Frontiers of Experimental Condensed Matter Physics

- Part B: Excitations
  - Electronic structure:
    - Revision of basic electronic properties
      - Atomic character
      - Bands and bandwidth
    - Processes and nomenclature.
  - X rays
    - Spectroscopy based on absorption
      - Structure from XAS and EXAFS
  - Photoemission and electron spectroscopies
    - 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
      - Photoelectron microscopy.

Atomic states

- Solids
  - The electronic character of the solid derives in large part form the atomic states of the constituent atoms.
  - Many, general aspects of the electronic properties can be understood from the basic properties of hydrogenic orbitals and bonding in the independent electron approximation.
- Atoms:
  - Hydrogenic wavefunctions:
    - Quantum numbers:

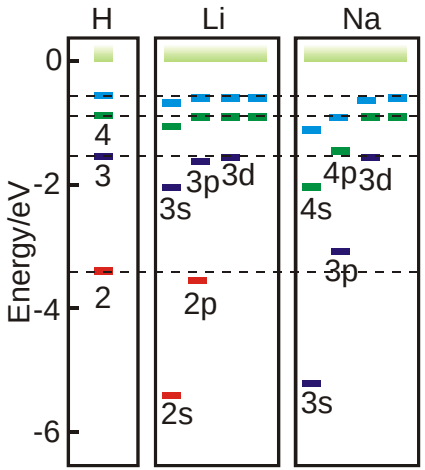
      n l m

      principal → n; angular momentum (s,p,d...) → l; projection of l → m
    - For hydrogen (z=1), the value of l and m does not affect the energy

1s	lowest energy
2s, 2p (degenerate)	
3s, 3p, 3d (")	increasing
4s, 4p, 4d, 4f (")	energy

Hydrogenic states

- $z>1$
  - In atoms heavier than hydrogen the l-degeneracy breaks down.

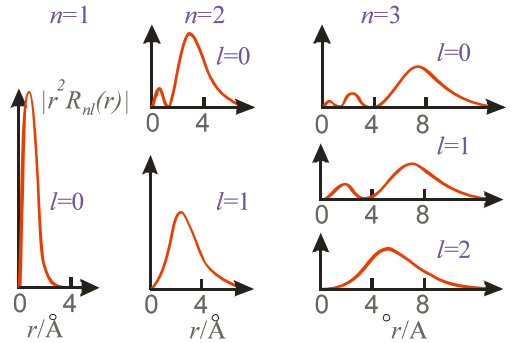


Note:

- As z increases penetration of wavefunction tail into the core lowers the binding energy. (Hence the $n = 3$ levels for Na overlap with the $n = 2$ levels in Li)
- The s-p gap for a given n increases with z. Hence, sp hybrids are more important in Gp. IV solids (Si, Ge) than Gp. VII (Cl, Br)

Spatial extent of orbitals

- Spatial extent of the wavefunctions is determined by their l-value.
- For example: hydrogen (again):



- Spatial extent increases with n, an obvious consequence of orthogonality.
- Higher l-values are more compact than lower l, for a given n. This too is a consequence of orthogonality. The angular variation in higher l-values allows orthogonality with the lower n-states without the need to expand in r.
- The spatial extent of an orbital determines the overlap with neighbouring atoms

Overlap and bandwidth

- Tight binding model
  - The simplest and most intuitive model describing the electronic structure of a solid comes from tight-binding theory.
  - Atomic orbits are used to construct Bloch states.
  - First write the wavefunction, for a Bloch state, labelled, **k**, as a sum of functions on lattice sites, j.

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_j \exp(i\mathbf{k}.\mathbf{r}_j)\varphi(\mathbf{r}-\mathbf{r}_j)$$

  - The expression defines $\phi(r)$, known as a Wannier function.
  - It is easy to show this has the correct, Bloch form

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \sum_j \exp(i\mathbf{k}.\mathbf{r}_j)\varphi(\mathbf{r}+\mathbf{R}-\mathbf{r}_j)$$

$$= \exp(i\mathbf{k}.\mathbf{R})\sum_j \exp(i\mathbf{k}.(\underbrace{\mathbf{r}_j-\mathbf{R}})\varphi(\mathbf{r}-(\underbrace{\mathbf{r}_j-\mathbf{R}}))$$

$$= \exp(i\mathbf{k}.\mathbf{R})\psi_{\mathbf{k}}(\mathbf{r})$$

simply another lattice vector, r_m, say

Tight-binding model

- $\phi(r)$ can be represented as a sum over atomic states

$$\varphi(\mathbf{r}) = \sum_{nlm} c_{nlm}\varphi_{nlm}(\mathbf{r}) \approx \varphi^o(\mathbf{r})$$

- The approximation, above, uses a single atomic state. It is the simplest and is useful provided the state is well localised.
- Then the energy of the state, **k** is

$$E_{\mathbf{k}} = \langle\psi_{\mathbf{k}}|H|\psi_{\mathbf{k}}\rangle = \sum_j\sum_m \exp(i\mathbf{k}.(\mathbf{r}_j-\mathbf{r}_m))\langle\varphi_m^o|H|\varphi_j^o\rangle$$

state, ϕ^o, at site m

- For simplicity take a 1-D solid with atoms at $r = ma$.
- We can neglect all terms except the nearest neighbours $j=m$, $m\pm1$, since the matrix elements decrease rapidly with the separation of the wavefunction centres. Hence we get 3 terms

$$E_k = \alpha\exp(ik.0) + \beta\exp(ika) + \beta\exp(-ika)$$

$\alpha = \langle\varphi_m^o|H|\varphi_m^o\rangle$

$\beta = \langle\varphi_m^o|H|\varphi_j^o\rangle$

overlap integral

Energy bands

- The energy band becomes

$$E_k = \alpha + 2\beta\cos(ka)$$

number of nearest neighbours

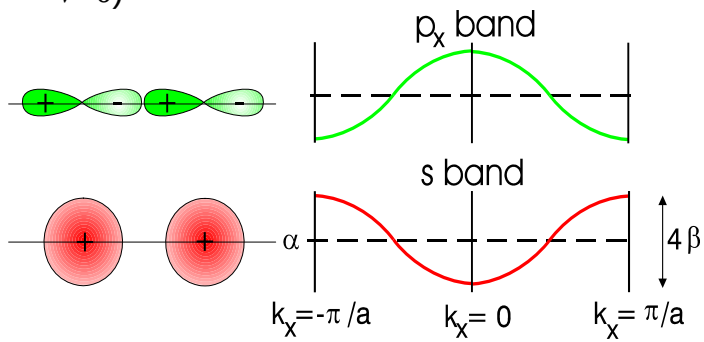
- Width of band directly proportional to the orbital overlap, β, and the bandwidth $\Delta E = 4\beta$.
- Note the factor 2 arises because we have two neighbours contributing. The analysis can easily be extended to 3-D. Assuming a cubic crystal we will have 6 neighbours (2 in x-direction, 2 in y and 2 in z). The band structure is

$$E_k = \alpha + 2\beta\{\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\}$$

- The bandwidth is now $\Delta E = 12\beta$.
- We note that the other factor in determining the bandwidth is the number of neighbours (coordination number).

Shells and bands

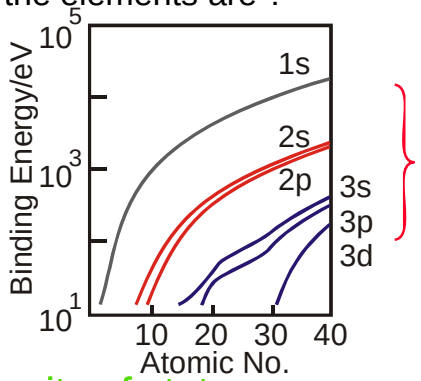
- Valence band
  - For s-states $\beta < 0$; p-states $\beta > 0$. (N.B. in H, $V<0$)



  - Spatially extended atomic states gives overlap and hence broad bands.
    - s-p bands typically 10-20eV
    - d bands usually narrower since d -states are more compact (less overlap)
- Core states
  - Highly compact with negligible overlap
    - bandwidth is negligible and the states are essentially the same as atomic states.

Generic density of states

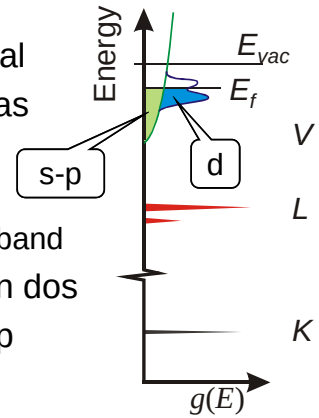
- Core levels
  - The measured binding energy of core levels of the elements are*:



Typical X ray energies

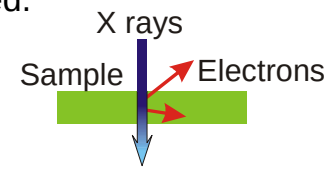
* based on fig. 3.15, Woodruff and Delchar

- Density of states
  - Eg. Typical transition metal
  - Note core levels notated as
    - K, for 1s level
    - L, for 2s, 2p
    - V indicates the valence band
  - s-p band has free-electron dos
  - d-states narrower than s-p
  - note E_f and E_{vac}.

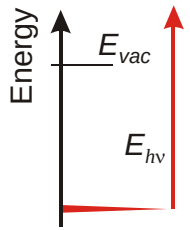


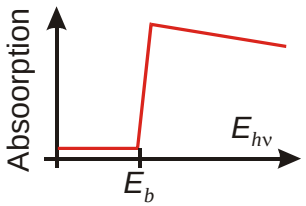
Core level spectroscopies

- X ray absorption / photoemission
  - If an incident x-ray has sufficient energy to excite a core electron into an empty state the x-ray is absorbed and (possibly) a photoelectron generated.



  - Both the absorption process and the photoelectron energy provide spectroscopic information about a sample.
- X ray Absorption (XAS, EXAFS)
  - XAS – x ray, absorption spectroscopy; EXAFS – extended, x ray, absorption fine structure.
  - An isolated atom gives a simple absorption edge





X ray absorption

- The absorption spectrum for an atom gives little information of value.

Absorption in a solid

- In a solid, the process is more complex and interesting.
- The outgoing photoelectron scatters from nearby atoms and interferes with the outgoing wave. The scattering defines the final state into which the transition occurs and, therefore, affects the transition probability.
- The transition rate, μ, is given by Fermi's Golden rule:

$$\mu(h\nu) \propto \sum_i |\langle f|H_i|i\rangle|^2 \delta(h\nu - E_f - E_i)$$

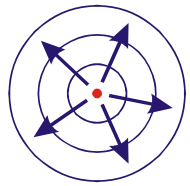
final state — initial state — energy conservation

- The wavelength of the x ray exceeds the spatial extent of the initial, core state. So the dipole approximation is valid and the matrix elements become $\langle f|H_i|i\rangle \approx \langle f|\mathbf{e.r}|i\rangle$ A

polarisation vector for the x-ray

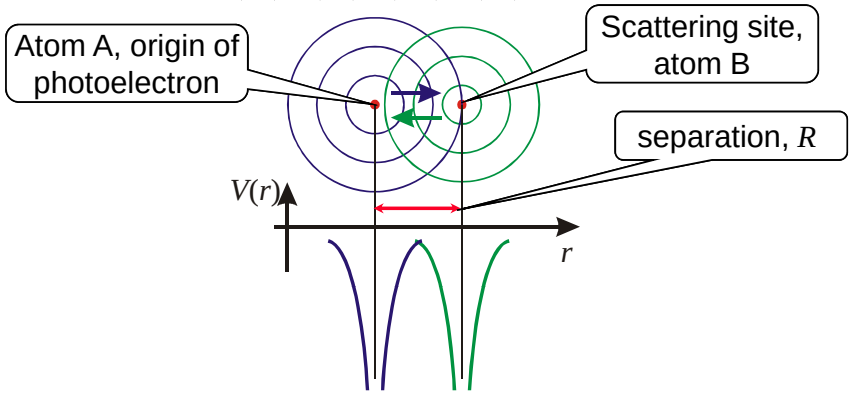
Electron backscattering

- For an isolated atom $|f\rangle$ is simply a spherical wave.



- If there is a single, neighbouring atom then $|f\rangle$ is modified by the scattered wave

$$|f\rangle = |f\rangle + |\delta f\rangle = |f\rangle(1+\chi)$$



- Note the spherical wave is travelling through a region where the potential varies strongly so that phase shifts arise because of the potentials, as well as the distances travelled.

- Amplitude of the wave at site B

$$\psi = \frac{\exp i(kR+\delta)}{R}$$

phase shift travelling R

phase shift due to potential

- The wave is reflected with a coefficient,

$$f_B(k) = |f_B(k)|\exp(i\delta_B(k)),$$

which includes a phase shift, δ_B, attributable to traversing potential V_B. Thus, the reflected amplitude at site A is

B

$$\chi = \frac{\exp i(kR+\delta)}{R}|f_B(k)|\exp(i\delta_B)\frac{\exp i(kR+\delta)}{R}$$

$$= |f_B(k)|\frac{\exp i(2kR+\phi(k))}{R^2}$$

$\phi(k) = 2\delta + \delta_B$

- Equations A and B contain the physics that allows the method to be used as a local, structural probe. Specifically
  - A shows that there is a polarisation dependence to the absorption
  - B shows there are interference terms with period $2kR$, where R is the distance to the neighbour.

XAS, EXAFS

Practical approach

- In addition to the structural information, we need to include thermal vibrations (through a Debye-Waller type expression) and inelastic scattering of the photoelectrons (through a mean-free-path)
- The usual expression used to analyse experiment is

polarisation term

oscillatory term (structure)

$$\chi(k) = \sum_j \cos^2(\mathbf{R}_j.\boldsymbol{\varepsilon}).\frac{|f_B(k)|}{R_j^2}.\sin(2kR_j + \varphi(k)).$$

$$\exp(-2\sigma^2k^2).\exp(-2R_j/\lambda(k))$$

damping due to thermal vibrations

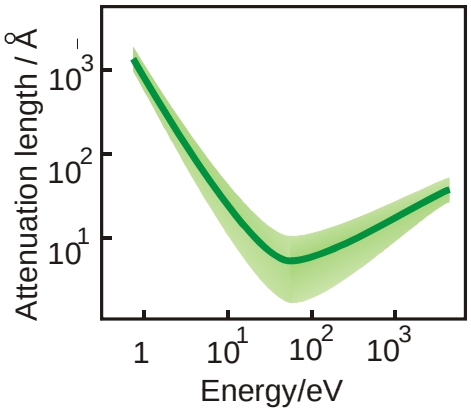
damping due to inelastic scattering

- The thermal vibration term contains an "effective" vibration amplitude, σ. In the harmonic approximation, $\sigma^2 \propto T$ (Debye-Waller type behaviour). However, we are sensitive to changes in the interatomic distance, which is unaffected by long-wavelength, acoustic phonons.

Inelastic scattering

Attenuation length

- The main contributions to inelastic scattering are single particle events and plasmon excitation. The latter tends to dominate at higher energies.
- There is a “universal curve” (with some scatter) that characterises all materials.

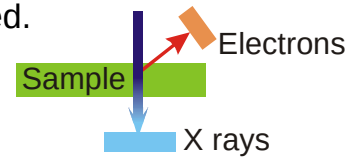


- For typical electron energies (10-1000eV), the attenuation length is extremely small ~10Å.
  - Interference effects are only appreciable for local scatterers.
  - Photoelectrons that leave the sample come from the near surface region.

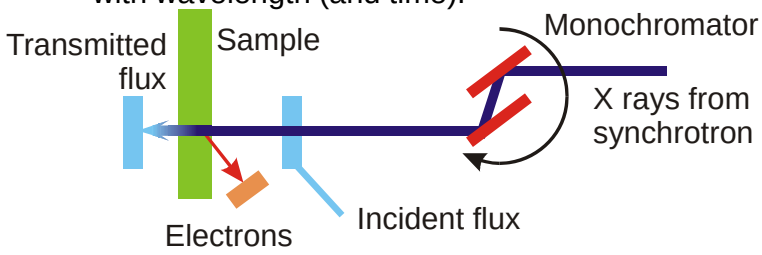
Methods

Bulk and surface studies

- The probe can be made sensitive either to the bulk or to the surface by changing the way absorption is measured.

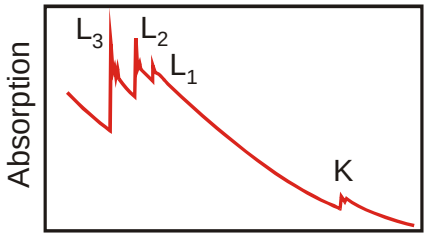


  - Direct measure of x-ray flux transmitted gives a bulk probe.
  - Measuring the photoelectron signal gives a surface probe.
- Experiment typically scans the x ray wavelength by monchromating the “white” synchrotron radiation. Crystal monochromater relies on diffraction (angle relates to wavelength)
  - Need to normalise signal to the incident flux (varies with wavelength (and time).

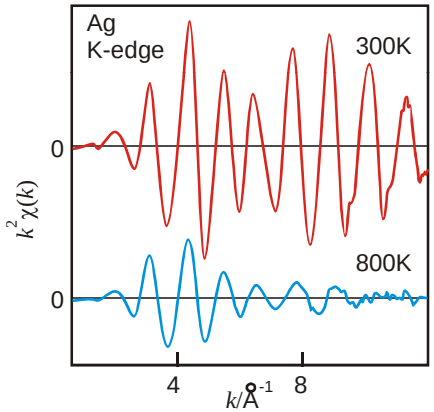


Examples

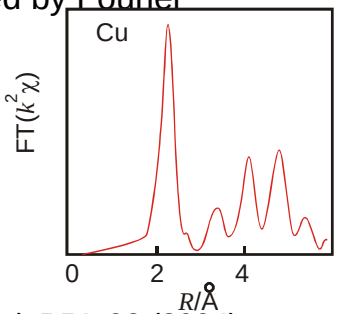
- Simple metals
  - Chosen to illustrate the method (See Rehr and Albers, Rev Mod Phys 72, (2000) 621)
  - Absorption edges



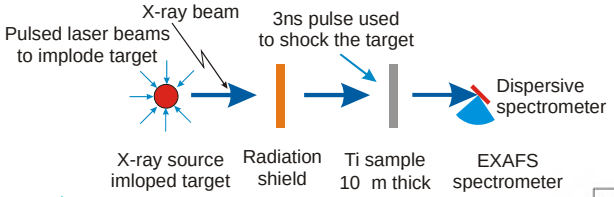
  - After removal of edge itself one is left with the fine structure. (Note the temperature dependence)



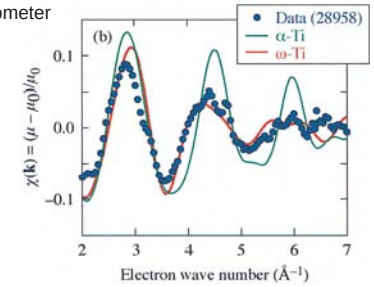
- Simplest analysis is achieved by Fourier Transforming (see fig.).
  - Spacing of shells given directly.
  - More sophisticated modelling, using multiple scattering theory also possible – not shown.



- Recent example (Yaakobi et al. PRL 92 (2004) 095504) EXAFS from shocked Ti.
  - Multiple laser beams: some generate x-rays in an imploded target; others shock the Ti sample

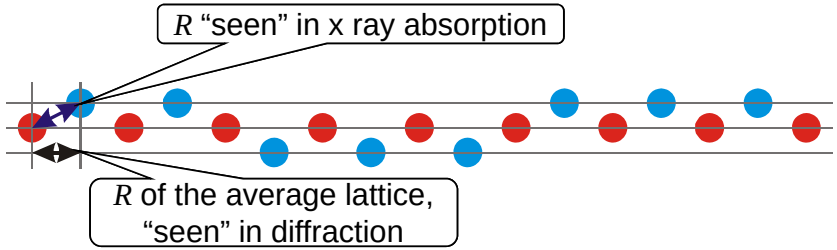


- Results indicate a phase change from α-Ti to ω-Ti. (The variety of nearest-neighbour distances in ω-Ti, explains the rapid decay in oscillations – it is not due to high T in the shock region)



Absorption vs diffraction

- Why use x ray absorption?
  - In principle all structural information is present in the x ray diffraction pattern. In practice, the combination of diffraction (sensitive to medium and long range order) with a probe giving nearest neighbour bond-angles and lengths is valuable.
  - For example, disordered structures clearly benefit from a local probe.
  - There are other subtleties; Take, for example, a structure with multiple conformations. Diffraction sees the average lattice



  - A further benefit of EXAFS is that it can be made surface sensitive (by measureing the photoelectron yield) and hence give bond lengths (and angles) for surface adsorption etc.

EXAFS

- Summary: X ray absorption
  - Simple probe of local structure
  - Has chemical sensitivity through the choice of the absorbing atom (which has its characteristics absorption edges)
  - Doesn't require a crystalline sample, hence useful in amorphous systems and those with poor long-range order.
  - Bond lengths (from the period of the oscillations) can be determined accurately ~ ± 0.02 Å
  - Bond directions (from the polarisation dependence of the signal) can be determined qualitatively.
  - Disadvantages:
    - Only appropriate for relatively simple structures.
    - Only sensitive to a few neighbouring shells.