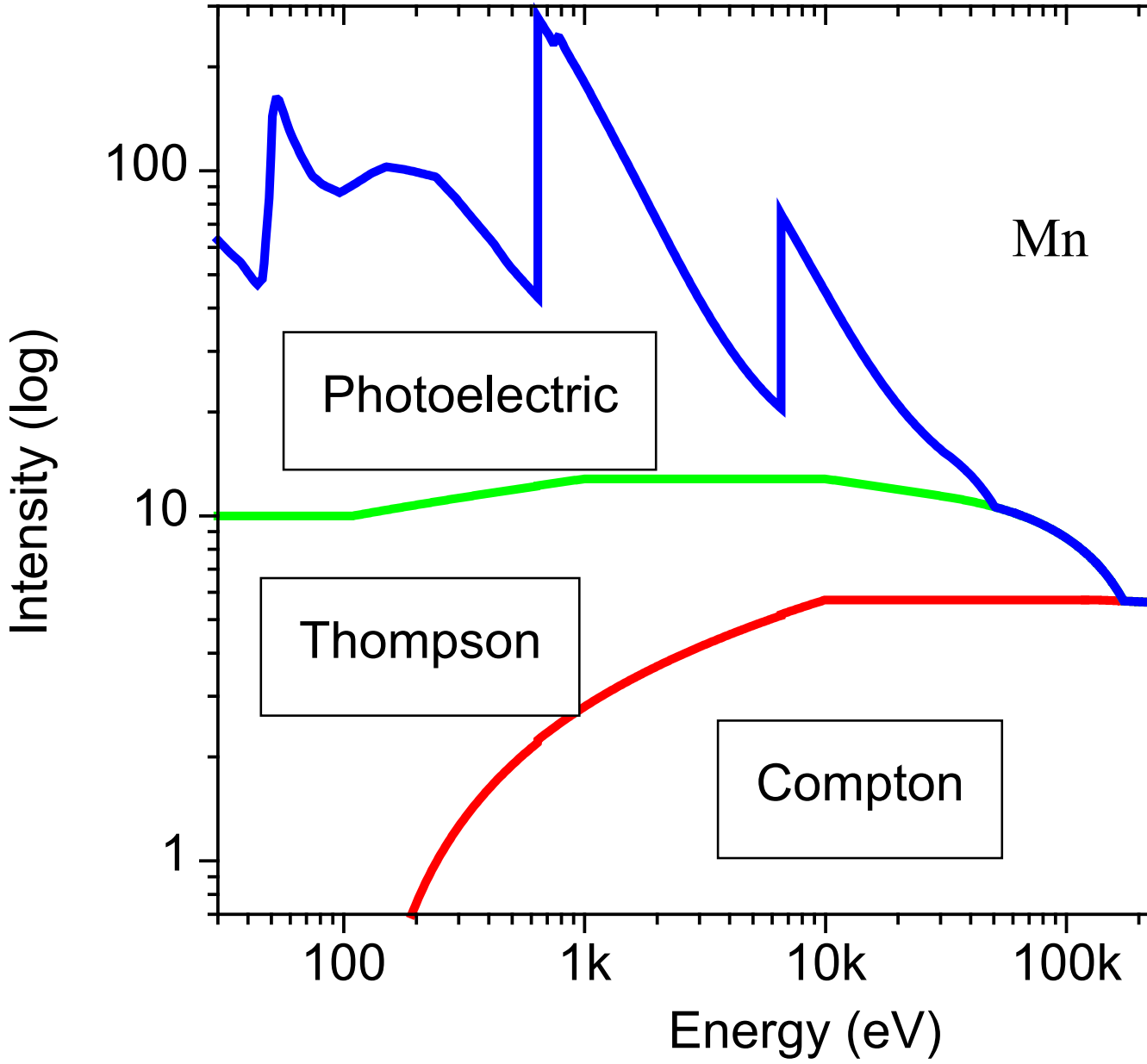
X-ray Absorption Spectroscopy

- Introduction to XAS
- XAS spectral shape
- multiplet calculations

X-ray Absorption Spectroscopy

- Photo-electric
  (X-ray annihilation)
- Elastic X-ray scattering
- Inelastic X-ray scattering



X-ray Absorption Spectroscopy

Label	Orbital	eV
K	1s	6539
L_I	2s	769
L_{II}	$2p_{1/2}$	650
L_{III}	$2p_{3/2}$	639
M_I	3s	82
M_{II}	$3p_{1/2}$	47
M_{III}	$3p_{3/2}$	47

sharp
principal
diffuse
fundamental

J. Chem. Educ. 84, 757 (2007)

BarKLa

The Nobel Prize in Physics 1917 was awarded to Charles Glover Barkla "for his discovery of the characteristic Röntgen radiation of the elements."

X-ray Absorption Spectroscopy

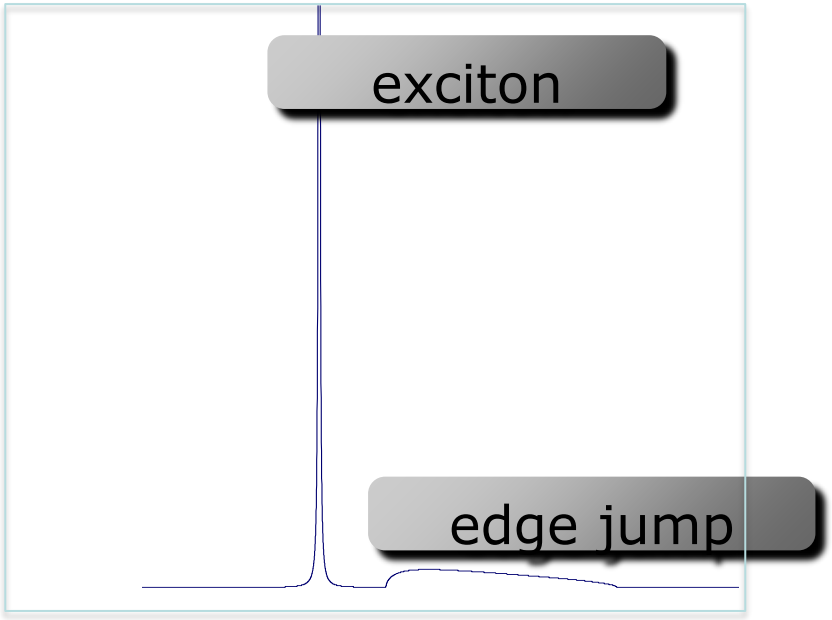
- Element specific
- Sensitive to low concentrations
- Applicable under extreme conditions

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

XAS: spectral shape

Excitations of core electrons to empty states

The XAS spectra are given by the Fermi Golden Rule



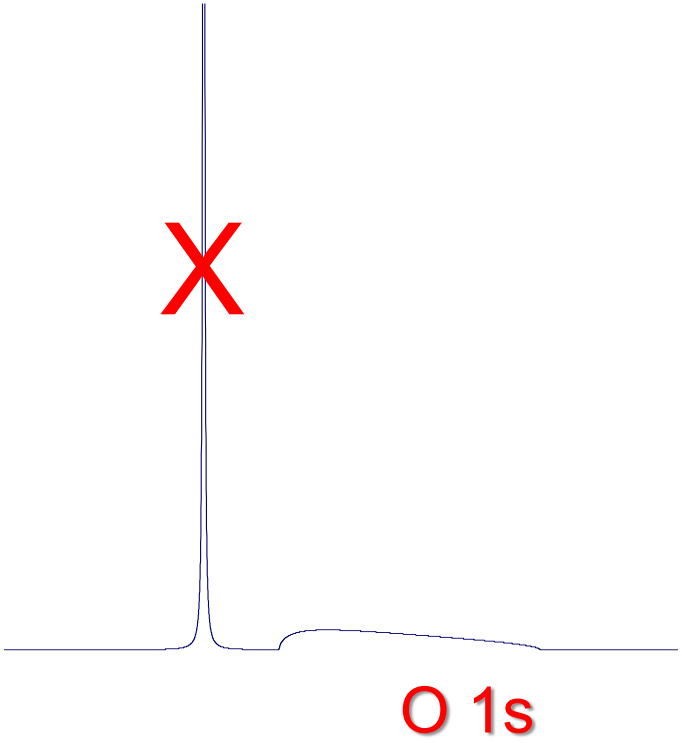
$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \left| \hat{e} \cdot r \right| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

XAS: spectral shape (oxygen 1s)

Fermi Golden Rule

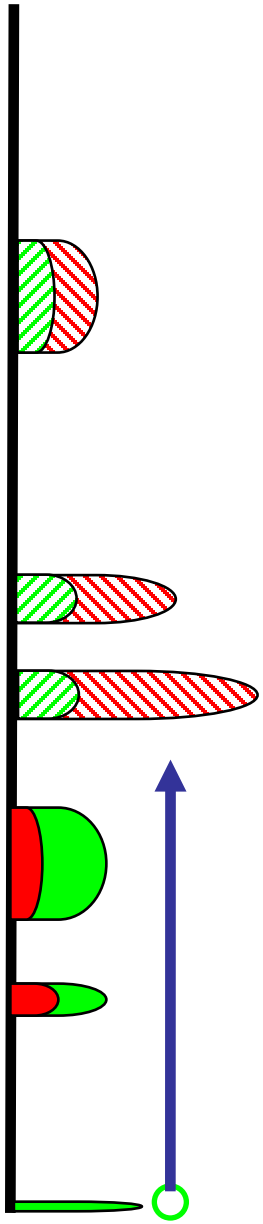
↓

Excitations to
empty states as calculated by
DFT



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

XAS: spectral shape (O 1s)



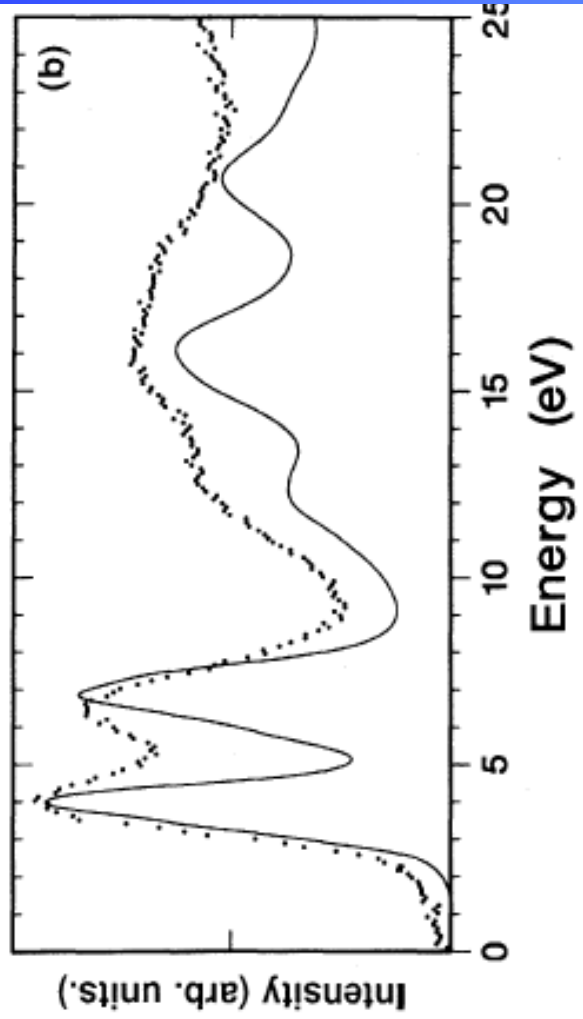
4sp

E_g

T_{2g}

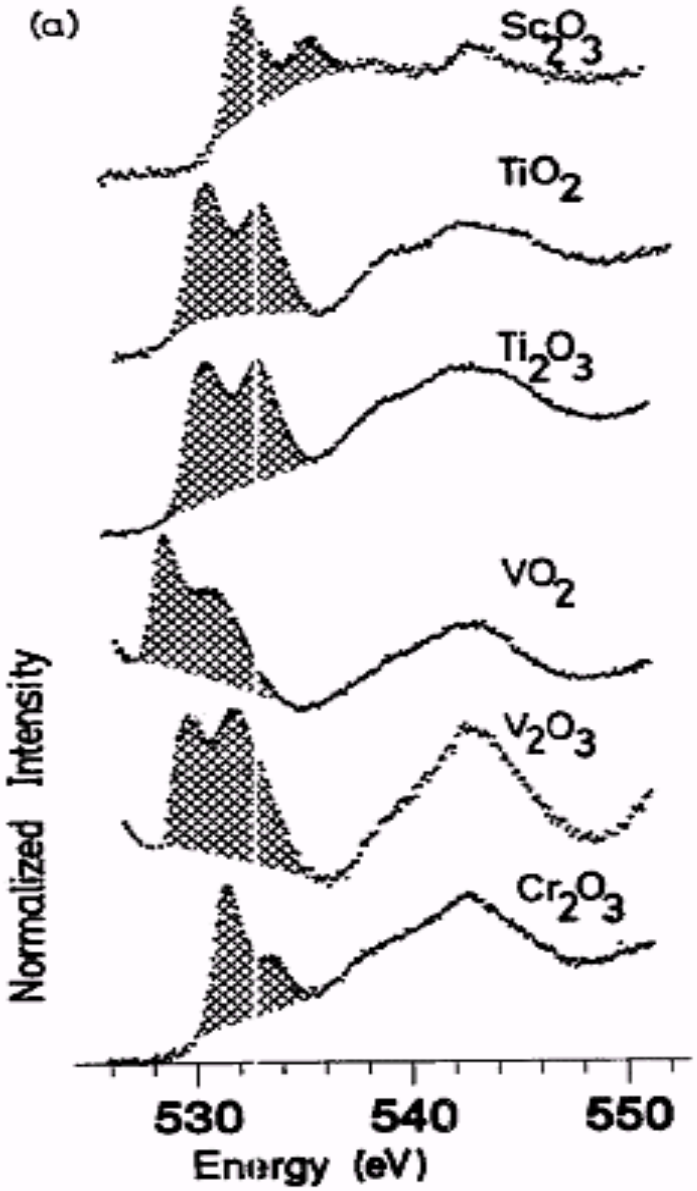
O2p

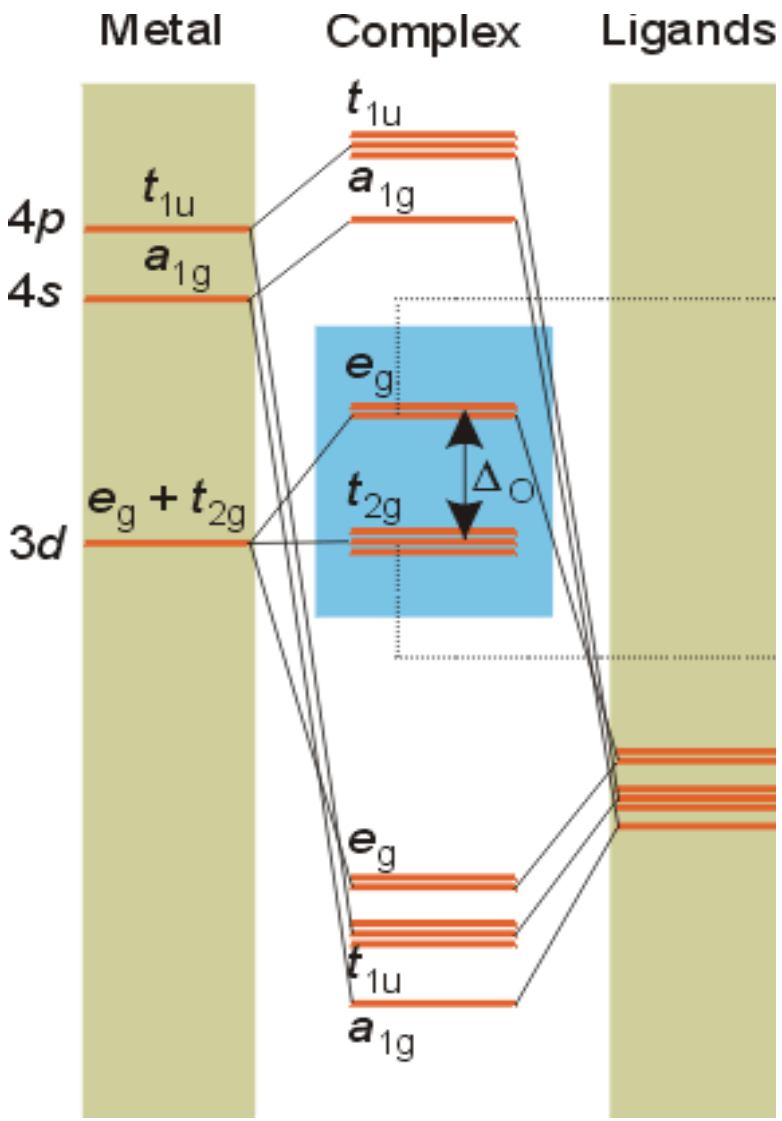
O2s



O 1s ~530 eV

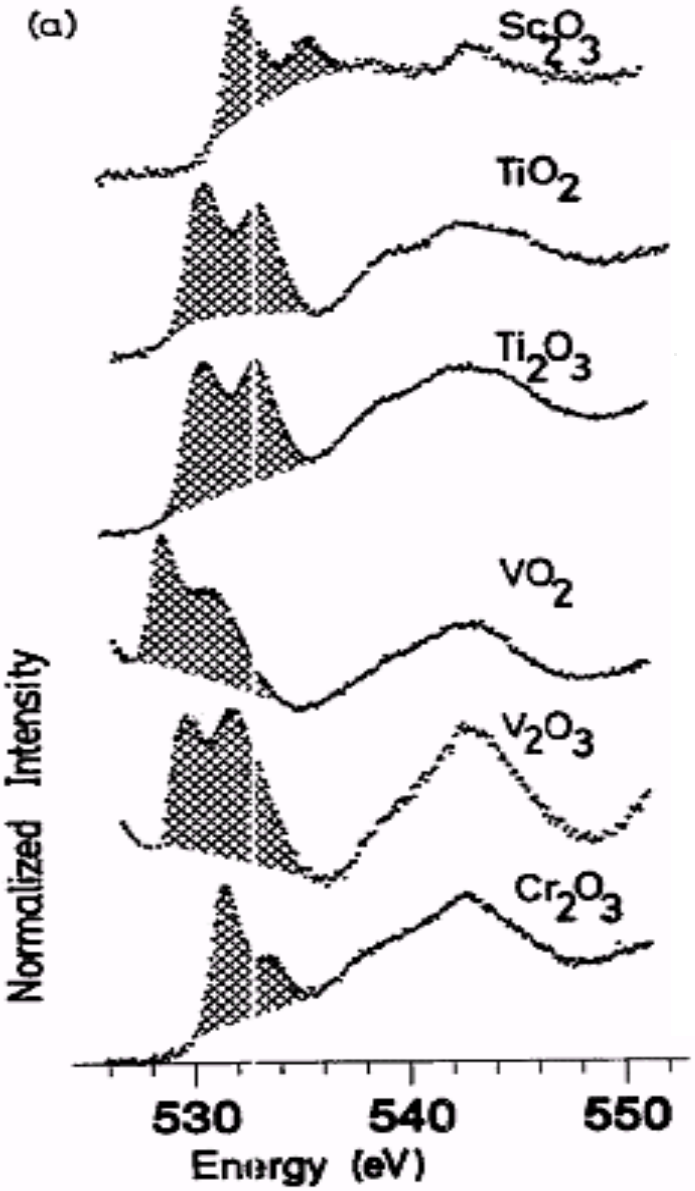
XAS: spectral shape (O 1s)

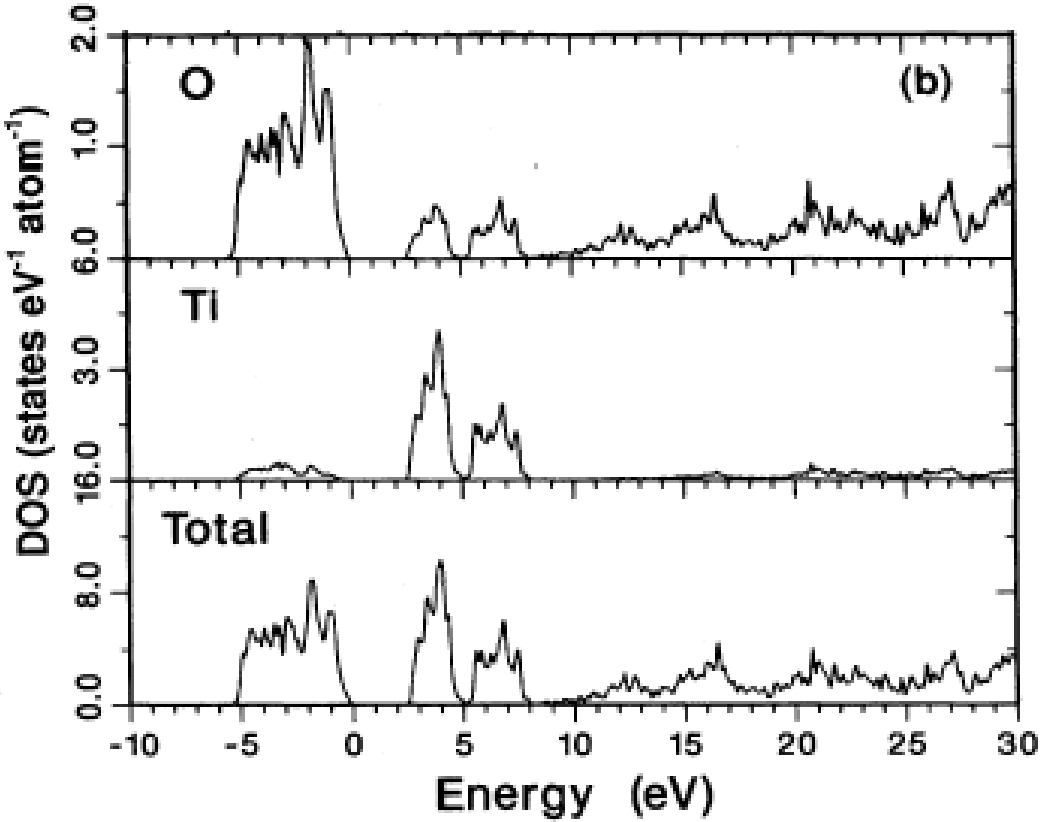




Phys. Rev. B.40, 5715 (1989)

XAS: spectral shape (O 1s)

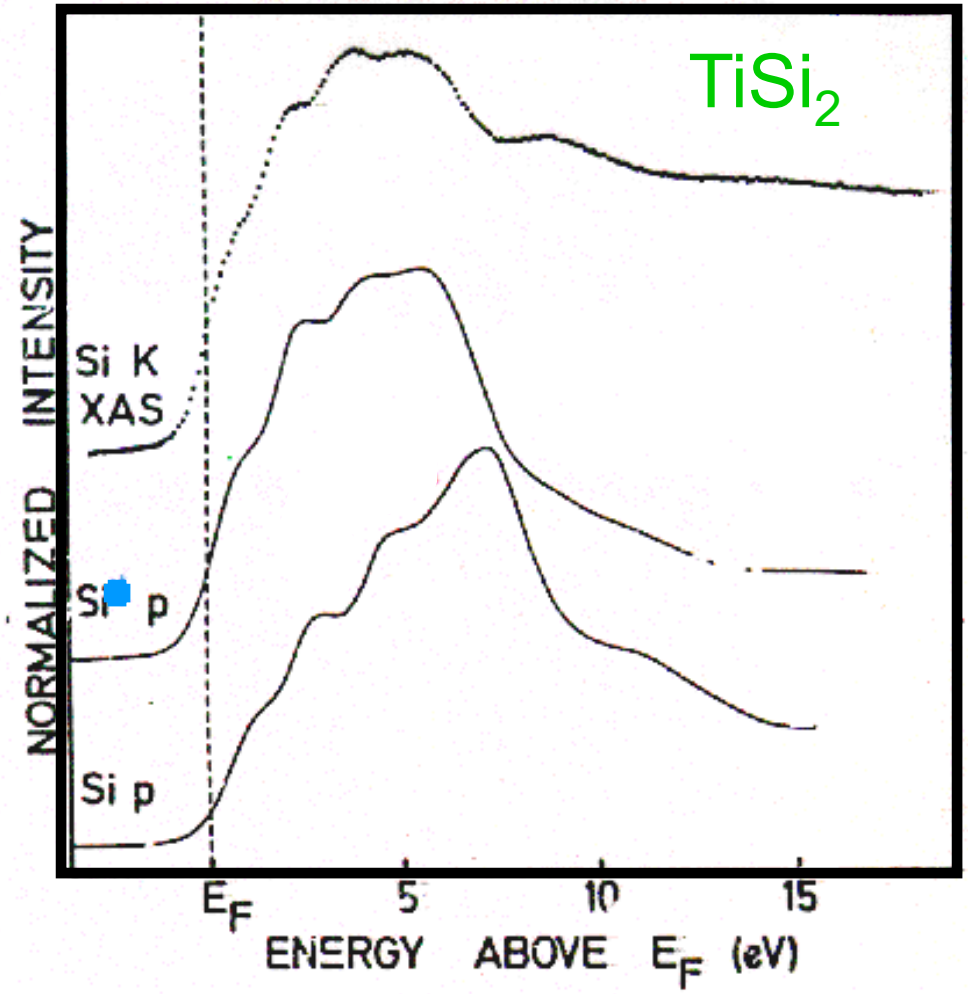




oxygen 1s > p DOS

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

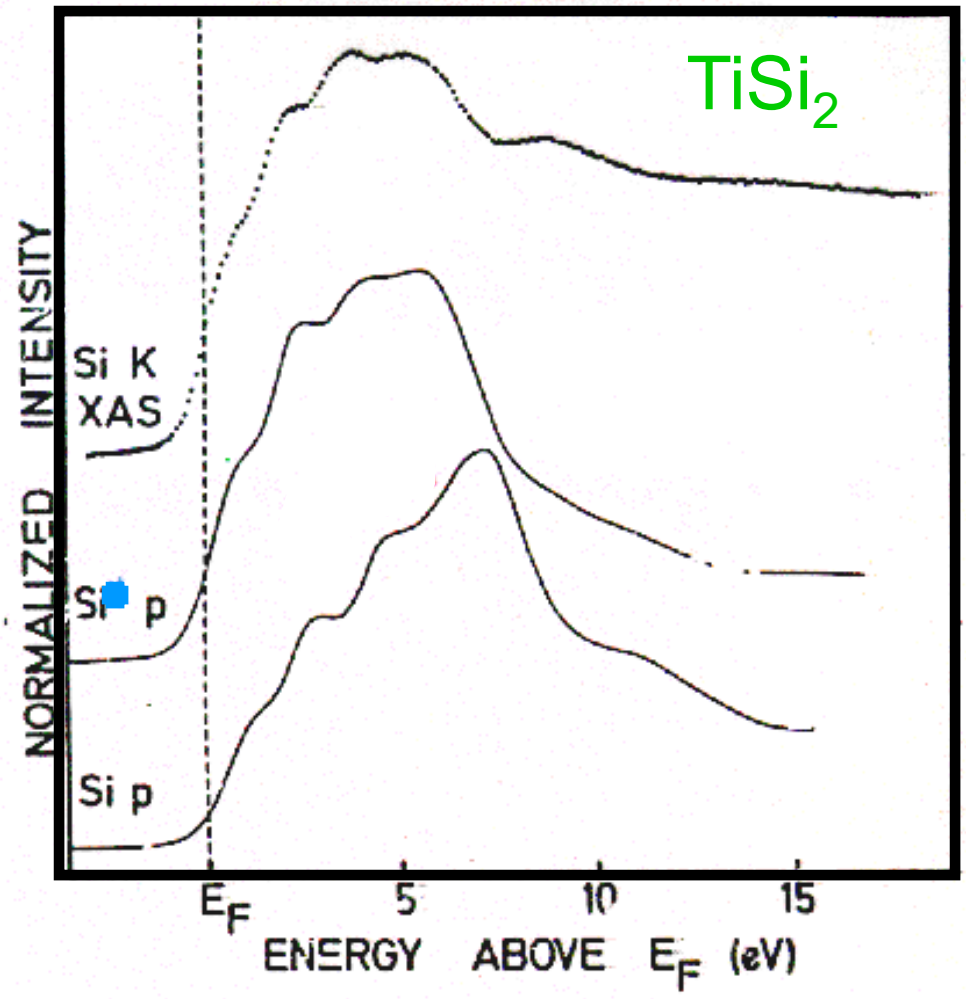
XAS: spectral shape



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

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

XAS: spectral shape



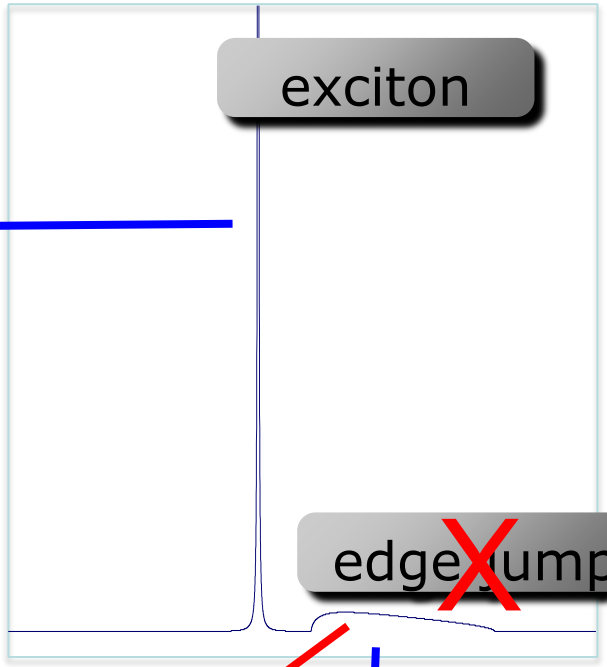
- **XAS codes:**
- Multiple scattering:
  FEFF, FDMNES, etc.
- Band structure:
  WIEN2K,
  Quantumespresso, etc.
- Real-space DFT:
  ADF,
  ORCA, etc.

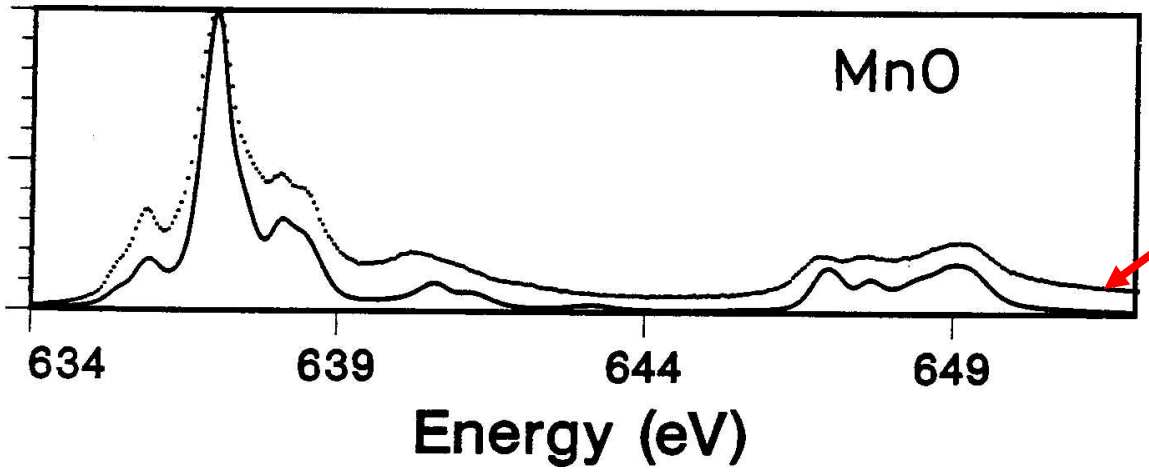
Phys. Rev. B. 41, 11899 (1991)

2p XAS of transition metal ions

2p > 3d

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



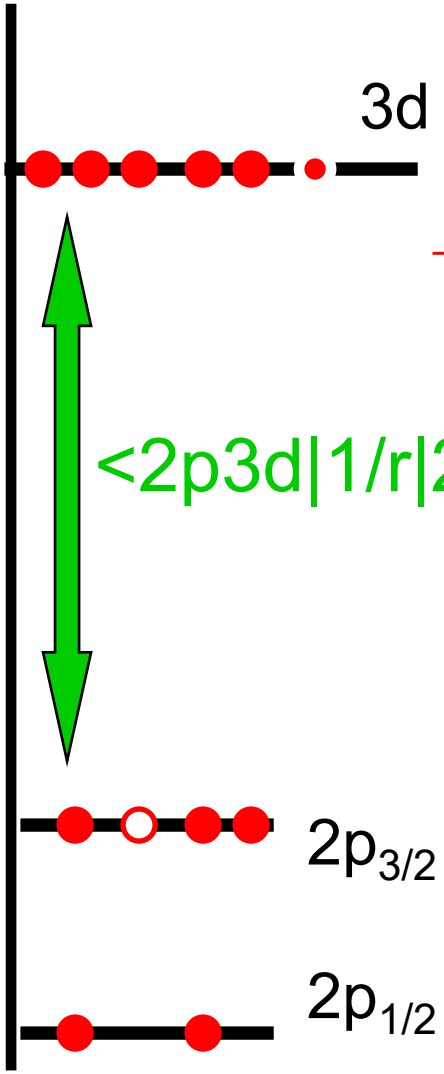


2p > s,d DOS

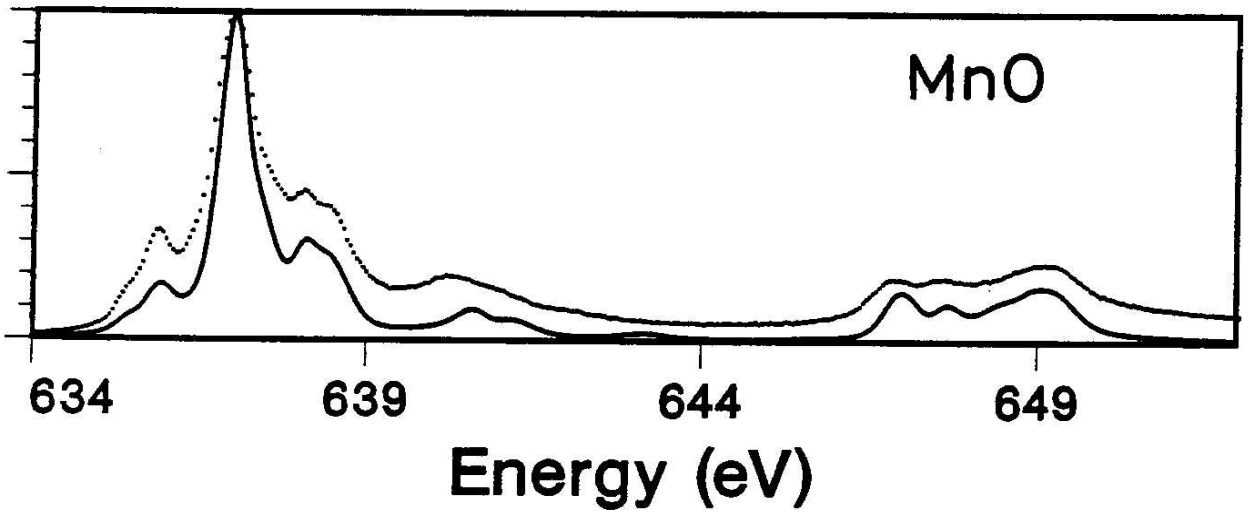
[Phys. Rev. B. 42, 5459 (1990)]

XAS: spectral shape

Interaction between core and valence wave functions

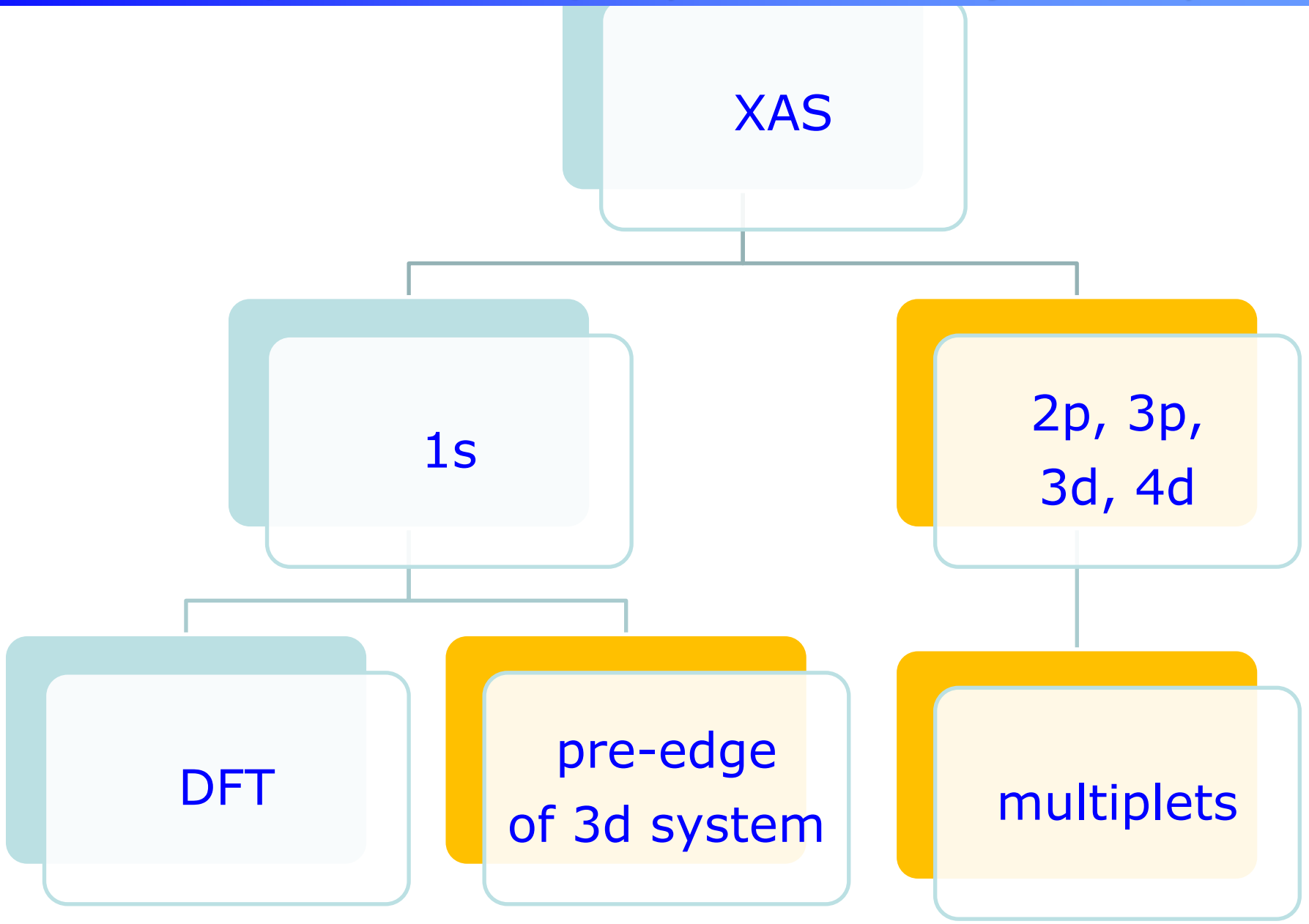


→ Spectral shape NOT improved in last 30 years!



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

XAS: spectral shape (of d and f systems)



CHARGE TRANSFER MULTIPLETS

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES

involving d and f-shells

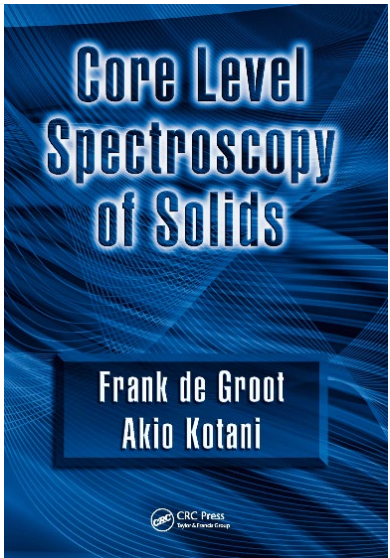
ATOMIC PHYSICS

⇓

GROUP THEORY

⇓

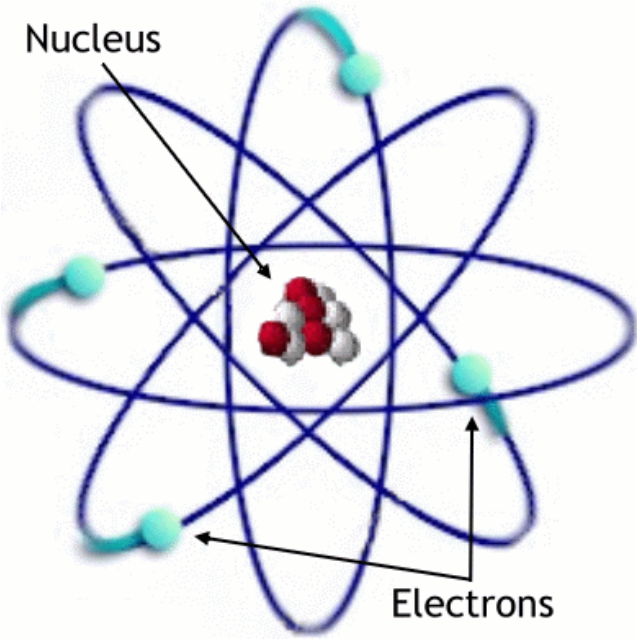
MODEL HAMILTONIANS



ATOMIC MULTIPLETS

$$H\Psi=E\Psi$$

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



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

ATOMIC MULTIPLETS

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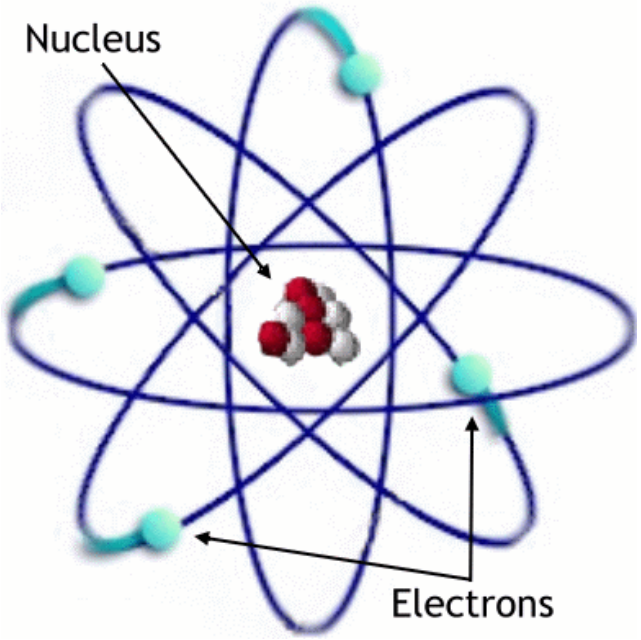
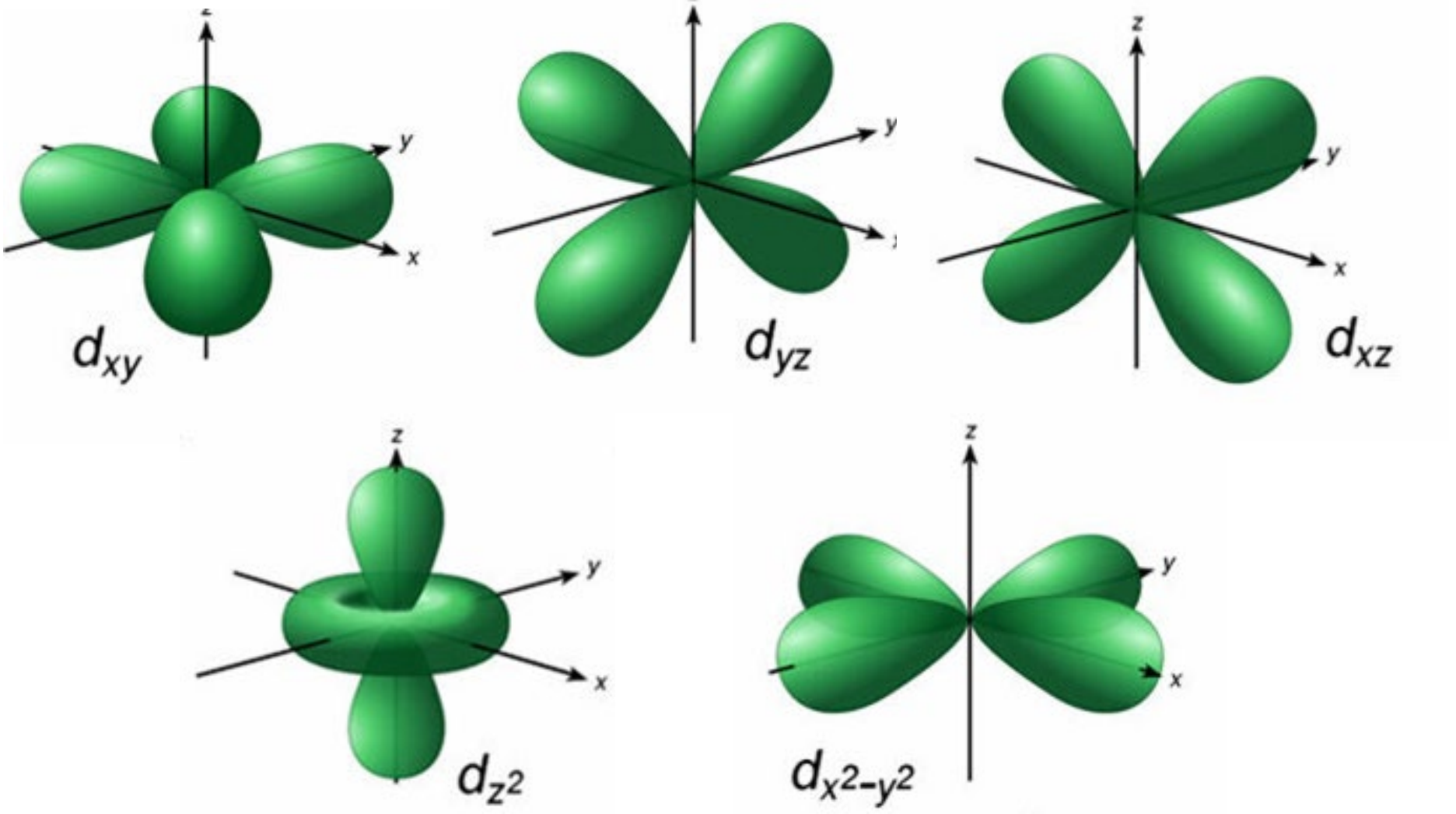


- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling

ATOMIC MULTIPLETS $3d^1$

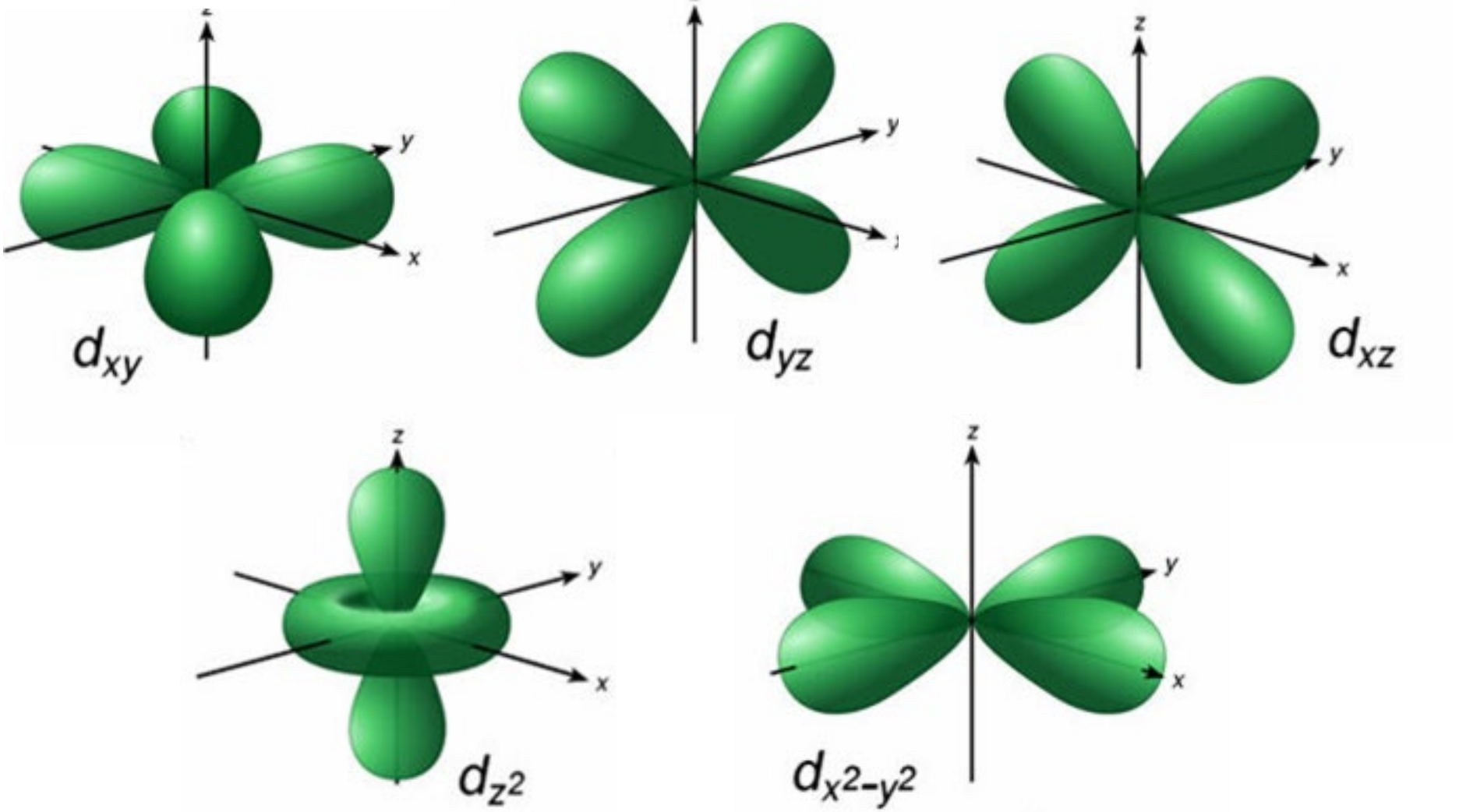


5 orbitals (each spin-up or spin-down) >> total 10 states

No electron-electron interaction: all states have the same energy

Quantum numbers: L=2 and S=½, notation as term symbol: $^{2S+1}L = {}^{2}D$

ATOMIC MULTIPLETS $3d^1$



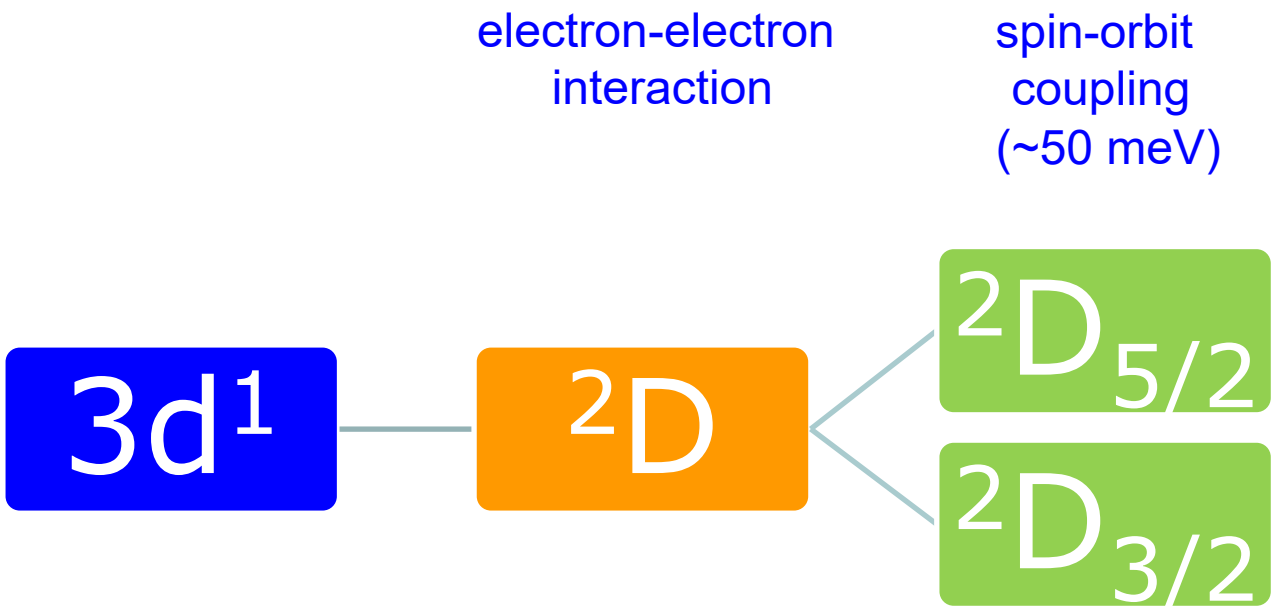
Spin-orbit coupling couples L and S quantum numbers to a total quantum number J

J_{max}= L+S = 5/2, J_{min}= |L-S|= 3/2, Integer steps of J.

Two term symbols: L=2, S=½, and J = 5/2 >> notation as term symbol: $^{2S+1}L_J = {}^2D_{5/2}$

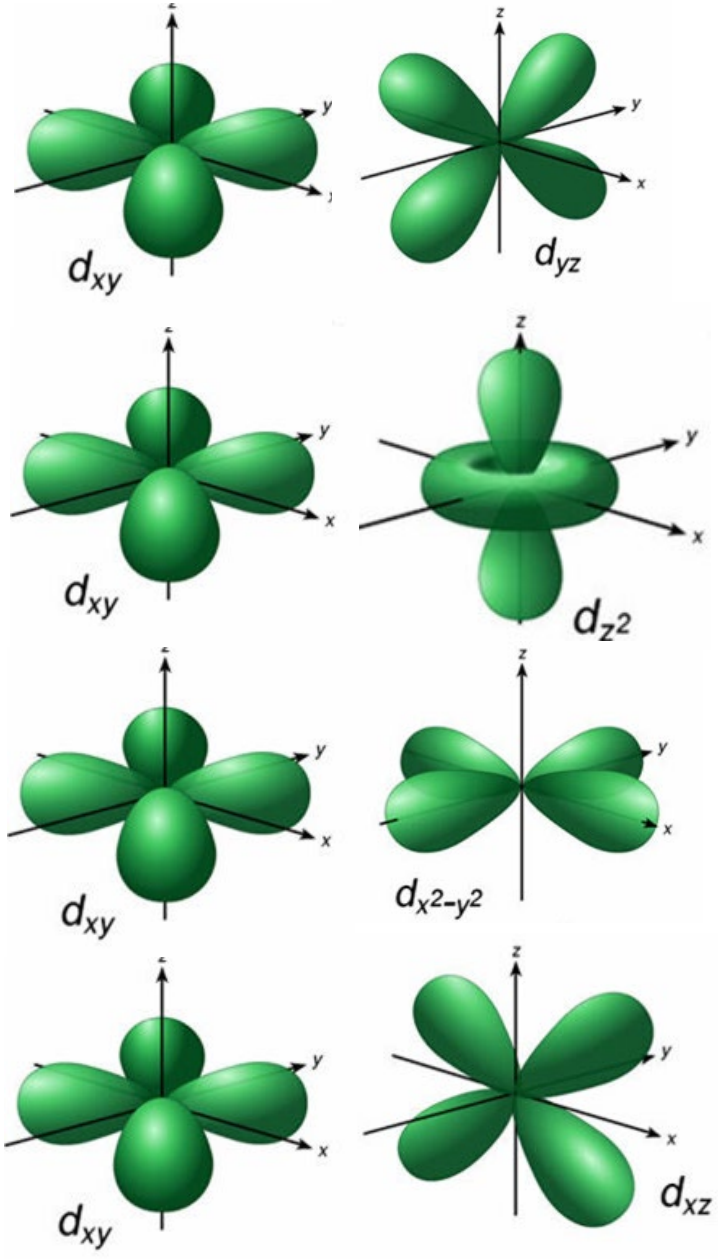
L=2, S=½, and J = 3/2 >> notation as term symbol: $^{2S+1}L_J = {}^2D_{3/2}$

ATOMIC MULTIPLETS $3d^1$



https://drive.google.com/file/d/1a-EOyCMw1AOGxlTnCVGfRQapi7w0KXCU/view?usp=sharing

ATOMIC MULTIPLETS $3d^2$



5 spin-up orbitals give 4 + 3 + 2 + 1 = 10 paired $3d^2$ states
5 spin-down orbitals give 10 paired down-down $3d^2$ states
There are 5x5 = 25 up-down states
In total 10+10+25 = 45 states

Can also be calculated as 10 x 9 / 2 = 45 states

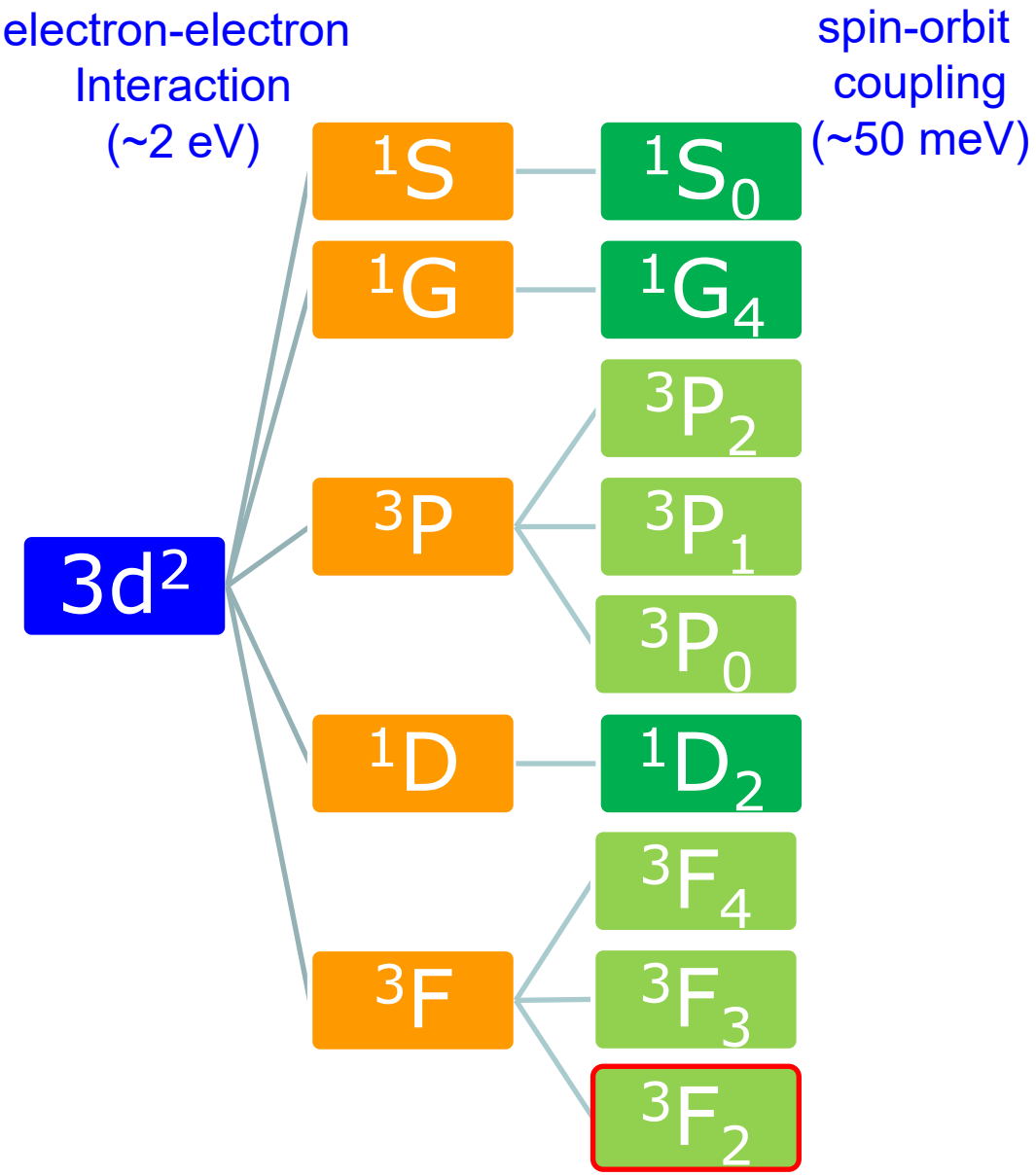
Electron-electron interaction is different for different orbital combinations

There will be a number of different states with different energies.

Analysis shows that the states are ^1S, ^3P, ^1D, ^3F and ^1G

https://drive.google.com/file/d/1a-EOyCMw1AOGxlTnCVGfRQapi7w0KXCU/view?usp=sharing

ATOMIC MULTIPLETS $3d^2$

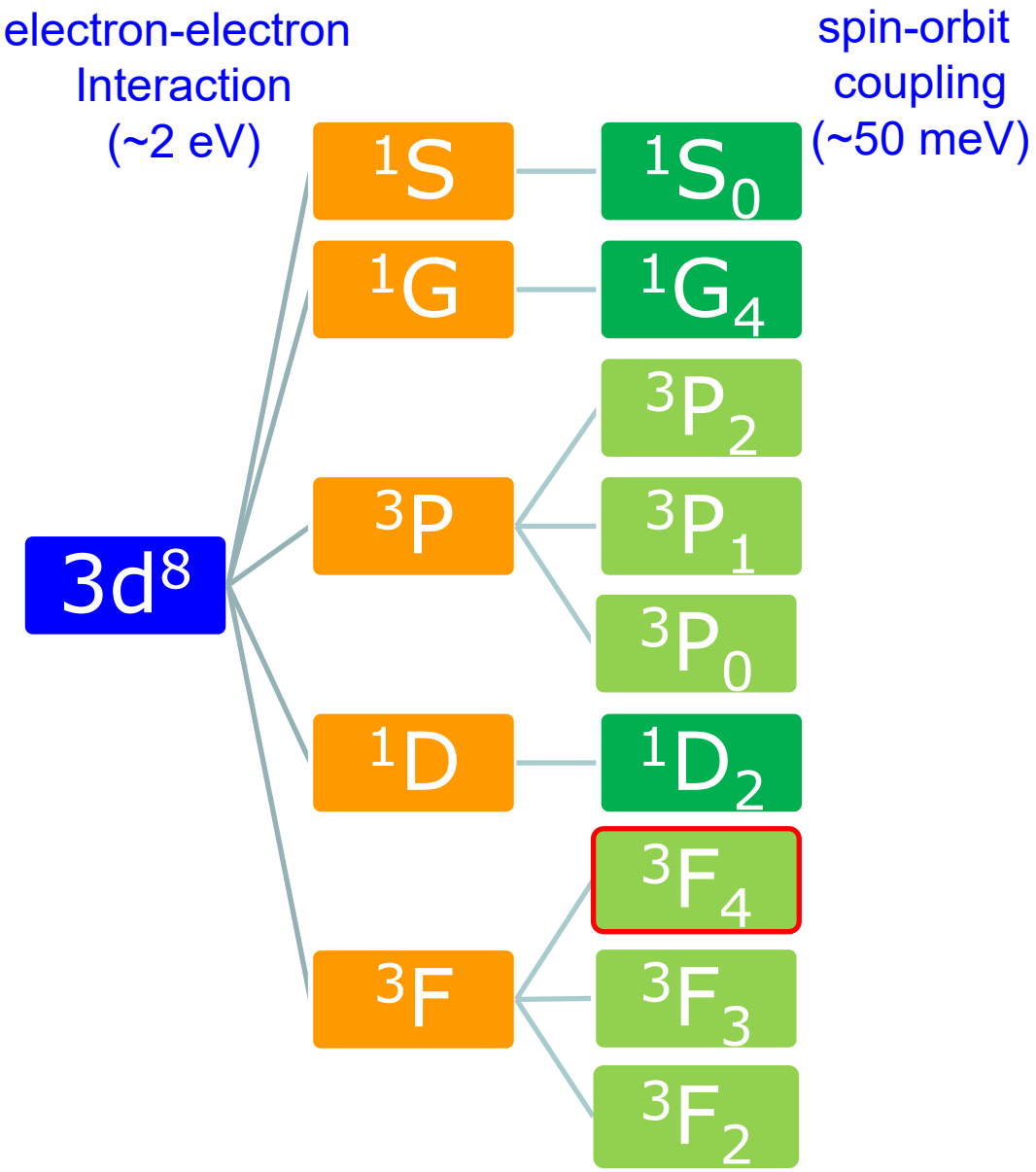


Ground state:

Given by **Hunds rules**

1. max S
2. max L
3. min J (if less than half full)

ATOMIC MULTIPLETS $3d^8$



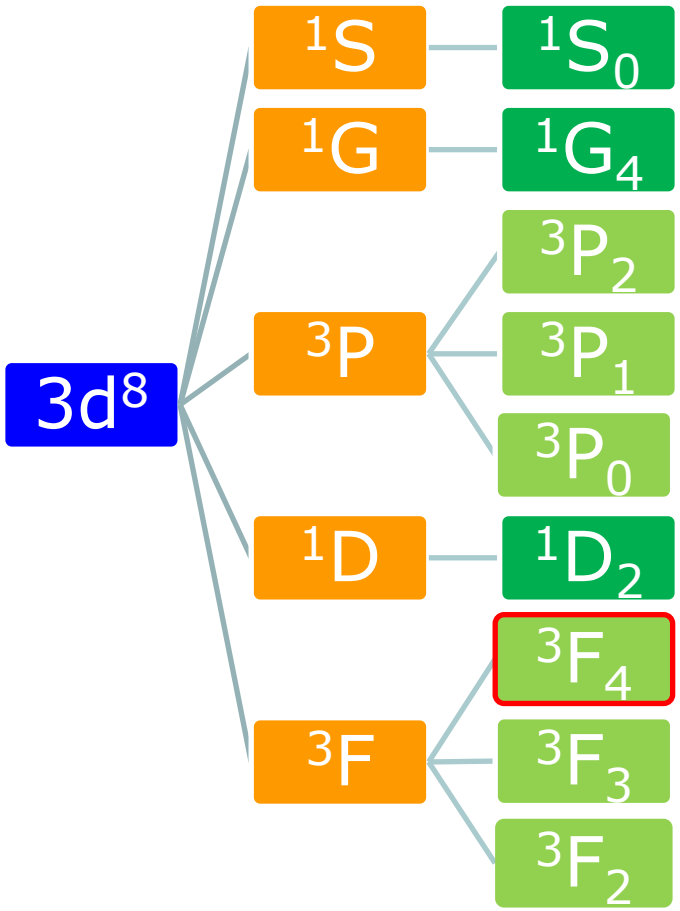
Ground state:

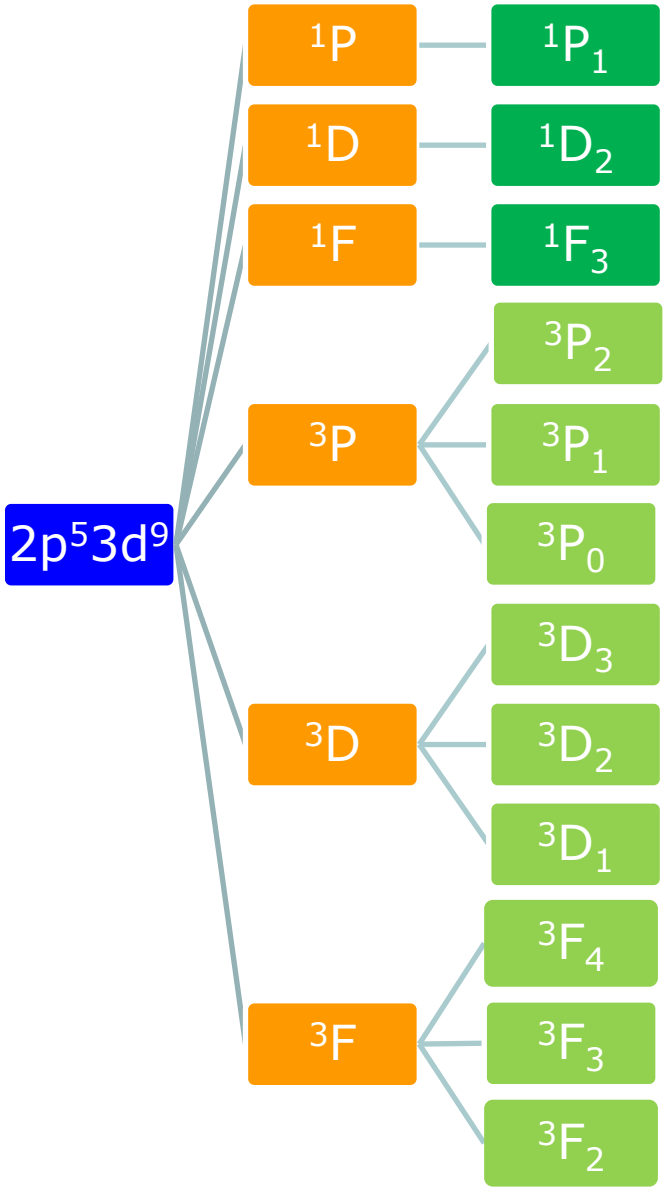
Given by **Hunds rules**

1. max S
2. max L
3. max J (if more than half full)

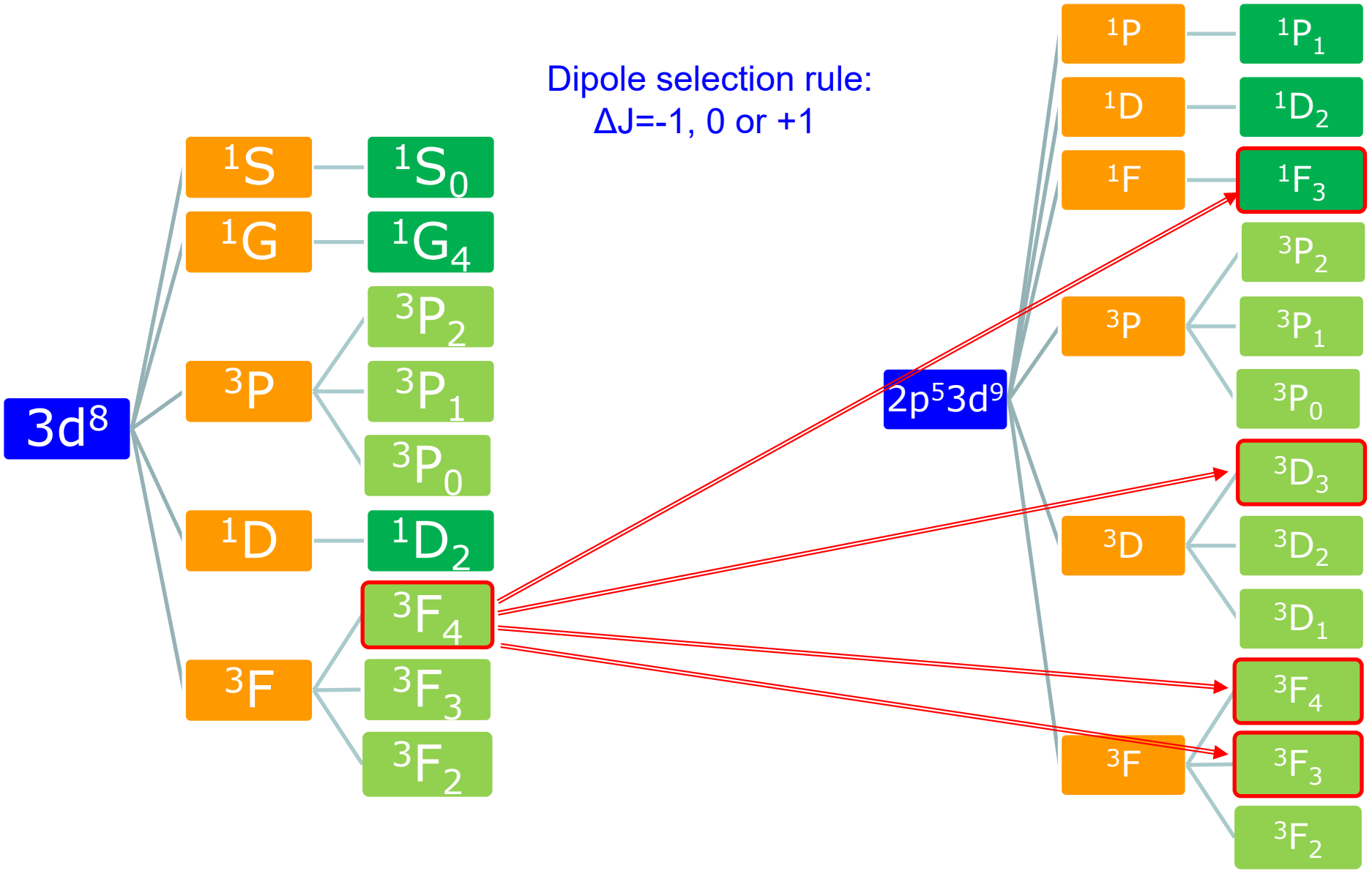
X-ray absorption from $3d^8$ to $2p^5 3d^9$

Dipole selection rule:
$\Delta J = -1, 0 \text{ or } +1$

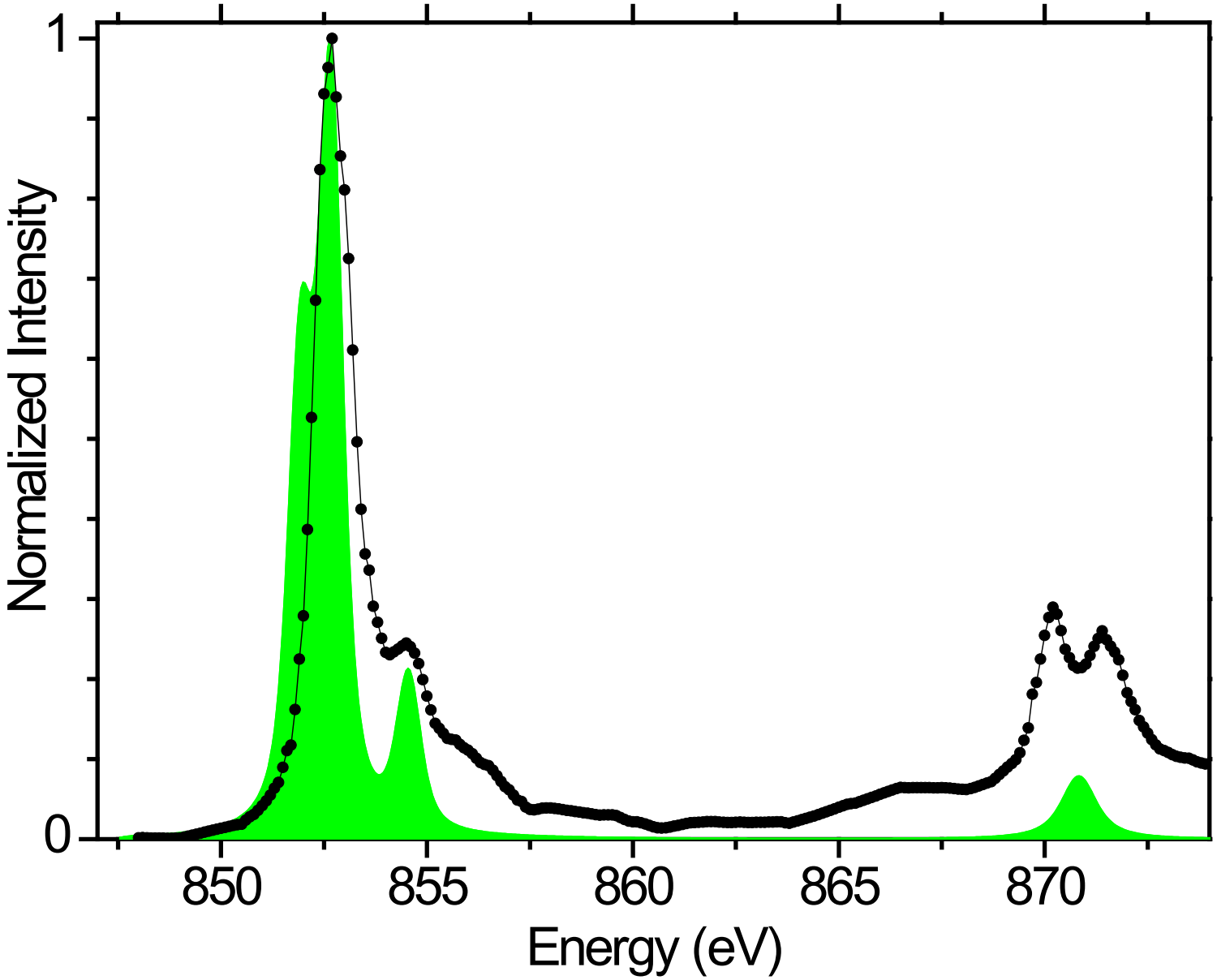




X-ray absorption from $3d^8$ to $2p^5 3d^9$



2p XAS of NiO with atomic multiplets



3d XAS of rare earths

4f electrons are localized

- No effect of surroundings (crystal field < lifetime broadening)
- 3d XAS is self screened > no charge transfer effect

Initial state

- electron-electron interaction.
- Valence spin-orbit coupling

Final state

- + core hole – valence hole 'multiplet' interaction.
- + core hole spin-orbit coupling

PHYSICAL REVIEW B VOLUME 32, NUMBER 8 15 OCTOBER 1985

$3d$ x-ray-absorption lines and the $3d^9 4f^{n+1}$ multiplets of the lanthanides

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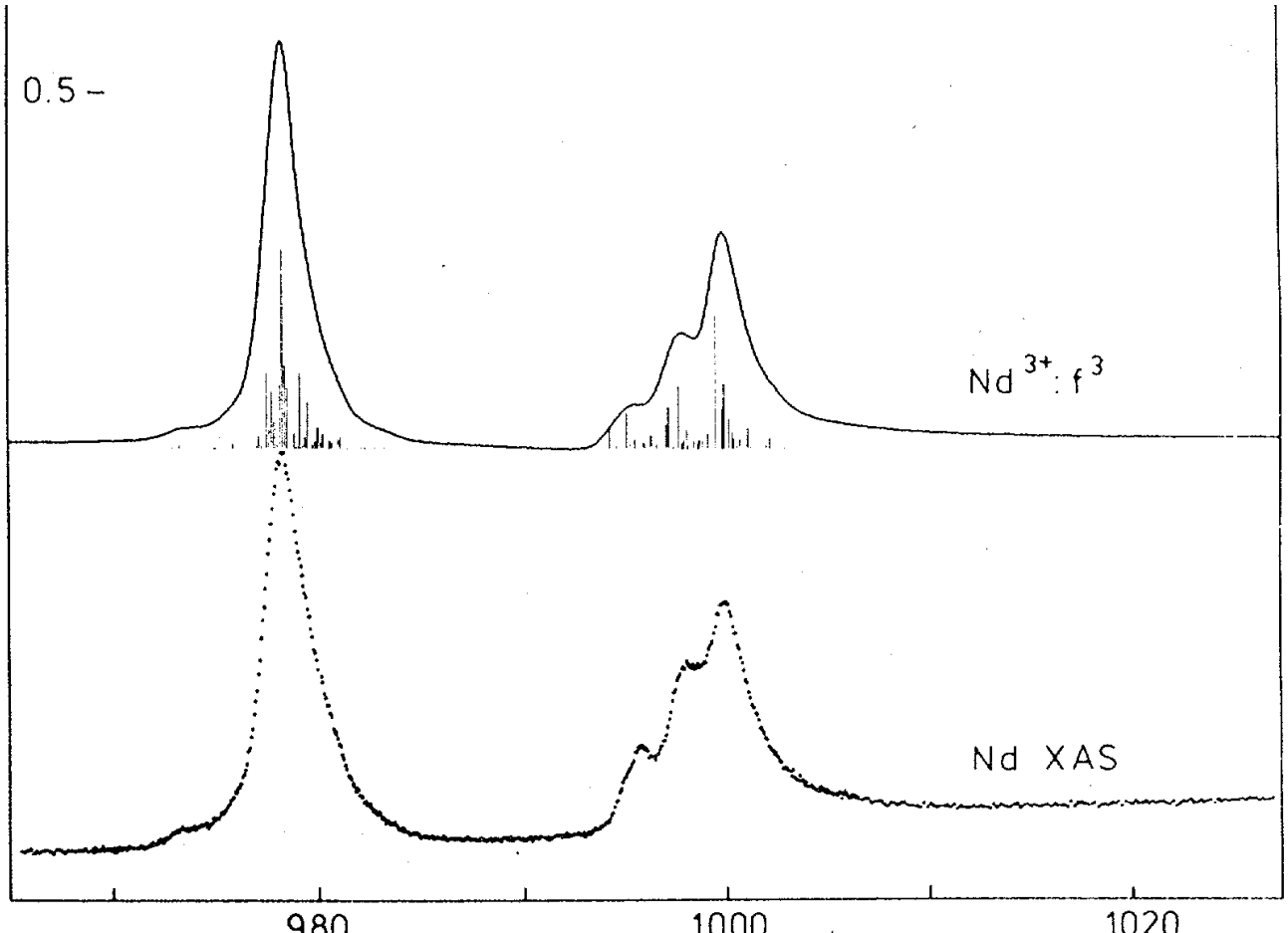
3d XAS of rare earths

Nd^{3+} $4f^3$ system: ground state is $^4I_{9/2}$



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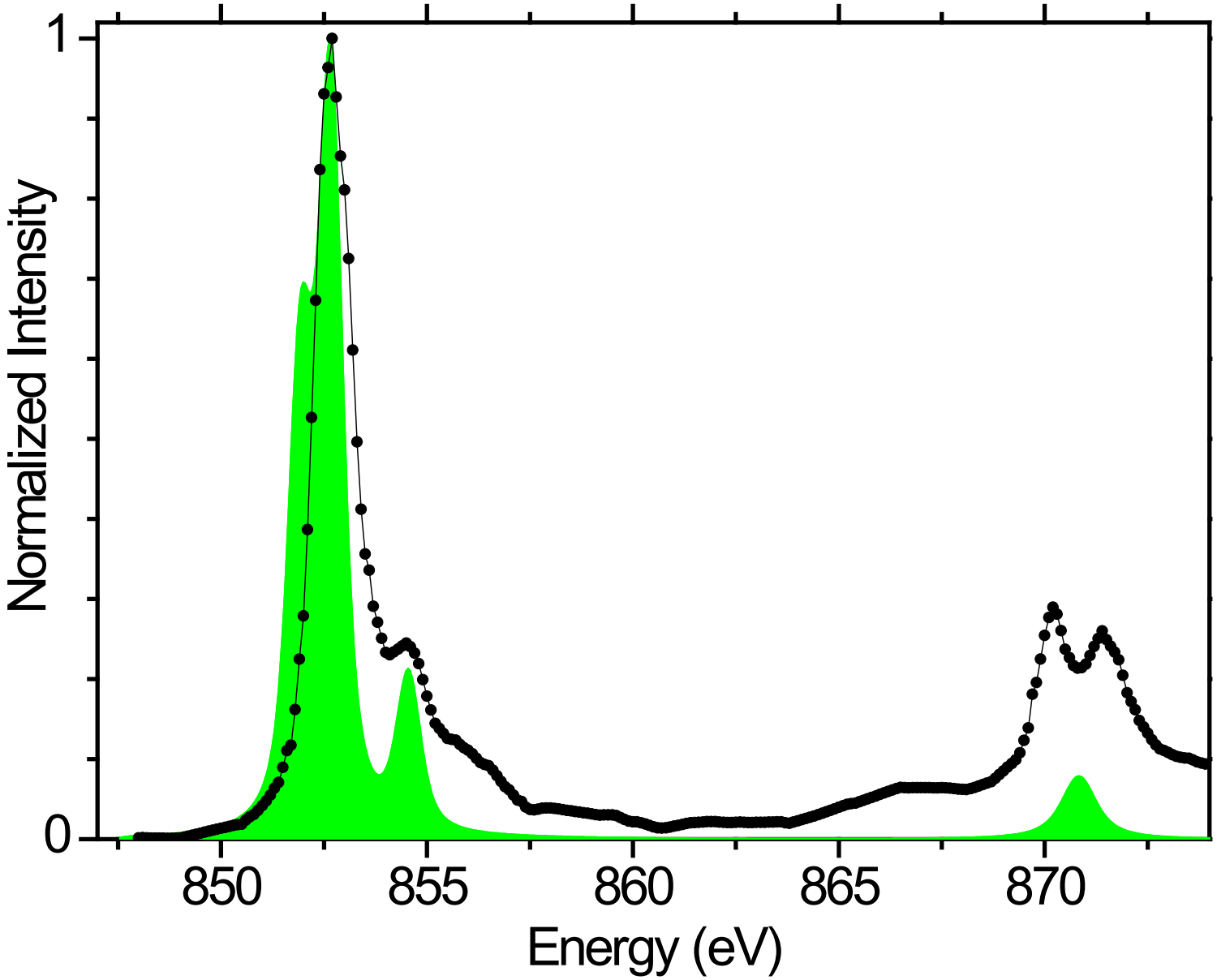


2p XAS of 3d transition metal oxides

3d electrons are less localized

- Effect of surroundings (crystal field effect)
- 3d XAS is self screened > weak charge transfer effect

Initial state

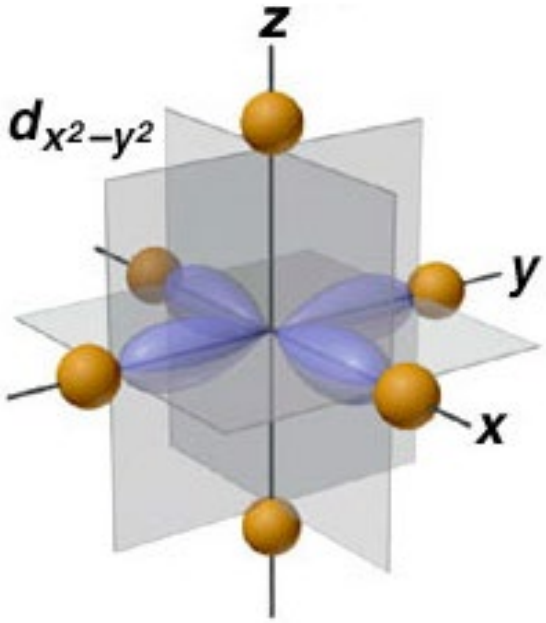
- electron-electron interaction.
- valence spin-orbit coupling
- crystal field effect

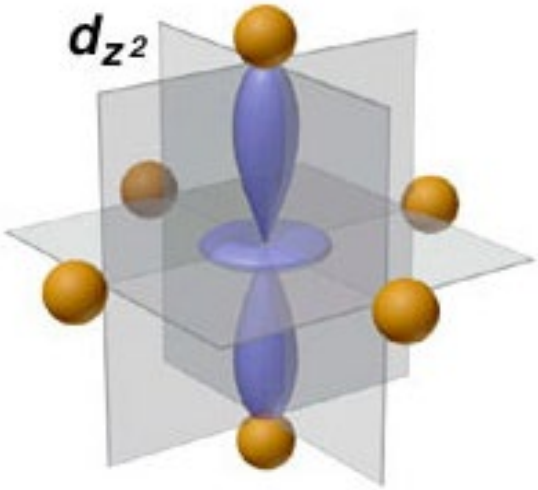
Final state

- core hole – valence hole ‘multiplet’ interaction.
- core hole spin-orbit coupling
- crystal field effect

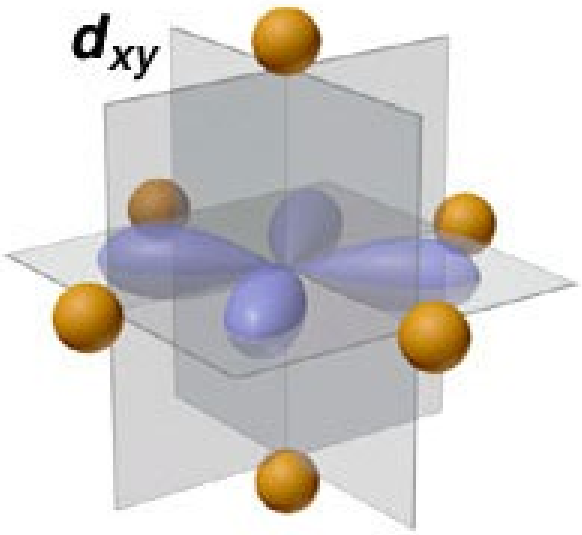
crystal field effect

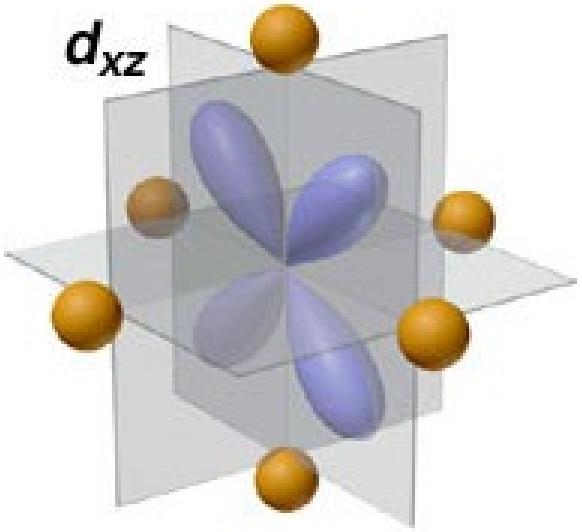
e_g states

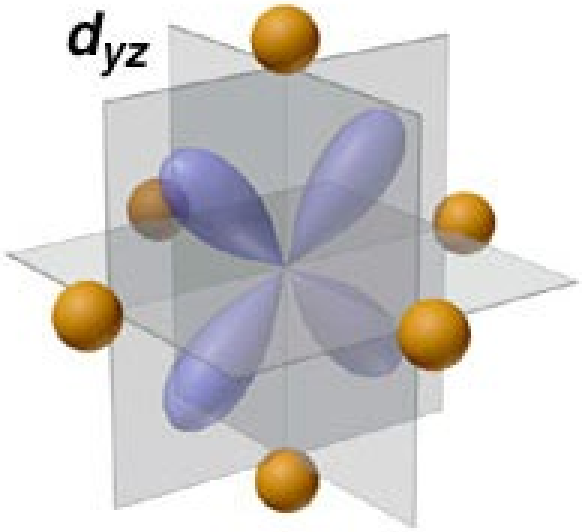




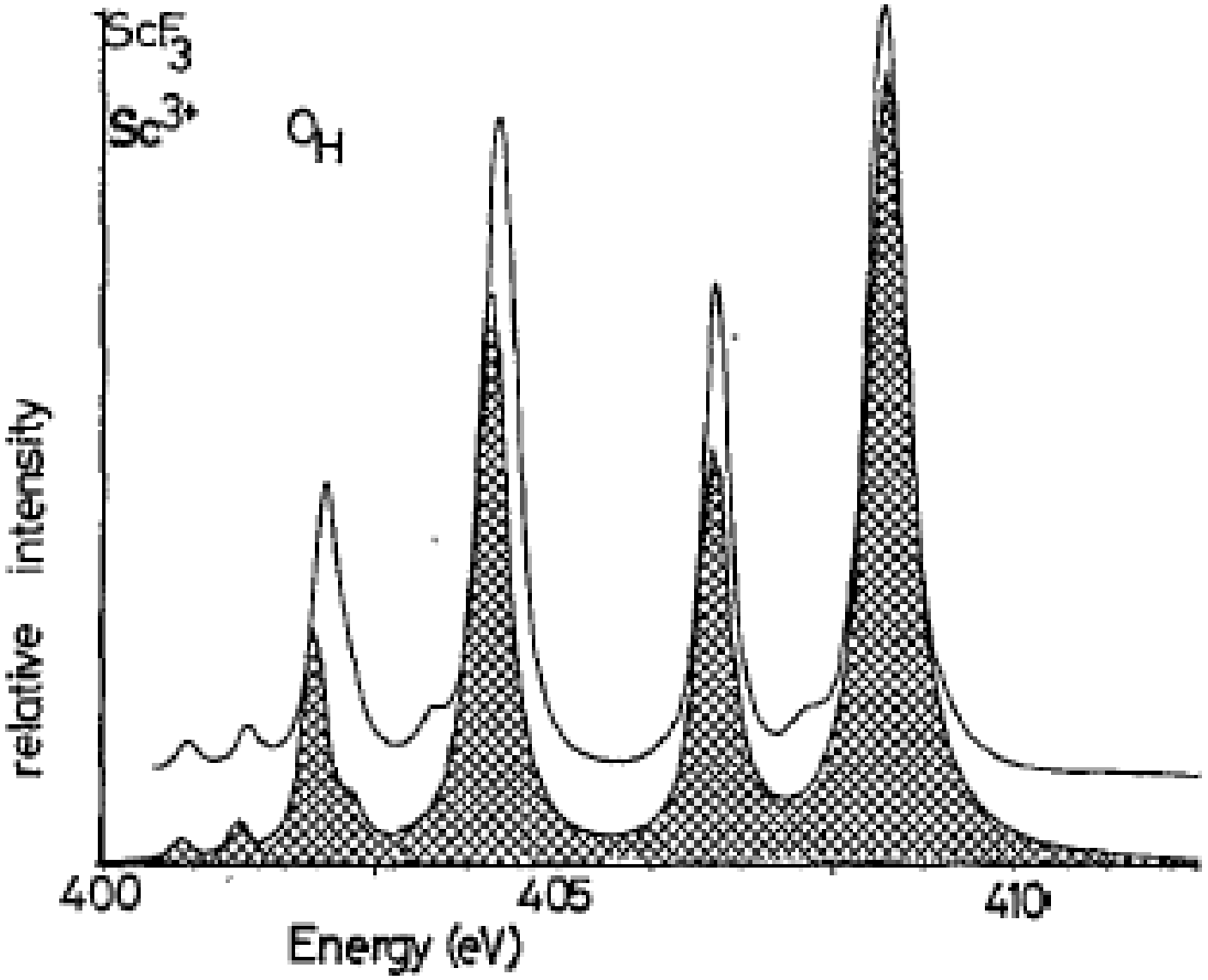
t_{2g} states







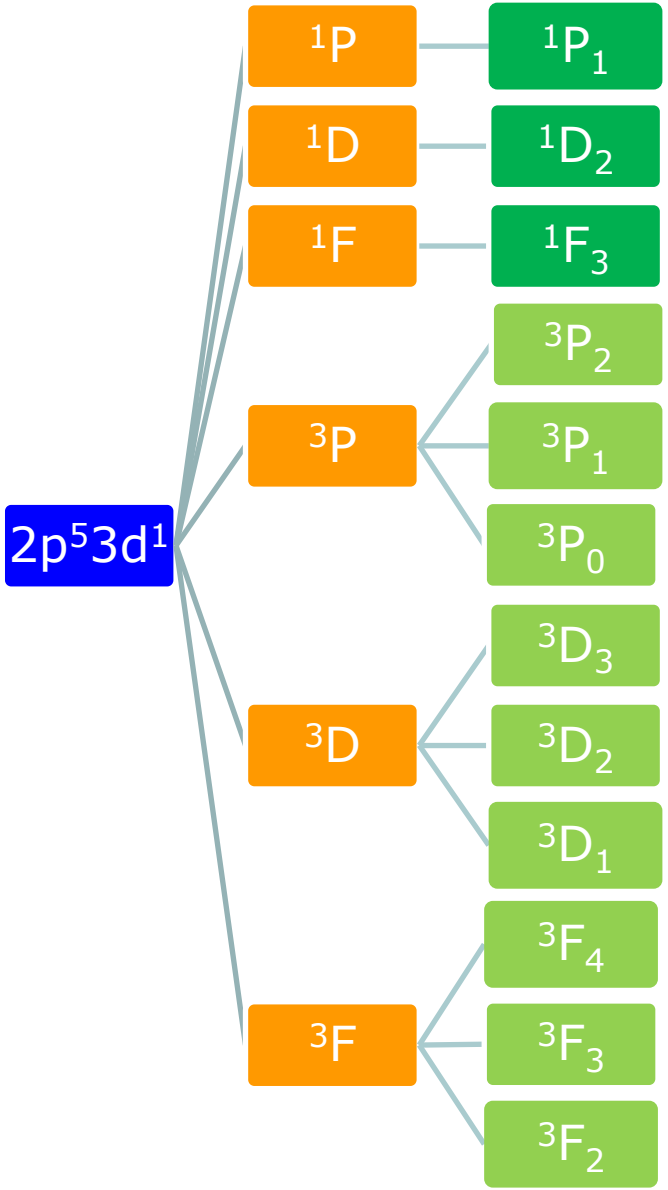
2p XAS of ScF3 with crystal field multiplets



PHYS. Rev. B. 41, 928 (1990) [google drive]

X-ray absorption from $3d^0$ to $2p^53d^1$

Dipole selection rule:
$\Delta J=-1, 0 \text{ or } +1$
$J=J' \neq 0$



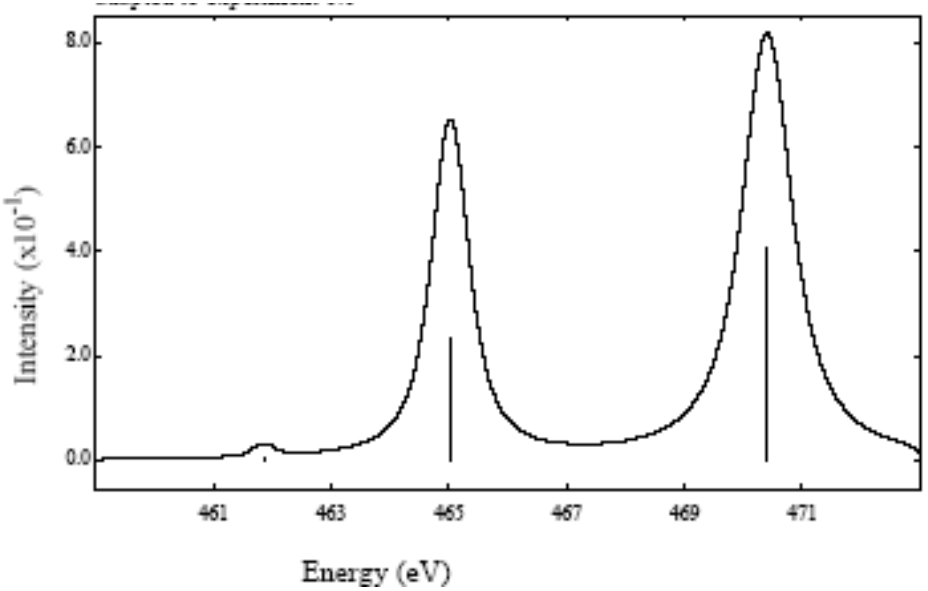
X-ray absorption from $3d^0$ to $2p^53d^1$

Dipole selection rule:
$\Delta J=-1, 0$ or $+1$
$J=J' \neq 0$

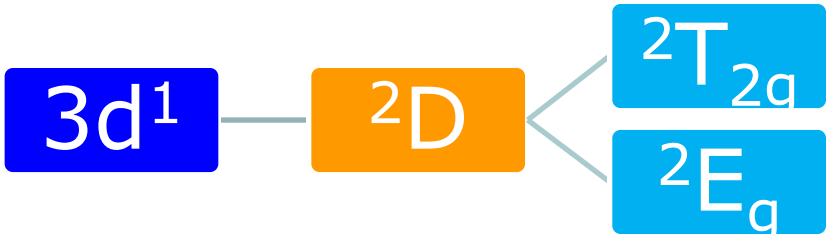
$3d^0$ — ^1S — $^1S_0$

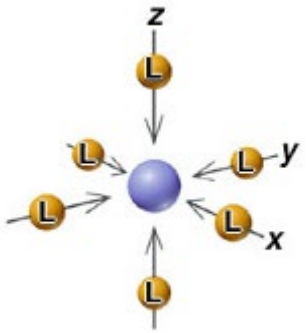
$2p^53d^1$

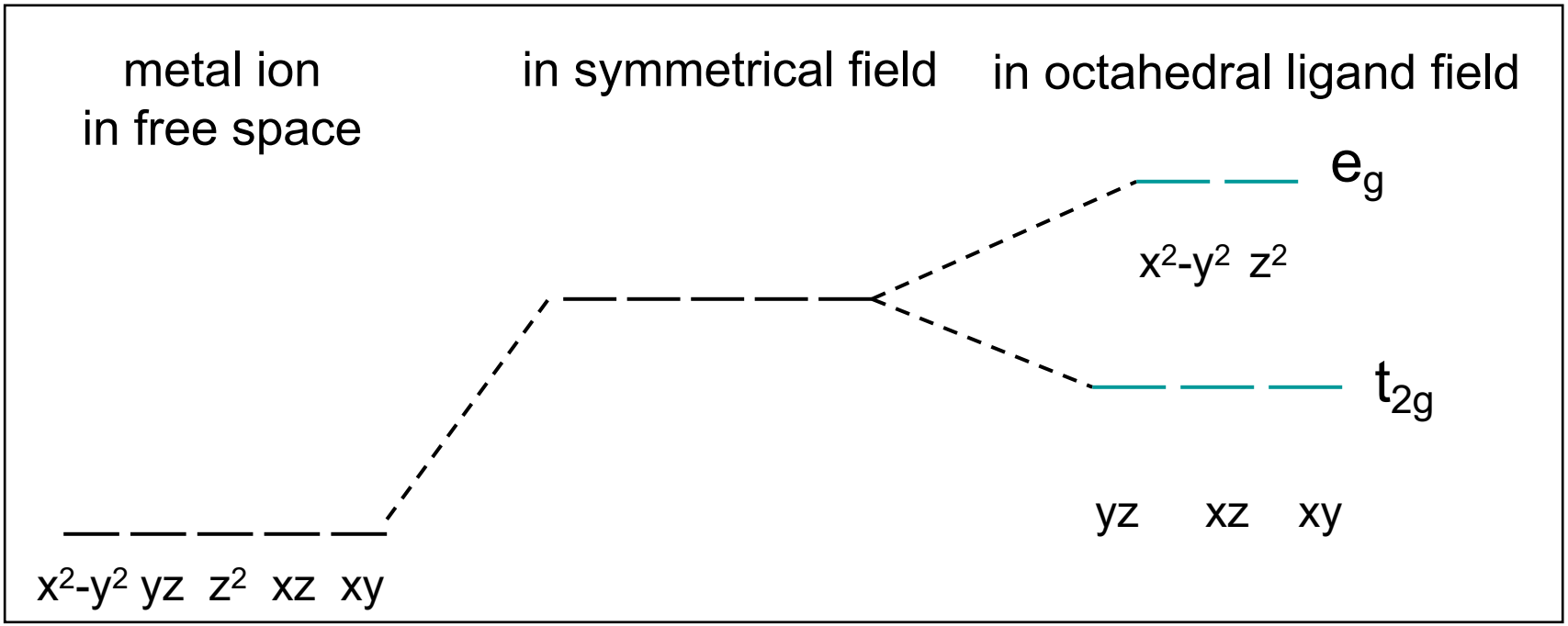
- ^1P → $^1P_1$
- ^1D → $^1D_2$
- ^1F → $^1F_3$
- ^3P → $^3P_2$, $^3P_1$, $^3P_0$
- ^3D → $^3D_3$, $^3D_2$, $^3D_1$
- ^3F → $^3F_4$, $^3F_3$, $^3F_2$



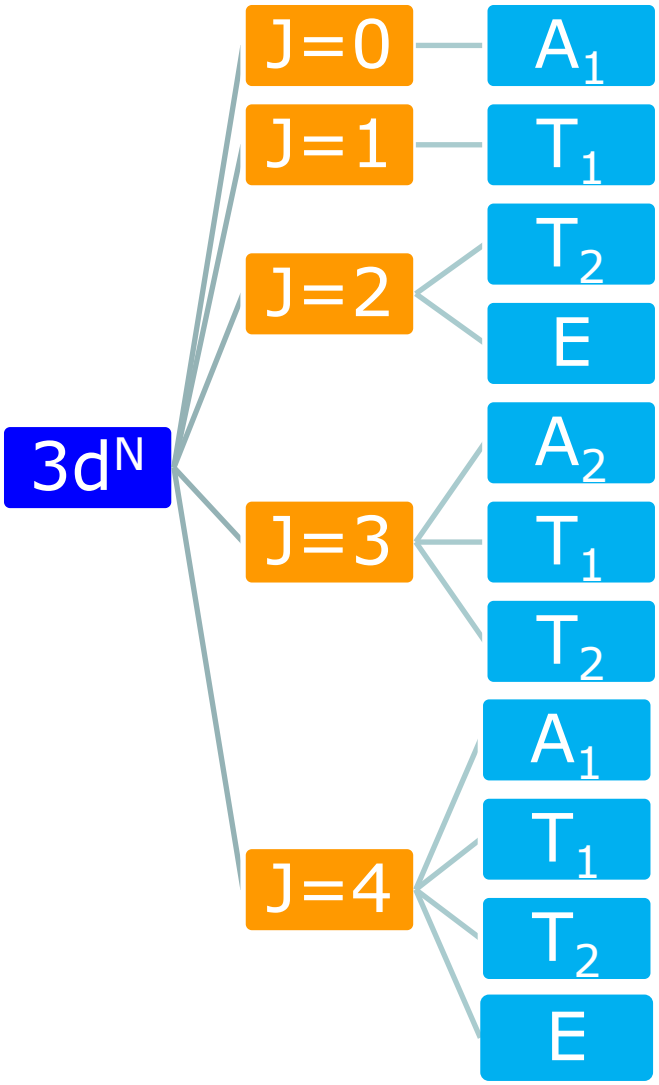
CRYSTAL FIELD EFFECT







CRYSTAL FIELD EFFECT

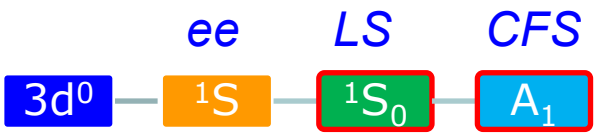


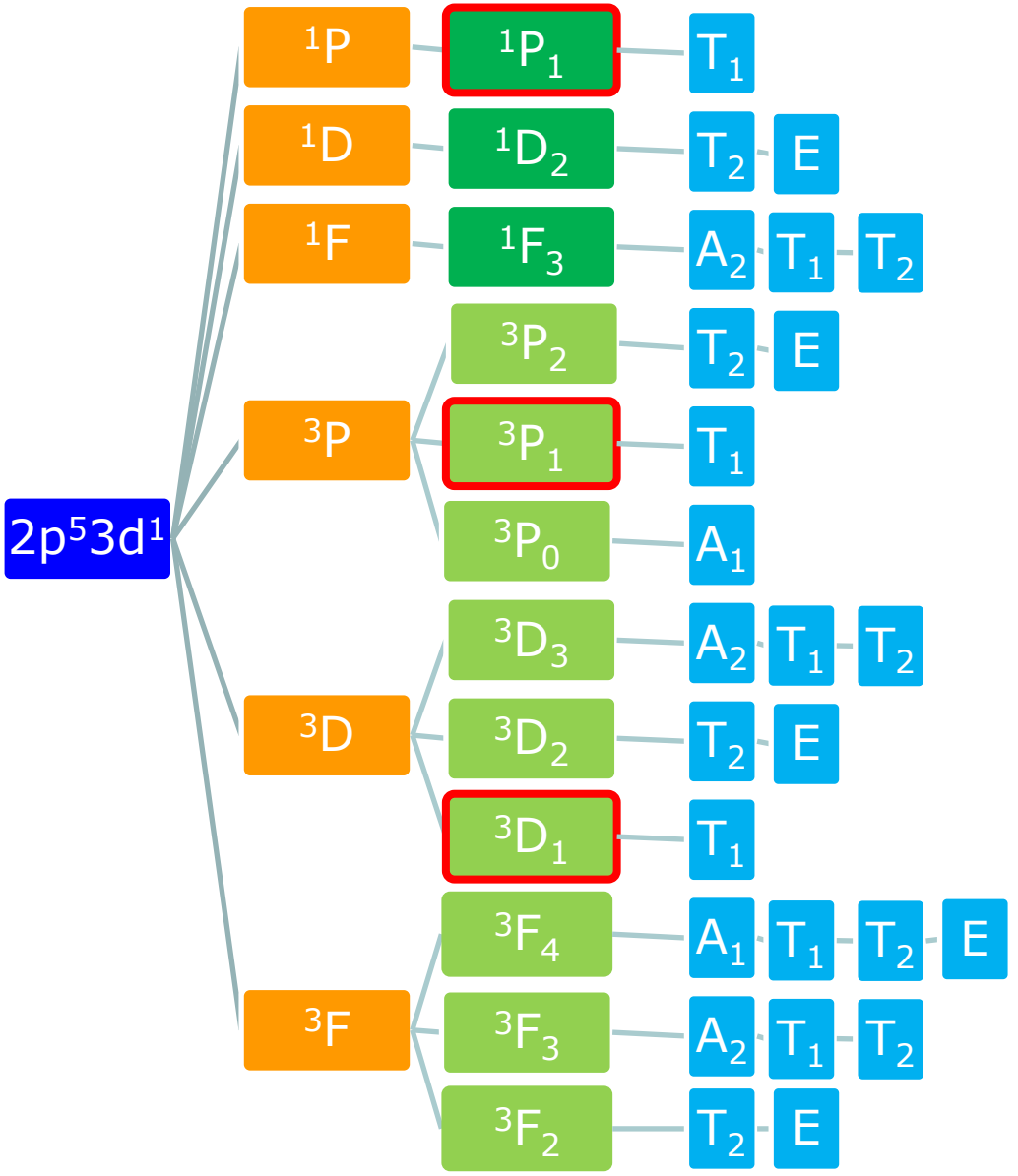
Branching rules:

Same rules for any quantum number

S, L or J

X-ray absorption from $3d^0$ to $2p^53d^1$



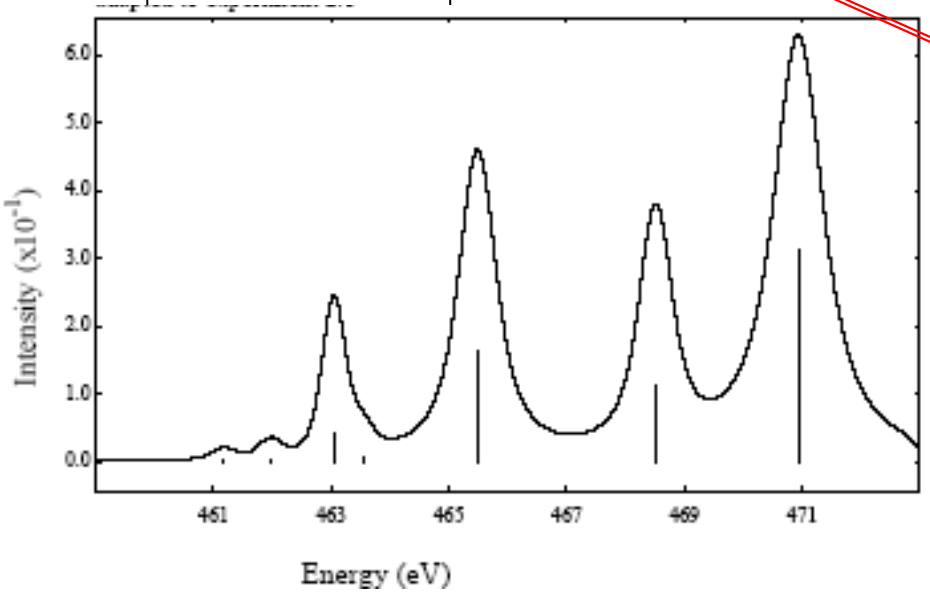


X-ray absorption from $3d^0$ to $2p^53d^1$

Dipole selection rule:
$\Delta J = T_1$
(cubic symmetry)

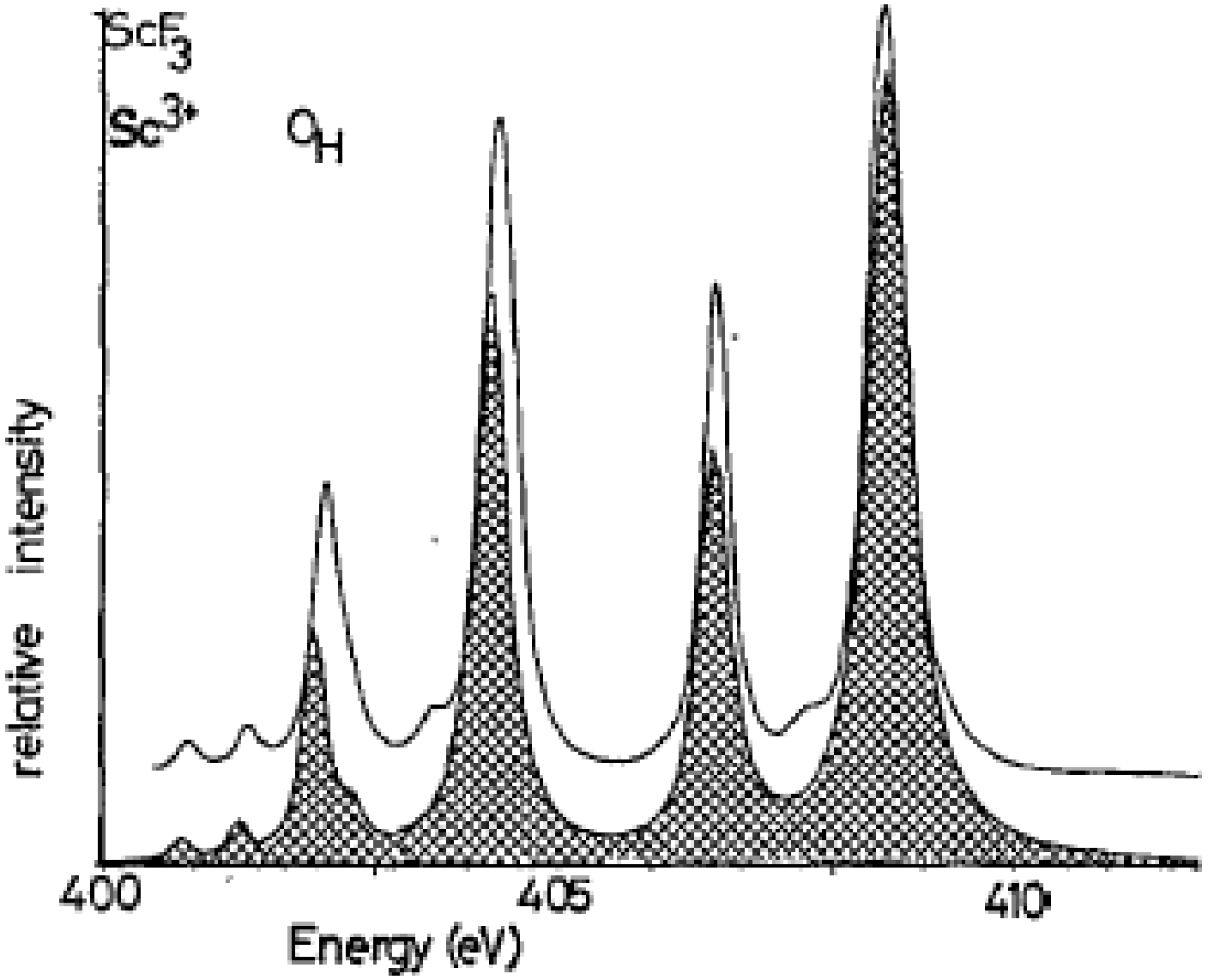
CFS

$3d^0$ — A_1 — $2p^53d^1$



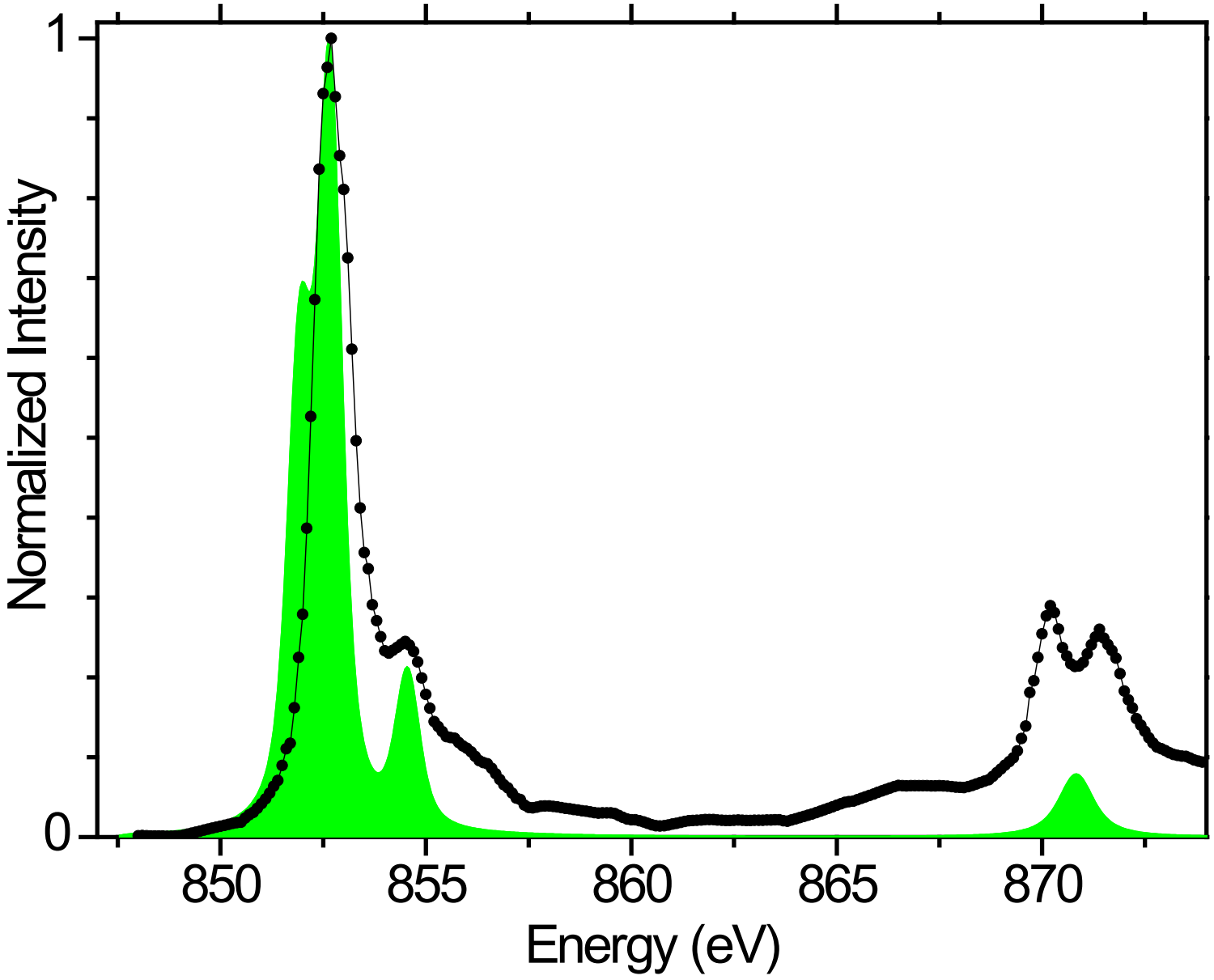
		T_1		
	T_2			E
A_2		T_1	T_2	
	T_2			E
		T_1		
A_1				
A_2		T_1	T_2	
	T_2			E
		T_1		
A_1		T_1	T_2	E
A_2		T_1	T_2	
	T_2			E
2	**3**	**7**	**8**	**5**

2p XAS of ScF3 with crystal field multiplets

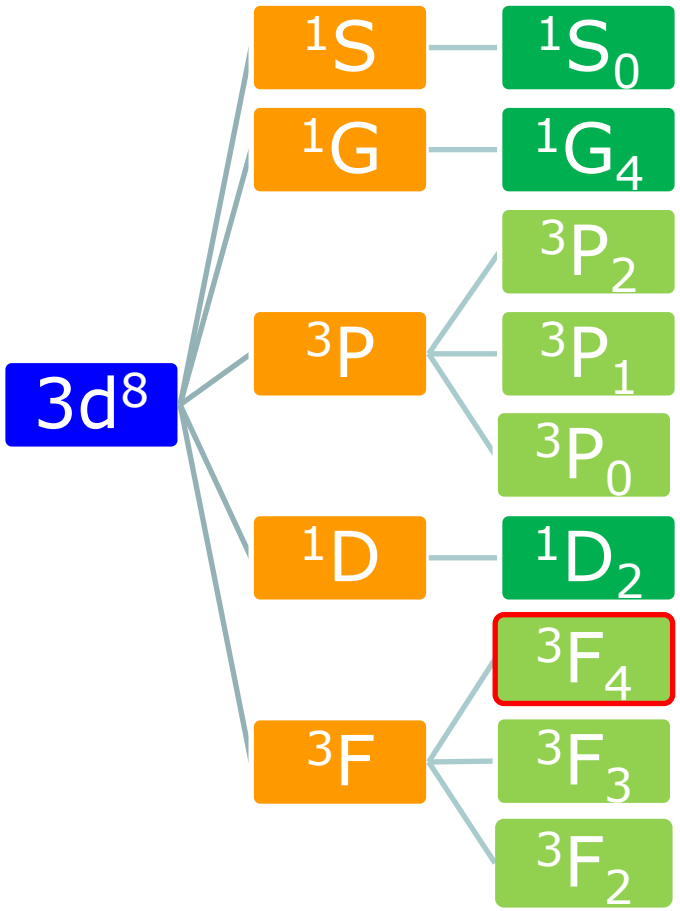


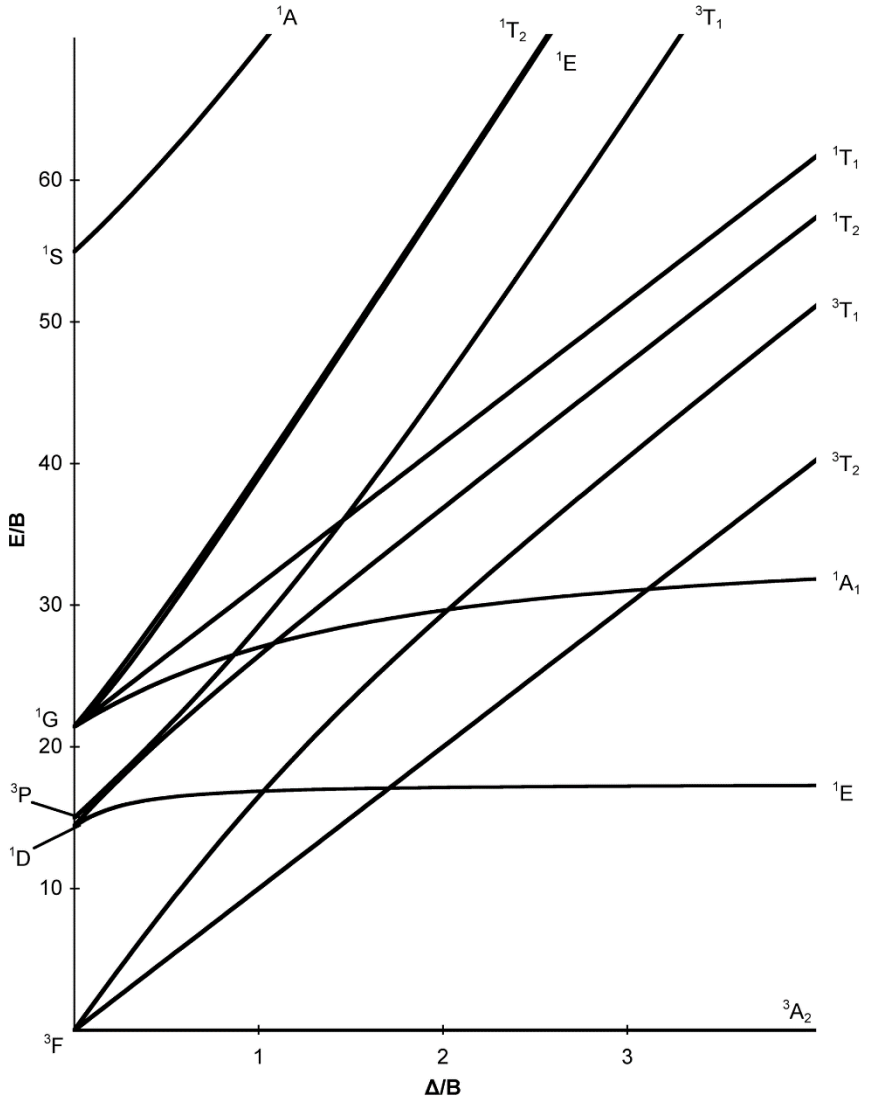
PHYS. Rev. B. 41, 928 (1990) [google drive]

2p XAS of NiO

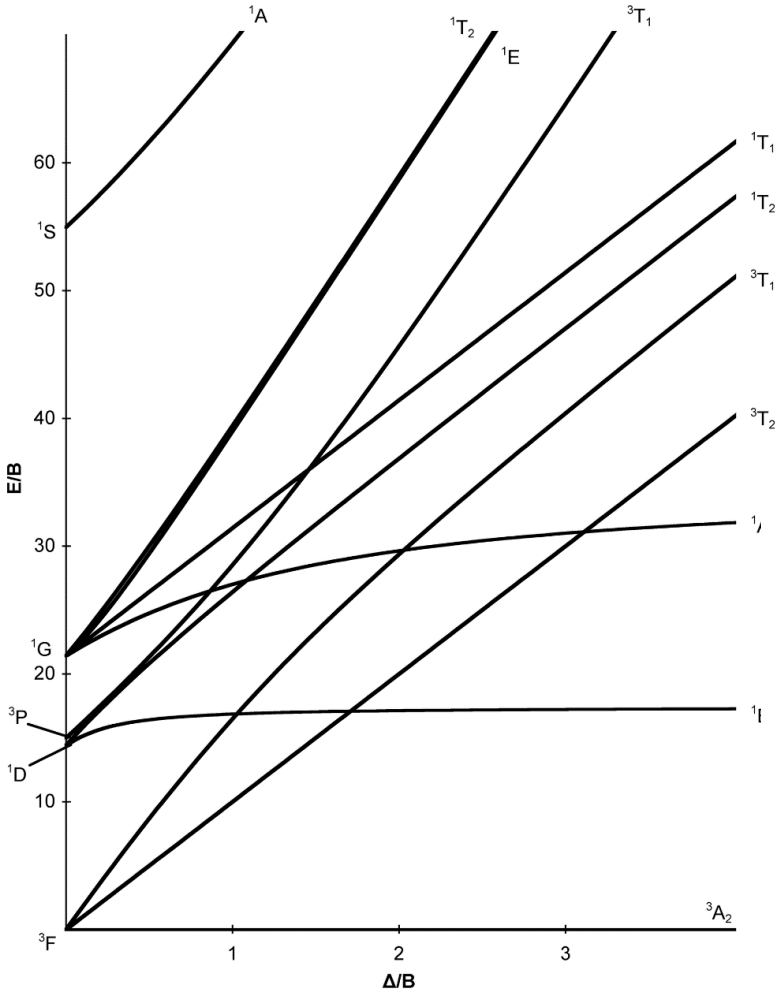


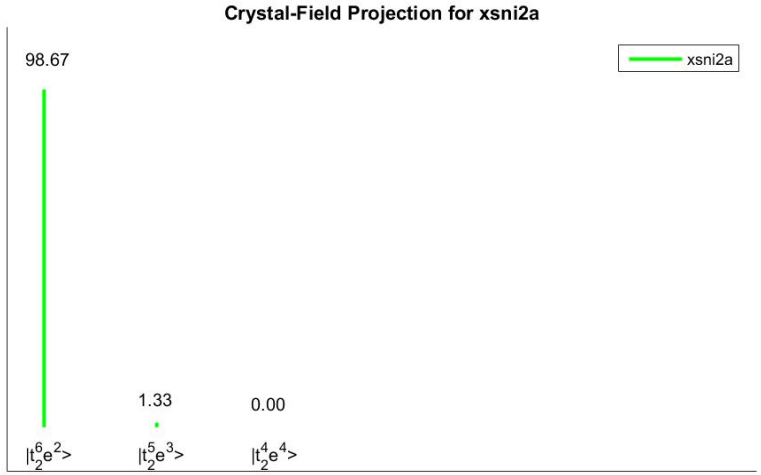
States of 3dN transition metal ions

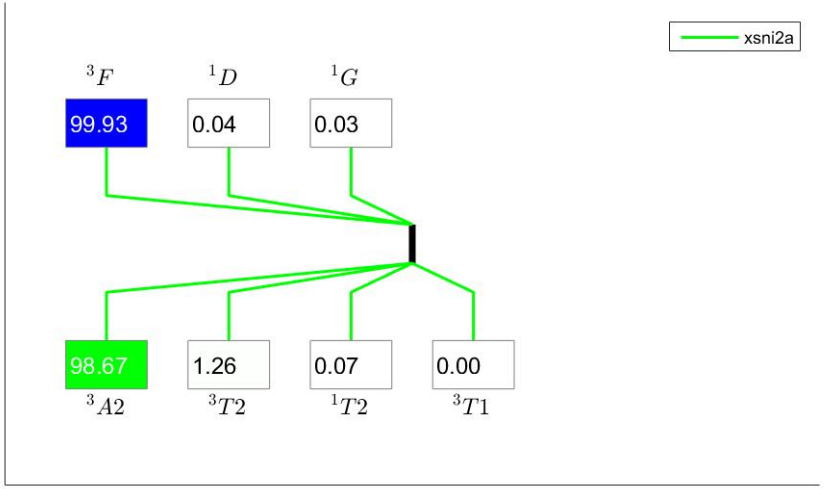




States of $3d^N$ transition metal ions

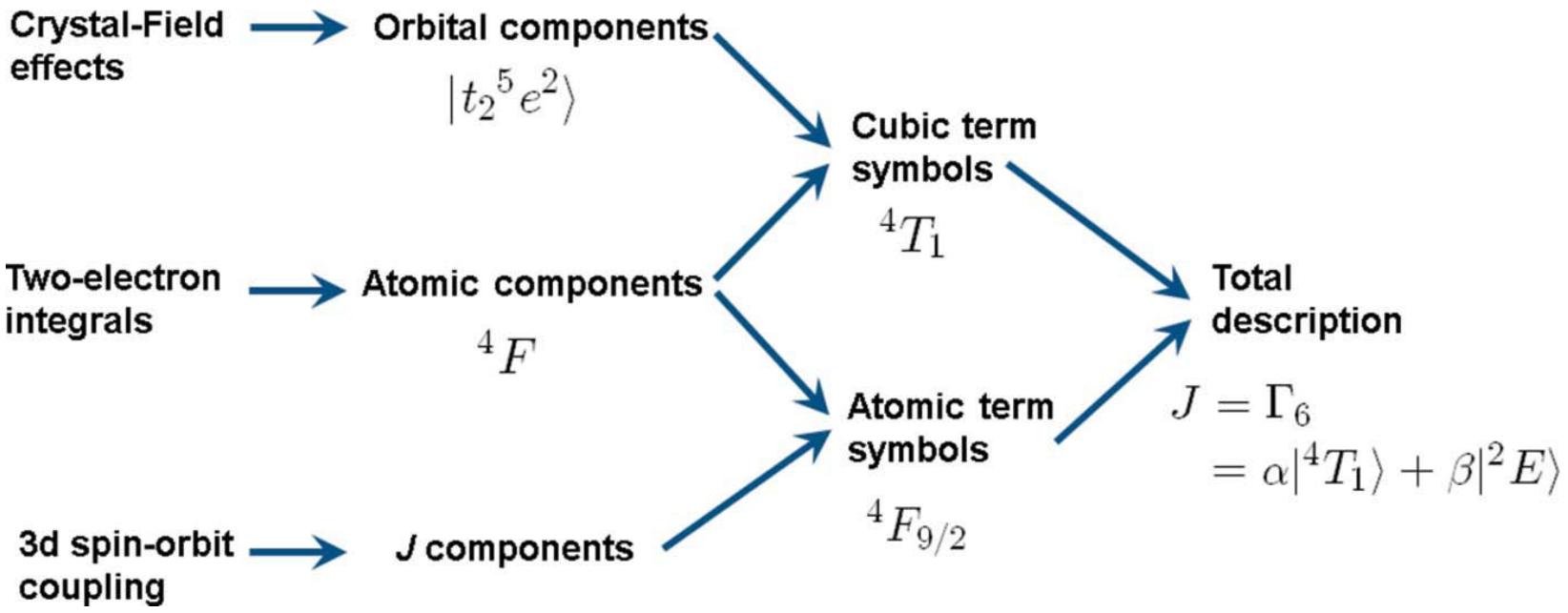






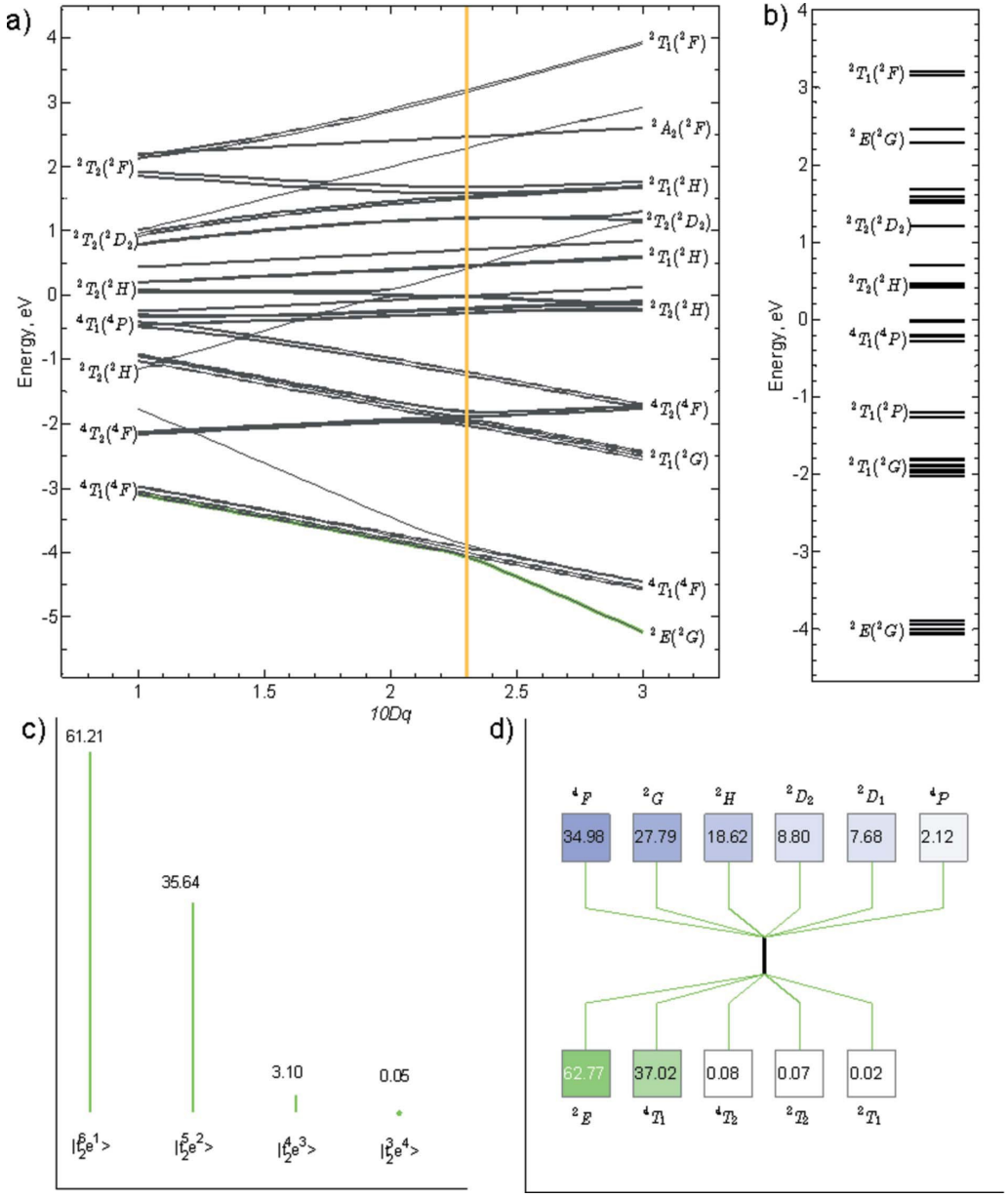
Symmetry labels are labels; they are (almost) never exact.

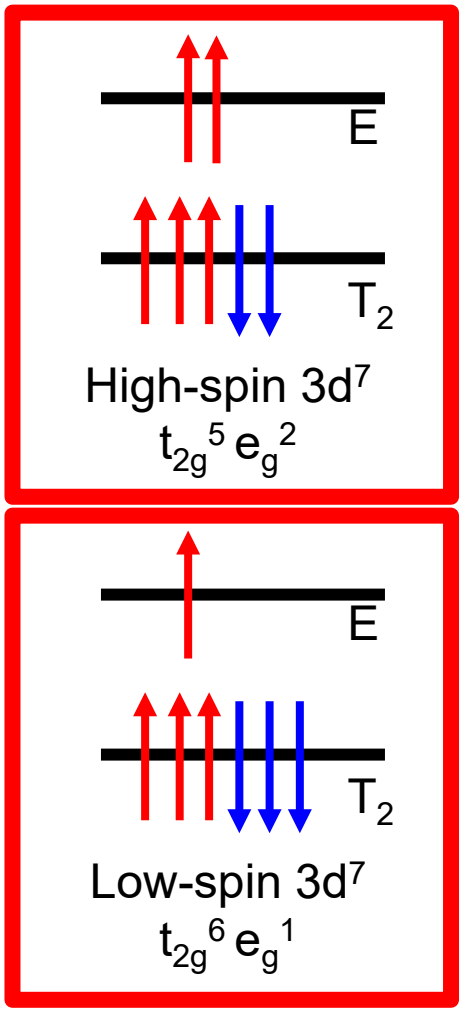
States of $3d^N$ transition metal ions



J. Synchrotron Rad. (2016). 23, 1264 (2016) [google drive]

States of 3dN transition metal ions



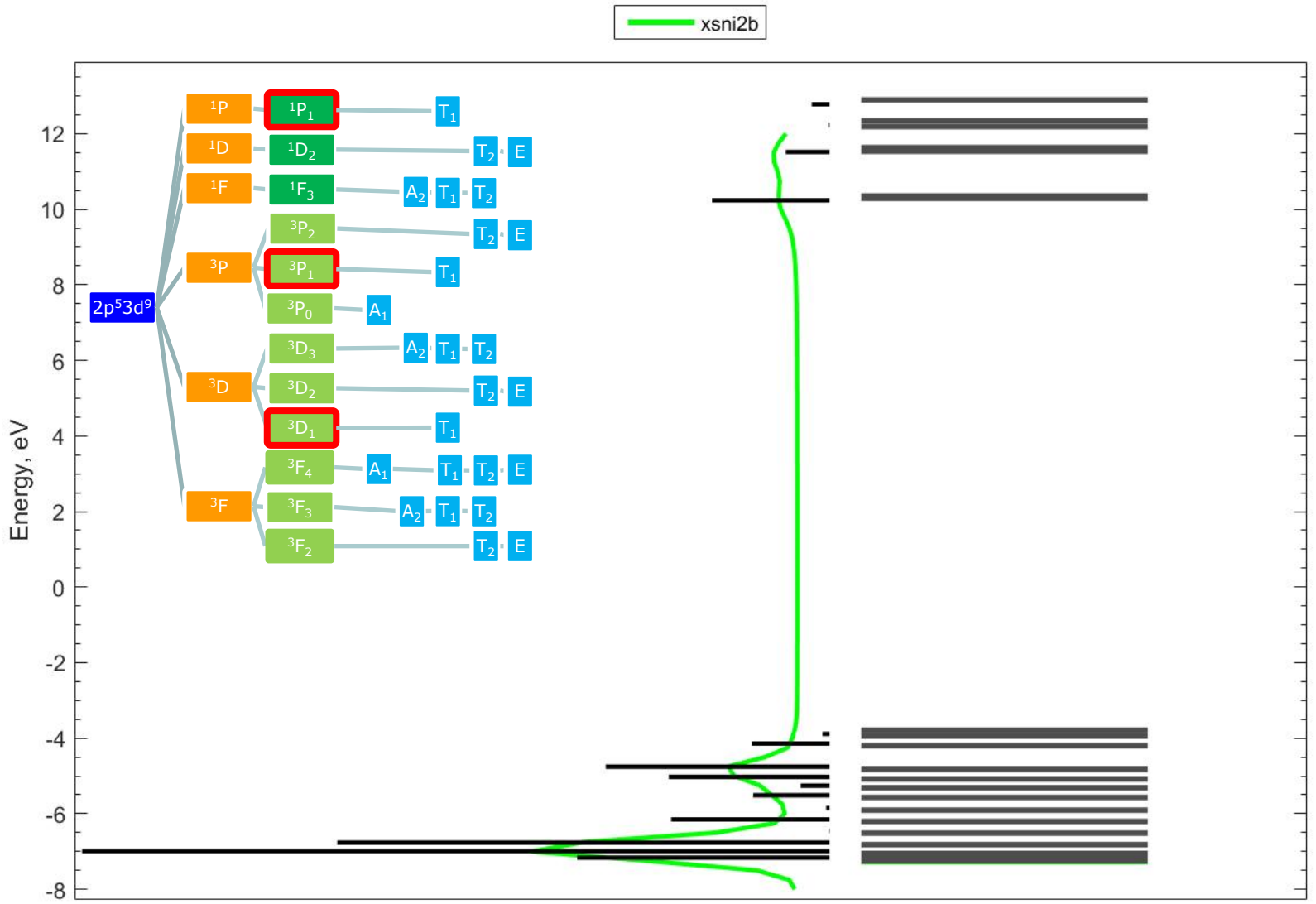


40%

60%

J. Synchrotron Rad. (2016). 23, 1264 (2016) [google drive]

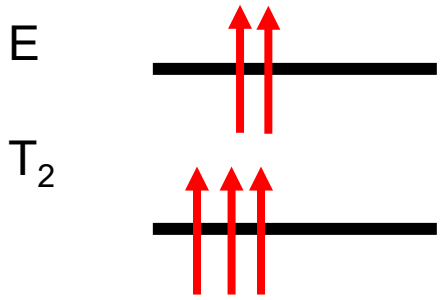
2p XAS of NiO



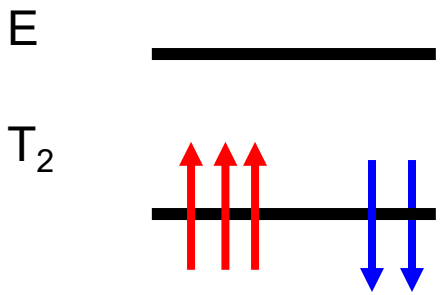
Calculate 2p XAS around 0.0 and shift to experiment

Crystal Field: High-spin or low-spin

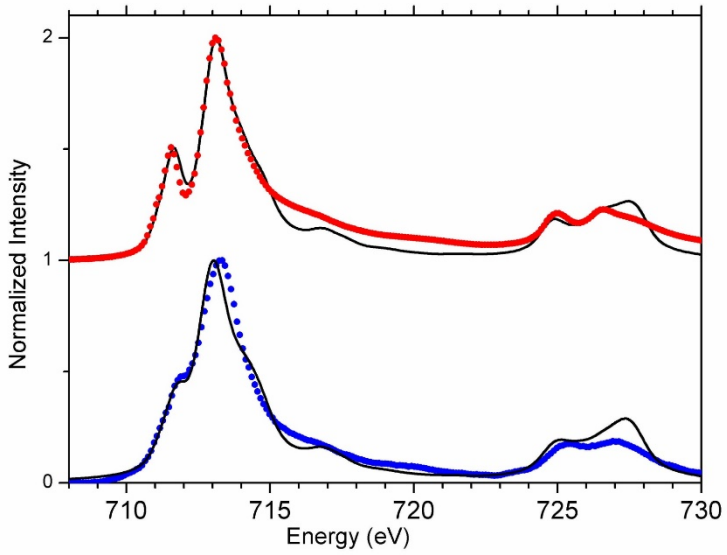
Large 10Dq will change the ground state to low-spin

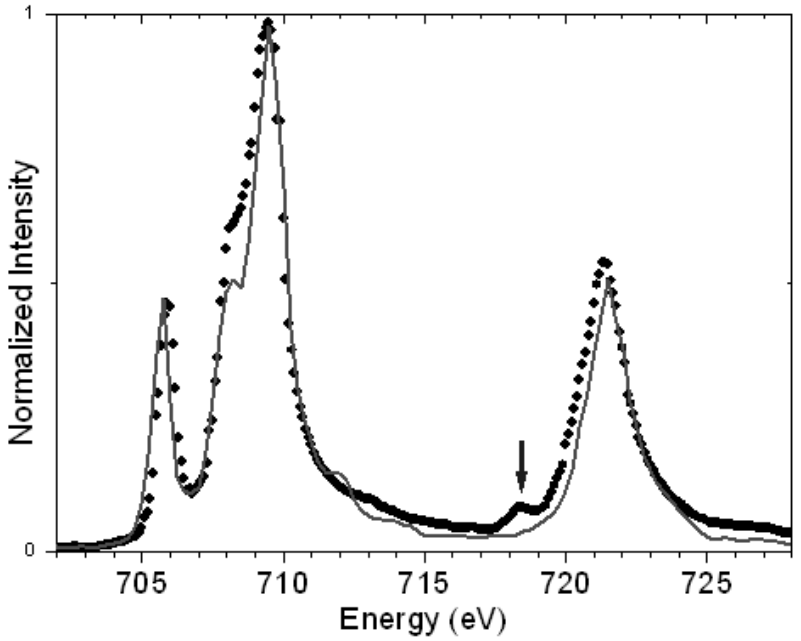


High-spin $3d^5$



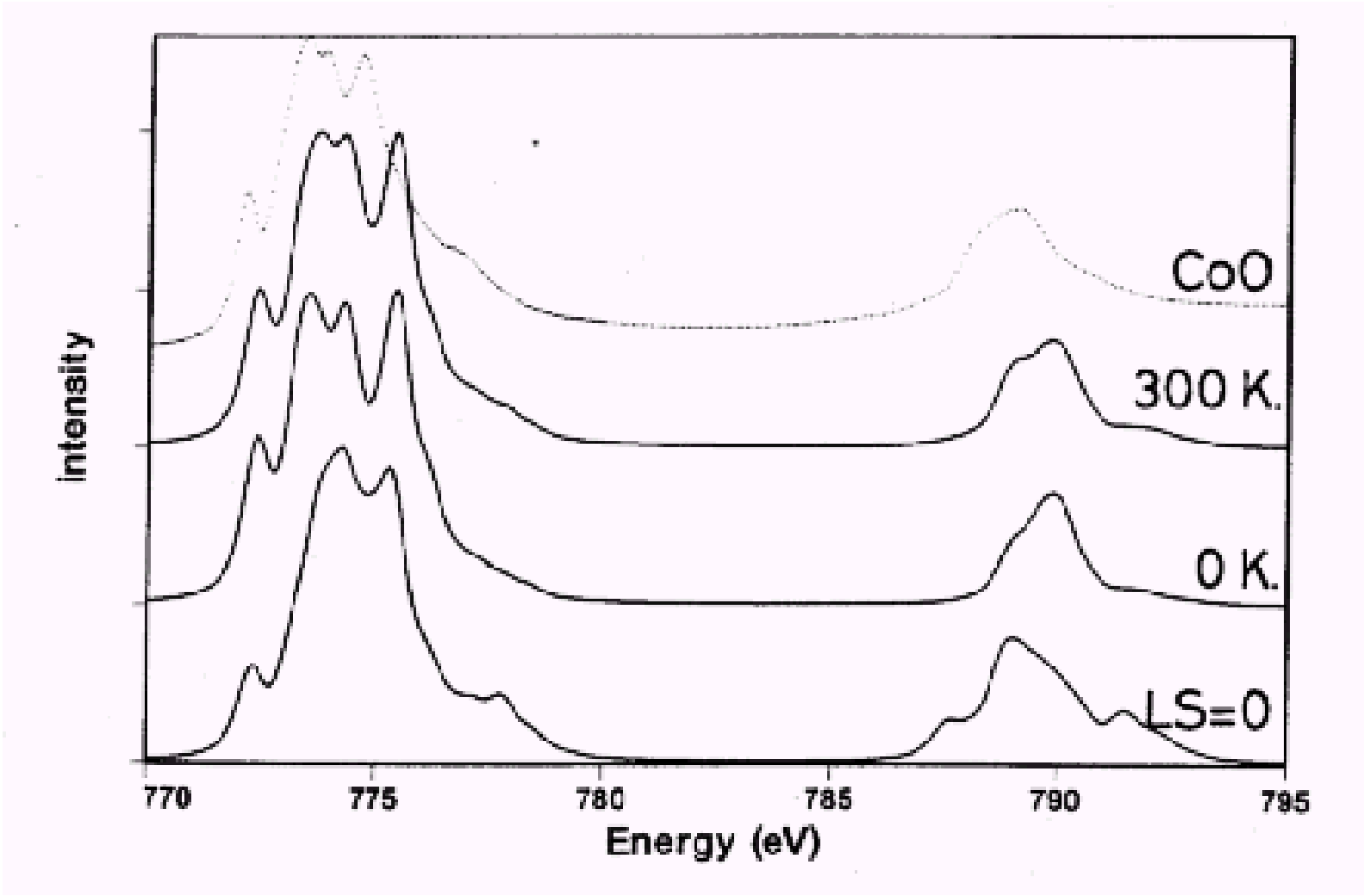
Low-spin $3d^5$



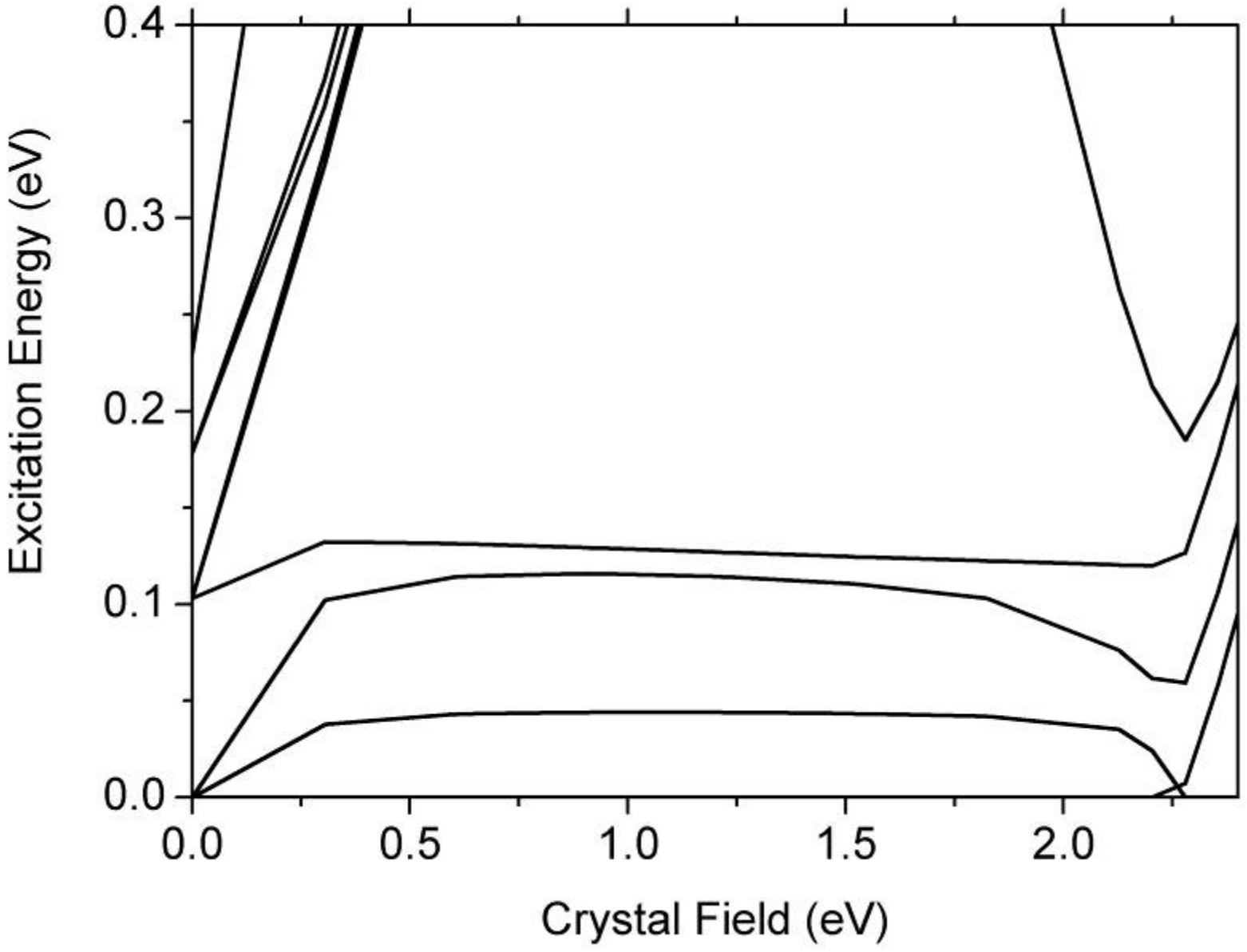


Crystal Field: Effect of 3d spin-orbit coupling

Spin-orbit coupling important for T_1 and T_2 symmetry ground states ($3d^1$, $3d^2$, $3d^6$, $3d^7$), for example Fe^{2+} and Co^{2+}



Crystal Field: Effect of 3d spin-orbit coupling

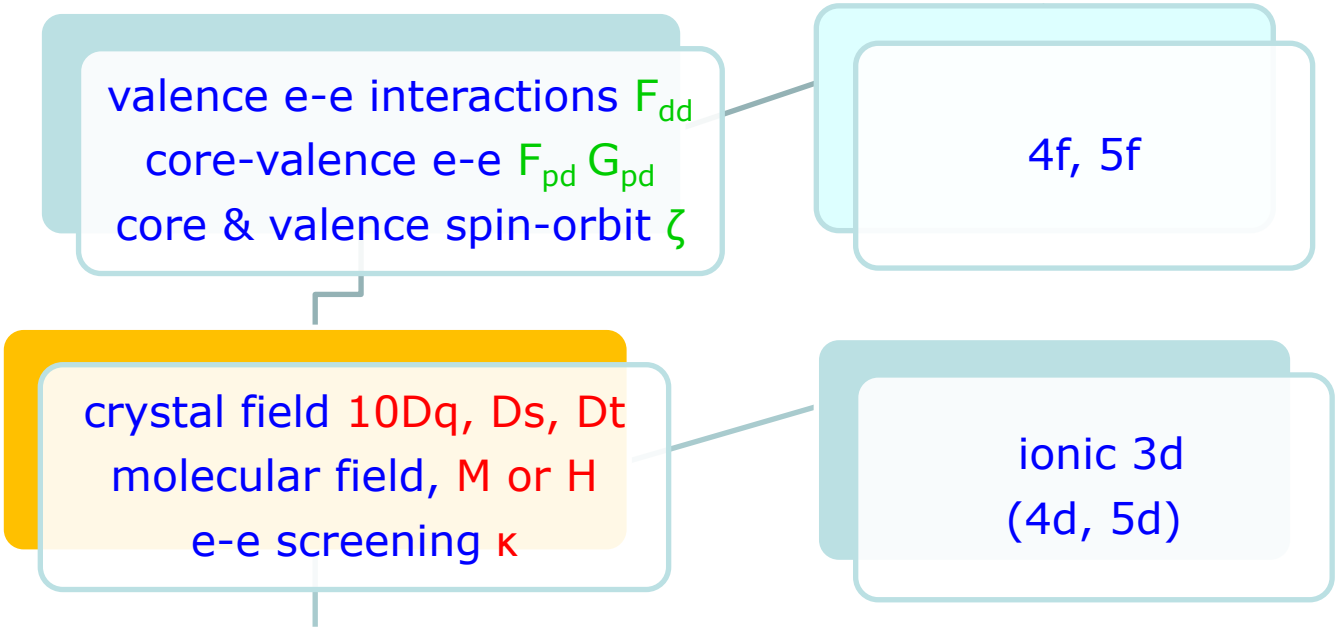


Multiplet calculations

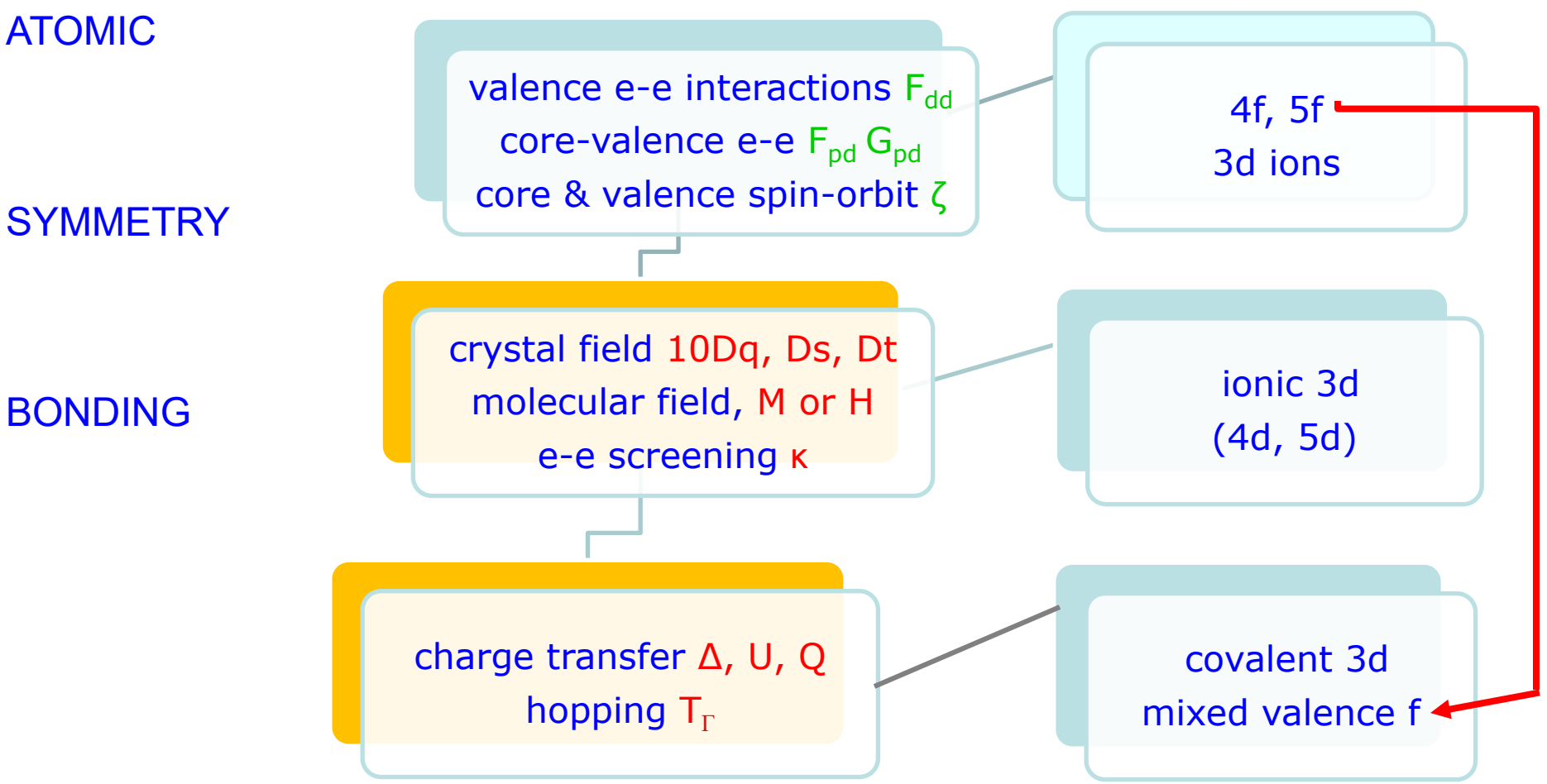
ATOMIC

SYMMETRY

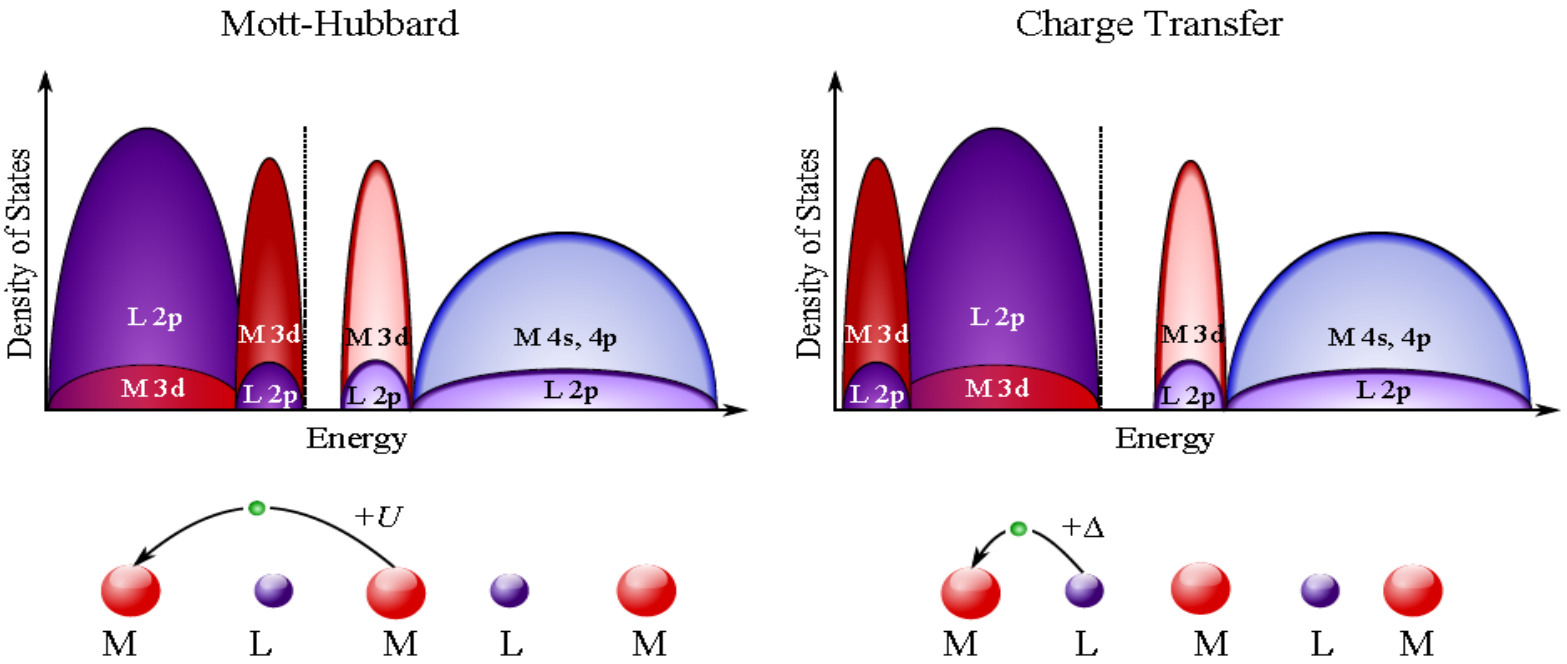
BONDING



Multiplet calculations



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):

Δ= $E(3d^9\underline{L}) - E(3d^8)$

Charge transfer effects

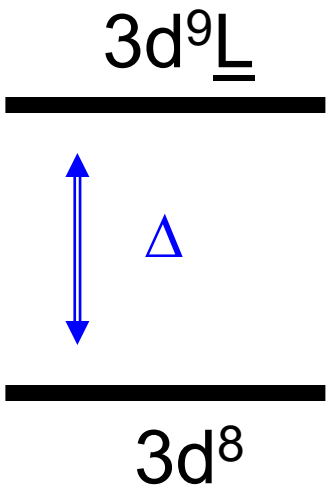
Main screening mechanism in XAS of oxides:
Ligand-to-metal charge transfer

Charge transfer energy Δ is important for XAS

Hubbard U is NOT important for XAS spectral shape

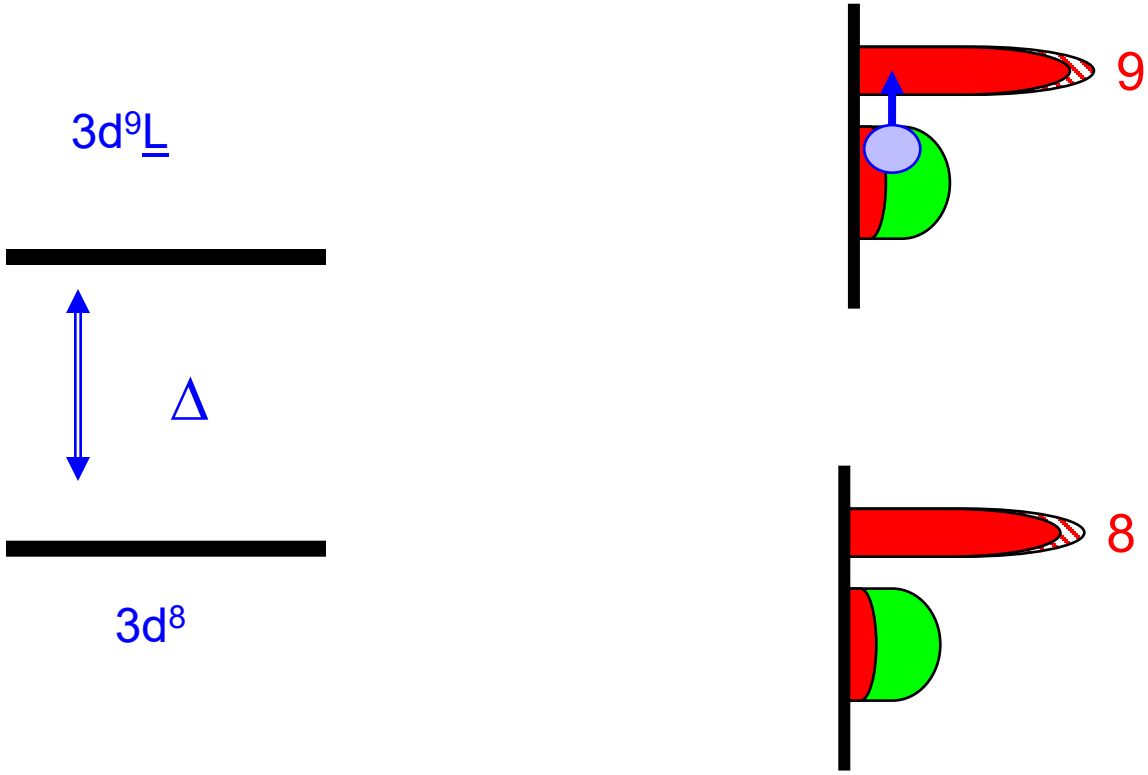
transition metal oxides

- Ground state: $3d^8 + 3d^9\underline{L}$
- Energy of $3d^9\underline{L}$: Charge transfer energy Δ



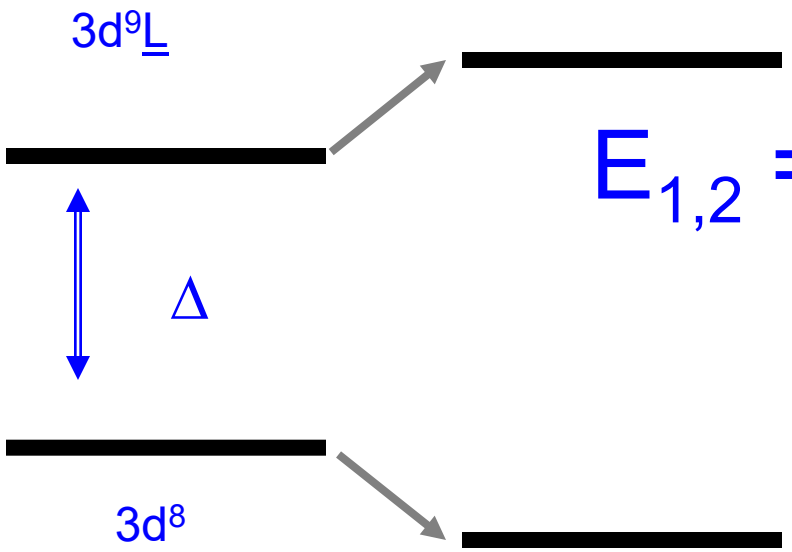
Ground State

Charge Transfer Effects



Charge Transfer Effects

$$H_{mix} = \begin{bmatrix} 0 & T_j \\ T_j & \Delta \end{bmatrix}.$$



$$E_{1,2} = \tfrac{1}{2}\left[\Delta \pm \sqrt{(\Delta^2 + 4T^2)}\right]$$

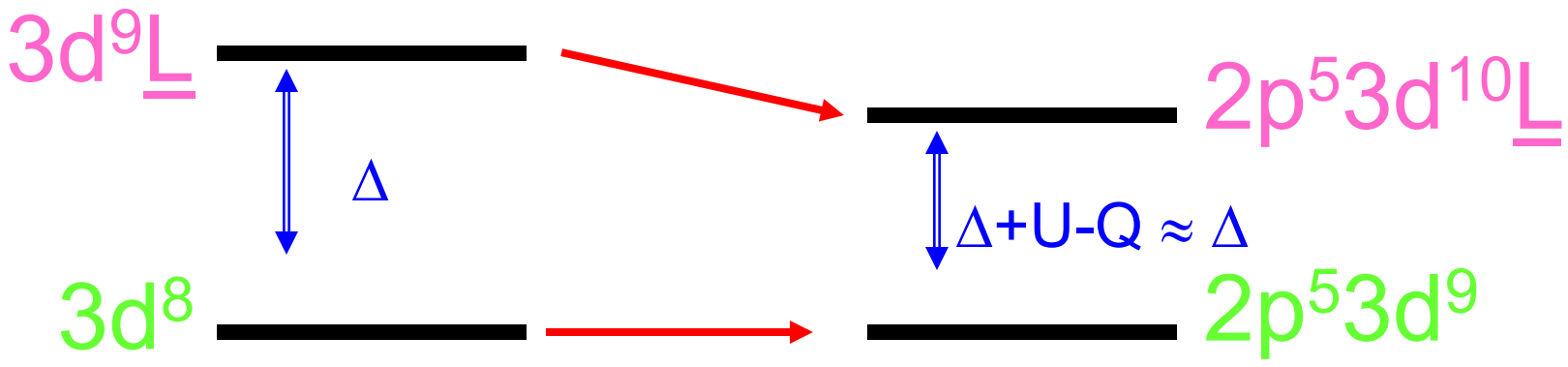
$\Delta = 2$ and $T = 1$

$$E_{1,2} = \tfrac{1}{2}\left[2 \pm \sqrt{(2^2 + 4)}\right] = 1 \pm \sqrt{2}$$

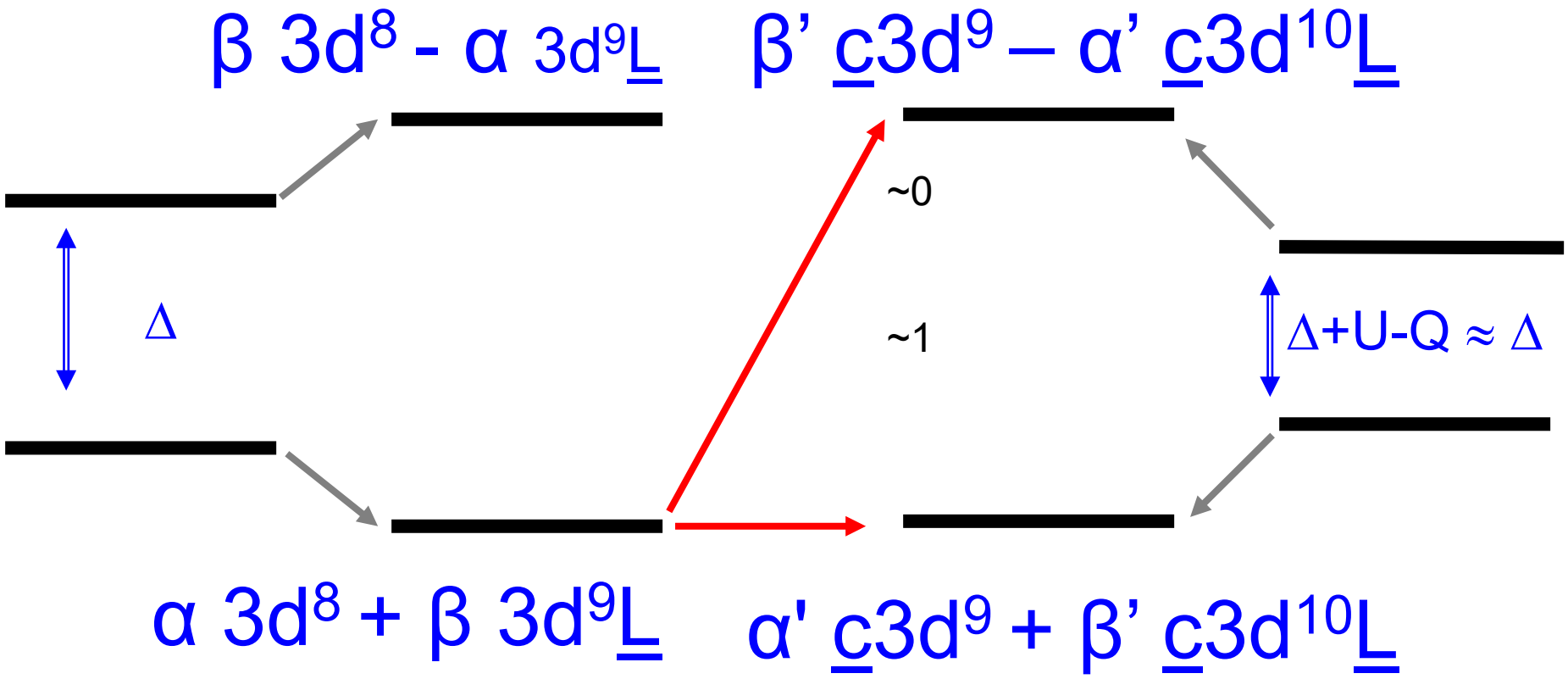
Charge transfer effects

NiO: Ground state: $3d^8$ + $3d^9\underline{L}$

Energy of $3d^9\underline{L}$: Charge transfer energy Δ



Charge transfer effects

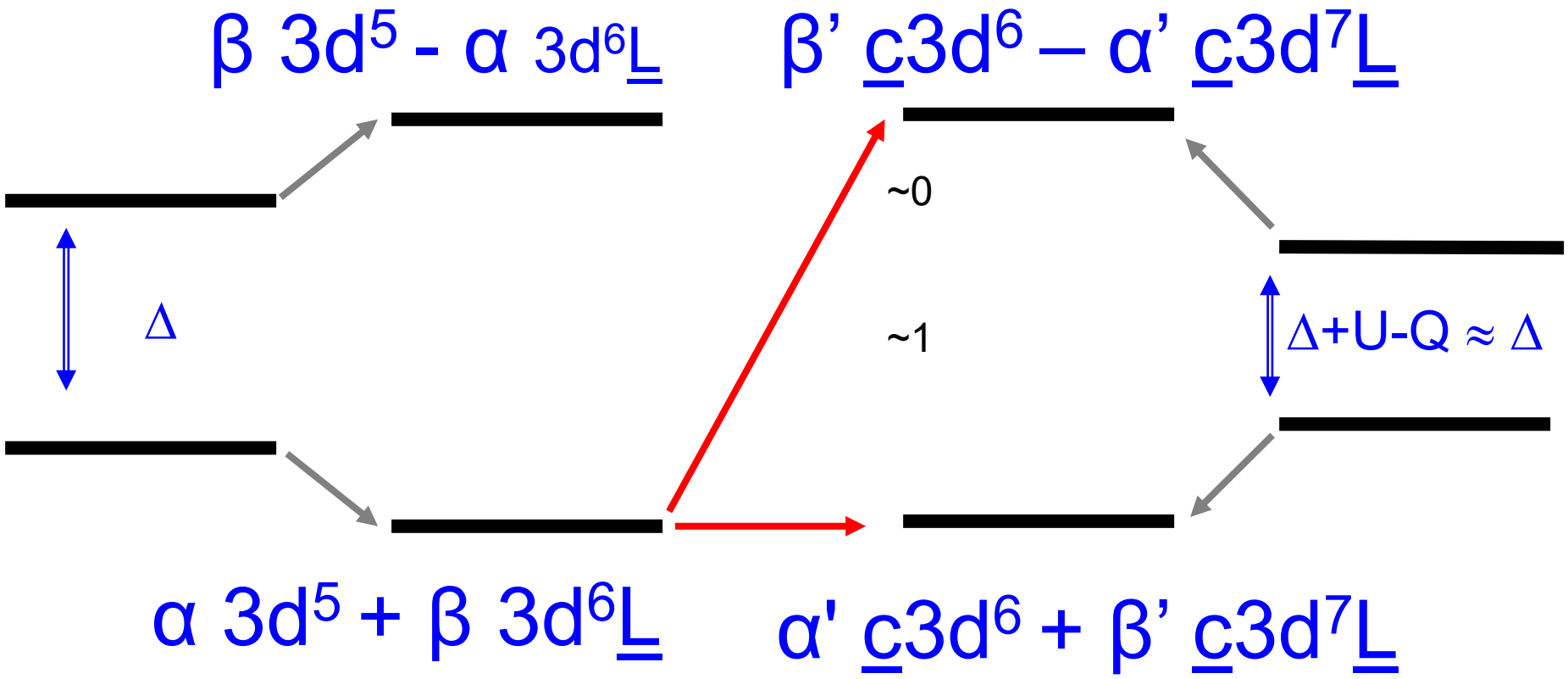


Intensity bonding combination: $[\alpha\,\alpha' + \beta\,\beta']^2$

$\alpha \approx \alpha'$

$\approx (\alpha^2 + \beta^{2)2} = 1$

Charge transfer effects



Intensity anti-bonding combination: $[\alpha\,\beta' - \beta\,\alpha']^2$

$\alpha \approx \alpha'$

$\approx (\alpha\beta - \beta\alpha)^2 = 0$

Charge transfer effects

Neutral experiments are self-screened

XAS, optical, EPR, EELS, RIXS

>> small screening satellites

>> crystal field theory can be used

Ionising experiments are not self-screened

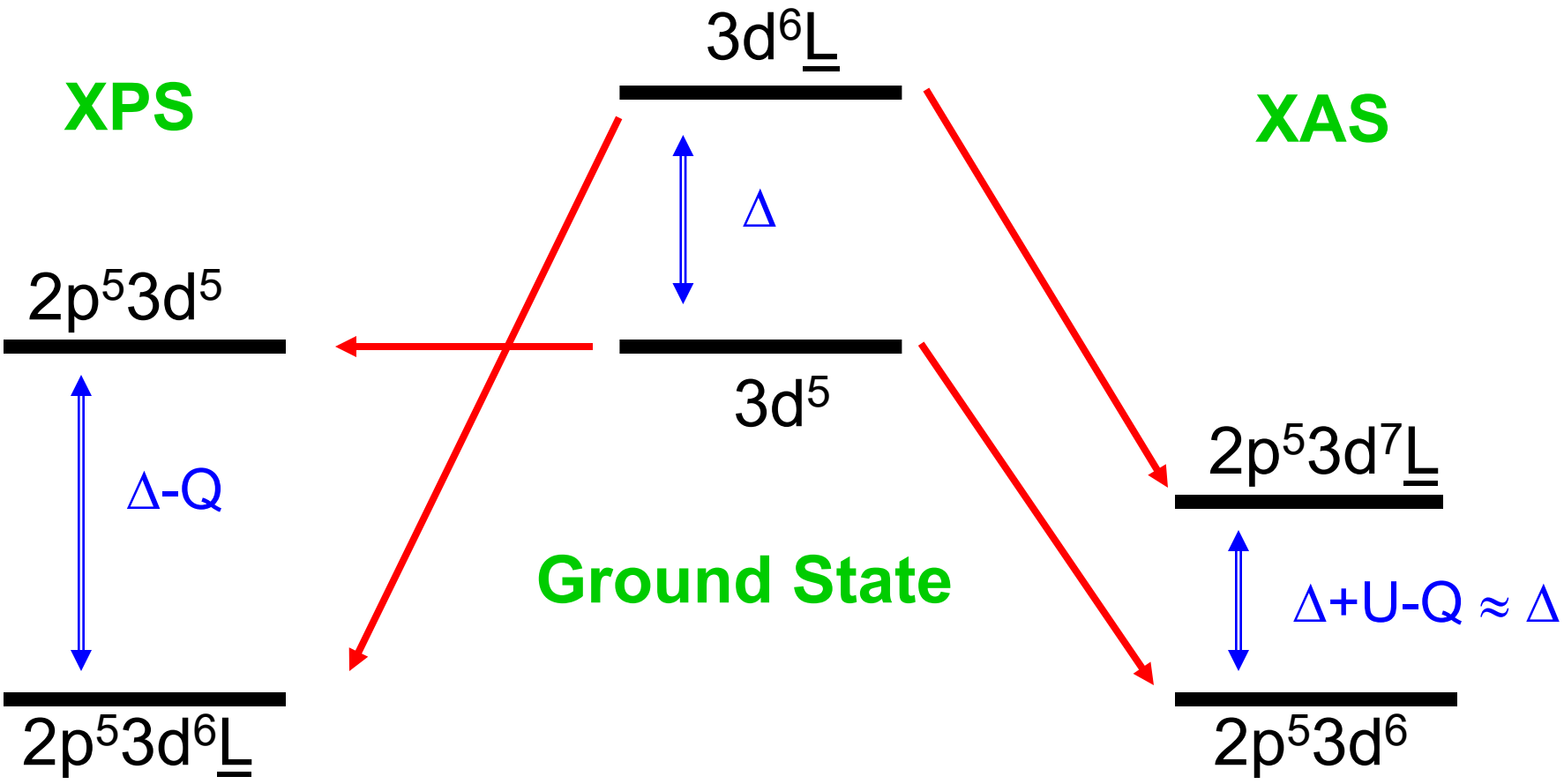
XPS, Auger, (metal K edge XAS)

>> large screening > large satellites

>> crystal field theory can not be used

Charge transfer effects in XAS and XPS

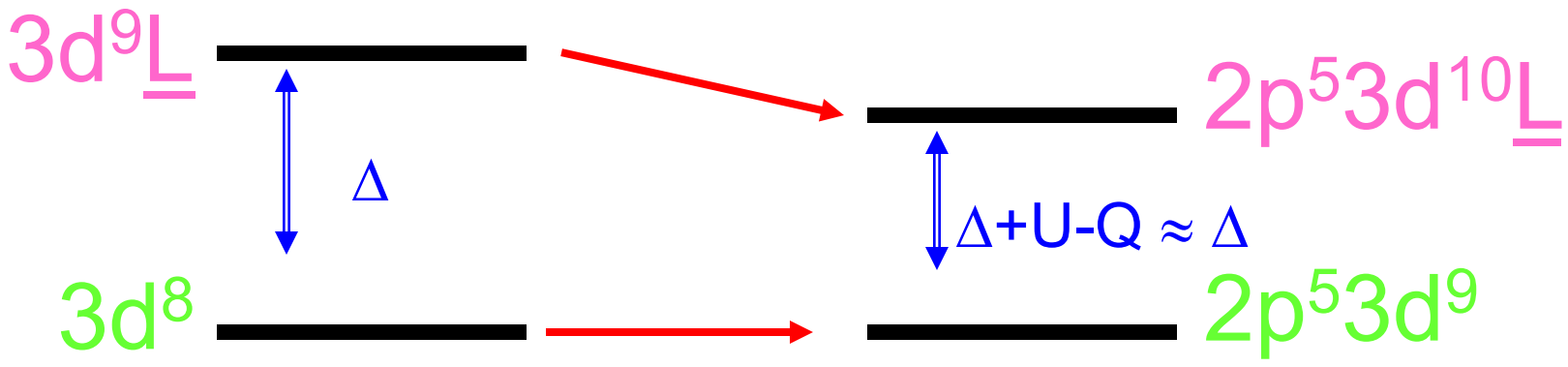
- Transition metal oxide: Ground state: $3d^5 + 3d^6\underline{L}$
- Energy of $3d^6\underline{L}$: Charge transfer energy Δ



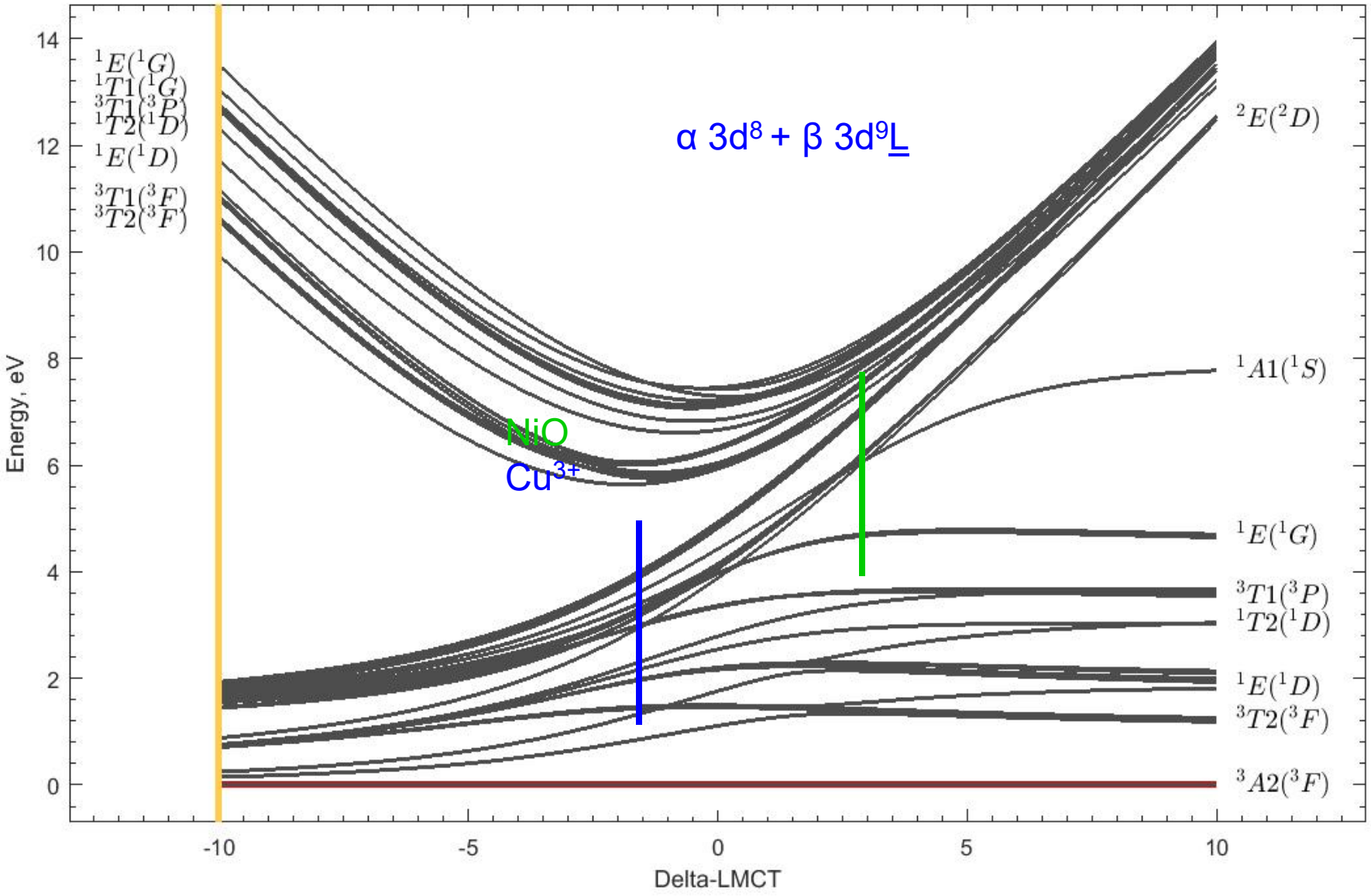
Charge transfer effects

NiO: Ground state: $3d^8$ + $3d^9\underline{L}$

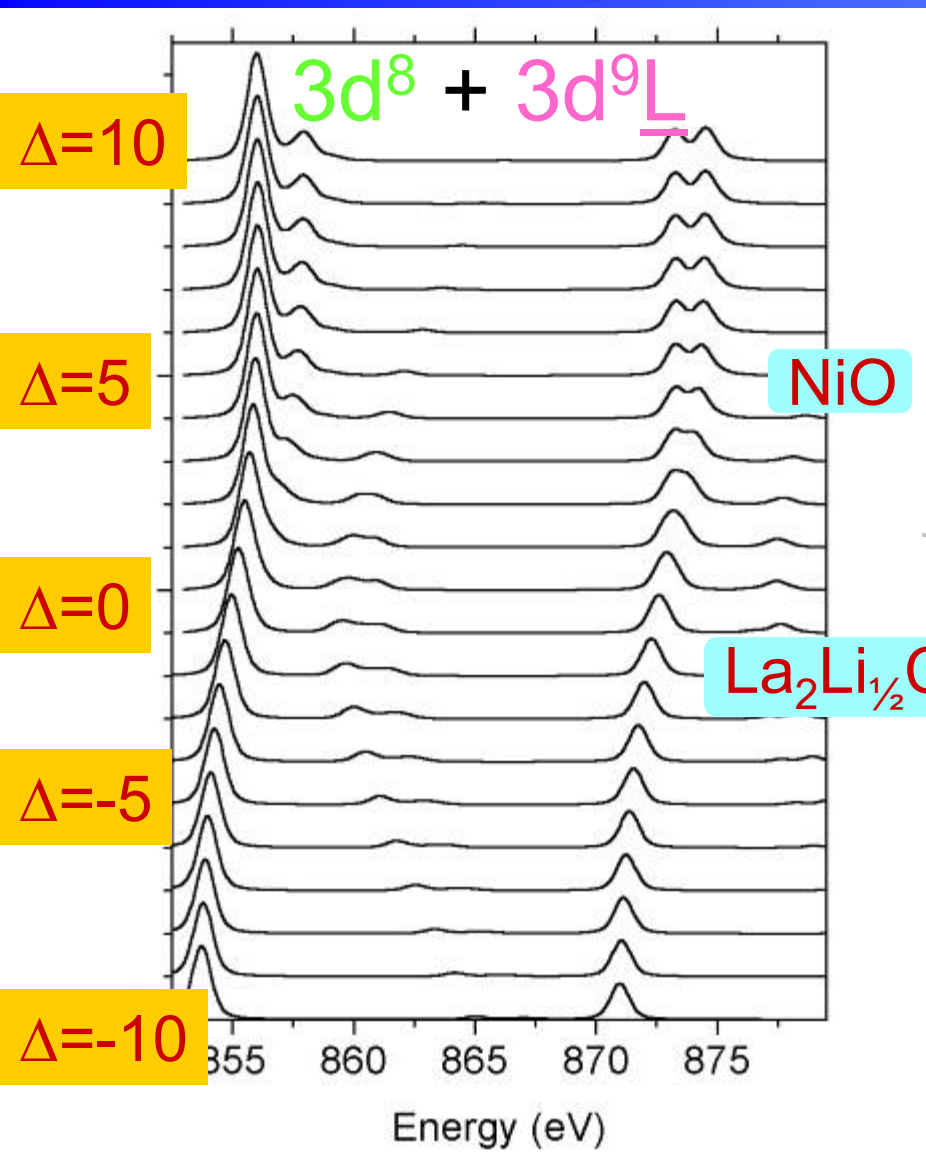
Energy of $3d^9\underline{L}$: Charge transfer energy Δ

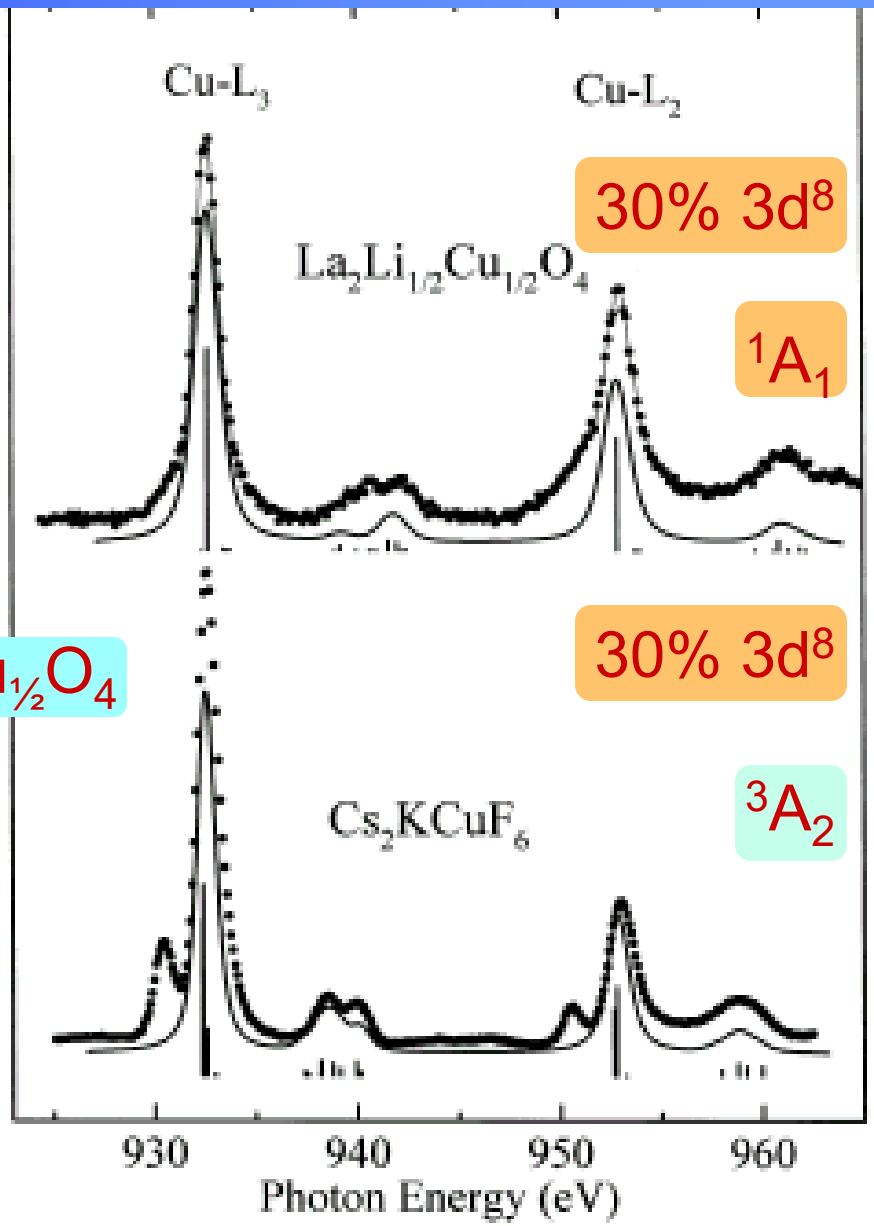


Tanabe-Sugano diagrams with charge transfer



Charge transfer effects in XAS

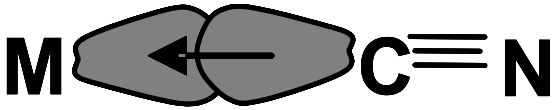


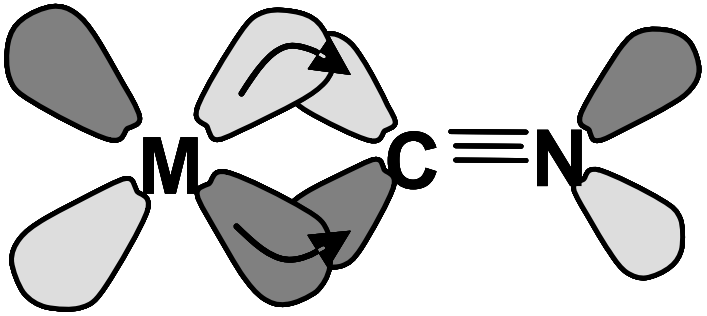


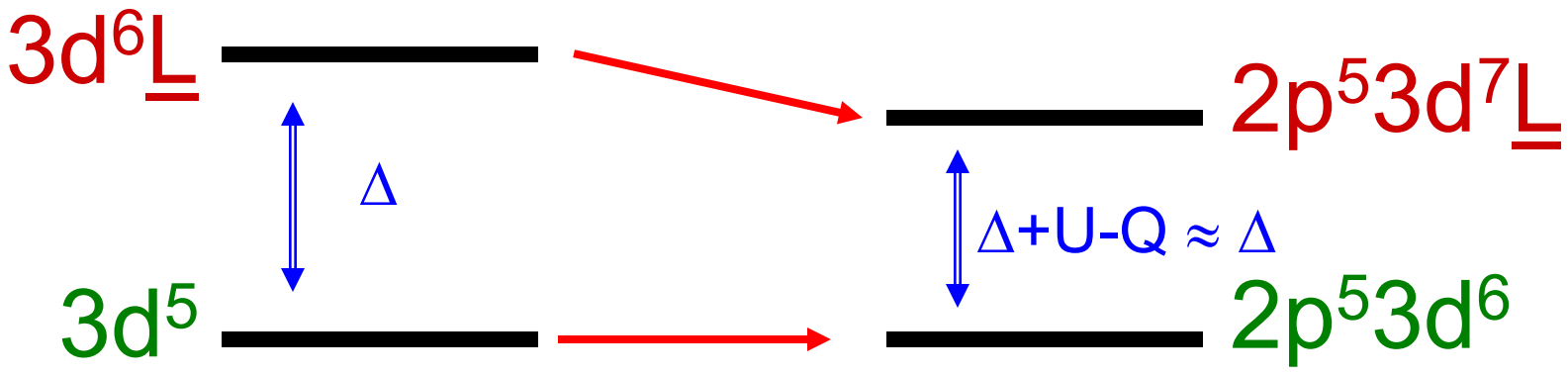
Chem. Phys. Lett. 297, 321 (1998)

LMCT and MLCT: π - bonding

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



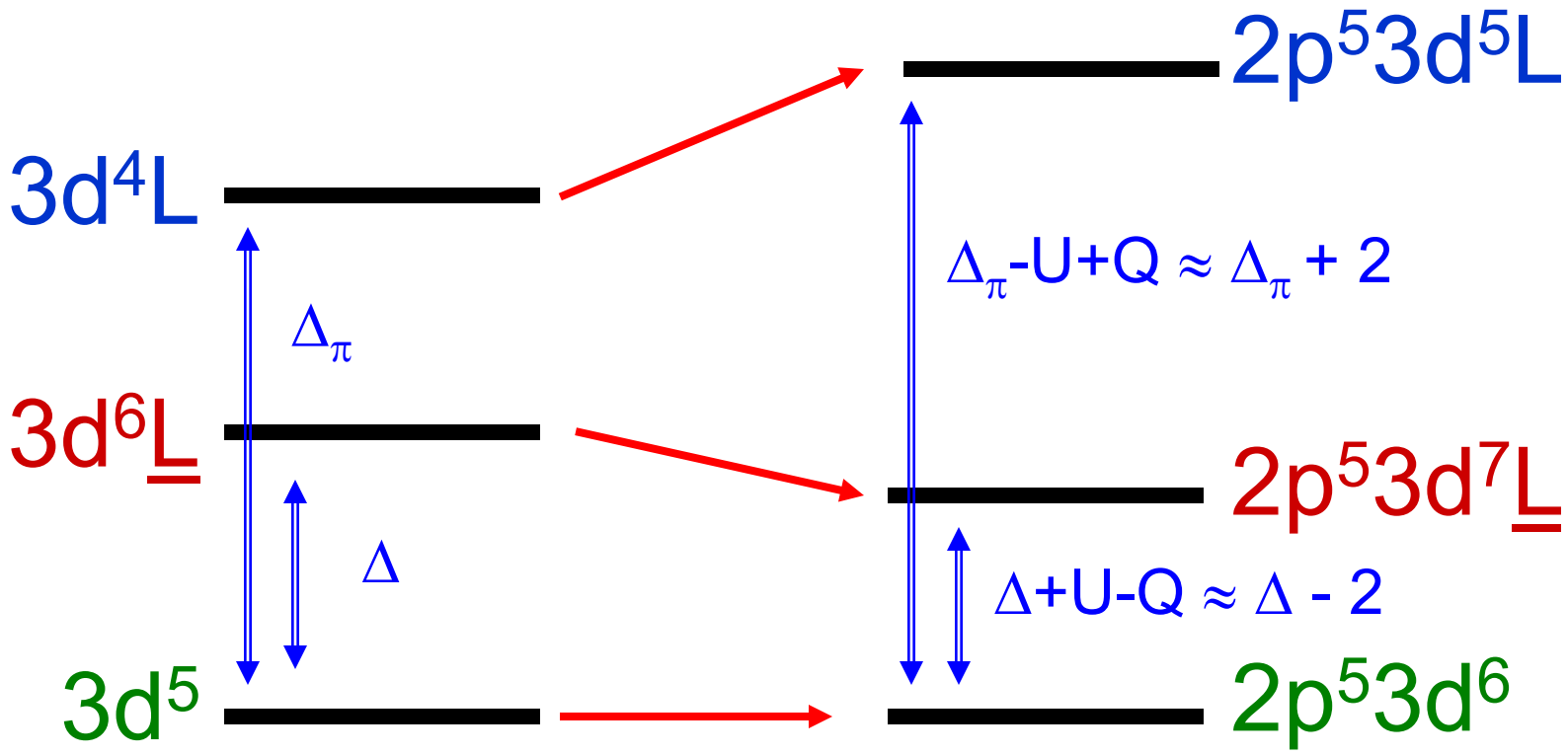




with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

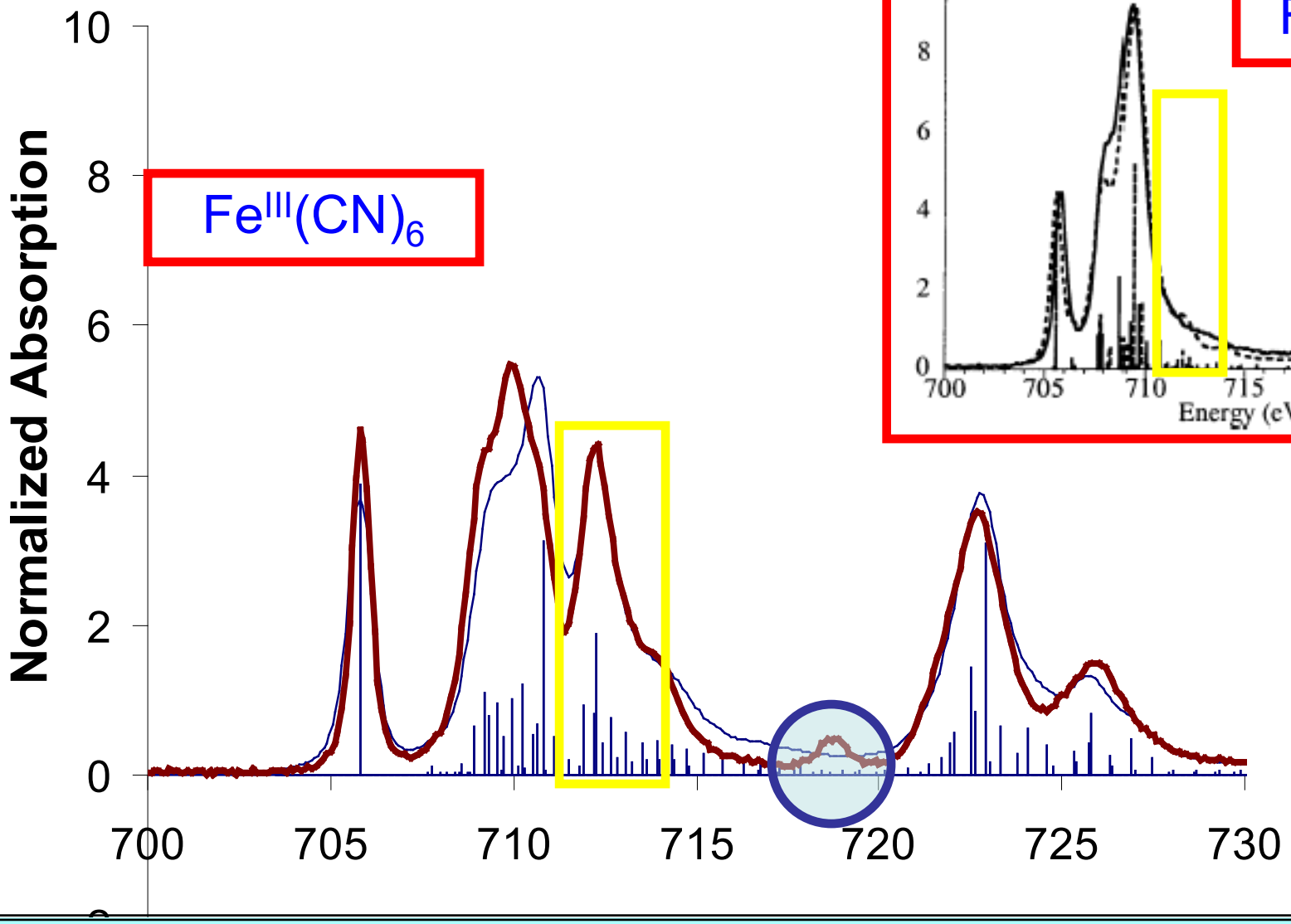
LMCT and MLCT: π - bonding

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)

Multiplet calculations

Calculated for an atom/ion

- Valence and core **spin-orbit coupling**
- Core and valence **electron-electron interaction**.

Comparison with experiment

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

First Principle Multiplet calculations

Calculated for an atom/ion

- Valence and core **spin-orbit coupling**
- Core and valence **electron-electron interaction**.

Comparison with experiment

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

2p XAS first-principle codes

SOLIDS

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

MOLECULES

- Restricted Active Space CI (Odelius, Kuhn, Lundberg)
- Restricted Open-shell CI + Multi Reference (Neese)

TDDFT/BSE

- *Time-Dependent DFT (Joly)*
- *Bethe-Salpeter (Rehr, Shirley)*
- *Multi-channel Multiple-scattering (Kruger)*