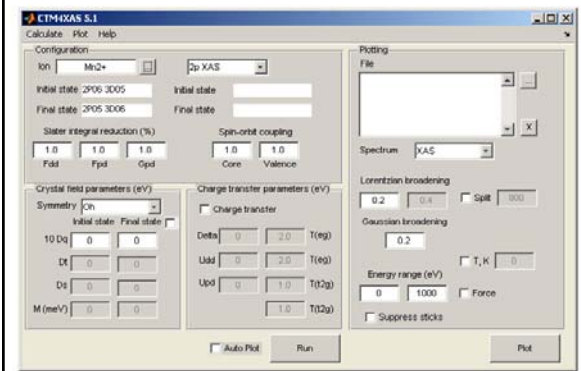## The CTM4XAS program

CTM4XAS 5.1

CHARGE TRANSFER MULTIPLET CALCULATIONS
FOR X-RAY ABSORPTION SPECTROSCOPY

© Eli Stavitski and Frank de Groot, 2008–2010
Synchrotron and Theoretical Spectroscopy, Utrecht University/ National Synchrotron Light Source

The CTM4XAS program (5.1)

CTM4XAS version 5.2

X-ray Absorption Spectroscopy

Excitations of
core electrons
to empty states

The XAS spectrum
is given by the
Fermi Golden Rule
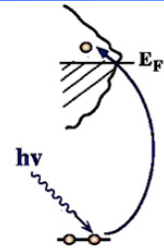
$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \left| \hat{e} \cdot r \right| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray Absorption Spectroscopy

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

X-ray Absorption Spectroscopy

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

Electronic Structure; TiO$_2$

Electronic Structure: TiO$_2$

X-ray absorption: core hole effect

TiSi$_2$

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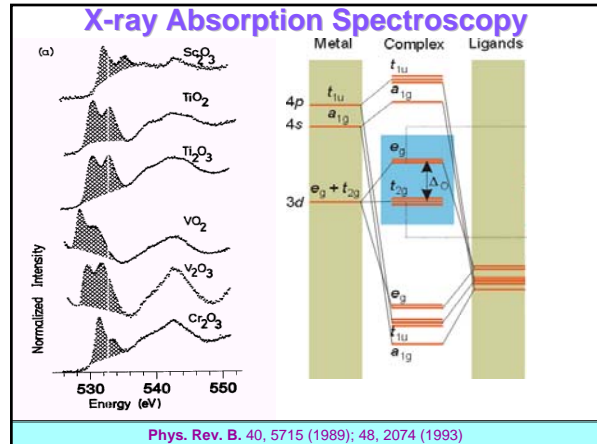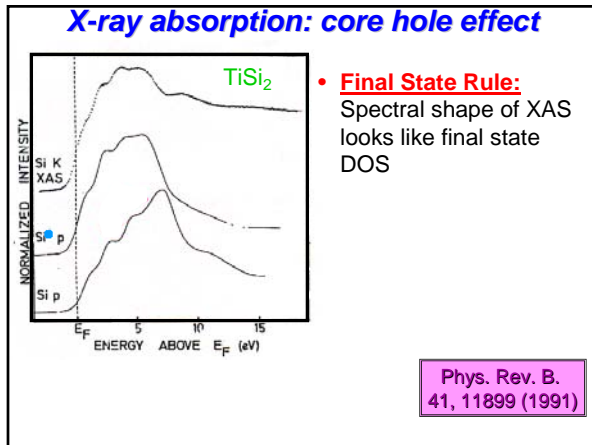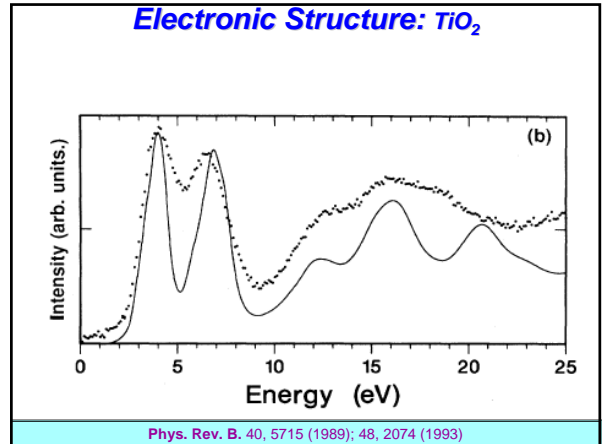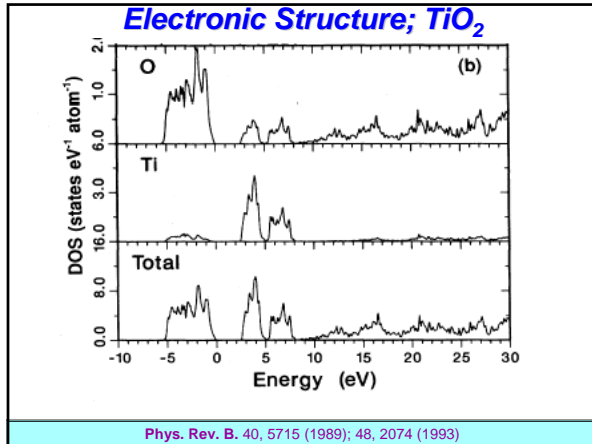
X-ray absorption

Fermi Golden Rule:
$I_{XAS} = |<\Phi_f|dipole|\Phi_i>|^2 \, \delta_{[\Delta E=0]}$

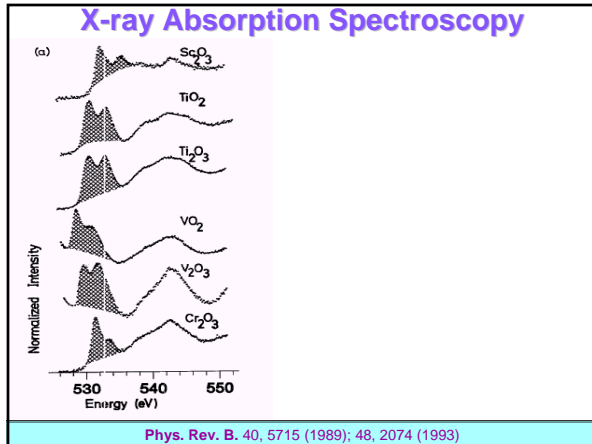$$\left| \left\langle \Phi_f \left| \hat{e}_q \cdot r \right| \Phi_i \right\rangle \right|^2 = \left| \left\langle \Phi_i \underline{c}\varepsilon \left| \hat{e}_q \cdot r \right| \Phi_i \right\rangle \right|^2$$

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

Single electron (excitation) approximation:
$I_{XAS} = |<\Phi_{empty}|dipole|\Phi_{core}>|^2 \, \rho$

Multiplet Effects in XAS

Overlap of core and valence wave functions

3d

$\rightarrow$ Single Particle model breaks down

$<2p3d|1/r|2p3d>$

2p$_{3/2}$

2p$_{1/2}$

MnO

XAS: multiplet effects

$2p^5 3d^{n+1}$ — Single Particle:
1s edges
(DFT + core hole (+U))

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

Multiplets:
2p, 3s, 3p edges
(CTM4XAS)

$2p^6 3d^n$
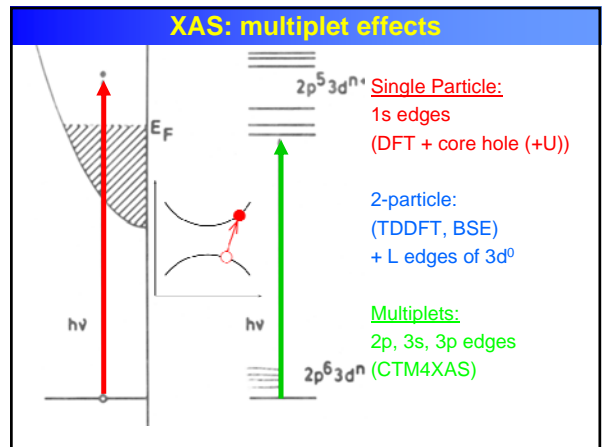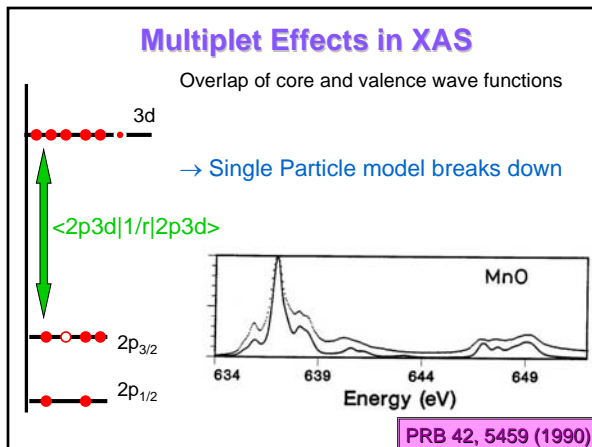
K edge (1s) XAS

Excitation of core electrons to empty states.

Spectrum identifies with the
(final state) empty Density of States

Calculate with DFT
(LDA+U, TDDFT, BSE)

+ add core hole potential
+ add U for strongly correlated systems

L edge (2p) XAS

Excitation of core electrons to empty states.

Empty Density of States

+ add core hole potential
+ add U for strongly correlated systems
+ add core hole spin-orbit coupling
+ add core-valence correlations
(a.k.a. multiplet effects)

Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

ATOMIC PHYSICS
⇓
GROUP THEORY
⇓
MODEL HAMILTONIANS

Atomic Multiplet Theory

$$H\Psi = E\Psi$$
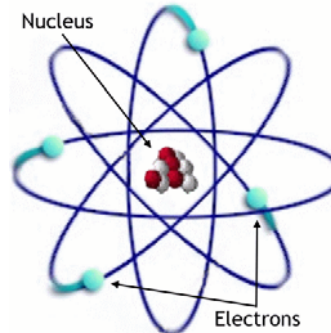
Atomic Multiplet Theory

$$H\Psi = E\Psi$$

$$H = \sum_N \frac{p_i^2}{2m}$$

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

Atomic Multiplet Theory

$$H\Psi = E\Psi$$

$$H = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i}$$

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

Atomic Multiplet Theory

$$H\Psi = E\Psi$$

$$H = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}}$$

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

Nucleus

Electrons

Atomic Multiplet Theory

$$H\Psi = E\Psi$$

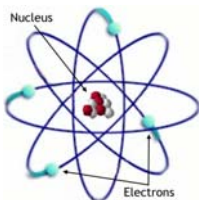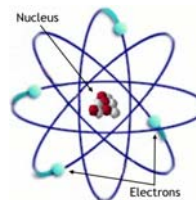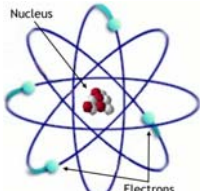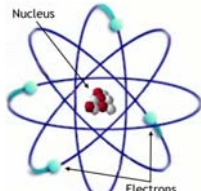$$H = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

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

Nucleus

Electrons

Atomic Multiplet Theory

$$H\Psi = E\Psi$$

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

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

Nucleus

Electrons

Atomic Multiplet Theory

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

$$H_{ee}^{'} = H_{ee} - \left\langle H_{ee} \right\rangle = \sum_{pairs} \frac{e^2}{r_{ij}} - \left\langle \sum_{pairs} \frac{e^2}{r_{ij}} \right\rangle$$

Atomic Multiplet Theory

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

Electron-electron interactions of Valence States

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

Valence Spin-orbit coupling

CTM4XAS version 5.2

4

Atomic Multiplet Theory

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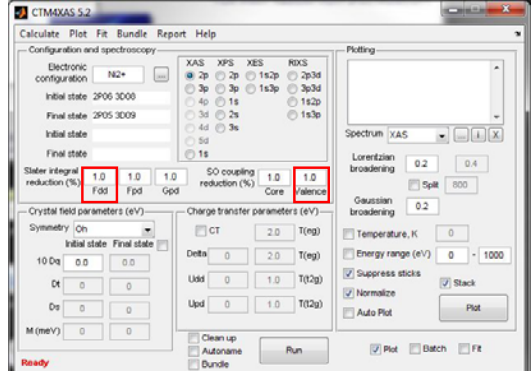
Core Valence Overlap

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

Core Spin-orbit coupling

CTM4XAS version 5.2
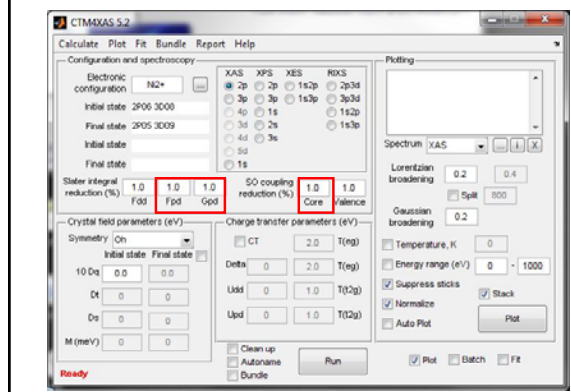
Multiplet Effects (Ni²⁺)

1s	2s	2p	3s	3p
0.07	**5**	**8**	**13**	**17**
	Core Valence Overlap			
0	**0**	**17**	**0**	**2**
	Core Spin-orbit coupling			

Quantum numbers

- Main   n   1,2,3,….
- Azimuthal   L   (orbital moment)
- Spin   S
- Magnetic m_L (orbital magnetic moment)
- Spin magnetic m_S (spin magnetic moment)
- Total moment   J
- Total magnetic m_J

Term Symbols ²ˢ⁺¹L_J

- **Term symbols of a 1s electron**
- S=1/2, L=0, J=1/2   → ${}^2S_{1/2}$ [(2S+1)(2L+1)=2]

- **Term symbols of a 2p electron**
- S=1/2, L=1, J=1/2 or J=3/2   → ${}^2P_{1/2}$ or ${}^2P_{3/2}$

      [Σ(2J+1)=2+4=6]

- **Term symbols of a 3d electron**
- S=1/2, L=2, J=3/2 or J=5/2   → ${}^2D_{3/2}$ or ${}^2D_{5/2}$

      [Σ(2J+1)=4+6=10]

Term Symbols

2p3p-configuration

Term symbols 2p: ${}^2P_{1/2}$ and ${}^2P_{3/2}$

Term symbols 3p: ${}^2P_{1/2}$ and ${}^2P_{3/2}$

Term symbols 2p3p: multiply L and S separately

L_{2p}=1, L_{3p}=1 L_{TOT} = 0, 1 or 2

S_{2p}=1/2, S_{3p}=1/2 S_{TOT} = 0 or 1

all combinations are possible:

      ${}^1S,{}^1P,{}^1D$ and ${}^3S,{}^3P,{}^3D$

Term Symbols

2p3p-configuration

all combinations are possible:

$^1S, ^1P, ^1D$ and $^3S, ^3P, ^3D$

In short: $^2P \otimes ^2P = ^{1,3}S,P,D$

Add J-quantum numbers:

$^1S_0, ^1P_1, ^1D_2 + ^3S_1$

$+ ^3P_0, ^3P_1, ^3P_2$

$+ ^3D_1, ^3D_2, ^3D_3,$

Term Symbols

• **Term symbols of a $2p^1 3d^1$ configuration**

• $2p^1 \rightarrow \quad ^2P_{1/2}, ^2P_{3/2}$ (S=1/2, L=1, J=1/2,3/2)

• $3d^1 \rightarrow \quad ^2D_{3/2}, ^2D_{5/2}$ (S=1/2, L=2, J=3/2,5/2)

• $2p^1 3d^1 \qquad \rightarrow S_{TOT} = 0$ or 1

$\rightarrow L_{TOT} = 1$ or 2 or 3

$\rightarrow ^1P_1 + ^3P_0, ^3P_1, ^3P_2$

$\rightarrow ^1D_2 + ^3D_1, ^3D_2, ^3D_3$

$\rightarrow ^1F_3 + ^3F_2, ^3F_3, ^3F_4$

[$\Sigma(2J+1)=3+1+3+5+5+3+5+7+7+5+7+9=60$]

Term Symbols

• **Term symbols of a $2p^2$ configuration**

Configurations of $2p^2$
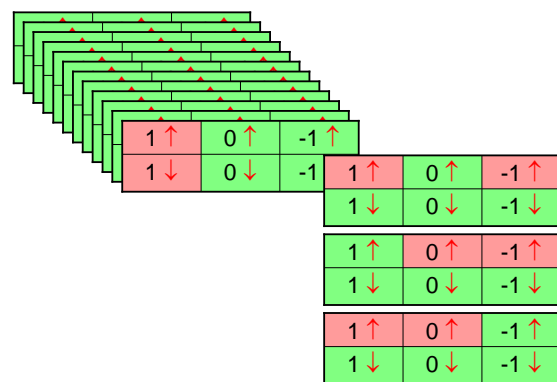
2p XAS of TiO₂

• Ground state is $3d^0$

• Dipole transition $3d^0 \rightarrow 2p^5 3d^1$

• Ground state symmetry: $^1S_0$

• Final state symmetry: $^2P \otimes ^2D$ gives

• $^1P, ^1D, ^1F,$ and $^3P, ^3D, ^3F$

Term Symbols of $2p^2$

	$M_S=1$	$M_S=0$	$M_S=-1$
$M_L=2$	0	1	0
$M_L=1$	1	2	1
$M_L=0$	1	3	1
$M_L=-1$	1	2	1
$M_L=-2$	0	1	0

LS term symbols: $^1S, ^1D, ^3P$

LSJ term symbols:

$^1S_0 \quad ^1D_2 \quad ^3P_0 \quad ^3P_1 \quad ^3P_2$

2p XAS of TiO$_2$

- Final state symmetries:

  ^1P, ^1D, ^1F, and ^3P, ^3D, ^3F

- Transition $<^1S_0|\Delta J=+1|$ $^1P_1$, $^3P_1$, $^3D_1>$

- 3 peaks in the spectrum

Calculate the 2p XAS spectrum of a Ti atom
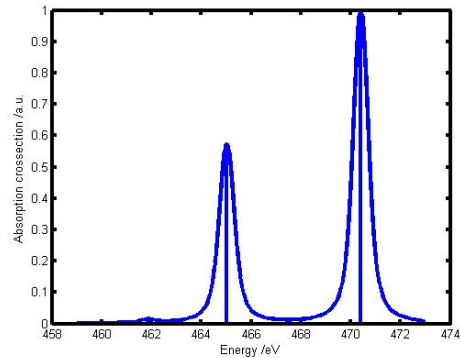
Hunds rules

- 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

3d^1 has $^2D_{3/2}$ ground state   3d^2 has $^3F_2$ ground state
3d^9 has $^2D_{5/2}$ ground state   3d^8 has $^3F_4$ ground state

Give the Hund's rule ground states for 3d^1 to 3d^9

Term Symbols and XAS

Ni^{II} ion in NiO:
Ground state: 3d^8
Final state: 2p^{5}3d^9
Dipole transition: p-symmetry

3d^8-configuration: ^1S, ^1D, ^3P,^1G, ^3F j=4
2p^{5}3d^9-configuration: $^2P\otimes^2D = ^{1,3}$PDF   j'=0,1,2,3,4
p-transition: ^1P Δj=+1,0,-1

ground state symmetry: ^3F $^3F_4$
transition: $^3F \otimes^1P = ^3$DFG
two possible final states: ^3D, ^3F $^3D_3,^3F_3,^3F_4, ^1F_3$

3d^8 XAS calculation

+LS$_{2p}$

+LS$_{3d}$: > $^3F_4$

O

+F^K, G^K: > ^3F
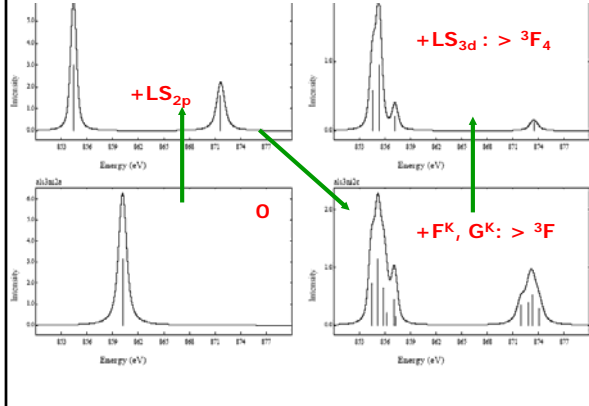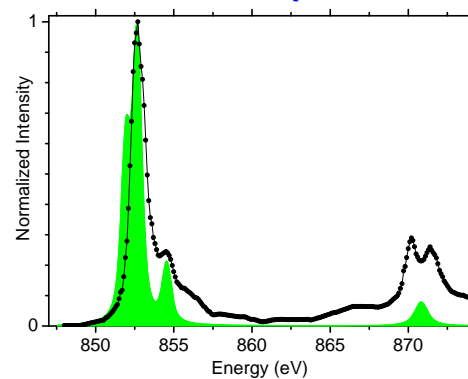
Atomic multiplets

Charge Transfer Multiplet program

EXERCISES

ATOMIC PHYSICS
⇓
GROUP THEORY
⇓
MODEL HAMILTONIANS

The CTM4XAS program
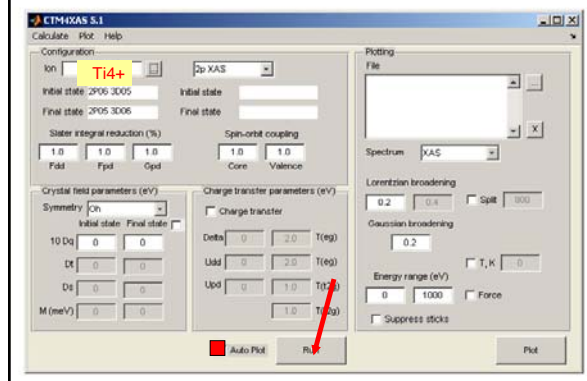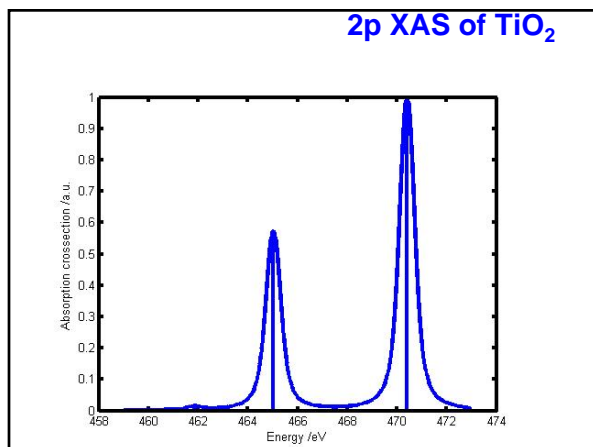
2p XAS of TiO$_2$

2p XAS of TiO$_2$

- Final state symmetries:
  ^1P, ^1D, ^1F, and ^3P, ^3D, ^3F
- Transition $<^1S_0|\Delta J=+1|$ $^1P_1$, $^3P_1$, $^3D_1>$
- 3 peaks in the spectrum

The CTM4XAS program
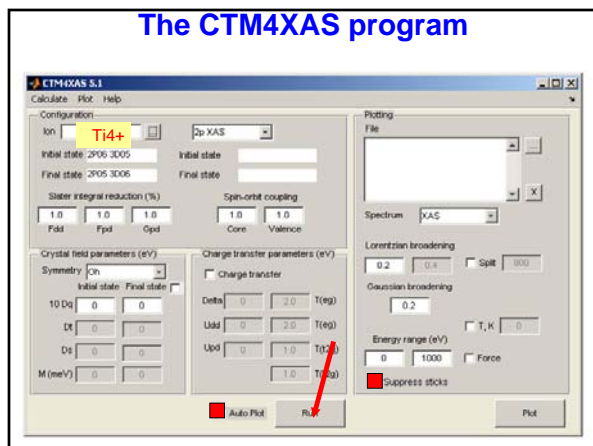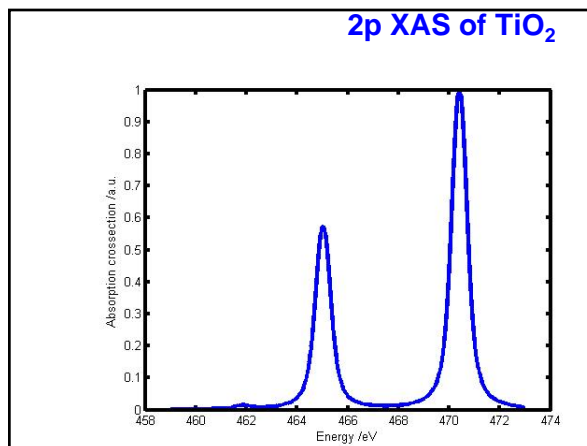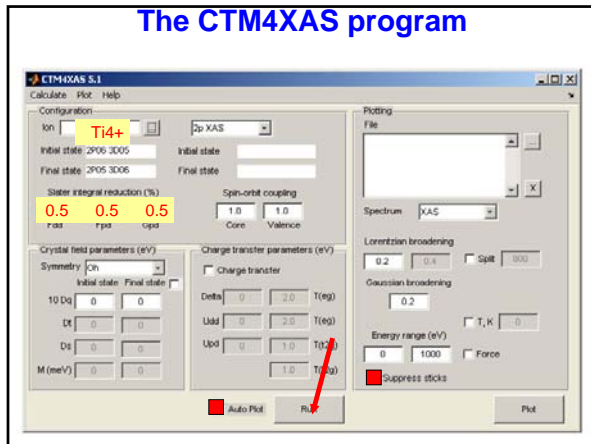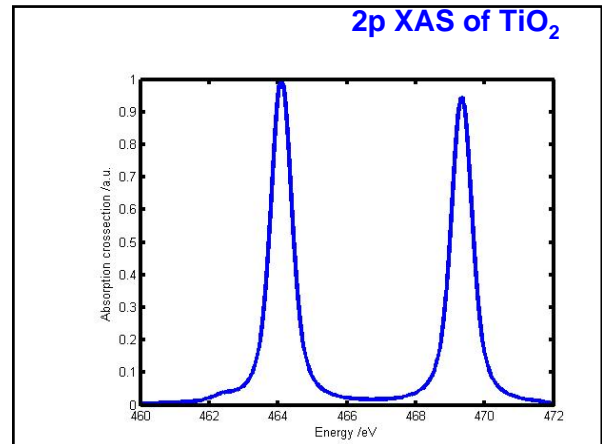
2p XAS of TiO$_2$

The CTM4XAS program

2p XAS of TiO$_2$

The CTM4XAS program

3d^0 XAS calculation

The CTM4XAS program

3d^0 XAS calculation

The CTM4XAS program

3d⁰ XAS calculation

$3d^0$ XAS calculation

0

+F^K, G^K

+LS$_{2p}$

+F^K, G^K
+LS$_{2p}$
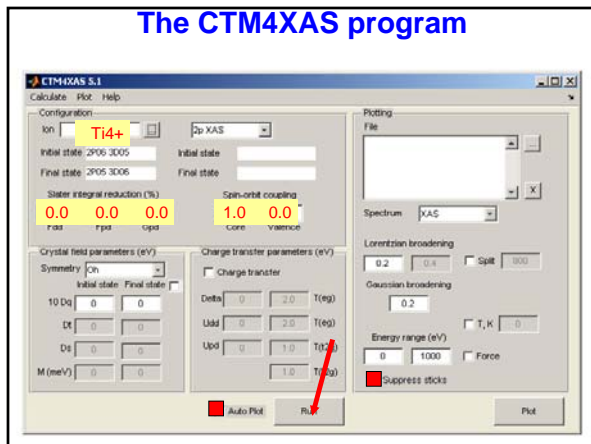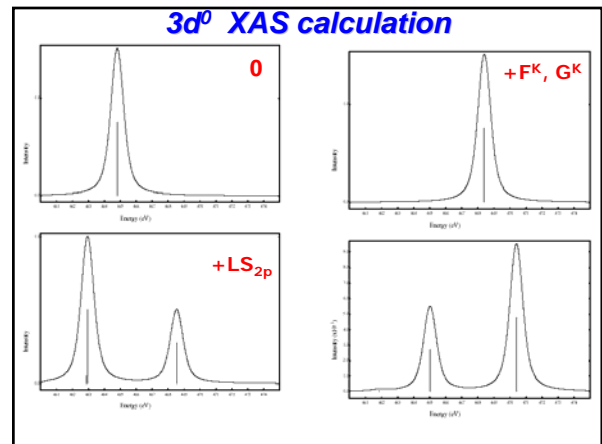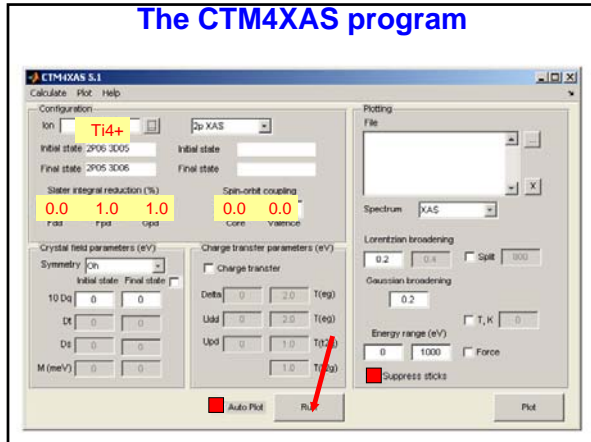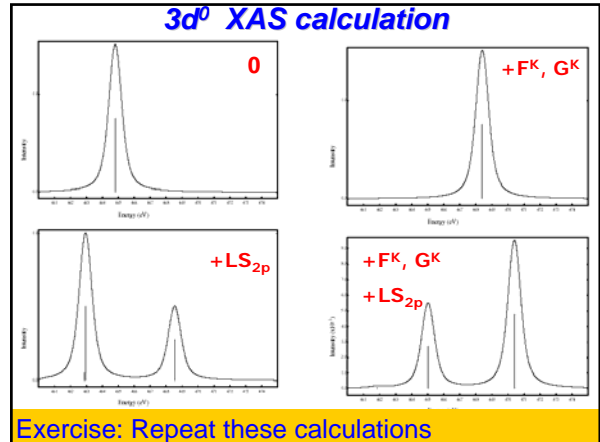
Exercise: Repeat these calculations

Exercise: Calculate the 2p XAS spectrum of Fe

Fe atom:
Ground state:
$3d^6$ ($4s^2$) ^5D j=4
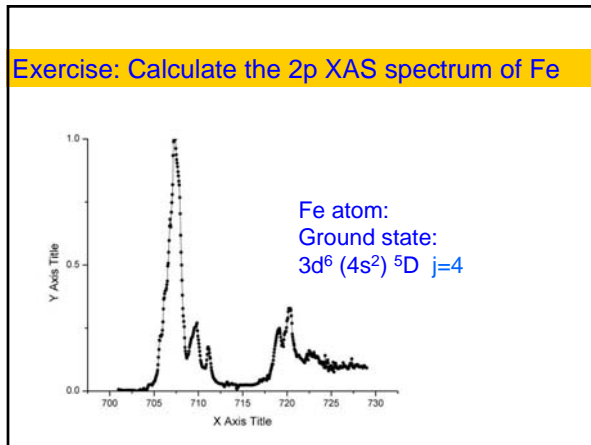
Term Symbols and XAS

Fe atom:
Ground state: $3d^6$ ($4s^2$)
Final state: $2p^5 3d^7$
Dipole transition: p-symmetry

$3d^6$-configuration: ^5D, etc.   j=4
$2p^5 3d^7$-configuration: 110 states   j'= 3,4, 5
p-transition: ^1P Δj=+1,0,-1

ground state symmetry: ^5D $^5D_4$
transition: $^5D \otimes {}^1P = {}^5PDF$
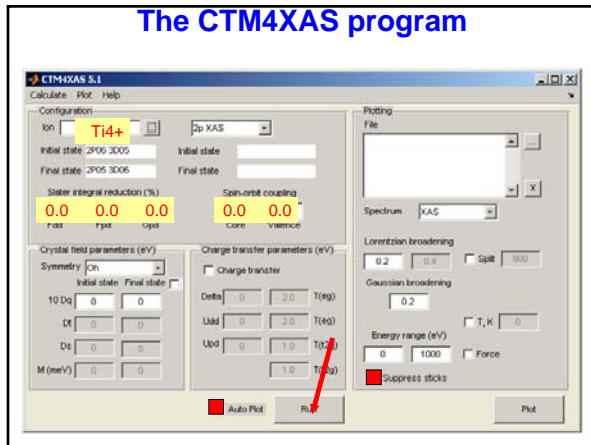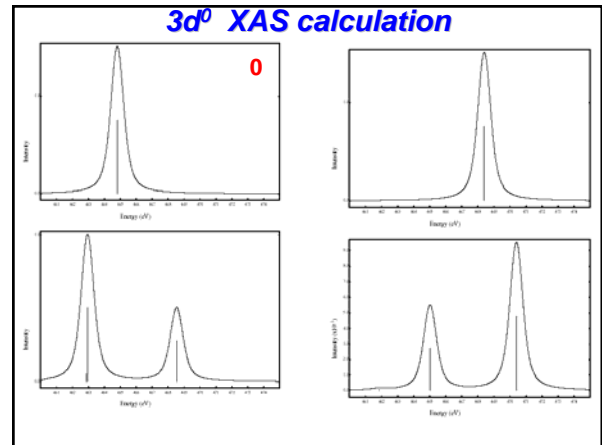possible final states: 68 states

Term Symbols and XAS

Fe atom:
Ground state: $3d^6$ ($4s^2$) ^5D j=4

$^5D_0$

^5D

$^5D_4$
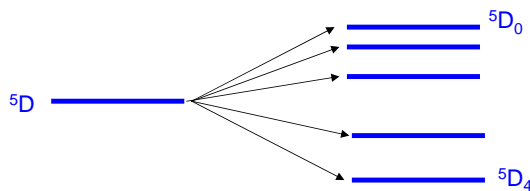
ora outputfile

```
H   H  AAA  M   M IIIII L      TTTTT  OOO  N   N IIIII  AAA  N   N
H   H A  A  MM MM  I    L        T   O   O NN  N   I   A   A NN  N
HHHHH AAAAA M M M  I    L        T   O   O N N N   I   AAAAA N N N
H   H A   A M   M  I    L        T   O   O N  NN   I   A   A N  NN
H   H A   A M   M IIIII LLLLL    T    OOO  N   N IIIII A   A N   N

CALCULATIONS for ACTOR:HAMILTONIAN     GROUND

     CALCULATING MATRIX for TRIAD  1  (  0+   0+   0+ )  (56*56)




    ---- EIGENVALUES ----

             1        2        3        4        5        6
  7        8        9       10       11       12
   KET/PURE    6 1.00    44 1.00   23 1.00   38 1.00   15 1.00   34 1.00
 1 1.00   13 1.00   55 1.00   32 1.00   30 0.99   51 0.99
    EIGVAL  -3.44286  -3.44286  -3.44286  -3.38906  -3.35125  -3.32693  -
 3.31500  -1.21676  -1.21676  -1.21676  -1.18897  -1.18897
```

10

Exercise: Calculate the 3d XAS spectrum of Tm

Tm metal:
Ground state: $4f^{12}$

Tm XAS

1460   1480   1500

Charge Transfer Multiplet program

ATOMIC PHYSICS
$\Downarrow$
GROUP THEORY
$\Downarrow$
MODEL HAMILTONIANS

Crystal Field Effects

e_g states

$d_{x^2-y^2}$ d_{z^2}

t_{2g} states

d_{xy} d_{xz} d_{yz}
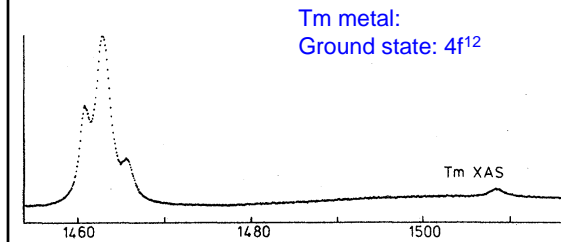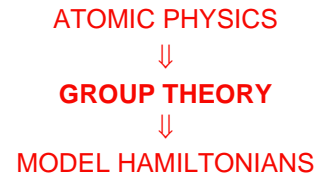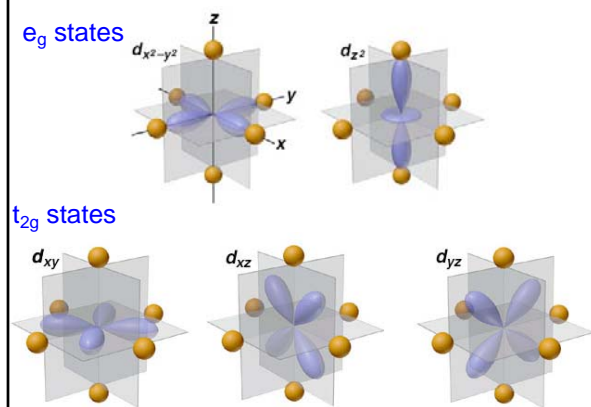
Octahedral crystal field splitting

metal ion in free space	in symmetrical field	in octahedral ligand field
		e_g
		x^2-y^2 z^2
		t_{2g}
x^2-y^2 yz z^2 xz xy		yz xz xy

Crystal Field Effects in CTM

0   7 = 2.13 eV

constant broadening 0.0   constant broadening 2.1
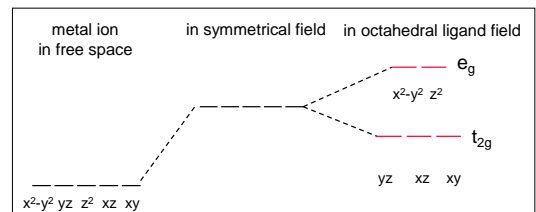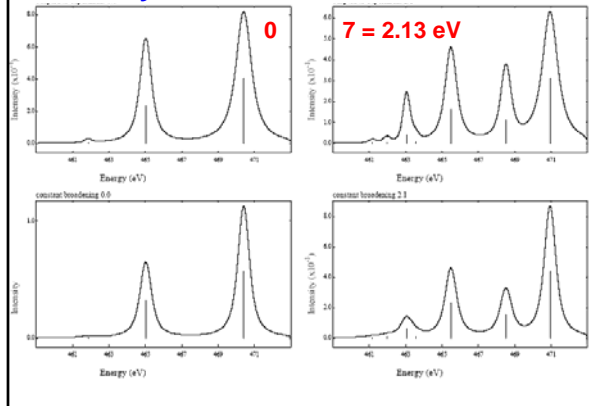
Crystal Field Effects

SO$_3$			O$_h$ (Mulliken)
S	0		A_1
P	1		T_1
D	2		$E + T_2$
F	3		$A_2 + T_1 + T_2$
G	4		$A_1 + E + T_1 + T_2$

2p XAS of TiO$_2$ (atomic multiplets)

Ti^{IV} ion in TiO$_2$:

3d^0-configuration:	^{1}S,		j=0
2p^{1}3d^9-configuration:	^{2}P$\otimes^2$D = ^{1,3}PDF		j'=0,1,2,3,4
p-transition:	^{1}P		Δj=+1,0,-1

Write out all term symbols:

$$
\begin{array}{ccc}
& \mathbf{^1P_1} & ^1D_2 \quad ^1F_3 \\
^3P_0 & ^3P_1 & ^3P_2 \\
& ^3D_1 & ^3D_2 \quad ^3D_3 \\
& & ^3F_2 \quad ^3F_3 \quad ^3F_4
\end{array}
$$

1   3   4   3   1

Crystal Field Effect on XAS

J in SO$_3$	Deg.			
0	1			
1	3			
2	4			
3	3			
4	1			
Σ	12			

<^{1}S$_0$|dipole|^{1}P$_1$> goes to <A$_1$|T$_1$|T$_1$>

Crystal Field Effect on XAS

J in SO$_3$	Deg.	Branchings		
0	1	A$_1$		
1	3	3×T$_1$		
2	4	4×E, 4×T$_2$		
3	3	3×A$_2$, 3×T$_1$, 3×T$_2$		
4	1	A$_1$, E, T$_1$, T$_2$		
Σ	12			

<^{1}S$_0$|dipole|^{1}P$_1$> goes to <A$_1$|T$_1$|T$_1$>

Crystal Field Effect on XAS

J in SO$_3$	Deg.	Branchings	Γ in O$_h$	Deg.
0	1	A$_1$	A$_1$	2
1	3	3×T$_1$	A$_2$	3
2	4	4×E, 4×T$_2$	T$_1$	7
3	3	3×A$_2$, 3×T$_1$, 3×T$_2$	T$_2$	8
4	1	A$_1$, E, T$_1$, T$_2$	E	5
Σ	12			25

<^{1}S$_0$|dipole|^{1}P$_1$> goes to <A$_1$|T$_1$|T$_1$>

Effect of 10Dq on XAS:3d^0
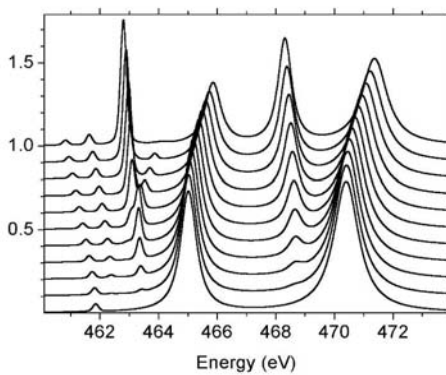
Comparison with Experiment
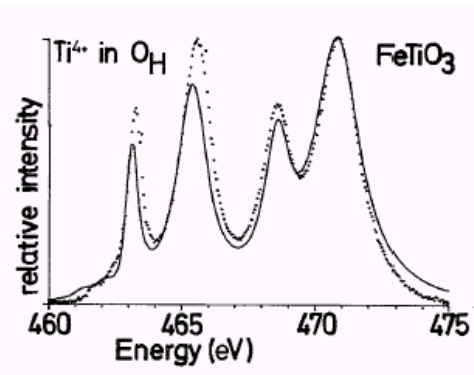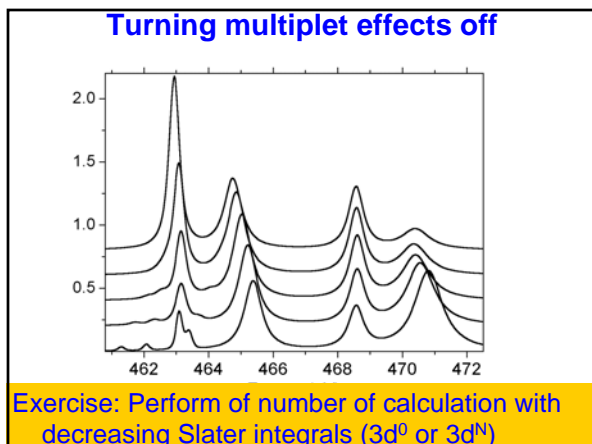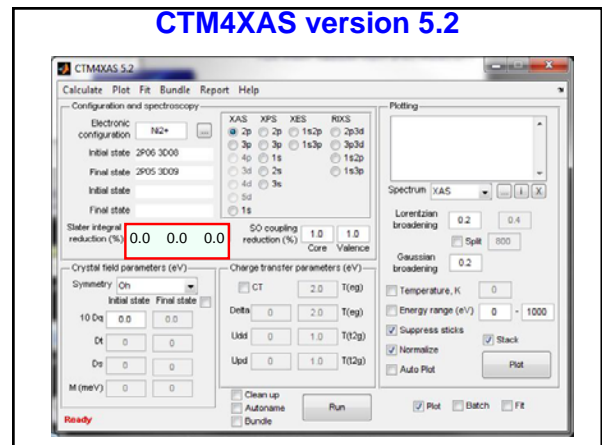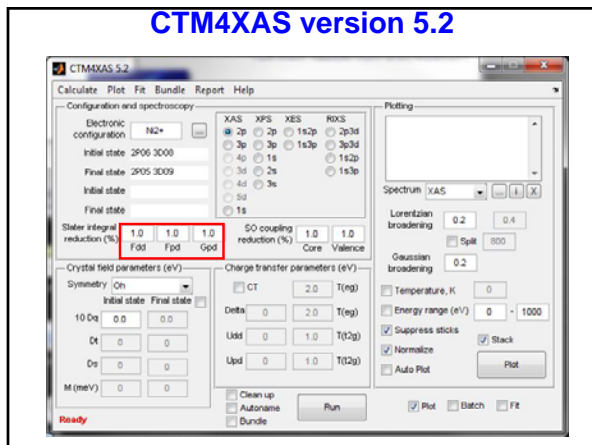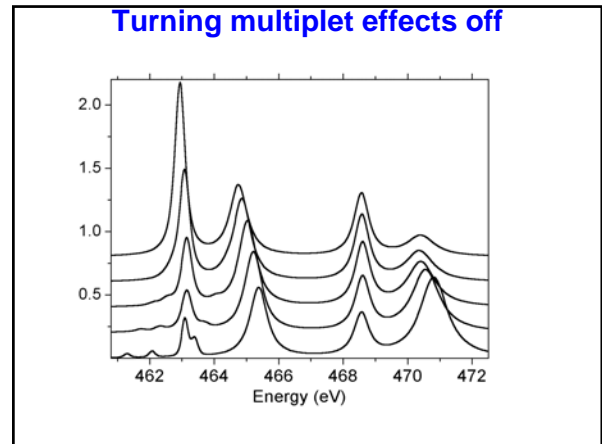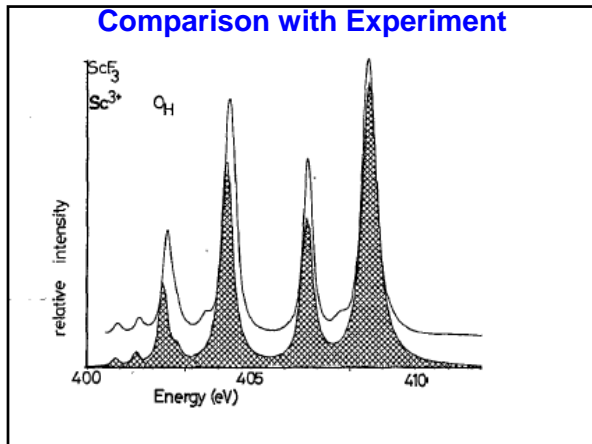
Comparison with Experiment

Turning multiplet effects off

CTM4XAS version 5.2

CTM4XAS version 5.2

Turning multiplet effects off

Exercise: Perform of number of calculation with decreasing Slater integrals ($3d^0$ or $3d^N$)

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

$3d^1$ has $^2D_{3/2}$ ground state $3d^2$ has $^3F_2$ ground state
$3d^9$ has $^2D_{5/2}$ ground state $3d^8$ has $^3F_4$ ground state

Crystal Field Effects on $3d^8$ states

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {}^1T_2$	
^3F	-1.8 eV	$^3A_2 + {}^3T_1 + {}^3T_2$	
^1G	0.8 eV	$^1A_1 + {}^1T_1 + {}^1T_2 + {}^1E$	

Crystal Field Effects

SO_3		O_h (Butler)	O_h (Mulliken)
S	0	0	A_1
P	1	1	T_1
D	2	$2 + {}^\wedge 1$	$E + T_2$
F	3	$^\wedge 0 + 1 + {}^\wedge 1$	$A_2 + T_1 + T_2$
G	4	$0 + 1 + 2 + {}^\wedge 1$	$A_1 + E + T_1 + T_2$

Crystal Field Effects on $3d^8$ states

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	$A_1 \otimes A_1 = A_1$
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {}^1T_2$	
^3F	-1.8 eV	$^3A_2 + {}^3T_1 + {}^3T_2$	$T_1 \otimes T_2 = T_1 + T_2 + E + A_2$
^1G	0.8 eV	$^1A_1 + {}^1T_1 + {}^1T_2 + {}^1E$	

The multiplication table of O_h symmetry

O	A_1	A_2	T_1	T_2	E
A_1	A_1	A_2	T_1	T_2	E
A_2	A_2	A_1	T_2	T_1	E
T_1	T_1	T_2	$T_1 + T_2 + E + A_1$	$T_1 + T_2 + E + A_2$	$T_1 + T_2$
T_2	T_2	T_1	$T_1 + T_2 + E + A_2$	$T_1 + T_2 + E + A_1$	$T_1 + T_2$
E	E	E	$T_1 + T_2$	$T_1 + T_2$	$A_1 + A_2 + E$

Crystal Field Effects on $3d^8$ states

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	$^{A1}A_1 = A_1$
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {}^1T_2$	
^3F	-1.8 eV	$^3A_2 + {}^3T_1 + {}^3T_2$	$(T_2) + (A_1 + E_1 + T_1 + T_2) + (A_2 + E + T_1 + T_2)$
^1G	0.8 eV	$^1A_1 + {}^1T_1 + {}^1T_2 + {}^1E$	

Crystal Field Effects: Tanabe-Sugano

Effect of 10Dq on XAS:3d^N

High-spin or Low-spin

10Dq > 3J
(d^4 and d^5)

10Dq > 2J
(d^6 and d^7)

2p XAS of Mn2+
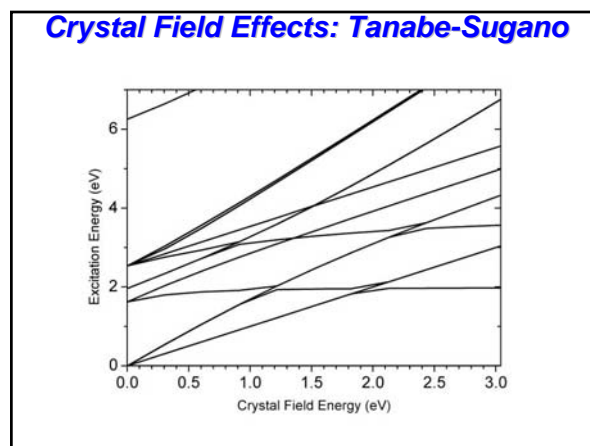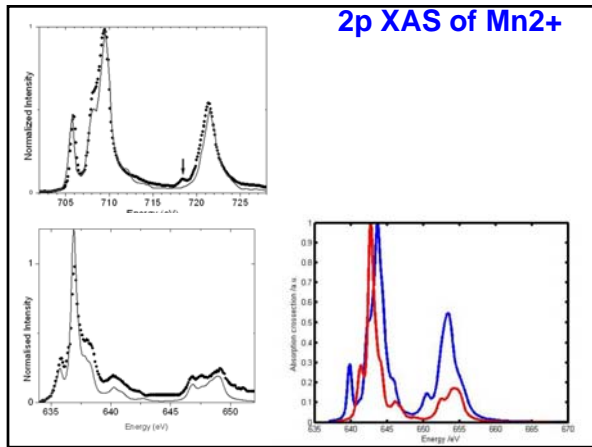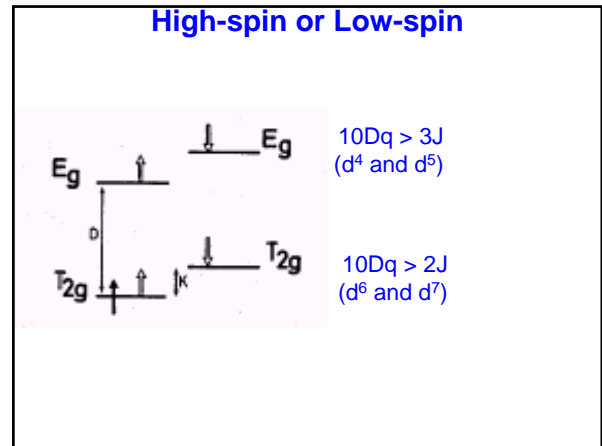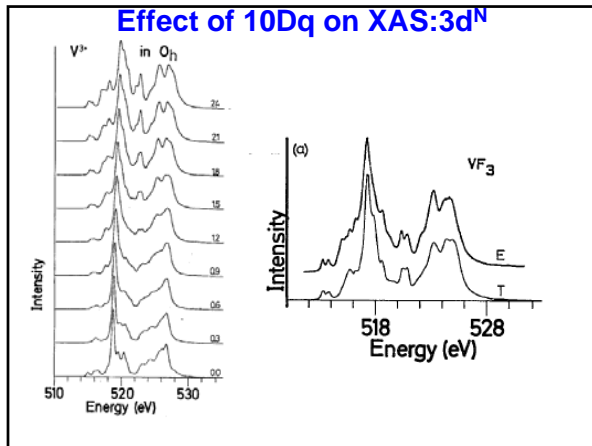
Exercise: Calculate the 2p XAS spectra of FePO4 and LiFePO4

Conf.	SO3	Oh	Spin in Oh	Deg.	Overall Symmetry in Oh
3d^0	$^1S_0$	$^1A_1$	A_1	1	A_1
3d^1	$^2D_{3/2}$	$^2T_2$	U_1	2	$U_2 + G$
3d^2	$^3F_2$	$^3T_1$	T_1	4	$E+T_1+T_2+A_1$
3d^3	$^4F_{3/2}$	$^4A2$	G	1	G
3d^4	$^5D_0$	^5E $3T_1$	$E + T_2$ T_1	5 4	$A_1+A_2+E+T_1+T_2$ $E+T_1+T_2+A_1$
3d^5	$^6S_{5/2}$	$^6A_1$ $2T_2$	$G+U_2$ U_1	2 2	$G+U_2$ $G+U_2$
3d^6	$^5D_2$	$^5T_2$ $1A_1$	$E+T_2$ A_1	6 1	$A_1+E+T_1+T_1+T_2+T_2$ A_1
3d^7	$^4F_{9/2}$	$^4T_1$ $2E$	G U_1	4 1	$U_1+U_2+G + G$ G
3d^8	$^3F_4$	$^3A_2$	T_1	1	T_2
3d^9	$^2D_{5/2}$	^2E	U_1	1	G

3d spin-orbit coupling

Exercise: Calculate the 2p XAS spectrum of CoO

15

3d spin-orbit coupling

RIXS of a 4 nm CoO nanoparticle

RIXS of a 4 nm CoO nanoparticle

Charge Transfer Effects

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

Charge fluctations

Charge Transfer Effects

$3d^N 3d^N \rightarrow 3d^{N-1} 3d^{N+1}$

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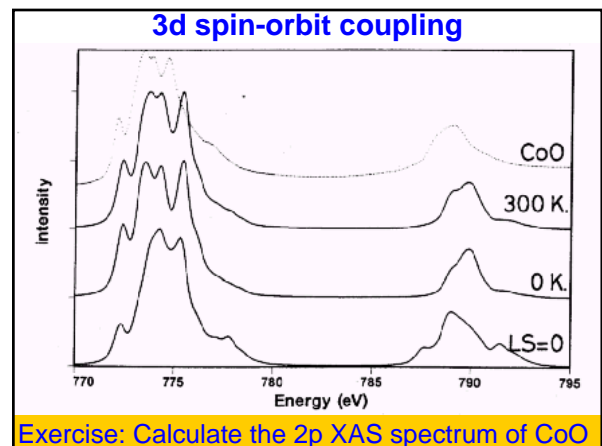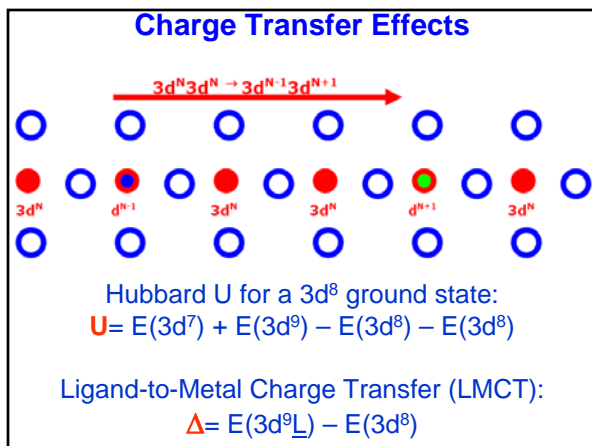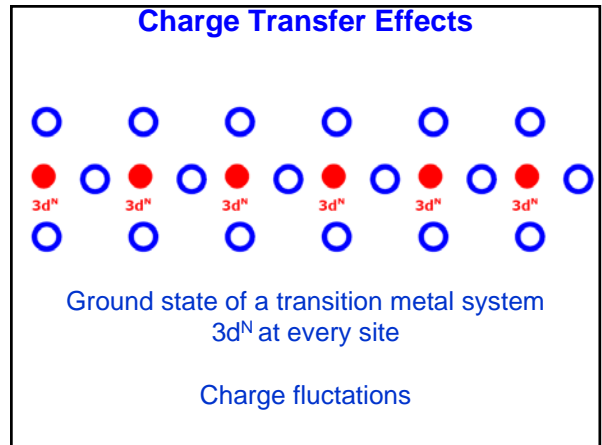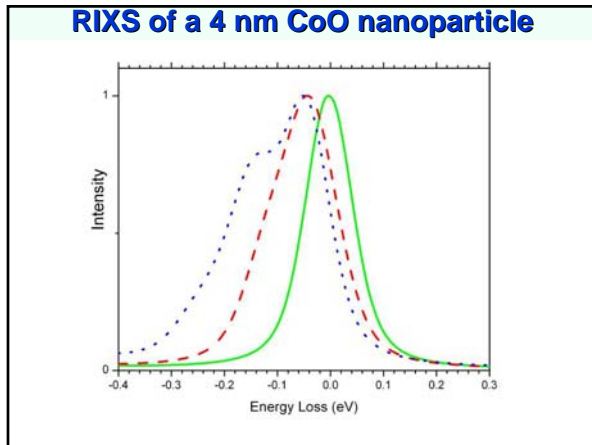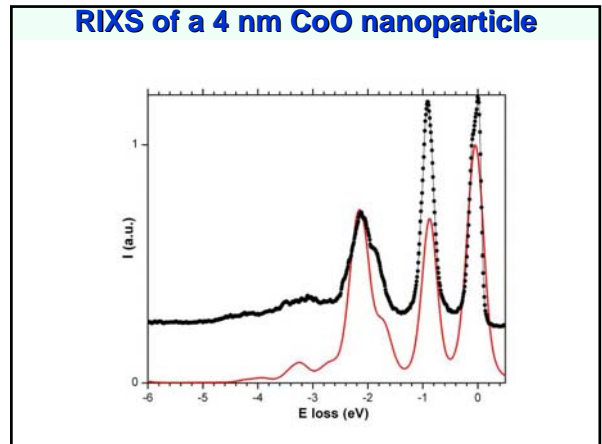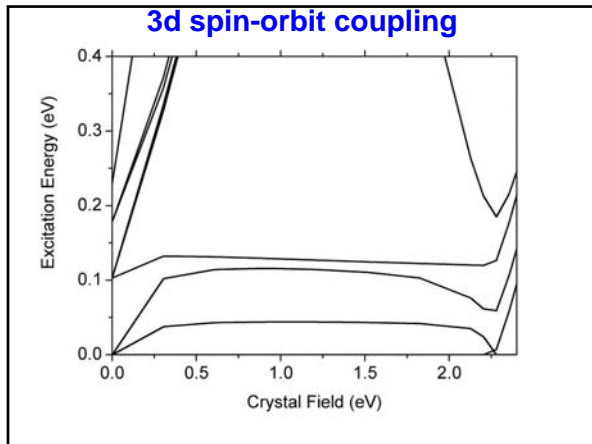
Charge Transfer Effects

$\Delta = E(3d^9\underline{L}) - E(3d^8)$
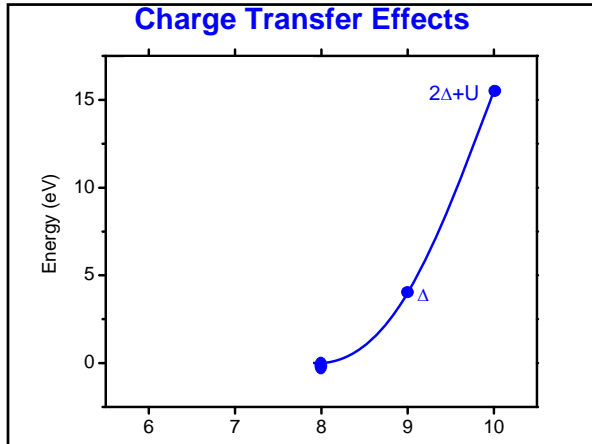
$E(3d^{10}\underline{LL}') - E(3d^8)$
Two times charge transfer:　　2Δ
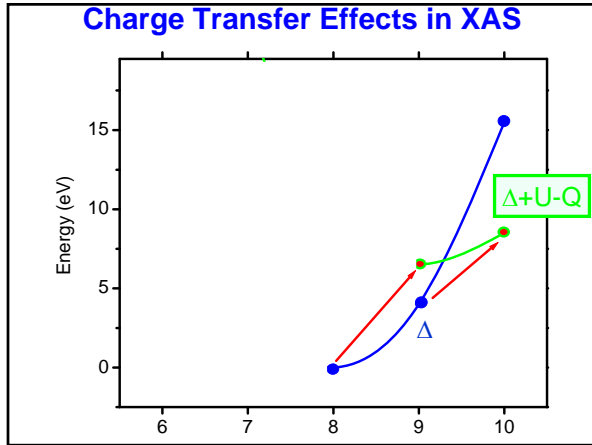Extra 3d3d interaction:　　　　U

$2\Delta + U$

Charge Transfer Effects

Energy (eV) vs axis (6–10)

$2\Delta+U$

Δ

Charge Transfer Effects in XAS

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

$E(3d^{10}\underline{L}\underline{L}') - E(3d^8) = 2\Delta + U$

2p XAS: $3d^8 \rightarrow 2p^5 3d^9$

$\qquad E(2p^53d^9) = E_{2p} + \Delta$

2p XAS: $3d^9\underline{L} \rightarrow 2p^5 3d^{10}\underline{L}$

$\qquad E(2p^53d^{10}\underline{L}) = E_{2p} - Q + 2\Delta + U$

Energy difference: $E_{2p} - Q + 2\Delta + U - E_{2p} - \Delta = \Delta + U - Q$

$Q \cong U + 2$ eV

Charge Transfer Effects in XAS

Energy (eV) vs axis (6–10)

$\Delta+U-Q$

Δ

Charge Transfer Effects

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

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

$3d^5$ —— → —— $2p^53d^6$

Charge Transfer Effects

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

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

$3d^6\underline{L}$ —— → —— $2p^53d^7\underline{L}$

Δ

$\Delta+U-Q \approx \Delta$

$3d^5$ —— → —— $2p^53d^6$

Charge Transfer Effects in XPS

Energy (eV) vs axis (6–10)

$\Delta-Q$

Δ

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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

XPS — $3d^6\underline{L}$ — XAS

Δ

$2p^53d^5$

$3d^5$

$2p^53d^7\underline{L}$

Ground State

$\Delta - Q$

$\Delta + U - Q \approx \Delta$

$2p^53d^6\underline{L}$

$2p^53d^6$
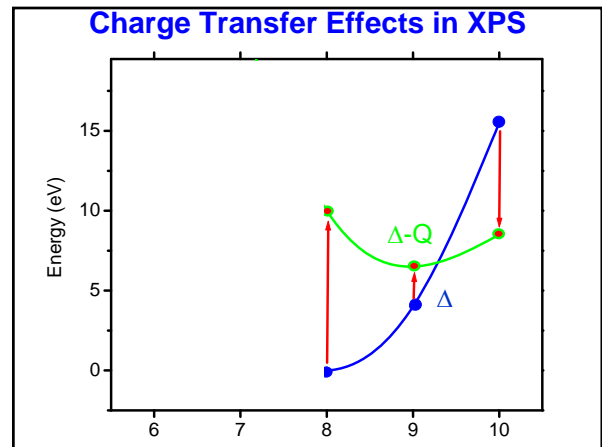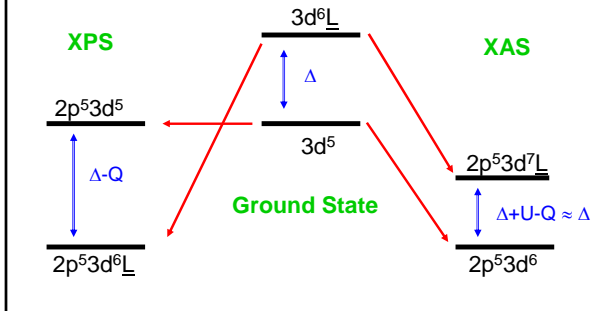
Charge Transfer Effects

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 Multiplets of Ni²⁺

$\Delta = 3$

$\Delta = 9$

$\Delta = 0$

$\Delta = 6$

Exercise: perform a series of charge transfer calculations changing Δ from +10 to -10.

X-ray Absorption Spectroscopy

NiO

Spectral shape:
(1) Multiplet effects
(2) Charge Transfer

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

Charge transfer

Ionic Conf.   Charge Transfer States

$3d^7$ $3d^8$ t=0   t=1   t=2

t=0.5

18

Charge transfer

$$2p^5 3d^{N+2}\underline{L} \qquad \boxed{\quad} \; 2p^5 3d^{N+2}\underline{L}$$

Δ

$$2p^5 3d^{N+1}[\Gamma_2]$$

$2p^5 3d^{N+1}$

δ

$$2p^5 3d^{N+1}[\Gamma_2] + 2p^5 3d^{N+2}\underline{L}$$

$$2p^5 3d^{N+1}[\Gamma_1]$$

$$2p^5 3d^{N+1}[\Gamma_1] + 2p^5 3d^{N+2}\underline{L}$$

Charge transfer

NiF$_2$, NiCl$_2$, NiBr$_2$, NiO

Charge Transfer effects

$3d^8$ + $3d^9\underline{L}$

$\Delta=10$
$\Delta=5$
$\Delta=0$
$\Delta=-5$
$\Delta=-10$

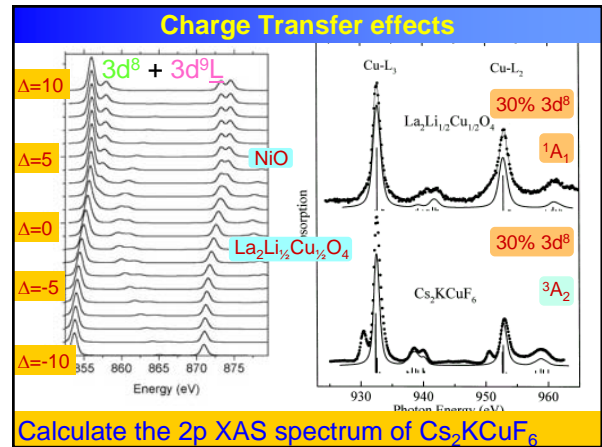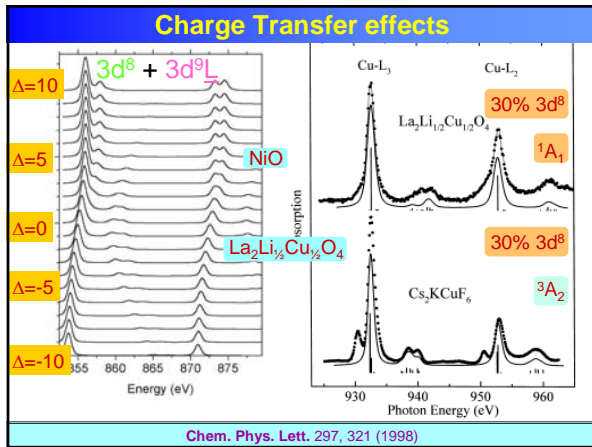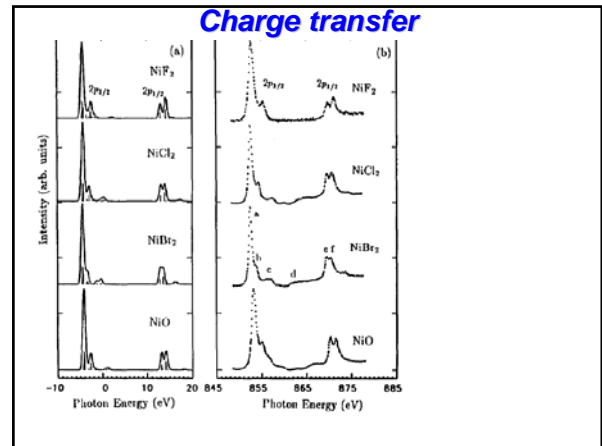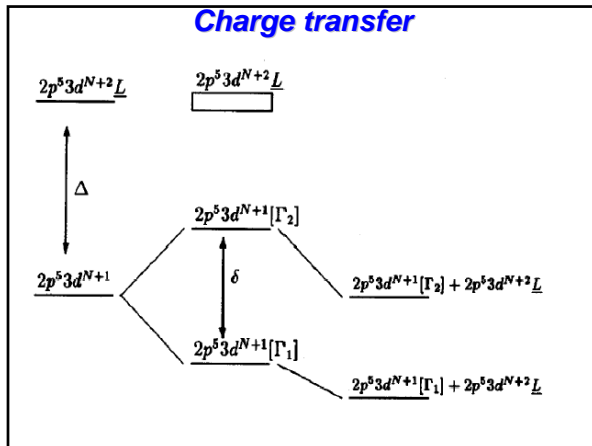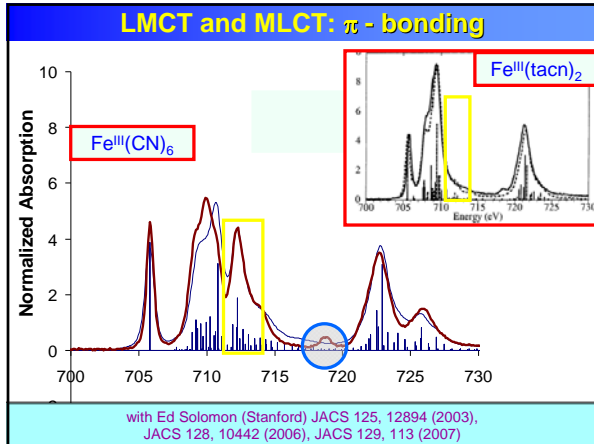NiO

La$_2$Li$_{1/2}$Cu$_{1/2}$O$_4$

Cu-L$_3$ Cu-L$_2$

30% 3d^8 $^1A_1$

30% 3d^8 $^3A_2$

Cs$_2$KCuF$_6$

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

Charge Transfer effects

$3d^8$ + $3d^9\underline{L}$

$\Delta=10$
$\Delta=5$
$\Delta=0$
$\Delta=-5$
$\Delta=-10$

NiO

La$_2$Li$_{1/2}$Cu$_{1/2}$O$_4$

Cu-L$_3$ Cu-L$_2$

30% 3d^8 $^1A_1$

30% 3d^8 $^3A_2$

Cs$_2$KCuF$_6$

Calculate the 2p XAS spectrum of Cs$_2$KCuF$_6$

LMCT and MLCT: π - bonding

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

M ← C≡N   M ... C≡N

$3d^6\underline{L}$ $2p^5 3d^7\underline{L}$

Δ $\Delta + U - Q \approx \Delta$

$3d^5$ $2p^5 3d^6$

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: $3d^5$ + $3d^6\underline{L}$ + $3d^4$L

$3d^4$L $2p^5 3d^5$L

Δ_π $\Delta_\pi - U + Q \approx \Delta_\pi + 2$

$3d^6\underline{L}$ $2p^5 3d^7\underline{L}$

Δ $\Delta + U - Q \approx \Delta - 2$

$3d^5$ $2p^5 3d^6$

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

LMCT and MLCT: π - bonding

Fe^{III}(CN)$_6$

Fe^{III}(tacn)$_2$

Normalized Absorption

(x-axis: 700, 705, 710, 715, 720, 725, 730)

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

XPS

Charge transfer effects in XAS and XPS

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

XPS   3d^{6}L   XAS

Δ

2p^{5}3d^5 3d^5

$\Delta-Q$ 2p^{5}3d^{7}L

Ground State $\Delta+U-Q \approx \Delta$

2p^{5}3d^{6}L   2p^{5}3d^6

Charge transfer effects in XPS

Intensity (arb. units)

(a) NiF$_2$ (b) NiCl$_2$ (c) NiBr$_2$ (d) NiO
2p$_{1/2}$ 2p$_{3/2}$

200   150   100   50   0
Relative Binding Energy (eV)

Exercise: Calculate the 2p XPS spectrum of NiCl$_2$

Charge transfer effects in XPS

$2w$ $d_i^{n-1} d_j^{n+1}$

U_{dd} $W+w$ $d_i^n d_j^{n+1}$ L

$d_i^n d_j^n$ Δ

Charge transfer effects in XPS

U/T_{eff}

CuO, FeO, NiO, NaCuO$_2$, LaFeO$_3$, SrFeO$_3$, Fe$_2$O$_3$, MnO, SrMnO$_3$, LaMnO$_3$, V$_2$O$_3$, LaCrO$_3$, V$_2$O$_3$, LaVO$_3$, Cr$_2$O$_3$, TiO$_2$, TiO, SrTiO$_3$, LaTiO$_3$, YTiO$_3$

$\Delta=U$

Δ/T_{eff}

Charge transfer effects in XPS

MCD

Polarization of X-rays

Linear polarization — Right circular polarization — Left circular polarization

space / time

defines axis

defines **handedness** (chirality) or **direction** (photon angular momentum)

X-MCD

+ helicity   − helicity

X-MCD

Cu^{2+}: $3d^9$ → $2p^5 3d^{10}$
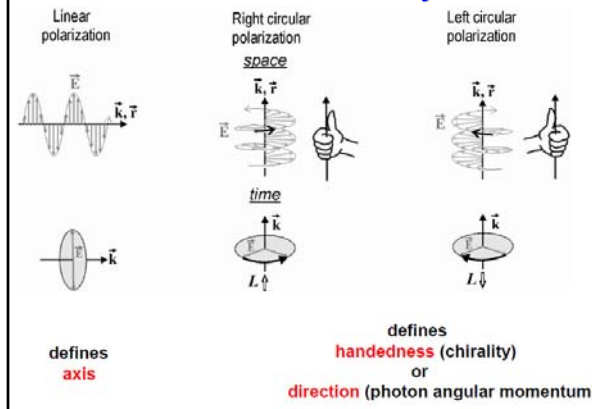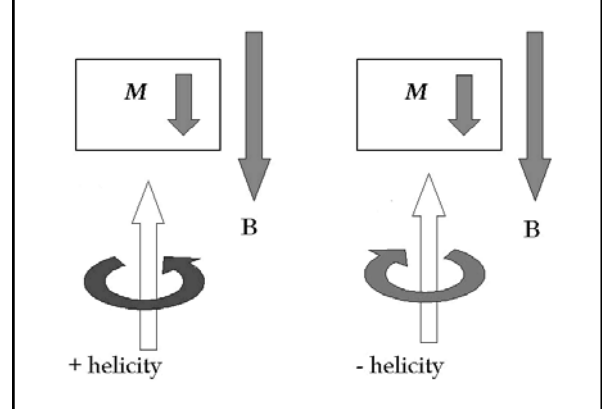
$[\underline{l}_1,\underline{s}_1]=[-2,-1/2]$
$L=2$, $S=1/2 \to {}^2D$
$J=5/2$ or $3/2$
More than half-full
$\to {}^2D_{5/2}$

$[\underline{l}_2,\underline{s}_2]=[-1,-1/2]$
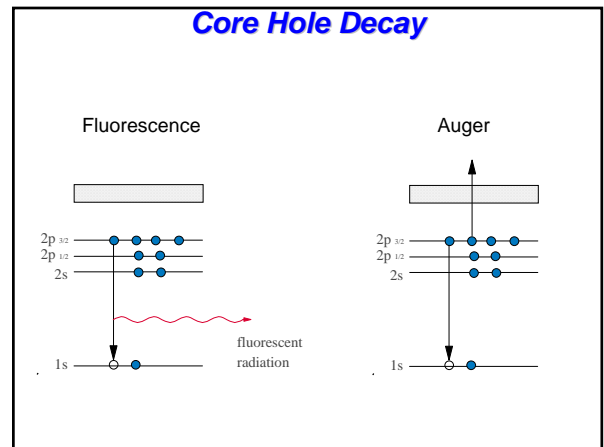$L=1$, $S=1/2 \to {}^2P$
$J=3/2$ or $1/2$

$\to {}^2P_{3/2}$ or ${}^2P_{1/2}$

$\Delta J= +1$ or 0 or -1
light polarization $q = m_J$

X-MCD

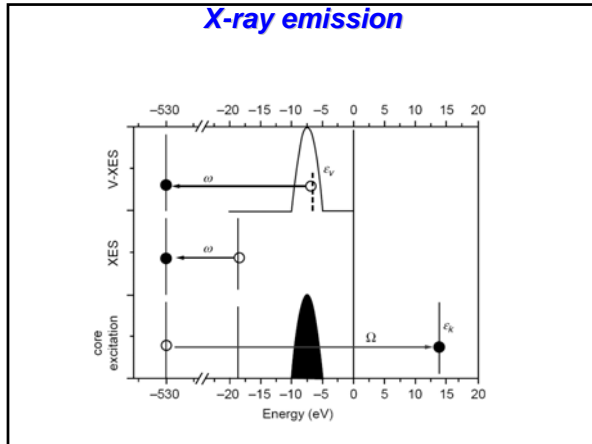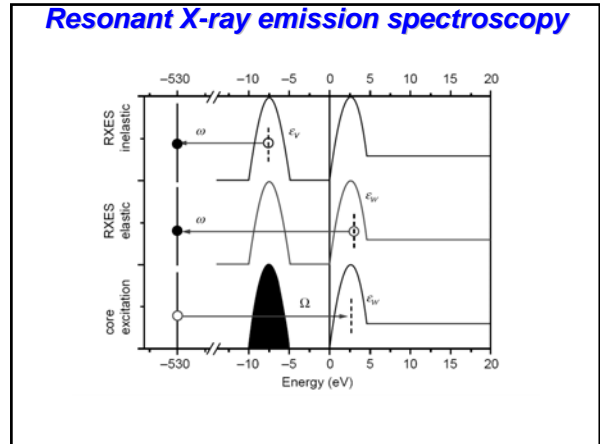Cu^{2+}: $3d^9$

$J=1/2$ L_2 edge
$2p^5$
$J=3/2$ L_3 edge $m_J=+3/2$ $m_J=-3/2$

$\Delta J = -1$
$\Delta m_J = +1$

$J=3/2$
$3d^9$
$J=5/2$ $m_J=+5/2$ $m_J=-5/2$

X-MCD

MCD

m_J=-5/2 to m_J=-3/2

MCD

no LS

Exercise: Repeat these calculations

X-MCD

MCD

no LS

MCD

+ crystal field

X-MCD

MCD

$^3F_4$ LS

^3F no LS

XES calculations

X-ray absorption and X-ray photoemission

XPS

XAS

DOS

Ω

ε_k

Ω

ε_w

Energy (eV)

Core Hole Decay

Fluorescence

Auger

2p 3/2
2p 1/2
2s
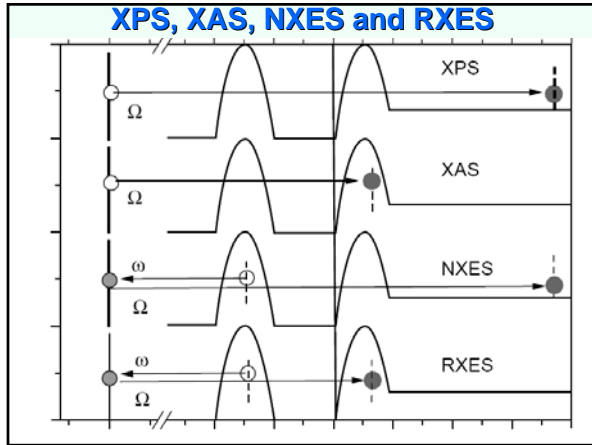
1s

fluorescent radiation

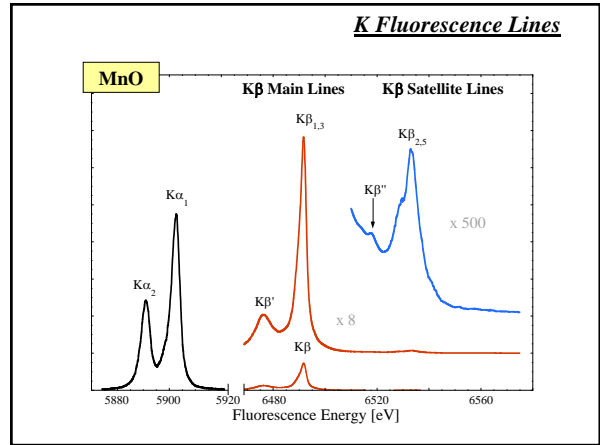2p 3/2
2p 1/2
2s
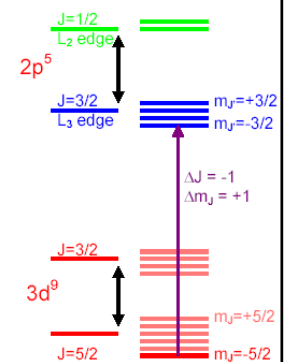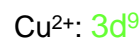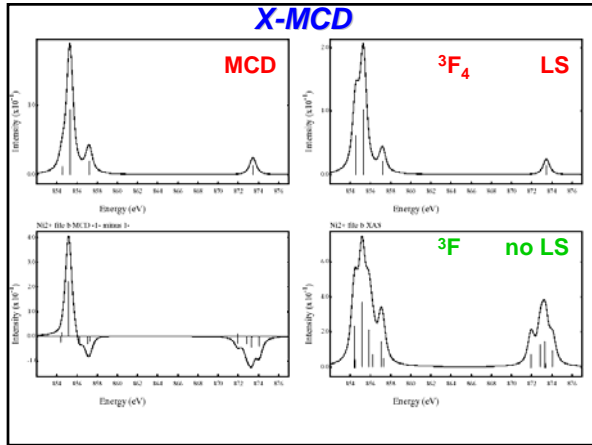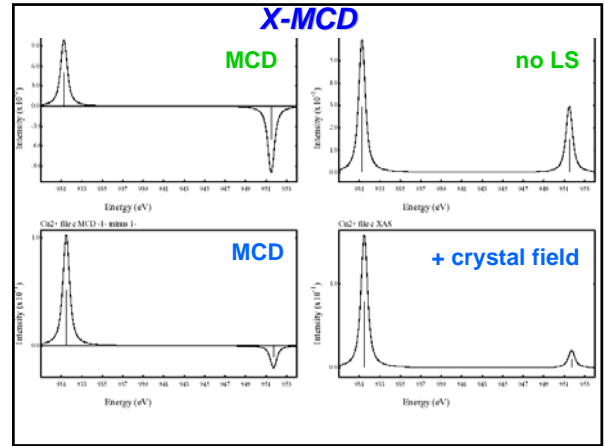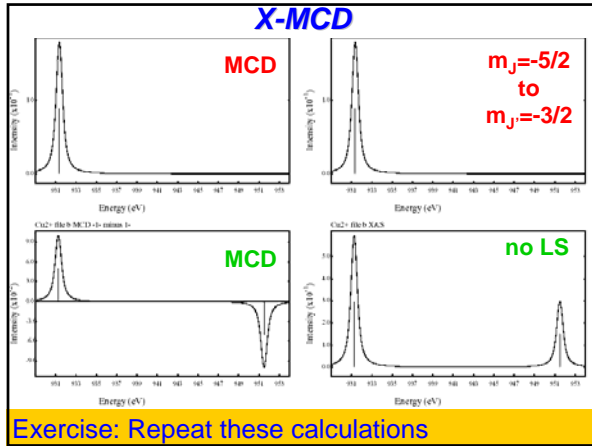
1s
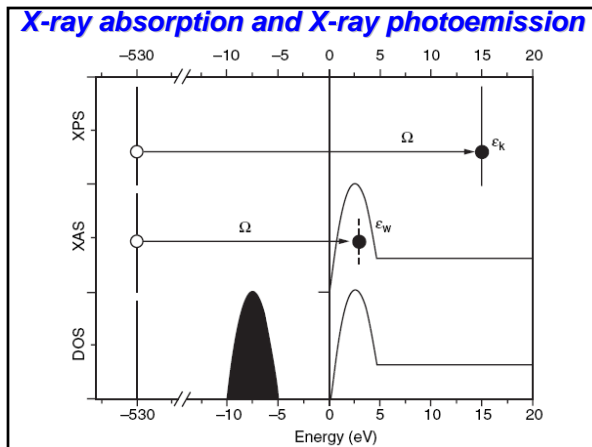
X-ray emission

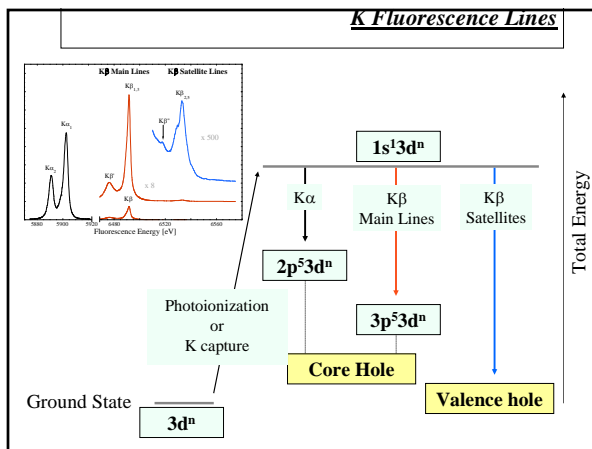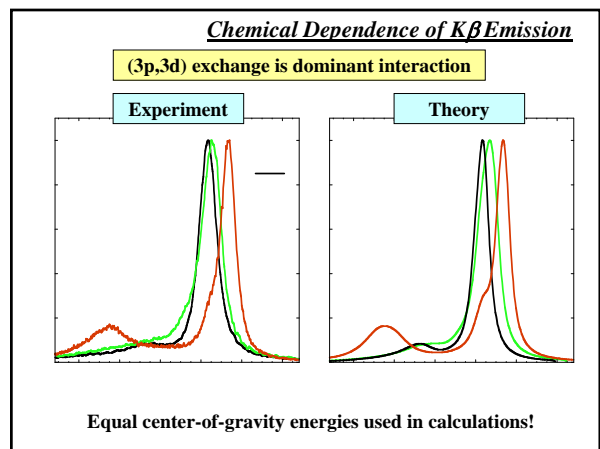## Resonant X-ray emission spectroscopy

XPS, XAS, NXES and RXES

K Fluorescence Lines

MnO

K Fluorescence Lines

Chemical Dependence of $K\beta$ Emission
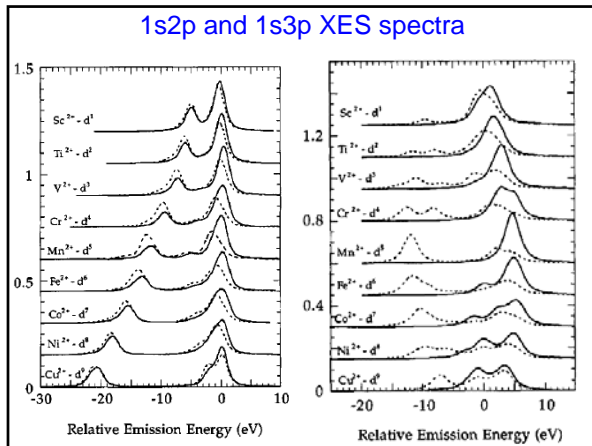
(3p,3d) exchange is dominant interaction

Experiment | Theory

Equal center-of-gravity energies used in calculations!

23

1s2p and 1s3p XES spectra

1s2p and 1s3p XES spectra

Approximations:

- $3d^N$ ground state (+ CT)

- XES only from lowest energy $1s^1 3d^N$ state (+CT)

- Charge transfer energy is Δ-Q

Charge transfer in 1s pre-edge and edge

• Transition metal oxide: Ground state: $3d^5 + 3d^6 \underline{L}$

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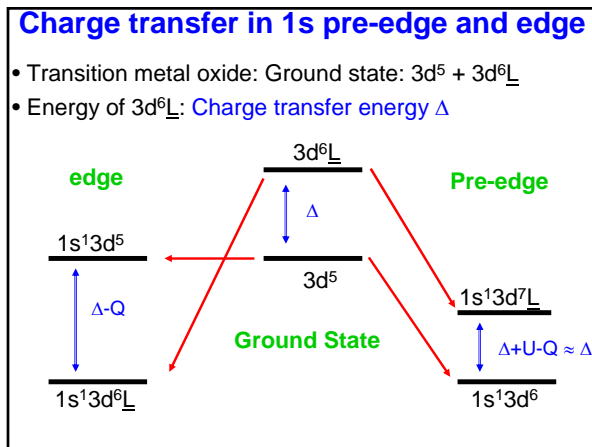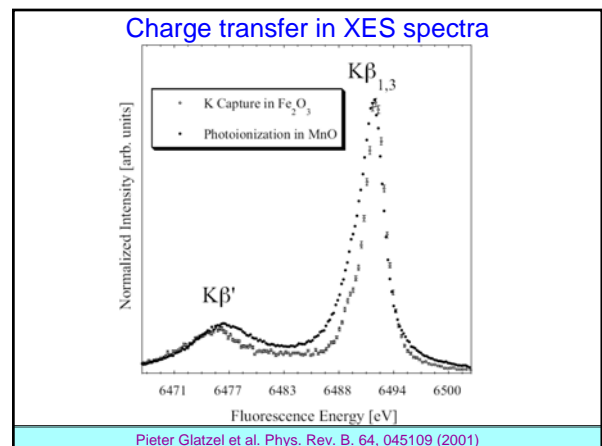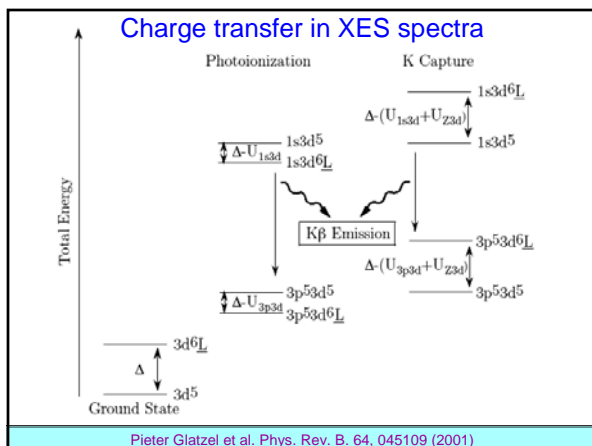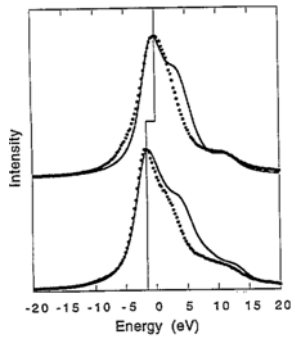

1s2p and 1s3p XES spectra

Approximations:

- $3d^N$ ground state (+ CT)

- XES only from lowest energy $1s^1 3d^N$ state (+CT)

- Charge transfer energy is Δ-Q

- Neglect 1s3d exchange interaction (needed for spin-pol.)

- Neglect of excitation process (a better approximation is to describe the excitation process with XPS)
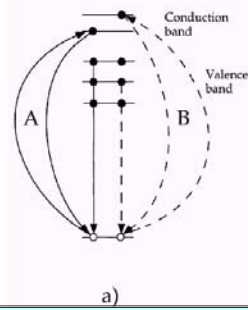
Charge transfer in XES spectra

Pieter Glatzel et al. Phys. Rev. B. 64, 045109 (2001)

Charge transfer in XES spectra

Pieter Glatzel et al. Phys. Rev. B. 64, 045109 (2001)

Charge transfer in XES spectra of NiF_2 and $NiBr_2$

Calculate the 1s3p XES spectrum of Fe2O3

RIXS

RIXS

Single-particle approach

a)

Resonant Inelastic X-ray Spectroscopy

Core-excited states

B

A

dd excitation

Ground state

$$I(\omega,\omega') = \sum_f \left| \sum_x \frac{\langle f|r_q|x\rangle\langle x|r_q|i_0\rangle}{E_{i_0}+\omega-E_x-i\Gamma_x} \right|^2 L_f(\omega-\omega')G_E$$

Resonant Inelastic X-ray Spectroscopy

2p XAS of CaF_2

$3d^0$

$\hbar\omega$

$2p^53d^1$

$\hbar\omega'$

$3s^13d^1$

Data

CaO

CaF_2

346   348   350   352   354   356
Photon energy (eV)

25

Resonant Inelastic X-ray Scattering

2p3s RIXS of CaF$_2$

3d^0

$\hbar\omega$

2p^{5}3d^1

$\hbar\omega'$

3s^{1}3d^1

45
46
47
48
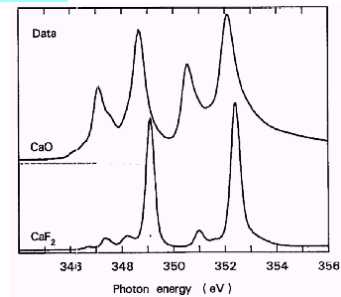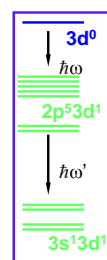49
50

w − w' (eV)

346 347 348 349 350 351 352 353 354

w (eV)

Phys. Rev. B. 53, 7099 (1996)

Resonant Inelastic X-ray Spectroscopy

NiO
Ni $L_{2,3}$

b
a c d e f g

e
d
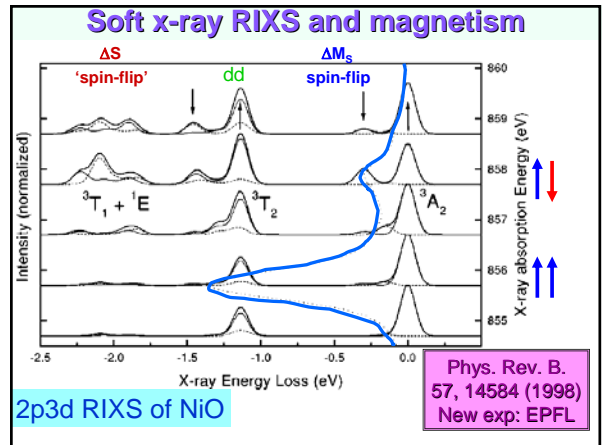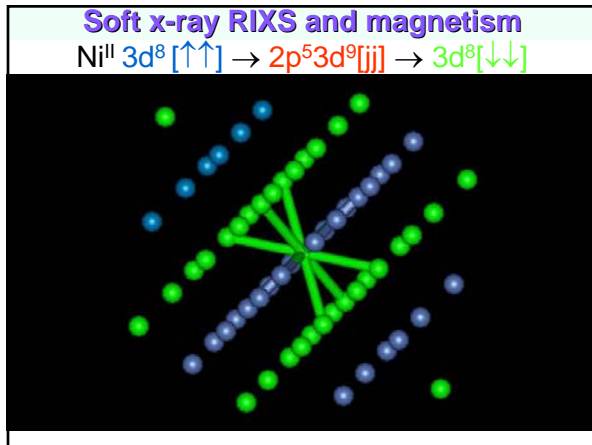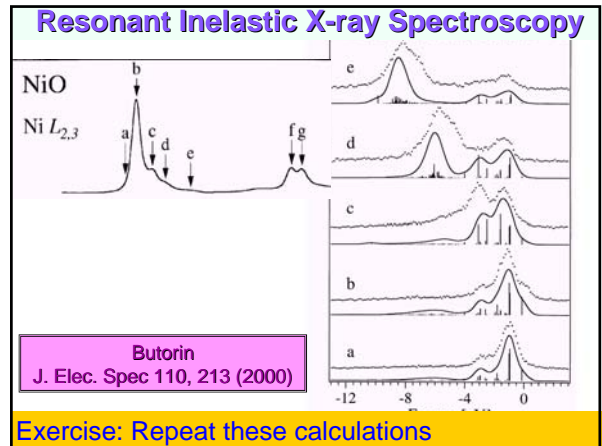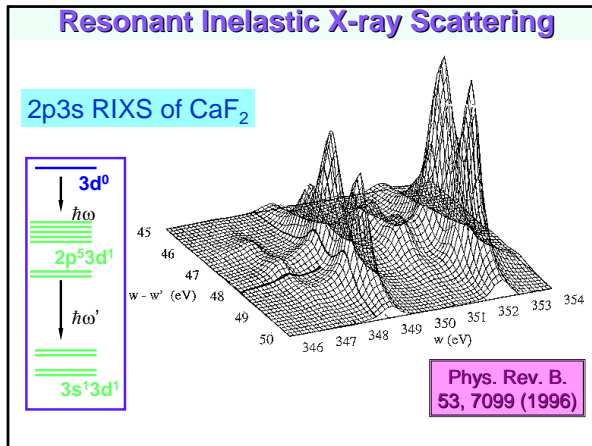c
b
a

−12 −8 −4 0

Butorin
J. Elec. Spec 110, 213 (2000)

Exercise: Repeat these calculations

Soft x-ray RIXS and magnetism
Ni^{II} 3d^8 [↑↑] → 2p^{5}3d^9[jj] → 3d^8[↓↓]

Soft x-ray RIXS and magnetism

ΔS
'spin-flip'

dd

ΔM$_S$
spin-flip

860
859
858
857
856
855

X-ray absorption Energy (eV)

$^3T_1 + ^1E$ $^3T_2$ $^3A_2$

Intensity (normalized)

−2.5 −2.0 −1.5 −1.0 −0.5 0.0

X-ray Energy Loss (eV)

2p3d RIXS of NiO

↑ ↓
↑ ↑

Phys. Rev. B. 57, 14584 (1998)
New exp: EPFL

Soft x-ray RIXS and magnetism

3p3d RIXS of Sr$_2$CuO$_2$Cl$_2$

400
300
200
100
0

Counts

76.3 eV
74.0 eV

x^2-y^2

M$_2$ xz   xy   M$_3$

z^2

−2.5 −2.0 −1.5 −1.0 −0.5 0.0

$\Phi_0 \rightarrow$ 3p $\rightarrow \Phi_0$ + dd + spin-flip

Phys. Rev. Lett. 80, 5204 (1998)

RIXS at metal K edges

Fe K pre-edges

Westre et al. JACS 119, 6297 (1997); Heyboer et al. J.Phys.Chem.B. 108, 10002 (2004)

Exercise: Repeat these calculations

CoO

high-spin Co^{II}
$3d^7$ [$^4T_2$]

Only quadrupole peaks visible
$3d^7 \rightarrow 1s^1 3d^8 \rightarrow 2p^5 3d^8$
Only correct with interference effects ON

RIXS-MCD at the K pre-edge

$L_{2,3}$ edges ($2p \rightarrow 3d$)

✓ Theoretical framework well established : sum rules giving access to magnetic moments

✓ Large intensity

✗ Not compatible with some sample environments : high-pressure cells, liquids

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RIXS-MCD at the K pre-edge

K pre-edge ($1s \rightarrow 3d$)

✓ Compatible with high-pressure cells

✗ Difficult to interpret (no SO coupling on *1s* orbital)

✗ XMCD at K pre-edge obscured by broadening and edge tail

✗ Very small intensity (a few 0.1 %)

Mathon et al (2004)

RIXS-MCD at the K pre-edge

Experimental setup

Si(311)mono

ID26
4x Ge(440) analyzers
vertical spectrometer

Quarter Wave Plate

Fe_3O_4

B

APD

$Nd_2Fe_{14}B$ magnet

RIXS-MCD at the K pre-edge of Fe_3O_4

$K\alpha_2$

$K\alpha_1$

Fe^{II} octa

27

ζ_{2p} (FS)

Fe^{II} oct

RIXS-MCD at the K pre-edge

Line scans

XMCD at high-pressure

La 2p XAS: effects of HERFD

2p5d dipole

2p4f quadrupole

Glatzel et al. PRB 72, 014117 (2005)

La 2p XAS: effects of HERFD

- HERFD makes pre-edge 2p4f transition visible

La 2p XAS: effects of HERFD

LaF$_3$

2p5d dipole

2p4f quadrupole

Suljoti et al. (new data from ID26)

Does FY does measure X-ray Absorption?

LaF$_3$

2p5d dipole

2p4f quadrupole

?

?

Suljoti et al. (new data from ID26)
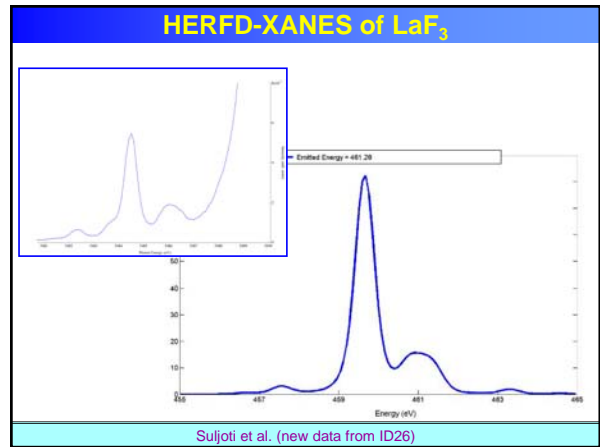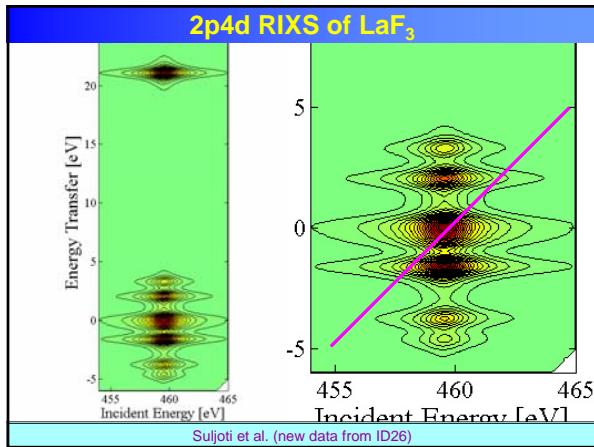
La 2p XAS: effects of HERFD

- HERFD makes pre-edge 2p4f transition visible

- Why has the 2p4f pre-edge 3 peaks?

Does HERFD measure X-ray Absorption?

2p4f quadrupole

$$4f^0 \rightarrow 2p^5\ 4f^1$$

$$4f^0 + 4f^1\underline{L} \rightarrow 2p^5\ 4f^1 + 2p^5\ 4f^2\underline{L}$$

$$4f^0 5d^0 + 4f^0\ 5d^1\underline{L} \rightarrow 2p^5\ 4f^1 + 2p^5 4f^1 5d^1\underline{L}$$

2p4d RIXS of LaF$_3$

Suljoti et al. (new data from ID26)

HERFD-XANES of LaF$_3$

Suljoti et al. (new data from ID26)

2p4d RIXS of LaF$_3$

measured with 2p4d XES

$$4f^0 \rightarrow 2p^5\ 4f^1 \rightarrow 4d^9\ 4f^1$$

one peak

multiplet structure