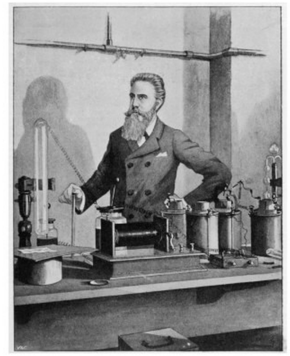
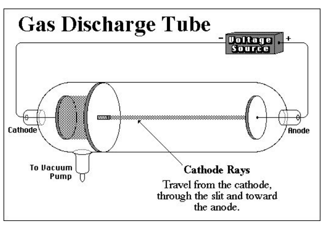
X-ray Spectroscopy

- Lecture 1: Introduction & experimental aspects
- Lecture 2: Atomic Multiplet Theory
  Crystal Field Theory
  CTM4XAS program
- Lecture 3: Charge Transfer Multiplet Theory
  Resonant Inelastic X-ray Scattering
  X-ray Spectroscopy on nanomaterials

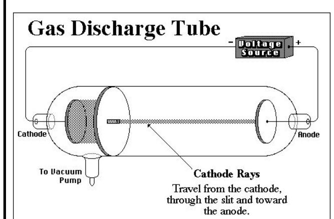
Röntgen's experiment in 1895



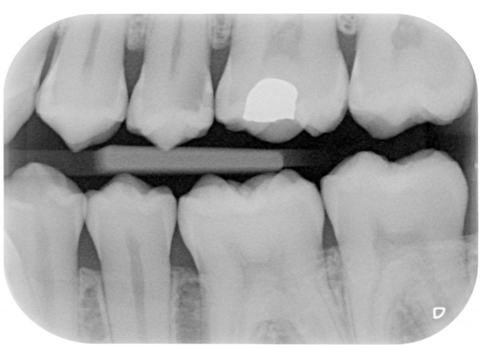
Röntgen's experiment



Röntgen's experiment



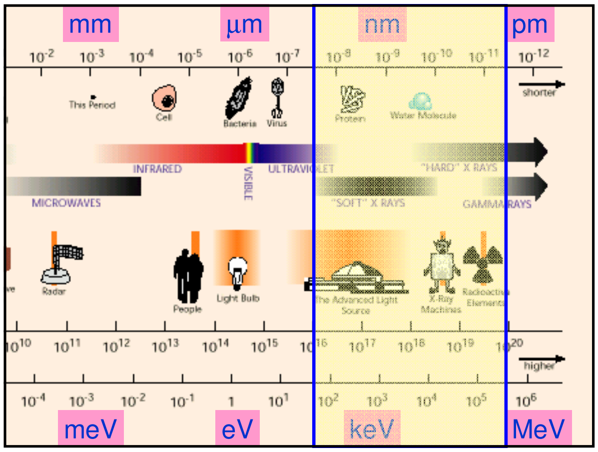
Interaction of x-rays with matter



x-rays

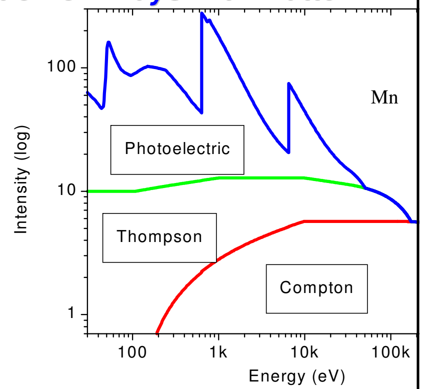
Wavelength: 10^{-10} m

Frequency: $C/\lambda = 3 \cdot 10^{18}$ Hz



Interaction of x-rays with matter

- XAFS studies photoelectric absorption
- Thompson scattering (Diffraction)
- Compton scattering



Interaction of x-rays with matter 1

The photon moves towards the atom

Interaction of x-rays with matter 1

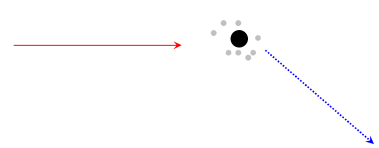
The photon meets an electron and is annihilated

Interaction of x-rays with matter 1

The electron gains the energy of the photon and is turned into a **blue electron**.

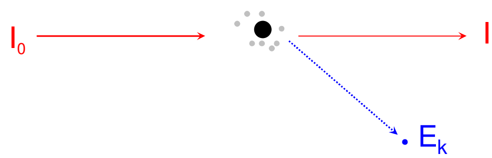
Interaction of x-rays with matter 1

The blue electron (feeling lonely) leaves the atom and scatters of neighbors or escapes from the sample

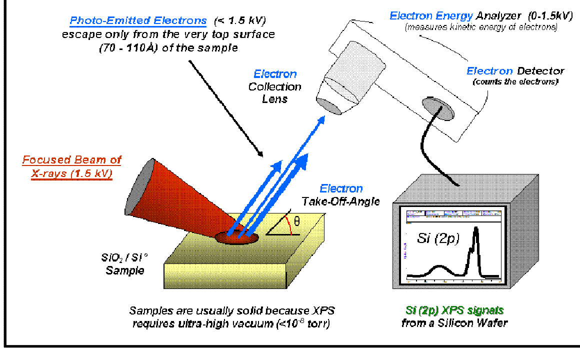


Interaction of x-rays with matter 1

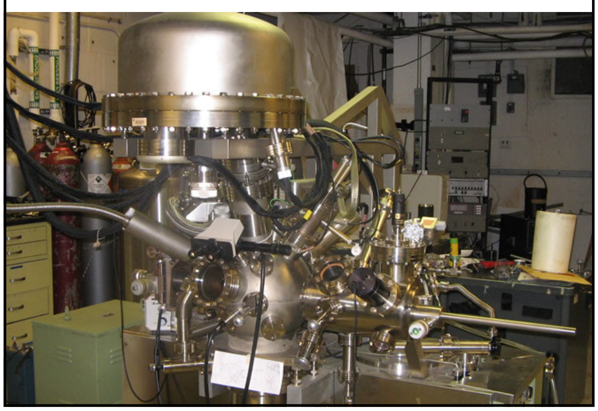
The probability of photon annihilation determines the intensity of the transmitted photon beam



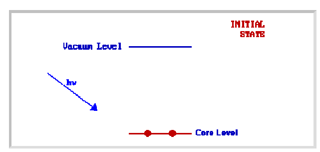
XPS machine



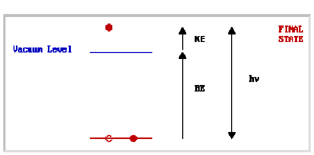
XPS machine

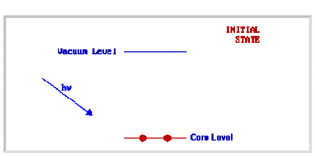


X-ray photoemission



X-ray photoemission





X-ray photoemission: workfunction

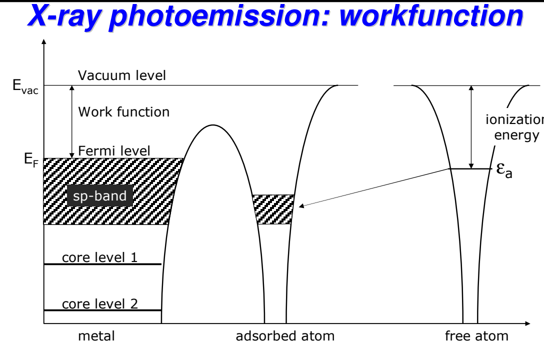
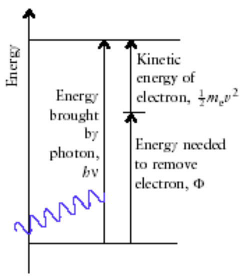
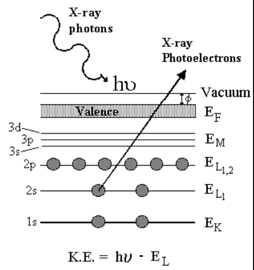


Figure 6.11

XPS and the photo-electric effect

Photo-electric effect | XPS





$h\nu = E_k + \Phi$ $\quad$ $h\nu = E_L + E_k + \Phi$

Binding Energy: defined versus highest occupied state

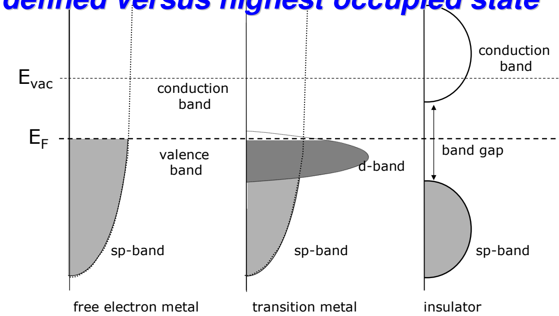
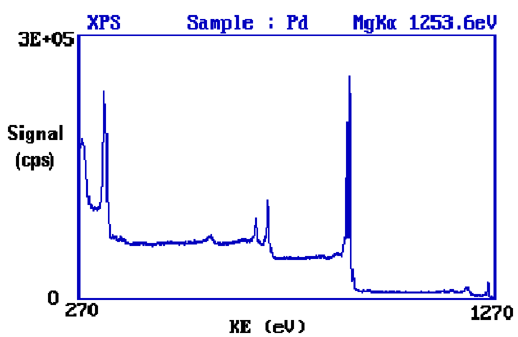


Figure 6.17

X-ray photoemission



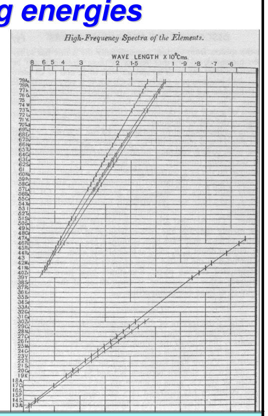
Atomic binding energies

THE HIGH FREQUENCY SPECTRA OF THE ELEMENTS (1913)

Moseley (1887-1915)

Atomic binding energies

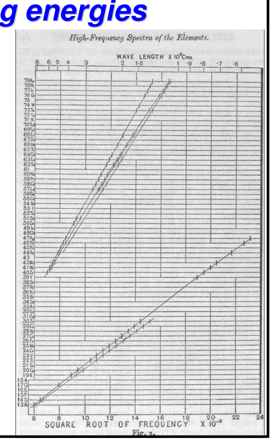
… simple laws have been found which […] make it possible to predict with confidence the position of the principal lines in the spectrum of any element from aluminum to gold.



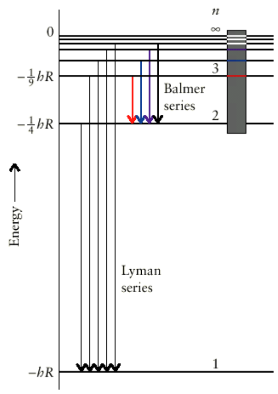
Moseley. **Phil. Mag.** 26, 156(1913); online link at website

Atomic binding energies

$\nu = 2.5 \cdot 10^{15} (Z-\alpha)^2$ Hz



Atomic binding energies



Bohr frequency condition:

$$h\nu = E_{upper} - E_{lower}$$

$$h\nu = h\mathcal{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Rydberg formula

Atomic binding energies

Transition from 1s to 2p in hydrogen:

$$h\nu = h\mathcal{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 13.6 * (1/1-1/4) \sim 10 \text{ eV}$$

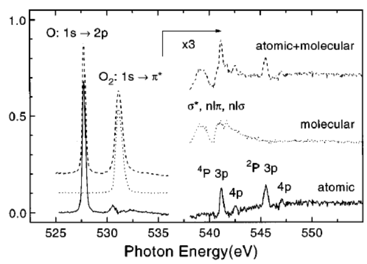
Transition from 1s to 2p in oxygen:

$$h\nu = h\mathcal{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \cdot Z^2$$

$= 10 * 8^2 = 10 * 64 = 640$ eV

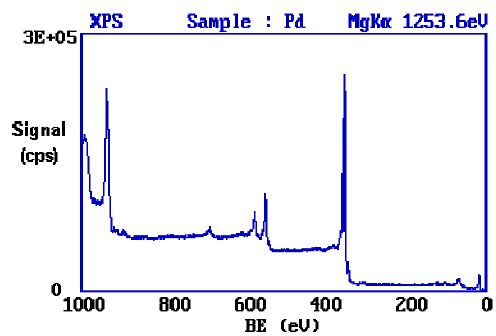
Atomic binding energies

Transition from 1s to 2p in oxygen: 528 eV;
Calculated as 640 eV



Screening of charge: $hC^*(Z_{eff})^2$ =528 eV, with Z_{eff}=7.2
$hC^*(Z-\alpha)^2$, with α=0.8

X-ray photoemission



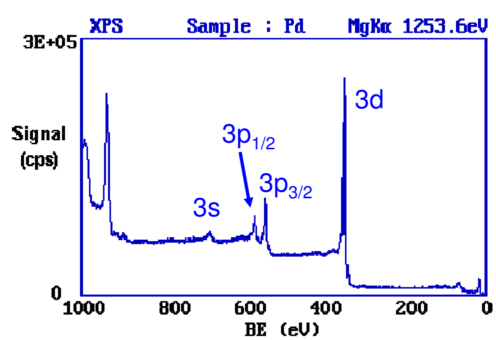
X-ray photoemission edges

Paladium Electron binding energies

M I	3s	671.6
M II	3p1/2	559.9
M III	3p3/2	532.3
M IV	3d3/2	340.5
M V	3d5/2	335.2
N I	4s	87.1
N II	4p1/2	55.7
N III	4p3/2	50.9

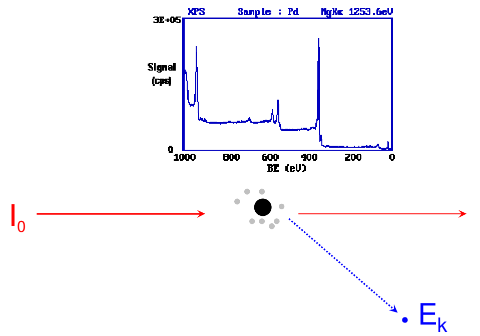
http://www.webelements.com/

X-ray photoemission

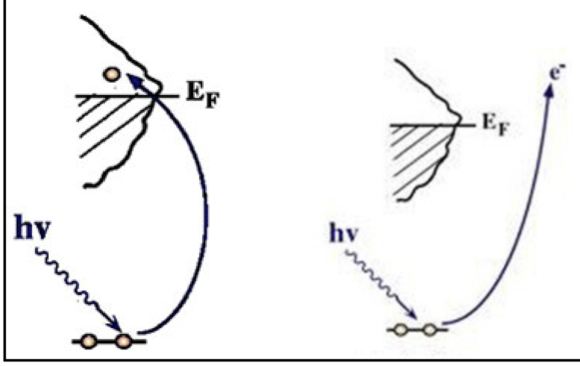


http://www.webelements.com/

Interaction of x-rays with matter 1



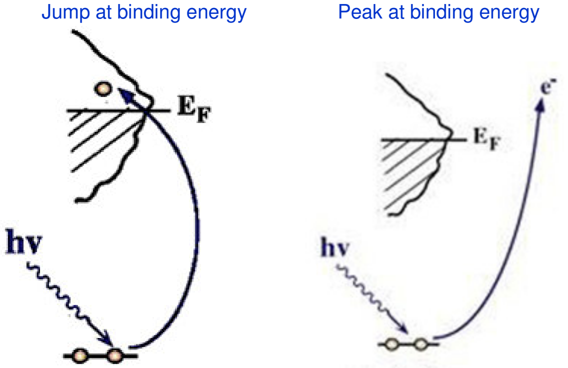
X-ray absorption and X-ray photoemission



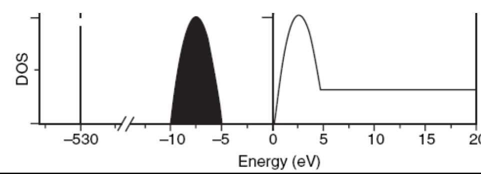
X-ray absorption and X-ray photoemission

Jump at binding energy

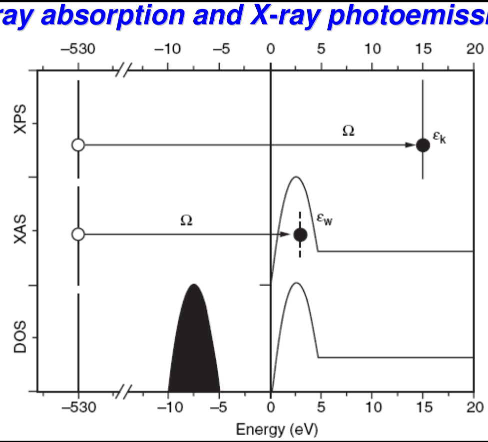
Peak at binding energy



X-ray absorption and X-ray photoemission



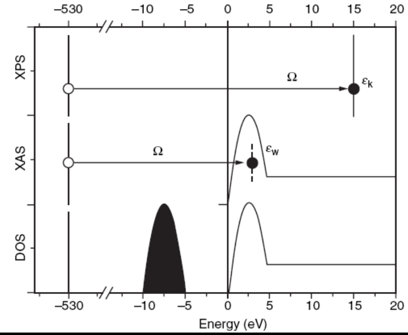
X-ray absorption and X-ray photoemission



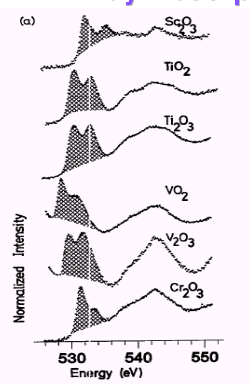
X-ray absorption experiments

X-ray absorption and X-ray photoemission

$$W_{fi} = \frac{e^2}{\hbar c}\frac{4\Omega^3}{3c^2} n |\langle \Phi_f | \mathbf{r} | \Phi_i \rangle|^2 \delta(E_f - E_i - \hbar\Omega).$$

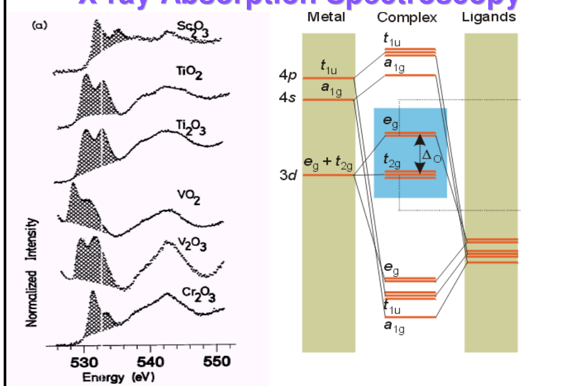


X-ray Absorption Spectroscopy



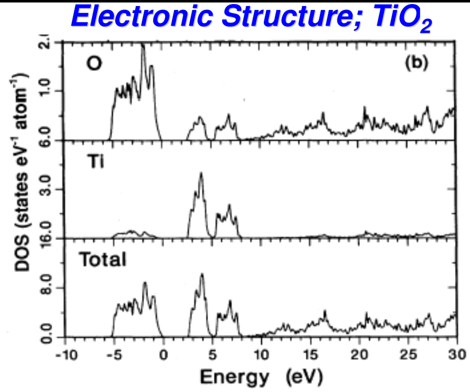
Phys. Rev. B. 40, 5715 (1989); 48, 2074 (1993)

X-ray Absorption Spectroscopy



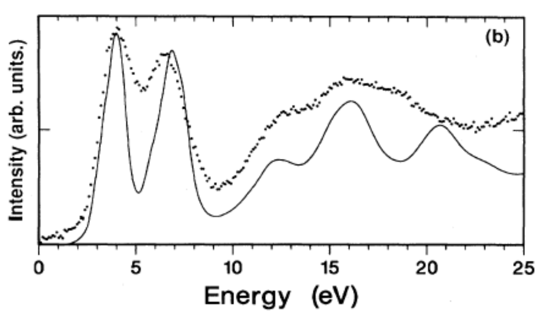
Phys. Rev. B. 40, 5715 (1989); 48, 2074 (1993)

Electronic Structure; TiO_2

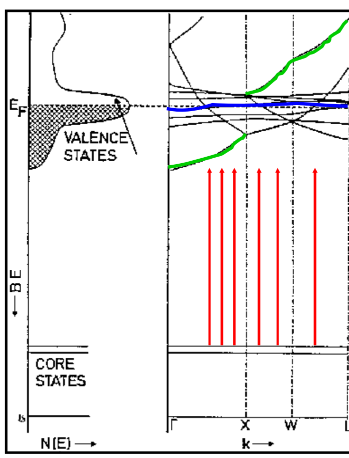


Phys. Rev. B. 40, 5715 (1989); 48, 2074 (1993)

Electronic Structure: TiO_2



Phys. Rev. B. 40, 5715 (1989); 48, 2074 (1993)



SOLID STATE
>> delocalised

ATOMIC
>> localised

X-ray absorption

Excitation of core electrons to empty states.

Spectrum given by the **Fermi Golden Rule**
(name Golden Rule given by Fermi; rule itself given by Dirac)

$$I_{XAS} \sim \Sigma_f \left|\left\langle \Phi_f \left| \hat{e}\cdot r \right| \Phi_i \right\rangle\right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray absorption

Fermi Golden Rule:

$I_{XAS} = |\langle\Phi_f|\text{dipole}|\Phi_i\rangle|^2 \; \delta_{[\Delta E=0]}$

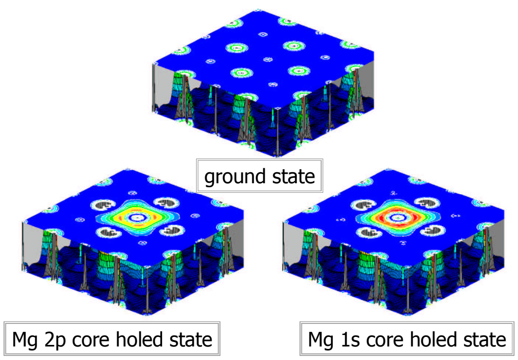
$$\left|\left\langle \Phi_f \left| \hat{e}_q \cdot r \right| \Phi_i \right\rangle\right|^2 = \left|\left\langle \Phi_i \underline{c}\varepsilon \left| \hat{e}_q \cdot r \right| \Phi_i \right\rangle\right|^2$$

$$= ?? \left|\left\langle \varepsilon \left| \hat{e}_q \cdot r \right| c \right\rangle\right|^2$$

Single electron (excitation) approximation:

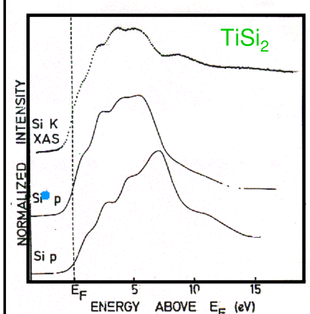
$I_{XAS} = |\langle\Phi_{empty}|\text{dipole}|\Phi_{core}\rangle|^2 \; \rho$

X-ray absorption: core hole effect



Tanaka et al, **J. Am. Ceram. Soc.** 88, 2013 (2005).

X-ray absorption: core hole effect

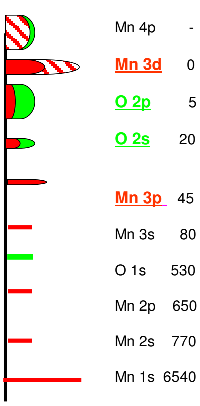


- **Final State Rule:** Spectral shape of XAS looks like final state DOS
- **Initial State Rule:** Intensity of XAS is given by the initial state

Phys. Rev. B. 41, 11899 (1991)

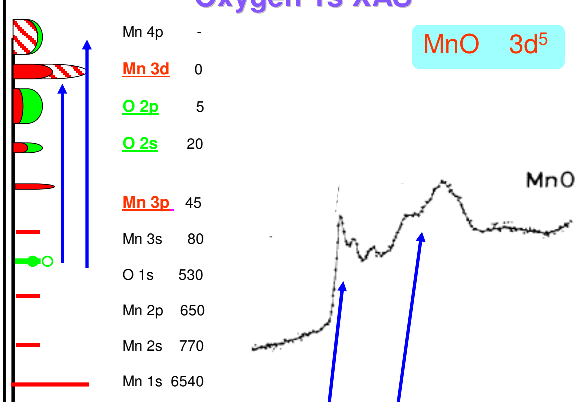
Ground State

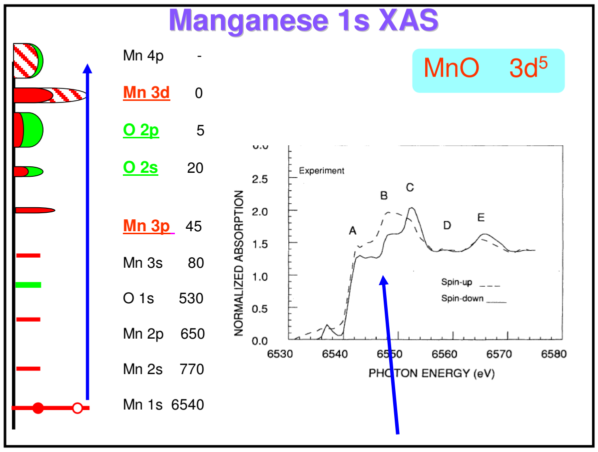
MnO $3d^5$

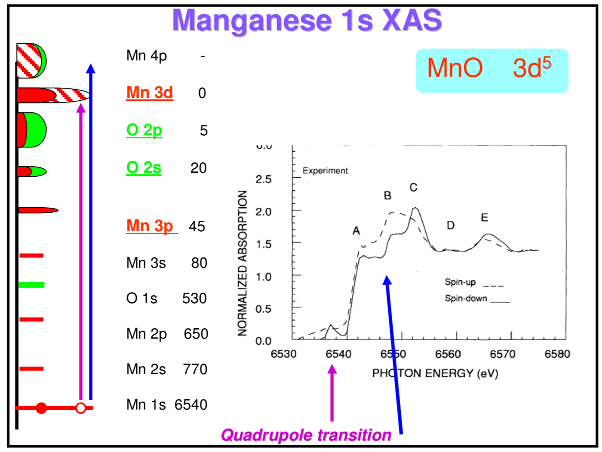


Oxygen 1s XAS

MnO $3d^5$



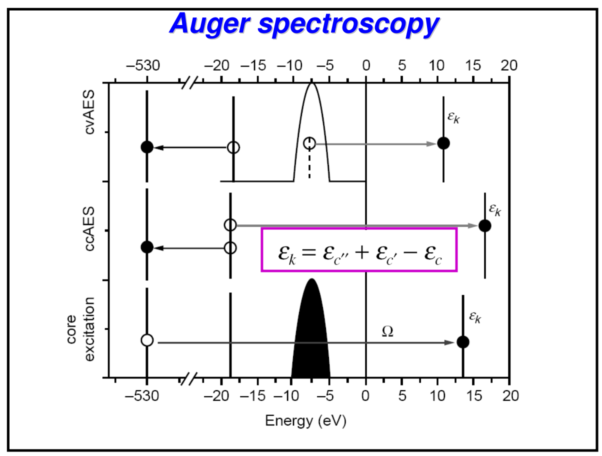


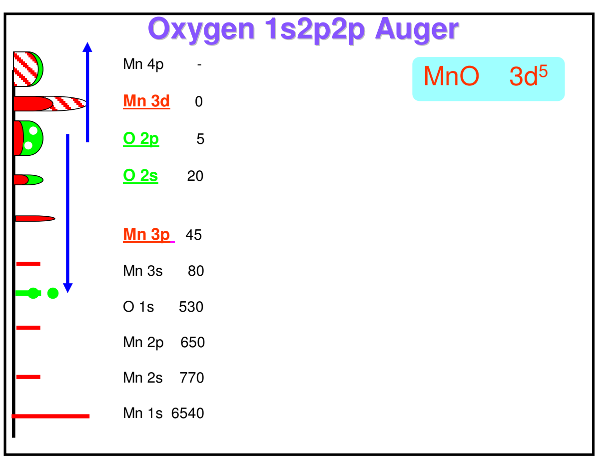


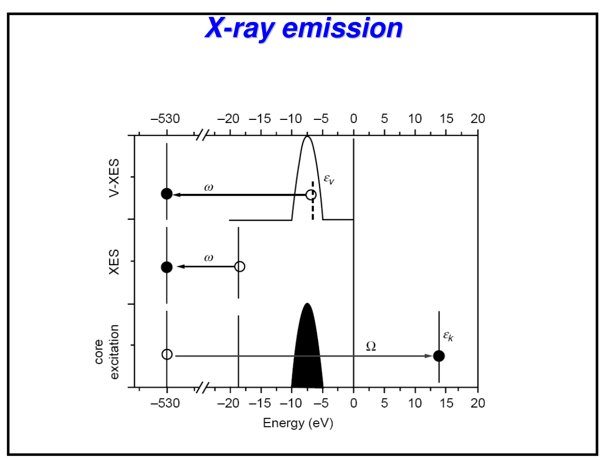
The life of a Core Hole

Heisenberg uncertainty relation
$\Gamma\tau \cong \hbar$ (~ 10^{-16} eV s).

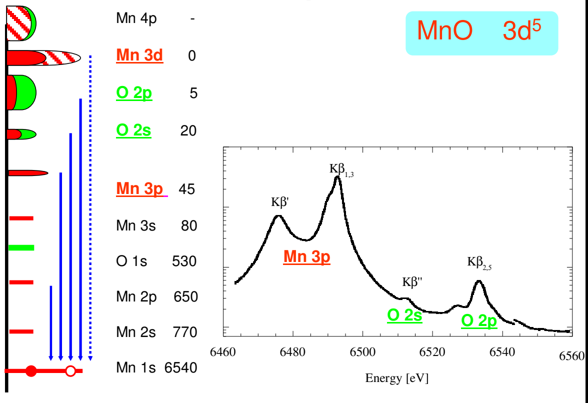
Broadening of XAS: ~0.1 eV
Lifetime = 1 femtosecond



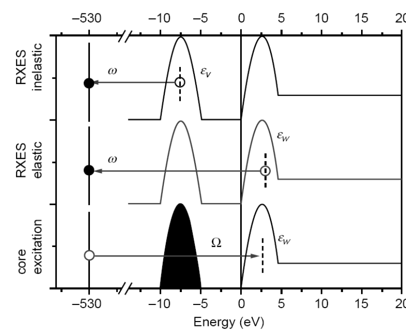


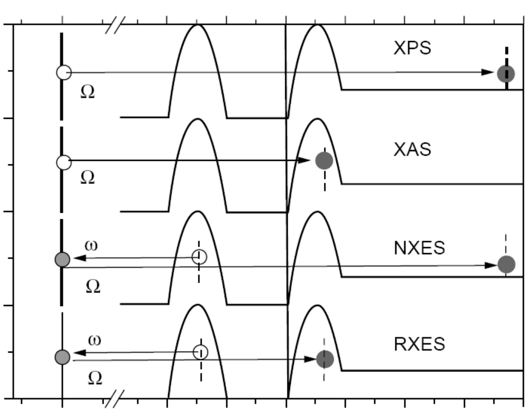


Mn 1s3p XES



Resonant X-ray emission spectroscopy





X-ray absorption

Fermi Golden Rule:

$I_{XAS} = |\langle\Phi_f|\text{dipole}|\Phi_i\rangle|^2 \, \delta_{[\Delta E=0]}$

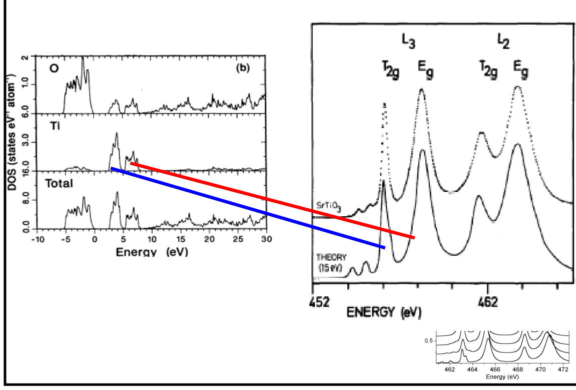
$$\left|\left\langle \Phi_f \middle| \hat{e}_q \cdot r \middle| \Phi_i \right\rangle\right|^2 = \left|\left\langle \Phi_i \underline{c}\varepsilon \middle| \hat{e}_q \cdot r \middle| \Phi_i \right\rangle\right|^2$$

$$= ?? \left|\left\langle \varepsilon \middle| \hat{e}_q \cdot r \middle| c \right\rangle\right|^2$$

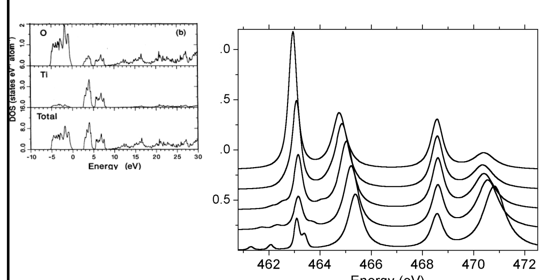
Single electron (excitation) approximation:

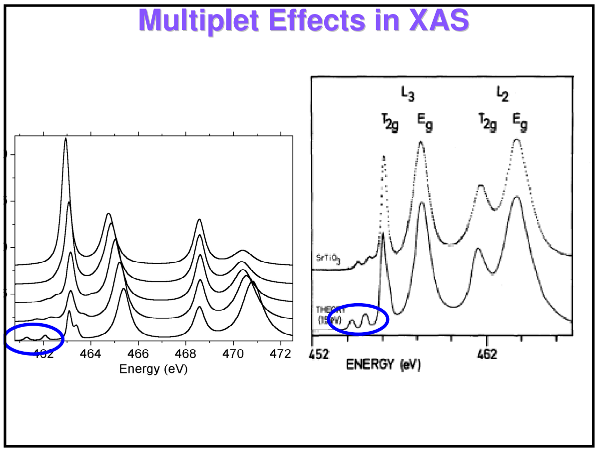
$I_{XAS} = |\langle\Phi_{empty}|\text{dipole}|\Phi_{core}\rangle|^2 \, \rho$

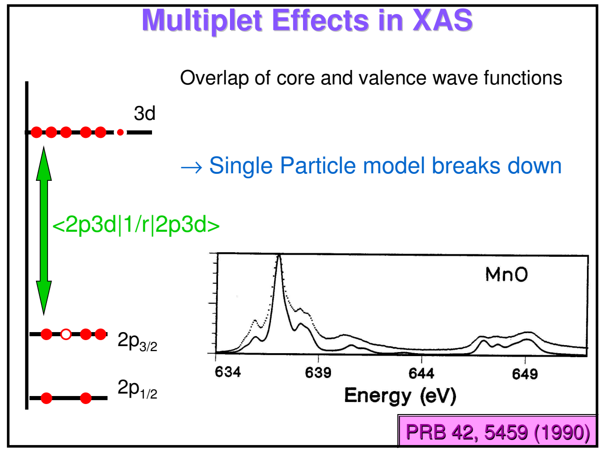
Multiplet Effects in XAS

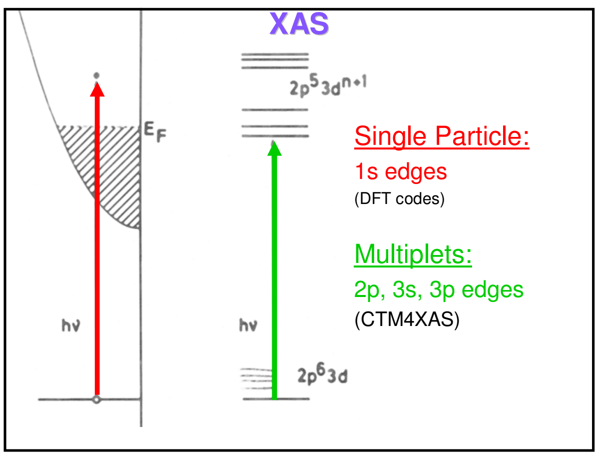


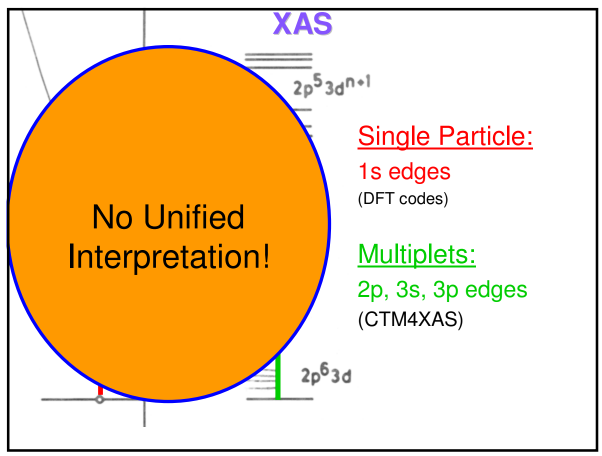
Multiplet Effects in XAS

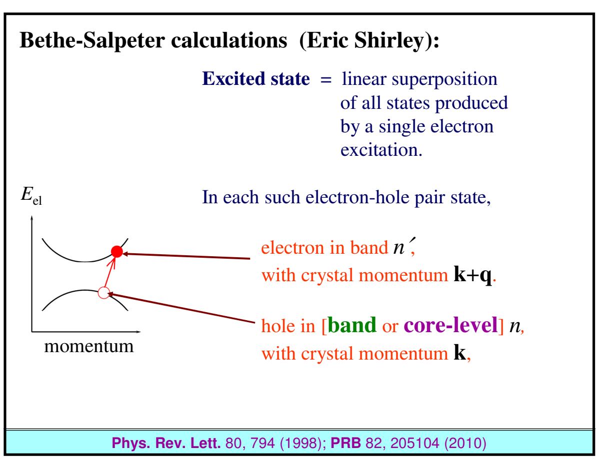


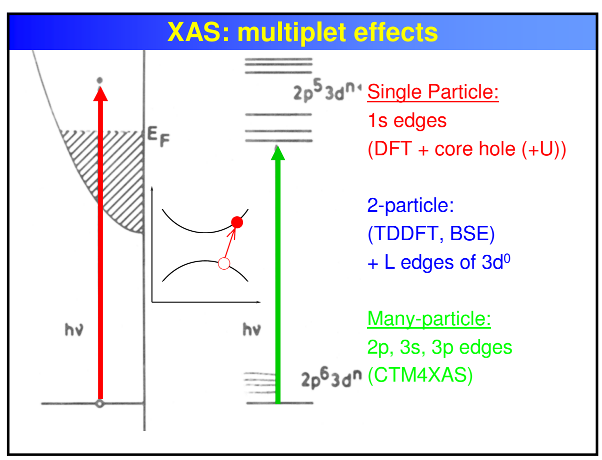

Multiplet Effects in XAS
L3
L2
T2g
Eg
SrTiO3
THEORY
462
464
466
468
470
472
Energy (eV)
452
462
ENERGY (eV)


Multiplet Effects in XAS
Overlap of core and valence wave functions
3d
→ Single Particle model breaks down
<2p3d|1/r|2p3d>
MnO
2p3/2
2p1/2
634
639
644
649
Energy (eV)
PRB 42, 5459 (1990)

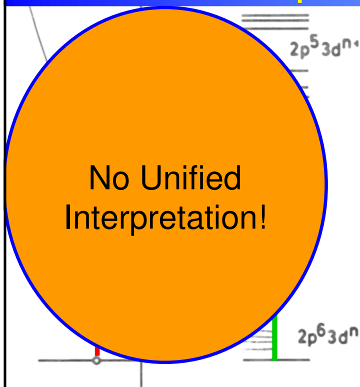

XAS
2p53dn+1
EF
Single Particle:
1s edges
(DFT codes)
Multiplets:
2p, 3s, 3p edges
(CTM4XAS)
hν
hν
2p63d


XAS
2p53dn+1
No Unified Interpretation!
Single Particle:
1s edges
(DFT codes)
Multiplets:
2p, 3s, 3p edges
(CTM4XAS)
2p63d


Bethe-Salpeter calculations (Eric Shirley):
Excited state = linear superposition of all states produced by a single electron excitation.
In each such electron-hole pair state,
Eel
electron in band n´, with crystal momentum k+q.
hole in [band or core-level] n, with crystal momentum k,
momentum
Phys. Rev. Lett. 80, 794 (1998); PRB 82, 205104 (2010)


XAS: multiplet effects
2p53dn+1
EF
Single Particle:
1s edges
(DFT + core hole (+U))
2-particle:
(TDDFT, BSE)
+ L edges of 3d0
Many-particle:
2p, 3s, 3p edges
(CTM4XAS)
hν
hν
2p63dn

XAS: multiplet effects

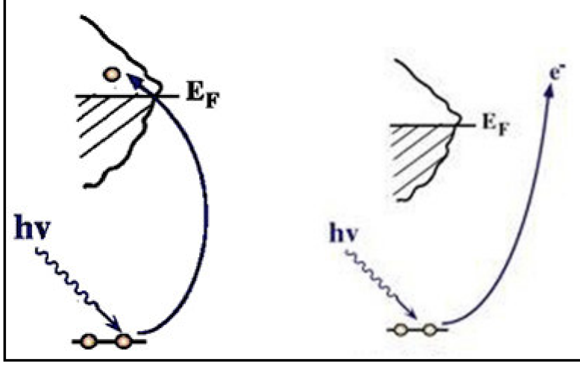


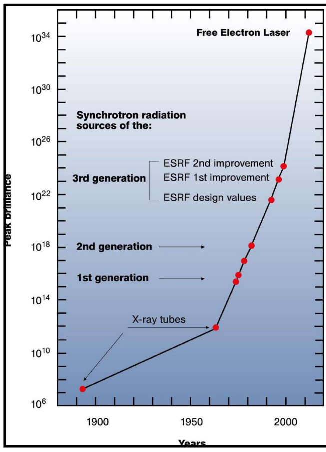
Single Particle:
1s edges
(DFT + core hole (+U))

2-particle:
(TDDFT, BSE)
+ L edges of $3d^0$

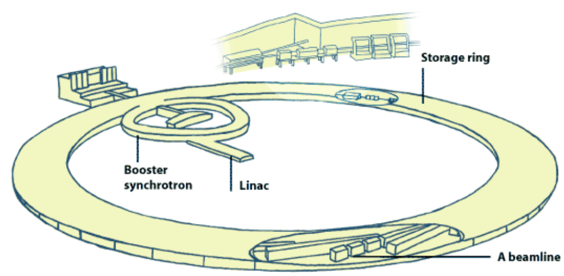
Many-particle:
2p, 3s, 3p edges
(CTM4XAS)

X-ray absorption and X-ray photoemission

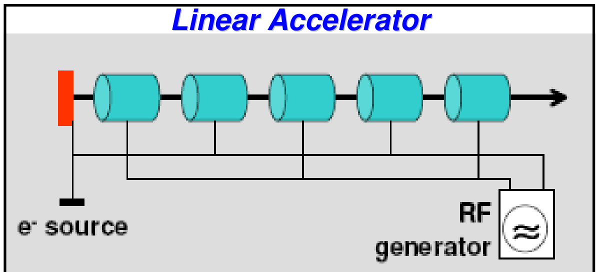




X-rays from synchrotrons



Linear Accelerator

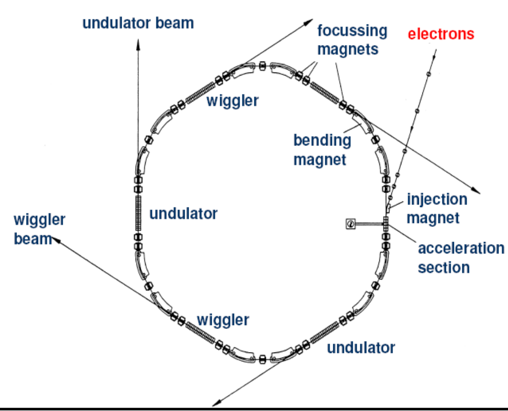


	1.5 V	~ 700 km/s
	12 V	~2000 km/s
20 000 V		~90 000 km/s
800 000 000 V		299 792,40 km/s
1 700 000 000 V		299 792,44 km/s

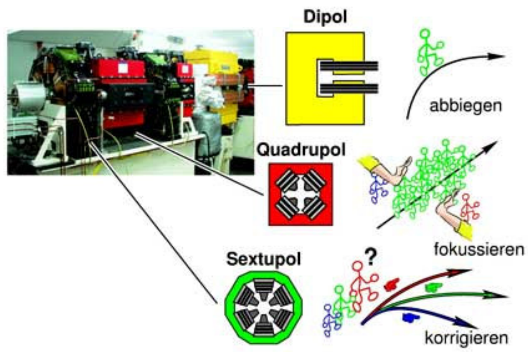
c=299 792,4581 km/s

1.7GeV synchrotron gives 0.9999999c

Storage Ring



Magnets in the storage ring



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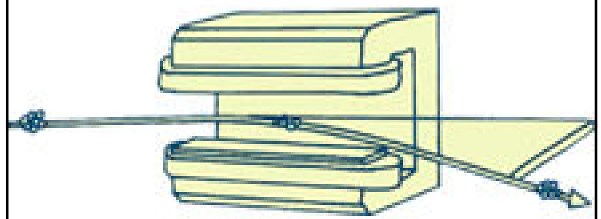
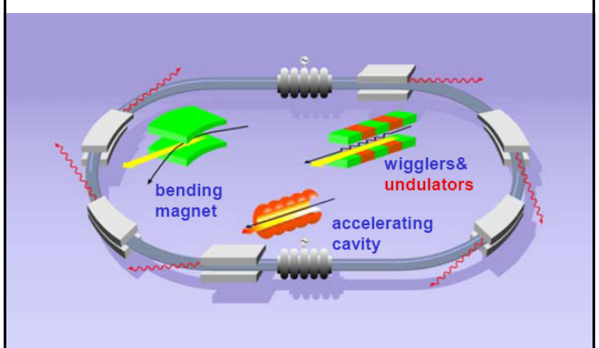
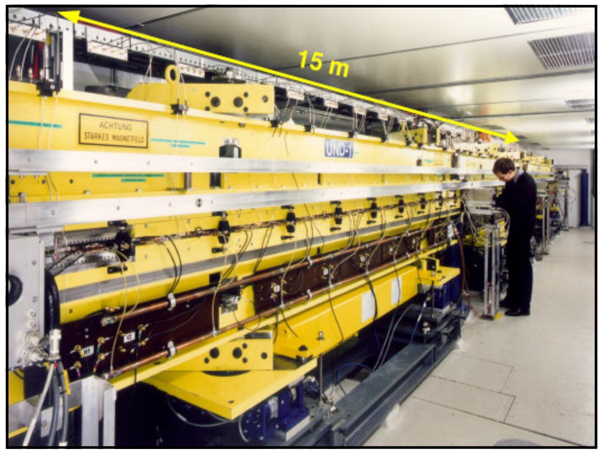


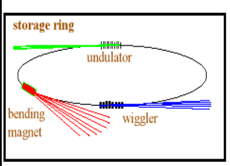
Magnetic Force

- F = q · v · B
- Perpendicular to Field and propagation direction



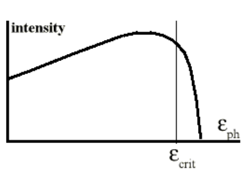


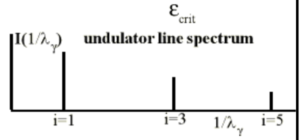
X-rays from synchrotrons

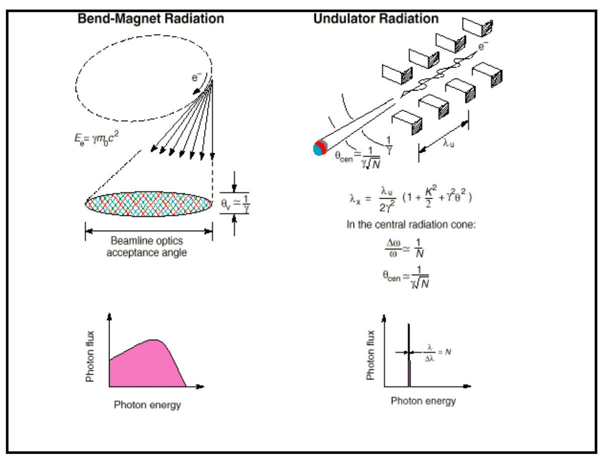


- Bending Magnets
- Insertion Devices:
  - Wiggler
  - Undulator

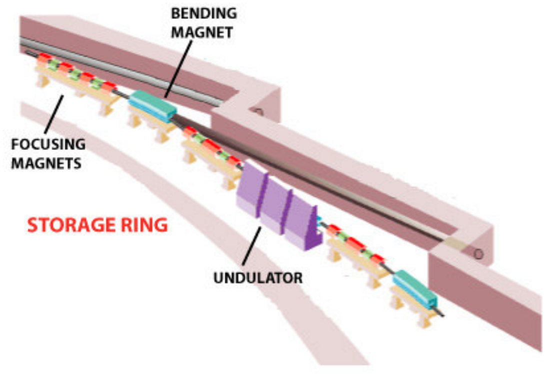
continuous spectrum for wiggler, bending magnet and wave length shifter:



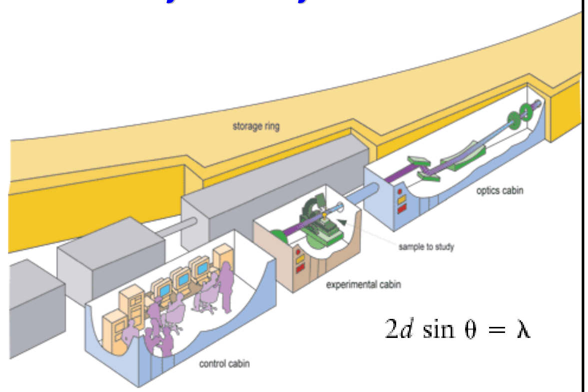




X-rays from synchrotrons

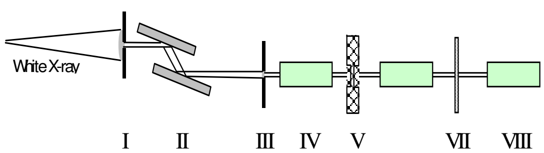


X-rays from synchrotrons



$$2d \sin \theta = \lambda$$

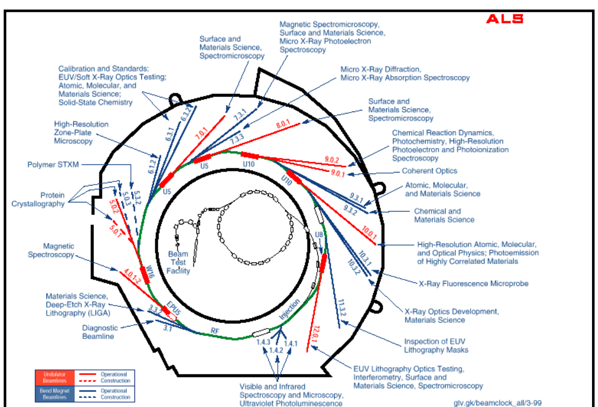
X-ray absorption beamline (transmission)



I Entrance slits	II Monochromator
III Exit slits	IV Ionisation chamber
V Sample	VI Ionisation chamber
VII Reference material	VIII Ionisation chamber

Beamline 18ID at the APS

Mirrors | Monochromator



http://www-als.lbl.gov/als/

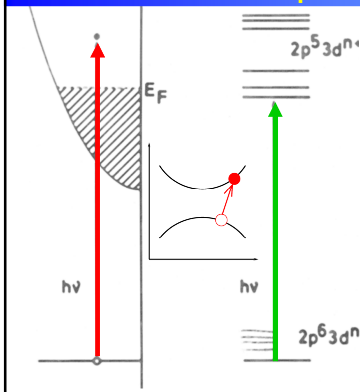
Why a synchrotron?

- **Energy**: tunable source
- **Intensity**: 10^6-10^{12} higher than x-ray tube
- **Space**: spot-size 1x1 mm (unfocussed)

  down to 20x20 nm (focussed)
- **Time**: pulse 50 ps, sliced down to 50 fs.
- **Polarization:**

  Angular dependence & Circular dichroism:
- NOT coherent (no laser)

XAS: multiplet effects



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Many-particle:
2p, 3s, 3p edges
(CTM4XAS)

Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

ATOMIC PHYSICS

⇓

GROUP THEORY

⇓

MODEL HAMILTONIANS

The CTM4XAS program