

IUCr Congress 2017.
XAFS Tutorial for Crystallographers.
Hyderabad Monday 21st August
XAFS Theory: XANES and EXAFS Spectra.

Chris. Chantler

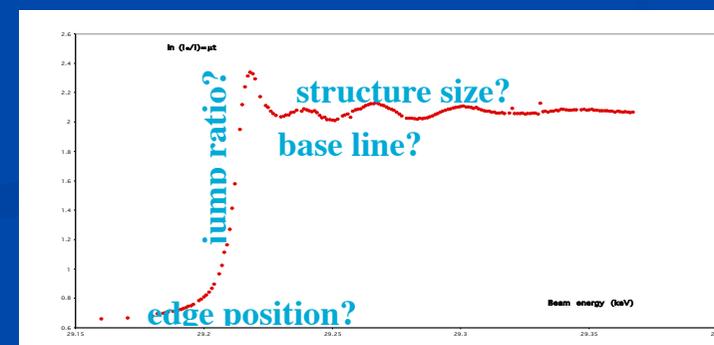
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[http://optics.ph.unimelb.edu.au/~chantler/
home.html](http://optics.ph.unimelb.edu.au/~chantler/home.html)



XAFS Theory: XANES and EXAFS Spectra

SESSION 1. Chair: Chris Chantler (Australia)

9:00 X-ray absorption spectroscopy for beginners. Overview - Farideh Jalilevand (Canada)

9:30 XAFS Theory: XANES and EXAFS Spectra – Chris Chantler (Australia)

10:00 Coffee

SESSION 2. Chair: Farideh Jalilevand (Canada)

10:30 XAS Experiment - Steve Heald (USA)

11:15 EXAFS Analysis - Boopesh Mishra (UK)

12:00 Summary of Software and Panel Discussion - Chris Chantler (Australia) and panel

12:20 Applications I: Materials - Guiliana Aquilanti (Elettra, Italy)

13:05 lunch

SESSION 3. Chair: Christopher Chantler (Australia)

14:55 Applications II: Biology - Ritimukta Sarangi (Stanford)

15:40 Applications III: Industry - Sohini Basu (Honeywell UOP, India)

16:00 Applications III: Environmental - Hugh Harris (Australia)

16:45 Proposal Preparation for Synchrotron Beamtime and Closing Notes – Chris Chantler (Australia) [Bruce Ravel]

16:55 Workshop Close. Congress Reception!

IUCr 2017. XAFS Tutorial. C.T. Chantler

XAFS Theory: XANES and EXAFS Spectra

Thanks for this initiative:

IUCr Commission on XAFS

International X-ray Absorption Society

IUCr Local Organising Committee

IUCr Congress

**Farideh Jalilehvand, Bruce Ravel, Dibyendu
Bhattacharyya**

All organisers, executive, etc.

Session leaders and presenters at IUCr Congress

Continuing engagement, collegial development



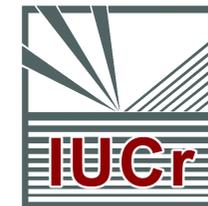
International Tables for Crystallography

Volume I

X-ray Absorption Spectroscopy

Editors: Chris Chantler, Federico Boscherini,
Bruce Bunker

1. Introduction
2. XAS Theory
3. Experimental Methods
4. Pre-processing of Experimental Data
5. Overview of Analysis of Experimental Data
6. Data Reduction, Theoretical Prediction and Data Analysis
7. Exchange of Data and Processed Outputs, Deposition
8. Applications



Volume I

- What [old and new] things can we do with XAS that we could not before, how can we do them, and what standards can we use?
- Research in core physics and condensed matter science are increasingly relevant for diverse fields
- Applications in chemistry, engineering and biological sciences, linking to experimental research at synchrotrons, reactors and specialized facilities
- A plethora of different approaches are popular in the literature
- The Volume will hope to capture great achievements and value by representation of leading groups from Europe, America, Asia, Australia plus elsewhere!
- traditional and new experiments, theory, analysis

Recent New Fields

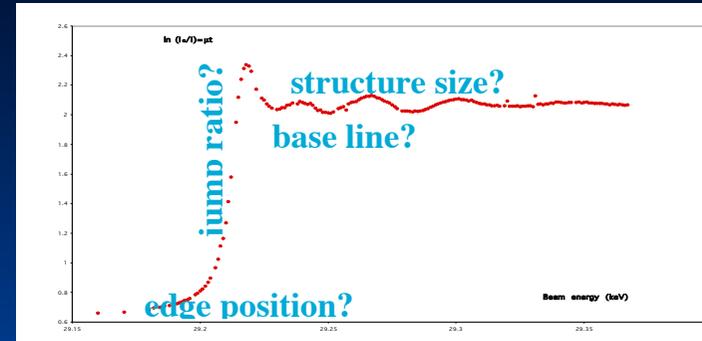
- Resonant Inelastic X-ray Scattering (Glatzel, numerous other groups, several important variant techniques) - scattering and resonant analysis; huge information content; complex but successful theory; insight well below hole width limits
- Ultra-fast XAS (Frahm, XFELs, MaxLab; SLS; Tsukuba) - dynamic processes; direct observation of catalysis; phase changes; ...
- X-ray Emission Spectroscopy - electronic structure, X-ray Raman spectroscopy...
- X-ray Excited Optical Luminescence - site specificity, optical properties
- High Energy Resolution Fluorescence - reduced lifetime broadening



VOTE MELBOURNE, AUSTRALIA
IUCr 2023



XAFS Theory: XANES and EXAFS Spectra



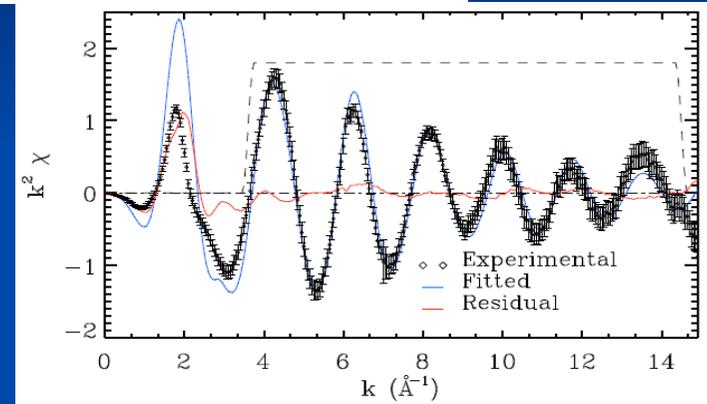
1. Why XAFS?
2. What is XAFS?
3. How does XAFS work?

Difficulties

Links with Crystallography

Realisation: A: Absorption

Realisation: B: Fluorescence



XAFS Theory: XANES and EXAFS Spectra

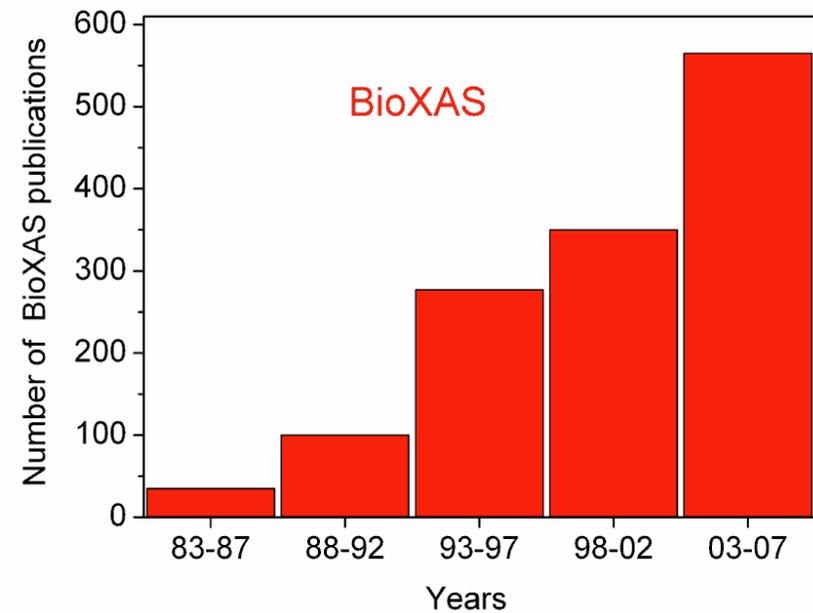
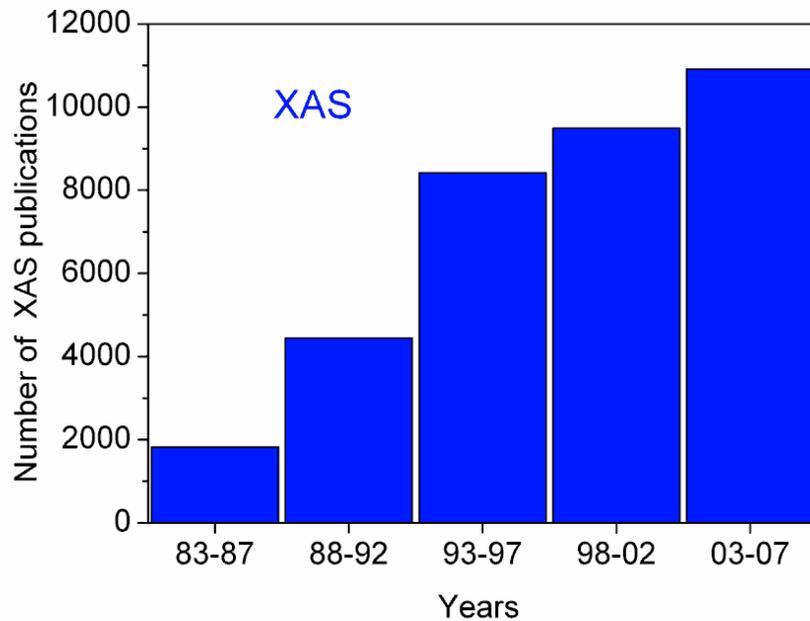
1. Why XAFS?

- **Crystallography - periodicity, symmetry and mean structure of perfect crystals [X-ray; Electron Diffraction; Neutron Diffraction]**
- **Nanocrystallites in advanced synchrotron beams; or [X-ray] Powder Diffraction**
- **TEM etc. of surfaces or slices [destructive].**
- **Great difficulties for disordered systems; solutions; dilute systems; local order; dynamic bond lengths; active centres.**
- **X-ray Absorption Fine Structure [XAFS] deals directly with these questions and more.**
- **Complementary for complex systems, organometallics, bioactive systems, ideal crystals or metals**

XAFS Theory: XANES and EXAFS Spectra

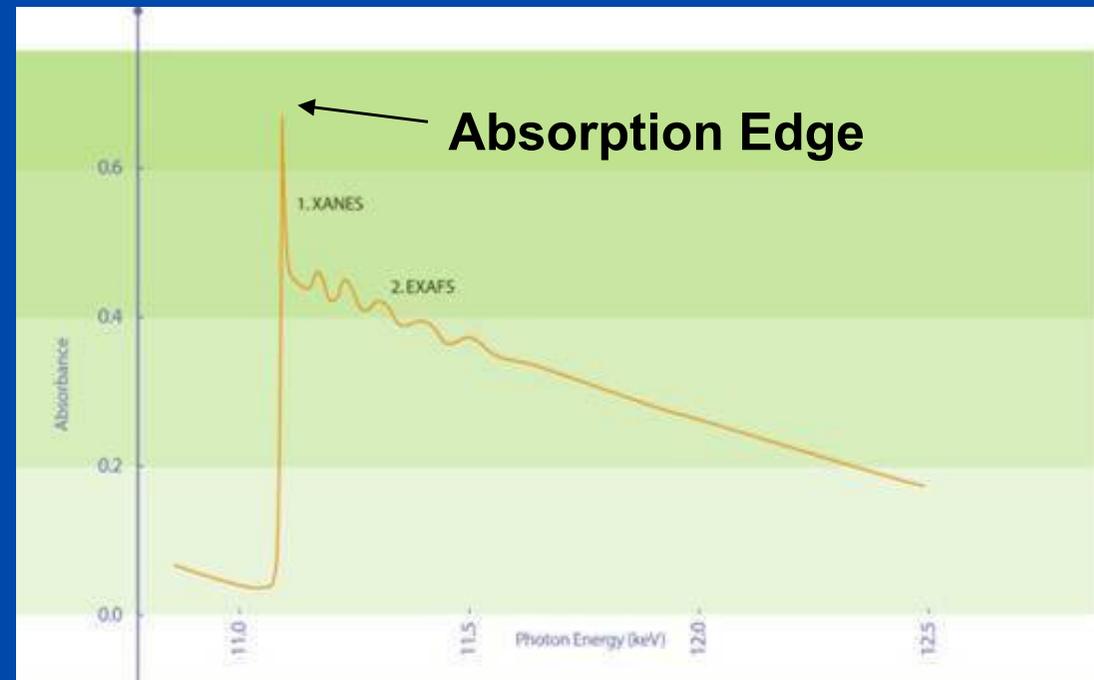
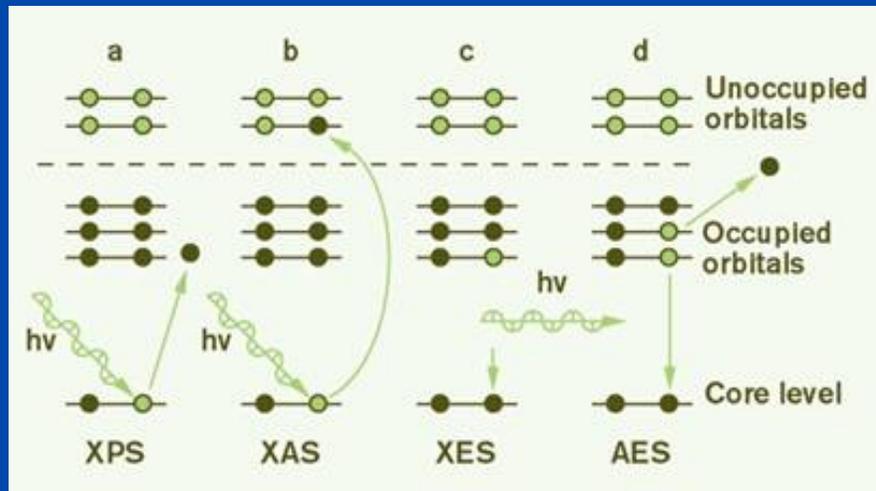
1. Why XAFS?

- Recent advances in synchrotron techniques,
- new opportunities in organometallic materials,
- dynamic bond investigation,
- thermal dependence of structure [especially disordered],
- complex phase systems
- cluster studies
- >12000 papers in the last 5 years.



Application to physics, earth science, chemistry and biology
Ascone et al. (2009). Journal of Synchrotron Radiation 16, 413-42

Spectroscopy

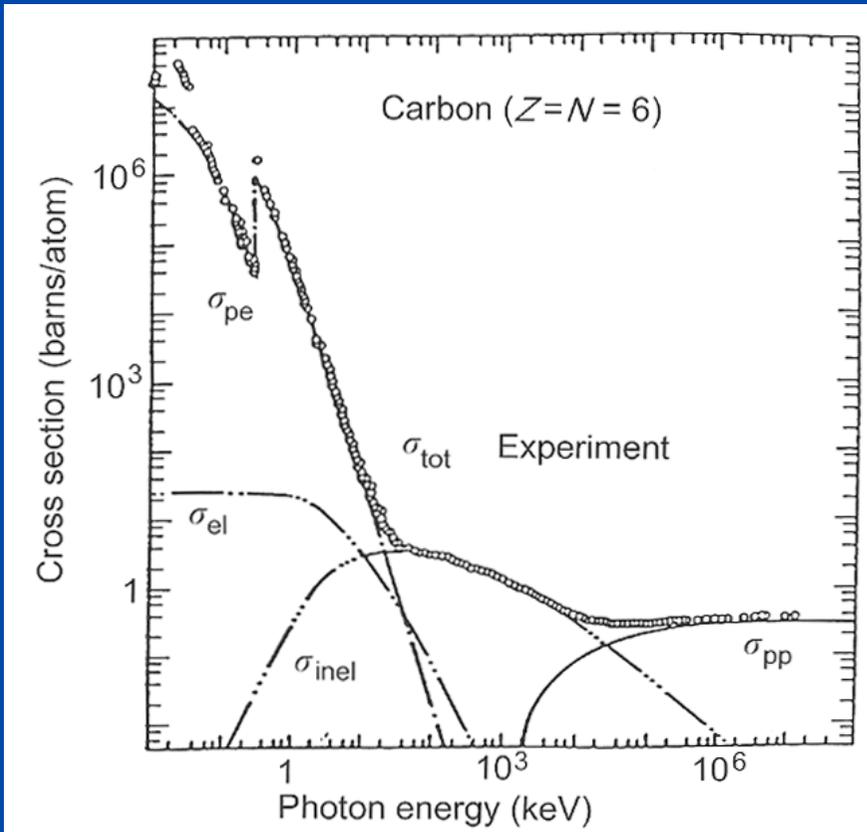


Changes in electron state when a photon is absorbed by an atom.

These mechanisms enable:

- a) x-ray photoelectron spectroscopy
- b) x-ray absorption spectroscopy
- c) x-ray emission spectroscopy
- d) auger electron spectroscopy

X-ray and photon interaction processes



Interactions include:

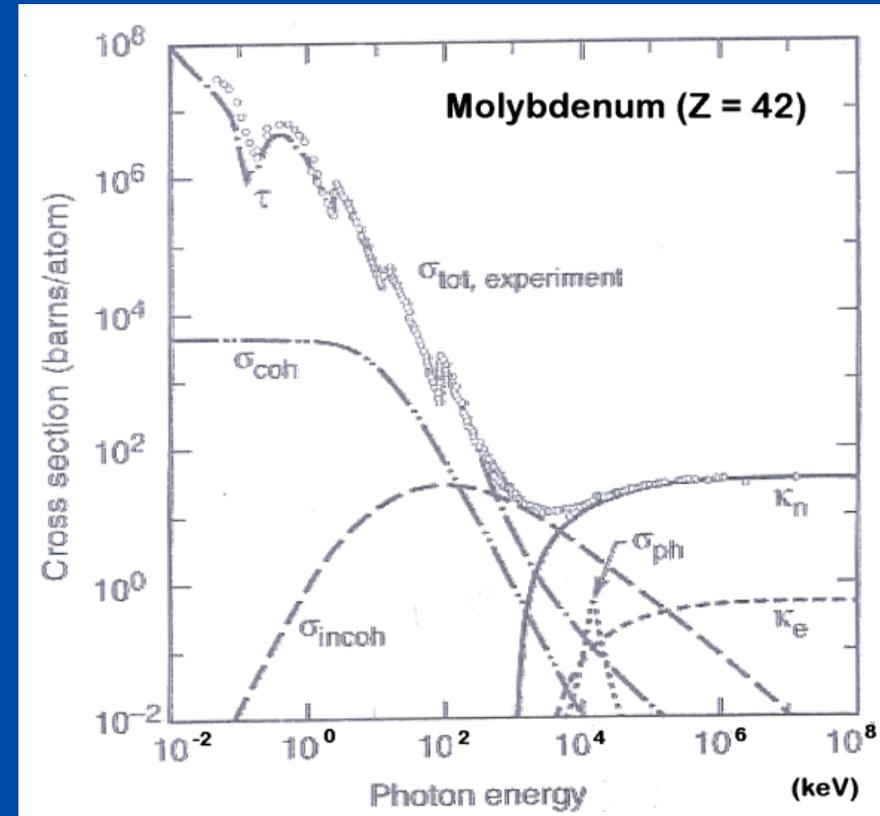
photoelectric absorption σ_{pe}, τ

inelastic scattering (Compton Effect) σ_{inel} (incoh)

including X-ray fluorescence

elastic scattering (Rayleigh) σ_{el} (coh)

pair production σ_{pp} (κ)



Links: X-ray Absorption Fine Structure and Crystallography Photoelectric Absorption; Coherent (elastic) Scattering; Inelastic (Compton) Scattering [e.g. Hubbell...]

Cross-sections (barns/atom): $\sigma_{tot} = \tau_{PE} + \sigma_{coh} + \sigma_{incoh} + \mathcal{K}_n + \mathcal{K}_e + \sigma_{p.n.}$

X-ray Absorption:

$$\tau_{PE}(E) = 2hcr_e \text{Im}(f) / E$$

mass absorption coefficient (cm²/g): $[\mu_{PE} / \rho](E) = \tau_{PE} / (uA)$

linear absorption coefficient (cm⁻¹): $\mu_{PE} = [\mu_{PE} / \rho]\rho$

Coherent (Rayleigh) scattering:

$$\sigma_{coh, Rayleigh} = \pi r_e^2 \int_{-1}^1 (1 + \cos^2 \theta) f^2(q, Z) d(\cos \theta)$$

Coherent (Bragg-Laue) scattering:

$$\sigma_{coh, BL} = \left(\frac{r_e^2 \lambda^2}{2NV_c} \right) \sum_H \left[\left(\frac{1 + \cos^2 \theta}{2} \right) md |F|^2 \right]_H$$

$$F(hkl) = \sum_j f_j e^{-M_j} e^{2\pi i(hx_j + ky_j + lz_j)}, (TDS = 0)$$

Coherent (Thermal Diffuse) Scattering:

$$\sigma_{coh, TDS} = \left(\frac{r_e^2 \lambda^2}{2NV_c} \right) \sum_H \left[\left(\frac{1 + \cos^2 \theta}{2} \right) md |F|^2 \{1 - e^{-2M}\} \right]_H$$

Inelastic (Compton):

$$\sigma_{incoh, Compton} = \pi r_e^2 \int_{-1}^1 \left(\frac{1 + \cos^2 \theta + \frac{k^2 (1 - \cos \theta)^2}{1 + k(1 - \cos \theta)}}{(1 + k(1 - \cos \theta))^2} \right) S(q, Z) d(\cos \theta), k = \frac{\hbar \omega}{mc^2}$$

Klein-Nishina (free electron)

$$I_e = I_0 r_e^2 \left[\frac{1 + \cos^2 \theta}{2} \right]$$

\mathcal{K}_n nuclear-field pair production \mathcal{K}_e triplet production $\sigma_{p.n.}$ photonuclear absorption

Links: X-ray Absorption Fine Structure and Crystallography ATTENUATION & THE (X-RAY) ATOMIC FORM FACTOR: One Example of usage: FFAST:

$$\mu_{PE}(E) = f_2(E)2hcr_0 / E$$

$$[\mu_{PE} / \rho](E) = \sigma_{PE} / (uA)$$

$$\text{Im}(f) = f''(E) = f_2(E) = \frac{E\mu_{PE}(E)}{2hcr_e}$$

$$\text{Re}(f) = f_0 + f' + f_{NT}, f' = f_1 + f_{rel} - Z$$

$$f_0(q, Z) = 4\pi \int_0^\infty \frac{\rho(r) \sin(qr) r^2 dr}{qr}$$

<http://physics.nist.gov/PhysRefData/FFast/Text/cover.html>

Chantler, CT, Olsen, K, et al. (2005) X-Ray Form Factor, Attenuation & Scattering Tables (v2.1) [Online]; Chantler, CT, JPhysChemRefData 29(4), 597-1048 (2000); Chantler, CT, JPhysChemRefData 24, 71-643 (1995).



[Version History - Disclaimer](#)

X-Ray Form Factor, Attenuation, and Scattering Tables

Detailed Tabulation of Atomic Form Factors, Photoelectric Absorption and Scattering Cross Section, and Mass Attenuation Coefficients for $Z = 1-92$ from $E = 1-10$ eV to $E = 0.4-1.0$ MeV

C.T. Chantler,¹ K. Olsen,² R.A. Dragoset,² J. Chang,² A.R. Kishore,² S.A. Kotochigova,² and D.S. Zucker²

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²NIST, Physics Laboratory, Office of Electronic Commerce in Scientific and Engineering Data

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[Database Search Form](#)

Updated values May 2003, see [Version History](#)

[Note on NIST X-ray Attenuation Databases](#)

Example of how to reference this online database: Chantler, C.T., Olsen, K., Dragoset, R.A., Chang, J., Kishore, A.R., Kotochigova, S.A., and Zucker, D.S. (2005), X-Ray Form Factor, Attenuation and Scattering Tables (version 2.1). [Online] Available: <http://physics.nist.gov/ffast> [2008, January 21]. National Institute of Standards and Technology, Gaithersburg, MD. Originally published as Chantler, C.T., J. Phys. Chem. Ref. Data 29(4), 597-1048 (2000); and Chantler, C.T., J. Phys. Chem. Ref. Data 24, 71-643 (1995).

Tables for form factors and anomalous dispersion are of wide general use in the UV, x-ray and γ -ray communities, and have existed for a considerable period of time. Much of the recent theoretical basis for these was contributed by Cromer, Mann and Liberman while much of the experimental data was synthesised by Henke et al. More recent developments in both areas have led to new and revised tables. The generality of these works has entailed numerous simplifications compared to detailed relativistic S-matrix calculations; however, the latter do not appear to give convenient tabular application for the range of Z and energy of general interest. Conversely, the former tables appear to have large regions of limited validity throughout the range of Z and energies, and in particular have limitations with regard to extrapolation to energies outside tabulated ranges.

Herein, the primary interactions of x-rays with isolated atoms from $Z = 1$ (hydrogen) to $Z = 92$ (uranium) are described and computed within a self-consistent Dirac-Hartree-Fock framework. This has general application across the range of energy from 1-10 eV to 400-1000 keV, with limitations (described below) as the low- and high-energy extremes are approached. Tabulations are provided for the f_1 and f_2 components of the form factors, together with the photoelectric attenuation coefficient for the atom, μ , and the value for the K-shell, μ_K , as functions of energy and wavelength. Also provided are estimated correction factors as described in the text, conversion factors, and a simple estimate for the sum of the scattering contributions (from an isolated atom).

Revised formulae can lead to significant qualitative and quantitative improvement, particularly above 30 keV to 60 keV energies, near absorption edges, and at 0.03 keV to 3 keV energies. Recent experimental syntheses are often complementary to this approach. Examples are given where the predictions underlying revised theoretical tables are in qualitative agreement with experiment, as opposed to results in experimental syntheses.

Links: X-ray Absorption Fine Structure and Crystallography (X-RAY)

ATOMIC FORM FACTOR: Resonant scattering amplitude of X-rays by charge (electron) density

$$\text{Re}(f) = f_0 + f' + f_{NT}, f' = f_1 + f_{rel} - Z$$

$$f_0(q, Z) = 4\pi \int_0^\infty \frac{\rho(r) \sin(qr) r^2 dr}{qr}$$

$$f'(E, Z) = f'(\infty) - \frac{2}{\pi} P \int_0^\infty \frac{\epsilon' f''(\epsilon')}{E^2 - (\epsilon')^2} d\epsilon'$$

$$\text{Im}(f) = f''(E) = f_2(E) = \frac{E \mu_{PE}(E)}{2hc r_e}$$

‘normal’ coherent scattering factor

‘anomalous’ scattering factor

Utility: X-ray Diffraction experiments, Crystallography...

$$F(hkl) = \sum_j f_j e^{-M_j} e^{2\pi i(hx_j + ky_j + lz_j)}, (TDS = 0)$$

Electronic wavefunction distribution, bonding...

$$\Delta\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l \Delta F(hkl) e^{-2\pi i(hx + ky + lz)}$$

VUV research, multilayer modelling, critical angle spectroscopy...

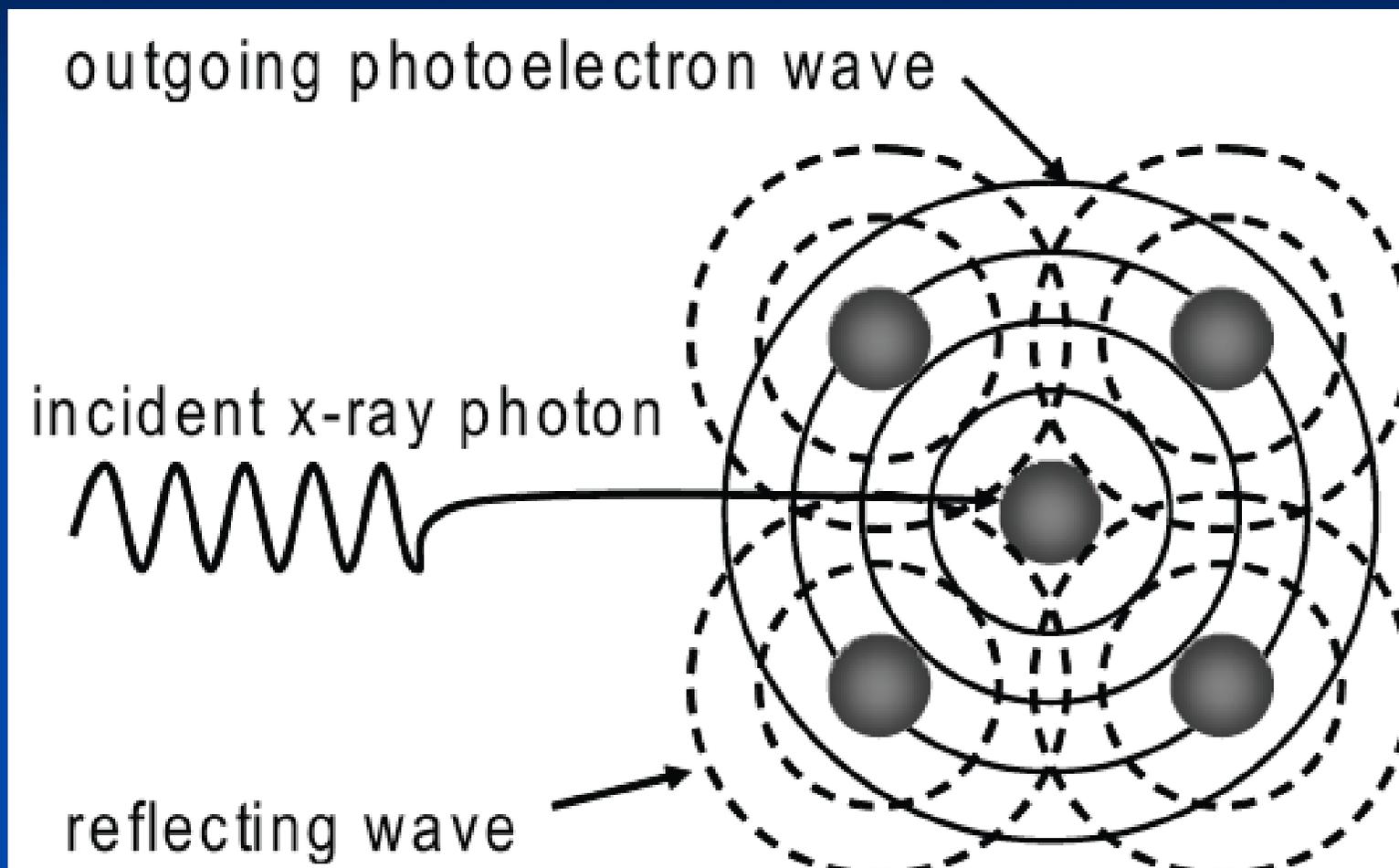
$$n_r = n + ik = \sqrt{\epsilon} = 1 - \delta - i\beta = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_j n_j f_j \quad n_j \text{ atom number density; } r_0 \text{ classical electron radius}$$

Transmission, attenuation experiments... $\mu_{PE}(E) = f_2(E) 2hc r_0 / E$

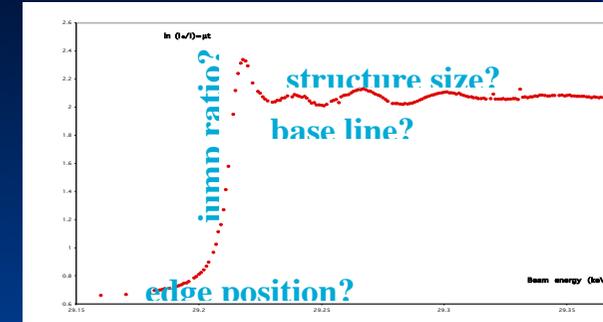
Electron form factor (Mott-Bethe)... $f^B(q, Z) = \frac{me^2}{2\pi\hbar^2\epsilon_0} \left\{ \frac{Z - f(q, Z)}{q^2} \right\}$

XAFS Theory: XANES and EXAFS Spectra

XAFS, XANES, XERT



XAFS Theory: XANES and EXAFS Spectra



2. What is X-ray Absorption Fine Structure XAFS?

- sharp oscillations in Absorption above a absorption edge [K, L_I, L_{II}, L_{III}, M...] of an element [Fe, Cu, Ni, C, Mo, Au, ...] in a material
- creation of electron holes in 1s, 2s, 2p_{1/2}, 2p_{3/2}
- The material may be an ideal crystal or metal, a nanocrystal or powder, or a non-ideal mixture or dilute solution.

See IUCr Commission on XAFS Definitions: <http://www.iucr.org/resources/commissions/xafs/xafs-related-definitions-for-the-iucr-dictionary> See also: <http://www.iucr.org/>

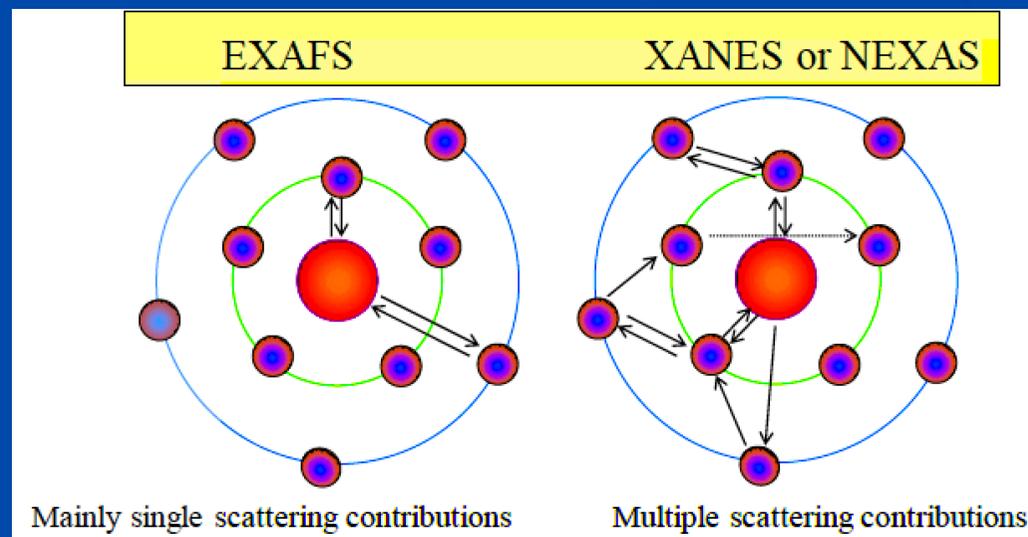
XAFS Theory: XANES and EXAFS Spectra

2. What is XAFS?

- modulation of absorption coefficient due to chemical state & structure of immediate surroundings.
- ‘near edge’ region (XANES or NEXAFS) to ~ 50 eV above the absorption edge
- ‘extended’ region (EXAFS) giving oscillations in the absorption coefficient from ~ 50 eV.

• XANES (X-ray Absorption Near Edge Spectroscopy) for X-ray edges (~ 1 keV and above); NEXAFS (Near-edge X-ray Absorption Fine Structure) for soft X-ray edges.

• Spectral features before the main absorption edge - ‘pre-edge’ features - are associated with transitions to bound states.



MODERN QUANTITATIVE THEORY – FMS

MULTIPLE SCATTERING

- Start with Fermi's Golden Rule:

$$\mu \propto \sum_f \left| \langle \psi_i | d | \psi_f \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

- Final (excited) state wavefunctions are difficult to treat directly in an arbitrary solid
- Use a trick: expand out...

$$\mu \propto \langle \psi_i | d \sum_f | \psi_f \rangle \langle \psi_f | \delta(E_f - E_i - \hbar\omega) d^* | \psi_i \rangle$$

$$\mu \propto -\frac{1}{\pi} \text{Im} \langle \psi_i | d G(\omega) d^* | \psi_i \rangle$$

MODERN QUANTITATIVE THEORY – FMS

- Green's function propagator:

$$G = [E - H_0 - V]^{-1}$$

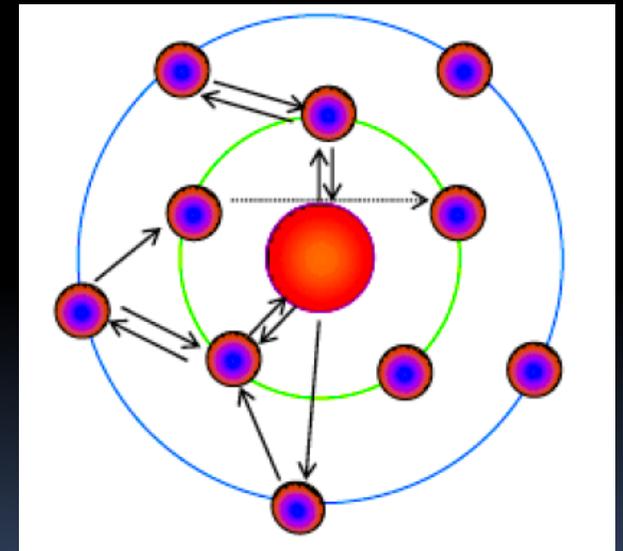
$$= [E - H_0]^{-1} \left\{ 1 + V(E - H_0)^{-1} + [V(E - H_0)^{-1}]^2 + \dots \right\}$$

$$G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \dots$$

- Muffin-tin approximation – V 's become site based block diagonal matrices T

$$G = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \dots$$

$$G(\omega) = [1 - G_0 T]^{-1} G_0$$



FULL MULTIPLE SCATTERING

* c/o Josh Kas, University of Washington

FDMNES – METHOD OF CALCULATION

- Sum over transition amplitudes

$$M_{gf} = \langle \psi_f | \boldsymbol{\varepsilon} \cdot \boldsymbol{r} \left(1 + \frac{i}{2} \boldsymbol{k} \cdot \boldsymbol{r} \right) | \psi_g \rangle$$

- To evaluate optical cross section

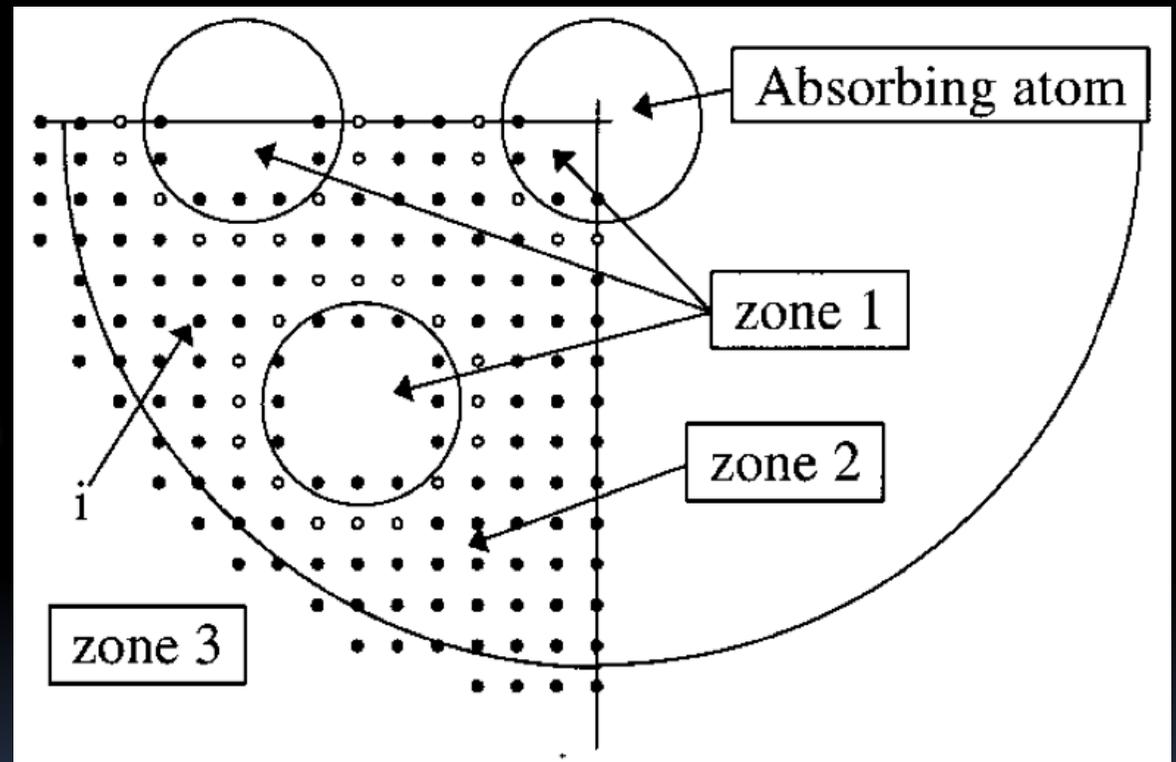
$$\sigma = 4\pi^2 \alpha \hbar \omega \sum_{f,g} |M_{gf}|^2 \delta(\hbar\omega - E_f + E_g)$$

- Require wavefunctions for final and initial states
- Initial state is a ground state – calculated atomistically with relativistic corrections
- Final state determined using the FDM

FDMNES – METHOD OF CALCULATION

- Cluster broken up into three zones – (1) near cores (small), (2) interstitial, (3) outside cluster

- Wave functions in zone 1 constructed from spherical harmonics, in zone 3 from Neumann and Bessel functions



- In zone 2 the FDM is used to determine the final-state photoelectron wave function

FDMNES – METHOD OF CALCULATION

- Potential in interstitial region may be determined from DFT internally or externally (WIEN2k), or from electron density values with exchange+correlation correction
- Once potential is found, evaluate wavefunctions using discretized Schrodinger Equation:

$$\nabla^2 \psi_i = \frac{1}{h^2} \left(\frac{4}{3} \sum_{j,\varepsilon} \psi_j^\varepsilon - \frac{1}{12} \sum_{j,\varepsilon} \psi_j^{\varepsilon\varepsilon} - \frac{15}{2} \psi_i \right)$$

$$(-\nabla^2 + V_i - E) \psi_i + \sum_j (-\nabla^2 \psi_j) = 0$$

FDMNES – EXAMPLES AND HANDS-ON

•/fdmnes/fdmfile.txt

```
fdmfile.txt
! General indata file for FDMNES
! with indata files examples

1
entree/test_stand/cu_inp2.txt

entree/test_stand/vo6_inp.txt
entree/test_stand/vo6_conv_inp.txt
entree/test_stand/vo6_nodipole_inp.txt
entree/test_stand/feo6_inp.txt
entree/test_stand/ni_inp.txt
entree/test_stand/ni_mg_inp.txt
entree/test_stand/v2o3_inp.txt
entree/test_stand/gan_inp.txt
entree/test_stand/fe3o4_inp.txt
entree/test_stand/fe3o4_dd_inp.txt
entree/test_stand/cr_inp.txt
entree/test_stand/cr_conv_inp.txt
entree/test_stand/ba2znuo6_inp.txt
entree/test_stand/ca3co2o6_inp.txt
entree/test_stand/fe2o3_inp.txt
entree/test_stand/fe2o3_selec_inp.txt
entree/test_stand/fe2o3_scf_inp.txt
entree/test_stand/fe2o3_hub_inp.txt
entree/test_stand/fe_bio_inp.txt
entree/test_stand/ndmg_inp.txt
entree/test_stand/pt13_inp.txt
entree/test_stand/mult_inp.txt
entree/test_stand/cuo_inp.txt
```

•/fdmnes/entree/
cu_inp.txt

```
cu_inp.txt
! Fdmnes indata file
! Calculation for the copper K-edge in copper cfc
! Finite difference method calculation with convolution

Filout
  xanout/test_stand/cu

Range          ! Energy range of calculation (eV)
-10. 0.2  0. 0.5 10. 1. 40. ! first energy, step, intermediary energy, step ..., last energy

Radius          ! Radius of the cluster where final state calculation is performed
  3.0           ! For a good calculation, this radius must be increased up to 6 or 7 Angstroms

Crystal         ! Periodic material description (unit cell)
  3.61  3.61  3.61  90. 90. 90. ! a, b, c, (Angstroem) alpha, beta, gamma (degree)
29  0.0  0.0  0.0           ! Z, x, y, z (unit cell unit)
29  0.5  0.5  0.0
29  0.5  0.0  0.5
29  0.0  0.5  0.5

! Convolution keyword : broadening with a width increasing versus energy as an arctangent

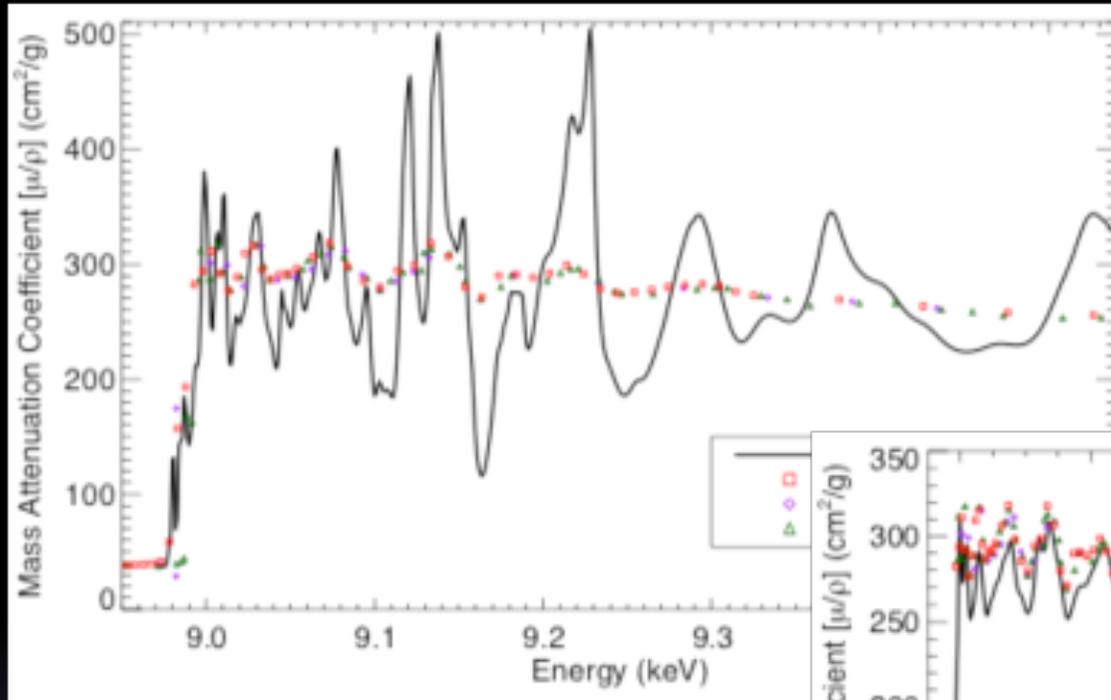
Convolution

End
```

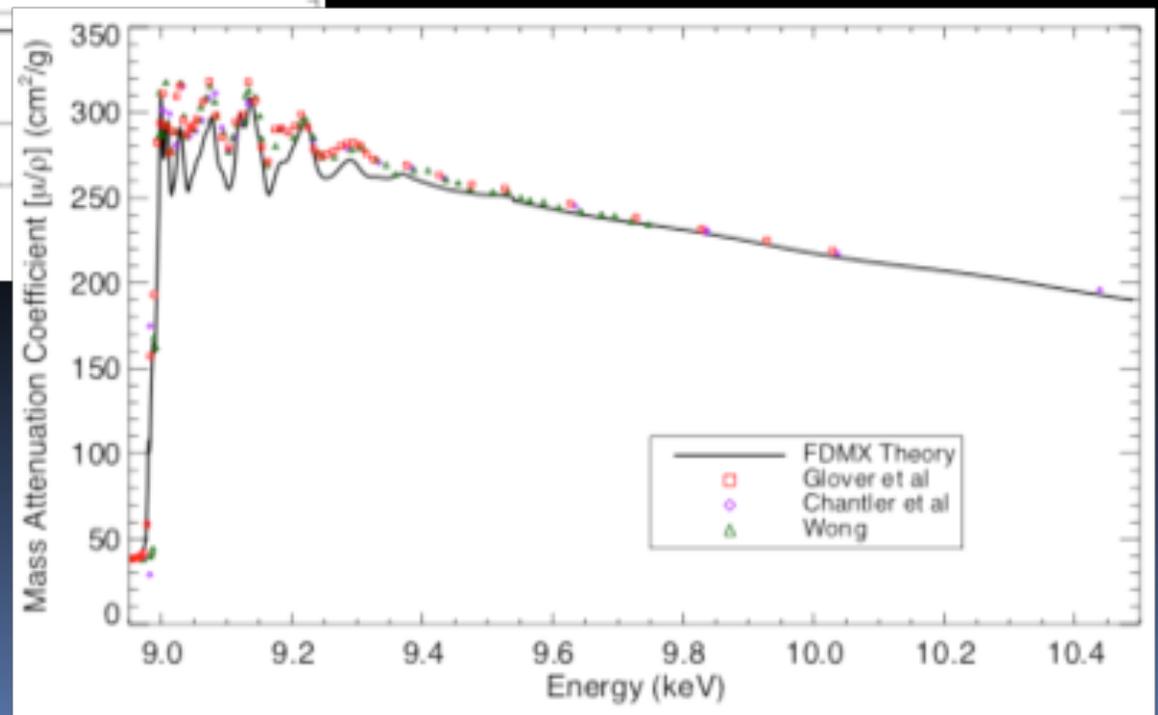
•Run
FDMNES.exe

FDMX OVERVIEW AND PURPOSE

- In a nutshell... we want to turn this:

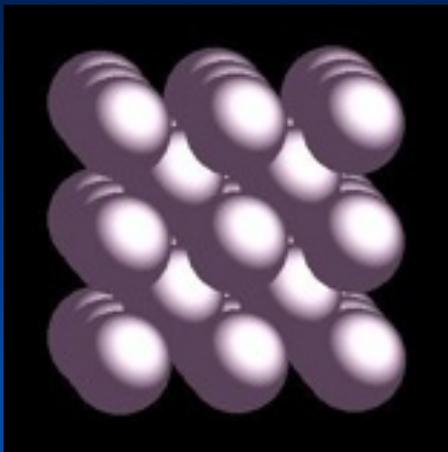


- Into this →



3. How does XAFS work?

Local Structure Guess



Metallic Molybdenum:
BCC Crystal

Program?

Model of XAFS Spectrum (XAFS Equation)

$$\chi_{th}(k) = \sum_j N_j S_0^2 F_j(k) \frac{\sin(2kr_j + \phi_j(k))}{kr_j^2} e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)}$$

$$r_j = (1 + \alpha)r_{0,j}$$

Expansion
Coefficient

Distance To
Coordination Shell
Based On Input

Backscattering
Amplitude and Phase

Many Body
Reduction
Factor

Coordination
Numbers

Mean
Free
Path

Debye-Waller
Factor

FDMX METHOD OF CALCULATION

- Inclusion of thermal disorder

$$\chi_j(k) = \dots e^{(-2\sigma_j^2 k^2)}$$

- Require *relative* mean-square displacement of neighbour atoms along a photoelectron scattering path R_j

$$\sigma_j^2 = \langle (u_0 \cdot R_j)^2 \rangle + \langle (u_j \cdot R_j)^2 \rangle - 2 \langle (u_0 \cdot R_j) \cdot (u_j \cdot R_j)^2 \rangle$$

- For N atoms of mass M in a crystal with resonant phonons of energy $\hbar\omega_{q\lambda}$, express as:

$$\sigma_j^2 = \frac{\hbar}{NM} \sum_{q\lambda} (e_{q\lambda} \cdot R_j)^2 \frac{1}{\omega_{q\lambda}} \left(\coth \left(\frac{\omega_{q\lambda}}{2k_B T} \right) \right) [1 - \cos(q \cdot R_j)]$$

* Gruneisen & Goens, *Z. Phys.* **29** 141(1924)

* Kittel, *Introduction to Solid State Physics*, Wiley, 1996

FDMX METHOD OF CALCULATION

- Substituting $\omega_{q\lambda}$ values from Debye Model, and Taylor expanding coth term enables “simple” equation for a correlated Debye model: Beni-Platzmann theory

$$\sigma_j^2 = \frac{6\hbar}{m\omega_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 D_1 \right] - \frac{6\hbar}{m\omega_D} \left\{ \frac{1 - \cos(q_D r_j)}{2(q_D r_j)^2} + \left(\frac{T}{\theta_D} \right)^2 \left[D_1 - \frac{1}{3!} \left(q_D r_j \frac{T}{\theta_D} \right)^2 D_3 + \frac{1}{5!} \left(q_D r_j \frac{T}{\theta_D} \right)^4 D_5 - \dots \right] \right\}$$

$$\omega_D = \frac{\theta_D k_B}{\hbar}$$

$$q_D = \left(\frac{6\pi^2}{V} \right)^{1/3}$$

$$D_n = \int_0^{\theta_D/T} \frac{x^n}{e^x - 1} dx$$

- Enables efficient calculation of Debye-Waller factor σ^2 for each atom in a cluster
- Only approximates density of phonon states – full account may be implemented with DFT but much more complex/inefficient!

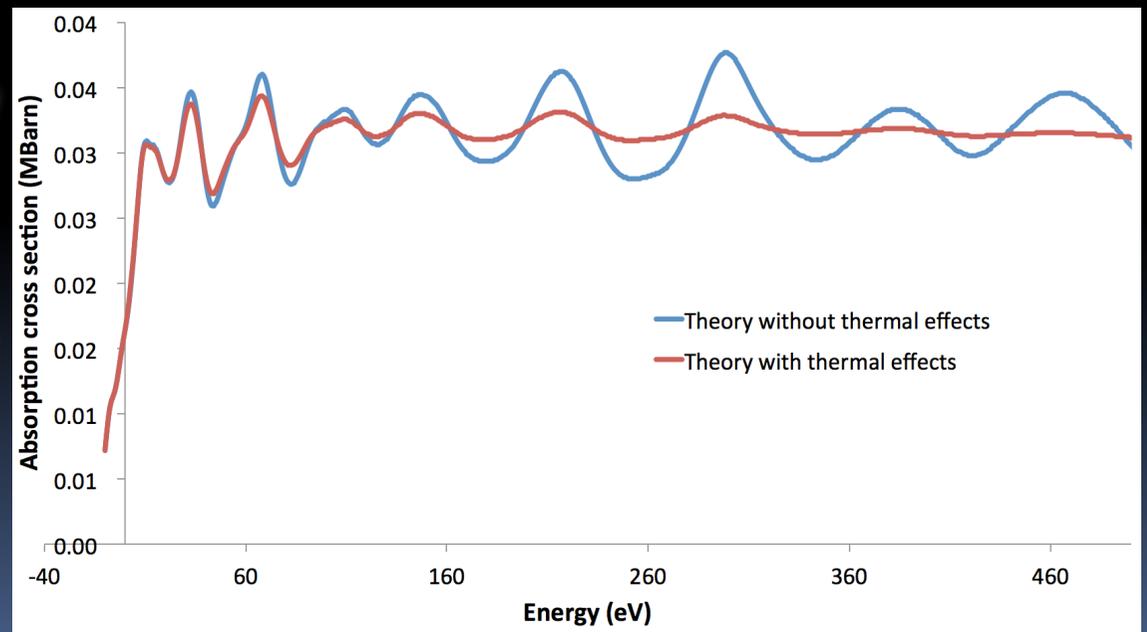
FDMX METHOD OF CALCULATION

- First order correction from nearest-neighbour (dominant) Debye-Waller factor

$$\chi_j(k) \rightarrow \chi_j(k)e^{(-2\sigma_j^2 k^2)}$$

- Accurate at high energies – area of maximum importance

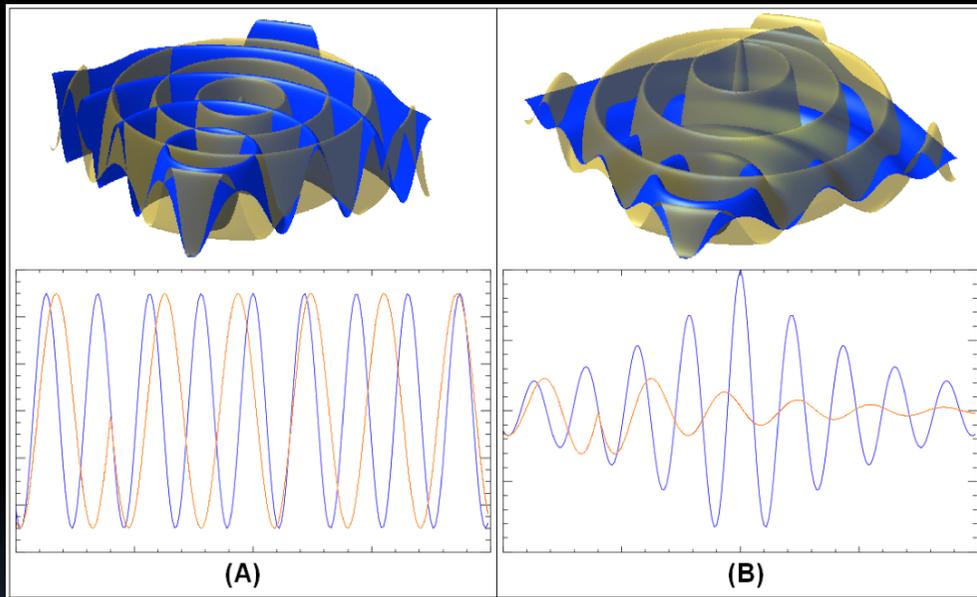
- Underestimate at low energies, but not a dominant effect in this region (i.e. compare with IMFPs, potential shape etc.)



FDMX METHOD OF CALCULATION

- Inelastic scattering causes an energy-dependent broadening of the XAFS

$$\Gamma(E) = \frac{\hbar}{\lambda(E)} \sqrt{\frac{2E}{m}} + \Gamma_H$$



- Core-hole lifetime also included
- Strong effect beyond 10 eV

- Use many-pole optical data model and generalized theory of Tanuma et al.

* S. Tanuma et al. *Surf. Interface Anal.* 43 689 (2011)

FDMX METHOD OF CALCULATION

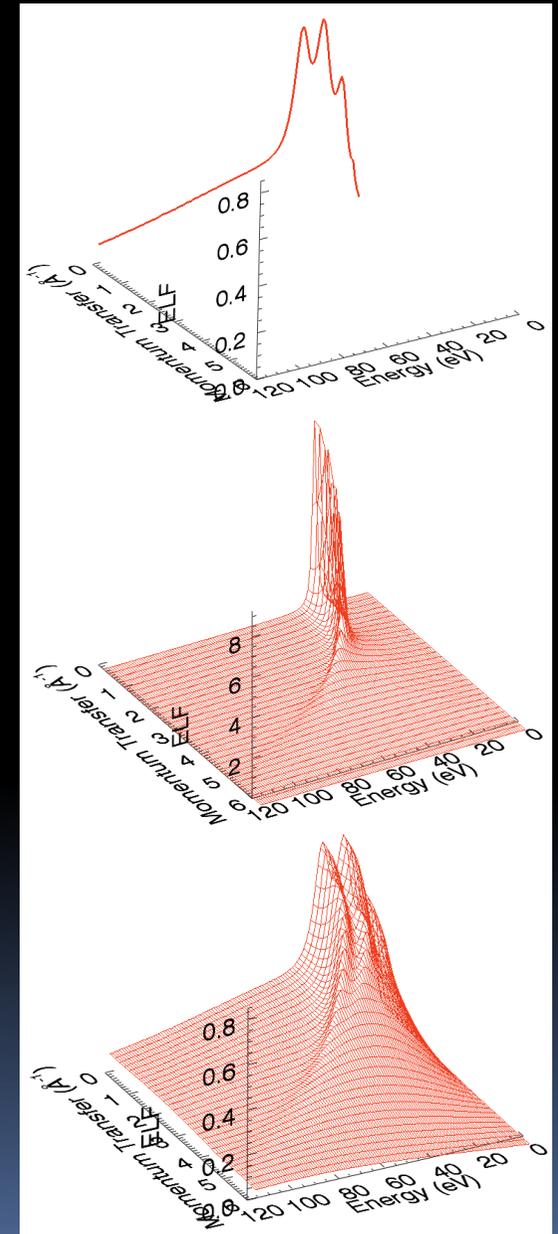
- IMFP determined from electron energy loss function (ELF)

$$\lambda^{-1}(E) = \frac{\hbar}{a_0 \pi E} \int_0^{\hbar} \int_{q_-}^{q_+} \frac{1}{q} \text{Im} \left[\frac{-1}{\varepsilon(q, \omega)} \right] dq d\omega$$

$$q_{\pm} = \sqrt{\frac{2mE}{\hbar^2}} \pm \sqrt{\frac{2m}{\hbar^2} (E - \hbar\omega)}$$

- Electron ELF built from transform of optical dielectric function $\varepsilon(0, \omega)$

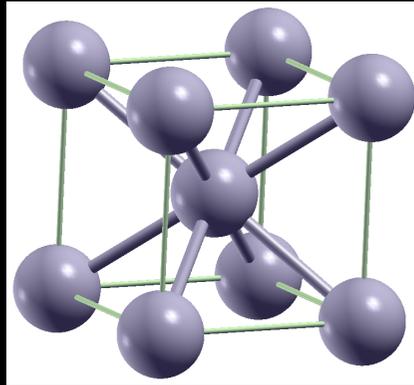
$$\text{Im} \left[\frac{-1}{\varepsilon(0, \omega)} \right] = \sum_i A_i \text{Im} \left[\frac{-1}{\varepsilon_{FEG}(0, \omega; \omega_p = \omega_i)} \right]$$



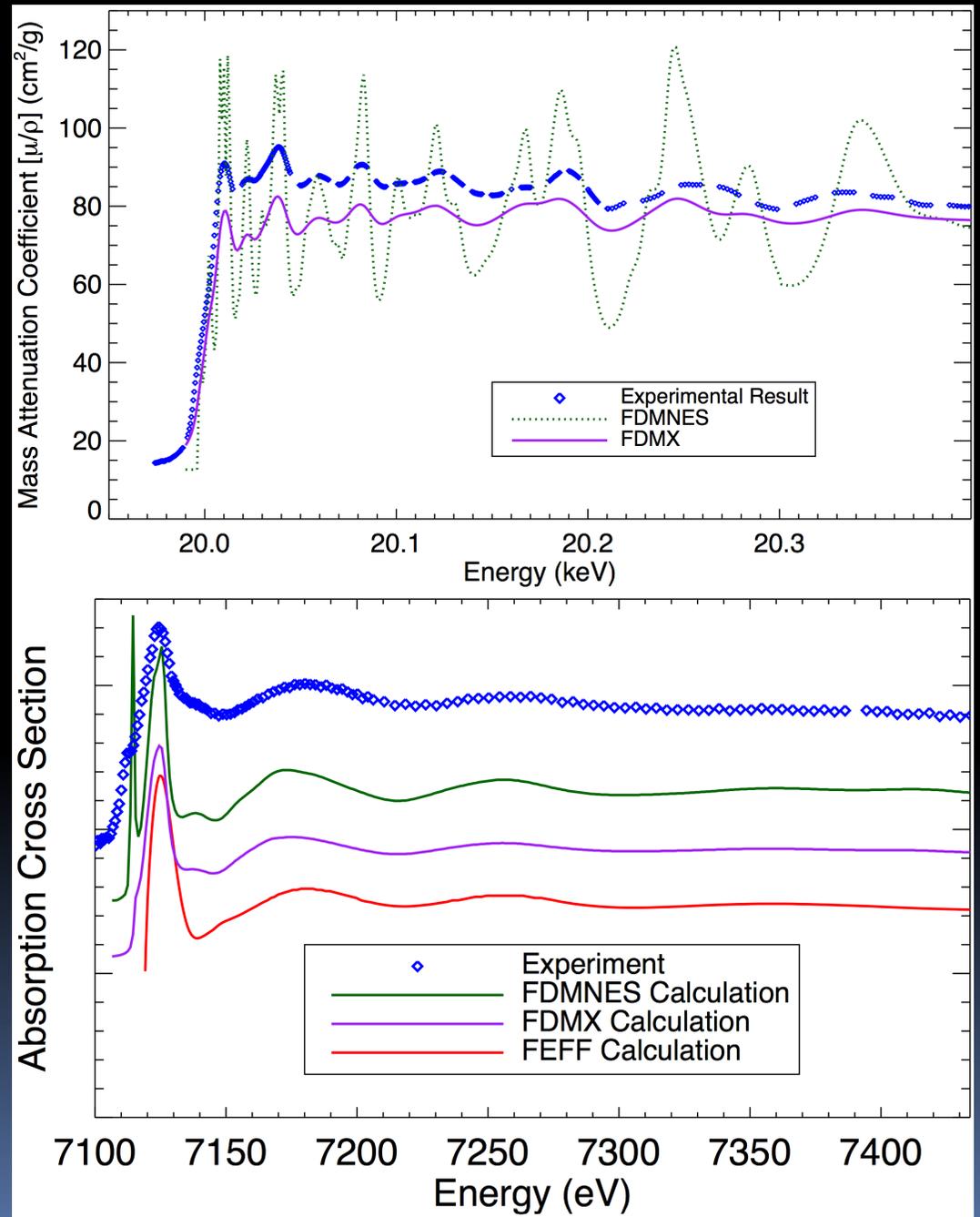
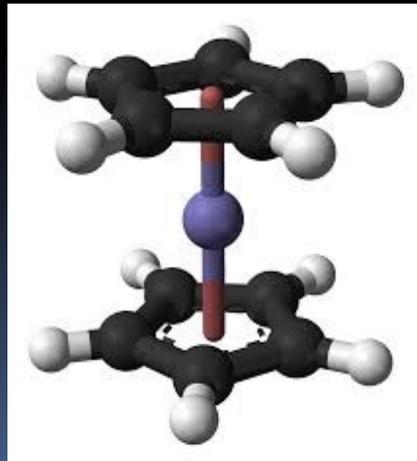
FDMX – EXAMPLES AND HANDS-ON

- Further examples of FDMX:

Molybdenum:



Ferrocene:



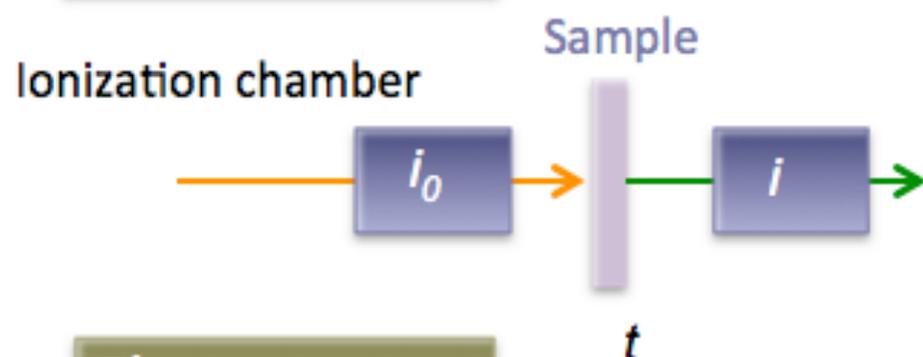
+ X-ray Absorption Spectroscopy

-how to measure

XANES, EXAFS, ...

Most fundamental technique is a transmission mode

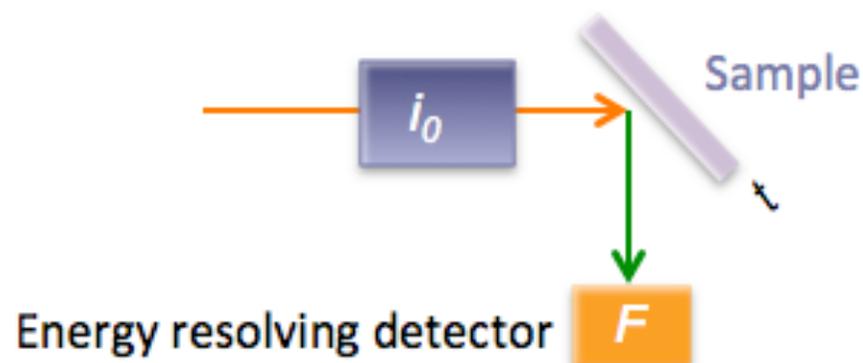
Transmission



$$\mu t (E) = \ln (i_0 / i)$$

You measure attenuated beam intensity, that "exponentially" decreases

Fluorescence



$$\mu t (E) = F / i_0$$

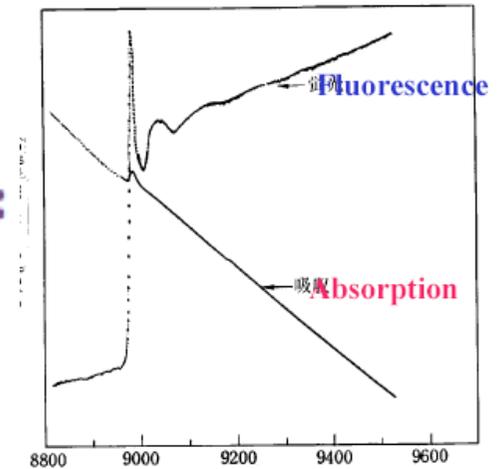
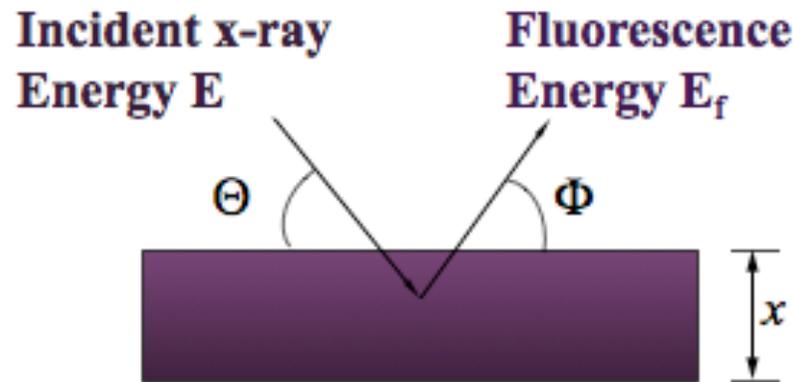
You measure emitted beam intensity
Which "linearly" proportional to conc.

Dilute system

Impurities, surfaces, thin films

+ Fluorescence intensity estimation

For x-rays incident on a slab of sample with thickness of x :



The fluorescence intensity $I_f(E)$ accepted by a detector with a solid angle of $\Omega/4\pi$ is:

$$I_f = \frac{\frac{fI_0\Omega[\mu/\rho]_{pe}^*}{4\pi \cos \theta_{inc}}}{\frac{[\mu/\rho]}{\cos \theta_{inc}} + \frac{[\mu_f/\rho]}{\cos \theta_{out}}} \left(A - \exp \left(-\frac{\left[\frac{\mu}{\rho} \right] [\rho t]}{\cos \theta_{inc}} - \frac{\left[\frac{\mu_f}{\rho} \right] [\rho t]}{\cos \theta_{out}} \right) \right)$$

$$I_f(E) \approx I_0 \times 8.8 \times 10^{-4} \times 0.012 \approx 1 \times 10^{-5} I_0, \text{ lower than } I_0 \text{ by 5 orders.}$$

EXPERIMENTAL ANALYSIS AND SYSTEMATICS

- Beer Law:

$$I_1 = I_0 e^{(-\mu t)}$$

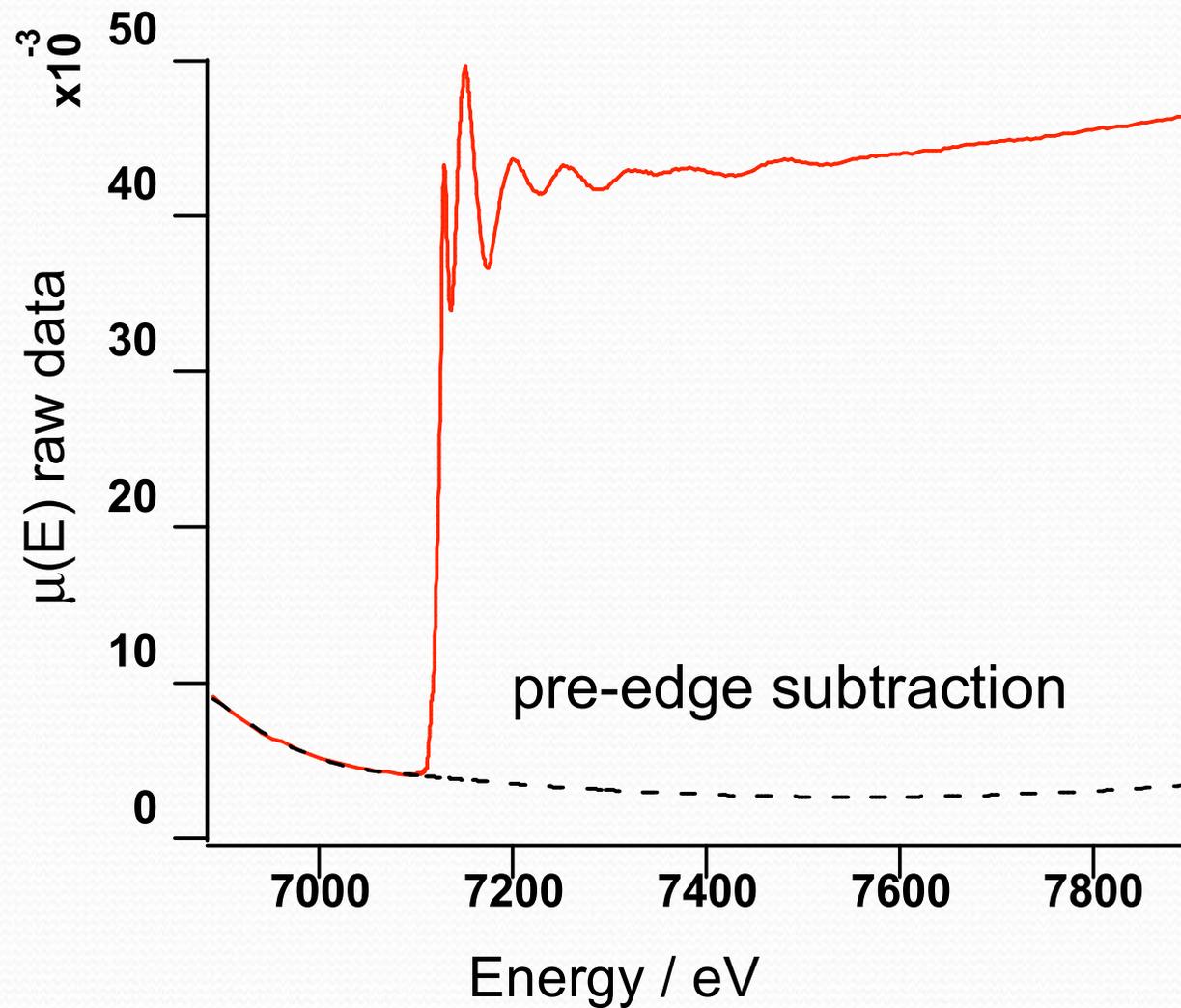
- Dark current (no beam through *each* detector)

$$\left[\frac{\mu}{\rho} \right] [\rho t] = -\ln \left(\frac{I_1 - D_1}{I_0 - D_0} \right)$$

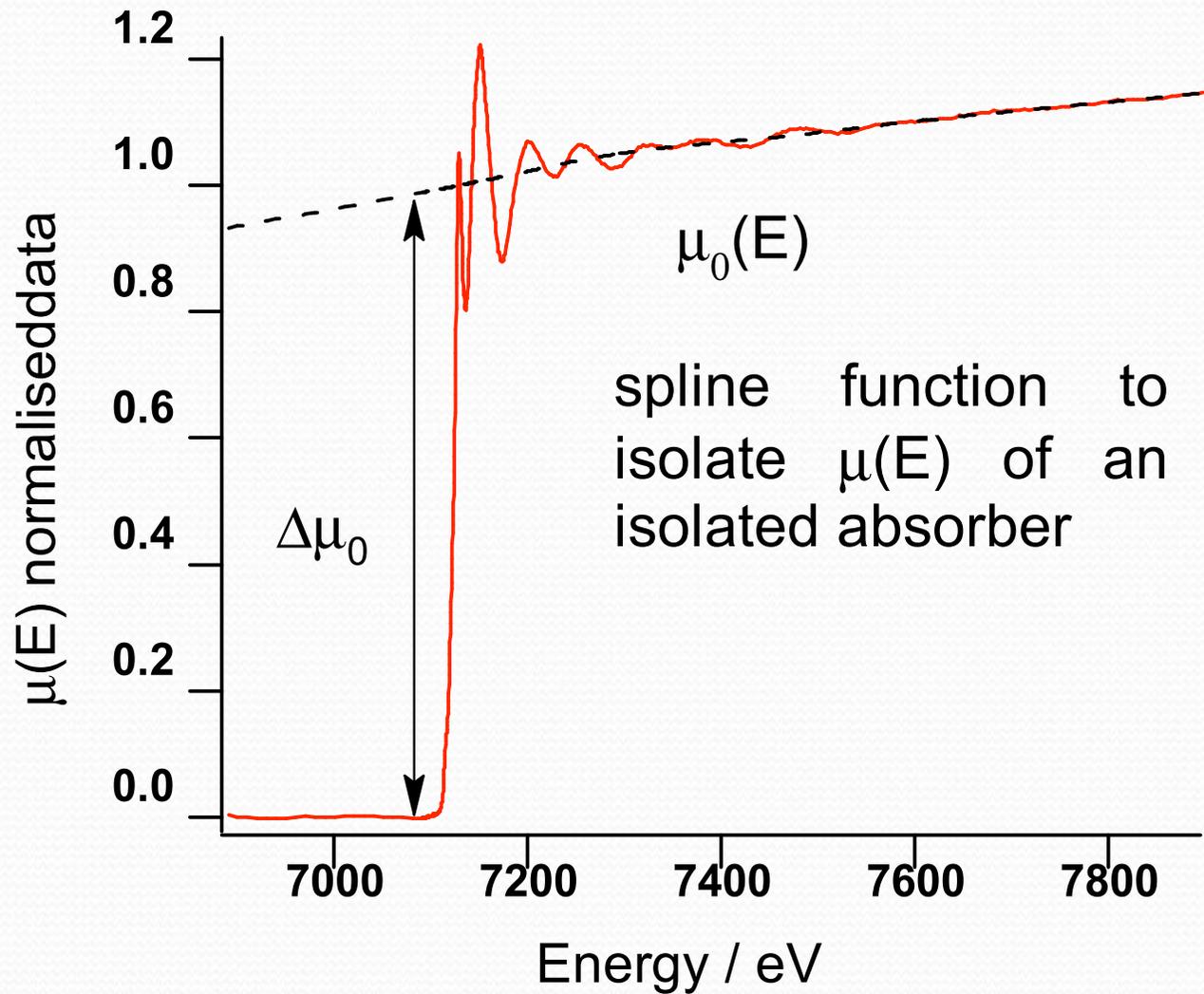
- Air path offset – blank in sample stage

$$\left[\frac{\mu}{\rho} \right] [\rho t]_s = \left[\frac{\mu}{\rho} \right] [\rho t]_{s+a} - \left[\frac{\mu}{\rho} \right] [\rho t]_a$$

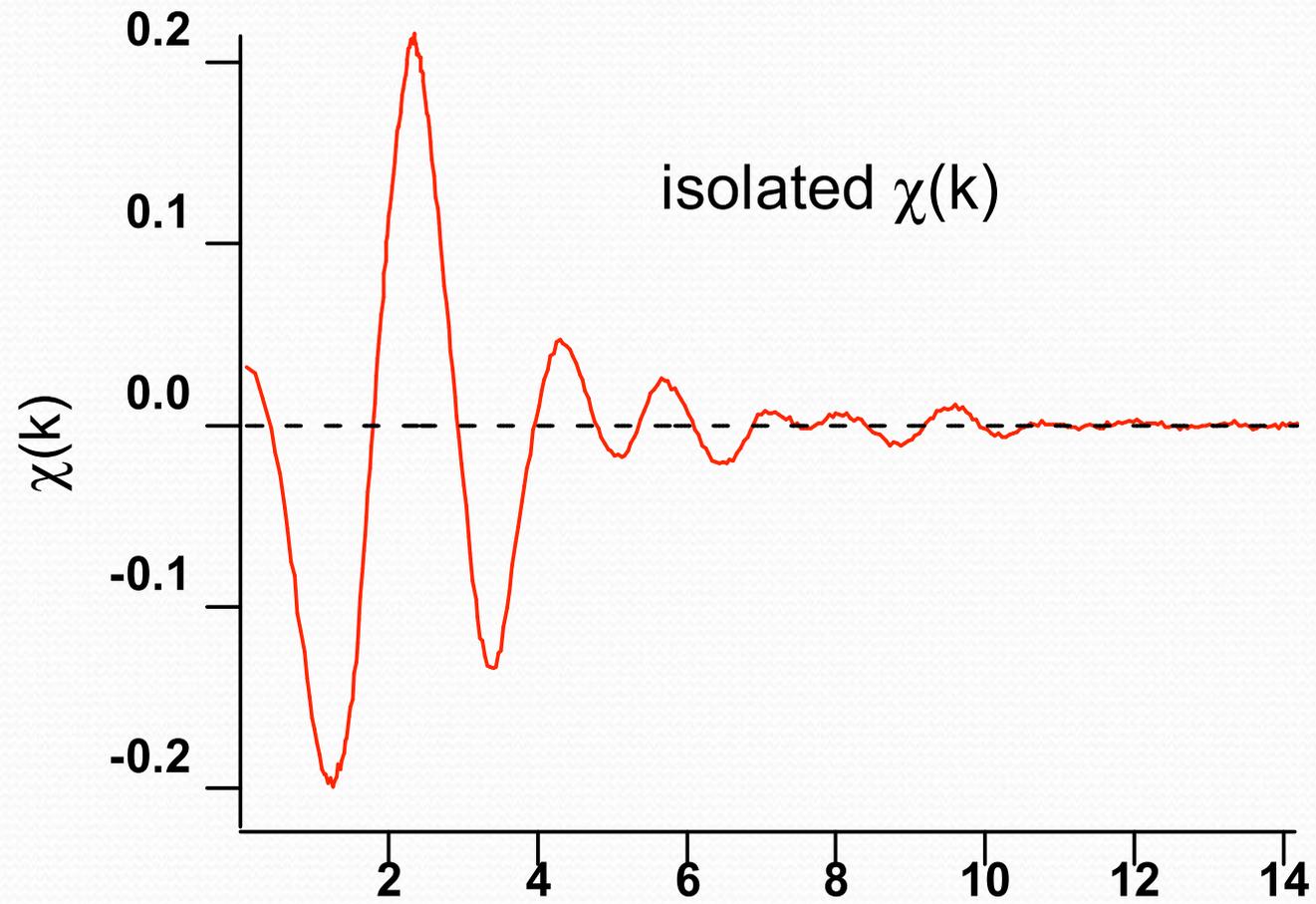
Data reduction



Data reduction



Data reduction

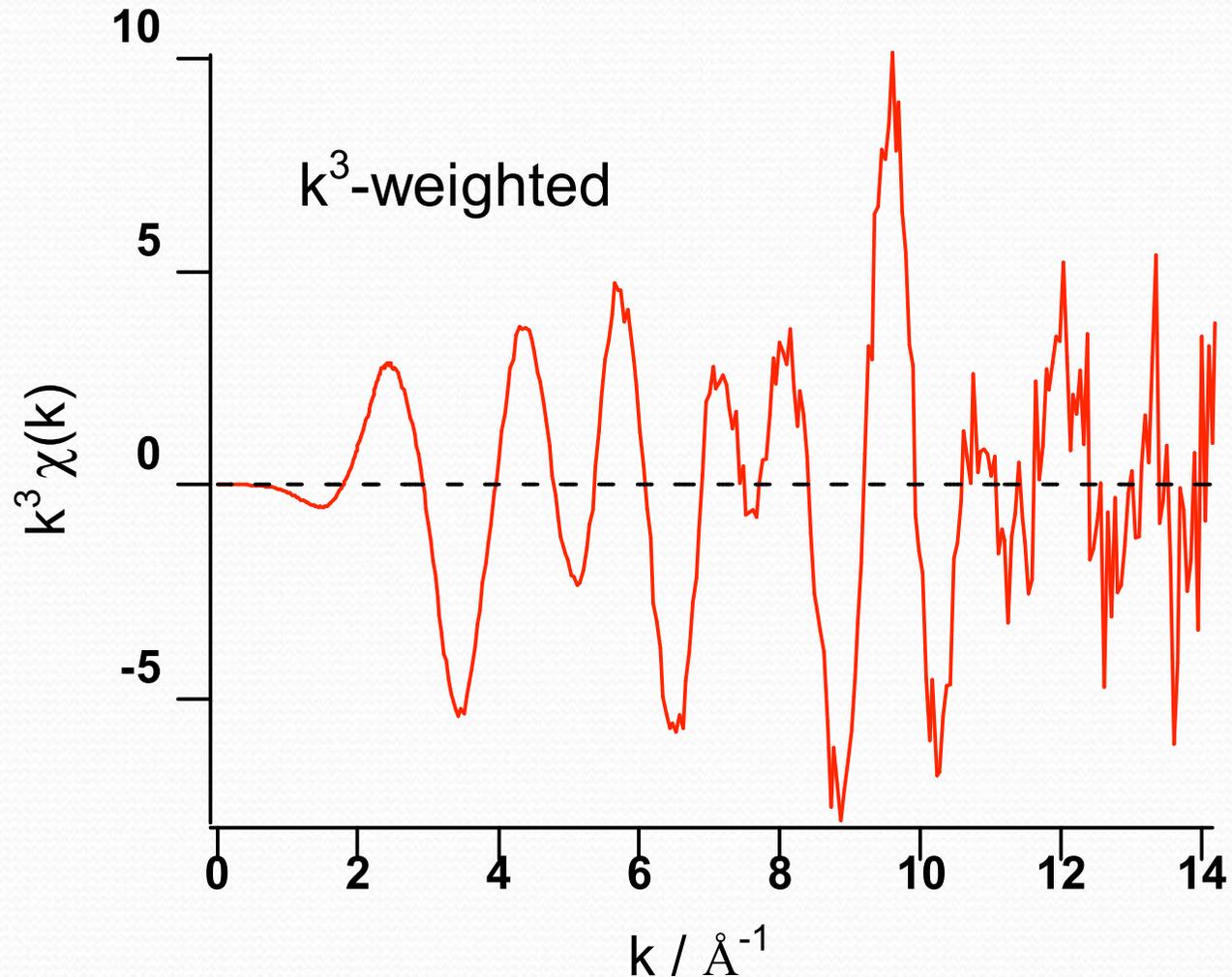


Data reduction

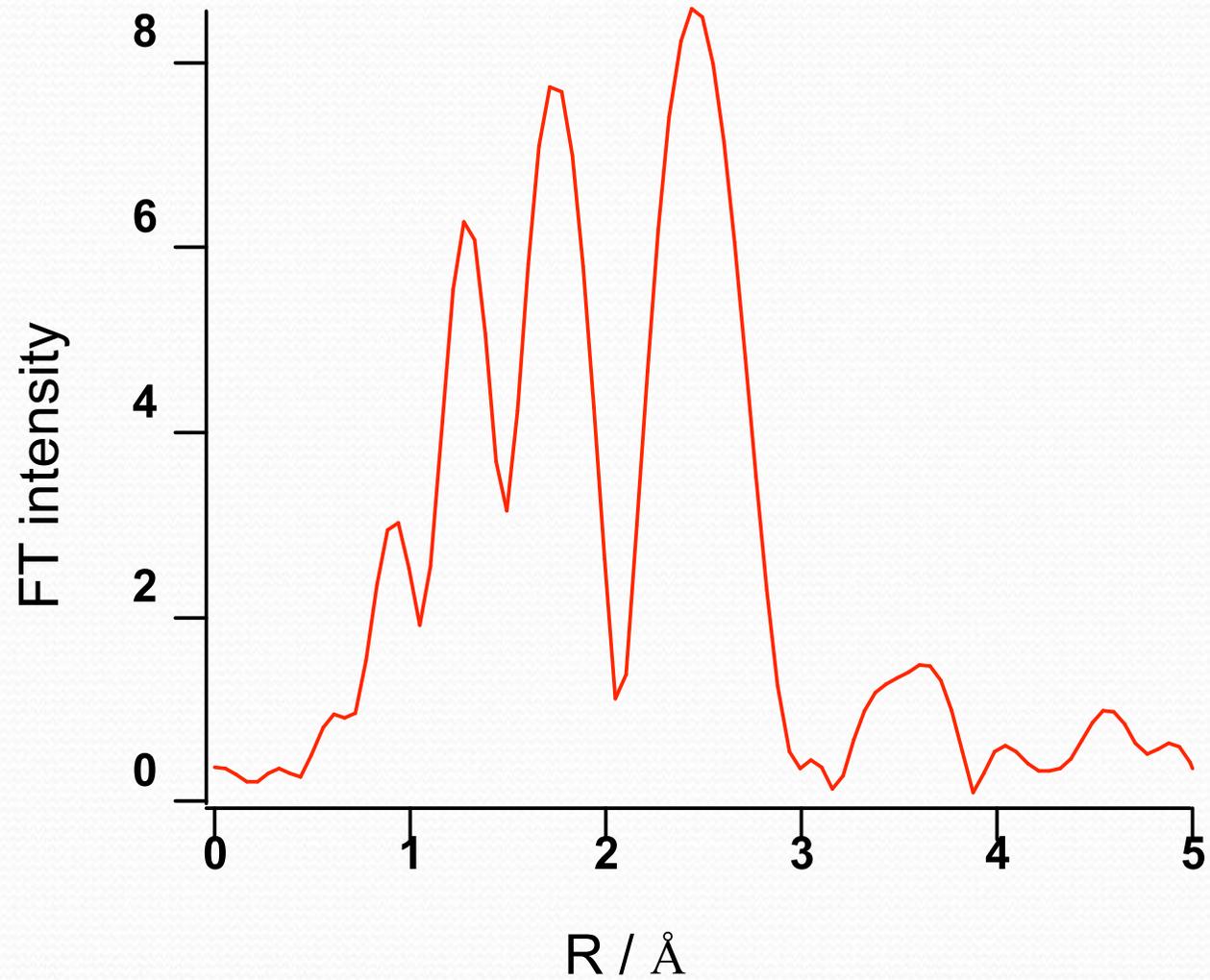
What are the uncertainties?

How much information content remains?

How much has been lost for hypothesis testing?



Data reduction



XAFS Theory: XANES and EXAFS Spectra

End

Software Packages

XAFS Theory: XANES and EXAFS Spectra

3. How does XAFS work?

$$\chi_{th}(k) = \sum_j N_j S_0^2 F_j(k) \frac{\sin(2kr_j + \phi_j(k))}{kr_j^2} e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)}$$

$$r_j = (1 + \alpha)r_{0,j}$$

- Lytle, F. W., 1999, *J. Synchrotron Radiat.* 6, 123
- Stumm von Bordwehr, R., 1989, *Ann. Phys. (Paris)* 14, 377.
- EXAFS Scattering Theory: Sayers, Stern, Lytle, *Phys. Rev. Lett.* 27 (1971) 1204
- Rehr, Albers, *Rev. Mod. Phys.* 72 (2000) 621-654
- Newville, M. (2004). *Fundamentals of XAFS. CARS, University of Chicago, Chicago IL*, pp. 23–24
- Bunker, G. (2010). In *Introduction to XAFS: A practical guide to X-ray Absorption Fine Structure Spectroscopy*, pp. 92–95. CUP
- Chantler et al., *J Synch. Rad.* 19 (2012) 145-158; *J Synch Rad* 19 (2012) 851-862. *International Tables for Crystallography Volume I*

ANALYSIS OF EXPERIMENTAL SPECTRA

- Ab Initio Theory codes – e.g. FEFF (FMS), FDMNES (FDM), GNXAS (FMS), CONTINUUM (FMS), WIEN2k (DFT)
- Analysis and Fitting Codes – e.g. IFEFFIT, MXAN, EXCURV*, XFIT
- Different approaches useful for different materials, energy ranges. Most commonly, FDM/DFT for near-edge (XANES), MS for high energies (EXAFS)

Different Approaches to Analysis

- **FEFF and related codes:** Spherically symmetric potentials (Muffin-tin (MT) approximation). Simulation of XANES spectra and fitting of EXAFS region. (developed in US) **IFEFFIT** (US, Australia) **Athena, Artemis etc.** (US)
- **EXCURVE** : Potentials and corresponding phase shifts are calculated for each constituent atom of the examined material sample from a superposition of neutral atomic solutions or potential files produced by *ab initio* codes are used. Simulation of XANES spectra and fitting of EXAFS region. (developed in UK)
- **MXAN:** Full multiple scattering calculations with MT approximation and **FPMS** (Non MT approximation). Structural and electronic properties are fitted in XANES region (developed in Italy)
- **FDMNES:** Finite Difference Method (FDM) to solve the Schrödinger equation (non MT approximation) and MT approximation. Pre-edge and XANES spectra are simulated (developed in France)
- **Fit-it:** Use FEFF and FDMNES to fit XANES (developed in Russian Federation)
- **FDMX:** Finite Difference Method (FDM) with full XAFS analysis. Pre-edge, XANES and XAFS spectra fitted, Inelastic mean free paths simulated and fitted, thermal broadening fitted or measured (developed in Australia from France)
- **Others** - Shirley et al.

6. Packages Data Collection, Reduction, Prediction, Analysis 130pp?

Part 6A Theoretical Prediction

Muffin-Tin Multiple scattering

- 6.1 EXCURVE
- 6.2 FEFF
- 6.3 GNXAS I: PHAGEN/GNPEAK/GNXAS

Non-Muffin-Tin Multiple scattering

- 6.4 FPMS - Full Potential Multiple Scattering

Non-Muffin-Tin Finite Difference Method

- 6.5 FDMNES Finite Difference Method for Near Edge Structure
- 6.6 FDMX Finite Difference Method for XAS

Multiplets

- 6.7 TT-Multiplets

Other Density Functional Theory (inc. 6.4-6.6)

- 6.9 QuantumEspresso/Xspectra (First Principles Calculations with DFT)
- 6.10 Wien2K
- 6.11 OCEAN (Abinit, DFT) Correlation Packages
- 6.12 Exciting (DFT full potential)

Part 6B Data Analysis

- 6.13 Athena and Artemis
- 6.14 EDA
- 6.15 ESTRA
- 6.16 FitIt
- 6.17 GNXAS II: FITHEO
- 6.18 IFEFFIT and Larch
- 6.19 IFEFFIT with errors
- 6.20 MAX
- 6.21 MXAN
- 6.22 PRESTOPRONT0
- 6.23 RSXAP and RSFIT
- 6.24 SixPACK
- 6.25 VIPER and XANDA
- 6.26 XAFSX
- 6.27 XFIT
- 6.28 LASE