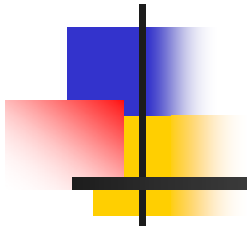


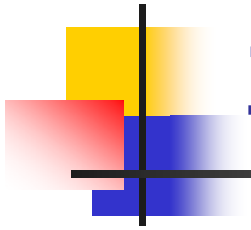
# *Core loss spectra*

## *(EELS, XAS)*

Kevin Jorissen

University of Washington (USA)

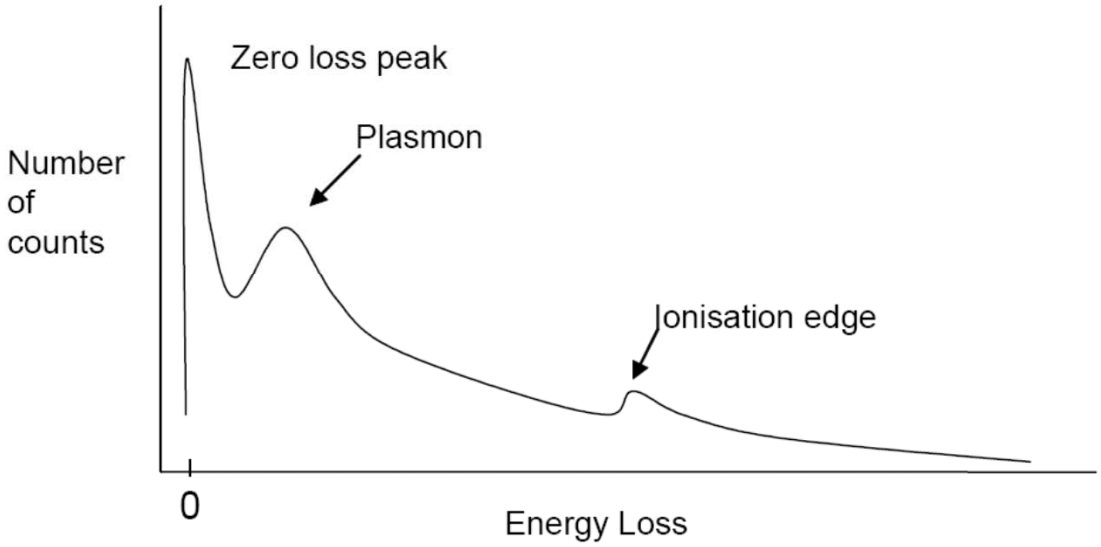
WIEN2k 2013 Penn State

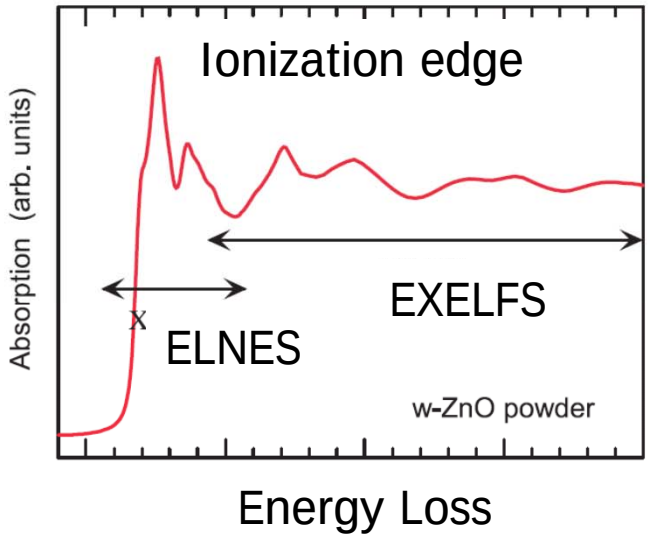


# 1. Concepts

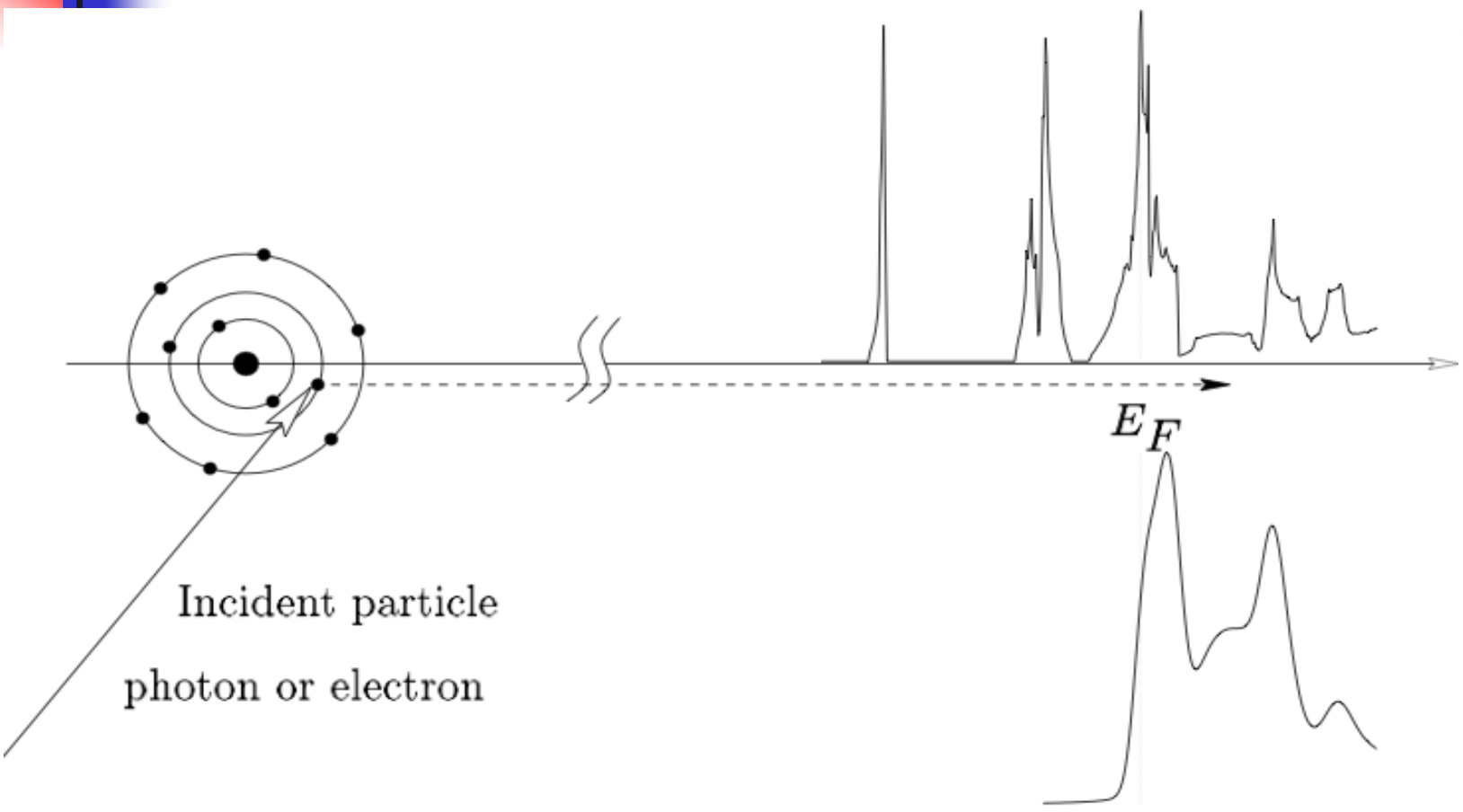
# WIEN2k calculates ELNES / XANES

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



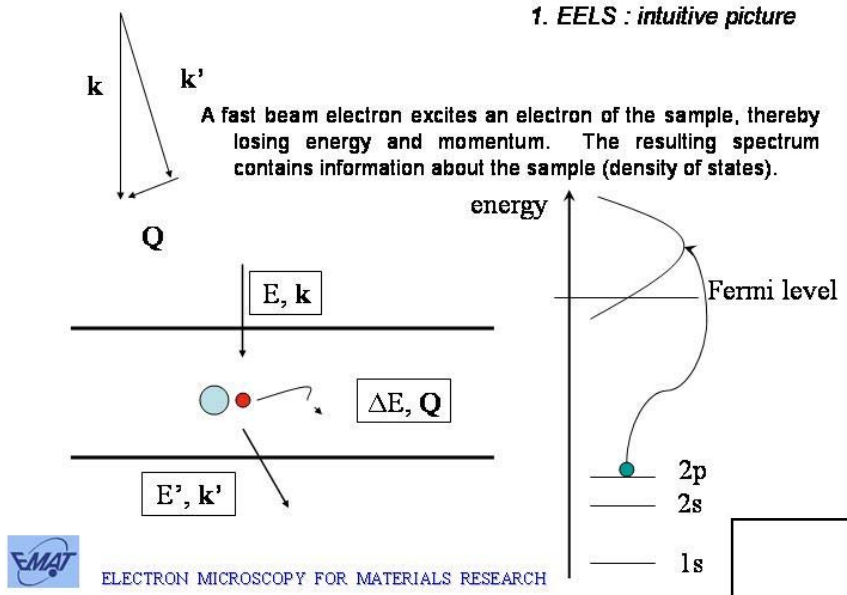



# the excitation process



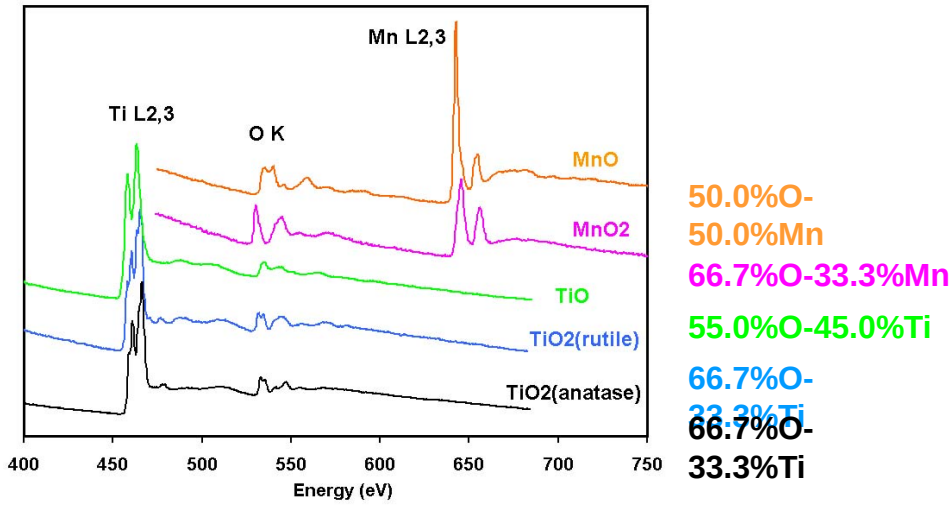
## *INTRODUCING EELS*

*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 (~0.5 Å).*
*Energy resolution is improving ( ~ 25meV).*




Intuitive picture of EELS

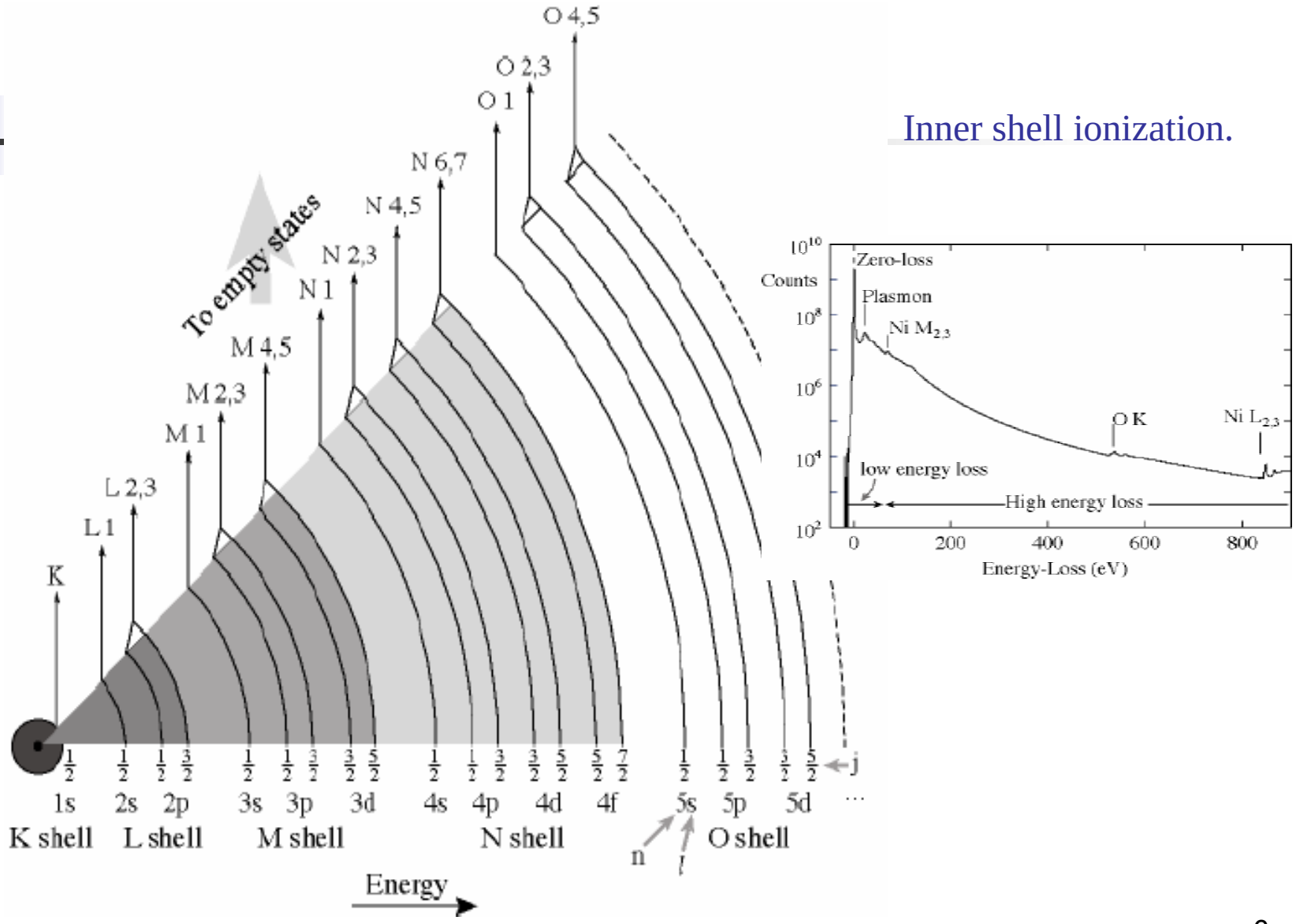
Electron microscope equipped with EELS-detector




EELS spectra of TM oxides
Probes local electronic structure

50.0%O-50.0%Mn
66.7%O-33.3%Mn
55.0%O-45.0%Ti
66.7%O-33.3%Ti
66.7%O-33.3%Ti

# Terminology for ionization edges

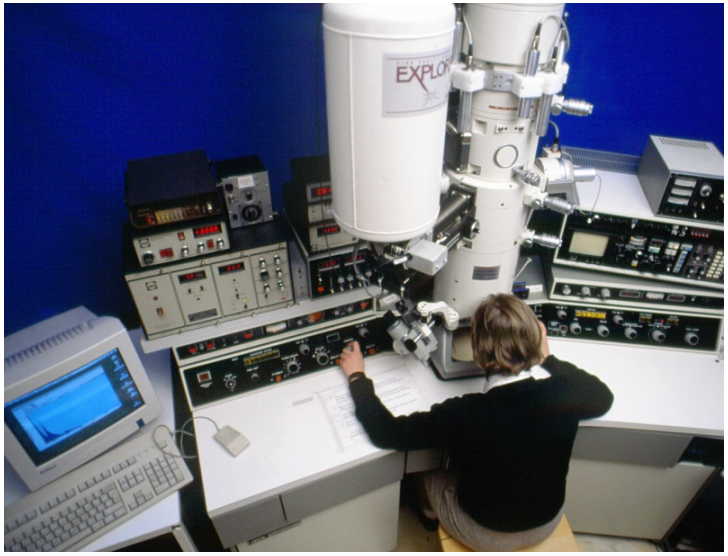



Inner shell ionization.

# 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.

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

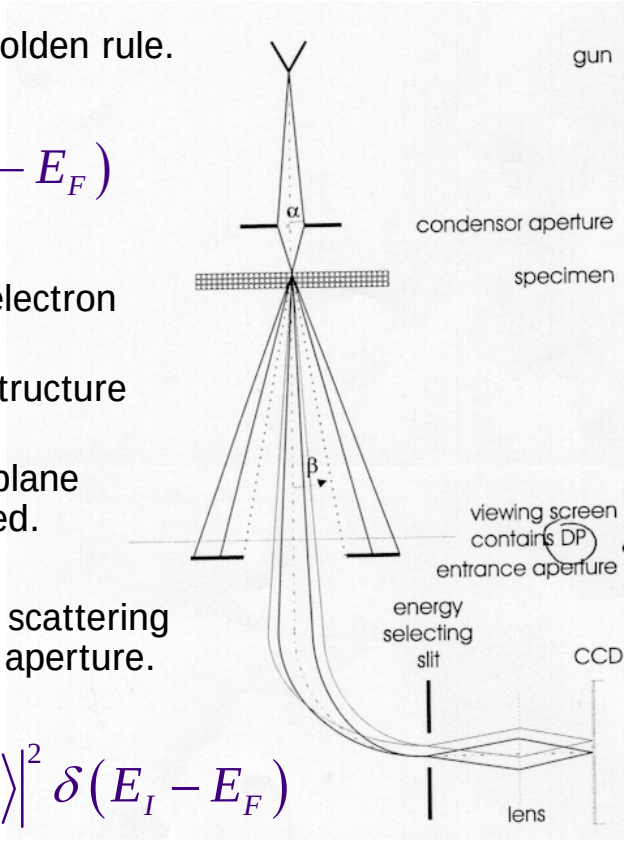
V is the interaction potential between the fast beam electron and an electron in the sample.

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

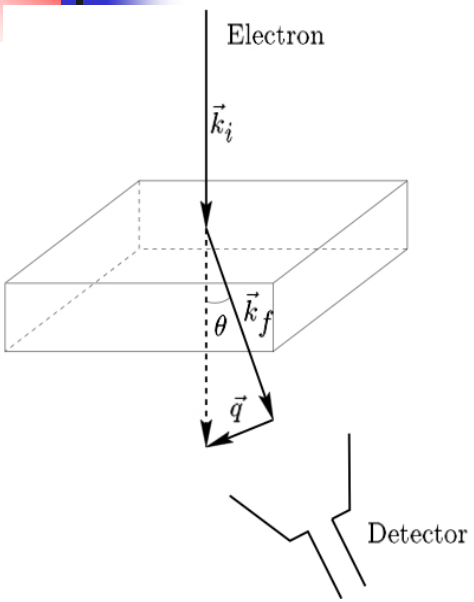
$k_F$ and $k_I$ the probe states, are typically described as plane waves when Bragg scattering effects are neglected.

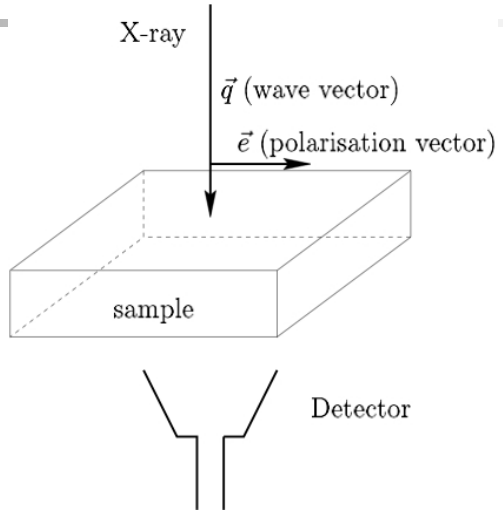
In experiment, one usually integrates over a range of scattering angles, due to the beam width and spectrometer aperture.
→ differential cross section :

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



# Theory (EELS --------- XAS)




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

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

# dipole approximation

$$\vec{q}.\vec{R} << 1 \rightarrow e^{i\vec{q}\vec{R}} = 1 + i\vec{q}.\vec{R} + \frac{(\vec{q}.\vec{R})^2}{2!} + \square$$

EELS

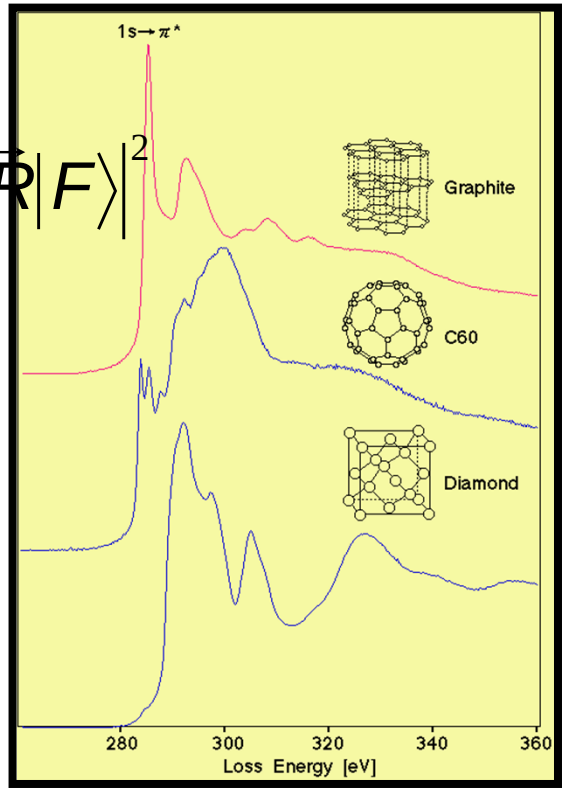
$$\frac{\partial^2\sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{q}.\vec{R} | F \rangle \right|^2$$

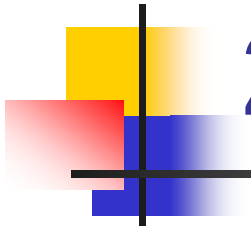
XAS

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

The polarization vector e in XAS plays the same role as momentum transfer q in ELNES within the dipole approximation.
This is why people say “XAS = EELS”.
(Beware - there are quite a few differences, too.)

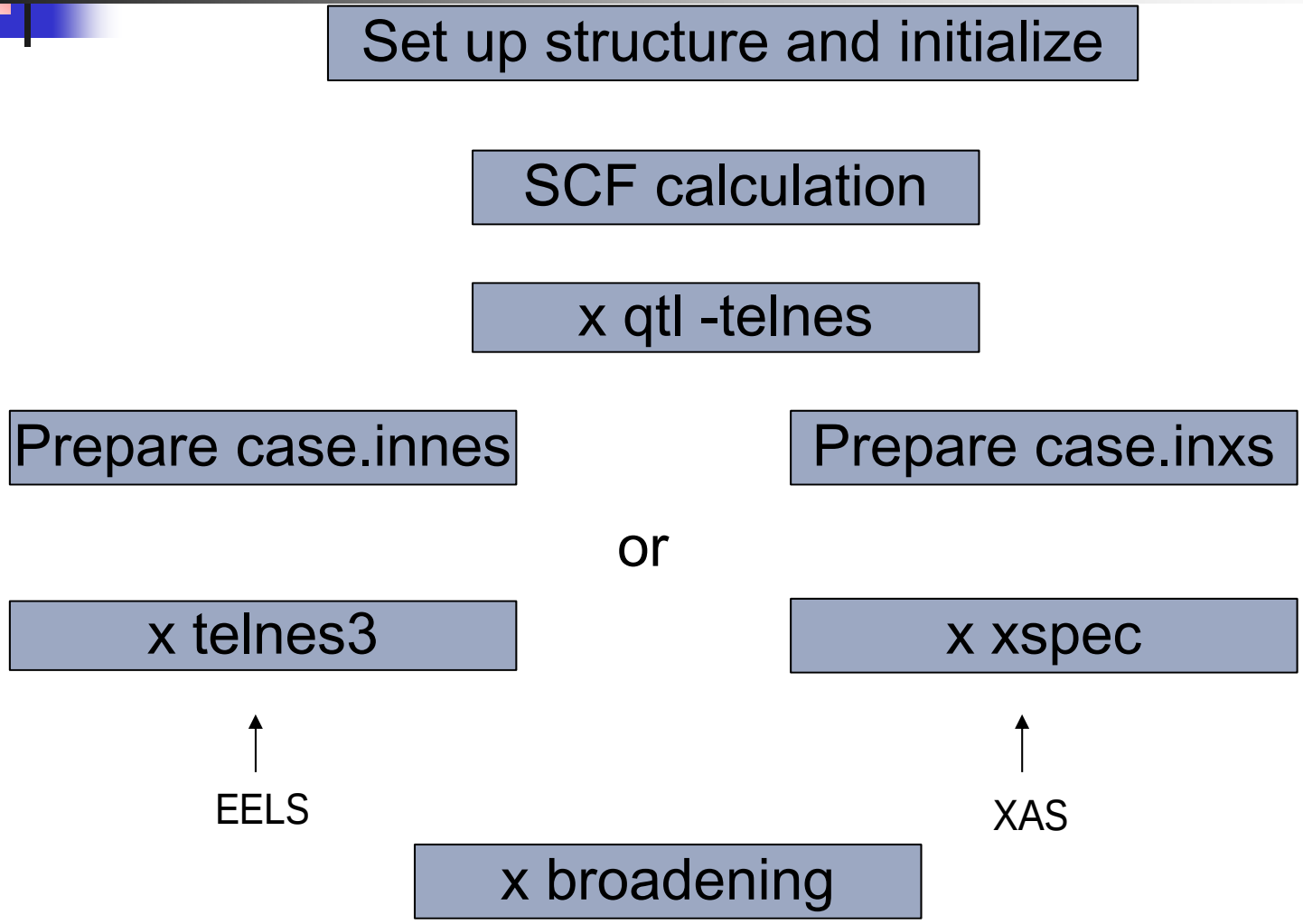
→ Probes local, symmetry-selected ($l_c$+1) unoccupied DOS



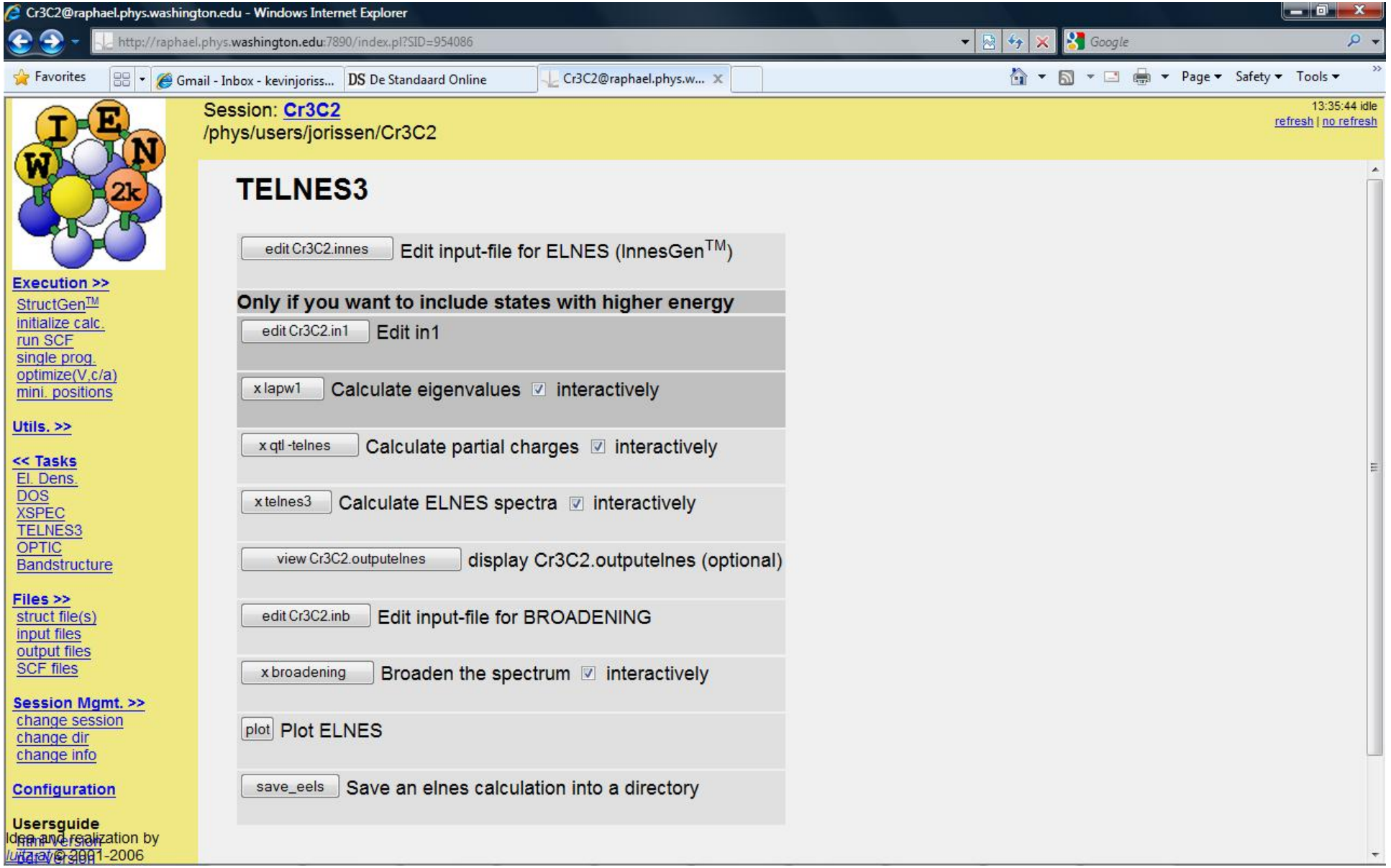


# 2. WIEN2k Calculations.

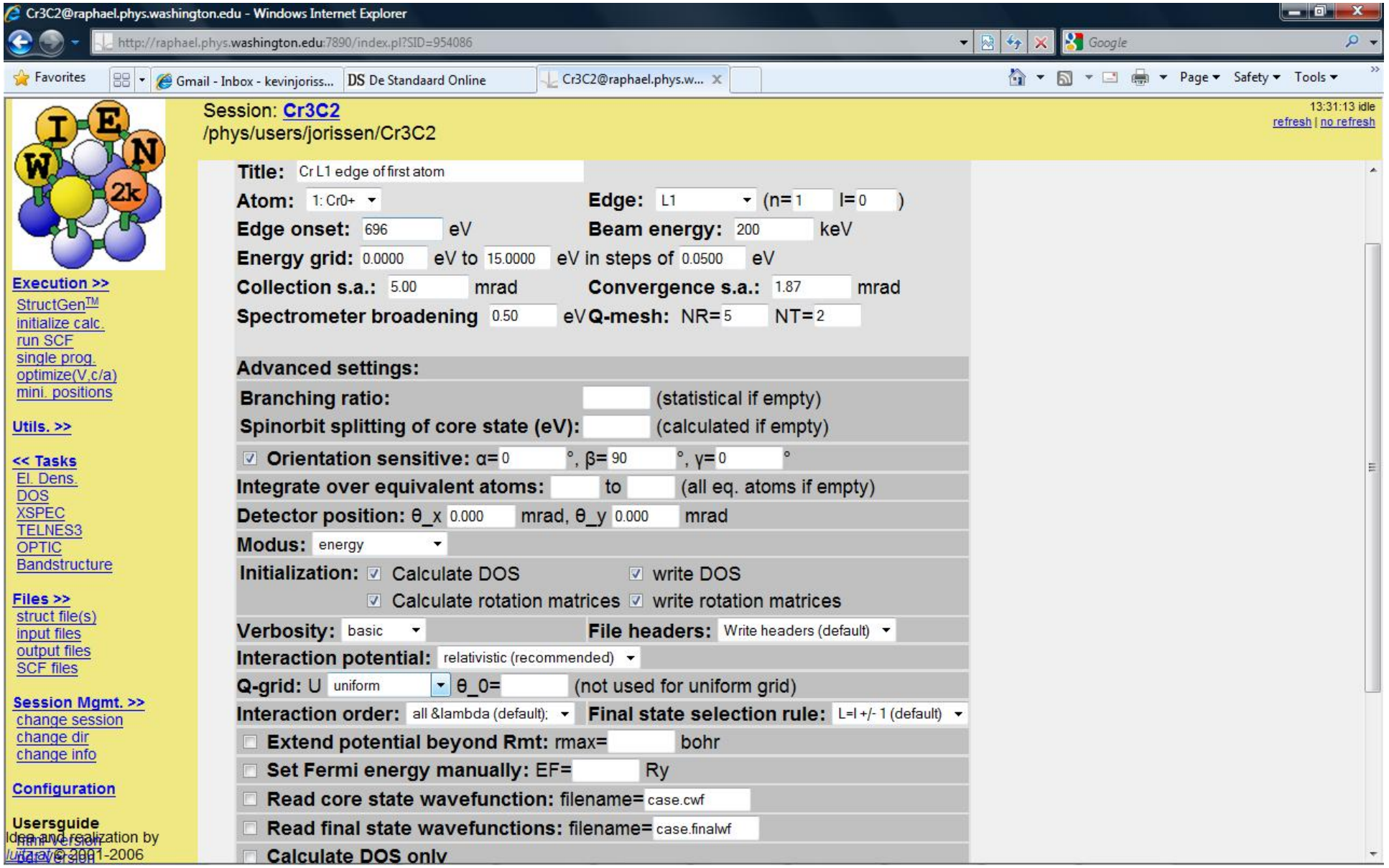
# *calculation of spectra using WIEN2k*



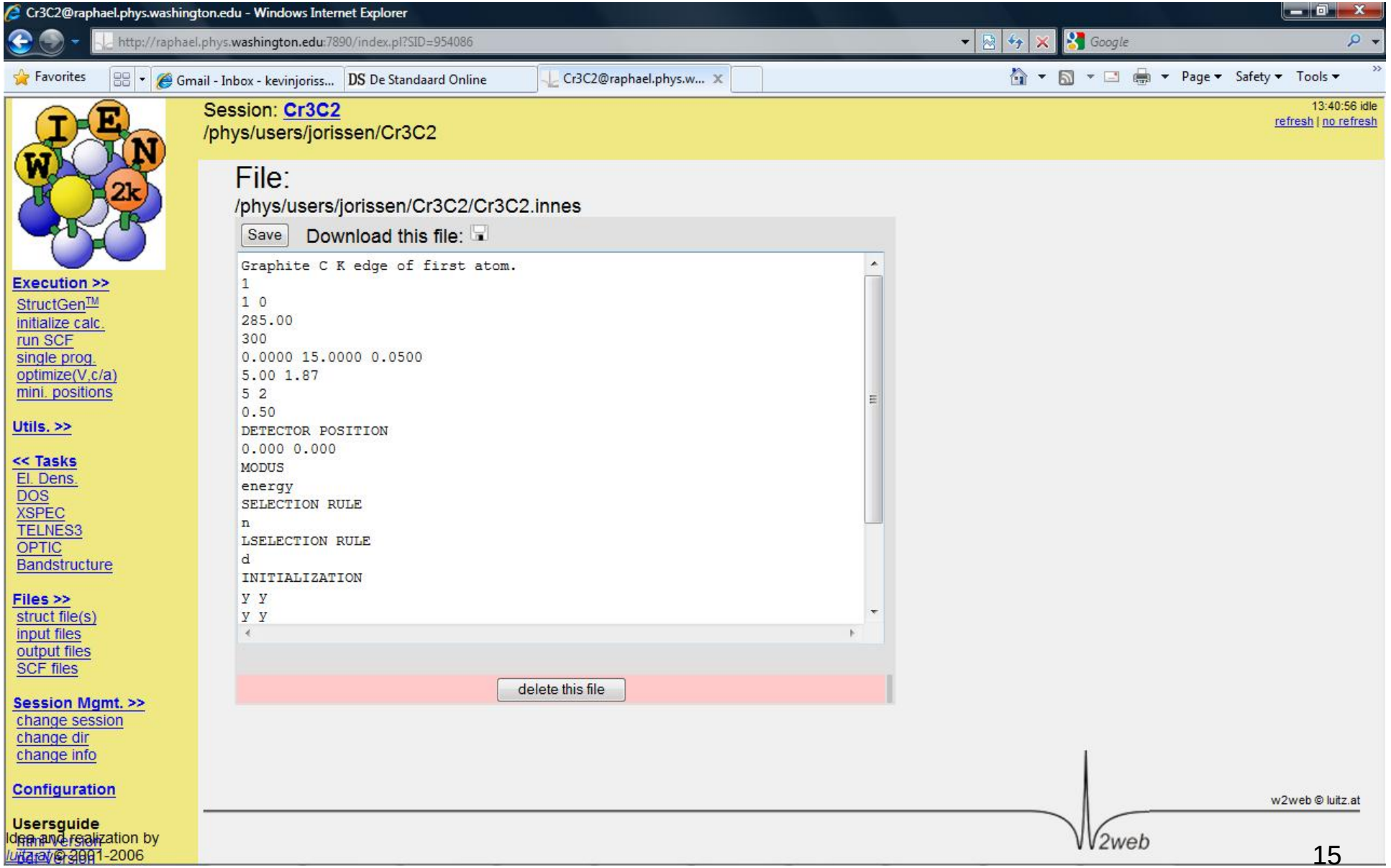
# ELNES workflow



# ELNES input w2web



# ELNES input file (case.innes)



# XSPEC-task

Session: [ magnetite ]
/area51/pblaha/lapw/correlated/magnetite

16:42:50 idle
[ refresh ] | [ no refresh ]


[ Execution >> ]
[ StructGen™ ]
[ view structure ]
[ initialize calc. ]
[ run SCF ]
[ single prog. ]
[ optimize(V,c/a) ]
[ mini. positions ]

[ Utils. >> ]

[ << Tasks ]
[ El. Dens. ]
[ DOS ]
[ XSPEC ]
[ TELNES.2 ]
[ OPTIC ]
[ Bandstructure ]

[ Files >> ]
[ struct file(s) ]
[ input files ]
[ output files ]
[ SCF files ]

[ Session Mgmt. >> ]
[ change session ]
[ change dir ]
[ change info ]

[ Configuration ]

Usersguide
[ html-Version ]
[ pdf-Version ]


## XSPEC

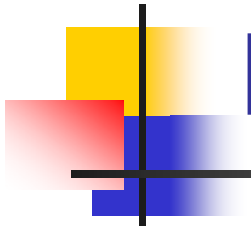
[ Spin UP ] [ Spin DOWN ]

**Spin UP selected.**

**If you want to include states with higher energy**

| | |
|---|---|
| edit magnetite.in1 | Edit in1 |
| x lapw1 -up | Calculate eigenvalues ☑ interactively |
| x lapw1 -dn | Calculate eigenvalues ☑ interactively |
| x lapw2 -qtl -up | Calculate partial charges ☑ interactively |
| edit magnetite.inxs | Edit input-file for XSPEC |
| x xspec -up | Calculate X-ray spectra ☑ interactively |
| plot | Plot XSPEC |

```
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
```



# 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

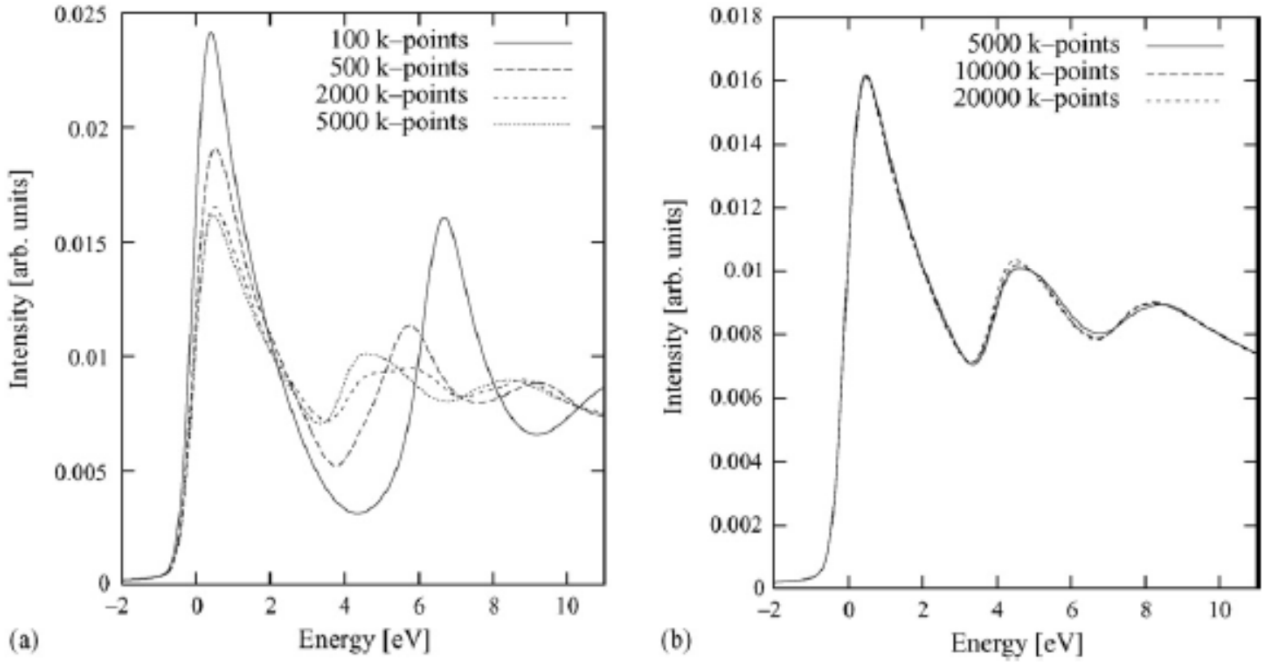



Fig. 8. Cu $L_3$ edge in fcc-Cu calculated for different number of *k*-points in the whole BZ. The calculation was performed with RKMAX = 8. The structures were broadened with a Gaussian of 0.7 eV to account for experimental broadening. Lifetime broadening was modeled with a linear approximation.

# Features of WIEN2k

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

For EELS:

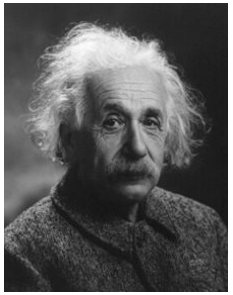
- Account for collection/convergence angle
- Output $\sigma$ (E) or $\sigma$ ($\theta$)
- Relativistic ELNES (→ anisotropic materials)

# EELS – Relativistic theory needed for anisotropic materials

Semi-relativistic theory :

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

V=|**r**-**r'**|-1
m -> γ m
$\theta_E$ -> $\theta_{E,rel}$



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

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

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

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 :

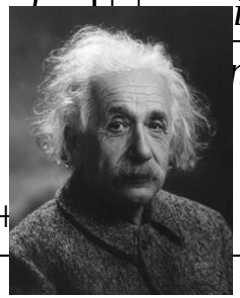
$$\frac{\partial^2\sigma}{\partial E\partial\Omega}=\left[\frac{4\gamma^2a_0^{-2}}{q^2-\left(E/\hbar c\right)^2}\right]^2\frac{k_f}{k_i}\sum_{i,f}\left|\left\langle f\left|e^{i\mathbf{q}.\mathbf{r}}\left(1-\frac{\mathbf{v_0}.\mathbf{p}}{m_ec^2}\right)\right|i\right\rangle\right|^2\delta\left(E_f-E_i-E\right)$$

$$\left\langle i\left|V\right|f\right\rangle=4\pi\sum_{\lambda\mu}\sum_{lm}i^\lambda d_{lm}^{f*}Y_{\lambda\mu}^*\left(\Omega_{\mathbf{q}}\right)\left[t_1+i\sum_{a=2}^{5}t_a\right]$$

$$=4\pi\sum_{\lambda\mu}\sum_{lm}i^\lambda d_{lm}^{f*}Y_{\lambda\mu}^*\left(\Omega_{\mathbf{q}}\right)\left\{\begin{Bmatrix}l & \lambda & l_i\\ -m & \mu & m_i\end{Bmatrix}\int j_\lambda u_l u_i+\frac{i\hbar v_0}{m_ec^2}\sqrt{\frac{4\pi}{3}}\int j_\lambda u_l\left(\frac{\partial u_i}{\partial r}-\frac{m_i}{r}u_i\right)\right.$$

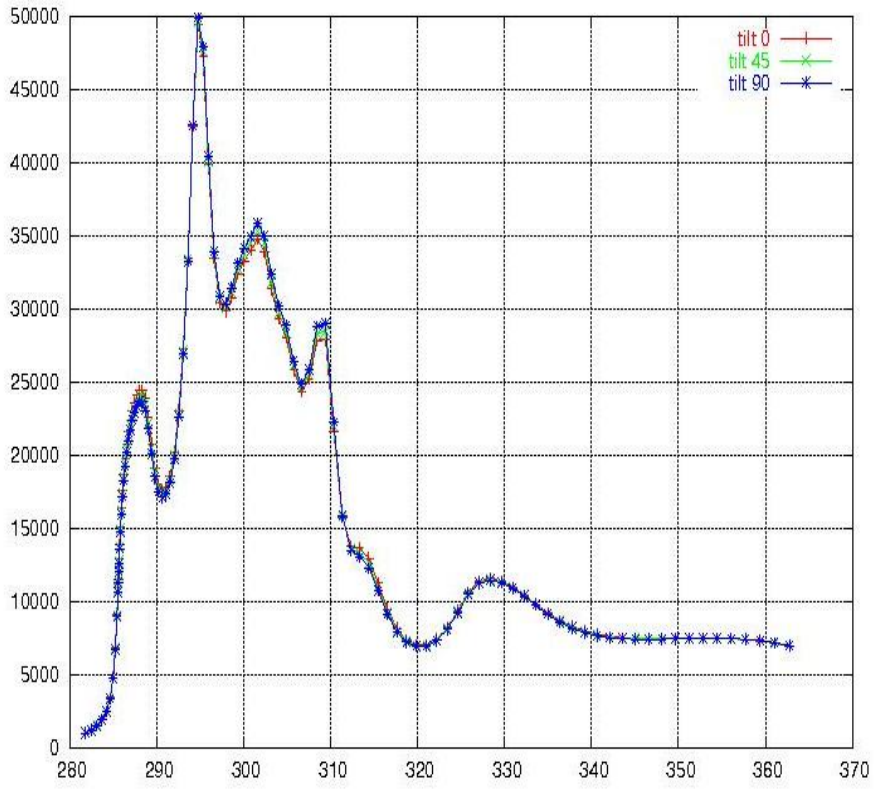
$$\left[\begin{Bmatrix}l_i+1 & l_i & 1\\ -m_i & m_i & 0\end{Bmatrix}\begin{Bmatrix}l & \lambda & l_i+1\\ -m & \mu & m_i\end{Bmatrix}+\begin{Bmatrix}l_i-1 & l_i & 1\\ -m_i & m_i & 0\end{Bmatrix}\begin{Bmatrix}l & \lambda & l_i-1\\ -m & \mu & m_i\end{Bmatrix}\right]\frac{i\hbar v_0}{m_ec^2}\sqrt{\frac{8\pi}{3}}\sqrt{\left(l_i-m_i\right)\left(l_i+m_i+1\right)}$$

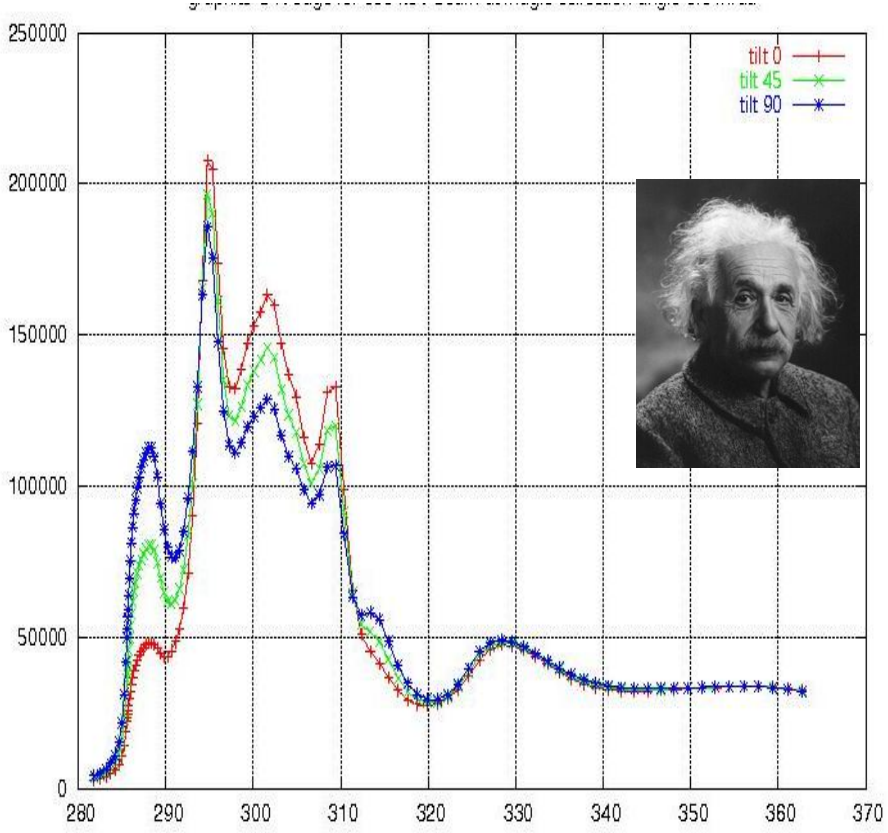
$$\left.\int j_\lambda u_l\frac{u_i}{r}\left[\begin{Bmatrix}l_i+1 & l_i & 1\\ -m_i & m_i+1 & -1\end{Bmatrix}\begin{Bmatrix}l & \lambda & l_i+1\\ -m & \mu & m_i\end{Bmatrix}+\begin{Bmatrix}l_i-1 & l_i & 1\\ -m_i & m_i+1 & -1\end{Bmatrix}\begin{Bmatrix}l & \lambda & l_i-1\\ -m & \mu & m_i\end{Bmatrix}\right]\right\}$$



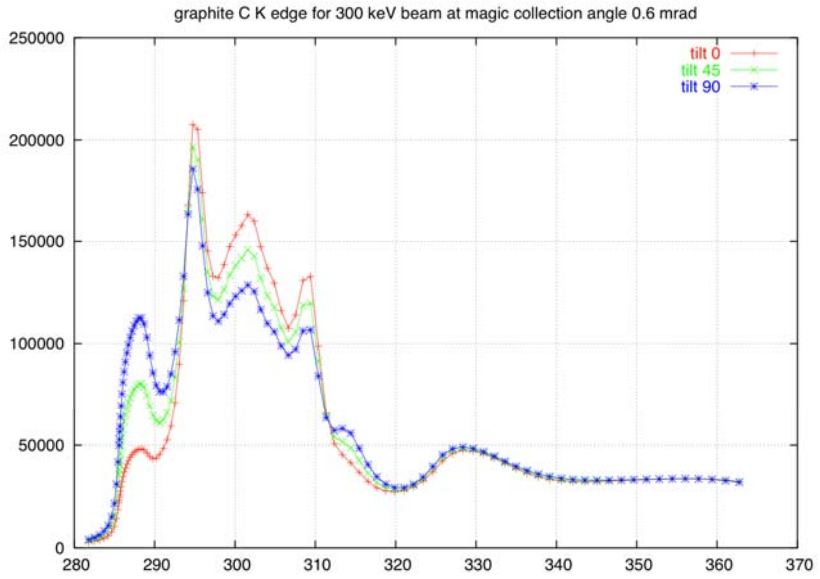
# Relativistic spectra

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

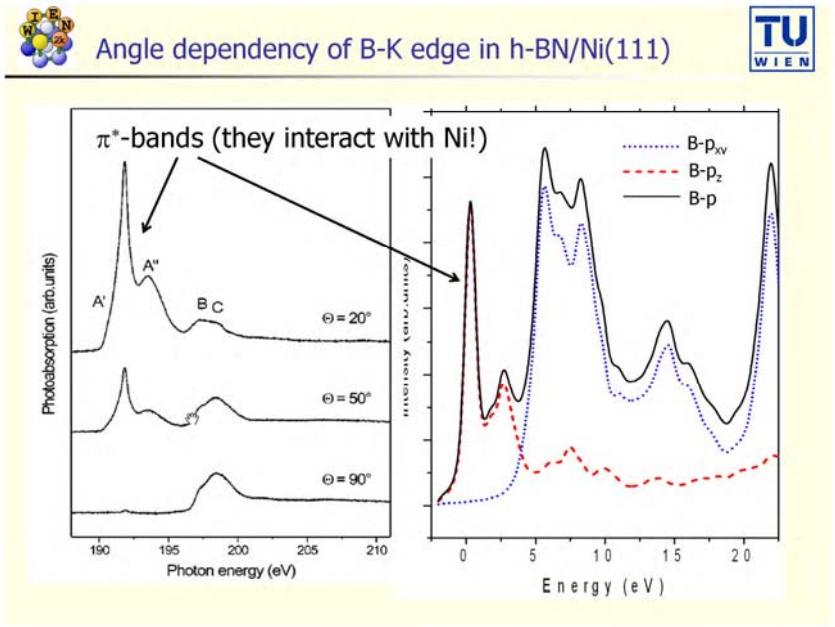


# Orientation dependence

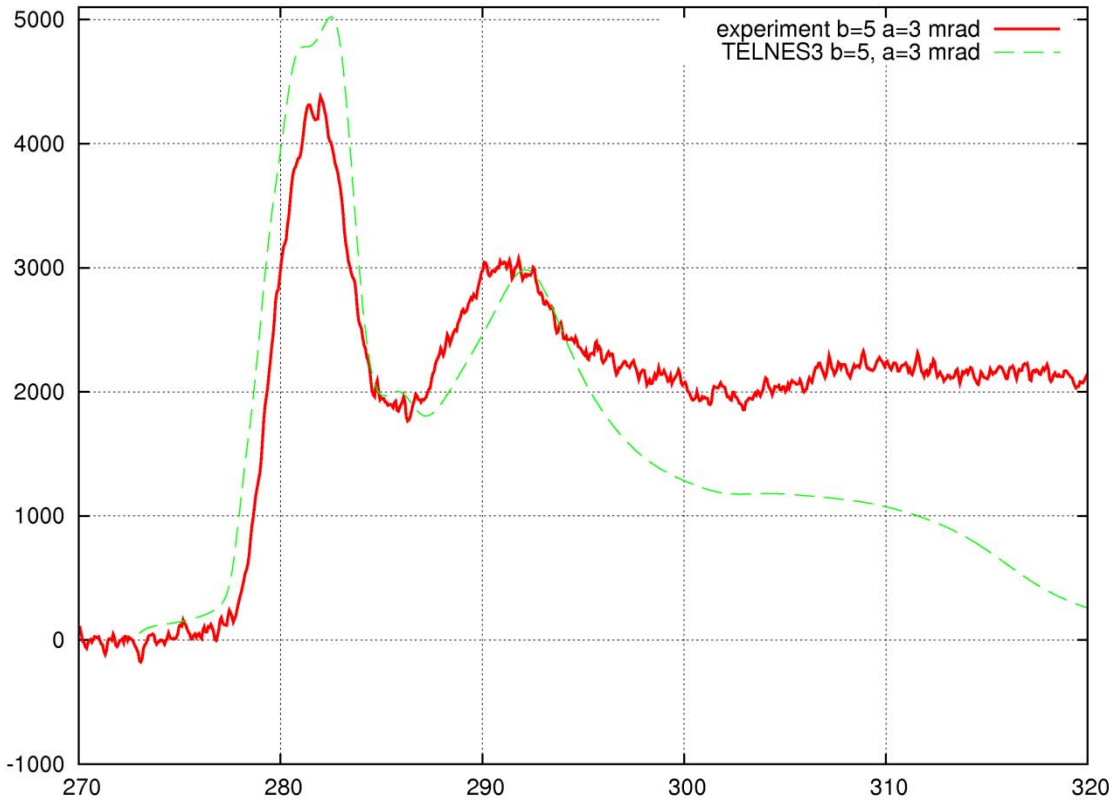



graphite C K EELS



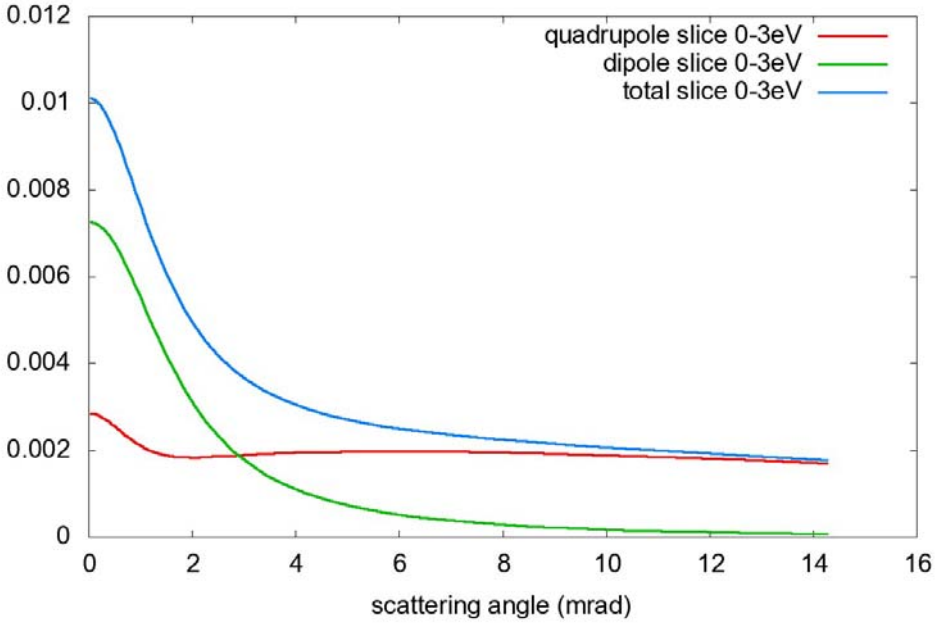

BN B K XAS

# Spectrum as a function of energy loss

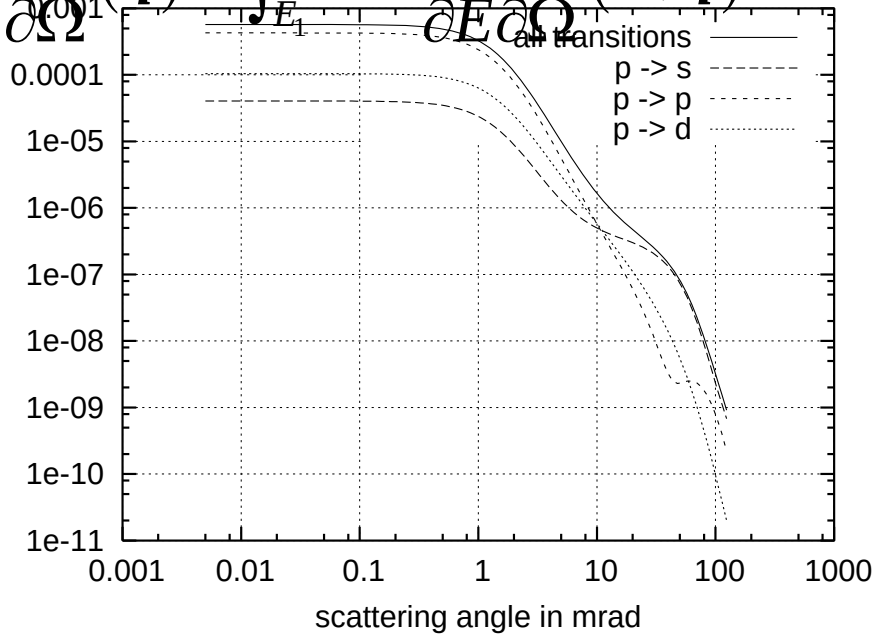



Cr3C2 C K edge

# Spectrum as a function of scattering angle




$$\frac{\partial\sigma}{\partial\Omega}(\boldsymbol{q}) = \int_{E_1}^{E_2} dE \frac{\partial^2\sigma}{\partial E\,\partial\Omega}(E,\boldsymbol{q})$$

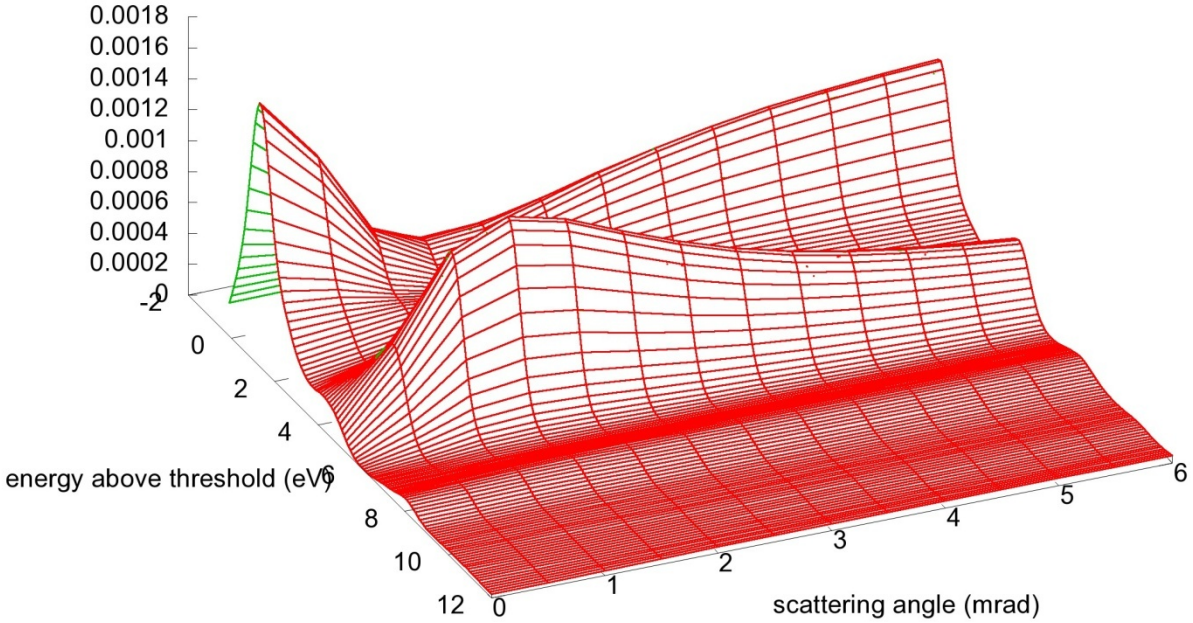



*Left :* L3 edge of Cr3C2

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

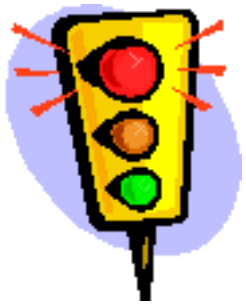
# Just the double-differential CS

Double differential scattering cross-section (DDSCS)



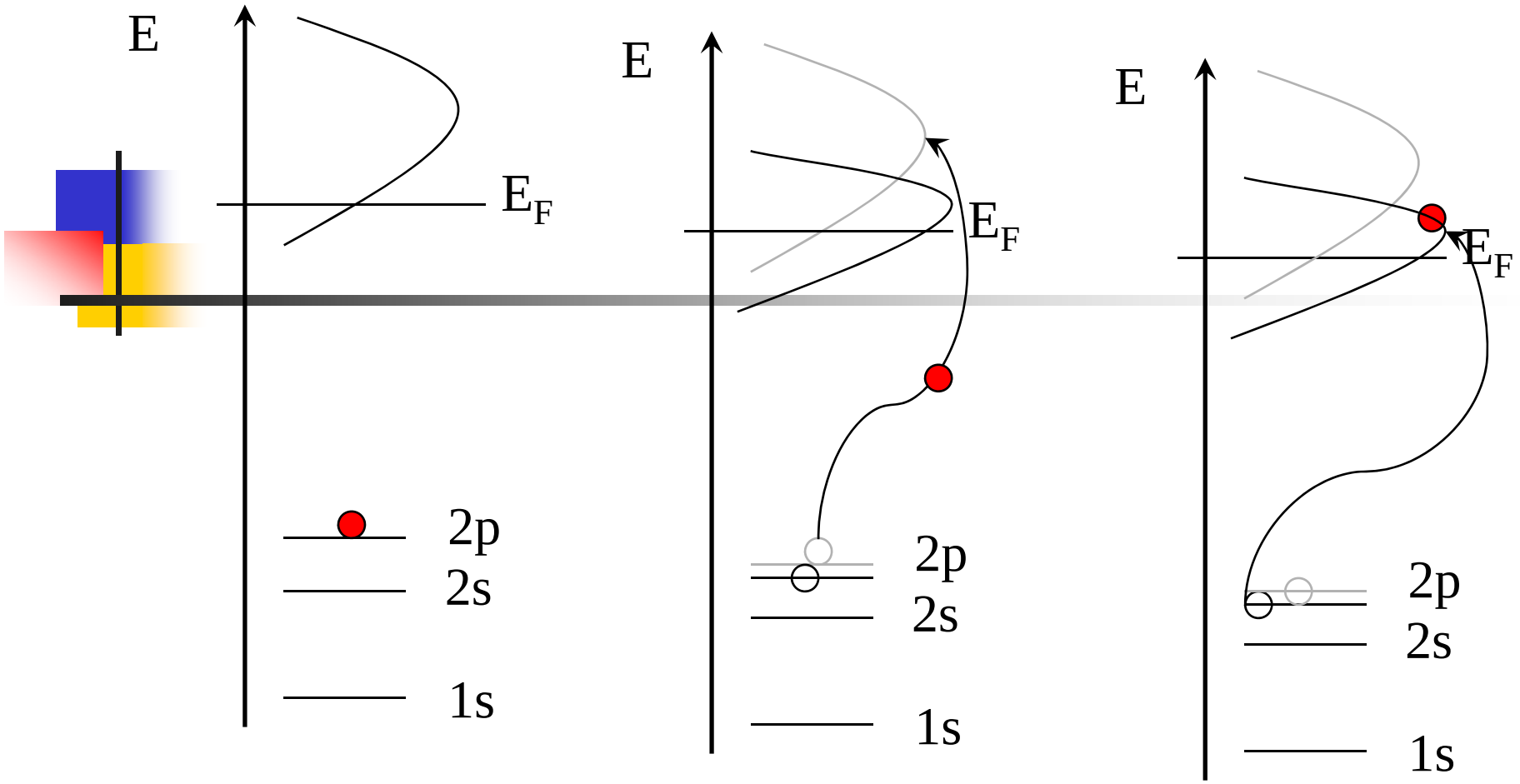

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}(E, \boldsymbol{q})$$

# Warning!

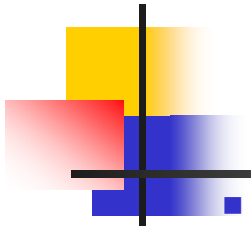


- ✗ DFT is a ground state theory !
- ➔ it should fail for the prediction of excited state properties
- ✔ *however: for many systems it works pretty well*

# The core hole



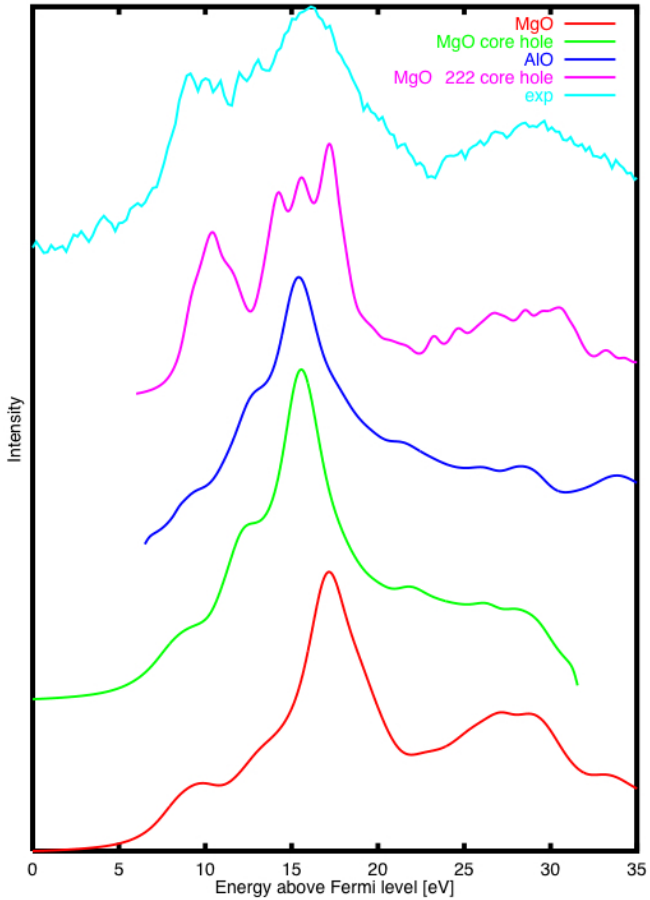
# Different ways of treating the core hole within WIEN2k



- 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



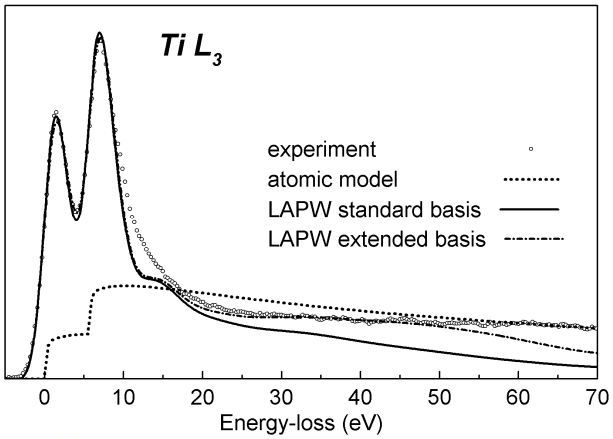

- mismatch between experiment and simulation
- introduction of core hole or Z+1 approximation does not help
- interaction between neighbouring core holes

➔ core hole in a supercell

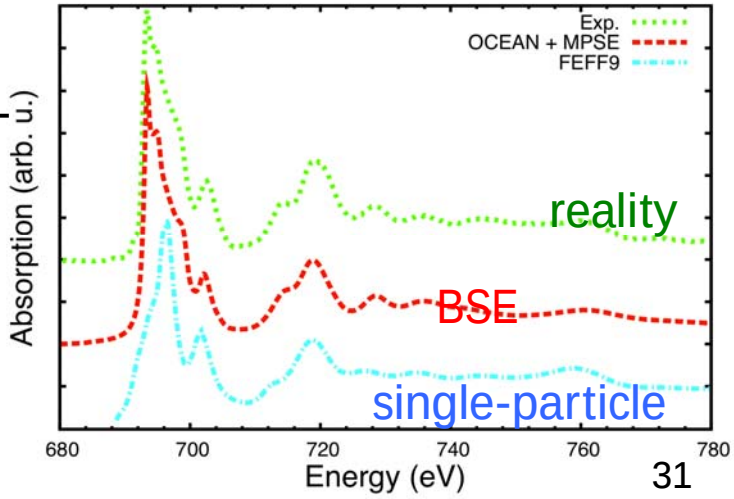
C. Hébert, J. Luitz, P. Schattschneider
Micron 34, 219 (2003)

# 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.

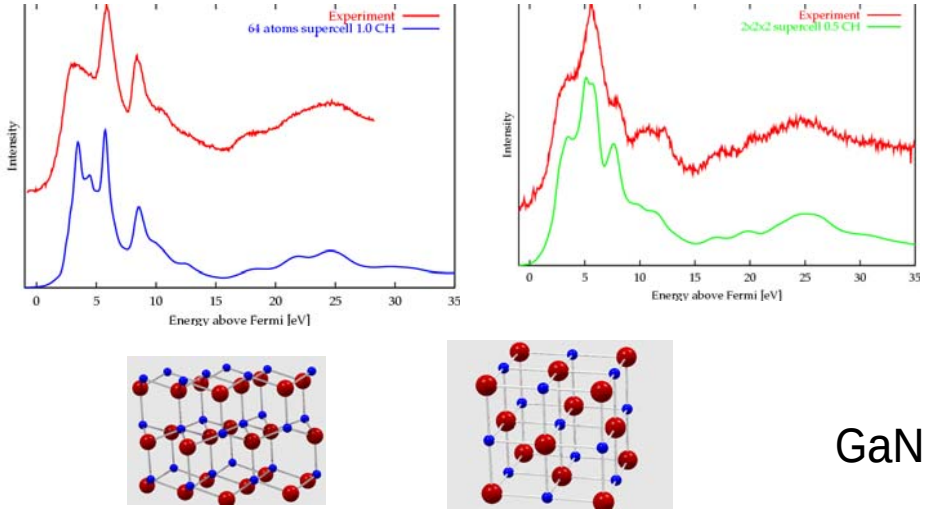



2. Sometimes Final State Rule (core hole) DFT just isn't good enough and you need Bethe-Salpeter (BSE) calculations
- codes : OCEAN, AI2NBSE, Exc!ting, "BSE"
- much more expensive
- not as "polished" as DFT
- gets L3/L2 ratios right

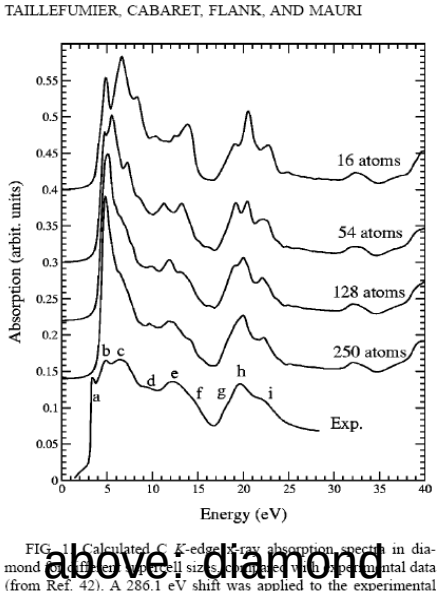


# Challenges of WIEN2k

3. 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

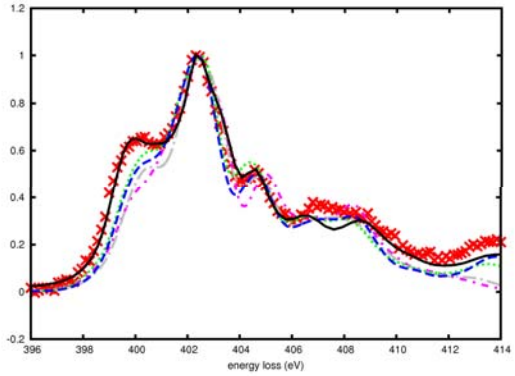



S. Lazar, C. Hébert, H. W. Zandbergen
Ultramicroscopy 98, 2-4, 249 (2004)

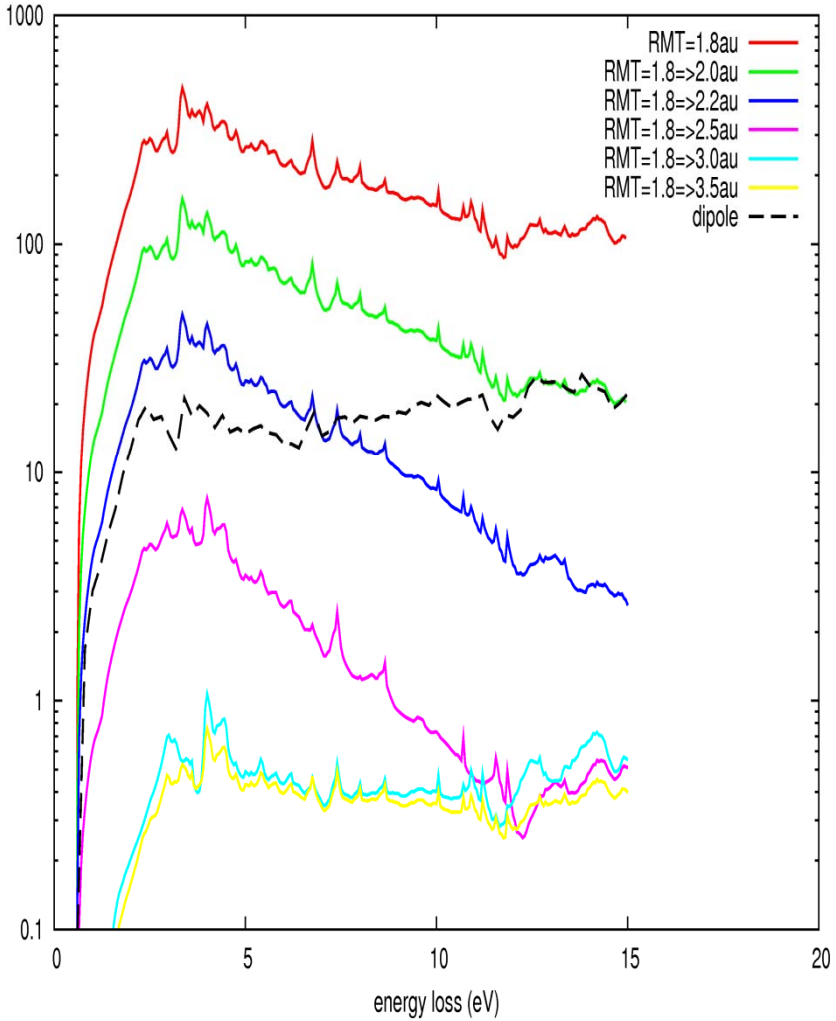


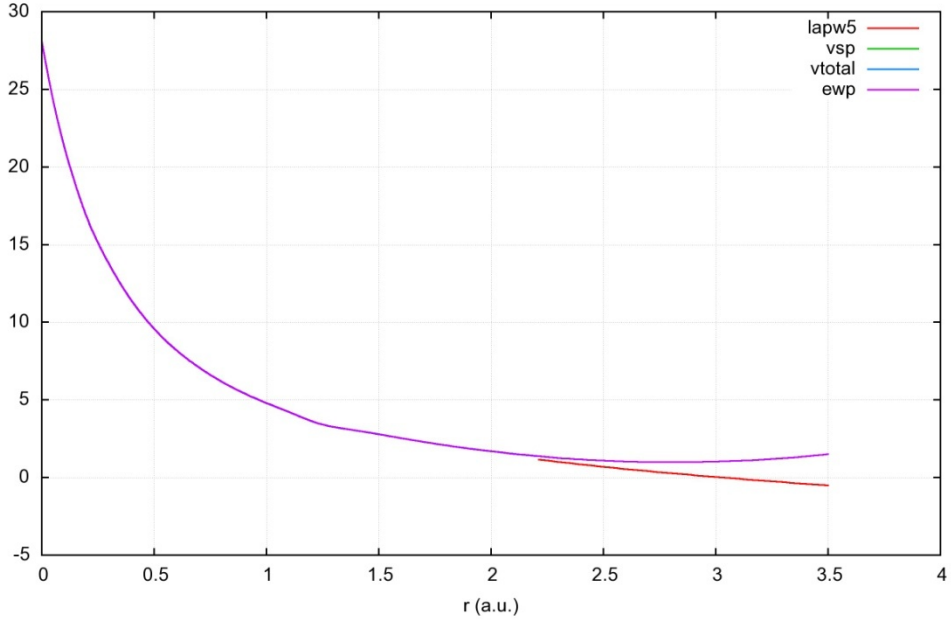

above: diamond

GaN N K edge



# 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.

# Thank you:

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- J. Rehr and the FEFF9 team
- WIEN2013 organizers