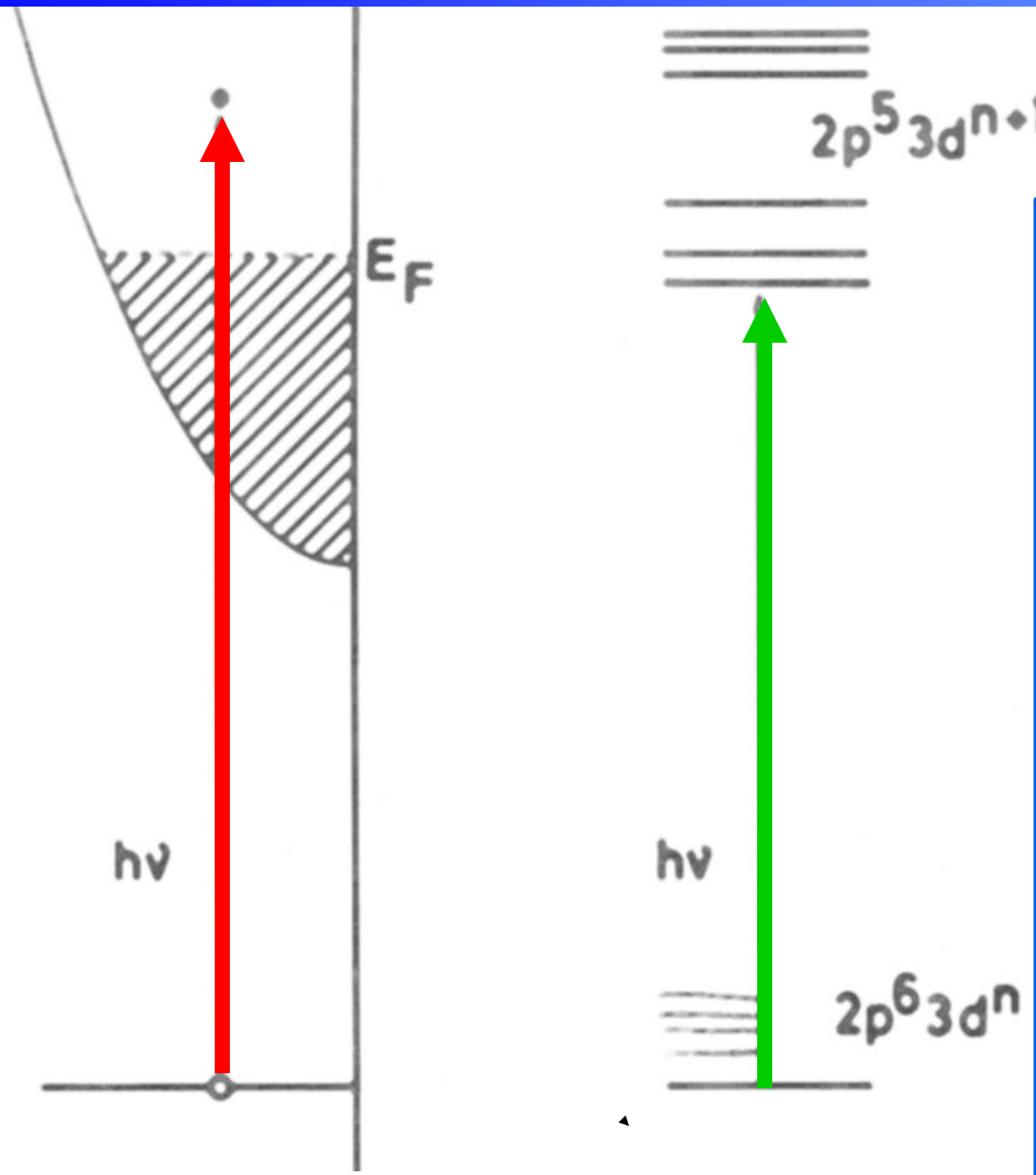
XAS: spectral shape



1-particle:

1s edges

(DFT + core hole +U)

many-particle:

open shell systems

(CTM4XAS)

Multiplet calculations (semi-empirical)

ATOMIC

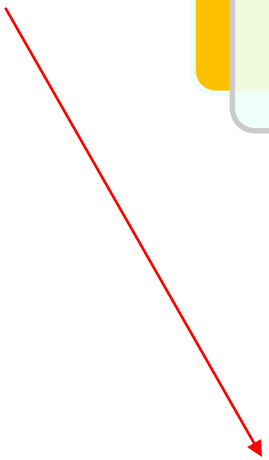
valence e-e interactions F_{dd}
core-valence e-e F_{pd} G_{pd}
core & valence spin-orbit ζ

4f, 5f
3d ions

SYMMETRY

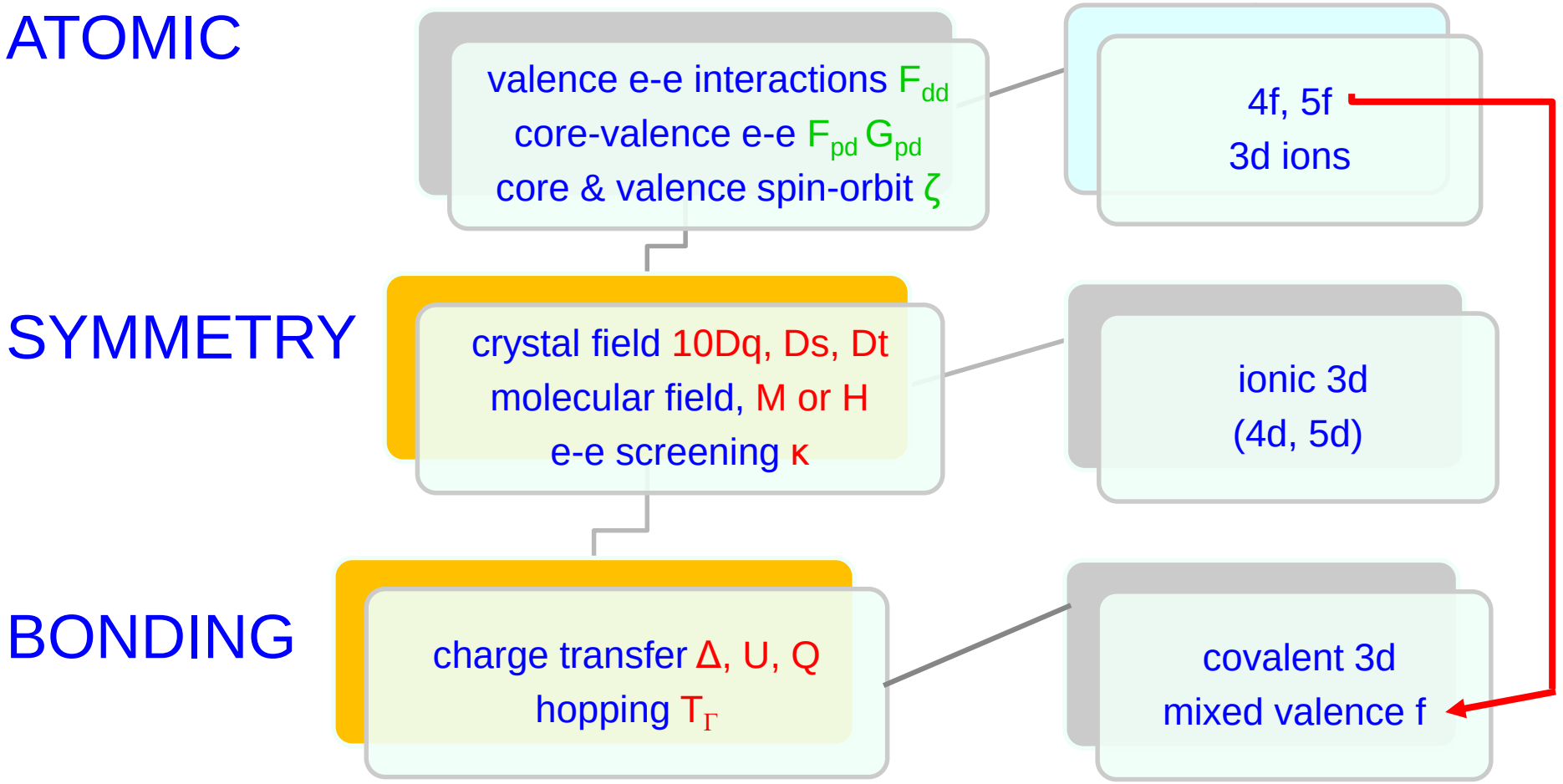
crystal field 10Dq, Ds, Dt
molecular field, M or H
e-e screening κ

ionic 3d
(4d, 5d)

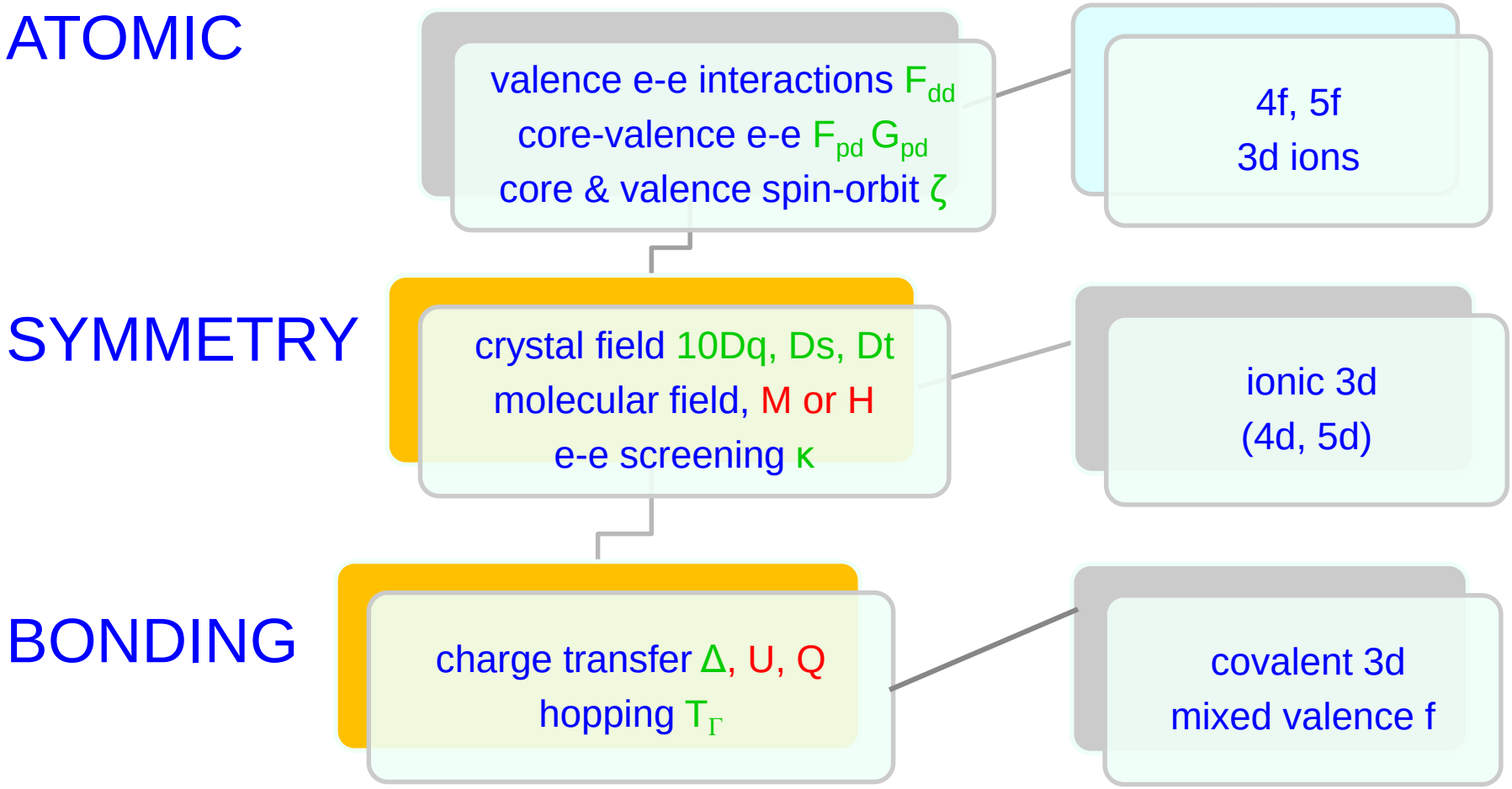


Tuesday
Lecture on ground states (CTM4DOC):
Hunds rules and Tanabe-Sugano diagrams

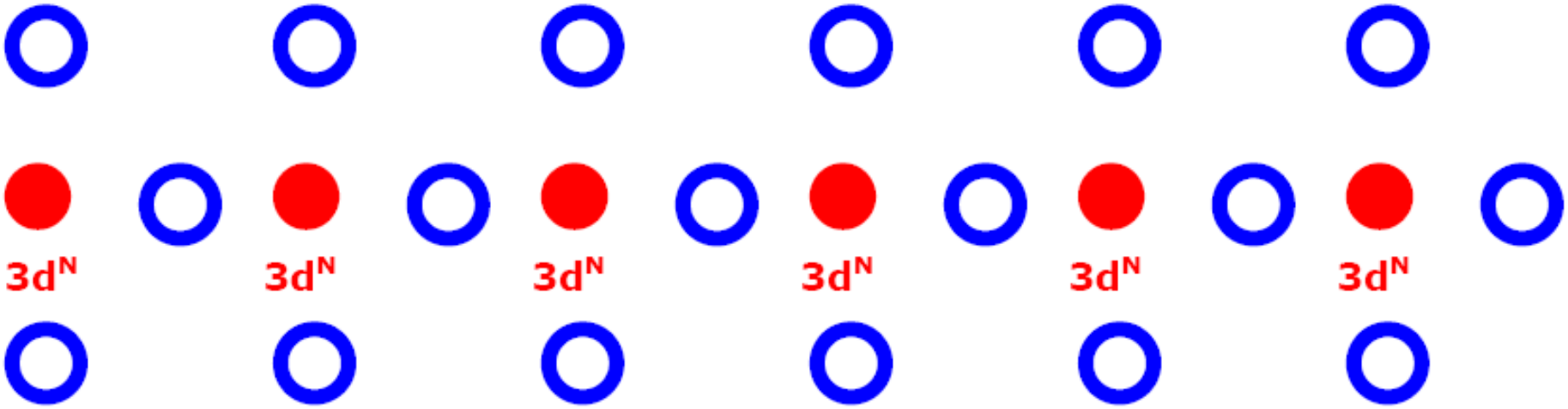
Multiplet calculations (semi-empirical)



Multiplet calculations (first-principle)



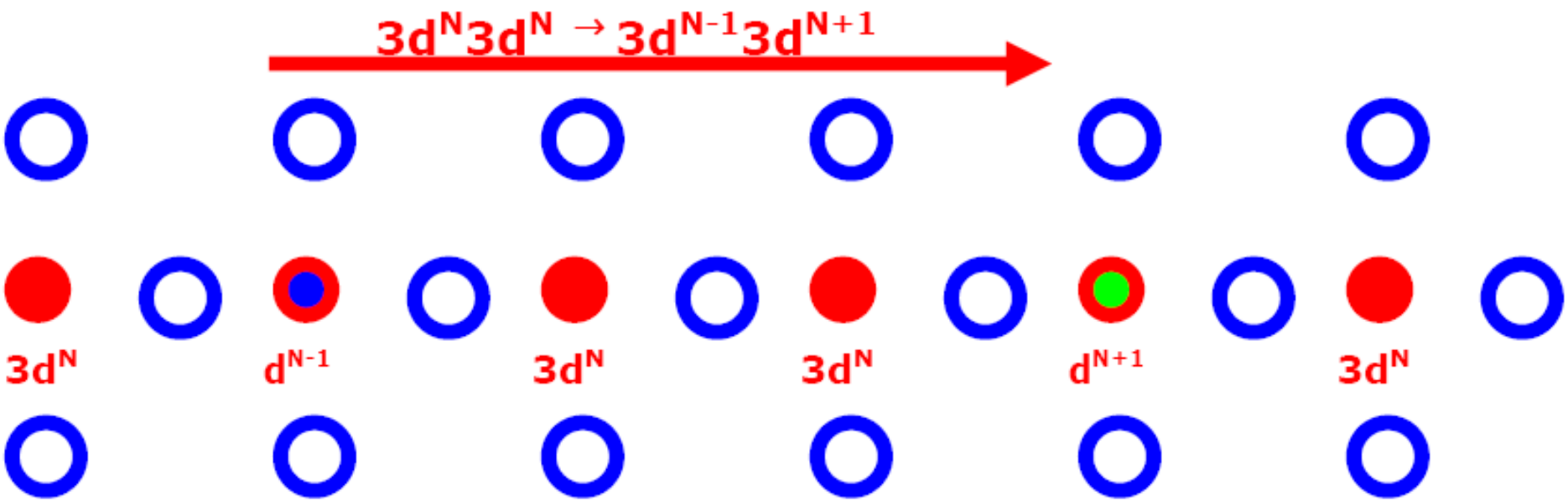
Charge transfer effects



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

Charge fluctations

Charge transfer effects



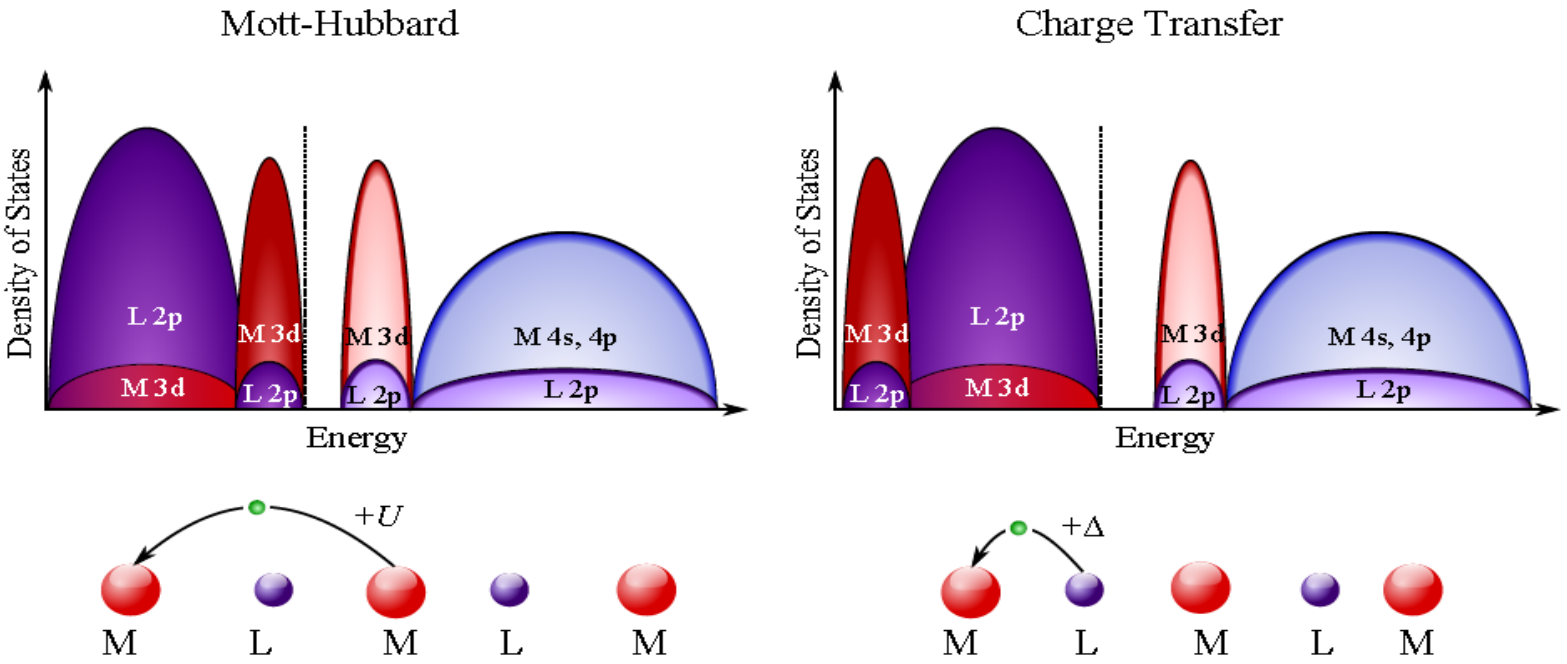
Hubbard U for a $3d^8$ ground state:

$\mathbf{U} = E(3d^7) + E(3d^9) - E(3d^8) - E(3d^8)$

Ligand-to-Metal Charge Transfer (LMCT):

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

Charge transfer effects



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= $E(3d^9\underline{L}) – E(3d^8)$

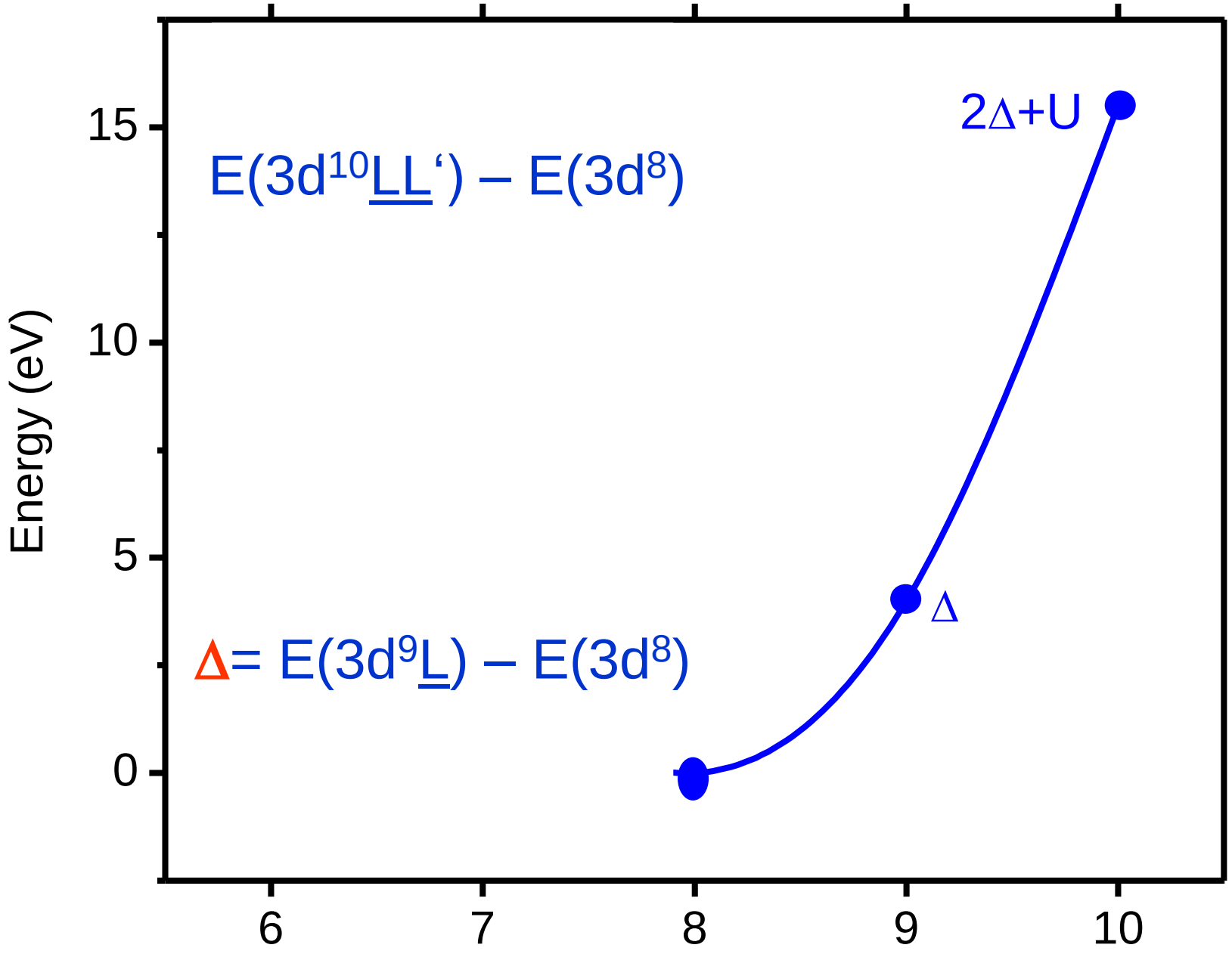
Charge transfer effects

Main screening mechanism in XAS and XPS:
Ligand-to-metal charge transfer

Charge transfer energy Δ is important for XAS/XPS

Hubbard U is NOT very important for XAS/XPS

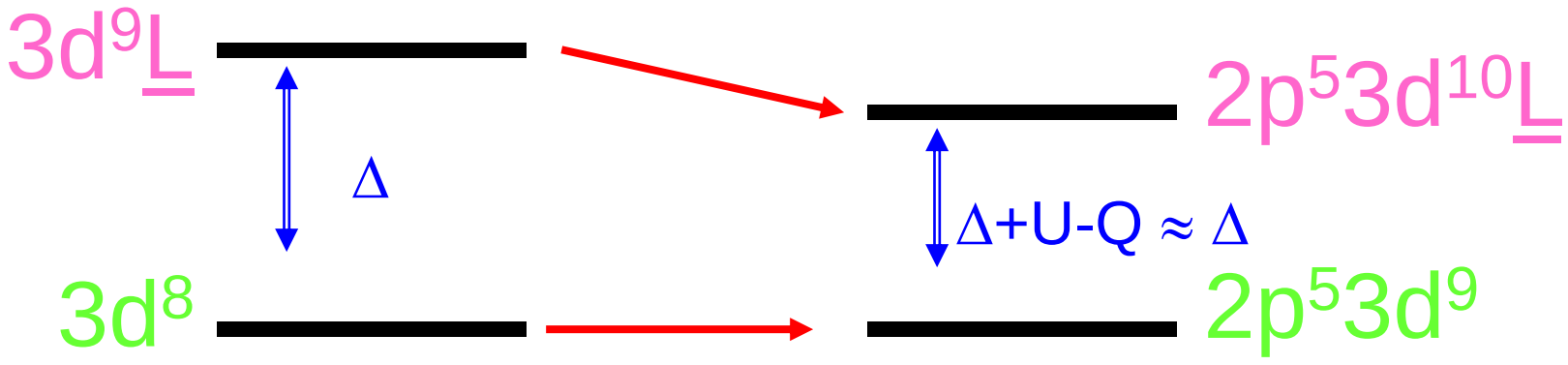
Charge transfer effects



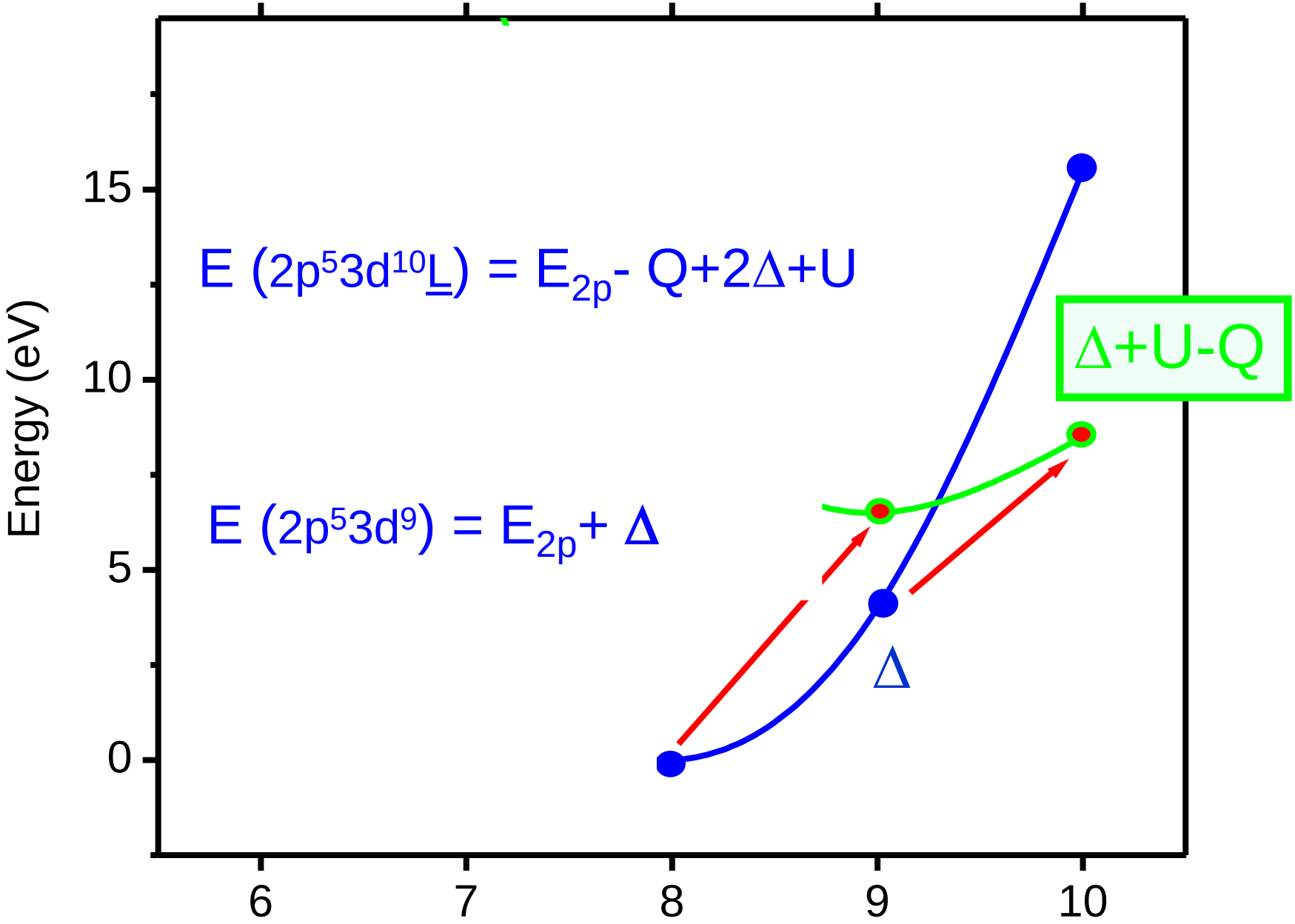
Charge transfer effects

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

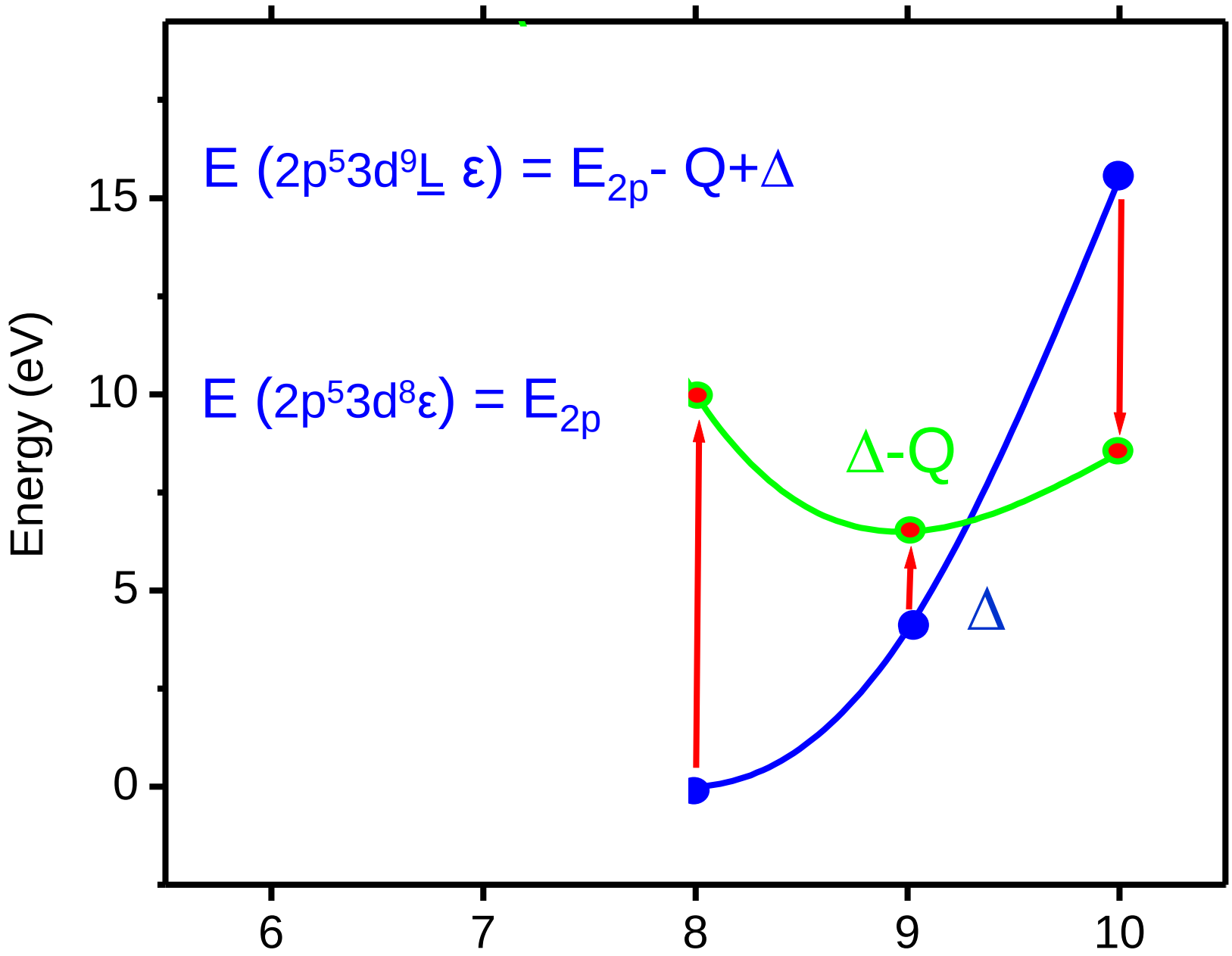
Energy of $3d^9\underline{L}$: Charge transfer energy Δ



Charge transfer effects

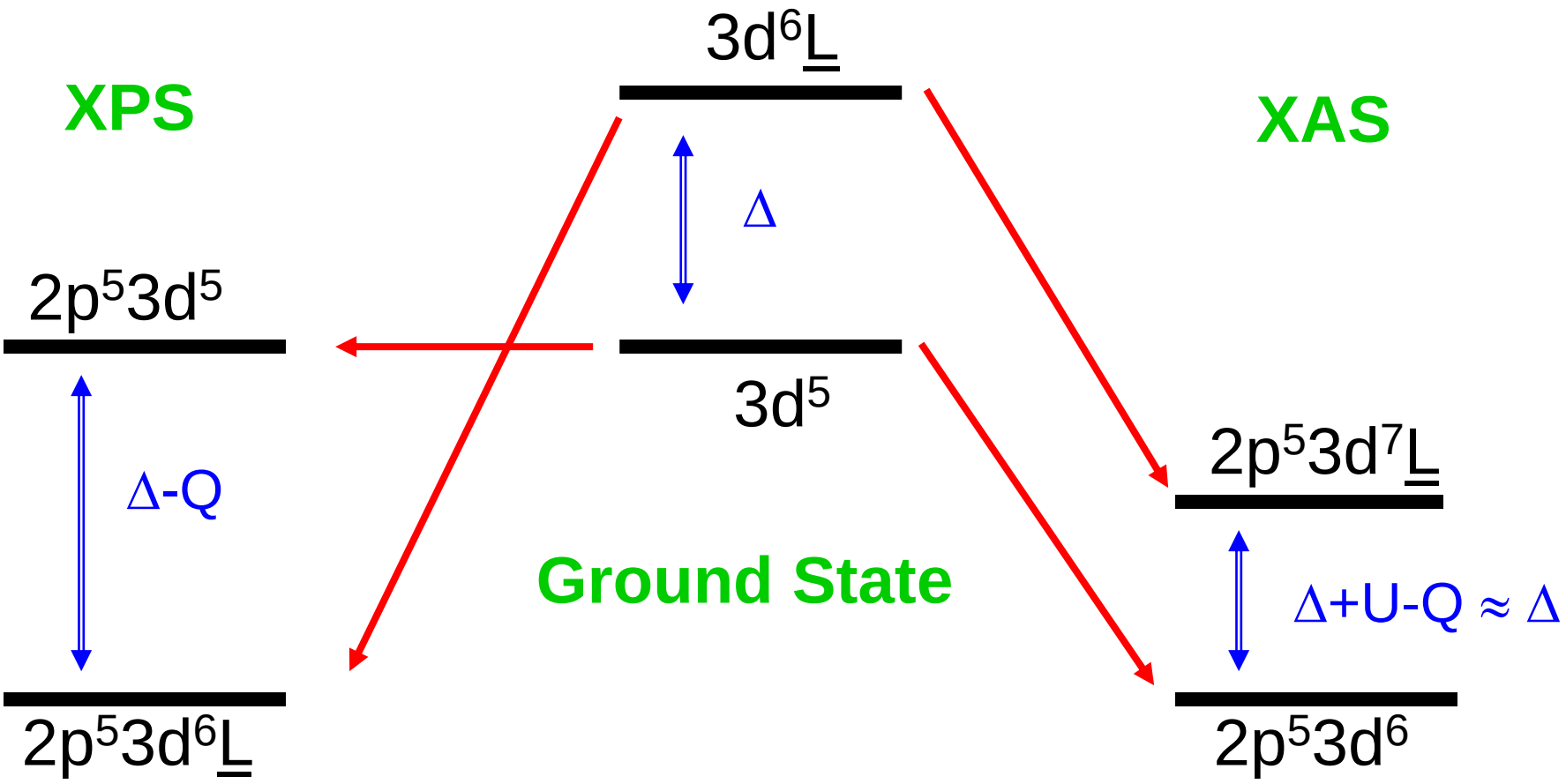


Charge transfer effects in XPS



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



Charge transfer effects

NiO: Ground state: $3d^8$ ($3d^8$)

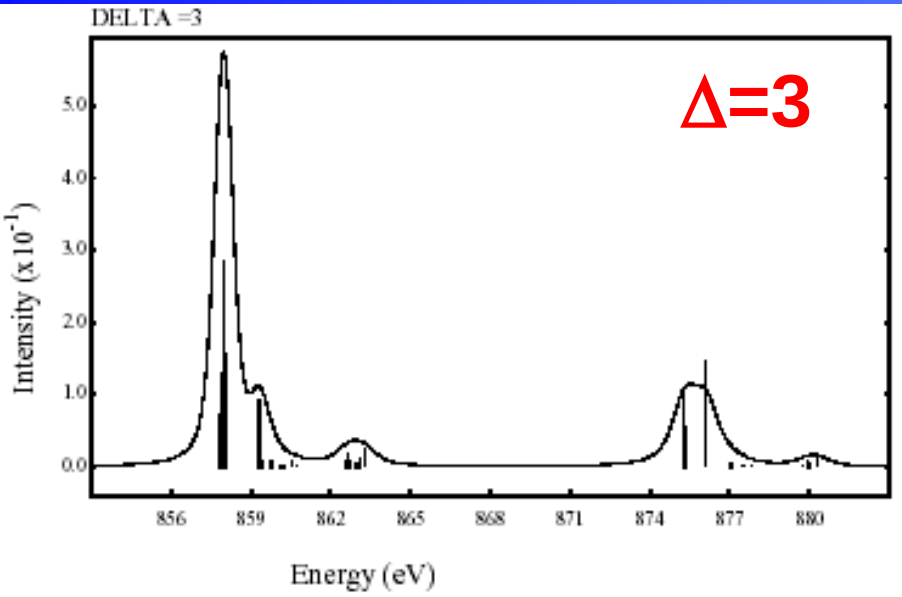
+ $3d^9\underline{L}$ Charge transfer energy Δ

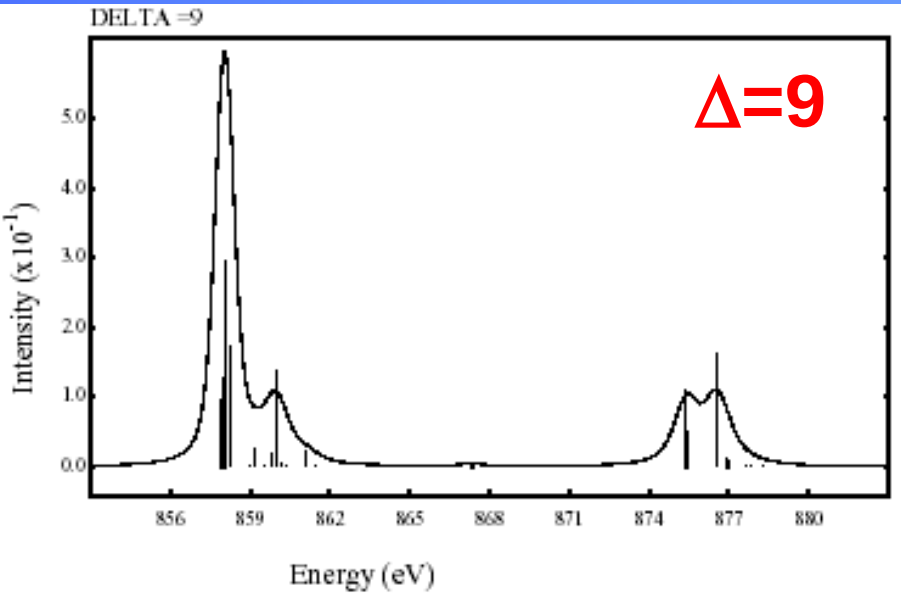
+ $3d^93d^7$ Hubbard U

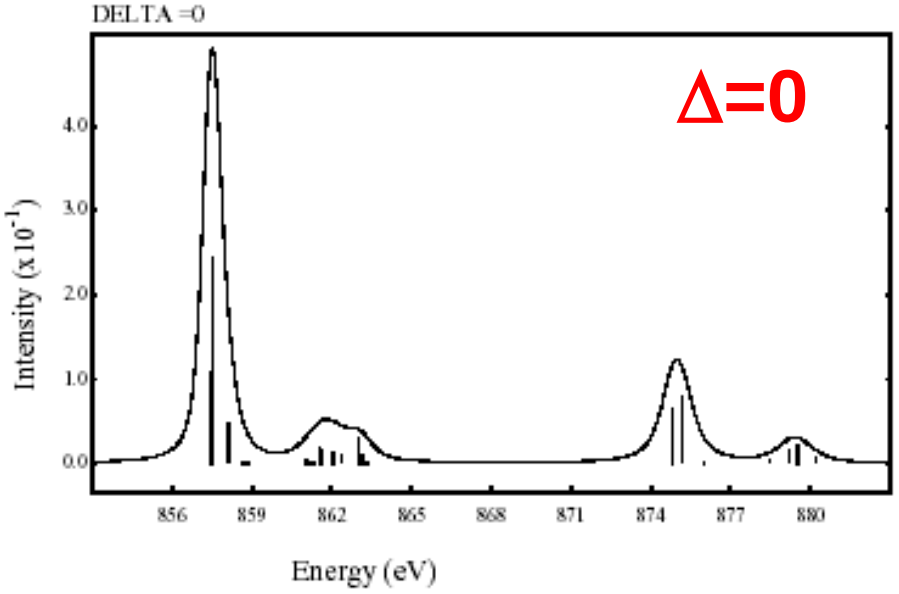
+ $3d^{10}\underline{L}^2$ $2\Delta+U$

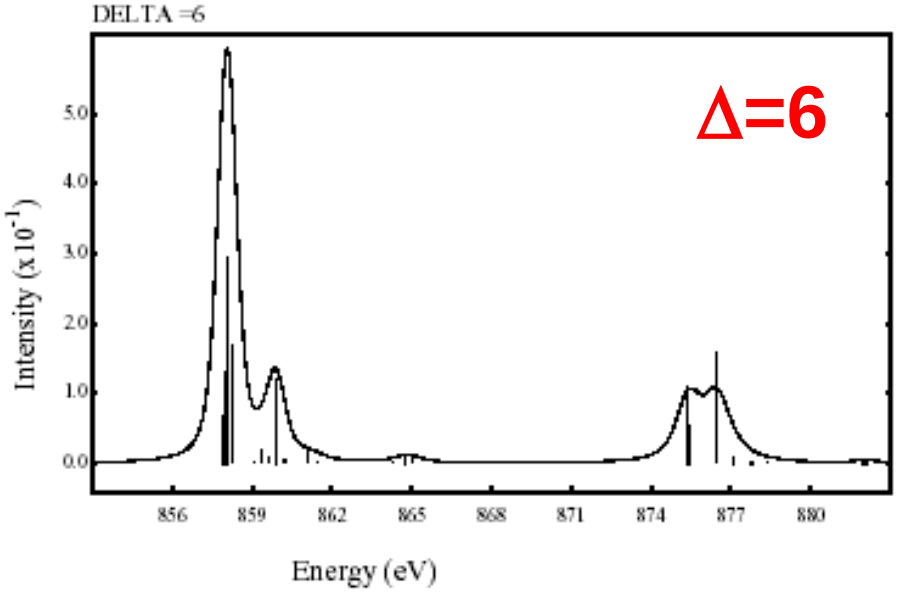
+ $3d^7L$ Metal-ligand CT Δ_{MLCT}

Charge transfer effects in XAS

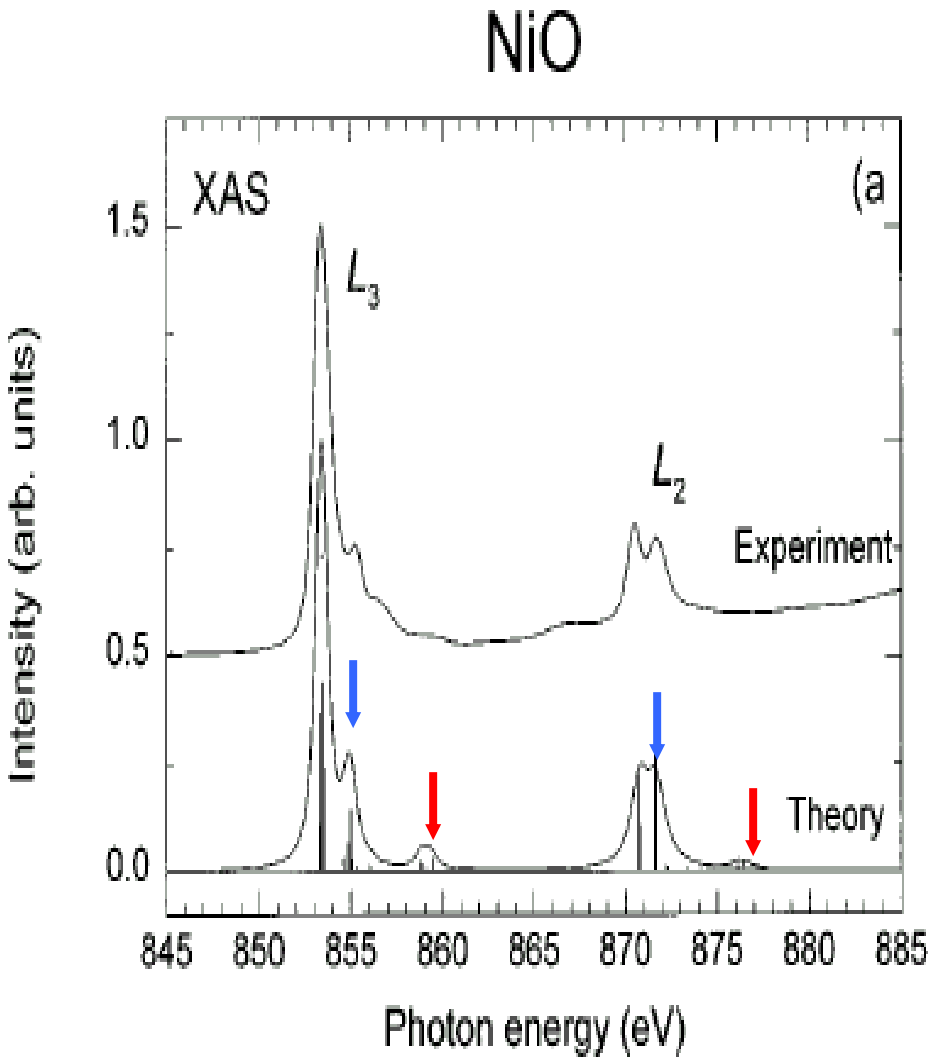








Charge transfer effects in XAS and XPS



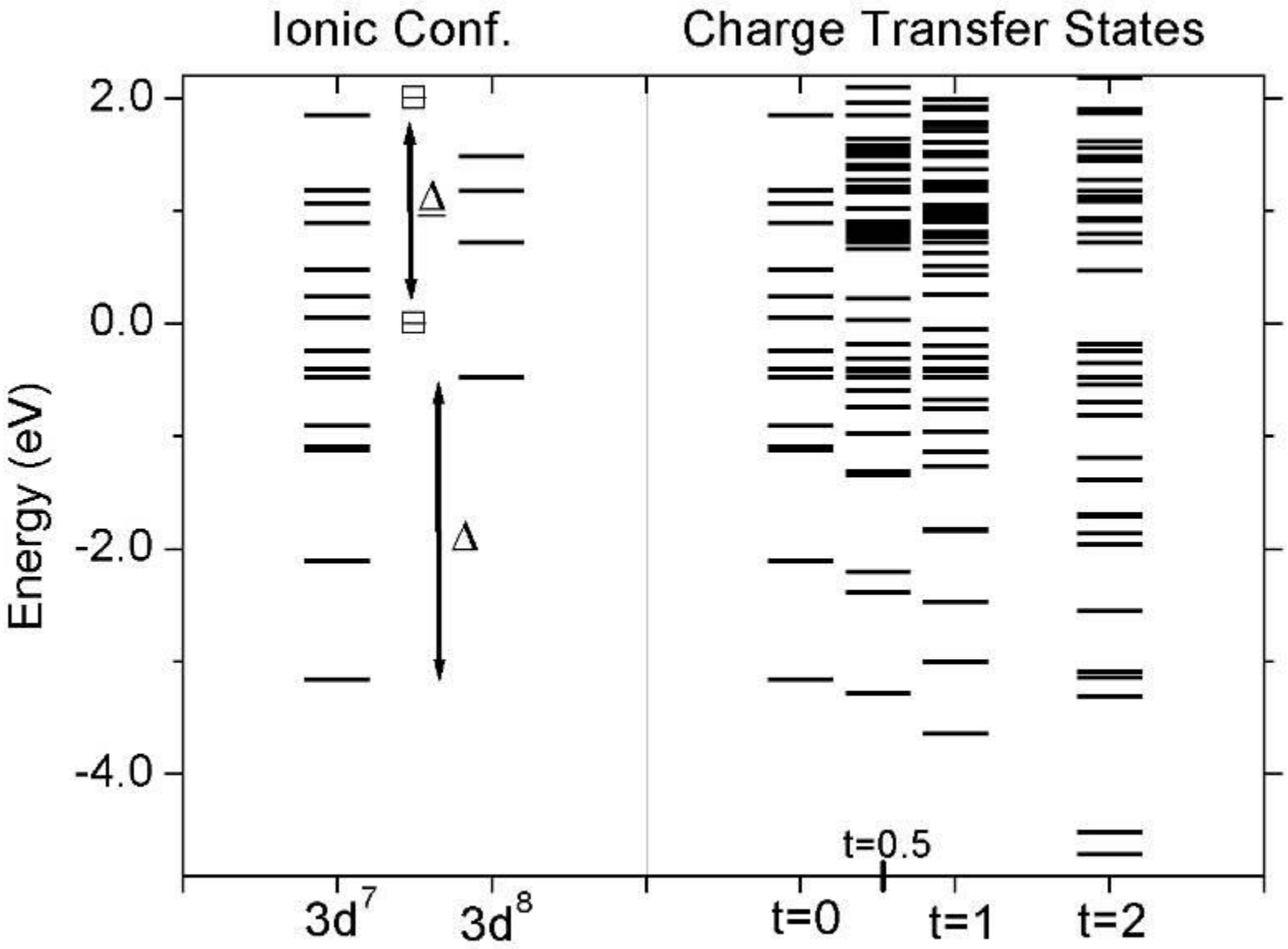
Spectral shape:

(1) Multiplet effects

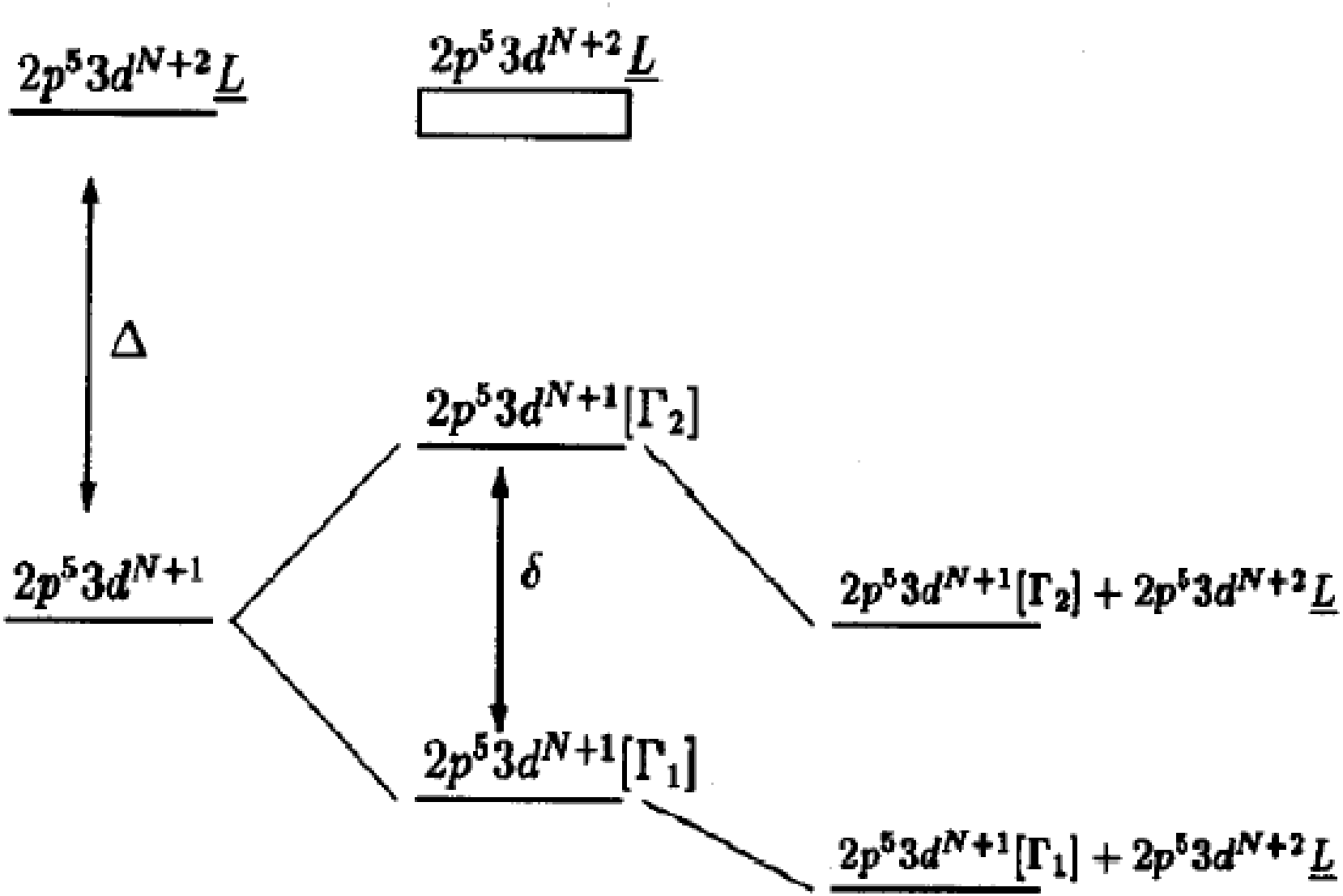
(2) Charge Transfer

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

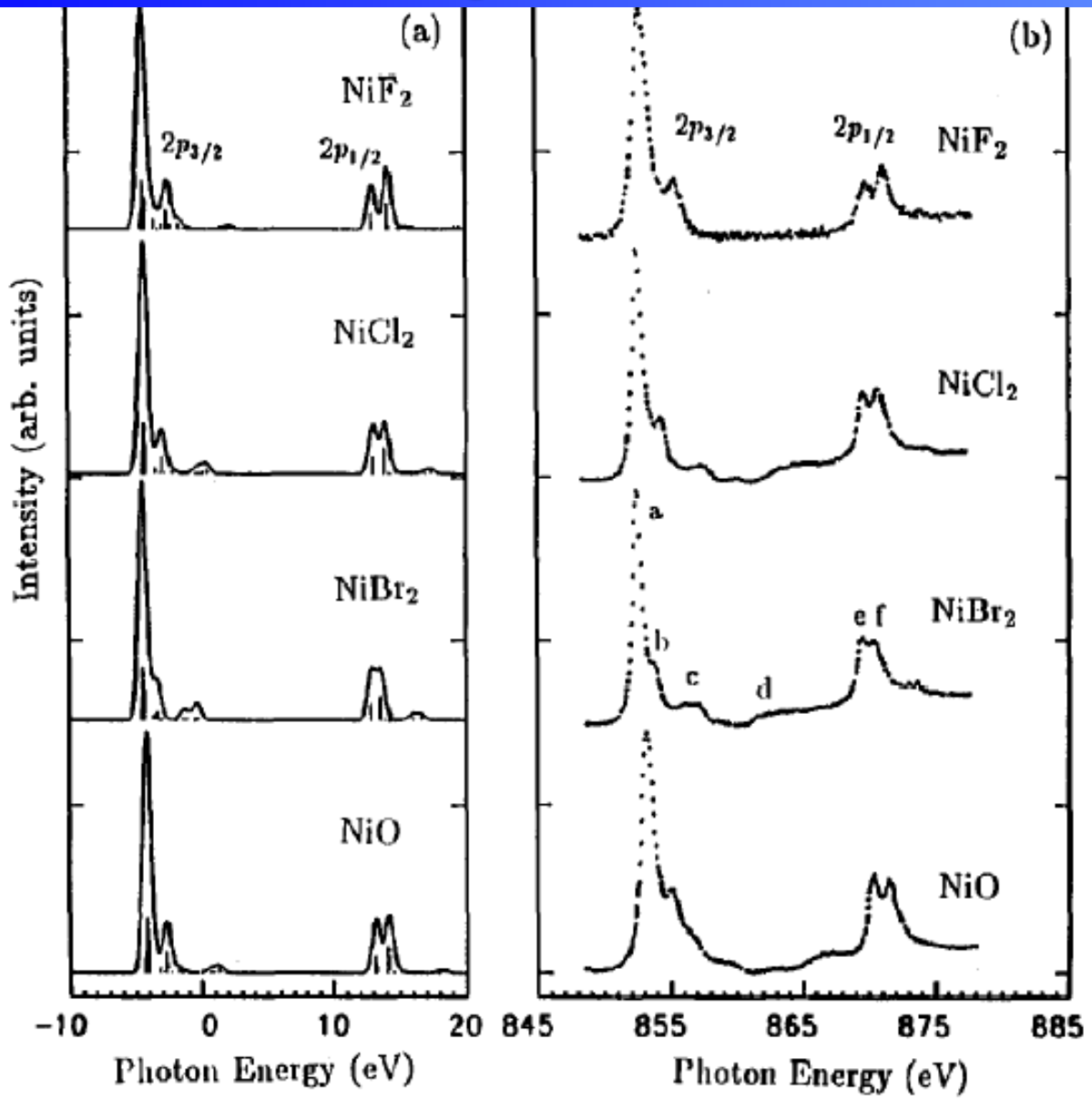
Charge transfer effects



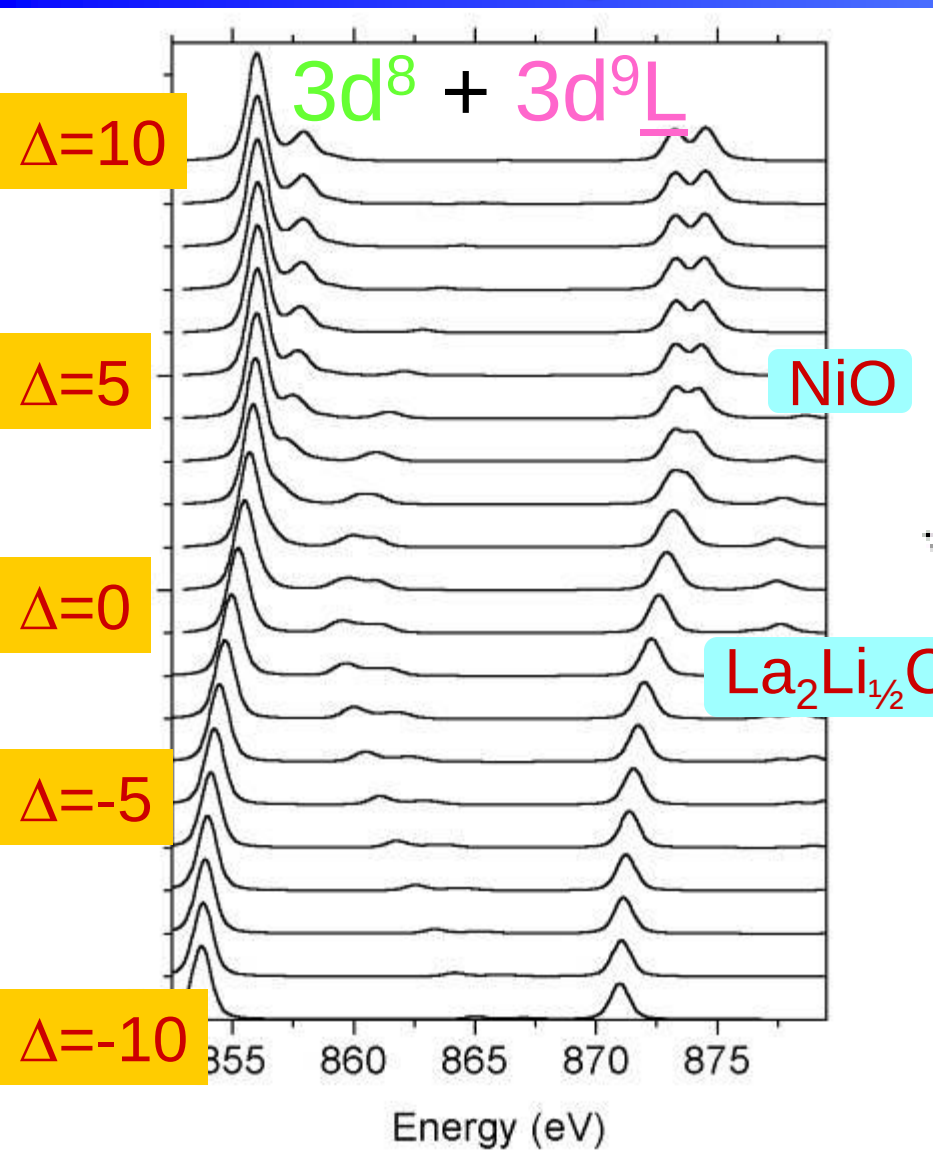
Charge transfer effects

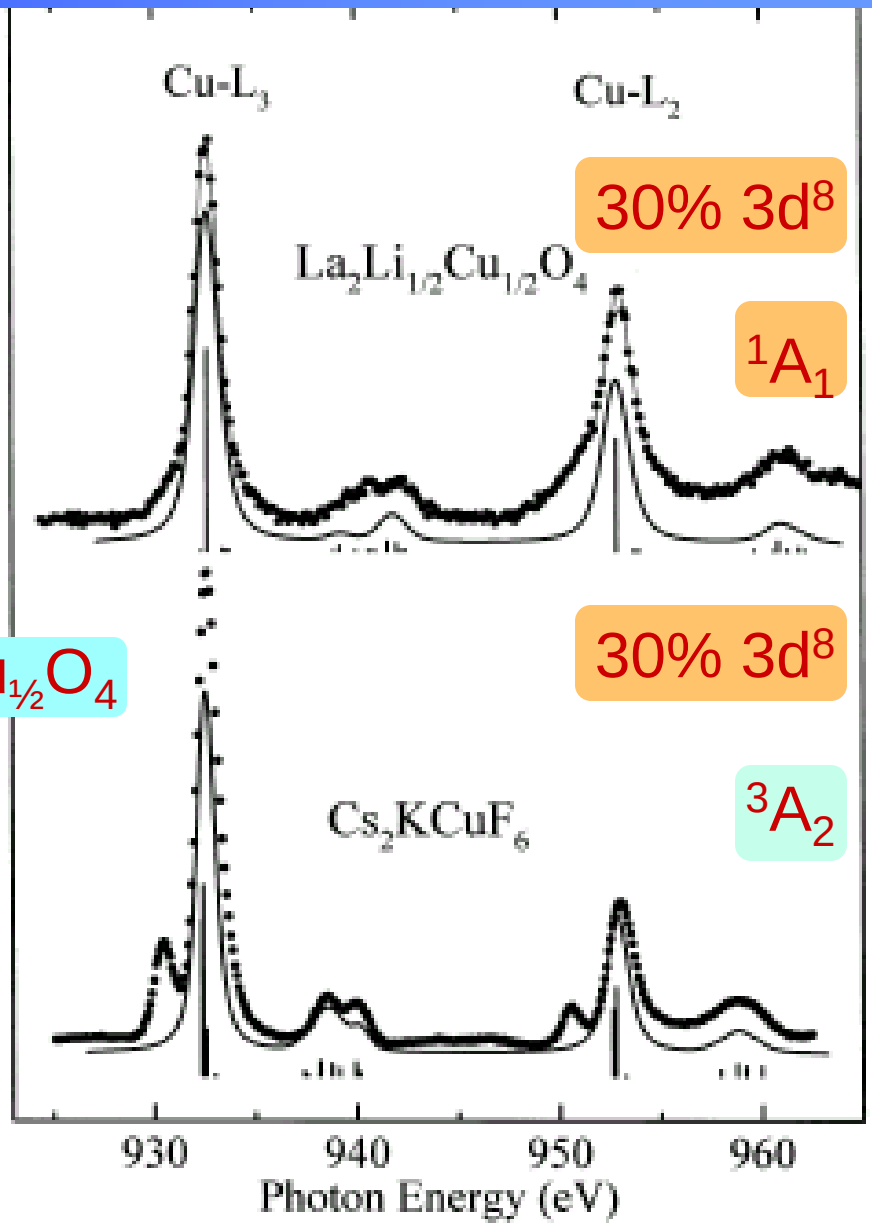


Charge transfer effects in XAS



Charge transfer effects in XAS

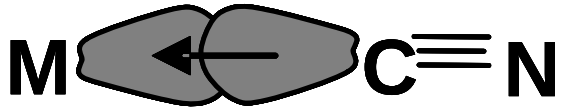


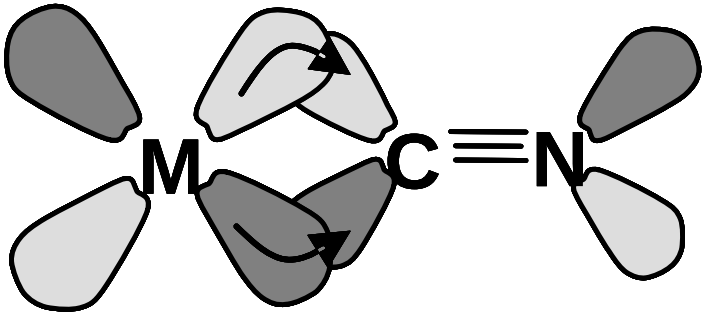


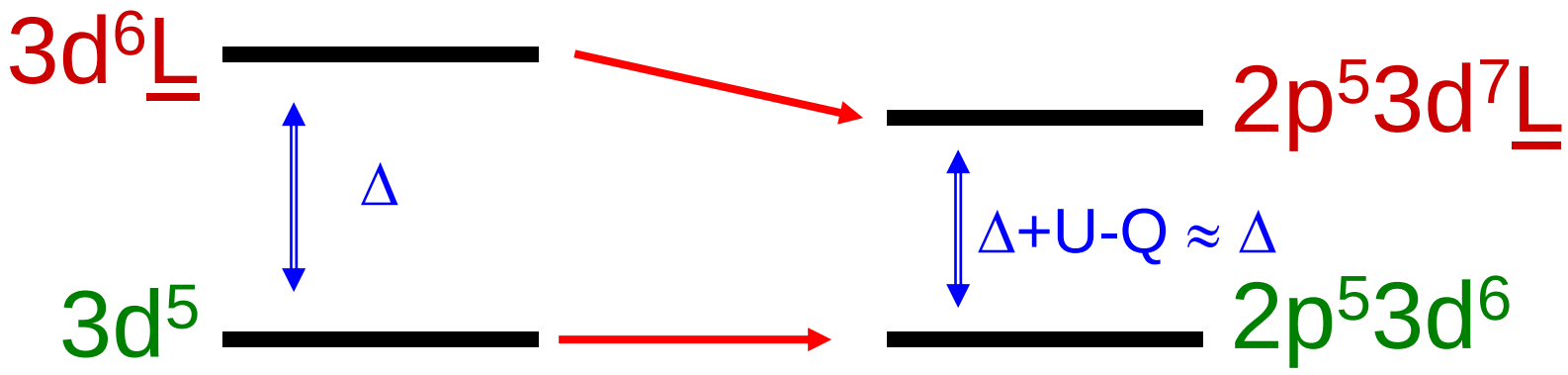
Chem. Phys. Lett. 297, 321 (1998)

LMCT and MLCT: π - bonding

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



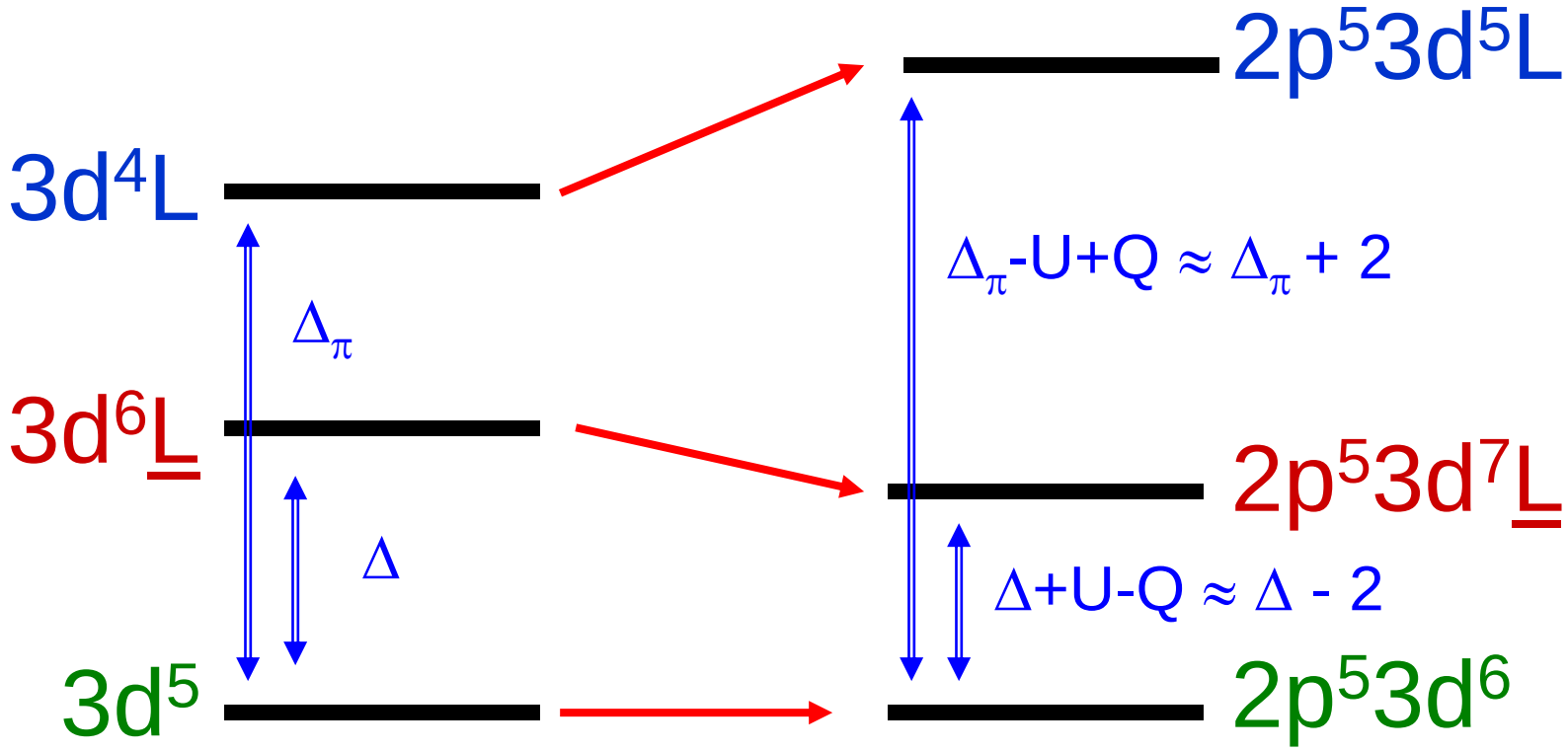




with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

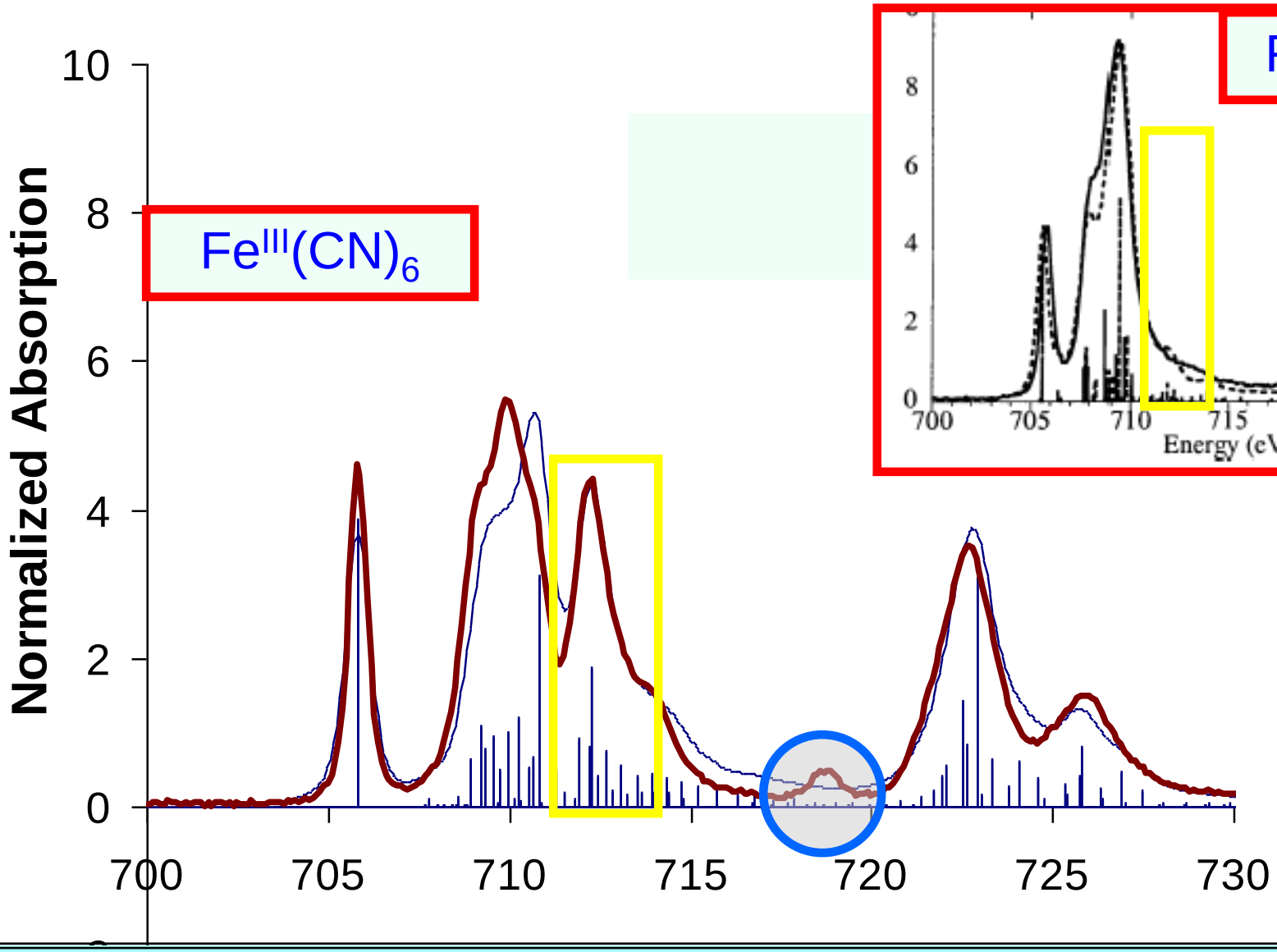
LMCT and MLCT: π - bonding

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)

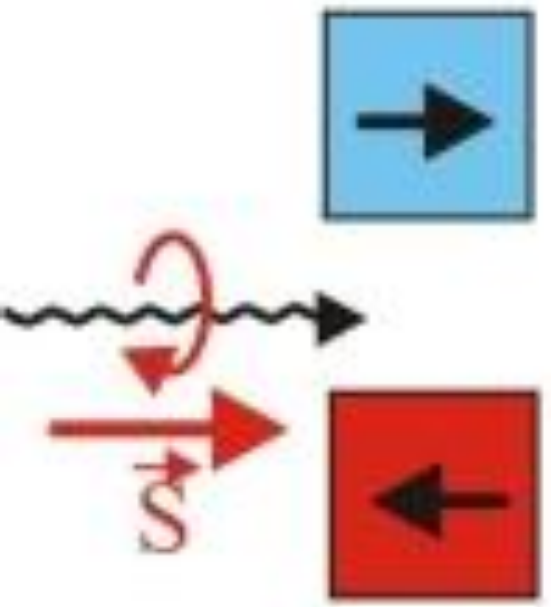
LMCT and MLCT: π - bonding

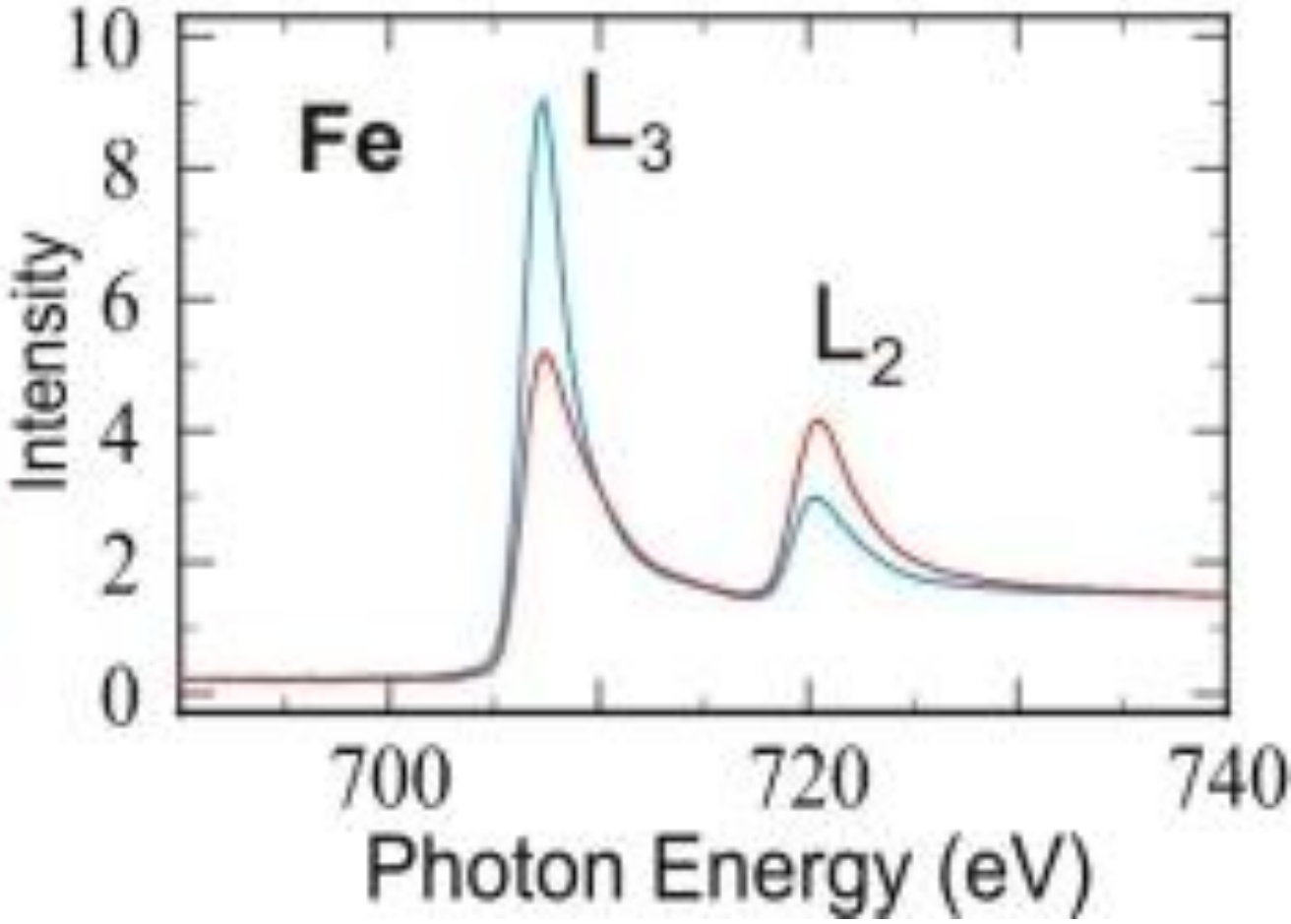


with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

X-ray MCD

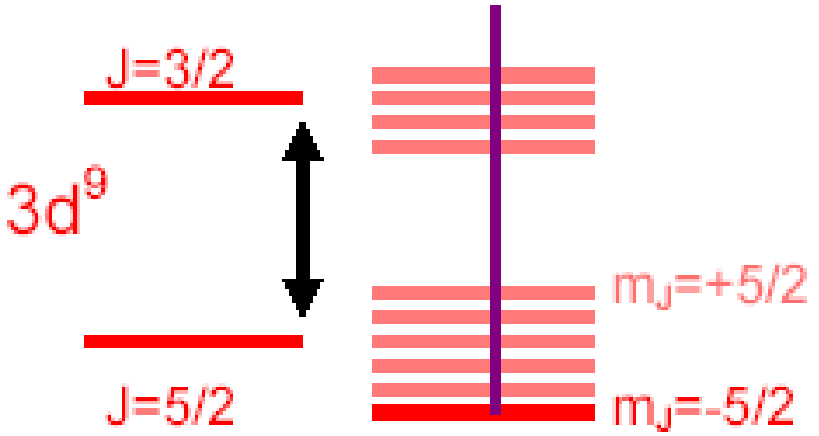
X-ray MCD





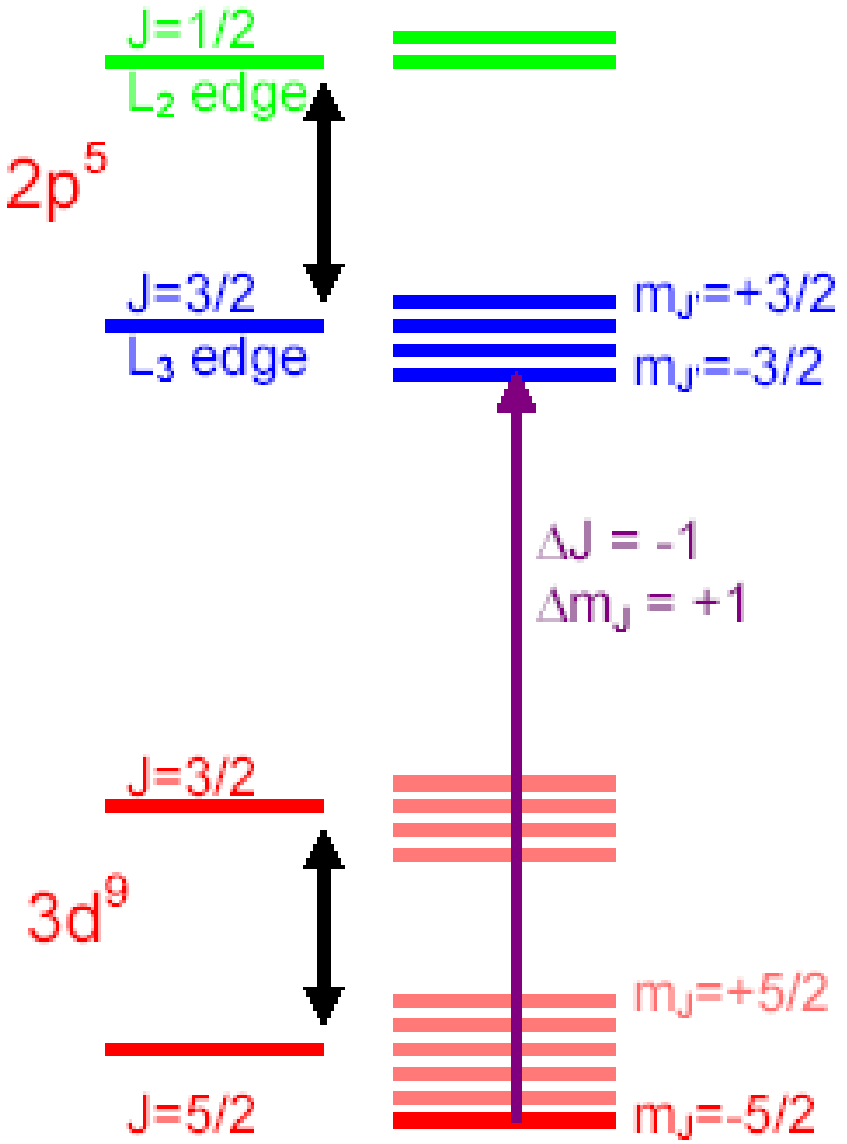
X-ray MCD

Cu^{2+}: $3d^9$

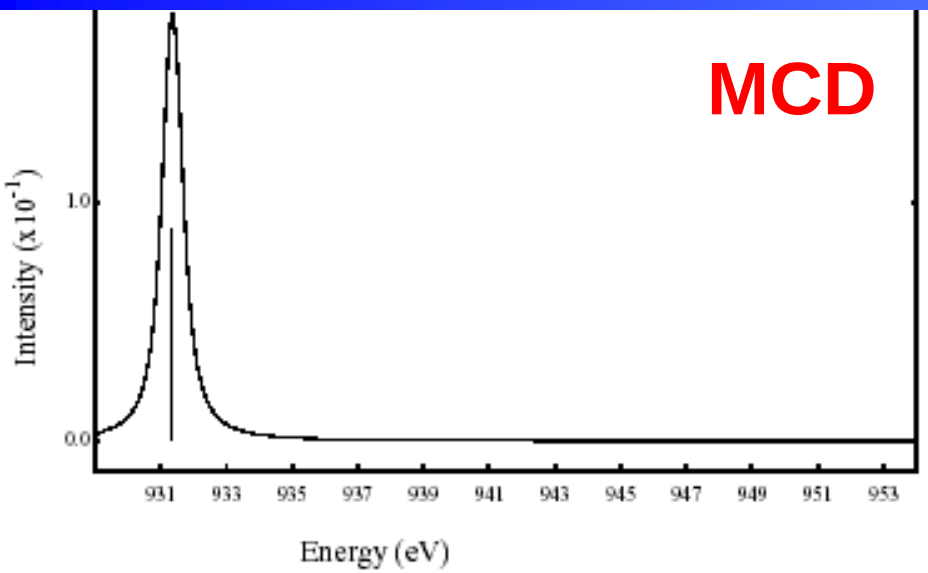


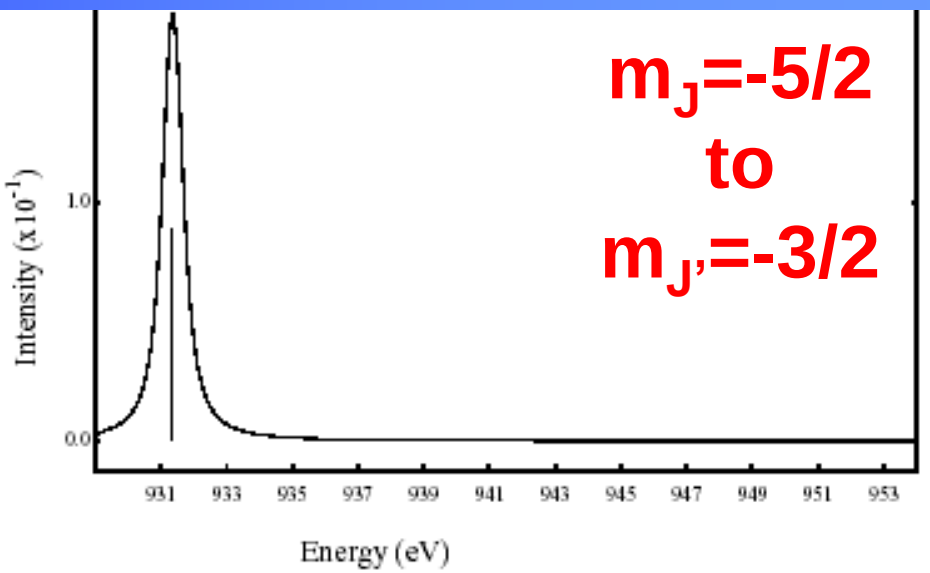
X-ray MCD

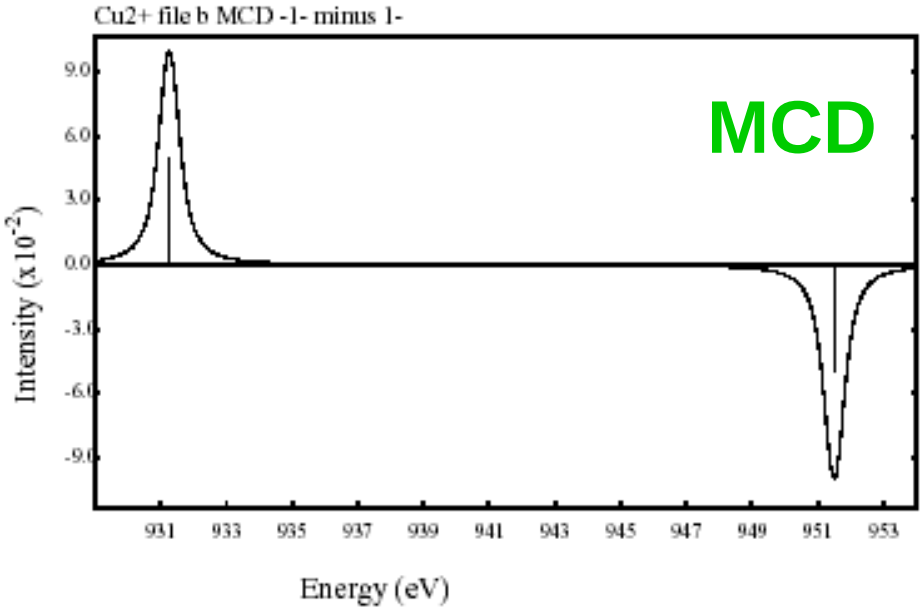
Cu^{2+}: $3d^9$

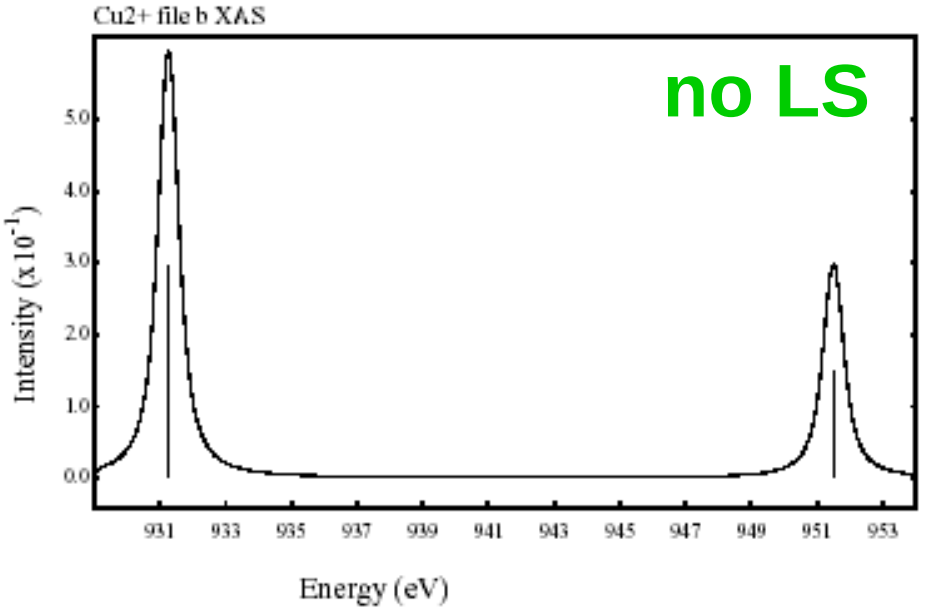


X-ray MCD


MCD
Intensity (x10^{-1})
1.0
0.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)


m_J=-5/2
to
$m_{J'}$=-3/2
Intensity (x10^{-1})
1.0
0.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)


Cu2+ file b MCD -1- minus 1-
MCD
Intensity (x10^{-2})
9.0
6.0
3.0
0.0
-3.0
-6.0
-9.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)


Cu2+ file b XAS
no LS
Intensity (x10^{-1})
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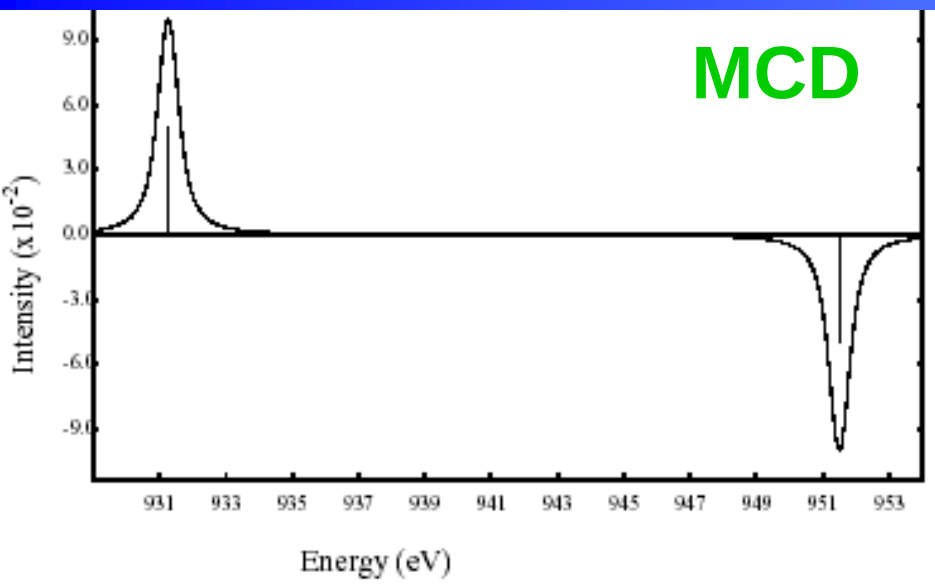
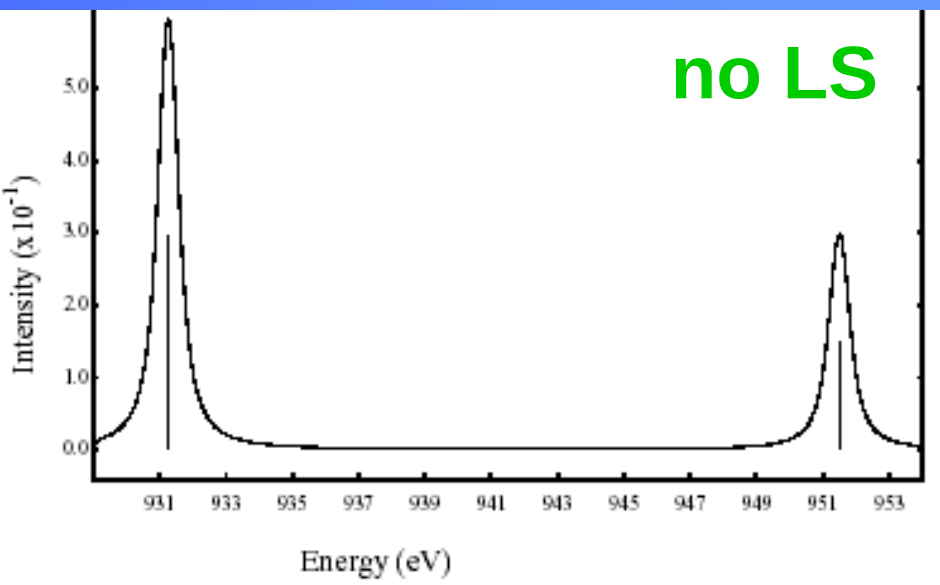
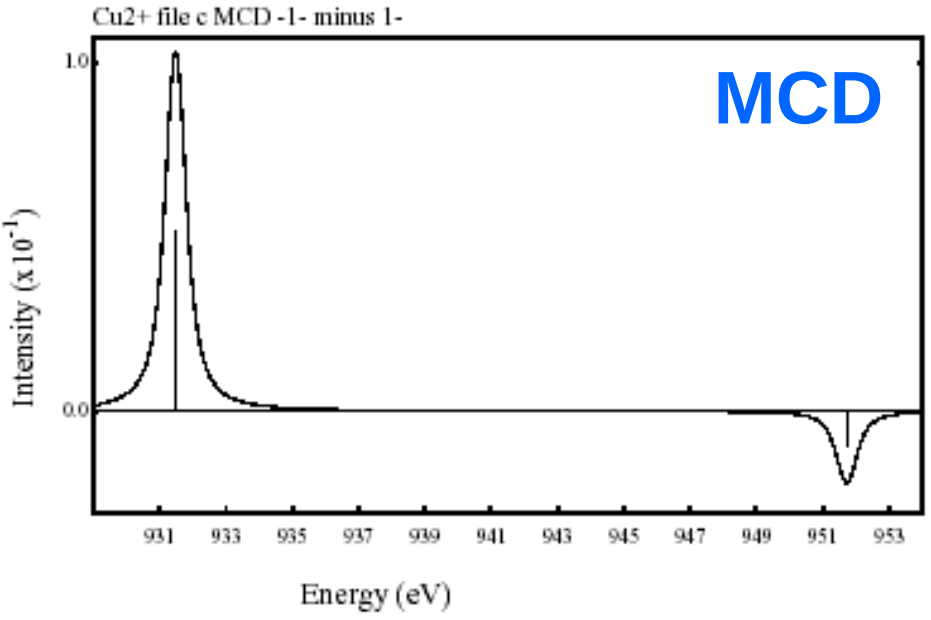
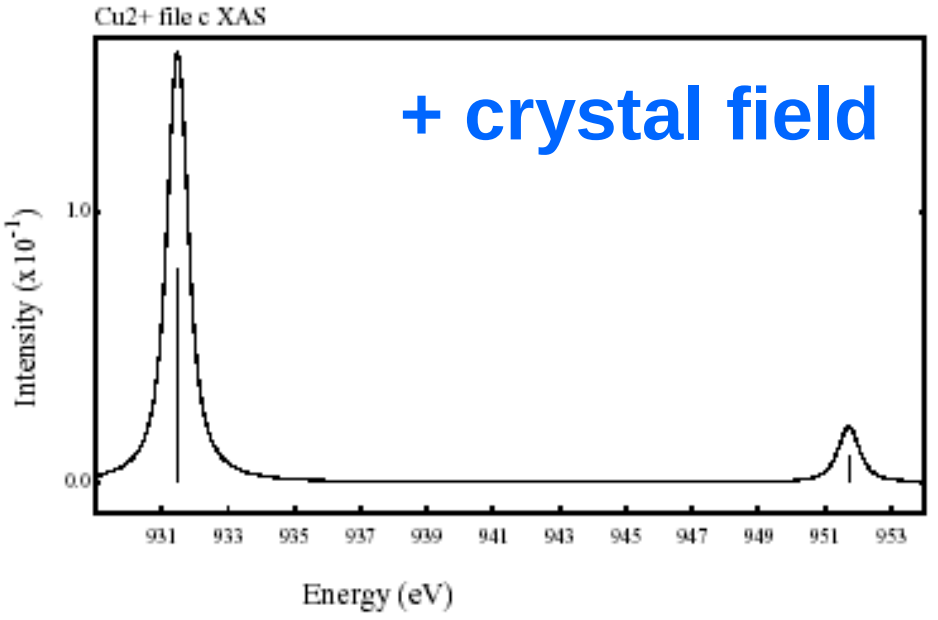
4.0
3.0
2.0
1.0
0.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)

X-ray MCD

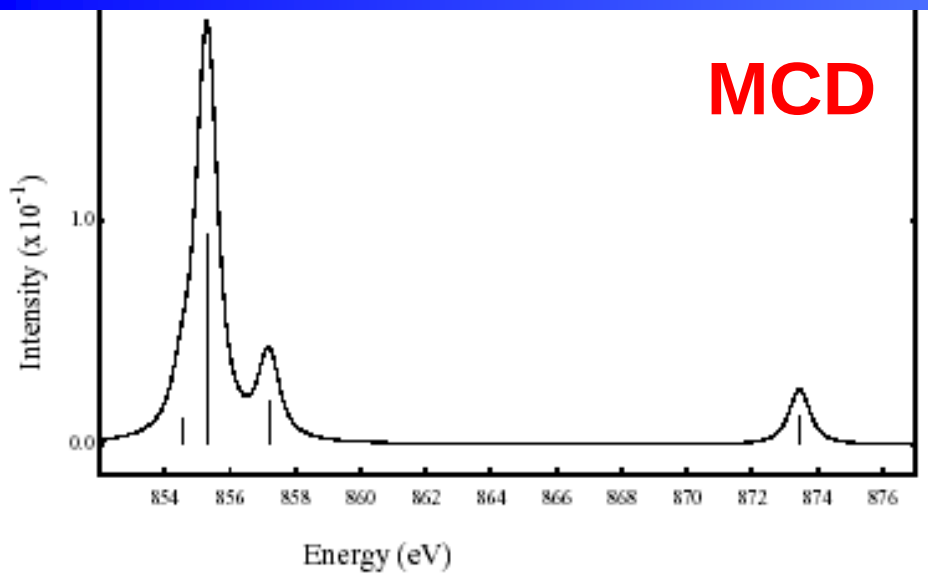

MCD
Intensity (x10^{-2})
9.0
6.0
3.0
0.0
-3.0
-6.0
-9.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)

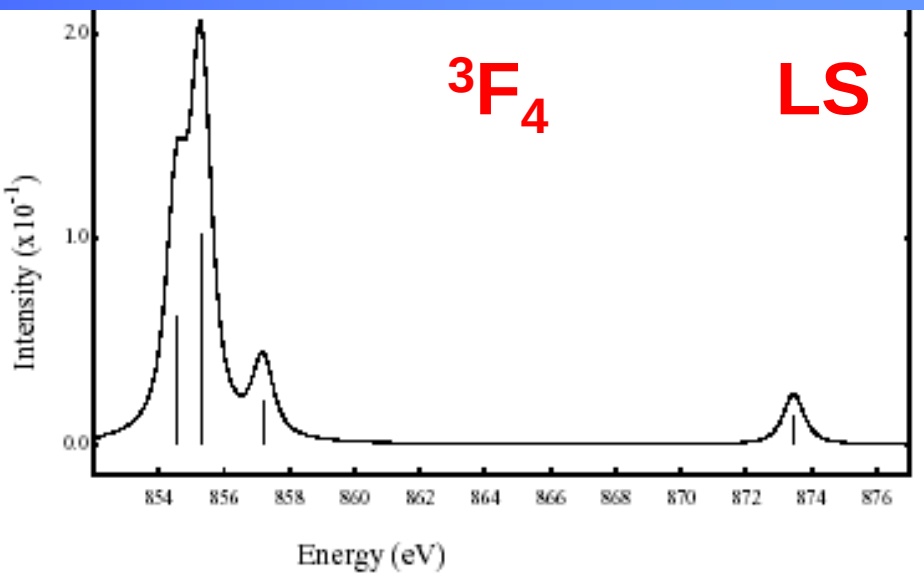

no LS
Intensity (x10^{-1})
5.0
4.0
3.0
2.0
1.0
0.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)

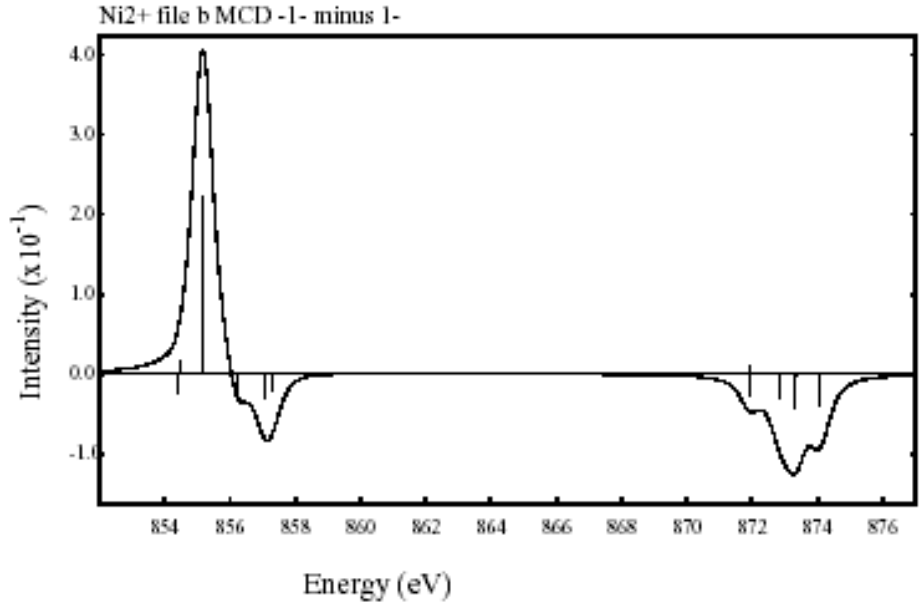

Cu2+ file c MCD -1- minus 1-
MCD
Intensity (x10^{-1})
1.0
0.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)

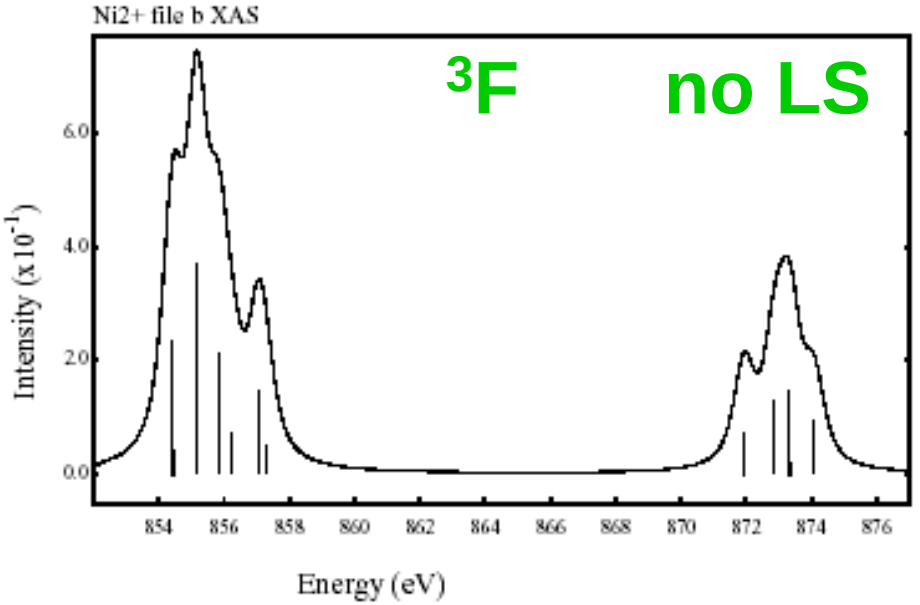

Cu2+ file c XAS
+ crystal field
Intensity (x10^{-1})
1.0
0.0
931 933 935 937 939 941 943 945 947 949 951 953
Energy (eV)

X-ray MCD

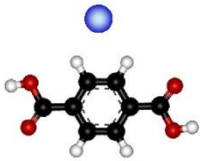

MCD
Intensity (x10^{-1})
1.0
0.0
854 856 858 860 862 864 866 868 870 872 874 876
Energy (eV)


$^3F_4$
LS
Intensity (x10^{-1})
2.0
1.0
0.0
854 856 858 860 862 864 866 868 870 872 874 876
Energy (eV)


Ni2+ file b MCD -1- minus 1-
Intensity (x10^{-1})
4.0
3.0
2.0
1.0
0.0
-1.0
854 856 858 860 862 864 866 868 870 872 874 876
Energy (eV)

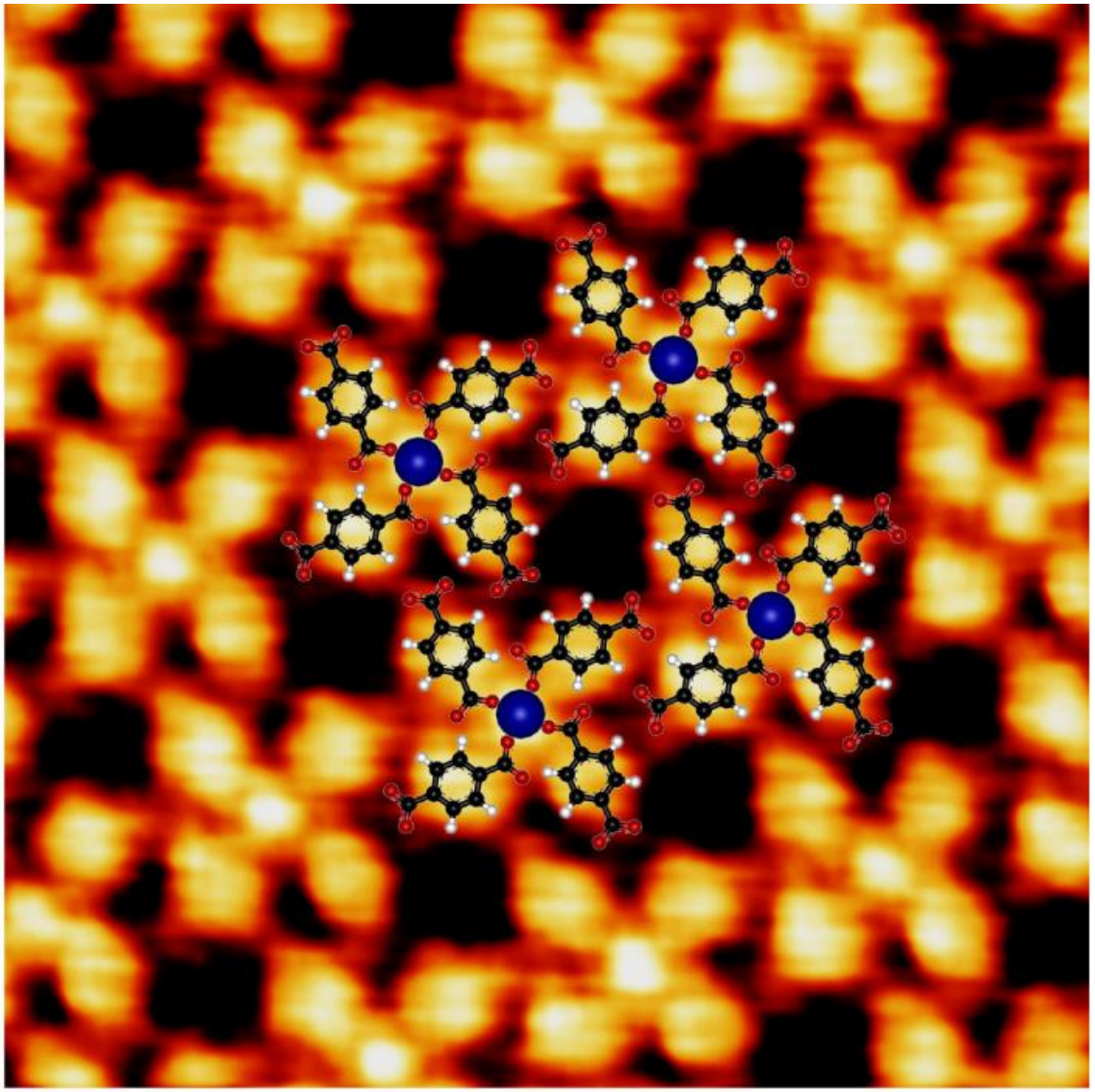

Ni2+ file b XAS
^3F
no LS
Intensity (x10^{-1})
6.0
4.0
2.0
0.0
854 856 858 860 862 864 866 868 870 872 874 876
Energy (eV)

Iron 2p XAS of Fe arrays



Fe

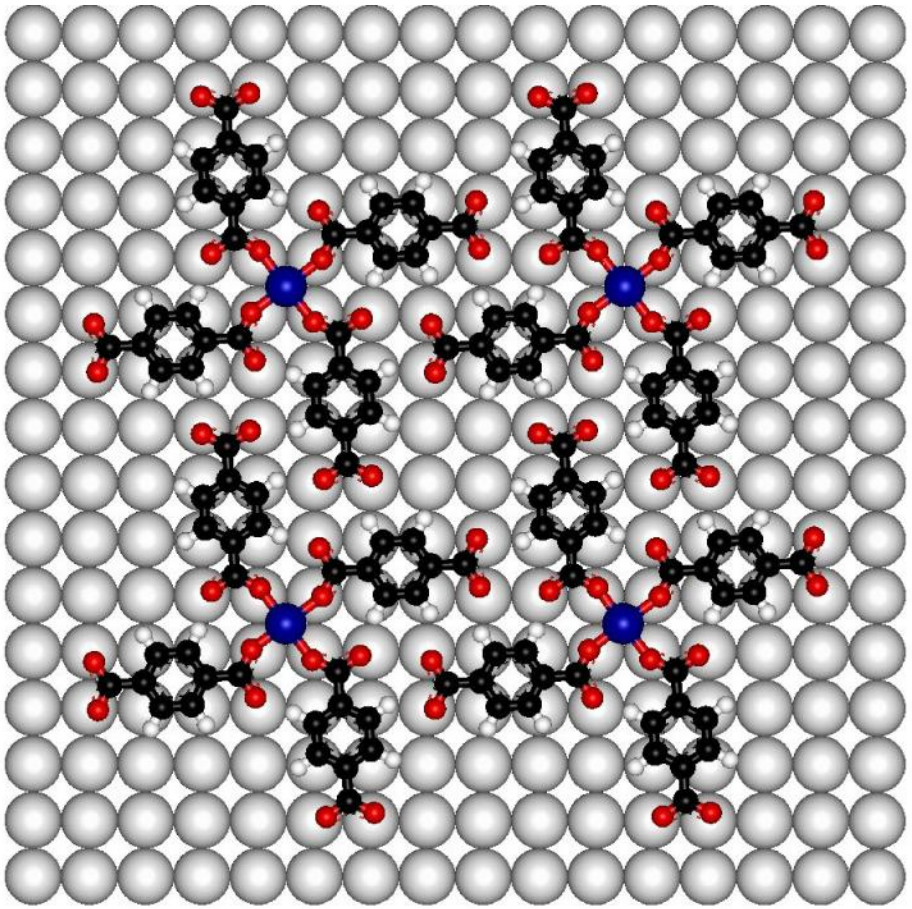
TPA

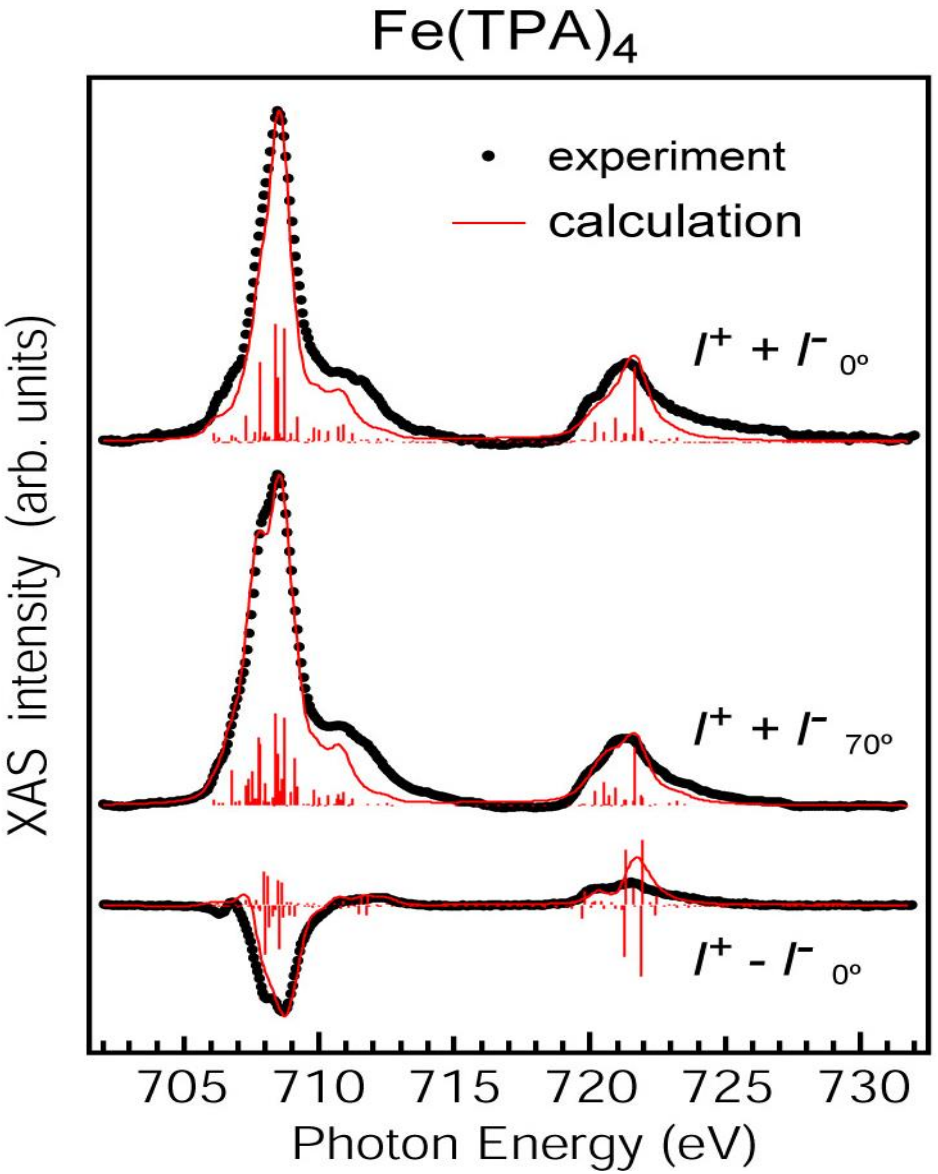


with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

Iron 2p XAS of Fe arrays

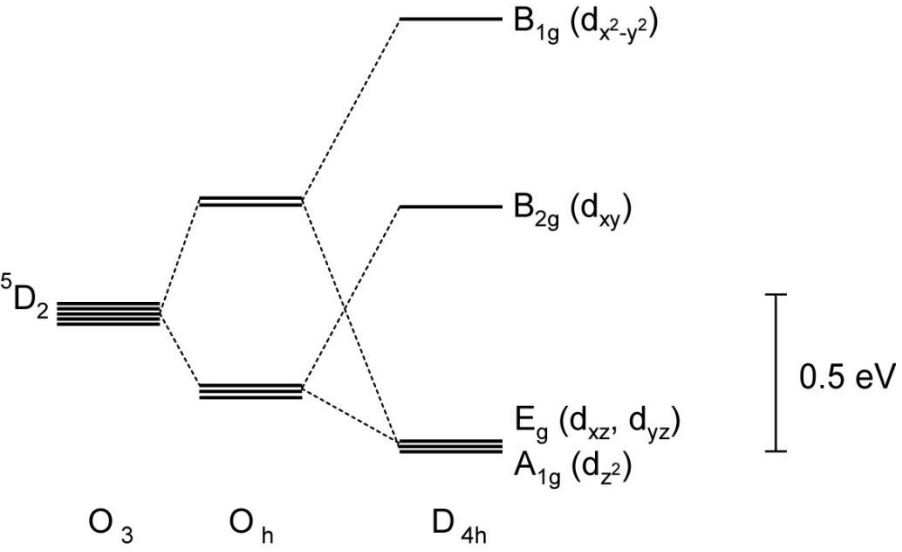
$Fe(TPA)_4$ on Cu(100)

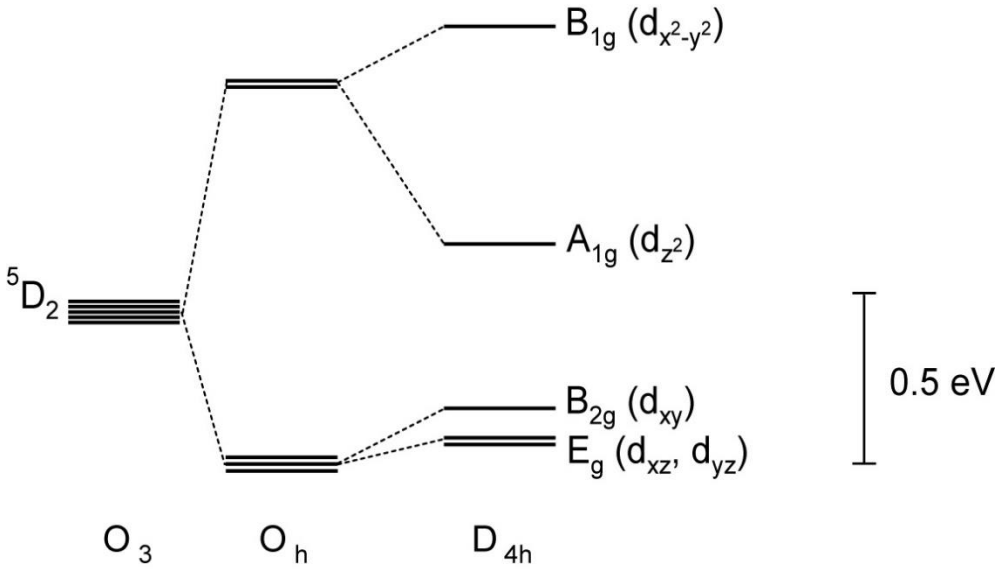


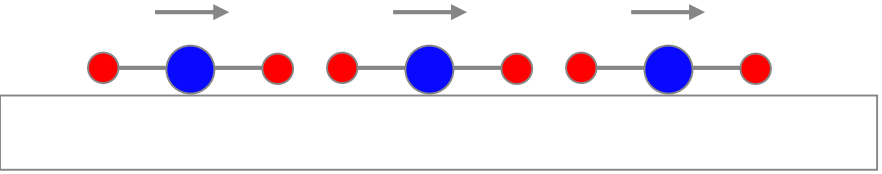


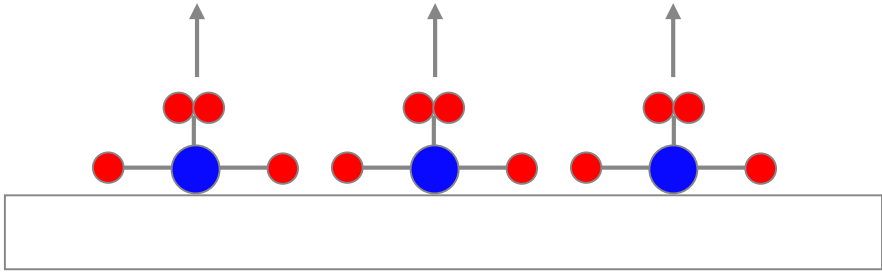
with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

Iron 2p XAS of Fe arrays







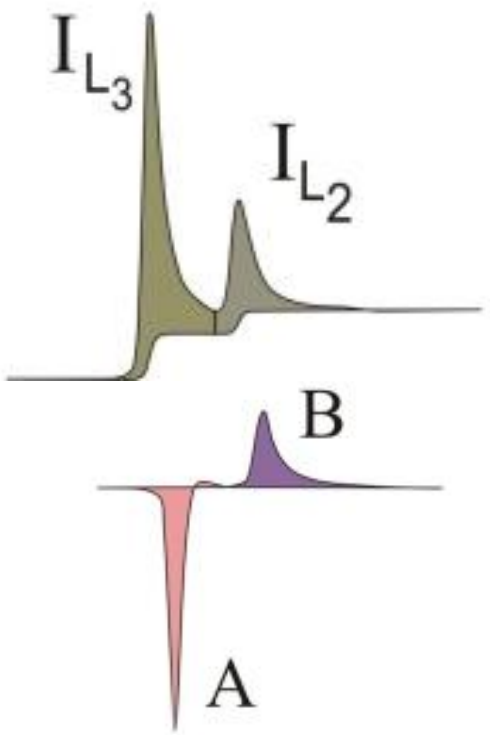


with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

X-ray MCD sum rules

XAS spectrum

XMCD spectrum



$$\int \mu = \int (\mu_1 + \mu_0 + \mu_{-1}) = \frac{C}{5} \langle N_h \rangle.$$

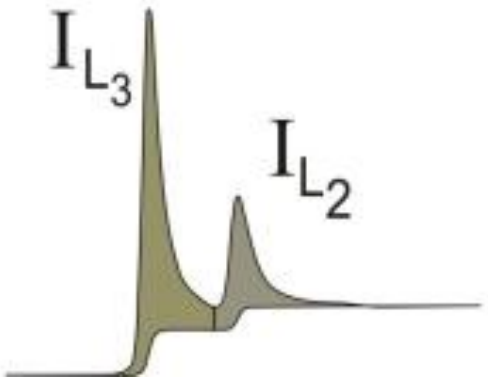
$$\int (\mu_+ - \mu_-) = -\frac{C}{10} \langle L_z \rangle.$$

$$\langle L_z \rangle = -\frac{\int (\mu_+ - \mu_-)}{\int \mu} \cdot 2\langle N_h \rangle.$$

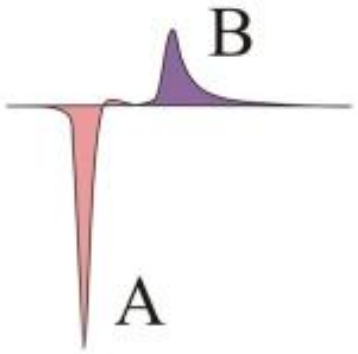
Thole et al. **PRL** 68, 1943 (1992); Carra et al. **PRL** 70, 684 (1993)

X-ray MCD sum rules

XAS spectrum



XMCD spectrum



Courtesy: J. Stöhr

magnetic dipole

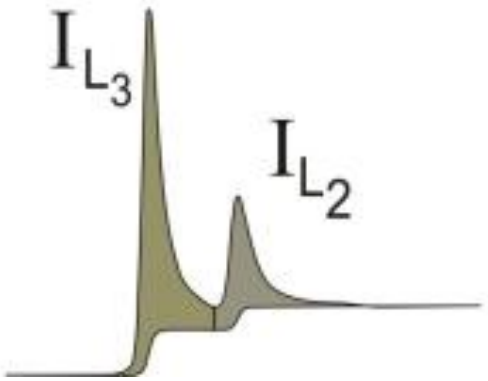
$$S_{eff} = \langle S_z \rangle + \frac{7}{2}\langle T_z \rangle = \frac{3}{2}\left(\frac{A-2B}{I_{L_3}+I_{L_2}}\right) \times n_h$$

$$\langle L_z \rangle = 2\left(\frac{A+B}{I_{L_3}+I_{L_2}}\right) \times n_h$$

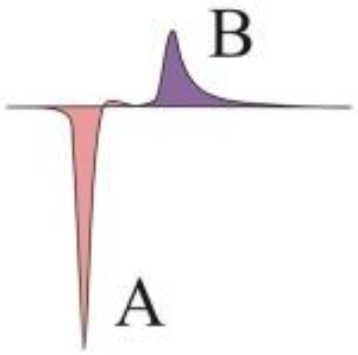
Thole et al. **PRL** 68, 1943 (1992); Carra et al. **PRL** 70, 684 (1993)

Effective spin sum rule

XAS spectrum



XMCD spectrum



Courtesy: J. Stöhr

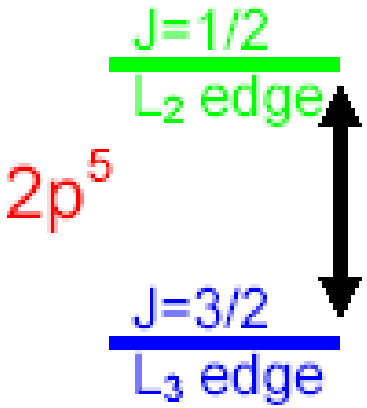
magnetic dipole

$$S_{eff} = \langle S_z \rangle + \frac{7}{2}\langle T_z \rangle = \frac{3}{2}\left(\frac{A-2B}{I_{L_3}+I_{L_2}}\right) \times n_h$$

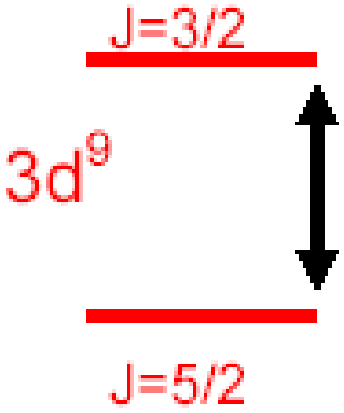
- separate L_3 from L_2?
- value of $\langle T_z \rangle$

Carra et al. **PRL** 70, 684 (1993)

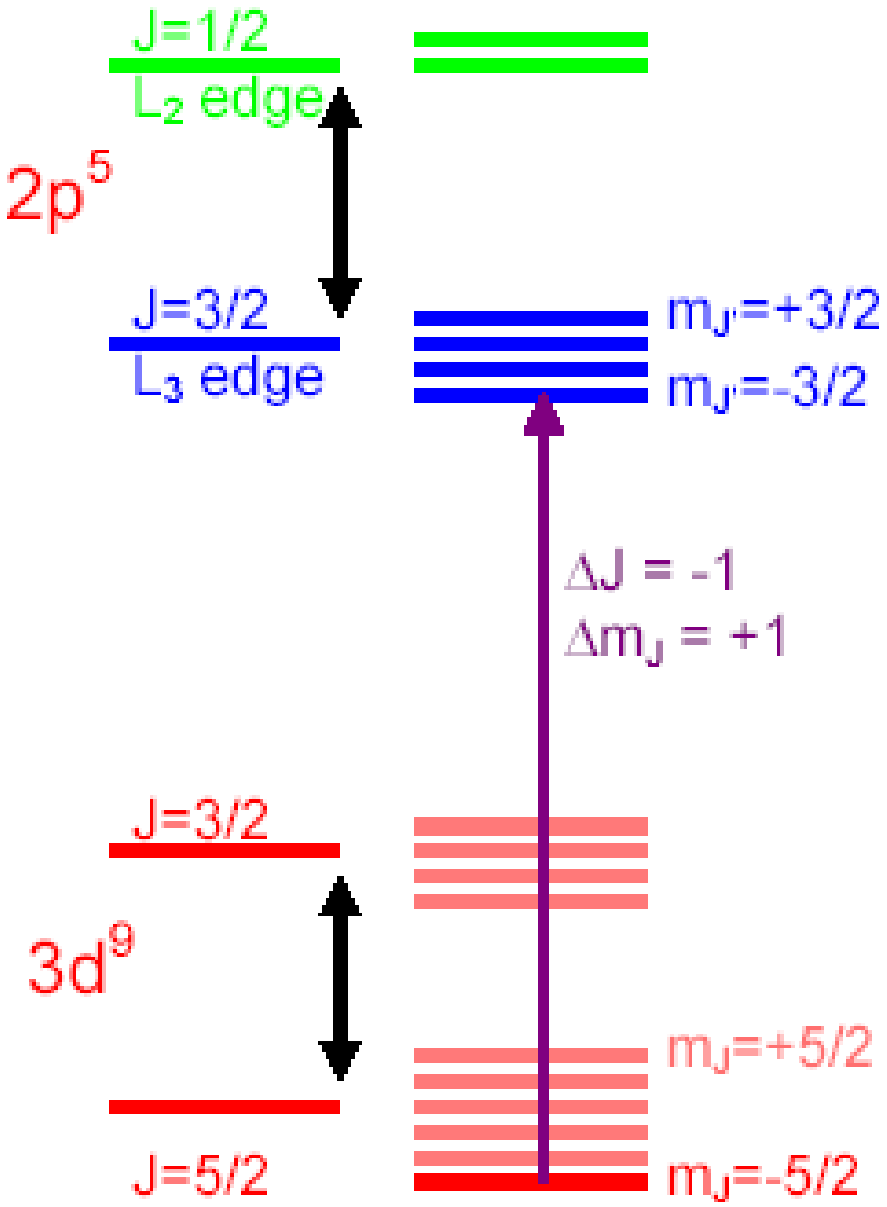
Effective spin sum rule for a $3d^9$ system



$$3d^9 \rightarrow 2p^5 3d^{10}$$



Effective spin sum rule for a $3d^9$ system



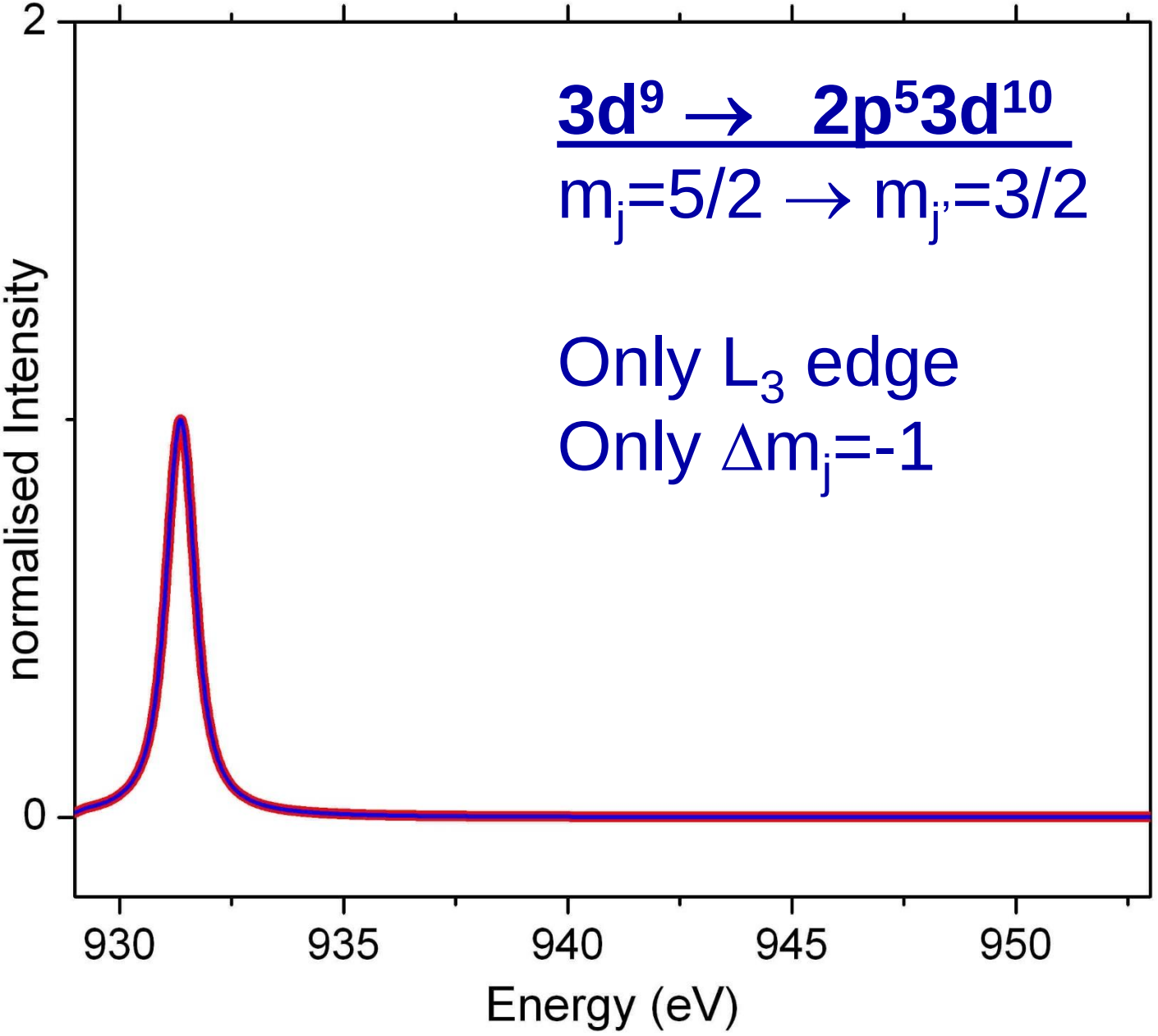
$3d^9 \rightarrow \ 2p^5 3d^{10}$

m_j=-5/2 $\rightarrow$ $m_{j'}$=-3/2

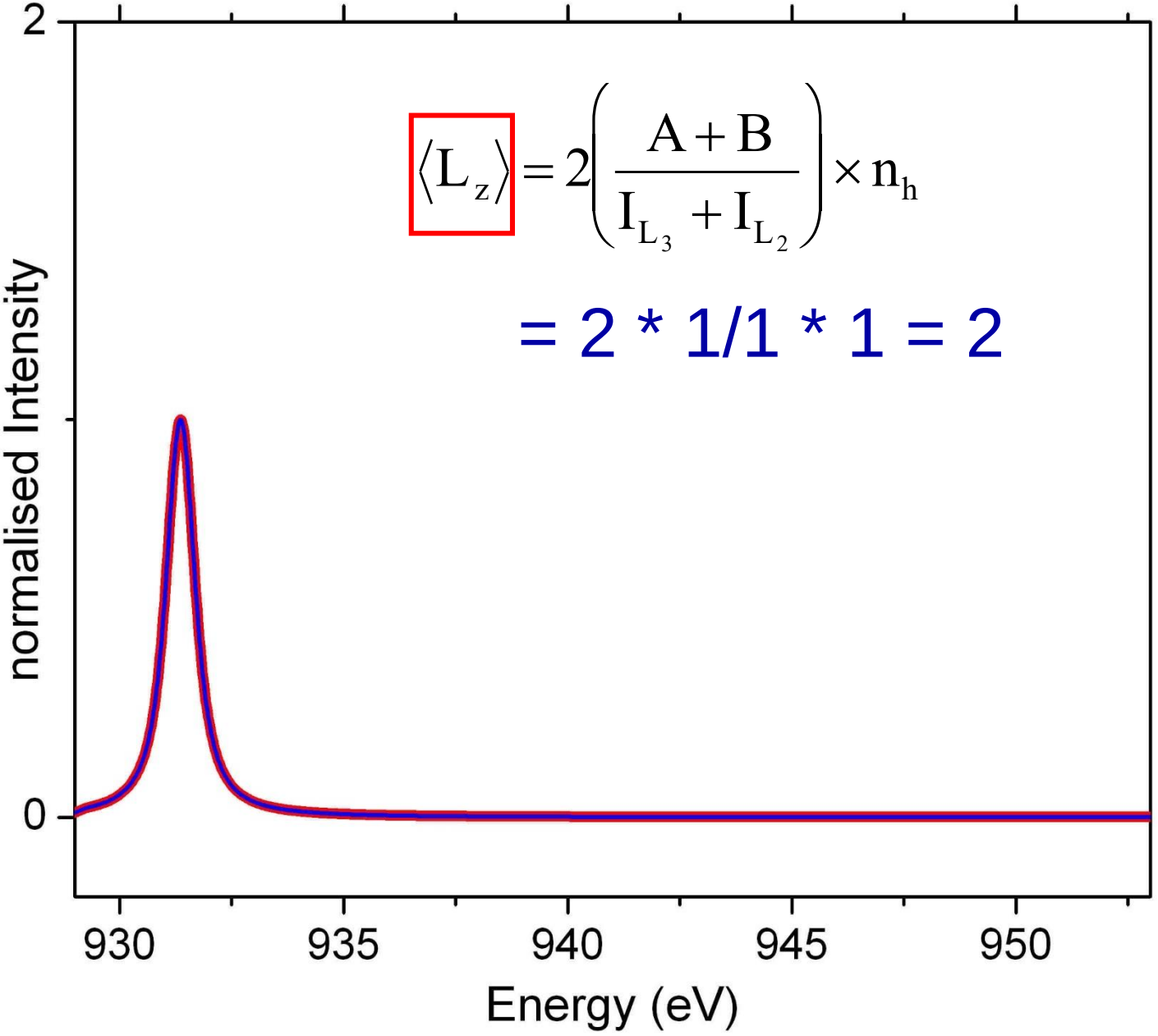
Only L_3 edge

Only Δm_j=+1

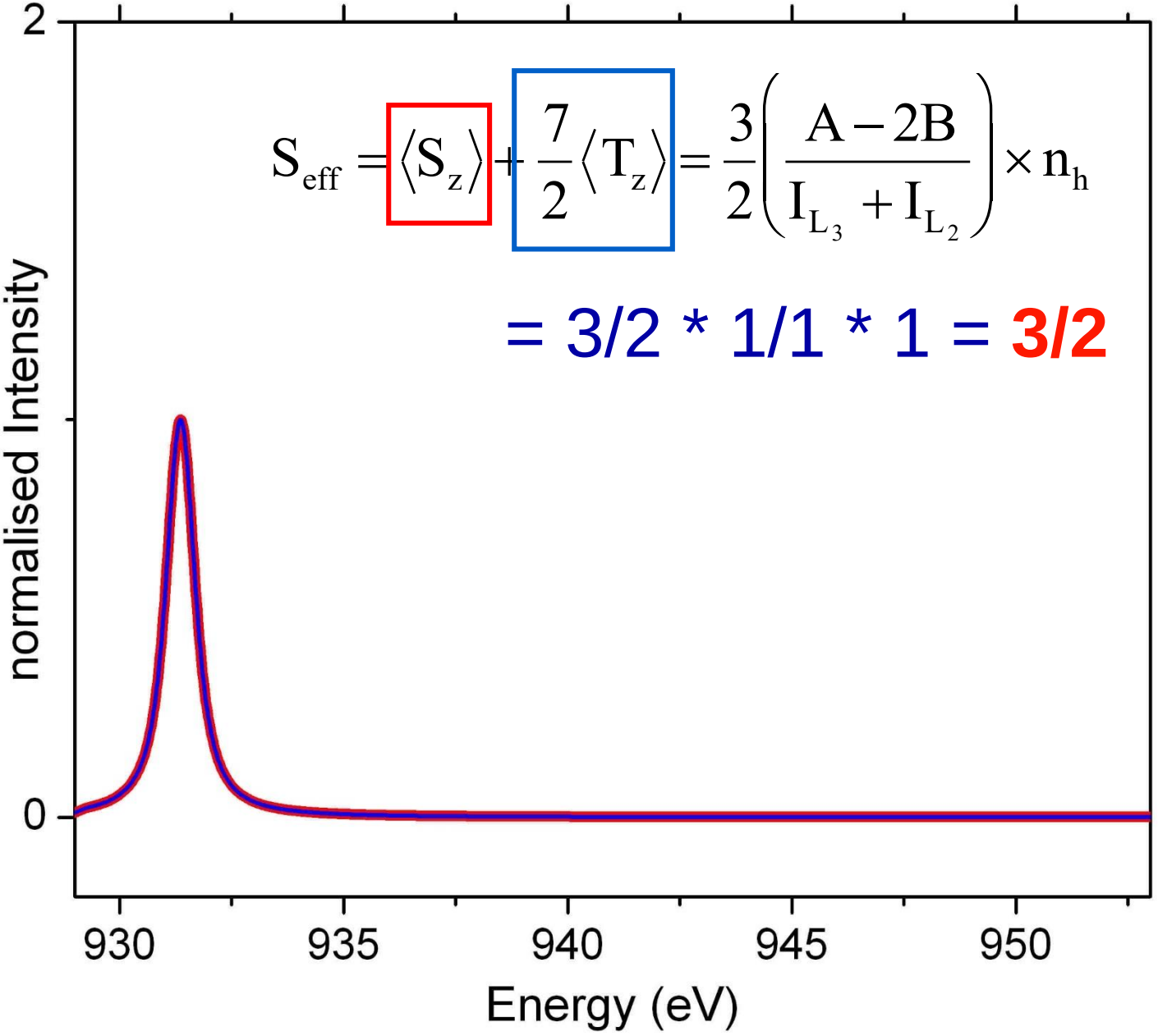
Effective spin sum rule for a $3d^9$ system



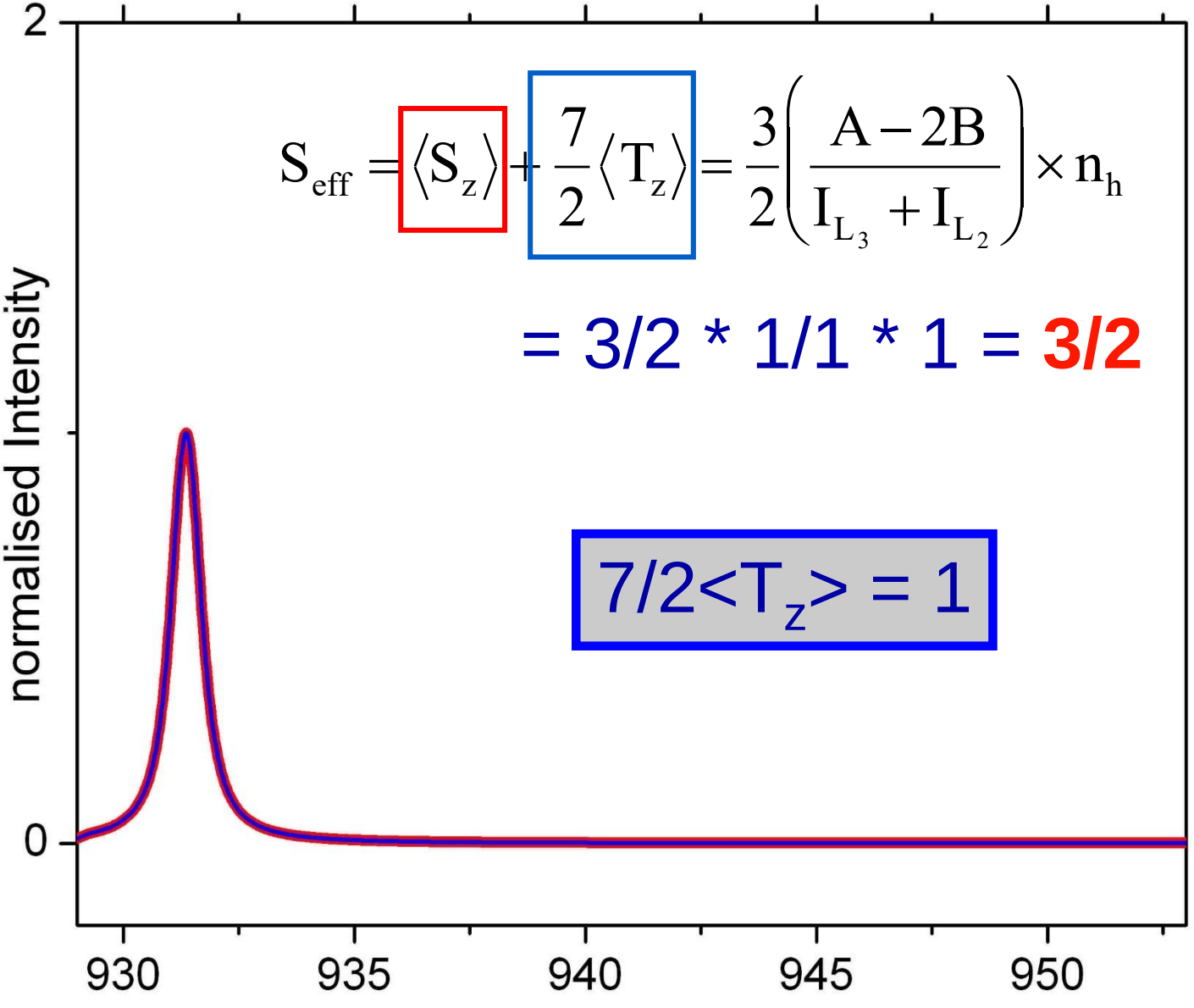
Effective spin sum rule for a $3d^9$ system



Effective spin sum rule for a $3d^9$ system



Effective spin sum rule for a $3d^9$ system



Phys. Rev. B. 80, 184410 (2009)