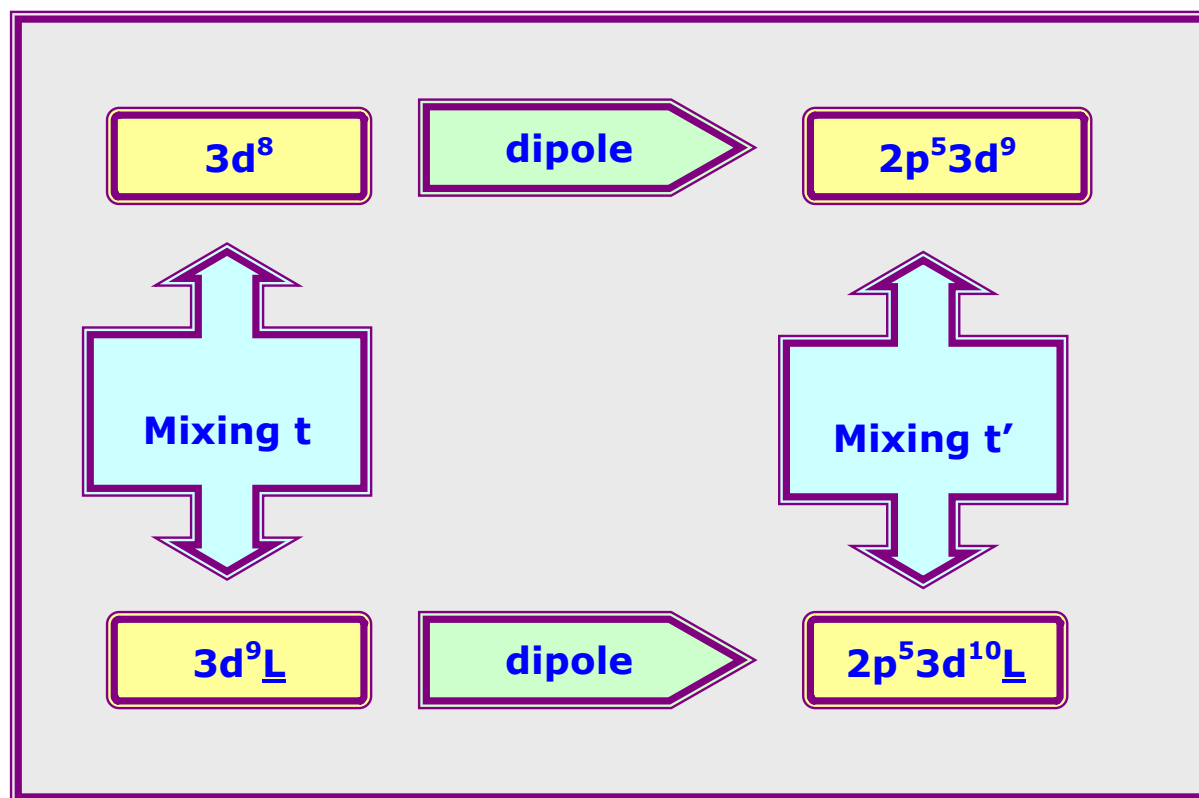


### The Charge Transfer Multiplet Model

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  $3d^9L$ . 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  $2p^5 3d^{10}L$ . However, if one would only perform the dipole calculations, the configurations would not mix. To mix the  $3d^8$  and  $3d^9L$  configurations we need an additional calculation. Effectively this is a monopole transition calculation between  $3d^8$  and  $3d^9L$ . A similar mixing occurs in the final state. We arrive at four calculations to be performed, as schematically indicated in this scheme.



The charge transfer multiplet calculations need an additional program TTBAN, where the four individual calculations are combined. The TTRCG and TTRAC calculations are performed four times, using a single inputfile. The results of TTRCG are again written to m14 matrix files. The results of TTRAC are written to

## Chapter 3

## CHARGE TRANSFER EFFECTS

m15 matrix files. The TTBAN program uses these matrices to generate the charge transfer multiplet spectrum.

We start with a Ni<sup>2+</sup> calculation in Oh symmetry. The files als6ni2x1.rcg, als6ni2x1.rac and als6ni2x1.ban generate the outputfile als6ni2x1.oba, which contains the spectrum. The file als6ni2x1.rcg consist of four parts, indicated with four colours.

```

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 colour is related to a single TTRCG calculation. Each sub-calculation is similar to a normal single configuration TTRCG 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<sup>8</sup> to 2p53d9, 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 3d9L to 2p53d10L, 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<sup>8</sup> and 3d9 configuration. A 3d<sup>8</sup> configuration has 4 parameters (energy, two Slater integrals and 3d spin-orbit) and a 3d9 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 2p53d9 configuration has 6 parameters (energy, three pd Slater integrals and two spin-orbit couplings) and a 2p5(3d10 = 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 Ni2+ calculation with two configurations. Later we will show three configuration calculations, for example 3d7 + 3d8L + 3d9L2 for a Ni3+ ground state. The next step in the TTRAC 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    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

```

Every colour is again related to a single TTRAC calculation, where the same colours have been used as for the TTRCG calculation.

- ☒ The blue calculation is the dipole transition from  $3d^8$  to  $2p53d9$ . 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 'hybridisations', respectively *eghybr* and *t2ghybr*. These two mixing parameters relate respectively to the mixing of an *eg* electron and a *t2g* electron. The numbers .894427191 and 3.286335345 take care that the interactions can be given in electronvolts in the TTBAN inputfile. 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 the consist of the atomic Hamiltonian and the cubic crystal field. Because the 3d-electrons were defined in the first shell in the TTRCG program, we use the operator SHELL1 in the TTRAC inputfile.

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 TTBAN 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

```

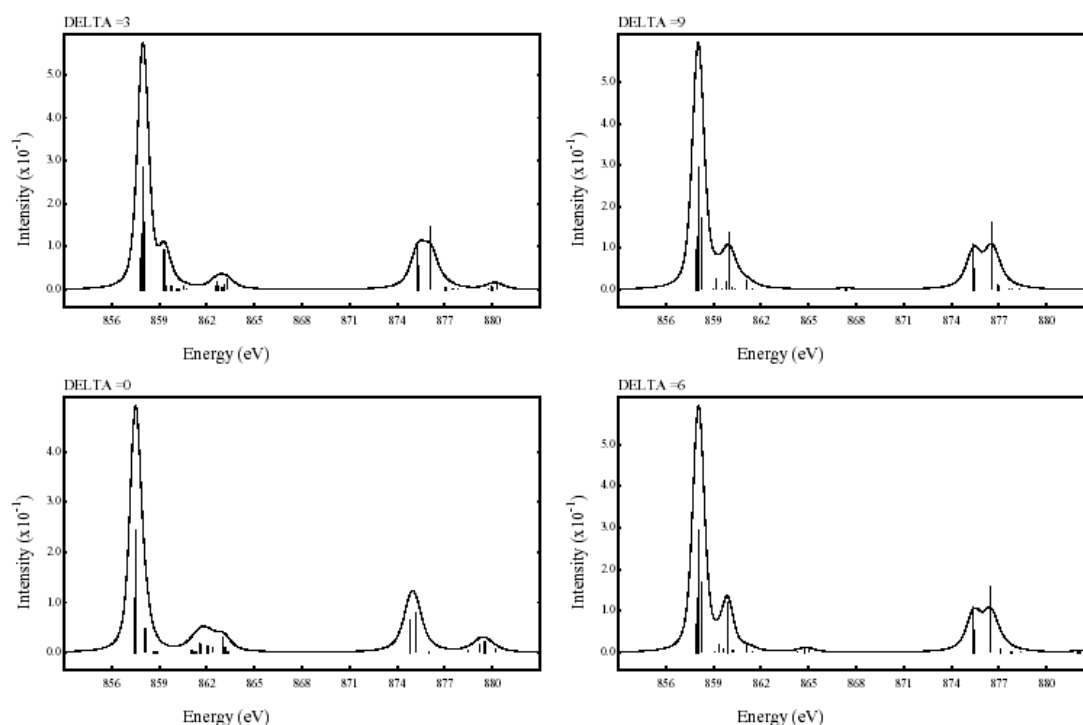
We will explain this file line by line.

- ⊗ 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 outputfiles (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 4<sup>th</sup> 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 5<sup>th</sup> 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 centres 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 eg mixing and 1.0 for t<sub>2g</sub> 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 inputfile, in this case first the atomic Hamiltonian (always set to 1.0) and the cubic crystal field, set to 1.12. In TTBAN all values are given in electronvolts.
- ⊗ 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 TTRAC 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.

Now, we know enough to run a TTBAN calculation. We have applied the file as given above to the Ni2+ system. The result is given in the figure below (left bottom; the value of DELTA is indicated above each sub-figure). We see a leading peak and a second multiplet structure some 5 eV higher. This does not look like the experimental NiO spectrum. With the value DELTA=0, we create a 50:50 mixture of 3d<sup>8</sup> and 3d9L. In contrast NiO should be described with much more 3d<sup>8</sup> than 3d9L in its ground state. This can be achieved by increasing DELTA. In the figure below we increased DELTA 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<sup>8</sup> character. This also implies that the calculated spectral shape is identical to the single configuration calculation 3d<sup>8</sup> > 2p53d9 (check with chapter 5). If we decrease the value of DELTA 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 L3 edge appears compressed. These two phenomena are explained in detail below and also in degroot94a.pdf.

If one would like to fit the experimental NiO spectrum (or another Ni2+ spectrum), in addition to EG2 (= DELTA), one could optimise EF2 (varying it between EG2-1.0 eV and EG2-2.0 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 mixing, see degroot94a.pdf). As a final step, one could vary the mixing parameters a little, say between 1.6 and 2.4 for eg mixing, keeping the 2:1 ratio between eg and t2g mixing.



One can quantify the amount of mixing between  $3d^8$  and  $3d^9L$ . It is given in `als6ni2x1.oba` file. We have saved the four oba-files for the figure above by renaming them to `als6ni2x19.oba`, etc. If one does not rename an oba-file before running again the TTBAN program, the oba-file is overwritten. Looking into `als6ni2x19.oba`, 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%  $3d^9L$ . However, note that this applies to  $A_1$  symmetry only. Actually, we have seen in chapter 5 that the ground state of  $Ni^{2+}$  in octahedral symmetry has  $3A_2$  ( $T_2$ )



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## CHARGE TRANSFER EFFECTS

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 much lower at  $-3.26$  eV. The ground state contains 94.4%  $3d^8$  and 5.6%  $3d^9L$  character, similar but not identical to the  $A_1$  symmetry numbers.

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

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

EXERCISE: Run the **als6ni2x1** calculation for a number of values of DELTA (EG2). Modify also the value of EF2, following the rule as mentioned above. Which value gives an experimental spectrum that looks like NiO? Which value gives a spectrum that looks like  $Cs_2KCuF_6$ ?



**Important concepts**

In short, the three important parameters (U, DELTA and Q) as used in the TTBAN program are introduced.

***The Hubbard U***

The Hubbard U is defined within the impurity model as a charge fluctuation between two metal sites. For example, the Ni sites in NiO have a  $3d^8$  configuration in the ionic limit of  $Ni^{2+}$  ions. A charge fluctuation can occur where an electron jumps from one Ni site to another site. This gives a  $3d^7$  site plus a  $3d^9$  site. The energy difference of the situations before and after the charge fluctuation define the value of the Hubbard U. In the initial state, the energy is given as twice the energy of  $3d^8$ . The final state energy is equal to the energy of  $3d^7$  plus the energy of  $3d^9$ , or:

$$U = E(3d^7) + E(3d^9) - E(3d^8) - E(3d^8).$$

U or  $U_{\text{eff}}$  is defined as the energy differences between the lowest multiplet states of the respective  $3dN$  configurations. One can define a related property  $\underline{U}$  or  $U_{\text{av}}$  as the energy difference between the centres of the respective  $3dN$  configurations.

In first approximation, the value of U is only dependent on the element, its valence and site symmetry. Typical values for the value of U for a divalent metal ion are between 3 eV and 8 eV, where the systematics over the 3d-band is given in figure xx.

The trends in U are caused mainly by the multiplet effects, which increases the values of U for the stable configurations  $3d^3$ ,  $3d^5$  and  $3d^8$  in high-spin octahedral symmetry. These configurations are relatively stable due to the filled (sub) bands, i.e. the ground states  $t_{2g}^3$ ,  $t_{2g}^3e_g^2$  and  $t_{2g}^3e_g^2t_{2g}^3$ .

***The charge transfer energy***

The charge transfer energy is defined within the impurity model as a charge fluctuation between a metal ion and a ligand anion. In NiO, an electron is excited from the oxygen 2p valence band to the 3d band of Ni.

Both the 3d band and the oxygen 2p valence band have a certain bandwidth that in turn yields a bandwidth of the charge transfer energy.

The charge transfer energies are dependent on the nature of the ligand atoms.

Figure with trend.

There can be two or more different charge transfer processes in a certain material. Systems with more than one neighbour atom, of course have charge transfer energies related to these neighbours, but also if all neighbour atoms are identical, there can be more than one charge transfer process. The best known

example are systems where in addition to the ligand-to-metal charge transfer (LM-CT), also the metal-to-ligand charge transfer (ML-CT) is important.

### ***The core hole potential $Q$***

In the final state of a core excitation experiment, be it XAS or XPS, one of the core states is not 100% filled anymore. The core hole creates an additional attractive interaction to all the core and valence levels that lie above it. The most important core hole potentials are the effects on the 3d states. Within the single impurity model, one finds that the core hole potential is usually one to two eV larger than the Hubbard  $U$  and, in addition the largest core hole potential is found for the deepest core state.

The core hole potential as used in the single impurity model is assumed to act only on the 3d-states. This is an approximation and the interactions of the core hole on other valence electrons is neglected. This accounts for ligand valence states as well as metal 4sp conduction states. In addition, off-diagonal interaction terms including the 3d-electron and a valence electron are neglected. It is assumed that the neglect of these interactions can be taken into account by renormalizing the core hole potential  $Q$  to an effective core hole potential  $Q_{\text{eff}}$ . This implies that the value of other parameters as determined from core spectroscopies will also be influenced by the value of  $Q_{\text{eff}}$ , which implies that these parameters can be different from parameters determined from experiments that do not involve core states.

In DFT calculations, the core hole potential is essentially an additional nuclear charge on the atom that absorbed the x-ray energy. This nuclear charge acts, in principle, on all valence states. Thus the core hole potential effect in DFT might also differ from the  $Q_{\text{eff}}$  value in CTM calculations.

### **Initial State Effects**

The charge transfer method is based on the Anderson impurity model and related short-range model Hamiltonians that were applied to core level spectroscopies. This line of approach has been developed in the eighties by the groups of Kotani and Jo<sup>23</sup>, Gunnarsson and Schönhammer<sup>24</sup>, Fujimori and co-workers<sup>25</sup> and Sawatzky and co-workers<sup>26-28,28</sup>. There are variations between the specific methods used, but in this review we sketch only the main line of reasoning behind these models. For details is referred to the original papers.

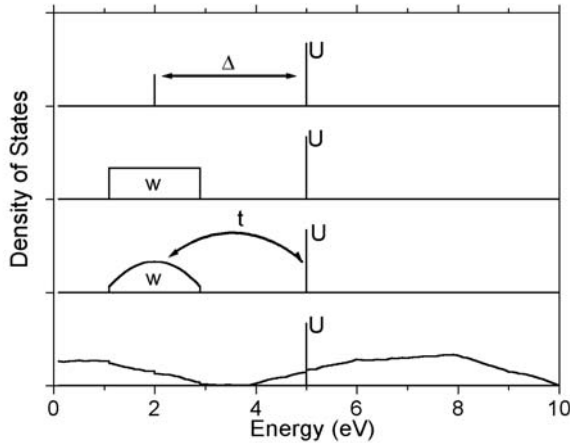
The Anderson impurity model describes a localized state, the 3d-state, which interacts with delocalised electrons in bands. The Anderson impurity model is usually written in second quantization. In second quantization one starts with the ground state  $|_0\rangle$  and acts on this state with operators that annihilate ( $a$ ) or create ( $a^\dagger$ ) a specific electron. For example a 2p to 3d x-ray absorption transition is written as  $|_0 a_{2p}^\dagger a_{3d}\rangle$ . With second quantization one can also indicate the mixing of configurations in the ground state. For example an electron can hop from the 3d-states to a state in the (empty) conduction band, i.e.  $|_0 a_{3d} a_{ck}^\dagger\rangle$ , where  $a_{ck}$  indicates an electron in the conduction band with reciprocal-space vector  $k$ . Comparison to experiment has shown that the coupling to the occupied valence band is more important than the coupling to the empty conduction band. In other

words the dominant hopping is from the valence band to the 3d-states. If one annihilates an electron in a state and then re-creates it one effectively is counting the occupation of that state, i.e.  $a_{3d}^\dagger a_{3d}$  yields  $n_{3d}$ . The Anderson impurity Hamiltonian can then be given as:

$$H_{AIM} = \epsilon_{3d} a_{3d}^\dagger a_{3d} + U_{dd} a_{3d}^\dagger a_{3d} a_{3d}^\dagger a_{3d} + \sum_k \epsilon_{vk} a_{vk}^\dagger a_{vk} + t_{v3d} \sum_k (a_{3d}^\dagger a_{vk} + a_{vk}^\dagger a_{3d})$$

These four terms represent respectively the 3d-state, the correlation of the 3d-state, the valence band and the coupling of the 3d-states with the valence band. One can further extend the Anderson Impurity model to include more than a single impurity, i.e. impurity bands. In addition one can include correlation in the valence band, use larger clusters, etc. In case of multiplet calculations of x-ray absorption these approaches lead in most cases to a too large calculation. There has been much work for the  $\text{Cu}^{\text{II}}$  case, in particular in connection to the high  $T_c$  superconductors<sup>29</sup>, and also there have been calculations concerning the effects of non-local screening on larger clusters for  $\text{Ni}^{\text{II}}$ <sup>30</sup>.

Figure 13 sketches the Impurity model with a semi-elliptical band of bandwidth  $w$ . Instead of a semi-elliptical band one can use the actual band structure that is found from DFT calculations (bottom). Actually, it has been demonstrated that the use of the real band structure instead of an approximate semi-elliptical or square band structure hardly affects the spectral shape<sup>31</sup>. The multiplet model approximates the band usually as a square of bandwidth  $w$ , where  $n$  number of points of equal intensity are used for the actual calculation. Often one simplifies the calculation further to  $n=1$ , i.e. a single state representing the band. In that case the bandwidth is reduced to zero. In order to simplify the notation we will in the following remove the  $k$ -dependence of the valence band and assume a single state describing the band. It must be remembered however that in all cases one can change back this single state to a real band with bandwidth  $w$ .



**Figure 13:** The interaction of a  $U$ -correlated localized state with delocalised bands. From bottom to top are respectively given: a general DOS, a semi-elliptical valence band, a square valence band and a single valence state.

Removing the  $k$ -dependence renders the Hamiltonian into:

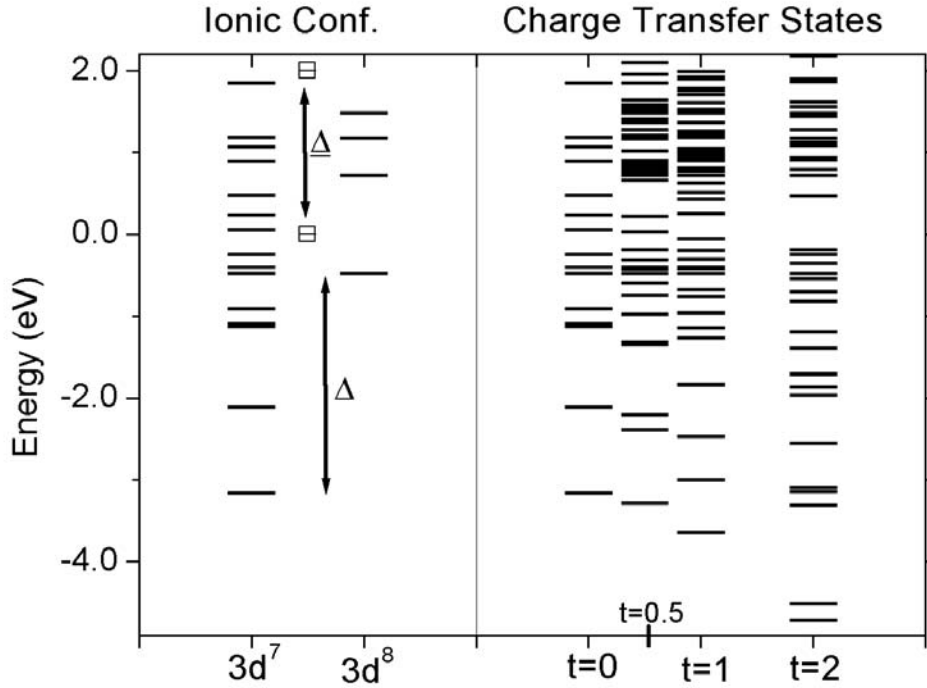
$$H_{AIM-1} = \epsilon_{3d} a_{3d}^\dagger a_{3d} + U_{dd} a_{3d}^\dagger a_{3d} a_{3d}^\dagger a_{3d} + \epsilon_k a_v^\dagger a_v + t_{v3d} (a_{3d}^\dagger a_v + a_v^\dagger a_{3d})$$

Bringing the multiplet description into this Hamiltonian implies that the single 3d state is replaced by all states that are part of the crystal field multiplet Hamiltonian of that particular configuration. This implies that the  $U_{dd}$ -term is replaced by a summation over four 3d-wavefunctions  $3d_1$ ,  $3d_2$ ,  $3d_3$  and  $3d_4$ :

$$H_{AIM} = \varepsilon_{3d} a_{3d}^\dagger a_{3d} + \varepsilon_k a_v^\dagger a_v + t_{v3d} (a_{3d}^\dagger a_v + a_v^\dagger a_{3d}) + \sum_{\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4} g_{dd} a_{3d1}^\dagger a_{3d2} a_{3d3}^\dagger a_{3d4} + \sum_{\Gamma_1, \Gamma_2} l \cdot s a_{3d1}^\dagger a_{3d2} + H_{CF}$$

The term  $g_{dd}$  describes all two-electron integrals and includes the Hubbard  $U$  as well as the effects of the Slater-Condon parameters  $F^2$  and  $F^4$ . In addition there is a new term in the Hamiltonian due to the 3d spin-orbit coupling.  $H_{CF}$  describes the effects of the crystal field potential. This situation can be viewed as a multiplet of localized states interacting with the delocalised density of states. One ingredient is still missing from this description that is if the electron is transferred from the valence band to the 3d-band, the occupation of the 3d-band changes by one. This  $3d^{N+1}$  configuration is again affected by multiplet effects, exactly like the original  $3d^N$  configuration. The  $3d^{N+1}$  configuration contains a valence band with a hole. Because the model is used mainly for transition metal compounds, the valence band is in general dominated by ligand character, for example the oxygen 2p valence band in case of transition metal oxides. Therefore the hole is considered to be on the ligand and is indicated with  $\underline{L}$ , i.e. a ligand hole. The charge transfer effect on the wave function is described as  $3d^N + 3d^{N+1}\underline{L}$ . If one includes the effects of the multiplets on the  $3d^{N+1}\underline{L}$ , a configuration-interaction picture is obtained coupling the two sets of multiplet states.

**Figure 14:** Left: The crystal field multiplet states of  $3d^7$  and  $3d^8$  configurations.



The multiplet states with energies higher than +2.0 eV are not shown.  $\underline{L}$  has been set to +2.0 eV. Right: The charge transfer multiplet calculations for the combination of crystal field multiplets as indicated on the left and with the hopping ranging from 0.0 eV to 2.0 eV as indicated below the states.

Figure 14 gives the crystal field multiplets for the  $3d^7$  and  $3d^8\underline{L}$  configurations of  $\text{Co}^{\text{II}}$ . The  $3d^7$  configurations is centred at 0.0 eV and the lowest energy state is the  $^4T_1$  state, where the small splittings due to the 3d spin-orbit coupling have

been neglected. The lowest state of the  $3d^8\bar{L}$  configuration is the  $^3A_2$  state, which is the ground state of  $3d^8$ . The centre of gravity of the  $3d^8$  configuration has been set at 2.0 eV, which identifies with a value of  $\bar{\epsilon}$  of 2.0 eV. The effective charge transfer energy  $\bar{\epsilon}$  is defined as the energy difference between the lowest states of the  $3d^7$  and the  $3d^8\bar{L}$  configurations as indicated in Figure 14. Because the multiplet splitting is larger for  $3d^7$  than for  $3d^8\bar{L}$ , the effective  $\bar{\epsilon}$  is larger than  $\bar{\epsilon}$ . The effect of charge transfer is to form a ground state that is a combination of  $3d^7$  and  $3d^8\bar{L}$ . The energies of these states have been calculated on the right half of the figure. If the hopping parameter  $t$  is set equal to zero, both configurations do not mix and the states of the mixed configuration are exactly equal to  $3d^7$ , and at higher energy to  $3d^8\bar{L}$ . Turning on the hopping parameter, one observes that the energy of the lowest configuration is further lowered. This state will still be the  $^4T_1$  configuration, but with increasing hopping, it will have increasing  $3d^8\bar{L}$  character. One can observe that the second lowest state is split by the hopping and the most bonding combination obtains an energy that comes close to the  $^4T_1$  ground state. This excited state is essentially a doublet state and if the energy of this state would cross with the  $^4T_1$  state one would observe a charge-transfer induced spin-transition. It has been shown that charge transfer effects can lead to new types of ground states, for example in case of a  $3d^6$  configuration, crystal field effects lead to a transition of a  $S=2$  high-spin to a  $S=0$  low-spin ground state. Charge transfer effects are also able to lead to an  $S=1$  intermediate spin ground state<sup>32</sup>.

Figure 14 can be expanded to Tanabe-Sugano like diagrams for two configurations  $3d^N + 3d^{N+1}\bar{L}$ , instead of the usual Tanabe-Sugano diagrams as a function of only one configuration. The energies of such two-configuration Tanabe-Sugano diagrams are affected by the Slater-Condon parameters (often approximated with the B Racah parameter), the cubic crystal field  $10Dq$ , the charge transfer energy  $\bar{\epsilon}$  and the hopping strength  $t$ . The hopping can be made symmetry dependent and one can add crystal field parameters related to lower symmetries, yielding to an endless series of Tanabe-Sugano diagrams. What is actually important is to determine the possible types of ground states for a particular ion, say  $Co^{II}$ . Scanning through the parameter space of  $F^2$ ,  $F^4$ ,  $10Dq$ ,  $Ds$ ,  $Dt$ ,  $LS_{3d}$ ,  $t$  and  $\bar{\epsilon}$  one can determine the nature of the ground state. This ground state can then be checked with 2p x-ray absorption. After the inclusion of exchange and magnetic fields one has also a means to compare the ground state with techniques like x-ray MCD, optical MCD and EPR.

Comparing figure 13 with figure 14 one observes the transition from a single particle picture to a multiplet configurational picture. One can in principle put more band character into this configurational picture and a first step is to make a transition from a single state to a series of  $3d^8\bar{L}$  states, each with its included multiplet but with each a different effective charge transfer energy. One can choose to use a more elaborate cluster model in which the neighbour atoms are actually included in the calculation<sup>29,30,33</sup>. These cluster models are not described further here.

### Final state effects

The final state Hamiltonian of x-ray absorption includes the core hole plus an extra electron in the valence region. One adds the energy and occupation of the 2p core hole to the Hamiltonian. The core hole potential  $U_{pd}$  and its higher order terms  $g_{pd}$  give rise to the overlap of a 2p wave function with a 3d wave function and is given as a summation over two 2p and two 3d-wavefunctions  $2p_1$ ,  $2p_2$ ,  $3d_1$  and  $3d_2$ :

$$H_{2p} = \varepsilon_{2p} a_{2p}^\uparrow a_{2p} + \sum_{\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4} g_{pd} a_{3d1}^\uparrow a_{2p1} a_{2p2}^\uparrow a_{3d2} + \sum_{\Gamma_1, \Gamma_2} l \cdot s a_{2p1}^\uparrow a_{2p2}$$

The term  $g_{pd}$  describes all two-electron integrals and includes  $U_{pd}$  as well as the effects of the Slater-Condon parameters  $F^2$ ,  $G^1$  and  $G^3$ . In addition there is a term in the Hamiltonian due to the 2p spin-orbit coupling. There is no crystal field effect on core states.

$$\begin{aligned} H_{AIM} = & \varepsilon_{3d} a_{3d}^\uparrow a_{3d} + \varepsilon_k a_v^\uparrow a_v + t_{v3d} (a_{3d}^\uparrow a_v + a_v^\uparrow a_{3d}) \\ & + \sum_{\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4} g_{dd} a_{3d1}^\uparrow a_{3d2} a_{3d3}^\uparrow a_{3d4} + \sum_{\Gamma_1, \Gamma_2} l \cdot s a_{3d1}^\uparrow a_{3d2} + H_{CF} \\ & + \varepsilon_{2p} a_{2p}^\uparrow a_{2p} + \sum_{\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4} g_{pd} a_{3d1}^\uparrow a_{2p1} a_{2p2}^\uparrow a_{3d2} + \sum_{\Gamma_1, \Gamma_2} l \cdot s a_{2p1}^\uparrow a_{2p2} \end{aligned}$$

The overall Hamiltonian in the final state is given. This equation is solved in the same manner as the initial state Hamiltonian. Using the two configuration description of Figure 14, one finds for  $\text{Co}^{II}$  two final states  $2p^5 3d^8$  and  $2p^5 3d^9 \underline{L}$ . These states mix in a manner similar to the two configurations in the ground state and as such give rise to a final state Tanabe-Sugano diagram. All final state energies are calculated from the mixing of the two configurations. This calculation is only possible if all final state parameters are known. The following rules are used:

- The 2p3d Slater-Condon parameters are taken from an atomic calculation. For trivalent ions and higher valences, these atomic values are sometimes reduced.
- The 2p and 3d spin-orbit coupling are taken from an atomic calculation.
- The crystal field values are assumed to be the same as in the ground state.
- The energies of the configurations, i.e. the charge transfer energy, are given by the values of  $U_{dd}$  and  $U_{pd}$ . Effectively  $\underline{\epsilon}_F = \underline{\epsilon}_I + U_{dd} - U_{pd}$ . Because in general  $U_{pd}$  is approximately 1 to 2 eV larger than  $U_{dd}$ , one often assumes  $\underline{\epsilon}_F = \underline{\epsilon}_I - 1$  eV or  $\underline{\epsilon}_F = \underline{\epsilon}_I - 2$  eV.
- The hopping parameter  $t$  is assumed to be equal in the initial and final states.

Detailed analysis of x-ray absorption and resonant x-ray emission spectra has shown that the crystal field values seem to be smaller by 10 to 20% in the final state<sup>34</sup>. The same observation has been made for the hopping parameters<sup>35</sup>. One can understand these trends from the (slight) compression of the 3d wave function in the final state. From the presence of the 2p core hole one would expect a significant compression of the 3d wave function, but the effect of the 2p core hole is counteracted by the effect of the extra 3d-electron in the final state. Because we have seen that  $U_{dd}$  is a bit smaller than  $U_{pd}$  this counteracting action is not complete and there will be a small compression of the 3d wave function. In conclusion it can be said that  $\underline{\epsilon}$ ,  $t$  and  $10Dq$  will all be slightly smaller in the final state. Because the reduction of these parameters has counteracting effects on the spectral shape, in most simulations one varies only  $\underline{\epsilon}$  and keeps  $t$  and  $10Dq$  constant.



### The x-ray absorption spectrum with charge transfer effects

The essence of the charge transfer model is the use of two or more configurations. Ligand field multiplet calculations use one configuration for which it solves the effective atomic Hamiltonian plus the ligand field Hamiltonian, so essentially the following matrices:

$$I_{XAS,1} \propto \langle 3d^N | p | 2p^5 3d^{N+1} \rangle^2$$

$$H_{INIT,1} = \langle 3d^N | \frac{e^2}{r_{12}} + \zeta_d l_d \cdot s_d + H_{LFM} | 3d^N \rangle$$

$$H_{FINAL,1} = \langle 2p^5 3d^{N+1} | \frac{e^2}{r_{12}} + \zeta_p l_p \cdot s_p + \zeta_d l_d \cdot s_d + H_{LFM} | 2p^5 3d^{N+1} \rangle$$

The charge transfer model adds a configuration  $3d^{N+1}\underline{L}$  to the  $3d^N$  ground state. In case of a transition metal oxide, in a  $3d^{N+1}\underline{L}$  configuration an electron has been moved from the oxygen 2p-valence band to the metal 3d-band. One can continue with this procedure and add  $3d^{N+2}\underline{L}^2$  configuration, etc. In many cases two configurations will be enough to explain the spectral shapes, but in particular for high valence states it can be important to include more configurations<sup>36,37</sup>. As far as x-ray absorption and x-ray emission is concerned, the consequences for the calculations are the replacement of  $3d^N$  with  $3d^N + 3d^{N+1}\underline{L}$  plus the corresponding changes in the final state. This adds a second initial state, final state and dipole transition:

$$I_{XAS,2} \propto \langle 3d^{N+1}\underline{L} | p | 2p^5 3d^{N+2}\underline{L} \rangle^2$$

$$H_{INIT,2} = \langle 3d^{N+1}\underline{L} | \frac{e^2}{r_{12}} + \zeta_d l_d s_d + H_{LFM} | 3d^{N+1}\underline{L} \rangle$$

$$H_{FINAL,2} = \langle 2p^5 3d^{N+2}\underline{L} | \frac{e^2}{r_{12}} + \zeta_p l_p s_p + \zeta_d l_d s_d + H_{LFM} | 2p^5 3d^{N+2}\underline{L} \rangle$$

The two initial states and two final states are coupled by monopole transitions, i.e. configuration interaction. The mixing parameter  $t$  couples both configurations and  $\Delta$  is the energy difference. The Hamiltonian is abbreviated with  $t/\Delta$  to describe the monopole interaction:

$$H_{MIX I1,I2} = \langle 3d^N | t/\Delta | 3d^{N+1}\underline{L} \rangle$$

$$H_{MIX F1,F2} = \langle 2p^5 3d^{N+1} | t/\Delta | 2p^5 3d^{N+2}\underline{L} \rangle$$

The x-ray absorption spectrum is calculated by solving the equations given above. If a  $3d^{N+2}\underline{L}\underline{L}'$  configuration is included its energy is  $2_{-} + U_{dd}$ , where  $U_{dd}$  is the correlation energy between two 3d-electrons<sup>28</sup>. The formal definition of  $U_{dd}$  is the energy difference one obtains when an electron is transferred from one metal site to another, i.e. a transition  $3d^N + 3d^N \rightarrow 3d^{N+1} + 3d^{N-1}$ . The number of interactions of two  $3d^N$  configurations is one more than the number of interactions of  $3d^{N+1}$  plus  $3d^{N-1}$ , implying that this energy difference is equal to the correlation energy between two 3d-electrons.

By analysing the effects of charge transfer it is found that, for systems with a positive value of  $\Delta$ , the main effects on the x-ray absorption spectral shape are:

- (1) The formation of small satellites.
- (2) The contraction of the multiplet structures.

The formation of small satellites or even the absence of visible satellite structures is a special feature of x-ray absorption spectroscopy. Its origin is the fact that x-ray absorption is a neutral spectroscopy and the local charge of the final state is equal to the charge of the initial state. This implies that there is little screening hence little charge transfer satellites. This effect can be explained by using a two-by-two problem as example. We follow the paper of Hu et al.<sup>38</sup> to describe the mixing of two configurations that are separated by  $\Delta$  and mixed by  $t$ . This mixing yields a two by two determinant:

$$H = \begin{vmatrix} 0 & t \\ t & \Delta \end{vmatrix}$$

Solving the determinant yields the two states after mixing: The ground state, or bonding combination,  $\Psi_B$  has a wave function:

$$\Psi_B = \alpha_i |3d^N\rangle + \beta_i |3d^{N+1}\underline{L}\rangle$$

The energy of the bonding combination is given as:

$$E_B = \frac{\Delta}{2} - \frac{1}{2}\sqrt{\Delta^2 + 4t}$$

The parameters  $\alpha_i$  and  $\beta_i$  can be defined in  $\Delta$  and  $t$ :

$$\alpha_i = \sqrt{1/1 + \left(\frac{X-\Delta}{2T}\right)^2}, \quad X = \sqrt{\Delta^2 + 4T^2}$$

$$\beta_i = \sqrt{1 - \alpha_i^2}$$

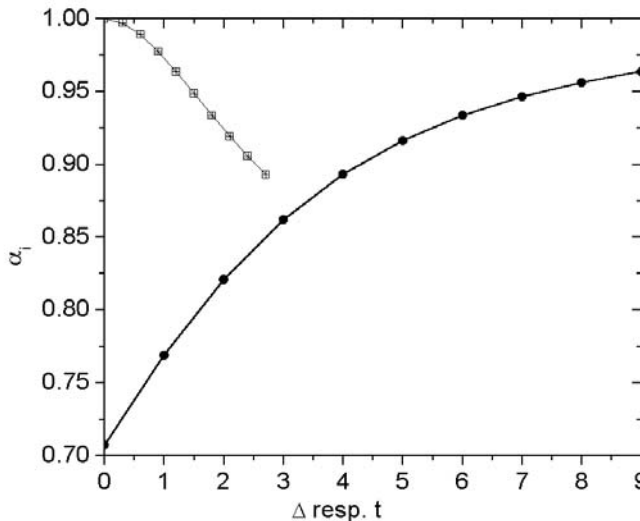
The anti-bonding combination is given as:

$$\Psi_B = \beta_i |3d^N\rangle - \alpha_i |3d^{N+1}\underline{L}\rangle$$

The energy of the anti-bonding combination is given as:

$$E_B = \frac{\Delta}{2} + \frac{1}{2}\sqrt{\Delta^2 + 4t}$$

It can be found that, apart from numerical deviations at small charge transfer energies, the value of  $\alpha_i$  is essentially proportional to  $\Delta/t$ . The dependence on  $\Delta$  and  $t$  is very clear in figure 15. A linear dependence of  $\alpha_i$  is observed as a function of  $t$  and a square root dependence is found as a function of  $\Delta$ . This implies for the percentage of  $3d^N$  character in the ground state, i.e.  $\alpha_i^2$  that it is proportional to  $\Delta/t^2$ .



**Figure 15:** The initial state value of  $\alpha_i$  as a function of the charge transfer energy for  $t=2.7$  eV (solid circles) and as a function of the hopping  $t$  for  $\Delta=5$  eV (open squares).

We have found that in the final state the value of  $\epsilon_F \sim -1$  eV. This implies that the final state determinant is approximately equal to the initial state determinant:

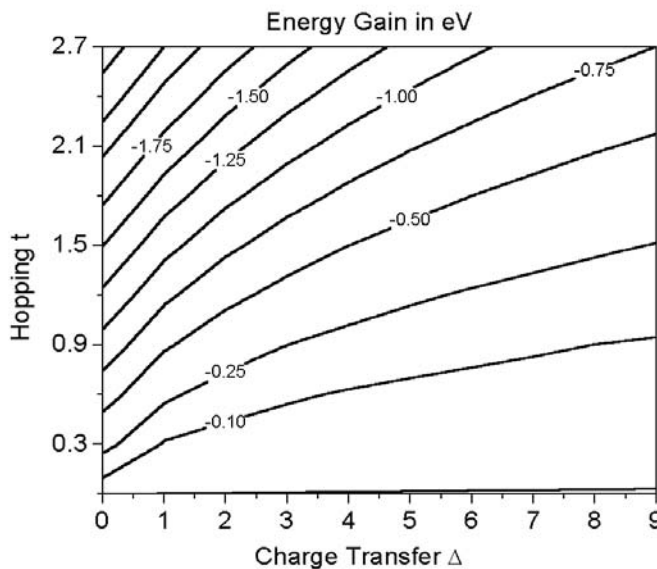
$$H = \begin{vmatrix} 0 & t_F \\ t_F & \Delta_F \end{vmatrix}$$

This yields for  $\epsilon_f$  and  $\epsilon_i$  that they are approximately equal to  $\epsilon_i$  and  $\epsilon_i$ . The results of the initial and final state equations can be used to calculate the x-ray absorption cross section. One can make a transition from  $3d^N$  to  $2p^5 3d^{N+1}$  and from  $3d^{N+1} \underline{L}$  to  $2p^5 3d^{N+2} \underline{L}$ . This implies that the intensity of the main peak is equal to  $(\epsilon_i f + \epsilon_i f)^2$  while the satellite intensity is equal to  $(\epsilon_i f - \epsilon_i f)^2$ . The contraction of the multiplet structure due to charge transfer can also be understood using the two by two matrices. Assume two multiplet states split by an energy  $\Delta$ . They both mix with a charge transfer state that is positioned  $\delta$  above the lowest energy multiplet state I. Consequently the charge transfer energy of the second multiplet state II is  $\Delta - \delta$ . Assuming that the hopping terms are the same for these two states, the energy gain of the bonding combination is:

$$E_B(I) = \frac{\Delta}{2} - \frac{1}{2} \sqrt{\Delta^2 + 4t}$$

$$E_B(II) = \frac{\Delta - \delta}{2} - \frac{1}{2} \sqrt{(\Delta - \delta)^2 + 4t}$$

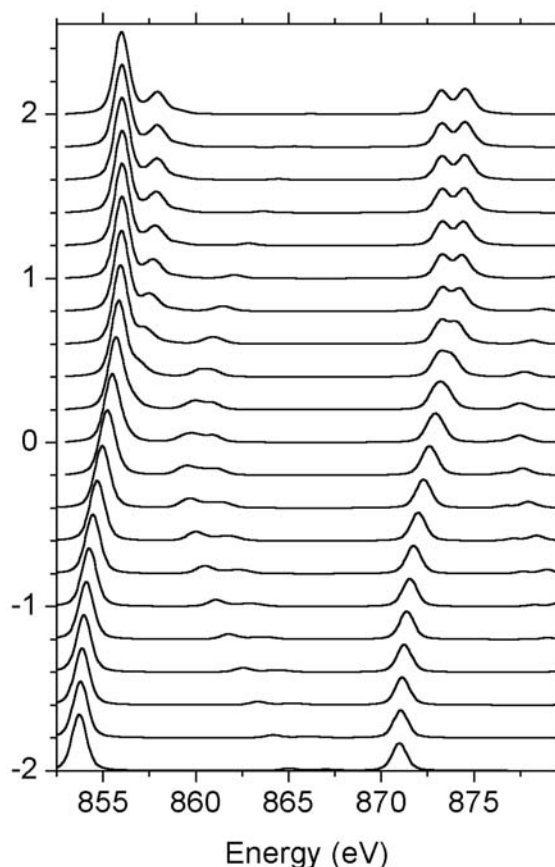
These trends are made visible in figure 16. One can observe that for zero hopping there is no energy gain. Consider for example a hopping of 1.5 eV. Then one observes the largest energy gain for the lowest value of  $\Delta$ . The higher lying multiplet states have a smaller effective  $\Delta$  and consequently a larger energy gain. As such their energy comes closer to the lowest energy state and the multiplet appears compressed.



**Figure 16:** The energy gain of the bonding combination of a two-state problem as a function of the charge transfer energy  $\Delta$  and the hopping  $t$

The two by two problem in the initial and final state explains the two main effects of charge transfer: a compression of the multiplet structure and the existence of only small satellites. These two phenomena are visible in the figures of  $\text{Ni}^{II}$  and

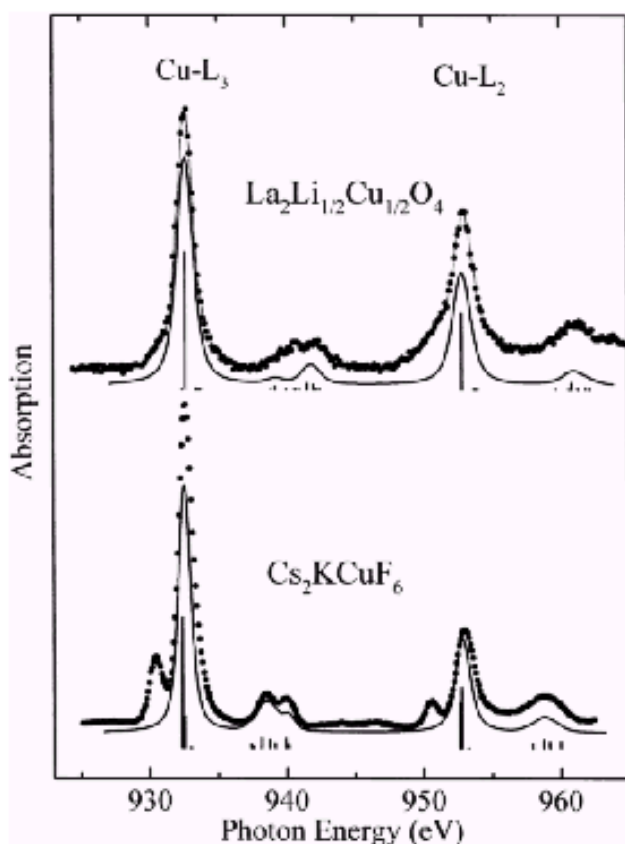
$\text{Co}^{\text{II}}$  as given below. In case that the charge transfer is negative, the satellite structures are slightly larger because then the final state charge transfer is increased with respect to the initial state and the balance of the initial and final state 's and 's is less good.



**Figure 17:** Series of charge transfer multiplet calculations for the  $\text{Ni}^{\text{II}}$  ground state  $|3d^8+3d^9\bar{L}\rangle$ . The top spectrum has a charge transfer energy of +10 eV. The bottom spectrum has a charge transfer energy of -10 eV and relates to an almost pure  $3d^9$  ground state.

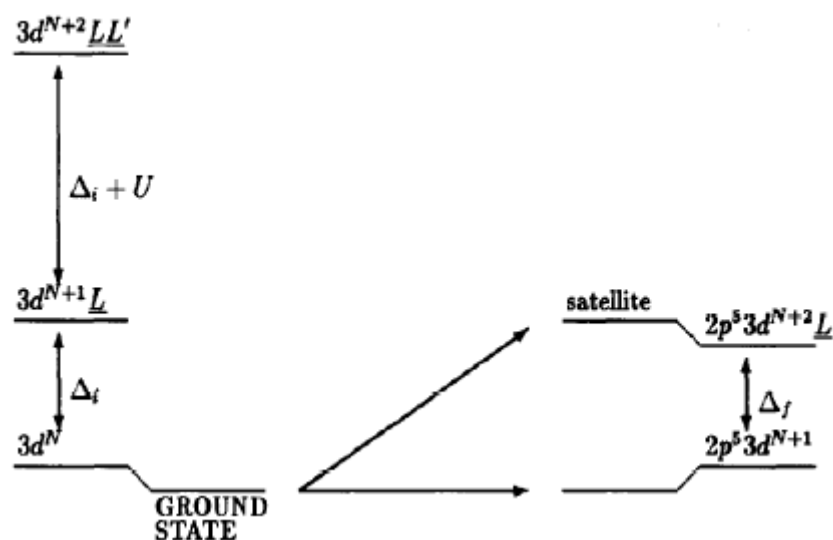
Figure 17 shows the effect of the charge transfer energy on divalent nickel. We have used the same hopping  $t$  for the initial and final state and reduced the charge transfer energy by one eV. In the top spectrum,  $\Delta = 10$  and the spectrum is essentially the ligand field multiplet spectrum of a  $\text{Ni}^{\text{II}}$  ion in its  $3d^8$  configuration. The bottom spectrum uses  $\Delta = -10$  and now the ground state is almost a pure  $3d^9\bar{L}$  configuration. Looking for the trends in Figure 17, one finds the increased contraction of the multiplet structure by going to lower values of  $\Delta$ . This is exactly what is observed in the series  $\text{NiF}_2$  to  $\text{NiCl}_2$  and  $\text{NiBr}_2$ <sup>16,17,27,39</sup>. Going from Ni to Cu the atomic parameters change very little, except the 2p spin-orbit coupling and the 2p binding energy. Therefore the spectra of  $3d^N$  systems of different elements are all very similar and the bottom spectrum is also similar to  $\text{Cu}^{\text{II}}$  systems. Therefore one can also use the spectra with negative  $\Delta$ -values for  $\text{Cu}^{\text{III}}$  compounds, such as  $\text{La}_2\text{Li}_{1/2}\text{Cu}_{1/2}\text{O}_4$  and  $\text{Cs}_2\text{KCuF}_6$ . Figure 18 shows the comparison of the 2p x-ray absorption spectrum of these two compounds with charge transfer multiplet calculations<sup>40,41</sup>. It can be checked in figure 4.8 that these calculations look similar to the calculations for  $\text{Ni}^{\text{II}}$  systems with negative values of  $\Delta$ . For such systems with negative  $\Delta$  values, it is important to carry out

charge transfer multiplet calculations, as no good comparison with crystal field multiplet spectra can be made.



**Figure 18:** Results of theoretical simulations of the copper 2p x-ray absorption spectra of  $\text{Cs}_2\text{KCuF}_6$  (bottom) and  $\text{La}_2\text{Li}_{1/2}\text{Cu}_{1/2}\text{O}_4$  (top), in comparison with the experimental spectra. (Reprinted with permission from ref.<sup>38</sup>. Copyright 1998 Elsevier Science).

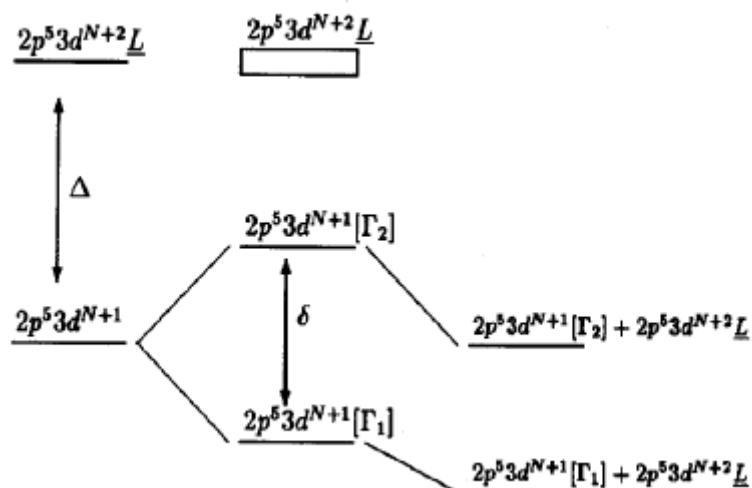
### Why there are small satellites in XAS



In the figure above the effects of hybridization are included for 2p XAS. The ground state is formed from a combination of  $3d^N$  and  $3d^{N+1}L$ . The two configurations in the final state form a bonding and antibonding combination. If  $f =$  (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  $2p^5 3d^N$  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 electronvolts (for details of multiplet calculations see Section 5.1). This spread implies that the energy difference of these different states with the  $2p^5 3d^{N+1} L$  band varies considerably. In the figure below a situation is sketched in which the multiplet splittings ( $\delta$ ) are less than the charge transfer energy ( $\Delta$ ). If hybridization is turned on, the energy-gain of the lowest multiplet state ( $\Gamma_1$ ) 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.



**Charge transfer in D4h symmetry with three configurations**

Until now we have used two configurations to describe the ground state of a system. In case of Ni<sup>2+</sup> and all other divalent systems, two configurations seem adequate to describe the XAS spectral shapes. Higher valent systems might need more configurations. We will discuss the differences between two and three configuration on the basis of Ni<sup>3+</sup> systems. In the ionic ansatz, Ni<sup>3+</sup> has a 3d<sup>7</sup> configuration. A 3d<sup>7</sup> configuration can be high-spin and low-spin depending. A high-spin ground state has 4T<sub>1</sub> symmetry, with all spin-up electrons filled plus two t<sub>2g</sub> spin-down electrons. A low-spin ground state has 2E symmetry, with all t<sub>2g</sub> electrons filled plus one e<sub>g</sub> spin-up electron.

We start with a description of two configurations. The als6ni3x2.rcg inputfile reads:

```

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
D 7  P 6
D 8  P 5
Ni3+    1 1
Ni3+    2 1
          -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
D 8  P 6 D09
D 9  P 5 D09
Ni3+    1 2
Ni3+    2 2
          -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
D 7  P 6 D10
D 8  P 6 D09
Ni3+2P3DXAS      4      0.0000      10.6211      6.6361      0.0912      0.0000HR99999999
Ni2+2P3DXAS      4      0.0000      9.7871      6.0781      0.0832      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
D 8  P 5 D10
D 9  P 5 D09
          8  862.3000      11.2171      7.0111      0.1122      11.5002HR99999999
        6.6803      5.0654      2.8824
          6  862.3000      0.1022      11.5002      6.1763      4.6294HR99999999
        2.6324
          -99999999.
-1

```

This inputfile is similar to the Ni<sup>2+</sup> inputfile, with the difference that the ground state starts from 3d<sup>7</sup> instead of 3d<sup>8</sup>. If the calculation would be performed in Oh

symmetry, the **als6ni3x2.rac** inputfile is completely identical to als6ni2x1.rac. We will however do the calculation in D4h symmetry, which implies that additional parameters have to be introduced in the TTRAC file. The als6ni3x2.rac file reads:

```

Y
  % vertical                1
racer O3
to   Oh
to   D4h
endchain
actor 1- perp              transi
  oper MULTIPOLE
    branch 1- > 0 1- > 1- 1.000
actor ^0- para              transi
  oper MULTIPOLE
    branch 1- > 0 1- > ^0- 1.000
actor 0+ HAMILTONIAN ground
actor 0+ 10Dq              ground
actor 0+ Dt                ground
actor 0+ Ds                ground
actor 0+ HAMILTONIAN excite
actor 0+ 10Dq              excite
actor 0+ Dt                excite
actor 0+ Ds                excite
RUN
  % vertical                2
racer O3
to   Oh
to   D4h
endchain
actor 1- perp              transi
  oper MULTIPOLE
    branch 1- > 0 1- > 1- 1.000
actor ^0- para              transi
  oper MULTIPOLE
    branch 1- > 0 1- > ^0- 1.000
actor 0+ HAMILTONIAN ground
actor 0+ 10Dq              ground
actor 0+ Dt                ground
actor 0+ Ds                ground
actor 0+ HAMILTONIAN excite
actor 0+ 10Dq              excite
actor 0+ Dt                excite
actor 0+ Ds                excite
RUN
  % horizontal              1
racer O3
to   Oh
to   D4h
endchain
  ACTOR 0+ Blhybr          transi
  OPER  MULTIPOLE

```



```

BRANCH 0+ > 0 0+ > 0+ 0.4472135955
BRANCH 4+ > 0 0+ > 0+ 1.643167673
BRANCH 4+ > 0 2+ > 0+ -1.388730150
BRANCH 2+ > 0 2+ > 0+ -1.195228609
  ACTOR 0+ A1hybr      transi
  OPER  MULTIPOLE
BRANCH 0+ > 0 0+ > 0+ 0.4472135955
BRANCH 4+ > 0 0+ > 0+ 1.643167673
BRANCH 4+ > 0 2+ > 0+ +1.388730150
BRANCH 2+ > 0 2+ > 0+ +1.195228609
  ACTOR 0+ B2hybr      transi
  OPER  MULTIPOLE
BRANCH 0+ > 0 0+ > 0+ 0.4472135955
BRANCH 4+ > 0 0+ > 0+ -1.095445115
BRANCH 4+ > 0 2+ > 0+ +1.851640200
BRANCH 2+ > 0 2+ > 0+ -1.195228609
  ACTOR 0+ Ehybr      transi
  OPER  MULTIPOLE
BRANCH 0+ > 0 0+ > 0+ 0.8944271910
BRANCH 4+ > 0 0+ > 0+ -2.190890230
BRANCH 4+ > 0 2+ > 0+ -1.851640200
BRANCH 2+ > 0 2+ > 0+ +1.195228609
actor 0+ HAMILTONIAN ground
  oper  HAMILTONIAN
    branch 0+ > 0 0+ > 0+ 1.000
actor 0+ 10Dq      ground
  oper  SHEll1
    BRANCH 4+ > 0 0+ > 0+ 3.28633
actor 0+ Dt      ground
  oper SHEll1
    BRANCH 4+ > 0 2+ > 0+ -16.2019
actor 0+ Ds ground
  oper SHEll1
    BRANCH 2+ > 0 2+ > 0+ -8.3666
actor 0+ HAMILTONIAN excite
  oper  HAMILTONIAN
    branch 0+ > 0 0+ > 0+ 1.000
actor 0+ 10Dq      excite
  oper  SHEll1
    BRANCH 4+ > 0 0+ > 0+ 3.28633
actor 0+ Dt      excite
  oper  SHEll1
    BRANCH 4+ > 0 2+ > 0+ -16.2019
actor 0+ Ds      excite
  oper  SHEll1
    BRANCH 2+ > 0 2+ > 0+ -8.3666
RUN
  % horizontal      2
racer O3
to Oh
to D4h

```

```

      ACTOR    0+ B1hybr      transi
endchain

```

```

      OPER     MULTIPOLE

```

```

BRANCH  0+ > 0 0+ > 0+    0.4472135955
BRANCH  4+ > 0 0+ > 0+    1.643167673
BRANCH  4+ > 0 2+ > 0+   -1.388730150
BRANCH  2+ > 0 2+ > 0+   -1.195228609

```

```

      ACTOR    0+ A1hybr      transi

```

```

      OPER     MULTIPOLE

```

```

BRANCH  0+ > 0 0+ > 0+    0.4472135955
BRANCH  4+ > 0 0+ > 0+    1.643167673
BRANCH  4+ > 0 2+ > 0+   +1.388730150
BRANCH  2+ > 0 2+ > 0+   +1.195228609

```

```

      ACTOR    0+ B2hybr      transi

```

```

      OPER     MULTIPOLE

```

```

BRANCH  0+ > 0 0+ > 0+    0.4472135955
BRANCH  4+ > 0 0+ > 0+   -1.095445115
BRANCH  4+ > 0 2+ > 0+   +1.851640200
BRANCH  2+ > 0 2+ > 0+   -1.195228609

```

```

      ACTOR    0+ Ehybr      transi

```

```

      OPER     MULTIPOLE

```

```

BRANCH  0+ > 0 0+ > 0+    0.8944271910
BRANCH  4+ > 0 0+ > 0+   -2.190890230
BRANCH  4+ > 0 2+ > 0+   -1.851640200
BRANCH  2+ > 0 2+ > 0+   +1.195228609

```

```

actor    0+ HAMILTONIAN ground

```

```

  oper    HAMILTONIAN

```

```

    branch 0+ > 0 0+ > 0+    1.000

```

```

actor    0+ 10Dq      ground

```

```

  oper    SHE111

```

```

    BRANCH 4+ > 0 0+ > 0+    3.28633

```

```

actor    0+ Dt      ground

```

```

  oper    SHE111

```

```

    BRANCH 4+ > 0 2+ > 0+   -16.2019

```

```

actor    0+ Ds      ground

```

```

  oper    SHE111

```

```

    BRANCH 2+ > 0 2+ > 0+   -8.3666

```

```

actor    0+ HAMILTONIAN excite

```

```

  oper    HAMILTONIAN

```

```

    branch 0+ > 0 0+ > 0+    1.000

```

```

actor    0+ 10Dq      excite

```

```

  oper    SHE111

```

```

    BRANCH 4+ > 0 0+ > 0+    3.28633

```

```

actor    0+ Dt      excite

```

```

  oper    SHE111

```

```

    BRANCH 4+ > 0 2+ > 0+   -16.2019

```

```

actor    0+ Ds      excite

```

```

  oper    SHE111

```

```
RUN
```

```
BRANCH 2+ > 0 2+ > 0+ -8.3666
```

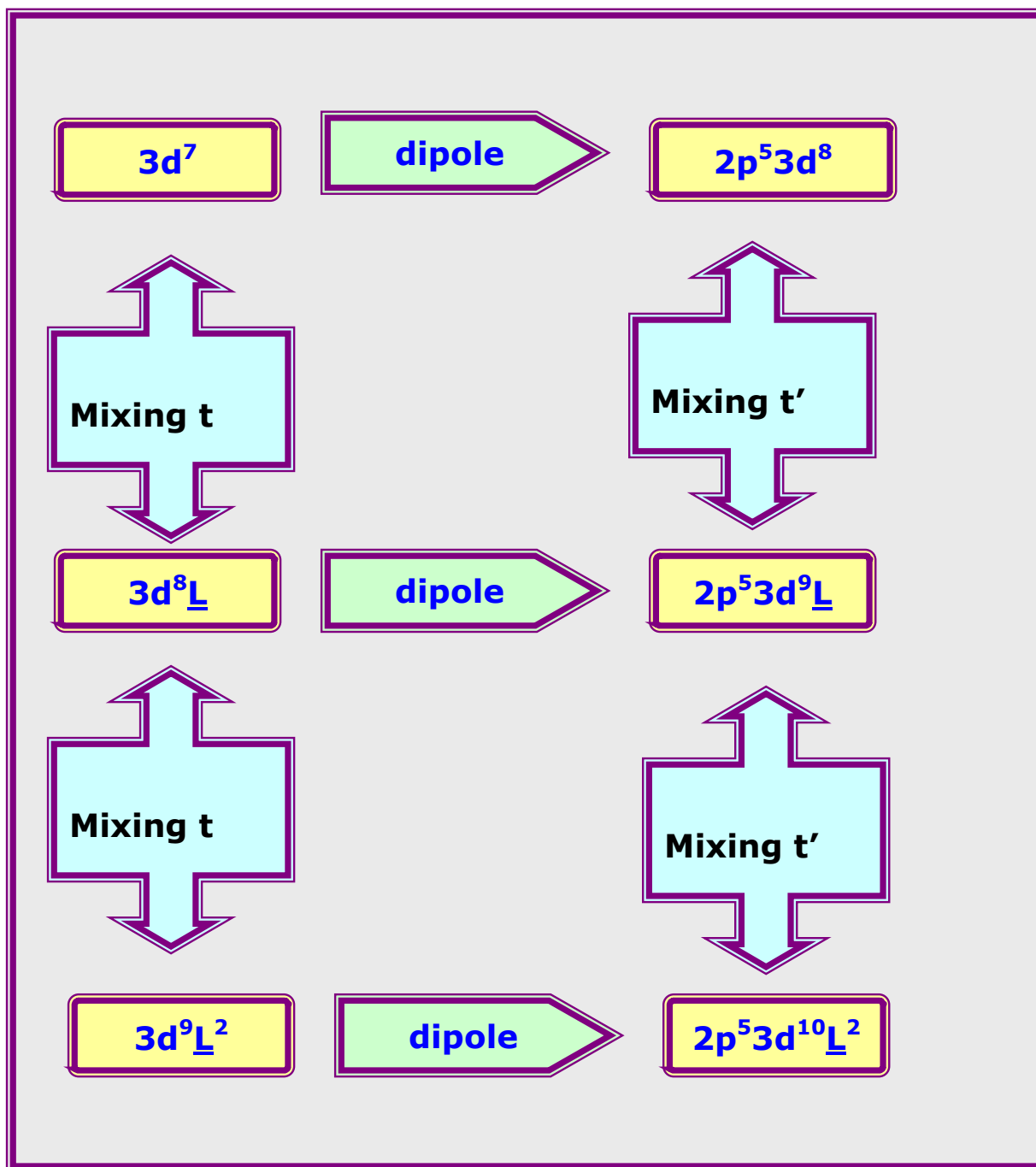
This file has additional branches for the Dt and the Ds parameters and also additional mixings for respectively A1, B1, B2 and E symmetry electrons. The numbers that are used in this file are all chosen in such a way to allow all parameters to be given in electronvolts in the TTBAN inputfile.

The als6ni3x2.ban file has a few new aspects:

```
erange 0.3000
NCONF 2 2
N2 1
def EG2 = -0.5 unity
def EF2 = -1.5 unity
XMIX 4 2 2 1 1.0
2 1 1 2 2 1 2
XHAM 4 1.0 1.1 0.2 0.1
4 1 1 1 2 2 1 2 2
TRAN 2 1 1 2 2
TRIADS
S0+ 1- S0-
S0+ 1- S1-
S1+ 1- S0-
S1+ 1- S1-
S0+ ^0- S0-
S1+ ^0- S1-
```

There are now 4 mixing parameters (B1, A1, B2, E), the Hamiltonian consists of four terms (atomic, 10Dq, Ds and Dt) and the triads have two different dipole operators (1- and ^0-, or respectively parallel and perpendicular to the z-axis). Because the numbers of electrons is odd, the symmetries relate to noninteger spin-states. These states are notated with an S in front of the symmetry. In D4h symmetry, there are only two possibilities S0+ and S1+.

A 3-configuration inputfile is essentially similar to the two-configuration inputfile, but now there are 7 instead of 4 sub-calculations.



This scheme explains why there are seven calculations. There are 3 configurations in the initial state and three in the final state. This implies that there are three dipole transitions to be calculated. In addition there are two mixings in the initial state (1) between  $3d^8$  and  $3d^9 \underline{L}$  and (2) between  $3d^9 \underline{L}$  and  $3d^{10} \underline{L}^2$ . Finally there are two mixings in the final state. In total this gives 7 transitions or mixings. The order in the TTRCG file is that first the dipole transitions are given, then the initial state mixings and then the final state mixings. In TTRAC the same order is maintained.

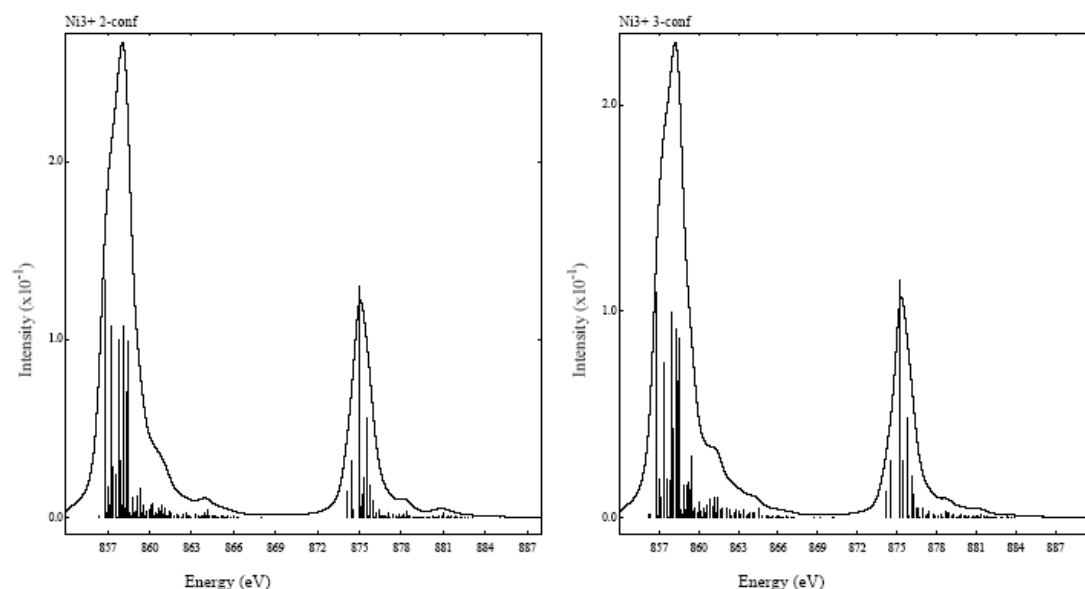
## Chapter 3

## CHARGE TRANSFER EFFECTS

The files als6ni3x3.rcg and als6ni3x3.rac are equivalent to the als6ni3x2 files given above. The file **als6ni3x3.ban** contains a number of changes:

```
erange 0.3
NCONF 3 3
N2 1
N3 1
def EG2 = 0.5 unity
def EF2 = -0.5 unity
def EG3 = 8.0 unity
def EF3 = 6.0 unity
XMIX 4 2.0 2.0 1.0 1.0
4 1 1 2 1 2 3 2 1 2 2 2 3
XHAM 4 1.0 1.1 0.2 0.1
6 1 1 1 2 1 3 2 1 2 2 2 3
TRAN 3 1 1 2 2 3 3
TRIADS
S0+ 1- S0-
S0+ 1- S1-
S1+ 1- S0-
S1+ 1- S1-
S0+ ^0- S0-
S1+ ^0- S1-
```

The changes are that NCONF reads 3 3 instead of 2 2 to indicate that one is using three configurations. N3 1 indicates that also the third configuration is used as a single state. EG3 and EF3 are the equivalents of EG2 and EF2, the Hamiltonian acts on 6 states and there are three dipole transitions. The calculation is equivalent to the 2-configuration calculation, with an additional configuration 3d9L2 at an energy of 8.0 eV above the 3d7 state.



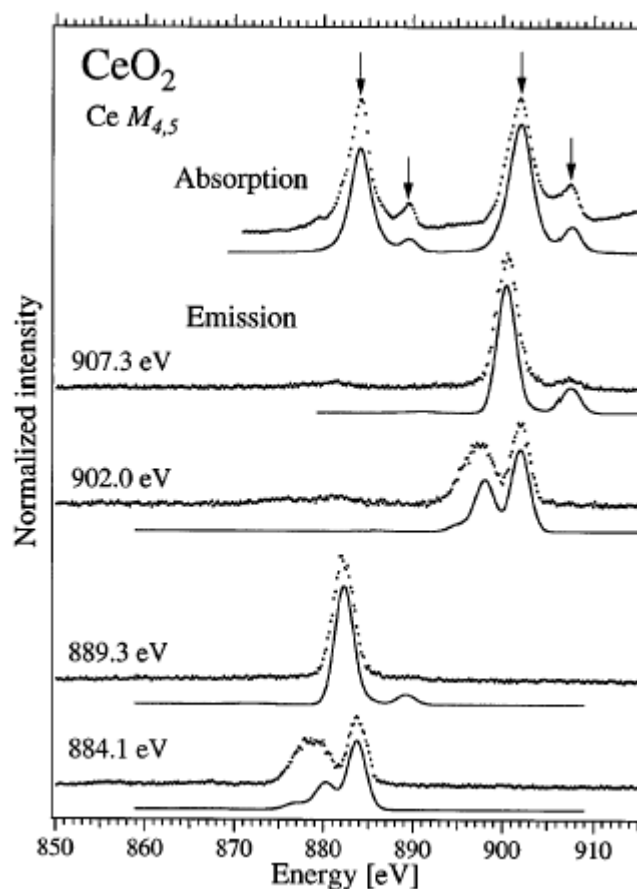
The two spectra are similar. The 2-configuration calculation has a more distinct shoulder at 864 eV, but the overall shape of the spectra is equivalent. The occupation of the configurations are respectively 59% 3d7 + 41% 3d8L for the 2-configuration calculation and 48% 3d7 + 48% 3d8L + 4% 3d9L2 for the 2-

configuration calculation. This result confirms the general rule that 2p XAS spectra can be calculated rather accurately with 2 configurations. We will show in chapter 8 that the situation for 2p XPS is completely different.

MORE SOON

The manual will be extended with:

1. CT in CeO<sub>2</sub>
2. CT with more than 3 configurations
3. Metal-to-Ligand CT: Interactions of 3dN with 3dN-1L
4. Both LMCT and MLCT for cyanides and pi-bonding systems
5. CT with two different CT channels

**Charge transfer effects in  $\text{CeO}_2$** 

$\text{CeO}_2$  is a famous example concerning its charge transfer effects. The figure above shows the  $M_{45}$  x-ray absorption spectrum (top) plus a series of resonant X-ray emission spectra (to be discussed in chapter 6).

How do we start a calculation to simulate this spectrum? We certainly need charge transfer between  $4f^0$  and  $4f^1L$ . Thus the first step is to calculate the parameters needed for the  $4f^0 > 3d^9 4f^1$  transition and the  $4f^1 > 3d^9 4f^2$  transition. These parameters are calculated with TTRCN. The inputfiles [als6ce3.rcn](#) and [als6ce4.rcn](#) read:

```
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
58      Ce3+ 4F01 3D10          4F01 3D10
58      Ce3+ 4F02 3D09          4F02 3D09
-1
```

and

```
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
58      Ce3+ 4F00 3D10          4F00 3D10
58      Ce3+ 4F01 3D09          4F01 3D09
-1
```

The outputfiles [als6ce3.rcf](#) and [als6ce4.rcf](#) contain the atomic parameters. They are reordered into the rcg-file for the charge transfer calculation.

**als6ce4.rcg** reads:

```

0          80998080          8065.47800          00000000
10         14      0      0      1      1 INTER0
1          2 1 12 1 10      00      9 00000000      8065.4780 .00      0 1
D10 F00
D09 F01
Ce4+ 4F00 3D10
Ce4+ 4F01 3D09
-999999999.
0          80998080          8065.47800          00000000
10         14      0      0      1      1 INTER0
1          3 1 13 1 10      00      9 00000000      8065.4780 .00      0 1
D10 F01 F13
D09 F02 F13
Ce3+ 4F01 3D10
Ce3+ 4F02 3D09
-999999999.
0          80998080          8065.47800          00000000
10         14      0      4      0      4 INTER2 shell100000000
1          3 1 13 1 10      00      9 00000000      8065.4780 .00      0 1
D10 F00 F14
D10 F01 F13
Ce4+ 4F00 3D10      1      0.0000      0.0000      0.0000      0.0000      0.0000HR99999999
Ce3+ 4F01 3D10      2      0.0000      0.0872      0.0000      0.0000      0.0000HR99999999
-999999999.
0          80998080          8065.47800          00000000
10         14      0      4      0      4 INTER2 shell100000000
1          3 1 13 1 10      00      9 00000000      8065.4780 .00      0 1
D09 F01 F14
D09 F02 F13
Ce3+ 4F01 3D09      8      890.0000      7.4422      0.1192      8.1943      3.7513HR99999999
      5.6584      3.3124      2.2874
Ce3+ 4F02 3D09      11      890.0000      12.6281      7.9401      5.7171      7.4462HR99999999
      0.1072      7.4863      3.3843      5.0734      2.9684      2.0484
-999999999.
-1

```

Note that the initial state has only a 4f spin-orbit parameter for the charge transfer state. The  $3d^9 4f^1$  final state has 8 parameters (2 spin-orbit, 5 Slater integrals from the df coupling) and the  $3d^9 4f^2$  final state has even 11 parameters (2 spin-orbit, 3 Slater integrals from the ff coupling, 5 Slater integrals from the df coupling). The Slater integrals are large and of the same order as the core hole (3d) spin-orbit coupling.

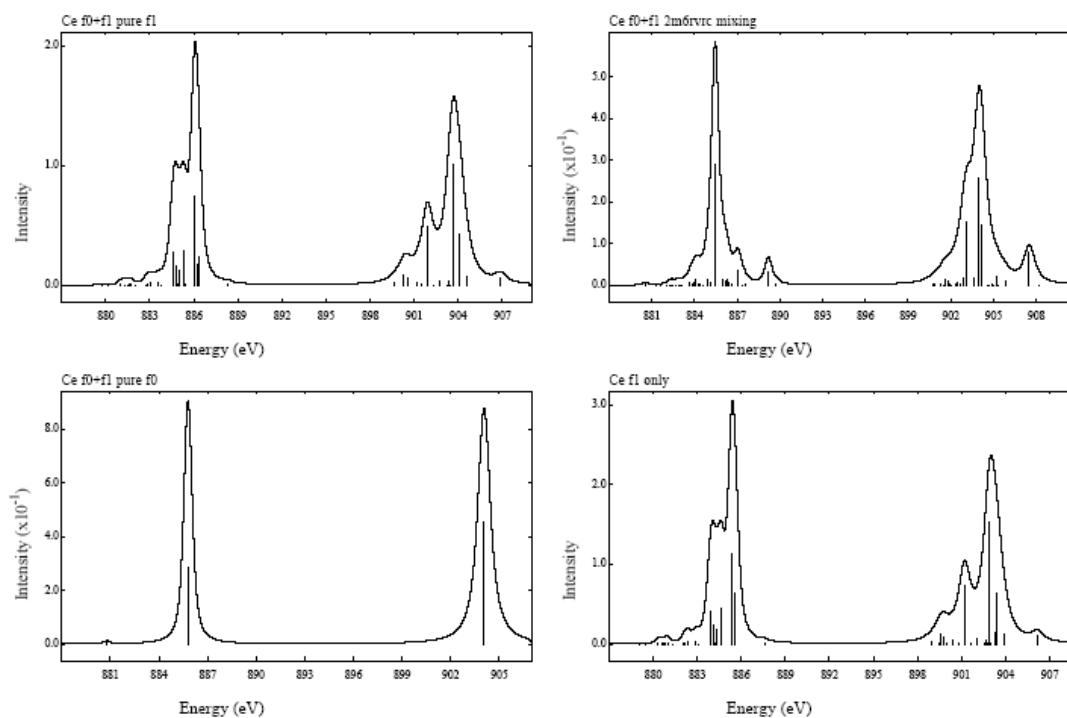
The **als6ce4.rac** file has no crystal field parameters included as the crystal field effect on 4f electrons is small.



The als6ce4.ban file reads:

```
PRMULT
erange 0.5
NCONF 2 2
N2 5 w 2
def EG1 = 0.0 unity
def EG2 = 2.0 unity
def EF1 = 0.0 unity
def EF2 = -0.6 unity
XMIX 2 0.925 0.925
1 1 1 2
XMIX 2 0.6 0.6
1 2 1 2
XHAM 1 1.0
4 1 1 1 2 2 1 2 2
TRAN 2 1 1 2 2
TRIADS
0+ 1- 1- 0
```

There is only one TRIAD as the ground state will remain the same as for a  $4f^0$  state, i.e.  $1S_0$  or  $0^+$ . There is a new feature in this ban-file, which is the command **N2 5 w 2**. Until now we always used N2 1 as command. N2 5 w 2 implies that we use 5 different  $4f^1L$  states that are spread over 2 eV. For example N2 20 w 5 would imply 20 charge transfer states spread over 5 eV, etc. It is noted that, in general, there will be only a minor effect on the spectral shape of these multi-charge transfer states. Because the computer time goes up (dramatically), these multi-charge transfer states are not often used, other than for didactical purposes. One could use them if there are two charge transfer states at different energy. Using this parameter one has no individual control over the other parameters, so if one would like to add two distinct charge transfer channels one has to explicitly add these two channels in the inputfiles.



This figure gives the result for the CeO<sub>2</sub> calculations. The left-bottom gives the pure  $4f_0$  ground state and left-top the pure  $4f_1$  state. The pure  $4f_0$  state has been discussed in chapter 1; it can be calculated from the als6ce4.ban file by

setting the mixing to zero and the 4f1 configuration at high energy. The pure 4f1 state is essentially the experimental spectrum of Ce<sub>2</sub>O<sub>3</sub>; it can be calculated from the als6ce4.ban file by setting the mixing to zero and the 4f0 configuration at high energy using EG1 100 unity. The bottom-right is an atomic multiplet calculation of Ce<sup>3+</sup> and the top-right is the simulation of CeO<sub>2</sub>, using the parameters as given in als6ce4.ban.