

## Chapter 1: ATOMIC MULTIPLETS

**Theoretical background of the 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. The review of John Rehr in this issue deals with the latest developments in the single electron codes using multiple scattering. Cabaret and coworkers describe the new developments in band structure codes and the recently developed PARATEC-based projection method promises to set a new standard for single electron XANES calculations. 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 metal and oxygen K edges, whereas for the other edges, in particular 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 that one does not observe the density of states in such x-ray absorption processes. The reason for the deviation from the density-of-states is the strong overlap of the core wave function with the valence wave functions. The overlap of core and valence wave functions is present also in the ground state, but because all core states are filled, it is not effective and one can approximate the core electrons with their charge. 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, these so-called multiplet effects are hardly screened in the solid state. This implies that the atomic multiplet effects are of the same order of magnitude in atoms and in solids.

**3d and 4d XAS of La<sup>3+</sup> ions****Term symbols**

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

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

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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 ML and MS 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 ML values between  $-2$  and  $+2$ . The only associated MS 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.

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### Exercise:

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

The term symbols of a  $2p^3$  configuration do not have to obey the Pauli principle. There will be  $6 \times 6 = 36$  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 Table 2.4, 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.											
$3d^1 4d^1$	$^1S$	$^1P$	$^1D$	$^1F$	$^1G$	$^3S$	$^3P$	$^3D$	$^3F$	$^3G$	$\Sigma$
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.

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

**X-ray Absorption Spectra described with Atomic Multiplets.**

We start with the description of the  $M_{45}$  edge of  $\text{La}^{3+}$ , for example in  $\text{La}_2\text{O}_3$ . 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  $3d^{10}4f^0 \rightarrow 3d^9 4f^1$ . We will at first only look at the symmetry aspects of the problem. The  $3d^{10}4f^0$  ground state contains only completely filled or completely empty shells and as such has  $^1S_0$  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  $^2D \otimes ^2F$ . 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  $^1P_1$ ,  $^1D_2$ ,  $^1F_3$ ,  $^1G_4$ ,  $^1H_5$  and  $^3P_{012}$ ,  $^3D_{123}$ ,  $^3F_{234}$ ,  $^3G_{345}$ ,  $^3H_{456}$ . Here we use  $^3H_{456}$  as shorthand notation of  $^3H_4$  plus  $^3H_5$  plus  $^3H_6$ . 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  $3 \times 35 = 105$ , adding up to 140 in total, confirming the  $10 \times 14$  possibilities of adding a 3d and a 4f electron.

$3d^1 4f^1$	$^1H$	$^1P$	$^1D$	$^1F$	$^1G$	$^3H$	$^3P$	$^3D$	$^3F$	$^3G$	$\Sigma$
Deg.	11	3	5	7	9	33	9	15	21	27	140
J-values		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

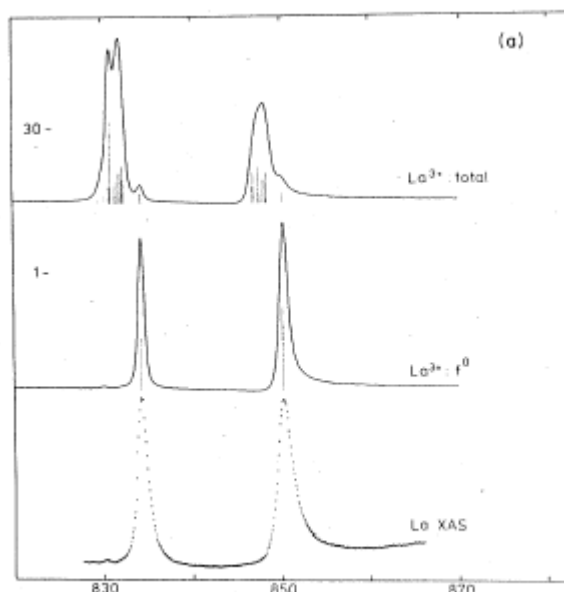
Note that the difference between the term symbols of  $3d^{14}d^1$  and  $3d^9 4f^1$  are small, essentially the replacement of  $1S$  and  $3S$  by  $1H$  and  $3H$ . The degeneracies in  $J$  are important because the x-ray absorption calculations are always performed in intermediate coupling, i.e. 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  $3d^{10}4f^0 \ ^1S_0$  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

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states:  $^1P_1$ ,  $^3P_1$  and  $^3D_1$ . This means that the  $M_{4,5}$  x-ray absorption spectrum of  $\text{La}_2\text{O}_3$  can have a maximum of only three peaks.



The figure above shows a calculation of the 3d x-ray absorption spectrum of  $\text{La}_2\text{O}_3$ , 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  $\text{La}^{3+}$ , 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 TTRCG 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 diagonalisation 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	DY3+ 3D10 4F00		---		DY3+ 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  $La_2O_3$  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

M<sub>5</sub> edge and 0.4 for the M<sub>4</sub> edge, plus a Gaussian of 0.25. M<sub>4,5</sub> spectra of rare earths have a special feature, which is there asymmetry of the M<sub>4</sub> edge. All rare earth M<sub>4,5</sub> edge spectra have a symmetric M<sub>5</sub> edge and a asymmetric M<sub>4</sub> edge. The reason is that the M<sub>4</sub> edge can interact with the continuum of the M<sub>5</sub> 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 M<sub>4</sub> edge of Lanthanum. More details on the Fano lineshape in [thole85a.pdf](#) and the book of Cowan [ref].

We will introduce the plotting program TTPLO. 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.

**als2la3.rcg**

**rcg2 als2la3**

**als2la3.org**

**als2la3.plo**

**plo2 als2la3**

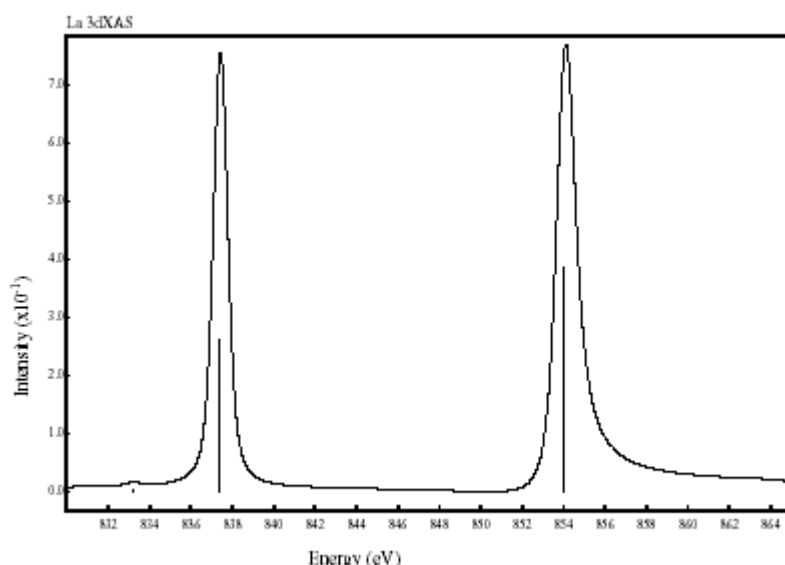
**als2la3.ps**

- ⊗ 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 M5 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 M4 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 M5 and M4 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.

## Chapter 1

## ATOMIC MULTIPLETS

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



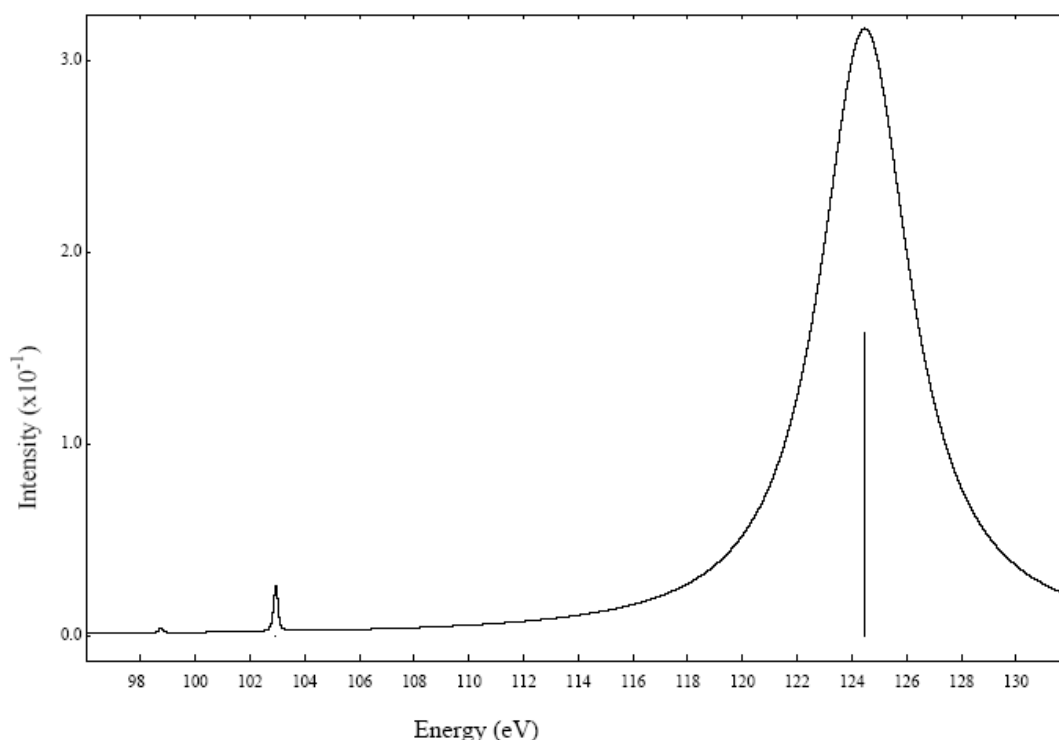
The result of this plotting program is given above. One finds the three peaks, essentially two big peaks, the M5 edge at 837 eV and the M4 edge at 854 eV. In addition, a small pre-edge is visible at 833 eV. From the output file we found that the M4 edge relates to a  $1P_1$  state, the M5 edge to a  $3D_1$  state, and the pre-edge to a  $3P_1$  state.

We next turn to the N45 XAS edge of La. The  $4f^0$  to  $4d^9 4f^1$  transition has exactly the same symmetry properties as the  $M_{45}$  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.

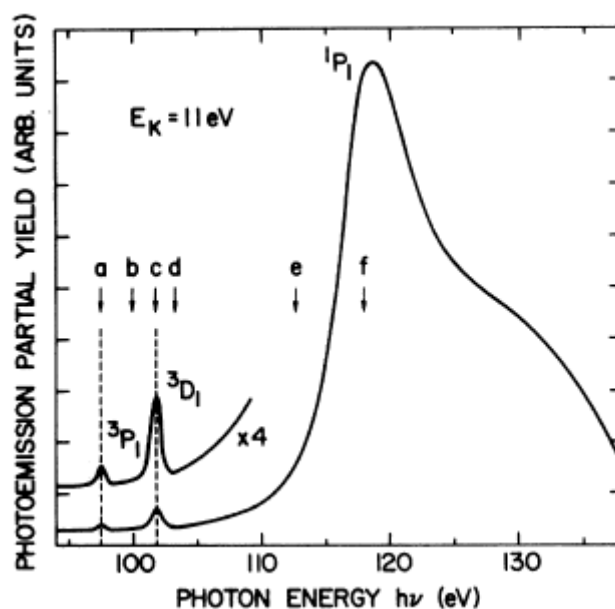
- The 4d binding energy is only 103 eV.
- The 4d spin-orbit coupling is only 1.1 eV, implying that the splitting between the  $N_5$  and  $N_4$  edge is only 2.7 eV.
- The Slater-Condon parameters are much larger for the  $4d4f$  interaction, implying that the energy separations between different (spin) states will be much larger for the N45 edge.
- Looking at the intensities. one finds small pre-edges for both the M45 and N45 edge, but where the M45 edge has an intensity ratio of 0.8:1.2, more than 99% of the intensity of the N45 edge goes to the N4 edge. In fact both the pre-edge and the N5 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

The calculation of the N45 edge is equivalent to that of the M45 edge. First run the input file `als2la34d.rcg` with the command `rcg2 als2la34d`. This yields again the `als2la34d.rcg` file that can be plotted with `rcg2 als2la34d`.



Note that one needs a rather good experimental resolution to observe the two peaks at 99 eV and 103 eV.



A detailed calculation and a comparison to experiments can be found in [aono80a.pdf](#). A detailed calculation of the 4d XAS spectrum as well as the related 4d5p resonant photoemission spectra can be found in [ogasawara92a.pdf](#). We will discuss resonant photoemission in chapter 9.

M<sub>4,5</sub> edge has much larger core spin-orbit that brings it closer to jj-coupling. N<sub>4,5</sub> edge has very small core spin-orbit coupling that brings it close to pure LS-coupling. In pure LS-coupling there is only one peak, the <sup>1</sup>P<sub>1</sub> peak. This is discussed below for Ti<sup>4+</sup> systems.

**The atomic multiplet spectrum of the  $L_{2,3}$  edge of  $Ti^{4+}$  and  $Ni^{2+}$** **The 2p x-ray absorption spectrum of  $TiO_2$** 

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  $2P \times 2D$  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:

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

The table below contains the result of an atomic multiplet calculation for  $Ti^{IV}$  ( $3d^0$ ) 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 (because of the selection rule  $|J-1| \leq J' \leq J+1$ ), but it is possible that another state decays to this  $^3P_0$  state via Coster-Kronig Auger decay.

	$^3P_0$	$^3P_1$	$^3D_1$	$^1P_1$	$^3P_2$	$^3D_2$	$^3F_2$	$^1D_2$	$^3D_3$	$^3F_3$	$^1F_3$	$^3F_4$
-3.281	<b>1.0</b>											
-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	-	0.01	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									-		0.5	
									0.21	0.77	9	
-1.369									0.81	-	0.5	
									-	0.19	4	
3.777									-	-	0.5	
									0.53	0.60	9	
-2.481												<b>1.0</b>

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

To reproduce this table from the inputfile we have to run a similar atomic multiplet calculation as for La3+. One can calculate the atomic parameters from an additional program TTRCN that we did not discuss till now. With the use of the TTRCN 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 Ti4+ 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** inputfile 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 Ti4+ 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 2p53d1. One can run the TTCN 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 TTRCG and TTRAC programs.

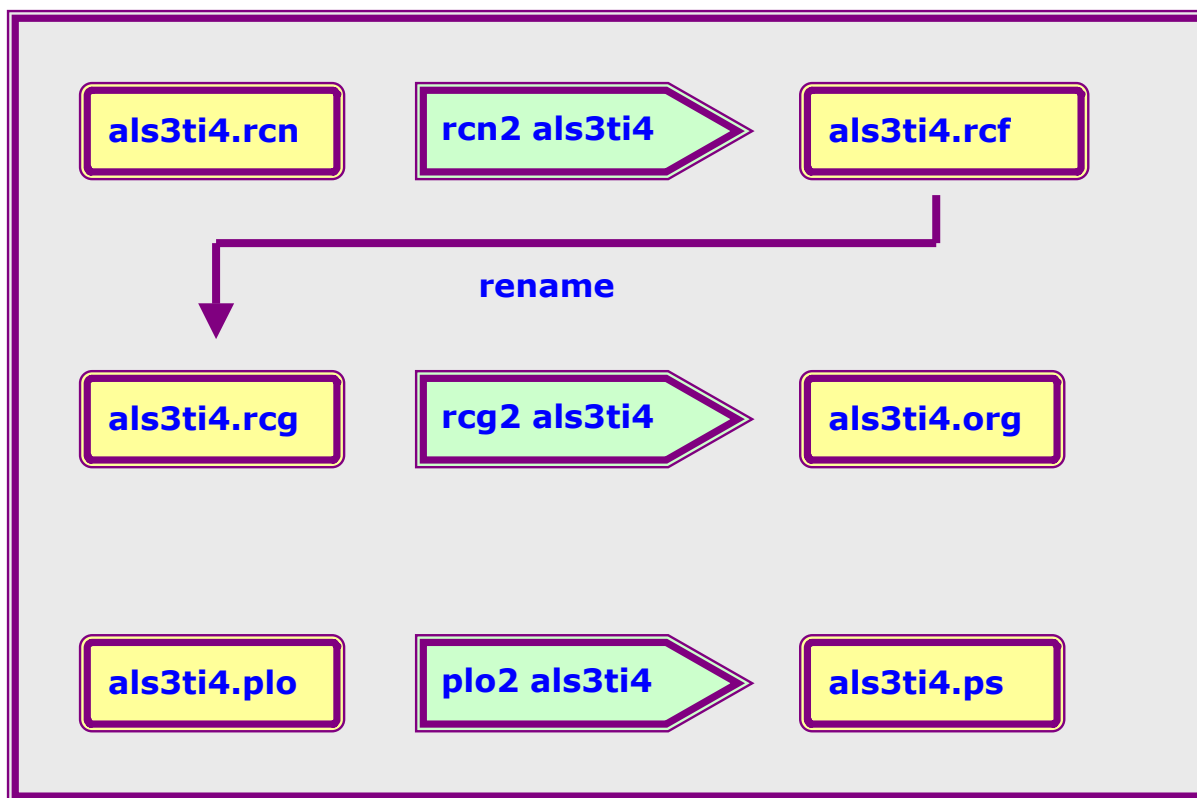
If one would like to calculate Ni2+ instead of Ti4+, the **als3ni2.rcn** file changes as follows:

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 TTRCG program with the command **rcg2 als3ti4** will yield an out file **als3ti4.org** that contains the atomic multiplet spectrum, similar to the case of La3+. The general scheme for the atomic multiplet calculation of a Ti4+ ion is given below.





If one would like 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 als3ti4p.rcg has been modified and will yield a file als3ti4p.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                                80998080                                8065.47800    0000000
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 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. They are indicated in table 2.8 in boldface. 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. As discussed above 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: Repeat the multiplet calculation for Ti4+ 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:  $H = H_{ELECTRO} + H_{LS-2p} + H_{LS-3d}$ .

We start by setting all final state interactions to zero. The file [als3ti4.rcg](#) has been modified to [als3ti4a.rcg](#) and all the final state interactions are switched off, except the final state energy of 464.811 eV. The printing command has been set to 6, which will show again all energy matrix, 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 '<sup>3</sup>D', '<sup>3</sup>P' and '<sup>1</sup>P' states, indicating the approximate term symbol related to the state. The original term symbols <sup>3</sup>P, <sup>3</sup>D and <sup>1</sup>P 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.

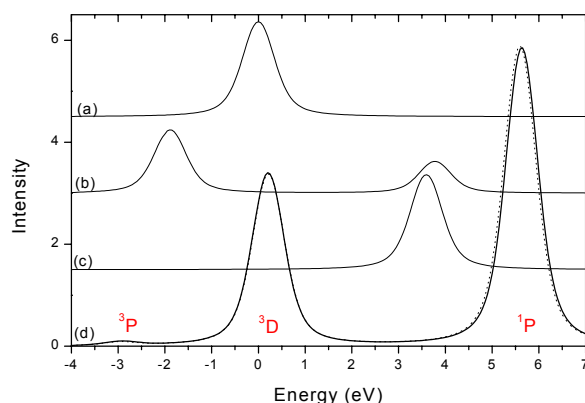


Figure: The effects of the Slater-Condon parameters and the spin-orbit coupling on the atomic multiplet spectrum of a  $3d^0$  system. (a) no interactions, (b) only 2p spin-orbit, (c) only Slater-Condon, (d) both Slater-Condon and 2p spin-orbit (solid). The dashed line includes the 3d

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 <sup>1</sup>P<sub>1</sub> character, which is given in the bottom line of the eigenvectors (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<sub>3/2</sub> states, have twice the intensity of the singlet, or 2p<sub>1/2</sub>, states. This has also been indicated in Figure 2.3.

(part of [als3ti4b.org](http://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](http://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](http://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

## Chapter 1

## ATOMIC MULTIPLETS

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](http://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](http://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	

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  $\text{Ti}^{\text{IV}}$

and  $\text{La}^{\text{III}}$  are respectively  $3d^0$  and  $4f^0$  and they share a  $^1S$  ground state. The transitions at the four edges are respectively:

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

These four calculations are equivalent and all spectra consist of three peaks with  $J=1$ . What changes are the values of the atomic Slater-Condon parameters and core hole spin-orbit couplings. They are given in table 6 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 in table 6 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

Table 2.1 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.

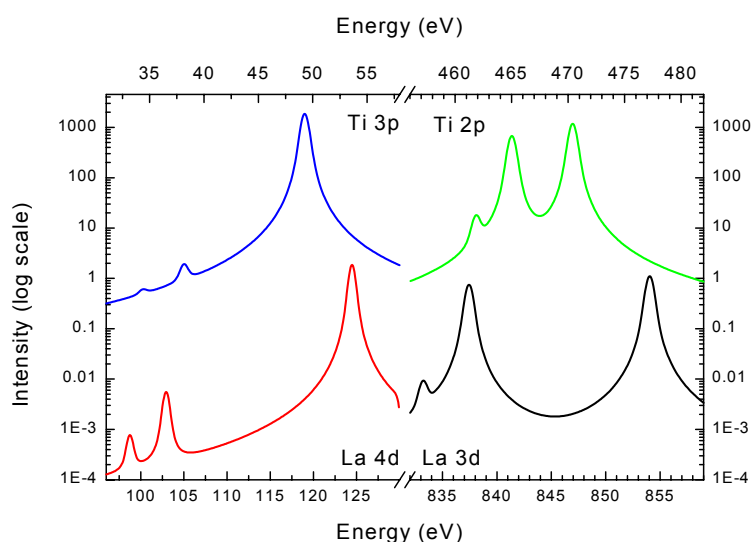


Figure 2.4 The  $\text{La}^{\text{III}}$  4d and 3d plus  $\text{Ti}^{\text{IV}}$  3p and 2p x-ray absorption spectra as calculated for isolated ions. The intensity is given on a logarithmic scale to make the pre-edge peaks visible.

*The intensities of titanium have been multiplied by 1000.*

## 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  $H_{\text{ATOM}}$ . As discussed in the previous section,  $H_{\text{ATOM}}$  consists of the effective electron-electron interaction  $H'_{\text{ee}}$  and the spin-orbit coupling  $H_{\text{is}}$ :

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

The electron-electron interaction commutes<sup>1</sup> 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. Table 2.5 gives the possible  $i$ -values for some important configurations.

The possible values of $f_i$ and $g_i$ for simple configurations								
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  $l_1+l_2$ . The general rules for the values of  $f_i$  and  $g_i$  can be found, for example, in [degroot01cr.pdf](#).

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

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

<sup>1</sup> 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 viceversa.

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

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  ${}^1G$ . Their energies are given in Table 2.6.  $f_0$  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 table 2.6 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 Hunds 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

Table 2.2 The relative energies of the term symbols for a  $3d^2$  configuration (see text).

Table 2.7 gives three related notations that are used to indicate the radial integrals. The Slater-Condon parameters  $F^k$ , the normalised Slater-Condon parameters  $F_k$  and the Racah parameters A, B and C. The bottom half of table 2.7 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.

Slater-Condon	Normalised	Racah
$F^0$	$F_0 = F^0$	$A = F_0 - 49F_4$
$F^2$	$F_2 = F^2/49$	$B = F_2 - 5F_4$
$F^4$	$F_4 = F^4/441$	$C = 35F_4$
$F^0 = 8.0$	$F_0 = 8.0$	$A = 7.3$
$F^2 = 10.0$	$F_2 = 0.41$	$B = 0.13$
$F^4 = 6.2$	$F_4 = 0.014$	$C = 0.49$

Table 2.3 A comparison of the Slater-Condon parameters  $F^k$ , with the normalised Slater-Condon parameters  $F_k$  and the Racah parameters.

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.

**Atomic multiplet ground states of 3d<sup>n</sup> systems**

The term symbols for a partly filled d-band with the lowest energy, found after calculating the matrix elements, are given in table 5. 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<sup>N</sup> configuration. The three Hunds rules are:

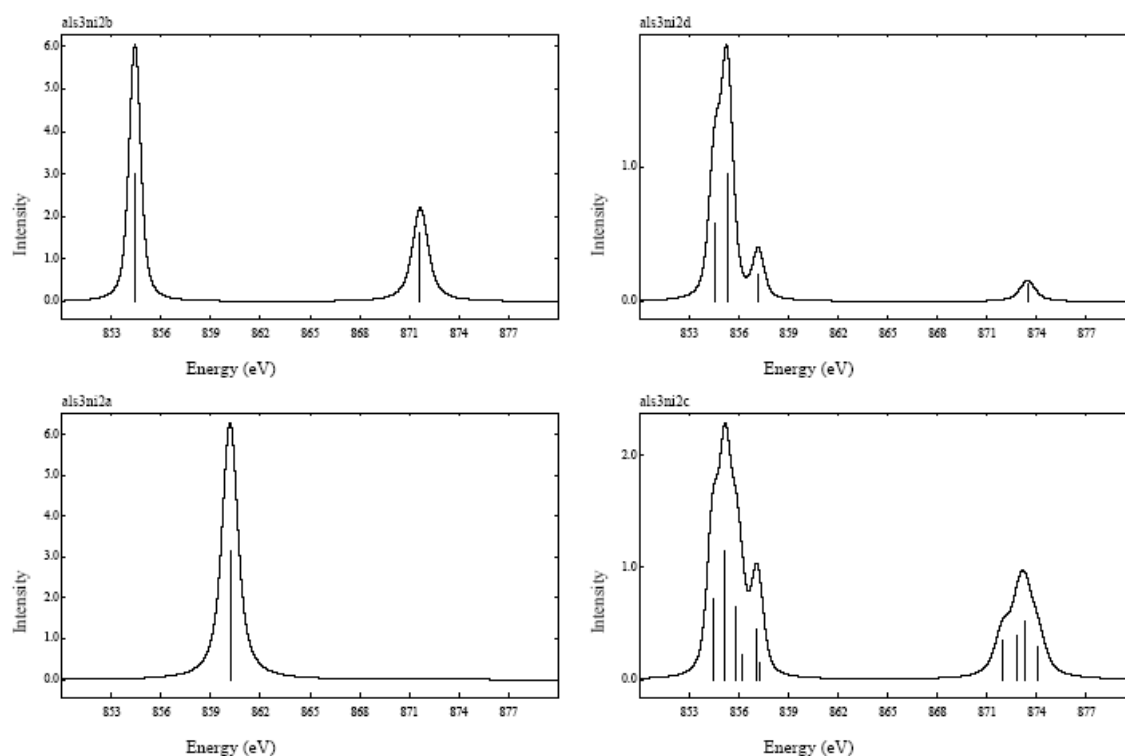
1. Term symbols with maximum spin  $S$  are lowest in energy,
2. Among these terms, the one with the maximum orbital moment  $L$  is lowest,
3. In the presence of spin-orbit coupling, the lowest term has  $J = |L-S|$  if the shell is less than half full and  $J = L+S$  if the shell is more than half 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<sup>5</sup> configuration, where the <sup>6</sup>S state has its five electrons divided over the five spin-up orbitals, which minimises their repulsion. In case of 3d<sup>2</sup>, the first Hunds rule implies that either the <sup>3</sup>P or the <sup>3</sup>F-term symbol must have lowest energy. From the previous section one finds that the <sup>3</sup>F term symbol is lower than the <sup>3</sup>P-term symbol, because the <sup>3</sup>F wave function tends to minimise electron repulsion. The effects of spin-orbit coupling are well known in case of core states. A 2p-core state has <sup>2</sup>P<sub>3/2</sub> and <sup>2</sup>P<sub>1/2</sub> states. The state with the lowest energy is <sup>2</sup>P<sub>3/2</sub>. Consider for example the 2p XAS or XPS spectrum of nickel. The <sup>2</sup>P<sub>3/2</sub> peak is positioned at approximately 850 eV and the <sup>2</sup>P<sub>1/2</sub> 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<sup>5</sup>, so more than half-full, implying that highest J-value has lowest energy. The third rule implies that the ground state of a 3d<sup>8</sup> configuration is <sup>3</sup>F<sub>4</sub>, while it is <sup>3</sup>F<sub>2</sub> in case of a 3d<sup>2</sup> configuration.

**Atomic multiplet calculations for Ni<sup>2+</sup>**

We repeat the multiplet calculation for Ni<sup>2+</sup> 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<sup>2+</sup> calculation.

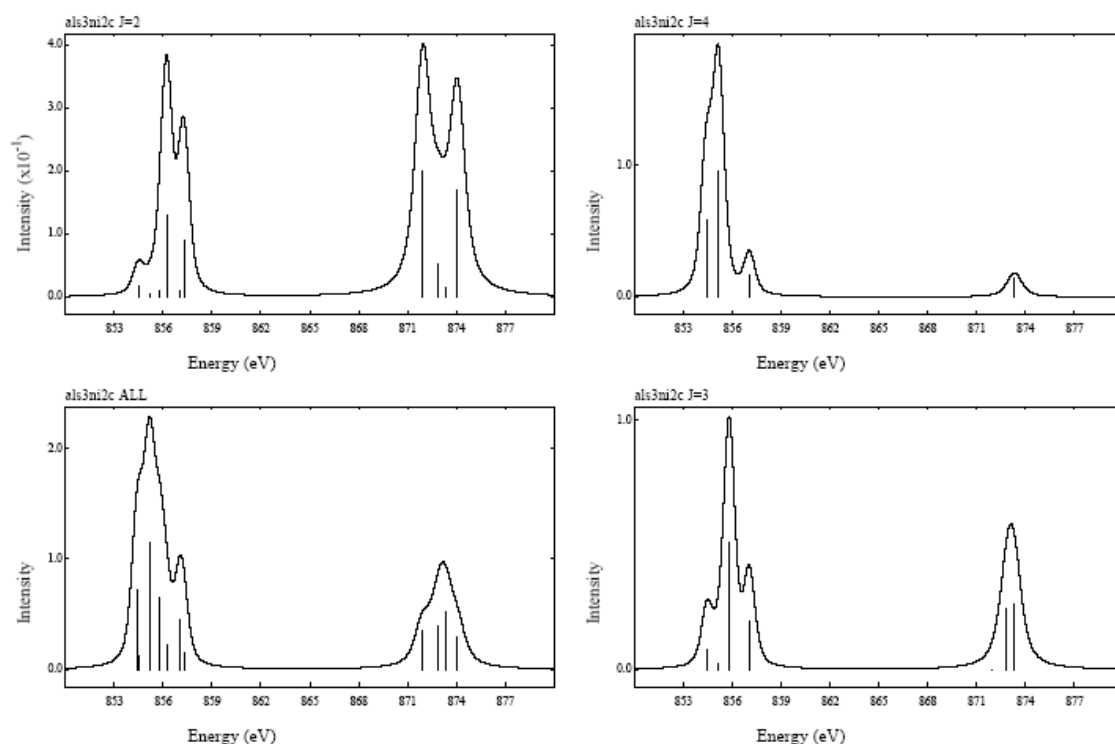


If all initial state and final state interactions are set to zero, one observes a single line (als3ni2a). This line is split into an L3 edge and an L2 edge by the spin-orbit coupling (als3ni2b). The introduction of multiplets generate a whole series of peaks (als3ni2c). These peaks are due to transitions 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<sub>4</sub> 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<sup>4+</sup> ions, we showed that there are three 2p53d1 final state with J=3 and one with J=4 (cf. the table on page 3.1). The same applies to a 2p53d9 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.

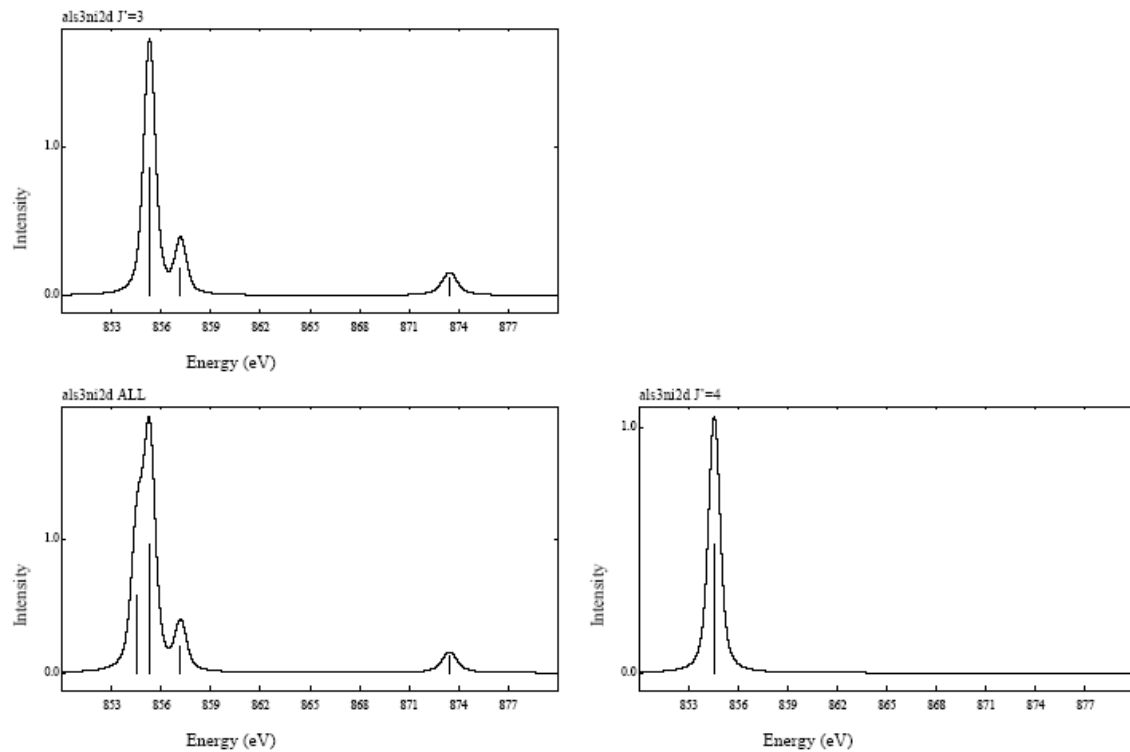


One observes that the spectra for  $J=2$ ,  $J=3$  and  $J=4$  are quite distinct. One finds that the  $J=4$  ground state mainly is excited to the L3 edge, while the  $J=2$  ground state has a larger L2 edge.

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  $\text{Ni}^{2+}$  ion with its  $3F_4$  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. This is exactly as found in the table on page 3.1. Note that if one asks for a final state that is not available (fstate 5), no spectrum is plotted.