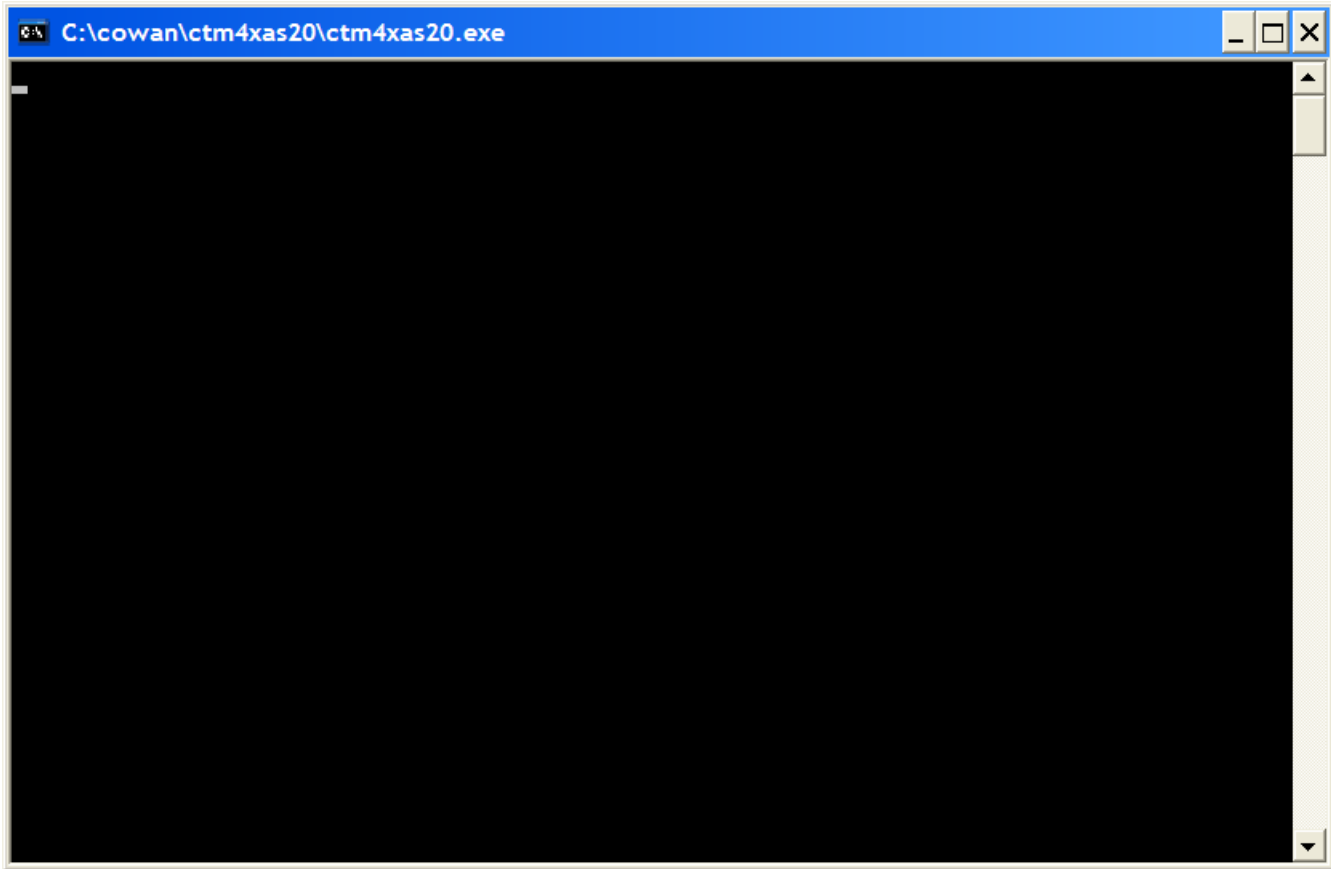Steps for successfully using the CTM4XAS20 Charge-Transfer Multiplet Program
Layout of inputs is different for the current CTM4XAS55 version, but this guide is still totally relevant and usable

• Go to http://www.anorg.chem.uu.nl/people/staff/FrankdeGroot/SLS/ctm4xas2008.htm. Follow the download and installation steps exactly. Finally, everything needed should be in the folder: c:\cowan\ctm4xas20\

•Go to this folder and run ctm4xas20.exe

•You will see a cmd window, as on slide 2, while the program gets ready to work

•After a while, you will then see the real input page, as on slide 3, where various inputs and options are indicated

•If you select charge transfer, which is optional for XAS since the excited electron is mostly excited into a 3d "screening" orbital, but required for XPS since the core hole will strongly polarize everything around it, other options appear, as shown on slide 4.

•Background on the method and the parameters is shown in slides 5-7

•If you now select XPS, you see something like slide 8

•Now input some parameters appropriate to your case. For example, for Mn^{2+} in MnO, with origins discussed in slides 9-12.

C:\cowan\ctm4xas20\ctm4xas20.exe

Use the curled arrow to enlarge for full viewing of all inputs. There is some overlap of inputs on my screen at the bottom, but maybe not yours; no big problem anyway.

Yes or no for ligand-metal charge transfer

XAS, unless this is clicked

Don't use

Chooses whether a core 2p or 3p electron is excited

U_{dd} cannot be changed in XPS

1.0 = free-atom 3d s-o

Crystal field strength

Simplest Octahedral symmetry, two others possible

Shows XAS even when XPS plotted

Click here to get rid of a file if you don't want to plot it

Don't force energy range, program selects it for plot

Lorentzian (lifetime) & Gaussian (instrumental) broadenings to simulate a true experimental spectrum. Set to zero to see details of states involved.

Just delete this advertisement!
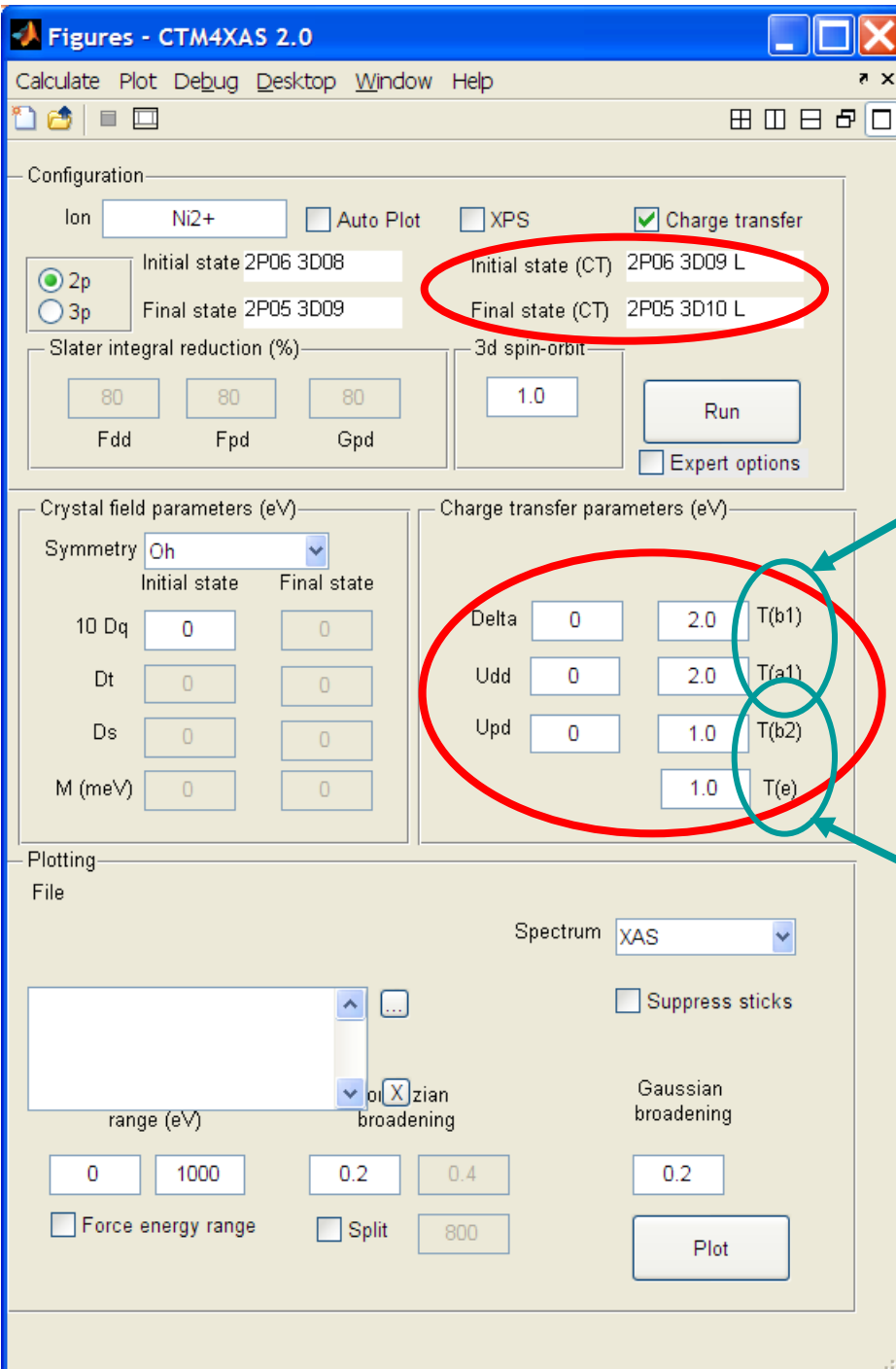
And with charge transfer selected

Initial and final states in XAS have some total number of electrons, and screened d^{n+1} configurations mixed in are now present

T_σ in some papers and of opposite sign to T_π in some papers. Just a sign convention in the codes.

Interaction parameters describing the charge transfer now have to be input. These are different for each case, and are mostly empirically derived by fitting to XAS a/o XPS spectra.

T_π in some papers and of opposite sign to T_σ in some papers

(SUGANO, LARSSON ~> SAWATZKY, VAN DER LAAN, FUJIMORI, OH, ET AL.)

$\underline{c}$ = CORE HOLE ON METAL

$\underline{L}$ = VALENCE (?) HOLE ON LIGAND

Good discussion of model: Bocquet & Fujimori, J. Elect. Spect. & Rel. Phen. 82, 87 (1996)

$$\rho(e_k) = \sum_f |\langle \Psi_f | c | \Psi_g \rangle|^2 \delta(h\nu - e_k - E_f)$$

**By now:
CTM4XAS program
for calculating this
for some cases:
http://www.anorg.chem.uu.nl/
people/staff/FrankdeGroot/
multiplet1.htm**

$$\psi_i = a_0 |d^n\rangle + \sum_m a_m |d^{(n+m)} \underline{L}^m\rangle$$

$$\psi_f = b_0 |\underline{c} d^n\rangle + \sum_m b_m |\underline{c} d^{(n+m)} \underline{L}^m\rangle$$

WITH INTERACTIONS OF:
10Dq = CRYSTAL FIELD (OFTEN NEGLECTED)

Δ = LIGAND-TO-METAL CHARGE TRANSF. ENERGY
$= E(d^{n+1} \underline{L}) - E(d^n)$

$U_{pd} = U = $ d-d COULOMB REPULSION ENERGY
$= E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$

$T = $ LIGAND p-TO-METAL d HYBRIDIZATION
$= \langle d_\alpha | \hat{H} | p_\alpha \rangle$ (α = SAME SYMMETRY)

$U_{dd} = Q = $ CORE-HOLE-TO-d INTERACTION: $\langle c | \hat{H} | d \rangle \approx \mathbf{J_{cd}}$ **= coulomb integral**

WITH INTENSITIES FROM SUDDEN APPROX.

AS:

$$I(E_{kin}) \propto \sum_{f,k} |\langle \psi_f (N-1, k) | \psi_R (N-1, k)\rangle|^2.$$

$$\delta(h\nu - E_f - E_{kin})$$

$= \underline{c} = $ CORE HOLE

WHERE: $\psi_R (N-1, k) = \psi_i$ (N WITH k HOLE = $\underline{c}$)

(SUGANO, LARSSON ⇝ SAWATZKY, VAN DER LAAN, FUJIMORI, OH, ET AL.)
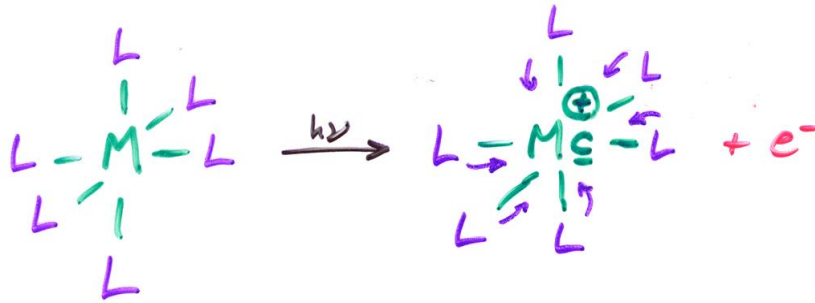
$\underline{c}$ = CORE HOLE ON METAL

$\underline{L}$ = VALENCE (?) HOLE ON LIGAND

$\psi_i = a_0 |d^n\rangle + \sum_m a_m |d^{(n+m)} \underline{L}^m\rangle$

$\psi_f = b_0 |\underline{c} d^n\rangle + \sum_m b_m |\underline{c} d^{(n+m)} \underline{L}^m\rangle$

WITH INTERACTIONS OF:

$10D_q$ = CRYSTAL FIELD (OFTEN NEGLECTED)

Δ = LIGAND-TO-METAL CHARGE TRANSF. ENERGY
$= E(d^{n+1} \underline{L}) - E(d^n)$

U_{pd} = U = d-d COULOMB REPULSION ENERGY
$= E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$

T = LIGAND p-TO-METAL d HYBRIDIZATION
$= \langle d_\alpha | \hat{H} | p_\alpha \rangle$ (α = SAME SYMMETRY)

U_{dd} = Q = CORE-HOLE-TO-d INTERACTION: $\langle c | \hat{H} | d \rangle \approx J_{cd}$ = coulomb integral

Good discussion of model: Bocquet & Fujimori, J. Elect. Spect. & Rel. Phen. 82, 87 (1996)

$$\rho(e_k) = \sum_f |\langle \Psi_f | c | \Psi_g \rangle|^2 \delta(h\nu - e_k - E_f)$$

By now: CTM4XAS program for calculating this for some cases: http://www.anorg.chem.uu.nl/people/staff/FrankdeGroot/multiplet1.htm

WITH INTENSITIES FROM SUDDEN APPROX.

AS:

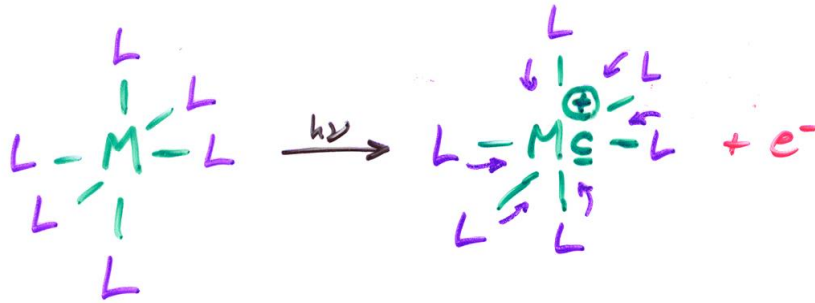$$I(E_{kin}) \propto \sum_{f,k} |\langle \psi_f (N-1, k) | \psi_R (N-1, k)\rangle|^2_0$$

$\downarrow = \underline{c}$ = CORE HOLE

$$\delta(h\nu - E_f - E_{kin})$$

WHERE: $\psi_R (N-1, k) = \psi_i (N$ WITH k HOLE $= \underline{c})$

From Bocquet & Fujimori, J. Elect.Spect. & Rel. Phen. 82, 87 (1996):

The electronic structures of transition-metal (TM) compounds, particularly the 3d TM halides, oxides and chalcogenides, have long provided intriguing problems for physicists and chemists. These compounds are highly correlated electron systems where the essential physics can be described in terms of a few interaction strengths, namely the on-site d–d coloumbic repulsion energy U, the ligand-to-metal charge-transfer energy Δ, and the ligand p–metal d hybridization strength T. Core-level X-ray photoemission spectroscopy (XPS) is a useful probe of the valence electronic structures of TM compounds, and has been successfully used in recent years to extract parame values for these interaction strengths [1–5]. In
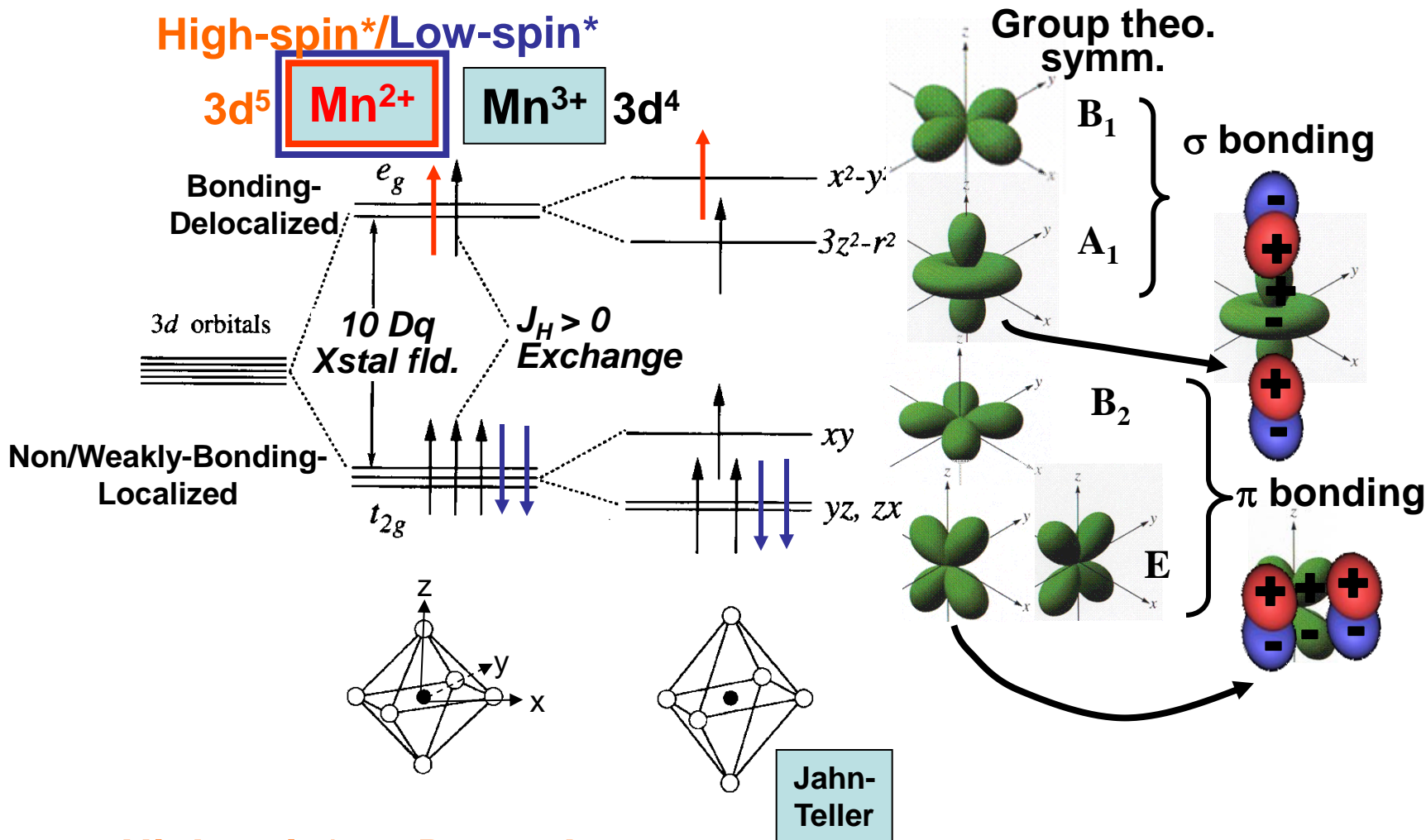
From CTM manual:

C: Charge Transfer Parameters

- **Delta:** This is the charge transfer parameter $\underline{\Delta}$, which gives the energy difference between the (centers of the) $3d^N$ and $3d^{N+1}\underline{L}$ configurations. The effective value of Δ (Δ_{eff}) is affected by the multiplet and crystal field effects on each configuration. In the next version, the value of Δ_{eff} will be given in a parameter-output file.
- **Udd:** This is the value of the Hubbard U.
- **Upd:** This is the core hole potential. In case of XAS spectra, only the difference between U_{pd} and U_{dd} is important.
- **Hopping T:** The hopping parameters are given for the 4 symmetries in tetragonal symmetry A_1, B_1, E and B_2. A_1 (z^2) and B1 (x^2-y^2) are part of the e_g-orbitals and E (xz, yz) and B_2 (xy) are part of the t_{2g} orbitals. In Oh symmetry the values of $A_1=B_1$ and $E=B_2$. (This is not yet automatic in the test-version).

Originated in the Hubbard Model: Ashcroft and Mermin, pp. 689-691

E.g.—Crystal field in Mn³⁺ & Mn²⁺ with negative octahedral ligands

High-spin*/Low-spin*

$3d^5$ Mn²⁺   Mn³⁺ $3d^4$

Group theo. symm.

Bonding-Delocalized

e_g

Non/Weakly-Bonding-Localized

$3d$ orbitals

10 Dq Xstal fld.

$J_H > 0$ *Exchange*

$x^2 - y^2$

$3z^2 - r^2$

xy

yz, zx

t_{2g}

B_1

A_1

σ bonding

B_2

E

π bonding

Jahn-Teller

High-spin*: 10Dq << J_H
Low-spin*: 10Dq >> J_H
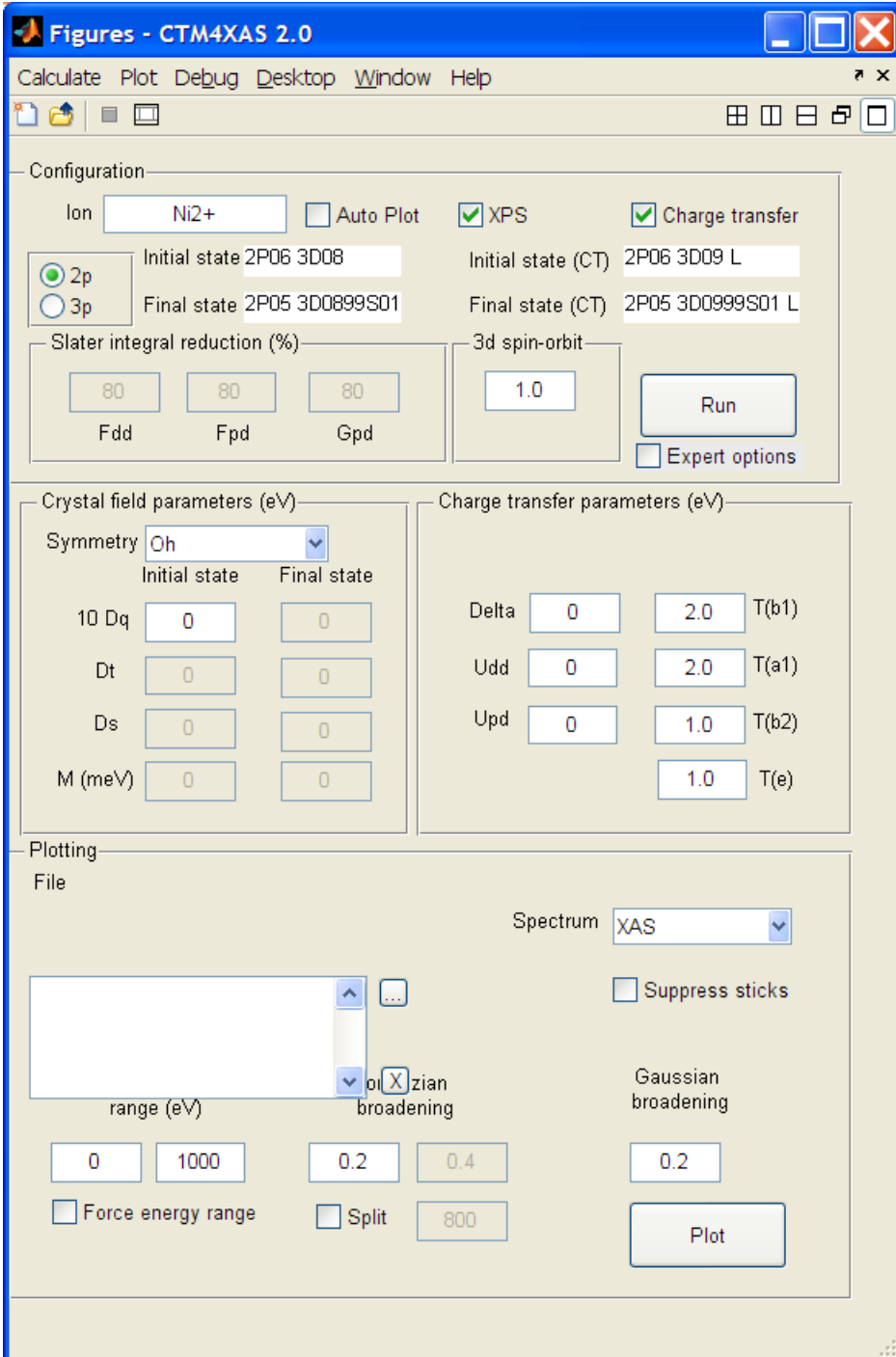
Initial and final states in XPS have different numbers of electrons, and screened d^{n+1} configurations mixed in are now present. Notation is odd for the latter.

Mn 2p XPS — ● Mn 2p XPS — Calculations

Intensity (arb. units) vs. Relative Binding Energy (eV)

More recent data:
Phys. Rev. B 63, 115119 (2001)
In problem set

MnO Mn 2p
d^5 ($^6A_1$)

$2p_{3/2}$ HOLE ... $3d^6$ + LIGAND HOLE "SCREENED" = "MAIN LINE"

EXPT.

Mn LMV THEO.

$2p_{3/2}$ HOLE ... $3d^5$ "UNSCREENED" = "SATELLITE LINE"

LaMnO$_3$
d^4 (^5E)

La LNN

Mn LMV

SrMnO$_3$
d^3 ($^4A_2$)

Mn LMV

BOUQUET ET AL., PHYS. REV. B 46, 3771 ('92)
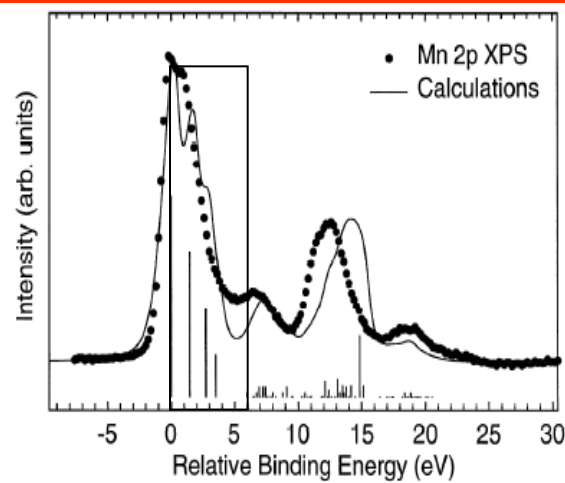
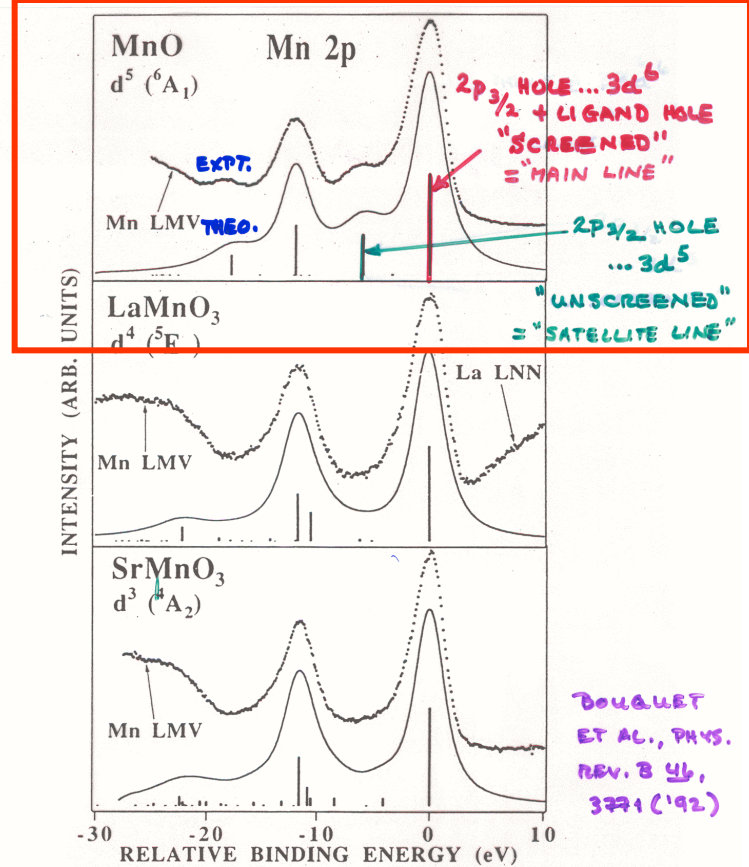INTENSITY (ARB. UNITS) vs. RELATIVE BINDING ENERGY (eV)

FIG. 1. Theoretical 2p core-level XPS spectra (solid line) compared with experimental data (dots) after background subtraction for Mn cations with varying valence. Emission due to the Mn LMV Auger peak is observed on the high-binding-energy side of the $2p_{1/2}$ spin-orbit peak, partially obscuring the $2p_{1/2}$ satellite structure.

For octahedral coord.:

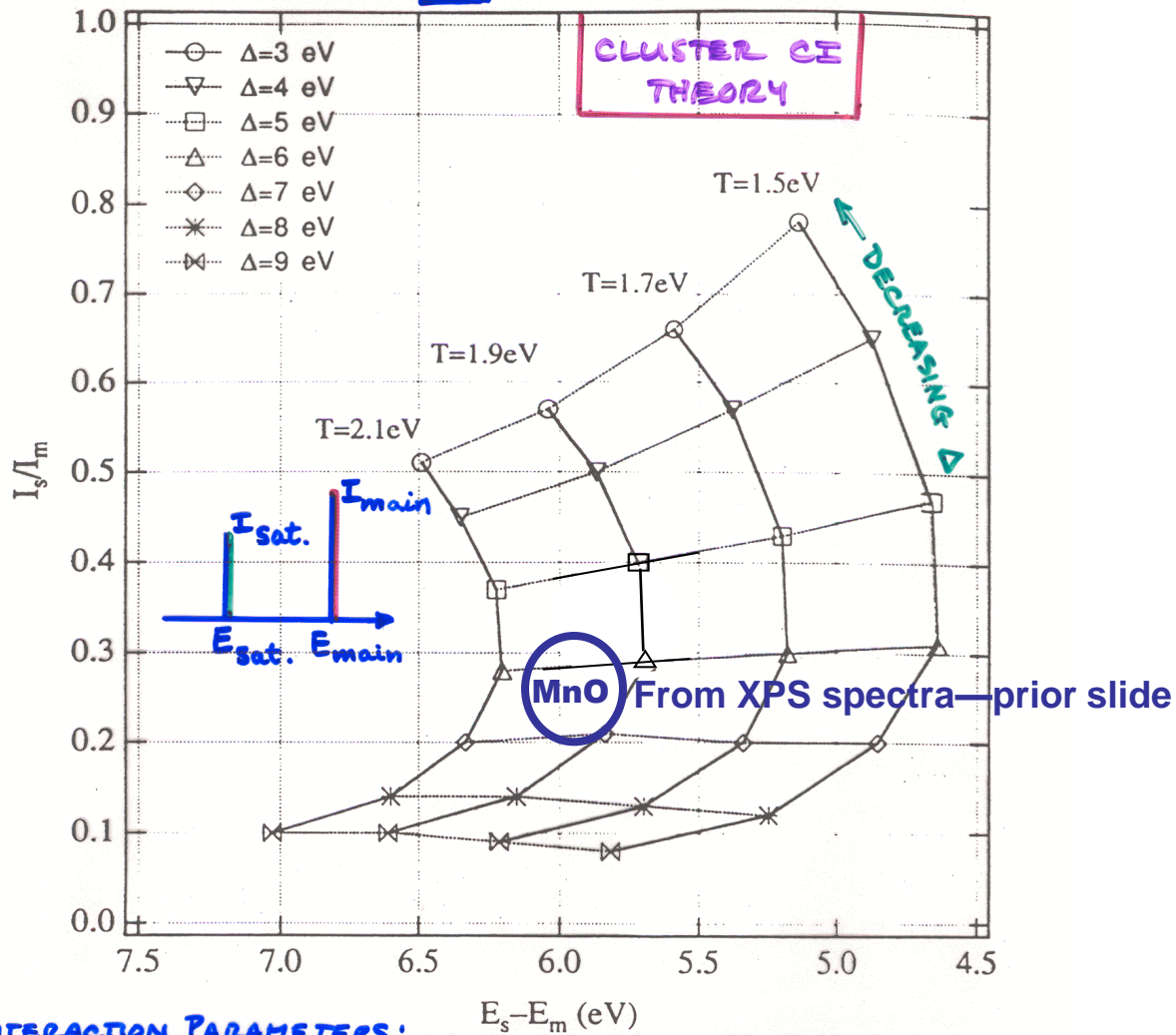$$T_\sigma = \sqrt{3}(pd\sigma), \ T_\pi = 2(pd\pi)$$

$$T_\sigma / T_\pi \propto (pd\sigma)/(pd\pi) \approx -2.2$$

Compound	d^n	Valence	Δ	U	$(pd\sigma)$	Δ_{eff}	U_{eff}	Main peak	Satellite peak	Ref.
SrMnO$_3$	d^3	4+	2.0	7.8	−1.5	−0.2	7.1	$d^4\underline{L}$	$d^4\underline{L}$	This work
LaMnO$_3$	d^4	3+	4.5	7.5	−1.8	1.8	6.8	$d^5\underline{L}$	$d^6\underline{L}^2$	This work
MnO	d^5	2+	6.5	7.0	−1.1	8.8	11.6	$d^6\underline{L}$	d^5	This work
			7.0	7.5	−0.9					3

From later paper (see next slides) 6.5   6.0   -1.99/√3 = -1.1   U/Q = 0.7-1.0, a best fit no. is 0.83.   10Dq is 1.0-2.0 eV

ANALYSIS VIA ANDERSON IMPURITY MODEL

Mn^{2+}(HS) U=6.0 eV

CLUSTER CI THEORY

INTERACTION PARAMETERS:

$U_{dd} \equiv \mathcal{U}$ = 3d-3d COULOMB REPULSION ENERGY

Δ = LIGAND-TO-METAL CHARGE TRANSFER ENERGY

T = LIGAND p — METAL 3d HYBRIDIZATION ENERGY

$U_{pd} \equiv Q$ = CORE HOLE–3d COULOMB

BOUQUET ET AL., J. EL. SP. 82, 87 ('96)

Estimating the parameters from fits to the experimental satellite intensity and spacing

From Bocquet & Fujimori, J. Elect.Spect. & Rel. Phen. 82, 87 (1996)
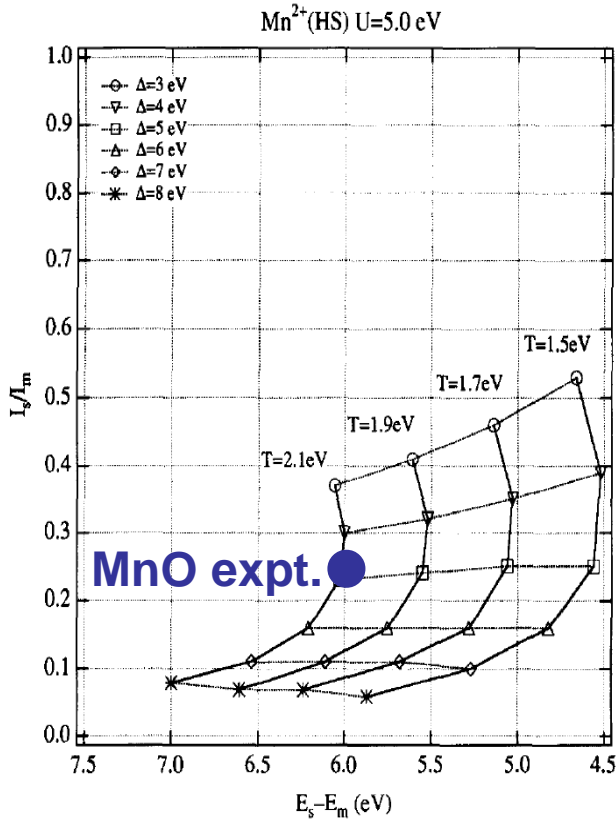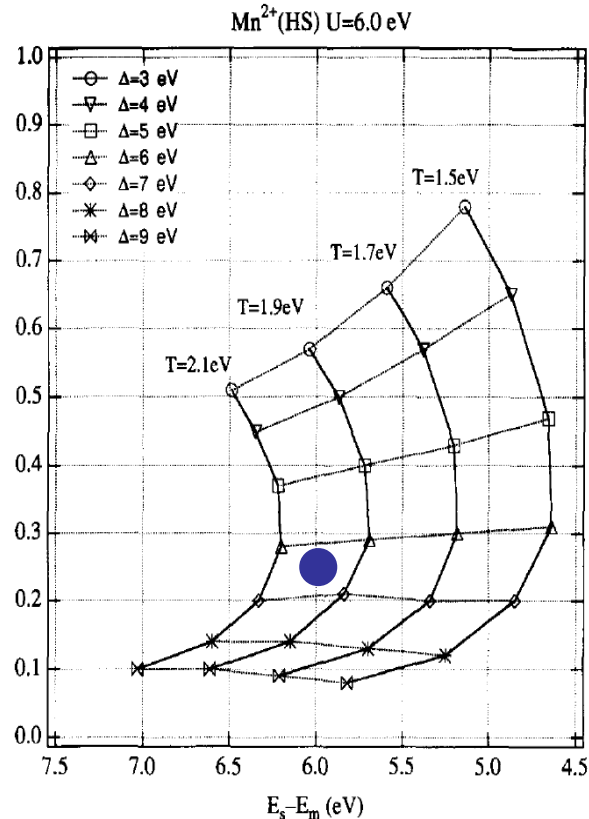
U = 5.0, T = 2.08, Δ = 4.8   **U = 6.0, T = 1.99, Δ = 6.5**   U = 7.0, T = 1.93, Δ = 8.0

**Crystal field 10Dq assumed zero in this study,
but a value of about ~1.0-2.0 eV has been estimated from previous
optical, XAS, and EELS measurements:
Garvie et al., Physical Chemistry of Materials 21, 191 (1994)
Muller et al., Phys. Rev. B 78, 085438 (2008)**

Figures - CTM4XAS 2.0

Calculate Plot Debug Desktop Window Help

Configuration

Ion: Mn2+   ☐ Auto Plot   ☑ XPS   ☑ Charge transfer

○ 2p   ● ... Initial state: 2P06 3D05   Initial state (CT): 2P06 3D06 L
○ 3p   Final state: 2P05 3D0599S01   Final state (CT): 2P05 3D0699S01 L

Slater integral reduction (%)
80 Fdd   80 Fpd   80 Gpd

3d spin-orbit
1.0

Run

☐ Expert options

Crystal field parameters (eV)

Symmetry: Oh

	Initial state	Final state
10 Dq	0	0
Dt	0	0
Ds	0	0
M (meV)	0	0

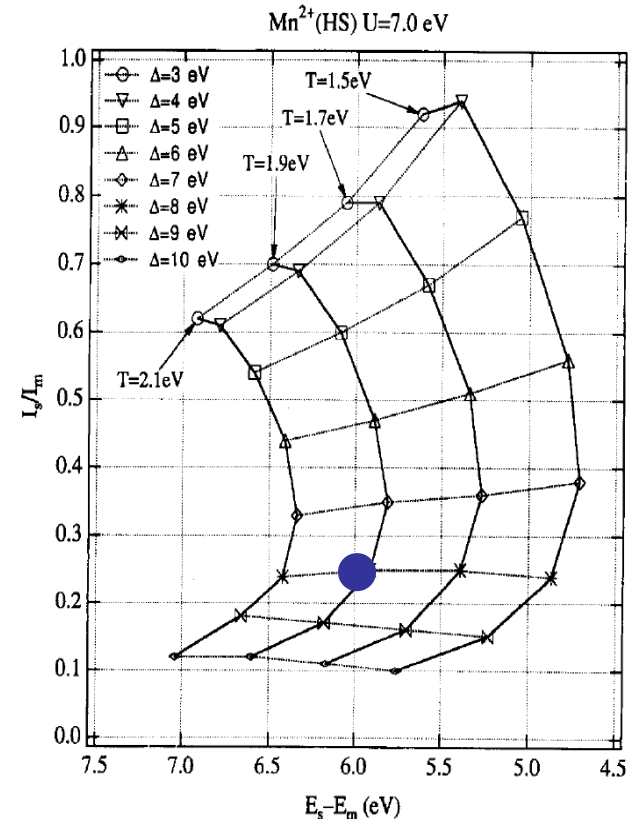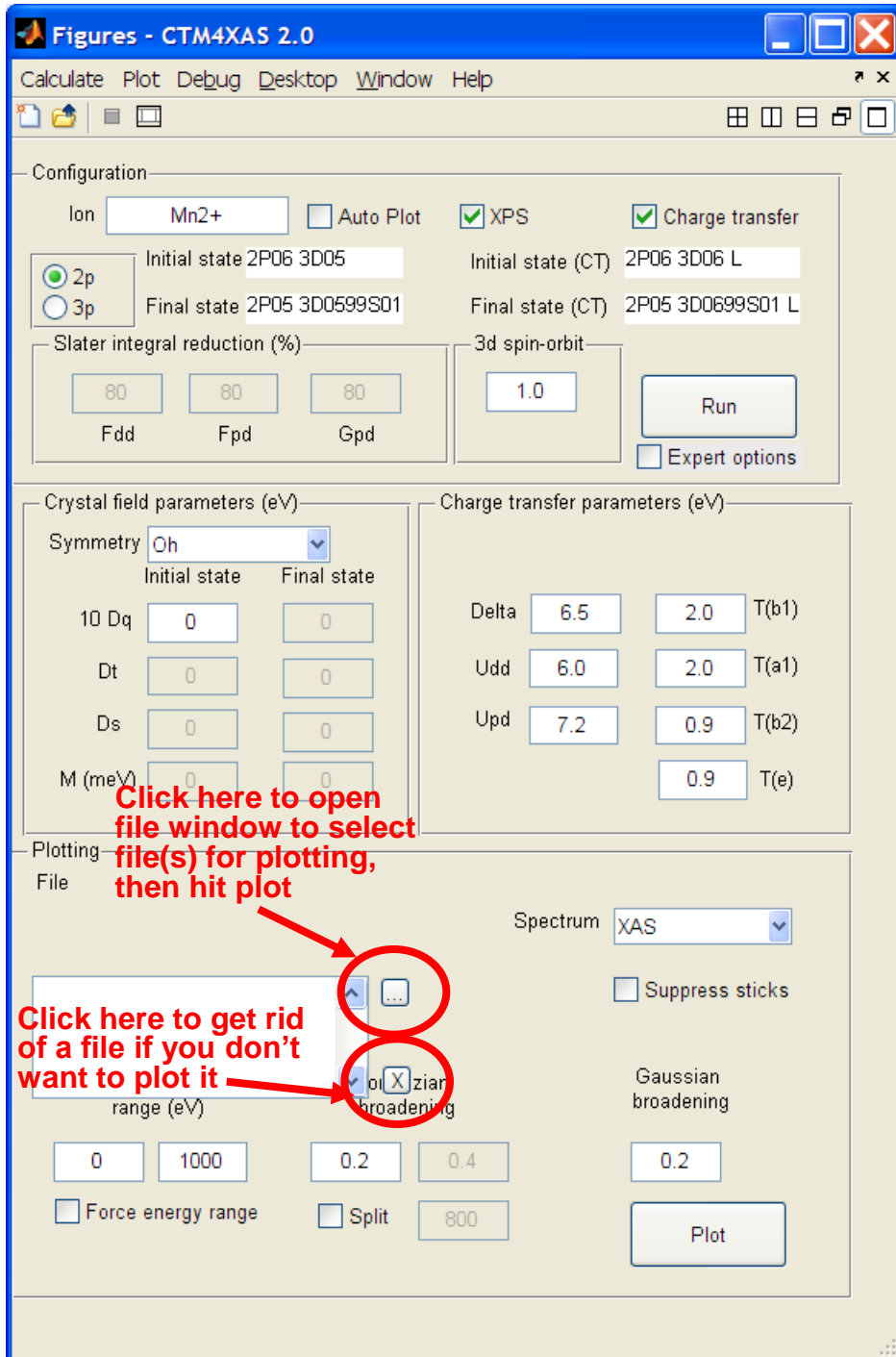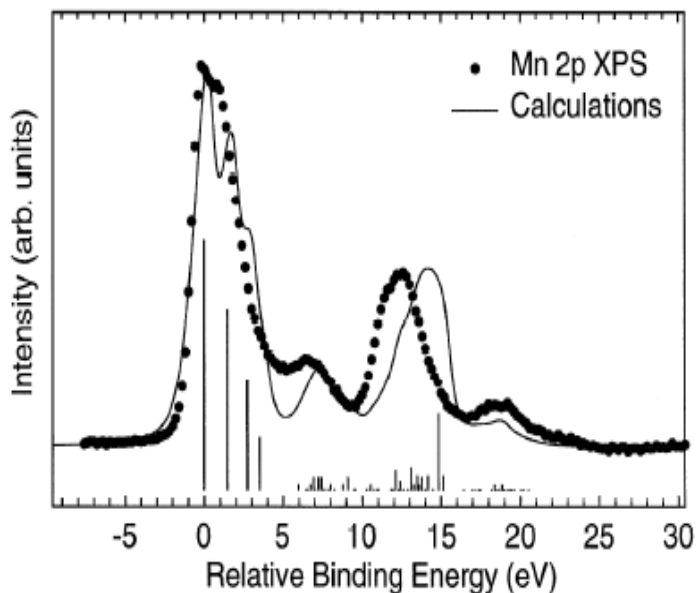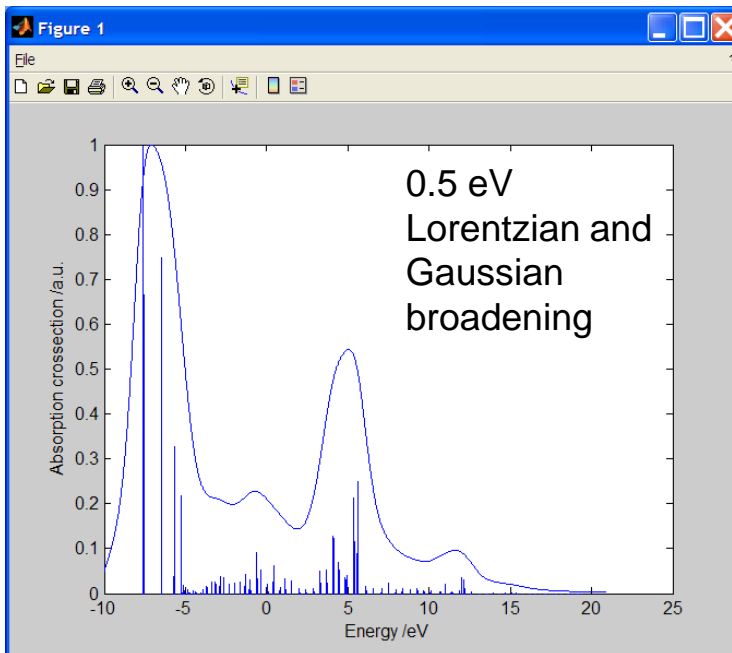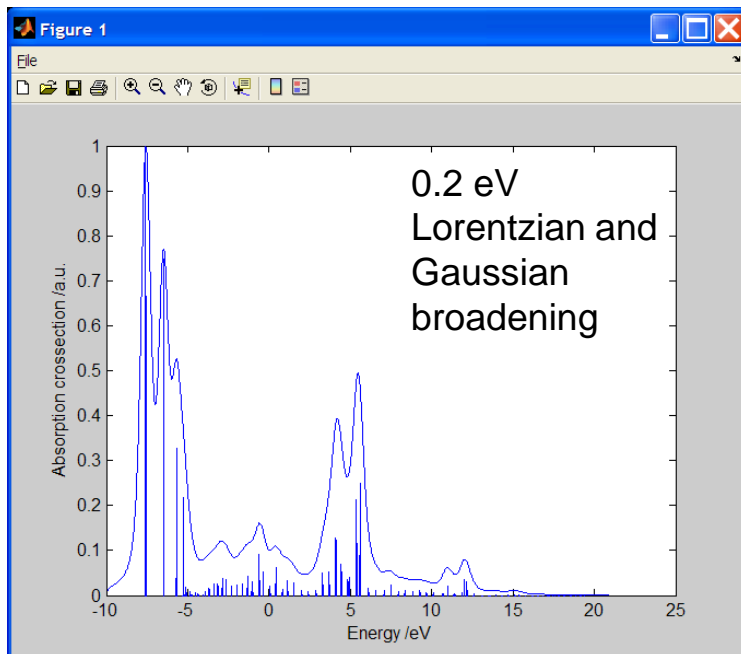### Charge transfer parameters (eV)

Delta	6.5	2.0	T(b1)
Udd	6.0	2.0	T(a1)
Upd	7.2	0.9	T(b2)
		0.9	T(e)

Plotting

Click here to open file window to select file(s) for plotting, then hit plot

Click here to get rid of a file if you don't want to plot it

Spectrum: XAS

☐ Suppress sticks

...or X zian broadening

Gaussian broadening

range (eV)
0   1000   0.2   0.4   0.2

☐ Force energy range   ☐ Split   800

Plot

Here is a reasonable choice of parameters for Mn^{2+}, with no crystal field splitting

Hit run, wait until program asks for a file name for the output, input this and run will begin. Wait while program steps are executing in command window, example below. XPS is much slower than XAS.

C:\cowan\ctm4xas20\ctm4xas20.exe

```
looking for   GROUND   S1-   0+   S1-     758  758 Factor =    0.0000000
routine=ETR                    file= 15 line= 20785 col= 66 =>
REDUCEDMATRIX GROUND       S1-   0+  S1-  DT              758 758<<
looking for   GROUND   S1-   0+   S1-     758  758 Factor =    0.0000000
routine=ETR                    file= 15 line= 22055 col= 66 =>
REDUCEDMATRIX GROUND       S1-   0+  S1-  DS              758 758<<
looking for   GROUND   S1-   0+   S1-     758  758 Factor =    0.0000000
routine=ETR                    file= 15 line= 22975 col= 66 =>
REDUCEDMATRIX GROUND       S1-   0+  S1-  SPIN            758 758<<
looking for   EXCITE   S1-   0+   S1-    6302 6302 Factor =    1.0000000
routine=ETR                    file= 15 line= 23517 col= 68 =>
REDUCEDMATRIX EXCITE       S1-   0+  S1-  HAMILTONIAN     6302 6302<<
looking for   EXCITE   S1-   0+   S1-    6302 6302 Factor =    0.0000000
routine=ETR                    file= 15 line= 24581 col= 68 =>
REDUCEDMATRIX EXCITE       S1-   0+  S1-  10DQ            6302 6302<<
looking for   EXCITE   S1-   0+   S1-    6302 6302 Factor =    0.0000000
routine=ETR                    file= 15 line= 26943 col= 68 =>
REDUCEDMATRIX EXCITE       S1-   0+  S1-  DT              6302 6302<<
looking for   EXCITE   S1-   0+   S1-    6302 6302 Factor =    0.0000000
routine=ETR                    file= 15 line= 29369 col= 68 =>
REDUCEDMATRIX EXCITE       S1-   0+  S1-  DS              6302 6302<<
looking for   EXCITE   S1-   0+   S1-    6302 6302 Factor =    0.0000000
routine=ETR                    file= 15 line= 31031 col= 68 =>
REDUCEDMATRIX EXCITE       S1-   0+  S1-  SPIN            6302 6302<<
```

And finally you will get something like this, with no crystal field splitting:

0.2 eV Lorentzian and Gaussian broadening

0.5 eV Lorentzian and Gaussian broadening

Which compares pretty well with expt. and another similar calculation from the literature, esp. if theory is broadened more.

Could try adding crystal field, as next slide suggests.

Now just switching to XAS gives you:

No crystal field

Crystal field = 1.0 eV

~Best fit

Crystal field = 2.0 eV

Optical constant, β

L₃ = 2p₃/₂ · · · MARPE theory

β — Experiment ∝ XAS

L₂ = 2p₁/₂