X-ray Absorption Spectroscopy

- Introduction to XAS
- XAS detection techniques
- XAS spectral shape
- 1s XAS (pre-edges)
- Overview of programs
- Overview of spectroscopies

X-ray Absorption Spectroscopy

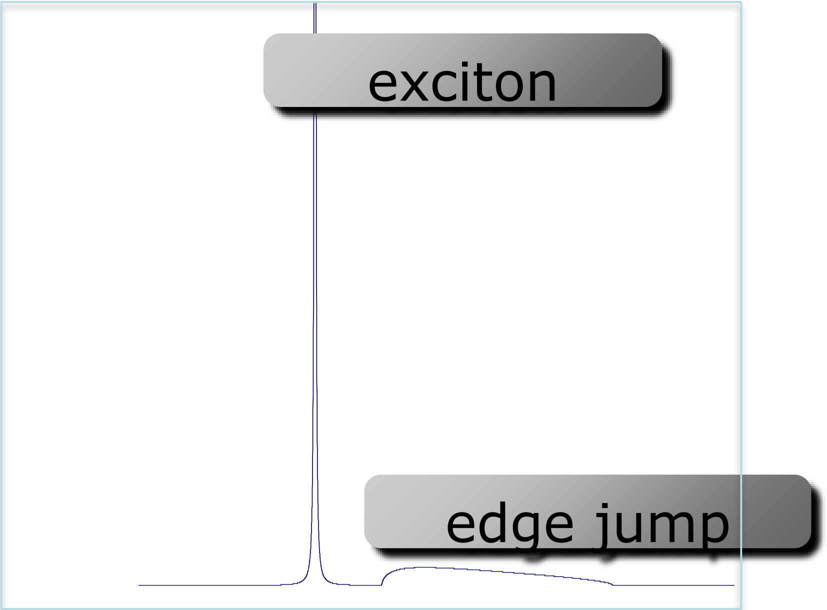
- Element specific
- Sensitive to low concentrations
- Applicable under extreme conditions

- SPACE: Combination with x-ray microscopy
- TIME: femtosecond XAS
- RESONANCE: RIXS, RPES, RAES, R scat.

XAS: spectral shape

Excitations of core electrons to empty states

The XAS spectra are given by the Fermi Golden Rule



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

X-ray Absorption Spectroscopy

The photon moves towards the atom

X-ray Absorption Spectroscopy

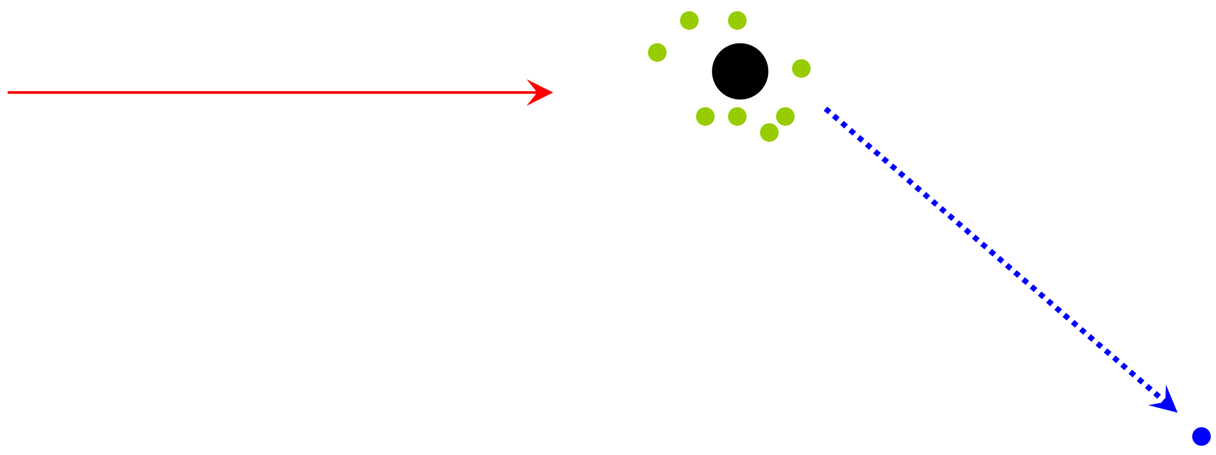
The photon meets an electron and is annihilated

X-ray Absorption Spectroscopy

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

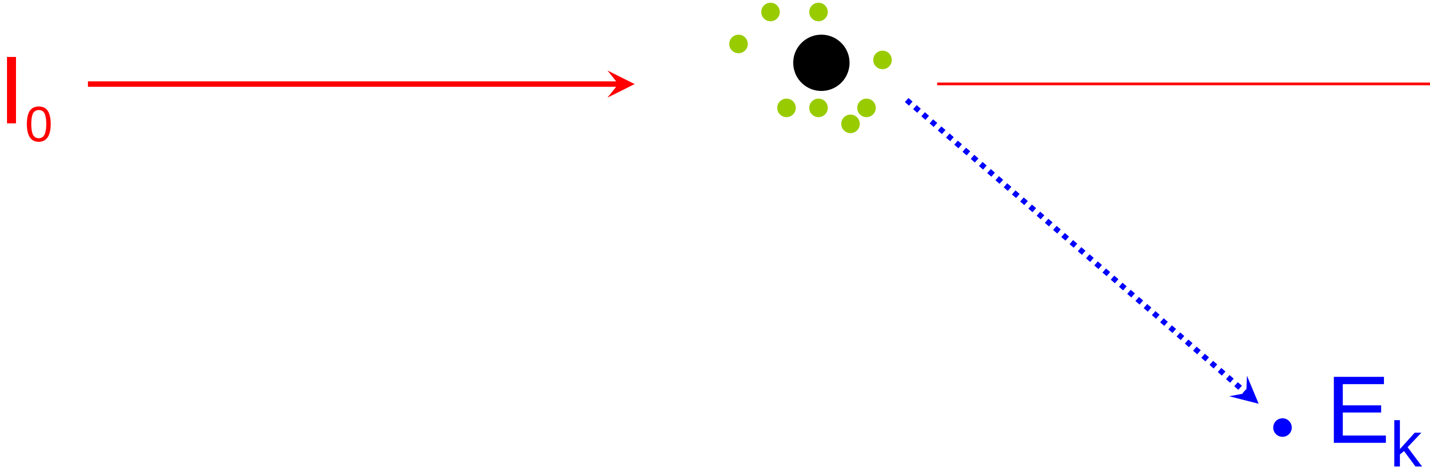
X-ray Absorption Spectroscopy

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

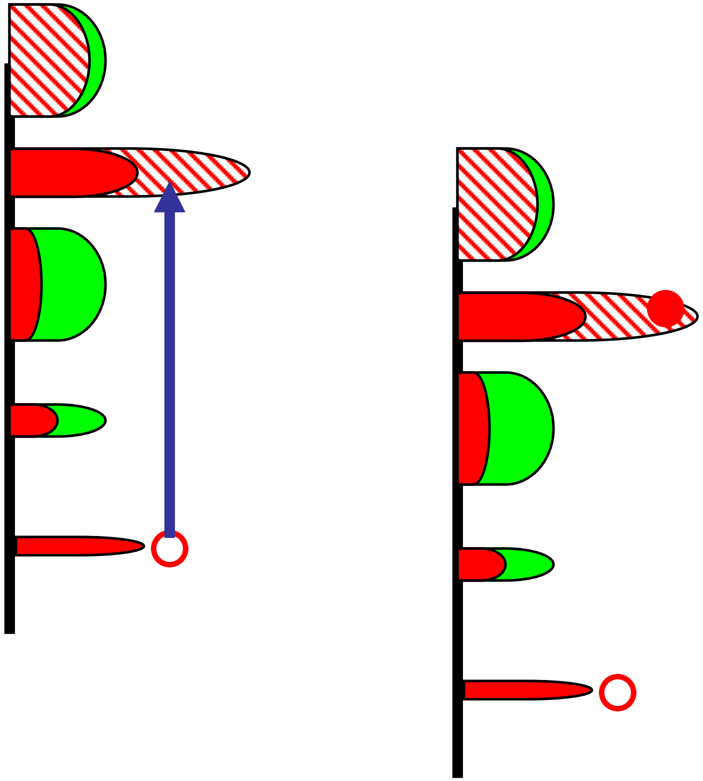


X-ray Absorption Spectroscopy

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

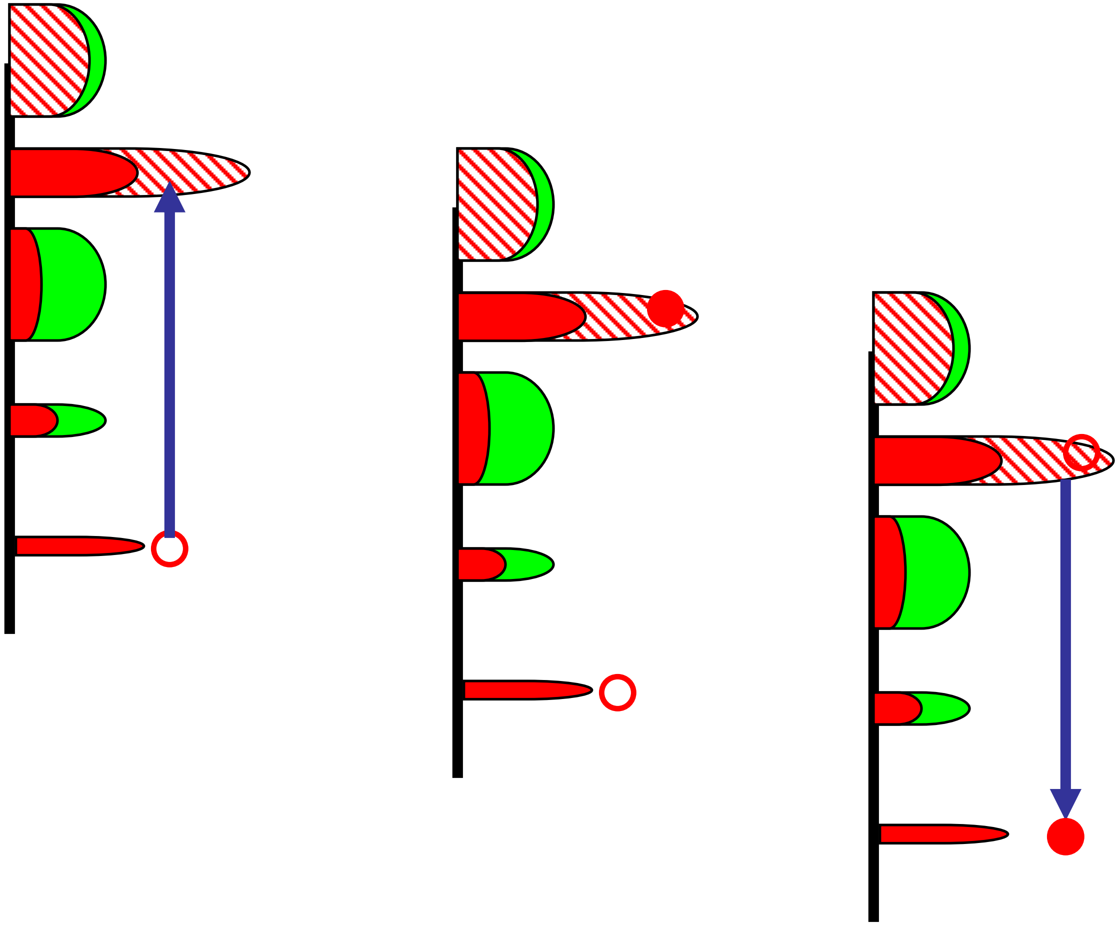


X-ray Absorption Spectroscopy



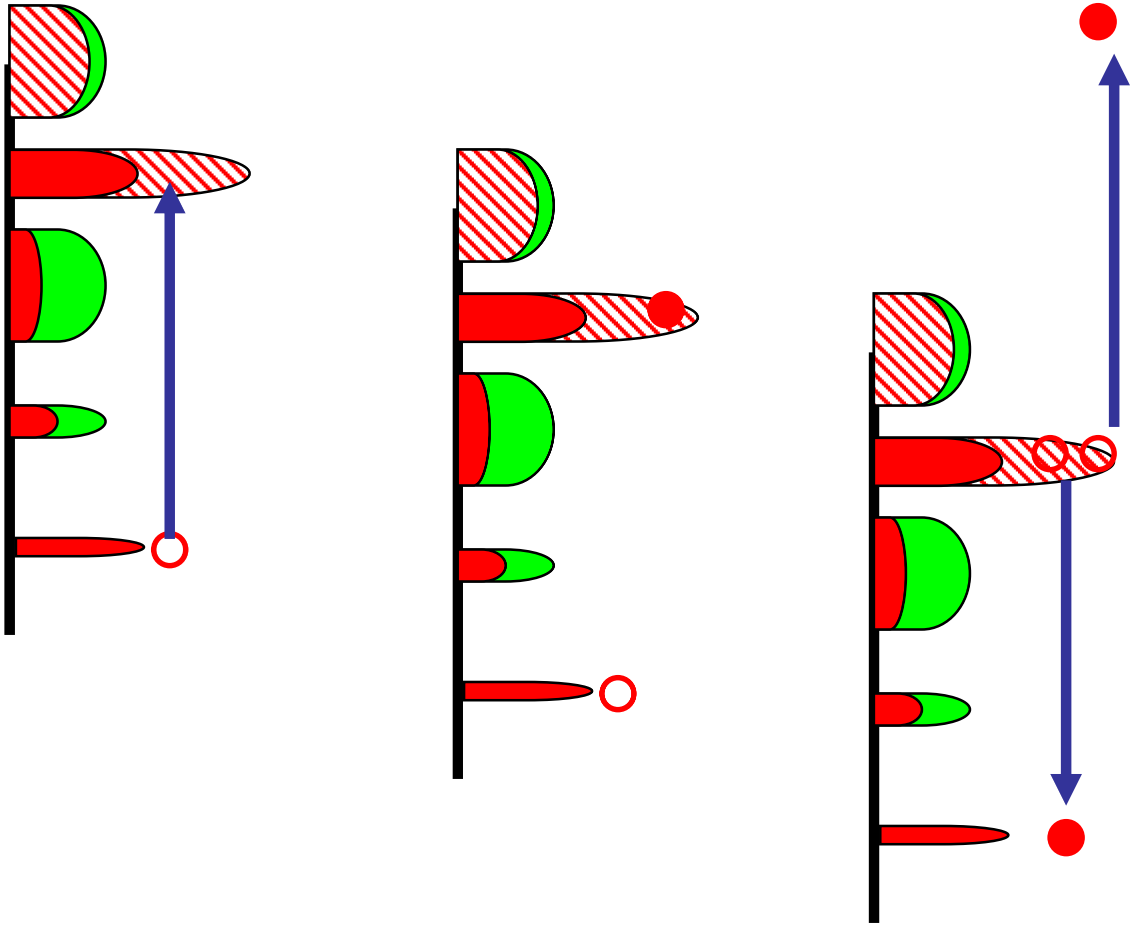
- Excitation of 2p to 3d state
- Lifetime of excitation is ~20 fs

X-ray Absorption Spectroscopy



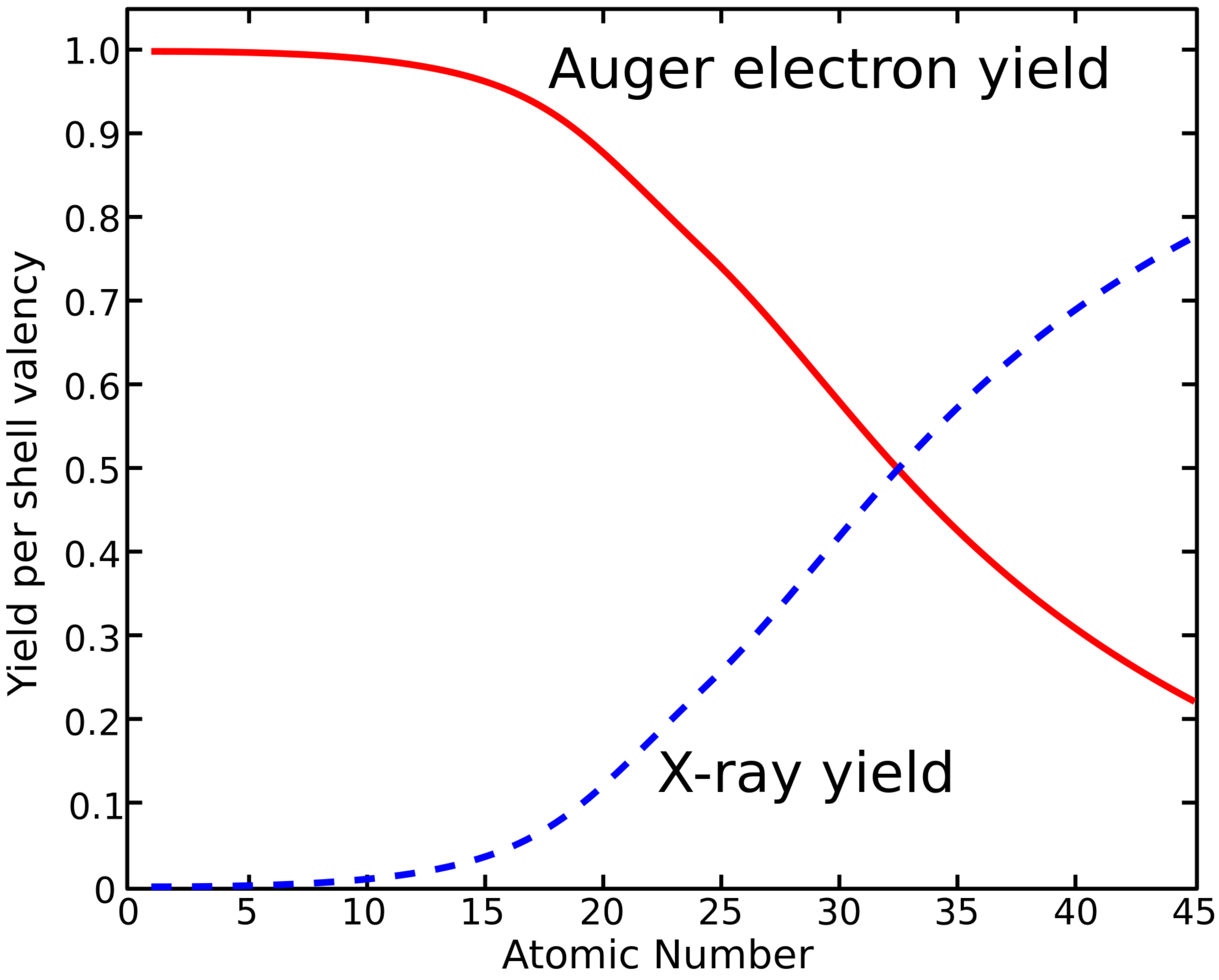
- Decay of 3d or 3s electron to 2p core state
- X-ray emission

X-ray Absorption Spectroscopy



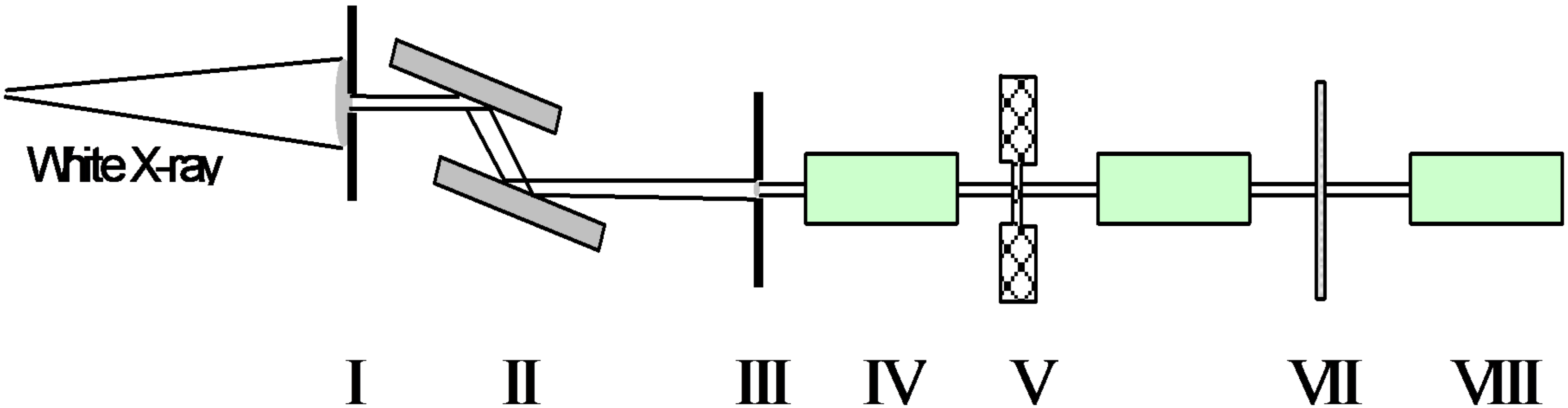
- Decay of 3d/3p/3s electron to 2p core state
- Energy used to excite a 3d/3p/3s electron
- Auger electron spectroscopy

X-ray Absorption Spectroscopy



XAS: detection techniques

XAS: detection techniques



I Entrance slits

II Monochromator

III Exit slits

IV Ionisation chamber

V Sample

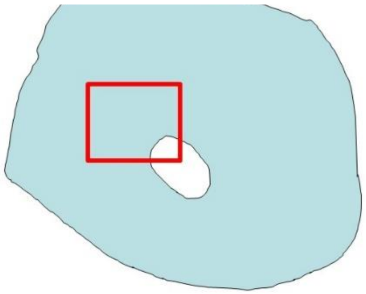
VI Ionisation chamber

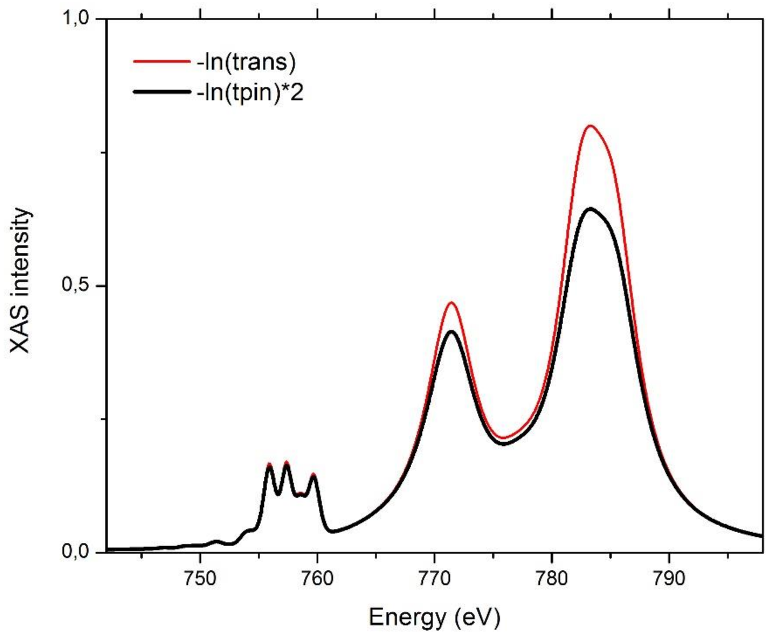
VII Reference material

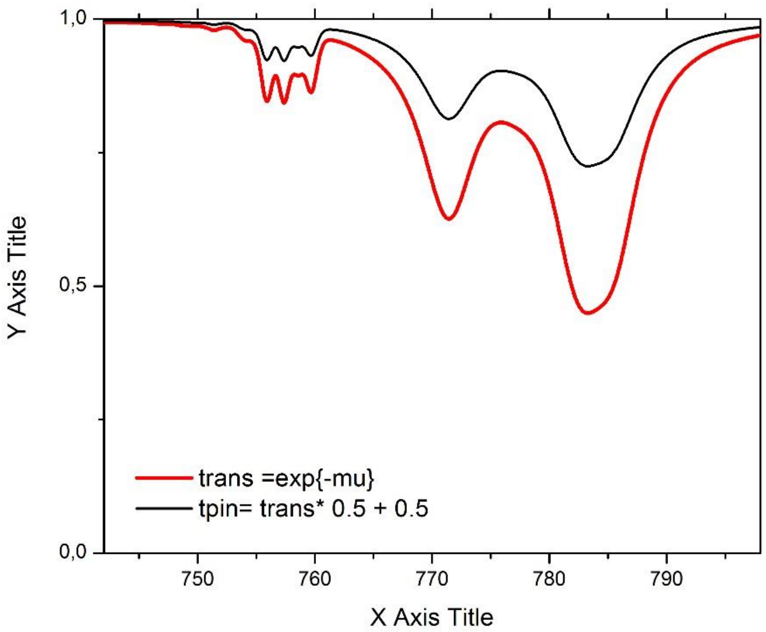
VIII Ionisation chamber

XAS: detection techniques

Pinhole effect in transmission

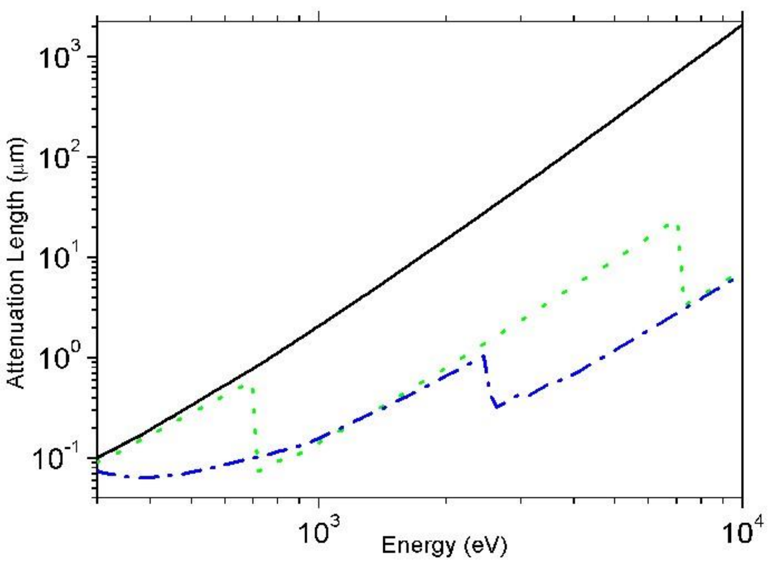


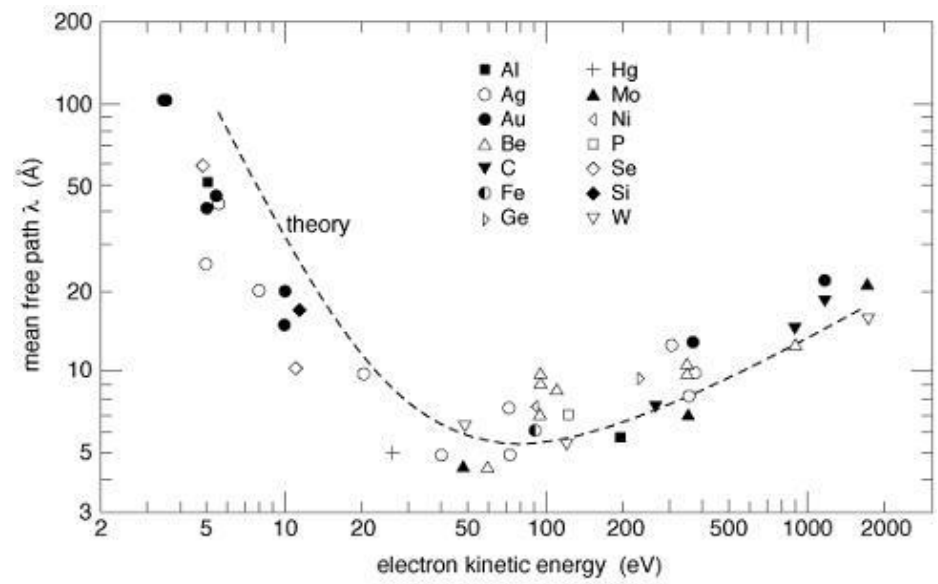




X-ray penetration lengths &

electron escape depths



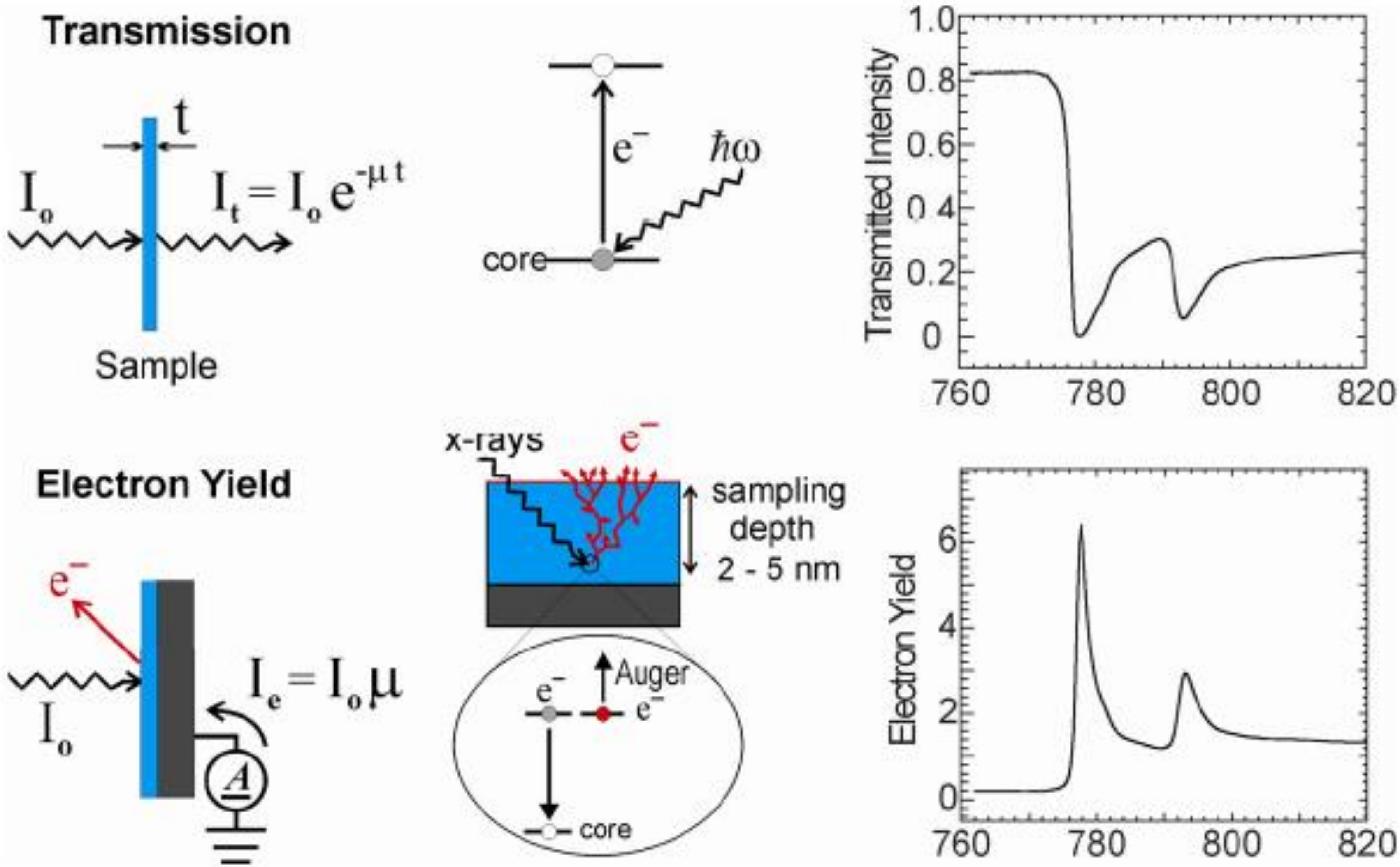


1000 nm

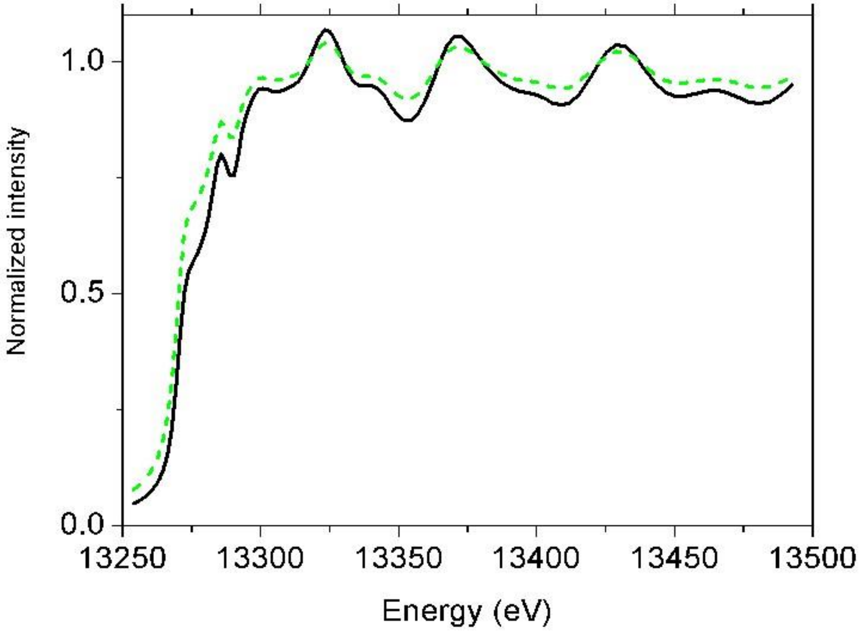
(CXRO, but 20 nm for L edges)

1 nm

XAS: detection techniques



XAS: detection techniques



$$I_{FY} \propto \frac{\mu(E)}{\mu(E) + \mu_B}$$

XAS: detection techniques

Transmission

(pinhole, saturation > thin samples)

Electron Yield

(surface sensitive)

Fluorescence Yield

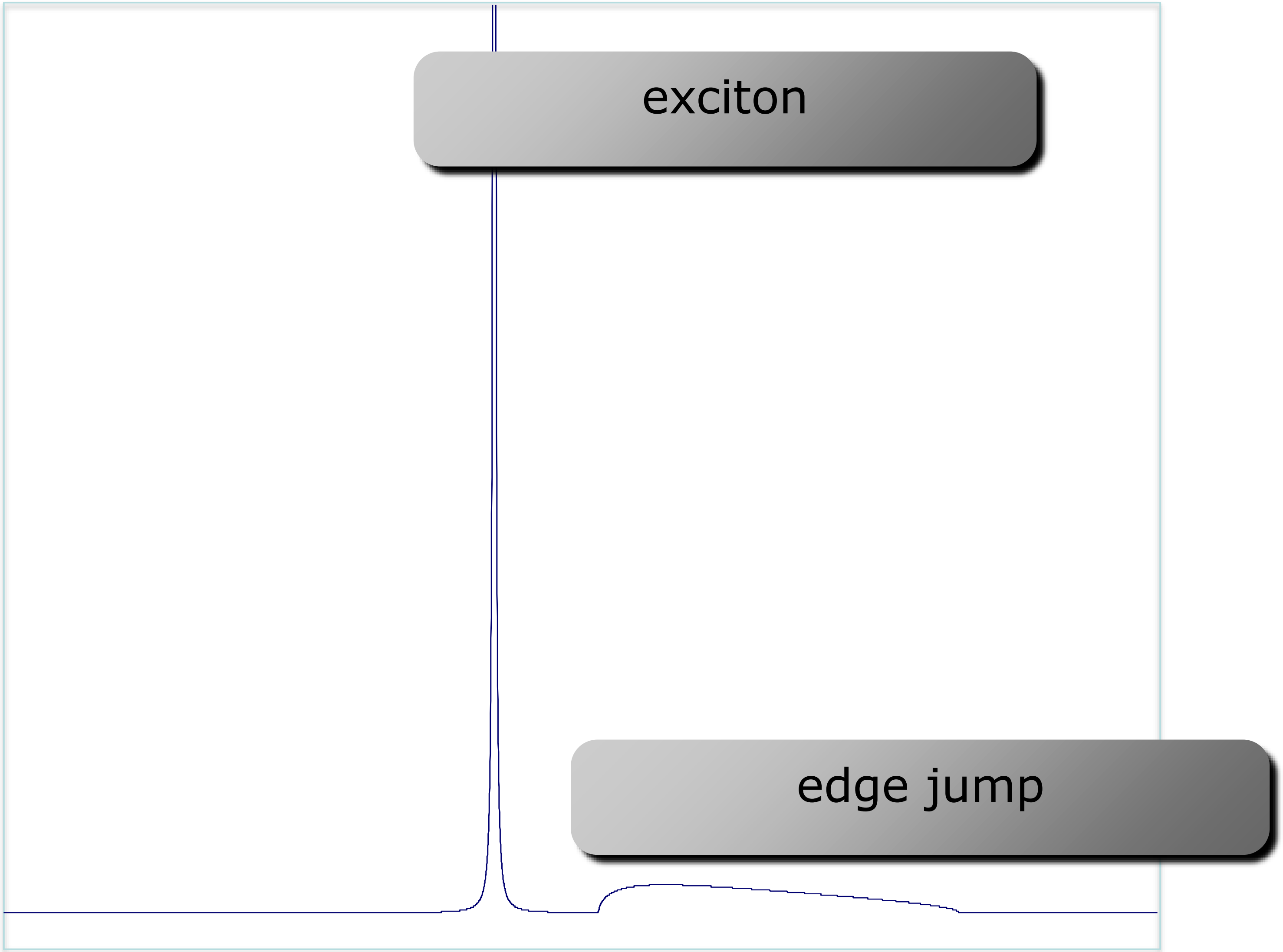
(saturation > dilute samples;

L edges are intrinsically distorted)

XAS: spectral shape

- Interpretation of spectral shapes

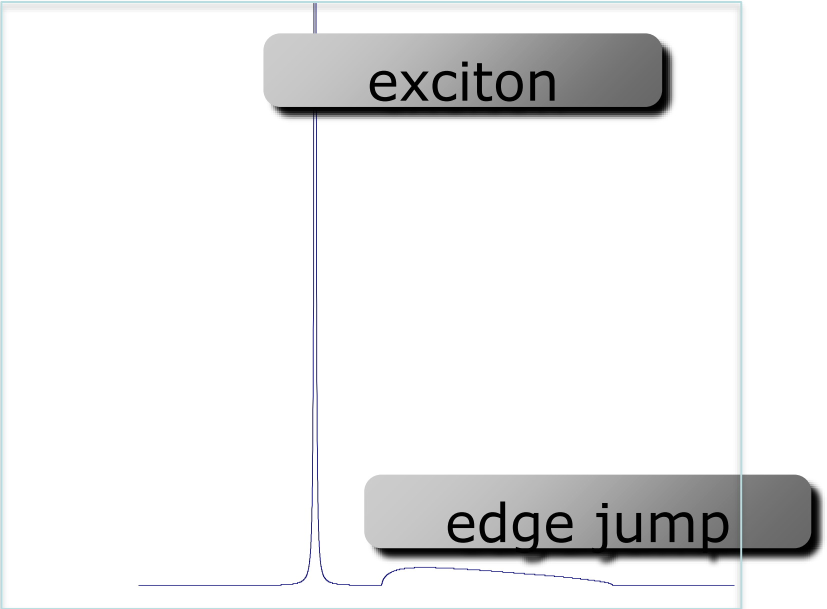
Metal K edges



XAS: spectral shape

Excitations of core electrons to empty states

The XAS spectra are given by the Fermi Golden Rule



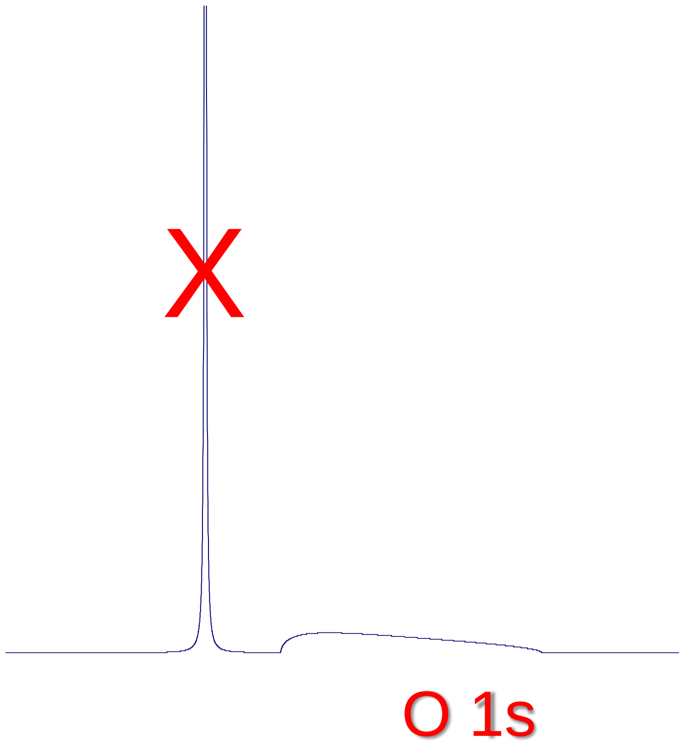
$$I_{XAS} \sim \sum_f \left| \left\langle \Phi_f \right| \hat{e} \cdot r \left| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

XAS: spectral shape (O 1s)

Fermi Golden Rule

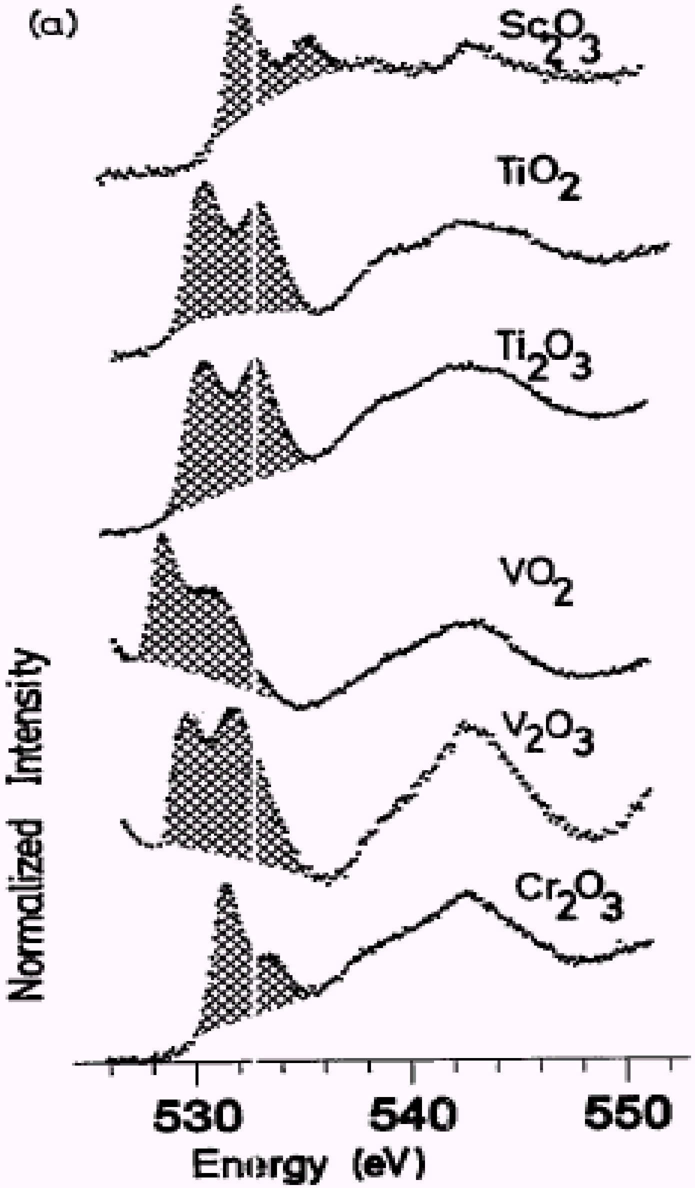
↓

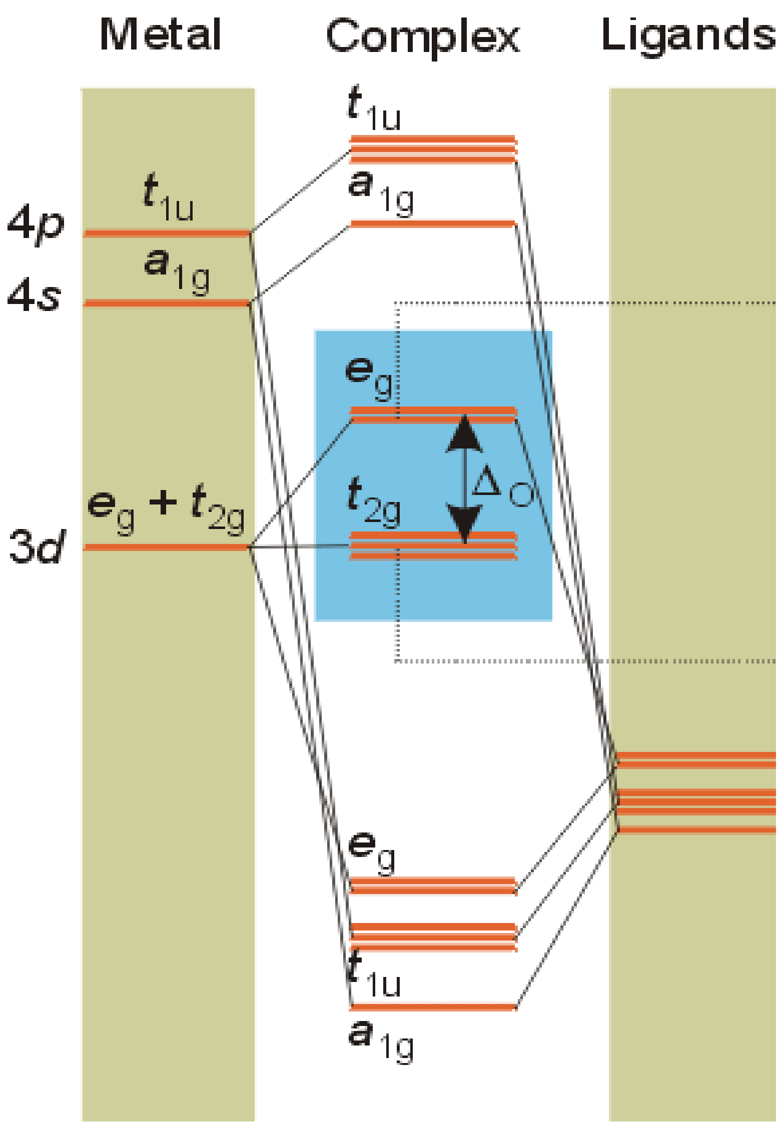
Excitations to
empty states as calculated by
DFT



$$I_{XAS} \sim M^2 \rho \approx \rho_{site,symmetry}$$

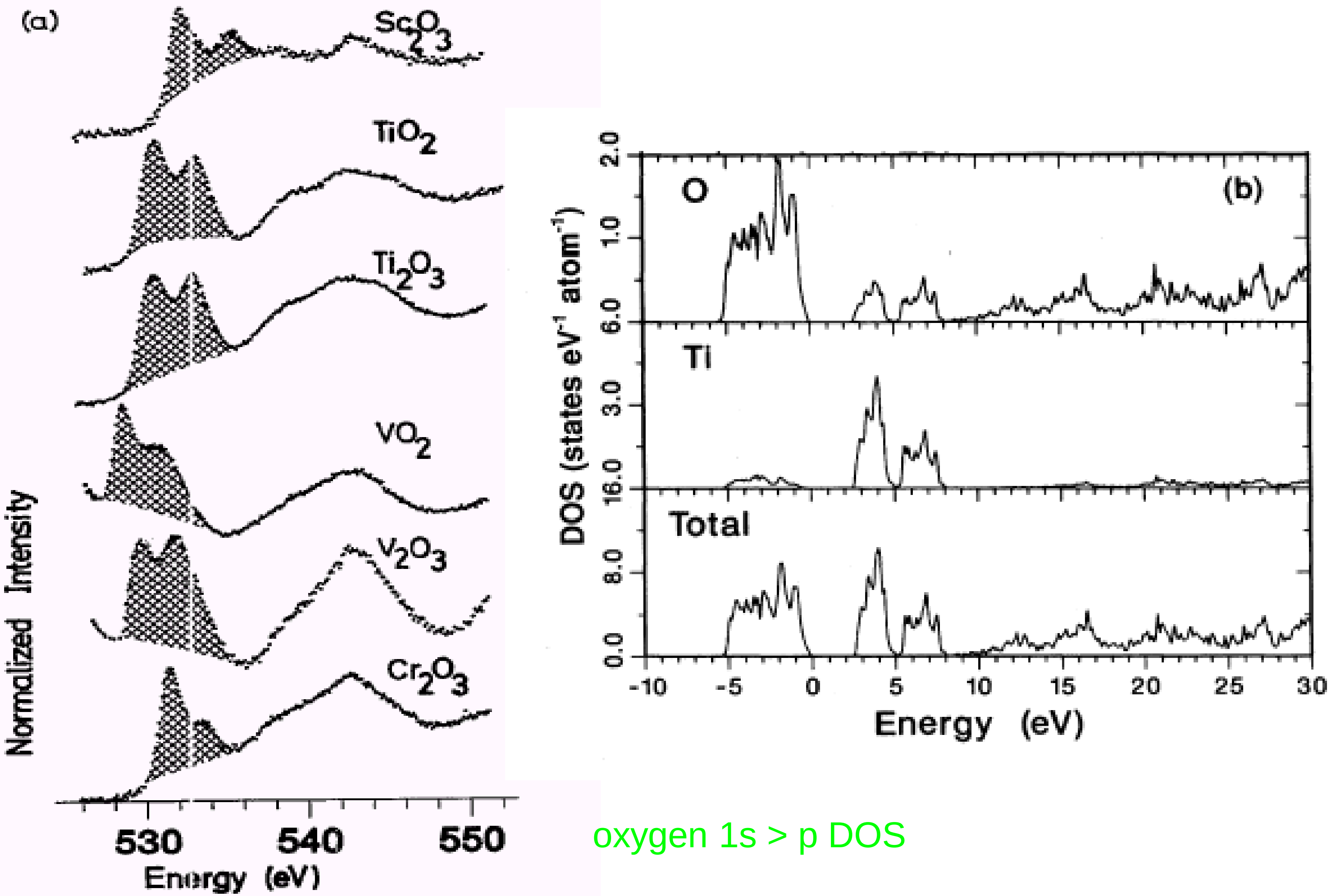
XAS: spectral shape (O 1s)





Phys. Rev. B.40, 5715 (1989)

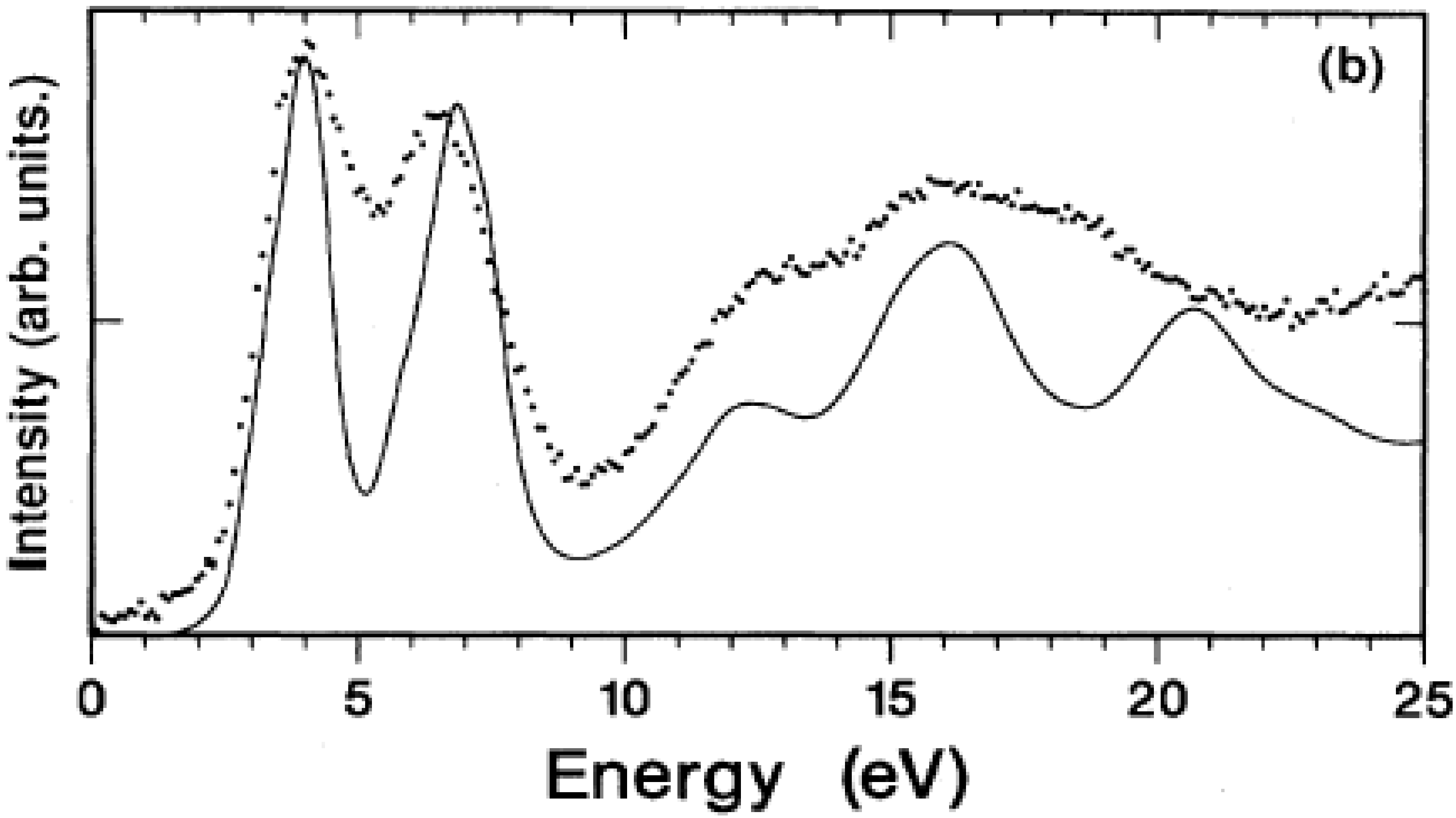
XAS: spectral shape (O 1s)



oxygen 1s > p DOS

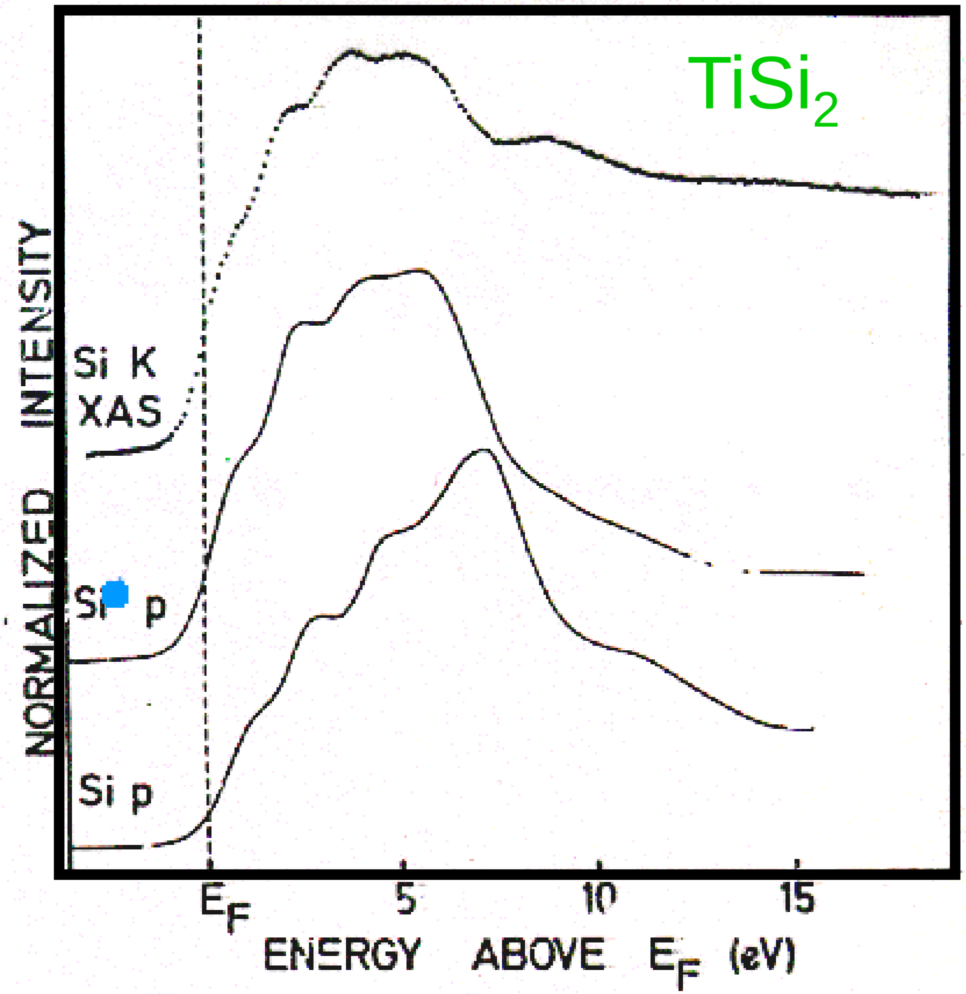
Phys. Rev. B.40, 5715 (1989); 48, 2074 (1993)

XAS: spectral shape (O 1s)



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

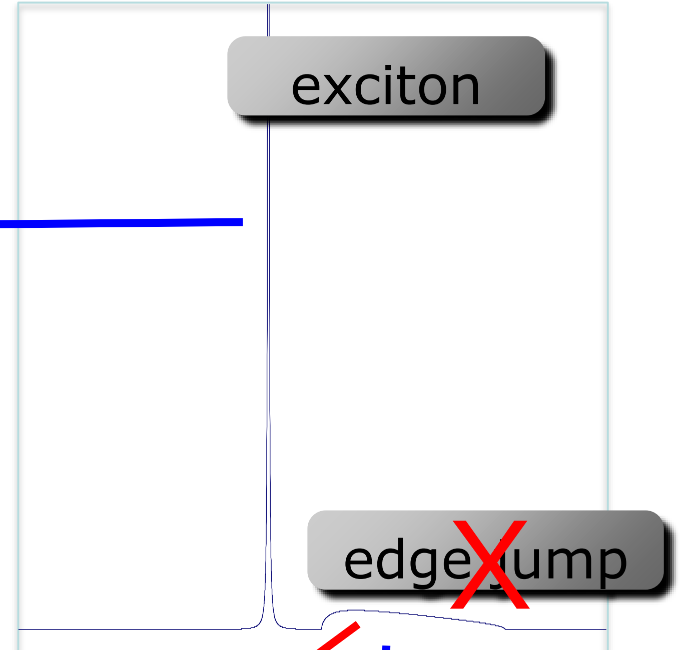
XAS: spectral shape



- **Final State Rule:** Spectral shape of XAS looks like final state DOS

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

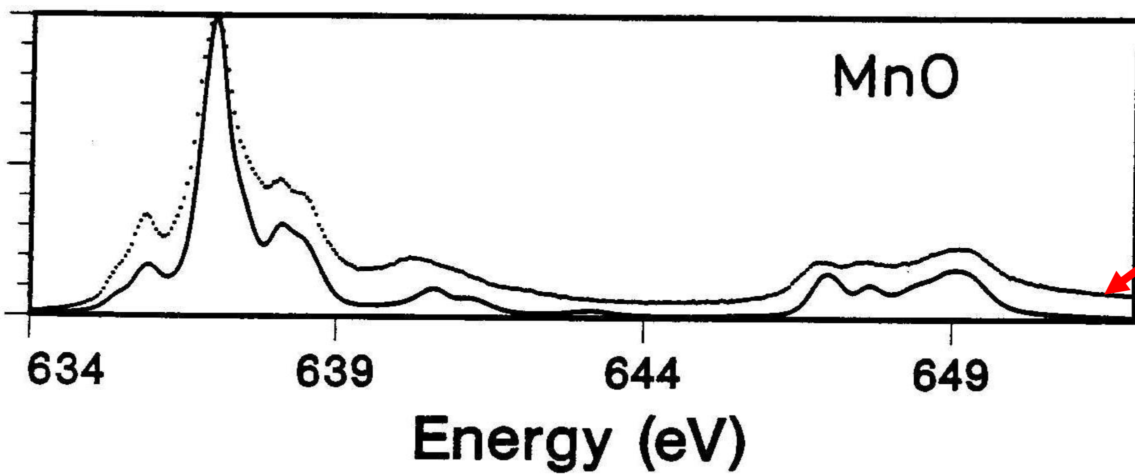
2p XAS of transition metal ions



2p > 3d

($3d^5 > 2p^5 3d^6$, self screened)

2p > s,d DOS

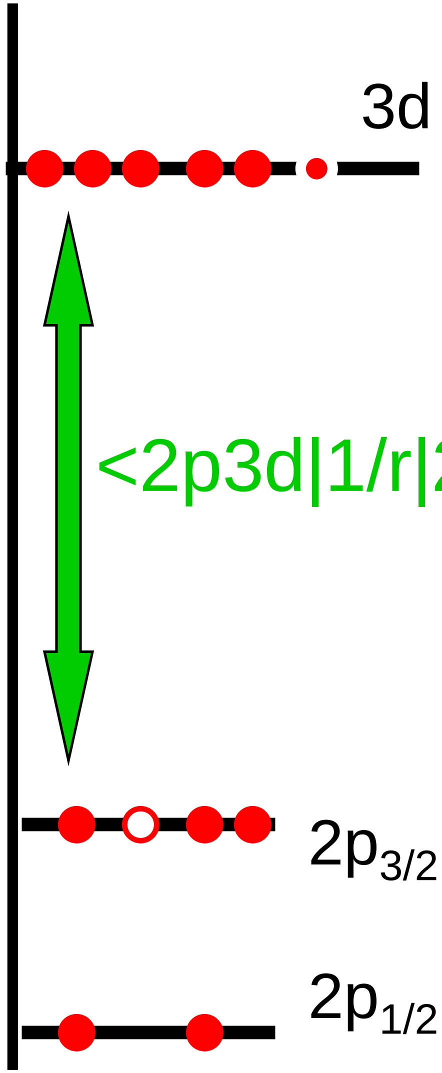


[Phys. Rev. B. 42, 5459 (1990)]

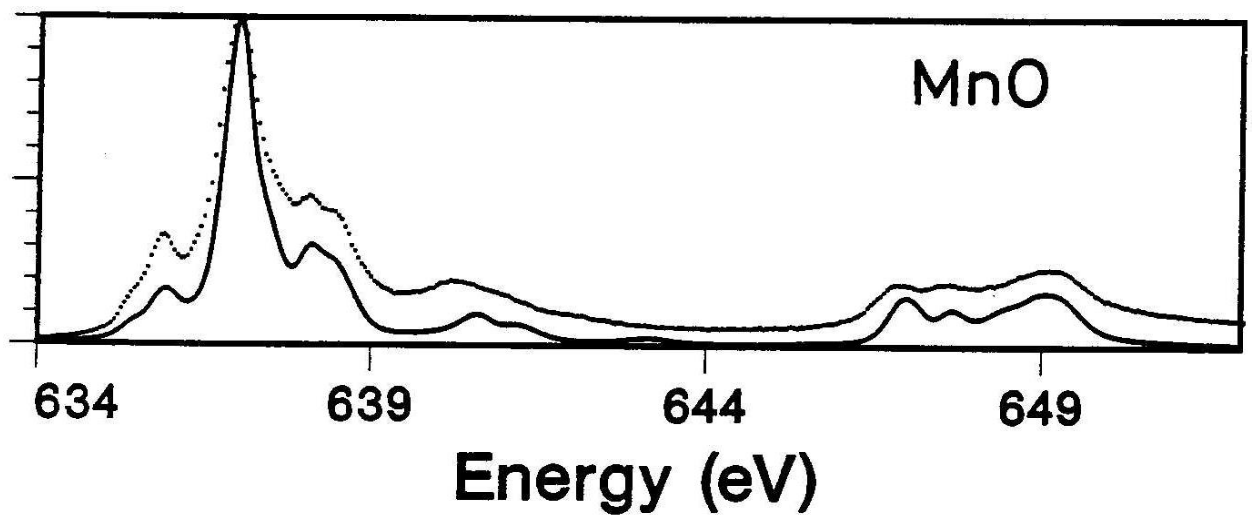
XAS: spectral shape

Overlap of core and valence wave functions

→ Single Particle model breaks down

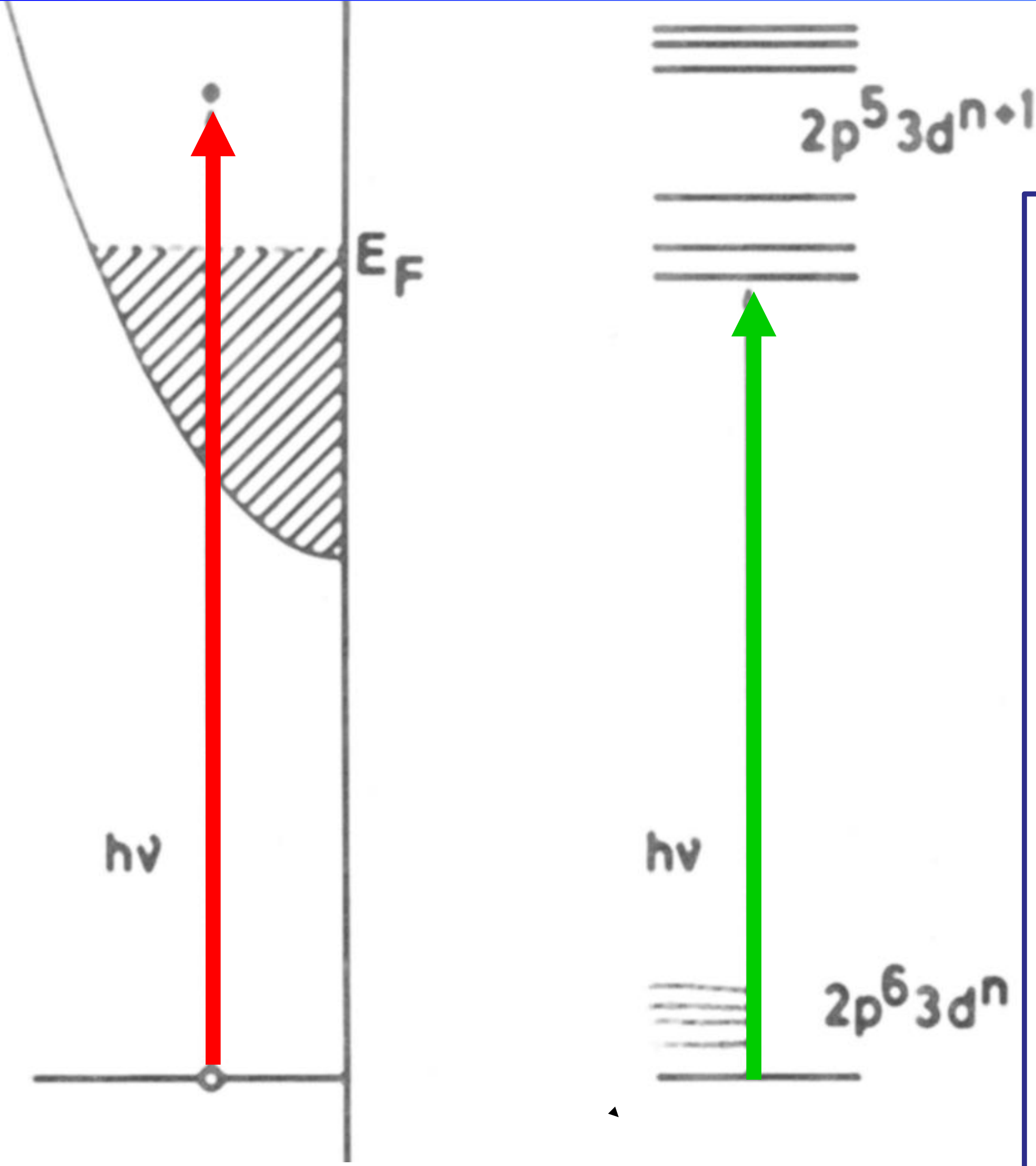


<2p3d|1/r|2p3d>



Phys. Rev. B. 42, 5459 (1990)

XAS: spectral shape



<u>1-particle:</u>

1s edges

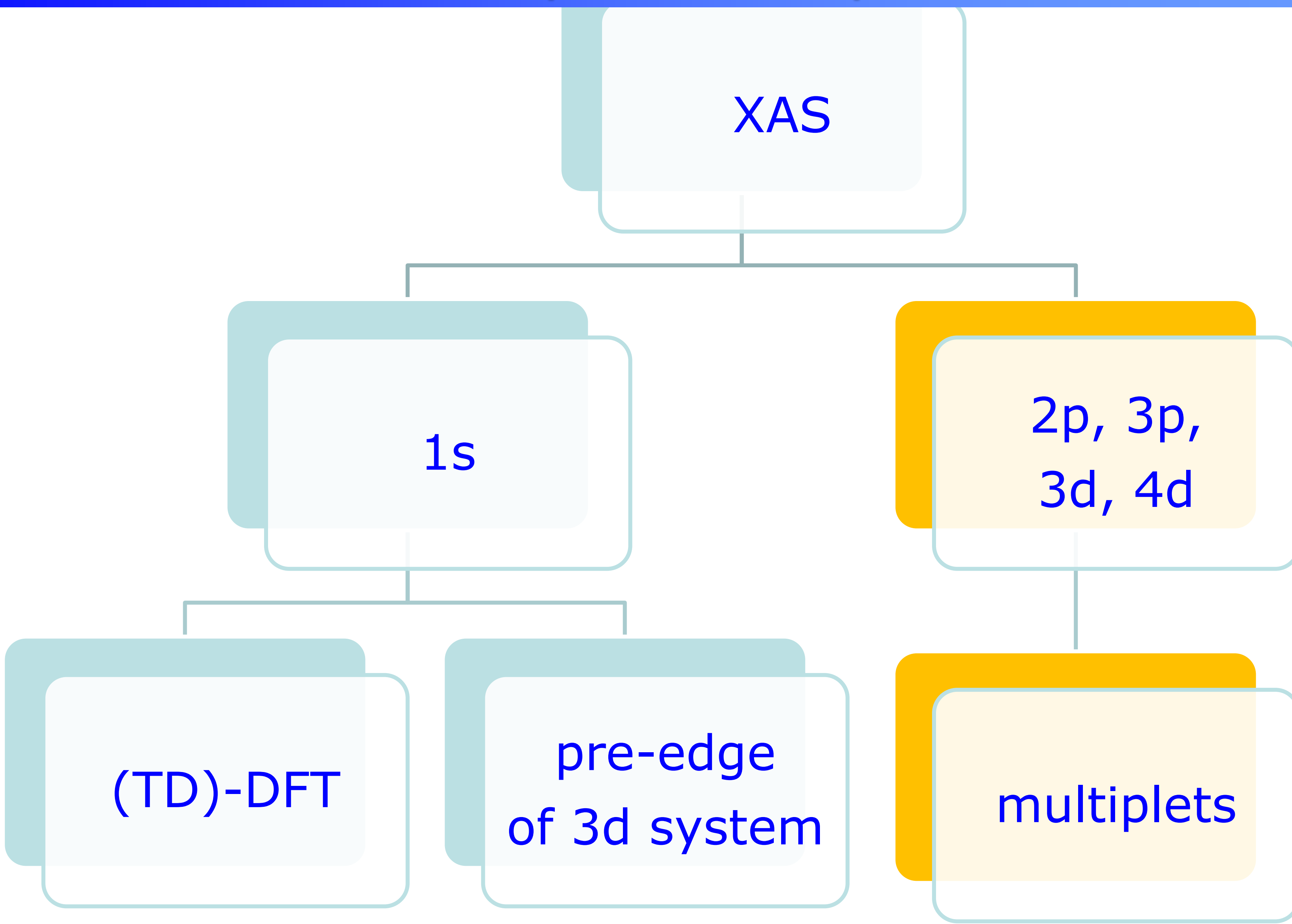
(DFT + core hole +U)

<u>many-particle:</u>

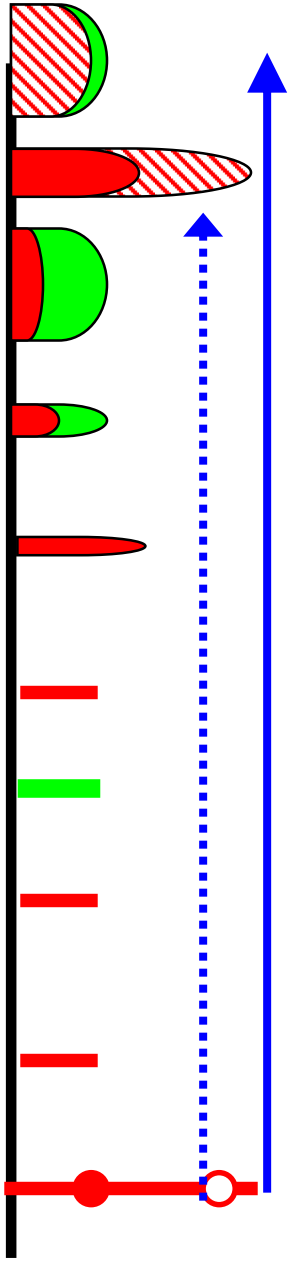
open shell systems

(CTM4XAS)

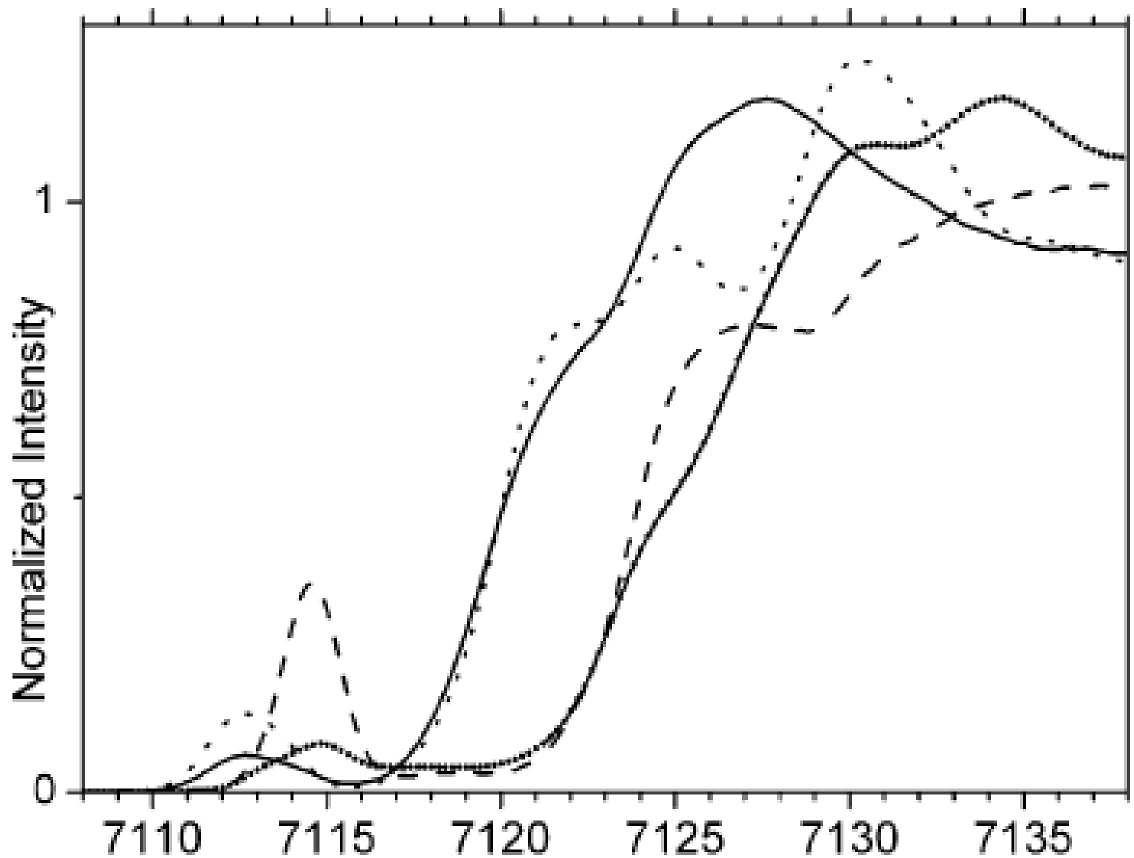
XAS: spectral shape



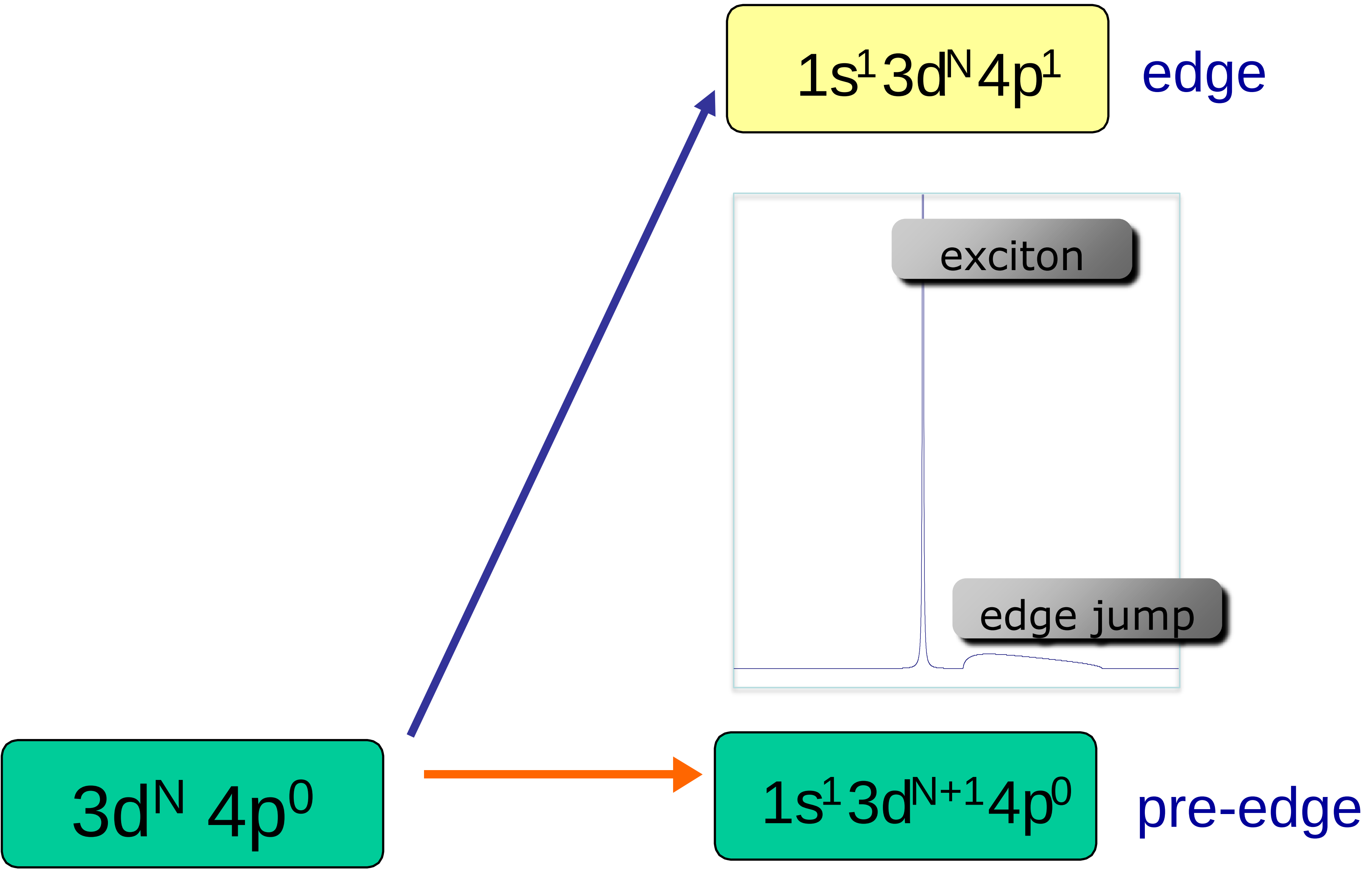
Pre-edges structures in 1s XAS



Fe 4p	-
Fe 3d	0
O 2p	5
O 2s	20
Fe 3p	50
Fe 3s	85
O 1s	530
Fe 2p	700
Fe 2s	800
Fe 1s	7115

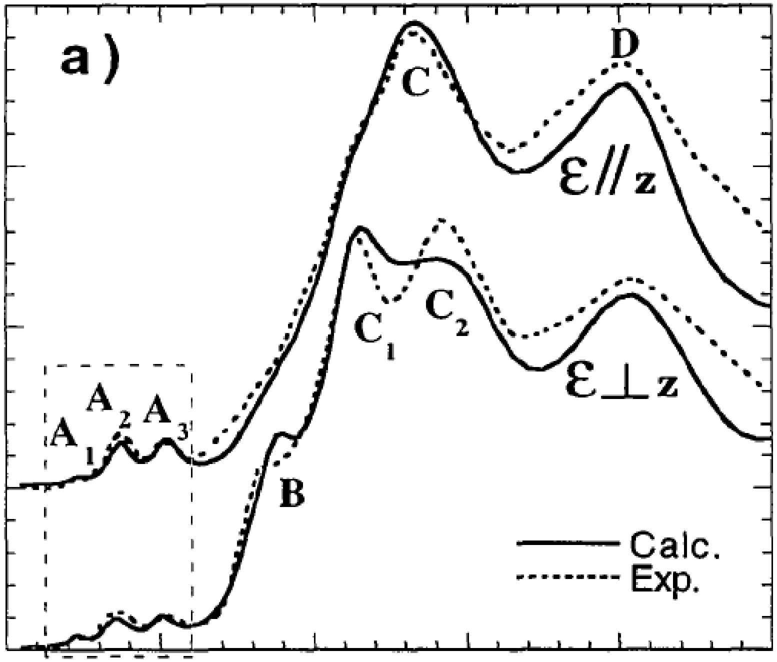


Pre-edges structures in 1s XAS



Pre-edges structures in 1s XAS

$1s^1 3d^N 4p^1$ edge

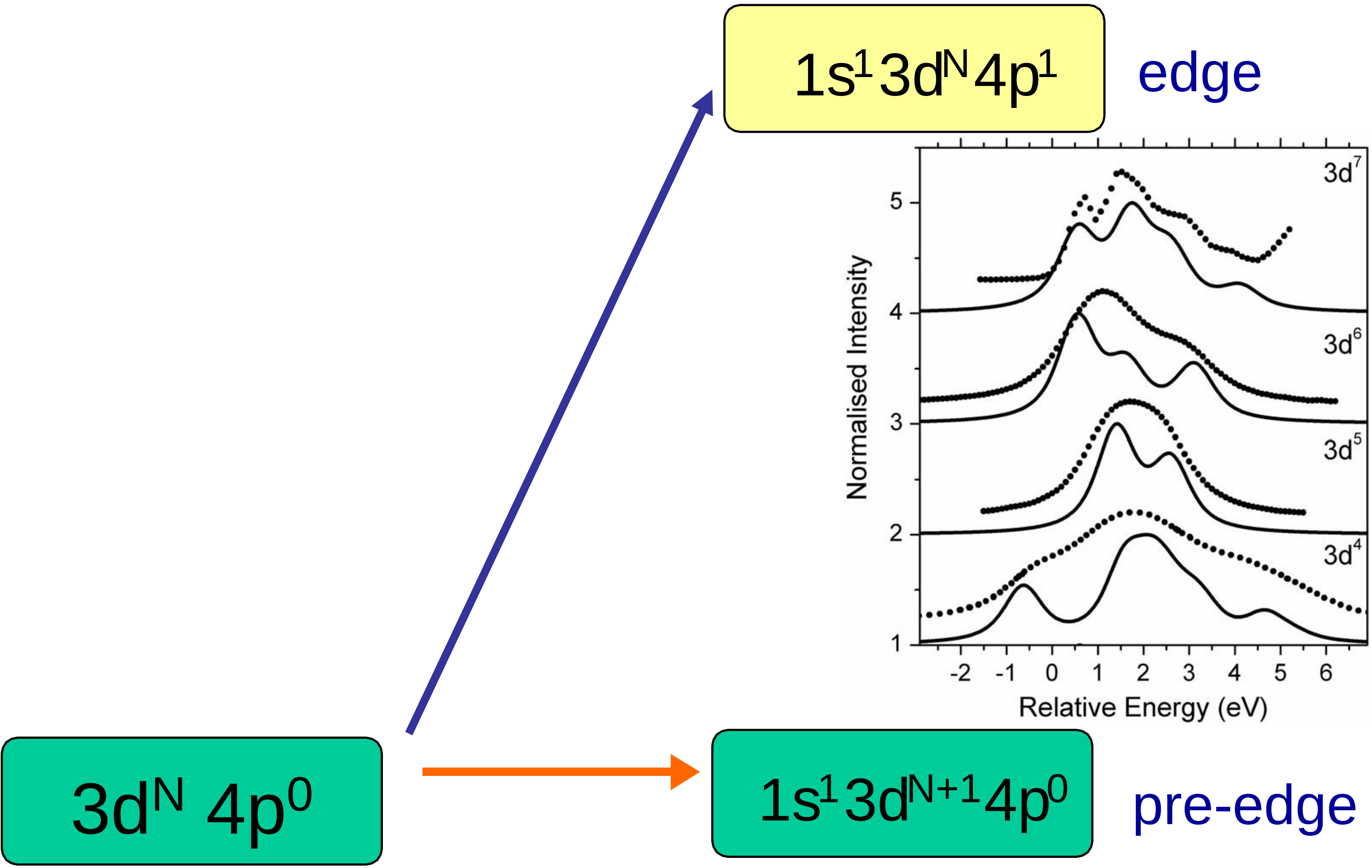


$3d^N\ 4p^0$

$1s^1 3d^{N+1} 4p^0$ pre-edge

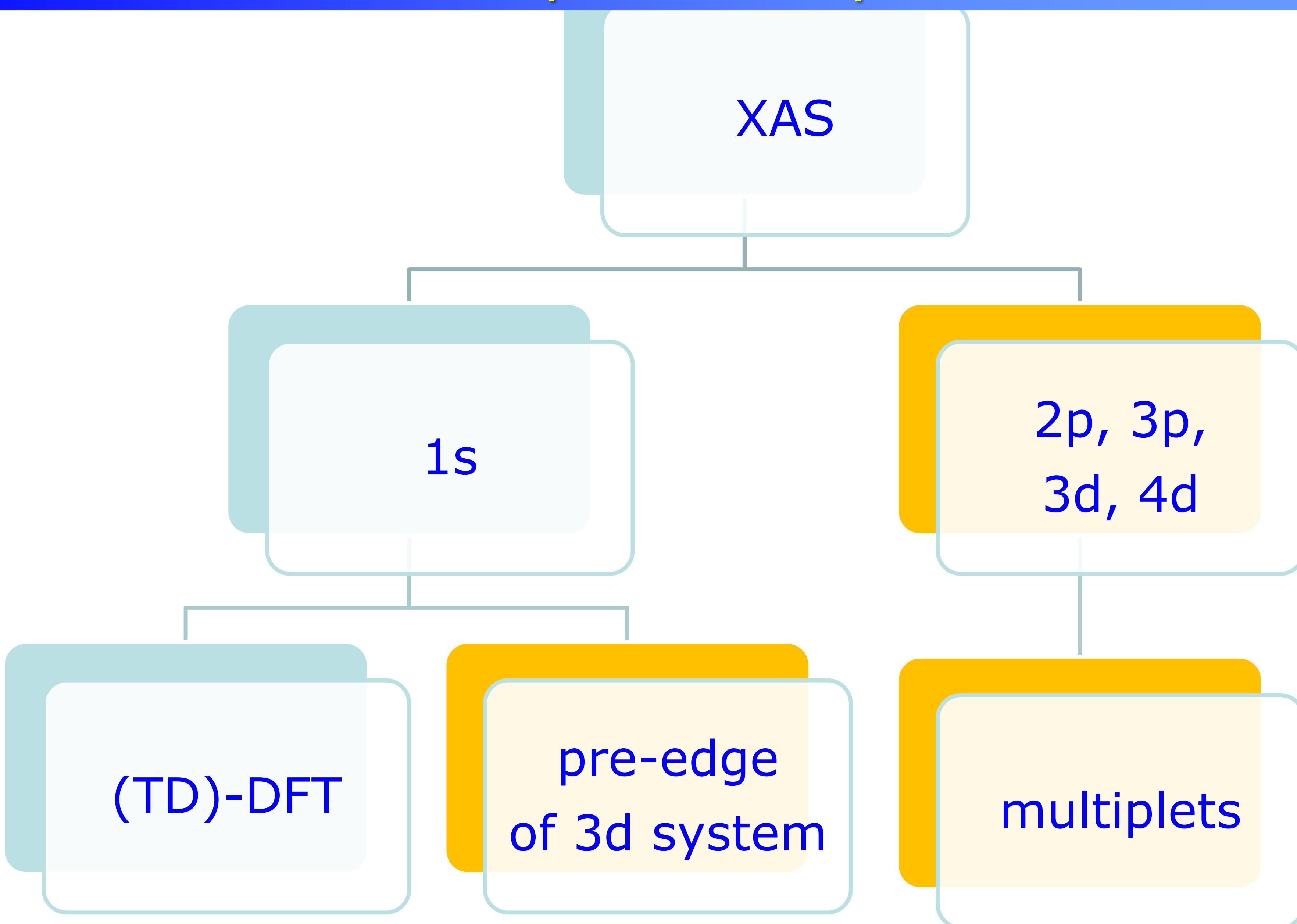
[Cabaret et al. j. Synchrot. Rad. 6, 258 (1999)]

Pre-edges structures in 1s XAS



[J. Phys. Cond. Matt. 21, 104207 (2009)]

XAS: spectral shape



Multiplet calculations

Calculated for an atom/ion

- Valence and core hole **spin-orbit coupling**
- Core hole – valence hole **'multiplet' interaction**.

Comparison with experiment

- Core hole **potential and lifetime**
- Local symmetry (**crystal field)**
- Spin-spin interactions (**molecular field**)
- Core hole screening effects (**charge transfer**)

Neglected

- The coupling of core hole excitations to **vibrations**

(available) 2p XAS semi-empirical codes

- Thole .cowan-racah-bander
- Haverkort .quanty

- Tanaka
- Van Veenendaal

(available) 2p XAS Interfaces

➢ Thole	> CTM4XAS, missing, ttmult(s)
➢ Tanaka	
➢ Haverkort	> **Crispy**, CTM4XAS6, Quanty4RIXS
➢ Van Veenendaal	> Xclaim

2p XAS first-principle codes

- Band structure multiplet (Haverkort, Green, Hariki)
- Cluster DFT multiplet (Ikeno, Ramanantoanina, Delley)

- Restricted Active Space CI (Odelius, Kuhn)
- Restricted Open-shell CI (Neese)
- Time-Dependent DFT (Joly)
- Bethe-Salpeter (Rehr, Shirley)
- Multi-channel Multiple-scattering (Kruger)

Quanty first principle multiplet calculations

Calculated for a solid

- The core hole **spin-orbit coupling**
- The core hole – valence hole **‘multiplet’ interaction**.
- The core hole induced **screening** effects [except U]
- The core hole **lifetime**

Comparison with experiment

- The core hole **potential**

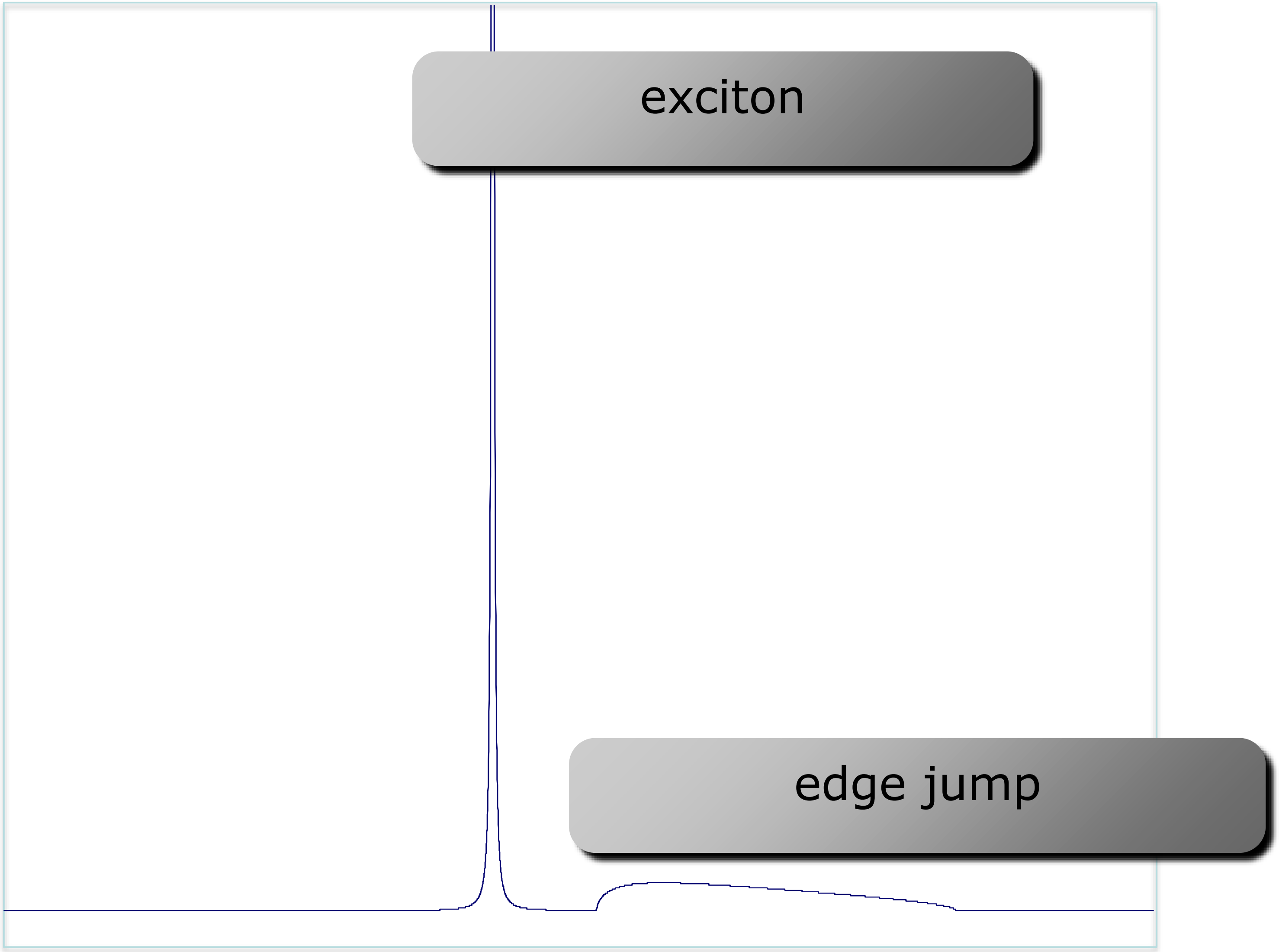
Neglected

- The coupling of core hole excitations to **vibrations**

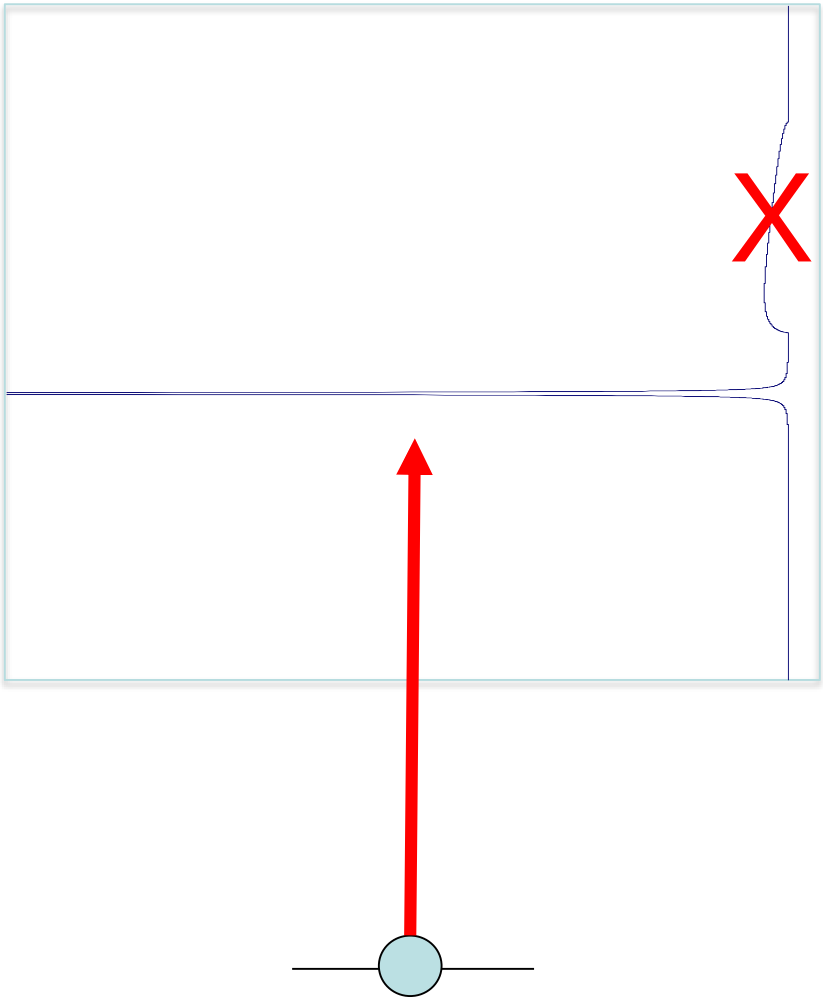
Overview

- XAS
- MCD
- XPS
- RIXS
- Ground state

Overview



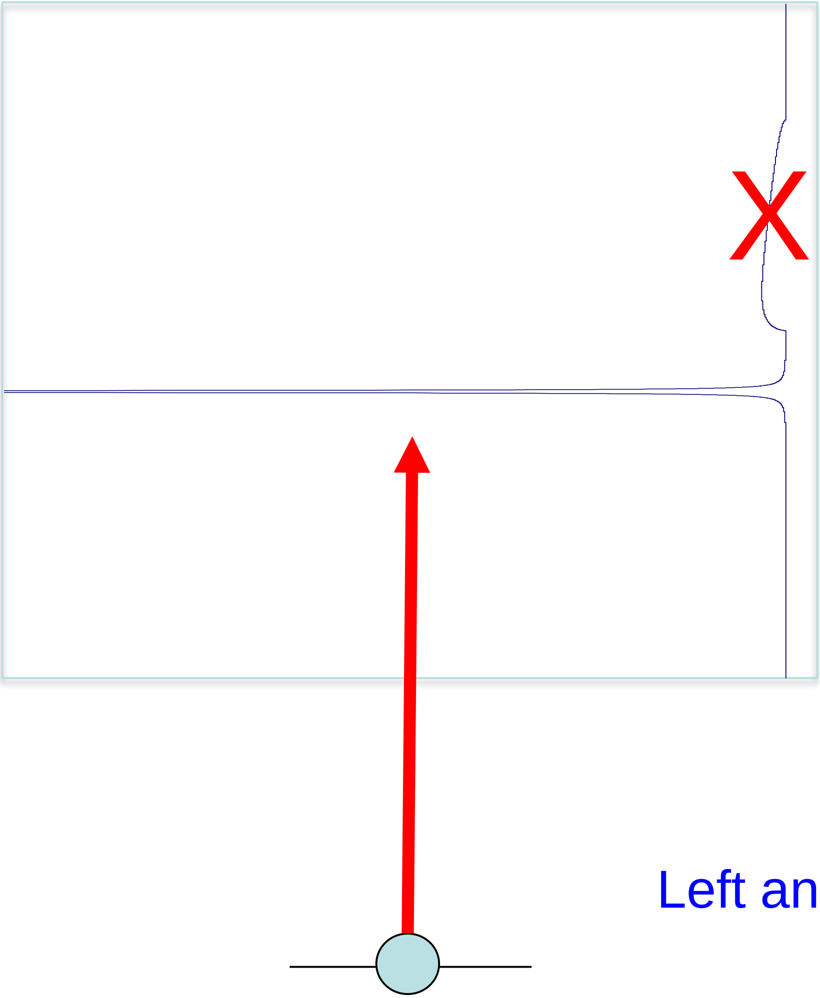
2p XAS



I(w)

Γ_{2p}= 0.2 eV

2p XMCD

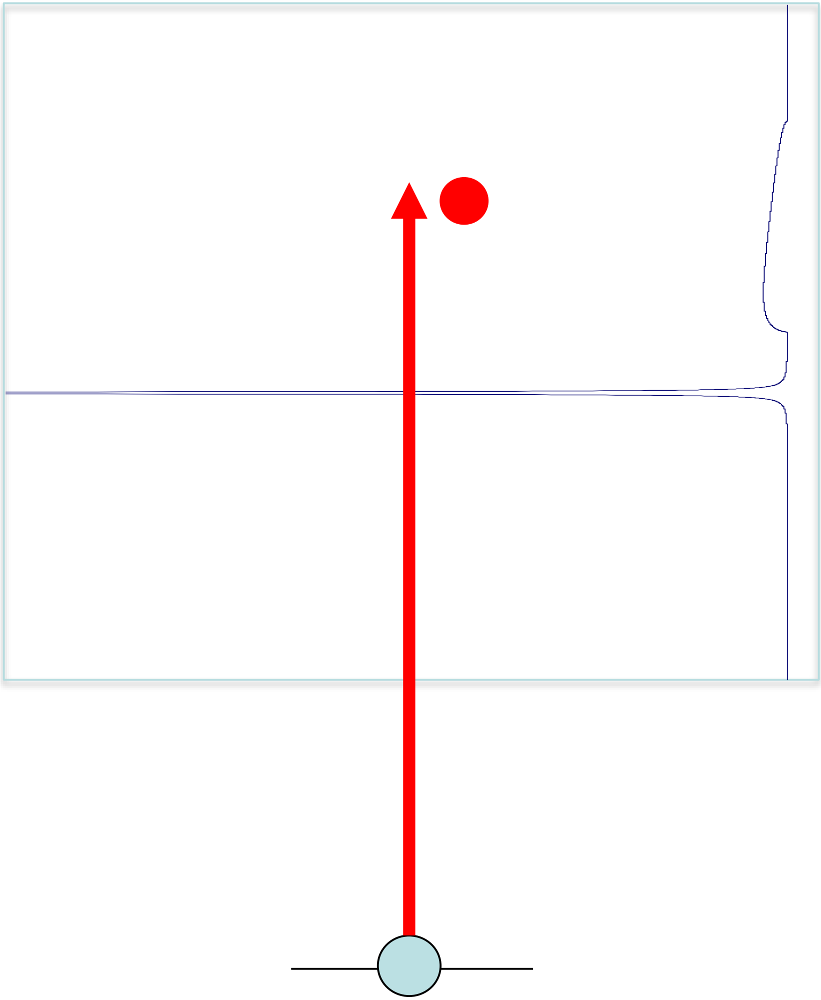


$I^+(w) - I^-(w)$

$\Gamma_{2p} = 0.2$ eV

Left and right polarized x-rays

2p XPS

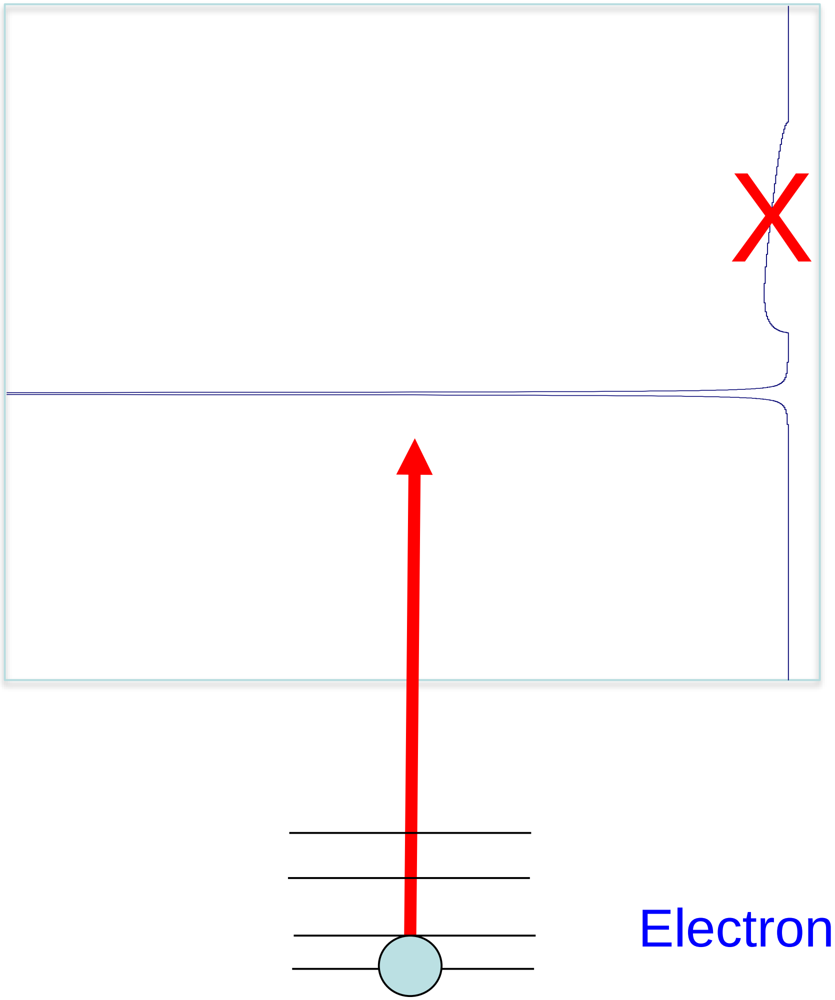


$I(E_k)$

Γ_{2p}= 0.2 eV

(additional broadening)

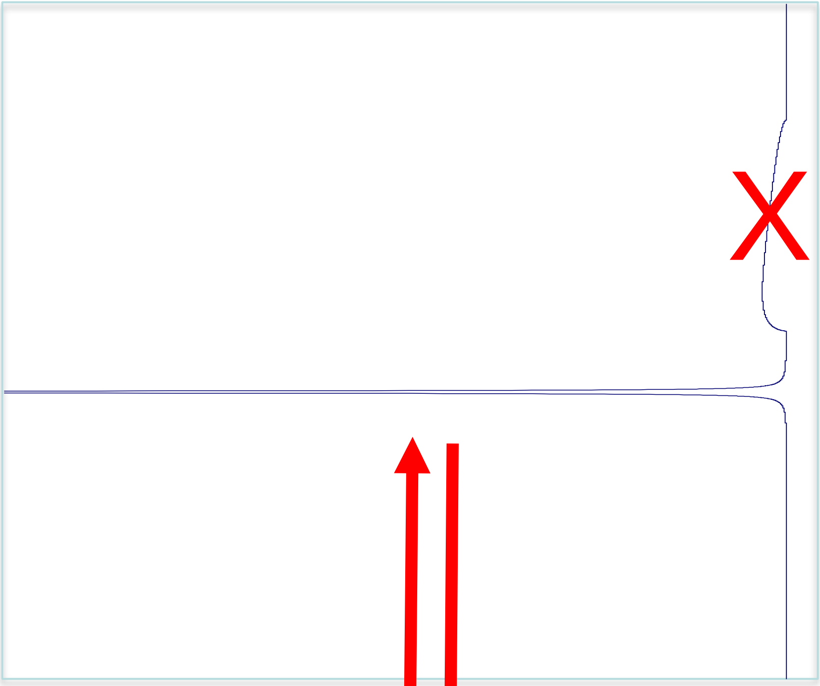
2p XAS



I(w)

Electronic, magnetic, vibrational

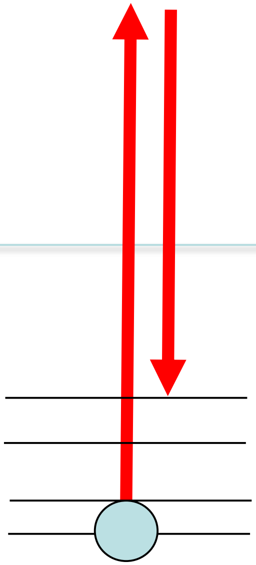
2p3d RIXS



I(w,w')

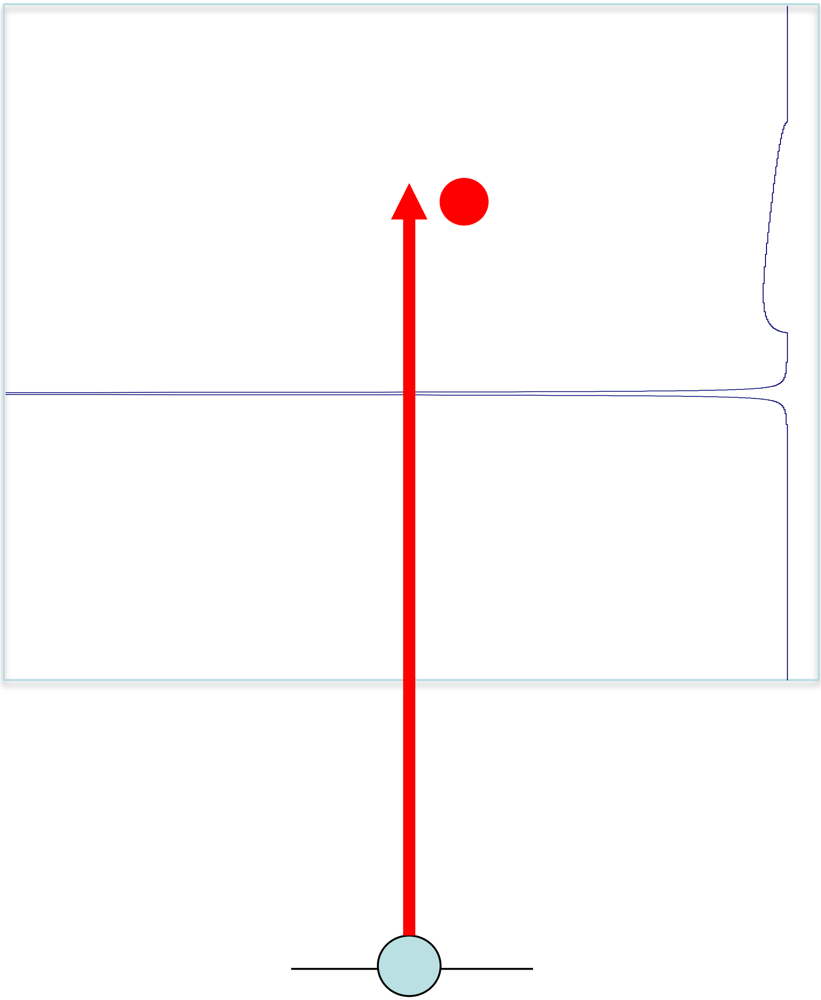
Fixed energy loss

Γ_{3d}= 10 meV?

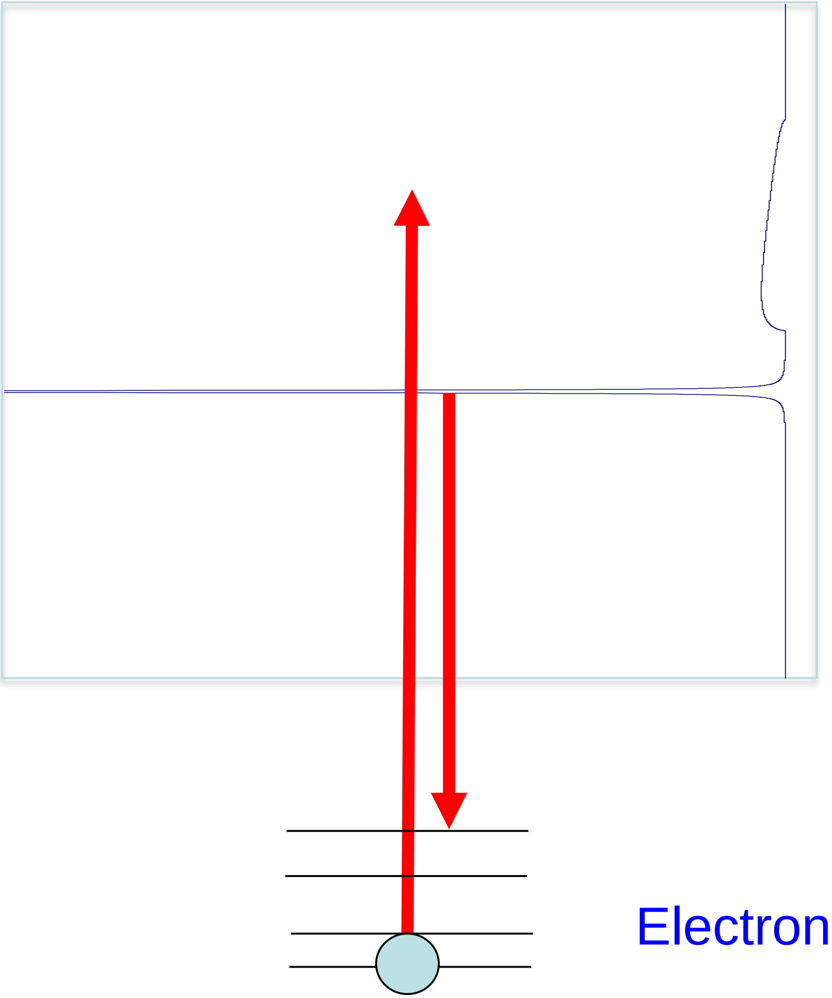


Electronic, magnetic, vibrational

2p XPS



2p3d fluorescence



I(w')

Fixed emission energy

Γ_{2p}= 0.2 eV

Electronic, magnetic, vibrational