



Core loss spectra

(EELS, XAS)

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University of Washington (USA)

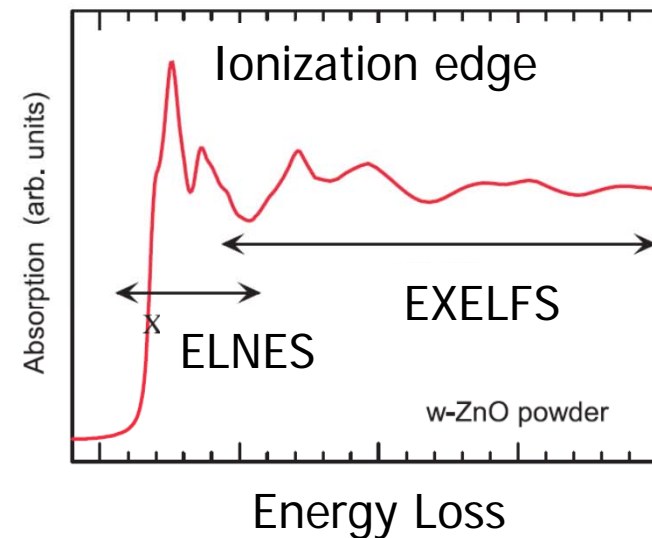
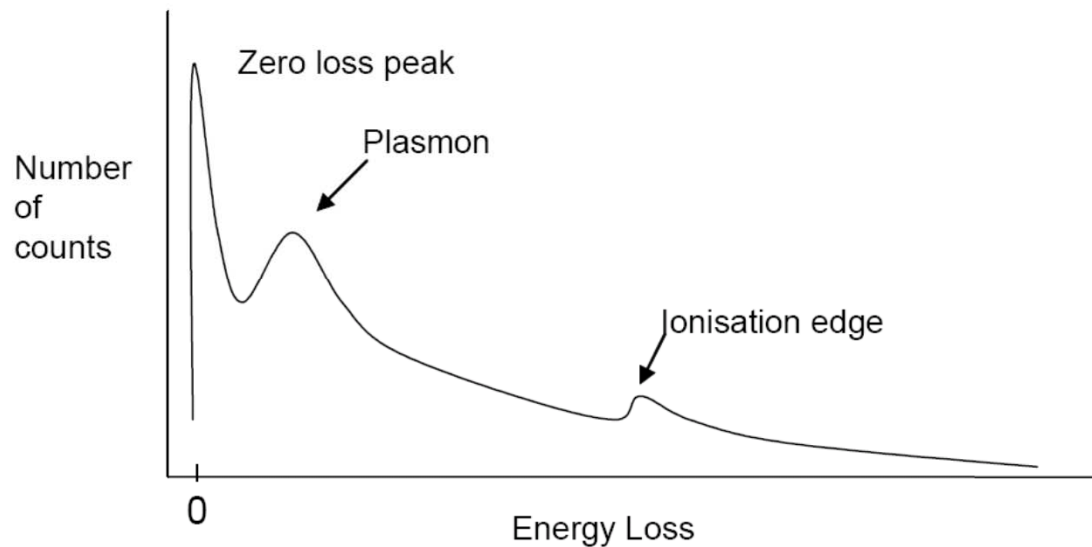
WIEN2k 2013 Penn State



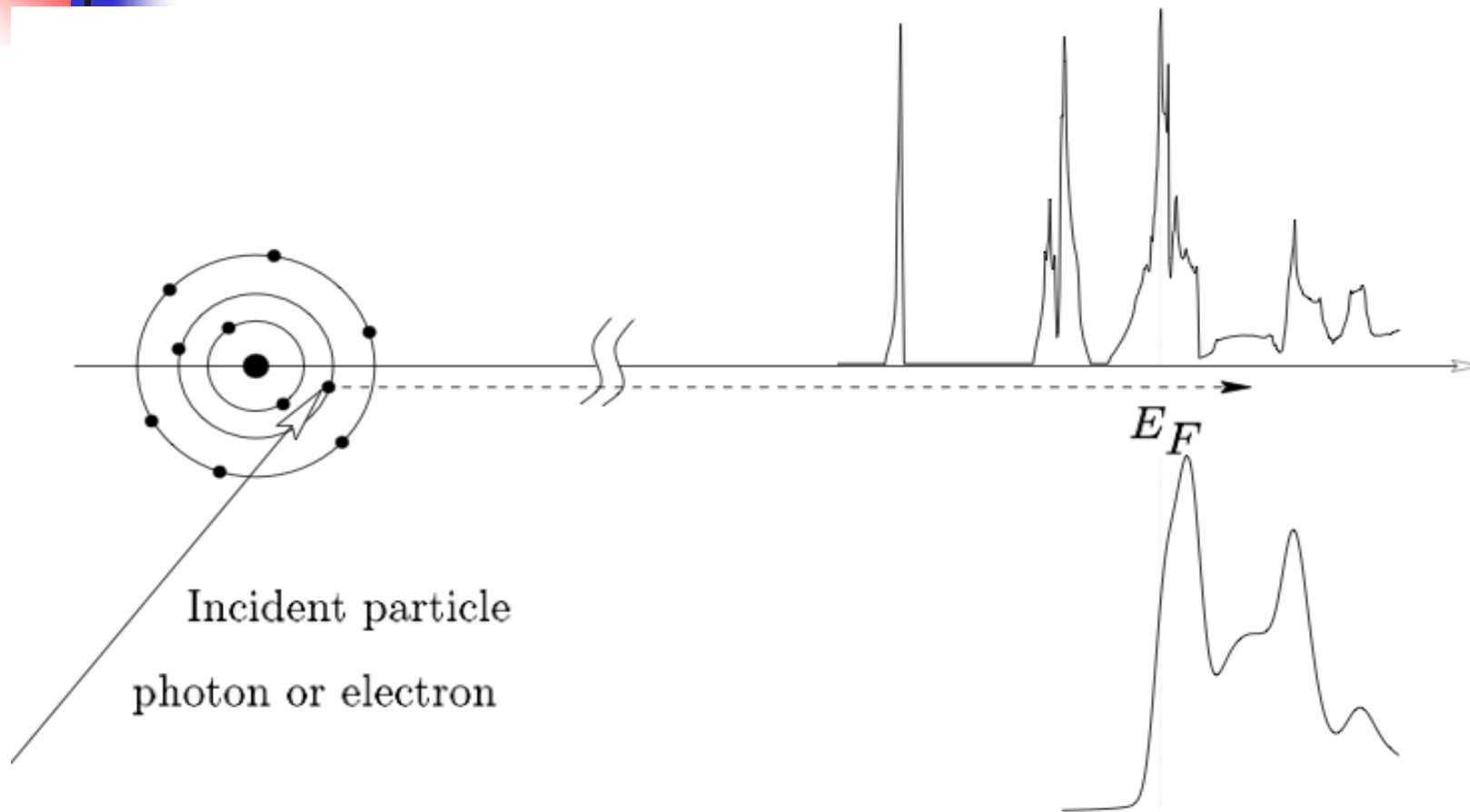
1. Concepts

WIEN2k calculates ELNES / XANES

- EELS : Electron Energy Loss Spectroscopy
- XAS: X-ray Absorption Spectroscopy



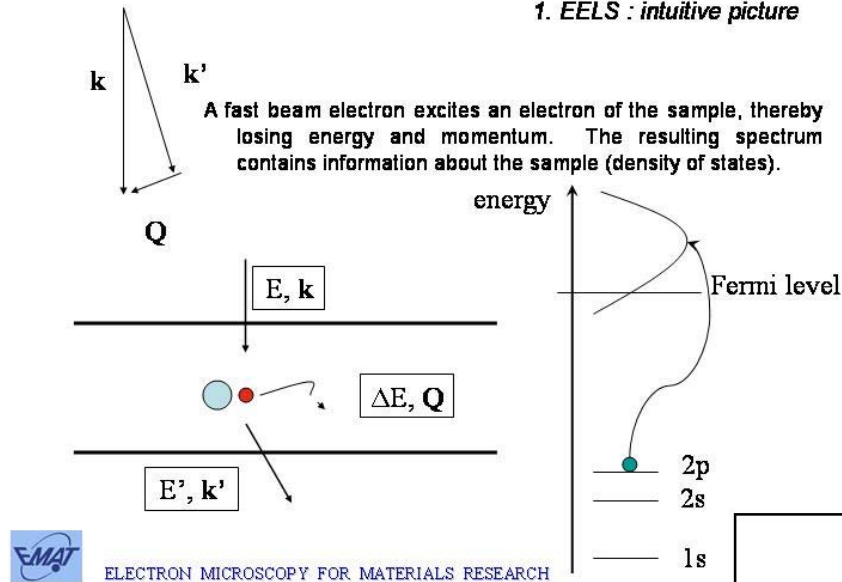
the excitation process



INTRODUCING EELS

Electron Energy Loss Spectroscopy is performed in a Transmission Electron Microscope, using a beam of high-energy electrons as a probe. The energy distribution of the beam gives a loss spectrum similar to XAS. Focussed probes give excellent spatial resolution ($\sim 0.5 \text{ \AA}$). Energy resolution is improving ($\sim 25 \text{ meV}$).

1. EELS : intuitive picture

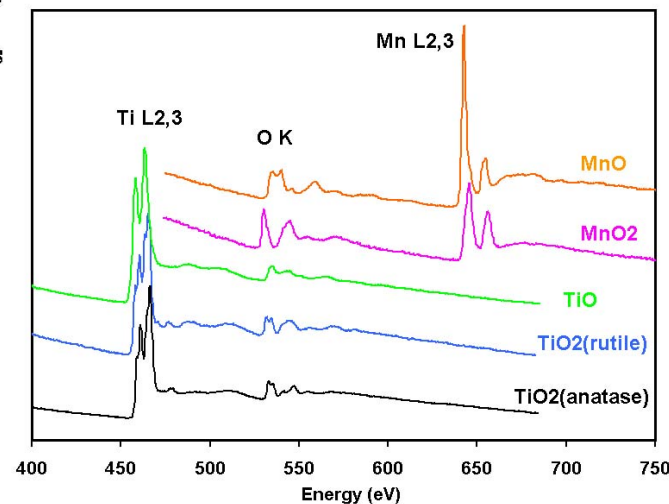


ELECTRON MICROSCOPY FOR MATERIALS RESEARCH

Intuitive picture of EELS

EELS spectra of TM oxides
Probes local electronic structure

Electron microscope
equipped with
EELS-detector



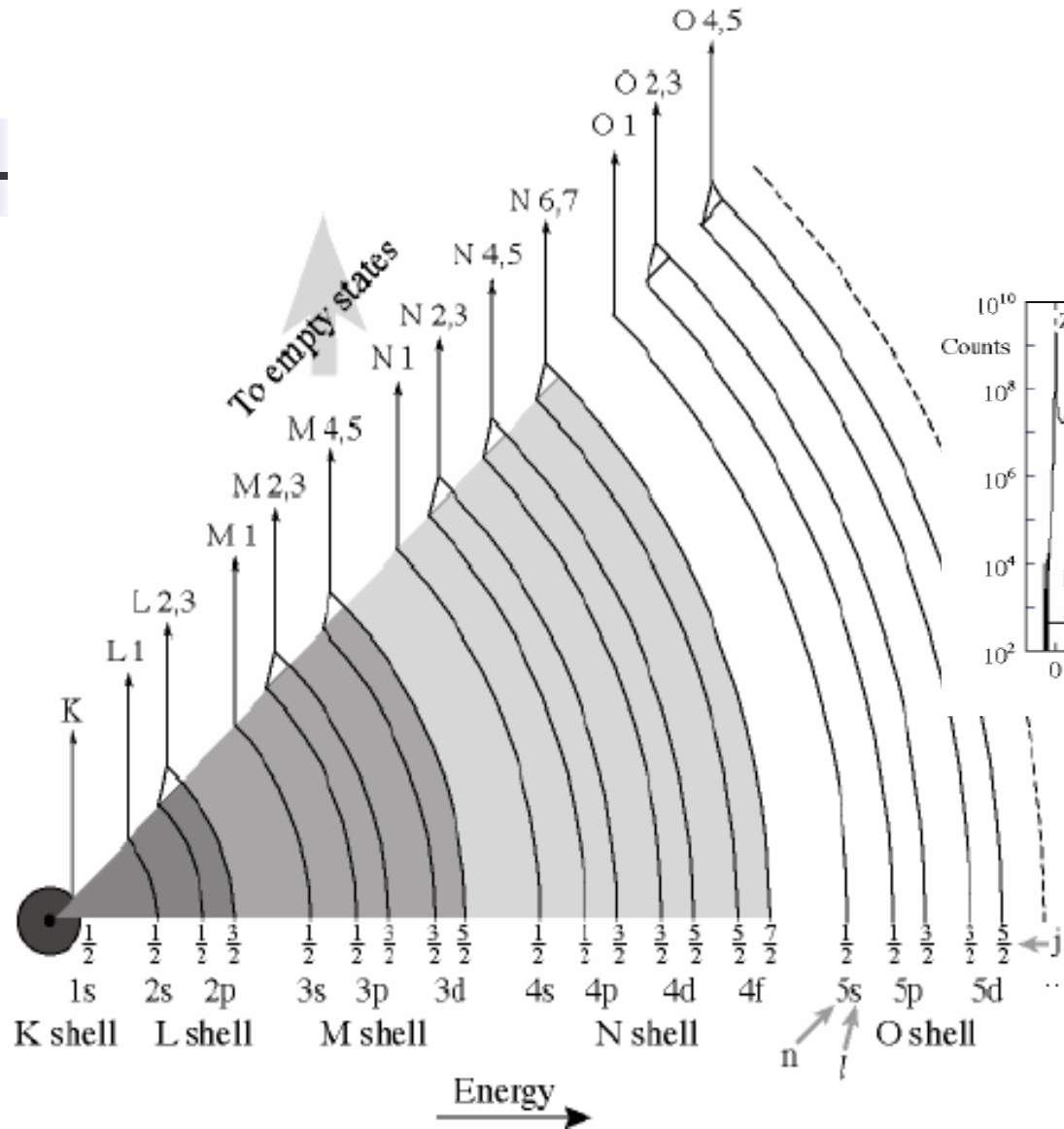
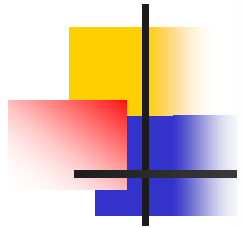
50.0%O-
50.0%Mn

66.7%O-33.3%Mn

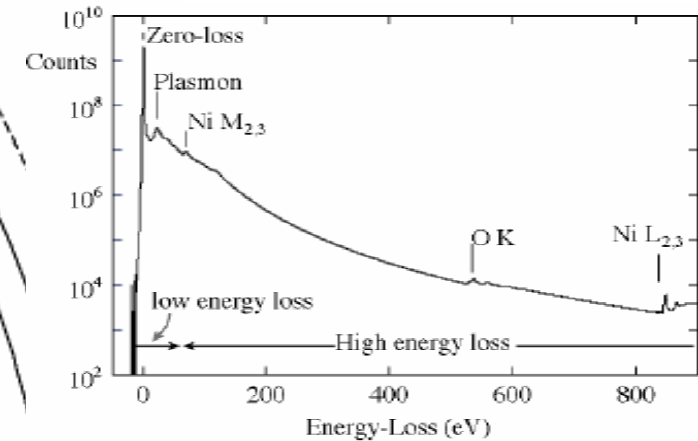
55.0%O-45.0%Ti

66.7%O-
33.3%Ti

Terminology for ionization edges



Inner shell ionization.

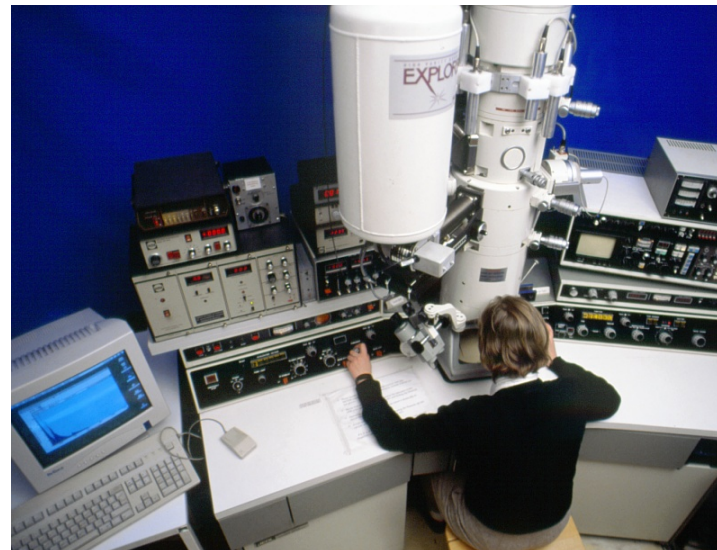


instrumentation

XAS: synchrotron



EELS: microscope



THEORY OF EELS : A double differential scattering cross-section is calculated by summing over all possible transitions between initial and final states.

The transition probabilities are described by Fermi's golden rule.

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}(E, \mathbf{Q}) = \zeta \sum_{I, F} \frac{k_F}{k_I} \left| \langle I k_I | V | k_F F \rangle \right|^2 \delta(E_I - E_F)$$

V is the interaction potential between the fast beam electron and an electron in the sample.

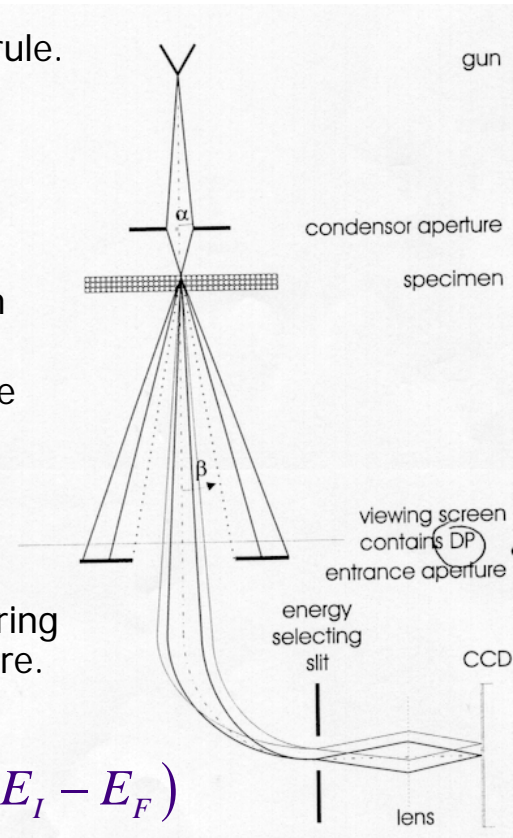
F, I the sample states, can be taken from electronic structure calculations.

k_F and k_I the probe states, are typically described as plane waves when Bragg scattering effects are neglected.

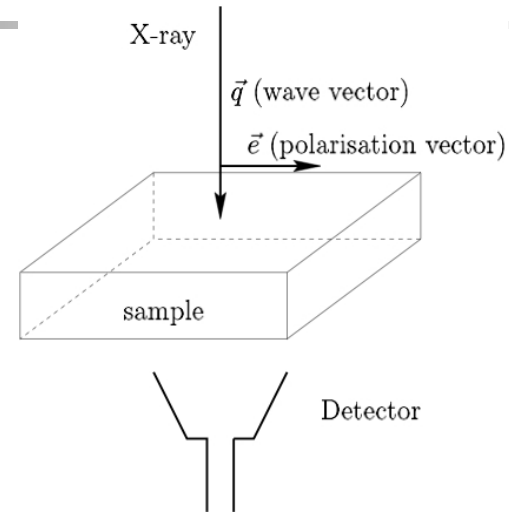
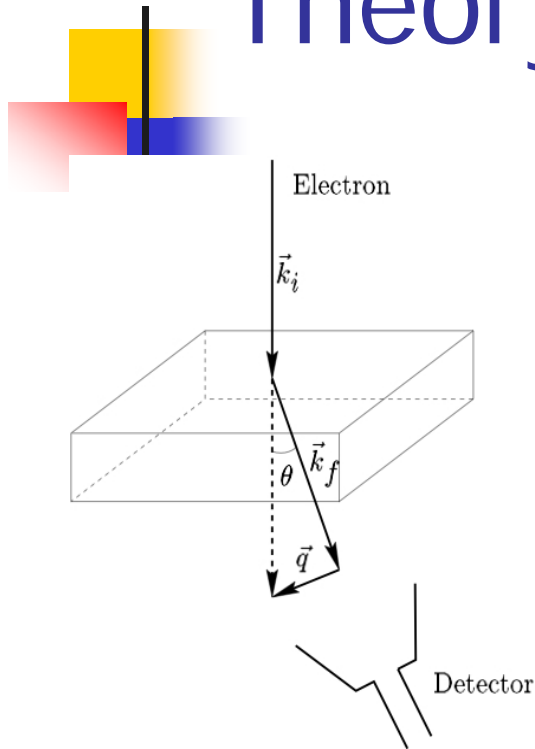
In experiment, one usually integrates over a range of scattering angles, due to the beam width and spectrometer aperture.

→ differential cross section :

$$\frac{\partial \sigma}{\partial E}(E; \alpha, \beta) = \int_{\alpha, \beta} d\Omega \zeta \sum_{I, F} \frac{k_F}{k_I} \left| \langle I k_I | V | k_F F \rangle \right|^2 \delta(E_I - E_F)$$



Theory (EELS ----- XAS)



$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I, F} \left| \langle I | e^{i\vec{q} \cdot \vec{R}} | F \rangle \right|^2$$

$$\frac{\partial \sigma}{\partial E} \propto \sum_{I, F} \left| \langle I | e^{i\vec{q} \cdot \vec{R}} \vec{e} \cdot \vec{R} | F \rangle \right|^2$$

dipole approximation

$$\vec{q} \cdot \vec{R} \ll 1 \rightarrow e^{i\vec{q} \cdot \vec{R}} = 1 + i\vec{q} \cdot \vec{R} + \frac{(\vec{q} \cdot \vec{R})^2}{2!} + \dots$$

EELS

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I, F} \left| \langle I | \vec{q} \cdot \vec{R} | F \rangle \right|^2$$

XAS

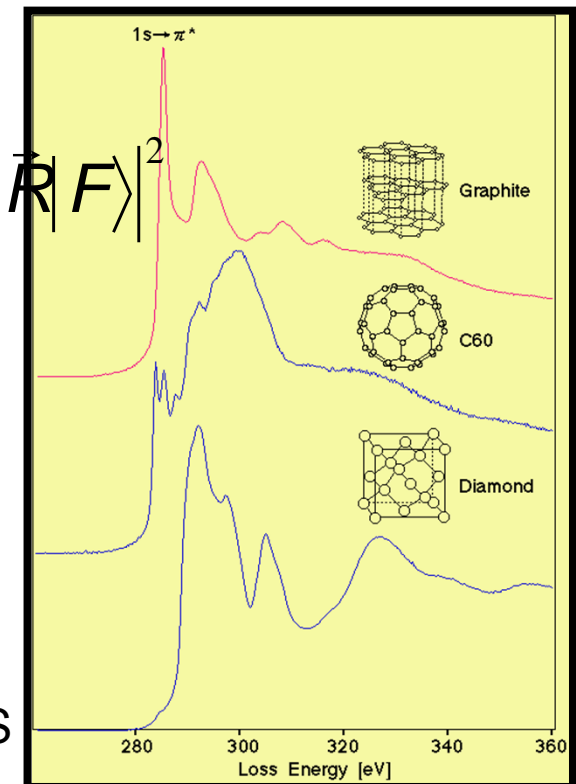
$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I, F} \left| \langle I | \vec{\epsilon} \cdot \vec{R} | F \rangle \right|^2$$

The polarization vector \mathbf{e} in XAS plays the same role as momentum transfer \mathbf{q} in EELS within the dipole approximation.

This is why people say “XAS = EELS”.

(Beware - there are quite a few differences, too.)

→ Probes local, symmetry-selected ($l_c + 1$) unoccupied DOS





2. WIEN2k Calculations.

calculation of spectra using WIEN2k

Set up structure and initialize

SCF calculation

x qtl -telnes

Prepare case.innes

Prepare case.inxs

or

x telnes3

x xspec

↑
EELS

↑
XAS

x broadening


ELNES workflow

Cr3C2@raphael.phys.washington.edu - Windows Internet Explorer
http://raphael.phys.washington.edu:7890/index.pl?SID=954086

Cr3C2@raphael.phys.w... x

Session: **Cr3C2**
/phys/users/jorissen/Cr3C2

13:35:44 idle
[refresh](#) | [no refresh](#)



TELNES3

Edit input-file for ELNES (InnesGen™)

Only if you want to include states with higher energy

Edit in1

Calculate eigenvalues interactively

Calculate partial charges interactively

Calculate ELNES spectra interactively

display Cr3C2.outputelnes (optional)

Edit input-file for BROADENING

Broaden the spectrum interactively

Plot ELNES

Save an elnes calculation into a directory

Execution >>
[StructGen™](#)
[initialize calc.](#)
[run SCF](#)
[single prog.](#)
[optimize\(V,c/a\)](#)
[mini_positions](#)

Utils. >>

<< Tasks
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[DOS](#)
[XSPEC](#)
[TELNES3](#)
[OPTIC](#)
[Bandstructure](#)

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[input files](#)
[output files](#)
[SCF files](#)

Session Mgmt. >>
[change session](#)
[change dir](#)
[change info](#)

Configuration

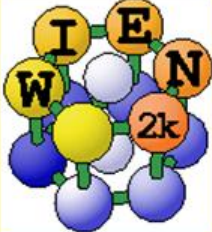
Usersguide
Idea and realization by
Ulrich Bauer
1991-2006

ELNES input w2web

Cr3C2@raphael.phys.washington.edu - Windows Internet Explorer
http://raphael.phys.washington.edu:7890/index.pl?SID=954086

Session: **Cr3C2**
/phys/users/jorissen/Cr3C2

13:31:13 idle
[refresh](#) | [no refresh](#)



Execution >>
[StructGen™](#)
[initialize calc.](#)
[run SCF](#)
[single prog.](#)
[optimize\(V,c/a\)](#)
[mini_positions](#)

Utils. >>

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Configuration

Usersguide
idea and realization by
Ulrich Bauer
1991-2006

Title: Cr L1 edge of first atom
Atom: 1: Cr0+ **Edge:** L1 (n=1 l=0)
Edge onset: 696 eV **Beam energy:** 200 keV
Energy grid: 0.0000 eV to 15.0000 eV in steps of 0.0500 eV
Collection s.a.: 5.00 mrad **Convergence s.a.:** 1.87 mrad
Spectrometer broadening: 0.50 eV **Q-mesh:** NR=5 NT=2

Advanced settings:

Branching ratio: (statistical if empty)
Spinorbit splitting of core state (eV): (calculated if empty)

Orientation sensitive: $\alpha=0^\circ$, $\beta=90^\circ$, $\gamma=0^\circ$

Integrate over equivalent atoms: (all eq. atoms if empty)

Detector position: θ_x 0.000 mrad, θ_y 0.000 mrad

Modus: energy

Initialization: Calculate DOS write DOS
 Calculate rotation matrices write rotation matrices

Verbosity: basic **File headers:** Write headers (default)

Interaction potential: relativistic (recommended)

Q-grid: U uniform $\theta_0=$ (not used for uniform grid)

Interaction order: all λ (default) **Final state selection rule:** L=l +/- 1 (default)

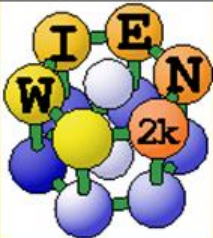
Extend potential beyond Rmt: rmax= bohr
 Set Fermi energy manually: EF= Ry
 Read core state wavefunction: filename= case.cwf
 Read final state wavefunctions: filename= case.finalwf
 Calculate DOS only

ELNES input file (case.innes)

Cr3C2@raphael.phys.washington.edu - Windows Internet Explorer
http://raphael.phys.washington.edu:7890/index.pl?SID=954086

Session: **Cr3C2**
/phys/users/jorissen/Cr3C2

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Execution >>
[StructGen™](#)
[initialize calc.](#)
[run SCF](#)
[single prog.](#)
[optimize\(V,c/a\)](#)
[mini_positions](#)

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[El. Dens.](#)
[DOS](#)
[XSPEC](#)
[TELNES3](#)
[OPTIC](#)
[Bandstructure](#)

Files >>
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Session Mgmt. >>
[change session](#)
[change dir](#)
[change info](#)


Configuration

Usersguide
Idea and realization by
Ulrich Bauer
1991-2006

File:
/phys/users/jorissen/Cr3C2/Cr3C2.innes

```
Graphite C K edge of first atom.  
1  
1 0  
285.00  
300  
0.0000 15.0000 0.0500  
5.00 1.87  
5 2  
0.50  
DETECTOR POSITION  
0.000 0.000  
MODUS  
energy  
SELECTION RULE  
n  
LSELECTION RULE  
d  
INITIALIZATION  
Y Y  
Y Y  
<
```

w2web © luitz.at



15



XSPEC-task



Session: [magnetite](#)
/area51/pblaha/lapw/correlated/magnetite

16:42:50 ide

[\[refresh\]](#) | [\[no refresh\]](#)



XSPEC

[\[Spin UP \]](#) | [\[Spin DOWN \]](#)

Spin UP selected.

If you want to include states with higher energy

Calculate eigenvalues interactively

Calculate eigenvalues interactively

Calculate partial charges interactively

Calculate X-ray spectra interactively

```

Title: Atom 1 L3 absorption spectrum
1          (atom)
2          (n core)
1          (l core)
0,0.5,0.5  (split, Int1, Int2)
-2,0.02,15 (EMIN,DE,EMAX)
ABS        (type of spectrum)
1.00       (s)
2.0        (gamma0)
1.50       (W only for EMIS)
AUTO       (AUTO or MANually select Energy)
-6.93
-10.16
-13.9

```

[Execution >>](#)

- [\[StructGen™ \]](#)
- [\[view structure \]](#)
- [\[initialize calc. \]](#)
- [\[run SCF \]](#)
- [\[single prog. \]](#)
- [\[optimize\(V,c/a\) \]](#)
- [\[mini_positions \]](#)

[\[Utils. >> \]](#)

[\[<< Tasks\]](#)

- [\[El. Dens. \]](#)
- [\[DCS \]](#)
- [\[XSPEC \]](#)
- [\[TELNES.2 \]](#)
- [\[OPTIC \]](#)
- [\[Bandstructure \]](#)

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- [\[struct file\(s\) \]](#)
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- [\[output files \]](#)
- [\[SCF files \]](#)

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[\[Configuration \]](#)

Usersguide

- [\[html-Version \]](#)
- [\[pdf-Version \]](#)



Practical considerations

- Spectra usually converge easily with respect to RKMAX, k-mesh, SCF criteria
- But you should check anyway (see Cu L3)
- Optimizing positions may be necessary
- You may need to sum over all “C” atoms in the unit cell. (Especially for orientation-resolved calculations.)
- You probably need to use a “core hole”. This can be a lot of work.
- Your results may be wrong even if you do everything right. (But often they are reasonably good.)
- To compare to experiment, you’ll probably fiddle with the broadening, the onset energy, and the branching ratio (L3/L2)

Convergence of Cu L₃ edge with # k-points

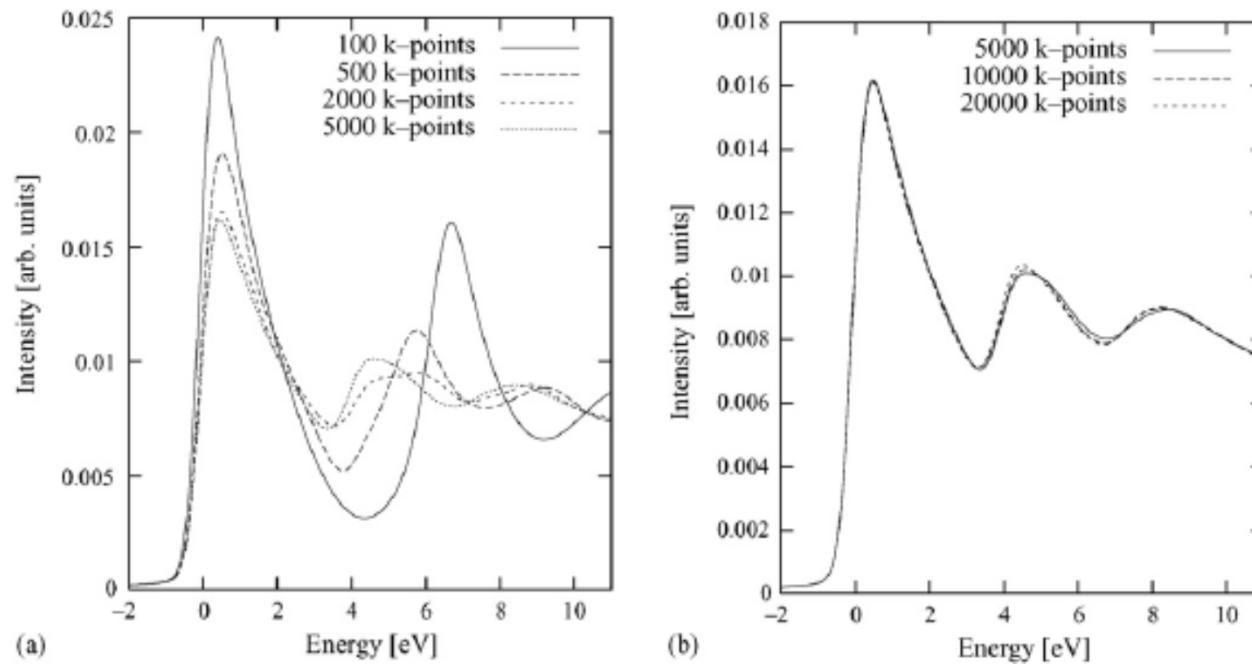


Fig. 8. Cu L₃ edge in fcc-Cu calculated for different number of k -points in the whole BZ. The calculation was performed with RKMAX = 8. The structures were broadened with a Gaussian of 0.7 eV to account for experimental broadening. Lifetime broadening was modeled with a linear approximation.



Features of WIEN2k

- Orientation dependence
- Beyond dipole selection rule
- Several broadening schemes
- All-electron

For EELS:

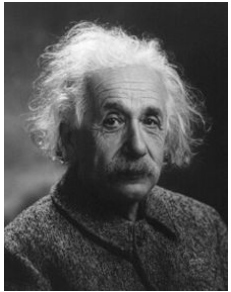
- Account for collection/convergence angle
- Output $\sigma(E)$ or $\sigma(\theta)$
- Relativistic ELNES (\rightarrow anisotropic materials)

EELS – Relativistic theory needed for anisotropic materials

Semi-relativistic theory :

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}(E, \mathbf{Q}) = \frac{4\gamma^2}{a_0^2} \frac{k'}{k} \frac{1}{Q^4} \sum_{I,F} \left| \langle I | \mathbf{Q} \cdot \mathbf{r} | F \rangle \right|^2 \delta(E_I - E_F - E)$$

$$\begin{aligned} V &= |\mathbf{r} - \mathbf{r}'|^{-1} \\ m &\rightarrow \gamma m \\ \theta_E &\rightarrow \theta_{E, \text{rel}} \end{aligned}$$



Fully relativistic theory (P. Schattschneider et al., Phys. Rev. B 2005) :

Up to leading order in c^{-2} and using the Lorentz gauge : $V = e\Phi \left(1 - \frac{\mathbf{p} \cdot \mathbf{v}_0}{mc^2} \right)$ $\Phi = \frac{-4\pi e \delta(\omega - \mathbf{q} \cdot \mathbf{v}_0)}{q^2 - \omega^2/c^2}$

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}(E, \mathbf{Q}) = \zeta \frac{k'}{k} \frac{1}{(Q^2 - E/\hbar c)^2} \sum_{I,F} \left| \langle I | \mathbf{r} \cdot (\mathbf{Q} - Q_z \beta^2 \mathbf{e}_z) | F \rangle \right|^2 \delta(E_I - E_F - E)$$

Geometrical interpretation : in the dipole limit, a relativistic Hamiltonian shrinks the impuls transfer in the direction of propagation. (The general case is more complex.)

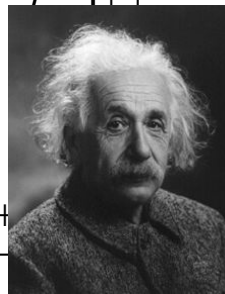
WIEN2k can also calculate non-dipole relativistic transitions. The equations are so long they make PowerPoint cry.

Beyond the small q approximation

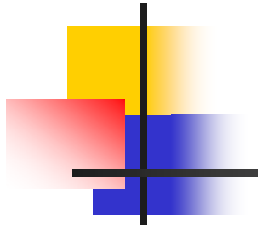
The relativistic DDSCS :

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \left[\frac{4\gamma^2 a_0^{-2}}{q^2 - (E/\hbar c)^2} \right]^2 \frac{k_f}{k_i} \sum_{i,f} \left| \left\langle f \left| e^{iq \cdot r} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{m_e c^2} \right) \right| i \right\rangle \right|^2 \delta(E_f - E_i - E)$$

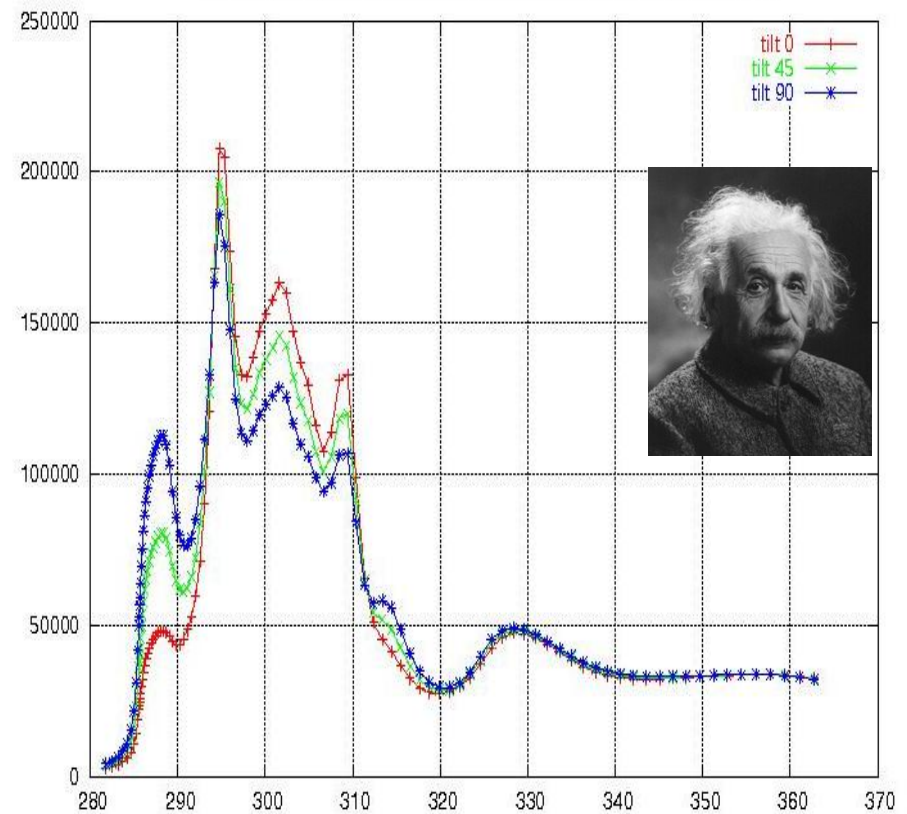
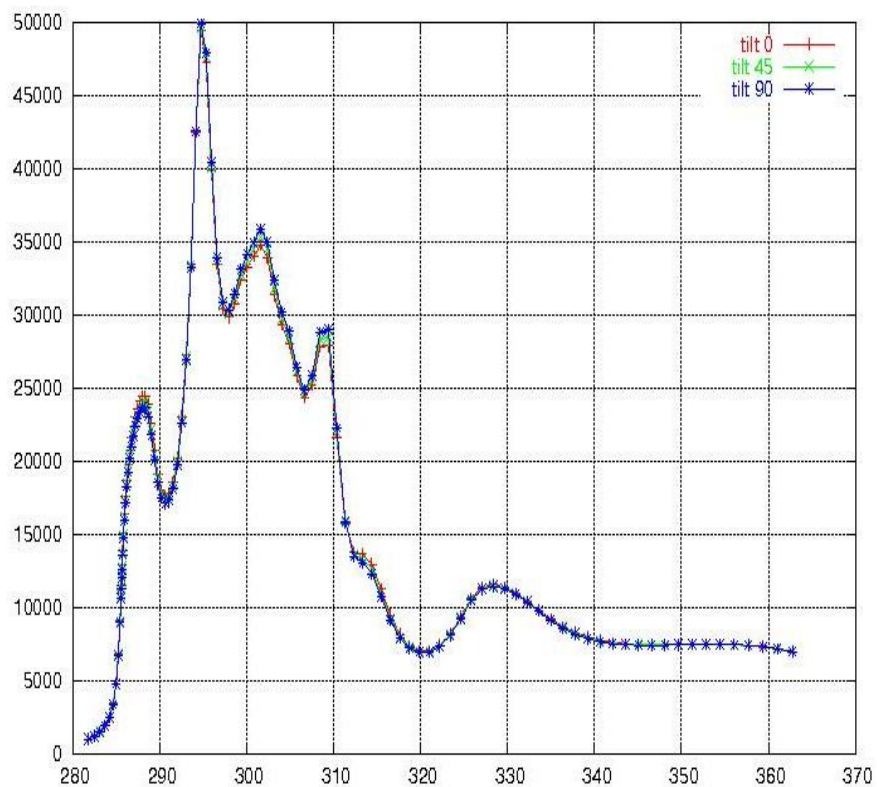
$$\begin{aligned} \langle i|V|f\rangle &= 4\pi \sum_{\lambda\mu} \sum_{lm} i^\lambda d_{lm}^{f*} Y_{\lambda\mu}^*(\Omega_q) \left[t_1 + i \sum_{a=2}^5 t_a \right] \\ &= 4\pi \sum_{\lambda\mu} \sum_{lm} i^\lambda d_{lm}^{f*} Y_{\lambda\mu}^*(\Omega_q) \left\{ \begin{Bmatrix} l & \lambda & l_i \\ -m & \mu & m_i \end{Bmatrix} \int j_\lambda u_l u_i + \frac{i\hbar v_0}{m_e c^2} \sqrt{\frac{4\pi}{3}} \int j_\lambda u_l \left(\frac{\partial u_i}{\partial r} - \frac{m_i}{r} u_i \right) \right. \\ &\quad \left[\begin{Bmatrix} l_i+1 & l_i & 1 \\ -m_i & m_i & 0 \end{Bmatrix} \begin{Bmatrix} l & \lambda & l_i+1 \\ -m & \mu & m_i \end{Bmatrix} + \begin{Bmatrix} l_i-1 & l_i & 1 \\ -m_i & m_i & 0 \end{Bmatrix} \begin{Bmatrix} l & \lambda & l_i-1 \\ -m & \mu & m_i \end{Bmatrix} \right] \\ &\quad \left. \int j_\lambda u_l \frac{u_i}{r} \left[\begin{Bmatrix} l_i+1 & l_i & 1 \\ -m_i & m_i+1 & -1 \end{Bmatrix} \begin{Bmatrix} l & \lambda & l_i+1 \\ -m & \mu & m_i \end{Bmatrix} + \begin{Bmatrix} l_i-1 & l_i & 1 \\ -m_i & m_i+1 & -1 \end{Bmatrix} \begin{Bmatrix} l & \lambda & l_i-1 \\ -m & \mu & m_i \end{Bmatrix} \right] \right\} \\ &\quad \int j_\lambda u_l \frac{u_i}{r} \left[\begin{Bmatrix} l_i+1 & l_i & 1 \\ -m_i & m_i+1 & -1 \end{Bmatrix} \begin{Bmatrix} l & \lambda & l_i+1 \\ -m & \mu & m_i \end{Bmatrix} + \begin{Bmatrix} l_i-1 & l_i & 1 \\ -m_i & m_i+1 & -1 \end{Bmatrix} \begin{Bmatrix} l & \lambda & l_i-1 \\ -m & \mu & m_i \end{Bmatrix} \right] \end{aligned}$$



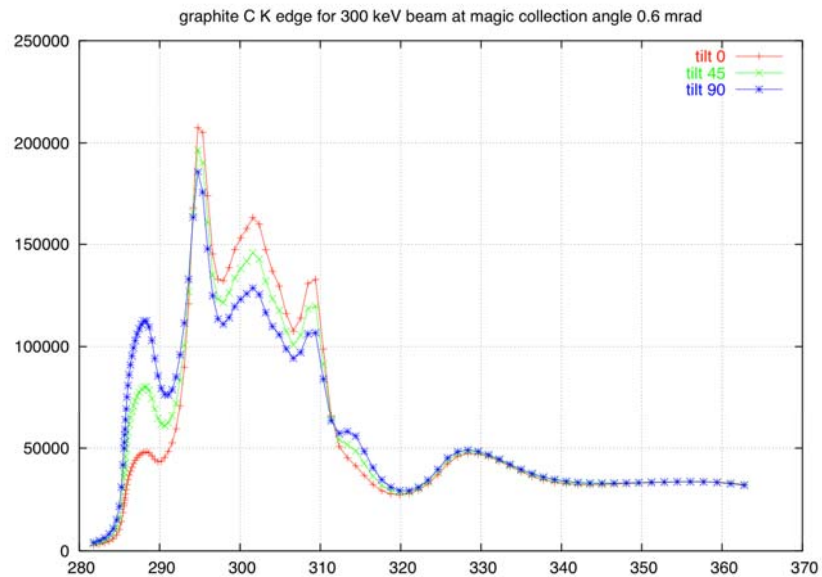
Relativistic spectra



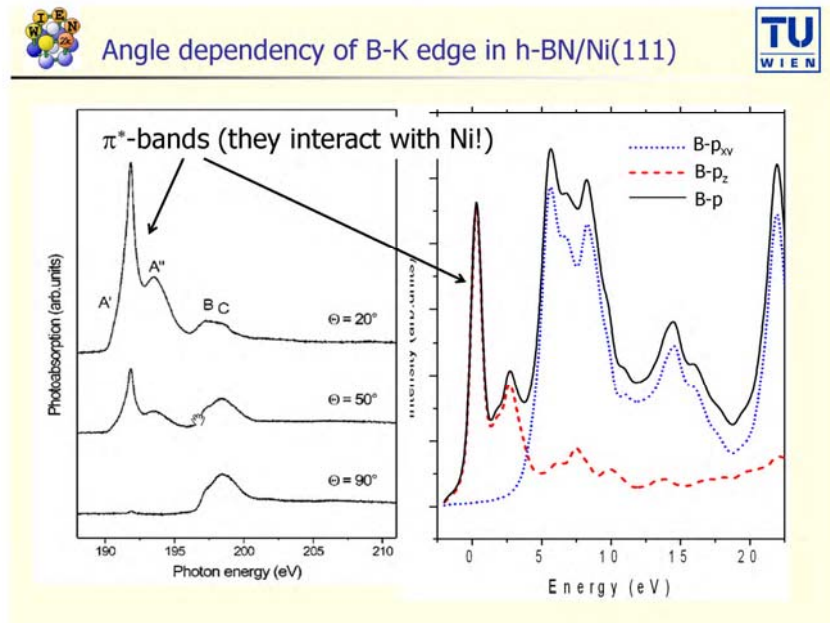
Graphite C K for 3 tilt angles. Beam energy 300 keV, collection angle = 2.4mrad.
Left: nonrelativistic calculation. Right: relativistic calculation.



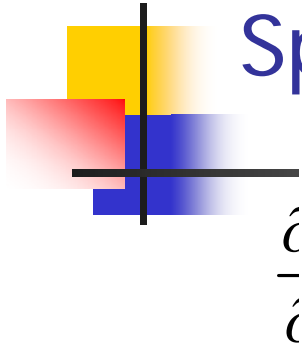
Orientation dependence



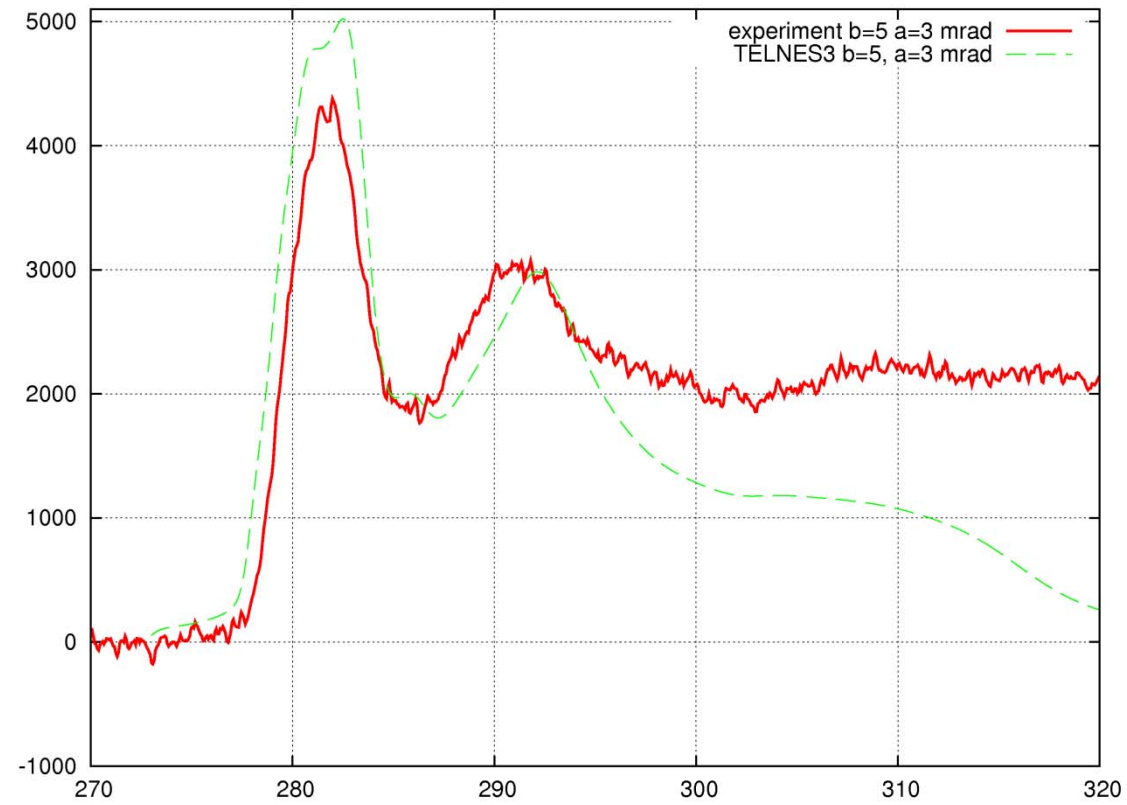
graphite C K EELS



BN B K XAS

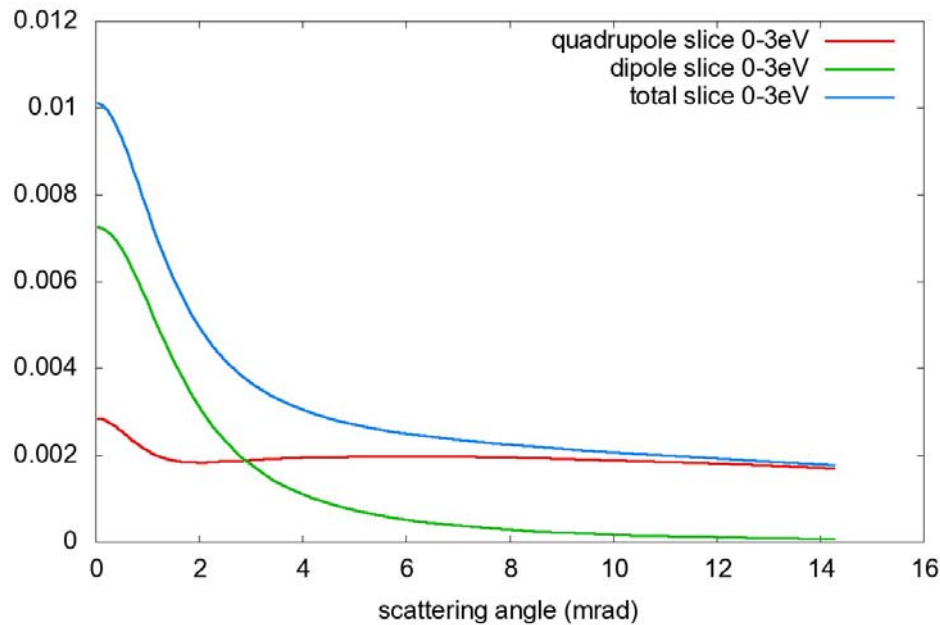


Spectrum as a function of energy loss

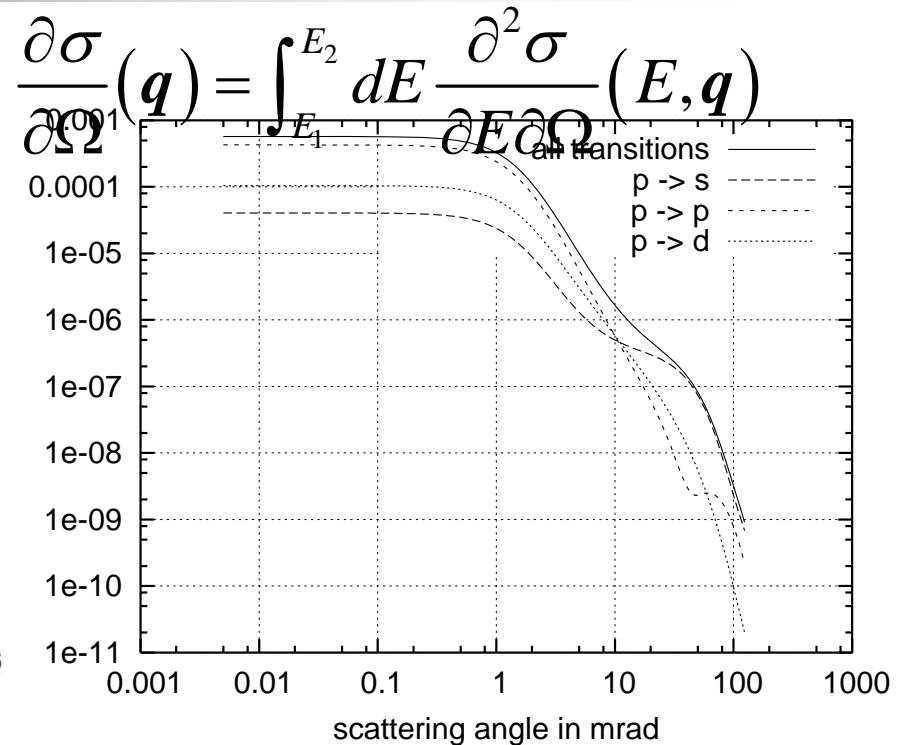


Cr₃C₂ C K edge

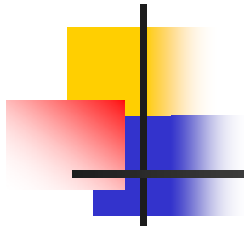
Spectrum as a function of scattering angle



Left : L3 edge of Cr3C2

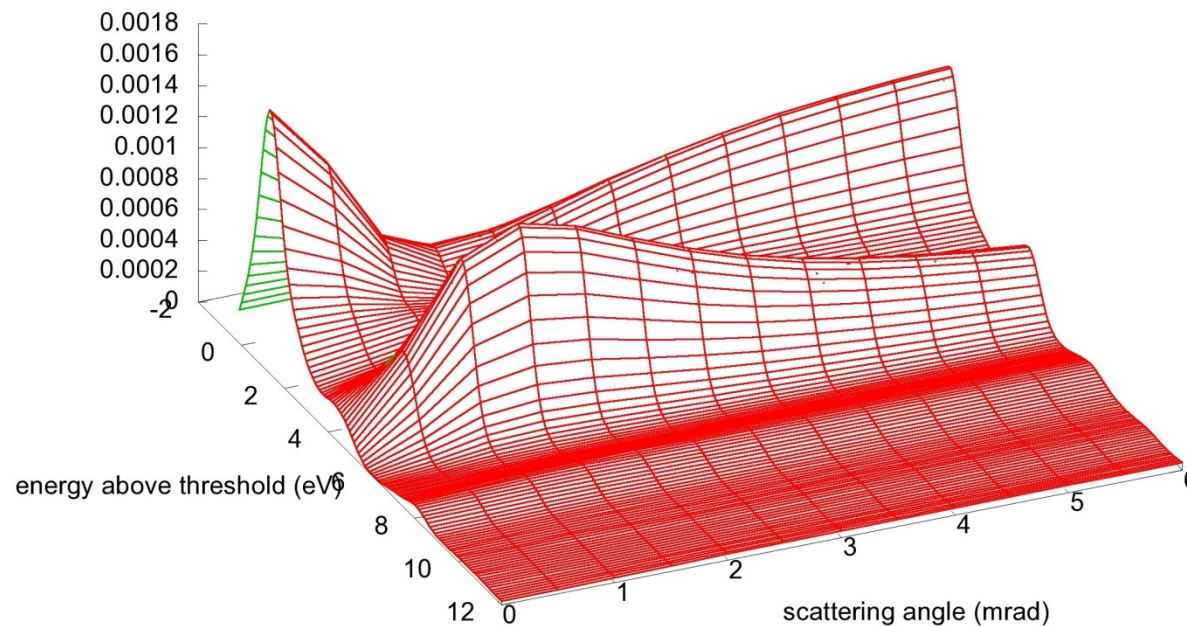


Right : the As L3 edge of NiAs (1324 eV)
Calculated using WIEN2k+TELNES2



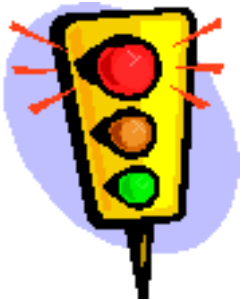
Just the double-differential CS

Double differential scattering cross-section (DDSCS)



$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} (E, \mathbf{q})$$

Warning!

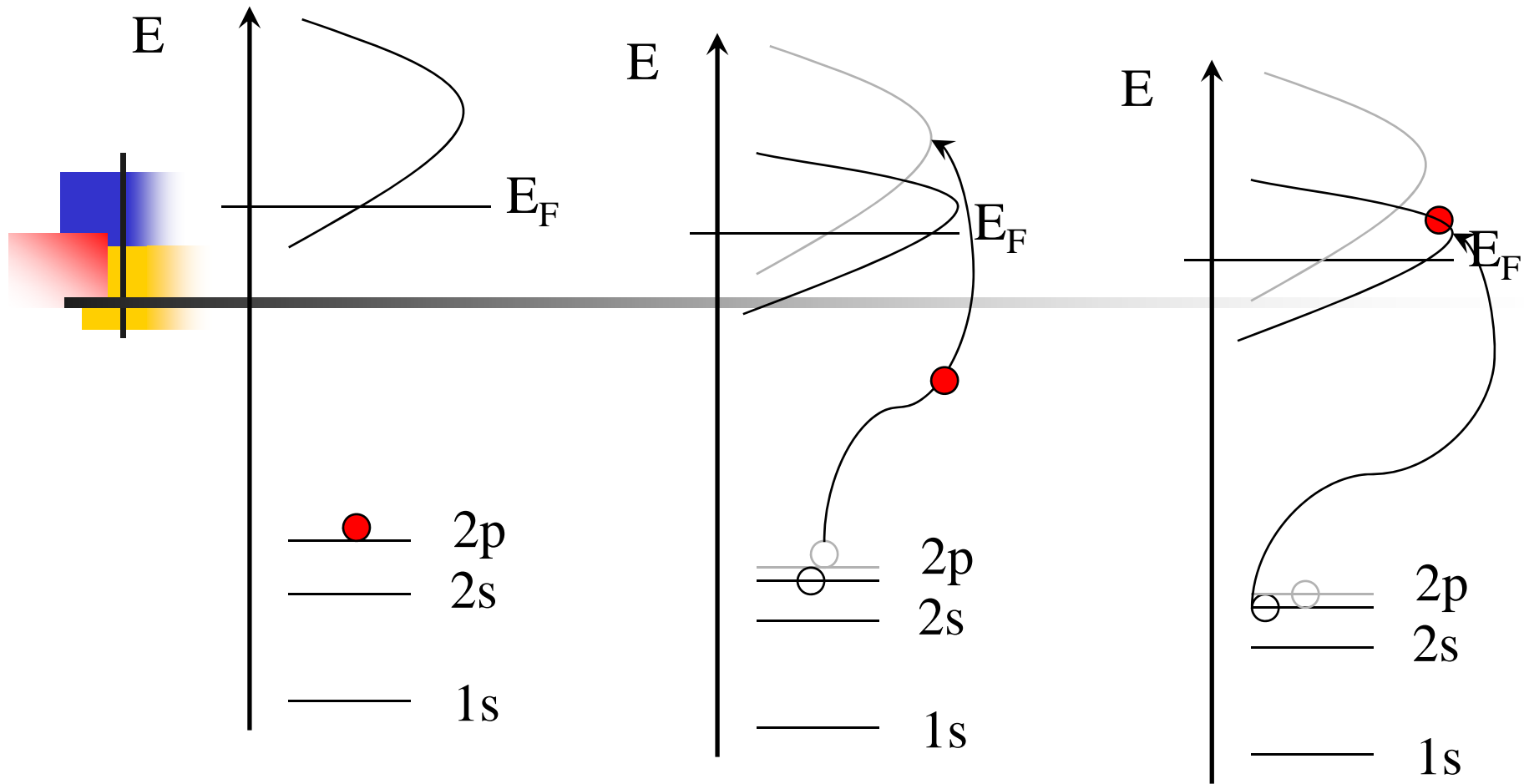


x DFT is a ground state theory !

→ it should fail for the prediction of excited state properties

✓ *however: for many systems it works pretty well*

The core hole

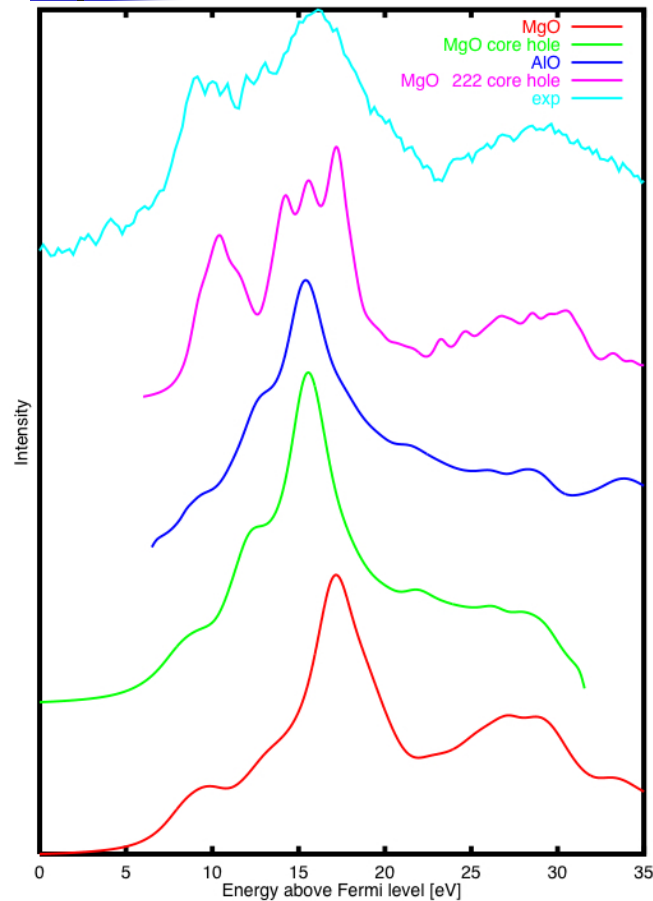


Different ways of treating the core hole within WIEN2k

- No core hole (= ground state, sudden approximation)
- $Z+1$ approximation (eg., replace C by N)
- Remove 1 core electron, add 1 electron to conduction band
- Remove 1 core electron, add 1 electron as uniform background charge
- Fractional core hole: remove between 0 and 1 electron charge (e.g. 0.5)
- *You may still get a bad result – correct treatment requires a more advanced theory, e.g. BSE treats electron-hole interaction explicitly (gold standard).*

Core hole calculations usually require a supercell !!!

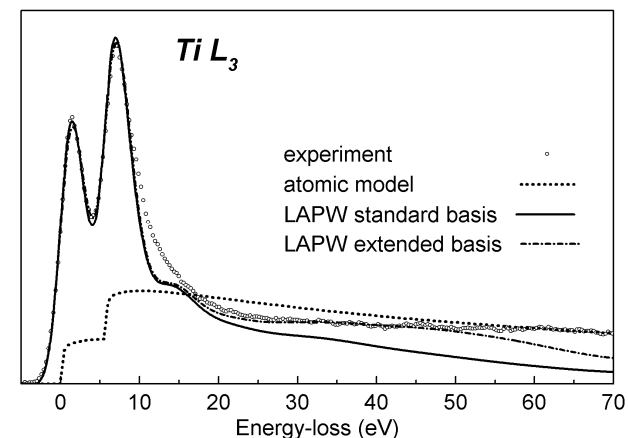
Mg-K in MgO



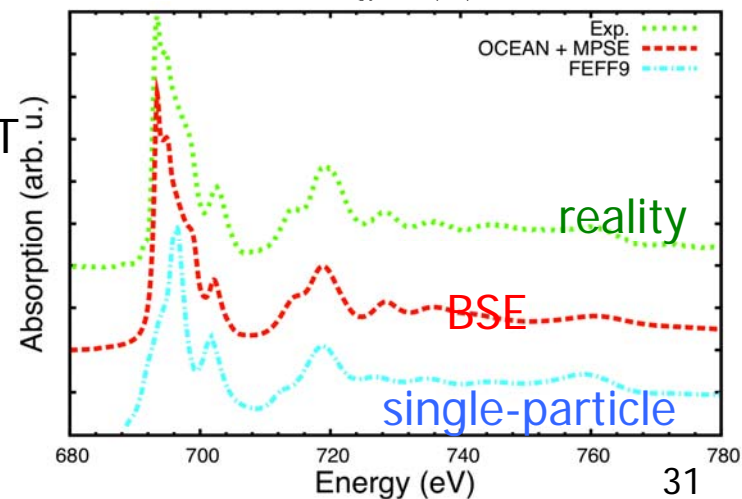
- mismatch between experiment and simulation
- introduction of core hole or $Z+1$ approximation does not help
- interaction between neighbouring core holes
- core hole in a supercell

Challenges of WIEN2k

1. Basis set only meant for limited energy range :
 - forget about EXAFS/EXELFS
 - sometimes adding a LO (case.in1) with a high linearization energy of 2.0 or 3.0 improves description of high-energy states.

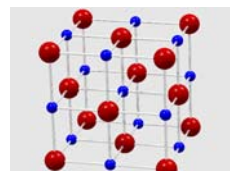
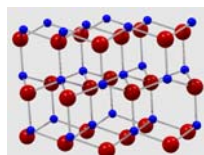
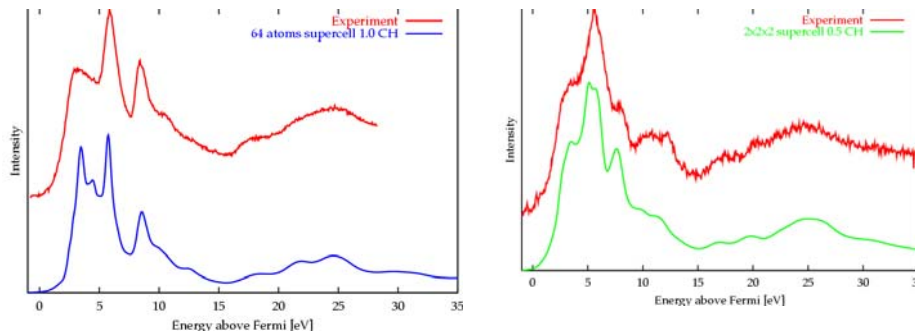


2. Sometimes Final State Rule (core hole) DFT just isn't good enough and you need Bethe-Salpeter (BSE) calculations
 - codes : OCEAN, AI2NBSE, Exc!ting, "BSE"
 - much more expensive
 - not as "polished" as DFT
 - gets L3/L2 ratios right



Challenges of WIEN2k

- Core hole supercell size can be hard to converge.
 - size of the cell
 - how much charge to remove?
 - optimal treatment can differ between similar materials; or even different edges in same material



GaN N K edge

S. Lazar, C. Hébert, H. W. Zandbergen
 Ultramicroscopy 98, 2-4, 249 (2004)

TAILLEFUMIER, CABARET, FLANK, AND MAURI

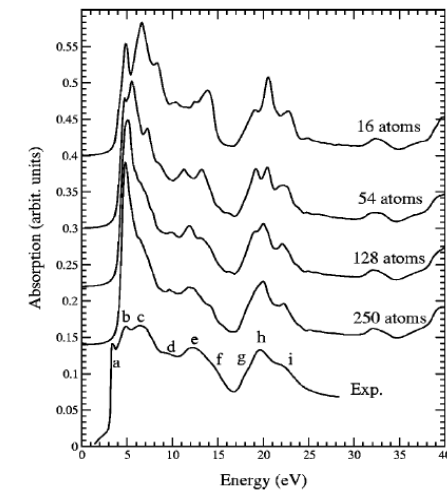
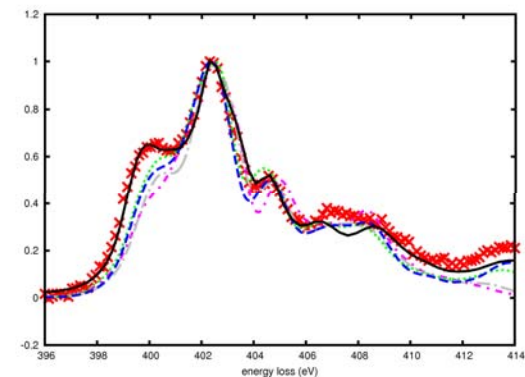
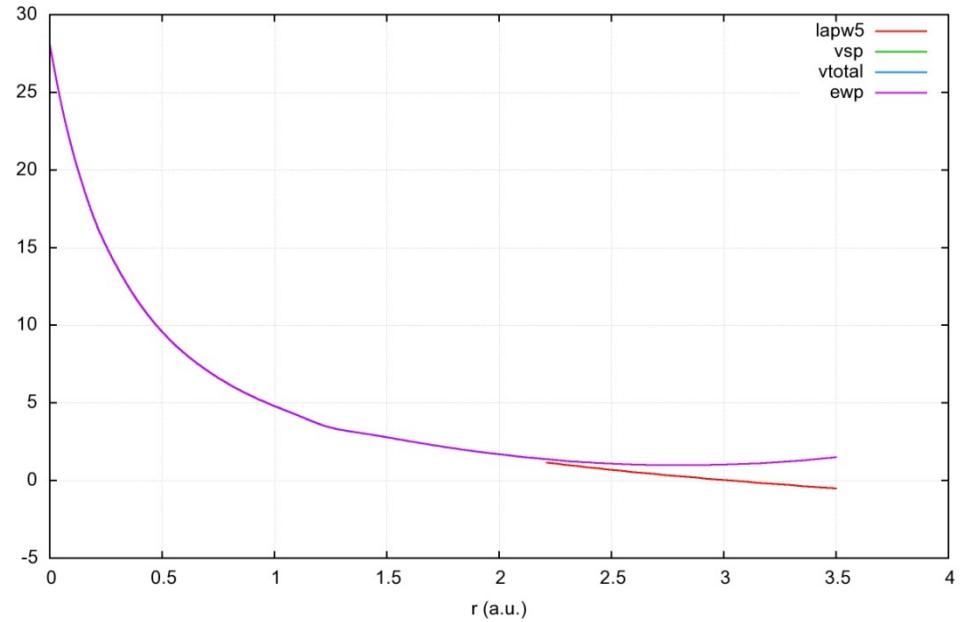
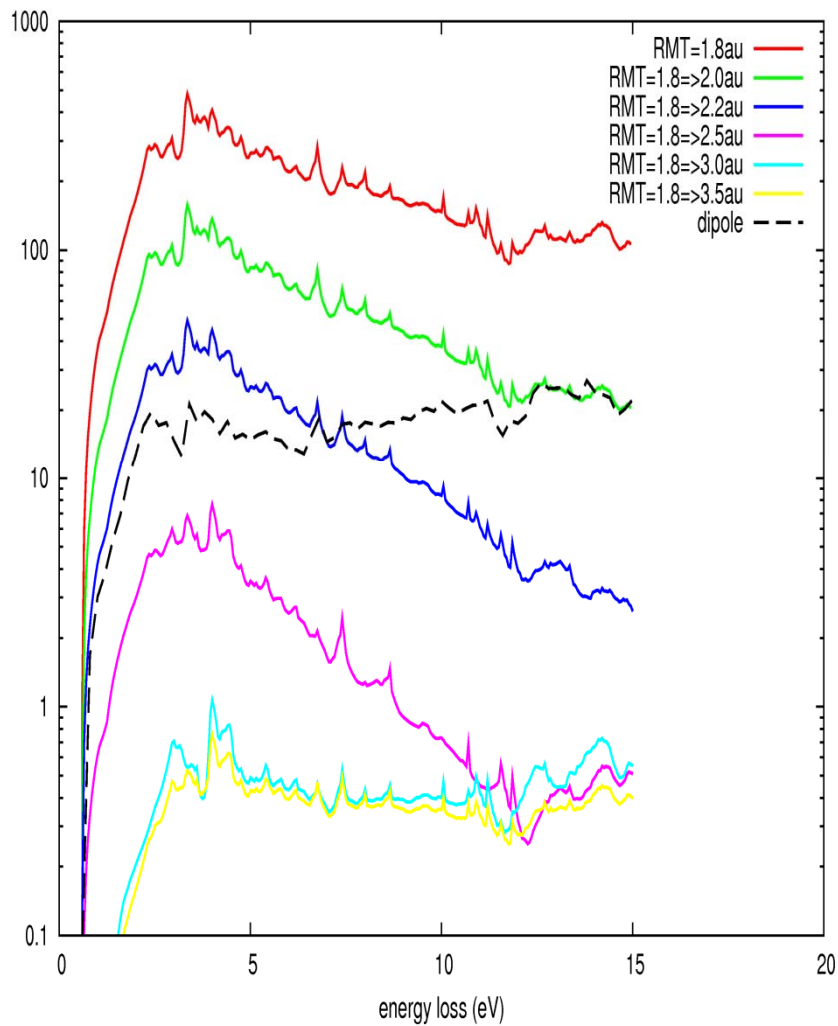


FIG. 11 Calculated C K-edge X-ray absorption spectra in diamond of different supercell sizes compared with experimental data (from Ref. 42). A 286.1 eV shift was applied to the experimental



Challenges of WIEN2k



4. Killing artifacts (unphysical monopoles) by “extending the RMT”



Documentation

- WIEN2k Users Guide!
- C. Hebert, Practical aspects of calculating EELS using the WIEN2k code, Ultramicroscopy, 2007
- Jorissen, Hebert & Luitz, submitting (http://leonardo.phys.washington.edu/feff/papers/dissertations/thesis_jorissen.pdf - Kevin's Ph.D. thesis)



3. Hands-on exercises

1. XAS of K edge of Cu.
2. averaged EELS of N K edge of GaN.
3. orientation sensitive, in-plane and out-of-plane EELS of N K edge of GaN.
4. core hole calculation for Cu K-edge XAS & compare.
5. initialize a $2*2*2$ supercell for TiC or TiN core hole EELS calculation.
6. Be K edge. Find the error.



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- WIEN2013 organizers