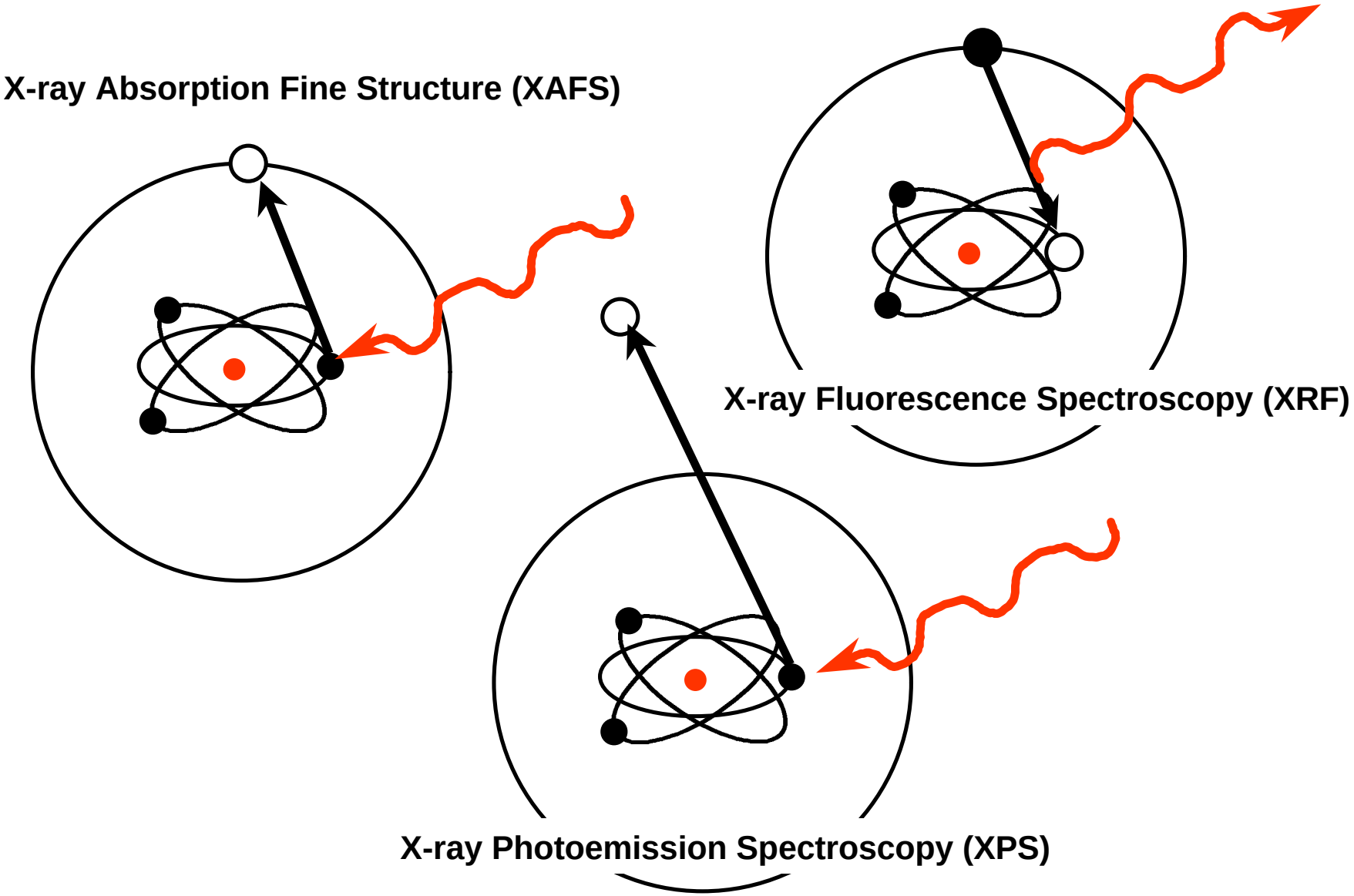
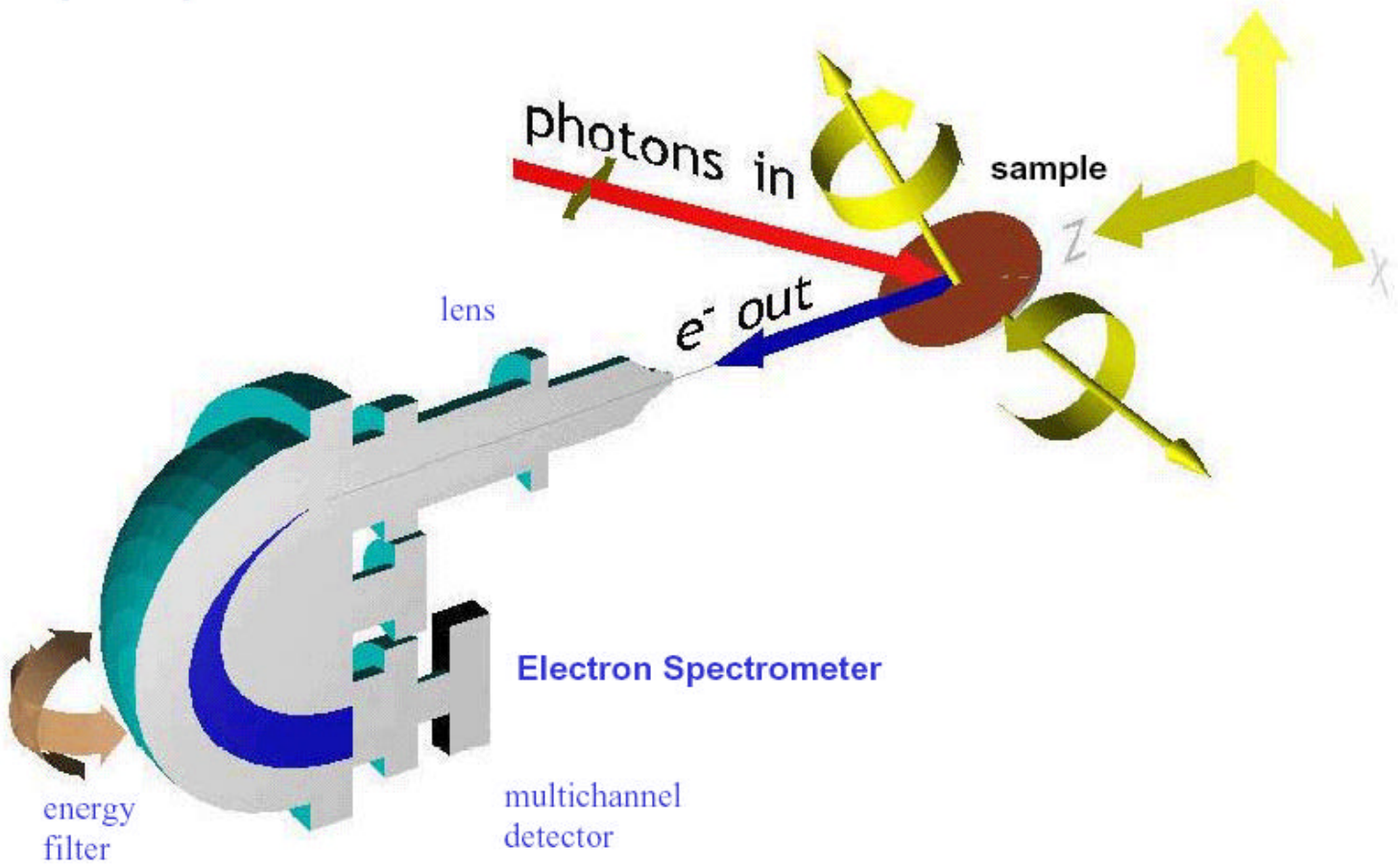
The Three Principle Soft X-ray Spectroscopies



Photoemission spectroscopy: experimental system



Terminology of Photoemission Spectroscopy

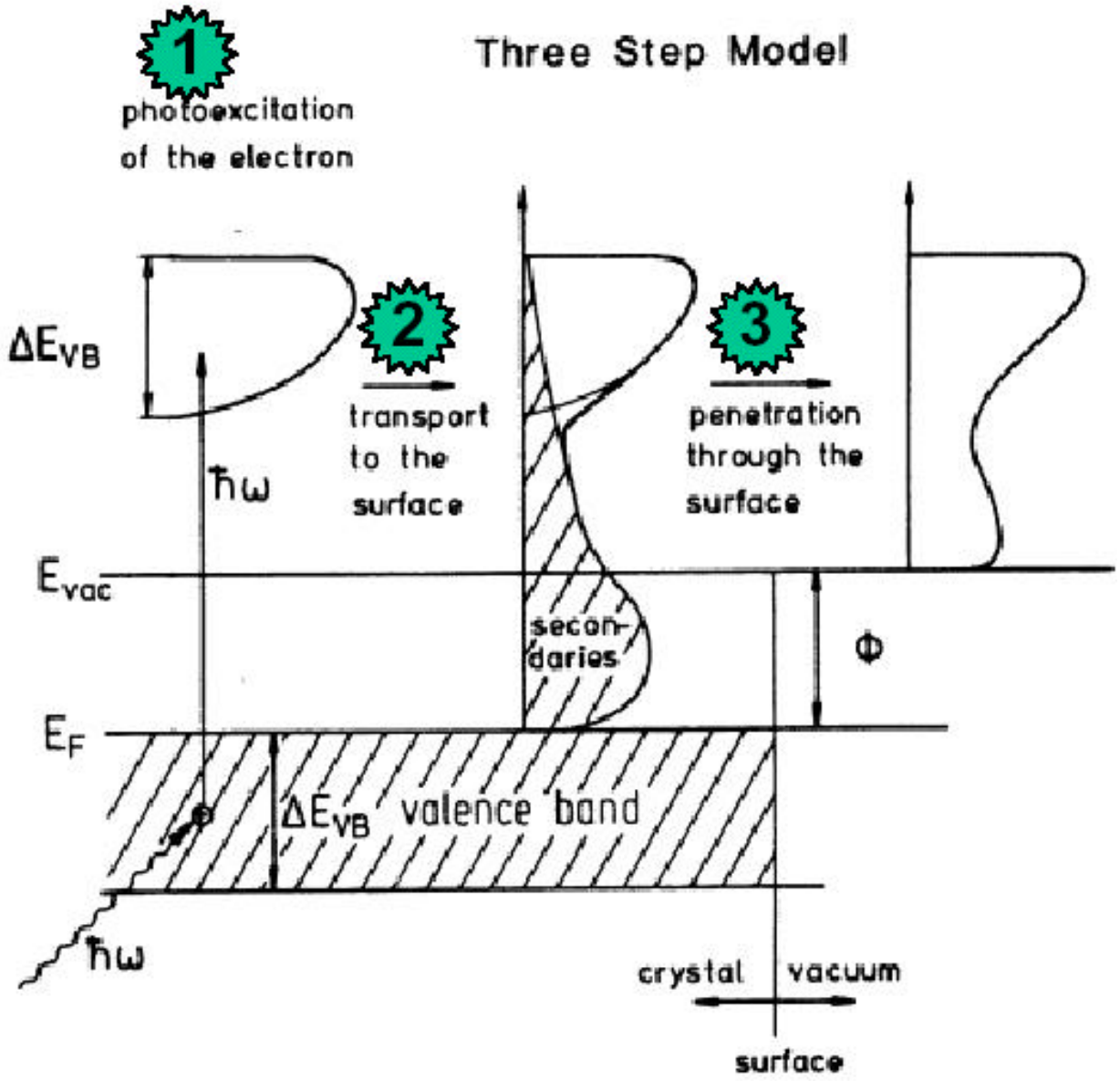
XPS: x-ray photoelectron spectroscopy. Used to determine binding energies of core-levels. These binding energies shift with chemical state (chemical-shift).

UPS: ultra-violet photoelectron spectroscopy. Used to measure binding energies of valence orbitals.

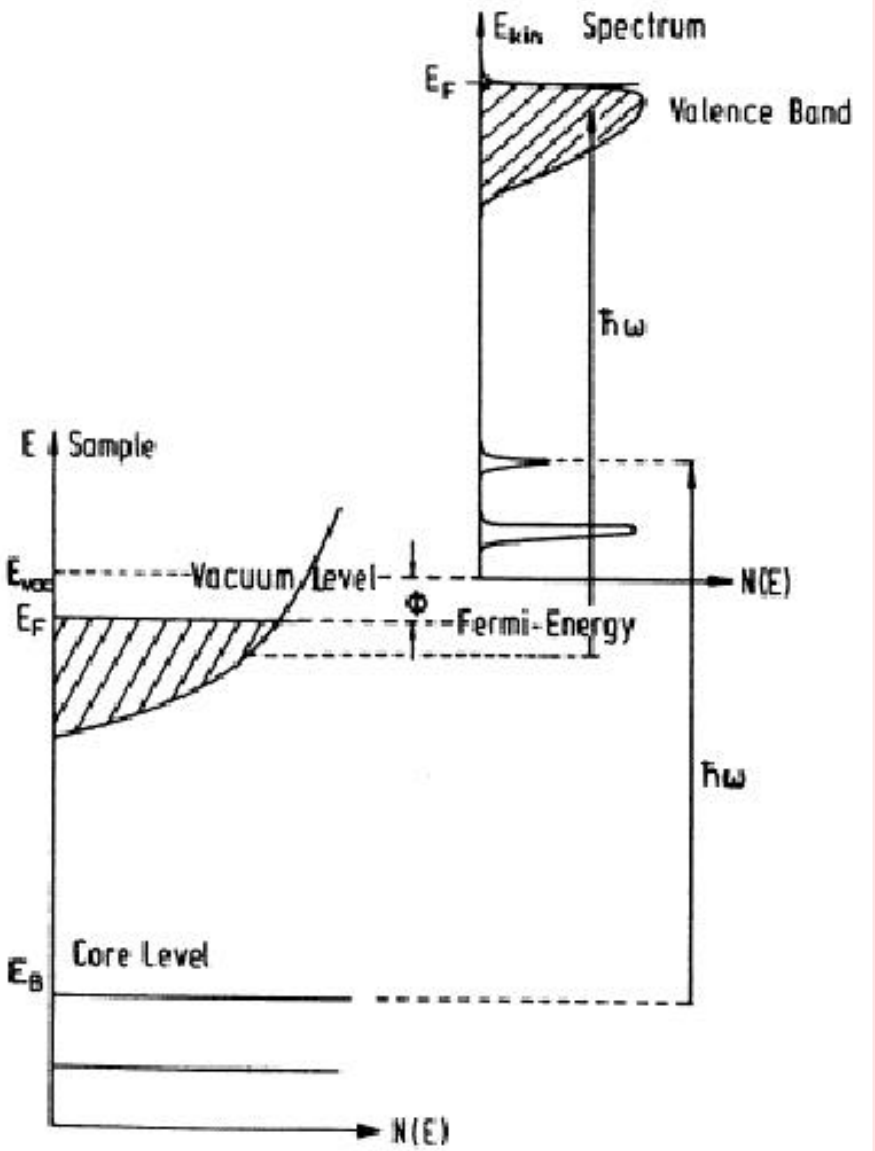
ARPES: angle-resolved photoemission spectroscopy. Measures the intensity of valence band features as a function of emission angle, which can be used to determine band-structure.

XPD: x-ray photoelectron diffraction. Measures the intensity of core-level features as a function of emission angle, which can be used to determine surface structure.

Basic model of photoemission physics



Energy conservation: measure binding energies



$$E_{kin} = \hbar\omega - \Phi - |E_B|$$

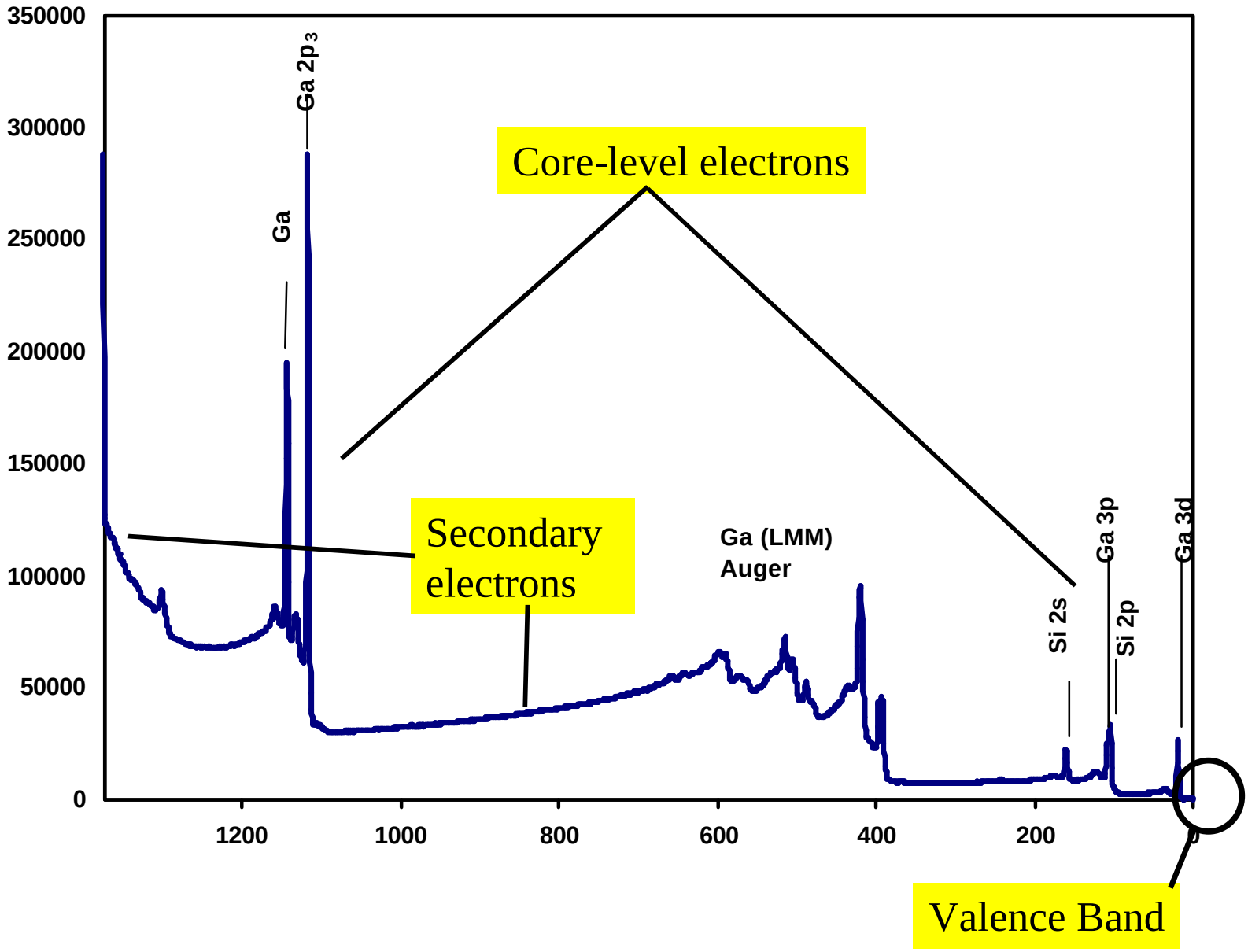
Measured Kinetic Energy

Measureed Photon Energy

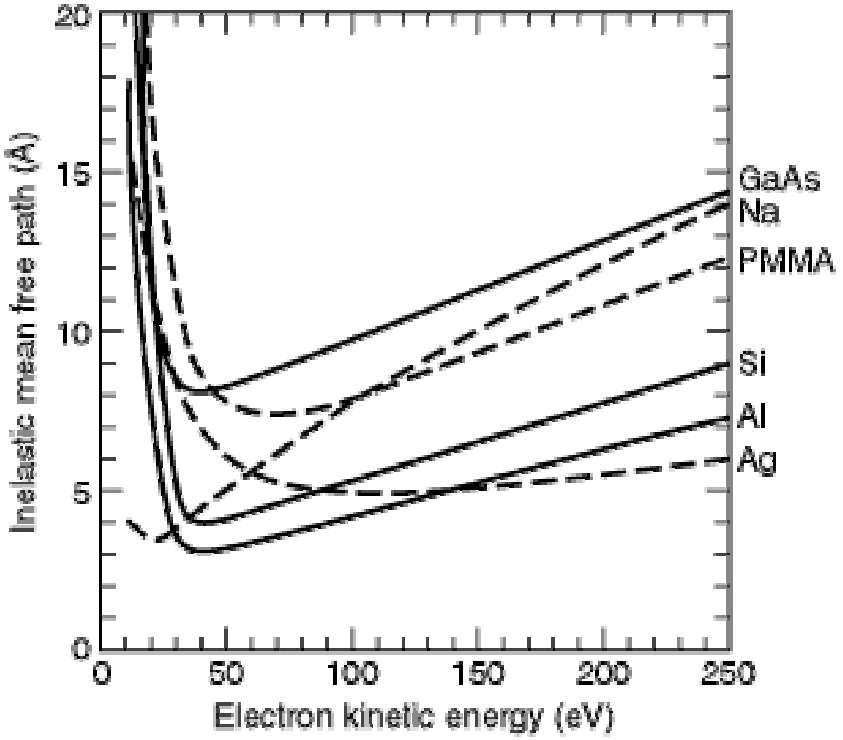
Measured Work Function

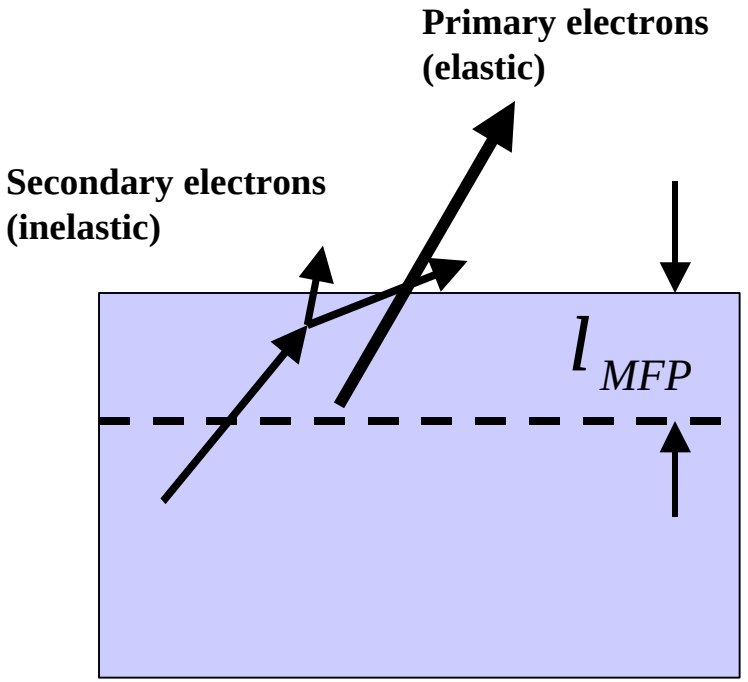
Electron Binding Energy

A typical X-ray Photoelectron Spectrum



The inelastic mean-free-path for an electron: Physical origin of surface sensitivity in electron spectroscopy

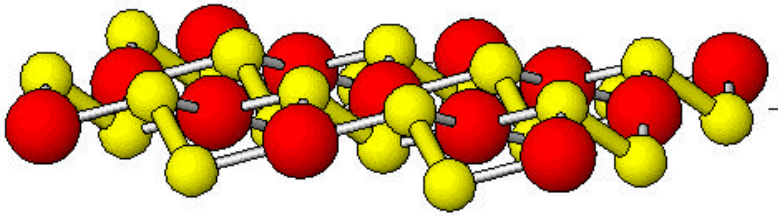




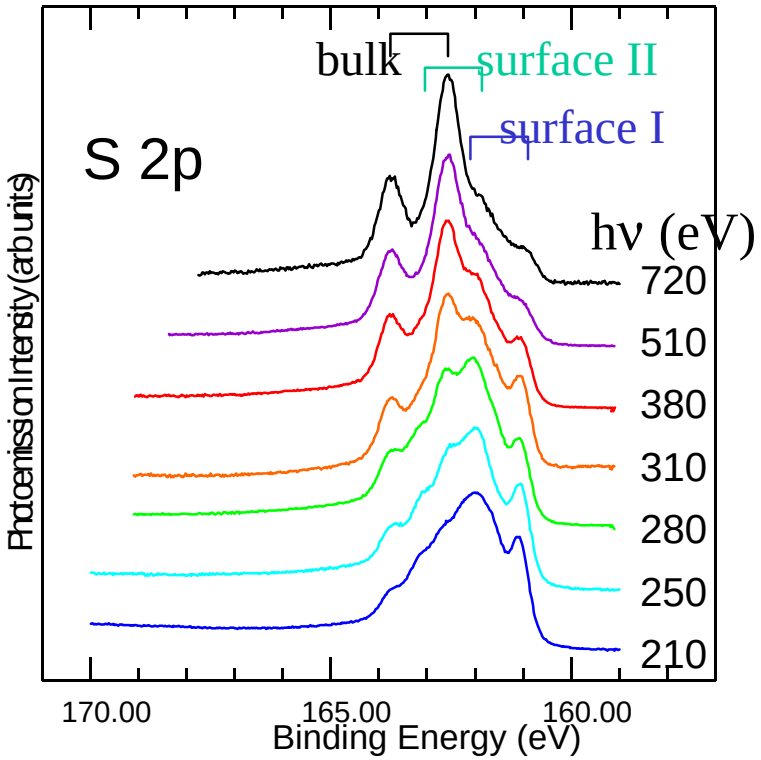
The minimum in the mean-free-path is as small as a single atomic layer.

Variable surface sensitivity by tunable photon energy: Case of pyrite (FeS_2)

side view, (100) surface plane

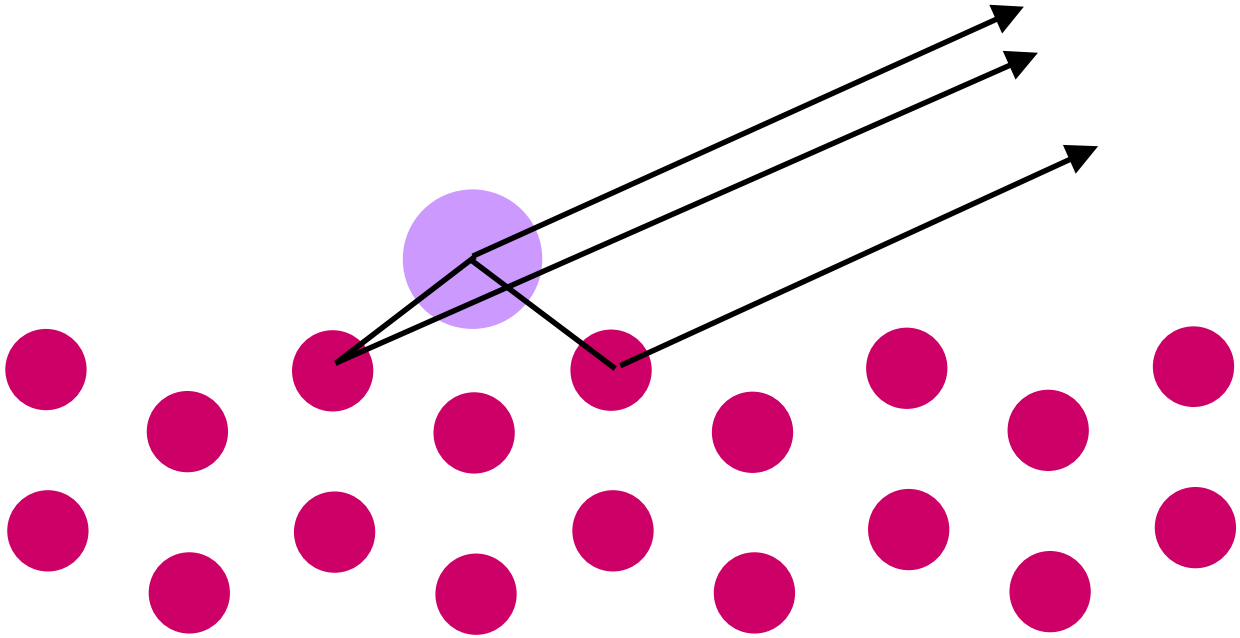


[100]

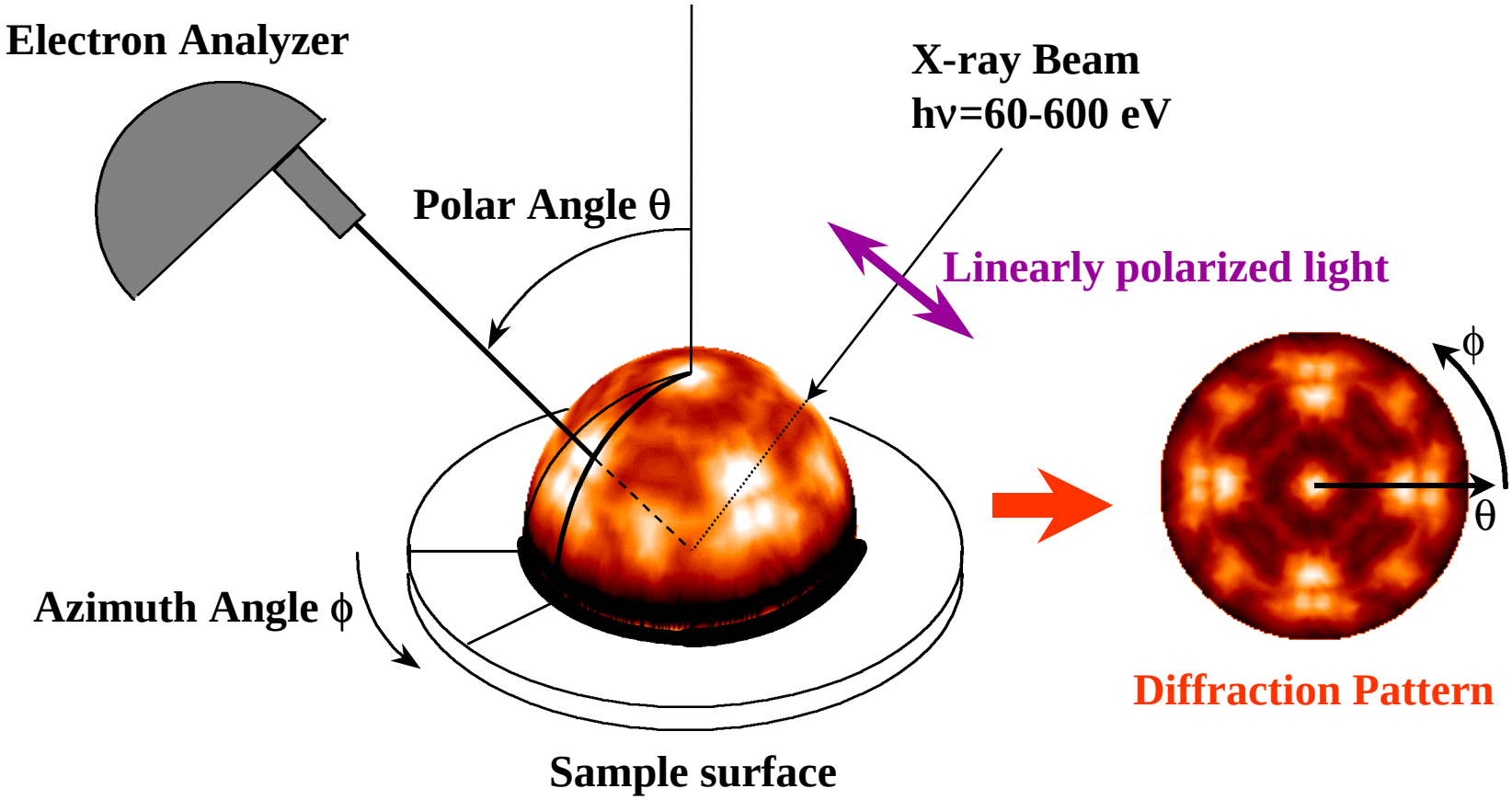


X-ray Photoelectron Diffraction (XPD)

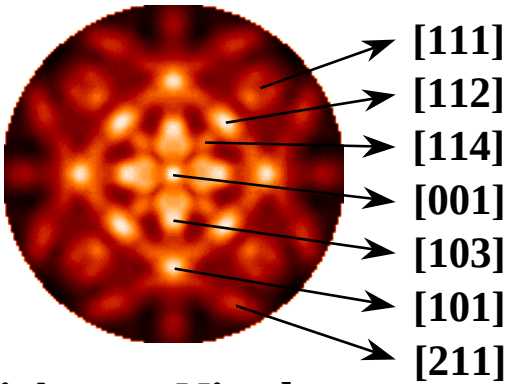
- A powerful tool for determining the atomic structure of surfaces
- Precision of bond-length measurement is about 0.02 Angstrom
- Source of electrons is known: determined by XPS binding energy
- Theory is a multiple-scattering theory; certain experimental conditions permit a single-scattering interpretation
- Has been used as a form of quantum holography: direct data inversion



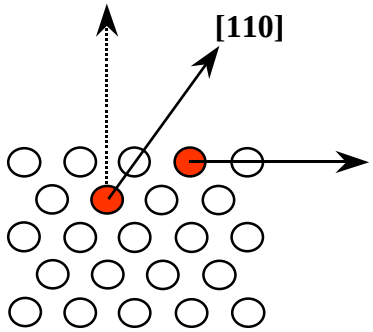
Experimental XPD Patterns



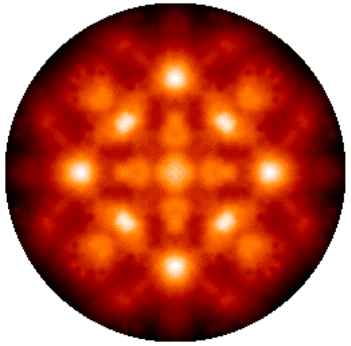
XPD of Mn/Ni, ESCA (MgK_α, $h\nu$=1253.6 eV)



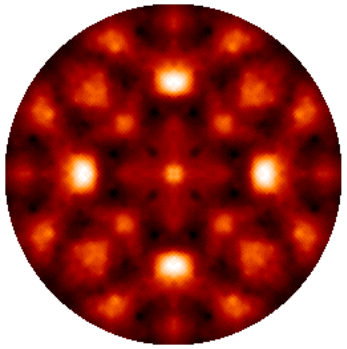
Ni Auger, Ni substate



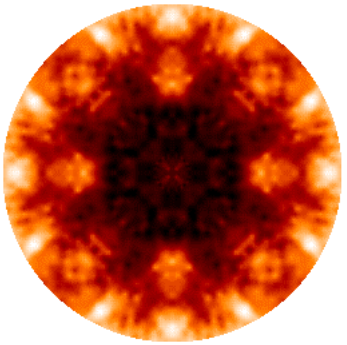
Map of the rows ABOVE the emitter



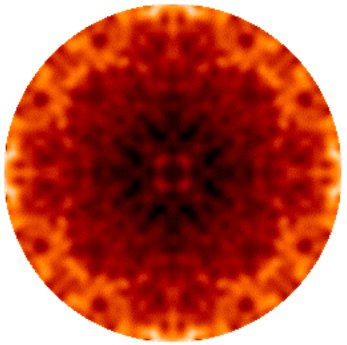
Mn 2p, 4 ML MnNi



Mn 2p, 3 ML MnNi

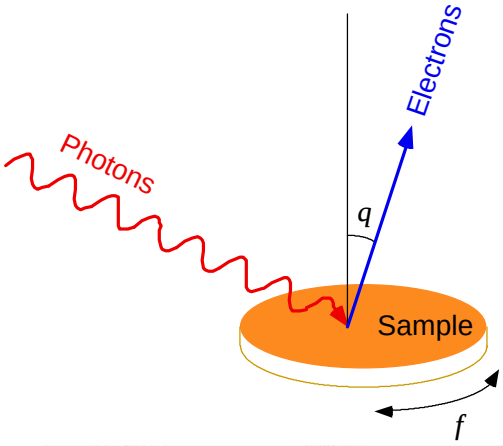


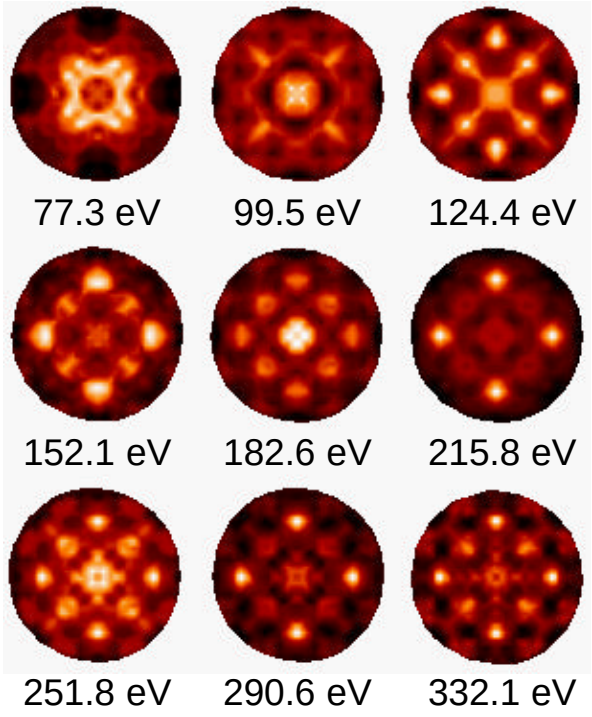
Mn 2p, 2 ML MnNi

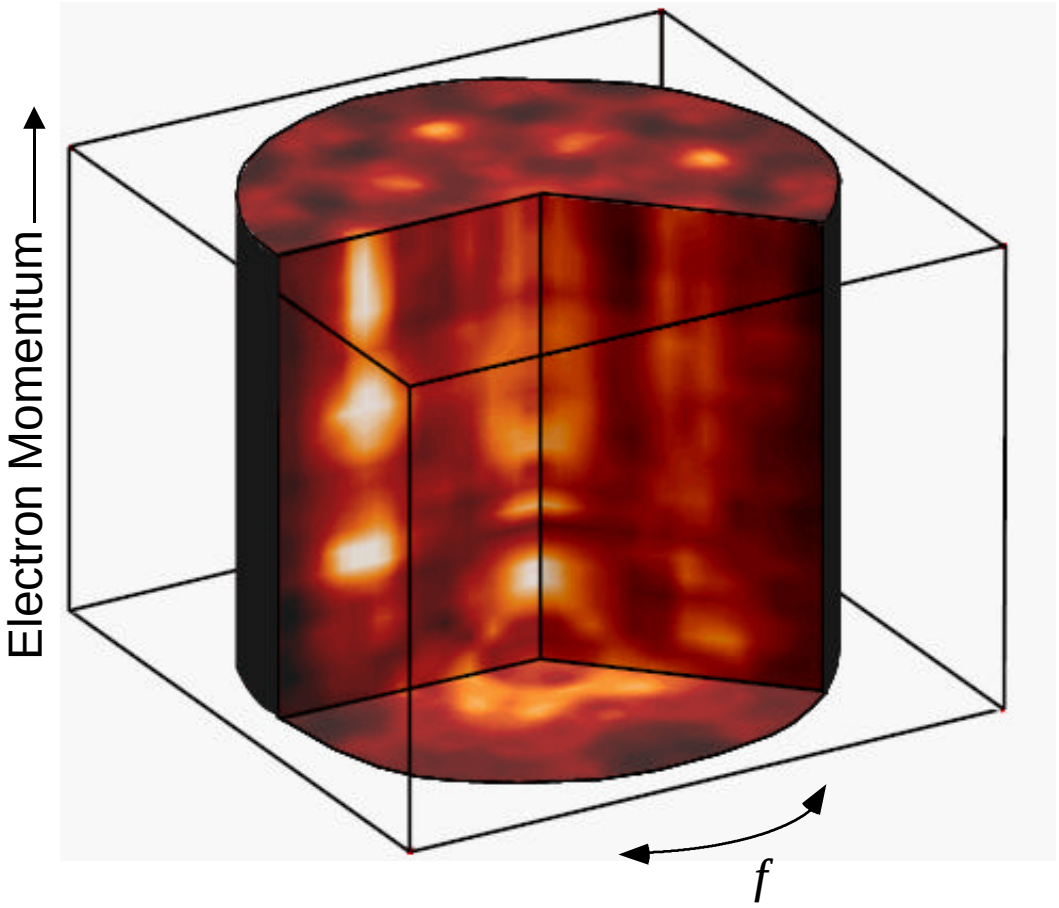


Mn 2p, 1 ML MnNi

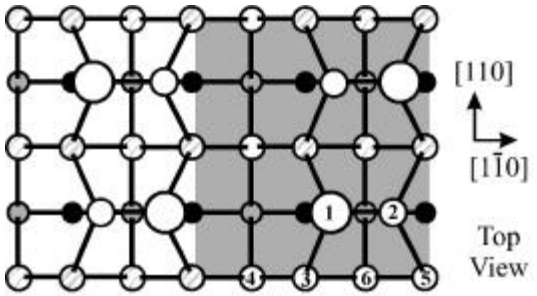
An XPD Diffraction "Volume"
Cu(100)

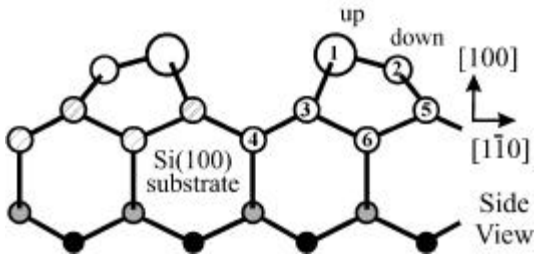


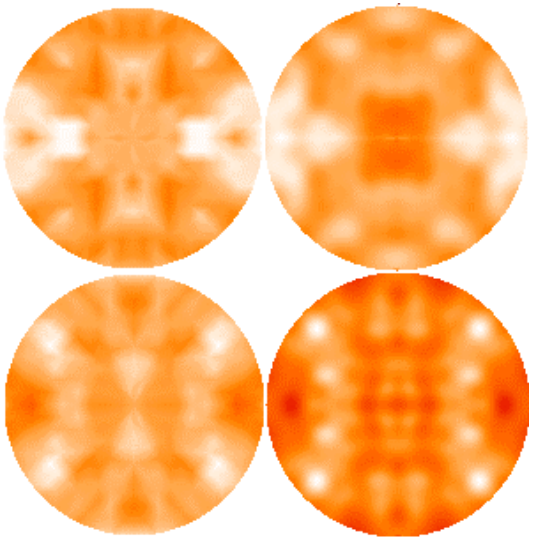


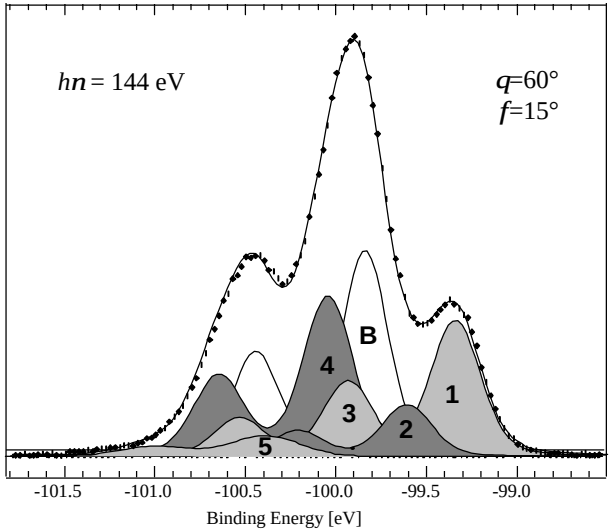


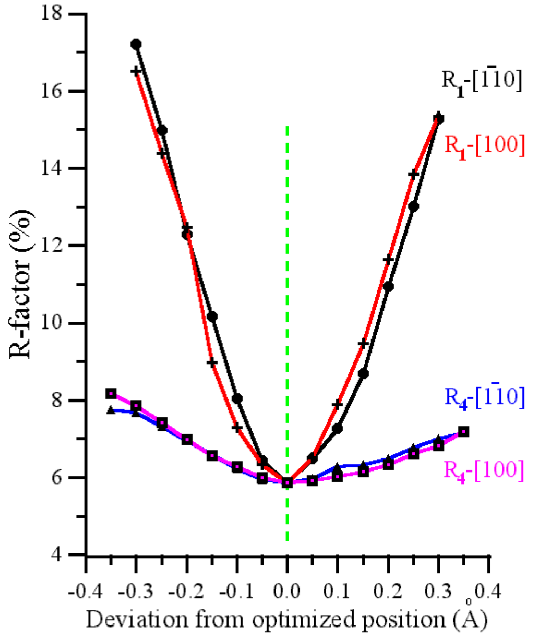
XPD for surface structure determination: The case of Si(100)c4x2







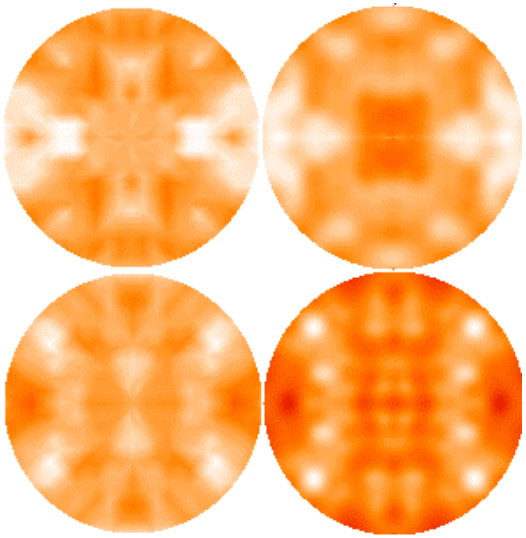




S1-XPD (left) and MS simulations (right) at hv=140 and 160 eV.
Dimer atoms only (Atom 1)

Si(100)c4x2: Dimers and Substrate

Fig.4 S_1-XPD (left) and MS simulations (right) at hv=140 and 160 eV. Emitters are dimer atoms at upper positions labeled as ATOM 1. In this figure, we only show the comparison at two energies.



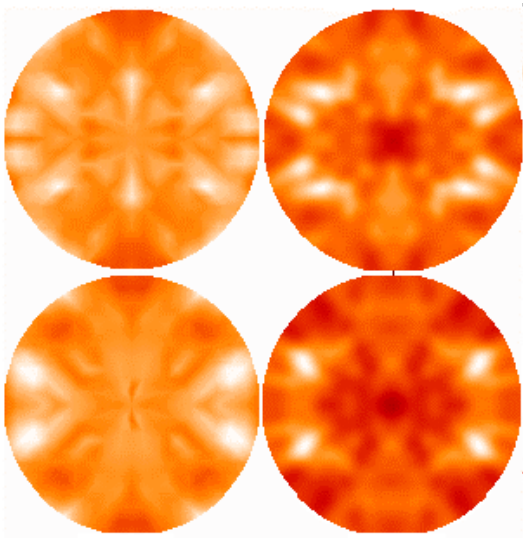
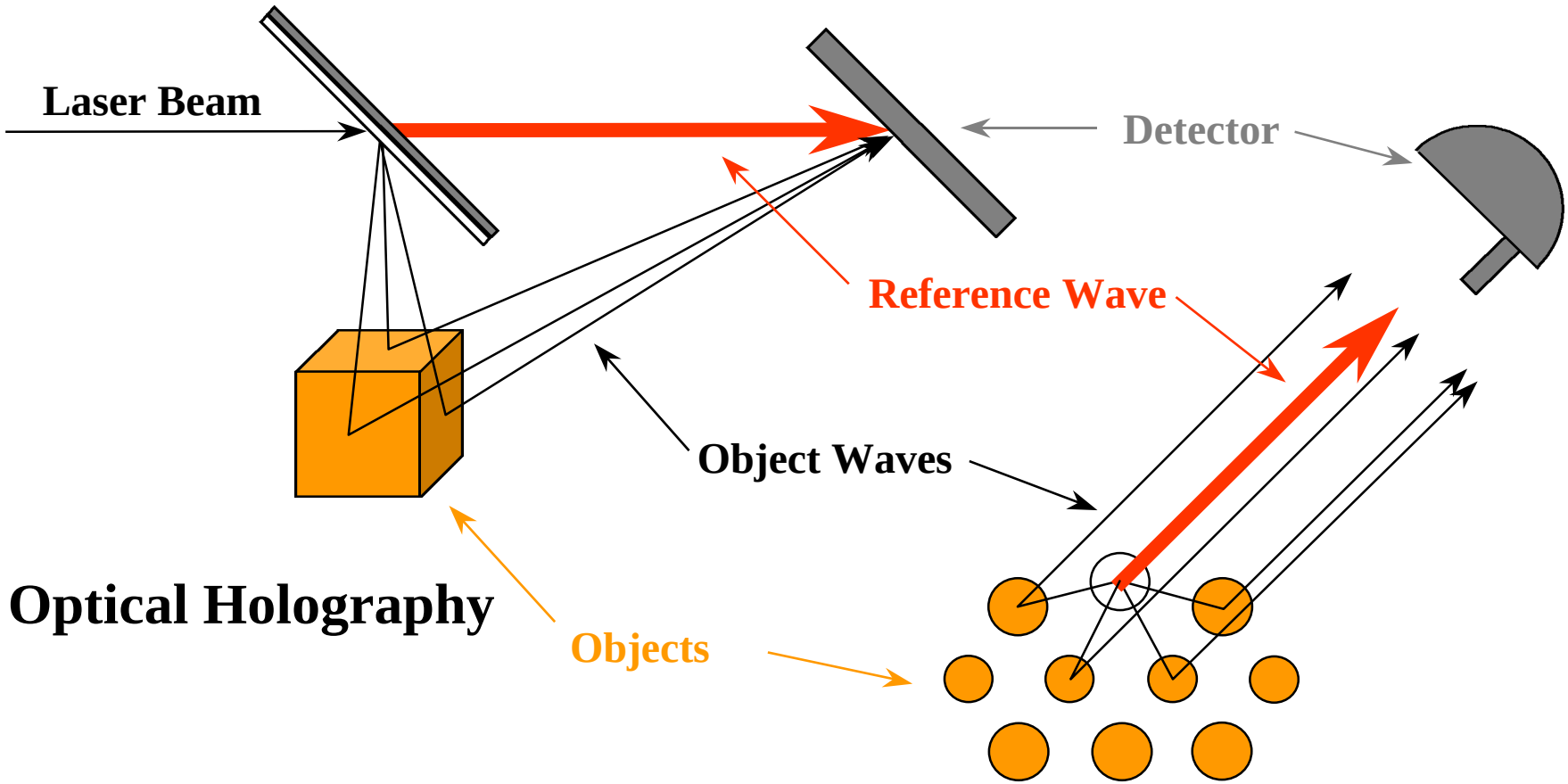
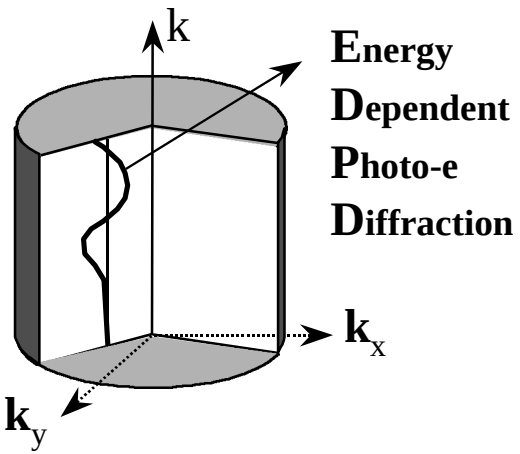


Fig.5 S_4-XPD (left) and MS simulations (right) at hv=145 and 160 eV. Emitters are those silicon atoms in the second layer substrate labeled as ATOM 4.

Photoelectron Holography: Analogy to Optical Holography



Method of Photoelectron Holography Inversions



•Barton Algorithm

$$A(\mathbf{r}) = \iiint_{k_x,k_y,k} c(k_x,k_y,k)\exp(i\mathbf{k}.\mathbf{r} - ikr)dk_x dk_y dk$$

•Synchrotron Data

$$A(\mathbf{r}) = \sum_{q,j,k} c(q,j,k)\exp(i\mathbf{k}.\mathbf{r} - ik.r)E_{out}\sin(q)\frac{1}{q_{out}}\frac{\cos(q_{out})}{\cos(q)}$$

•Geometric corrections (Data, angular integration)

•Refraction effects (Low energy)

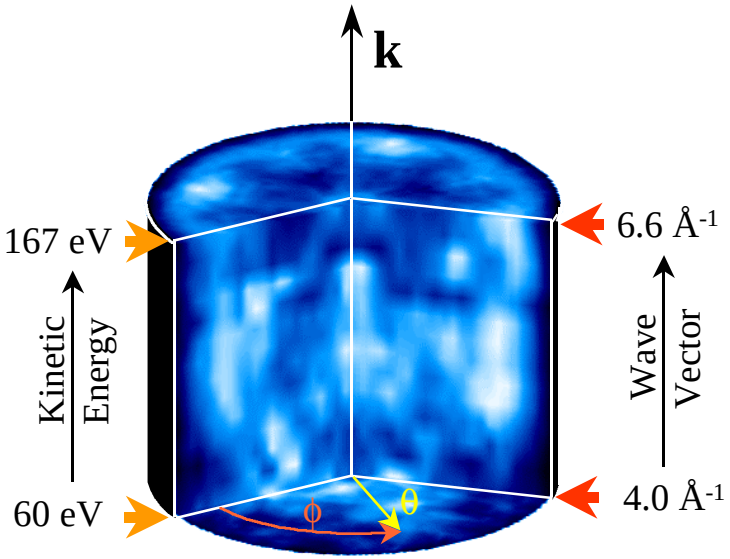
•Improvements

$$c(q,j,k) \rightarrow \frac{c(q,j,k)}{f(q,j,k)\exp(ia(q,j,k))S(q,j,k)}$$

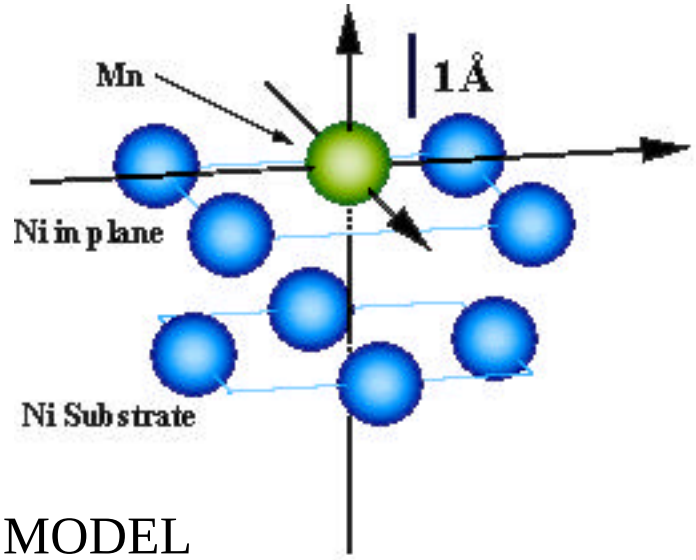
• s/d ratio (shift)
• Polarization (asymmetry)

•Scattering factor, phase (SWIFT)

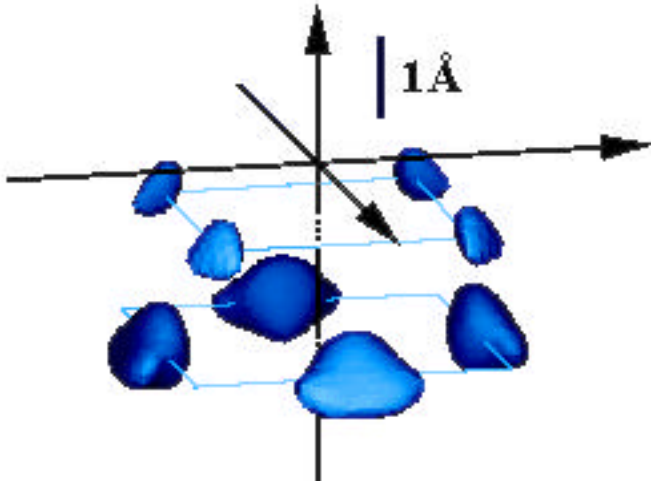
XPH example: Mn on Ni(100)



Direct inversion of XPD volumes, using a model called “photelectron holography.” The case of Mn atoms on a Ni(100) substrate is shown.



MODEL

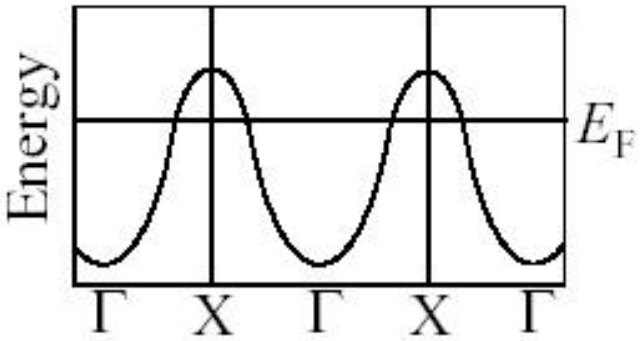


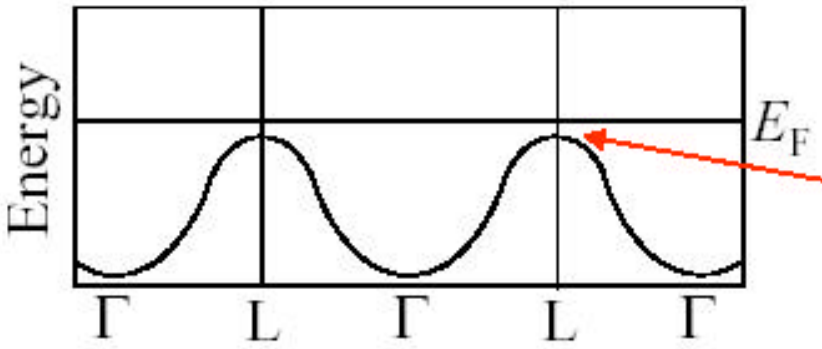
EXPERIMENTAL HOLOGRAM

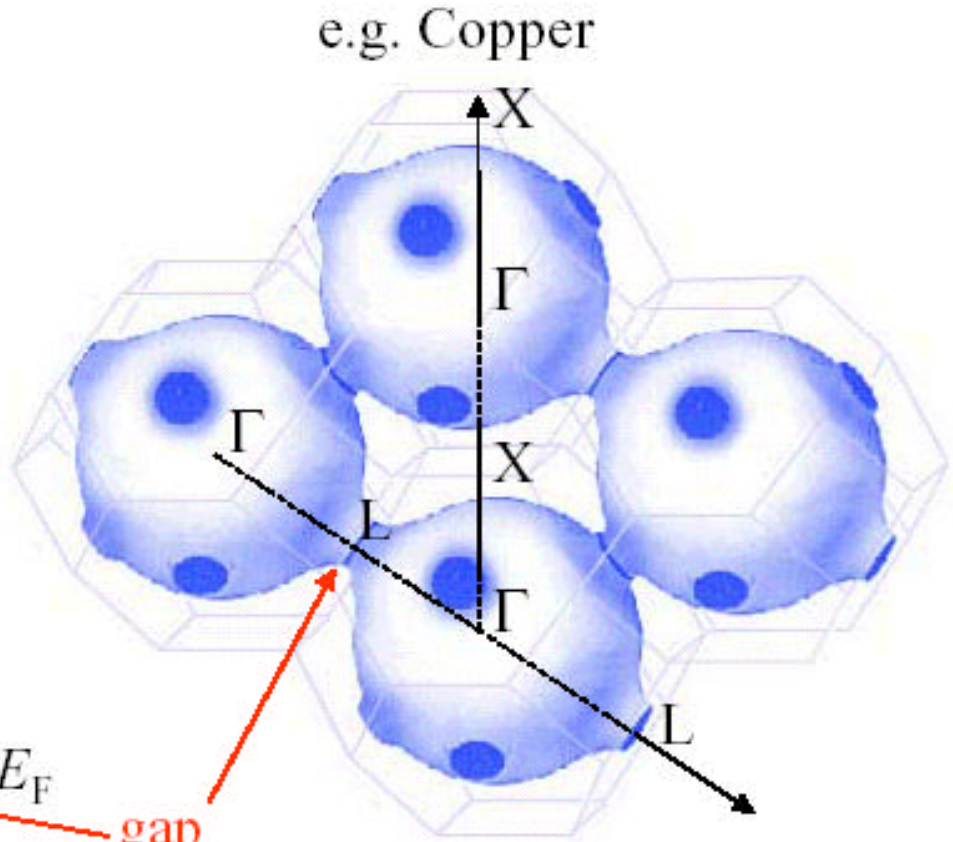
Energy bands and Fermi Surfaces in solids

$$E_{Bind} = \frac{1}{2}mv^2$$

$$= p^2/2m = \hbar^2 k^2/2m$$

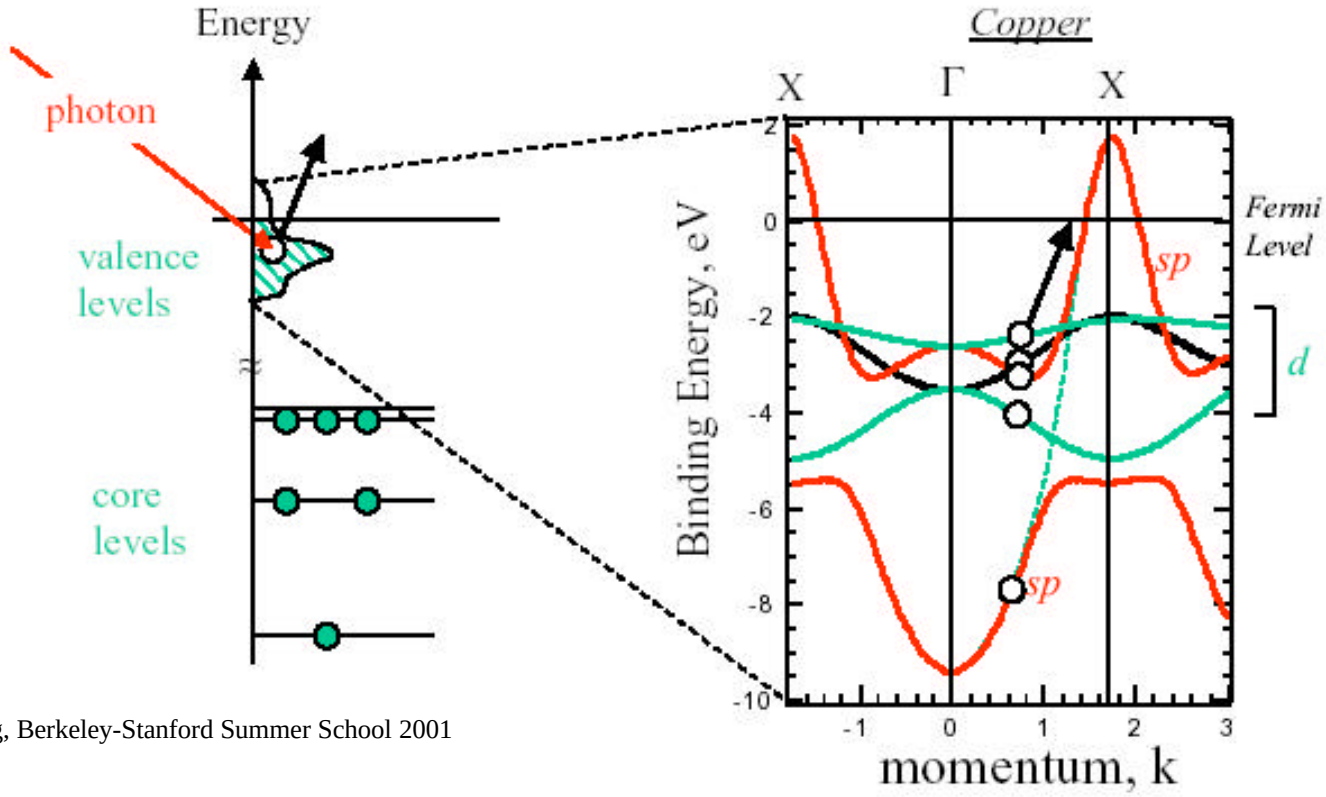






From Eli Rotenberg, Berkeley-Stanford Summer School 2001

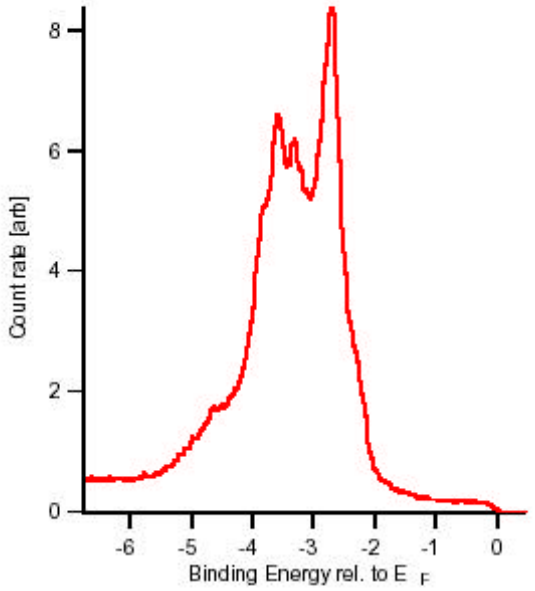
Angle-Resolved Photoemission Spectroscopy (ARPES): A way to directly measure band-structure



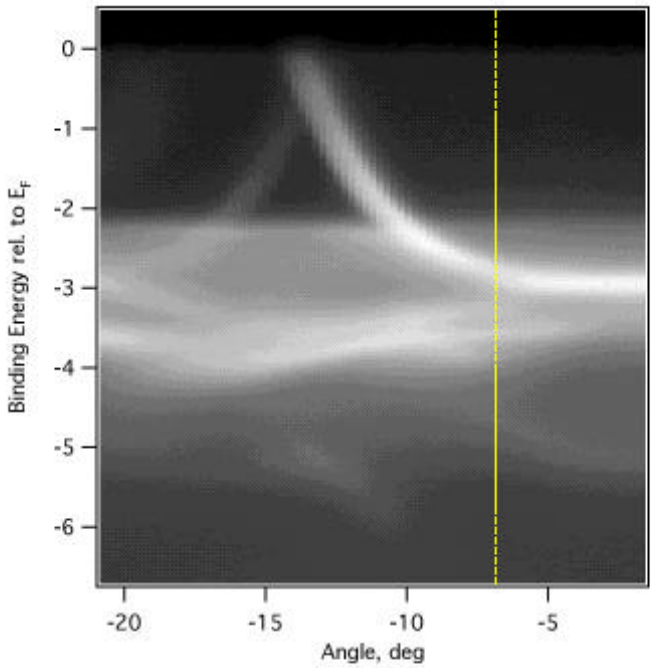
From Eli Rotenberg, Berkeley-Stanford Summer School 2001

- Conservation of energy: determine energy position of bands
- Conservation of parallel momentum: determine momentum position
- Symmetry selection rules: determine parity of band

Measurement of energy bands by scanned-angle ARPES



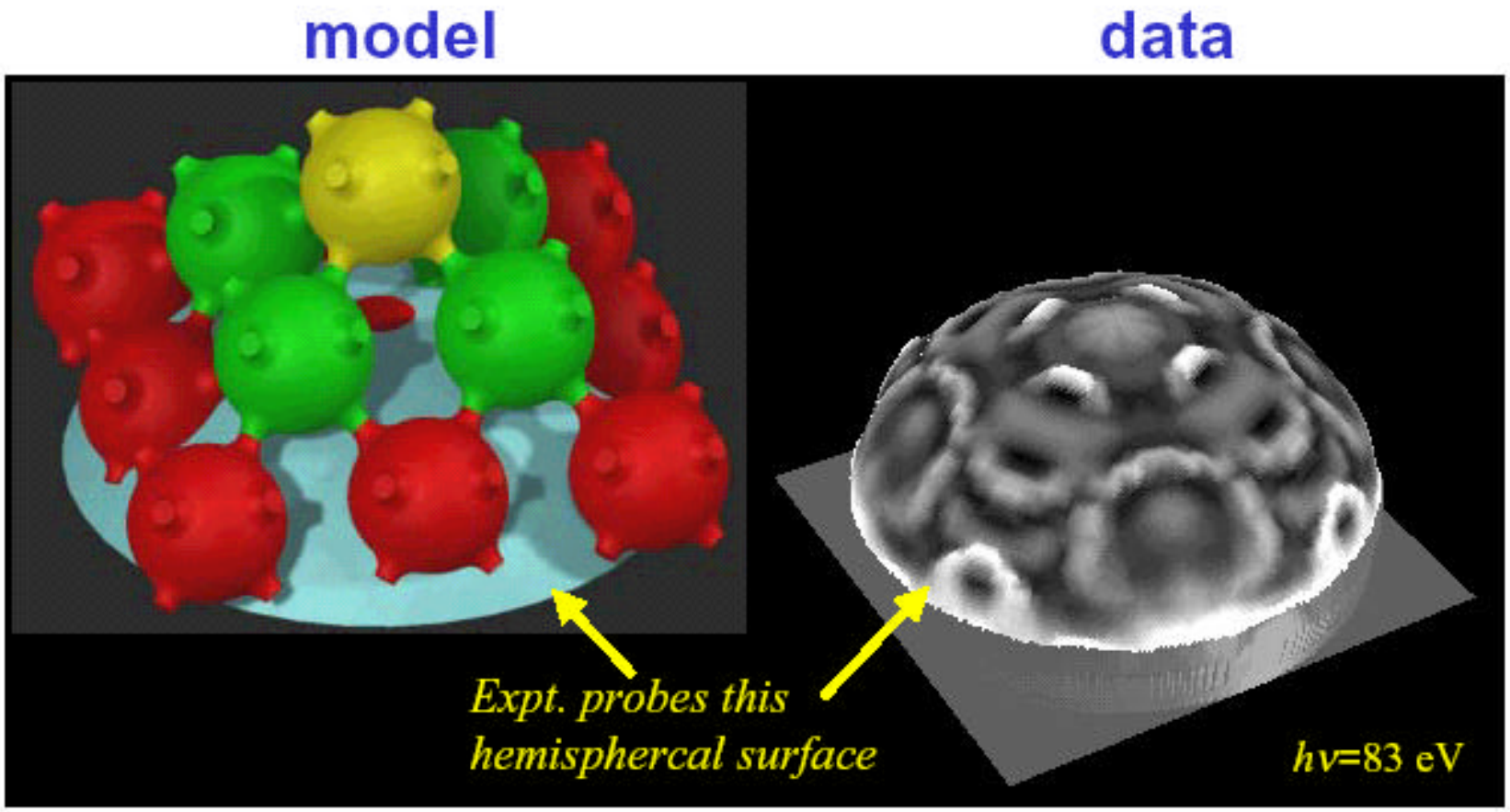
A spectrum at a single polar angle



Accumulate spectra as the angle is scanned

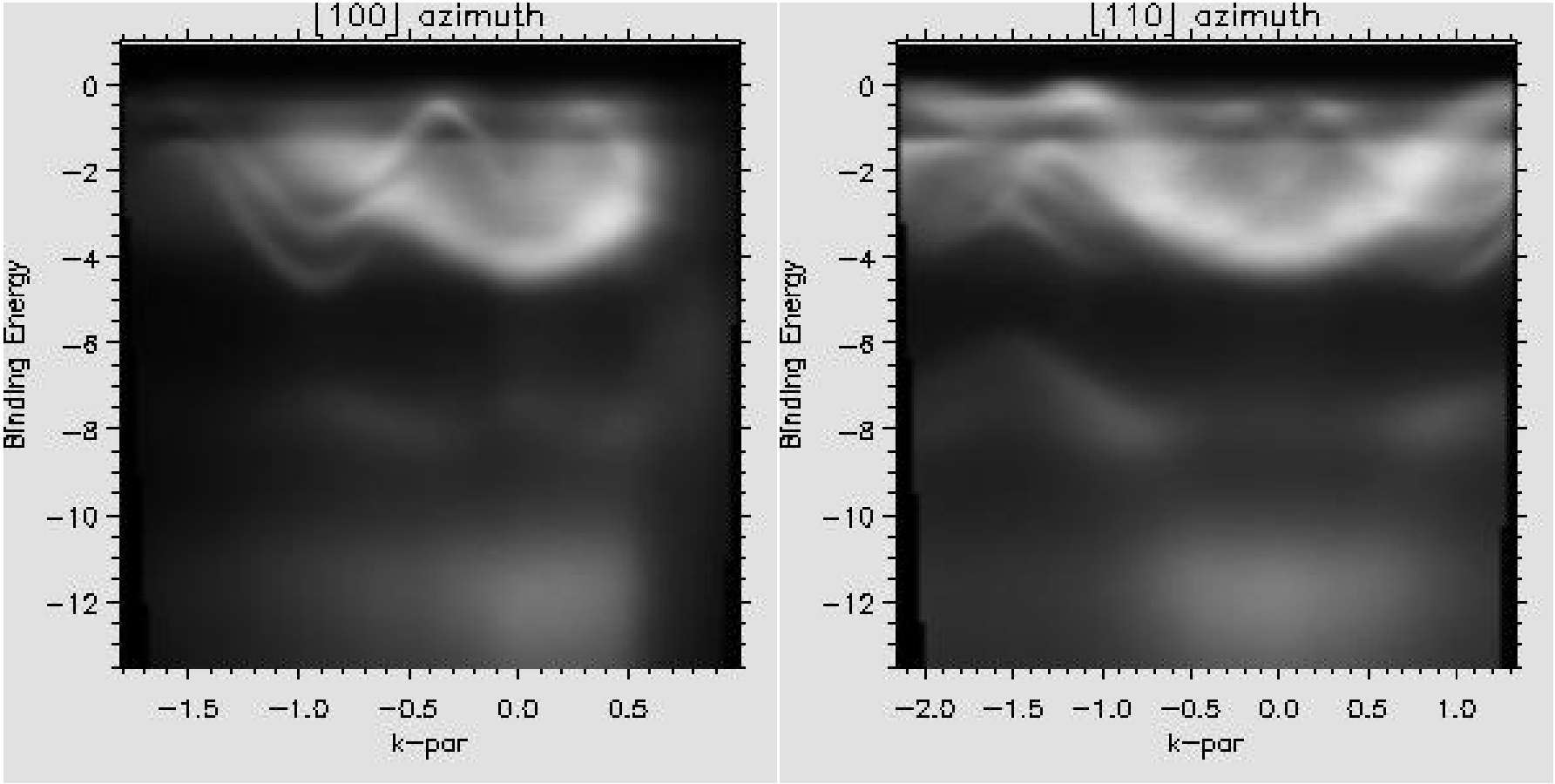
From Eli Rotenberg, Berkeley-Stanford Summer School 2001

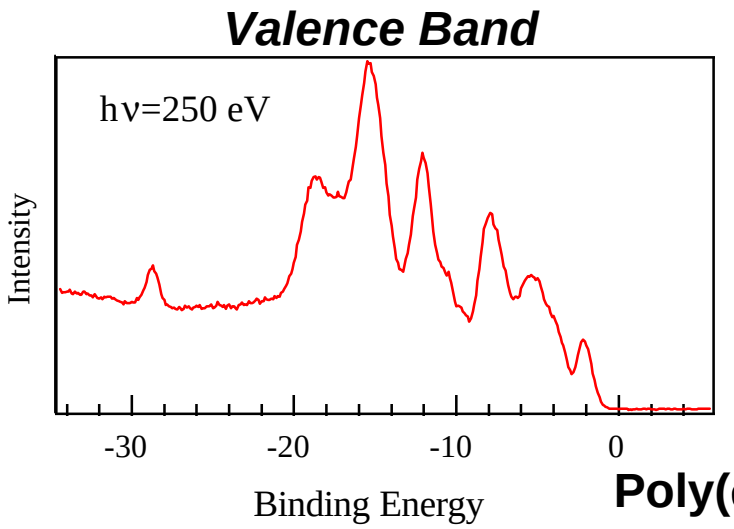
Example: Cu(100)



From Eli Rotenberg, Berkeley-Stanford Summer School 2001

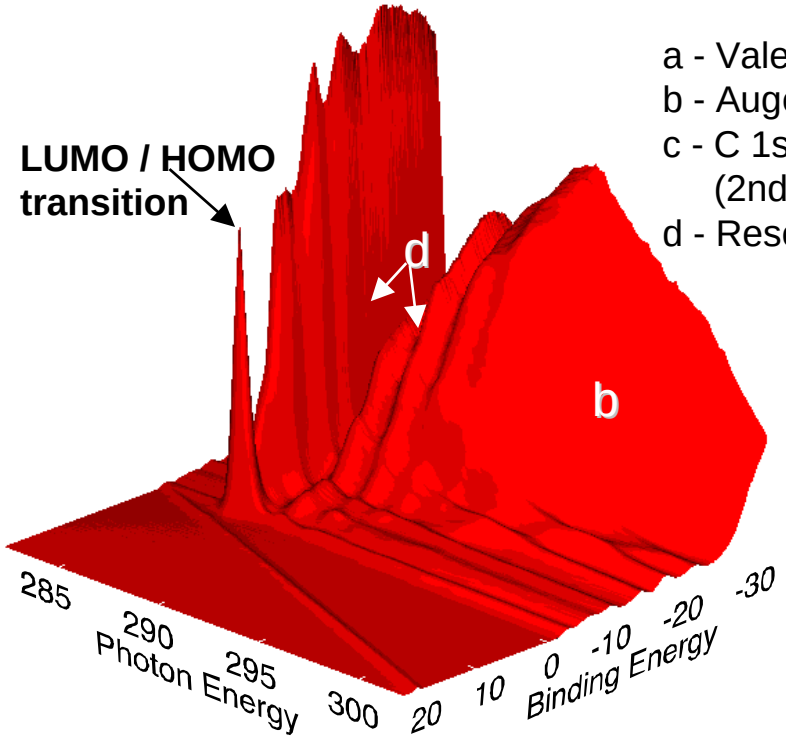
ARPES of a single crystal of PbS (galena)





Resonant Photoemission

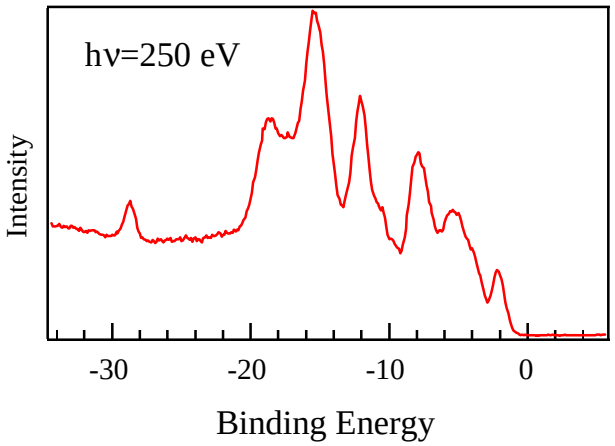
Poly(α-methylstyrene) Resonant Photoemission



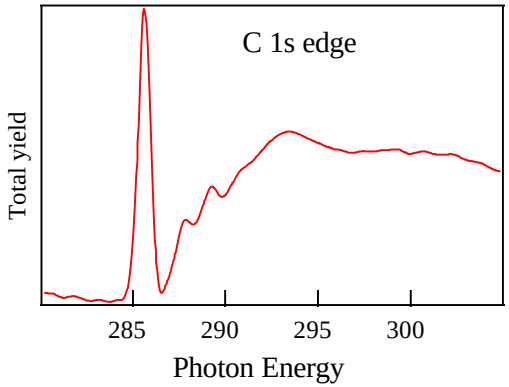
a - Valence Band Photoemission
b - Auger Emission
c - C 1s photoemission
(2nd harmonic radiation)
d - Resonant Photoemission

Mechanism of resonant photoemission

Valence Band

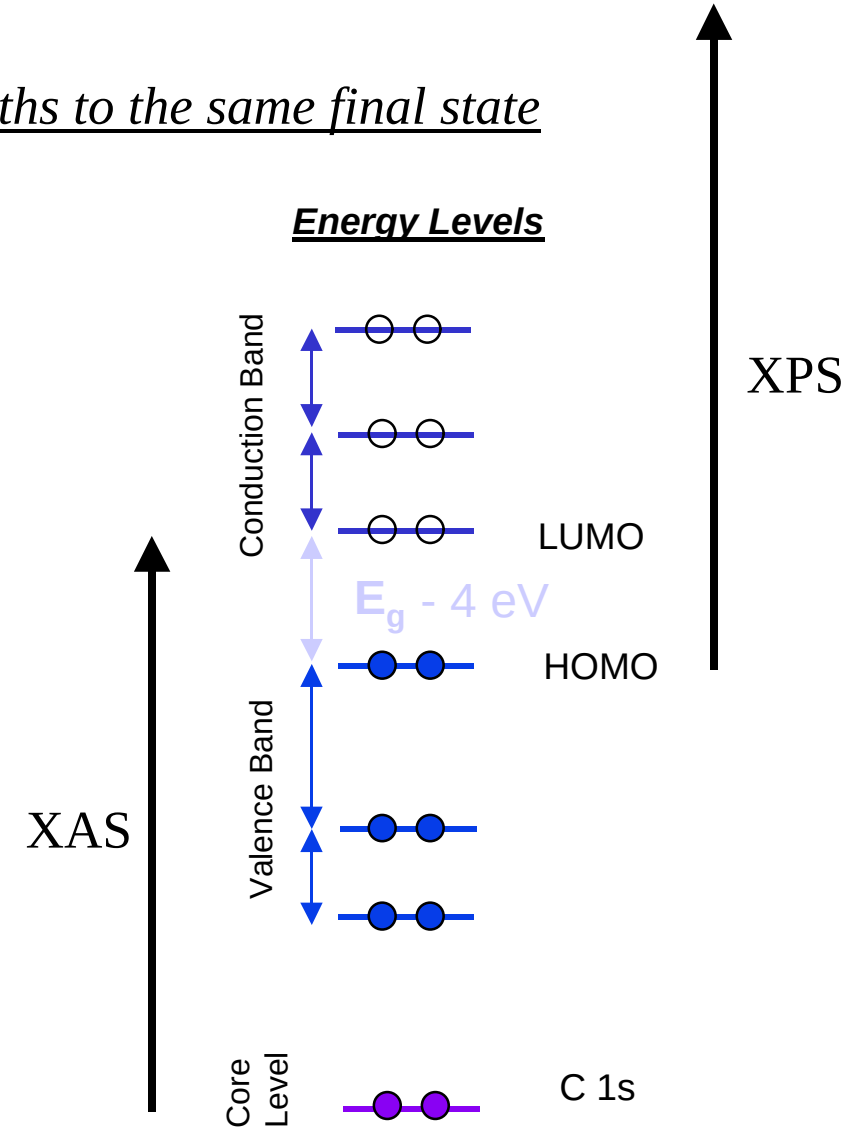


Absorption Profile



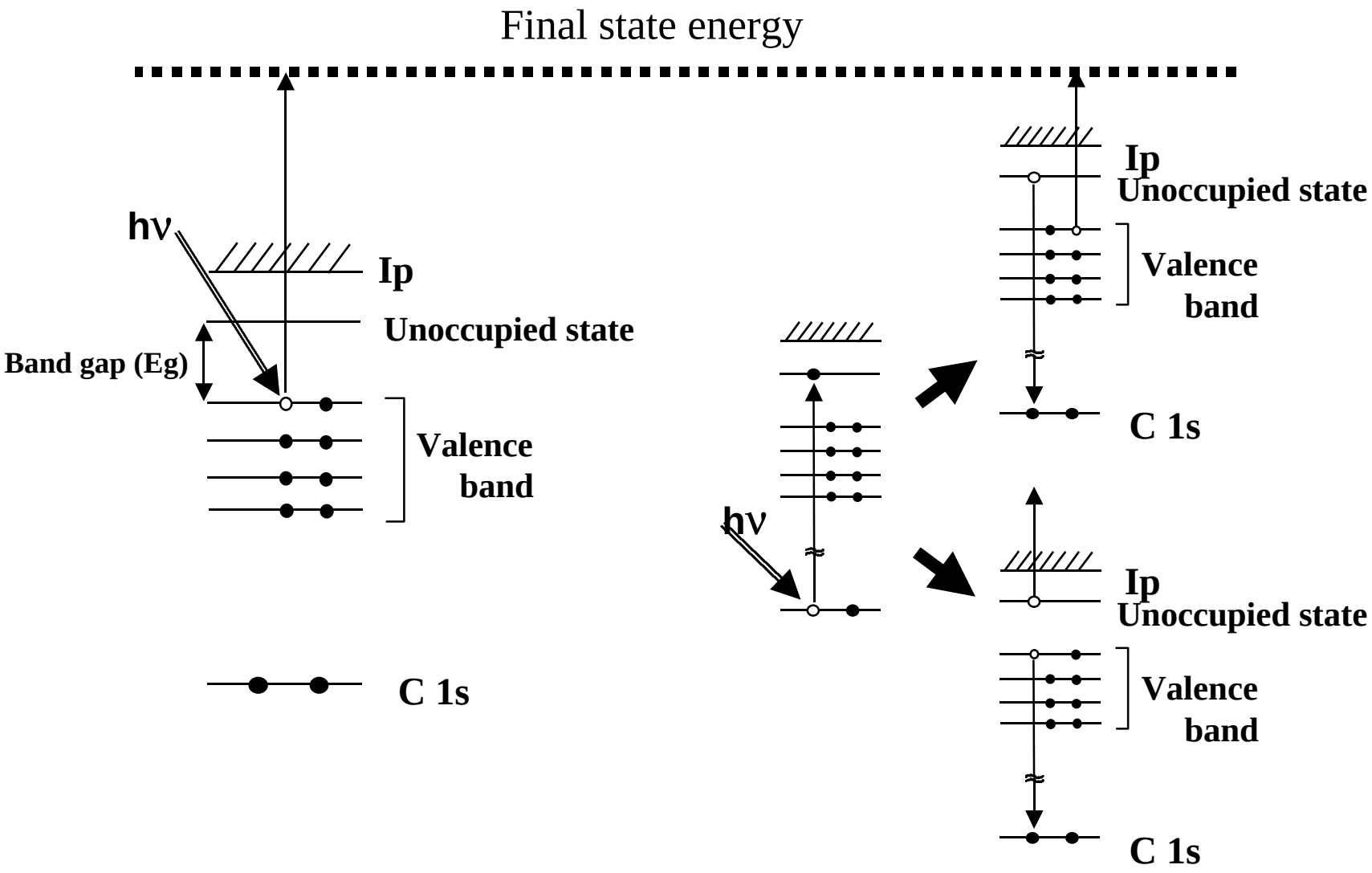
Two paths to the same final state

Energy Levels



Transitions in Resonant Photoemission

Two (or more) paths to the same final state



X-ray Absorption Spectroscopy

Note the increases in absorption at characteristic energies.