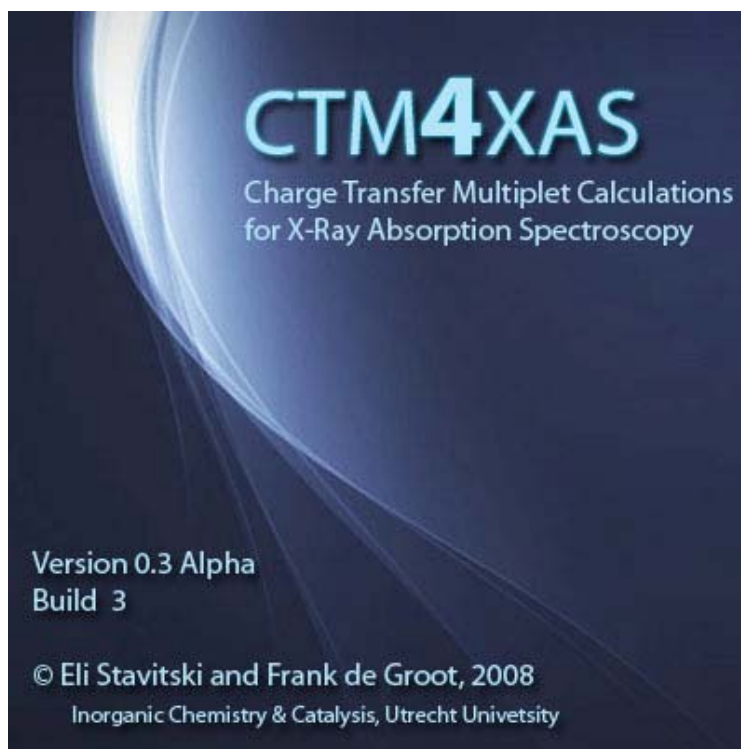


This document is a preliminary manual for the use of the CTM4XAS program.

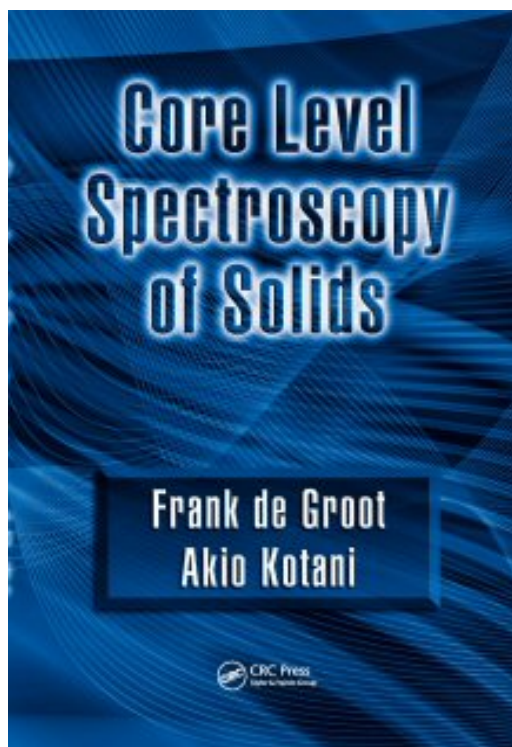


The present version of the CTM4XAS program calculates the 2p and 3p XAS spectra of the 3d and 4d transition metal ions.

We would like to ask all users to give suggestions what kind of options to include in future extensions of the program. This could include:

- Ground State: Providing an output table with all parameters, including the values for expectation values and the spectral sum rule values in case of MCD.
- New experiments: Adding the 1s3d pre-edge XAS, 2p XPS, 3s XPS, 3p XPS will follow soon. Later we intend to include RIXS and resonant photoemission, Auger and fluorescence.
- Adding 5d, 4f and 5f elements.
- More possibilities: symmetries, charge transfer configurations and channels, etc.

CTM4XAS is written by Eli Stavitski and Frank de Groot



The theoretical background to the charge transfer multiplet model has been described in **Core Level Spectroscopy of Solids**, Frank de Groot and Akio Kotani (Taylor And Francis, 2008). More information on my website: <http://www.anorg.chem.uu.nl/people/staff/FrankdeGroot/>

About the book:

Core level spectroscopy has become a powerful tool in the study of electronic states in solids. From fundamental aspects to the most recent developments, *Core Level Spectroscopy of Solids* presents the theoretical calculations, experimental data, and underlying physics of x-ray photoemission spectroscopy (XPS), x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD), and resonant x-ray emission spectroscopy (RXES).

Starting with the basic aspects of core level spectroscopy, the book explains the many-body effects in XPS and XAS. The authors explore more advanced features of XPS, XAS, XMCD, and RXES. Topics discussed include hard XPS, resonant photoemission, spin polarization, electron energy loss spectroscopy (EELS), and resonant inelastic x-ray scattering (RIXS). The authors also use the charge transfer multiplet theory to interpret core level spectroscopy for transition metal and rare earth metal systems.

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1 Using the CTM4XAS program

CTM4XAS 0.3

Calculate Plot Help

Configuration

Ion: ☐ Auto Plot ☐ Expert options ☐ Charge transfer

☒ 2p Initial state: Initial state (CT):

☐ 3p Final state: Final state (CT):

Slater integral reduction (%)

Fdd Fpd Gpd

3d spin-orbit:

Crystal field parameters (eV)

Symmetry:

	Ground state	Excited state
10 Dq	<input type="text" value="0"/>	<input type="text" value="0"/>
Dt	<input type="text" value="0"/>	<input type="text" value="0"/>
Ds	<input type="text" value="0"/>	<input type="text" value="0"/>
M (meV)	<input type="text" value="0"/>	<input type="text" value="0"/>

Charge transfer parameters (eV)

Delta	<input type="text" value="0"/>	<input type="text" value="2.0"/>	T(b1)
Udd	<input type="text" value="0"/>	<input type="text" value="2.0"/>	T(a1)
Upd	<input type="text" value="0"/>	<input type="text" value="1.0"/>	T(b2)
		<input type="text" value="1.0"/>	T(e)

Plotting

File: Spectrum:

☐ Suppress sticks

Energy range (eV):

Lorentzian broadening:

Gaussian broadening:

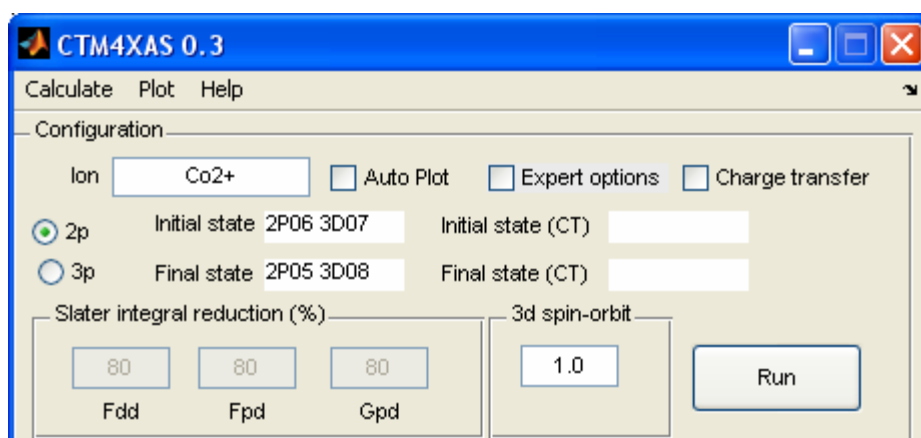
☐ Force energy range ☐ Split

This is the CTM4XAS parameters window

The next two pages explain how to run the CTM4XAS program. The CTM4XAS program makes use of the TT-MULTIPLY charge transfer multiplet programs as have been originally developed by Theo Thole. The background of the calculations is explained, with examples, starting on page 3. The program is started by running the CTM4XAS.exe file. This opens a parameter window, from which all programs can be executed. The CTM4XAS credits window can be closed. The CTM4XAS program starts executing the requested program with the command RUN. This starts a series of calculations that include the original RCN2, RCG2, RAC2, BAN2 and PLO2 programs.

The window consists of 4 parts:

- Top: Atomic Multiplet and General commands
- Middle-Left: Crystal Field parameters
- Middle-Right: Charge Transfer parameters
- Bottom: Plotting parameters



A: Atomic Multiplet and General Commands

- **Configuration:** Give here the element and valence. In the present program, only a limited set of elements are allowed. This includes the 3d (K to Cu) and 4d (Rb to Ag) metal ions in their common valences.
- **Auto Plot:** This automatically runs the plotting program after the calculation. Alternatively the plotting program can be executed with the PLOT command.
- **Expert Options:** This allows the reduction of Slater integrals and the use of different crystal field parameters in the final state.
- **Charge Transfer:** This includes a $3d^{N+1}\underline{L}$ configuration to the $3d^N$ ground state. Three configuration charge transfer and metal ligand charge transfer has not yet been included.
- **2p** creates a 2p core hole and **3p** creates a 3p core hole. Further core levels (1s, 2s, 3s) will be included in the next version, including the option to calculate XAS or XPS.
- The initial state and final state windows show the included configurations.
- **Slater integral reduction:** The F_{dd} , F_{pd} and G_{pd} Slater integrals can be reduced to any other value. The default value is 80% of their Hartree-Fock calculated value. This 80% value has been shown to be close to the optimized value to simulate the multiplet spectra of atoms.
- **3d Spin-orbit:** This value can be changed from 0 to 1. The default value of 1.0 includes the atomic 3d/4d spin-orbit coupling. A value of 0.0 sets the 3d/4d spin-orbit coupling to zero, which gives a better description of the spectral shape for many transition metal systems.

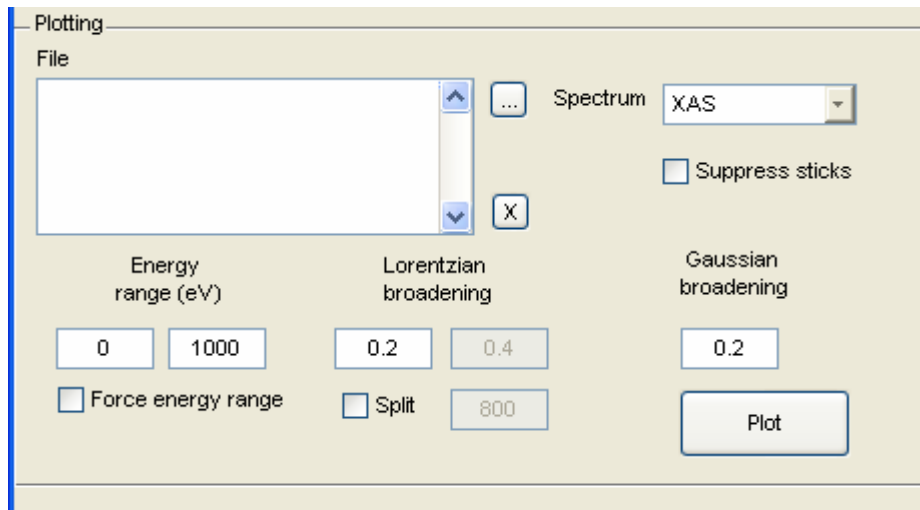
B: Crystal Field Parameters

- **Symmetry:** As yet, three symmetries can be calculated, octahedral (O_h), tetragonal (D_{4h}) and C_4 . All calculations are performed in C_4 symmetry, but the choice for a higher symmetry automatically limits the parameter choice. If all crystal field values are zero, the symmetry is spherical (SO_3) and a negative value for $10Dq$ effectively yields tetrahedral (T_d) symmetry.
- The values of $10Dq$, Ds and Dt are given in eV.
- A molecular (exchange) field can be included in meV.

Crystal field parameters (eV)			Charge transfer parameters (eV)		
Symmetry	Oh				
	Ground state	Excited state			
10 Dq	<input type="text" value="0"/>	<input type="text" value="0"/>	Delta	<input type="text" value="0"/>	<input type="text" value="2.0"/> T(b1)
Dt	<input type="text" value="0"/>	<input type="text" value="0"/>	Udd	<input type="text" value="0"/>	<input type="text" value="2.0"/> T(a1)
Ds	<input type="text" value="0"/>	<input type="text" value="0"/>	Upd	<input type="text" value="0"/>	<input type="text" value="1.0"/> T(b2)
M (meV)	<input type="text" value="0"/>	<input type="text" value="0"/>		<input type="text" value="1.0"/>	T(e)

C: Charge Transfer Parameters

- **Delta:** This is the charge transfer parameter Δ , which gives the energy difference between the (centers of the) $3d^N$ and $3d^{N+1}\underline{L}$ configurations. The effective value of Δ (Δ_{eff}) is affected by the multiplet and crystal field effects on each configuration. In the next version, the value of Δ_{eff} will be given in a parameter-output file.
- **Udd:** This is the value of the Hubbard U .
- **Upd:** This is the core hole potential. In case of XAS spectra, only the difference between U_{pd} and U_{dd} is important.
- **Hopping T:** The hopping parameters are given for the 4 symmetries in tetragonal symmetry A_1 , B_1 , E and B_2 . A_1 (z^2) and B_1 (x^2-y^2) are part of the e_g -orbitals and E (xz , yz) and B_2 (xy) are part of the t_{2g} orbitals. In O_h symmetry the values of $A_1=B_1$ and $E=B_2$. (This is not yet automatic in the test-version).



D: Plotting Parameters

- **File:** The File window contains all files that are plotted. All broadened spectra and also all sticks are normalized to 1.0.
- **Spectrum:** Here one can choose XAS, (M)LD or (M)CD, respectively the XAS spectrum (L+R+Z), linear dichroism ($\frac{1}{2}L + \frac{1}{2}R - Z$) and circular dichroism or XMCD (L-R).
- **Force Energy Range:** One can choose an energy range for the spectrum. The plotting program by default plots an energy range that contains the whole spectrum. This option can, for example, be used to plot individually the L_3 and L_2 edges of the 4d metals that are separated by a large energy.
- **Lorentzian broadening:** This value gives the Lorentzian broadening.
- **Split:** Two separate Lorentzian broadenings can be included with the provided energy separating the two regions. If one would like to include more broadening ranges, one has to use to original programs with the appropriate **plo** input file.
- **Gaussian broadening:** This value gives the Gaussian broadening, simulating the experimental resolution.
- **Suppress sticks:** Only the broadened spectrum is plotted.
- **Plot:** This command plots all files in the file window.

2 Atomic Multiplet Calculations

2.1 Origin of Multiplet effects

The single particle description of x-ray absorption works well for all K edges and a range of dedicated computer codes exist to calculate the x-ray absorption cross section, including Wien2K, FEFF, STOB, etc. Applying these one-electron codes (where one-electron applies to a one-electron core excitation, not to the treatment of the valence electrons) to systems such as transition metal oxides one finds excellent agreement for the oxygen K edges, whereas for the metal $L_{2,3}$ edges the agreement is poor. The reason for this discrepancy is not that the density-of-states is calculated wrongly, but rather that one does not observe the density of states in the 2p x-ray absorption process. The main reason for the deviation from the density-of-states is the strong overlap of the core wave function with the valence wave functions. In the final state of an x-ray absorption process one finds a partly filled core state, for example a $2p^5$ configuration. In case one studies a system with a partly filled 3d-band, for example NiO, the final state will have an incompletely filled 3d-band. For NiO this can be approximated as a $3d^9$ configuration. The 2p-hole and the 3d-hole have radial wave functions that overlap significantly. This wave function overlap is an atomic effect that can be very large. It creates final states that are found after the vector coupling of the 2p and 3d wave functions. This effect is well known in atomic physics and actually plays a crucial role in the calculation of atomic spectra. Experimentally it has been shown that while the direct core hole potential is largely screened in condensed phase systems, these so-called multiplet effects are hardly screened from their atomic values. This implies that the atomic multiplet effects are of the same order of magnitude in atoms and in solids. As such, they have to be included in the calculation of the 2p XAS spectra in any open shell system.

As yet, no ab-initio multiplet program exists that can deal with molecular or solid state open shell systems. Steps towards an ab-initio treatment are the molecular orbital-based program of Isao Tanaka's group, the multi-channel multiple scattering approach developed by Peter Kruger and the Bethe-Salpeter approach from Eric Shirley.

2.2 Term symbols

A term symbol is written as $^{2S+1}X_J$, where X corresponds to a letter according to the value of L. X = s, p, d, f and g for L = 0, 1, 2, 3 and 4. An s-electron has L=0 and only one J-value, equal to +1/2. In the absence of spin-orbit coupling, all terms with the same L and S have the same energy, giving an energy level that is (2L+1)(2S+1)-fold degenerate. When spin-orbit coupling is important, the terms are split in energy according to their J-value with a degeneracy of 2J+1. The quantity 2S+1 is called the spin multiplicity of the term, and the terms are called singlet, doublet, triplet, quartet, etc. according to S = 0, 1/2, 1, 3/2, etc.

For more details see appendix 2.B.

Examples of term symbols for 1- and 2-electron configurations.										
1s ¹	² S _{1/2}									
2p ¹	² P _{1/2} ² P _{3/2}									
3d ¹	² D _{3/2} ² P _{5/2}									
2p ¹ 3p ¹ (² P⊗ ² P)	¹ S ₀	¹ P ₁	¹ D ₂	³ S ₁	³ P ₀ ³ P ₁ ³ P ₂	³ D ₁ ³ D ₂ ³ D ₃				
2p ²	¹ S ₀		¹ D ₂		³ P ₀ ³ P ₁ ³ P ₂					
3d ¹ 4d ¹ (² D⊗ ² D)	¹ S ₀	¹ P ₁	¹ D ₂	¹ F ₃	¹ G ₄	³ S ₁	³ P ₀ ³ P ₁ ³ P ₂	³ D ₁ ³ D ₂ ³ D ₃	³ F ₂ ³ F ₃ ³ F ₄	³ G ₃ ³ G ₄ ³ G ₅
3d ²	¹ S ₀		¹ D ₂		¹ G ₄		³ P ₀ ³ P ₁ ³ P ₂		³ F ₂ ³ F ₃ ³ F ₄	
2p ¹ 3d ¹ (² P⊗ ² D)		¹ P ₁	¹ D ₂	¹ F ₃			³ P ₀ ³ P ₁ ³ P ₂	³ D ₁ ³ D ₂ ³ D ₃	³ F ₂ ³ F ₃ ³ F ₄	

2.3 The atomic multiplet spectrum of the $L_{2,3}$ edge of Ti^{4+}

The 2p x-ray absorption process excites a 2p core electron into the empty 3d shell and the transition can be described as $2p^6 3d^0 \rightarrow 2p^5 3d^1$. This transition is rather similar to the $3d^{10} 4f^0 \rightarrow 3d^9 4f^1$ transitions in rare earths as both have a ground state that has 1S_0 symmetry. For the final state we have a single p hole and a single d electron and 2Px2D gives the term symbols 1P_1 , 1D_2 , 1F_3 , $^3P_{012}$, $^3D_{123}$ and $^3F_{234}$. (We use the short hand notation $^3F_{234}$ for 3F_2 plus 3F_3 plus 3F_4). The energies of the final states are affected by the 2p3d Slater-Condon parameters, the 2p spin-orbit coupling and the 3d spin-orbit coupling. The x-ray absorption transition matrix elements to be calculated are:

$$I_{XAS} \propto \langle 3d^0 | p | 2p^5 3d^1 \rangle^2 \quad (2.9)$$

The symmetry aspects are:

$$I_{XAS} \propto \langle [^1S_0] || [^1P_1] || [^1,3PDF] \rangle^2 \quad (2.10)$$

The table below contains the result of an atomic multiplet calculation for Ti^{4+} ($3d^0$) using the atomic parameters. The twelve states are built from the twelve term symbols according to the matrix given. The irreducible representations, i.e. the states with the same J-value block out in the calculation. It is found that the lowest energy state is the pure 3P_0 state. This state has zero intensity in an x-ray absorption process.

	3P_0	3P_1	3D_1	1P_1	3P_2	3D_2	3F_2	1D_2	3D_3	3F_3	1F_3	3F_4
-3.281	1.0											
-2.954		-0.94	0.30	0.08								
0.213		-0.19	-0.77	0.60								
5.594		0.24	0.55	0.79								
-2.381					0.81	-0.46	0.01	0.34				
-1.597					-0.03	-0.50	0.56	-0.65				
3.451					0.04	-0.30	-0.82	-0.47				
3.643					-0.57	-0.65	-0.06	0.48				
-2.198									-0.21	0.77	0.59	
-1.369									0.81	-0.19	0.54	
3.777									-0.53	-0.60	0.59	
-2.481												1.0

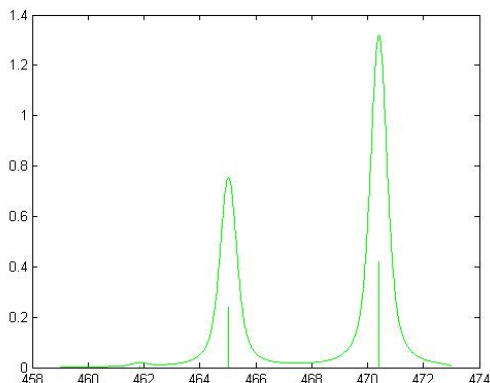
The relative energies of an atomic multiplet calculation for Ti^{IV} . The J=1 states (which have finite intensity) are given in boldface.

The symmetry of the dipole transition is given as 1P_1 , according to the dipole selection rules, which state that $\Delta J = +1, 0, -1$ but not $J' = J = 0$. Within LS coupling also $\Delta S = 0$ and $\Delta L = 1$. The dipole selection rule reduces the number of final states that can be reached from the ground state. The J-value in the ground state is zero. In this case, the dipole selection rule proclaims that the J-value in the final state must be one, thus only the three term symbols 1P_1 , 3P_1 and 3D_1 can obtain finite intensity. The problem of calculating the 2p absorption spectrum is effectively reduced to solving the three by three energy matrix of the final states with J=1.

Exercise 2.1:

Calculate the atomic multiplet spectrum of the 2p XAS spectrum of Ti^{4+} (or Sc^{3+})

Run CTM4XAS with the configuration Ti^{4+} (or Sc^{3+}) and Autoplot ON. Leave all other parameters at the provided default settings. (Choose any name; the program saves the appropriate rcn, rcg, rac, ban, plo and xy files with this name).

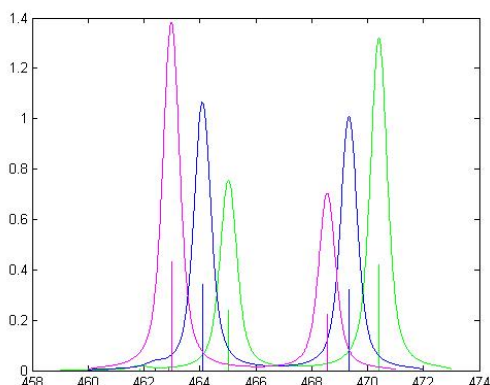


The atomic multiplet spectrum of Ti^{4+}

Exercise 2.2:

(a) Calculate the atomic multiplet spectrum of Ti^{4+} (or Sc^{3+}) with the Slater integrals reduced to 40% instead of 80%. Run CTM4XAS with the configuration Ti^{4+} (or Sc^{3+}), Autoplot ON and expert options ON. Set the three Slater integrals to 40.

(b) Calculate the atomic multiplet spectrum of Ti^{4+} (or Sc^{3+}) with the Slater integrals reduced to 1% instead of 80%. Run CTM4XAS with the configuration Ti^{4+} (or Sc^{3+}), Autoplot ON and expert options ON. Set the three Slater integrals to 40. (It is not possible to set the Slater integrals to 0%, because 00 is interpreted as 100%; The Slater integrals can be set to zero using the original programs).



The atomic (green), 40% reduced (blue) and 1% reduced (purple) spectra.

In the 40% spectrum, the pre-edge is shifted closer to the L_3 edge.

In the 1% spectrum, the branching ratio has changed to the statistical ratio of 2:1. The pre-edge has merged with the L_3 edge.

2.4 Atomic multiplet spectra of 3d0 and 4f0 systems

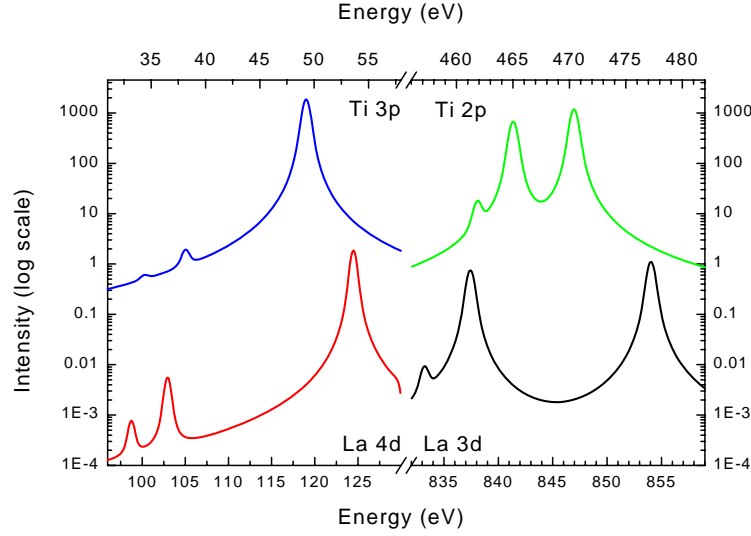
We compare a series of x-ray absorption spectra of tetravalent titanium 2p and 3p edges and the trivalent lanthanum 3d and 4d edges. The ground states of Ti^{4+} and La^{3+} are respectively $3d^0$ and $4f^0$ and they share a 1S ground state. The transitions at the four edges are respectively:

- Ti^{4+} L_{2,3} edge: $3d^0 \rightarrow 2p^5 3d^1$
- Ti^{4+} M_{2,3} edge: $3d^0 \rightarrow 3p^5 3d^1$
- La^{3+} M_{4,5} edge: $4f^0 \rightarrow 3d^9 4f^1$
- La^{3+} N_{4,5} edge: $4f^0 \rightarrow 4d^9 4f^1$

These four calculations are equivalent and all spectra consist of three peaks with $J=1$. The values of the atomic Slater-Condon parameters and core hole spin-orbit coupling are different for these 4 systems.. They are given for the four situations. The G^1 and G^3 Slater-Condon parameters have an approximately constant ratio with respect to the F^2 value. The important factor for the spectral shape is the ratio of the core spin-orbit coupling and the F^2 value. Finite values of both the core spin-orbit and the Slater-Condon parameters cause the presence of the pre-peak. It can be seen that the 3p and 4d spectra have small core spin-orbit couplings, implying small $p_{3/2}$ ($d_{5/2}$) edges and extremely small pre-peak intensities. The deeper 2p and 3d core levels have larger core spin-orbit splitting with the result of a $p_{3/2}$ ($d_{5/2}$) edge of almost the same intensity as the $p_{1/2}$ ($d_{3/2}$) edge and a larger pre-peak. Note that none of these systems comes close to the single-particle result of a 2:1 ratio of the p edges or the 3:2 ratio of the d edges. Figure 2.4 shows the x-ray absorption spectral shapes. They are given on a logarithmic scale to make the pre-edges visible.

Edge	Ti 2p	Ti 3p	La 3d	La 4d
Average Energy (eV)	464.00	37.00	841.00	103.00
Core spin-orbit (eV)	3.78	0.43	6.80	1.12
F^2 Slater-Condon (eV)	5.04	8.91	5.65	10.45
<u>Intensities:</u>				
Pre-peak	0.01	10^{-4}	0.01	10^{-3}
$p_{3/2}$ or $d_{5/2}$	0.72	10^{-3}	0.80	0.01
$p_{1/2}$ or $d_{3/2}$	1.26	1.99	1.19	1.99

The relative intensities, energy, core hole spin-orbit coupling and F^2 Slater-Condon parameters are compared for four different 1S_0 systems. The last two columns repeat the results of situation (b) and (c) as given above.



The La^{3+} 4d and 3d plus Ti^{4+} 3p and 2p x-ray absorption spectra as calculated for isolated ions. The intensity is given on a logarithmic scale to make the pre-edge peaks visible. The intensities of titanium have been multiplied by 1000.

2.5 Matrix elements

Above we have found the number of states of a certain $3d^n$ configuration and their term symbols. The next task is to find the relative energies of the different terms, calculating the matrix elements of these states with the Hamiltonian H_{ATOM} . As discussed in the previous section, H_{ATOM} consists of the effective electron-electron interaction H'_{ee} and the spin-orbit coupling H_{ls} :

$$H_{\text{ATOM}} = \sum_{\text{pairs}} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i) l_i \cdot s_i \quad (2.5)$$

The electron-electron interaction commutes¹ with L^2 , S^2 , L_z and S_z , which implies that all its off-diagonal elements are zero. The general formulation of the matrix elements of two-electron wave functions is given as:

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k \quad (2.6)$$

F^i (f_i) and G^i (g_i) are the Slater-Condon parameters for the radial (angular) part of the direct Coulomb repulsion and the Coulomb exchange interaction, respectively. f_i and g_i are non-zero only for certain values of i , depending on the configuration.

The possible values of f_i and g_i for simple configurations

¹ Two operators **A** and **B** are said to commute if they have common eigenfunctions, i.e. the eigenfunctions of **A** are eigenfunctions of **B**, and vice versa.

Conf.	f_i	g_i	Conf.	f_i	g_i	Conf.	f_i	g_i
$1s^2$	0	-	$1s2s$	0	0	$1s2p$	0	1
$2p^2$	0 2	-	$2p3p$	0 2	0 2	$2p3d$	0 2	1 3
$3d^2$	0 2 4	-	$3d4d$	0 2 4	0 2 4	$3d4f$	0 2 4	1 3 5

It can be seen that the exchange interaction g_i is present only for electrons in different shells. f_0 is always present and the maximum value for i equals two times the lowest value of l . For g_k , i is even if l_1+l_2 is even, and i is odd if l_1+l_2 is odd. The maximum value of i equals l_1+l_2 .

A $1s2s$ configuration consists of 1S and 3S term symbols. The value of both f_0 and g_0 is 1, and the respective energies are given by:

$$\left\langle ^1S \left| \frac{e^2}{r_{12}} \right| ^1S \right\rangle = F^0(1s2s) + G^0(1s2s) \quad (2.7)$$

$$\left\langle ^3S \left| \frac{e^2}{r_{12}} \right| ^3S \right\rangle = F^0(1s2s) - G^0(1s2s) \quad (2.8)$$

This result can be stated as “the singlet and the triplet state are split by the exchange interaction”. This energy difference is $2G^0(1s2s)$. An analogous result is found for a $1s2p$ state for which the singlet and triplet states are split by $(2/3)G^0(1s2p)$. The $2/3$ prefactor is determined by the degeneracy of the $2p$ -state.

For a $3d^2$ configuration, the electrons come from the same shell hence there are no exchange interactions. There are five term symbols 1S , 3P , 1D , 3F and 1G . f_0 is equal to the number of permutations $(N(N-1)/2)$ of n electrons, i.e. equal to 1.0 for two electron configurations. The Slater-Condon parameters F^2 and F^4 have approximately a constant ratio: $F^4 = 0.62 F^2$. The last column in the table gives the approximate energies of the five term symbols. In case of the $3d$ transition metal ions, F^2 is approximately equal to 10 eV. This gives for the five term symbols the energies respectively as 3F at -1.8 eV, 1D at -0.1 eV, 3P at +0.2 eV, 1G at +0.8 eV and 1S at +4.6 eV. The 3F -term symbol has lowest energy and is the ground state of a $3d^2$ system. This is in agreement with the Hund's rules, which will be discussed in the next section. The three states 1D , 3P and 1G are close in energy some 1.7 to 2.5 eV above the ground state. The 1S state has a high energy of 6.4 eV above the ground state, the reason being that two electrons in the same orbit strongly repel each other.

		Relative Energy	Relative Energy
1S	$F^0 + 2/7 F^2 + 2/7 F^4$	$0.46F^2$	4.6 eV
3P	$F^0 + 3/21 F^2 - 4/21 F^4$	$0.02F^2$	0.2 eV
1D	$F^0 - 3/49 F^2 + 4/49 F^4$	$-0.01F^2$	-0.1 eV
3F	$F^0 - 8/49 F^2 - 1/49 F^4$	$-0.18F^2$	-1.8 eV
1G	$F^0 + 4/49 F^2 + 1/441 F^4$	$0.08F^2$	0.8 eV

The relative energies of the term symbols for a $3d^2$ configuration (see text).

The table gives three related notations that are used to indicate the radial integrals. The Slater-Condon parameters F^k , the normalized Slater-Condon parameters F_k and the Racah parameters A, B and C. The bottom half uses the relationship between F^2 and F^4 and it further uses a typical F^2 value of 10 eV and a F^0 value of 8 eV.

A comparison of the Slater-Condon parameters F^k , with the normalized Slater-Condon parameters F_k and the Racah parameters.		
Slater-Condon	Normalized	Racah
F^0	$F_0 = F^0$	$A = F_0 - 49F_4$
F^2	$F_2 = F^2/49$	$B = F_2 - 5F_4$
F^4	$F_4 = F^4/441$	$C = 35F_4$
$F^0 = 8.0$	$F_0 = 8.0$	$A = 7.3$
$F^2 = 10.0$	$F_2 = 0.41$	$B = 0.13$
$F^4 = 6.2$	$F_4 = 0.014$	$C = 0.49$

For three and more electrons the situation is considerably more complex. It is not straightforward to write down an anti-symmetrized three-electron wave function. It can be shown that the three-electron wave function can be build from two-electron wave functions with the use of the so-called coefficients of fractional parentage.

2.6 Atomic multiplet spectra of partly filled 3d systems

The term symbols for a partly filled d-band with the lowest energy, found after calculating the matrix elements, are given in the table below. They are in agreement with the so-called Hunds rules. Based on experimental information Hund formulated three rules to determine the ground state of a $3d^N$ configuration. The three Hunds rules are:

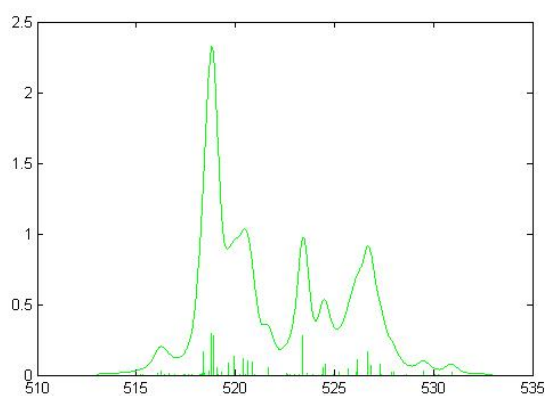
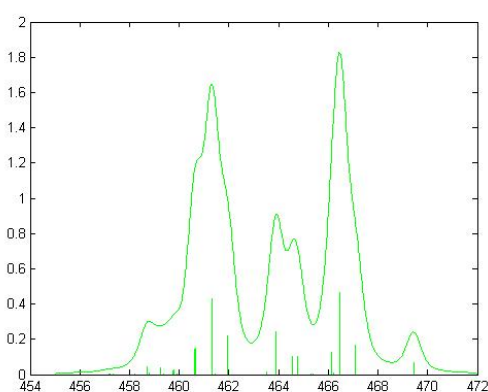
1. Term symbols with maximum spin S are lowest in energy,
2. Among these terms, the one with the maximum orbital moment L is lowest,
3. In the presence of spin-orbit coupling, the lowest term has $J = |L-S|$ if the shell is less than half full and $J = L+S$ if the shell is more than half full.

A configuration has the lowest energy if the electrons are as far apart as possible. The first Hunds rule 'maximum spin' can be understood from the Pauli principle: Electrons with parallel spins must be in different orbitals, which on overall implies larger separations, hence lower energies. This is for example evident for a $3d^5$ configuration, where the 6S state has its five electrons divided over the five spin-up orbitals, which minimizes their repulsion. In case of $3d^2$, the first Hunds rule implies that either the 3P or the 3F -term symbol must have lowest energy. From the previous section one finds that the 3F term symbol is lower than the 3P -term symbol, because the 3F wave function tends to minimize electron repulsion. The effects of spin-orbit coupling are well known in case of core states. A 2p-core state has $^2P_{3/2}$ and $^2P_{1/2}$ states. The state with the lowest energy is $^2P_{3/2}$. Consider for example the 2p XAS or XPS spectrum of nickel. The $^2P_{3/2}$ peak is positioned at approximately 850 eV and the $^2P_{1/2}$ at about 880 eV. Note that the state with the lowest binding energy is related to the lowest energy of the final state configuration. This is in agreement with Hunds third rule: the configuration is $2p^5$, so more than half-full, implying that highest J -value has lowest energy. The third rule implies that the ground state of a $3d^8$ configuration is 3F_4 , while it is 3F_2 in case of a $3d^2$ configuration.

Exercise 2.3:

Calculate the atomic multiplet spectrum of $3d^1 \text{Ti}^{3+}$, $3d^2 \text{V}^{3+}$ and $3d^3 \text{Cr}^{3+}$.

Run CTM4XAS with the configuration Ti^{3+} and Autoplot ON, etc. Leave all other parameters at the provided default settings.

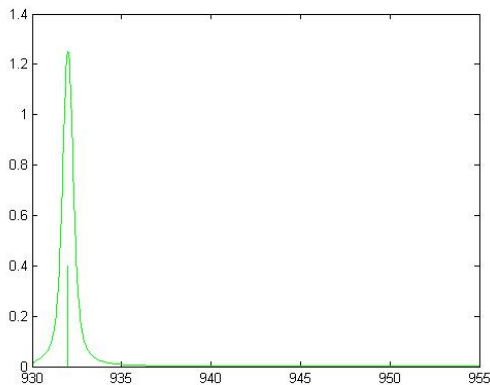


The $3d^1 \text{Ti}^{3+}$ (left) and $3d^2 \text{V}^{3+}$ atomic multiplet spectra.

All 3d ions can be calculated in this way. For example look at the $3d^4$ to $3d^9$ systems Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} .

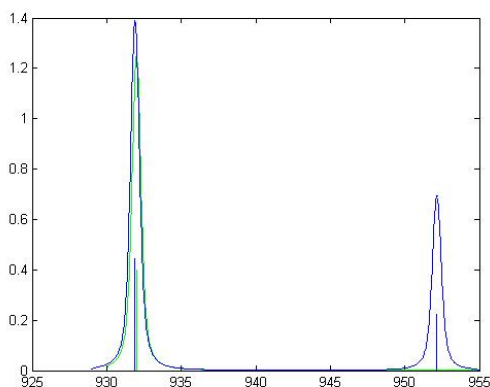
Exercise 2.4:

Calculate the atomic multiplet spectrum of $3d^9 \text{Cu}^{2+}$. Run CTM4XAS with the configuration Cu^{2+} and Autoplot ON, etc. Leave all other parameters at the provided default settings.



The $3d^9 \text{Cu}^{2+}$ atomic multiplet spectrum. Note that the Cu^{2+} spectrum has only a single final state because from the $3d^9$ ($J=5/2$) ground state only the $2p^5 3d^{10}$ ($J'=3/2$) final state can be reached.

The 3d spin-orbit coupling in the ground state is in some systems reduced or quenched by solid state effects. The value of the 3d spin-orbit coupling can be set between 0.0 and its atomic value (given as 1.0).

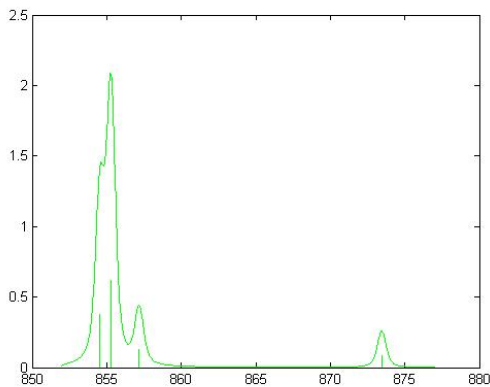


The $3d^9 \text{Cu}^{2+}$ atomic multiplet spectra, with the ground state 3d spin-orbit coupling set to zero (blue) and with the atomic 3d spin-orbit coupling (green).

Without the 3d spin-orbit coupling the $3d^9$ states with J -values of $J=5/2$ and $J=3/2$ are degenerate. Adding the atomic multiplet spectrum of $J=3/2$ yields two peaks with a ratio of 2:1, as there are no multiplet effects to modify this result.

Exercise 2.5:

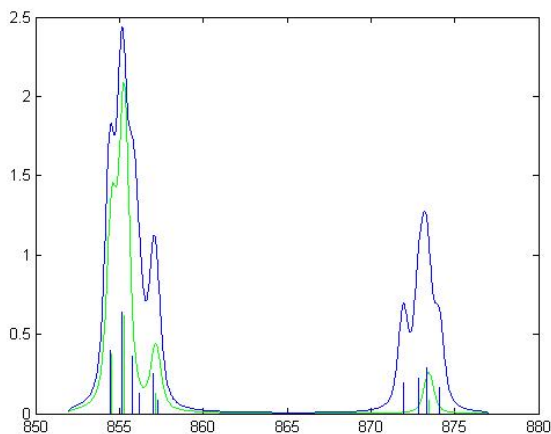
Calculate the atomic multiplet spectrum of $3d^8 \text{Ni}^{2+}$. Run CTM4XAS with the configuration Ni^{2+} and Autoplot ON, etc. Leave all other parameters at the provided default settings.



The $3d^8 \text{Ni}^{2+}$ atomic multiplet spectra.

The Ni^{2+} spectrum has 4 peaks. The Hunds rule ground state is 3F_4 . The final state has a $2p^5 3d^9$ configuration, which is equivalent to the $2p^1 3d^1$ configuration. A $J=4$ ground state can reach $J'=3, 4$ or 5 final states. There is no final state with $J'=5$, one with $J'=4$ and three with $J'=3$, yielding a total of 4 transitions.

If the 3d spin-orbit coupling in the ground state is set to zero, more peaks are allowed, due to the degeneracy of the 3F_4 , 3F_3 and 3F_2 ground states.



The $3d^8 \text{Ni}^{2+}$ atomic multiplet spectra with (green) and without (blue) 3d spin-orbit coupling.

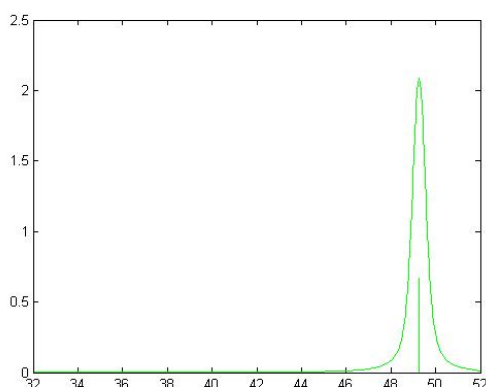
2.7 The 3p X-ray absorption spectra

With the button 3p the 3p X-ray absorption spectra are calculated.

Exercise 2.6:

Calculate the atomic multiplet spectrum of the 3p XAS spectrum of Ti^{4+}

Run CTM4XAS with the configuration Ti^{4+} , Button 3p ON and Autoplot ON. Leave all other parameters at the provided default settings.

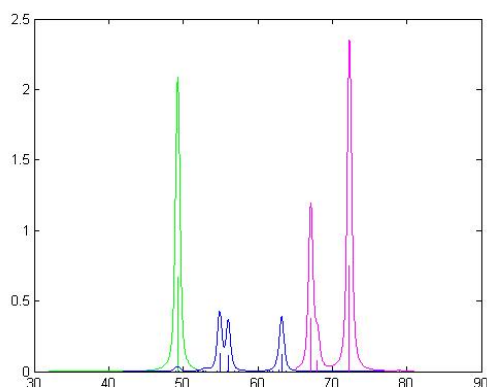


The atomic multiplet calculation of the 3p XAS spectrum of Ti^{4+} . Only one peak is visible. The other two peaks are too small to be visible on this scale; see figure with logarithmic scale on page 9.

Exercise 2.7:

Calculate the atomic multiplet spectrum of the 3p XAS spectrum of Mn^{4+} and Ni^{2+} .

Run CTM4XAS with the configuration Mn^{4+} (Ni^{2+}), Button 3p ON and Autoplot ON. Leave all other parameters at the provided default settings.



The atomic multiplet calculations of the 3p XAS spectrum of Ti^{4+} , Mn^{4+} and Ni^{2+} . The large 3p3d exchange interaction dominates over the small 3p spin-orbit coupling.

2.8 Appendix A: Finding the term symbols of configurations

We repeat some basic quantum mechanics concerning the quantum numbers and their nomenclature.

name	symbol	values (single electron)	values (two electrons)
Principal Quantum Number	n	$n_{(\max)} = \infty$ steps of 1 $n_{(\min)} = 1$	n_1, n_2^*
Azimuthal Quantum Number or Orbital Moment	L	$L_{(\max)} = n-1$ steps of 1 $L_{(\min)} = 0$	$L_{(\max)} = l_1 + l_2$ steps of 1 $L_{(\min)} = l_1 - l_2 $
Magnetic Quantum Number	m_L	$m_{L(\max)} = L$ steps of 1 $m_{L(\min)} = -L$	$m_{L(\max)} = L$ steps of 1 $m_{L(\min)} = -L$
Spin Quantum Number or Spin Moment	S	$1/2$	$S_{(\max)} = 1$ $S_{(\min)} = 0$
Spin Magnetic Quantum Number	m_s	$m_{S(\max)} = 1/2$ $m_{S(\min)} = -1/2$	$m_{S(\max)} = S$ $m_{S(\min)} = -S$
Total Quantum Number, or Total Moment	J	$J_{\max} = L + 1/2$ $J_{\min} = L - 1/2$	$J_{\max} = L + S$ steps of 1 $J_{\min} = L - S $
Total Magnetic Quantum Number	m_J	$m_{J(\max)} = J$ steps of 1 $m_{J(\min)} = -J$	$m_{J(\max)} = J$ steps of 1 $m_{J(\min)} = -J$

The main quantum number is not important for the angular symmetry of a state. For a single electron, the quantum numbers are indicated with the orbital moment L , the spin moment S of $1/2$ and total moment J , with two values $L+1/2$ and $L-1/2$. A term symbol is written as $^{2S+1}X_J$, where X corresponds to a letter according to the value of L . $X = s, p, d, f$ and g for $L = 0, 1, 2, 3$ and 4 . An s-electron has $L=0$ and only one J -value, equal to $+1/2$.

For a 2-electron configuration, similar rules apply. The maximum orbital moment L is equal to the addition of the two individual orbital moments, l_1 and l_2 . The same rule applies to the spin moment, implying that the spin moment of two electrons can be either 1 or 0. In case of multi-electron configurations there are more possibilities for the spin moment and the same rules for m_s apply as far m_l . In the absence of spin-orbit coupling, all terms with the same L and S have the same energy, giving an energy level that is $(2L+1)(2S+1)$ -fold degenerate. When spin-orbit coupling is important, the terms are split in energy according to their J -value with a degeneracy of $2J+1$. The quantity $2S+1$ is called the spin multiplicity of the term, and the terms are called singlet, doublet, triplet, quartet, etc. according to $S = 0, 1/2, 1, 3/2$, etc.

A single s electron has an orbital moment $L=0$, a spin moment $S=1/2$ and a total moment $J=1/2$. There is only one term symbol $^2S_{1/2}$. For one p electron, $L=1$, $S=1/2$, and J can be $1/2$ or $3/2$, corresponding to term symbols $^2P_{1/2}$ and $^2P_{3/2}$. Similarly a single d electron has term symbols $^2D_{3/2}$ and $^2D_{5/2}$ and a single f-electron $^2F_{5/2}$ and $^2F_{7/2}$. The degeneracy of these states is given by $2J+1$, which gives the well known 2:1 ratio for $^2P_{1/2}$ and $^2P_{3/2}$ (L_2 and L_3 edges) and 3:2 for $^2D_{3/2}$ and $^2D_{5/2}$ (M_4 and M_5 edges).

In the case of a transition metal ion, the important configuration for the initial state of the absorption process is $3d^n$. In the final state with a 3s or a 3p core hole, the configurations are $3s^1 3d^{n+1}$ and $3p^5 3d^{n+1}$. The main quantum number has no influence on the coupling scheme, so the same term symbols can be found for 4d and 5d systems, or for 2p and 3p core holes. In case of a $2p^2$ configuration, the first electron has six quantum states available, the second electron only five. This is due to the Pauli exclusion principle that forbids two electrons to have the same quantum numbers n , M_L and M_S . Because the sequence of the two electrons is not important, one divides the number of combinations by two and obtains fifteen possible combinations.

The m_l and m_s quantum numbers of the six 2p electrons are given as $|m_{la}, m_{sa}\rangle$ in this table:

$ 1, +\rangle$	$ 0, +\rangle$	$ -1, +\rangle$
$ 1, -\rangle$	$ 0, -\rangle$	$ -1, -\rangle$

One can create a 2-electron state by adding two of these $|m_{la}, m_{sa}\rangle$ combinations, for example $|1, +\rangle + |1, -\rangle$. This yields a state with $|M_L, M_S\rangle$ quantum numbers equal to $|2, 0\rangle$, i.e. $m_{l1} + m_{l2} = 1+1=2$ and $m_{s1} + m_{s2} = +1/2 + (-1/2) = 0$. The fifteen combinations of adding two 2p electrons are indicated in the table.

The 15 combinations of states $ m_{la}, m_{sa}\rangle$ and $ m_{lb}, m_{sb}\rangle$ of a $2p^2$ configuration. The fourth column counts the degeneracy of the total symmetry $ M_L, M_S\rangle$ states							
$ m_{la}, m_{sa}\rangle$	$ m_{lb}, m_{sb}\rangle$	$ M_L, M_S\rangle$	#	$ m_{la}, m_{sa}\rangle$	$ m_{lb}, m_{sb}\rangle$	$ M_L, M_S\rangle$	#
$ 1, +\rangle$	$ 1, -\rangle$	$ 2, 0\rangle$	1	$ 1, -\rangle$	$ -1, -\rangle$	$ 0, -1\rangle$	1
$ 1, +\rangle$	$ 0, +\rangle$	$ 1, 1\rangle$	1	$ 0, +\rangle$	$ 0, -\rangle$	$ 0, 0\rangle$	3
$ 1, +\rangle$	$ 0, -\rangle$	$ 1, 0\rangle$	1	$ 0, +\rangle$	$ -1, +\rangle$	$ -1, 1\rangle$	1
$ 1, +\rangle$	$ -1, +\rangle$	$ 0, 1\rangle$	1	$ 0, +\rangle$	$ -1, -\rangle$	$ -1, 0\rangle$	1
$ 1, +\rangle$	$ -1, -\rangle$	$ 0, 0\rangle$	1	$ 0, -\rangle$	$ -1, +\rangle$	$ -1, 0\rangle$	2
$ 1, -\rangle$	$ 0, +\rangle$	$ 1, 0\rangle$	2	$ 0, -\rangle$	$ -1, -\rangle$	$ -1, -1\rangle$	1
$ 1, -\rangle$	$ 0, -\rangle$	$ 1, -1\rangle$	1	$ -1, +\rangle$	$ -1, -\rangle$	$ -2, 0\rangle$	1
$ 1, -\rangle$	$ -1, +\rangle$	$ 0, 0\rangle$	2				

These fifteen $|M_L, M_S\rangle$ states can be put into a table collecting their overall M_L and M_S quantum numbers. This yields the following result:

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

It can be seen that there are three states with $|M_L, M_S\rangle = |0,0\rangle$, two states $|M_L, M_S\rangle = |1,0\rangle$ and $|-1,0\rangle$ and a number of other states. If one works out the symmetry properties of these states, one will find a number of so-called irreducible representations, or irrep. An irrep defines a single configuration with a defined L and S value. The energies of all the $|M_L, M_S\rangle$ states within an $|L, S\rangle$ irrep is the same. The rules on quantum numbers as outlined above apply also for irreps. This gives a lead to derive the irreps directly from the number of $|M_L, M_S\rangle$ states as given in the table. The presence of a $|2,0\rangle$ implies that this state is part of an irrep with L equal to, at least, 2. An irrep with L=2 has five states with M_L values between -2 and +2. The only associated M_S value is $M_S=0$, which implies that there is an irrep with $|L, S\rangle = |2,0\rangle$, which is a 1D term symbol.

One can remove these five states from the table and then one is left with ten states, containing $M_L = \pm 1$ and $M_S = \pm 1$. The next term symbol one finds has $|L, S\rangle = |1,1\rangle$, which is a 3P term symbol. A 3P term symbol has nine states and one is left with one additional state with $M_S = M_L = 0$. This state belongs to an $|L, S\rangle = |0,0\rangle$ term symbol, or 1S . We have found that the $2p^2$ configuration contains the terms 3P , 1D and 1S , with respective degeneracies of $3 \times 3 = 9$, $1 \times 5 = 5$ and $1 \times 1 = 1$. It can be checked that total degeneracy adds up to fifteen. Including J in the discussion we have the values 1D_2 , 1S_0 and 3P_2 plus 3P_1 plus 3P_0 . Focusing on the J-values, we have two J=0, one J=1 and two J=2 values. Because x-ray absorption calculations are carried out in intermediate coupling, the J-value is important; the total calculation is split into its various J-values.

Exercise 2.8:

- (a) determine the degeneracy for a $2p^3$ configuration
- (b) determine all LS term symbols
- (c) check that the degeneracies of the term symbols add up correctly.
- (d) determine the J values
- (e) count the degeneracies of the respective J states.

The term symbols of a $2p3p$ configuration do not have to obey the Pauli principle. There will be 6×6 is 36 combinations of terms. The term symbols can be determined directly from multiplying the individual term symbols. Multiplication of terms A and B is written as $A \otimes B$. Since both L and S are vectors, the resulting terms have possible values of $|L_A - L_B| \leq L \leq L_A + L_B$ and $|S_A - S_B| \leq S \leq S_A + S_B$. For $^2P \otimes ^2P$, this gives $L = 0, 1, 2$ and $S = 0$ or 1 . This gives the term symbols 1S , 1P , 1D and 3S , 3P and 3D . The respective degeneracies are 1, 3, 5 and 3, 9, 15 adding up to 36. Adding the J-values, one finds for the singlet states just a single J, i.e. 1S_0 , 1P_1 , 1D_2 . The triplet states each form three J-term symbols 3P_2 plus 3P_1 plus 3P_0 and 3D_3 plus 3D_2 plus 3D_1 . The 3S state has $L=0$, hence also only one J state as $3S_1$. We find two term symbols with J=0 (1S_0 and 3P_0), four with J=1, three with J=2 and one with J=3. The degeneracies can be checked by adding the $2J+1$ values, yielding $2 \times 1 + 4 \times 3 + 3 \times 5 + 1 \times 7 = 36$.

The LS term symbols for a $3d^1 4d^1$ configuration can be found similarly by "multiplying" the term symbols for the configurations $3d^1$ and $4d^1$. For $^2D \otimes ^2D$, this gives $L = 0, 1, 2, 3$ or 4 and $S = 0$ or 1 . The ten LS term symbols of the $3d^1 4d^1$ configuration are given in the table below, together with their degeneracy and possible J-values. The total degeneracy of the $3d^1 4d^1$ configuration is 100. In the presence of spin-orbit coupling, a total of eighteen term symbols are found.

Possible term LS term symbols for a $3d^1 4d^1$ configuration, with their degeneracy and possible J values.											
$3d^1 4d^1$	1S	1P	1D	1F	1G	3S	3P	3D	3F	3G	Σ
Deg.	1	3	5	7	9	3	9	15	21	27	100
J-values	0	1	2	3	4	1	0 1 2	1 2 3	2 3 4	3 4 5	2 4 4 4 3 1

Due to the Pauli exclusion principle, a $3d^2$ configuration does not have the same degeneracy as the $3d^1 4d^1$ configuration. In total there are $10 \times 9 / 2 = 45$ possible states. Following the same procedure as for the $2p^2$ configuration, one can write out all 45 combinations of a $3d^2$ configuration and sort them by their M_L and M_S quantum numbers. Analysis of the combinations of the allowed M_L and M_S quantum numbers yields the term symbols 1G , 3F , 1D , 3P and 1S . This is a sub-set of the term symbols of a $3d^1 4d^1$ configuration. The term symbols can be divided into their J-quantum numbers as 3F_2 , 3F_3 , 3F_4 , 3P_0 , 3P_1 , 3P_2 , 1G_4 , 1D_2 and 1S_0 .

In case of a $3d^3$ configuration a similar approach shows that the possible spin-states are doublet and quartet. By adding the degeneracies, it can be checked that a $3d^3$ configuration has 120 different states, i.e. $10 \times 9 / 2 \times 8 / 3$. The general formula to determine the degeneracy of a $3d^n$ configuration is:

$$\binom{10}{n} = \frac{10!}{(10-n)!n!} \quad (2.3)$$

One can show that the term symbols of a configuration $3d^n$ do also exist in a configuration $3d^{n+2}$, for $n+2 \leq 5$. Thus the term symbols of $3d^4$ contain all term symbols of $3d^2$ that contains the 1S term symbol of $3d^0$. Similarly the term symbols of $3d^5$ contain all term symbols of $3d^3$ that contains the 2D term symbol of $3d^1$. In addition there is a symmetry equivalence of holes and electrons, hence $3d^3$ and $3d^7$ have exactly the same term symbols.

Important for the $2p$ x-ray absorption edge are the configurations of the $2p^5 3d^n$ final states. The term symbols of the $2p^5 3d^n$ states are found by multiplying the configurations of $3d^n$ with a 2P term symbol. The total degeneracy of a $2p^5 3d^n$ state is given in equation 2.4. For example, a $2p^5 3d^5$ configuration has 1512 possible states. Analysis shows that these 1512 states are divided into 205 term symbols, implying in principle 205 possible final states. If all these final states have finite intensity then depends on the selection rules.

$$6 \times \binom{10}{n} = 6 \times \frac{10!}{(10-n)!n!} \quad (2.4)$$

2.9 Appendix B: Using the RCN program

One can calculate the atomic parameters from an additional program RCN2 that we did not discuss till now. With the use of the RCN2 program one can calculate any element and any transition in the periodic table. The only information needed is the atomic number and the initial state and final state configurations. We will use Ti^{4+} as an example.

```
22 -9      2   10  1.0    5.E-06    1.E-09-2    130    1.0  0.65  0.0 0.50 0.0  .70
22      Ti4+ 2p06 3d00          2P06 3D00
22      Ti4+ 2p05 3d01          2P05 3D01
-1
```

The `als3ti4.rcn` input file contains four lines. We will skip the function of the first line for the moment. In case of XAS calculations, it is always the same. The second line contains first the atomic number followed by a name of the initial state Ti^{4+} 2p06 3d00. Behind it the initial state configuration 2p63d0 is given for a second time as 2P06 3D00. This command is used by the program. The third line repeats the input for the final state configuration $2p^53d^1$. One can run the RCN2 program by the command `rcn2 als3ti4`. This will yield an out file `als3ti4.rcf`. This file should be modified to `als3ti4.rcg` by hand. Below it will be explained what must be changed in the `als3ti4.rcf` file to be used in the RCG2 and RAC2 programs.

If one would like to calculate Ni^{2+} instead of Ti^{4+} , the `als3ni2.rcn` file changes as follows:

```
22 -9      2   10  1.0    5.E-06    1.E-09-2    130    1.0  0.65  0.0 0.50 0.0  0.70
28      Ni2+ 2p06 3d08          2P06 3D08
28      Ni2+ 2p05 3d09          2P05 3D09
-1
```

Running the TTCN program with `rcn2 als3ni2` yields again an output file `als3ni2.rcf`.

If one would like to calculate the atomic multiple spectrum the `als3ti4.rcf` file does not have to be modified and it can just be renamed to `als3ti4.rcg`. Running the RCG2 program with the command `rcg2 als3ti4` will yield an out file `als3ti4.org` that contains the atomic multiplet spectrum, similar to the case of La^{3+} . The general scheme for the atomic multiplet calculation of a Ti^{4+} ion is given below.

2.10 Appendix C: Turning off atomic interactions

This is only possible using the original programs in the command prompt.

- Open the command prompt
(click "START", then "Run" and type "cmd")
- Go to the directory c:xxxxx

To print all results of the calculation, one has to change a single number in the `als3ti4.rcg` file. Below we show the file and in `green` the modified number, which must be changed from a 9 to a 6. This will not affect the atomic spectrum; it will just print the energy matrix, the eigen values and the eigen vectors. With these numbers one can create the complete table as given above. The file `als3ti4.rcg` has been modified and will yield a file `als3ti4.org` that contains all this information. Note that in case of a calculation with a larger number of states, printing the energy matrices and the eigen vectors will yield enormous files.

```

10      1      0      00      4      4      1      1 SHELL00000000 SPIN00000000 INTER8
0
1      2 1 12 1 10      00      6 00000000 0 8065.4790 .00      1
P 6 S 0
P 5 D 1
Ti4+ 2p06 3d00      1      0.0000      0.0000      0.0000      0.0000      0.0000HR99999999
Ti4+ 2p05 3d01      6 464.8110      3.7762      0.0322      6.3023      4.6284HR99999999
2.6334
Ti4+ 2p06 3d00      Ti4+ 2p05 3d01      -0.26267( 2P//R1// 3D) 1.000HR 38-100
-99999999.
-1

```

The atomic energy matrix consists of terms related to the two-electron Slater integrals ($H_{ELECTRO}$) and the spin-orbit couplings of the 2p (H_{LS-2p}) and the 3d electrons (H_{LS-3d}):

$$H_{eff} = H_{ELECTRO} + H_{LS-2p} + H_{LS-3d}$$

$$H_{ELECTRO} = \left\langle 2p^5 3d^1 \left| \frac{e^2}{r_{12}} \right| 2p^5 3d^1 \right\rangle$$

$$H_{LS-2p} = \left\langle 2p \left| \zeta_p l_p \cdot s_p \right| 2p \right\rangle$$

$$H_{LS-3d} = \left\langle 3d \left| \zeta_d l_d \cdot s_d \right| 3d \right\rangle$$

Exercise 1.9:

Repeat the multiplet calculation for Ti^{4+} for the following conditions:

- (a) All final state interactions are set to zero: $H = 0$
- (b) The 2p spin-orbit coupling is included: $H = H_{LS-2p}$
- (c) The Slater-Condon parameters are included: $H = H_{ELECTRO}$
- (d) The 2p spin-orbit coupling and Slater-Condon parameters are included: $H = H_{ELECTRO} + H_{LS-2p}$
- (e) The 3d spin-orbit coupling is included: $H = H_{ELECTRO} + H_{LS-2p} + H_{LS-3d}$.

The file `als3ti4.rcg` has been modified to `als3ti4a.rcg` and all the final state interactions are set to zero, except the final state energy of 464.811 eV. The printing command has been set to 6, which will show all energy matrixes, the eigen values and the eigen vectors. One observes that all energy matrices are diagonal with 464.811 on the diagonal axis and all other interactions zero. Consequently all eigen values are equal to 464.811 and all eigenvectors are diagonal with 1.0 on the diagonal and 0.0 elsewhere.

The output file `als3ti4a.org` contains for J=1 the following line.

```
1 ENERGY MATRIX ( LS COUPLING) J= 1.0
```

```

      1      1      1
      (2P) 3D (2P) 3P (2P) 1P (
      1      2      3
1 (2P) 3D 1 464.811 0.000 0.000
1 (2P) 3P 2 0.000 464.811 0.000
1 (2P) 1P 3 0.000 0.000 464.811
```

```
STAMP at 0.020 min
```

```
0 EIGENVALUES (J= 1.0)
```

```

      464.811 464.811 464.811
CONFIG. NO.
```

```
G-VALUES
```

```

      0.499 1.501 1.000
```

```
EIGENVECTORS ( LS COUPLING)
```

```

      1      P05 3D P05 3D P05 3D
      (2P) 3D (2P) 3P (2P) 1P (
1 (2P) 3D 1 1.00000 0.00000 0.00000
1 (2P) 3P 2 0.00000 1.00000 0.00000
1 (2P) 1P 3 0.00000 0.00000 1.00000
```

```
PURITY=1.000 1.00000 1.00000 1.00000
```

The results of the 2p x-ray absorption spectrum can be given with two 3x3 matrices. The energy matrix are labelled from top to bottom '3D', '3P' and '1P' states, indicating the approximate term symbol related to the state. The original term symbols ³P, ³D and ¹P are given in respectively the first

row, second row and bottom row of the eigenvector matrix. The intensity of the states is indicated in boldface; it is given by the 1P state as the other two states have no intensity in LS coupling.

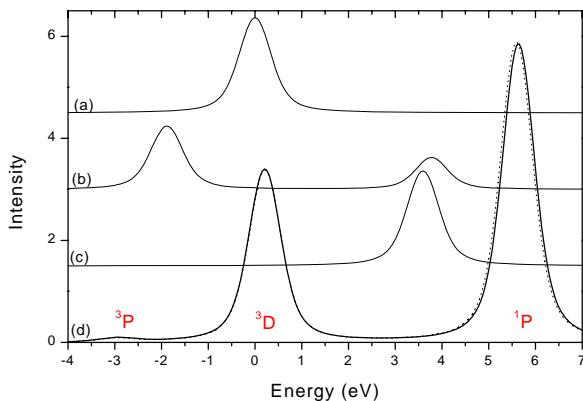


Figure: The effects of the Slater-Condon parameters and the spin-orbit coupling on the atomic multiplet spectrum of a $3d^0$ system. (a) no interactions, (b) only 2p spin-orbit, (c) only Slater-Condon, (d) both Slater-Condon and 2p spin-orbit (solid). The dashed line includes the 3d spin-orbit coupling.

Inclusion of the 2p spin-orbit coupling H_{LS-2p} of 3.776 eV creates non-diagonal elements in the energy matrix. In other words the LS-character of the individual states is mixed. In case only 2p spin-orbit coupling is included the result is rather simple, with the triplet states at $-1/2\zeta_p$ ($464.811 - 1/2 \cdot 3.776 = 462.923$) and the singlet state at $+\zeta_p$ (468.587). This relates to a pure jj-coupling scheme. The eigenvector matrix shows that the three states are mixtures of the three pure states. The intensities of the three states are given by the square of percentage of 1P_1 character, which is given in the bottom line of the eigen vectors (in green). The square of these numbers are respectively 0.533, 0.134 and 0.333. The first two states are degenerate and adding the two intensities yields 0.666. This gives the familiar result that the triplet states, or $2p_{3/2}$ states, have twice the intensity of the singlet, or $2p_{1/2}$, states. This has also been indicated in Figure 2.3.

```
(part of als3ti4b.org)
.
      (2P) 3D  (2P) 3P  (2P) 1P  (
      1      2      3
1 (2P) 3D  1  465.755   1.635   2.312
1 (2P) 3P  2    1.635  463.867   1.335
1 (2P) 1P  3    2.312   1.335  464.811
.
0 EIGENVALUES      (J= 1.0)
      462.923  462.923  468.587
.
EIGENVECTORS      (      LS COUPLING)
      1      P05 3D  P05 3D  P05 3D
      (2P) 1P  (2P) 3P  (2P) 3D  (
1 (2P) 3D  1  -0.67098  0.22312 -0.70711
1 (2P) 3P  2   0.12977 -0.90360 -0.40826
1 (2P) 1P  3   0.73003  0.36569 -0.57734
```

Next we include only the pd Slater-Condon parameters, keeping the 2p spin-orbit coupling zero. The Slater-Condon parameters are reduced to 80% of their atomic Hartree-Fock values and F^2 , G^1 and G^3 are respectively 5.042 eV, 3.702 eV and 2.106 eV. This gives the three states at respectively 463.466, 465.482 and 468.402 eV (in green). Only the 1P_1 state has a finite intensity and its energy is shifted to an energy of 468.402 eV as indicated in figure 2.3. The two other states have zero intensity. It can be seen that the pd Slater-Condon parameters are diagonal in the LS-terms, hence the three states are pure in character.

```
(part of als3ti4c.org)
.
      (2P) 3D  (2P) 3P  (2P) 1P  (
      1      2      3
1 (2P) 3D  1  465.482    0.000    0.000
1 (2P) 3P  2    0.000  463.466    0.000
1 (2P) 1P  3    0.000    0.000  468.402
.
0 EIGENVALUES      (J= 1.0)
      463.466  465.482  468.402
.
EIGENVECTORS      (      LS COUPLING)
      1      P05 3D  P05 3D  P05 3D
      (2P) 3P  (2P) 3D  (2P) 1P  (
1 (2P) 3D  1  0.00000  1.00000  0.00000
1 (2P) 3P  2  1.00000  0.00000  0.00000
1 (2P) 1P  3  0.00000  0.00000  1.00000
```

Above we have seen that the non-diagonal terms of the 2p spin-orbit coupling makes that all three states are mixtures of the individual term symbols. 2p spin-orbit coupling by itself creates the 2:1 intensity ratio, thereby shifting most of the 1P character to lower energy. In als3ti4c.org it was found that the Slater-Condon parameters shift the 1P state to higher energy and that the triplet states have a considerably lower energy. If one includes both the 2p spin-orbit coupling and the pd Slater-Condon parameters, the result will depend on their relative values. In case of the 2p core hole of Ti^{IV} , the Slater-Condon parameters are relatively large and most intensity goes to the $2p_{1/2}$ state. The triplet states are separated by 3 eV and the lowest energy state is extremely weak, gaining less than 1 % of the total intensity, i.e. $0.08946 \times 2 = 0.008$. Figure 2.3d shows the typical spectral shape with three peaks. In the next section we compare four similar spectra with different ratios of Slater-Condon parameters and core hole spin-orbit couplings to show the variations in their spectral shapes.

(part of als3ti4d.org)						
	1	1	1			
	(2P) 3D	(2P) 3P	(2P) 1P	(
	1	2	3			
1 (2P) 3D 1	466.426	1.635	2.312			
1 (2P) 3P 2	1.635	462.522	1.335			
1 (2P) 1P 3	2.312	1.335	468.402			
.						
0 EIGENVALUES	(J= 1.0)					
.						
	461.886	465.019	470.446			
.						
EIGENVECTORS	(LS COUPLING)					
1	P05 3D	P05 3D	P05 3D			
	(2P) 3P	(2P) 3D	(2P) 1P	(
1 (2P) 3D 1	0.29681	-0.77568	0.55698			
1 (2P) 3P 2	-0.95074	-0.18539	0.24845			
1 (2P) 1P 3	0.08946	0.60328	0.79250			

For completeness we include in the final calculation also the 3d spin-orbit coupling. Because the 3d spin-orbit coupling is only 32 meV, its influence on the spectral shape is negligible in the present case. The energy positions shift respectively by -39 meV, +5 meV and -41 meV. The intensities are also slightly affected. It is noted that the GROUND STATE 3d spin-orbit coupling can have very significant effects on the spectral shape in those cases where the 3d-shell is partly filled.

(part of als3ti4d.org)						
	1	1	1			
	(2P) 3D	(2P) 3P	(2P) 1P	(
	1	2	3			
1 (2P) 3D 1	466.386	1.649	2.293			
1 (2P) 3P 2	1.649	462.498	1.301			
1 (2P) 1P 3	2.293	1.301	468.402			
.						
0 EIGENVALUES	(J= 1.0)					
.						
	461.857	465.024	470.405			
.						
EIGENVECTORS	(LS COUPLING)					
1	P05 3D	P05 3D	P05 3D			
	(2P) 3P	(2P) 3D	(2P) 1P	(
1 (2P) 3D 1	0.30391	-0.77467	0.55455			
1 (2P) 3P 2	-0.94915	-0.19596	0.24641			
1 (2P) 1P 3	0.08222	0.60123	0.79483			

2.11 Appendix D: The M_{4,5} edge in La³⁺

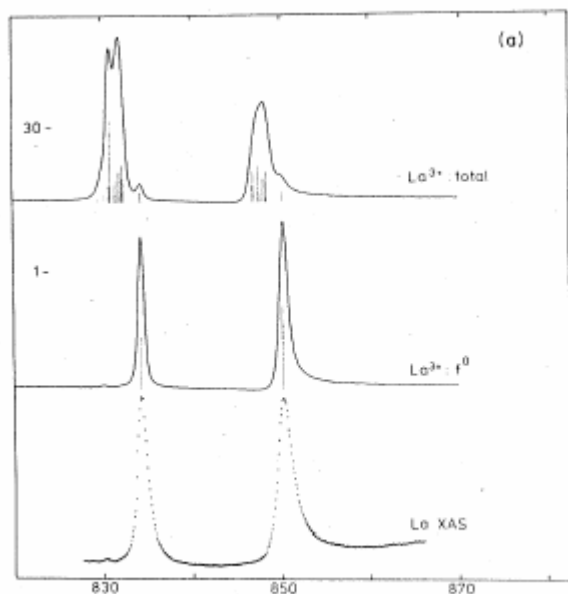
We start with the description of the M₄₅ edge of La³⁺, for example in La₂O₃. In this closed shell system, the 3d x-ray absorption process excites a 3d core electron into the empty 4f shell and the transition can be described as 3d¹⁰4f⁰ → 3d⁹4f¹. We will at first only look at the symmetry aspects of the problem. The 3d¹⁰4f⁰ ground state contains only completely filled or completely empty shells and as such has ¹S₀ symmetry. That is, all its quantum numbers are zero, S=0, L=0, J=0. This automatically means that all magnetic moments are zero too.

We next have to determine all term symbols in the final state. Because there is again a single 4f electron (with term symbol ²F) and a single 3d hole (with term symbol ²D), we have to multiply ²D ⊗ ²F. For the spin this gives singlet S=0 states and triplet S=1 states. The maximum L value is given by (l_{3d}=2) + (l_{4f}=3) = 5. The minimum L value is |(l_{3d}=2) - (l_{4f}=3)| = 1. Thus L takes any value from 5, 4, 3, 2 or 1. This gives as term symbols ¹P₁, ¹D₂, ¹F₃, ¹G₄, ¹H₅ and ³P₀₁₂, ³D₁₂₃, ³F₂₃₄, ³G₃₄₅, ³H₄₅₆. Here we use ³H₄₅₆ as shorthand notation of ³H₄ plus ³H₅ plus ³H₆. The overall degeneracies of the singlet term symbols are respectively 3, 5, 7, 9 and 11, in total 35. The overall degeneracies of the triplet states are 3x35 = 105, adding up to 140 in total, confirming the 10x14 possibilities of adding a 3d and a 4f electron.

3d ¹ 4f ¹	¹ H	¹ P	¹ D	¹ F	¹ G	³ H	³ P	³ D	³ F	³ G	Σ
Deg.	11	3	5	7	9	33	9	15	21	27	140
J-values	5	1	2	3	4	4 5 6	0 1 2	1 2 3	2 3 4	3 4 5	1 3 4 4 3 1

Note that the difference between the term symbols of 3d¹4d¹ and 3d⁹4f¹ are small, essentially the replacement of ¹S and ³S by ¹H and ³H. The degeneracies in J are important because the x-ray absorption calculations are always performed in intermediate coupling, i.e. the degeneracies in J set the sizes of the sub-matrices to be diagonalised. The reason behind this is the large core hole spin-orbit coupling that makes any LS-nomenclature impossible for the final states.

The important next step is to realize the dipole selection rules. If one works in intermediate coupling, only the J-selection rule matters. This rule states that J is changed by −1, 0 or +1 with respect to the initial state J, with the addition that if J is zero in the initial state it cannot be zero in the final state. J can also not be negative, so for a 3d¹⁰4f⁰ ¹S₀ ground state, the only allowed final state values of J is 1. Looking into the table this implies that there are only three allowed final states: ¹P₁, ³P₁ and ³D₁. This means that the M_{4,5} x-ray absorption spectrum of La₂O₃ can have a maximum of only three peaks.



The figure above shows a calculation of the 3d x-ray absorption spectrum of La_2O_3 , from the original paper of Theo Thole and coworkers attached as [thole85a.pdf](#).

```

10  1  0  00  4  4  1  1 SHELL00000000 SPIN00000000 INTER8
0                                     80998080          8065.47800      0000000
1    2 1 12 1 10          00          9 00000000 0 8065.4790 .00      1
D10  S 0
D 9  F 1
La³⁺ 3D10 4F00      1      0.0000      0.0000      0.0000      0.0000      0.0000HR99999999
La³⁺ 3D09 4F01      8      841.4990      6.7992      0.0922      7.0633      3.1673HR99999999
      4.7234      2.7614      1.9054
La³⁺ 3D10 4F00      Dy³⁺ 3D09 4F01      -0.24802( 3D//R1// 4F) 1.000HR 34-100
      -99999999.
-1

```

To calculate the spectrum of La^{3+} , we use the input file [als2la3.rcg](#). Lines 4 and 5 contain the initial state and final state configurations. Line 6 contains all initial state parameters. In the present case, there is only one parameter, the energy set to 0.0000 eV. Lines 7 and 8 contain the final state parameters. For a $3d^9 4f^1$ configuration there are 8 parameters, respectively the final state energy 841.499, the 3d spin-orbit coupling of 6.799 and the 4f spin-orbit coupling of 0.092 eV. Then follow five 3d4f Slater-Condon parameters (more details later).

After running RCG2 with the command [rcg2 als2la3](#), one obtains (in a fraction of a second) the [als2la3.org](#) output file. This file contains all information on the calculation, including the atomic x-ray absorption spectrum. The lines of this output file run over 132 characters and below the relevant part of the output is given, where the part in italic should be read behind the line above it. The calculation gives first all possible transitions (in blue), in the present case only from $J=0.0$ to $JP=1.0$, where J is used for the initial state, JP for the final state. The column J - JP gives the number of transitions, three as we worked out from term symbols above. The main part of the calculation is the diagonalization of the final state matrices, in the present case these are all small, with a size between 1 and 4 as found from the degeneracies of the JP states.

The output file then gives for each atomic transition, its initial state energy (= 0.0000) and J value (=0.0). The configuration is then approximated as good as possible in LS-terms. For the initial state this is exact and one finds 1S. In brackets before that the symmetry of only the 3d core electrons is given, in this case also (1S). The final state energy is given as EP and the energy difference with the ground state as DELTA E. In the present case both numbers are identical, as the initial state energy is 0.0000. Then follow a number of ways to express the intensity. The intensity is proportional to the number S/PMAX**2. We find (in red) the three intensities of the transitions to the final states. The symmetries of these states are given with CONFP and all 3d symmetries are (2D). The final state configurations, are respectively 3P, 3D and 1P. These names are determined from the largest fraction of each term symbol. Final states are mixed combinations of term symbols and are not pure term symbol states. This will be explained in more detail in example 3.

		NO. OF LINES									
J	JP	J-JP	TOTAL	KLAM	ILOST						
0.0	1.0	3	3	3000	0						
1											
ELEC DIP SPECTRUM											
(ENERGIES IN UNITS OF 8065.5 CM-1 = 1.00 EV)											
1	DY ³⁺	3D10	4F00	---	DY ³⁺	3D09	4F01				
0											
E	J	CONF	EP	JP	CONFP	DELTA E					
LAMBDA(A)	S/PMAX**2	GF	LOG GF	GA(SEC-1)	CF,BRNCH						
1	0.0000	0.0	1 (1S)	1S	833.2133	1.0	1 (2D)	3P	833.2133		
14.8804	0.00690+	0.0087	-2.062	2.611E+11	1.0000						
2	0.0000	0.0	1 (1S)	1S	837.4330	1.0	1 (2D)	3D	837.4330		
14.8054	0.80480+	1.0157	0.007	3.091E+13	1.0000						
3	0.0000	0.0	1 (1S)	1S	854.0414	1.0	1 (2D)	1P	854.0414		
14.5175	1.18829+	1.5294	0.185	4.840E+13	1.0000						

The M_{4,5} XAS spectrum of La₂O₃ is then generated from this output file by taking the energies DELTA E and the S/PMAX**2 values for the intensities. This generates a so-called stick spectrum. To compare with an experimental spectrum, we add again the lifetime broadening as Lorentzians and the experimental resolution as Gaussian. In the generated figure we use Lorentzians of 0.2 for the M₅ edge and 0.4 for the M₄ edge, plus a Gaussian of 0.25. M_{4,5} spectra of rare earths have a special feature, which is there asymmetry of the M₄ edge. All rare earth M_{4,5} edge spectra have a symmetric M₅ edge and an asymmetric M₄ edge. The reason is that the M₄ edge can interact with the continuum of the M₅ edge. This gives rise to so-called Fano lineshapes, which can be understood as asymmetric Lorentzians. We use a Fano parameter of nine for the M₄ edge of Lanthanum. More details on the Fano lineshape in thole85a.pdf and the book of Cowan [ref].

We will introduce the plotting program PLO2. With this program one can collect the required information from the output files of the multiplet calculations. In case of an atomic multiplet calculation the output can be found in an *.org file, in this case the als2la3.org file. The file used for plotting is called als2la3.plo and with the command plo2 als2la3 it is executed. The file is explained below.


```

1  postscript la3.ps
2  portrait
3  energy_range 830 865
4  columns_per_page 1
5  rows_per_page 2
6  frame_title La 3dXAS
7  lorentzian 0.2 999. range 0 845
8  lorentzian 0.4 9.   range 845 999
9  gaussian 0.25
10 rcg9 la3.org
11 spectrum
12 end

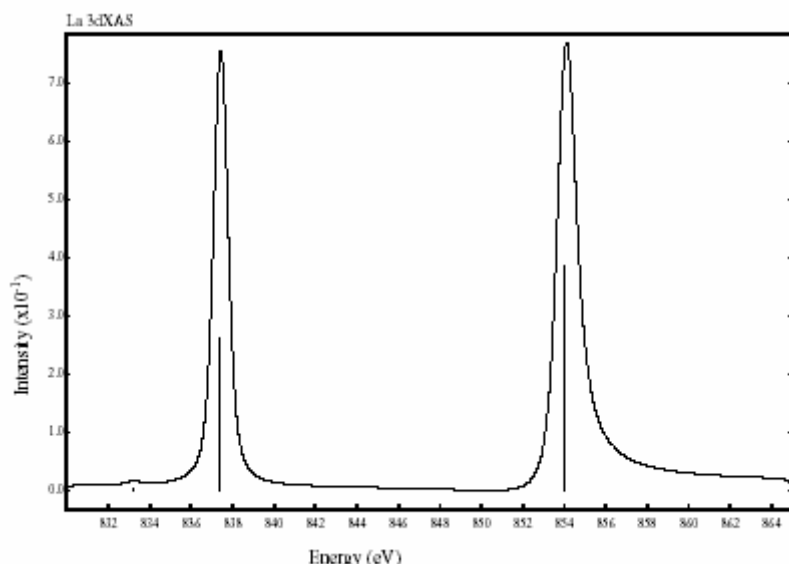
```

- ⊗ Line 1 gives the way the output is produced. There are two important options, postscript gives a postscript file with the name as given behind la3.ps. The postscript file can be plotted and/or watched on screen. Depending on available software, one could first transfer the postscript file to a PDF file, etc. An important alternative is the command xy, which yields an xy-file. For example the command xy la3.xy 500 gives an xy-file with the name la3.xy and 501 points. This is useful if one would like to use the output in plotting programs to compare with experiments. The xy-file contains the broadened spectrum with the number of points as requested (501 in this case), followed by an empty line, a line with the word 'sticks', followed by all individual original stick results, i.e. energies plus intensities.
- ⊗ Line 2 determines that the page has a portrait orientation; the alternative is landscape.
- ⊗ Line 3 determines the energy range. If this line is omitted, the program will determine an appropriate energy range. In case of new calculations, it is useful to first run the plotter program without an energy range, let the program decide the range and then adapt it to make a final spectrum. Once an energy range is set for a certain edge, it can always be kept the same.
- ⊗ Line 4 defines the number of columns per page and line 5 the number of rows per page. These commands thus allow on a single page to plot multiple (rows x columns) spectra. This is a useful command if one runs a number of simulations and plots them on a single page. In later examples we will use this also to plot spectra at various temperatures, plot the combined XAS, MCD and MLD spectra, compare the ground state to excited states, etc.
- ⊗ Line 6 defines the title that is given above each frame.
- ⊗ Line 7 defines the Lorentzian broadening for the M_5 edge with a hwhm of 0.2 eV, a Fano parameter of 999. This broadening is applied to the range from 000 eV to 845 eV. A large Fano parameter turns the Fano lineshape into a perfect Lorentzian.
- ⊗ Line 8 repeats the broadening for the M_4 edge. It is convenient to always use for the ranges 000 to EB, respectively EB to 999, where EB is the binding energy of the core state. In this way, one never forgets a line, assuming that the core state lies between zero and 1000 eV. Effectively it defines the binding energy as the border between the M_5 and M_4 edge. This issue is important in case of X-MCD and its related sum rules. This will be discussed in section 7.
- ⊗ Line 9 defines the Gaussian broadening.
- ⊗ Line 10 defines the file name that contains the results of the calculation. In case of atomic multiplets, one reads the input with the command rcg9. In case of crystal field calculations, the command is old_racah and in case of charge transfer calculations the command is band.
- ⊗ Line 11 gives the command spectrum. This generates the actual spectrum in the plot. Many options are possible here. They will be discussed in later examples. An example is the

command spectrum temp 300, which will give the spectrum at 300 Kelvin. Default is zero Kelvin.

☒ Line 12 defines the end of the file.

The scheme above shows the program overview for the atomic multiplet calculation of La^{3+} . We have skipped the crystal field program and directly plot the output of the atomic multiplet program



The result of this plotting program is given above. One finds the three peaks, essentially two big peaks, the M_5 edge at 837 eV and the M_4 edge at 854 eV. In addition, a small pre-edge is visible at 833 eV. From the output file we found that the M_4 edge relates to a 1P_1 state, the M_5 edge to a 3D_1 state, and the pre-edge to a 3P_1 state.

We next turn to the $N_{4,5}$ XAS edge of La. The $4f^0$ to $4d^9 4f^1$ transition has exactly the same symmetry properties as the $M_{4,5}$ edge. So, we again expect three peaks related to the 1P_1 , 3D_1 and 3P_1 states. We compare the parameters of the 3d edge with the 4d edge in the table on the right.

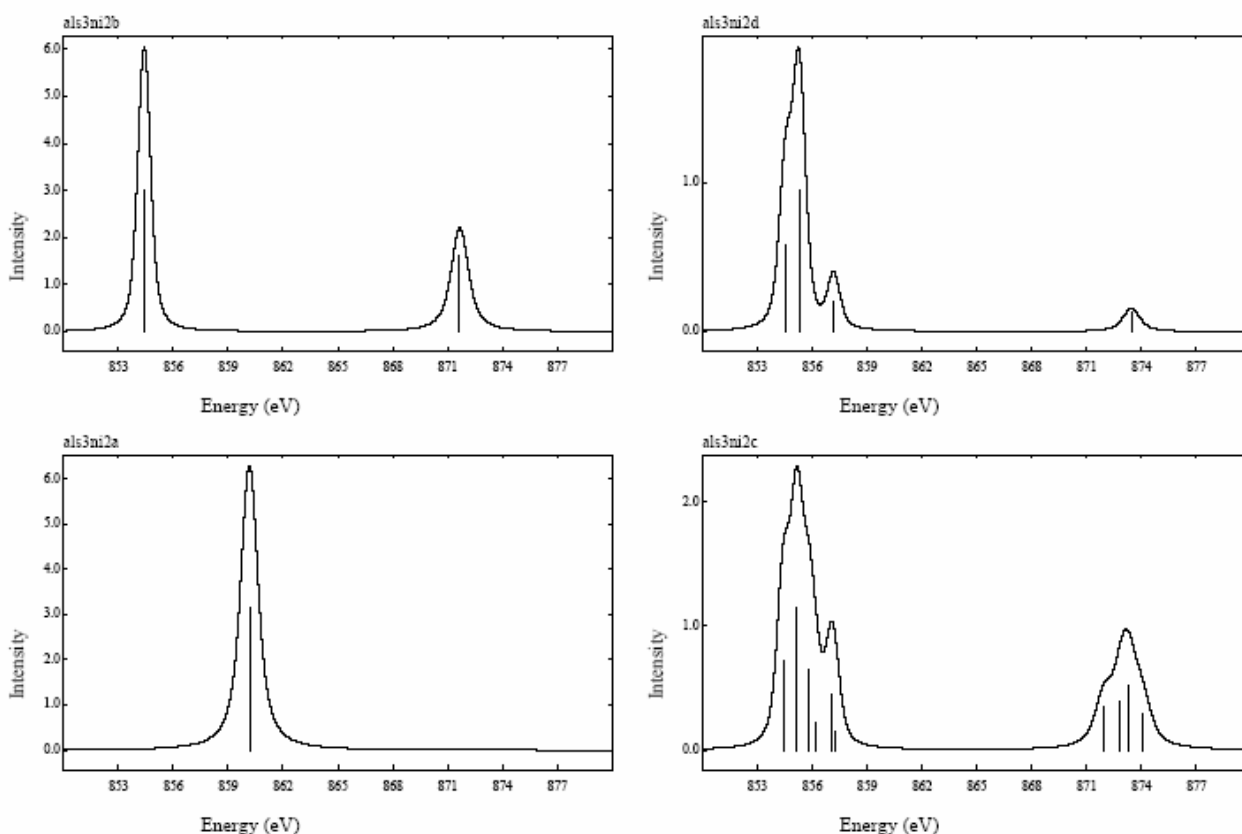
- The 4d binding energy is only 103 eV.
- The 4d spin-orbit coupling is only 1.1 eV, implying that the splitting between the N_5 and N_4 edge is only 2.7 eV.
- The Slater-Condon parameters are much larger for the 4d4f interaction, implying that the energy separations between different (spin) states will be much larger for the $N_{4,5}$ edge.
- Looking at the intensities, one finds small pre-edges for both the $M_{4,5}$ and $N_{4,5}$ edge, but where the $M_{4,5}$ edge has an intensity ratio of 0.8:1.2, more than 99% of the intensity of the N_5 edge goes to the N_4 edge. In fact both the pre-edge and the N_5 edge will be very small.

Edge	La 3d	La 4d
Average Energy (eV)	841.00	103.00
Core spin-orbit (eV)	6.80	1.12
F_{df}^2 Slater-Condon (eV)	4.72	12.42
<u>Intensities:</u>		
Pre-peak	0.01	10^{-3}
$p_{3/2}$ or $d_{5/2}$	0.80	0.01
$p_{1/2}$ or $d_{3/2}$	1.19	1.99

2.12 Appendix E: Atomic multiplet calculations for Ni^{2+}

We repeat the multiplet calculation for Ni^{2+} for the following conditions:

- The file `als3ni2a.rcg` calculates the case that all initial state and final state interactions are set to zero.
- The file `als3ni2b.rcg` calculates the case that the 2p spin-orbit coupling is included.
- The file `als3ni2c.rcg` calculates the case that the Slater-Condon parameters are included.
- The file `als3ni2d.rcg` calculates the case that the 3d spin-orbit coupling is added in the initial state. This yields the full Ni^{2+} calculation.

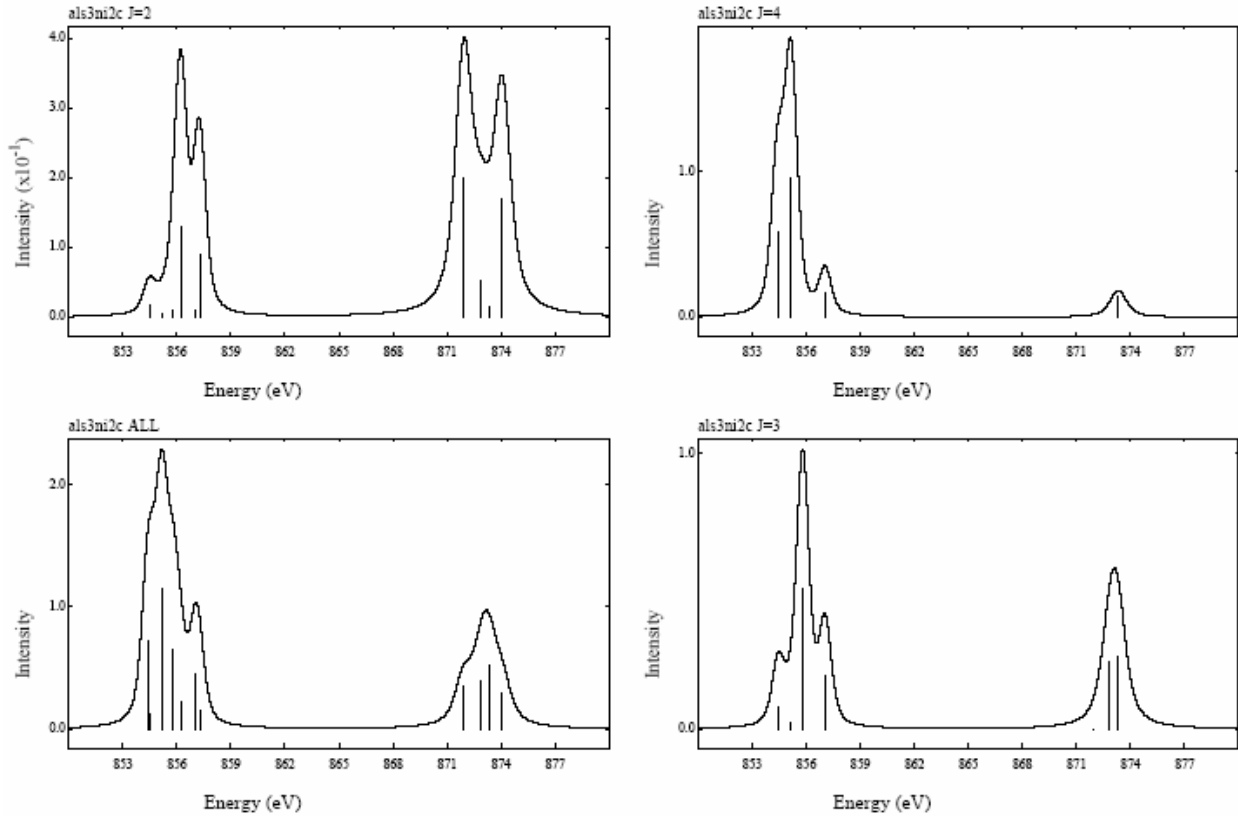


If all initial state and final state interactions are set to zero, one observes a single line (als3ni2a). This line is split into an L_3 edge and an L_2 edge by the spin-orbit coupling (als3ni2b). The introduction of multiplets generate a whole series of peaks (als3ni2c). These peaks are due to transitions of the $3F$ ground state to all possible final states that are allowed by the dipole selection rules. Introducing the 3d spin-orbit coupling in the initial state selects a few of the $4F$ states; in fact the new ground state is 3F_4 and the $J=4$ ground state can make a transition to $J=3$, $J=4$ and $J=5$ final states. In the discussion of Ti^{4+} ions, we showed that there are three $2p^5 3d^1$ final state with $J=3$ and one with $J=4$. The same applies to a $2p^5 3d^9$ final state, which explains the 4 peaks.

The file `als3ni2cj.plo` selects the different J-values in the initial state and plots their spectra individually. This is done by the following lines:

```
frame_title als3ni2c J=2
spectrum istate 2
```

The addition `istate 2` behind `spectrum` indicates that only those ground states with J equal to 2 have to be included in the figure. If the command `istate` is not included all J states will be chosen automatically.

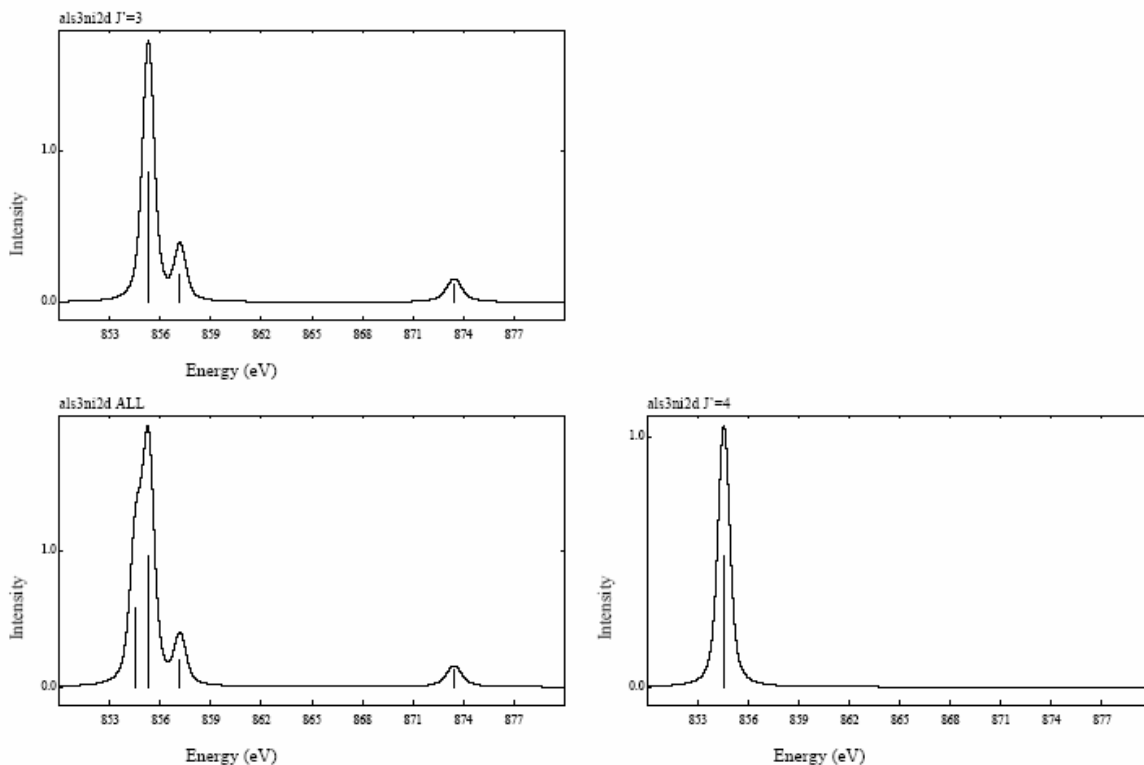


One observes that the spectra for J=2, J=3 and J=4 are quite distinct. One finds that the J=4 ground state mainly is excited to the L₃ edge, while the J=2 ground state has a larger L₂ edge.

The file `als3ni2dj.plo` selects the different J' -values in the final state and plots their spectra individually. This is done by the following lines:

```
frame_title als3ni2d J'=3
spectrum fstate 3
```

The addition `fstate 3` behind `spectrum` indicates that only those final states with J' equal to 3 have to be included in the figure. If the command `fstate` is not included all J' states will be chosen automatically.



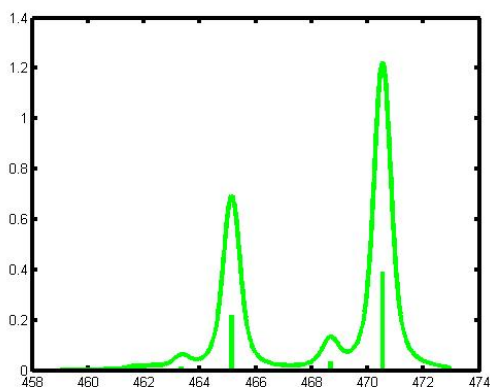
One observes that the complete 2p XAS spectrum of a Ni^{2+} ion with its 3F4 ground state, is split into a spectrum with 3 lines related to a final state J' value of 3 and a spectrum with one line related to a final state J' value of 4. Note that if one asks for a final state that is not available (`fstate 5`), no spectrum is plotted.

3 Crystal Field Multiplet Calculations

3.1 $3d^0$ systems in octahedral symmetry

Exercise 3.1:

Calculate the crystal field multiplet spectrum of the 2p XAS experiment of Ti^{4+} .
Run CTM4XAS with the configuration Ti^{4+} and Autoplot ON.
Add a cubic crystal field value $10Dq$ of 1.0 eV.
Leave all other parameters at the provided default settings.



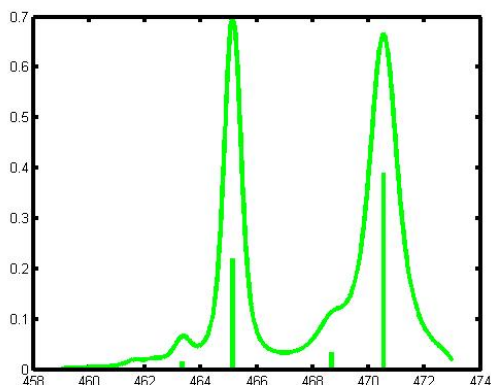
Crystal field multiplet calculation of the 2p XAS spectrum of Ti^{4+}

The plotting section of CTM4XAS allows for a different broadening of the L_2 part of the spectrum with respect to the L_3 part.

Exercise 3.2:

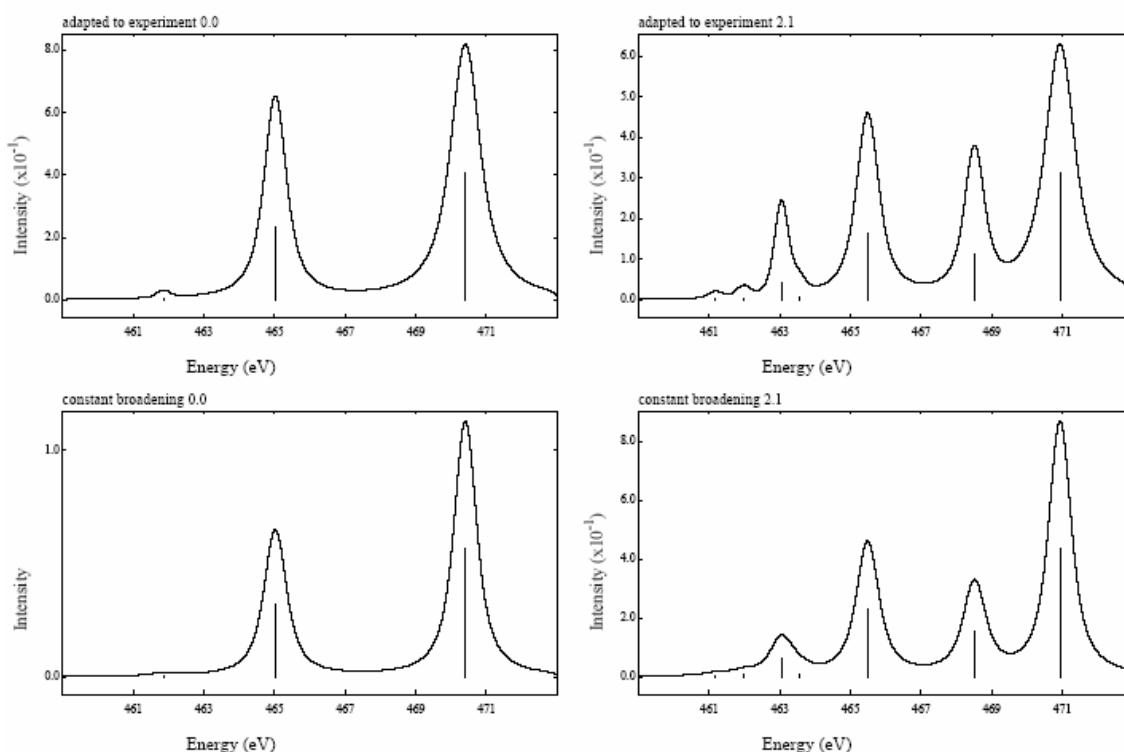
Add different broadening and plotting options in CTM4XAS.

- Turn split ON and modify the energy to 467 to split the Ti^{4+} 2p XAS spectrum; Modify the Lorentzian of the L_2 edge to 0.5.
- The energy range can be changed by hand, using the Force Energy range button; Set the energy range to 458 to 478 eV.



Modifying the broadening of the L_2 edge.

In experiment it is found that the small peaks are sharper than the large peaks. This can be corrected by adding a broadening to each line. This is not possible within CTM4XAS, but the created plo-file can be modified to treat each line-broadening individually.



This figure shows the result of the atomic multiplet calculation (left) and the crystal field multiplet calculation (right). Two different settings for the broadenings are used: The bottom figures use a constant broadening, while the top figures use a broadening that is different for every peak. In this way, the spectrum can be adapted to the experiment, as it turns out that in experiment there are different broadenings for different peaks. This state-by-state broadening is only possible for 3d0 systems, because other systems have too much.

Appendix 3.A explains the step-by-step programs that are used by CTM4XAS in a crystal field multiplet calculation.

The 3d⁰ systems are special because they are not affected by ground state effects of the multiplets, spin-orbit coupling and crystal field. The 3d⁰→2p⁵3d¹ transition can be calculated from a single transition matrix $\langle A_1 | T_1 | T_1 \rangle$ in O_h symmetry. The ground state A₁ matrix is 1x1 and the final state T₁ matrix is 7x7, making the transition matrix 1x7. In other words the spectrum consists of a maximum of seven peaks. Chapter 3 showed the complete calculation in SO₃ symmetry. Below the branching from SO₃ to O_h symmetry will be explained; for the moment we just use them. The respective degeneracies of the J-values in SO₃ symmetry and the degeneracies of the representations in O_h symmetry are collected in this table.

J in SO ₃	Deg.	Branching	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

It can be seen that a $2p^5 3d^1$ configuration has twelve representations in SO₃ symmetry that are branched to 25 representations in a cubic field. The overall degeneracy of the $2p^5 3d^1$ configuration is $6 \times 10 = 60$, implying a possibility of 60 transitions in a system without any symmetry. From these 25 representations, only seven are of interest for the calculation of the x-ray absorption spectral shape, because only these T₁ symmetry states obtain a finite intensity.

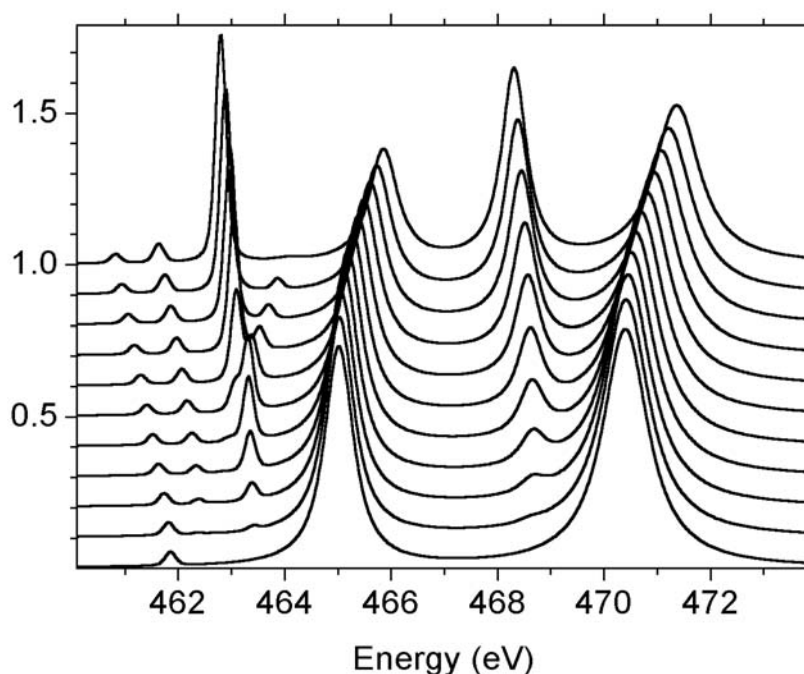
	461.856	462.329	462.613	463.442	465.024	468.588	470.405
1	0.0924	0.0000	0.0000	0.0000	0.6001	0.0000	0.3075
2	0.9009	0.0000	0.0000	0.0000	0.0384	0.0000	0.0607
3	0.0068	0.0000	0.0000	0.0000	0.3615	0.0000	0.6318
4	0.0000	0.0000	0.6019	0.0364	0.0000	0.3617	0.0000
5	0.0000	0.0000	0.0459	0.6674	0.0000	0.2867	0.0000
6	0.0000	0.0000	0.3521	0.2963	0.0000	0.3516	0.0000
7	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0001	0.0000	0.0000	0.0000	0.2466	0.0000	0.7533

This table shows the seven T₁ symmetry states calculated with a crystal field splitting of 0.0 eV. One finds the three peaks that are related to J=1 final states, build from vector rows one, two and three. The third row is related to the ¹P₁ state and the intensity of the peak as given in the bottom row is equal to the square of this row, where the total intensity is normalized to 1.0. Rows four, five and six are related to the J=3 states and row seven is related to a J=4 state. It can be seen that with a value of 10Dq of 0.0 eV, the 7x7 matrix blocks out to two 3x3 and one 1x1 matrices because one essentially is calculating a spectrum in SO₃ symmetry.

The T_1 final states of the $2p^5 3d^1$ configuration with $10Dq=3.04$ eV. The top row gives the energies and the bottom row the relative intensities of the seven final states that are build from seven basis-vectors.							
	460.828	461.641	462.806	464.048	465.859	468.313	471.369
1	0.0662	0.0037	0.1550	0.0124	0.4916	0.0404	0.2308
2	0.5944	0.0253	0.0007	0.2972	0.0280	0.0078	0.0466
3	0.0046	0.0091	0.1128	0.0046	0.1845	0.2666	0.4178
4	0.0161	0.4460	0.0340	0.0980	0.0097	0.2923	0.1039
5	0.0020	0.2973	0.2980	0.0791	0.0331	0.2191	0.0714
6	0.0044	0.0404	0.3986	0.0116	0.2417	0.1738	0.1294
7	0.3124	0.1781	0.0009	0.4972	0.0113	0.0000	0.0001
	0.0001	0.0003	0.0435	0.0001	0.1164	0.2430	0.5968

This table shows the seven T_1 symmetry states calculated with a crystal field splitting of 3.04 eV. One finds the seven peaks that are all build from the seven basis vectors. The third row is again related to 1P_1 symmetry and its square yields the intensity as given in the bottom row. Essentially one observes four main peaks, peaks 3, 5, 6 and 7. Peak 6 and 7 are essentially the L_2 edge peaks of respectively t_{2g} and e_g character. They are split by 3.05 eV, essentially the value of $10Dq$. Peaks 3 and 5 are the L_3 peaks of t_{2g} and e_g character, also split by 3.05 eV. Peaks 1, 2 and 4 are low-intensity peaks that originate from the 'spin-forbidden transition' in the atomic multiplet calculation.

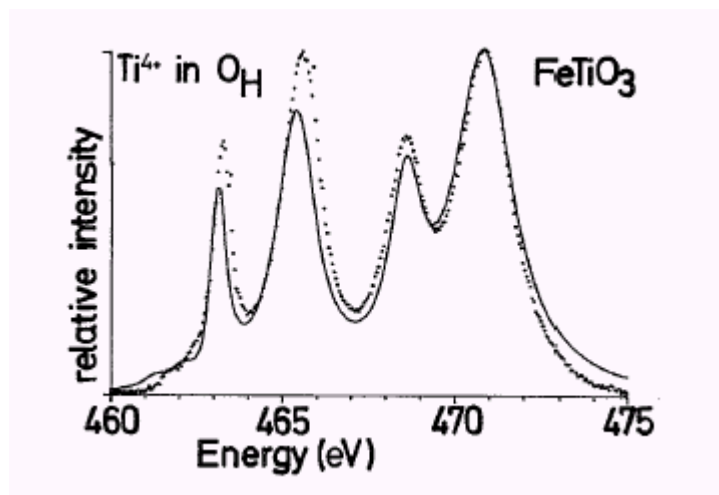
This figure shows the crystal field multiplet calculations for the $3d^0 \rightarrow 2p^5 3d^1$ transition in Ti^{4+} . The



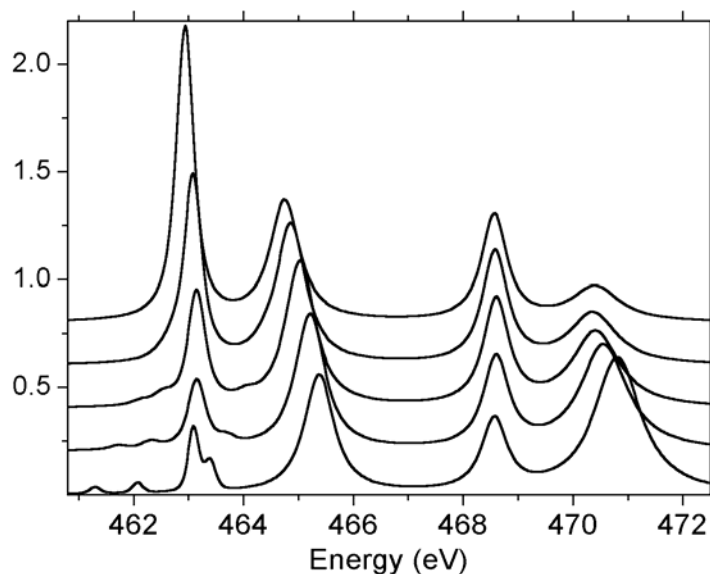
result of each calculation is a set of seven energies with seven intensities.

Exercise 3.3:

- Try to reproduce the figure on the previous page by calculating the crystal field multiplet spectrum of Ti^{4+} as a function of the crystal field strength.
- What happens if one changes the initial state crystal field value and the final state crystal field value independently?
- What happens if one sets the crystal field values to negative numbers?
- What happens if one uses very large crystal field values, say a value of 100 eV?



This figure compares the crystal field multiplet calculation of the $3d^0 \rightarrow 2p^5 3d^1$ transition in Ti^{4+} with the experimental 2p x-ray absorption spectrum of FeTiO_3 . The titanium ions are surrounded by six oxygen atoms in a (little) distorted octahedron. The value of $10Dq$ has been set to 1.8 eV. The calculation is able to reproduce all peaks that are experimentally visible. In particular the two small pre-peaks can be nicely observed. The similar spectrum of SrTiO_3 has an even sharper spectral shape, related to the perfect octahedral surrounding of Ti^{4+} by oxygen.



This figure shows the effect of the pd Slater-Condon parameters on the spectral shape of the $3d^0 \rightarrow 2p^5 3d^1$ transition in Ti^{IV} . The bottom spectrum uses the 80% reduction of the Hartree-Fock

values in order to obtain a good estimate of the values in the free atom. In most solids the 2p3d Slater-Condon parameters have essentially the same values as for the free atom, in other words the solid state screening of the 2p3d Slater-Condon parameters is almost zero. The five spectra are calculated by using the same values for the 3d- and 2p-spin-orbit coupling and the same crystal field value of 1.8 eV. The Slater-Condon parameters are rescaled to respectively 80% (bottom), 60%, 40%, 20% and 1% (top). The top spectrum corresponds closely to the single particle picture, where one expects four peaks, respectively the L_3 - t_{2g} , the L_3 - e_g , the L_2 - t_{2g} and the L_2 - e_g peak, with respective intensities given by their degeneracies, i.e. 6:4:3:2. This is exactly what is observed in the top spectrum, where it is noted that the intensity ratio is a little obscured by the differences in line width. One can conclude that there is a large difference between the single particle result (top spectrum) and the multiplet result (bottom spectrum). The Slater-Condon parameters have the effect to lower the intensity of the t_{2g} peaks and shift intensity to the e_g peaks. An even larger intensity shift can be observed from the L_3 edge to the L_2 edge and a very clear effect is the creation of additional (pre-)peaks, because additional transitions become allowed.

Exercise 3.4:

- (a) Try to reproduce the figure above by reducing the Slater integrals. Change the values from 80% to 60%, 40%, 20% and 1%. (0% does not work correctly as the program assumes it to be read as 100%).
- (b) Modify only the 3d3d integrals.
- (c) Modify only the 2p3d Coulomb + exchange integrals.

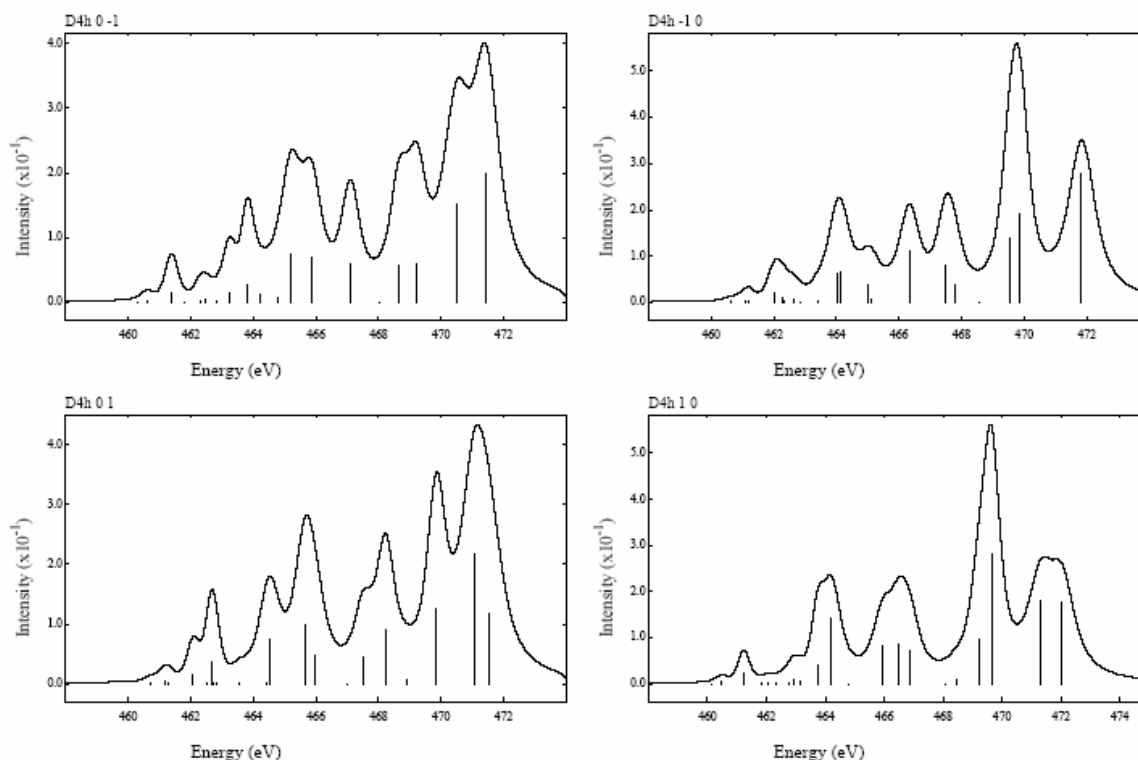
Appendix 3.B explains how the Slater integral reduction is implemented in the RCG2 program.

3.2 $3d^0$ systems in tetragonal symmetry

If one reduces the symmetry further from O_h to D_{4h} the seven lines in the x-ray absorption spectrum of Ti^{4+} split further. The respective degeneracies of the representations in O^h symmetry and the corresponding symmetries in D_{4h} symmetry are collected in this table.

Γ in O_h	Deg.		Γ in D_{4h}		Deg.
A_1	2	A_1	A_1	2+5	7
A_2	3	B_1	A_2	7	7
T_1	7	$E+A_2$	B_1	3+5	8
T_2	8	$E+B_2$	B_2	8	8
E	5	A_1+B_1	E	7+8	15
Σ	25				45

A $2p^5 3d^1$ configuration has twelve representations in SO_3 symmetry that are branched to 25 representations in a cubic field. These 25 representations are further branched to 45 representations in D_{4h} symmetry, of the overall degeneracy of 60. From these 45 representations, 22 are of interest for the calculation of the x-ray absorption spectral shape, because they have either E or A_2 symmetry. There are now two different final state symmetries possible because the dipole operator is split into two representations. The spectrum of two-dimensional E-symmetry relates to the in-plane direction of the tetragonal structure, while the one-dimensional A_2 -symmetry relates to the out-of-plane direction.



This figure shows the crystal field multiplet calculation of Ti^{4+} in D_{4h} symmetry, using the files als4ti4d4h.rcg and als4ti4d4h.rac. Four calculations have been performed. The value of the X40 branch was set to 7.0 in all cases and for the two other parameters X42 and X22 the combinations (5,0), (-5,0), (0,5) and (0,-5) were made. The four output files have been saved as als4ti4d4hm0.ora, etc. The figure is made with the file als4ti4d4h.plo. One can use the expressions on the previous page to calculate the values of $10Dq$, Ds and Dt and the energy positions of the different 3d-orbitals. For example, the parameters $(X40, X42, X22) = (7, 0, 5)$ relate to $(10Dq, Dt, Ds) = (2.13, 0, 0.597)$, etc.

Exercise 3.5:

Add a tetragonal symmetry to the calculation of the 2p XAS spectrum of Ti^{4+} ; Use atomic Slater integrals and $10Dq = 2.5$ eV.

(d) Modify Dt between -0.6 and +0.6 eV, in steps of 0.3 eV.

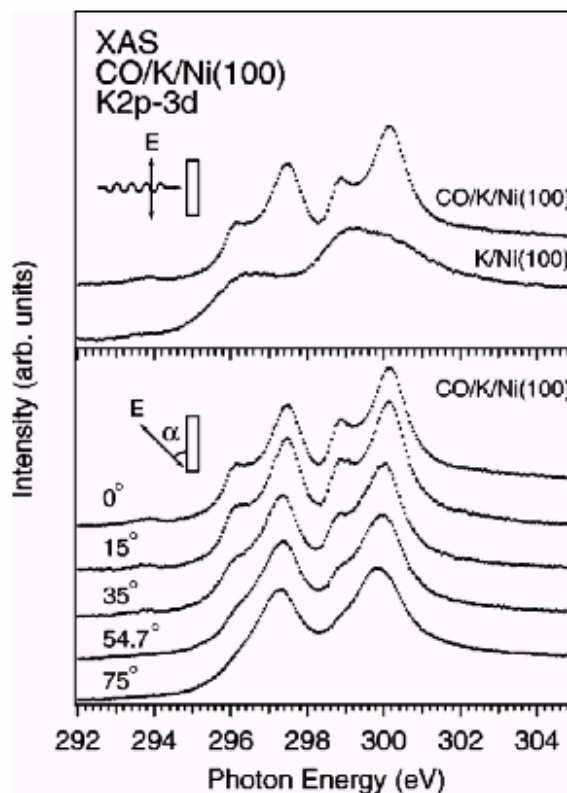
(e) Modify Ds between -0.6 and +0.6 eV, in steps of 0.3 eV; It is also possible that both Dt and Ds are non-zero.

(f) Change the plotting option from XAS to MLD. This shows the linear dichroism as is discussed below.

3.3 Lower symmetry and angular dependence

Examples of this angular dependence in D_{4h} and lower symmetries can be found in the study of interfaces, surfaces and adsorbates. A detailed study of the symmetry effects on the calcium 2p x-ray absorption spectra at the surface and in the bulk of CaF_2 did clearly show the ability of the multiplet calculations to reproduce the spectral shapes both in the bulk as at the reduced C_{3v} symmetry of the surface.

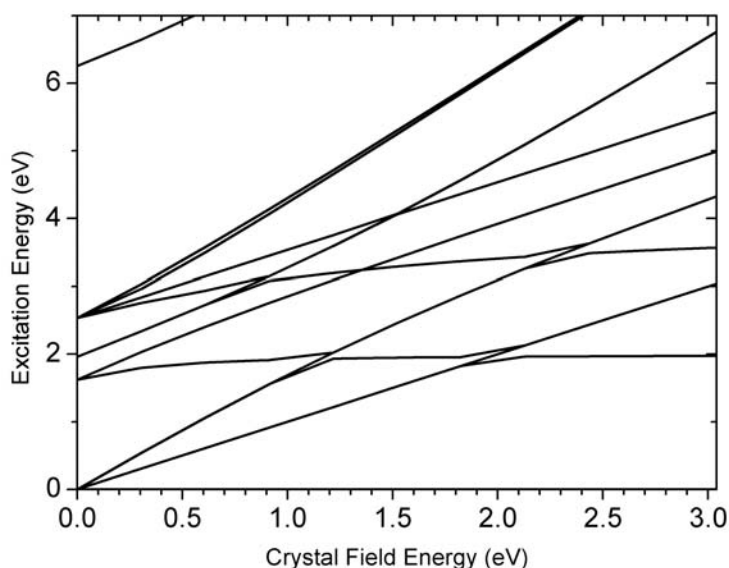
The figure shows the K 2p x-ray absorption spectra of K/Ni(100) compared with CO/K/Ni(100).. Note that potassium can be considered as K^+ , which is a 3d0 system similar to Ti^{4+} . The co-adsorption system shows significantly more structural details, which is caused by the strong (crystal) field of the CO molecules on the K ions. The CO and K adsorbates can be considered to be placed on respectively the black and white squares of a checkers game. Each K ion is surrounded by the four CO molecules in plane as well as the nickel surface below and vacuum above. This C_{4v} symmetry field is expected to have significant angular dependence between the x-ray absorption spectral shape in plane and out-of-plane. This is shown in the bottom half of the figure. Two asymmetric peaks are visible for (near) grazing incidence and four peaks are visible at normal incidence.



3.4 The energies of the $3d^8$ configuration

The table below gives the energy levels of a $3d^8$ configuration. The crystal field effect modifies these energy levels by the additional terms in the Hamiltonian. We will use the $3d^8$ configuration as an example to show the effects of the O_h and D_{4h} symmetry. Assuming for the moment that the 3d spin-orbit coupling is zero, in O_h symmetry the five term symbols in spherical symmetry split into eleven term symbols. Their respective energies can be calculated by adding the effect of the cubic crystal field $10Dq$ to the atomic energies. The diagrams of the respective energies with respect to the cubic crystal field (normalized to the Racah parameter B) are known as the Tanabe-Sugano diagrams.

	Relative Energy	Symmetries in O_h	Symmetries in D_{4h}
1S	4.6 eV	1A_1	1A_1
3P	0.2 eV	3T_1	$^3E + ^3A_2$
1D	-0.1 eV	$^1E + ^1T_2$	$^1A_1 + ^1B_1 + ^1E + ^1B_2$
3F	-1.8 eV	$^3A_2 + ^3T_1 + ^3T_2$	$^3B_1 + ^3E + ^3A_2 + ^3E + ^3B_2$
1G	0.8 eV	$^1A_1 + ^1T_1 + ^1T_2 + ^1E$	$^1A_1 + ^1E + ^1A_2 + ^1E + ^1B_2 + ^1A_1 + ^1B_1$



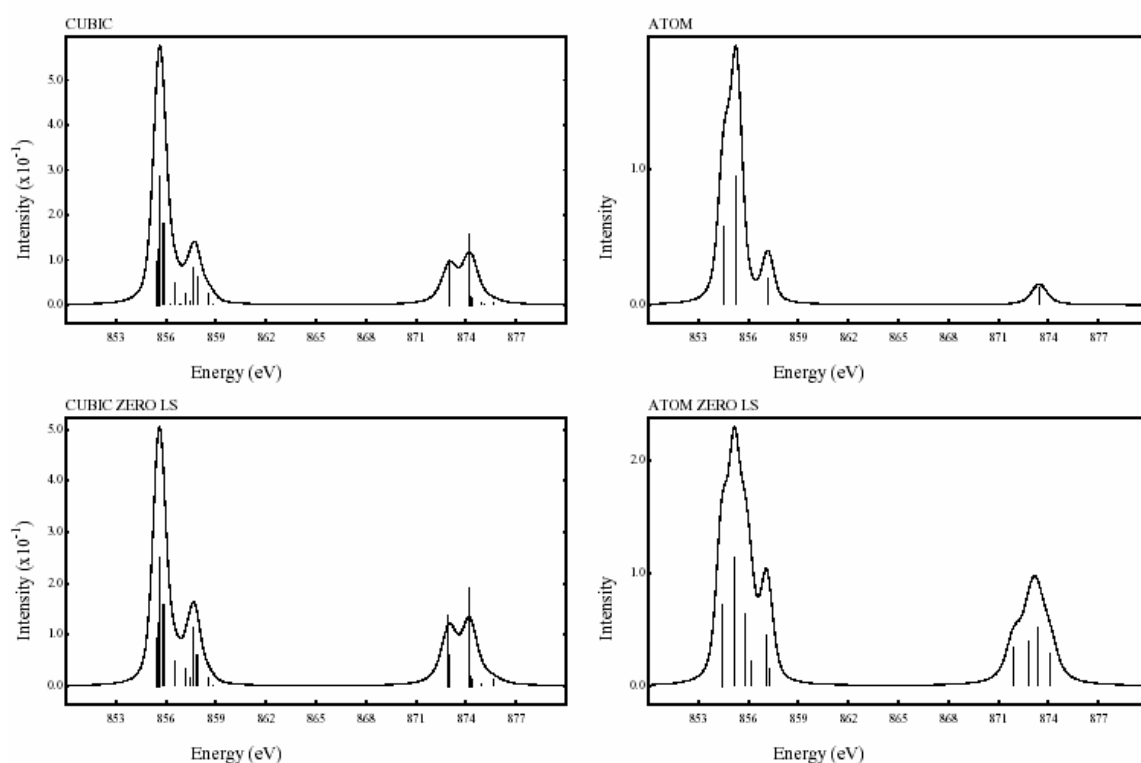
This figure gives the Tanabe-Sugano diagram for the $3d^8$ configuration. The ground state of a $3d^8$ configuration in O_h symmetry has 3A_2 symmetry. If the crystal field energy is 0.0 eV one has effectively the atomic multiplet states. From low energy to high energy, one can observe respectively the 3F , 1D , 3P , 1G and 1S states. Including a finite crystal field strength splits these states, for example the 3F state is split into $^3A_2 + ^3T_1 + ^3T_2$, etc. At higher crystal field strengths states start to change their order and they cross. If states actually cross each other or show non-crossing behavior depends on the fact if their symmetries allow them to form a linear combination of states. This also depends on the inclusion of the 3d spin-orbit coupling.

Appendix E shows how Tanabe-Sugano diagrams can be generated from the ora output file. This will be automatized in a future version of CTM4XAS.

X-ray absorption calculations of 3d⁸ systems

In octahedral symmetry one has to calculate five matrices for the initial and final states and thirteen transition matrices. Note that this is a general result for all even numbers of 3d electrons, as there are only these five symmetries in O_h symmetry. The case of an odd number of electrons will be described below. In the 3d⁰ case, the ground state branches to 1A_1 , with total symmetry $A_1 \times A_1 = A_1$. This again limits the calculation to only one transition matrix $\langle A_1 | T_1 | T_1 \rangle$. We have seen this in the ora output files that contain the seven lines of the $\langle A_1 | T_1 | T_1 \rangle$ transition at the end. In the 3d⁸ case the ground state is 3A₂, which in total symmetry yields a T₂ ground state. Using the table above, this implies that four dipole matrix elements must be calculated for the ground state $\langle T_2 | T_1 | T_1 \rangle$, $\langle T_2 | T_1 | E \rangle$, $\langle T_2 | T_1 | T_2 \rangle$ and $\langle T_2 | T_1 | A_2 \rangle$.

Appendix F explains where to find these symmetries in the ora output file and how to plot the different matrix elements independently.



The figure shows that the influence of the 3d spin-orbit coupling is large for a Ni²⁺ ion in spherical symmetry, while it is small for a Ni²⁺ ion in cubic symmetry. The reason is that for an atom, the 3F₄ ground state is made degenerate with the 3F₃ and 3F₂ states. In cubic symmetry, the 3A₂ ground state is not split by the 3d spin-orbit coupling, and another important factor is that the energy difference to the next state is over 1.0 eV. Although the spectra of cubic Ni²⁺ look rather similar with and without 3d spin-orbit coupling, they are not identical. With good experimental data quality, one could use these calculations to check whether the 3d spin-orbit coupling should be switched off or on, for example from the L₃ and L₂ peak ratios. In other systems, for example Co²⁺ and Cr⁴⁺, the role of the 3d spin-orbit coupling is much more significant, as will be discussed below.

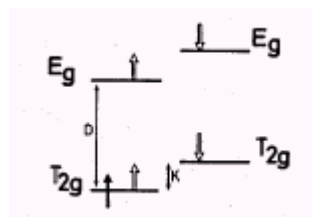
Exercise 3.6:

Calculate the Ni²⁺ spectrum for:

- (a) Atomic multiplets without 3d spin-orbit coupling
- (b) Atomic multiplets with 3d spin-orbit coupling
- (c) Crystal field multiplets without 3d spin-orbit coupling; $10Dq = 1.0$ eV
- (d) Crystal field multiplets with 3d spin-orbit coupling; $10Dq = 1.0$ eV
- (e) Crystal field multiplets in tetrahedral symmetry without 3d spin-orbit coupling; $10Dq = -1.0$ eV
- (f) Crystal field multiplets in tetrahedral symmetry with 3d spin-orbit coupling; $10Dq = -1.0$ eV
- (g) Why is the effect of spin-orbit coupling for 3d⁸ systems larger for tetrahedral symmetry?

The ground states of 3d^N systems

The ground state of a 3d⁸ configuration in O_h symmetry always remains ³A₂. The reason is clear if one compares these configurations to the single particle description of a 3d⁸ configuration. In a single particle description a 3d⁸ configuration is split by the cubic crystal field into the t_{2g} and the e_g configuration. The t_{2g} configuration has the lowest energy and can contain six 3d electrons. The remaining two electrons are placed in the e_g configuration, where both have a parallel alignment according to Hunds rule. The result is that the overall configuration is t_{2g}⁶e_g(up)². This configuration identifies with the ³A₂ configuration.



The splitting of 3d-electron states under influence of the cubic crystal field D and the Stoner exchange interaction J . A second electron is indicated with an empty arrow to indicate the energy effects.

This figure shows the splitting of a 3d configuration into an e_g and a t_{2g} configuration. Both configurations are further split by the Stoner exchange splitting J . The Stoner exchange splitting J is given as a linear combination of the Slater-Condon parameters as $J=(F_2+F_4)/14$. The Stoner exchange splitting is an approximation to the effects of the Slater-Condon parameters and in fact a second parameter C , the orbital polarization, can be used in combination with J . The orbital polarization C is given as $C=(9F_2-5F_4)/98$. Often this orbital polarization is omitted from single particle descriptions. In that case the multiplet configuration ³A₂ is not exactly equal to the single particle configuration t_{2g}⁶e_g(up)².

The configurations $3d^0$ to $3d^9$ are given in O_h symmetry for all possible high-spin (HS) and low-spin (LS) states. The third column gives the HS term symbols and the last column the LS term symbols. The fourth and fifth columns give the respective occupations of the t_{2g} and e_g orbitals.					
Conf.	Ground State in SO_3	HS Ground State in O_h	HS Ground State in Single particle models	LS Ground State in Single particle models	LS Ground State in O_h
$3d^0$	1S_0	1A_1	-	-	-
$3d^1$	$^2D_{3/2}$	2T_2	t_{2g+}^1	-	-
$3d^2$	3F_2	3T_1	t_{2g+}^2	-	-
$3d^3$	$^4F_{3/2}$	4A_2	t_{2g+}^3	-	-
$3d^4$	5D_0	5E	$t_{2g+}^3 e_{g+}^1$	$t_{2g+}^3 t_{2g-}^1$	3T_1
$3d^5$	$^6S_{5/2}$	6A_1	$t_{2g+}^3 e_{g+}^2$	$t_{2g+}^3 t_{2g-}^2$	2T_2
$3d^6$	5D_2	5T_2	$t_{2g+}^3 e_{g+}^2 t_{2g-}^1$	$t_{2g+}^3 t_{2g-}^3$	1A_1
$3d^7$	$^4F_{9/2}$	4T_1	$t_{2g+}^3 e_{g+}^2 t_{2g-}^2$	$t_{2g+}^3 t_{2g-}^3 e_{g+}^1$	2E
$3d^8$	3F_4	3A_2	$t_{2g+}^3 e_{g+}^2 t_{2g-}^3$	-	-
$3d^9$	$^2D_{5/2}$	2E	$t_{2g+}^3 e_{g+}^2 t_{2g-}^3 e_{g-}^1$	-	-

This table shows that for the configurations $3d^4$, $3d^5$, $3d^6$ and $3d^7$ there are two possible ground state configurations in O_h symmetry. A high-spin ground state that originates from the Hunds rule ground state plus a low-spin ground state for which first all t_{2g} levels are filled. One can directly relate the symmetry of a configuration to the partly filled sub-shell in the single particle model. A single particle configuration with one t_{2g} electron has T_2 symmetry, two t_{2g} electrons imply T_1 symmetry and one e_g electron implies E symmetry. If the t_{2g} electrons are filled and the e_g electrons (of the same spin) are empty the symmetry is A_2 . Finally, if both the t_{2g} and e_g states (of the same spin) are filled the symmetry is A_1 . The nature of the ground state is important, as we will show below that E symmetry states are susceptible to Jahn-Teller distortions and T_1 and T_2 symmetry states are susceptible to the effects of the 3d spin-orbit coupling.

Exercise 3.7:

Calculate the 2p XAS spectrum for:

- V^{5+} with and without 3d spin-orbit coupling; $10Dq=1.2$ eV.
- V^{4+} with and without 3d spin-orbit coupling; $10Dq=1.2$ eV.
- V^{3+} with and without 3d spin-orbit coupling; $10Dq=1.2$ eV.
- V^{2+} with and without 3d spin-orbit coupling; $10Dq=1.2$ eV.
- Explain why the effect of 3d spin-orbit coupling is large, small or zero for the calculations (a) to (d).

Appendix G discusses more details regarding the effects of the 3d spin-orbit coupling.

3.5 High-Spin Low-Spin Transitions

The transition from high-spin to low-spin ground states is determined by the cubic crystal field $10Dq$ and the exchange splitting J . The exchange splitting is present for every two parallel electrons. The $3d^4$ and $3d^7$ configuration differ by one t_{2g} versus e_g electron hence one time the crystal field splitting D . The $3d^5$ and $3d^6$ configurations differ by $2D$. The exchange interaction J is slightly

different for $e_g e_g$, $e_g t_{2g}$ and $t_{2g} t_{2g}$ interactions and column 5 contains the overall exchange interactions. The last column can be used to estimate the transition point. For this column the exchange splittings were assumed to be equal, yielding the simple rules that for $3d^4$ and $3d^5$ configurations high-spin states are found if the crystal field splitting is less than $3J$. In case of $3d^6$ and $3d^7$ configurations the crystal field value should be less than $2J$ for a high-spin configuration. Because J can be estimated as 0.8 eV, the transition points are approximately 2.4 eV for $3d^4$ and $3d^5$, respectively 1.6 eV for $3d^6$ and $3d^7$. In other words $3d^6$ and $3d^7$ materials have a tendency to be low-spin compounds. This is particularly true for $3d^6$ compounds because of the additional stabilizing nature of the $3d^6 {}^1A_1$ low spin ground state.

The high-spin and low-spin distribution of the 3d electrons for the configurations $3d^4$ to $3d^7$. The fourth column gives the difference in crystal field energy, the fifth column the difference in exchange energy. For the last column, we have assumed that $J_{te} \sim J_{ee} \sim J_{tt} = J$.					
Conf.	High-Spin	Low-Spin	10Dq (D)	Exchange (J)	J/D
$3d^4$	$t_{2g+}^3 e_{g+}^1$	$t_{2g+}^3 t_{2g-}^1$	1D	$3J_{te}$	3
$3d^5$	$t_{2g+}^3 e_{g+}^2$	$t_{2g+}^3 t_{2g-}^2$	2D	$6J_{te} + J_{ee} - J_{tt}$	~ 3
$3d^6$	$t_{2g+}^3 e_{g+}^2 t_{2g-}^1$	$t_{2g+}^3 t_{2g-}^3$	2D	$6J_{te} + J_{ee} - 3J_{tt}$	~ 2
$3d^7$	$t_{2g+}^3 e_{g+}^2 t_{2g-}^2$	$t_{2g+}^3 t_{2g-}^3 e_{g+}^1$	1D	$3J_{te} + J_{ee} - 2J_{tt}$	2

Exercise 3.8:

Calculate the 2p XAS spectrum with the 3d spin-orbit coupling set to zero for:

- Mn^{4+} with 10Dq=1.0, 2.0, 3.0 and 4.0 eV.
- Mn^{3+} with 10Dq=1.0, 2.0, 3.0 and 4.0 eV.
- Mn^{2+} with 10Dq=1.0, 2.0, 3.0 and 4.0 eV.
- At which energy is the high-spin low-spin transition?
- Try to determine the transition point by calculating in 0.1 energy steps of 10Dq.
- Repeat the calculations across the transition point, but now with the atomic spin-orbit coupling switched on. What is different?

3.6 Symmetry effects in D_{4h} symmetry

In D_{4h} symmetry the t_{2g} and e_g symmetry states split further into e_g and b_{2g} respectively a_{1g} and b_{1g} . Depending on the nature of the tetragonal distortion either the e_g or the b_{2g} state have the lowest energy. The table below shows that all configurations from $3d^2$ to $3d^8$ have a low-spin possibility in D_{4h} symmetry. Only the $3d^2$ configuration with the e_g state as ground state does not possess a low-spin configuration. The $3d^1$ and $3d^9$ configurations contain only one unpaired spin thus they have no possibility to obtain a low-spin ground state. It is important to notice that a $3d^8$ configuration as for example found in Ni^{2+} and Cu^{3+} can yield a low-spin configuration. Actually this low-spin configuration is found in the trivalent parent compounds of the high T_C superconducting oxides (Hu and others 1998). The D_{4h} symmetry ground states are particularly important for those cases where O_h symmetry yields a half-filled e_g state. This is the case for $3d^4$ and $3d^9$ plus low-spin $3d^7$. These ground states are unstable in octahedral symmetry and will relax to, for example, a D_{4h} ground state, the well-known Jahn-Teller distortion. This yields the Cu^{2+} ions with all states filled except the $^1A_{1g}$ -hole.

Ground State in Single particle models in D_{4h} symmetry				
Conf.	High-Spin $e_g < b_{2g}$	High-Spin $b_{2g} < e_g$	Low-Spin $e_g < b_{2g}$	Low-Spin $b_{2g} < e_g$
$3d^1$	e_{g+}	b_{2g+}	-	-
$3d^2$	e_{g+}^2	$b_{2g+} e_{g+}$	-	b_{2g+} b_{2g-}
$3d^3$	$e_{g+}^2 b_{2g+}$	$b_{2g+} e_{g+}^2$	e_{g+}^2 e_{g-}	$b_{2g+} e_{g+}$ b_{2g-}
$3d^4$	$e_{g+}^2 b_{2g+} a_{1g+}$	$b_{2g+} e_{g+}^2 b_{1g+}$	e_{g+}^2 e_{g-}^2	$b_{2g+} e_{g+}^2$ b_{2g-}
$3d^5$	$e_{g+}^2 b_{2g+} a_{1g+} b_{1g+}$	$b_{2g+} e_{g+}^2 b_{1g+} a_{1g+}$	$e_{g+}^2 b_{2g+}$ e_{g-}^2	$b_{2g+} e_{g+}^2$ $b_{2g-} e_{g-}^2$
$3d^6$	$e_{g+}^2 b_{2g+} a_{1g+} b_{1g+}$ e_{g-}	$b_{2g+} e_{g+}^2 b_{1g+} a_{1g+}$ b_{2g-}	$e_{g+}^2 b_{2g+}$ $e_{g-}^2 b_{2g-}$	$b_{2g+} e_{g+}^2$ $b_{2g-} e_{g-}^2$
$3d^7$	$e_{g+}^2 b_{2g+} a_{1g+} b_{1g+}$ e_{g-}^2	$b_{2g+} e_{g+}^2 b_{1g+} a_{1g+}$ $b_{2g-} e_{g-}^2$	$e_{g+}^2 b_{2g+} a_{1g+}$ $e_{g-}^2 b_{2g-}$	$b_{2g+} e_{g+}^2 b_{1g+}$ $b_{2g-} e_{g-}^2$
$3d^8$	$e_{g+}^2 b_{2g+} a_{1g+} b_{1g+}$ $e_{g-}^2 b_{2g-}$	$b_{2g+} e_{g+}^2 b_{1g+} a_{1g+}$ $b_{2g-} e_{g-}^2$	$e_{g+}^2 b_{2g+} a_{1g+}$ $e_{g-}^2 b_{2g-} a_{1g-}$	$b_{2g+} e_{g+}^2 b_{1g+}$ $b_{2g-} e_{g-}^2 b_{1g-}$
$3d^9$	$e_{g+}^2 b_{2g+} a_{1g+} b_{1g+}$ $e_{g-}^2 b_{2g-} a_{1g-}$	$b_{2g+} e_{g+}^2 b_{1g+} a_{1g+}$ $b_{2g-} e_{g-}^2 b_{1g-}$	-	-

Exercise 3.9:

Calculate the 2p XAS spectrum for:

- V^{3+} with $10Dq=2.0$ eV and with Ds is respectively -0.1 eV and +0.1 eV; Which calculation yields a e_{g+}^2 ground state?
- How can one bring a $3d^2$ system to a low-spin ground state?

3.7 Appendix A: Running the crystal field multiplet programs step-by-step

The CTM4XAS program runs the atomic multiplet program RCG2, followed by the crystal field multiplet program RAC2. All modifications to the files are made automatically. Exercise 2.1 performs the same calculation as given by the files `als4ti4a.rcg` and `als4ti4a.rac`. The file `als4ti4a.rcg` has the following lines:

```

10    1    0    14    2    4    1    1 SHELL03000000 SPIN03000000 INTER8
0
1      2 1 12 1 10      00      9 00000000 0 8065.4790 .00      1
P 6  S 0
P 5  D 1
Ti4+ 2p06 3d00      1      0.0000      0.0000      0.0000      0.0000      0.0000HR99999999
Ti4+ 2p05 3d01      6  464.8110      3.7762      0.0322      6.3023      4.6284HR99999999
      2.6334
Ti4+ 2p06 3d00      Ti4+ 2p05 3d01      -0.26267( 2P//R1// 3D) 1.000HR 38-100
      -99999999.

-1

```

Compared with the original file `als3ti4.rcg`, some changes have been made in this input file with the goal to continue with the crystal field calculation afterwards. The changes one has to make are all in the first line:

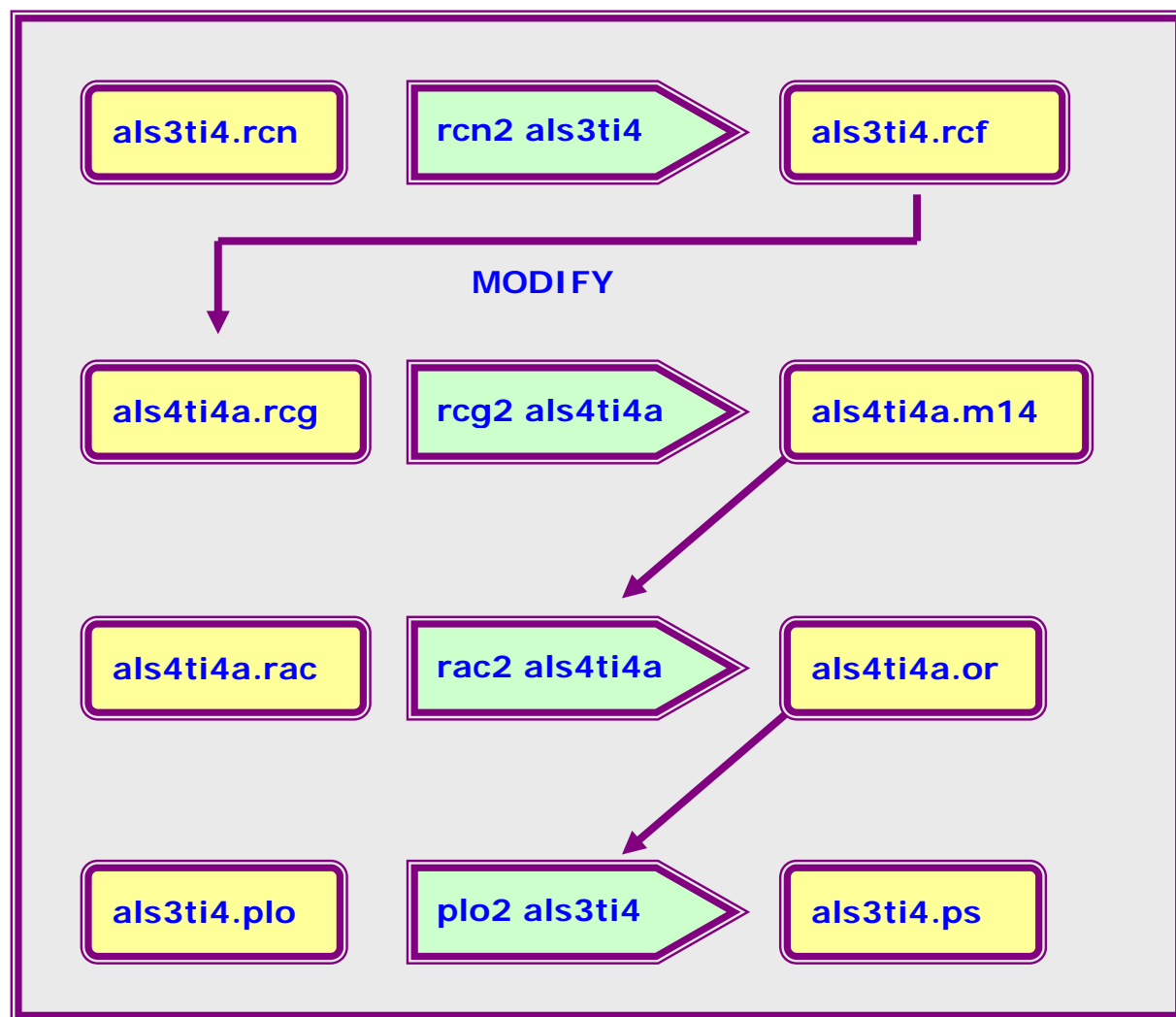
```

10    1    0    00    4    4    1    1 SHELL00000000 SPIN00000000 INTER8
10    1    0    14    2    4    1    1 SHELL03000000 SPIN03000000 INTER8

```

The 14 indicates the name of the output file that is used in RAC. It is renamed to `als4ti4a.m14`. The change to 2 is needed for calculations in low symmetry. It tells the program to calculate the additional matrices (see below). The SHELL comment has its second 0 changed to a 3. This implies that a crystal field can be added on the second shell as defined in the RCG file, which is the 3d-shell. These changes have to be made in all cases where one would like to add a crystal field and/or a magnetic field. The general procedure is to start from a RCN2 calculation and modify the `.rcf` file according to the procedure given above. (These modifications are automatic in CTM4XAS)

CTM4XAS performs the following series of calculations:



The
files

als4ti4b.rcg and als4ti4b.rac calculate the crystal field multiplet spectrum for a crystal field of 2.218 eV. The file als4ti4b.rcg is identical to als4ti4a.rcg. The only change that is made in the file als4ti4b.rac is the change of the crystal field values from 0.0 to 7.0. A value of 7.0 indicates a crystal field of $7.0 * 0.304 = 2.218$ eV.

```

Y
  % vertical 1 1
butler 03
to Oh
endchain
actor 0+ HAMILTONIAN ground PRINTEIG
  OPER HAMILTONIAN
    BRANCH 0+ > 0 0+ 1.0
  OPER SHELL2
    BRANCH 4+ > 0 0+ 0.00
actor 0+ HAMILTONIAN excite PRINTEIG
  OPER HAMILTONIAN
    BRANCH 0+ > 0 0+ 1.0
  OPER SHELL2
    BRANCH 4+ > 0 0+ 0.00
actor 1- plane transi PRINTTRANS
  oper MULTIPOLE
    branch 1- > 0 1- 1.000
RUN

```

The als4ti4b calculation shows seven peaks; after broadening the third and fourth peak overlap and one finds six peaks in the spectrum. These seven peaks are given at the bottom of the [als4ti4b.ora](#) file.

```

TRANSFORMED MATRIX for TRIAD 2 ( 0+ 1- 1- 0) (1*7) DIM :1:3:3 ACTOR
PLANE

      ---- MATRIX ----      PRINTTRANS

BRA/KET : 461.1850 461.9710 463.0501 463.5387 465.4900 468.5141 470.9370
-----
0.00000: 0.009445 0.015776 0.137714 0.021110 0.505803 0.346162 0.963990

TRANSFORMATION FINISHED

```

This part of the [als4ti4b.ora](#) file gives the 'transformed matrix for triad2', where 'triad2' is the transition from 0+ via 1- to 1- symmetry. Then follows a matrix with seven energies and seven intensities, which constitutes the complete result from the calculation. These seven sticks are then broadened in the plotting program. The meaning of 'triad2' and the respective symmetries will be explained below. A complication is the notation of the RAC2 program, which uses BUTLER notation, instead of the more familiar notation for group symmetries. The translation between the two notations is given below in the character table of O_h symmetry. Here we note that 0+ identifies with A_{1g} and 1- with T_{1u} , which means that triad2 is the calculation of the transition matrix $\langle A_{1g} | T_{1u} | T_{1u} \rangle$ in O_h symmetry. The dipole transition has T_{1u} symmetry in an octahedral field.

3.8 Appendix B: The Slater integrals reduction factors in the RCG2 program.

The files `als4ti4c.rcg` and `ti4ti4c.rac` reproduce the calculation for a reduction to 50% of the atomic values. The only parameters that should be changed are the reduction factors in the `als4ti4c.rcg` file. That is, the second line must be changed from 80998080 to 40994040.

0	80998080	8065.47800	0000000
0	40994040	8065.47800	0000000

These numbers are used to multiply the parameters with, before the calculation starts. There are four numbers that are respectively used for the four types of parameters, indicated with a 1, 2, 3 or 4 at the end, i.e.

1. The numbers with a 1 at the end are the 3d3d Slater integrals
2. The numbers with a 2 at the end are the spin-orbit couplings
3. The numbers with a 3 at the end are the 2p3d direct Slater integrals
4. The numbers with a 4 at the end are the 2p3d exchange Slater integrals

Instead of using the reduction factor, one can also change the individual numbers by hand to the required number. One can check in the `als4ti4c.org` file that the reductions have been performed in the correct manner. The file repeats first the input line and then reports the corrected values. the file gives the "PARAMETER VALUES IN 8065.5 CM-1", which identifies with electron volts and then tells that the values were multiplied with respectively 0.40, 1.00, 0.40 and 0.40, yielding the values for the respective parameters as given below. That is, the blue values are modified to the red values.

ECHO:							
TI4+	2P05	3D01	6	464.8110	3.7762	0.0322	6.3023
							4.6284HR9999999
			9				
ECHO:							
				2.6334			
TI4+	2P05	3D01		PARAMETER VALUES IN 8065.5 CM-1 (HR TIMES 0.40 1.00 0.40			
0.40)		1	P 5	D 1			
				EAV		ZETA 1	ZETA 2
F2(12)		G1(12)					
		G3(12)					
				464.811		3.776	0.032
2.521		1.851					
		1.053					

3.9 Appendix C: The Crystal Field Multiplet Hamiltonian

The crystal field multiplet Hamiltonian consists of the atomic Hamiltonian as outlined in the previous chapter, to which an electrostatic field is added:

$$H_{CF} = H_{ATOM} + H_{FIELD} \quad (3.2)$$

$$H_{ATOM} = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i) l_i \cdot s_i \quad (3.3)$$

$$H_{FIELD} = -e\phi(r) \quad (3.4)$$

The only term added to the atomic Hamiltonian is an electrostatic field, which consists of the electronic charge e times, a potential that describes the surroundings $\phi(r)$. The potential $\phi(r)$ is written as a series expansion of spherical harmonics Y_{LM} 's:

$$\phi(r) = \sum_{L=0}^{\infty} \sum_{M=-L}^L r^L A_{LM} Y_{LM}(\psi, \phi) \quad (3.5)$$

The crystal field is regarded as a perturbation to the atomic result. This implies that it is necessary to determine the matrix elements of $\phi(r)$ with respect to the atomic 3d orbitals $\langle 3d | \phi(r) | 3d \rangle$. One can separate the matrix elements into a spherical part and a radial part, as was done also for the atomic Hamiltonian in equation 2.6. The radial part of the matrix elements yields the strength of the crystal field interaction. The spherical part of the matrix element can be written completely in Y_{LM} symmetry, where the two 3d-electrons are written as Y_{2m} . This gives:

$$\langle Y_{2m_2} | Y_{LM} | Y_{2m_1} \rangle = (-1)^{m_2} \sqrt{15(2L+1)/4\pi} \begin{pmatrix} 2 & L & 2 \\ -m_2 & M & m_1 \end{pmatrix} \begin{pmatrix} 2 & L & 2 \\ 0 & 0 & 0 \end{pmatrix} \quad (3.6)$$

The second 3J-symbol is zero unless L is equal to 0, 2 or 4. This limits the crystal field potential for 3d electrons to:

$$\phi(r) = A_{00}Y_{00} + \sum_{M=-2}^2 r^2 A_{2M}Y_{2M} + \sum_{M=-4}^4 r^4 A_{4M}Y_{4M} \quad (3.7)$$

The first term $A_{00}Y_{00}$ is a constant. It will only shift the atomic states and it is not necessary to include this term explicitly if one calculates the spectral shape.

Cubic crystal fields

A large range of systems possess a transition metal ion surrounded by six or eight neighbours. The six neighbours are positioned on the three Cartesian axes, or in other words on the six faces of a cube surrounding the transition metal. They form a so-called octahedral field. The eight neighbours are positioned on the eight corners of the cube and form a so-called cubic field. Both these systems belong to the O_h point group. The character table of O_h symmetry is given above. O_h symmetry is a subgroup of the atomic SO_3 group.

The calculation of the x-ray absorption spectral shape in atomic symmetry involved the calculation of the matrices of the initial state, the final state and the transition. The initial state is given by the matrix element $\langle 3d^N | H_{ATOM} | 3d^N \rangle$, which for a particular J -value in the initial state gives $\sum_J \langle J | 0 | J \rangle$. The same applies for the final state matrix element $\langle 2p^5 3d^{N+1} | H_{ATOM} | 2p^5 3d^{N+1} \rangle$, where $\sum_J \langle J' | 0 | J' \rangle$.

is calculated for the values of J' that fulfill the selection rule, i.e. $J'=J-1, J$ and $J+1$. The dipole matrix element $\langle 3d^N | p | 2p^5 3d^{N+1} \rangle$ implies the calculation of all matrices that couple J and J' : $\sum_{J,J'} \langle J || J' \rangle$. To calculate the x-ray absorption spectrum in a cubic crystal field, these atomic transition matrix elements must be branched to cubic symmetry. This is essentially the only task to fulfill.

SO ₃		O _h (Butler)	O _h (Mulliken)
S	0	0	A ₁
P	1	1	T ₁
D	2	2 + $\hat{1}$	E+T ₂
F	3	$\hat{0}$ + 1 + $\hat{1}$	A ₂ +T ₁ +T ₂
G	4	0 + 1 + 2 + $\hat{1}$	A ₁ +E+T ₁ +T ₂

Branching rules for the symmetry elements by going from SO₃ symmetry to O_h symmetry.

This table gives the branching from SO₃ to O_h symmetry. This table can be determined from group theory (Butler 1981). This table implies that an S symmetry state in atomic symmetry branches only to a A₁ symmetry state in octahedral symmetry. This is the case, because the symmetry elements of an s-orbital in O_h symmetry are determined by the character table of A₁ symmetry, i.e. whatever symmetry operation one applies an s-orbital remains an s-orbital. This is not the case for the other orbitals. For example, a p-orbital can be described with the characters of the T₁ symmetry state in O_h symmetry, for example the class G₃, a two-fold rotation around x, inverts the p-orbital. A d-orbital or a D symmetry state in SO₃, branches to E plus T₂ symmetry states in octahedral symmetry. This can be related to the character table by adding the characters of E and T₂ symmetry, yielding the overall characters 5, -1, 1, -1 and 1, which describe the properties of d-orbitals in O_h symmetry, i.e. the dimension of a d-orbital is 5 and the class G₄ (a fourfold rotation around x) inverts the d-orbitals. This is a well-known result: A 3d electron is separated into t_{2g} and e_g electrons in octahedral symmetry, where the symmetries include the gerade-notation of the complete O_h character table.

One can make the following observations: The dipole transition operator has p-symmetry and is branched to T₁ symmetry. Having a single symmetry in O_h symmetry, there will be no dipolar angular dependence in x-ray absorption. The quadrupole transition operator has d-symmetry and is split into two operators in O_h symmetry, in other words there will be different quadrupole transitions in different directions. The Hamiltonian is given by the unity representation A₁ of the symmetry under consideration. In O_h symmetry the atomic G-symmetry state branches into the A₁ Hamiltonian, which is a confirmation of equation 3.7 as given above.

We can lower the symmetry from octahedral O_h to tetragonal D_{4h} and describe this symmetry lowering again with a branching table.

O _h (Butler)	O _h (Mulliken)	D _{4h} (Butler)	D _{4h} (Mulliken)
0	A ₁	0	A ₁
$\hat{0}$	A ₂	2	B ₁
1	T ₁	1 + $\hat{0}$	E + A ₂
$\hat{1}$	T ₂	1 + $\hat{2}$	E + B ₂
2	E	0 + 2	A ₁ + B ₁

Branching rules for the symmetry elements by going from O_h symmetry to D_{4h} symmetry.

An atomic s-orbital is branched to D_{4h} symmetry according to the branching series $S \rightarrow A_1 \rightarrow A_1$. In other words it is still the unity element, and it will always be the unity element in all symmetries. An atomic p-orbital is branched according to $P \rightarrow T_1 \rightarrow E + A_2$. Adding the characters of E and A_2 yields 3, -1, 1, -1 and -1, implying that a two-fold rotation around the z-axis inverts a p-orbital, etc. Similarly an atomic d-orbital is branched according to $D \rightarrow E + T_2 \rightarrow A_1 + B_1 + E + B_2$. Adding the characters of these four representations yields 5, 1, -1, 1 and 1. The dipole transition operator has p-symmetry and hence is branched to $E + A_2$ symmetry, in other words the dipole operator is described with two operators in two different directions implying an angular dependence in the x-ray absorption intensity. The quadrupole transition operator has d-symmetry and is split into four operators in D_{4h} symmetry, in other words there will be four different quadrupole transitions in different directions/symmetries. The Hamiltonian is given by the unity representation A_1 . Similarly as in O_h symmetry, the atomic G-symmetry state branches into the Hamiltonian in D_{4h} symmetry according to the series $G \rightarrow A_1 \rightarrow A_1$. In addition it can be seen that the E symmetry state of O_h symmetry branches to the A_1 symmetry state in D_{4h} symmetry. The E symmetry state in O_h symmetry is found from the D and G atomic states. This implies that also the series $G \rightarrow E \rightarrow A_1$ and $D \rightarrow E \rightarrow A_1$ become part of the Hamiltonian in D_{4h} symmetry. This is again a confirmation of equation 3.6, where we find that the second term $A_{2M}Y_{2M}$ is part of the Hamiltonian in D_{4h} symmetry. The three branching series in D_{4h} symmetry are in Butlers notation given as $4 \rightarrow 0 \rightarrow 0$, $4 \rightarrow 2 \rightarrow 0$ and $2 \rightarrow 2 \rightarrow 0$ and the radial parameters related to these branches are indicated as X_{400} , X_{420} , and X_{220} . The X_{400} term is important already in O_h symmetry. This term is closely related to the cubic crystal field term $10Dq$ as will be discussed below.

3.10 Appendix D: The definitions of the Crystal Field parameters

In order to compare the X_{400} , X_{420} , and X_{220} definition of crystal field operators to other definitions like Dq, Ds, Dt, we compare their effects on the set of 3d-functions. The most straightforward way to specify the strength of the crystal field parameters is to calculate the energy separations of the 3d-functions. In O_h symmetry there is only one crystal field parameter X_{40} . This parameter is normalized in a manner that creates unitary transformations in the calculations. The result is that it is equal to $1/18 \cdot \sqrt{30}$ times 10Dq, or 0.304 times 10Dq.

In tetragonal symmetry (D_{4h}) the crystal field is given by three parameters, X_{400} , X_{420} and X_{220} . An equivalent description is to use the parameters Dq, Ds and Dt. This table gives the action of the X_{400} , X_{420} and X_{220} on the 3d-orbitals and relates the respective symmetries to the linear combination of X parameters, the linear combination of the Dq, Ds and Dt parameters and the specific 3d-orbital(s) of that particular symmetry.

Γ	Energy expressed in X-terms	Energy in D-terms	orbitals
b_1	$30^{-1/2} \cdot X_{400} - 42^{-1/2} \cdot X_{420} - 2 \cdot 70^{-1/2} \cdot X_{220}$	$6Dq + 2Ds - 1Dt$	$3d_{x^2-y^2}$
a_1	$30^{-1/2} \cdot X_{400} + 42^{-1/2} \cdot X_{420} + 2 \cdot 70^{-1/2} \cdot X_{220}$	$6Dq - 2Ds - 6Dt$	$3d_{z^2}$
b_2	$-2/3 \cdot 30^{-1/2} \cdot X_{400} + 4/3 \cdot 42^{-1/2} \cdot X_{420} - 2 \cdot 70^{-1/2} \cdot X_{220}$	$-4Dq + 2Ds - 1Dt$	$3d_{xy}$
e	$-2/3 \cdot 30^{-1/2} \cdot X_{400} - 2/3 \cdot 42^{-1/2} \cdot X_{420} + 70^{-1/2} \cdot X_{220}$	$-4Dq - 1Ds + 4Dt$	$3d_{xz}, 3d_{yz}$

The energy of the 3d orbitals is expressed in X_{400} , X_{420} and X_{220} in the second column and in Dq, Ds and Dt in the third column.

From this table we can relate both notations and write X_{400} , etc as a function of Dq, Ds and Dt.

- $X_{400} = 6 \cdot 30^{1/2} \cdot Dq - 7/2 \cdot 30^{1/2} \cdot Dt$
- $X_{420} = -5/2 \cdot 42^{1/2} \cdot Dt$
- $X_{220} = -70^{1/2} \cdot Ds$

The inverse relationship imply:

- $Dq = 1/6 \cdot 30^{-1/2} \cdot X_{400} - 7/30 \cdot 42^{-1/2} \cdot X_{420}$
- $Ds = -70^{-1/2} \cdot X_{220}$
- $Dt = -2/5 \cdot 42^{-1/2} \cdot X_{420}$

These relations allow the quick transfer from for example the values of Dq, Ds and Dt from optical spectroscopy to the X-values as used in x-ray absorption.

3.11 Appendix E: Tanabe-Sugano diagrams from the multiplet calculations

The crystal field multiplet calculations use a single configuration as their ground state, in other words its ground state can be found from the Tanabe Sugano diagram. This also implies that the energies of the TSD are calculated in the crystal field multiplet calculation. The numbers are given in the ora files. If we use the files `als5ni2.rcg` and `als5ni2.rac` (which are identical to the als1ni2 files), we find in the `als5ni2.ora` file the following lines:

```
CALCULATIONS for ACTOR:HAMILTONIAN      GROUND

      CALCULATING MATRIX for TRIAD  1  (  0+   0+   0+ 0)  (4*4)
      MATRIX HAS 4 ZERO, 12 REAL and 0 COMPLEX ELEMENTS

      DIAGONALIZATION

      ---- EIGENVALUES ----

              1          2          3          4
KET/PURE      3 0.92      4 0.93      1 0.92      2 0.94
EIGVAL  -0.801748  0.603819  0.943165  5.315486
```

```
      CALCULATING MATRIX for TRIAD  6  (  1+   0+   1+ 0)  (4*4)
```

```
      MATRIX HAS 4 ZERO, 12 REAL and 0 COMPLEX ELEMENTS
```

```
      DIAGONALIZATION
```

```
      ---- EIGENVALUES ----
```

```
              1          2          3          4
KET/PURE      2 0.52      3 0.47      1 0.91      4 0.99
EIGVAL  -1.472040 -0.734825  0.914685  1.097910
```

```
      CALCULATING MATRIX for TRIAD 21 (  2+   0+   2+ 0)  (5*5)
```

```
      MATRIX HAS 6 ZERO, 19 REAL and 0 COMPLEX ELEMENTS
```

```
      DIAGONALIZATION
```

```
      ---- EIGENVALUES ----
```

```
              1          2          3          4          5
```

```
KET/PURE      4 0.76      3 0.40      1 0.41      2 0.90      5 0.74
EIGVAL -1.492799 -0.730041 -0.515086  0.855732  1.906725
```

```
CALCULATING MATRIX for TRIAD 31 ( ^1+ 0+ ^1+ 0) (6*6)
MATRIX HAS 10 ZERO, 26 REAL and 0 COMPLEX ELEMENTS
```

```
DIAGONALIZATION
```

```
----- EIGENVALUES -----
```

```

      1      2      3      4      5      6
KET/PURE  5 0.52  1 0.47  4 0.53  3 0.79  2 0.83  6 0.84
EIGVAL -2.572434 -1.420765 -0.629293  0.391811  0.886141  1.968931
```

```
CALCULATING MATRIX for TRIAD 46 ( ^0+ 0+ ^0+ 0) (1*1)
MATRIX HAS 0 ZERO, 1 REAL and 0 COMPLEX ELEMENTS
```

```
DIAGONALIZATION
```

```
----- EIGENVALUES -----
```

```

      1
KET/PURE  1 1.00
EIGVAL -1.400139
```

The numbers in bold red are the respective energies from the TSD. Collecting the energies yields:

```
A1 -0.801748 0.603819 0.943165 5.315486
T1 -1.472040 -0.734825 0.914685 1.097910
E  -1.492799 -0.730041 -0.515086 0.855732 1.906725
T2 -2.572434 -1.420765 -0.629293 0.391811 0.886141 1.968931
A2 -1.400139
```

The energies and symmetries are given in total symmetry. The ground state is found at -2.572434 eV and has T_2 symmetry. This is the 3A_2 ground state of a $3d^8$ configuration, which in total symmetry gives $A_2 \times T_1 = T_2$ symmetry. The next lowest states are a number of states around -1.45 eV. In total there are four of these states with the symmetries T_1 , E, T_2 and A_2 . Adding the degeneracies yields a $3+2+3+1=9$ -fold degenerate state. This is the 3T_2 state, which can be checked by multiplying T_1 with T_2 , yielding the 4 symmetries as given. Below the lowest 5 states have been identified. Continuing in this way yields the complete TSD.

A1	-0.801748	0.603819	0.943165	5.315486
T1	-1.472040	-0.734825	0.914685	1.097910
E	-1.492799	-0.730041	-0.515086	0.855732 1.906725
T2	-2.572434	-1.420765	-0.629293	0.391811 0.886141 1.968931
A2	-1.400139			
3A2	3T2	3T1	1E	1T2

The determination of the TSD symmetries using the method as given above becomes rather complex if the ground state has many states, say between $3d^3$ and $3d^7$. Things become significantly simpler if one switches the ground state $3d$ spin-orbit coupling off. In doing so, the states of a certain symmetry state become exactly degenerate.

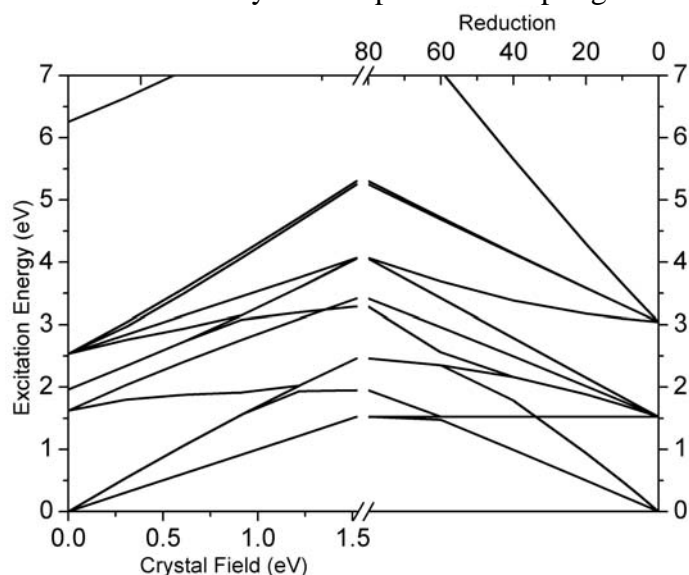
The files `als5ni2z.rcg` and `als5ni2z.rac` use a zero $3d$ spin-orbit coupling. The only change that must be made is changed the value 0.0832 in the ground state to 0.0002. (check that this is done by inspecting the file `als5ni2z.rcg`).

Ni2+ 2p06 3d08	4	0.0000	12.2341	7.5981	0.0832	0.0000HR99999999
Ni2+ 2p06 3d08	4	0.0000	12.2341	7.5981	0.0002	0.0000HR99999999

This yields an `als5ni2z.ora` file that has the TSD without the inclusion of the $3d$ spin-orbit coupling.

A1			-0.687617			0.599870	0.883427		5.306541
T1			-1.441638	-0.687618			0.883427	1.093059	
E			-1.441639	-0.687617	-0.630865		0.883427	1.901225	
T2	-2.558384	-1.441639	-0.687618			0.422527	0.883427		1.964579
A2			-1.441639						
	3A2	3T2	3T1	1E	1A1	3T1	1T1	1A1	
					1T2		1E	1T2	

The symmetries one finds are exactly those as determined from group theory arguments above. Note that the ground state is a pure T_2 symmetry state in double group symmetry. This implies that it cannot be split and as such is not affected by the $3d$ spin-orbit coupling.



The figure shows the effect of the reduction of the Slater-Condon parameters. The figure is the same as figure 3.1 up to a crystal field of 1.5 eV. Then for this crystal field value the Slater-Condon parameters have been reduced from their atomic value, indicated with 80% of their Hartree-Fock value to 0%. The spectrum for 0% has all its Slater-Condon parameters reduced to zero. In other words the $2p3d$ coupling has been turned off and one essentially observes the energies of a $3d^8$ configuration, i.e. of a two $3d$ -holes. This single particle limit has three configurations, respectively the two holes in $e_g e_g$, $e_g t_{2g}$ and $t_{2g} t_{2g}$ states. The energy difference between $e_g e_g$ and $e_g t_{2g}$ is exactly the

crystal field value of 1.5 eV. This figure shows nicely the transition from the single particle picture to the multiplet picture for the $3d^8$ ground state.

With the files `als5ni2b.rcg` and `als5ni2b.rac` we can reproduce the case that the 3d3d Slater-integrals are switched off. One obtains the following result for the eigenvalues in the initial state:

A1	-1.340094	-0.223349		0.893396	0.893396
T1		-0.223349	-0.223349	-0.223349	0.893396
E	-1.340094	-0.223349	-0.223349		0.893396
T2	-1.340095	-0.223349	-0.223349	-0.223349	0.893396
A2		-0.223349			

The lowest energy state has two holes in the e_g level. Its dimension is $1+2+3=6$. The next level has a hole in e_g and a hole in t_{2g} . Its dimension is $1+9+4+9+1=24$. The highest energy state has two holes in the t_{2g} level with dimension $2+3+4+6=15$. These degeneracies can be determined from the calculation of the possible number of ways one can put two holes in an e_g level. There are 4 e_g orbitals, implying that the first hole has 4 possibilities, the second 3 and their product must be divided by 2, giving $4*3/2 = 6$. Similarly for two t_{2g} holes this gives $6*5/2=15$. For a hole in e_g plus a hole in t_{2g} the number of possibilities is $6*4=24$.

The intermediate states on the right side of figure 3.2 can be determined using the files `als5ni2z.rcg` and `als5ni2z.rac`, by setting the first reduction factor from 80 to, for example, 60, 40 and 20, i.e. the following line in `als5ni2z.rcg` is changed.

0	80998080	8065.47800	0000000
0	40 998080	8065.47800	0000000

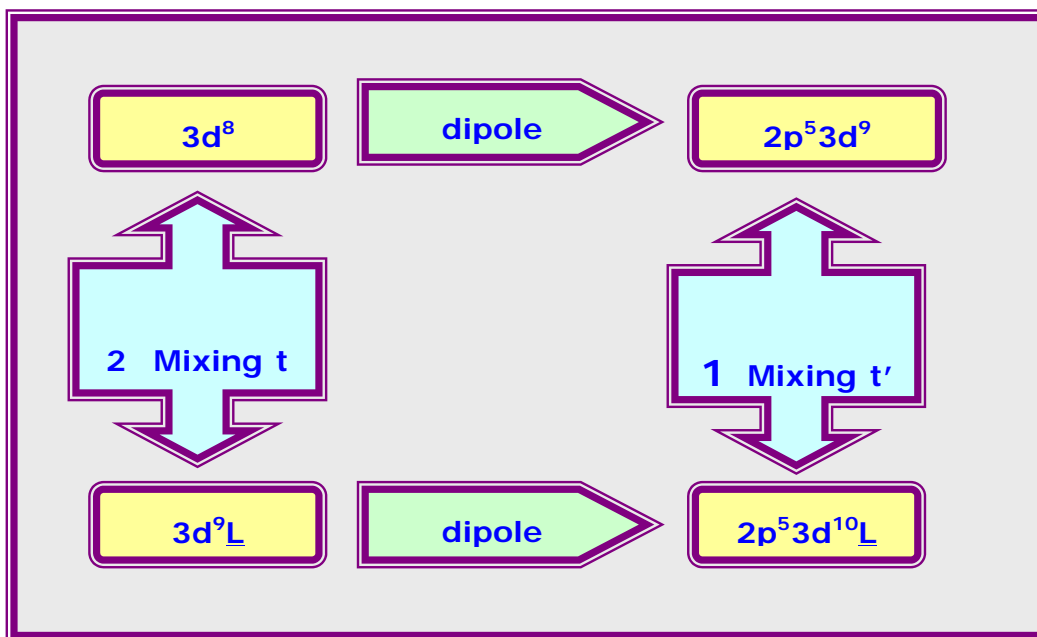
One can make the grid of the TSD as fine as one likes by calculating a large number of states. Interesting things happen if one is close to a crossing point, for example a high-spin to low-spin transition. If the 3d spin-orbit coupling is set to zero high-spin and low-spin states just cross as they are not coupled. However, if the 3d spin-orbit coupling is switched on, the ground state could become a mixture of high-spin and low-spin.

4 Charge Transfer Multiplet Calculations

4.1 The Charge Transfer Multiplet Model

Charge transfer effects are the effects of charge fluctuations in the initial and final states. The atomic multiplet and crystal field multiplet model use a single configuration to describe the ground state and final state. One can combine this configuration with other low-lying configurations similar to the way configuration-interaction works with a combination of Hartree-Fock matrices.

We start with a charge transfer multiplet calculation of NiO. Instead of a ground state that consists of a single $3d^8$ configuration, we add a second configuration where an electron has moved from a filled oxygen 2p-band to the e3d-band. This creates a $3d^9$ configuration with a hole on the oxygen ligand. This is notated as $3d^9\bar{L}$. There is a big difference between a single configuration calculation and a charge transfer calculation. In a single configuration calculation, one needs only a single dipole transition matrix calculation. With two configurations, we need two dipole calculations, from $3d^8$ to $2p^5 3d^9$ and from $3d^9$ to $2p^5 3d^{10}$. However, if one would only perform the dipole calculations, the configurations would not mix. To mix the $3d^8$ and $3d^9\bar{L}$ configurations we need an additional calculation. Effectively this is a monopole transition calculation between $3d^8$ and $3d^9\bar{L}$. A similar mixing occurs in the final state. We arrive at four calculations to be performed, as schematically indicated in this scheme.



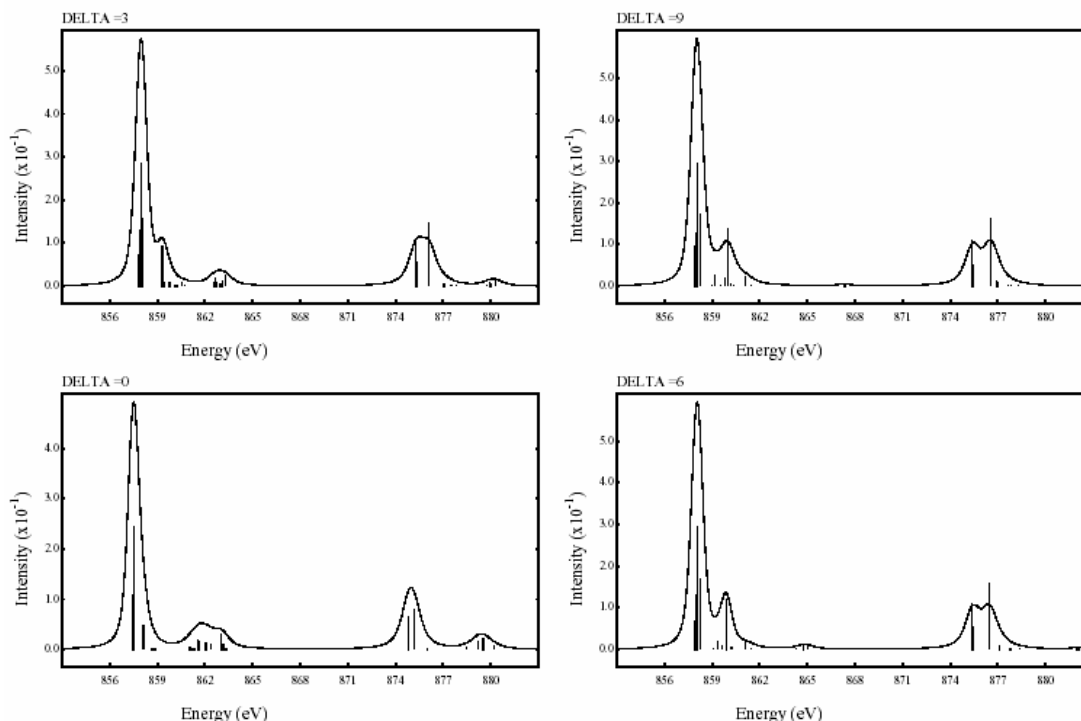
Charge transfer multiplet calculations can be performed by adding the second configuration with the Charge Transfer button. Details of the individual programs that are used with this option are given in appendix A.

The new parameters in a charge transfer

multiplet calculation are the charge transfer energy Δ , indicated as DELTA, The Hubbard Udd and the core hole potential Upd. In case of 2p XAS, only the difference between Udd and Upd is important. The other new parameters are the hopping terms that are symmetry dependent. Initially, we assume Oh symmetry, implying that $T(e_g) = T(b_1) = T(a_1)$ and $T(t_{2g}) = T(b_2) = T(e)$, using a 2:1 ratio between e_g and t_{2g} mixing. Effectively this yields only three new parameters: Δ , Udd-Upd and T.

With the value $\Delta=0$, we create a 50:50 mixture of $3d^8$ and $3d^9\bar{L}$. In contrast NiO should be described with much more $3d^8$ than $3d^9\bar{L}$ in its ground state. This can be achieved by increasing Δ . In the figure

below we increased Δ from 0.0, via 3.0 and 6.0 to 9.0, as indicated. The value of 9.0 eV creates a ground state that is essentially pure in $3d^8$ character. This also implies that the calculated spectral shape is identical to the single configuration calculation $3d^8 > 2p^5 3d^9$ (check with chapter 5). If we decrease the value of Δ from 9.0 to 6.0, some admixture occurs and in the spectrum we can observe a satellite at 865 eV. In addition the multiplet structure of the L_3 edge appears compressed.



If one would like to fit the experimental NiO spectrum (or another Ni^{2+} spectrum), in addition to Δ , one could optimize Udd-Upd (varying it between -2.0 and 0.0 eV), the crystal field (set to the overall value of 1.12 eV; it should be lowered because there is an additional contribution due to the non-spherical mixing. In addition, one could vary the mixing parameters, say between 1.6 and 2.4 for $T(e_g)$.

Exercise 4.1:

- (e) Calculate the charge transfer multiplet spectrum of Ni^{2+} , using $T(e_g) = 2.0$, $10Dq = 1.0$ eV and Udd-Upd=-1.0 eV, with $T(e_g)=2* T(t_{2g})$; Vary Δ between 0.0 and 10.0 eV.
 (f) What happens for negative values of Δ ? (Try -10.0 eV)

The amount of mixing between $3d^8$ and $3d^9\bar{L}$ is given in the **oba** file. In the **oba** file we find the first triad given as:

```

0+   1-   1-  0
Ground state energy Eg0= -1.138234258      ( 1 times)
Weight of configurations 1,2,3 in the ground state: 0.96709 0.03291 0.00000
Lowest few energies      -1.13823  -0.21210   0.54317   4.65561   8.40510
      9.34407   9.61269   9.87314   9.97790
energies and purities
-1.13823 0.967  -0.21210 0.912   0.54317 0.958   4.65561 0.878   8.40510 0.007
 9.34407 0.103   9.61269 0.026   9.87314 0.073   9.97790 0.077

```

```

TRANSFORMED MATRIX FOR TRIAD ( 0+      1-      1-      ) (1*      10) DIM : 1
: 0 : 3 ACTOR MULTIPOLE
BRA/KET : 854.64648 856.27197 856.76636 857.11066 858.35681 863.68793 864.12854
-1.13823: 0.053427 0.178937 0.080075 0.044825 0.000084 0.000398 0.000950
BRA/KET : 873.27112 875.03711 881.34369
-1.13823: 0.031072 0.003446 0.000203
Total intensity 0.39342

```

First the ground state energy is given for 0+ (A_1) symmetry. It is -1.13 eV. The next line gives the weights of the configurations, i.e. 96.7% $3d^8$ and 3.3% $3d^9\bar{L}$. However, note that this applies to A_1 symmetry only. The ground state of Ni^{2+} in octahedral symmetry has 3A_2 (T_2) symmetry, which will not change by charge transfer. So, we have to look for the T_2 ($^1+$) symmetry output lines in the **oba**-file:

```

^1+  1-  1-  0
Ground state energy Eg0= -3.264462233      ( 1 times)
Weight of configurations 1,2,3 in the ground state: 0.94391 0.05610 0.00000
Lowest few energies      -3.26446 -1.87305 -0.98539 -0.11271 0.50011
 1.68275 8.32094 8.39507 8.40402 8.40845 9.00927
energies and purities
-3.26446 0.944 -1.87305 0.961 -0.98539 0.965 -0.11271 0.948 0.50011 0.960
 1.68275 0.965 8.32094 0.000 8.39507 0.005 8.40402 0.007 8.40845 0.007
 9.00927 0.056 9.41960 0.001 9.49206 0.000 9.67276 0.022 9.72025 0.028
 9.80985 0.042 9.89024 0.040 9.94698 0.049
TRANSFORMED MATRIX FOR TRIAD ( ^1+      1-      1-      ) (1*      11) DIM : 3 : 0
: 3 ACTOR MULTIPOLE
BRA/KET : 854.64655 856.27197 856.76648 857.11084 858.35760 863.71844 864.01837
-3.26446: 0.085617 0.000523 0.119927 0.000824 0.000043 0.000014 0.000369
BRA/KET : 864.12927 873.27106 875.03693 881.34351
-3.26446: 0.002623 0.141123 0.002856 0.001015
Total intensity 0.35493

```

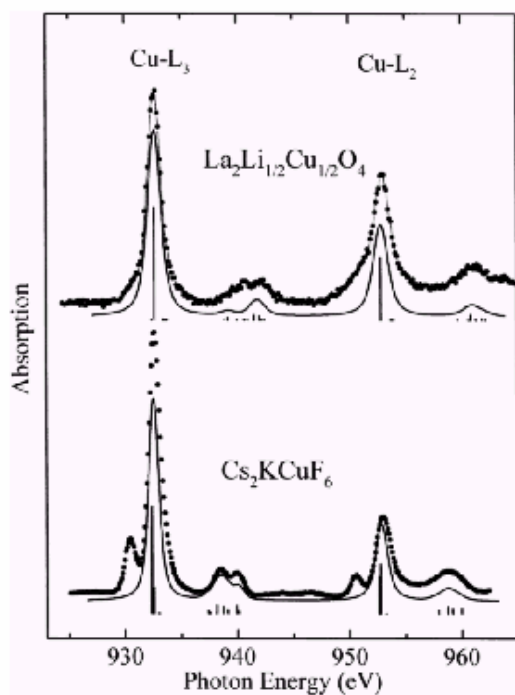
We see that the ground state energy is indeed lower at -3.26 eV.

The ground state contains 94.4% $3d^8$ and 5.6% $3d^9\bar{L}$ character, similar but not identical to the A_1 symmetry numbers.

DELTA	% $3d^8$	% $3d^9\bar{L}$
0	66	34
3	83	17
6	91	9
9	94	6

One observes that only small Δ values allow for significant mixing of $3d^8$ and $3d^9\bar{L}$. In principle, Δ can become negative, which could lead to a ground state that has over 50% $3d^9\bar{L}$. Such ground states are actually found for Cu^{3+} ions, as will be discussed below.

This figure shows the comparison of the 2p x-ray absorption spectrum of these two compounds with charge transfer multiplet calculations. These calculations look similar to the calculations for Ni^{2+} systems with negative values of Δ . For such systems with negative Δ values, it is important to carry out charge transfer multiplet calculations, as no good comparison with crystal field multiplet spectra can be made.



Results of theoretical simulations of the copper 2p x-ray absorption spectra of Cs_2KCuF_6 (bottom) and $\text{La}_2\text{Li}_{1/2}\text{Cu}_{1/2}\text{O}_4$ (top), in comparison with the experimental spectra.

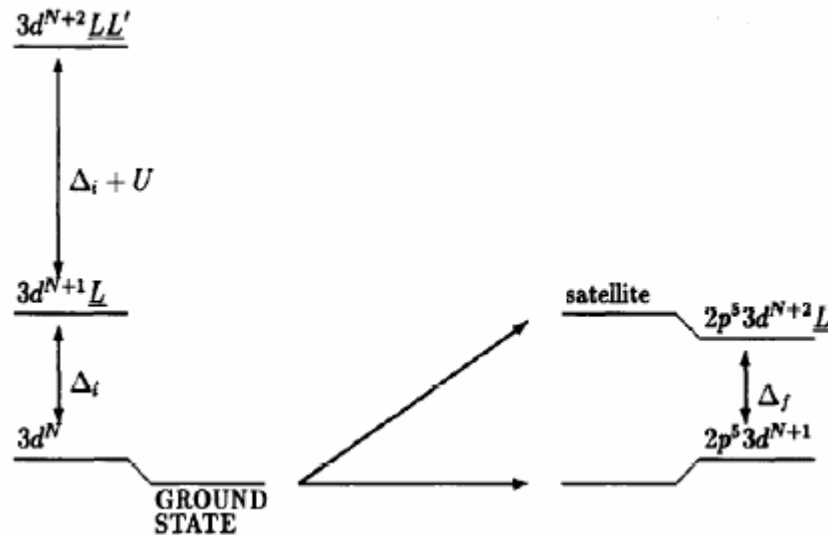
Exercise 4.2:

- Try to reproduce the Cu 2p XAS spectrum of Cs_2KCuF_6 .
The symmetry is octahedral; Use $T(e_g) = 2.0$, $T(e_g) = 2 * T(t_{2g})$ and $\text{Udd-Upd} = -1.0$ eV. Optimize $10Dq$ and Δ .
- Try to reproduce the Cu 2p XAS spectrum of $\text{La}_2\text{Li}_{1/2}\text{Cu}_{1/2}\text{O}_4$.
The symmetry is square planar and the ground state is low-spin; Use $Ds = 0.3$, $T(b1) = 3.0$, $T(a1) = 1.73$, $T(b2) = 1.5$, $T(e) = 1.05 *$ and $\text{Udd-Upd} = -1.0$ eV. Optimize $10Dq$ and Δ .

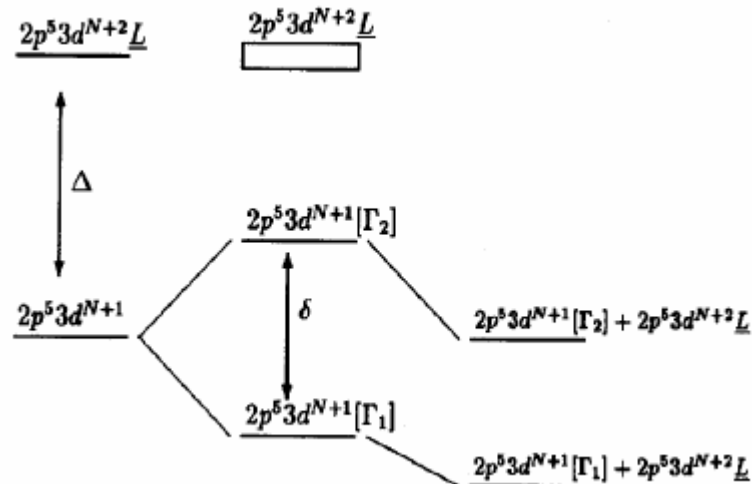
*The relations between the hopping terms are described by Eskes and Sawatzky, Phys. Rev. B 43, 119 (1991).

4.2 Why are the charge transfer satellites in XAS small?

In the figure below the effects of hybridization are included for 2p XAS. The ground state is formed from a combination of $3d^N$ and $3d^{N+1}\underline{L}$. The two configurations in the final state form a bonding and antibonding combination. If $\Delta_f = \Delta$ (and $t_f = t$), all intensity goes to the bonding combination of the two final state configurations and no satellite is present.



In the case of 2p XPS the situation is rather different. In general there are three low-lying states in the final state and their ordering has been changed with respect to the ground state. Under complete neglect of hybridization only the $2p^5 3d^{N+1}$ final state can be reached. If hybridization is turned on the two lower states gain in intensity, partly due to ground state hybridization but mainly due to final state hybridization and additionally due to the interference terms.



We assume that in a final state of 2p XAS the multiplet lines are spread out over an energy range of several electron volts (for details of multiplet calculations see Section 5.1). This spread implies that the energy difference of these different states with the $2p^5 3d^{N+2}\underline{L}$ band varies considerably. In the figure below a situation is sketched in which the multiplet splittings (δ) are less than the charge transfer energy (Δ). If hybridization is turned on, the energy-gain of the lowest multiplet state (Γ_1) will be less than the energy-gain of the highest multiplet state, because the effective energy

difference with the band is much smaller in the latter case. In the case of a multiplet with 100 lines instead of 2 this principle remains valid. The consequence is that the multiplet structure is “compressed” with respect to the atomic multiplet. If the spread of multiplet states is larger than the charge transfer energy, some of the multiplet states will be located within and above the band and the effects of charge transfer will be more complex.

Exercise 4.3:

- (a) Modify the relation $U_{dd}-U_{pd}=-1.0$ eV to values between 0.0 and 10.0.
- (a) What is the effect of the spectral shape?

4.3 Appendix A: Charge transfer calculations with BAN2

The charge transfer multiplet calculations need an additional program BAN2, where the four individual calculations are combined. The RCG2 and RAC2 calculations are performed four times, using a single input file. The results of RCG2 are again written to m14 matrix files. The results of RAC2 are written to m15 matrix files. The BAN2 program uses these matrices to generate the charge transfer multiplet spectrum.

We start with a Ni²⁺ calculation in Oh symmetry. The files als6ni2x1.rcg, als6ni2x1.rac and als6ni2x1.ban generate the output file als6ni2x1.oba, which contains the spectrum. The file als6ni2x1.rcg consists of four parts, indicated with four colors.

```

0                                80998080                                8065.47900      000000
10                               14      0      0      1      1 INTER0
1      2 1 12 1 10              00          9 00000000 0 8065.4790 .00          1
D08 P06
D09 P05
Ni3+ 1 2
Ni3+ 2 2
-99999999.

0                                80998080                                8065.47900      000000
10                               14      0      0      1      1 INTER0
1      3 1 13 1 10              00          9 00000000 0 8065.4790 .00          1
D09 P06 D09
D10 P05 D09
Ni3+ 1 3
Ni3+ 2 3
-99999999.

0                                80998080                                8065.47900      000000
10                               14      0      4      0      4 SHELL30000000 SPIN30000000 INTER2
1      3 1 13 1 10              00          9 00000000 0 8065.4790 .00          1
D08 P06 D10
D09 P06 D09
Ni3+P6D8L      4      0.0000      12.2341      7.5981      0.0832      0.0000HR99999999
Ni3+P6D9L2     2      0.0000      0.0742      0.0000      0.0000      0.0000HR99999999
-99999999.

0                                80998080                                8065.47900      000000
10                               14      0      4      0      4 SHELL30000000 SPIN30000000 INTER2
1      3 1 13 1 10              00          9 00000000 0 8065.4790 .00          1
D09 P05 D10
D10 P05 D09
Ni3+P5D9L      6      862.3000      00.1022      11.5072      7.7213      5.7874HR99999999
3.2914
Ni3+P5D10L2    2      862.3000      11.5092      0.0000      0.0000      0.0000HR99999999
-99999999.

-1

```

Every color is related to a single RCG2 calculation. Each sub-calculation is similar to a normal single configuration RCG2 calculation, where each sub-calculation ends with the line `–99999999`. and the file ends with the command `–1`.

- ⊗ The blue calculation is the dipole transition from $3d^8$ to $2p^5 3d^9$, as indicated with the initial state configuration (blue line 4) `D08 P06` and final state configuration (blue line 5) `D09 P05`. The blue and the green calculation are empty, in the sense that no parameters are given. Only the dipole matrix elements for the defined dipole transition are calculated.
- ⊗ The green calculation is the dipole transition from $3d^9 \underline{L}$ to $2p^5 3d^{10} \underline{L}$, as indicated with the initial state configuration (green line 4) `D09 P06 D09` and final state configuration (green line 5) `D10 P05 D09`. Note that the ligand hole state `L` is indicated as a d-electron. This is needed because this ligand hole state should mix with the 3d-states and as such bear the symmetries of this 3d-state when viewed from the metal centre. Later we will see that this ligand hole d-electron is described in a non-correlated way.
- ⊗ The red calculation is the monopole mixing in the initial state. The initial state first configuration (red line 4) `D08 P06 D10` and initial state second configuration (red line 5) `D09 P06 D10` are mixed. The parameters given relate to these two configurations, where it is noted that the ligand hole d-electron has no parameters. In addition, the 2p-state is completely full in the initial state, so the parameters relate to respectively $3d^8$ and $3d^9$ configuration. A $3d^8$ configuration has 4 parameters (energy, two Slater integrals and 3d spin-orbit) and a $3d^9$ configuration has 2 parameters (energy and 3d spin-orbit). The initial state energies are set to zero. Later in the `als6ni2x1.ban` file the energy difference (= charge transfer energy) is defined. Note that the 3d electrons have been set to the first shell and the corresponding `SHELL` command gives a 3 also in the first position.
- ⊗ The black calculation is the monopole mixing in the final state. The final state first configuration (black line 4) `D09 P05 D10` and final state second configuration (black line 5) `D10 P05 D10` are mixed. The parameters given relate again to these two configurations. A $2p^5 3d^9$ configuration has 6 parameters (energy, three pd Slater integrals and two spin-orbit couplings) and a $2p^5(3d^{10} = \text{full})$ configuration has 2 parameters (energy and 2p spin-orbit). The final state energies are set to the identical value of 862.300 eV, the (as such defined) centre of gravity of the 2p to 3d transition. Later in the `als6ni2x1.ban` file the final state energy difference is defined.

The `als6ni2x1.rcg` file is always the same for a Ni^{2+} calculation with two configurations. Later we will show three configuration calculations, for example $3d^7 + 3d^8 \underline{L} + 3d^9 \underline{L}^2$ for a Ni^{3+} ground state. The next step in the RAC2 calculation. This file has the following form:

```
Y
    % vertical 1 1
racer O3
TO      OH
ENDCHAIN
ACTOR    1-  MULTIPOLE    TRANSI
OPER      MULTIPOLE
BRANCH   1-  > 0 1-    1.000
ACTOR    0+  HAMILTONIAN  GROUND
ACTOR    0+  10Dq         GROUND
ACTOR    0+  HAMILTONIAN  EXCITE
ACTOR    0+  10Dq         EXCITE
RUN
```

```

      % vertical 2 2
racer O3
TO      OH
ENDCHAIN
ACTOR   1- MULTIPOLE   TRANSI
      OPER      MULTIPOLE
      BRANCH   1- > 0 1- 1.000
ACTOR   0+ HAMILTONIAN GROUND
ACTOR   0+ 10Dq        GROUND
ACTOR   0+ HAMILTONIAN EXCITE
ACTOR   0+ 10Dq        EXCITE
RUN
      % horizontal ground 1 2
racer O3
TO      OH
ENDCHAIN
ACTOR   0+ eghybr      TRANSI
      OPER      MULTIPOLE
      BRANCH   0+ > 0 0+ .894427191
      BRANCH   4+ > 0 0+ 3.286335345
ACTOR   0+ t2ghybr     TRANSI
      OPER      MULTIPOLE
      BRANCH   0+ > 0 0+ 1.341640787
      BRANCH   4+ > 0 0+ -3.286335345
ACTOR   0+ HAMILTONIAN GROUND

```

```

      OPER      HAMILTONIAN
      BRANCH   0+ > 0 0+ 1.000
ACTOR   0+ 10Dq        GROUND
      OPER      Shell1
      BRANCH   4+ > 0 0+ 3.286335345
ACTOR   0+ HAMILTONIAN EXCITE
      OPER      HAMILTONIAN
      BRANCH   0+ > 0 0+ 1.000
ACTOR   0+ 10Dq        EXCITE
      OPER      Shell1
      BRANCH   4+ > 0 0+ 3.286335345
RUN
      % horizontal excite 1 2
racer O3
TO      OH
ENDCHAIN
ACTOR   0+ eghybr      TRANSI
      OPER      MULTIPOLE
      BRANCH   0+ > 0 0+ .894427191
      BRANCH   4+ > 0 0+ 3.286335345
ACTOR   0+ t2ghybr     TRANSI
      OPER      MULTIPOLE

```



```

    BRANCH  0+ > 0 0+  1.341640787
    BRANCH  4+ > 0 0+ -3.286335345
  ACTOR    0+ HAMILTONIAN GROUND
    OPER    HAMILTONIAN
      BRANCH  0+ > 0 0+  1.000
  ACTOR    0+ 10Dq      GROUND
    OPER    Shell11
      BRANCH  4+ > 0 0+  3.286335345
  ACTOR    0+ HAMILTONIAN EXCITE
    OPER    HAMILTONIAN
      BRANCH  0+ > 0 0+  1.000
  ACTOR    0+ 10Dq      EXCITE
    OPER    Shell11
      BRANCH  4+ > 0 0+  3.286335345
  RUN

```

Every color is again related to a single RAC2 calculation, where the same colors have been used as for the RCG2 calculation.

- ☒ The blue calculation is the dipole transition from $3d^8$ to $2p^5 3d^9$. The only treatment that is done to the file is the projection of the dipole operator from atomic (1-) to cubic (1-) symmetry.
- ☒ The green calculation is an exact copy of the blue calculation.
- ☒ Also the red and the black calculations are exact copies of each other. The red calculation shows the branching of the mixing and the Hamiltonian in respectively the ground and the final state. The mixing is given with two separate 'hybridizations', respectively eghybr and t2ghybr. These two mixing parameters relate respectively to the mixing of an e_g electron and a t_{2g} electron. The numbers .894427191 and 3.286335345 take care that the interactions can be given in electron volts in the BAN2 input file. Their origin will be explained later. Below the ground state Hamiltonian (HAMILTONIAN GROUND) and the excited state Hamiltonian (HAMILTONIAN EXCITE) are given. In this case they consist of the atomic Hamiltonian and the cubic crystal field. Because the 3d-electrons were defined in the first shell in the RCG2 program, we use the operator SHELL1 in the RAC2 input file.

After running the files with `rcg2 als6ni2x1` and `rac2 als6ni2x1`, we have created the files `als6ni2x1.m14` and `als6ni2x1.m15`. These files contain the matrices that are needed in the third program where the configurations are mixed. We will look later into these files.

The BAN2 program is run with the command `ban2 als6ni2x1`. The file that is used is called `als6ni2x1.ban`.

```

PRMULT
  erange 1.0
  NCONF 2 2
  N2 1
  def EG2 = 0.0 unity
  def EF2 = -2.0 unity
  XMIX 2      2.0    1.0
  2    1 1 2          2 1 2
  XHAM 2    1.0    1.12
  4    1 1    1 2    2 1    2 2

```

```

TRAN  2      1 1      2 2
TRIADS
 0+    1-    1-  0
 1+    1-    0-  0
 1+    1-    1-  0
 1+    1-    2-  0
 1+    1-    ^1- 0
 2+    1-    1-  0
 2+    1-    ^1- 0
 ^1+    1-    1-  0
 ^1+    1-    2-  0
 ^1+    1-    ^1- 0
 ^1+    1-    ^0- 0
 ^0+    1-    ^1- 0

```

We will explain this file line by line.

- ⊗ The first line PRMULT indicates that the symmetry is Oh (more later).
- ⊗ The second line erange 1.0 indicates that all states within 1.0 eV of the lowest energy state (within a certain symmetry) are calculated. In principle one only needs the ground state, and if the erange command is omitted only the lowest energy state is calculated. In case of AS calculations, one in principle needs only the ground state or at finite temperature all those states that are populated. At room temperature (= 25 meV), a value of 0.1 is in principle large enough. Large erange values could yield very large output files (with useless information).
- ⊗ The third line NCONF 2 2 indicates that there are two configurations in the initial state and two configurations in the final state.
- ⊗ The 4th line N2 1 indicates that the second configuration is included once. Effectively this means that no finite bandwidth is chosen for the ligand hole state. If this command is changed to, for example, N2 5 w 3 one includes a bandwidth of 3.0 eV in which 5 states are chosen that each interact with the first configuration.
- ⊗ The 5th line **def EG2 = 0.0 unity** sets the value of DELTAAV, that is the energy difference between the first (EG1) and the second (EG2) configuration in the ground state. This energy difference is defined between the centers of the multiplets of each configuration, which means that it is different from the value of DELTA. DELTA is defined between the lowest energy states within two configurations. Below it will be explained how to calculate DELTA from DELTAAV. The energy of the first configuration (EG1) is in most cases set to its default value of 0.0 eV, but in principle it could be set to a non-zero value with an additional inputline, for example **def EG1 = 1.0 unity**
- ⊗ The 6th line repeats this procedure for the final state. As we will see below, in XAS EF2 is closely related to EG2. The formal relation is that $EF2 = EG2 + U_{dd} - U_{pd}$. The core hole potential U_{pd} is always larger than the 3d3d-correlation U_{dd} . As a rule, one can assume that U_{pd} is 1 to 2 eV larger than U_{dd} . This implies that EF2 is 1 to 2 eV smaller than EG2.
- ⊗ The line **XMIX 2 2.0 1.0** defines the mixing strength (t). In case of oxides in an octahedral surrounding, one can use the values 2.0 for e_g mixing and 1.0 for t_{2g} mixing. See degroot94a.pdf for details.
- ⊗ The line **2 1 1 2 2 1 2** defines that the mixing (as defined in the line above) acts on both the initial and the final state. (more details later)
- ⊗ The line **XHAM 2 1.0 1.12** defines the Hamiltonian that acts on all configurations. The first number gives the number of parts of the Hamiltonian (2), followed by the values as defined in the rac input file, in this case first the atomic Hamiltonian (always set to 1.0) and the cubic crystal field, set to 1.12. In BAN2 all values are given in electron volts.

- ⊗ The line `4 1 1 1 2 2 1 2 2` defines that the Hamiltonian acts 4 times, on all the four configurations. A modification that is possible is to define different Hamiltonians for the initial and final states. An example will be given later.
- ⊗ The line `TRAN 2 1 1 2 2` defines that there are two dipole transitions, between the first configurations in the initial and final state (1 1) and also between the second configurations in the initial and final state (2 2).
- ⊗ The line `TRIADS` indicates that below all matrices are given that must be calculated. For example, the first triad `0+ 1- 1- 0` indicates the transition from 0+ with 1- to 1- symmetry. In RAC2 the symmetry was defined as Oh, which means that the matrix is calculated from A1 with the dipole approximation (= 1-) to T1 final states. The TRIADS that are given in this example are all possible triads for a system with an even number of electrons in Oh symmetry. The fourth number (0) should only be given in Oh symmetry, because Oh symmetry has the special feature that there could be two identical triads. The fourth number is then used to distinguish these two triads.

5 XMCD calculations

In this section we discuss the polarization dependence of x-ray absorption spectral shapes. This includes both linear dichroism and circular dichroism.

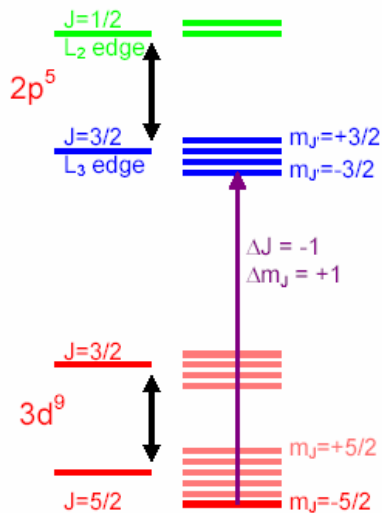
As examples we will use the Cu^{2+} and Ni^{2+} ground state. Cu^{2+} is given as a $3d^9$ configuration and Ni^{2+} as a $3d^8$ configuration. We will discuss MCD with atomic multiplets, crystal field effect on XMCD, charge transfers on XMCD, the input files for XMCD calculations and the difference between exchange fields and magnetic fields. At the end we will give a number of examples from 3d-systems, 4d-systems and 4f-systems. Before starting with the examples, XMCD will be introduced.

Dichroism is the property of certain objects showing different colors according to their orientation with respect to the light. It is due to the dependence of the optical response of the object on the relative orientation between the polarization direction of the light and the symmetry axes of the object. With x-rays, in some cases a difference can be observed between the absorption of left and right circularly polarized light (Circular Dichroism) or for different orientations of the polarization vector of linearly polarized light with respect to a given quantization axis (Linear Dichroism). Dichroism can only occur when the spherical symmetry of the free atom is broken due to a magnetic field and/or an electric field such as crystal field effects. Magnetic fields can cause both circular and linear dichroism, while a crystal field can only induce linear dichroism.

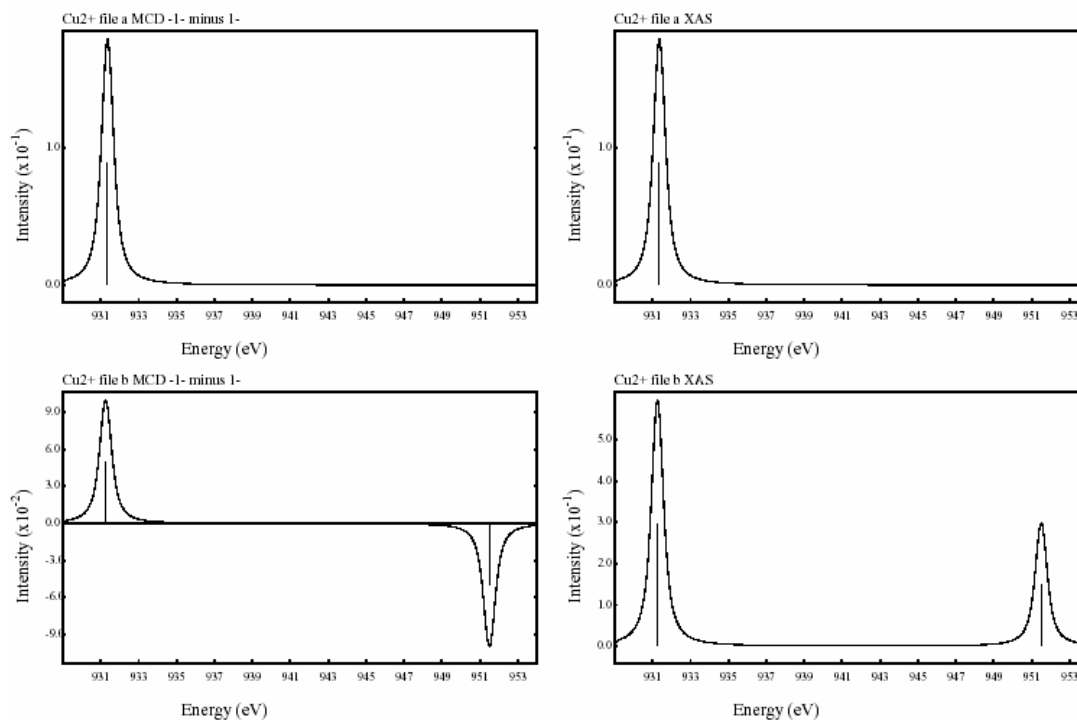
5.1 XMCD of Cu^{2+} systems

The initial state of Cu^{2+} has a $2p^6 3d^9$ configuration that is it contains a single 3d-hole. This implies that the 3d3d multiple interactions are absent and one only has the crystal field effects, the 3d spin-orbit coupling and the Zeeman exchange field or an external magnetic field. In the final state the 2p core hole spin-orbit coupling is an important factor for the dichroic effects. The final state has a $2p^5 3d^{10}$ configuration, hence no 3d-holes implying no 2p3d multiplets and no effects of the crystal field, exchange field and 3d spin-orbit coupling.

The initial state has a $3d^9$ configuration, hence the single 3d-hole ground state has $L=2$ and $S=1/2$. Following Hunds rules, its J-value is equal to $L+S = 5/2$. There is an excited state with $J=3/2$. The final state has a single 2p-hole, hence it has a $J=3/2$ state and a $J=1/2$ state, respectively the L_3 and the L_2 edge. Applying an exchange field splits the J states into their respective M_J sublevels, with the $M_J=-5/2$ as the ground state. The final states have M_J values between $-3/2$ and $+3/2$ and the selection rule states that ΔM_J is equal to -1 , 0 or $+1$ dependent on the polarization of the x-ray. This implies that for this ground state there will be only a single transition. This is the transition from $M_J=-5/2$ to $M_J'=-3/2$, with the $\Delta M_J=+1$ operator. The J-value of the ground state is $5/2$ and the J-values of the final states are $J=3/2$ and $J=1/2$. With the dipole selection rules $\Delta J = +1, 0$ or -1 , this implies that there is only a transition to the $J=3/2$ final state. That is, the only allowed transition has $\Delta J = -1$ and $\Delta M_J = -1$. The figure below sketches the situation of the various states.

**Exercise 5.1:**

- (c) Run CTM4XAS for Cu^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV; Plot the XAS spectrum and the MCD spectrum; They should look like the top panels of the figure below.
- (d) Run CTM4XAS for Cu^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV and with the 3d spin-orbit coupling set to 0.0; Plot the XAS spectrum and the MCD spectrum; They should look like the bottom panels of the figure below.



The top images show the atomic case with the single $J=5/2$ to $J'=3/2$ transition. The XAS is given on the right and the identical XMCD spectrum is given on the left. The XMCD spectrum is identical because there is only a $\Delta m_J = -1$ transition. The bottom images show the XAS (right) and its MCD (left) for an initial state that is not affected by 3d spin-orbit coupling. Effectively this implies

that the transitions from the $J=3/2$ state are added to those of the $J=5/2$ state. If we look into the **ora** output file, we find the following eigen values for the $3d^9$ ground state:

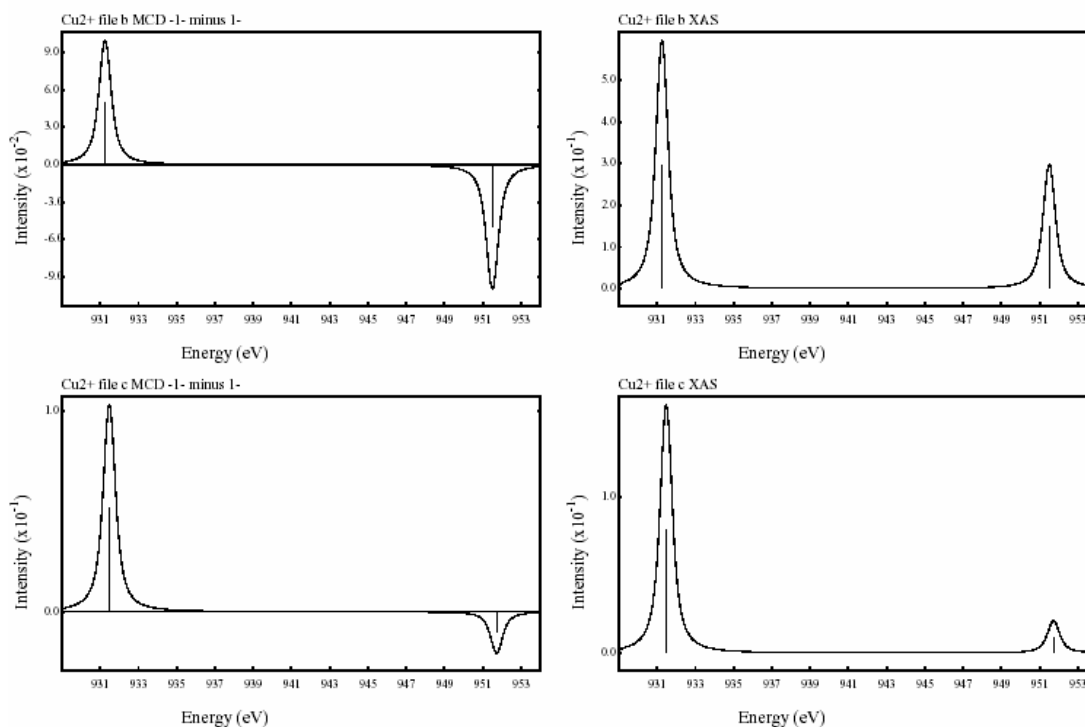
EIGVAL	-0.101095	0.152095	
EIGVAL	-0.103093	0.154093	
EIGVAL	-0.107000	-0.099064	0.150064
EIGVAL	-0.105061	-0.097000	0.156061

The six $J=5/2$ states are found between -0.107 and -0.097 eV and the four $J=3/2$ states are found between 0.150 and 0.156 eV. The $J=3/2$ state will have transitions to both the L_3 edge and the L_2 edge. If the $3d$ spin-orbit coupling is zero, the ratio of the XAS of the L_3 edge to the L_2 edge is 2:1, while their XMCD ratio is +1:-1 (or -1 to $+1$ depending on the definition used).

Exercise 5.2:

- Run CTM4XAS for Cu^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV, adding a crystal field value $10Dq$ of 0.3 eV.; Plot the XAS spectrum and the MCD spectrum; They should look like the bottom panels of the figure below.
- Perform a number of calculations for varying values of $10Dq$, in steps of 0.3 eV from 0.0 to 1.5 eV. What does one observe for the XAS and MCD spectra?
- Perform a calculation for negative values of $10Dq$, for example -0.3 , -0.5 and -0.9 eV. What does one observe? Explain.

If a crystal field of 0.3 eV is added to the ground state, one finds a small L_2 edge and also a small XMCD at the L_2 edge. Effectively one finds a result that is in between the situation with and without spin-orbit coupling. The reason for this is that if one includes a cubic crystal field, one effectively mixes the $J=5/2$ and $J=3/2$ states of the $3d$ -band. In fact, this is the reason that the $3d$ spin-orbit coupling can/must be neglected in many cases. Due to the crystal field (and other effects, for example translational symmetry), the $J=5/2$ and $J=3/2$ states in the $3d$ -band are completely mixed.

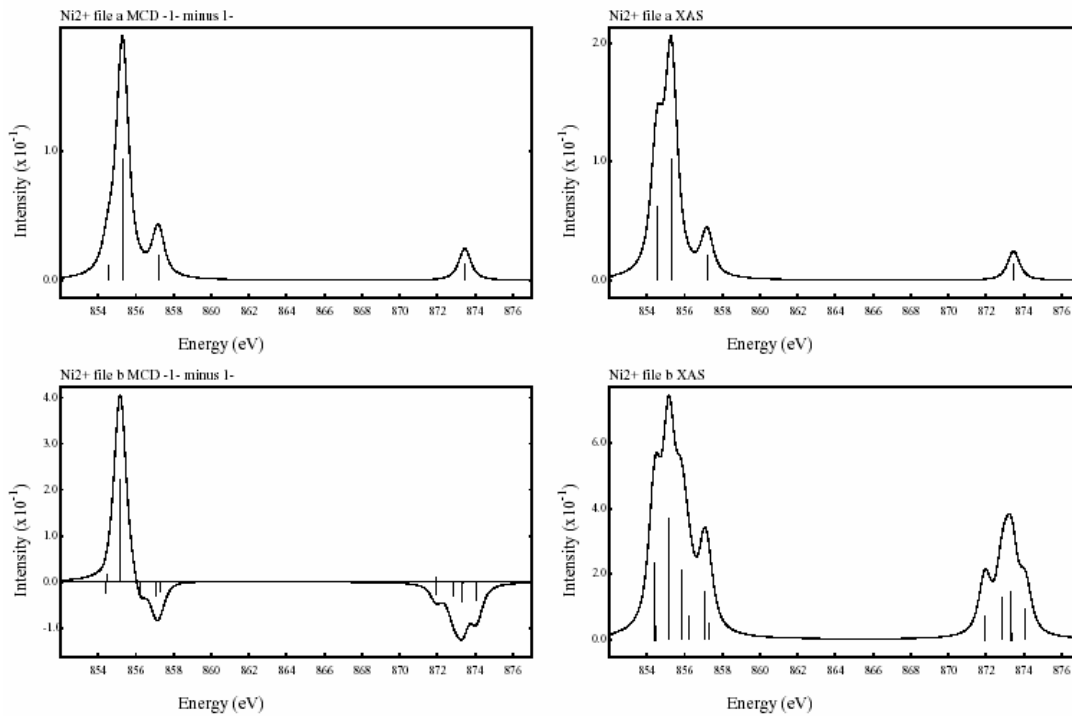


5.2 XMCD of Ni^{2+} systems

Next we switch to a Ni^{2+} ground state. The difference between Ni^{2+} and Cu^{2+} is that the $3d^8$ ground state is affected by $3d3d$ multiplet effects. In addition, the $2p^53d^9$ final state is affected by $2p3d$ multiplet effects. This will completely modify the $2p$ XAS and XMCD spectra of Ni^{2+} compared with Cu^{2+} . We start with the same calculation as for Cu^{2+} , which is a pure atomic calculation, including all atomic effects (multiplet effects, spin-orbit couplings).

Exercise 5.3:

- Run CTM4XAS for Ni^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV; Plot the XAS spectrum and the MCD spectrum; they should look like the top panels of the figure below.
- Run CTM4XAS for Ni^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV and with the 3d spin-orbit coupling set to 0.0; Plot the XAS spectrum and the MCD spectrum; they should look like the bottom panels of the figure below.



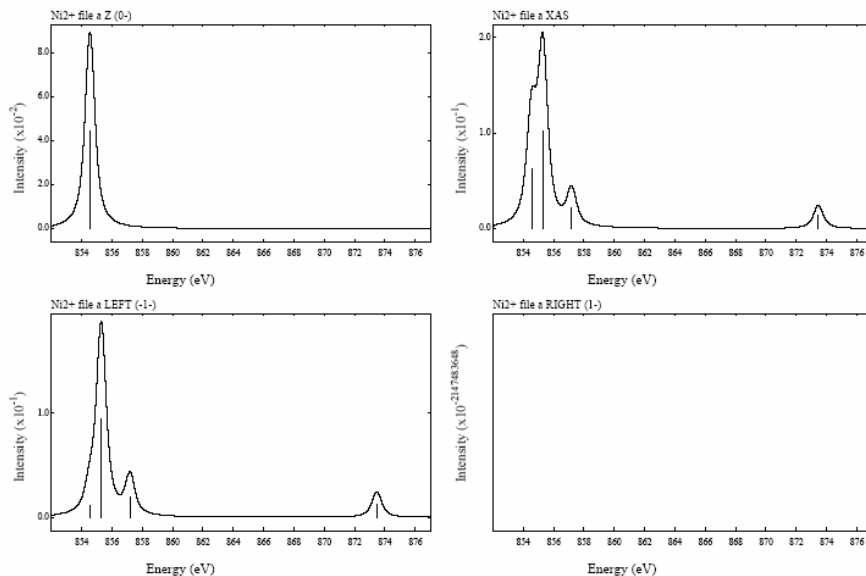
The MCD effect for atomic Ni^{2+} including the 3d spin-orbit coupling is completely positive. The reason is that there are no allowed transitions for right polarized x-rays. The first peak relates to a transition from the ground state 3F_4 state to a $J'=4$ final state. The other three peaks relate to $J'=3$ final state. The $\Delta J=-1$ transitions are purely left polarized ($\Delta m_J=-1$), cf the table as given on the right. The transition from $J=4$ to $J'=4$ can have either $\Delta m_J=-1$ or $\Delta m_J=0$ transitions, but no $\Delta m_J=+1$ transitions. This implies that the whole MCD spectrum (left-right) is positive.

Table 17

Correlation between ΔJ and ΔM_J

ΔJ	$(\Delta M_J = -q)$		
	-1	0	+1
-1	1	0	0
0	$\frac{1}{J+1}$	$\frac{J}{J+1}$	0
+1	$\frac{1}{(2J+3)(J+1)}$	$\frac{2J+1}{(2J+3)(J+1)}$	$\frac{(2J+1)(J+1)}{(2J+3)(J+1)}$

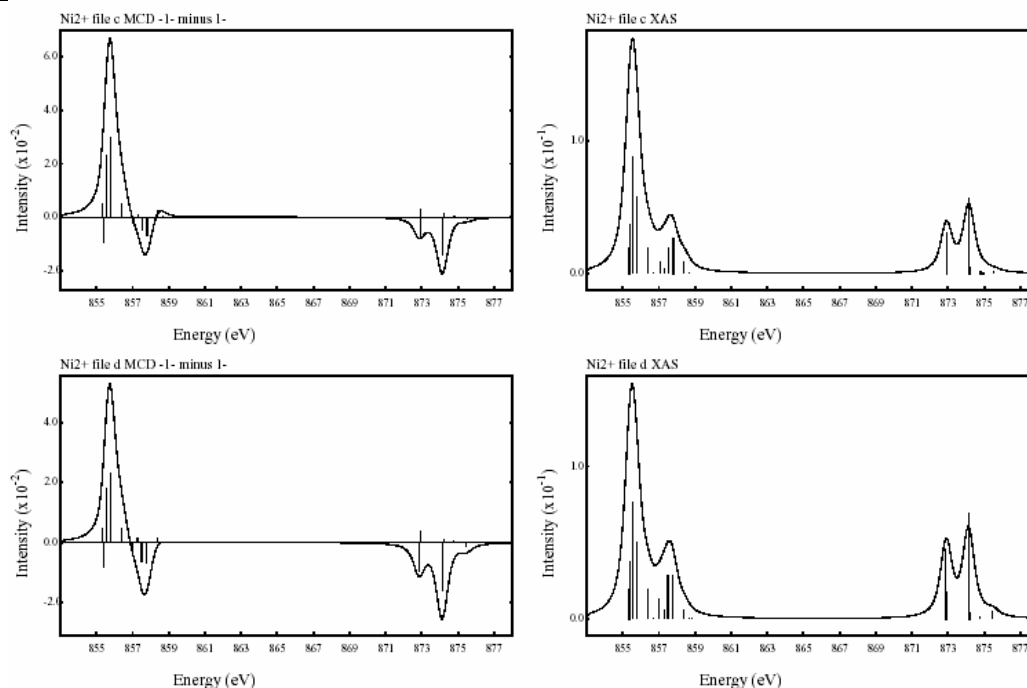
This figure shows the individual transitions for LEFT, RIGHT and Z-polarized X-rays for Ni^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV.



Applying a cubic crystal field modifies the ground state to 3A_2 . We have seen in chapter 5 that the 3d spin-orbit coupling has only a minor effect in case of a 3A_2 ground state. This is confirmed in the XMCD spectra of Ni^{2+} in octahedral symmetry.

Exercise 5.4:

- Run CTM4XAS for Ni^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV, adding a crystal field of 1.2 eV; Plot the XAS spectrum and the MCD spectrum; they should look like the top panels of the figure below.
- Run CTM4XAS for Ni^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV, adding a crystal field of 1.2 eV and with the 3d spin-orbit coupling set to 0.0; Plot the XAS spectrum and the MCD spectrum; they should look like the bottom panels of the figure below.



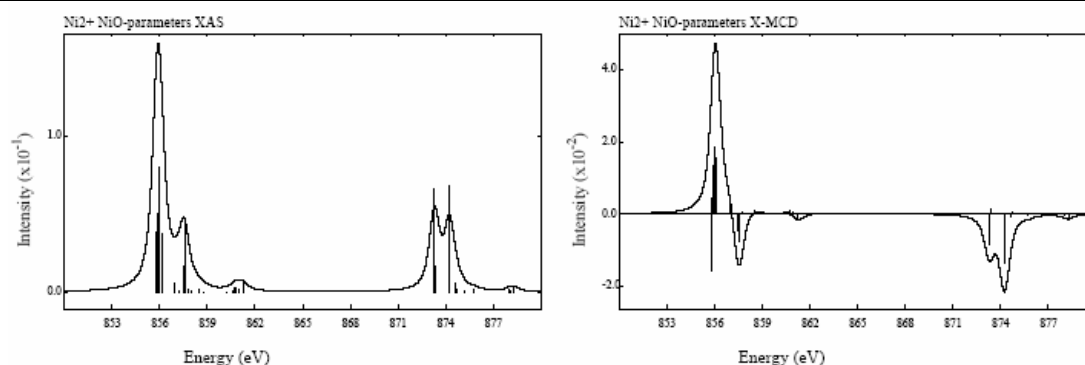
The figures show the similar 2p XAS and XMCD spectra of Ni^{2+} in an octahedral crystal field with (top) and without (bottom) the inclusion of 3d spin-orbit coupling. It is interesting to note that though the ground state has 3A_2 character, there is still a visible effect of the 3d spin-orbit coupling. The reason is the admixture of states of other character. This implies that the ground state is not 100% 3A_2 symmetry if 3d spin-orbit coupling is included. (It is 100% a T_2 symmetry state in the double group description, but the 3A_2 -type T_2 state has a little admixture of T_2 states of other excited T_2 states; In total there are 6 T_2 states)

5.3 Charge transfer and the XMCD spectral shape for Ni^{2+} ions

The next step is to include charge transfer for XMCD calculations. The procedure is analogous to the XAS calculations.

Exercise 5.5:

(a) Run CTM4XAS for Ni^{2+} in C_{4v} symmetry, with a magnetic field (M) of 1 meV, adding a crystal field of 1.0 eV. Set 'charge transfer' ON and use DELTA=3.5, Udd=7, Upd = 8.5 en hopping terms A_1 , B_1 , E and B_2 . equal to 2, 2, 1 and 1; Plot the XAS spectrum and the MCD spectrum; they should look like the bottom panels of the figure below.



5.4 Appendix A: The Ni^{2+} XMCD calculation with the original BAT files.

The files `als7ni2a.rcg` and `als7ni2a.rac` calculate the atomic transition for Ni^{2+} and the files `als7ni2b.rcg` and `als7ni2b.rac` calculate the same transition without the inclusion of the 3d spin-orbit coupling. The input of the rcg-file for XMCD calculations is analogous to a normal XAS calculation. The only addition is the inclusion of the operator spin and in some cases also orbit. The first line reads:

```
10      14      2      4      1      1  INTER2 shell03000000 %
spin03000000 orbit03000000
```

The % can be used if a line becomes too long. In addition to the crystal field (SHELL), this file adds an exchange field (SPIN) or a magnetic field (SPIN and ORBIT) to the matrices that are calculated. The `als7ni2a.rac` file is modified a bit more. It reads:

```
Y
      % vertical 1 1
butler 03
```

```

to      Oh
to      D4h
to      C4h
endchain
actor    0+ HAMILTONIAN ground  PRINTEIG
  OPER HAMILTONIAN
    BRANCH 0+ > 0 0+ > 0+      > 0+    1.0
  OPER SHELL2
    BRANCH 4+ > 0 0+ > 0+      > 0+    0.0
    BRANCH 4+ > 0 2+ > 0+      > 0+    0.0
    BRANCH 2+ > 0 2+ > 0+      > 0+    0.0
  OPER SPIN2
    BRANCH 1+ > 0 1+ > ^0+    > 0+    0.01
  OPER ORBIT2
    BRANCH 1+ > 0 1+ > ^0+    > 0+    0.00
actor    0+ HAMILTONIAN excite  PRINTEIG
  OPER HAMILTONIAN
    BRANCH 0+ > 0 0+ > 0+      > 0+    1.0
  OPER SHELL2
    BRANCH 4+ > 0 0+ > 0+      > 0+    0.0
    BRANCH 4+ > 0 2+ > 0+      > 0+    0.0
    BRANCH 2+ > 0 2+ > 0+      > 0+    0.0
  OPER SPIN2
    BRANCH 1+ > 0 1+ > ^0+    > 0+    0.01
  OPER ORBIT2
    BRANCH 1+ > 0 1+ > ^0+    > 0+    0.00
actor    1- left      transi PRINTTRANS
  oper MULTIPOLE
    branch 1- > 0 1- > 1- > 1- 1.000
actor    -1- right    transi PRINTTRANS
  oper MULTIPOLE
    branch 1- > 0 1- > 1- > -1- 1.000
actor    0- parallel  transi PRINTTRANS
  oper MULTIPOLE
    branch 1- > 0 1- > ^0- > 0- 1.000
RUN

```

Important is that the symmetry is changed from O3, via Oh and D4h to C4H. This allows one to add an exchange field with the operator SPIN2. The exchange field is added in electron volts and has a value of 0.01, or 10 meV. Note that the dipole operator splits into left (1-), right (-1-) and parallel (0-) due to the symmetry lowering from O3 to C4H. C4H symmetry implies that the magnetic field is added in the z-direction of the tetragonal symmetry. This input files allows one to add crystal field parameters (X40, X42 and X22) and an exchange or magnetic field.

The file als7ni2ab.plo generates a combined figure for both cases, which is given below. The new commands/lines for XMCD calculations are:

```

frame_title N2+1 file b MCD -1- minus 1-
addlines operator -1-
spectrum operator 1- scale -1

```

These three lines give the XMCD spectrum in a separate figure. `frame_title` gives the title of the frame. `Addlines` makes a spectrum for the operator $-1-$, but instead of plotting it, it saves the spectrum in memory. The command `spectrum` creates the spectrum for operator $1-$ multiplied with the scale factor of -1 . In addition it adds all stored spectra. Together these two lines create a spectrum of the operator $-1-$ minus the operator $1-$. Alternatively, one can just calculate the spectra of the three individual operators ($-1-$, $0-$ and $1-$) and use their spectra in separate software to create the figures.