Topics

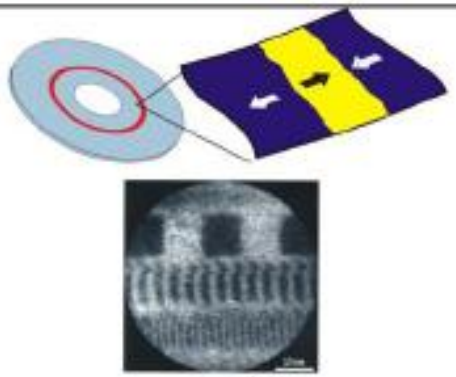
- Interaction of X-rays with matter
- Overview of core level spectroscopies
- XAS analysis of spectral features
- Interpretation of X-ray absorption

Why are X-Rays so Useful ?

Why are X-Rays so Useful ?

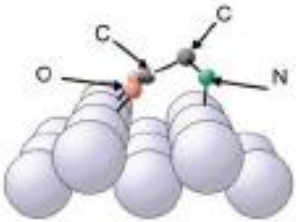
Imaging - Seeing the Invisible

1895

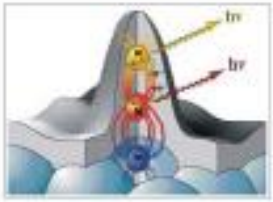


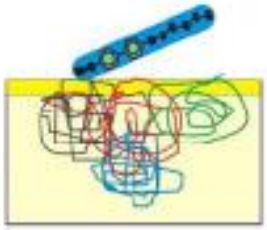
1993

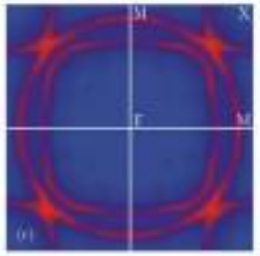
Atomic and Molecular Structure
- where are the atoms -



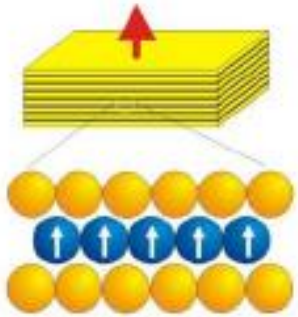
Electronic Structure and Bonding
- where are the electrons -

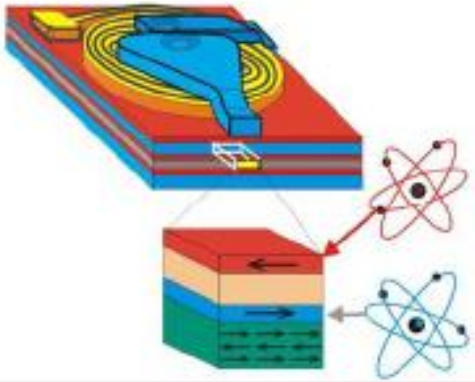






Magnetic Structure and Properties
- where are the spins-





Interaction of X-rays with matter

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

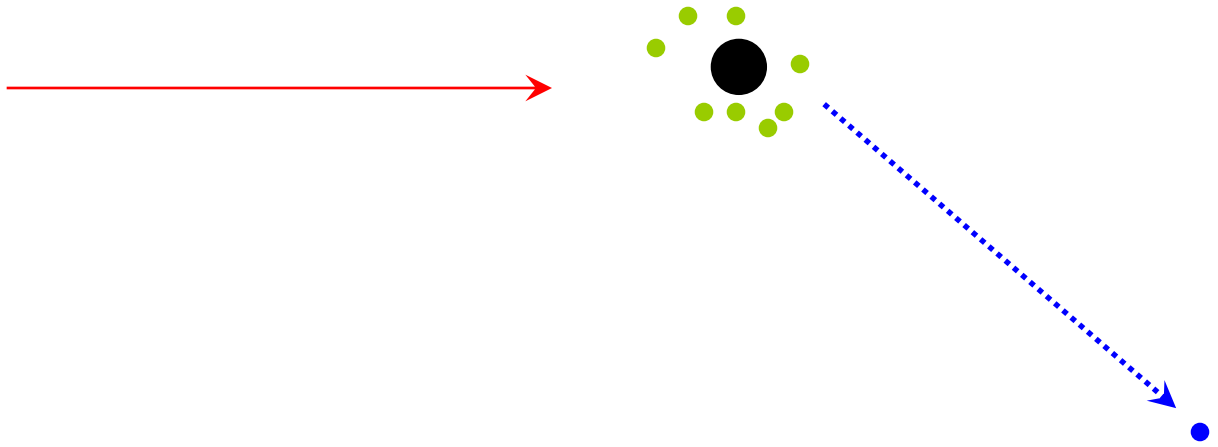
Interaction of x-rays with matter 1

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

Beyond the one-electron model: von Almbladh and Hedin,
Handbook of synchrotron radiation 1, chapter 8, pages 607-900 (1983)

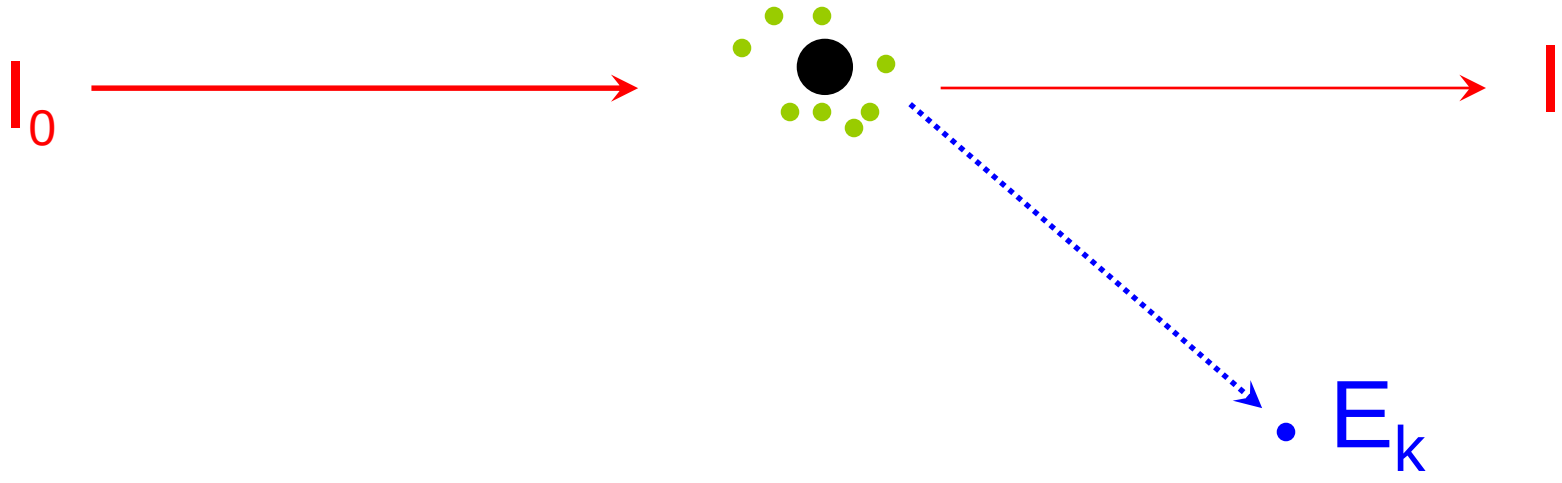
Interaction of x-rays with matter 1

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



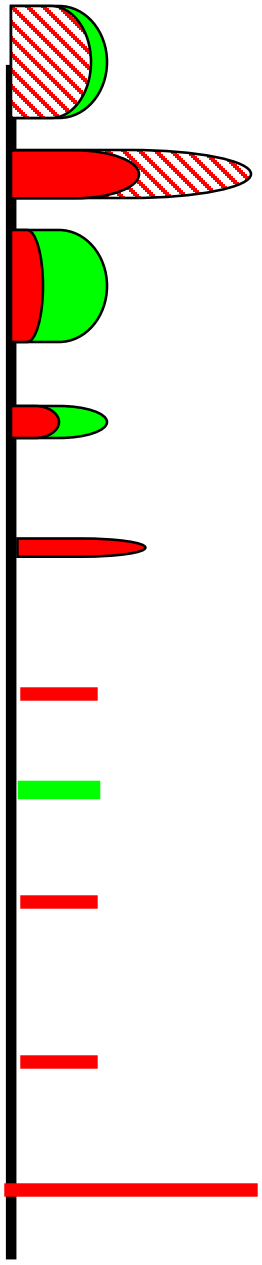
Interaction of x-rays with matter 1

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



Overview of core level spectroscopies

Ground State



Mn 4p -

Mn 3d 0

O 2p 5

O 2s 20

Mn 3p 45

Mn 3s 80

O 1s 530

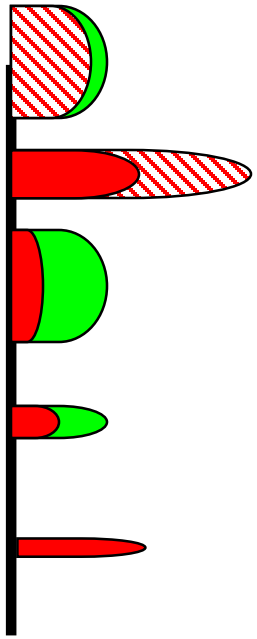
Mn 2p 650

Mn 2s 770

Mn 1s 6540

MnO $3d^5$

Ground State



Mn 4p -

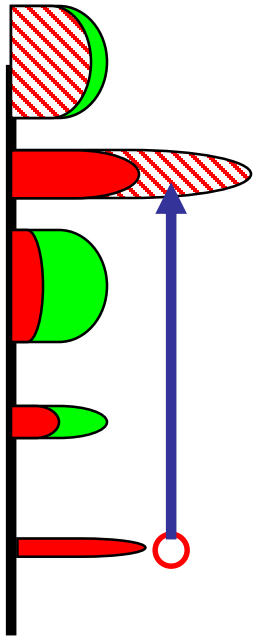
Mn 3d 0

O 2p 5

O 2s 20

Mn 3p 45

X-ray absorption



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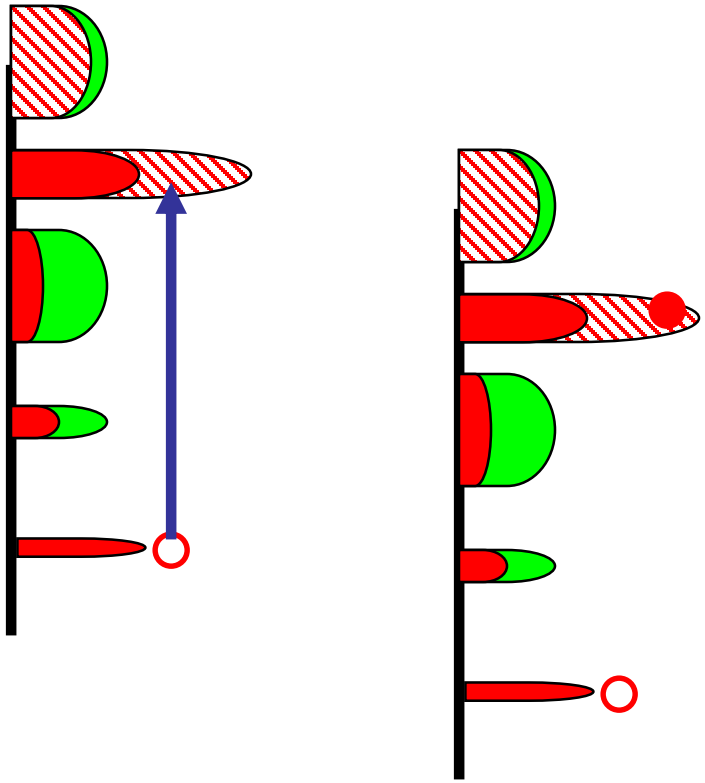
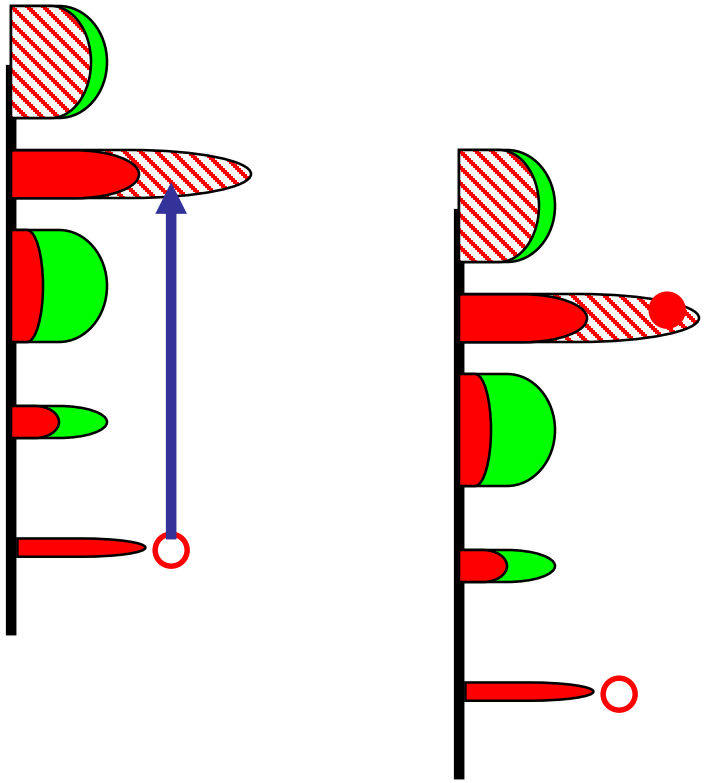
X-ray absorption

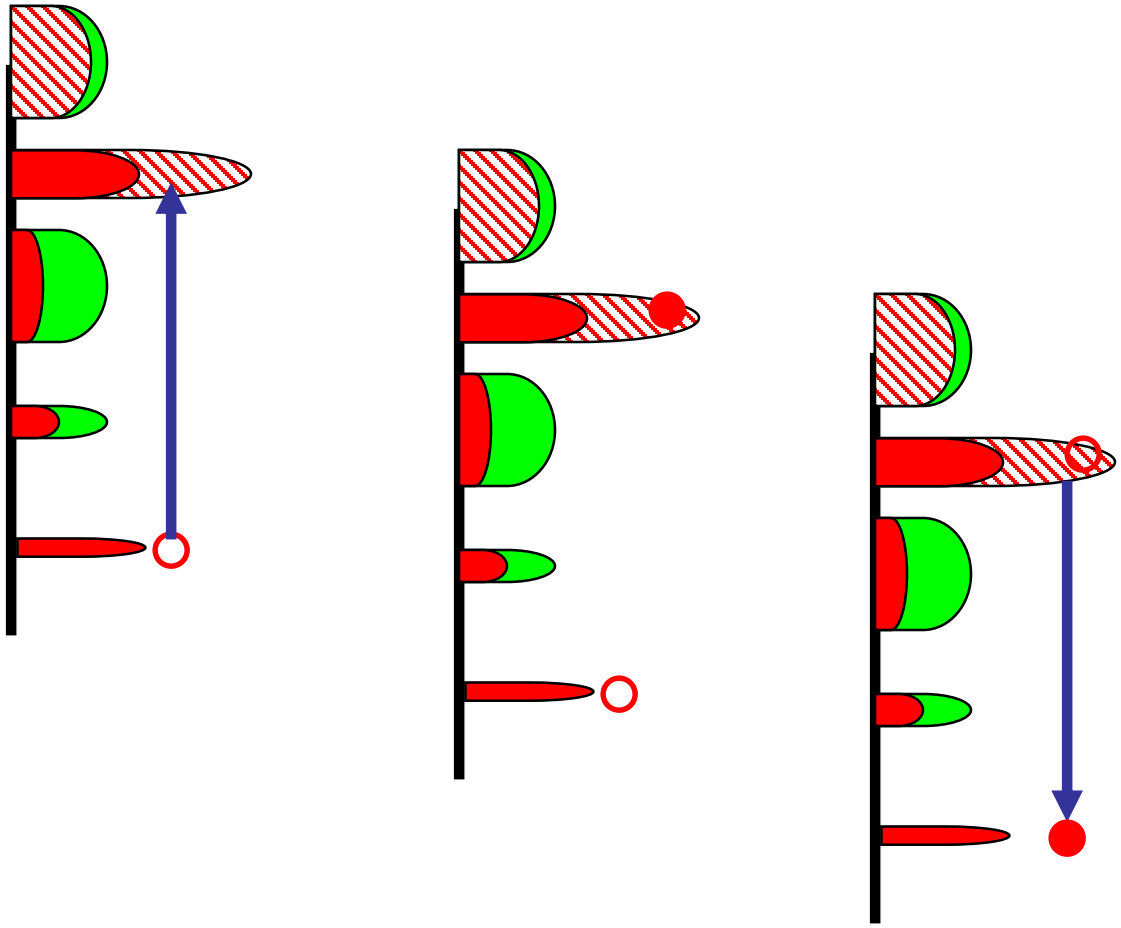


X-ray absorption

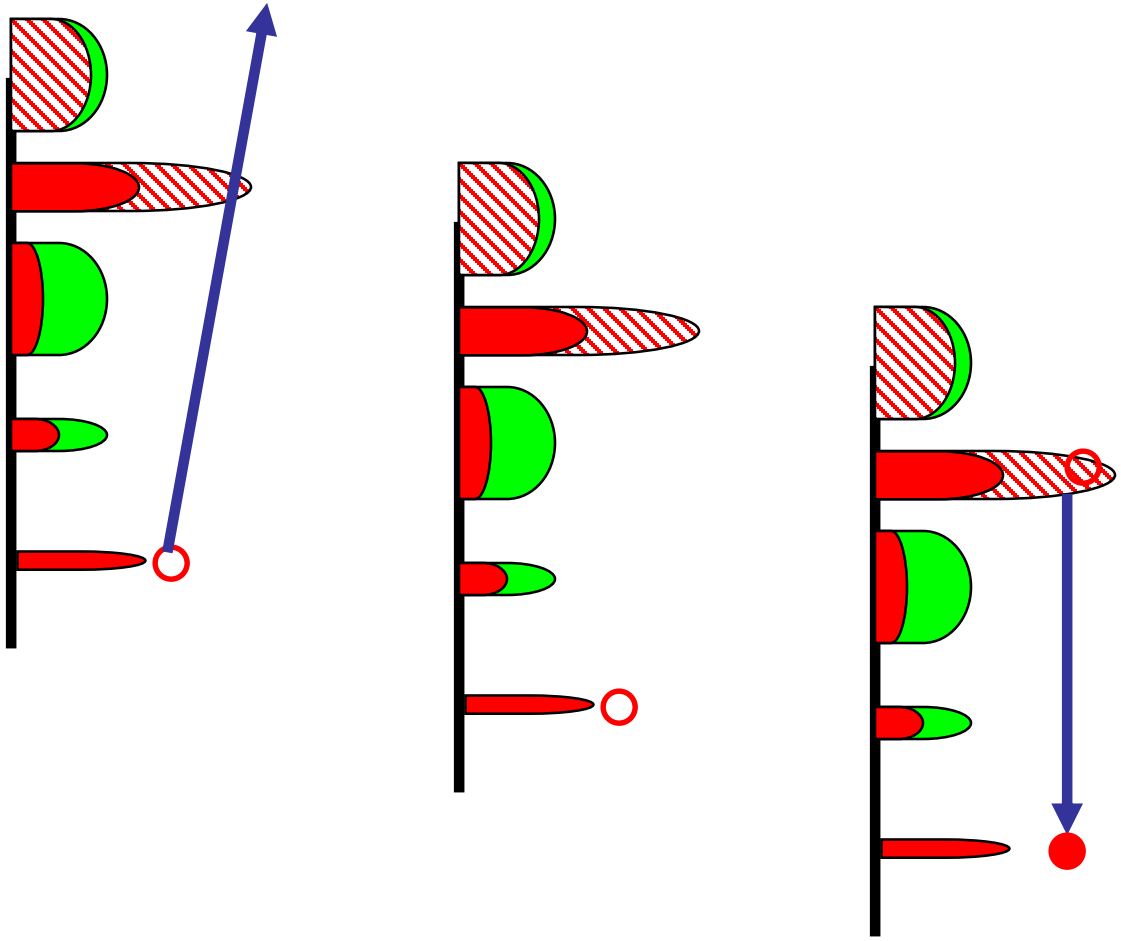


The life of a core hole is rather short:
~few femtoseconds

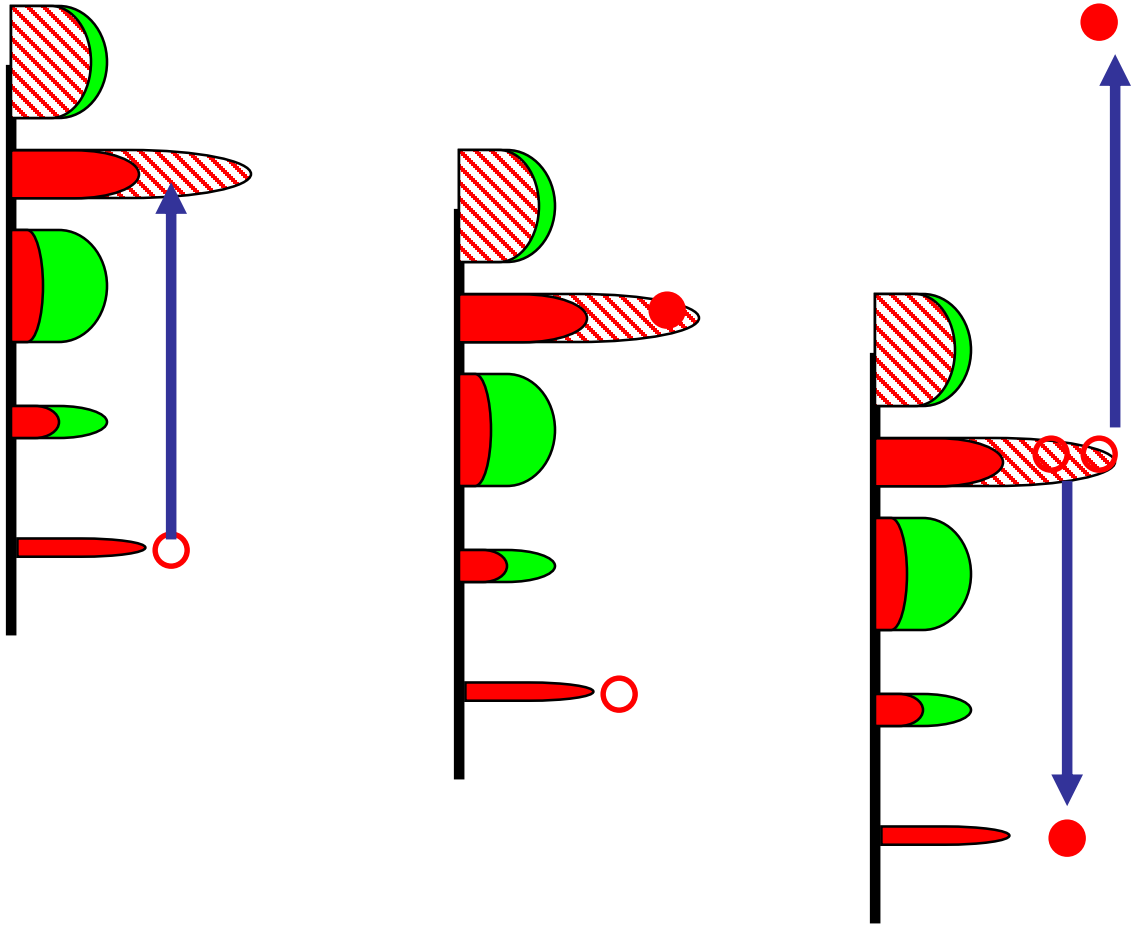
X-ray emission after x-ray absorption



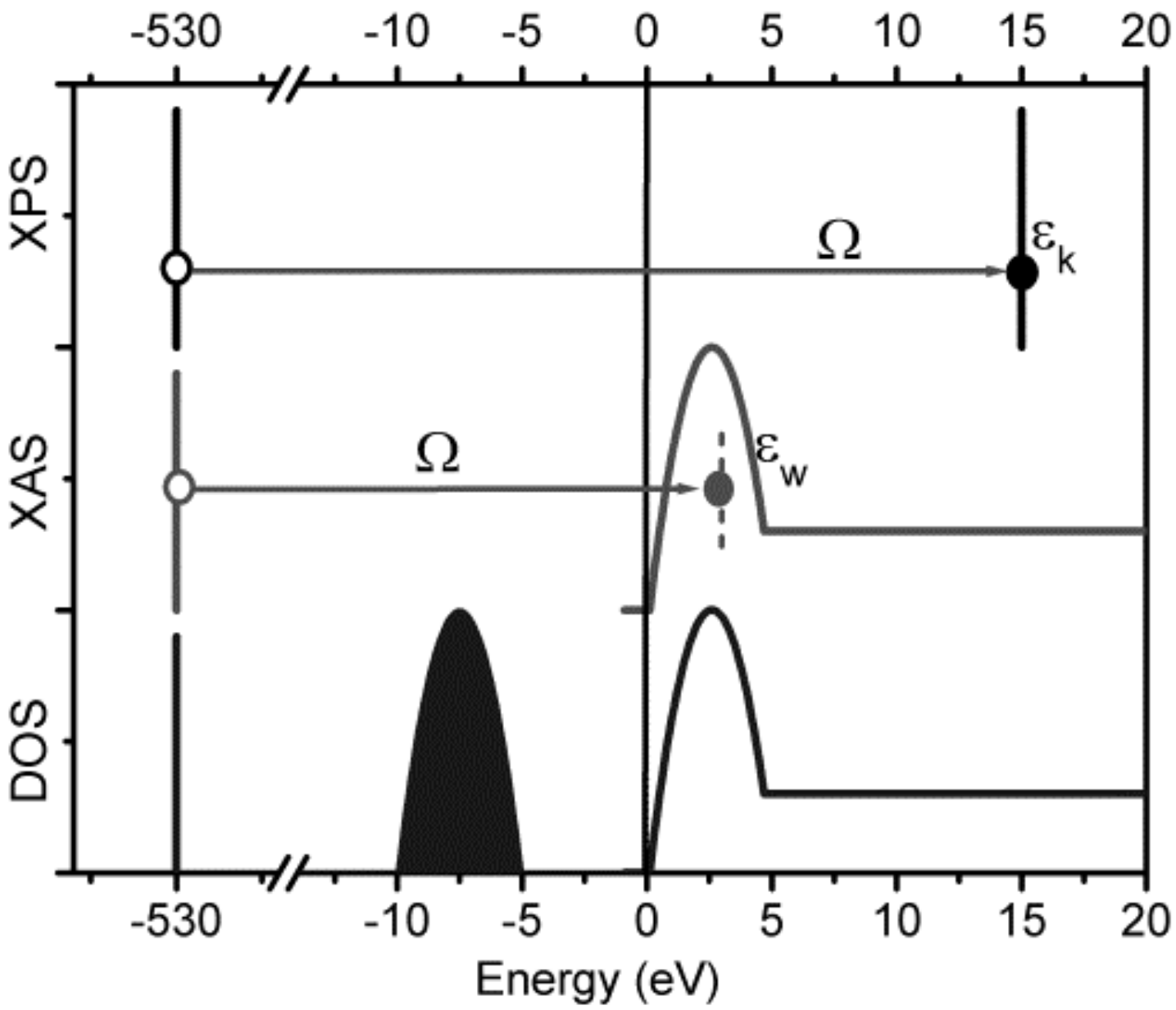
X-ray emission after electron excitation



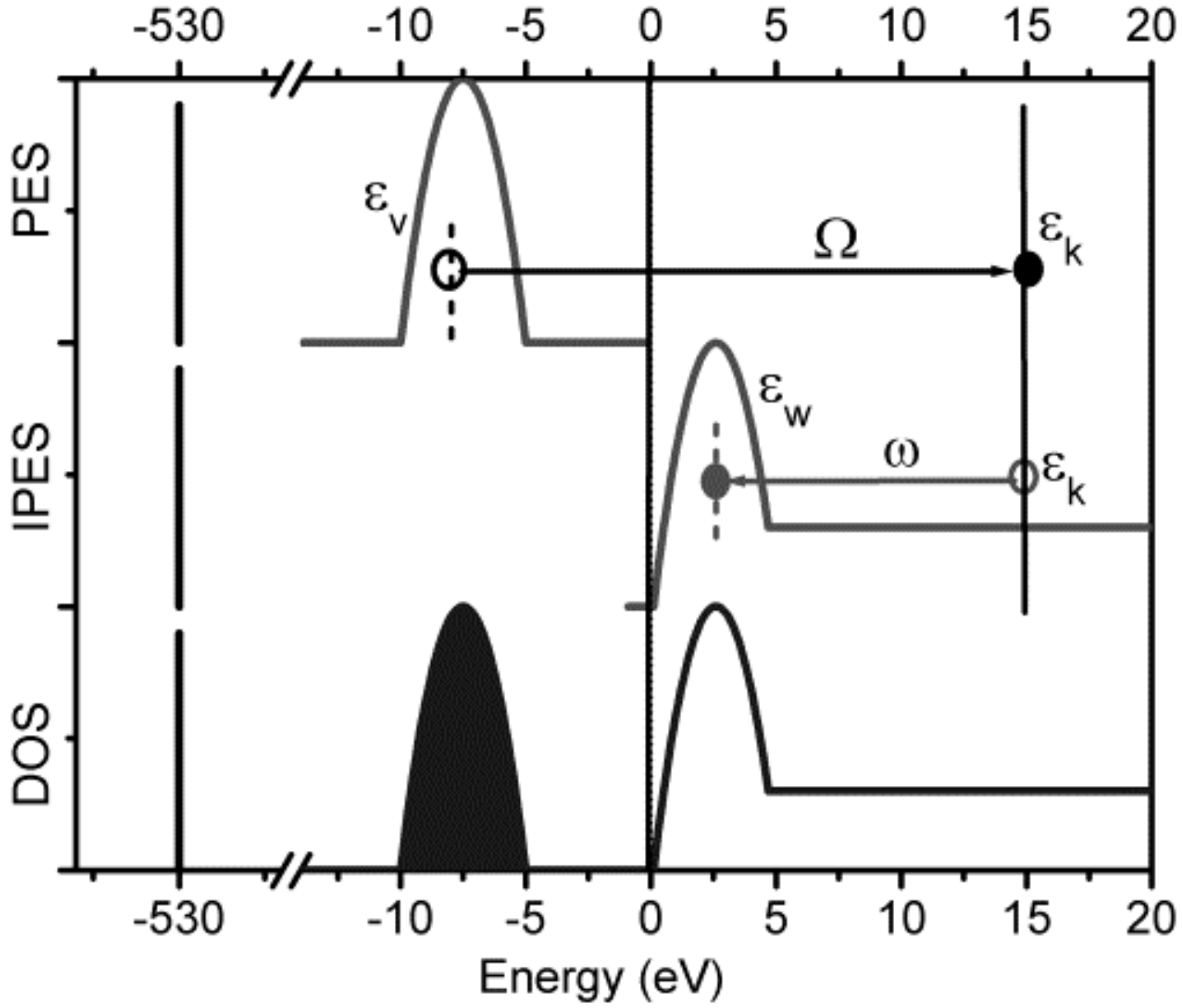
Auger



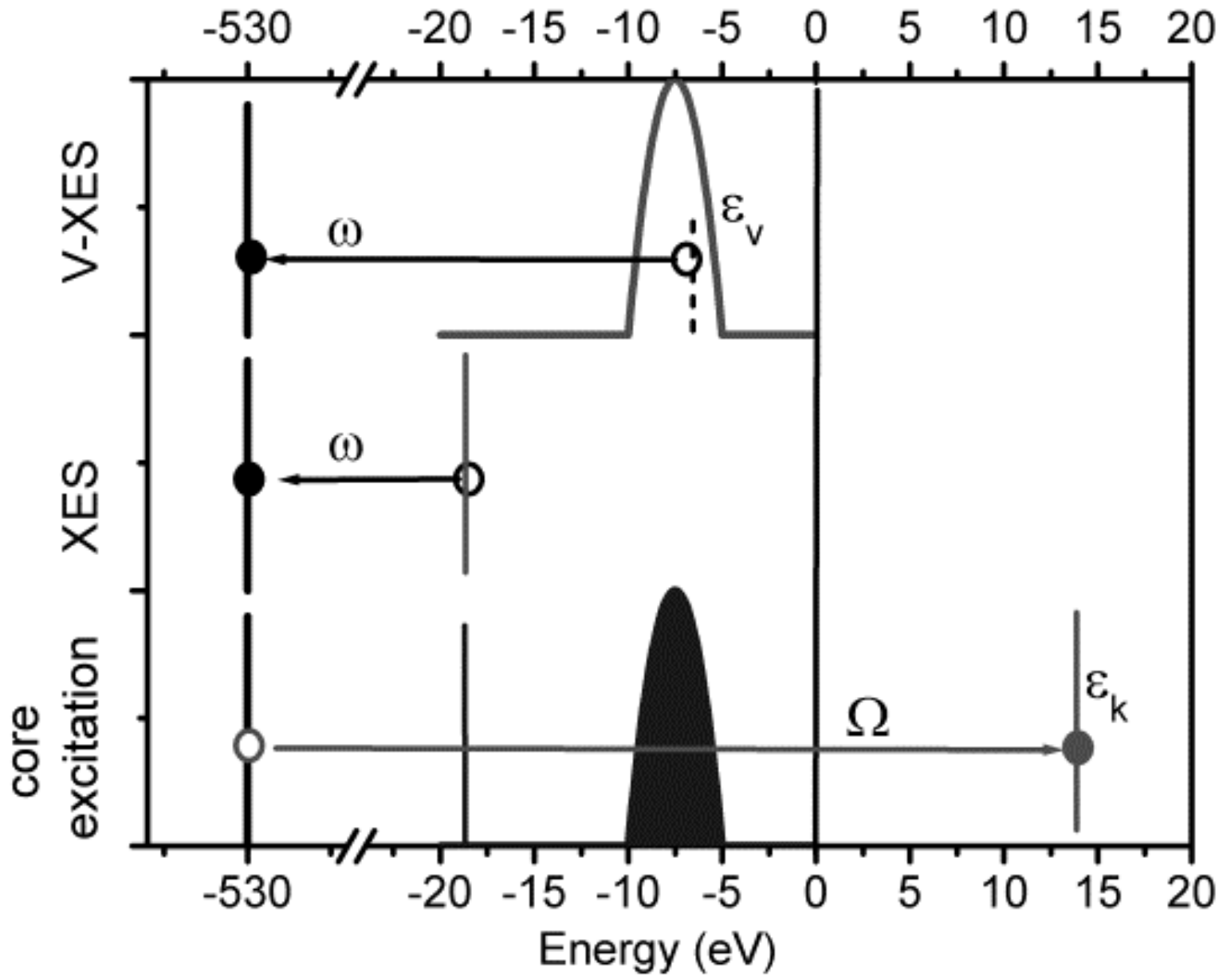
XAS and XPS


-530
-10
-5
0
5
10
15
20
XPS
XAS
DOS
Ω
ε_k
Ω
ε_w
-530
-10
-5
0
5
10
15
20
Energy (eV)

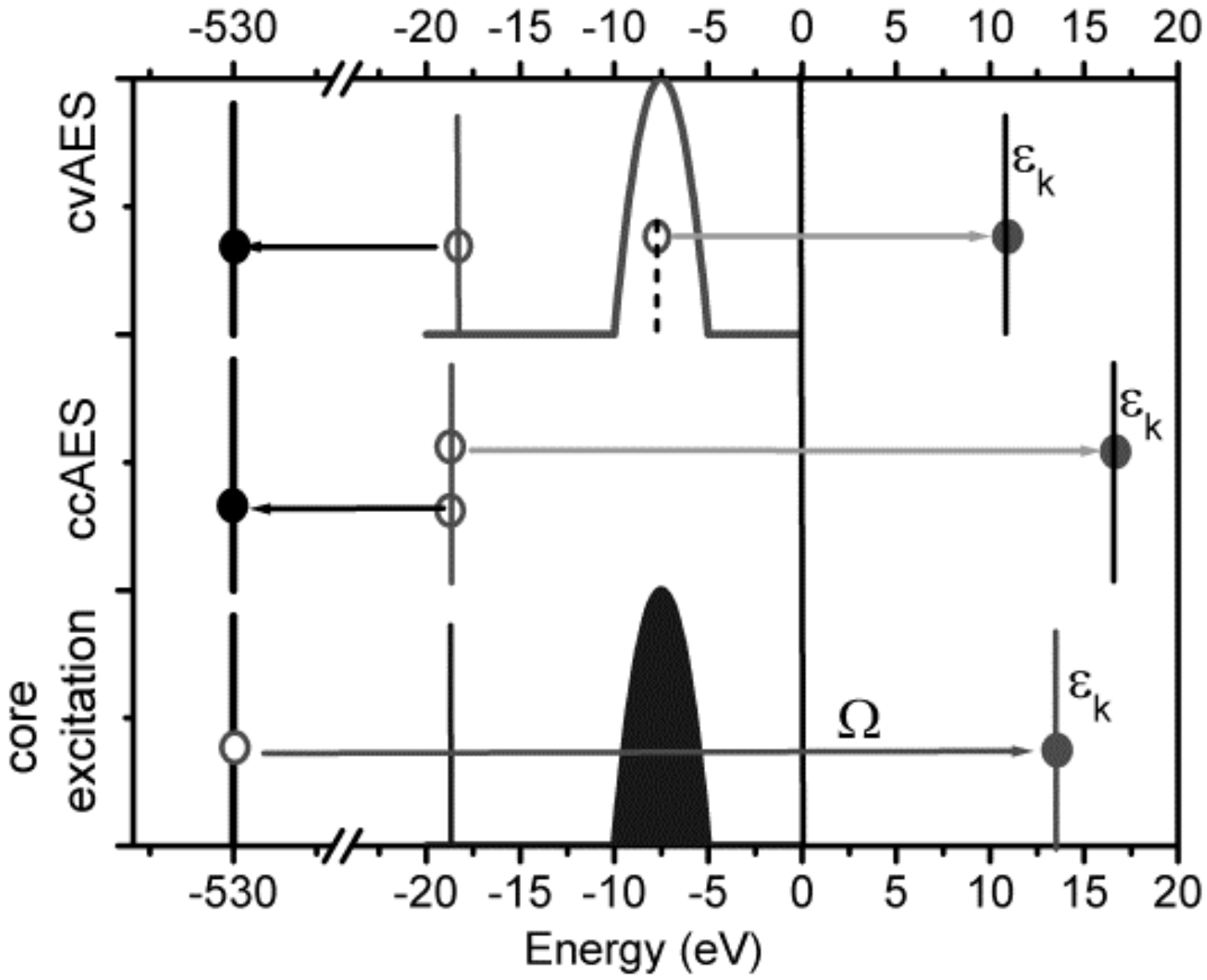
XPS (PES) and Inverse PES



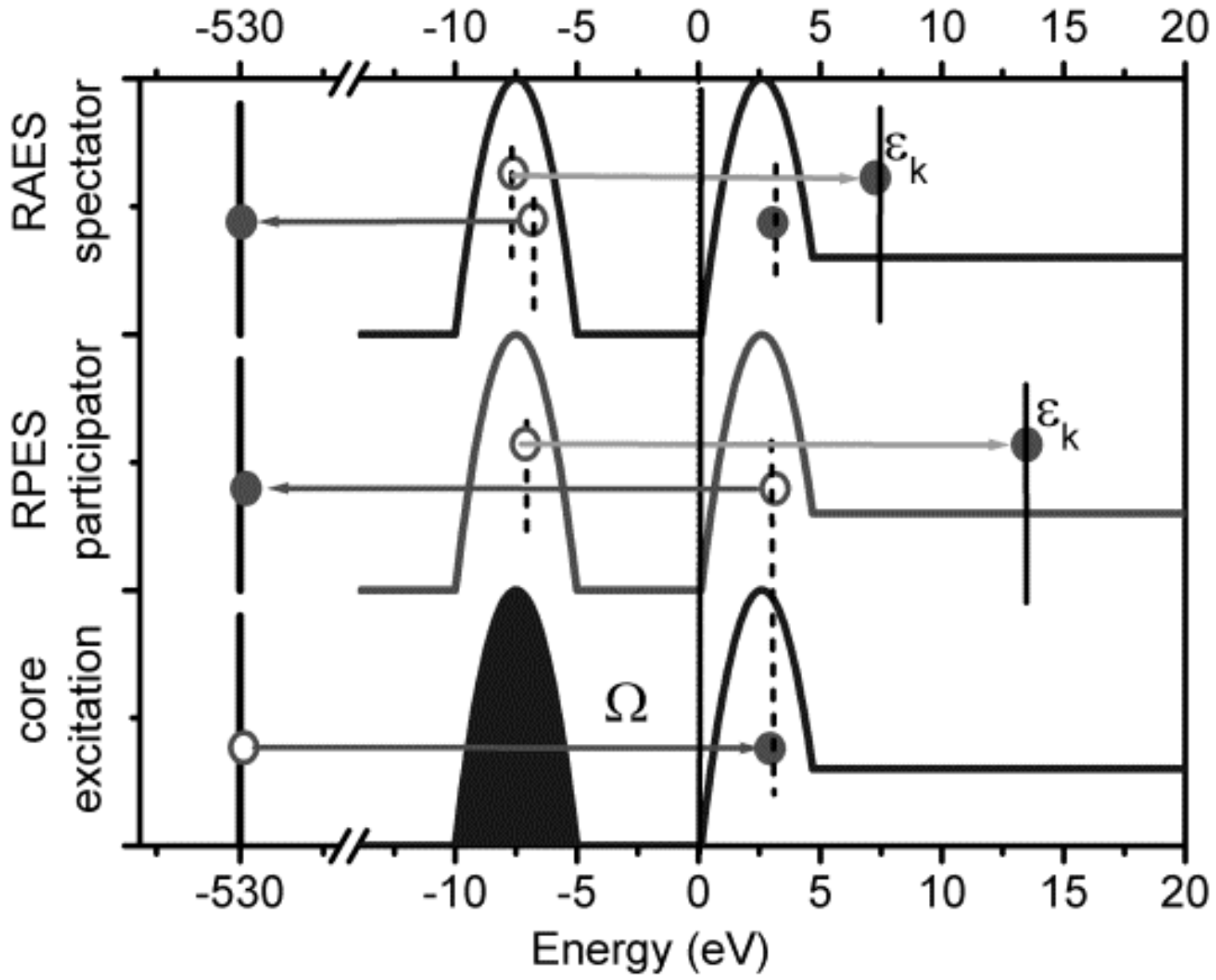
X-ray emission decay



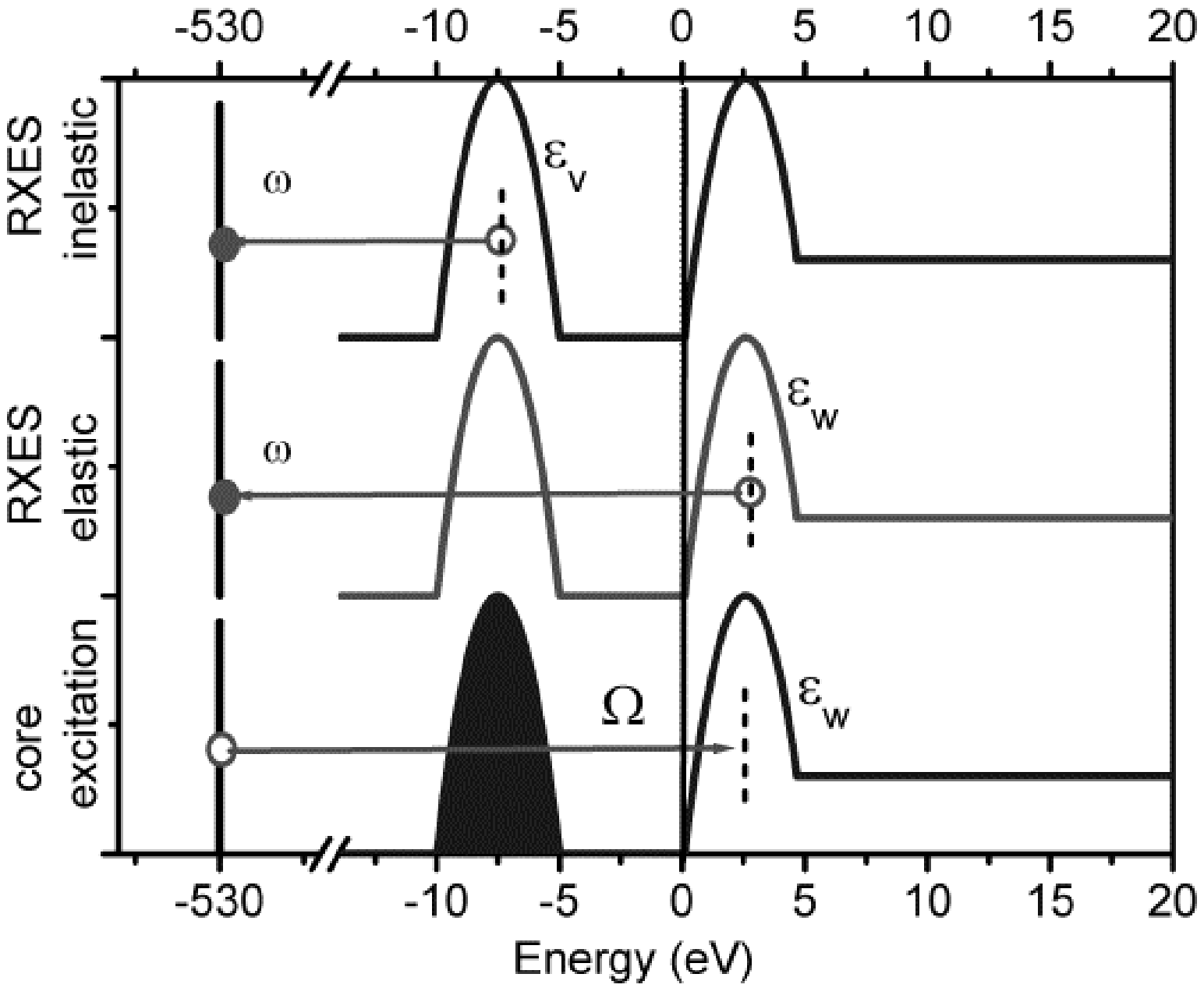
Auger electron decay



Resonant Auger decay (resonant PES)



Resonant X-ray emission decay



Binding Energies

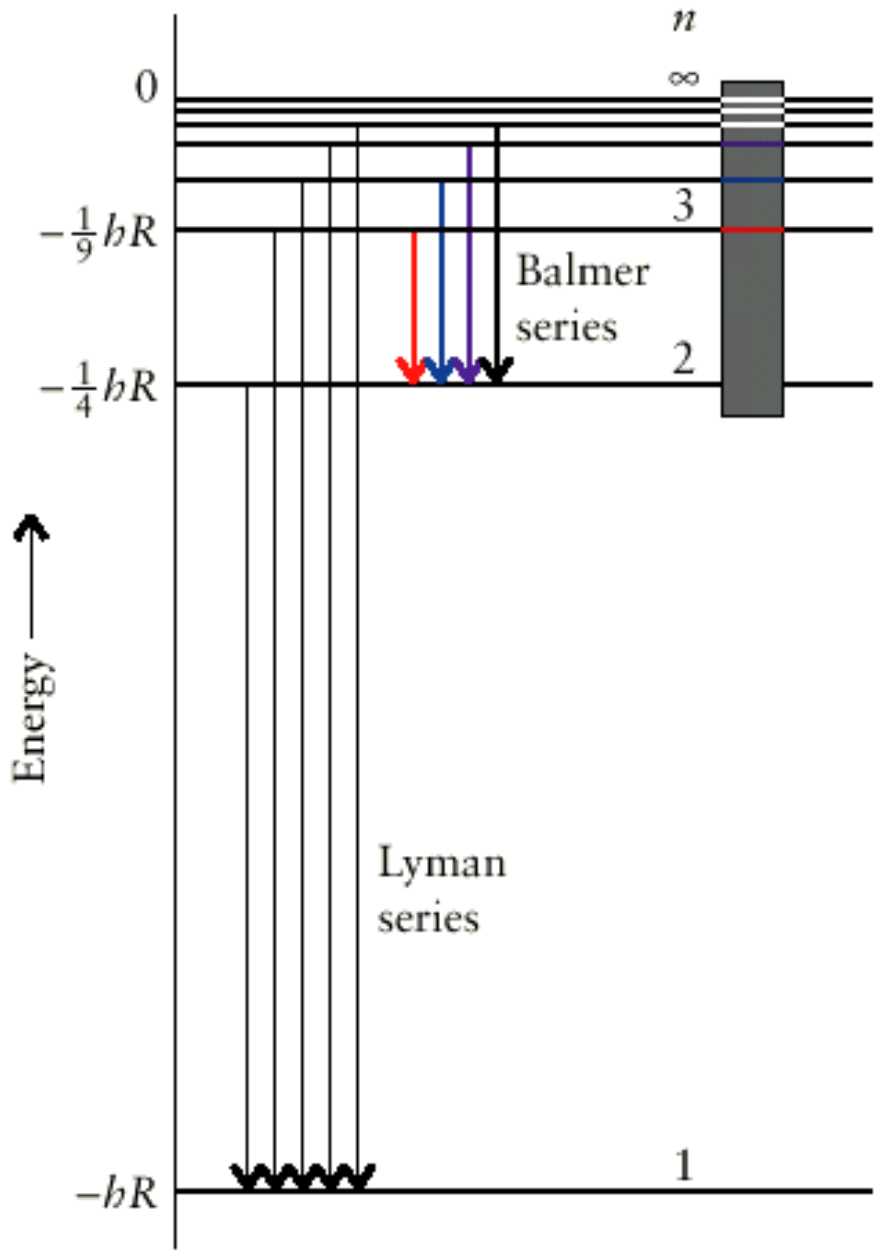
X-ray absorption edges

Manganese Electron binding energies

	Label	Orbital	eV [literature reference]
view	K	1s	6539 [1]
view	L_{I}	2s	769.1 [3]
view	L_{II}	$2p_{1/2}$	649.9 [3]
view	L_{III}	$2p_{3/2}$	638.7 [3]
view	M_{I}	3s	82.3 [3]
view	M_{II}	$3p_{1/2}$	47.2 [3]
view	M_{III}	$3p_{3/2}$	47.2 [3]

http://www.webelements.com/

Atomic binding energies in hydrogen



Bohr frequency condition:

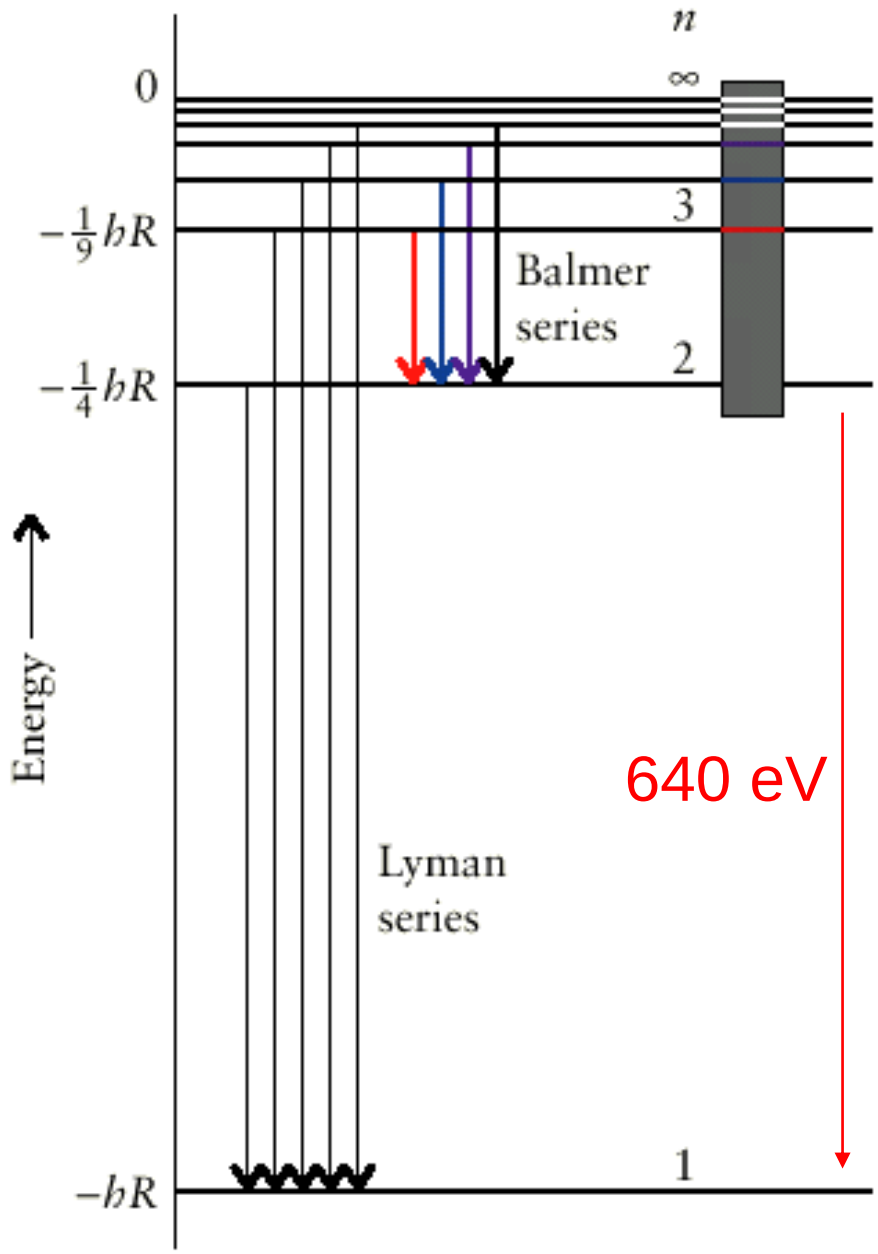
$$h\nu = E_{\text{upper}} - E_{\text{lower}}$$

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

Rydberg formula

13.6 eV

Atomic binding energies in oxygen



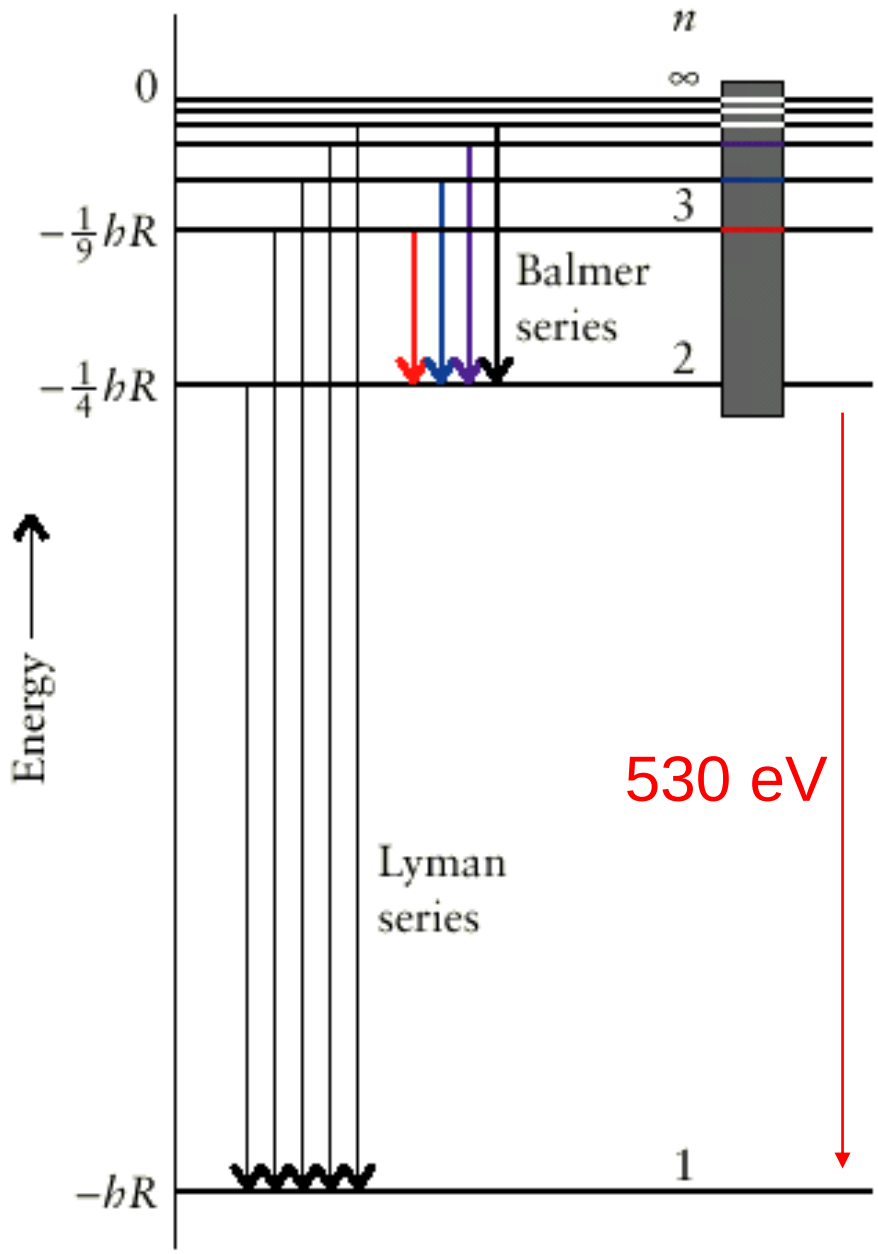
Bohr frequency condition:

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

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

Rydberg formula

Atomic binding energies in oxygen



Bohr frequency condition:

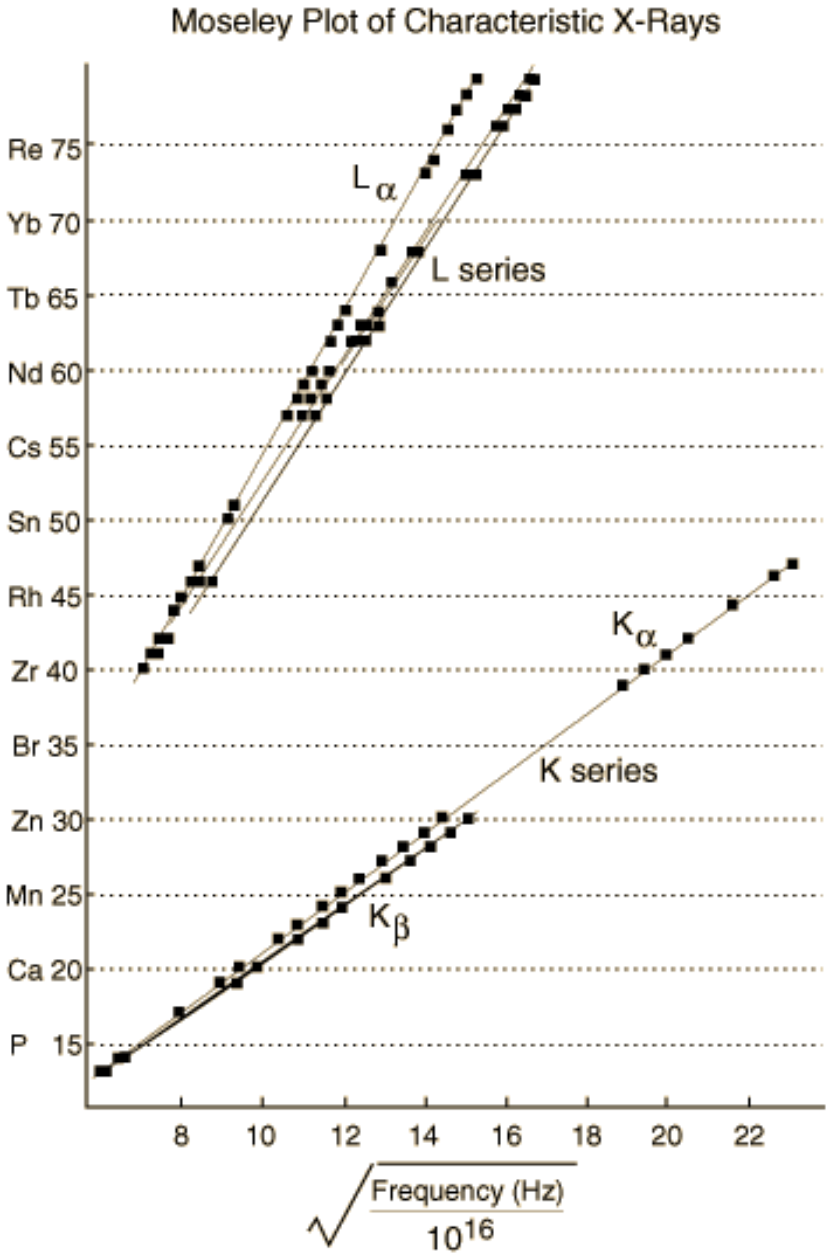
$$h\nu = E_{\text{upper}} - E_{\text{lower}}$$

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

Rydberg formula

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.



Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

X-ray absorption edges

Manganese Electron binding energies

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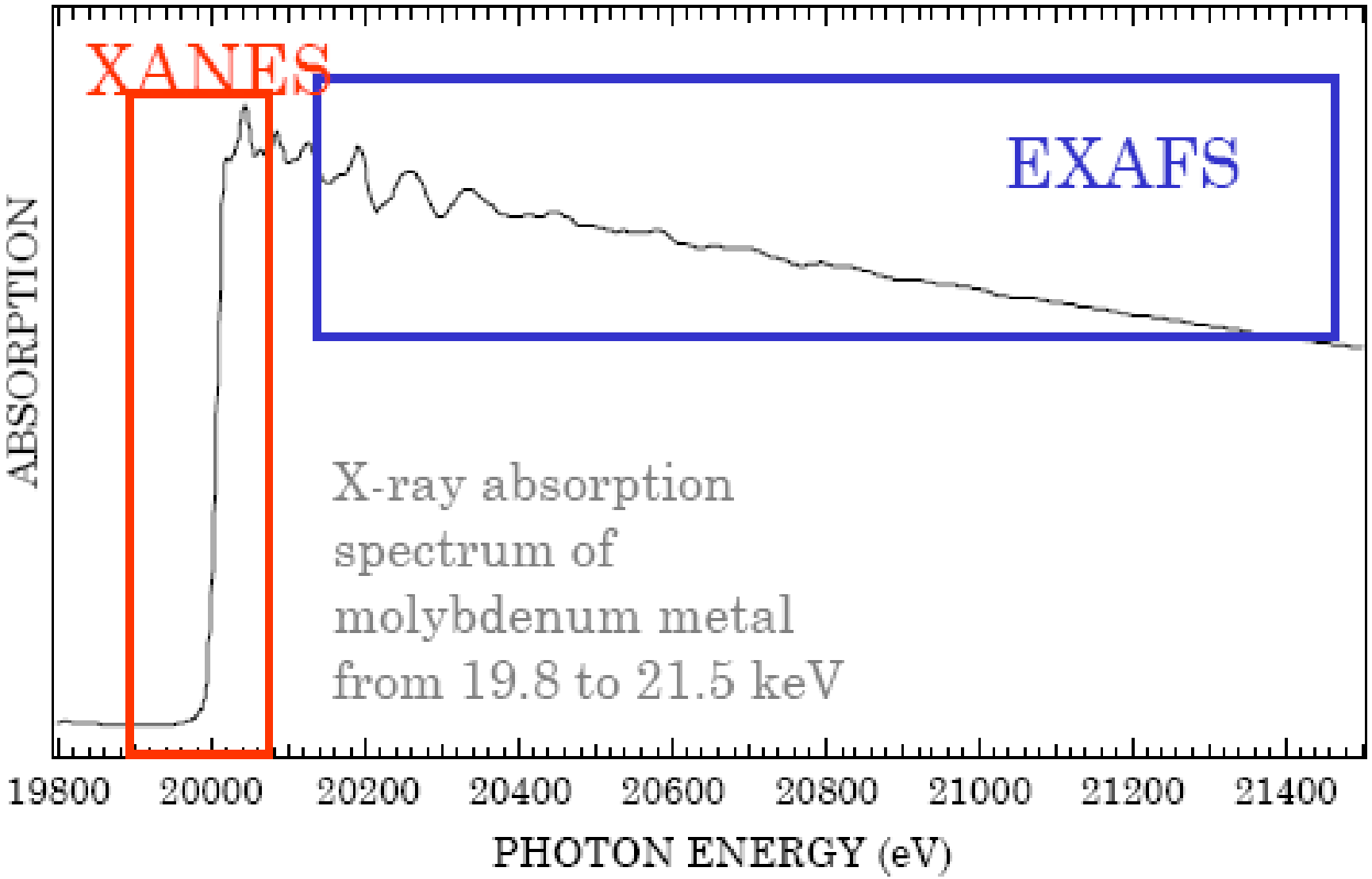
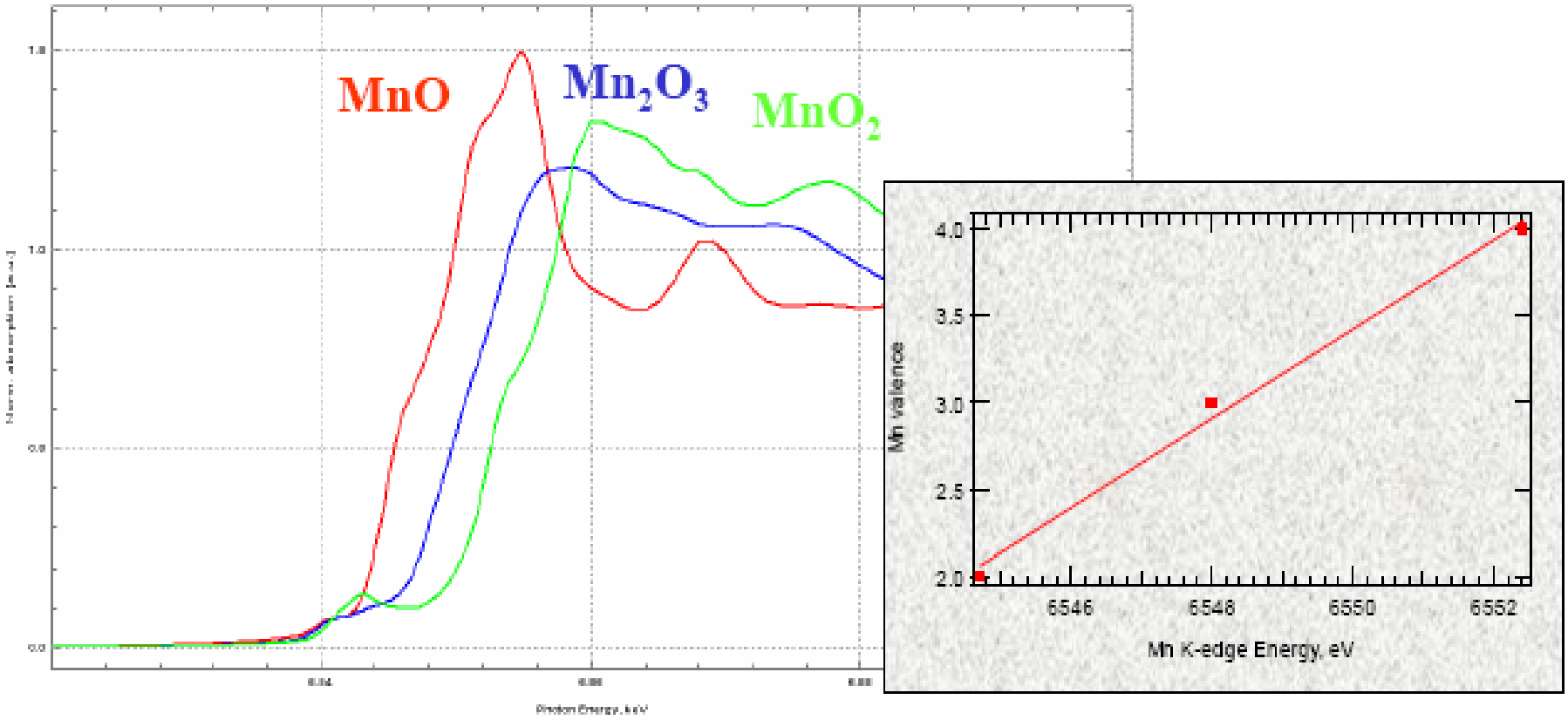
http://www.webelements.com/

Qualitative XAS analysis

X-ray absorption: XANES and EXAFS

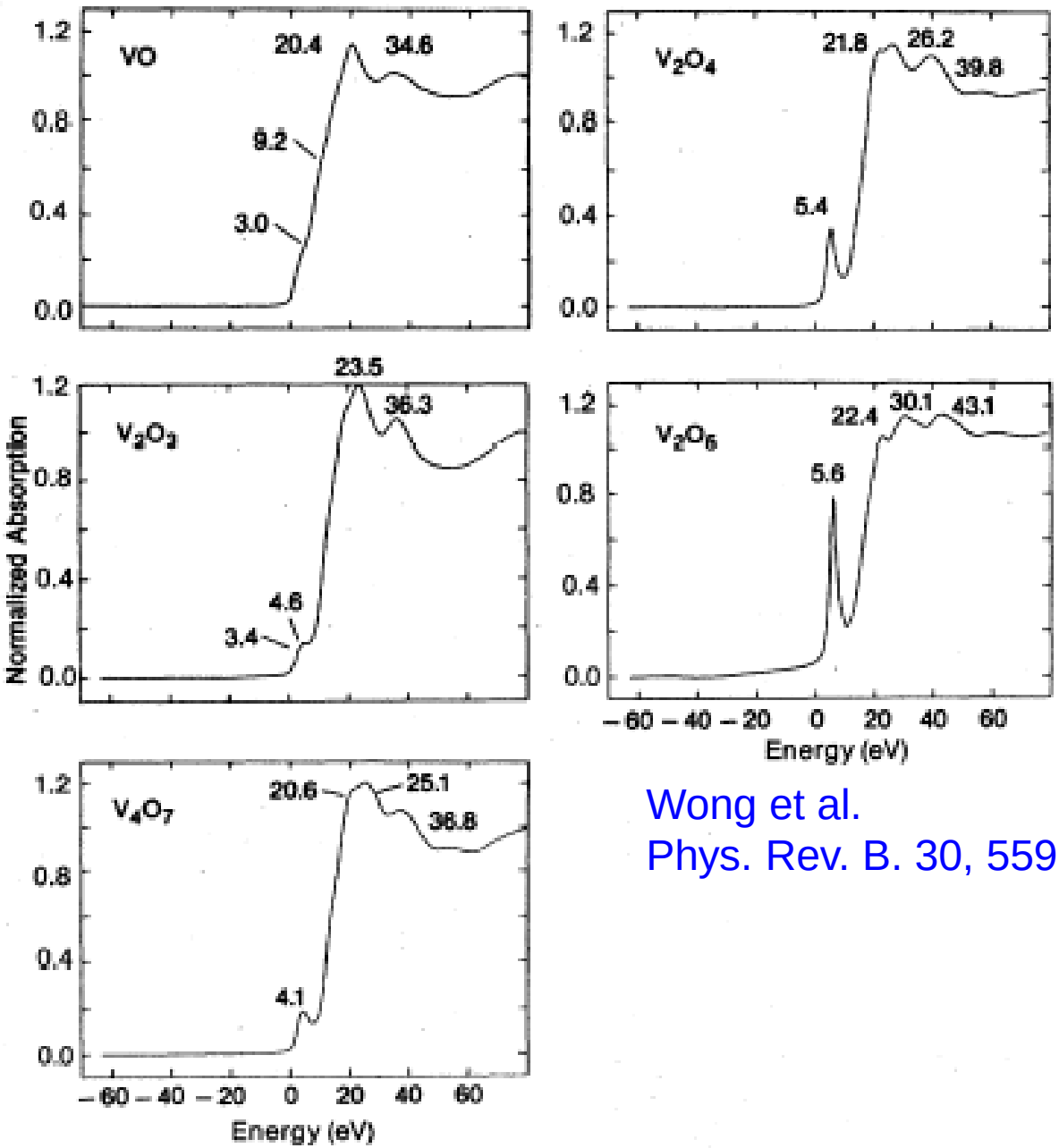


XANES: qualitative analysis



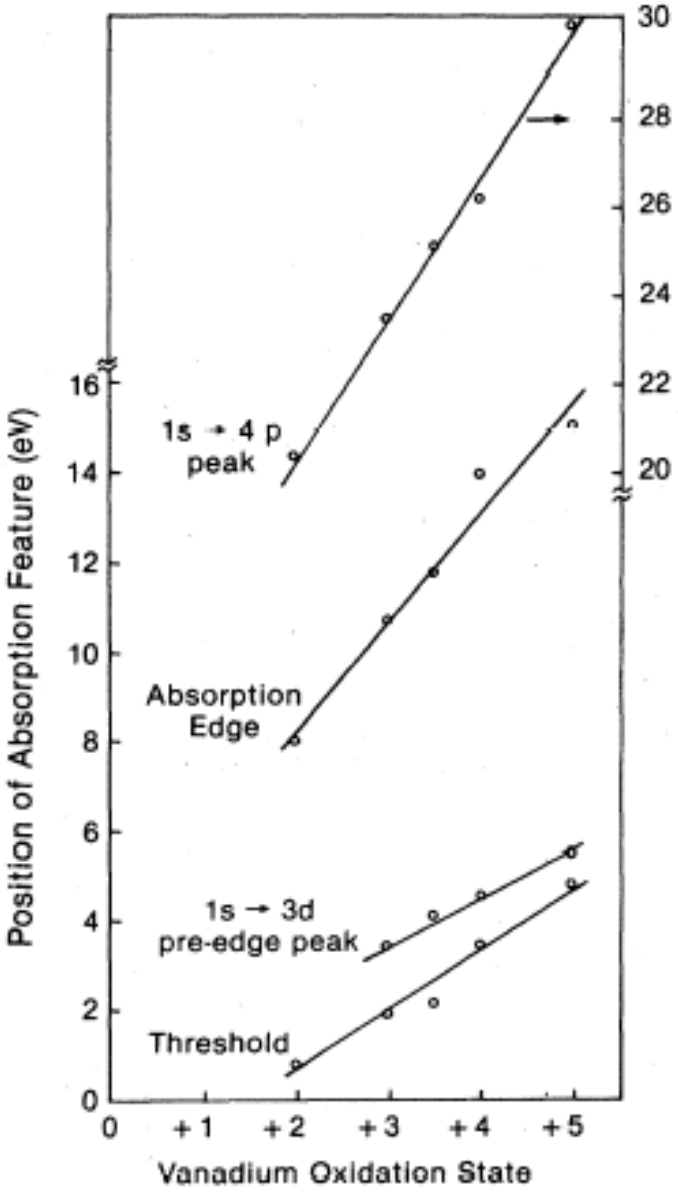
Edge position gives valence

XANES: qualitative analysis



Wong et al.
Phys. Rev. B. 30, 5596 (1984)

XANES: qualitative analysis

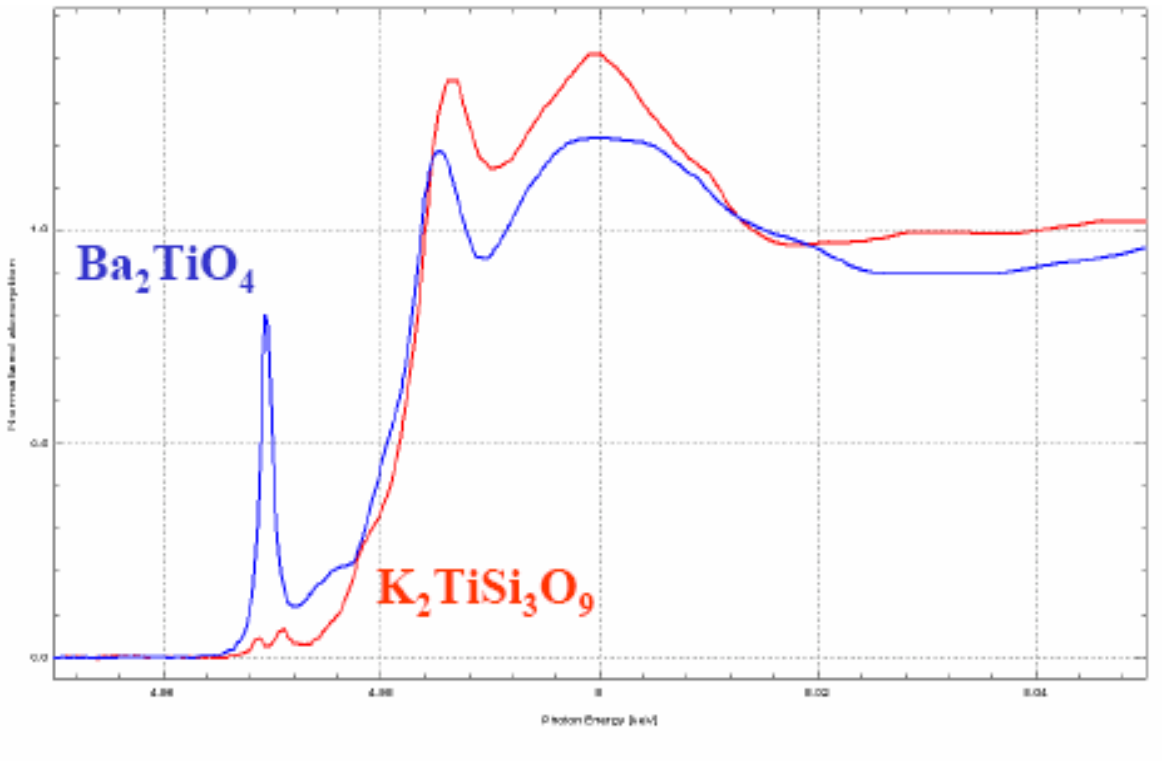


Edge position gives valence

Pre-edge gives valence

Different slopes

XANES: qualitative analysis



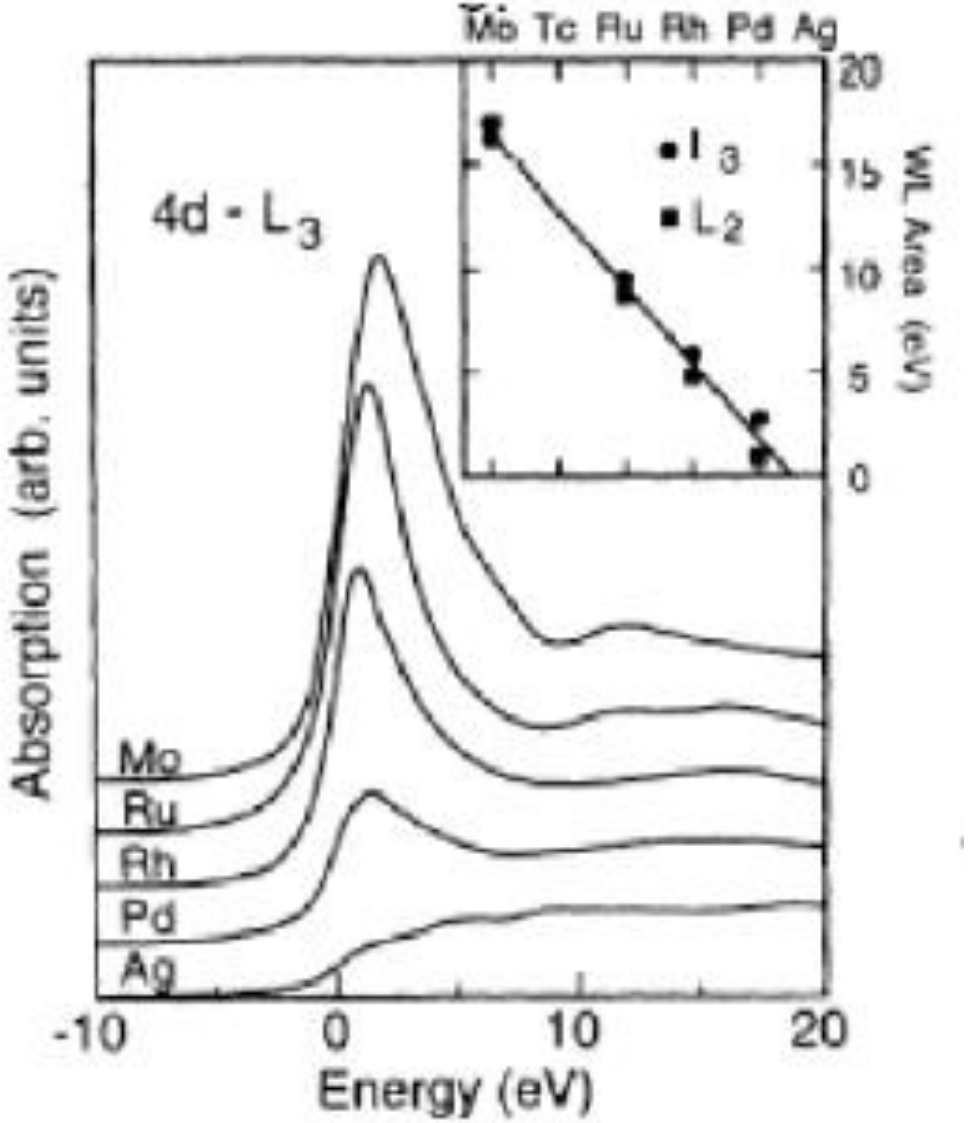
Both Ti^{4+}

Ba_2TiO_4

$K_2TiSi_3O_9$

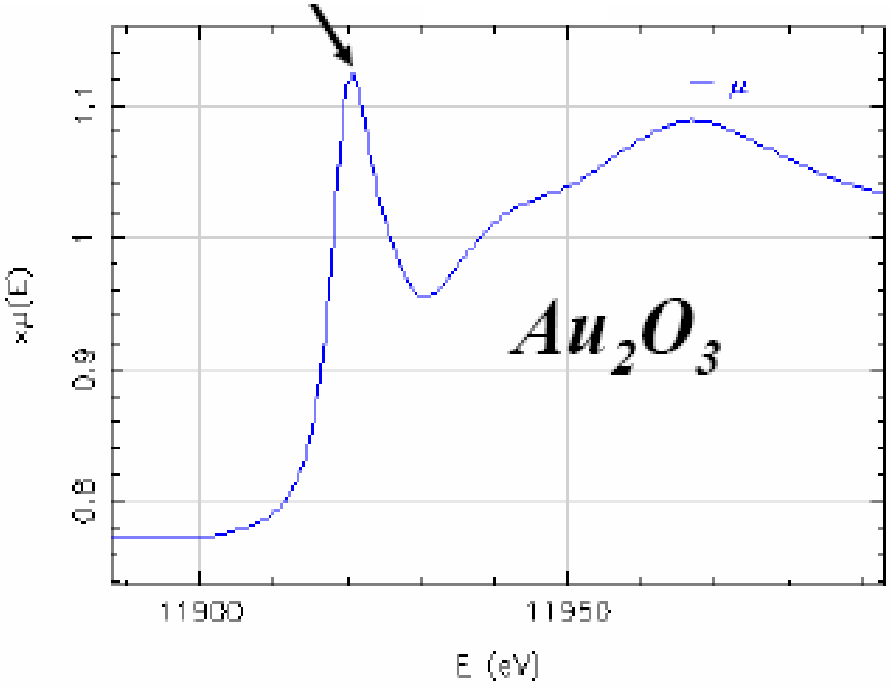
Pre-edge intensity gives site symmetry

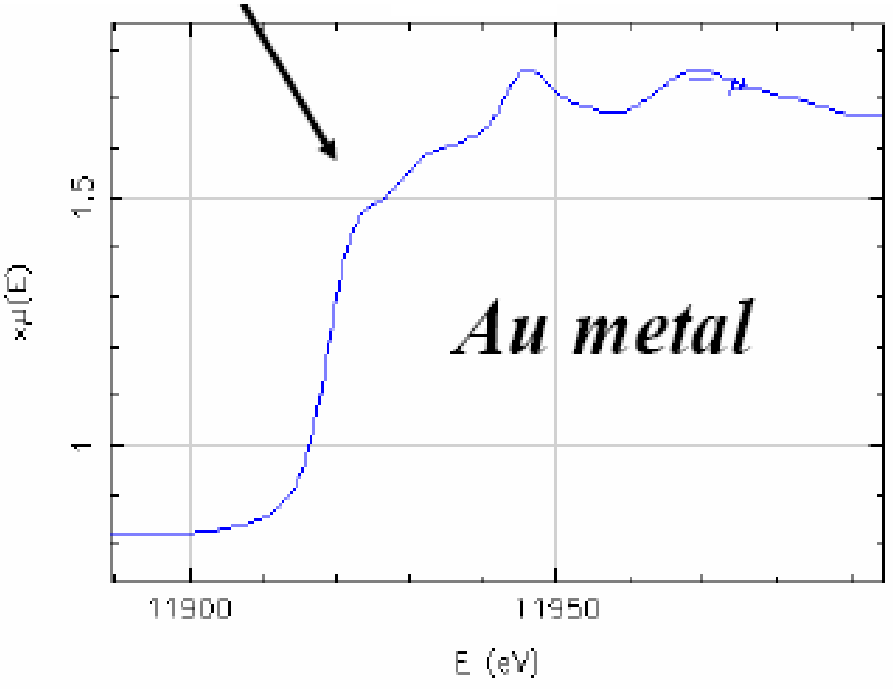
XANES: qualitative analysis



L edge of 4d-systems > number of empty 4d states

XANES: qualitative analysis





L edge of 5d-systems > number of empty 5d states

Difference between metal and oxide

Quantitative XAS interpretation

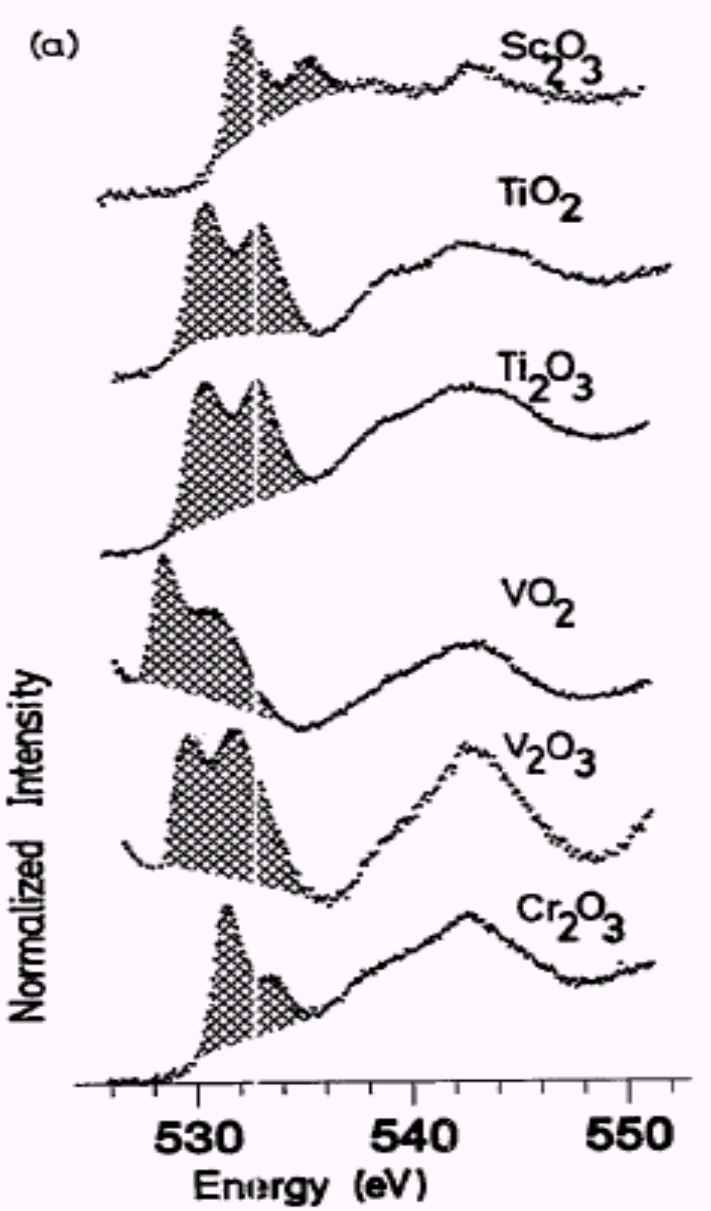
X-ray absorption

Excitation of core electrons to empty states.

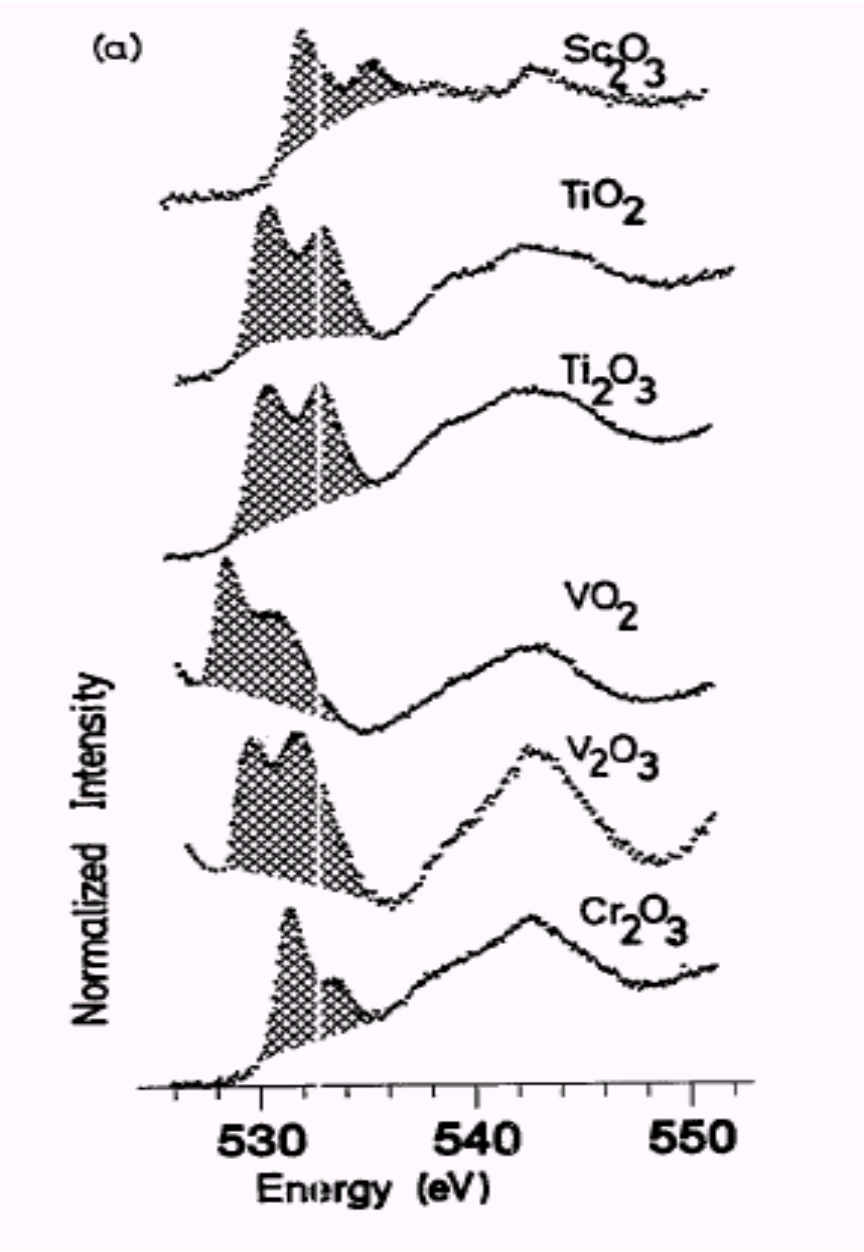
Spectrum given by the **Fermi Golden Rule**
(name Golden Rule given by Fermi; rule itself given by Dirac)

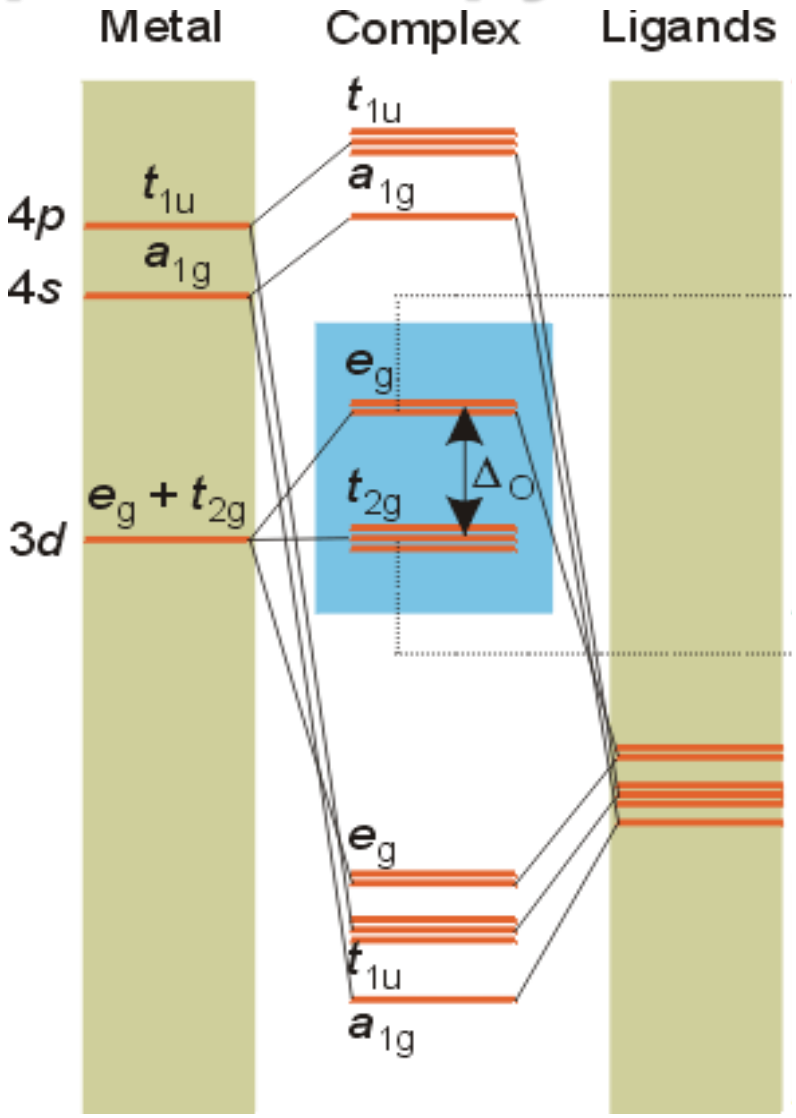
$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \left| \hat{e} \cdot r \right| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray Absorption Spectroscopy

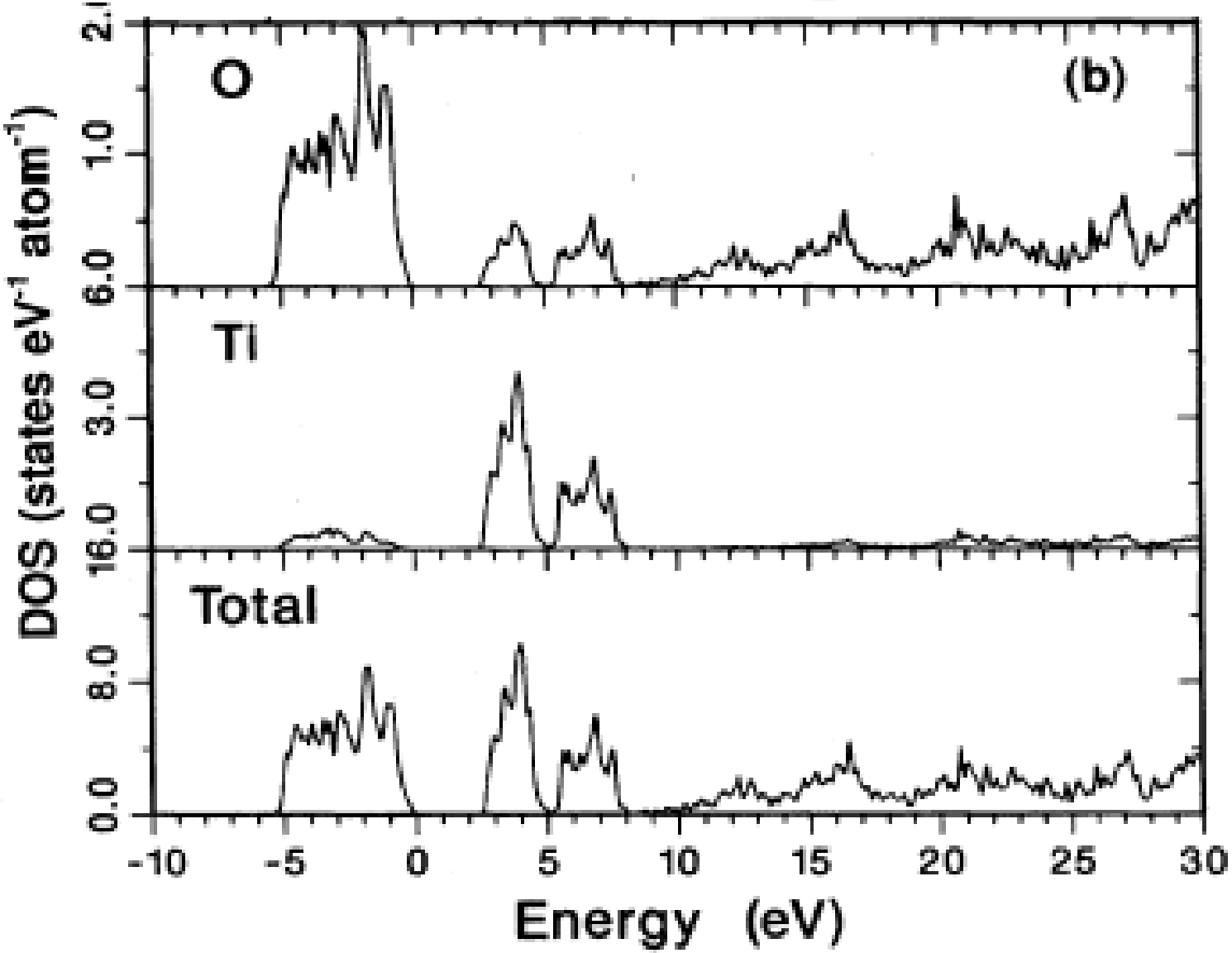


X-ray Absorption Spectroscopy

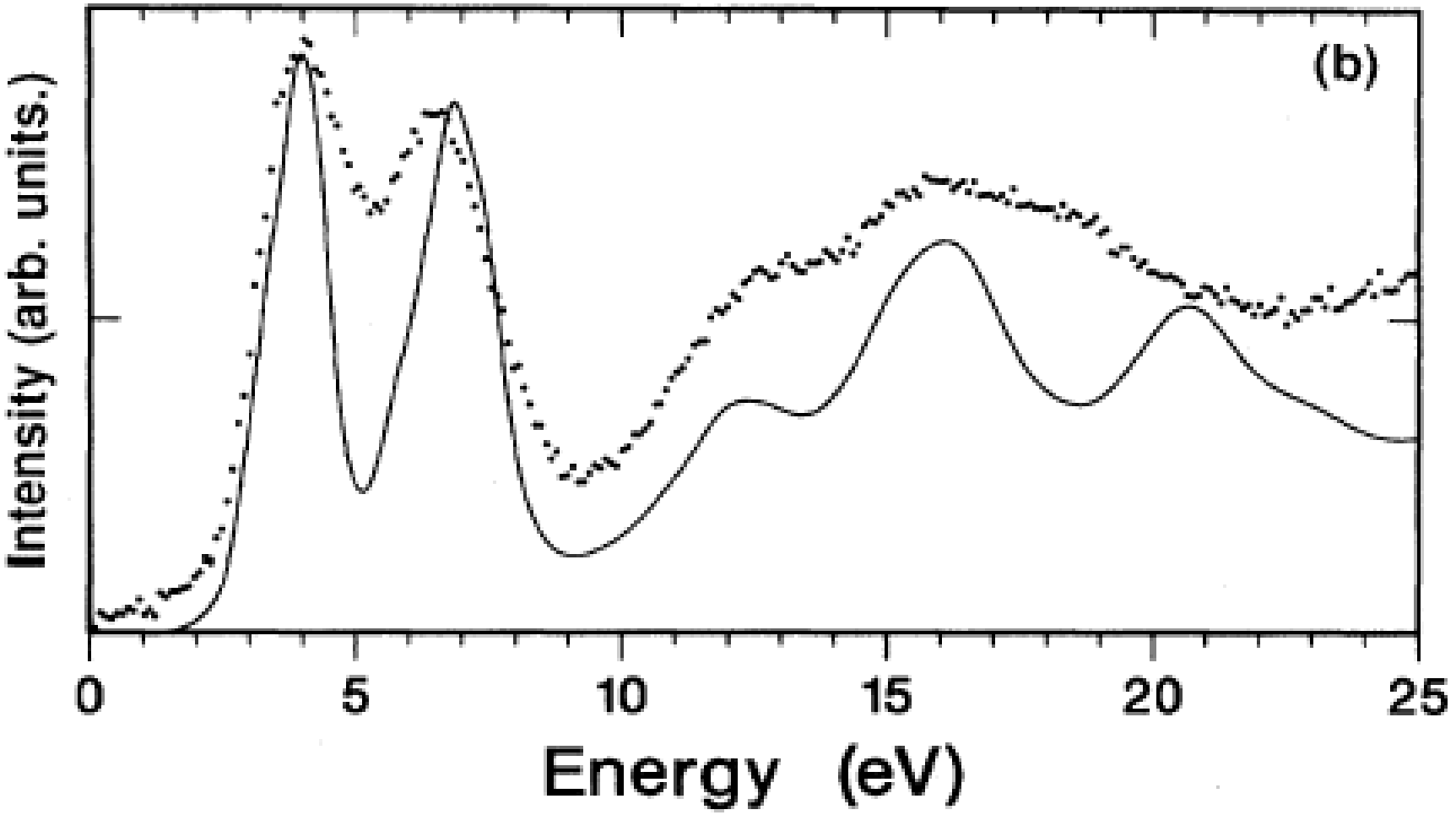




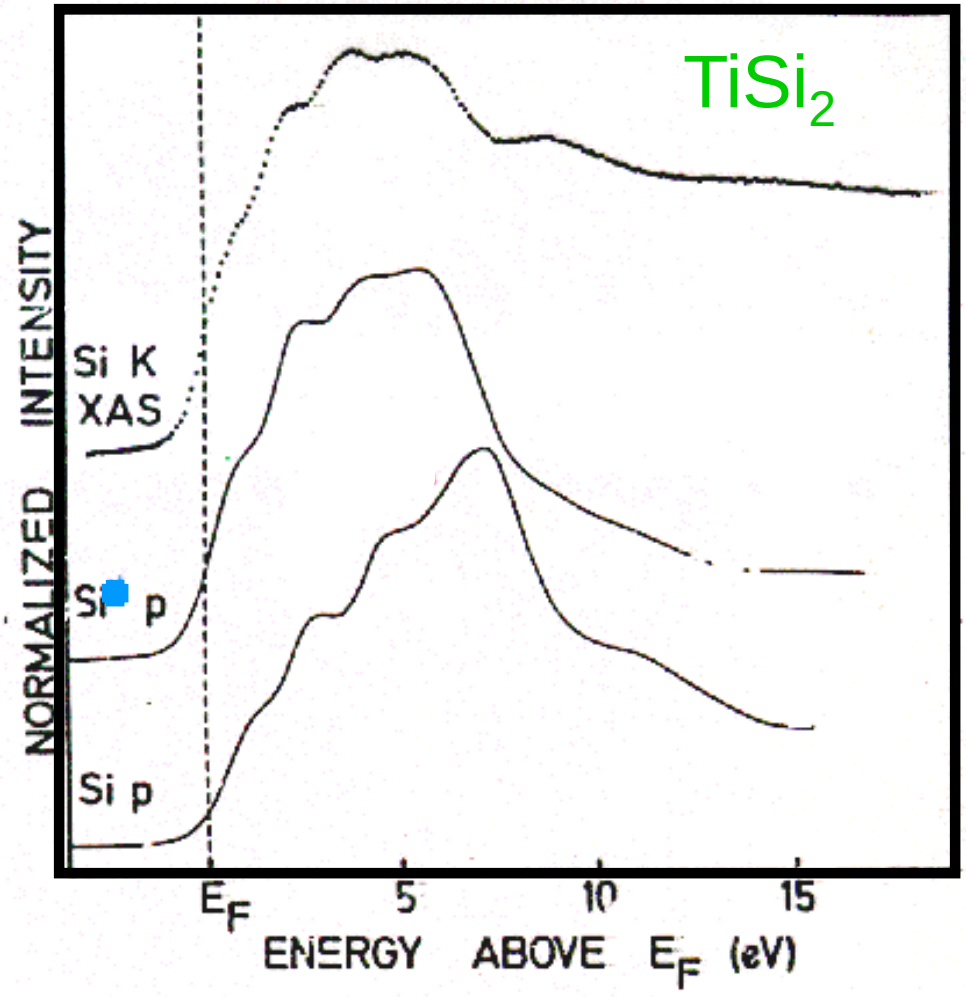
Electronic Structure; TiO_2



Electronic Structure: TiO_2



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

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:

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

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

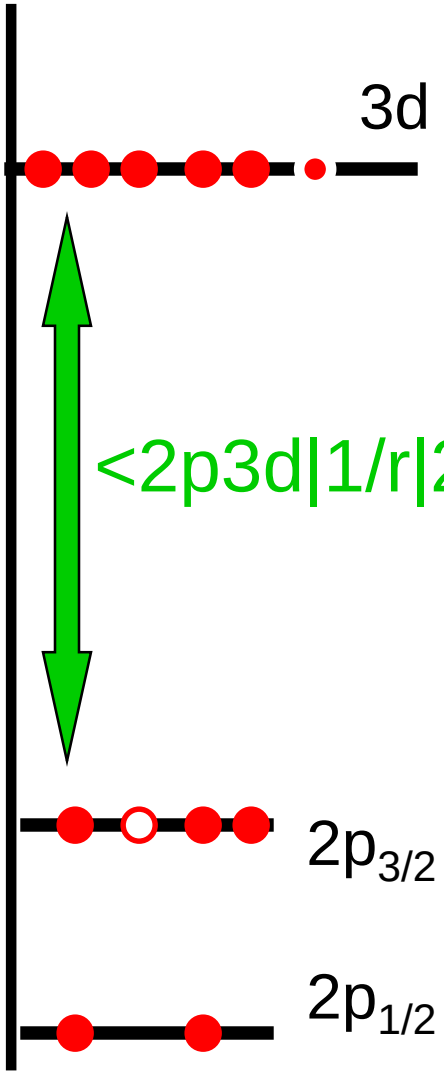
$$= ?? \left| \left\langle \varepsilon \left| \hat{e}_q \cdot r \right| c \right\rangle \right|^2$$

Single electron (excitation) approximation:

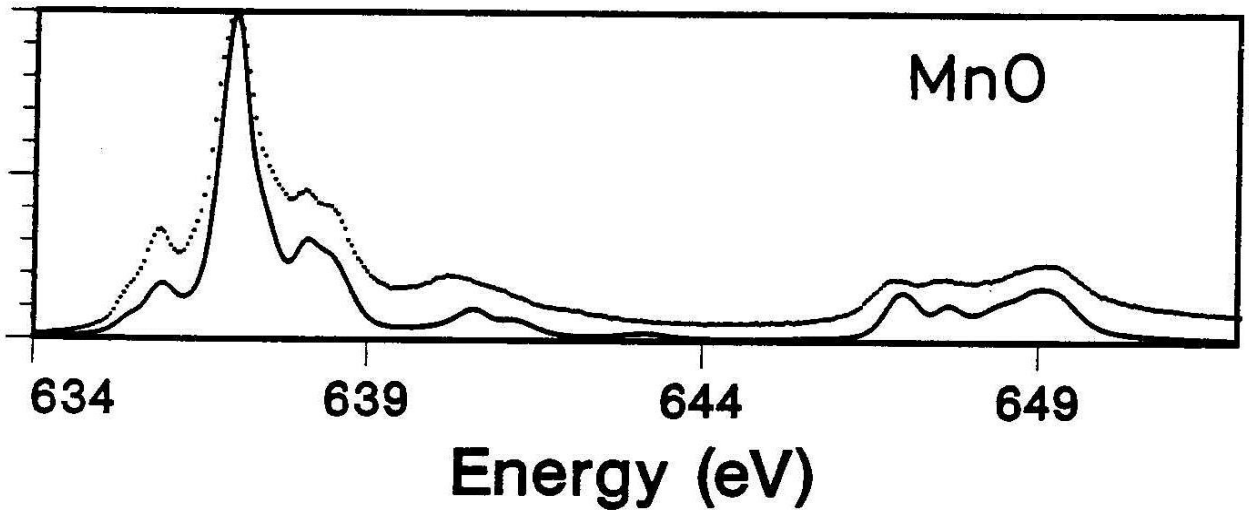
$I_{XAS} = |\langle \varphi_{empty} | \text{dipole} | \varphi_{core} \rangle|^2 \; \rho$

XAS: multiplet effects

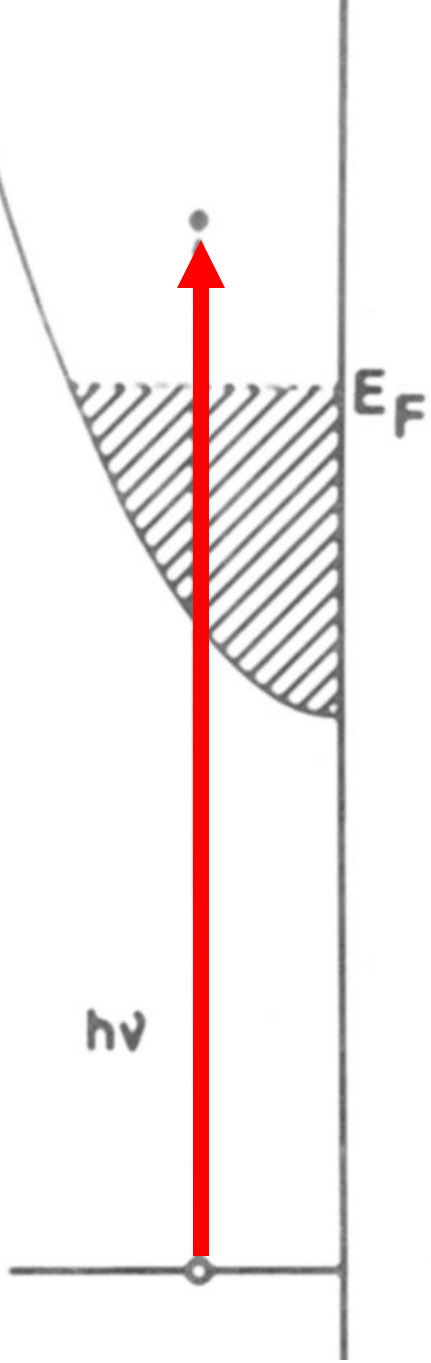
Overlap of core and valence wave functions



→ Single Particle model breaks down



XAS



Single Particle:

1s edges

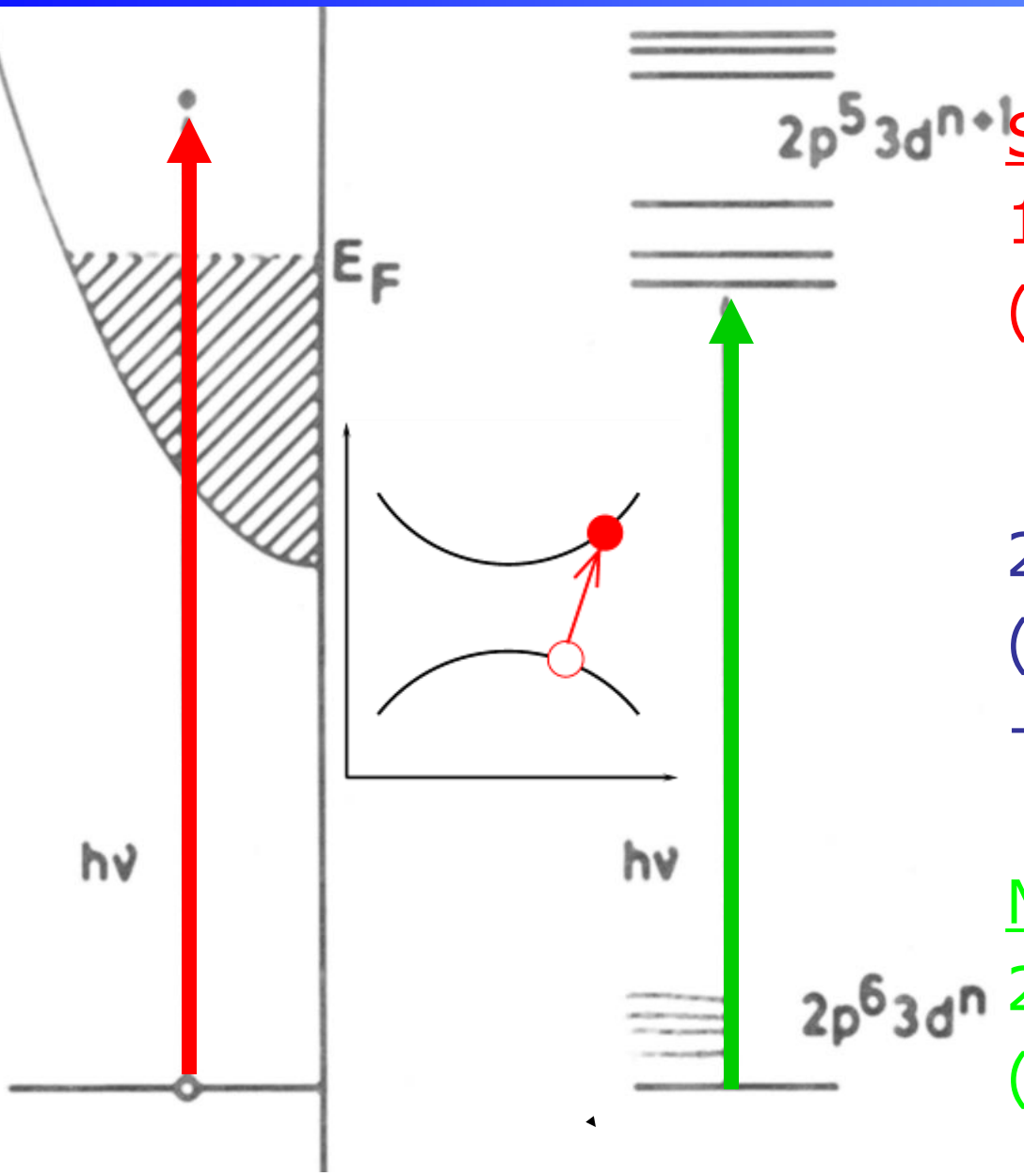
(DFT codes)

Multiplets:

2p, 3s, 3p edges

(CTM4XAS)

XAS: multiplet effects



Single Particle:

1s edges

(DFT + core hole (+U))

2-particle:

(TDDFT, BSE)

+ L edges of $3d^0$

Multiplets:

2p, 3s, 3p edges

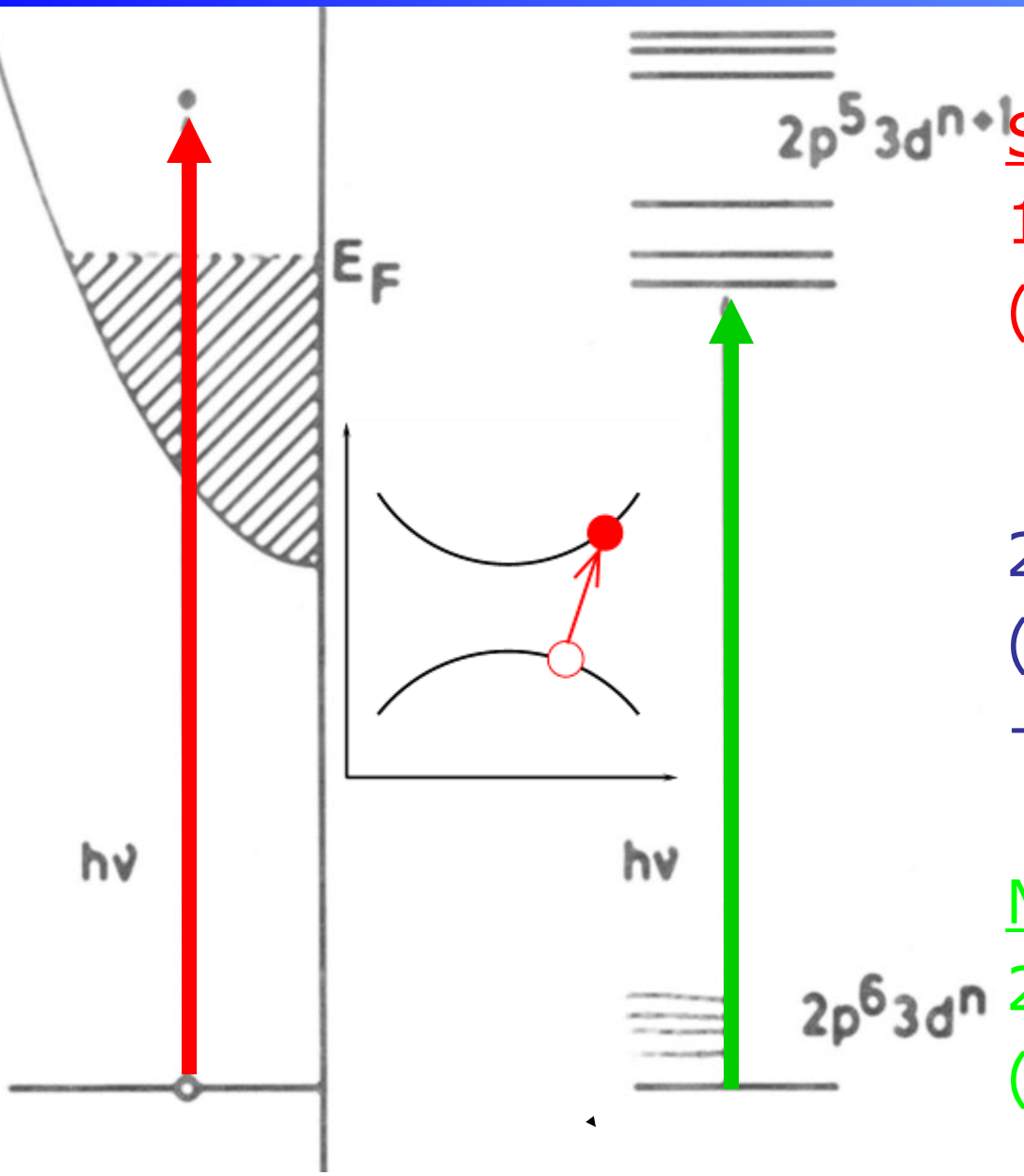
(CTM4XAS)

XAS: recent first principle developments for L edges

- *DFT + projection to cluster multiplet (Haverkort, Uozumi)*
- *Restricted-Active-Space (Odelius, Broer, Kuhn, Neese)*
- *ab-initio multiplets [DFT+CI] (Ikeno, Uldry)*

- *extended BSE (Rehr, Shirley, Joly, Laskowski)*

XAS: multiplet effects



Single Particle:

1s edges

(DFT + core hole (+U))

2-particle:

(TDDFT, BSE)

+ L edges of $3d^0$

Multiplets:

2p, 3s, 3p edges

(CTM4XAS)

Charge Transfer Multiplet program

XAS, EELS, Photoemission, Auger, XES,

Resonant PES, RIXS

ATOMIC PHYSICS

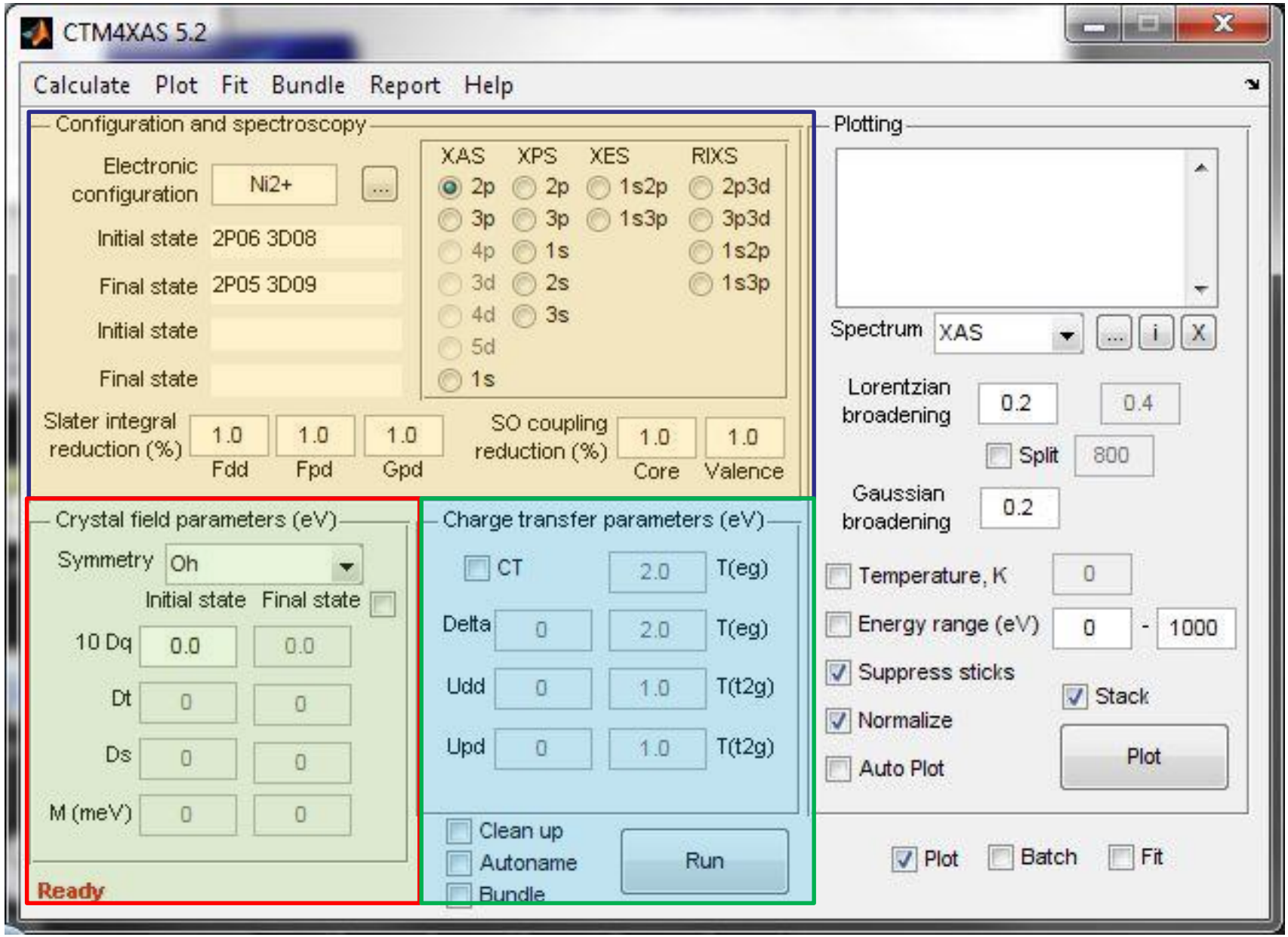
⇓

GROUP THEORY

⇓

MODEL HAMILTONIANS

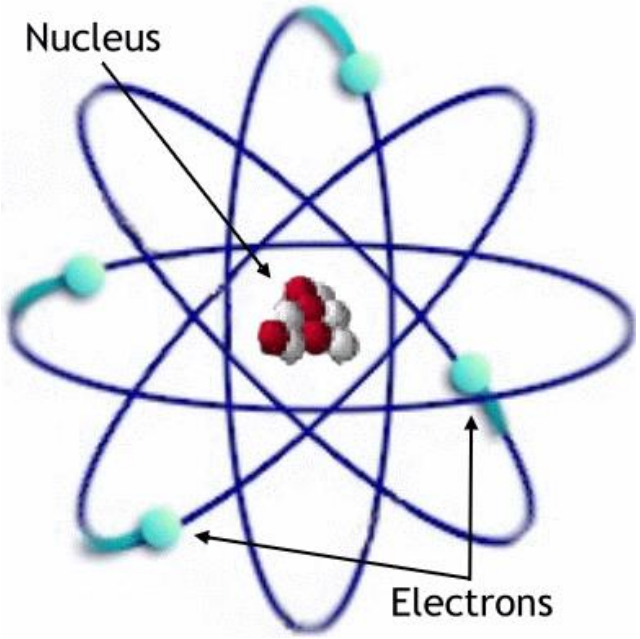
CTM4XAS (semi-empirical)



Atomic Multiplet Theory

$$H\Psi=E\Psi$$

$$H = \sum_{N} \frac{p_i^2}{2m} + \sum_{N} \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_{N} \zeta(r_i)\, l_i \cdot s_i$$

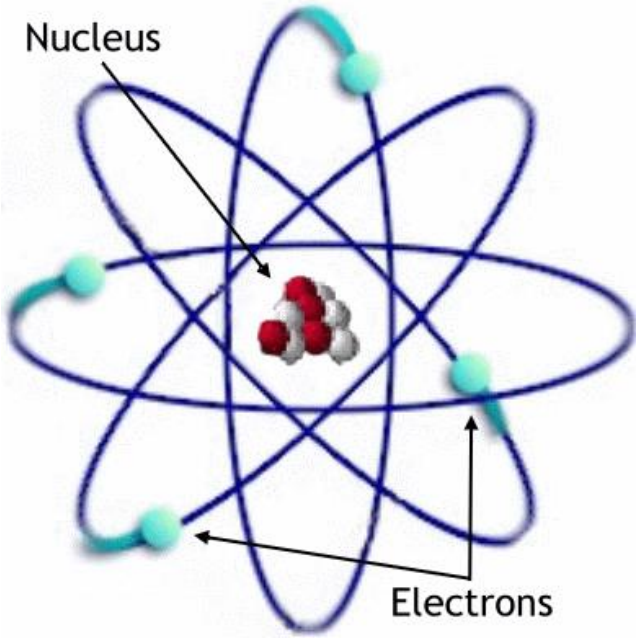


- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling

Atomic Multiplet Theory

$$H\Psi=E\Psi$$

$$H = \sum_{N} \frac{p_i^2}{2m} + \sum_{N} \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_{N} \zeta(r_i)\, l_i \cdot s_i$$



- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling

Atomic Multiplet Theory

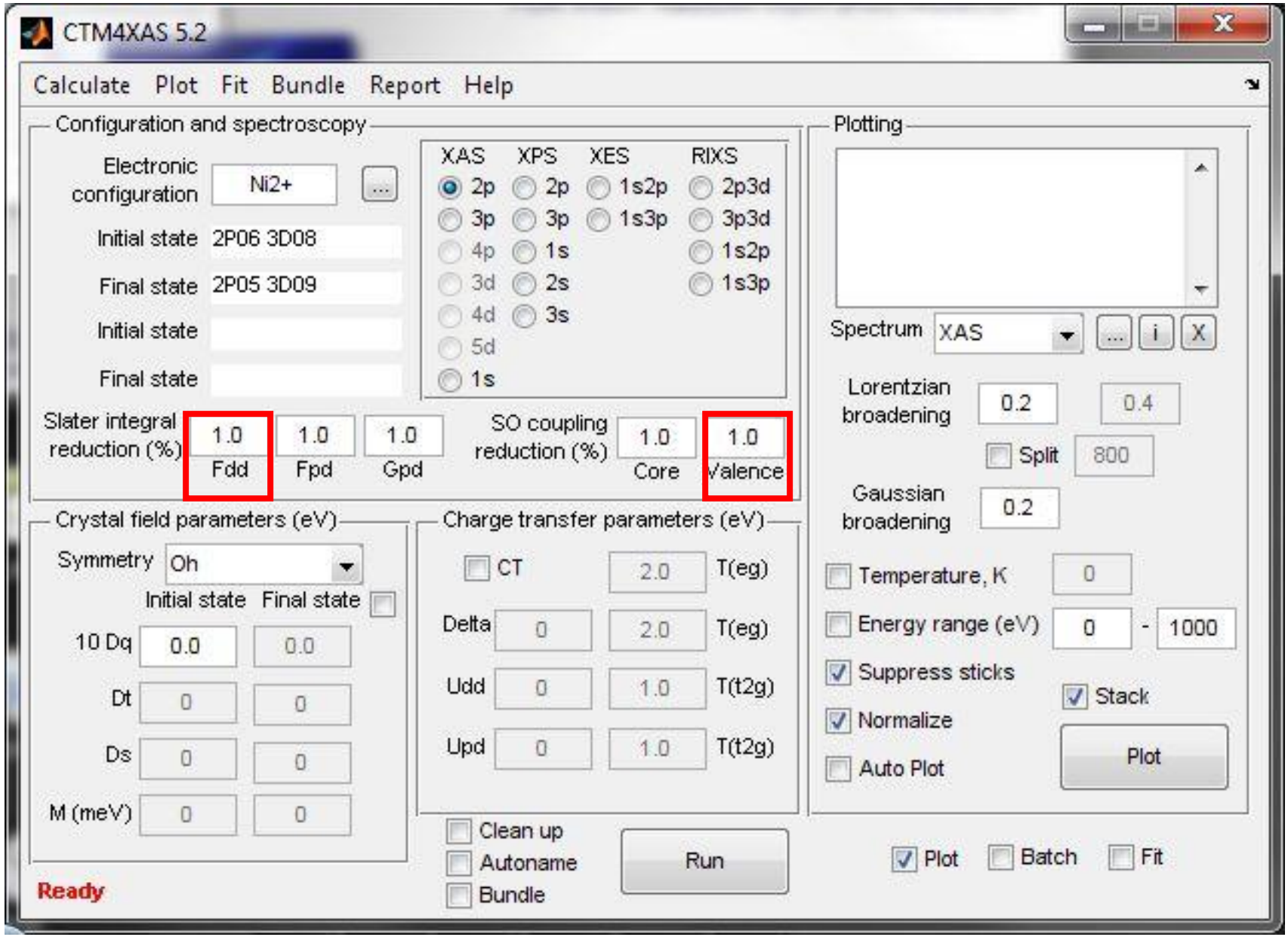
$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k$$

Electron-electron interactions of Valence States

$$H_{ATOM} = \sum_N \zeta(r_i)\, l_i \cdot s_i$$

Valence Spin-orbit coupling

CTM4XAS version 5.2



Atomic Multiplet Theory

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

Core Valence Overlap

$$H_{ATOM} = \sum_N \zeta(r_i)\, l_i \cdot s_i$$

Core Spin-orbit coupling

Hunds rules

- Term symbols with **maximum spin** S are lowest in energy,
- Among these terms:

Term symbols with **maximum L** are lowest in energy

- In the presence of spin-orbit coupling, the lowest term has
- J = |L-S| if the shell is less than half full
- **J = L+S** if the shell is more than half full

Hunds rules

max S > max L > max J (if more than half full)

What is the Hund's rule ground states for $3d^2$?

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

Hunds rules

max S > max L > max J (if more than half full)

What is the Hund's rule ground states for $3d^2$?

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

L=3, S=1

J=2 Term symbol = $^3F_2$

Hunds rules

max S > max L > max J (if more than half full)

What is the Hund's rule ground states for $3d^2$?

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

$$f_k = (2l_1 + 1)(2l_2 + 1)(-1)^L \begin{pmatrix} l_1 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix}$$

See the slides **EXTRA Slater Integrals** for more information

Hunds rules

What is the Hund's rule ground states for $3d^2$?

	f_2		f_4		Energy
^1S	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 0\\ 2 & 2 & 2\end{Bmatrix}$	2/7	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 0\\ 2 & 2 & 4\end{Bmatrix}$	2/7	$0.46F^2$
^3P	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 1\\ 2 & 2 & 2\end{Bmatrix}$	3/21	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 1\\ 2 & 2 & 4\end{Bmatrix}$	–4/21	$0.02F^2$
^1D	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 2\\ 2 & 2 & 2\end{Bmatrix}$	–3/49	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 2\\ 2 & 2 & 4\end{Bmatrix}$	4/49	$-0.01F^2$
^3F	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 3\\ 2 & 2 & 2\end{Bmatrix}$	–8/49	$-\frac{10}{7}\begin{Bmatrix}2 & 2 & 3\\ 2 & 2 & 4\end{Bmatrix}$	–1/49	$-0.18F^2$
^1G	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 4\\ 2 & 2 & 2\end{Bmatrix}$	4/49	$\frac{10}{7}\begin{Bmatrix}2 & 2 & 4\\ 2 & 2 & 4\end{Bmatrix}$	1/441	$0.08F^2$

Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

ATOMIC PHYSICS

⇓

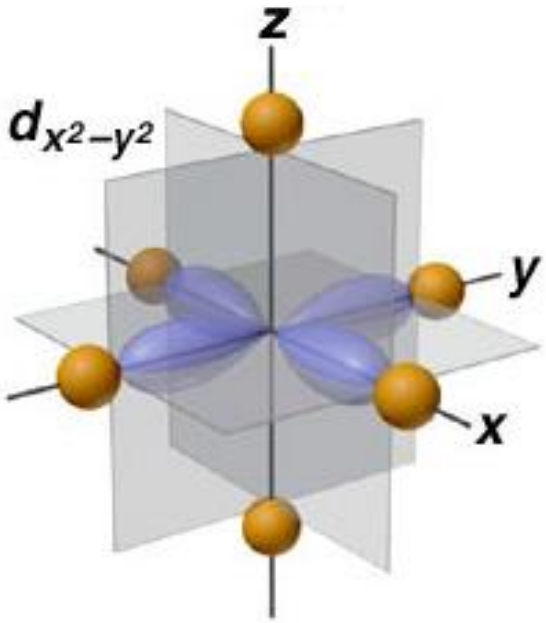
GROUP THEORY

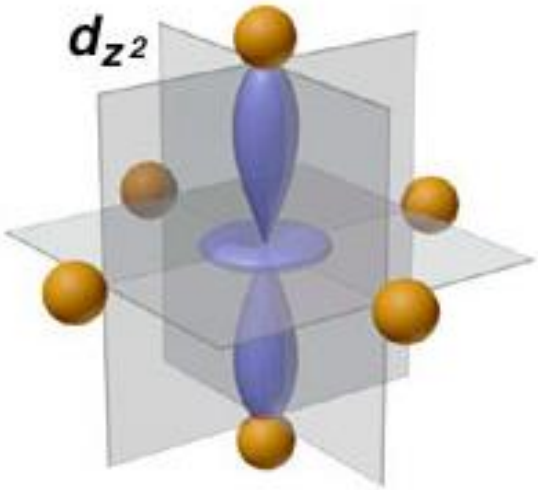
⇓

MODEL HAMILTONIANS

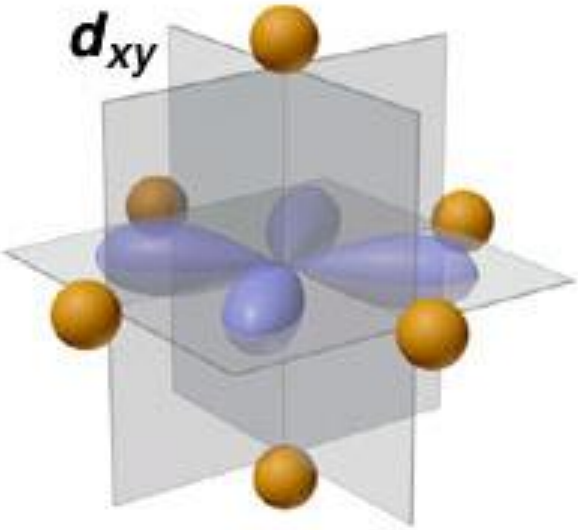
Crystal Field Effects

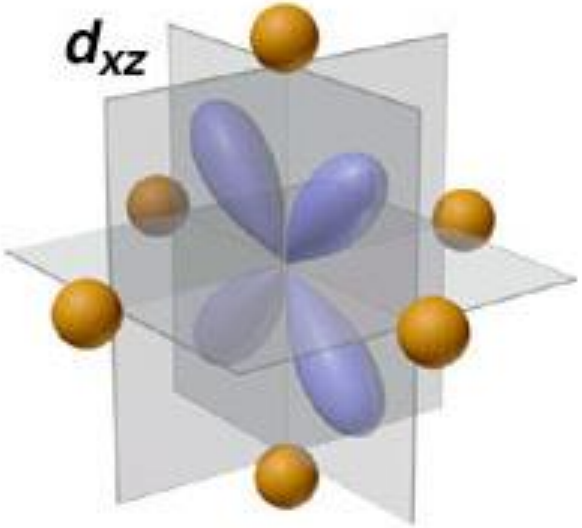
e_g states

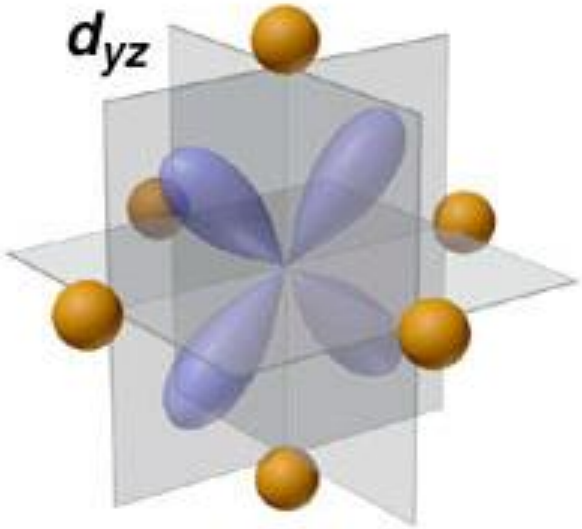




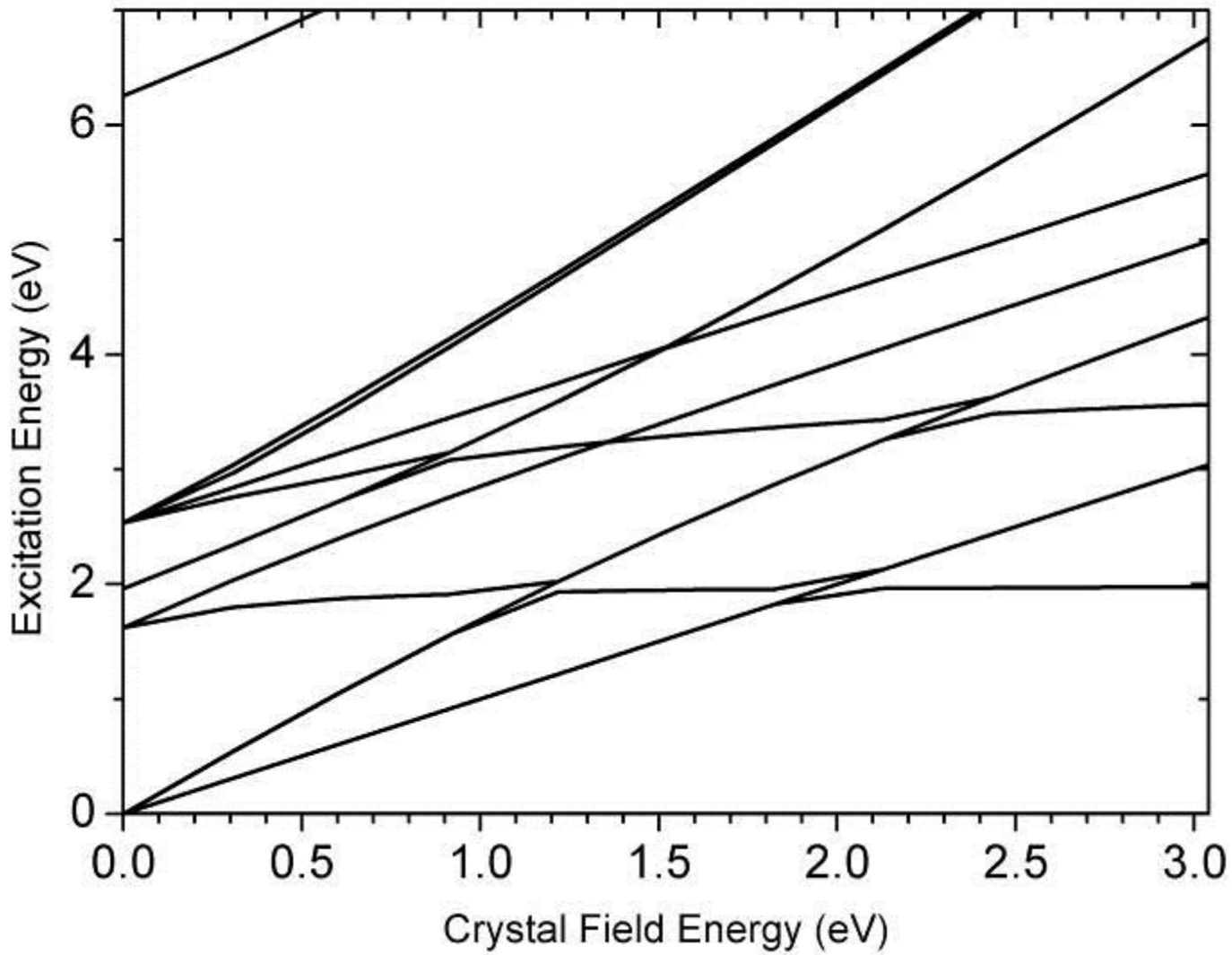
t_{2g} states



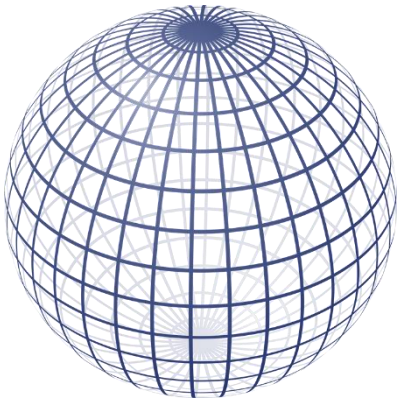


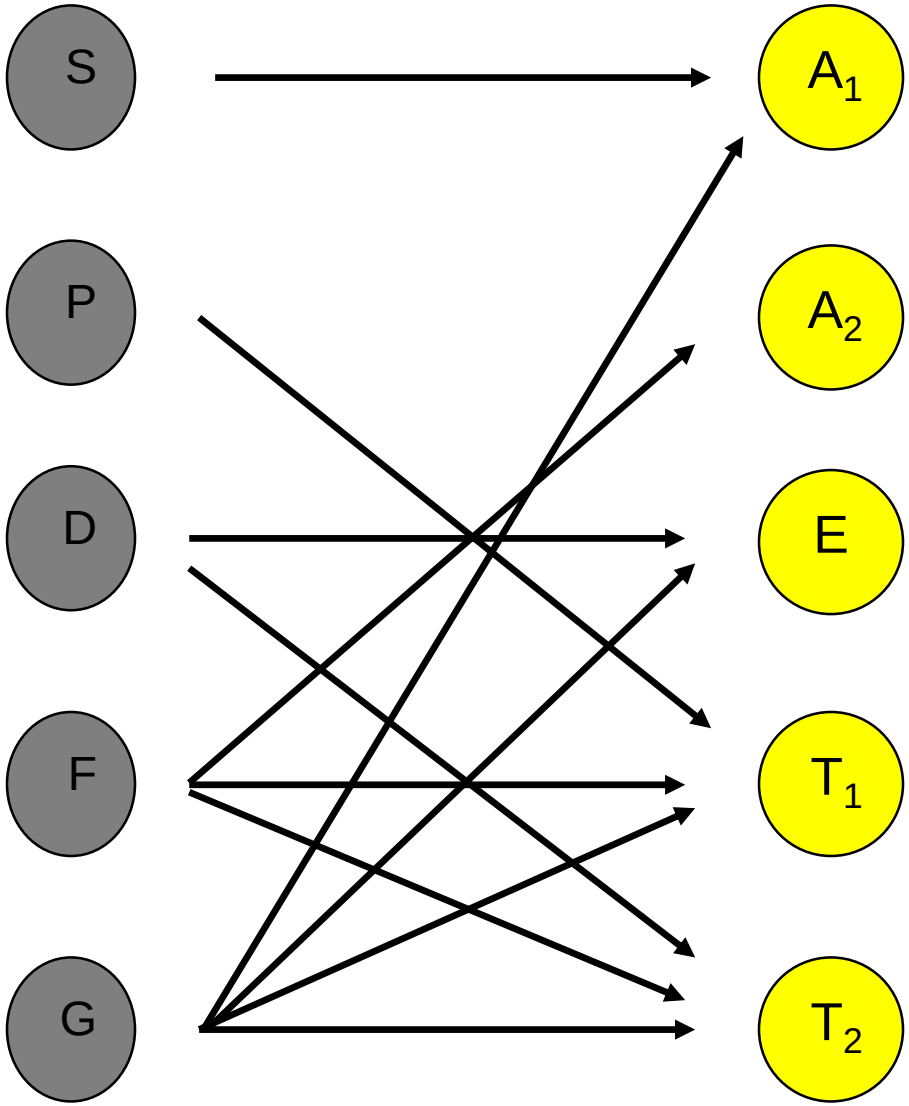


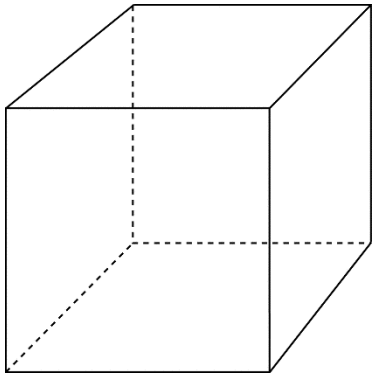
Crystal Field Effects: Tanabe-Sugano



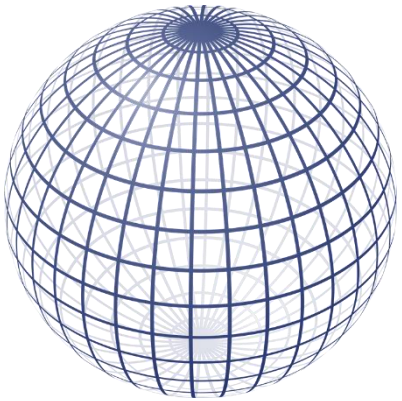
Crystal Field Effects: branching rules

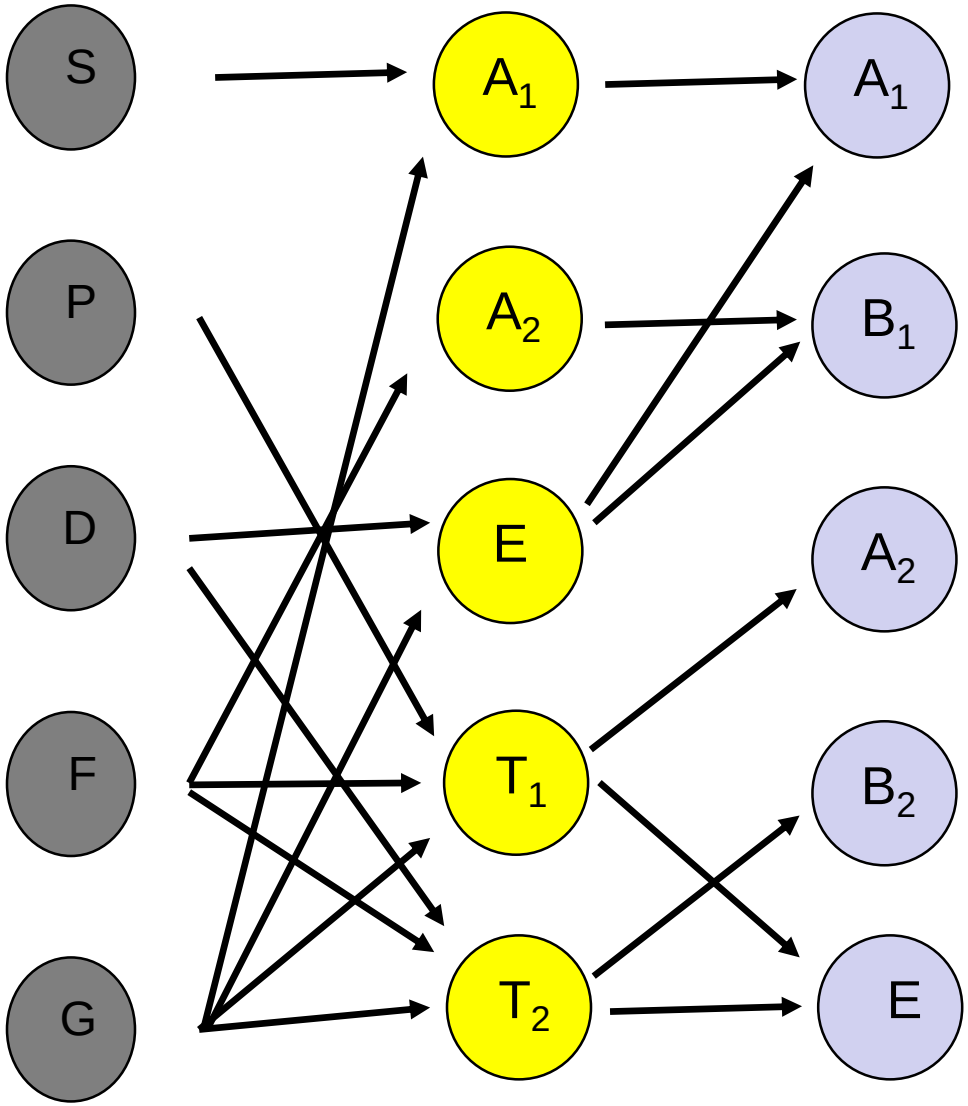


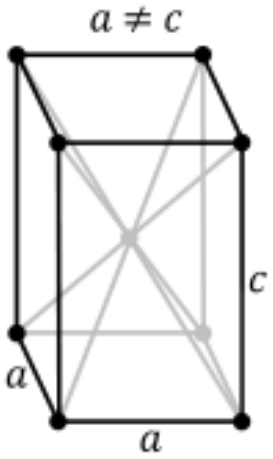




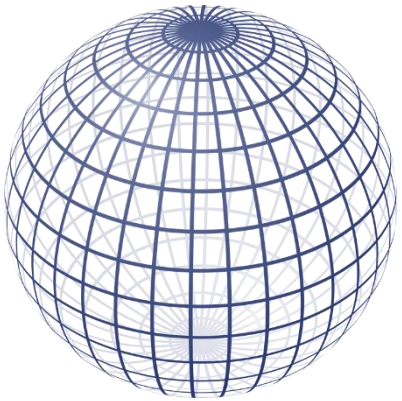
Crystal Field Effects: branching rules

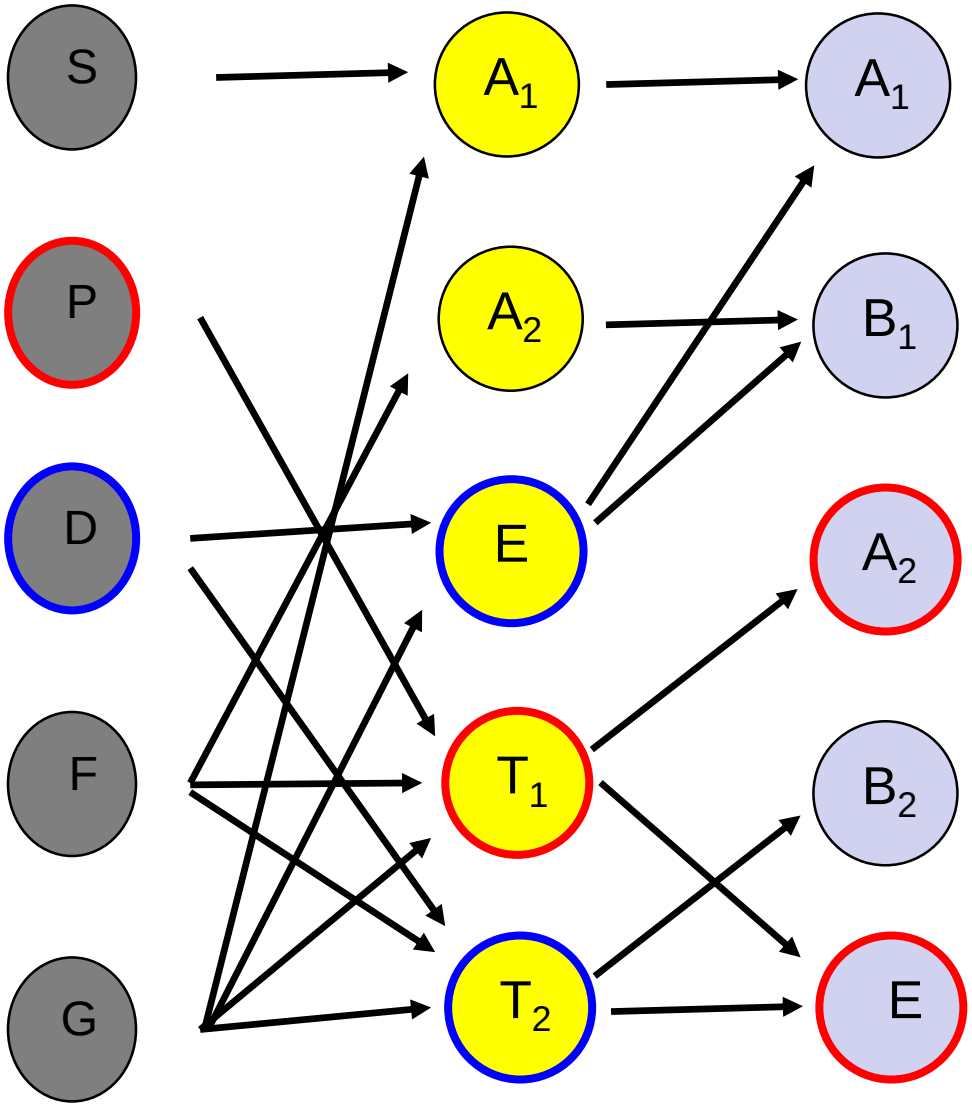


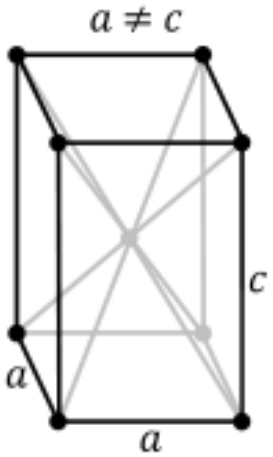




Crystal Field Effects: branching rules

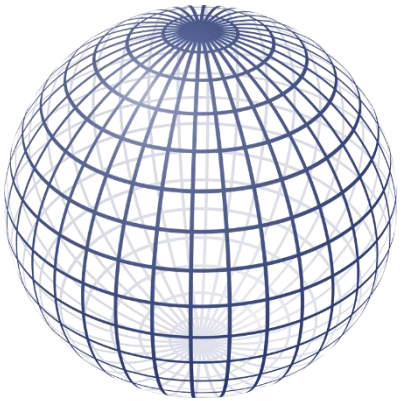


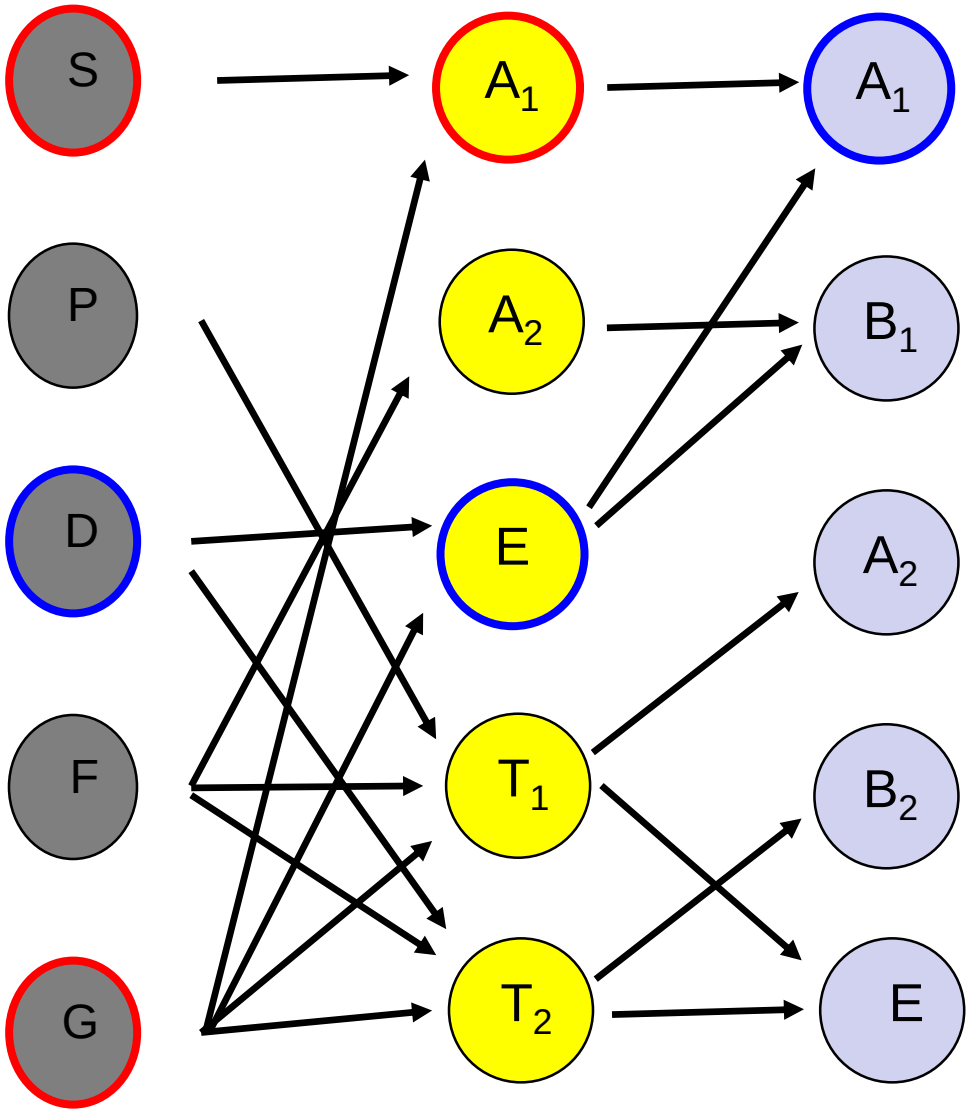


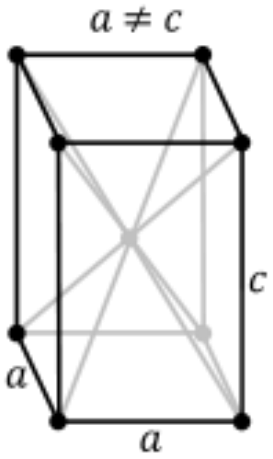


Dipole & Quadrupole

Crystal Field Effects: branching rules

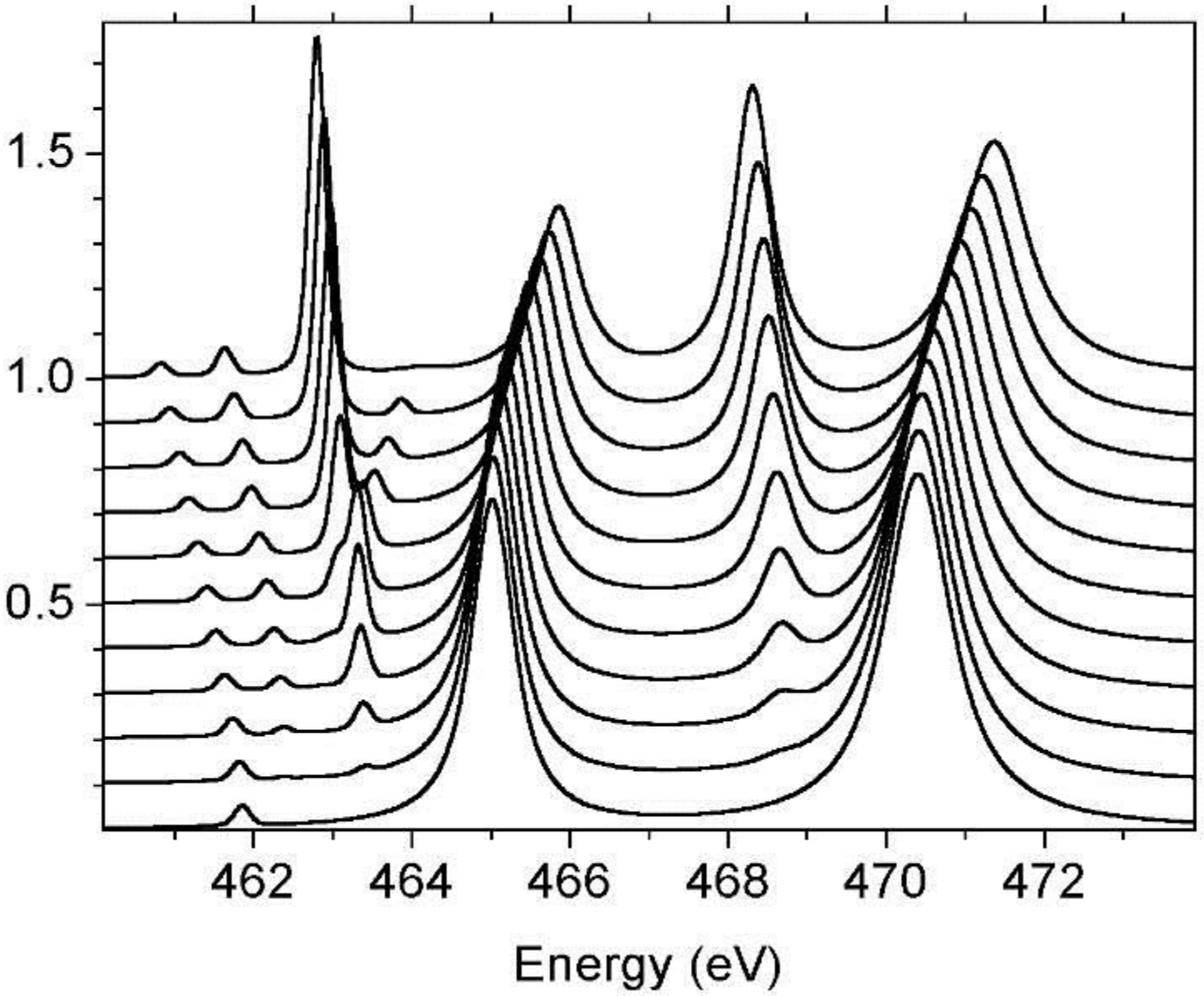




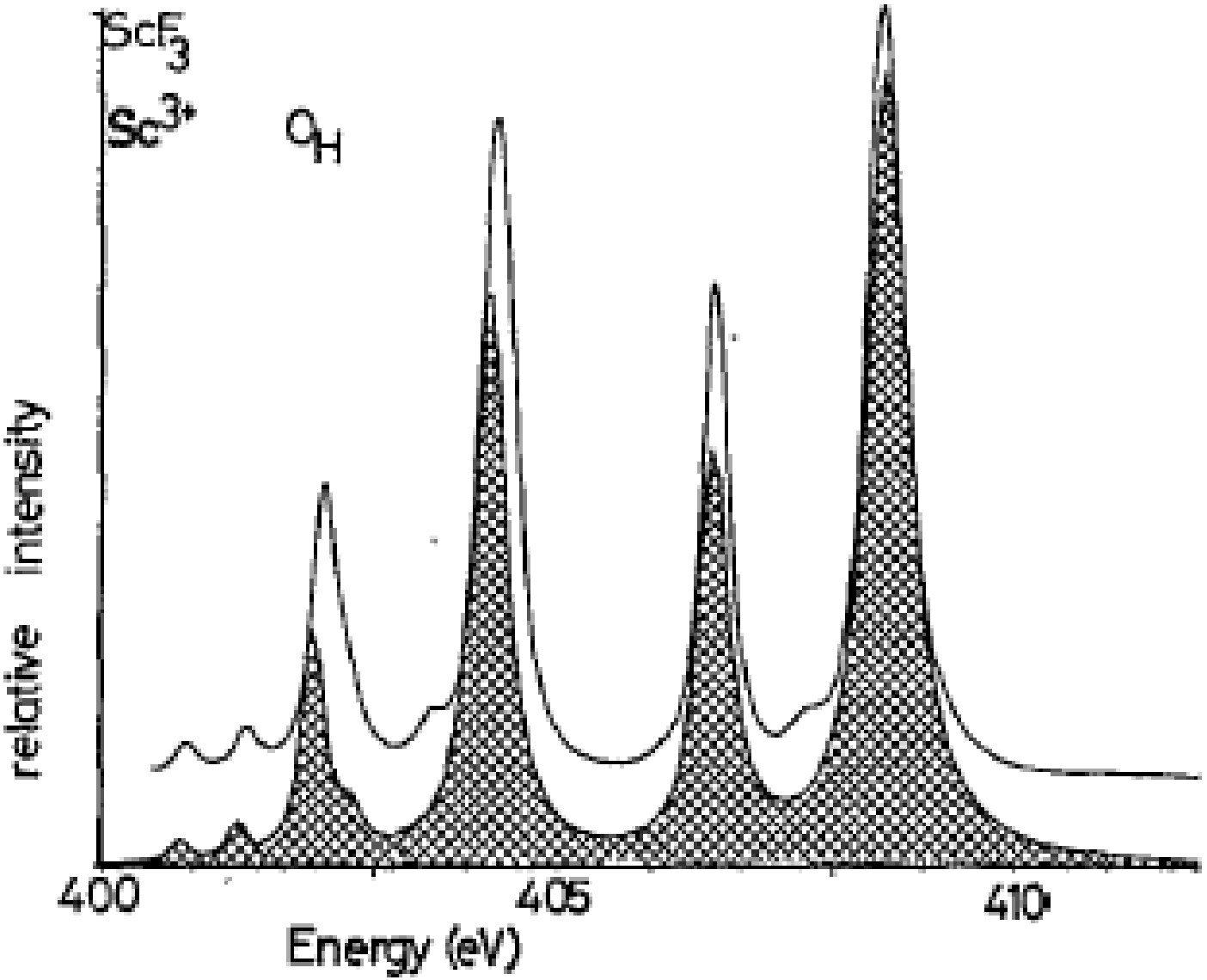


Hamiltonian (atomic, 10Dq, Ds, Dt)

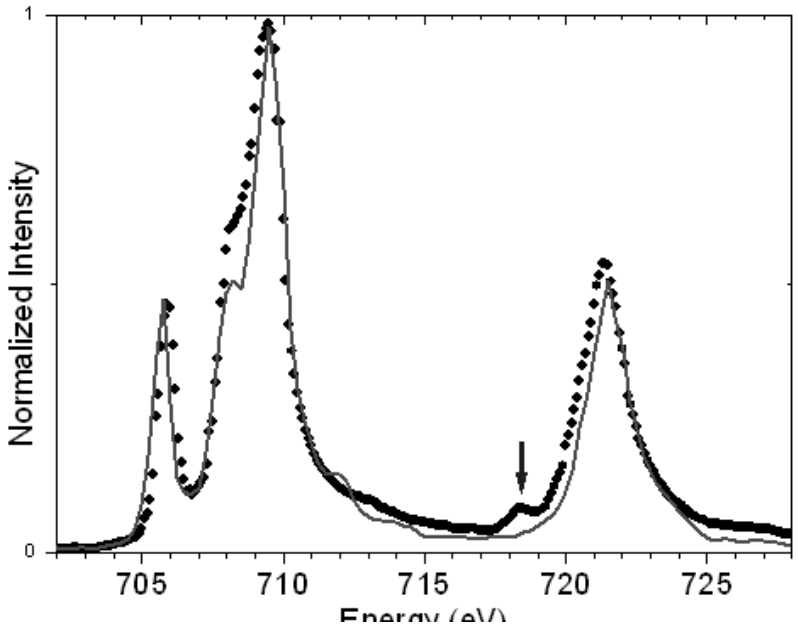
Effect of 10Dq on XAS:$3d^0$

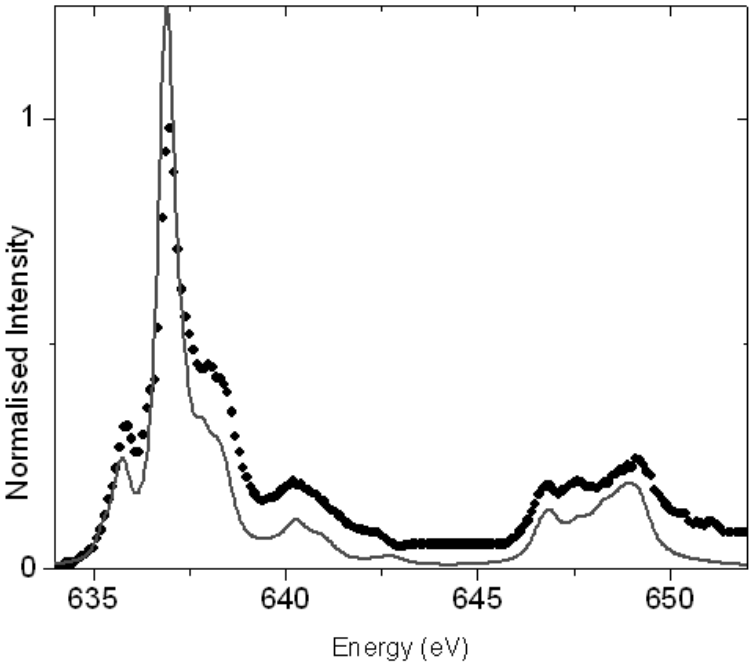


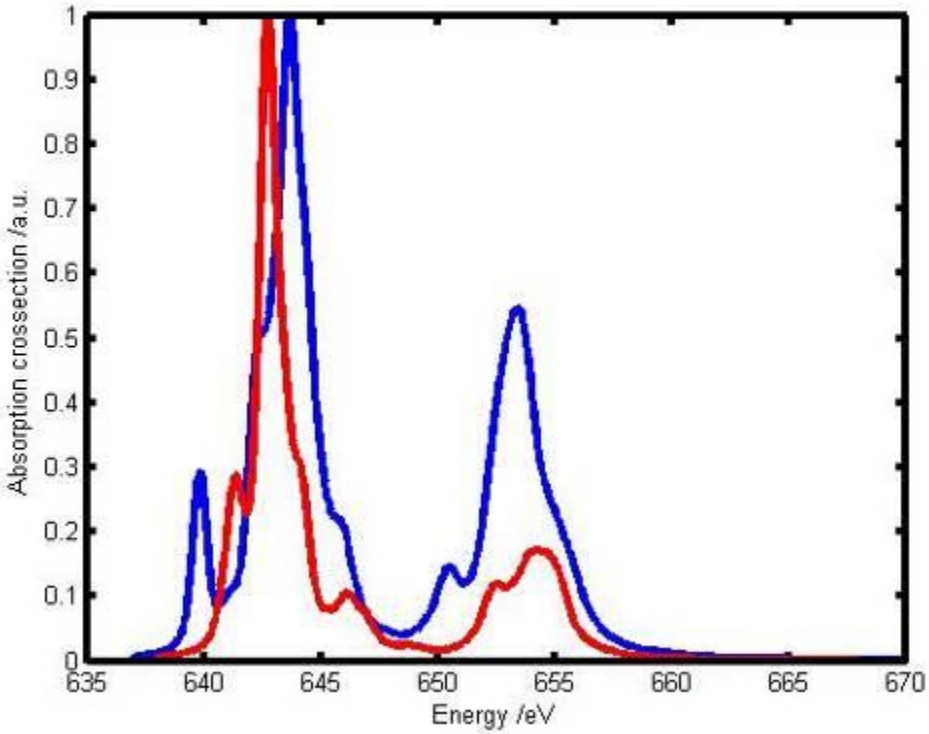
Comparison with Experiment



2p XAS of Mn2+


Normalized Intensity
1
0
705
710
715
720
725


Normalised Intensity
1
0
635
640
645
650
Energy (eV)


Absorption crossection /a.u.
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
635
640
645
650
655
660
665
670
Energy /eV

Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

ATOMIC PHYSICS

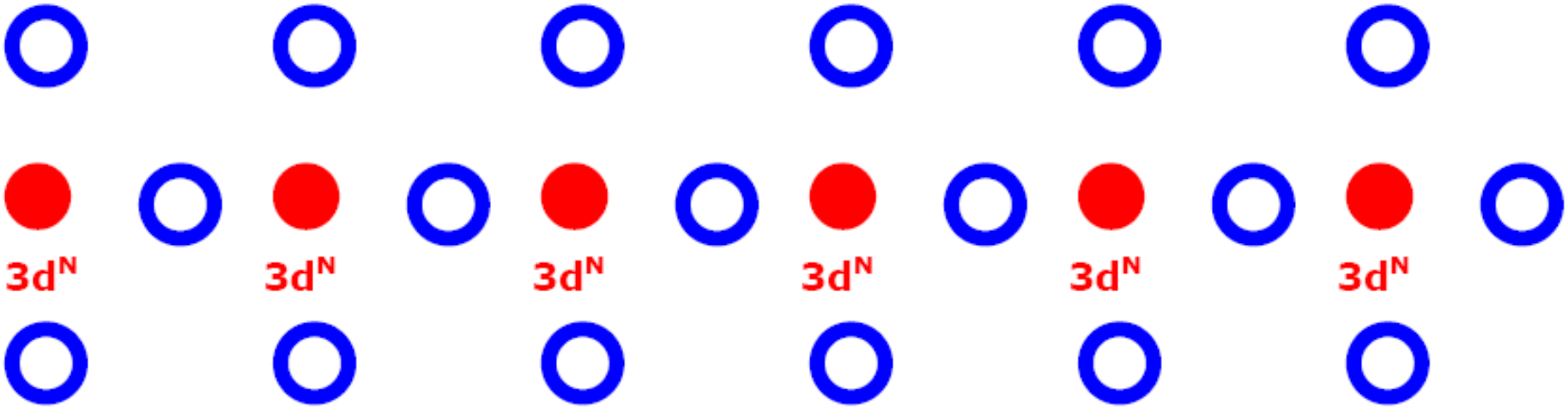
⇓

GROUP THEORY

⇓

MODEL HAMILTONIANS

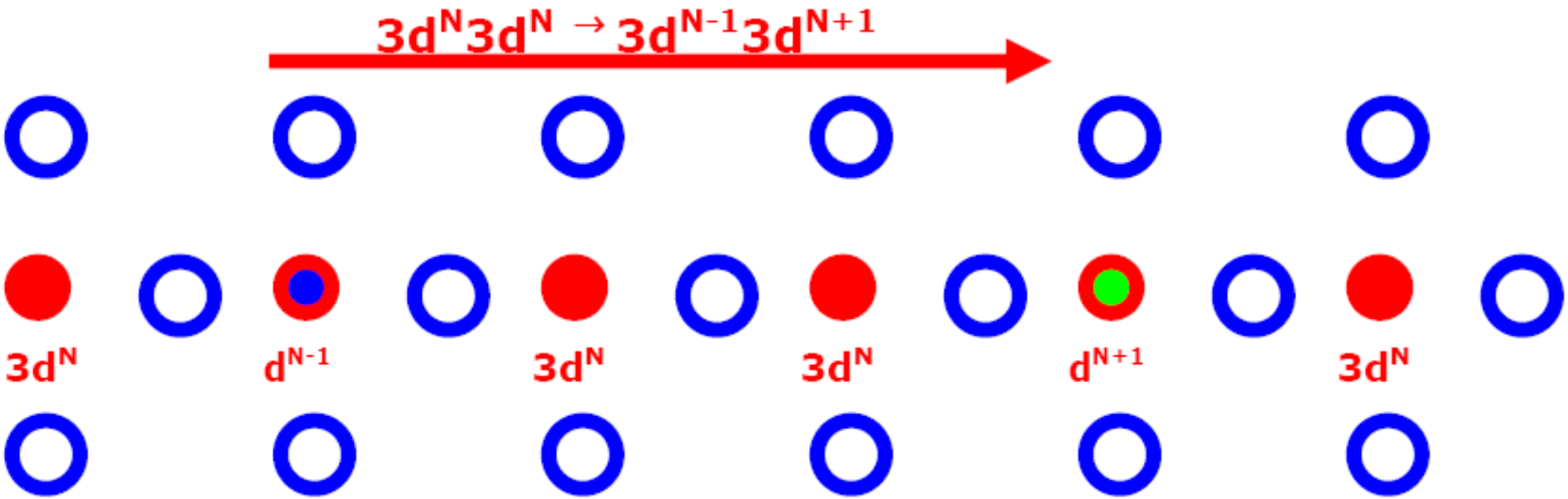
Charge Transfer Effects



Ground state of a transition metal system
$3d^N$ at every site

Charge fluctations

Charge Transfer Effects



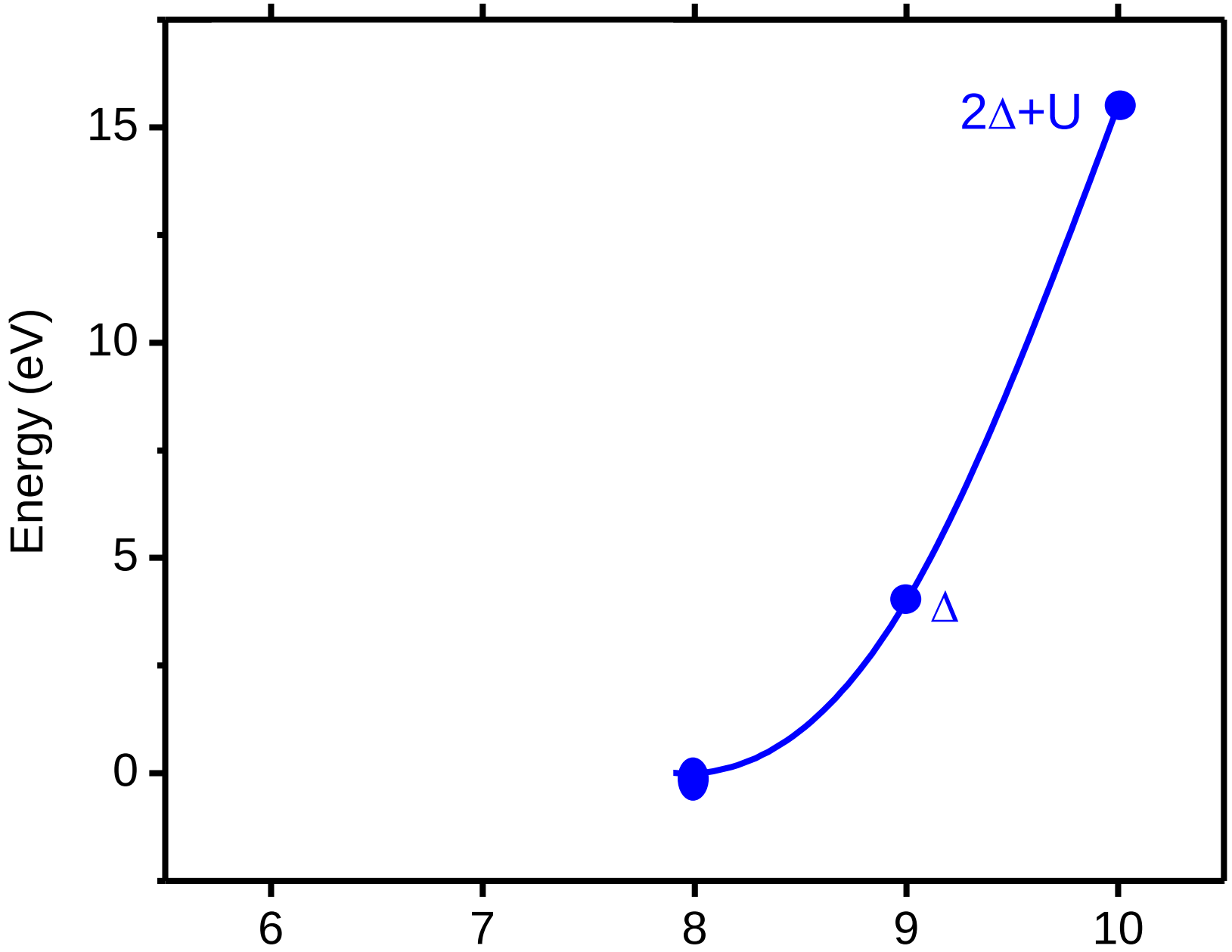
Hubbard U for a $3d^8$ ground state:

U= $E(3d^7) + E(3d^9) – E(3d^8) – E(3d^8)$

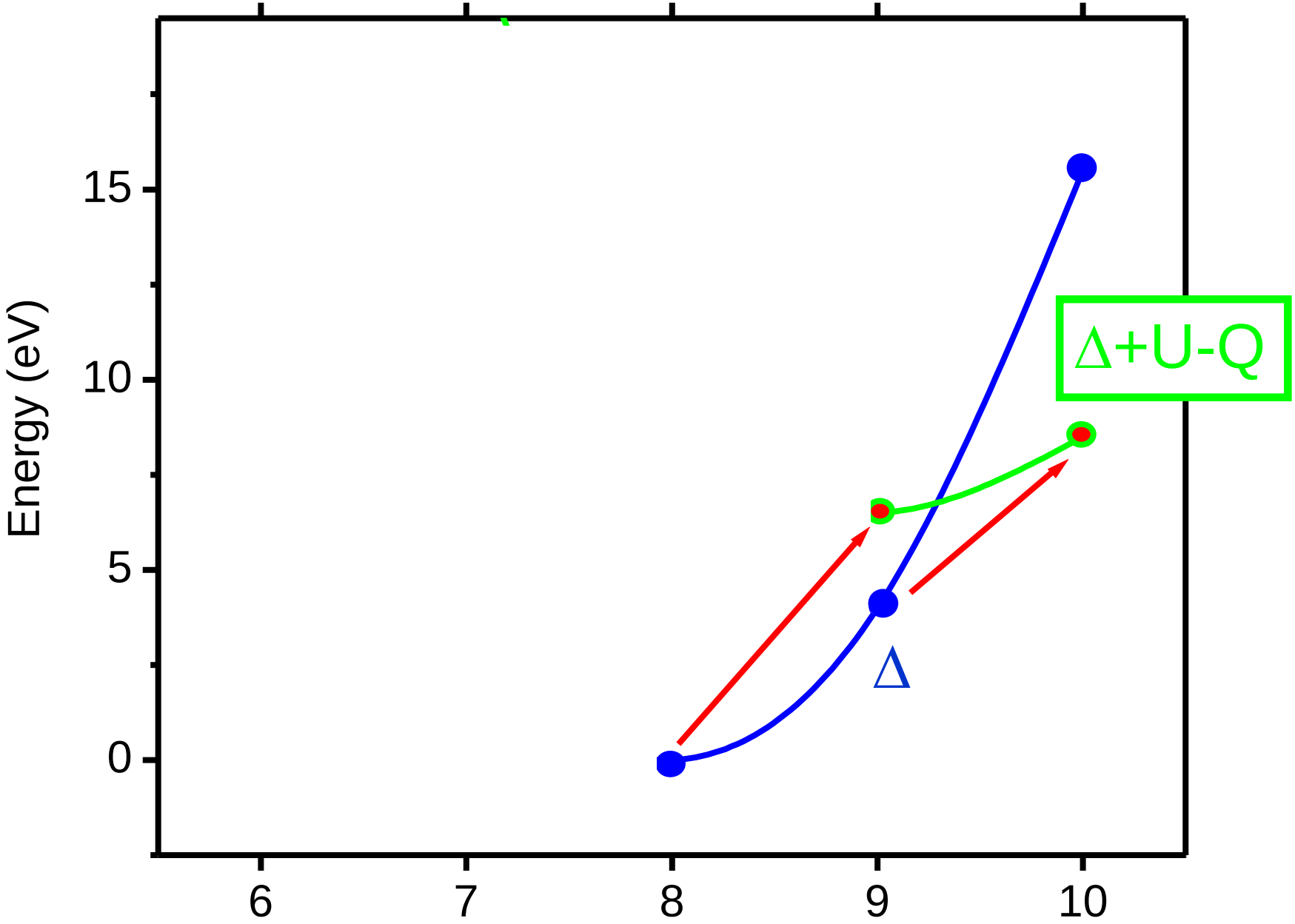
Ligand-to-Metal Charge Transfer (LMCT):

$\Delta = E(3d^9\underline{L}) – E(3d^8)$

Charge Transfer Effects



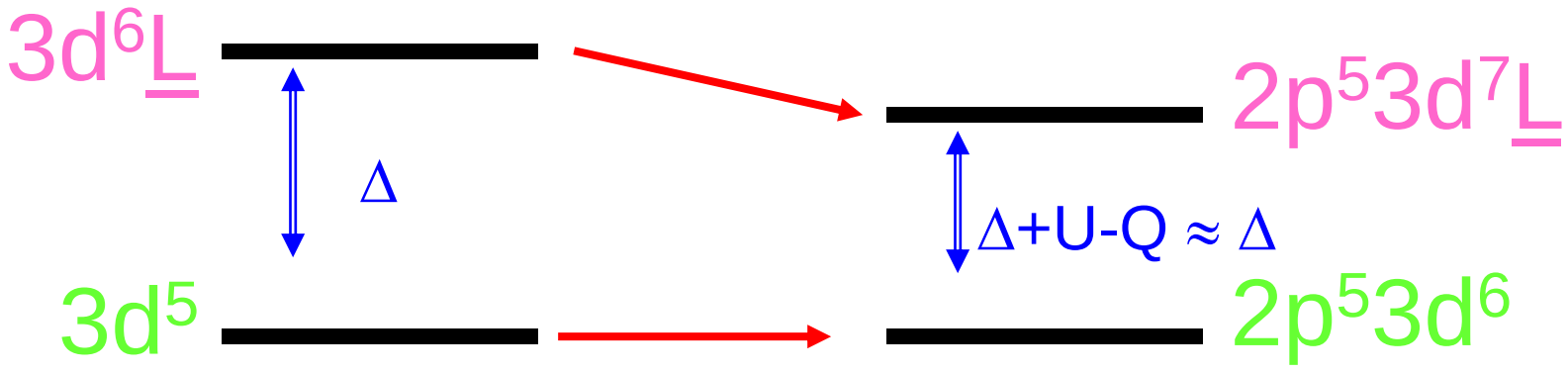
Charge Transfer Effects in XAS



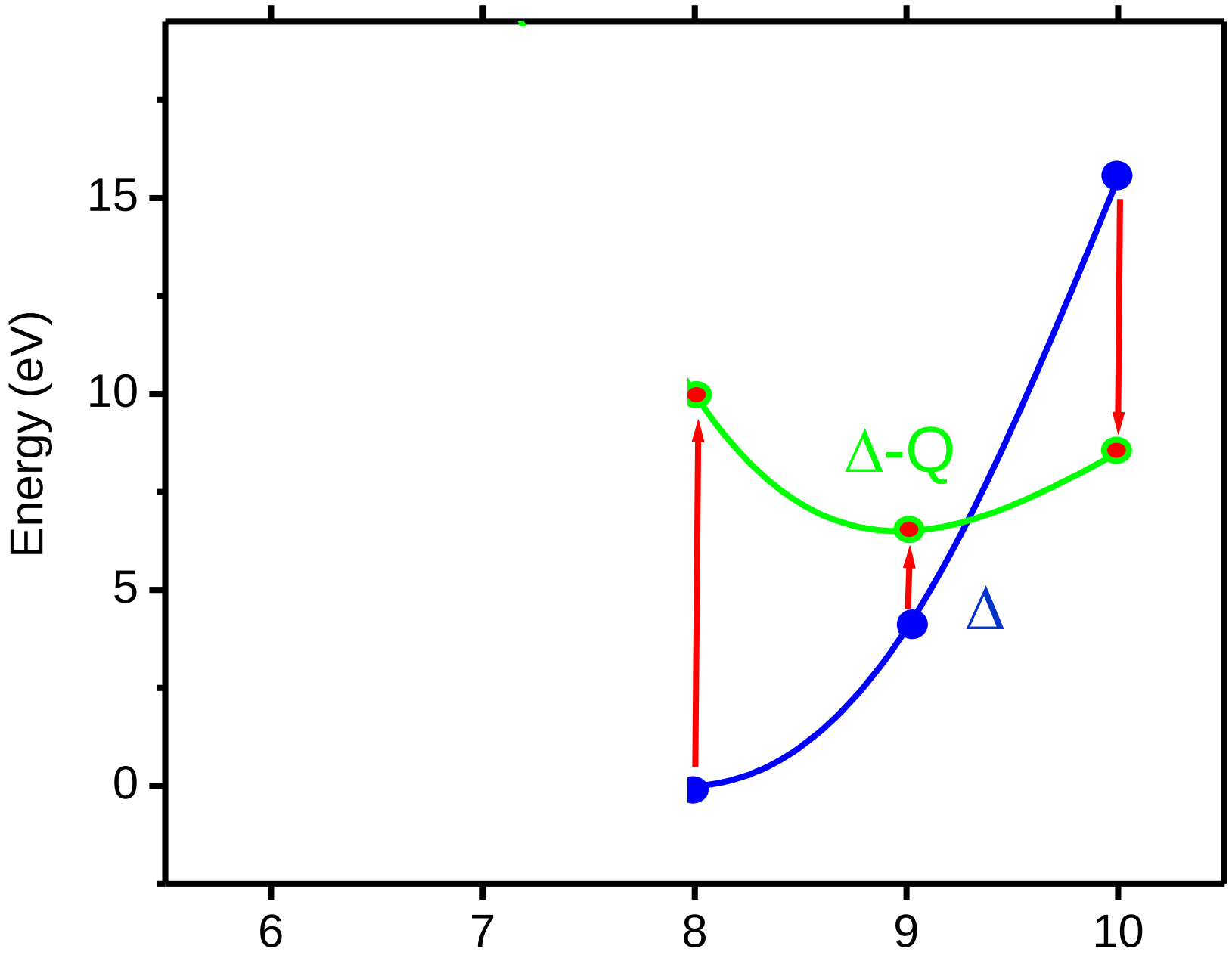
Charge Transfer Effects

MnO: Ground state: $3d^5 + 3d^6\underline{L}$

Energy of $3d^6\underline{L}$: Charge transfer energy Δ

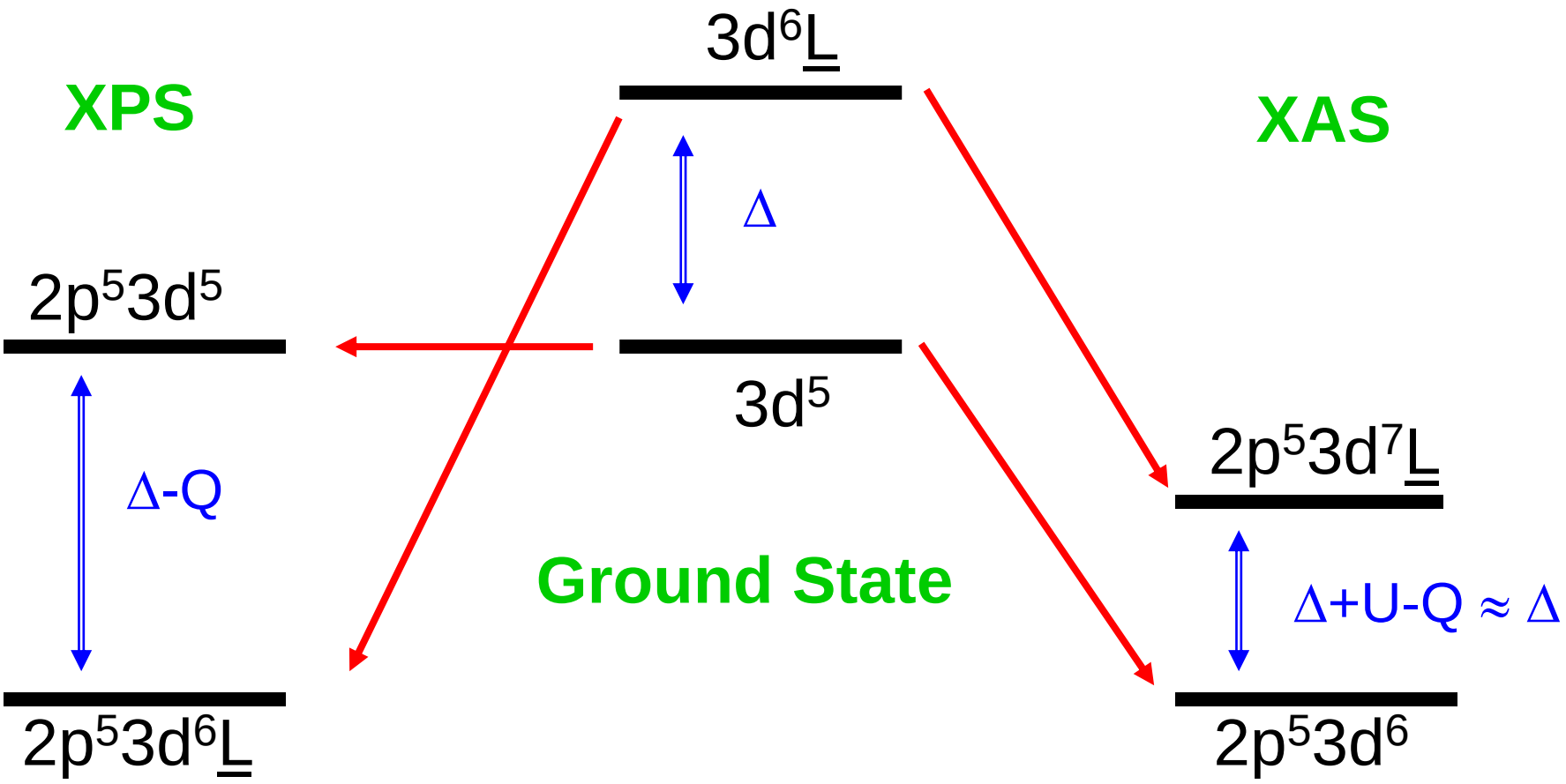


Charge Transfer Effects in XPS

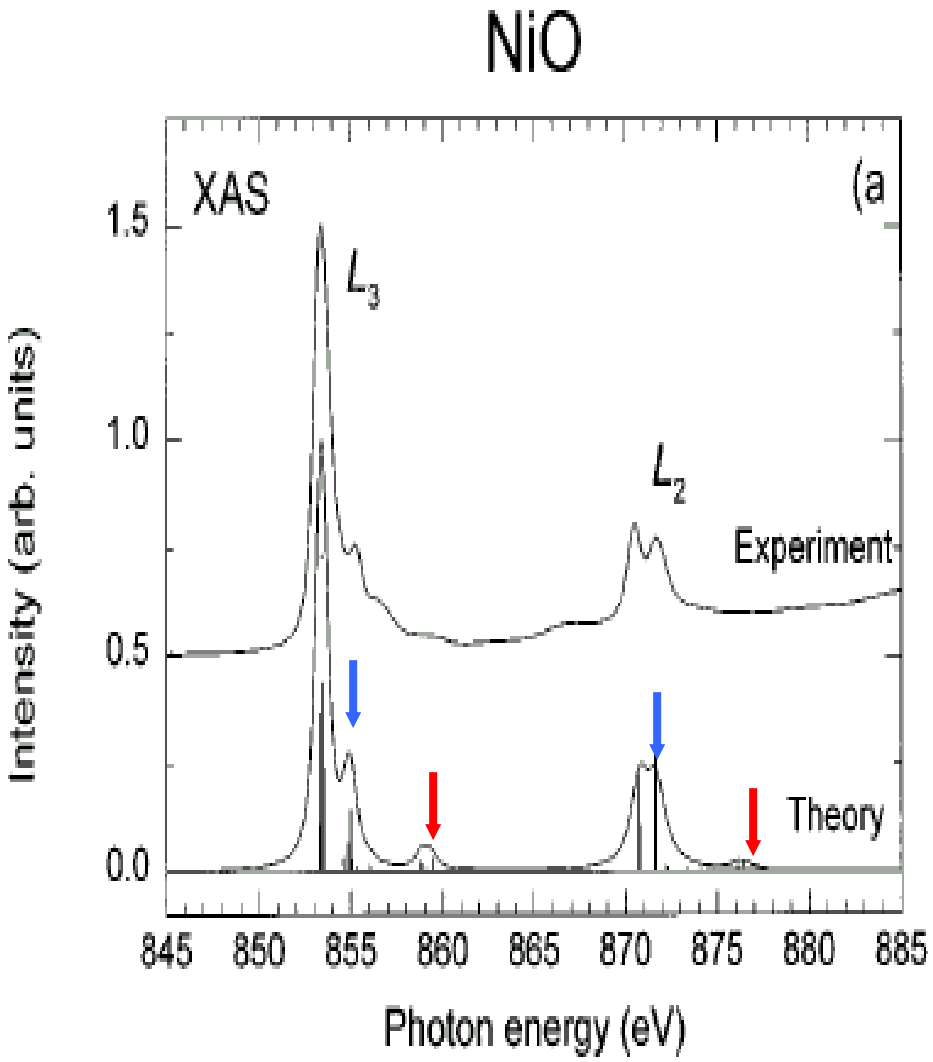


Charge transfer effects in XAS and XPS

- Transition metal oxide: Ground state: $3d^5 + 3d^6\underline{L}$
- Energy of $3d^6\underline{L}$: Charge transfer energy Δ



X-ray Absorption Spectroscopy



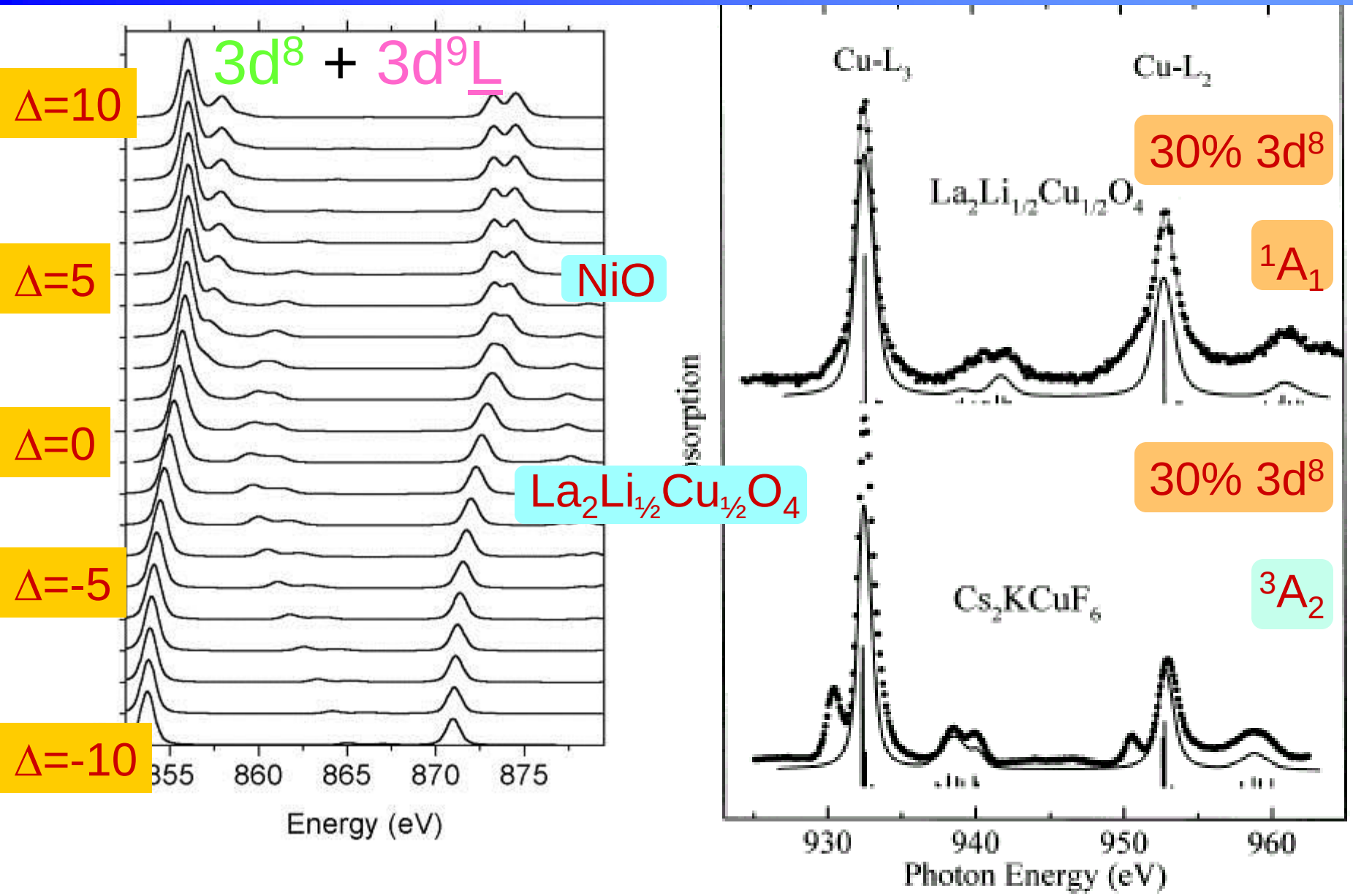
Spectral shape:

(1) Multiplet effects

(2) Charge Transfer

J. Elec. Spec. 67, 529 (1994)

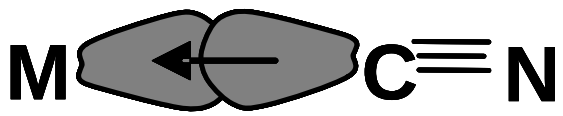
Charge Transfer effects

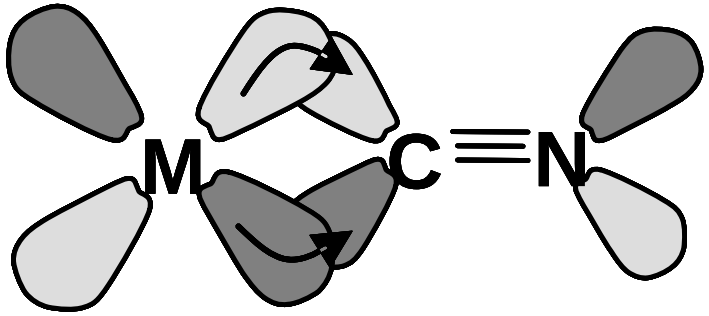


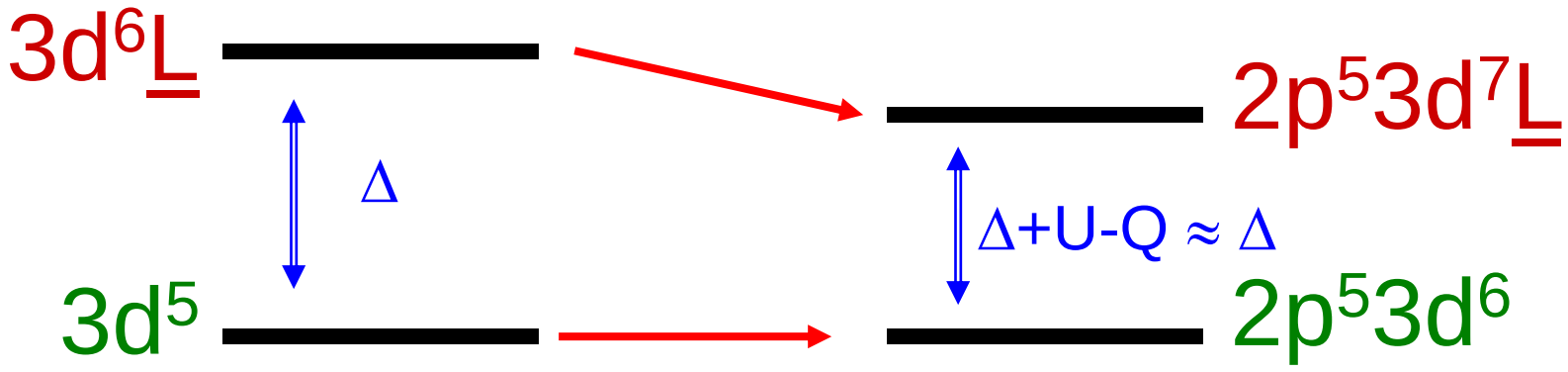
Chem. Phys. Lett. 297, 321 (1998)

LMCT and MLCT: π - bonding

Fe^{III}: Ground state: $3d^5 + 3d^6\underline{L}$



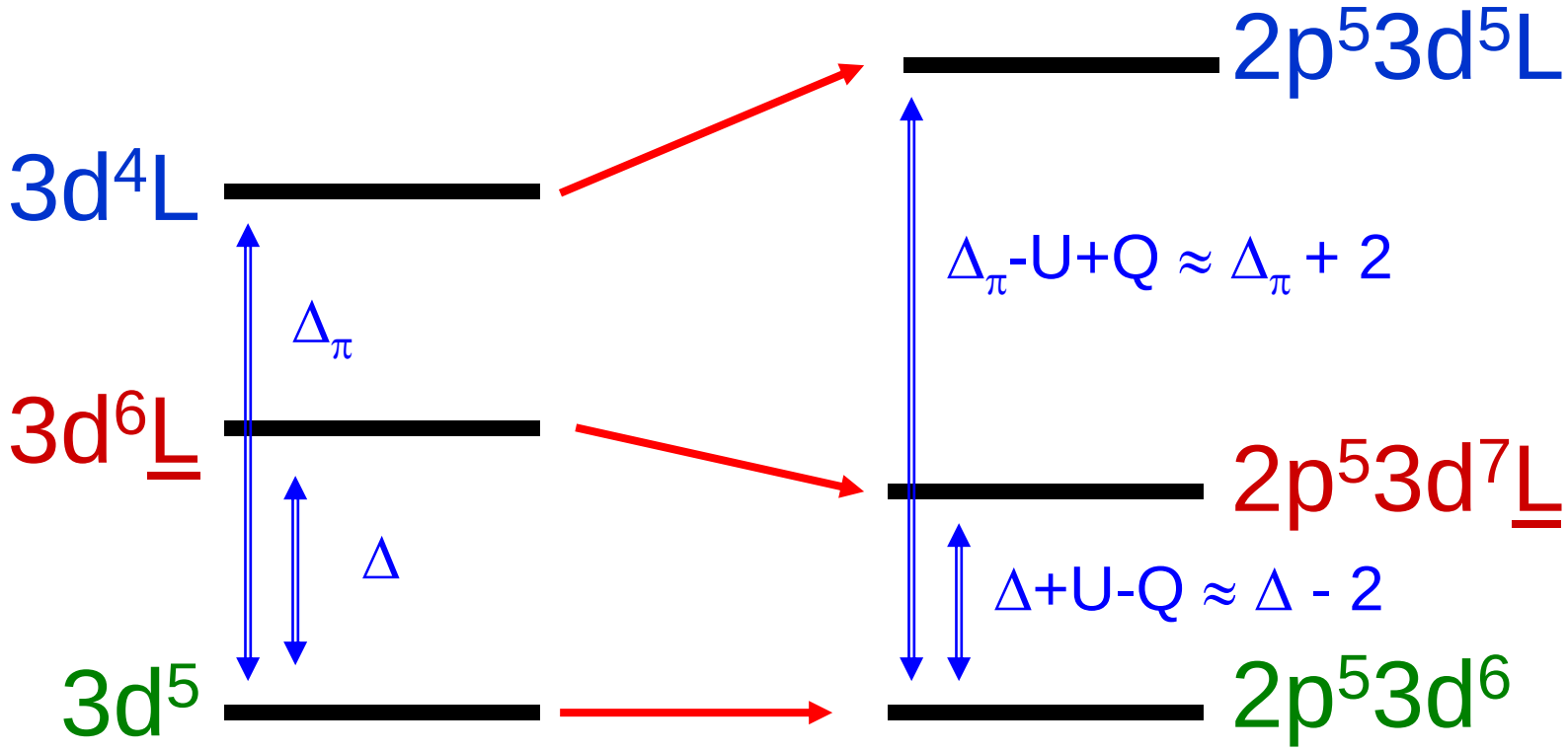




with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

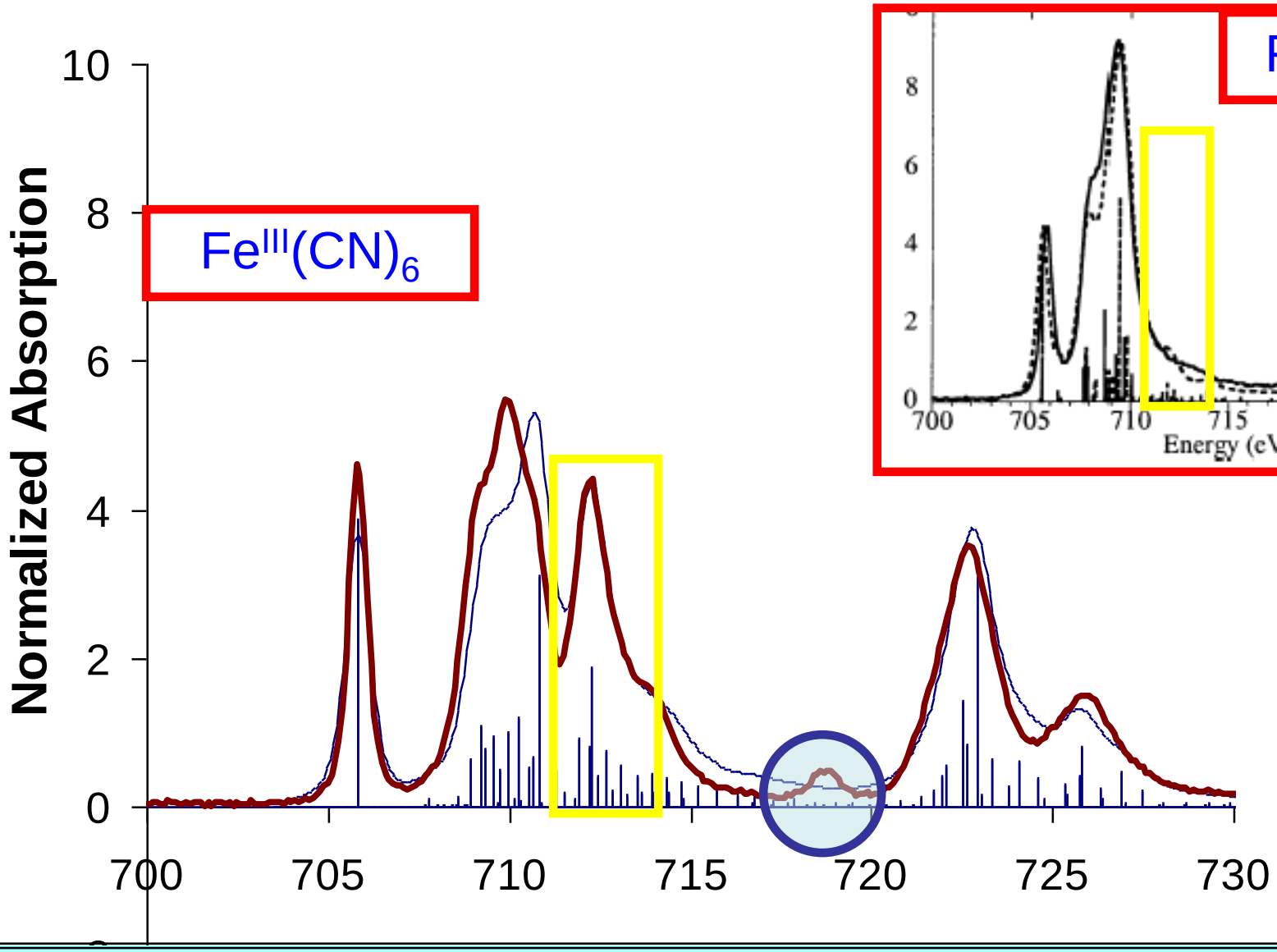
LMCT and MLCT: π - bonding

Fe^{III}: Ground state: $3d^5$ + $3d^6\underline{L}$ + $3d^4L$



with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

LMCT and MLCT: π - bonding



with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

resonant inelastic x-ray *scattering*

resonant inelastic x-ray *scattering*

10^{-10}

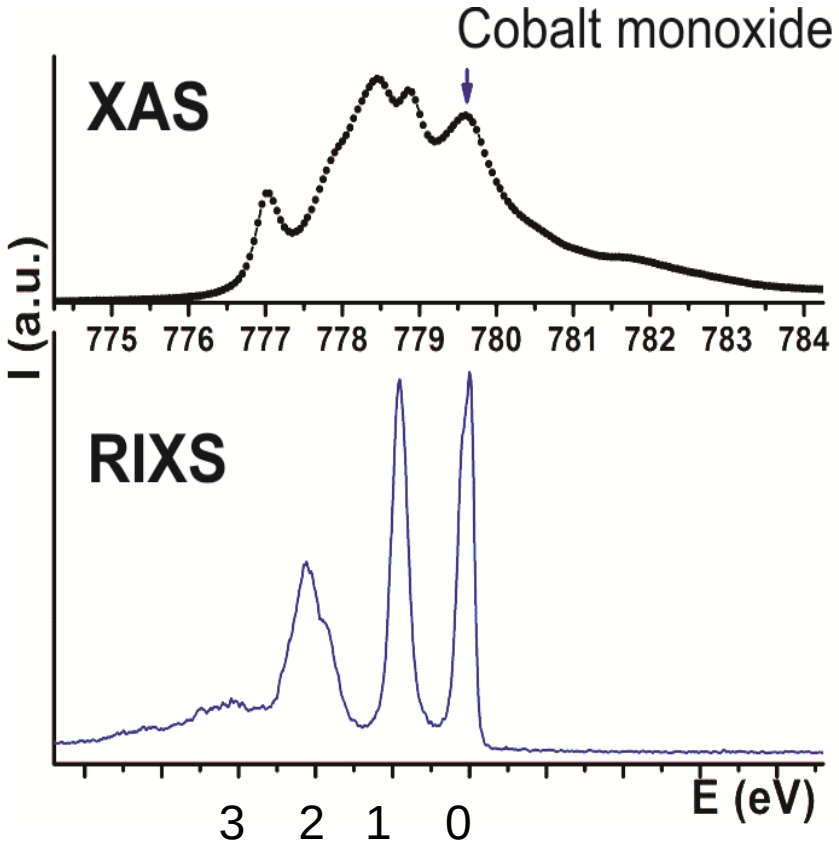
10^{-8}

$.5 \times 10^{-6}$

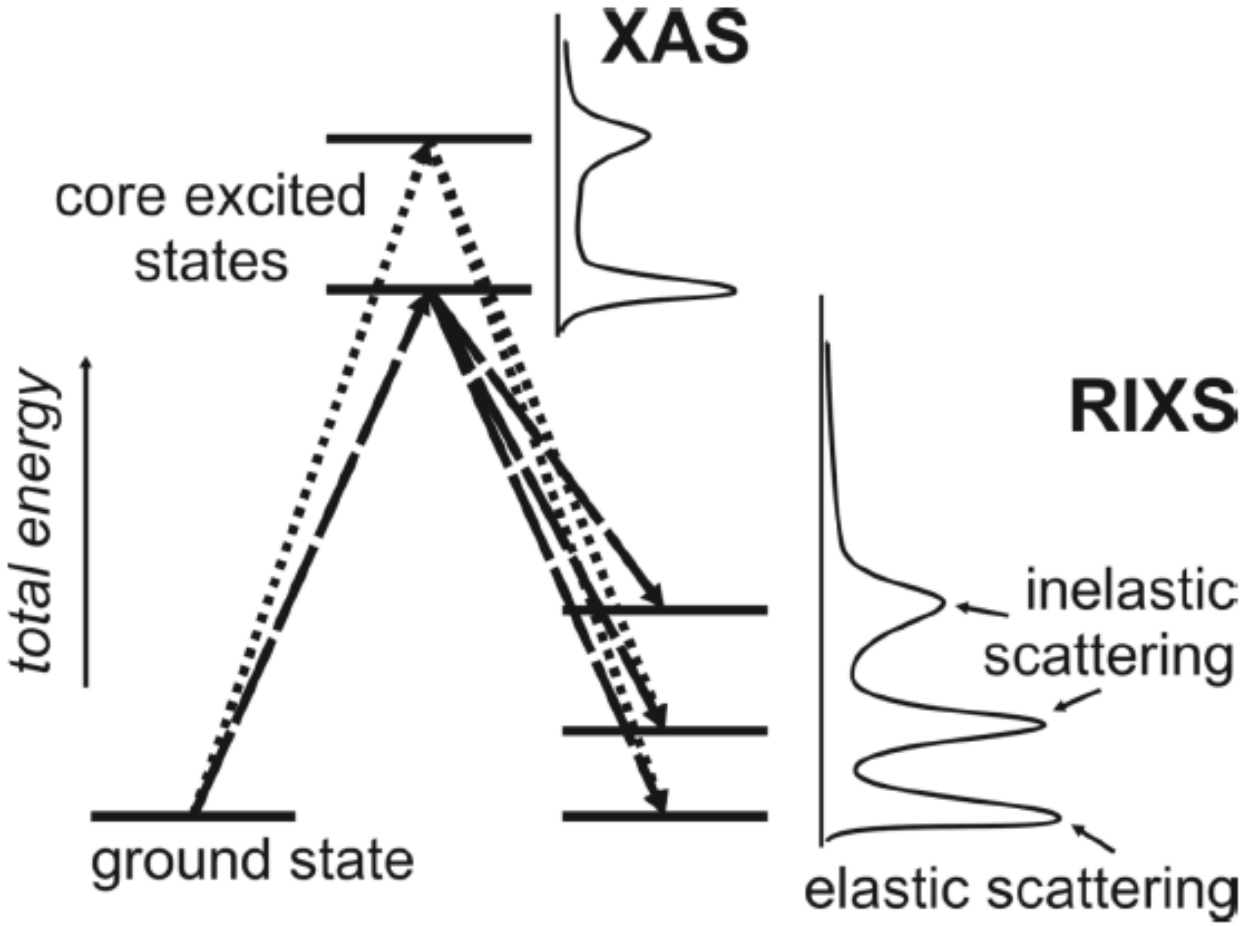
10^{-5}

Ψ_0

a.k.a. resonant x-ray Raman



resonant inelastic x-ray *scattering*



$$F(\Omega,\omega)=\sum_j\left|\sum_i\frac{<f|T_2|i><i|T_1|g>}{E_g+\hbar\Omega-E_i+\mathrm{i}\Gamma_i}\right|^2\times\frac{\Gamma_f/2\pi}{(E_g+\hbar\Omega-E_f-\hbar\omega)^2+\Gamma_f{}^2/4}$$

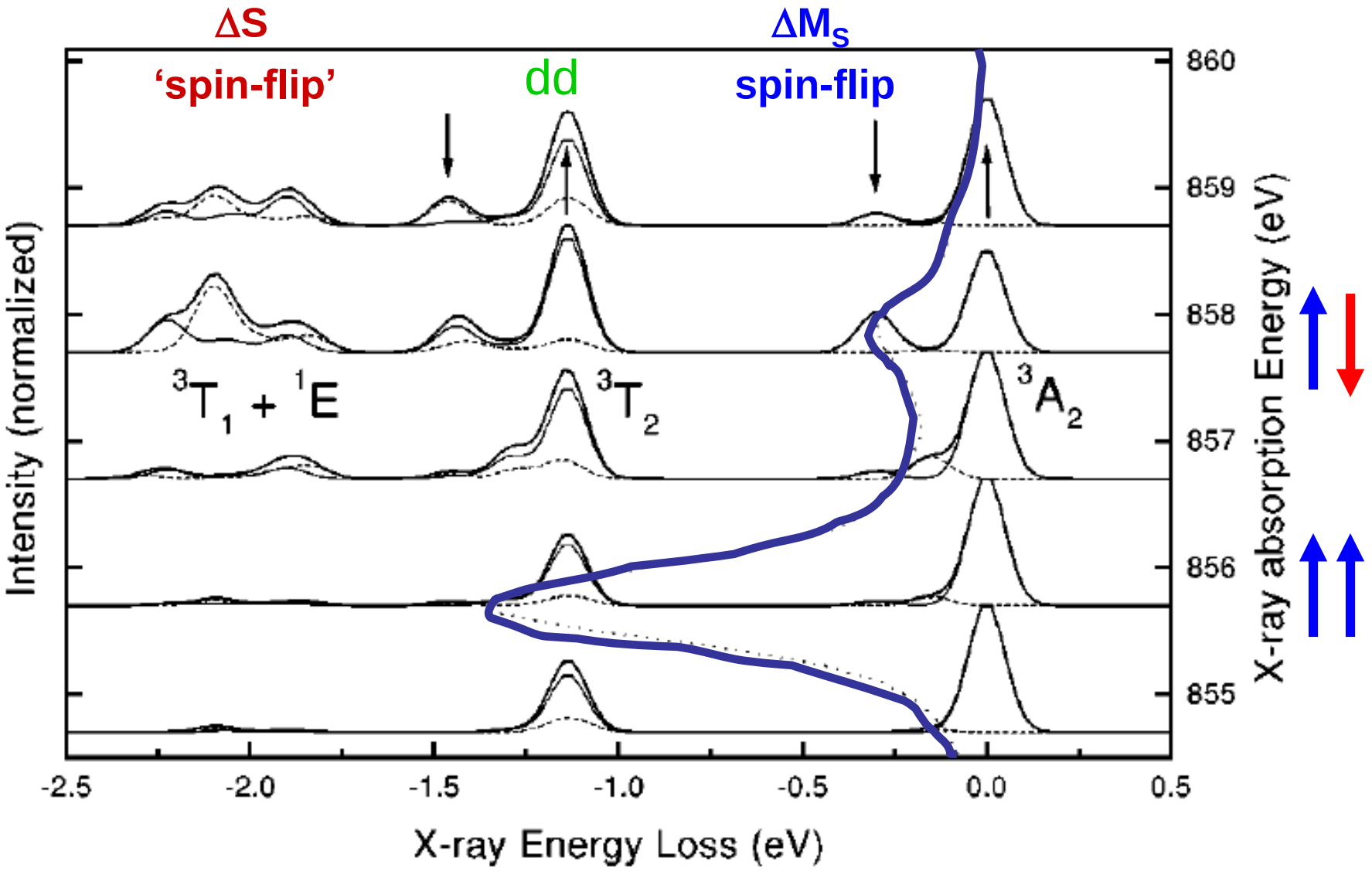
Why RIXS?

- Measure optical spectra with x-rays

  >> in-situ, element/valence specific
- dd-transitions > electronic structure
- Magnetic excitations
- Select specific states (active sites)

(only soft x-ray RIXS)

2p3d RIXS and magnetic excitations (NiO)



[Phys. Rev. B. 57, 14584 (1998)]

2p3d RIXS of CoO

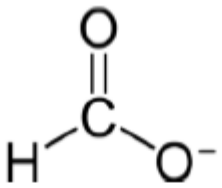
MCD, spin, angles
polarization,
angular-dependence
(in, sample, out)

eV
2-electron integrals
crystal field
charge transfer

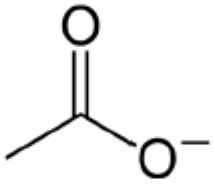
meV
spin-orbit, magnetic
distortions
vibrations

2p3d resonant XES of Co-carboxylates

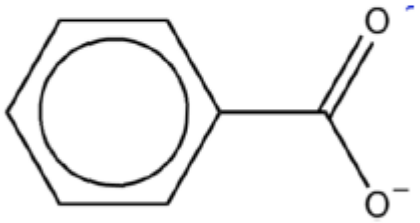
(1)



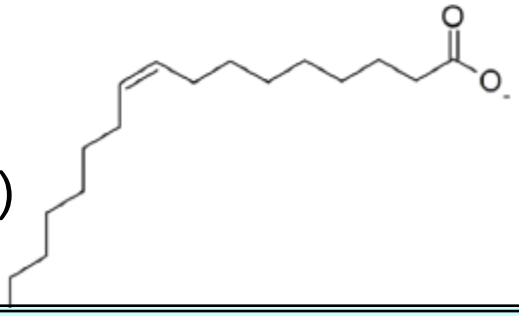
(2)

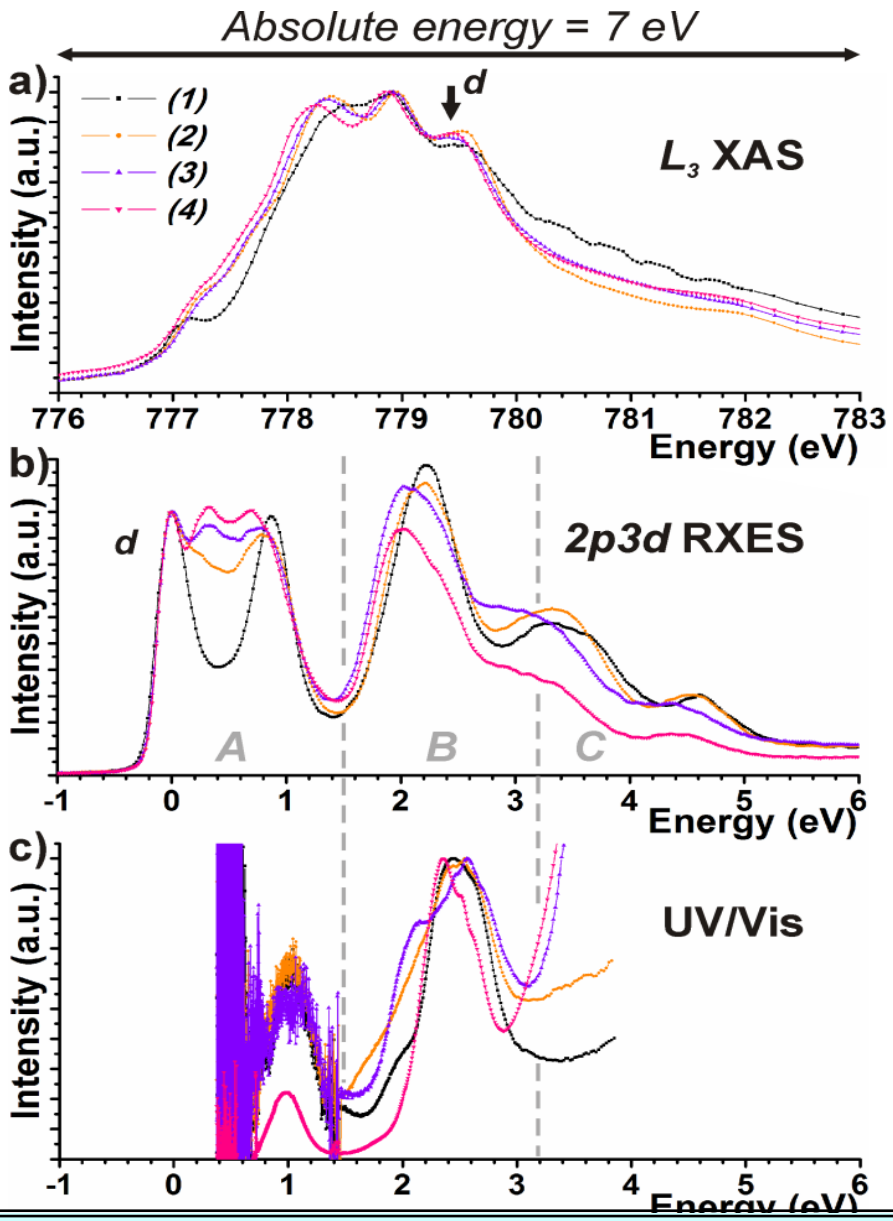


(3)



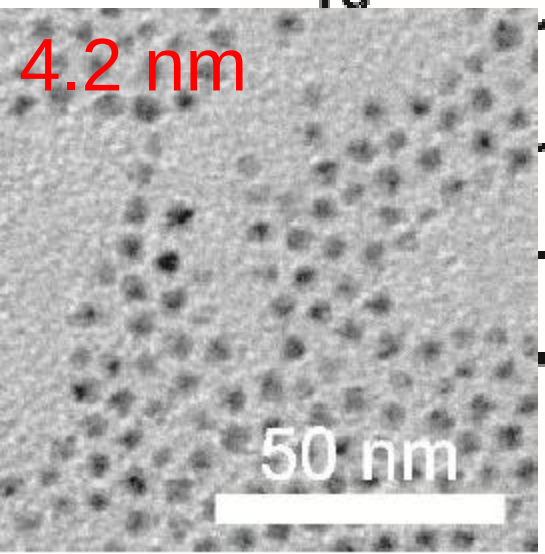
(4)





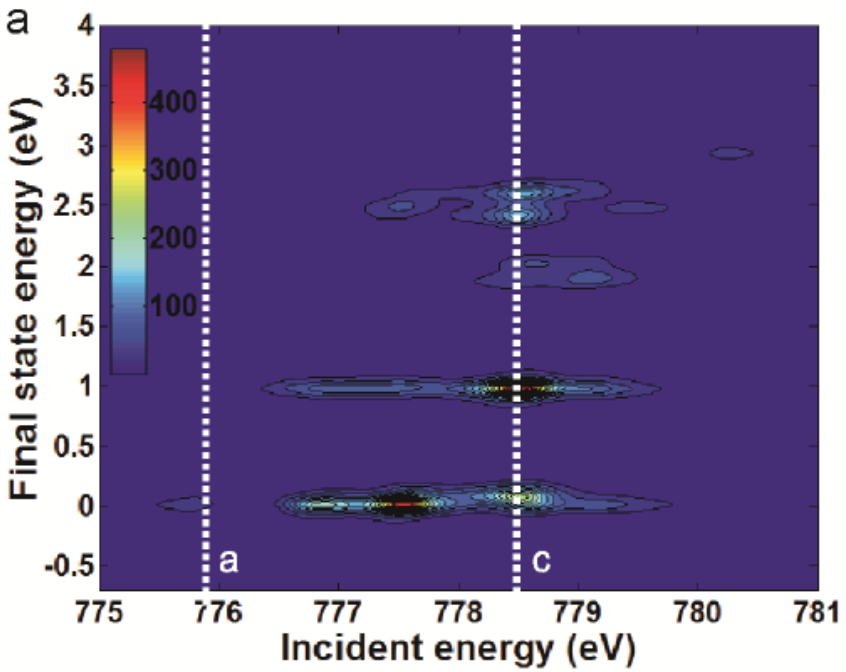
van Schooneveld et al., Angew. Chem. 52, 1170 (2012)

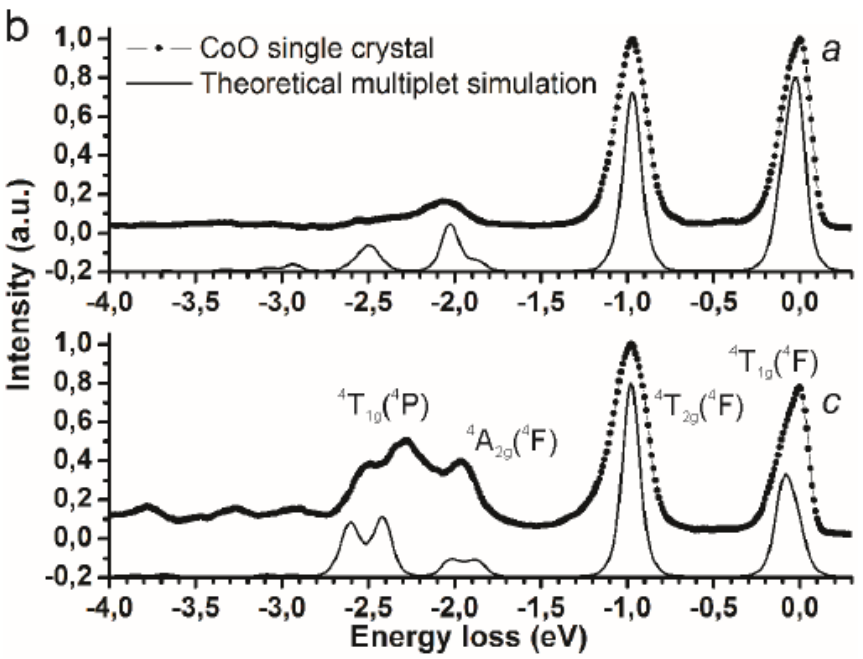
2p3d RIXS of CoO

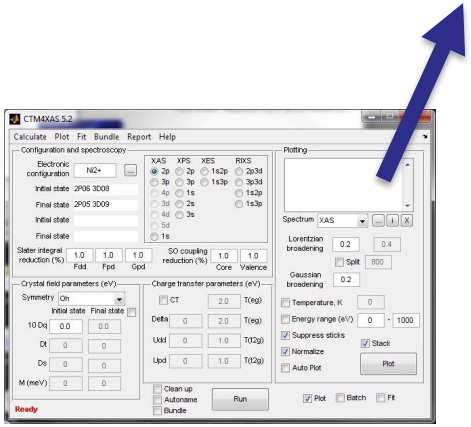


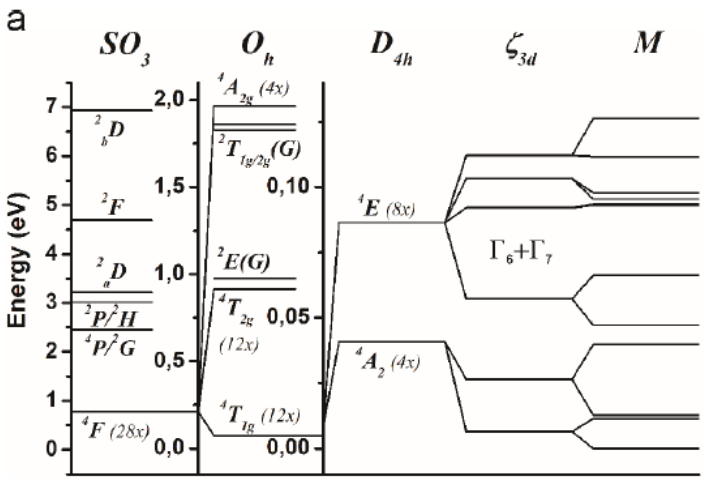
[van Schooneveld, J. Phys. Chem. C. 116, 15218 (2012)]

2p3d RIXS of CoO

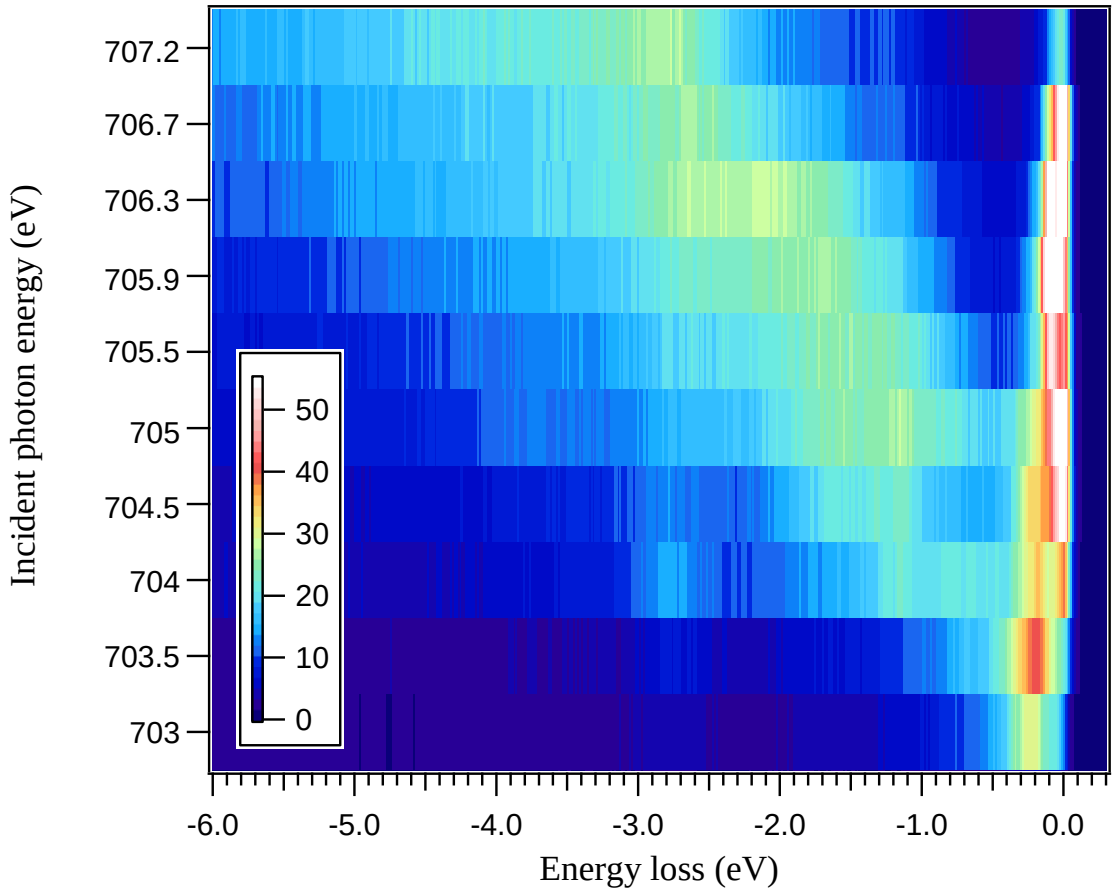


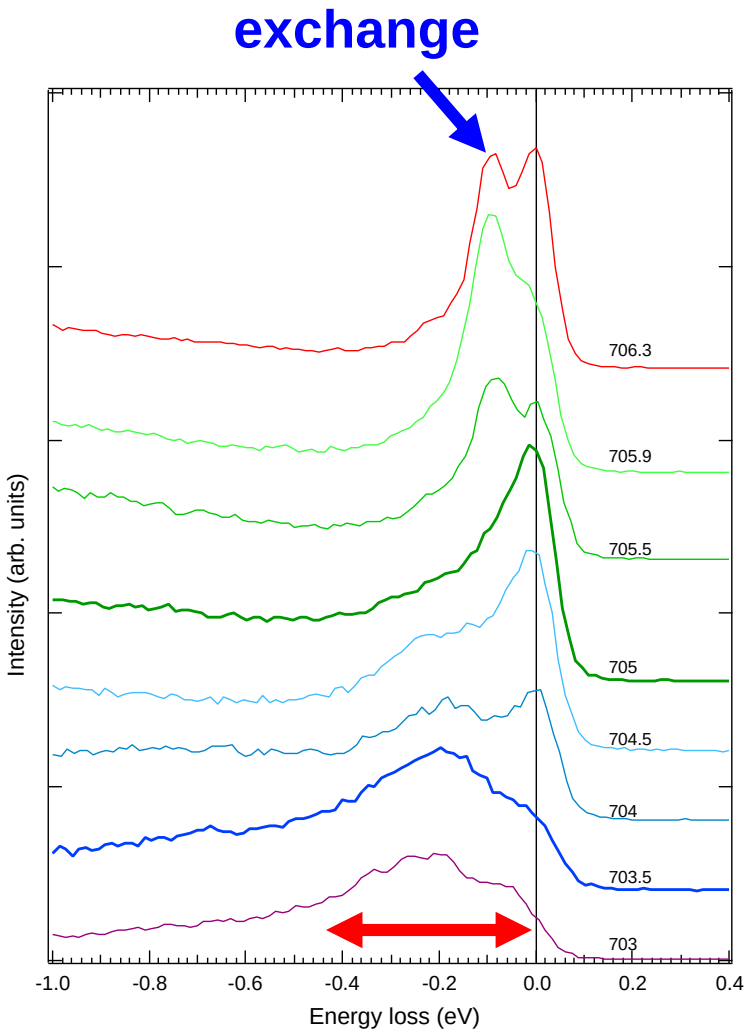






Select specific states in 2p3d RIXS (Fe_3O_4)

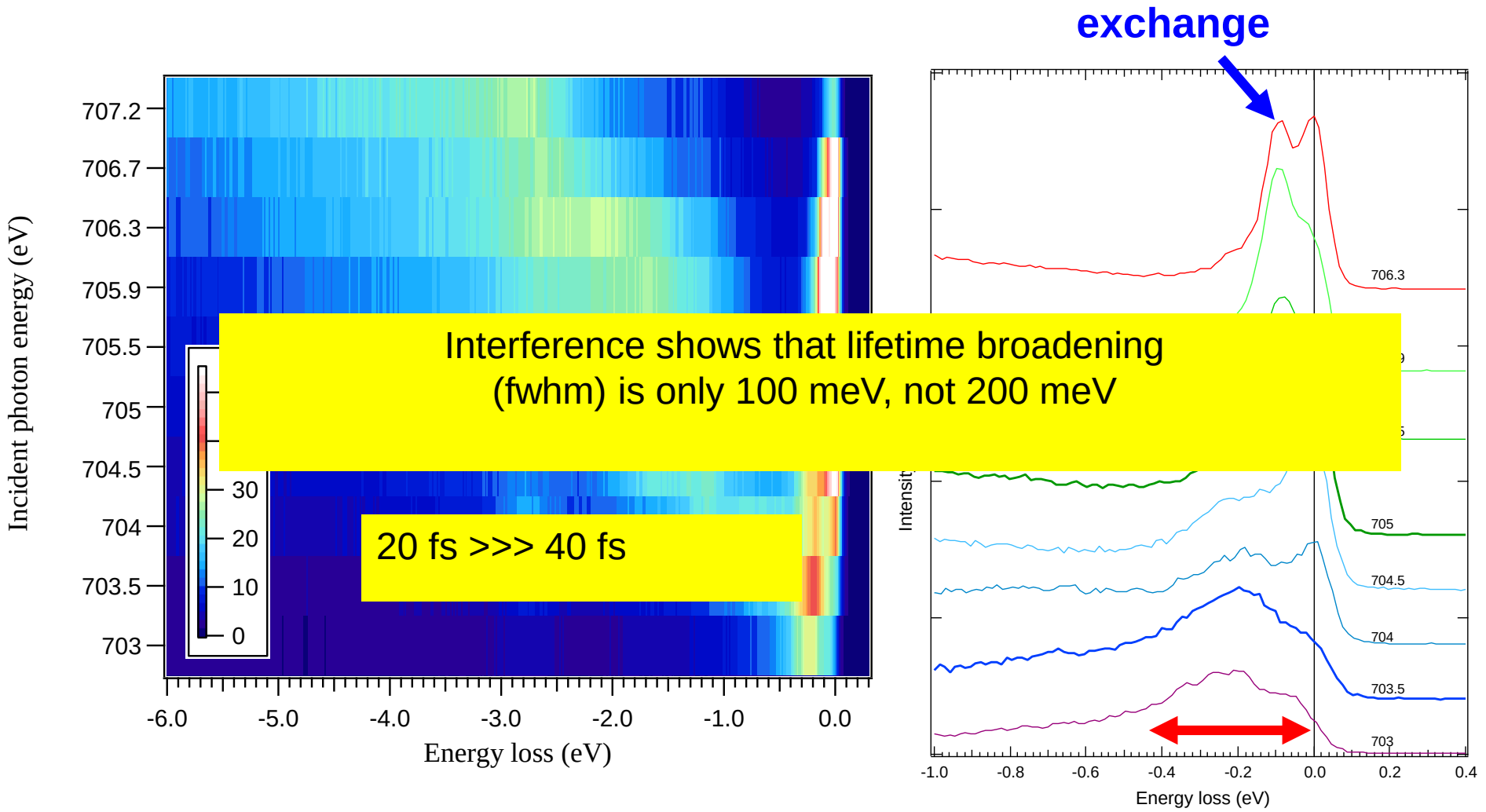




spin-orbit + exchange

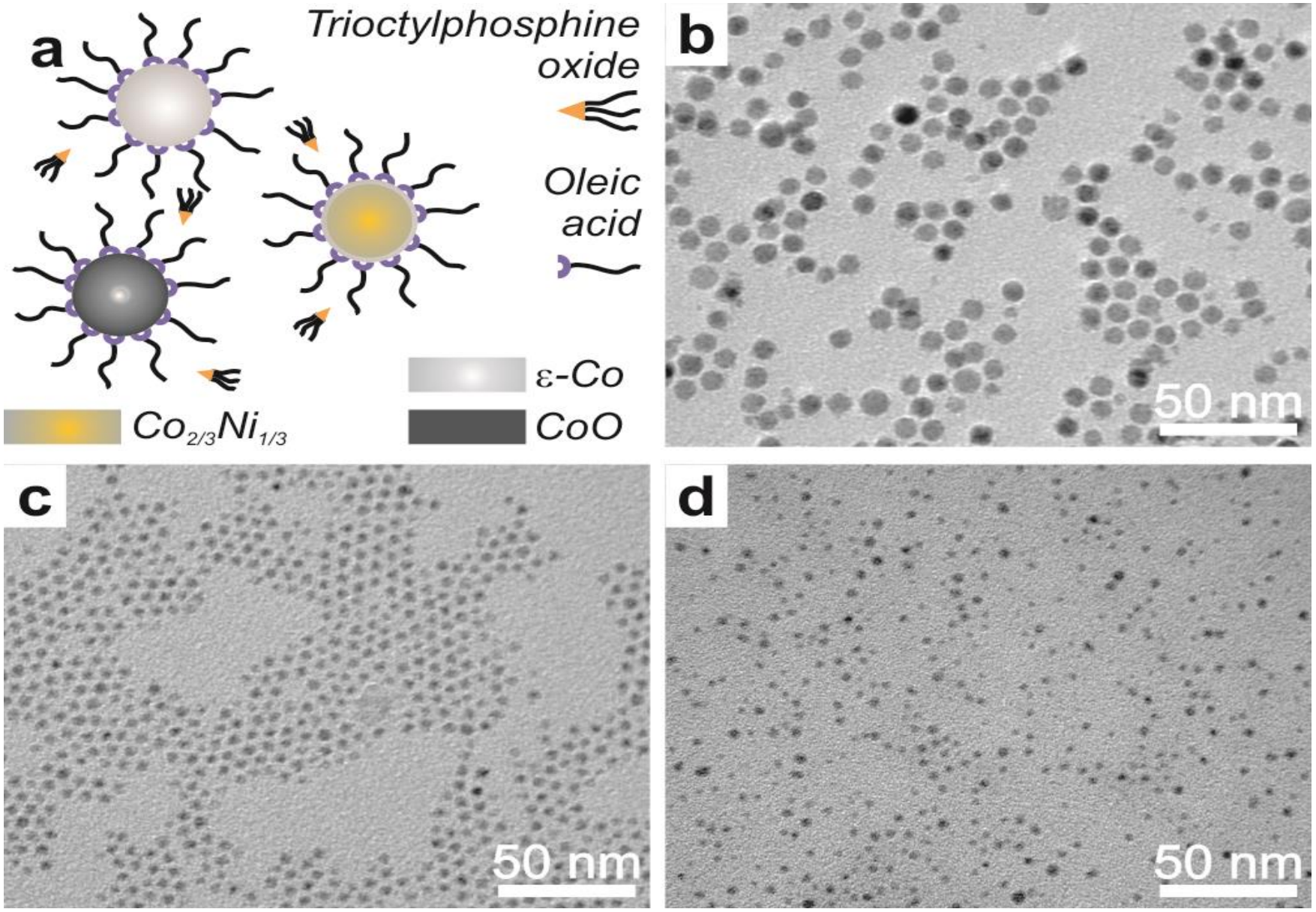
[Huang et al. arXiv:1512.07957]

Select specific states in 2p3d RIXS (Fe_3O_4)



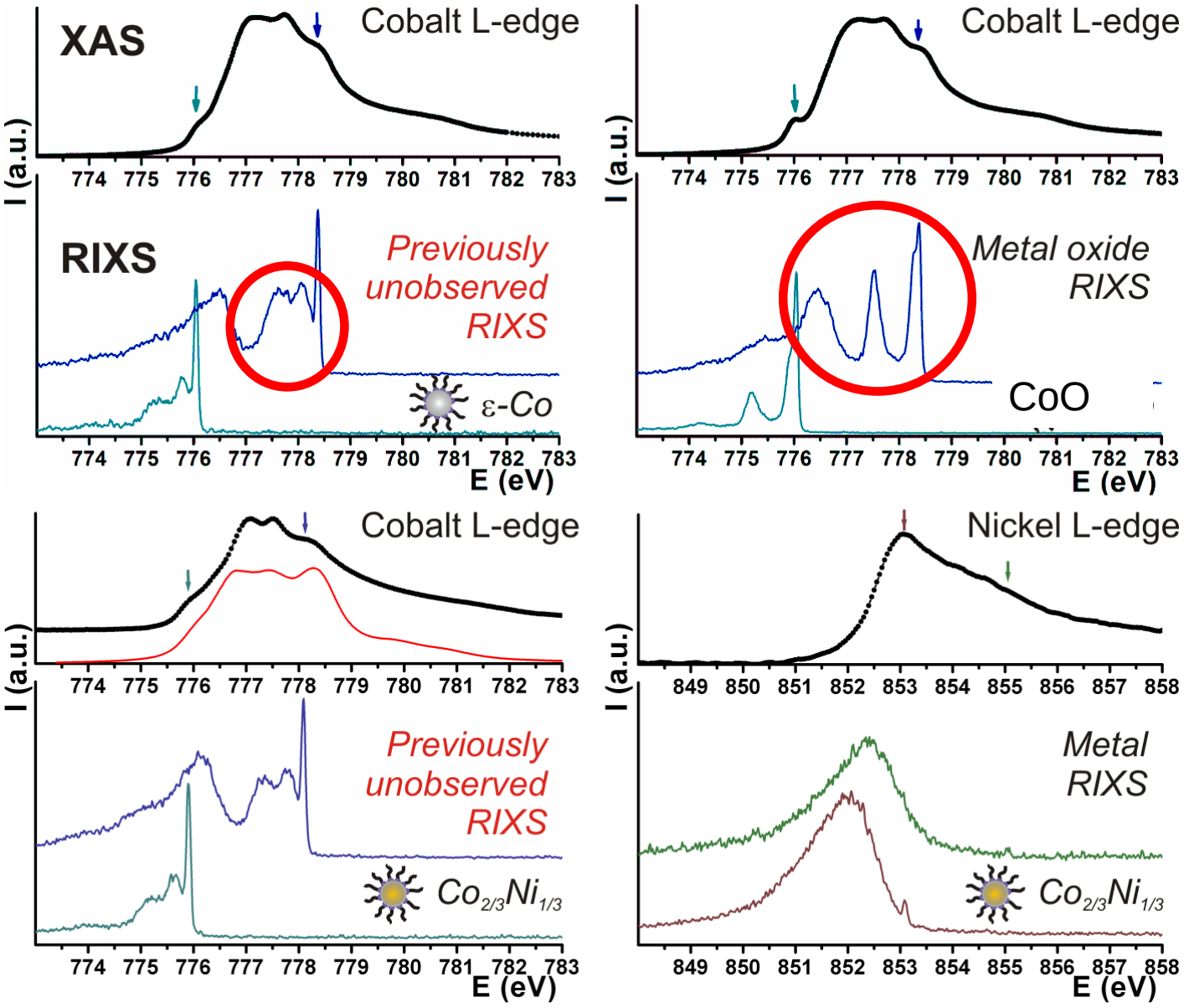
[Huang et al. arXiv:1512.07957]

2p3d resonant XES of metal Co nanoparticles



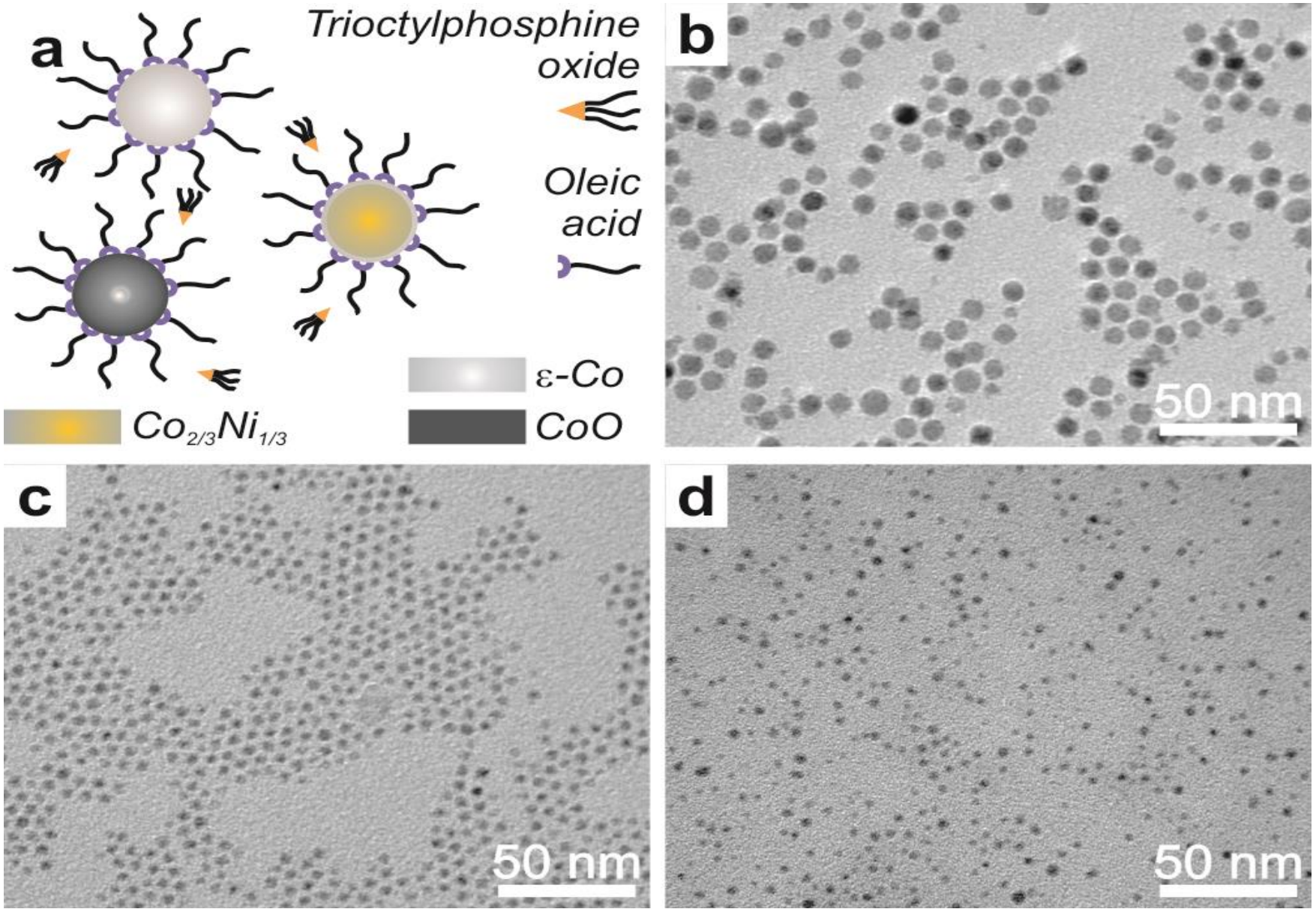
[van Schooneveld, J. Phys. Chem. Lett 4, 1161 (2013)]

2p3d resonant XES of metal Co nanoparticles



[van Schooneveld, J. Phys. Chem. Lett 4, 1161 (2013)] van Schooneveld *et al.*, submitted

2p3d resonant XES of metal Co nanoparticles



van Schooneveld et al., J. Phys. Chem. Lett. 4, 1161 (2013)

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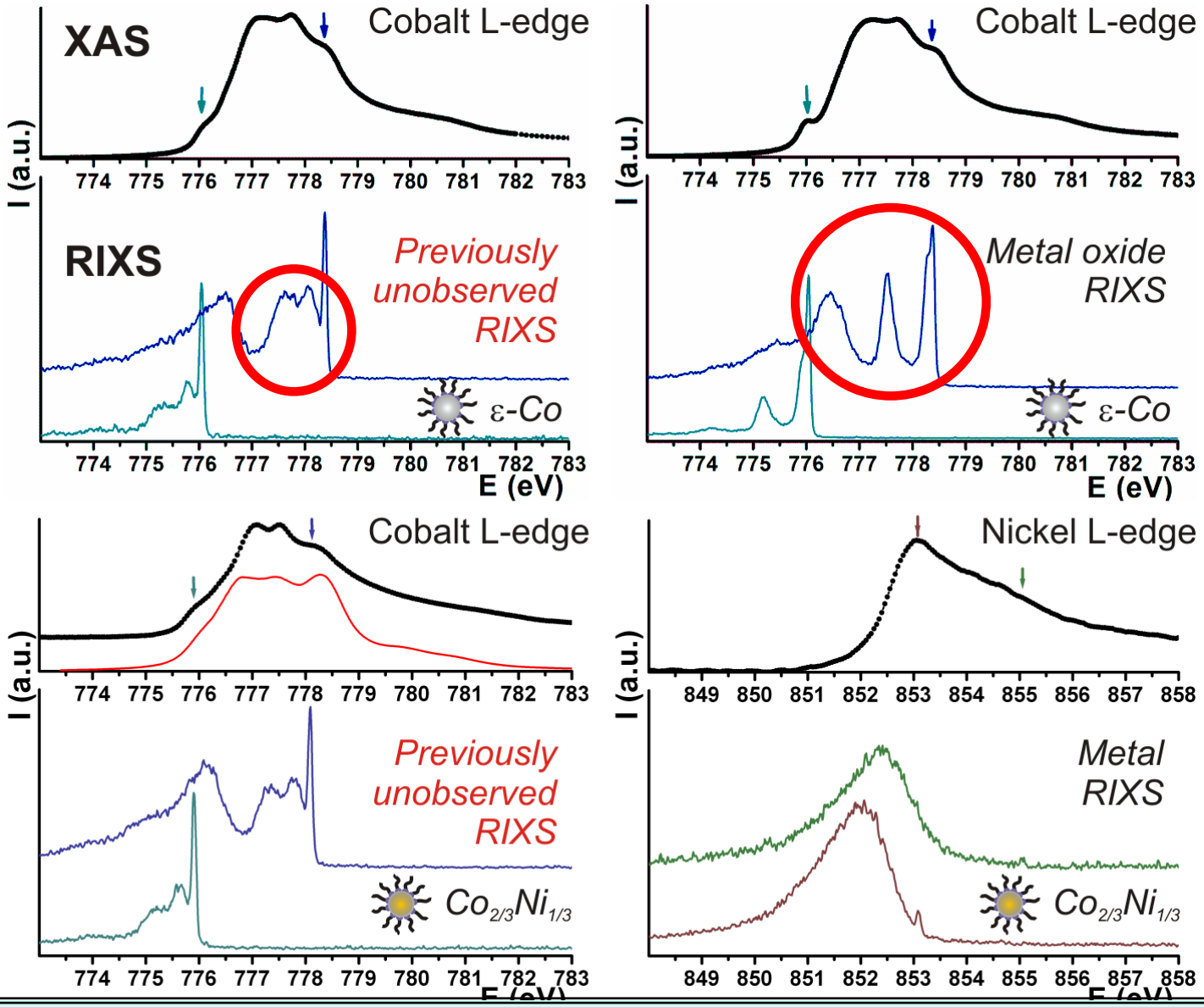
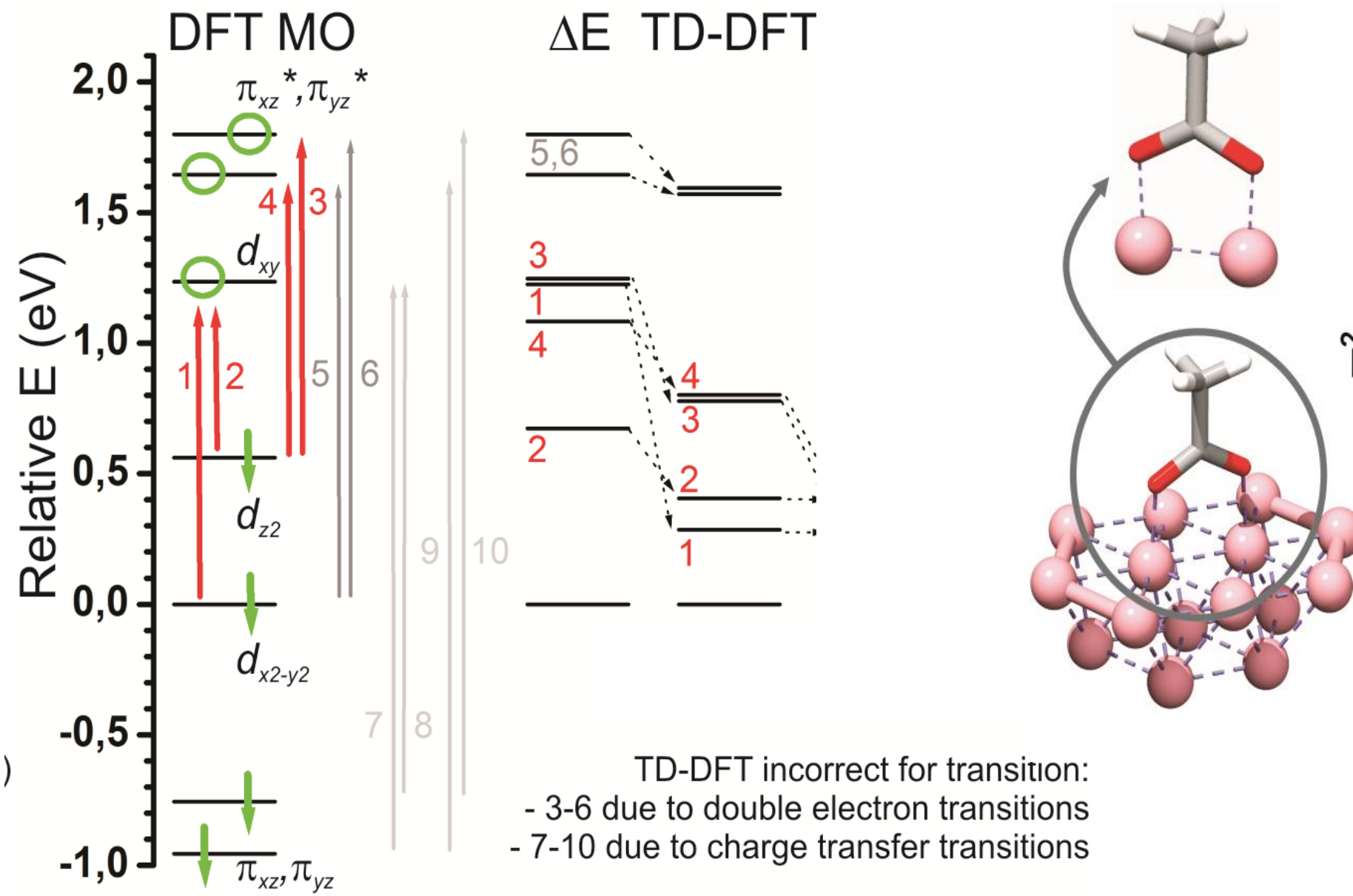


van Schooneveld et al., J. Phys. Chem. Lett. 4, 1161 (2013)

2p3d resonant XES of metal Co nanoparticles



van Schooneveld et al., J. Phys. Chem. Lett. 4, 1161 (2013)

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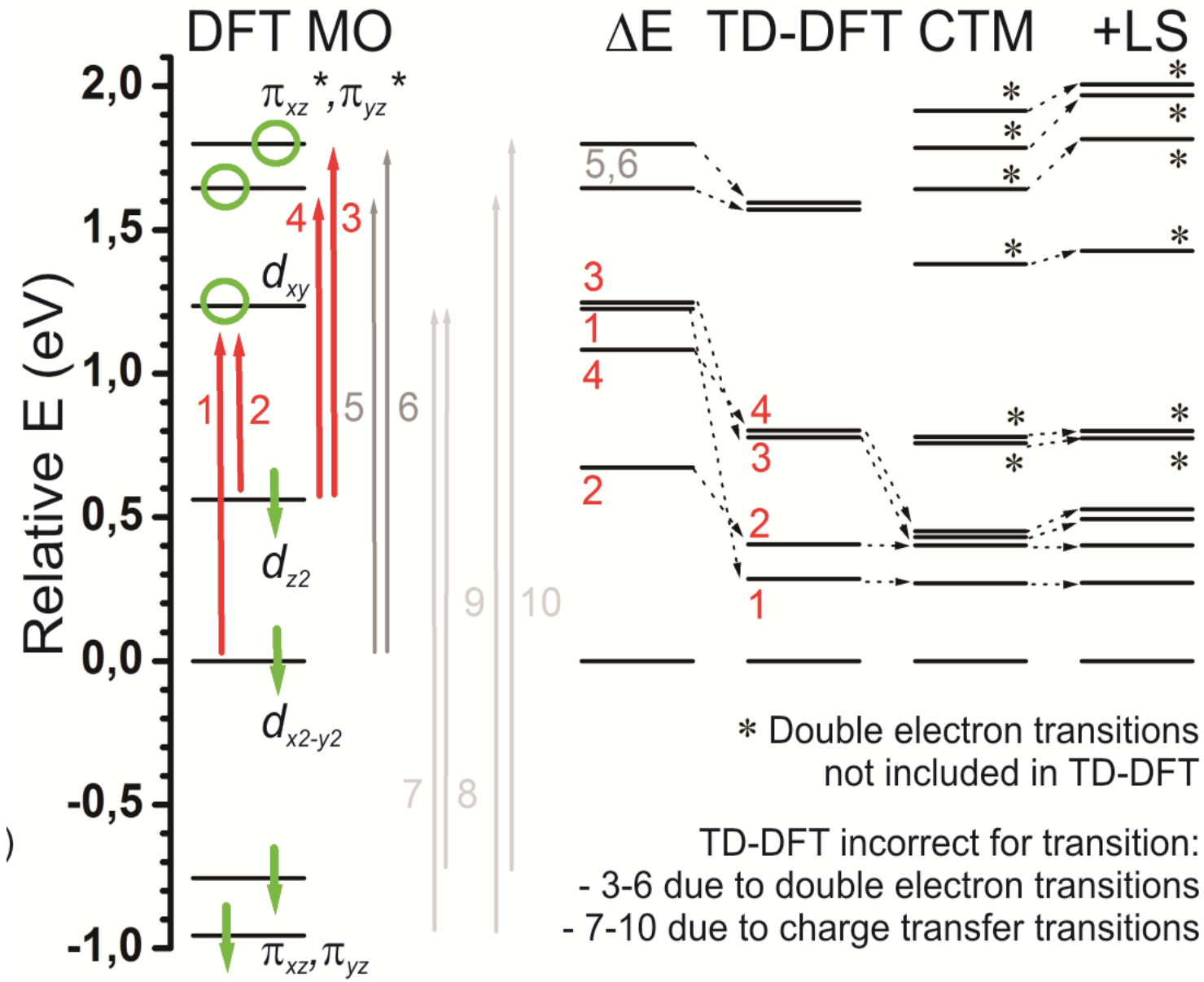
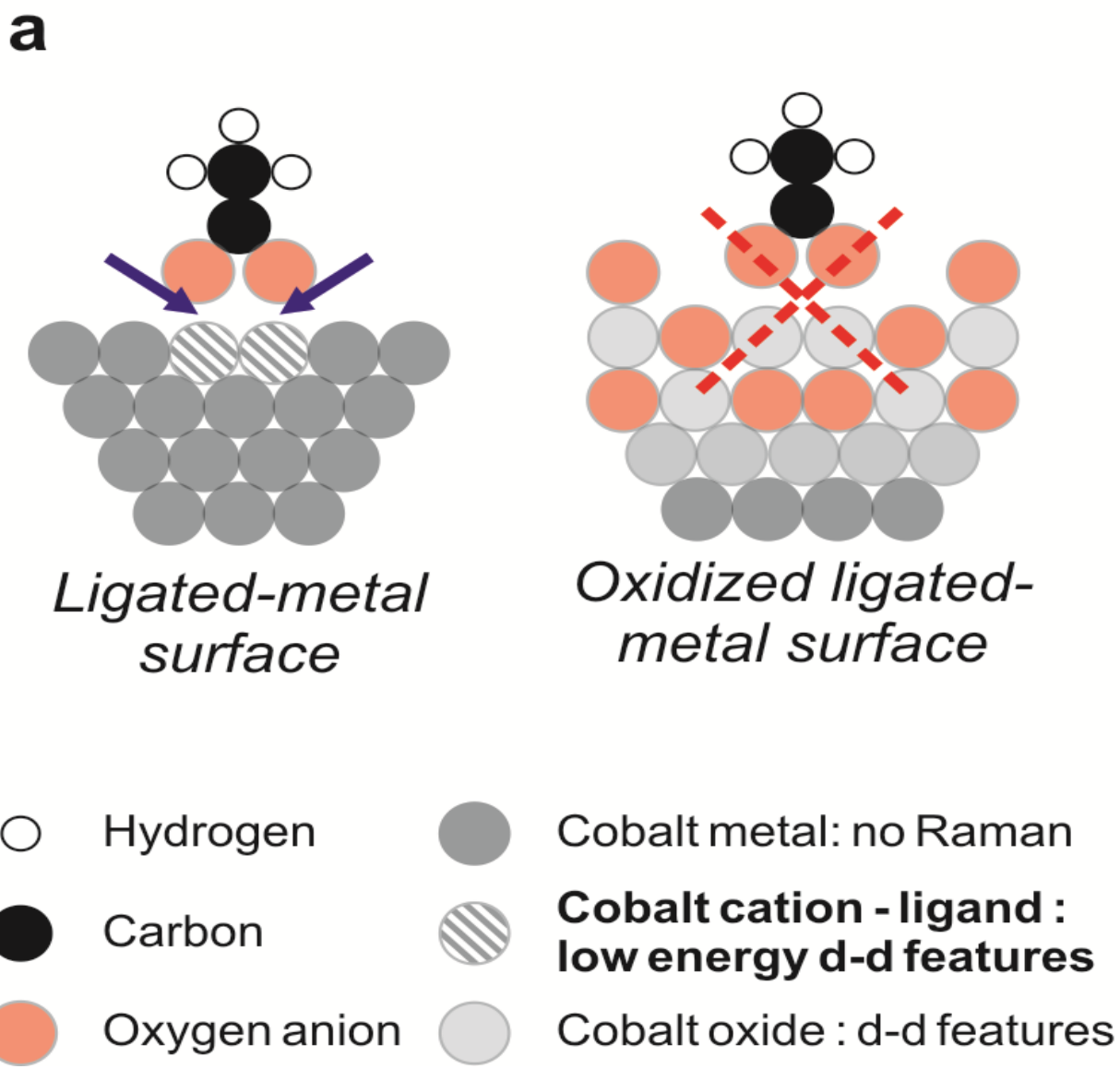


van Schooneveld et al., J. Phys. Chem. Lett. 4, 1161 (2013)

2p3d resonant XES of metal Co nanoparticles



van Schooneveld et al., J. Phys. Chem. Lett. 4, 1161 (2013)

Removing the silent majority