HANDS-ON TUTORIAL: FINITE DIFFERENCE METHOD CALCULATIONS FOR NEAR-EDGE AND EXTENDED RANGE X-RAY ABSORPTION FINE STRUCTURE

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OUTLINE

- Finite Difference Method for Near-Edge Structure (FDMNES)
- Overview and Purpose
- Method of Calculation (FDM mode)
- Examples and Hands-on
- Finite Difference Method for XAFS (FDMX)
- Overview and Purpose
- Method of Calculation
- Examples and Hands-on

FINITE DIFFERENCE METHOD FOR NEAR-EDGE STRUCTURE (FDMNES)

- Written by Y. Joly – Institut Néel, CNRS, Grenoble, France

  yves.joly@grenoble.cnrs.fr

- Available from

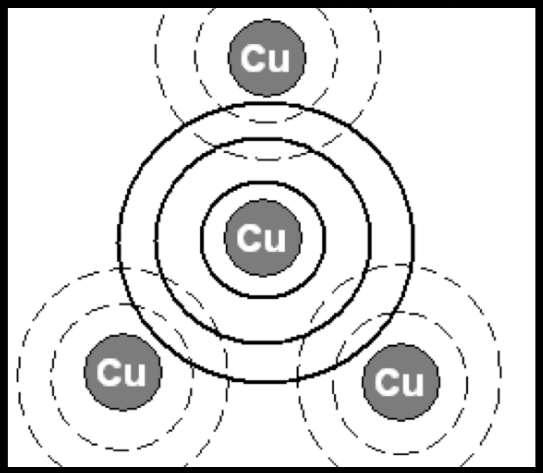
  http://www.neel.cnrs.fr/fdmnes

* Y. Joly, *Phys. Rev. B* **63** 125120 (2001)

FINITE DIFFERENCE METHOD FOR NEAR-EDGE STRUCTURE (FDMNES)

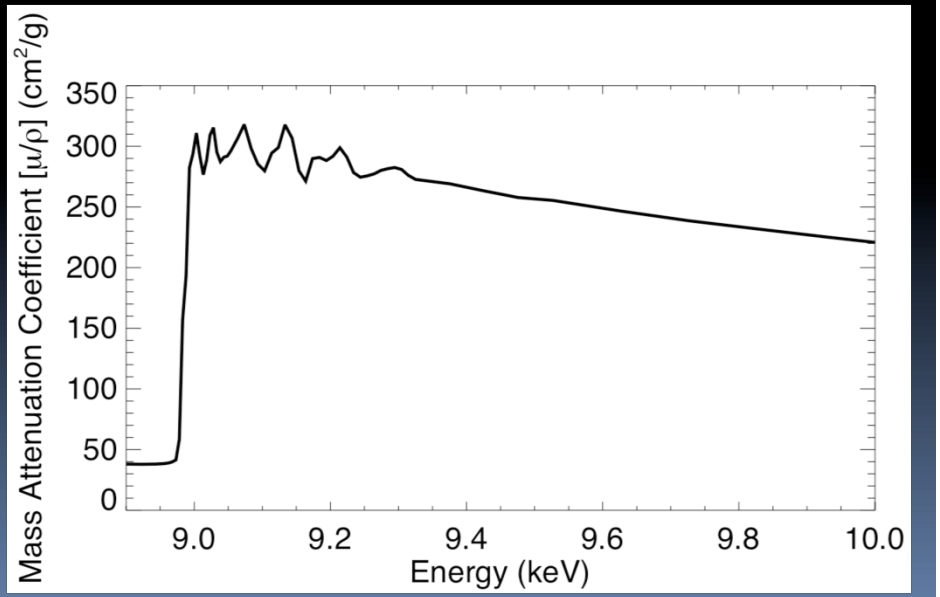
- Cluster-based calculation for the determination of x-ray spectroscopies
- Many applications – X-ray Absorption Near-Edge Structure (XANES), X-ray Absorption Fine Structure (XAFS), Diffraction Anomalous Fine Structure (DAFS), Resonant X-ray Diffraction/Scattering (RXD/RXS)
- Our focus is on XANES – XAFS – EXAFS

FDMNES OVERVIEW AND PURPOSE

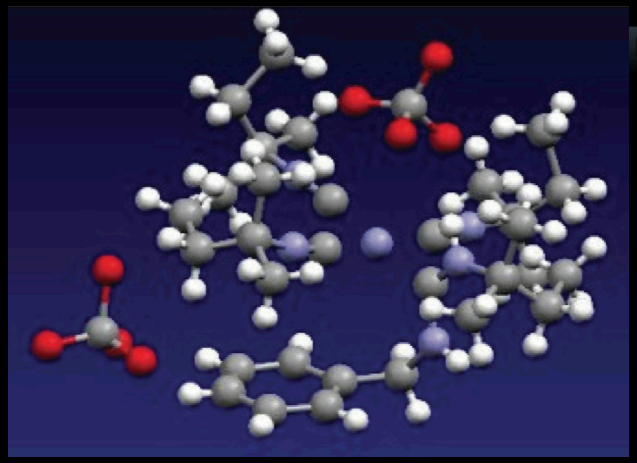


- Originally used for near-edge structure (XANES) calculations
- Two operational modes – Finite Difference Method (FDM) and Full-Multiple Scattering (FMS)

- FDM mode avoids muffin-tin approximation
- Useful in XANES region and for complex molecules

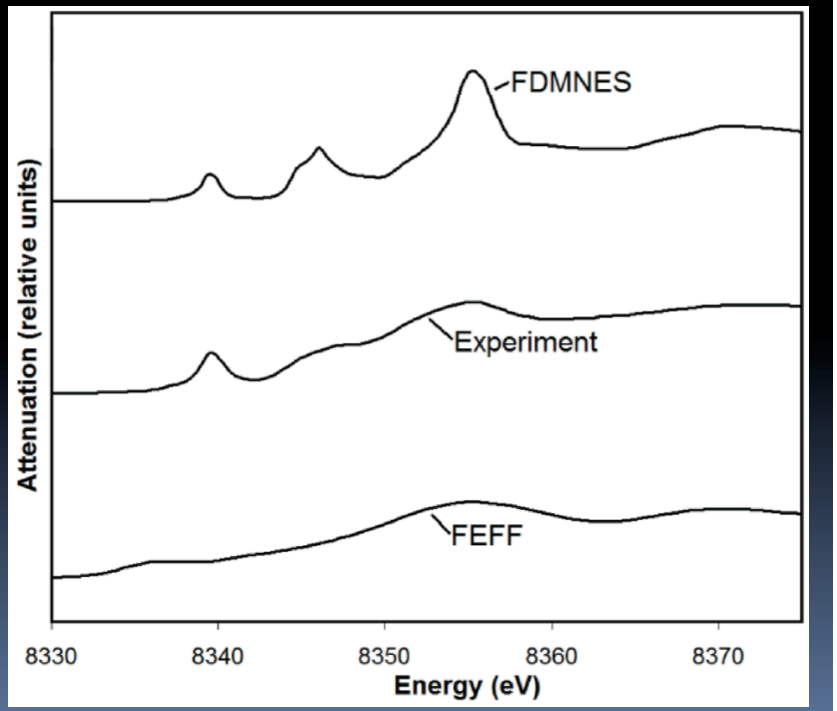


FDMNES OVERVIEW AND PURPOSE



- Example of FDM application – Activated Nickel (t-Amylisocyanide) molecule

- Full-potential calculation predicts extra near-edge structure
- Very computationally intensive
- Structures can be overestimated – see FDMX



* J. L. Glover et al. *AIP Conf. Proc.* **882** 625 (2007)

FDMNES – METHOD OF CALCULATION

- Sum over transition amplitudes

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

- To evaluate optical cross section Fermi's Golden Rule

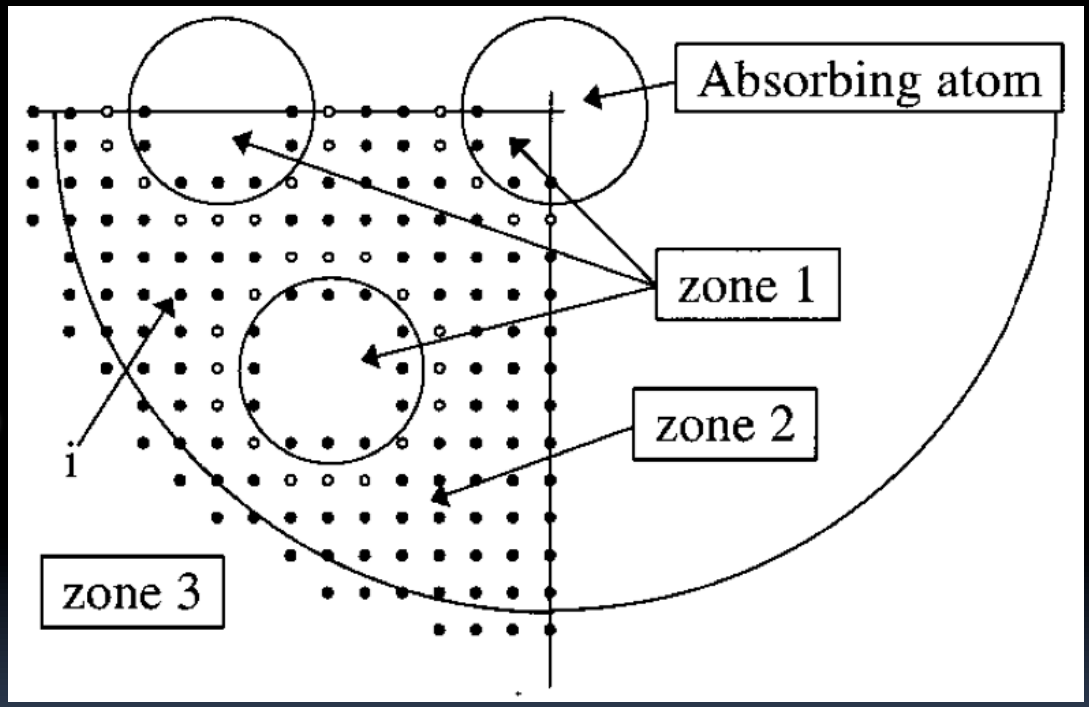
$$\sigma = 4\pi^2 \alpha \hbar\omega \sum_{f,g} \left| M_{gf} \right|^2 \delta\left(\hbar\omega - E_f + E_g \right)$$

- Require wavefunctions for final + 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 Schrödinger Equation:

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

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

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 Angstroems

 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

FDMNES – EXAMPLES AND HANDS-ON

- KEYWORDS (Mandatory)
- Filout – output file
- Range – energy range of calculation
- Radius – cluster radius
- Crystal – atomic co-ordinates
- KEYWORDS (Important)
- Convolution – Lorentzian convolution
- Adimp – interpoint distance
- Edge – absorption edge (K, L1, L2, etc)
- Green – MS calculation (fast)

FDMNES – EXAMPLES AND HANDS-ON

- Outputs /fdmnes/xanout/test_stand/
- Cu.txt
- Cu_bav.txt
- Cu_conv.txt

cu_bav.txt

```
  FDMNES II program, Revision 18 July 2014
  Date = 02 08 2014
  Time = 17 h 19 mn 35 s

Threshold: Copper K1 edge
Radius =  3.00
icheck = 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Range = -10.000   0.200   0.000   0.500  10.000   1.000  40.000
Dipole component
Non-relativistic calculation
Non-magnetic calculation
Real bases
Finite difference method calculation
  iord = 4, adimp =  0.25
  lmaxso0 = -5
  Eclie =  1.000 eV

Calculation in double precision

Crystal
  ngroup =    4, ntype = 1
  a, b, c =   3.61000   3.61000   3.61000
  alfa, beta, gamma =   90.000   90.000   90.000
   Z  Typ    posx      posy      posz      popats
  29   1   0.00000   0.00000   0.00000
  29   1   0.50000   0.50000   0.00000
  29   1   0.50000   0.00000   0.50000
```

cu_conv.txt

```
   Energy    <xanes>
 -10.000  5.0259349E-03
  -9.800  5.2667609E-03
  -9.600  5.5352524E-03
  -9.400  5.8365972E-03
  -9.200  6.1773302E-03
  -9.000  6.5657709E-03
  -8.800  7.0126206E-03
  -8.600  7.5317714E-03
  -8.400  8.1413749E-03
  -8.200  8.8651683E-03
  -8.000  9.7338710E-03
  -7.800  1.0785959E-02
  -7.600  1.2065966E-02
  -7.400  1.3616577E-02
  -7.200  1.5460152E-02
  -7.000  1.7572514E-02
  -6.800  1.9870821E-02
  -6.600  2.2239606E-02
  -6.400  2.4577676E-02
  -6.200  2.6826421E-02
  -6.000  2.8962402E-02
  -5.800  3.0979226E-02
  -5.600  3.2875021E-02
  -5.400  3.4647108E-02
  -5.200  3.6290995E-02
  -5.000  3.7801478E-02
  -4.800  3.9174379E-02
  -4.600  4.0407854E-02
  -4.400  4.1502963E-02
```

cu.txt

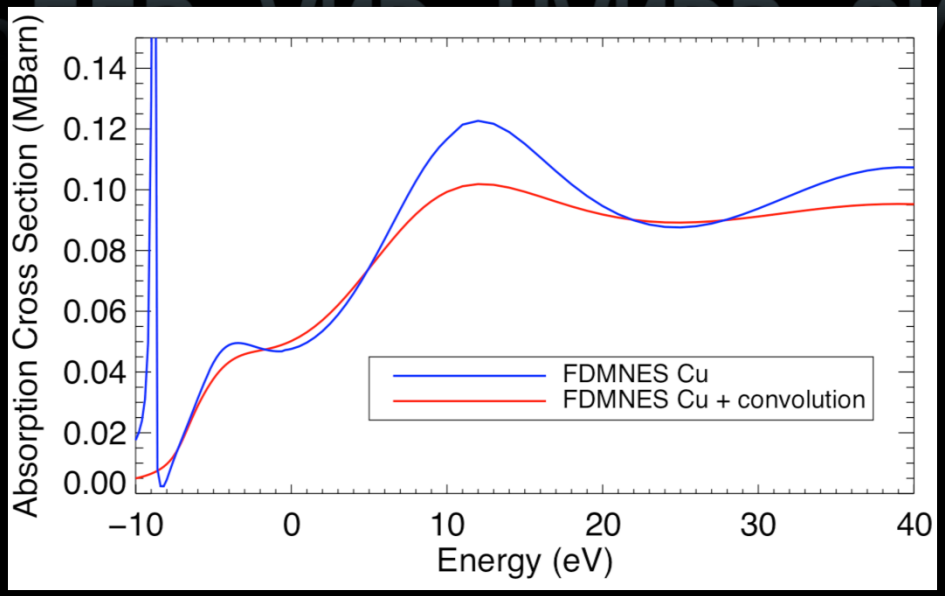
```
  8979.000   29  1  1     0.00000   -12.19174    -6.92535  1  1     8838.311  0.012599168
0.00000 = E_edge, Z, n_edge, j_edge, Abs_before_edge, VO_interstitial, E_Fermi, ninitl,
ninit1, Epsii, Atom_density, f0_forward
   Energy    <xanes>
 -10.000  1.7563421E-02
  -9.800  1.9998719E-02
  -9.600  2.3894525E-02
  -9.400  3.1032405E-02
  -9.200  4.9535182E-02
  -9.000  1.2873099E-01
  -8.800  2.8192980E-01
  -8.600  8.0071356E-03
  -8.400  2.4017761E-03
  -8.200  2.3759765E-03
  -8.000  4.5577548E-03
  -7.800  7.5060174E-03
  -7.600  1.0407134E-02
  -7.400  1.3139177E-02
  -7.200  1.5759159E-02
  -7.000  1.8331884E-02
  -6.800  2.0902525E-02
  -6.600  2.3493499E-02
  -6.400  2.6109023E-02
  -6.200  2.8737112E-02
  -6.000  3.1352415E-02
  -5.800  3.3920285E-02
  -5.600  3.6398098E-02
  -5.400  3.8741293E-02
  -5.200  4.1145219E-02
```

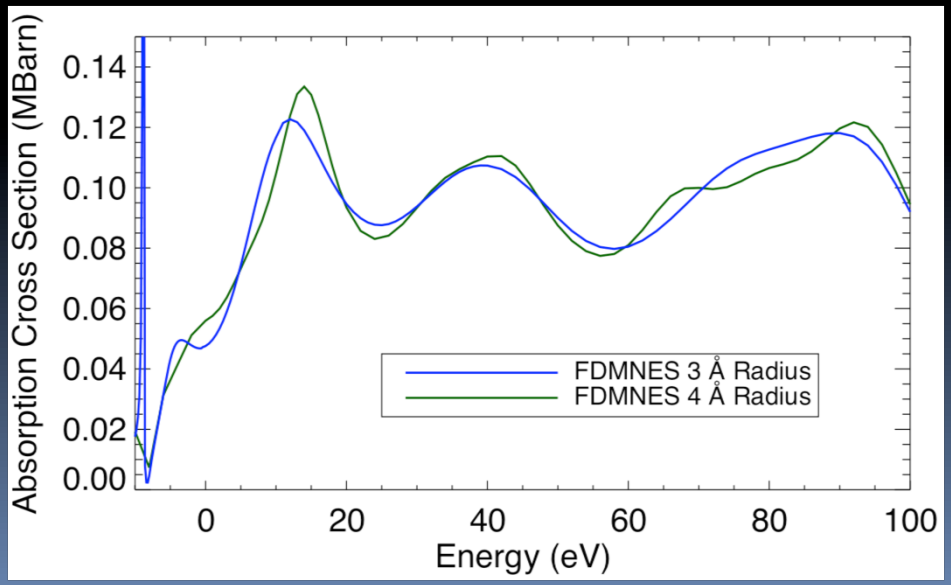
FDMNES – EXAMPLES AND HANDS-ON

- Output from copper example:

- Try increased energy range, Radius 3.0 Å -> 4.0 Å

- Extra structure appears from second co-ordination shell





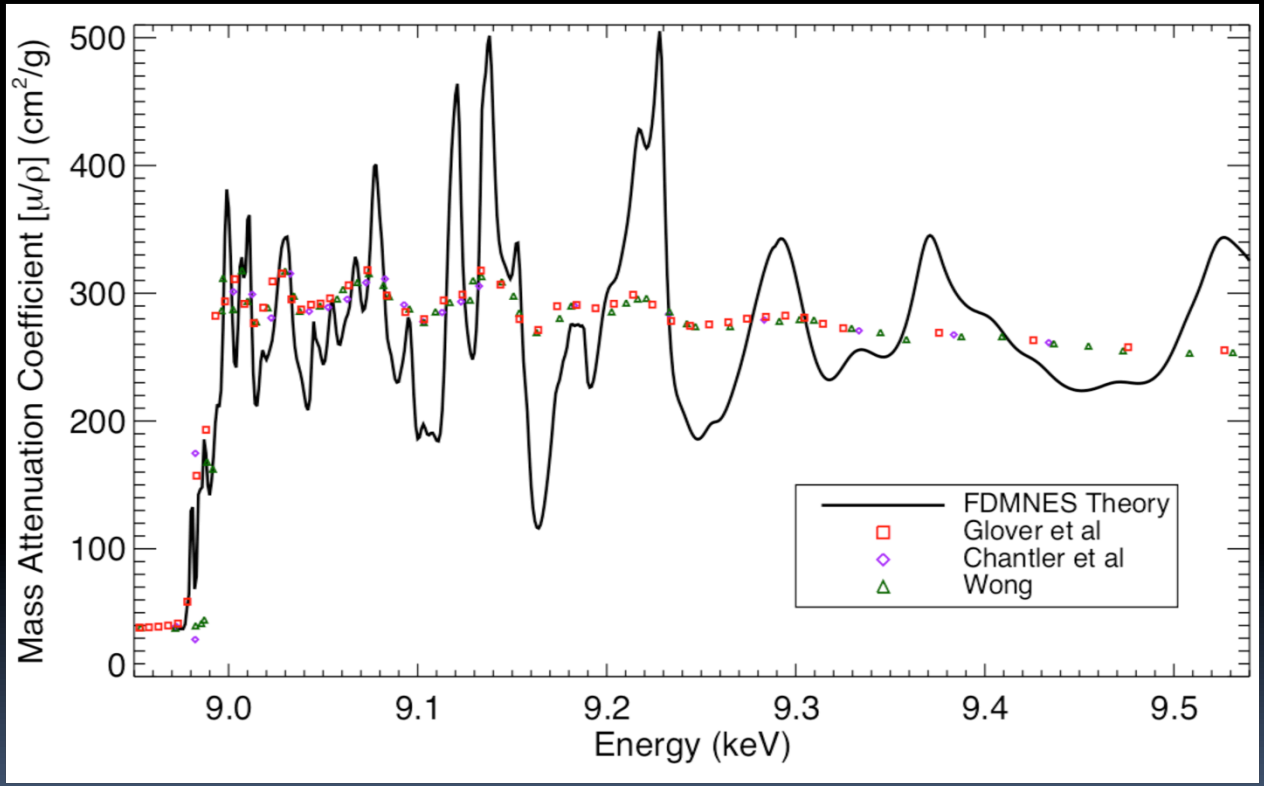
FINITE DIFFERENCE METHOD FOR XAFS (FDMX)

- Jay Bourke, Chris Chantler, Yves Joly
- School of Physics, University of Melbourne, Australia
- Available jayb@unimelb.edu.au and from IUCr 2014 - online soon!

- Designed to enable ab initio full energy range XAFS, XAS calculations from a full potential base
- Includes extra physics!

FDMX – EXAMPLES AND HANDS-ON

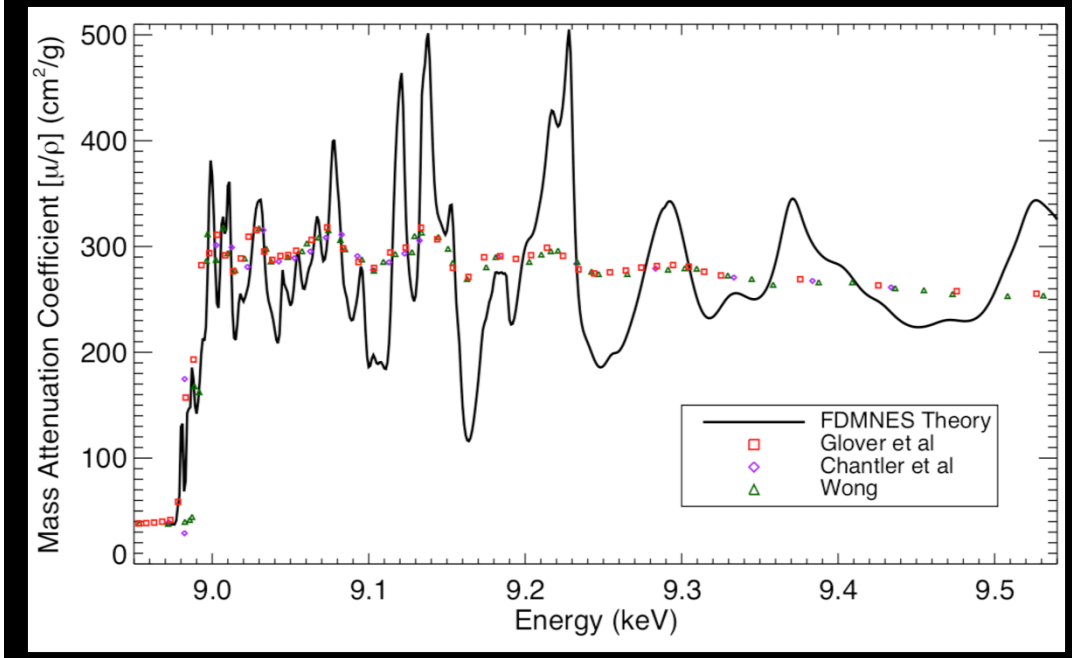
- FDMNES: increase Radius to 8.3 Å, reduce grid spacing (adimp), increase energy



- Match to experiment not so good! – Need extended theory

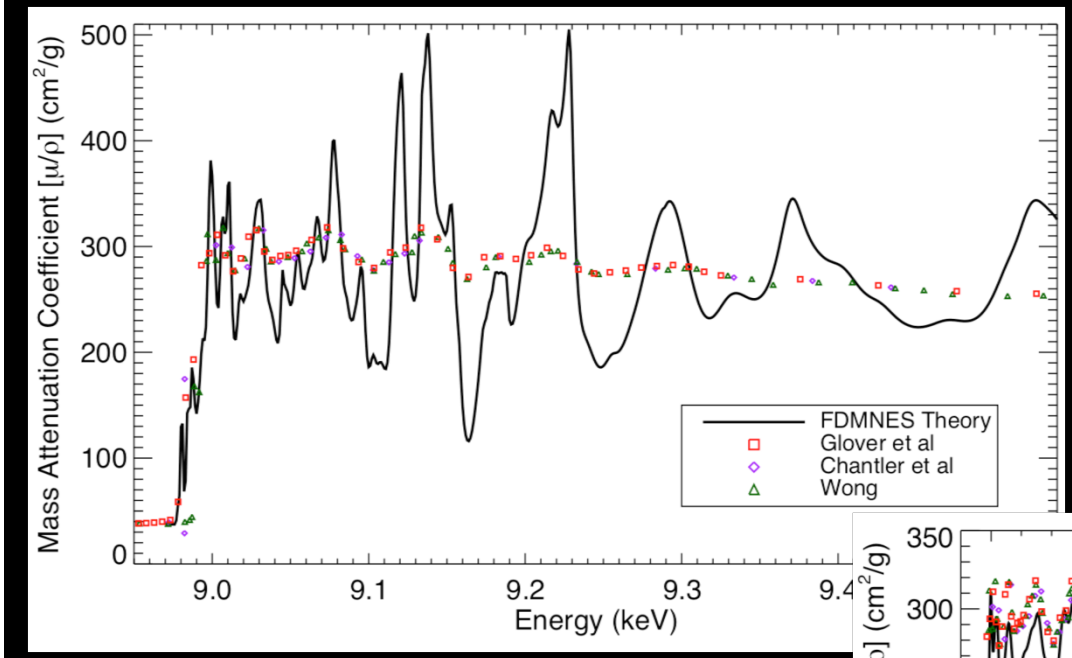
FDMX OVERVIEW AND PURPOSE

- In a nutshell… we want to turn this:

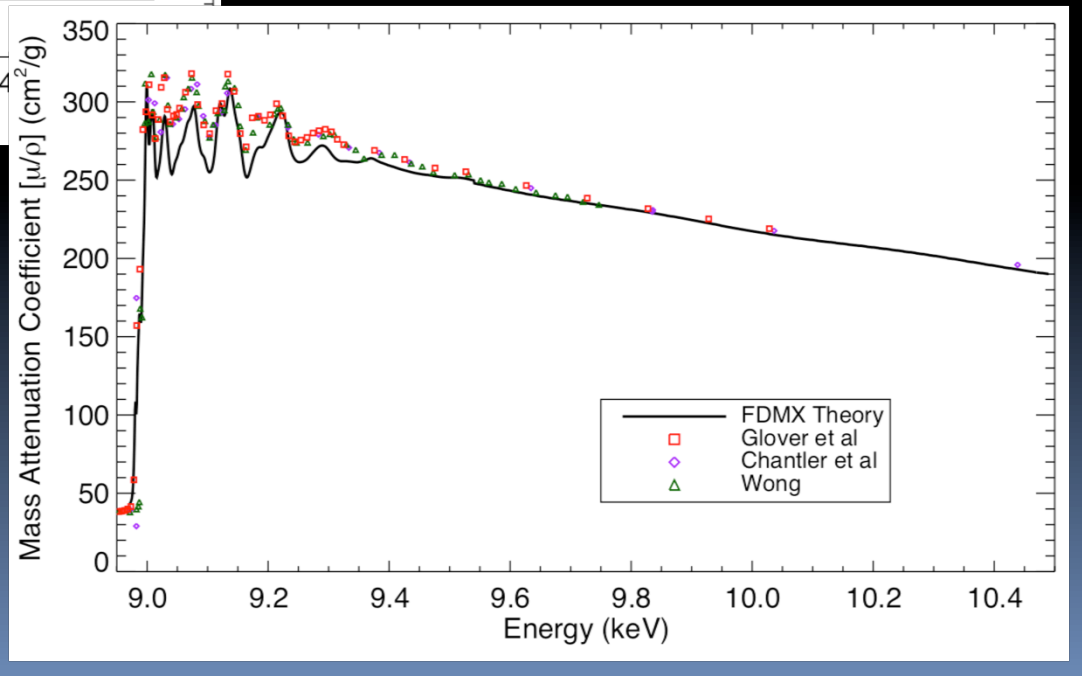


FDMX OVERVIEW AND PURPOSE

- In a nutshell… we want to turn this:



- Into this →



FDMX OVERVIEW AND PURPOSE

- XAFS Equation – convenient parameterization

$$\chi(k) = \sum_j N_j S_0^2 F_j(k) \frac{\sin[2kr_j + \phi_j(k)]}{kr_j^2} e^{\left(-2\sigma_j^2 k^2\right)} e^{\left(-2r_j/\lambda_j(k)\right)}$$

- Make sure all of the physics is there!

N_j Degeneracy of scattering paths

σ_j Debye-Waller factor (thermal disorder)

r_j Scattering path length (bond lengths)

λ_j Electron inelastic mean free path

FDMX METHOD OF CALCULATION

- Inclusion of thermal disorder

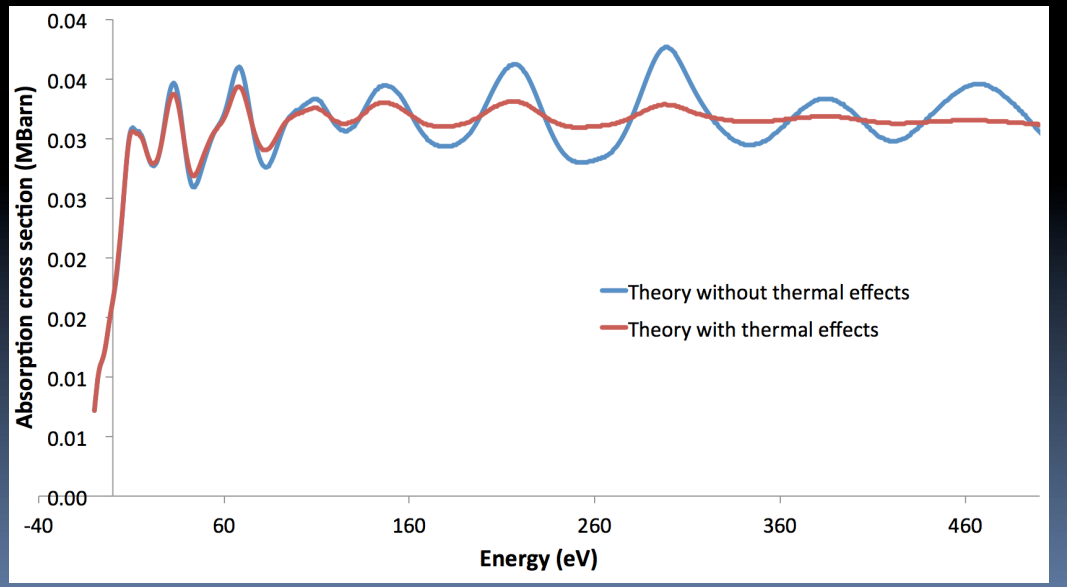
$$\chi_j(k) \rightarrow \chi_j(k) e^{\left(-2\sigma_j^2 k^2\right)}$$

- Beni-Platzmann theory

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

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

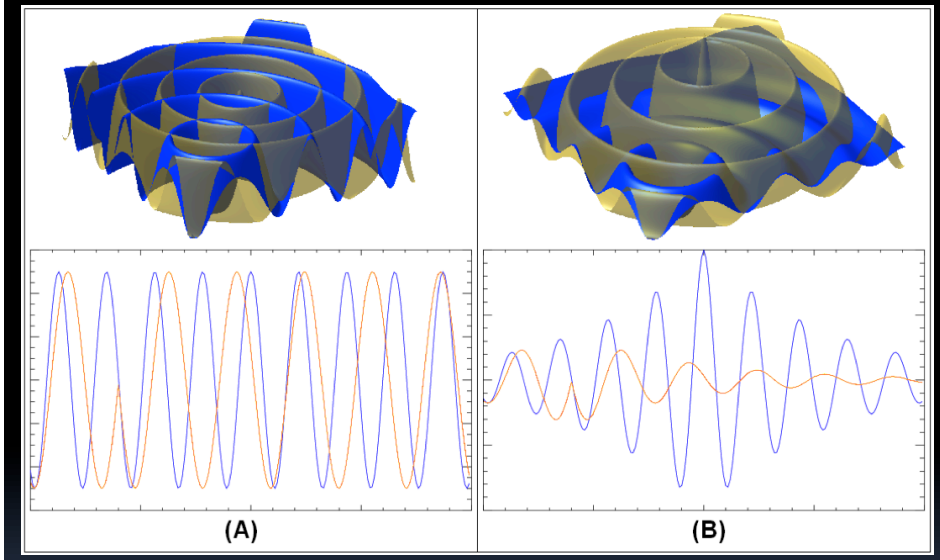
- Evaluate DW factor from neighbour positions
- Includes correlated motion



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

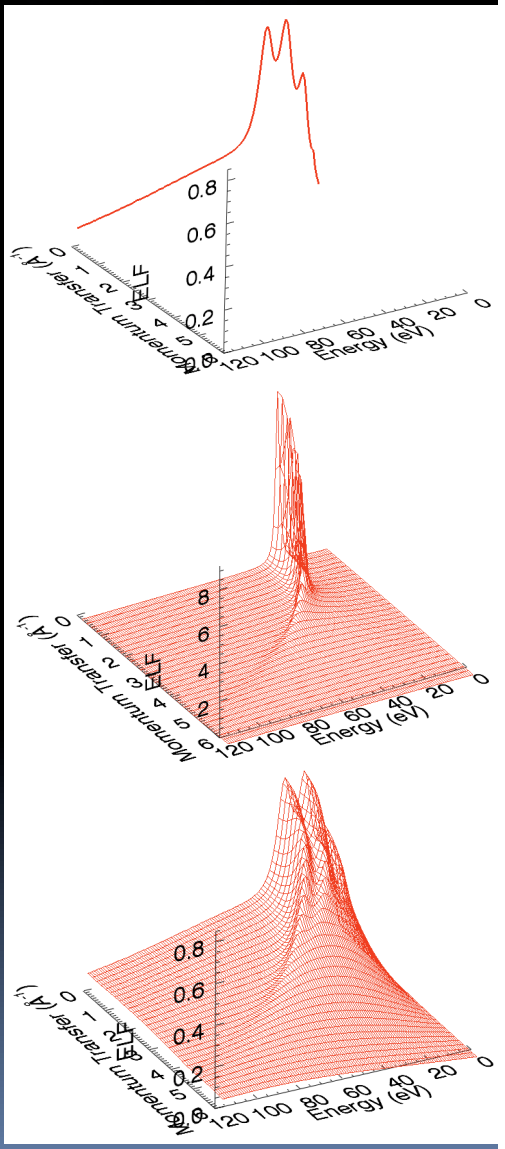
- IMFP determined from electron energy loss function (ELF)

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

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

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

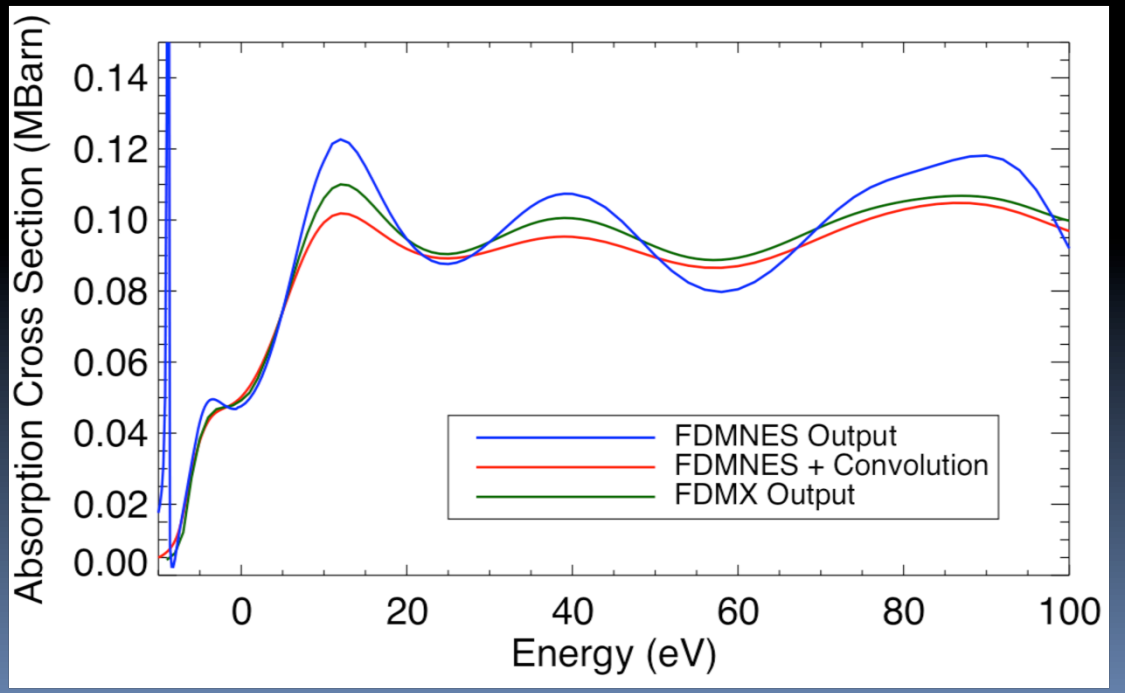
$$\mathrm{Im}\left[\frac{-1}{\varepsilon(0,\omega)}\right] = \sum_i A_i \, \mathrm{Im}\left[\frac{-1}{\varepsilon_{FEG}(0,\omega;\omega_p = \omega_i)}\right]$$



FDMX – EXAMPLES AND HANDS-ON

- Run FDMX.exe
- Uses fdmnes inputs (fdmfile.txt etc) to establish material data e.g. crystal structure
- implements physical effects to produce accurate XAFS theory over an extended range

Cu Example:



FDMX – EXAMPLES AND HANDS-ON

- Custom parameters may be included with optional input fdmxfile.txt
- Can exclude effects using keywords nohole, noDW, noIMFP
- Recommended for low & high T measurements, complex molecules, exotic materials

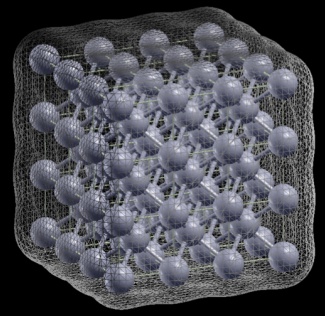
fdmxfile.txt

```
! FDMX indata file
! Contains keywords (if needed) to define parameters for FDMX post-processing

 Hole
   1.4

 Efermi
   -6.0

 IMFPin
   CuIMFPtable.txt

 TDebye
   343

 Tmeas
   100
```

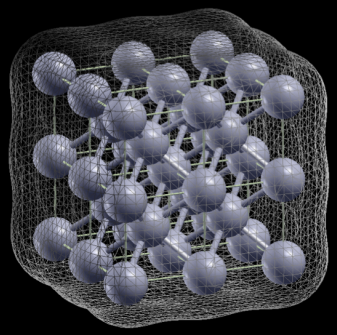
FDMXReadme.txt

```
<USAGE>

Program will automatically detect your FDMNES input from fdmfile.txt, and find data from
that and your FDMNES output(s). An optional input file, fdmxfile.txt, may be used with
keywords to set parameters

-

<KEYWORDS FOR FILE fdmxfile.txt>

Hole
 On next line - value in eV

Efermi
 On next line - value in eV

IMFPin
 On next line - filename

DWFactor
 On next line - value in angstrom

TDebye
 On next line - value in Kelvin

Tmeas
 On next line - value in Kelvin

nohole
 Use to not implement hole-width broadening
```

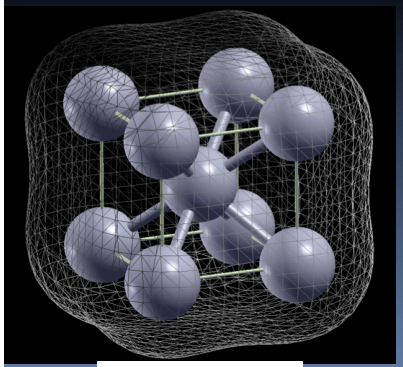
FITTING – ELECTRON IMFP



$\lambda = 12\text{Å}$

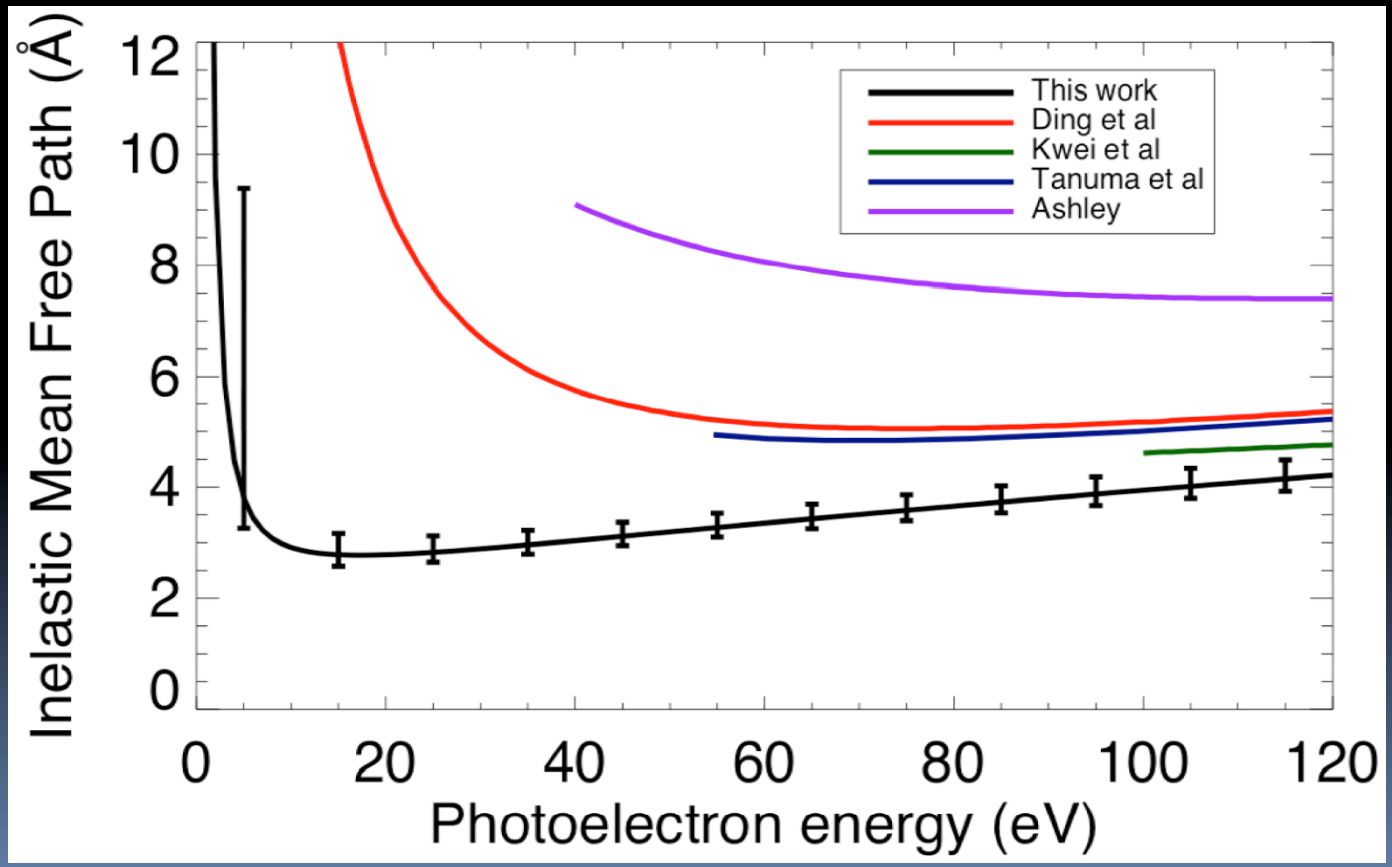


$\lambda = 8\text{Å}$



$\lambda = 4\text{Å}$

- May be extracted with sufficiently high measurement density **and** absolute accuracy



THANK YOU!