial} = \hbar \omega \quad E = E_{final} - E_f - \phi$$

$$\mathbf{K}_{initial}^{\parallel} + \mathbf{G} = \mathbf{P}^{\parallel} / \hbar$$

- There are 5 unknowns:
 \mathbf{k} of the initial state (3),
 E_i and E_f .

photoelectron energy, E , and momentum, \mathbf{P}

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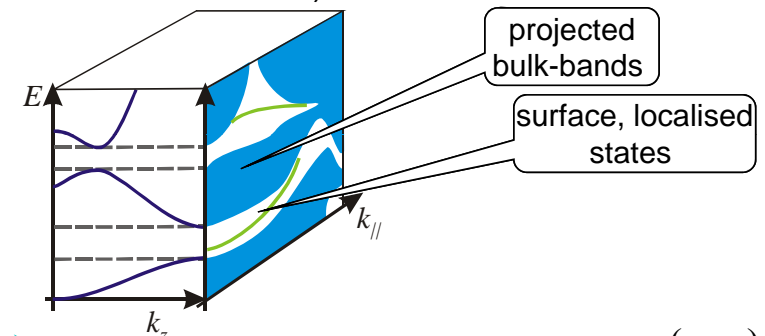
- There are several methods to overcome the difficulty. The simplest is to assume a **free-electron final state**,

$$E_{final}(\mathbf{k}) = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 - E_o$$

- E_o is the bottom of the final state band. It is not known *a priori* but can be deduced indirectly.

■ Projection of bulk bands at the surface

- The lack of information about the perpendicular wavevector, k_z , means that states with the same k_{\parallel} , but different k_z are projected onto the surface and can be observed (provided the kinematic conditions are correct)

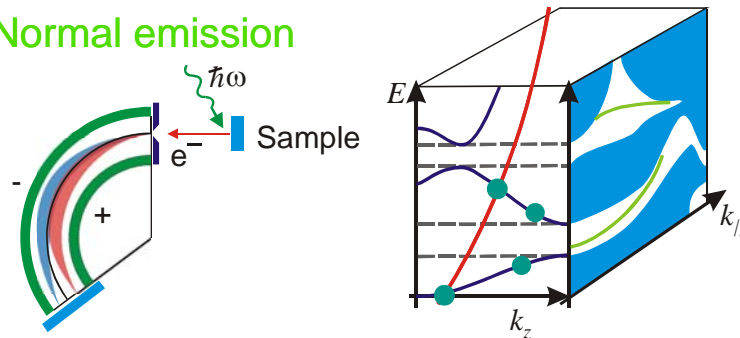


- surface states have imaginary k_z , i.e. $\psi \sim \exp(-\alpha z)$ and the state is localised at the surface

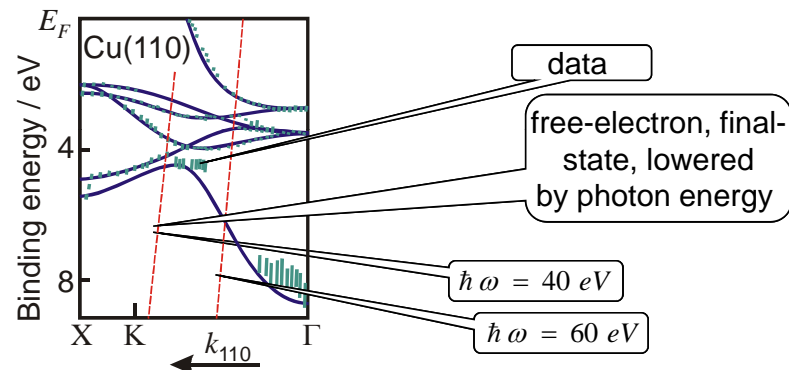
20

Bulk band structure

Normal emission



- Choosing normal emission and measuring over a range of photon energies (synchrotron) means we map the bands along k_z . The first measurement of this type 1979 was for copper (Thiry et al PRL, **43**, 82).



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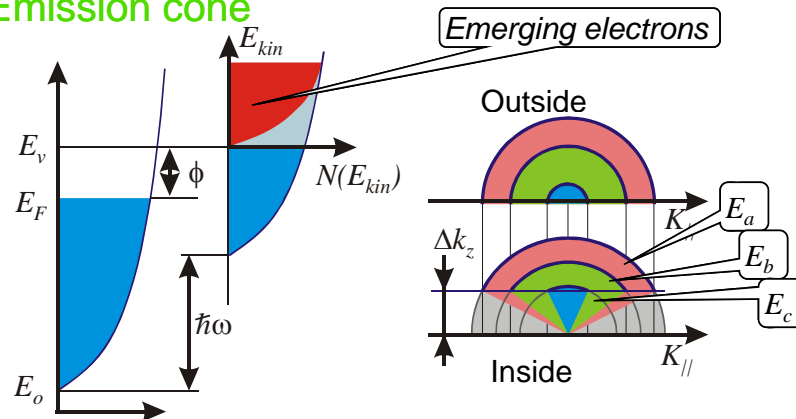
Photoelectron microscopy

- Since photoelectron energies are characteristic of the local electronic environment, an image offers the prospect of mapping chemical environment (on a length scale $\sim \mu\text{m}$)
- The obvious approach is to look at characteristic emission energies from particular initial states; however, that approach is rarely used. Instead, local variations in the work function are often used as a contrast mechanism.
- Work function changes manifest themselves in emergence (threshold) of the lowest energy electrons.
- It is instructive to understand why the approach works. There are 2 key aspects:
 - Emission probability increases rapidly (\sim linearly) above threshold. i.e. it is sensitive to work function variations.
 - The work function itself is very sensitive to the state of the surface. eg. it is changed by adsorption of gases.
- We deal with these two points separately:

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Work function

Emission cone



- Free electron model shows that, since $K_{||}$ is conserved, only a fraction of the electrons can emerge. Consider those emerging parallel to the surface:

- Outside: $E_{kin} = \hbar^2 K_{||}^2 / 2m$

- Inside: $E_{kin} + E_v - E_o = \hbar^2 (K_{||}^2 + \Delta k_z^2) / 2m$

so $\Delta k_z^2 = 2m(E_v - E_o) / \hbar^2$

- the right figure shows that a cone of electrons in the solid is defined. The cone, solid angle

$$\Omega = \pi E_{kin} / (E_v - E_o)$$

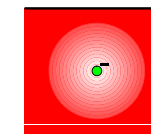
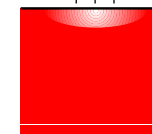
shrinks rapidly as the electron energy reduces.

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Work function

- There are two natural energies in a solid:
 - chemical potential – a bulk property
 - work function – a property of both the bulk and the surface (different surfaces of the same material exhibit a different work function)
- Electrons lower their energy by behaving cooperatively.

Electron approaching a metal



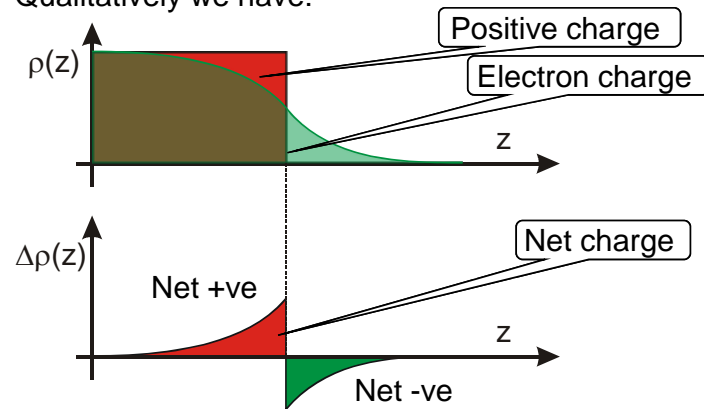
Electron inside a metal

- Electron approaching a metal: Electrostatics tells us the metal electrons will move to “screen” the external field. This happens by depleting the surface electrons below the incident electron.
- Electron inside a metal: Again the metal electrons move away from the incoming electron leaving an “exchange correlation hole”.
- The bulk part of the work function can be thought of as the energy to release an electron from its exchange-correlation hole.

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■ Surface dipole layer (in the Jellium model)

- At a surface the electrons spill into the vacuum.
- Here, the positive, nuclear charge is spread uniformly and it stops abruptly at the surface. Qualitatively we have:



- The result is a *dipole layer* at the surface (+ve on the inside, -ve outside). Its electrostatic field contributes to the work function.
- The detail of how electrons spill-out depends on the surface structure and hence different surfaces of the same material have different work functions.

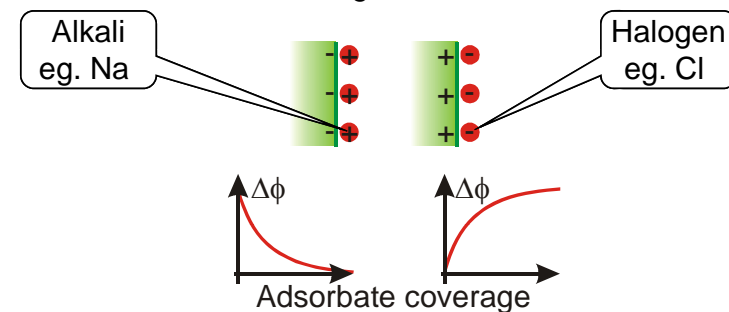
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Work function variation

- Note: the field is localised to the region of charge separation and electrons have to do work to escape.

■ Additional surface dipoles

- Atoms or molecules adsorbed on the surface are usually slightly polarised. They change the strength of the dipole layer and hence change the work function.
- Classic example: Alkali atoms decrease the work function while halogens increase the work function.

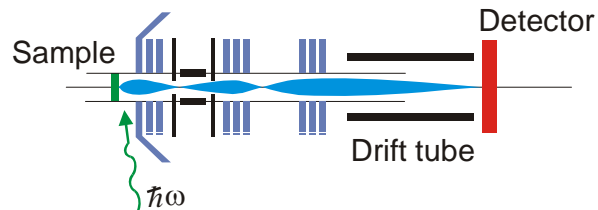


- It is the variation of work function, with the coverage of an adsorbate that lends sensitivity to the photoelectron microscope

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Photoelectron microscope

- Two basic requirements:
 - Imaging – electron lenses (resolution $\sim 1\mu\text{m}$)
 - Energy selection – electrostatic deflection was used in early instruments. It is now superseded.
- Recent instruments use lasers or synchrotrons as the excitation and exploit the fact that both are (or can be pulsed). Hence, time-of-flight methods are now used to measure the electron energy.



- Arrival time of photon pulse starts the clock.
- Detector determines the arrival time, and position, of individual photoelectrons. Typically less than one photoelectron per light pulse.
- For recent images see: www.omicron.de

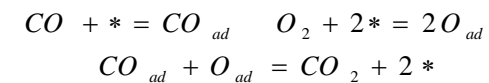
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Reactions at surfaces

- The first experiments exploited contrast in the image arising from local work function changes.

CO oxidation on Pt(110)

- A classic example where a simple chemical reaction shows complex behaviour due to non-linear dynamical effects that have been shown to arise from structural changes at the surface driven by adsorption of the reactants.



- The additional dipole from O_{ad} increases the work function, while CO_{ad} lowers the work function. Hence CO_{ad} rich regions appear bright.

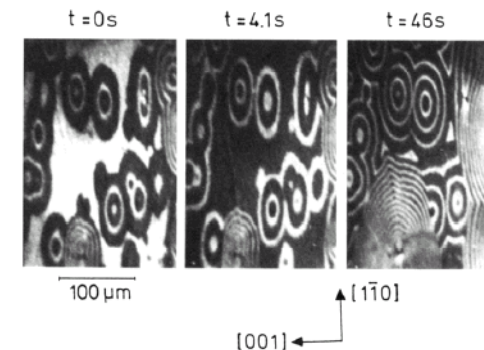


Fig. 21 Imbihl and Ertl, Chem. Rev. **95** (1995) 697

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Nanoparticles

- Illustrative results from (J. of Electron Spectroscopy and Related Phenomena 137–140 (2004) 249–257)

Photoemission time-of-flight spectromicroscopy
of Ag nanoparticle films on Si(1 1 1)

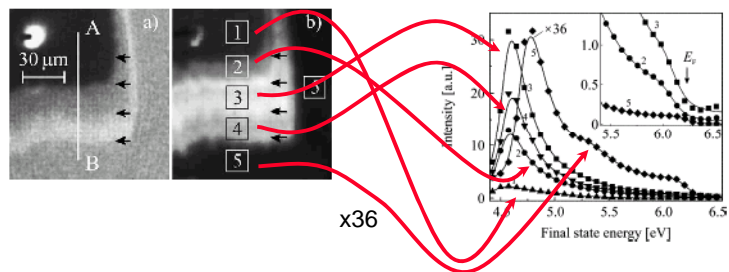
M. Cinchetti*, D.A. Valdaitsev, A. Gloskovskii, A. Oelsner,
S.A. Nepijko, G. Schönhense

Institut für Physik, Johannes Gutenberg-Universität, Staudingerweg 7, 55099 Mainz, Germany

- Silver nanoparticles ($\phi \sim 4.5\text{-}4.9\text{ eV}$) shown
 - (left, image) illuminated with 5eV photons from a continuous mercury lamp. Single photon photoemission, no energy resolution
 - (right, image) 200fs, pulsed, frequency-doubled Ti:Sa laser. Photons of energy 31.eV. Hence the emission is by 2 photon photoemission
 - Spectra show photoelectron energies at different thickness of the silver layer.

Images

Energy spectra



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