Australian Government

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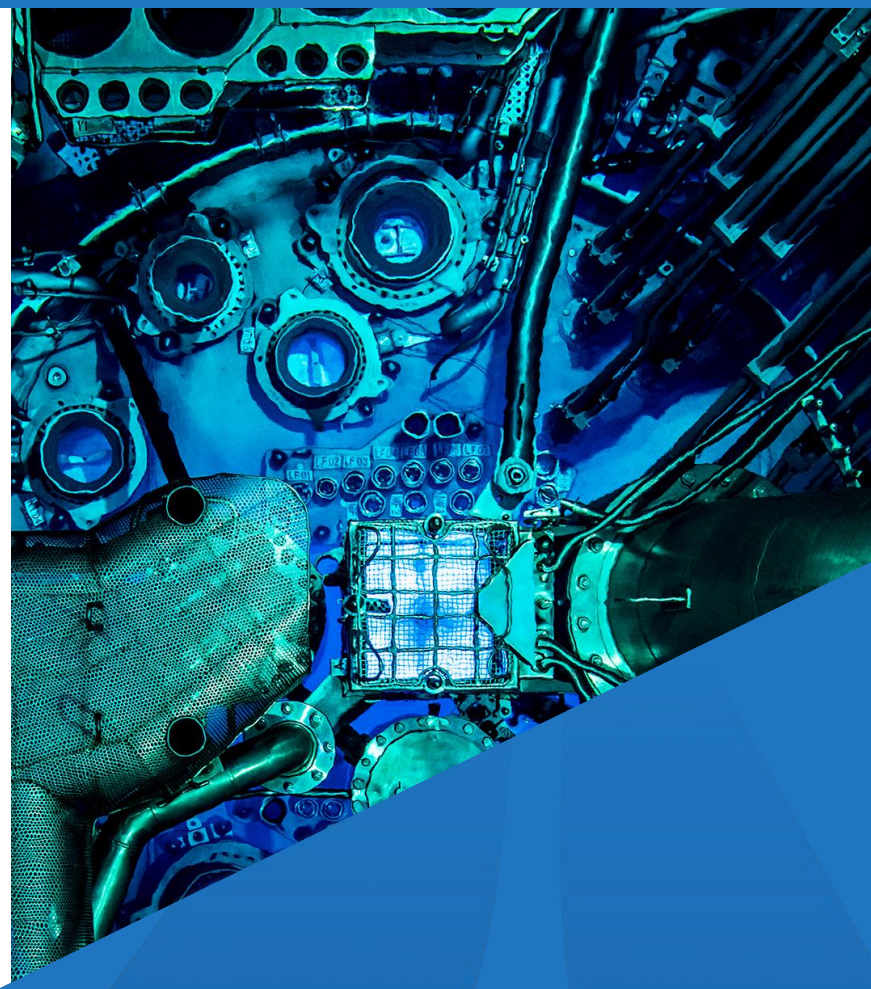
next step:

EXAFS



Bernt Johannessen

Senior Scientist

XAS Beamline ANSTO

15 August 2024

Science. Ingenuity. Sustainability.

Australian Government

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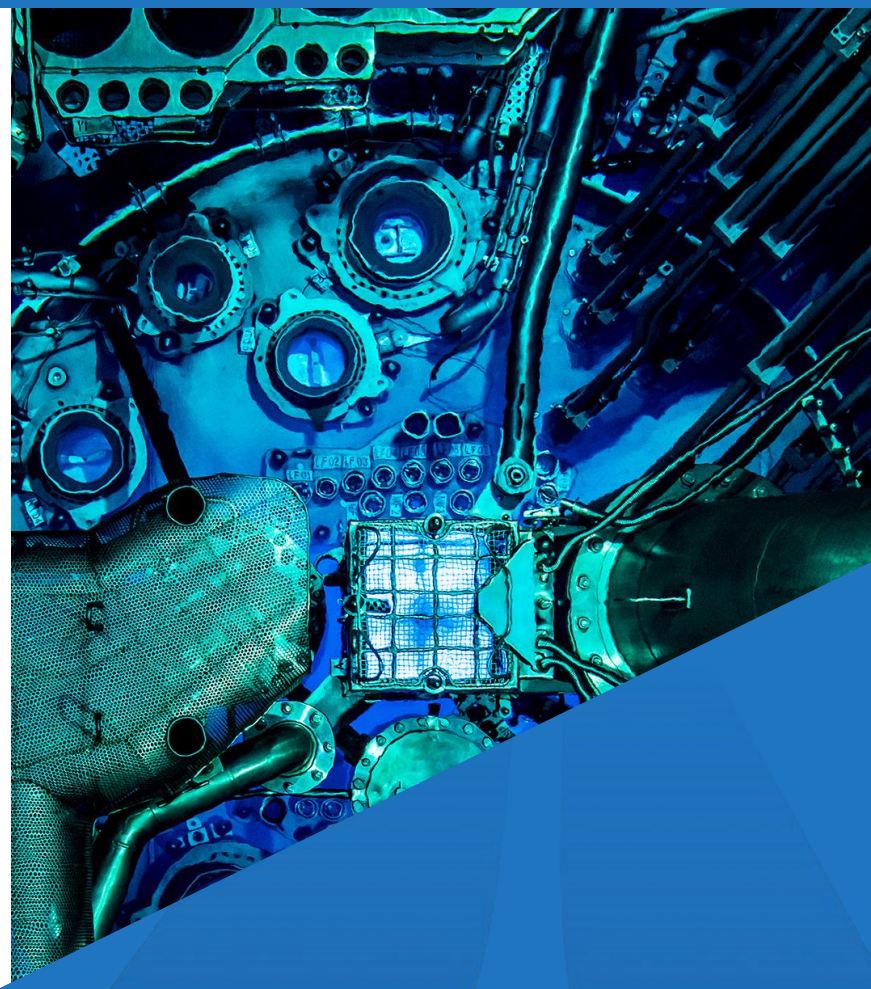

It takes years to learn

EXAFS

but hey, let's do it in under 20 min!

Bernt Johannessen

Senior Scientist

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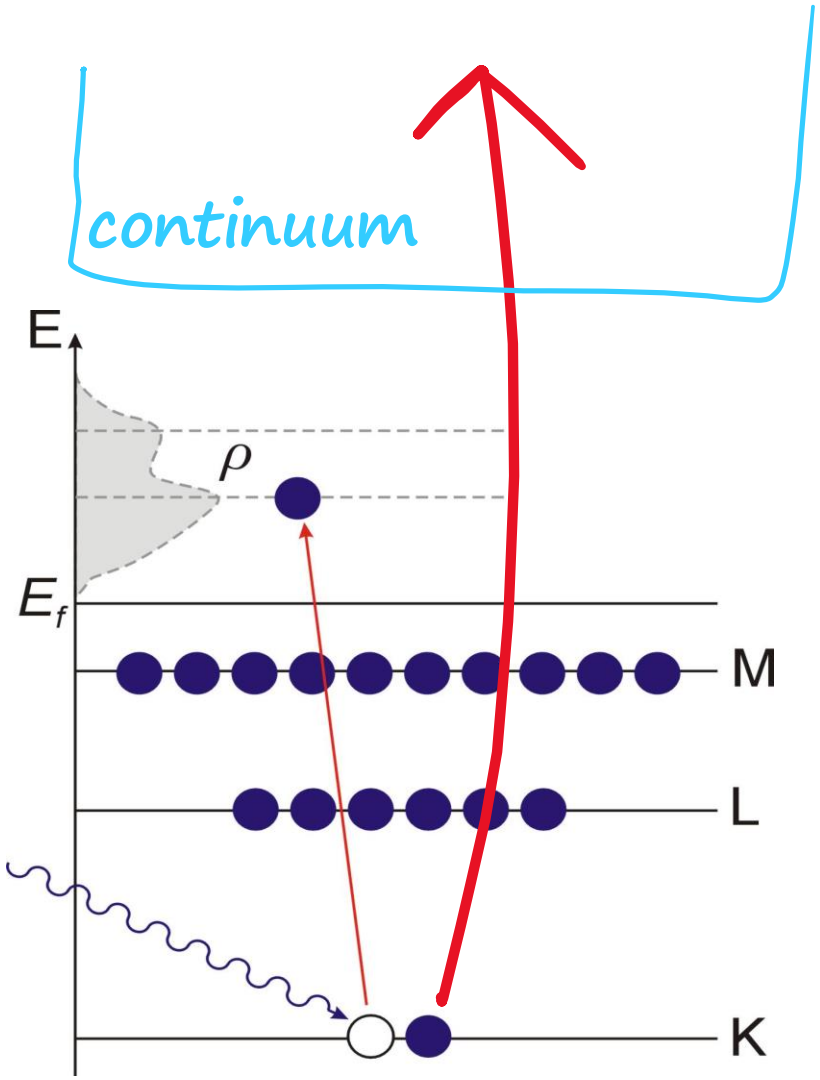
Science. Ingenuity. Sustainability.

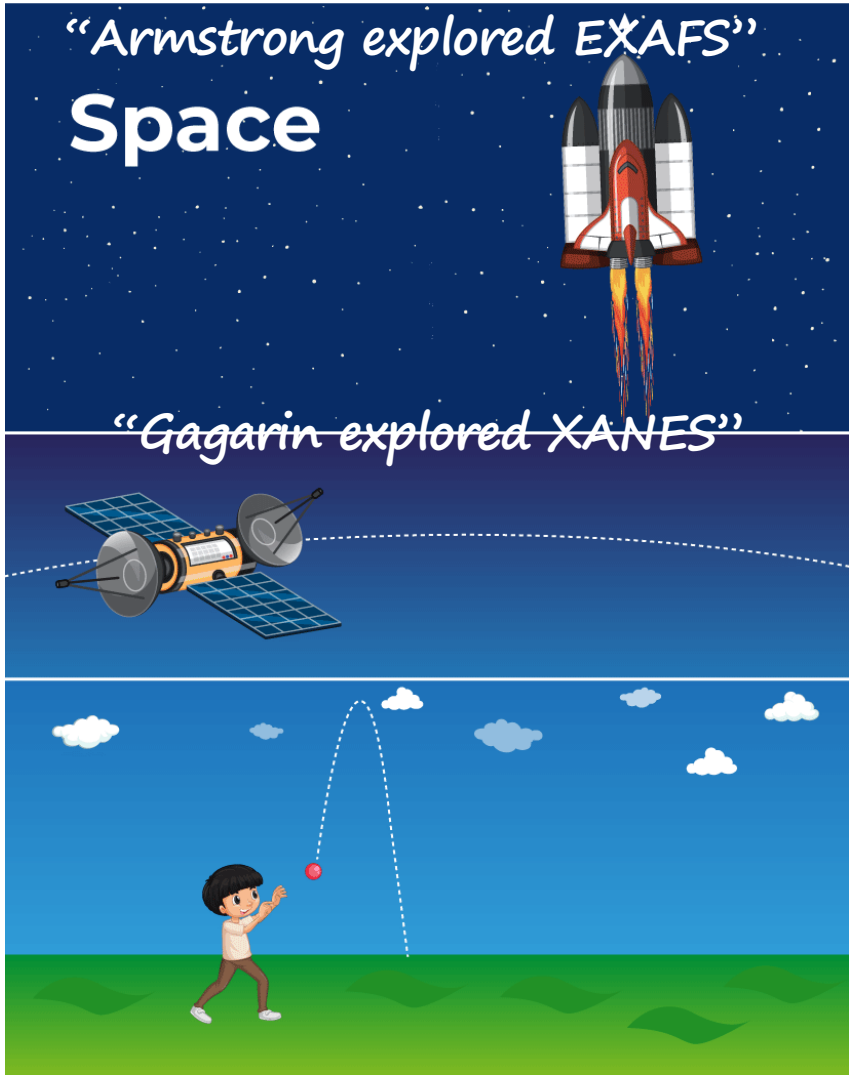
next step:

EXAFS

Photoelectron:

an x-ray is absorbed, and a core-level electron is promoted out of the atom





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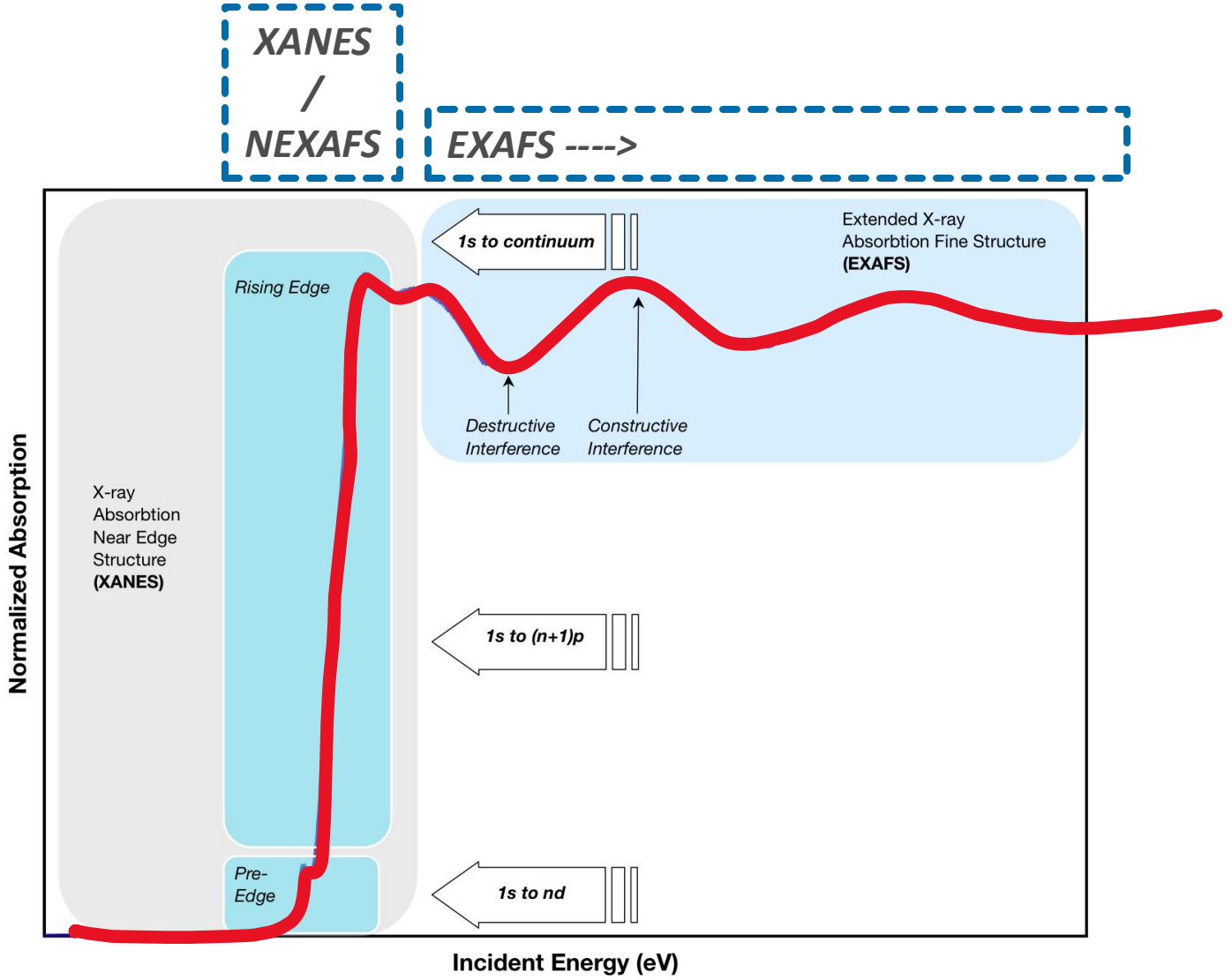
next step:

EXAFS



if we understand why the EXAFS looks that way,
we can model and interpret it

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The EXAFS equation

$$\chi(k) = \sum_i \frac{N_i S_0^2}{kR_i^2} f_i(k) e^{-2k^2\sigma_i^2} e^{-2R_i/\lambda(k)} \sin(2kR_i + \delta_i(k))$$

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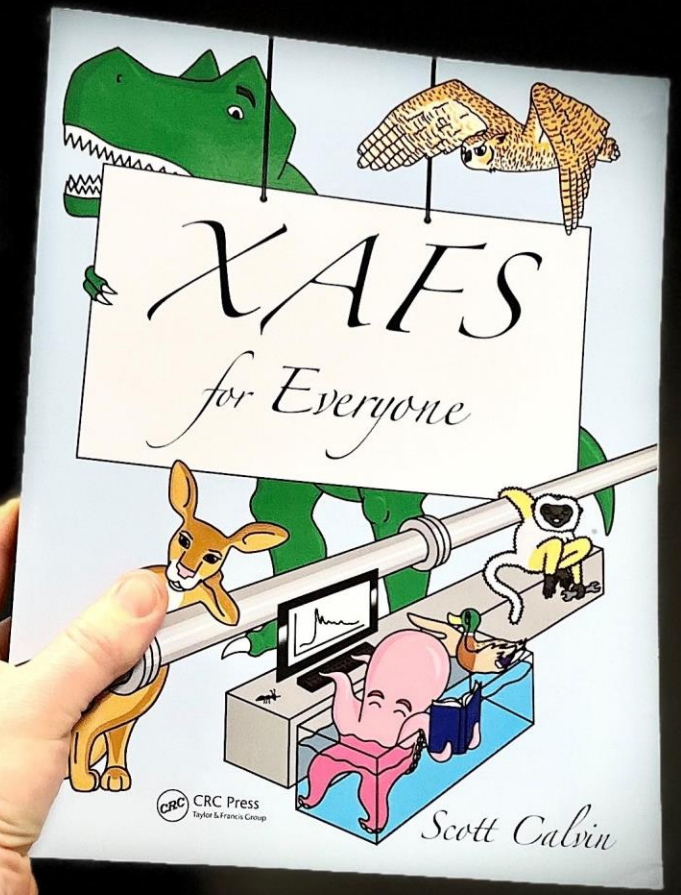
"EXAFS is due to interference of an electron with itself"



Scott Calvin

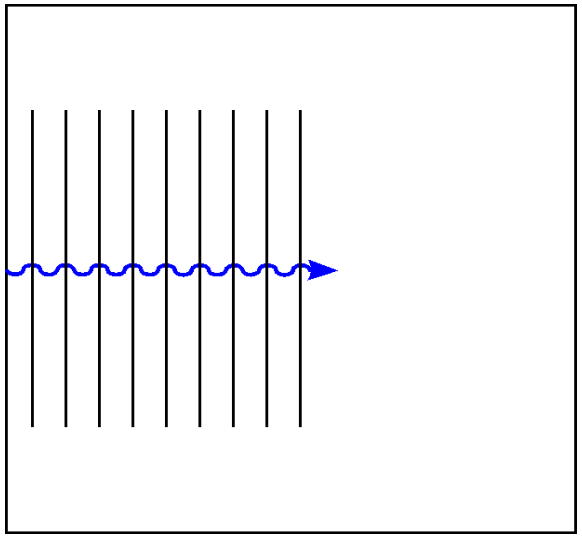
Lambert's Law

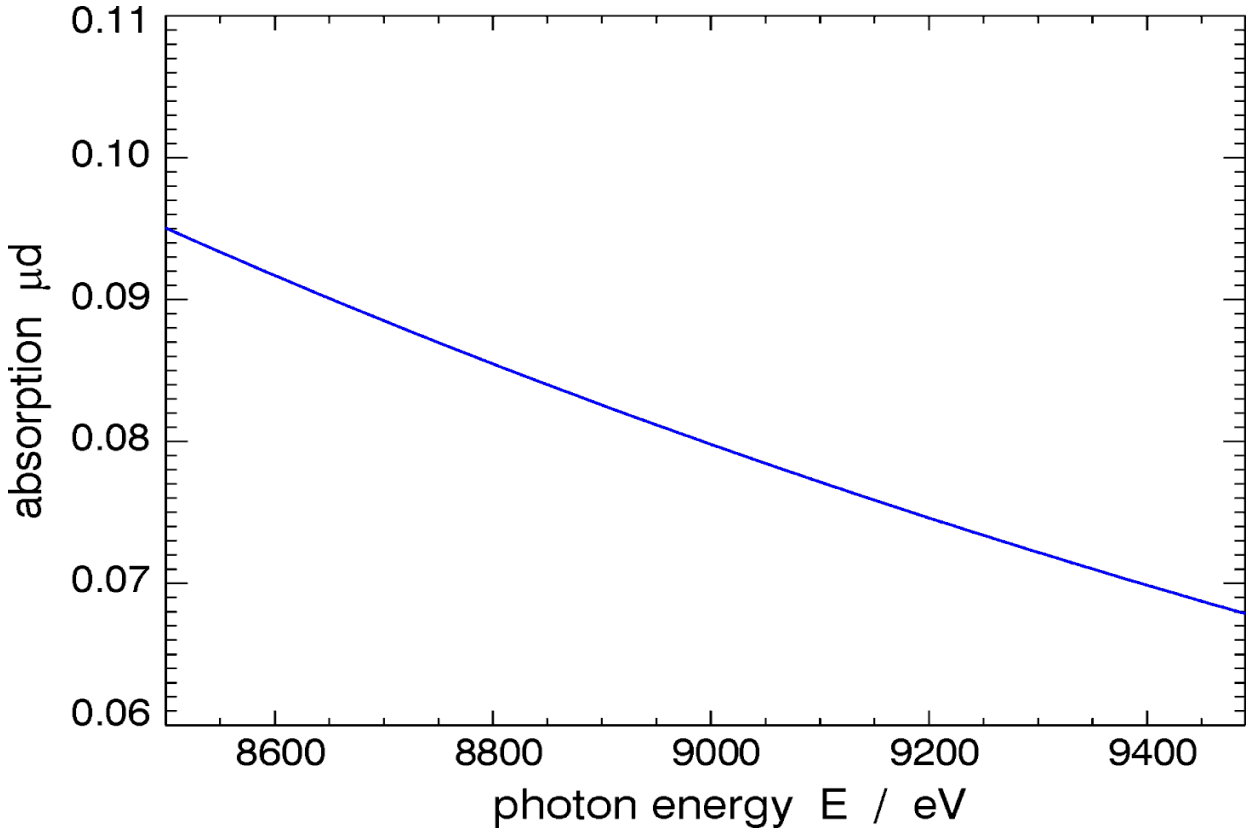
Intensity after passing through a medium:

$$I = I_0 e^{-\mu d}$$

- I_0: initial intensity
- d: path length
- μ: absorption coefficient

passing through air: *boring*





$\mu(E)$ **is a function of energy**

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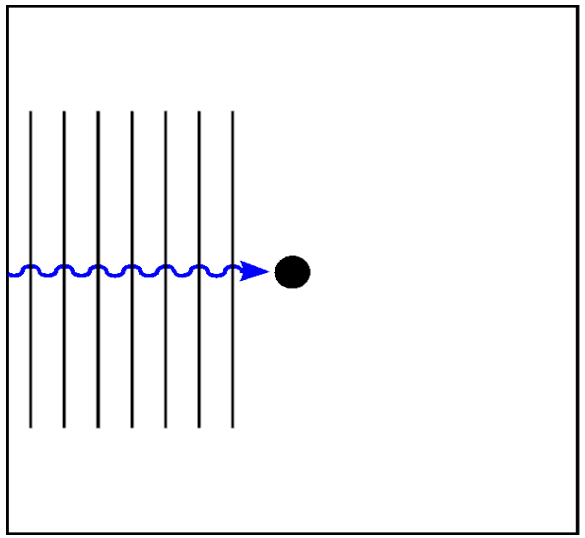
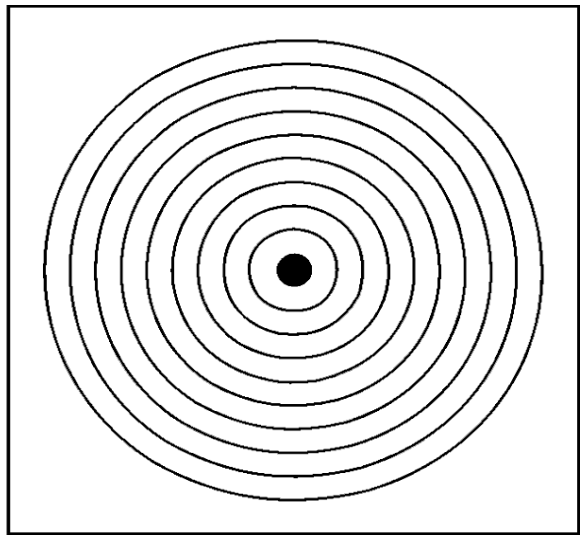
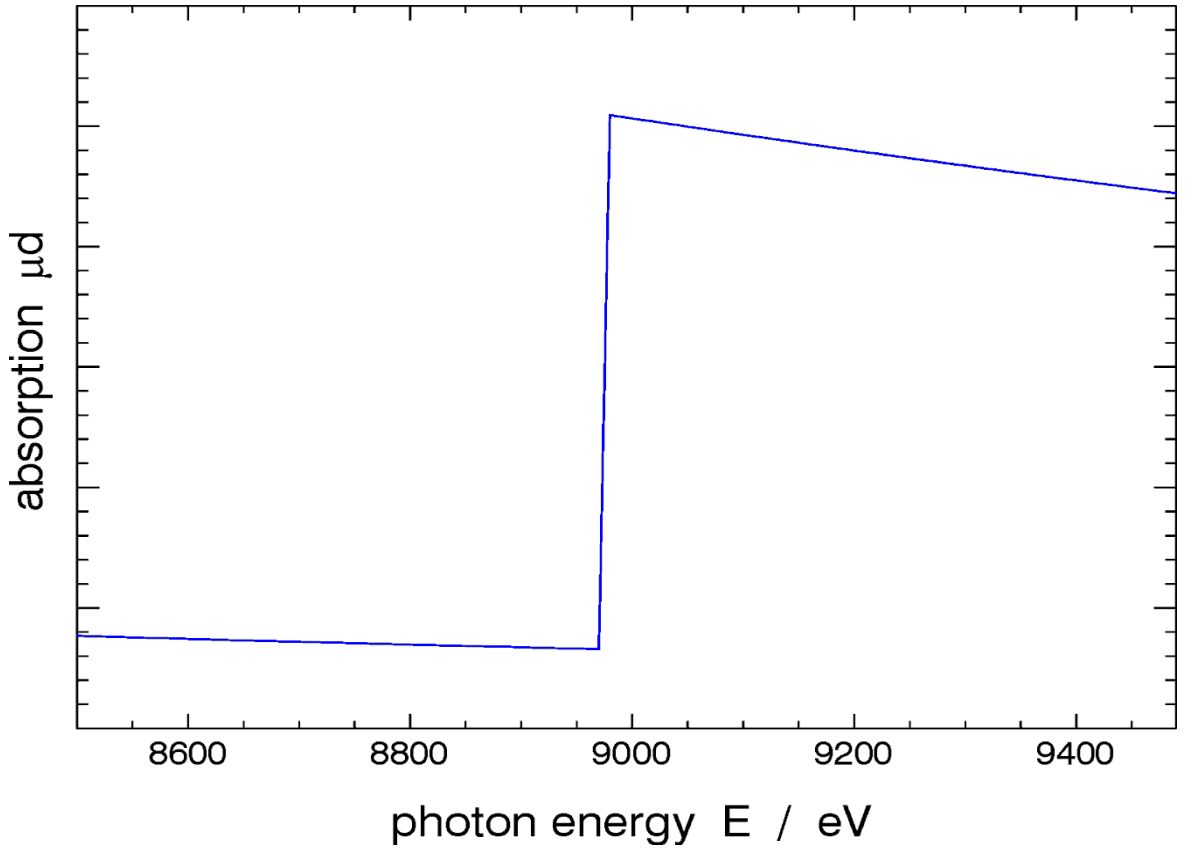
we encounter a lonely atom: *interesting*







photoelectron – dual particle/wave nature

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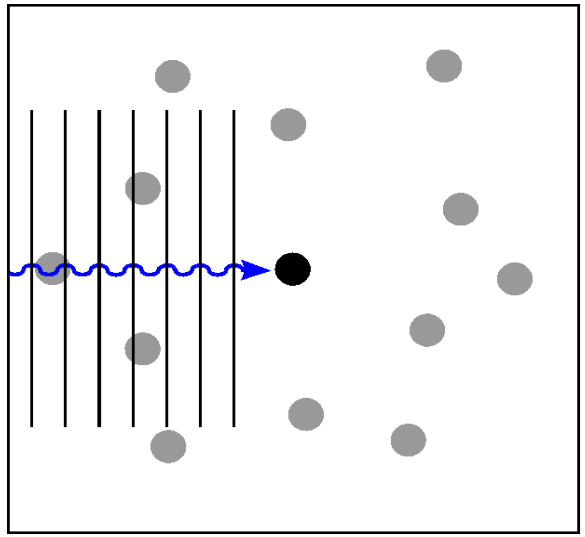
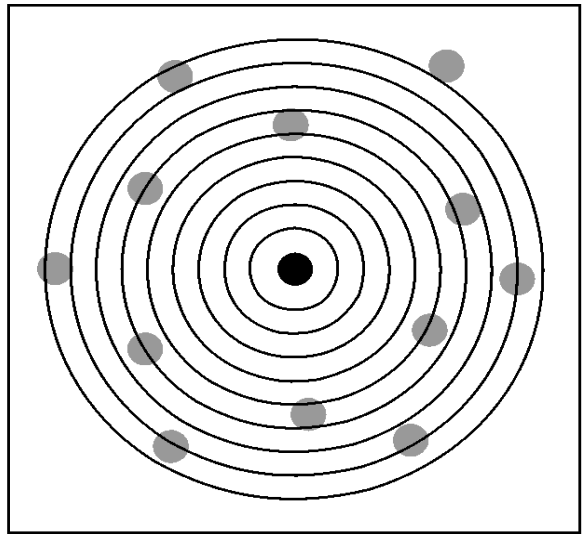
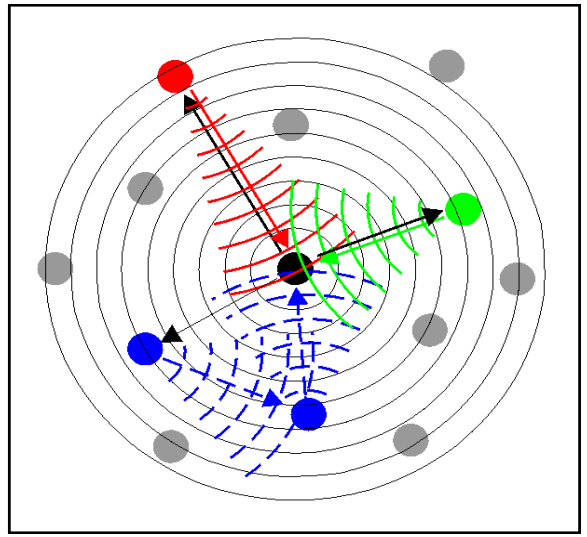
we encounter a group of atoms: *now you're talking!*







the photoelectron now interacts with the absorber's neighborhood

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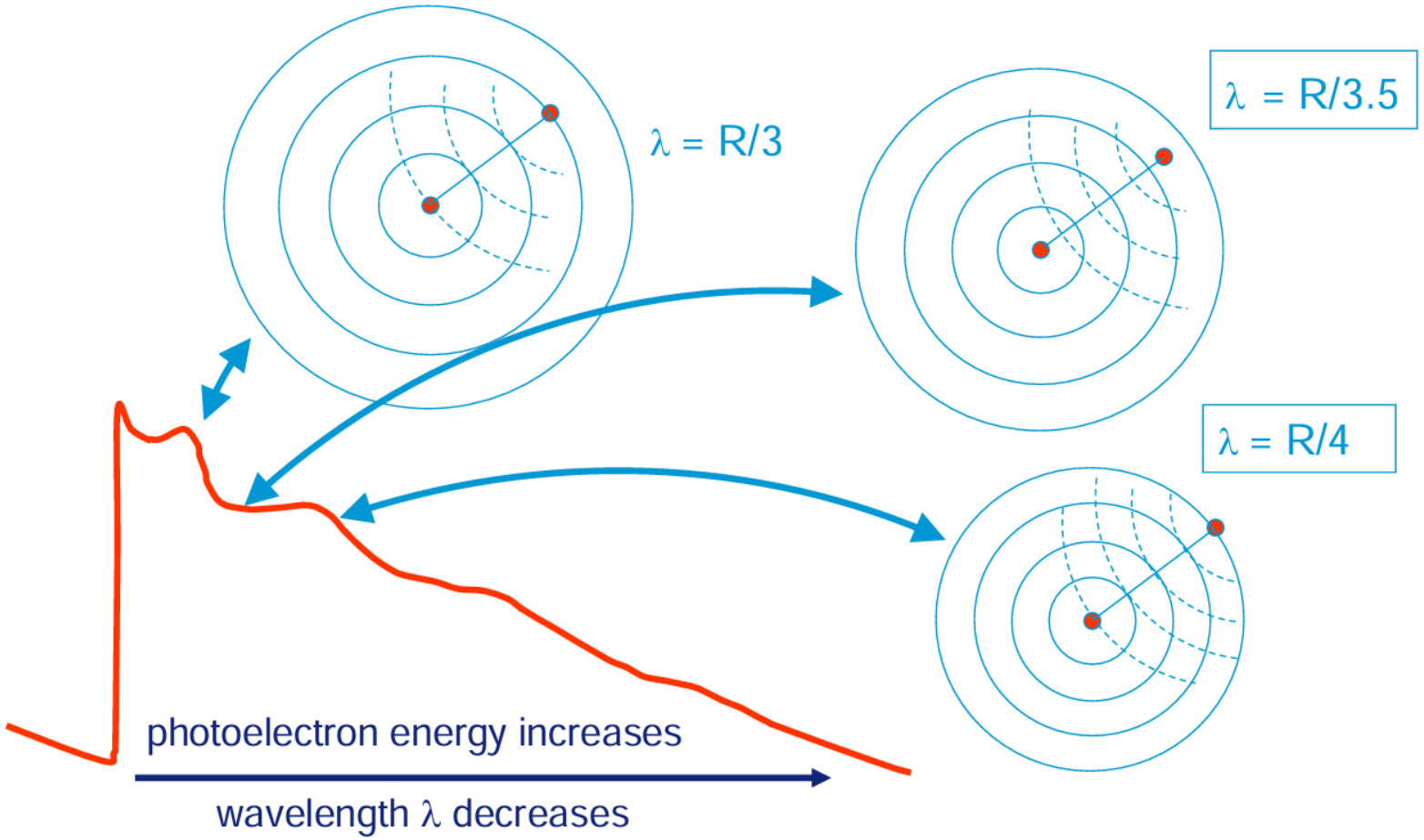
we encounter a group of atoms: *now you're talking!*



it is the interference between outgoing and incoming waves that gives rise to the sinusoidal variation of the absorption coefficient

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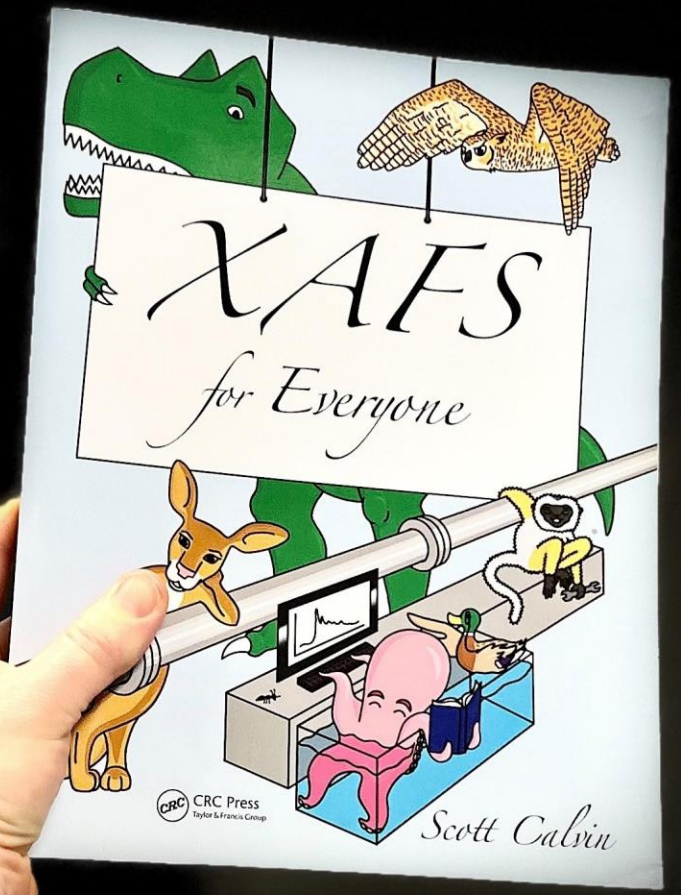
"EXAFS is due to interference of an electron with itself"



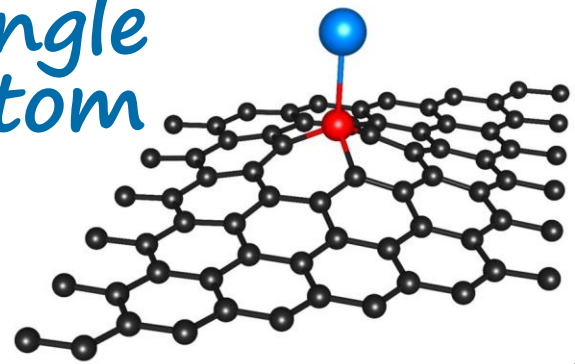
Scott Calvin

Example:

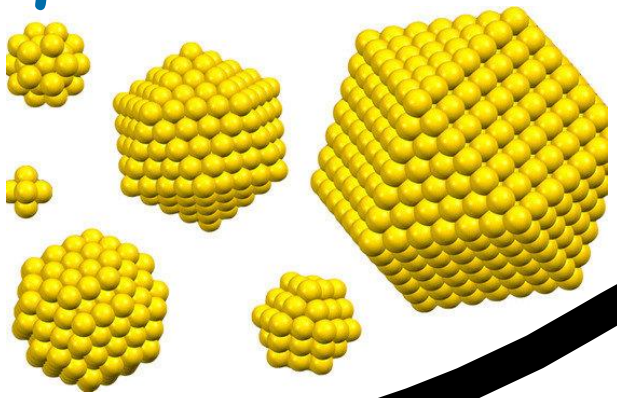
size effects in EXAFS

-> increasing catalytic efficiencies

single atom



nanoparticles



bulk metal

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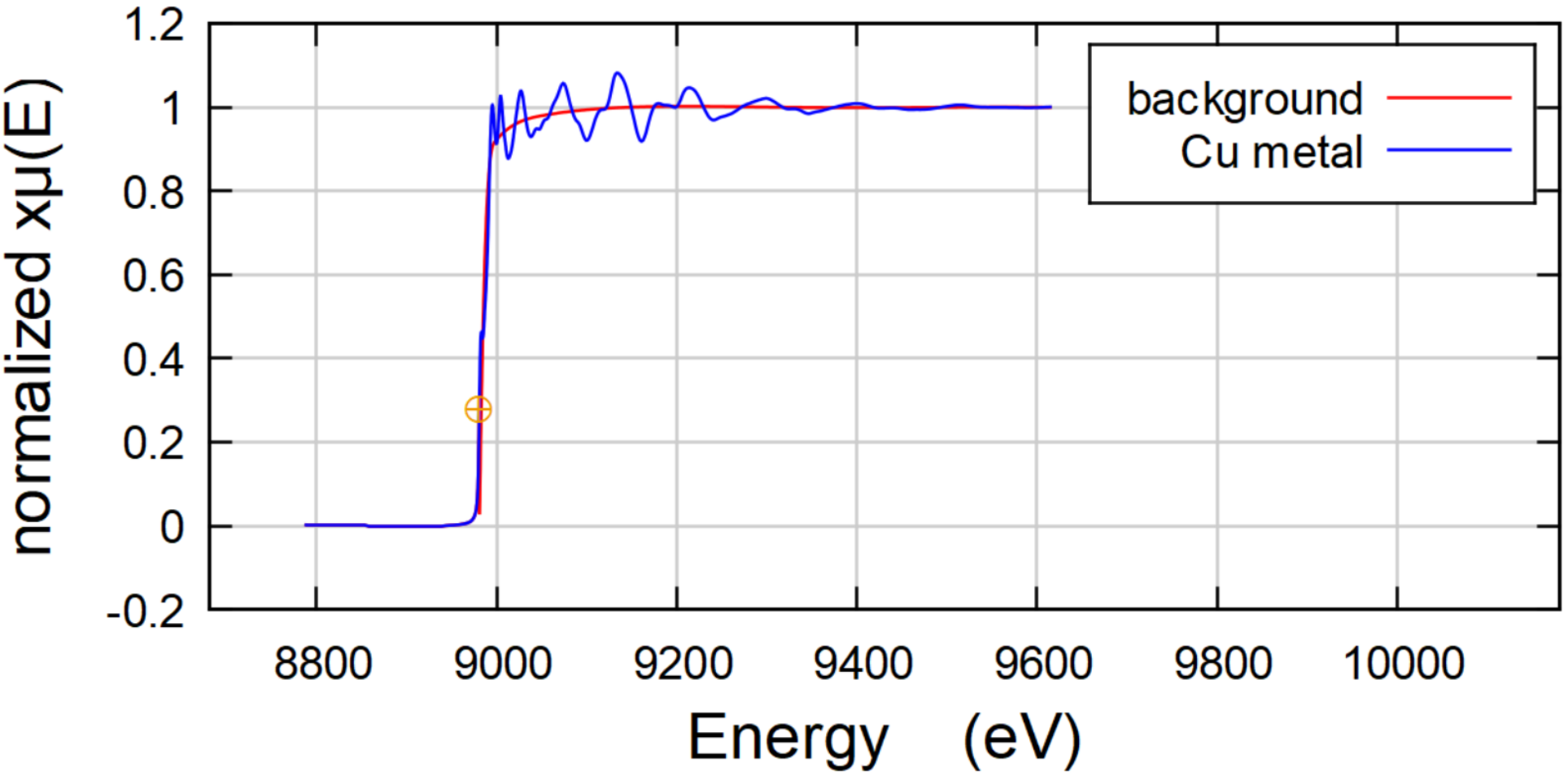
EXAFS: data normalisation & background removal



Normalise to account for variations in X-ray beam intensity and sample thickness, and remove the non-oscillatory part of the EXAFS spectrum

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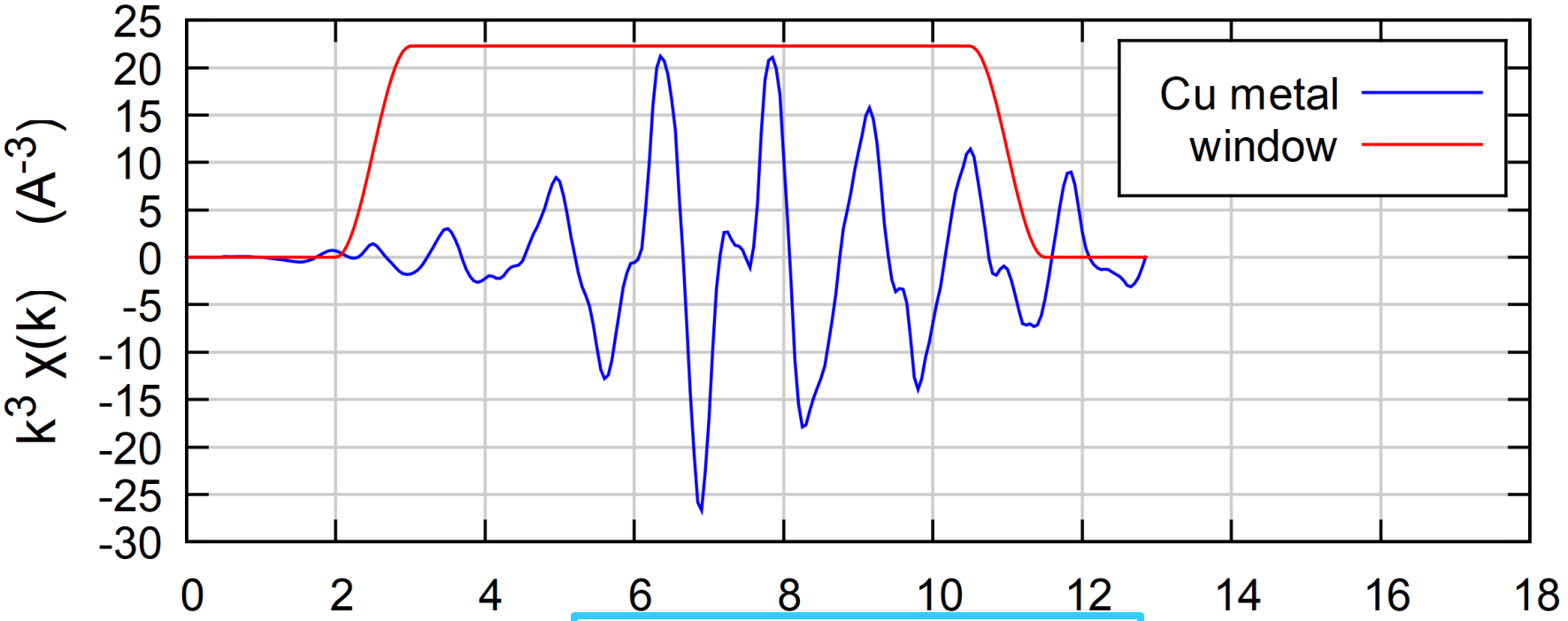
EXAFS: isolation of the fine structure ("wiggles")



$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}} \approx 16\sqrt{E - E_0}$$

The Wiggles
1991 –

Wavenumber is a measure of the momentum of a photoelectron after it has been ejected from an atom. Think of it simply as a non-linear energy scale.

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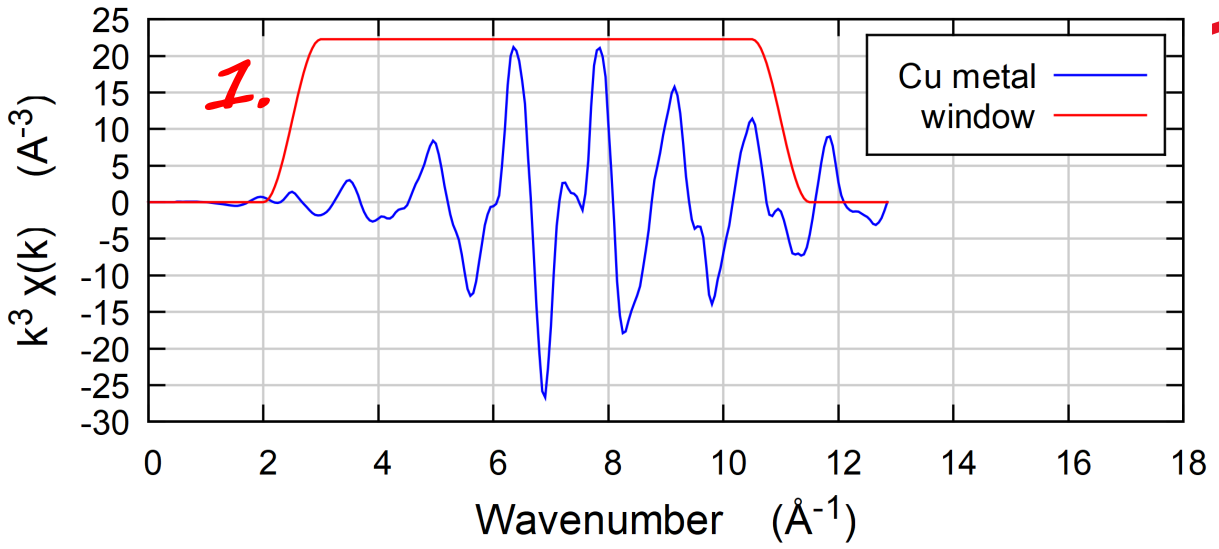
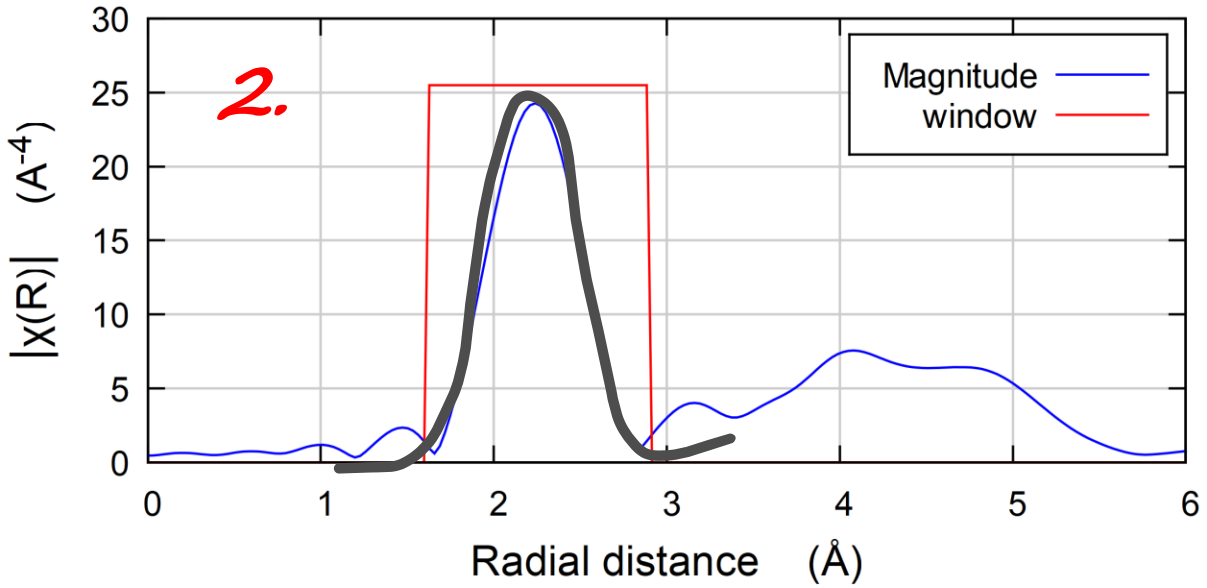
EXAFS: isolation of the fine structure

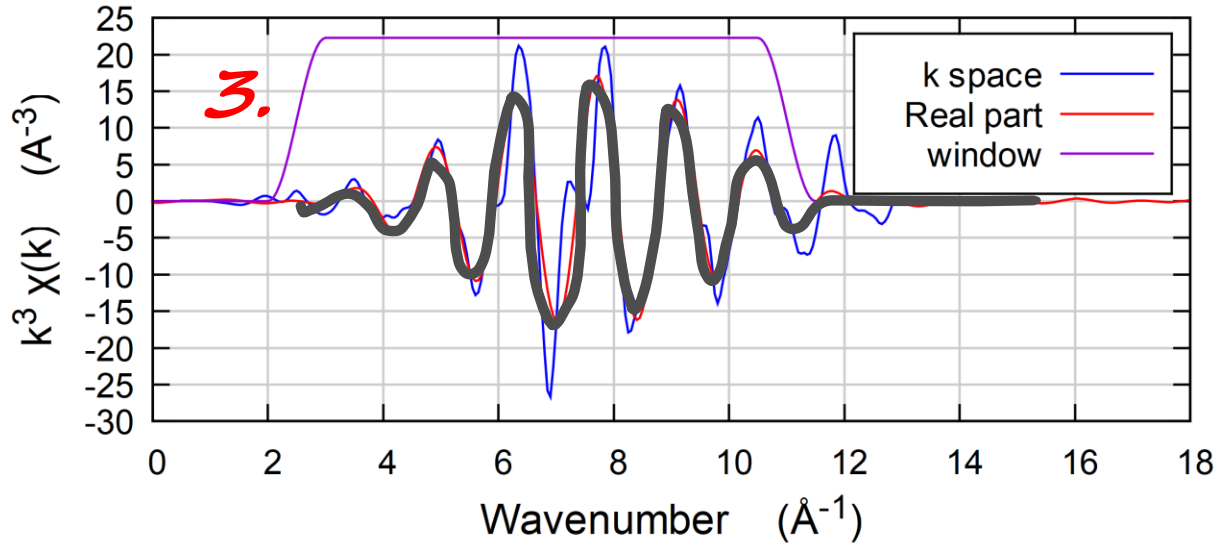


J. Fourier, 1822

$$f(\omega) = \int_{-\infty}^{\infty} f(x) e^{-i2\pi x\omega}\, dx$$

(forward) Fourier Transform





Back Transform

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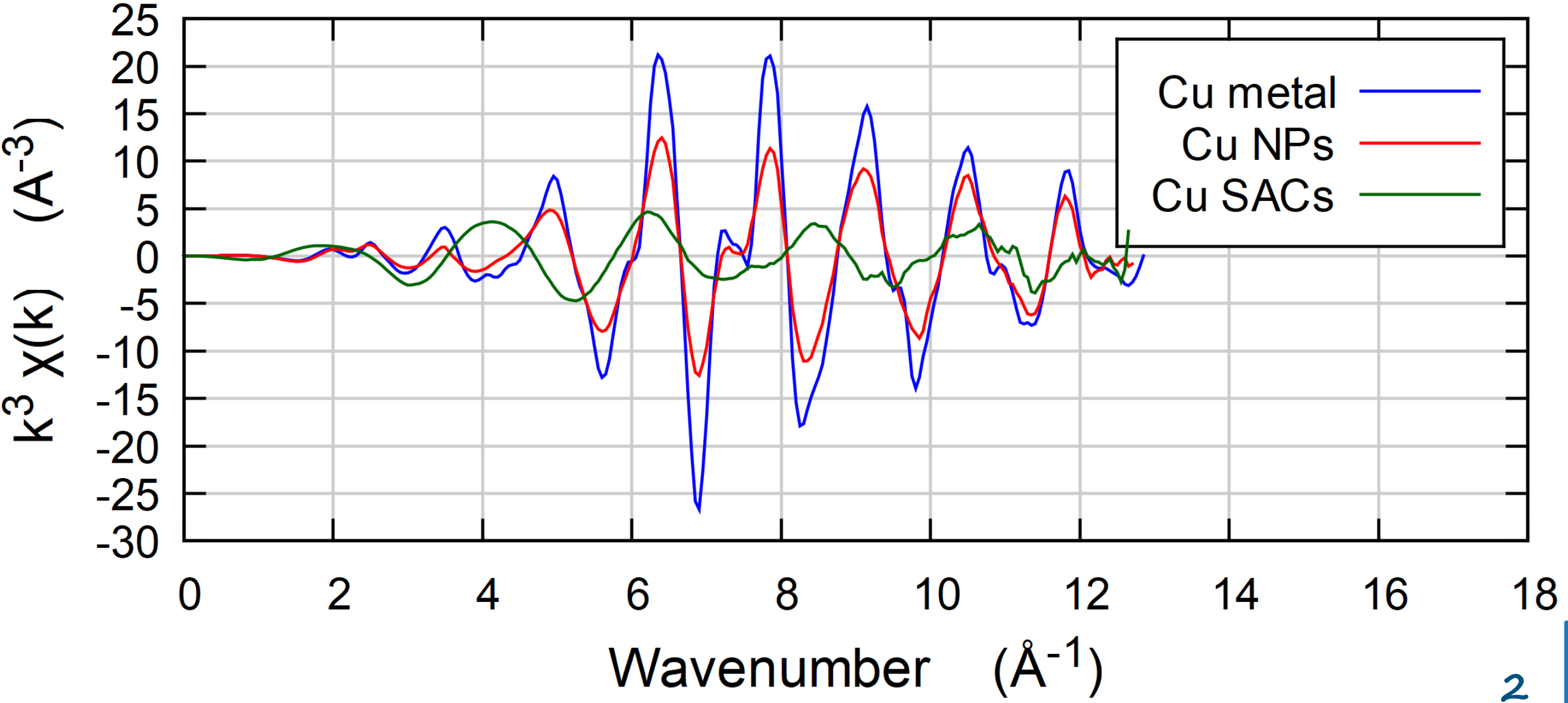
EXAFS: comparing spectra



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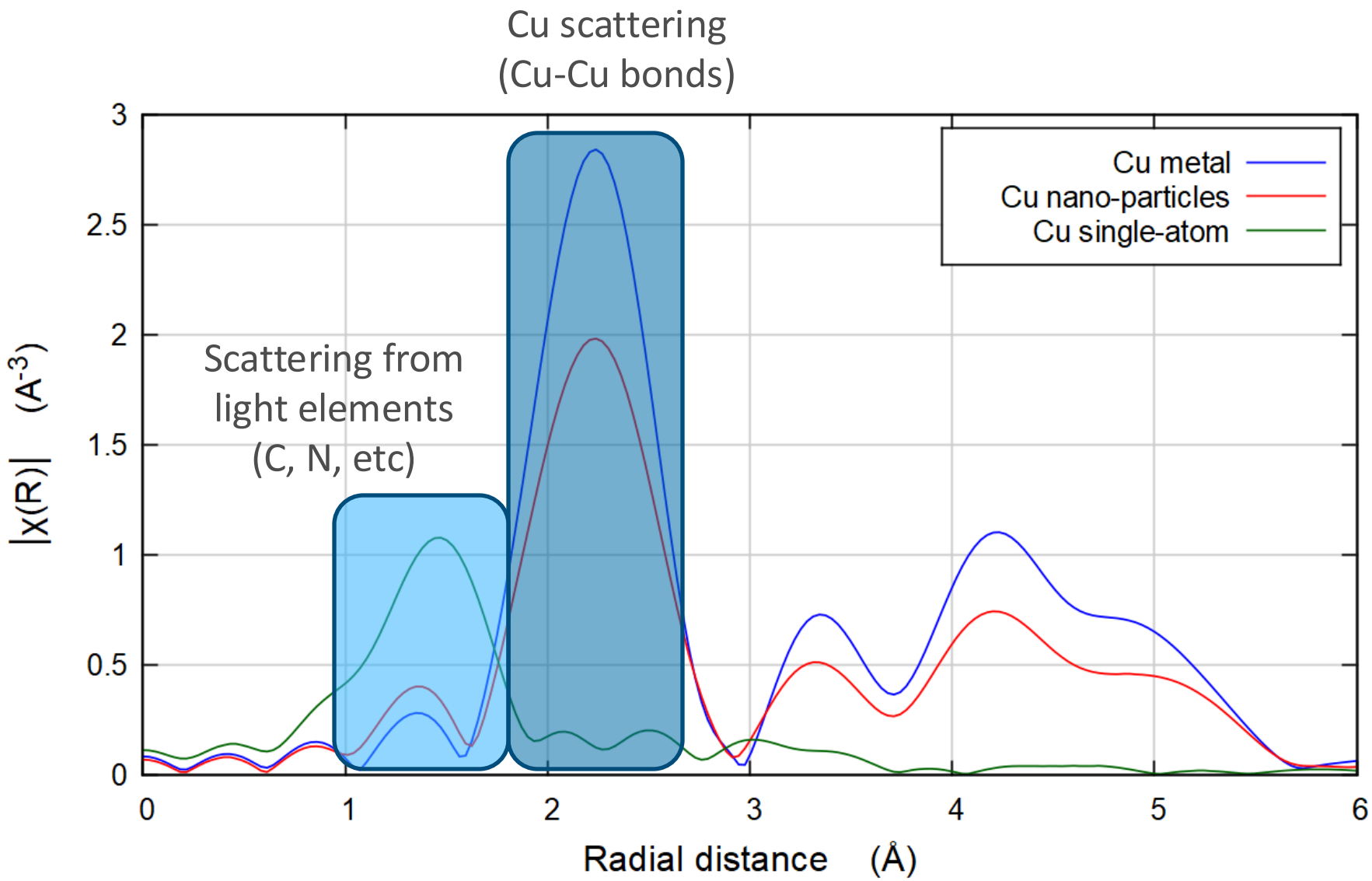
EXAFS: comparing spectra



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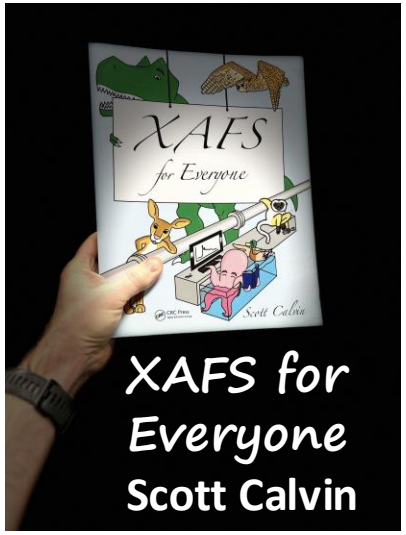
EXAFS: comparing spectra

For some systems, the qualitative interpretation of EXAFS is rather quick and easy!

We can now understand (parts of) the EXAFS equation



normalised oscillatory part of the absorption coefficient

coordination number

$$\chi(k) = \sum_i \frac{N_i S_0^2}{k R_i^2} f_i(k) e^{-2k^2\sigma_i^2} e^{-2R_i/\lambda(k)} \sin(2kR_i + \delta_i(k))$$

summed over all shells/atoms

bond length

Debye-Waller factor (disorder)

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