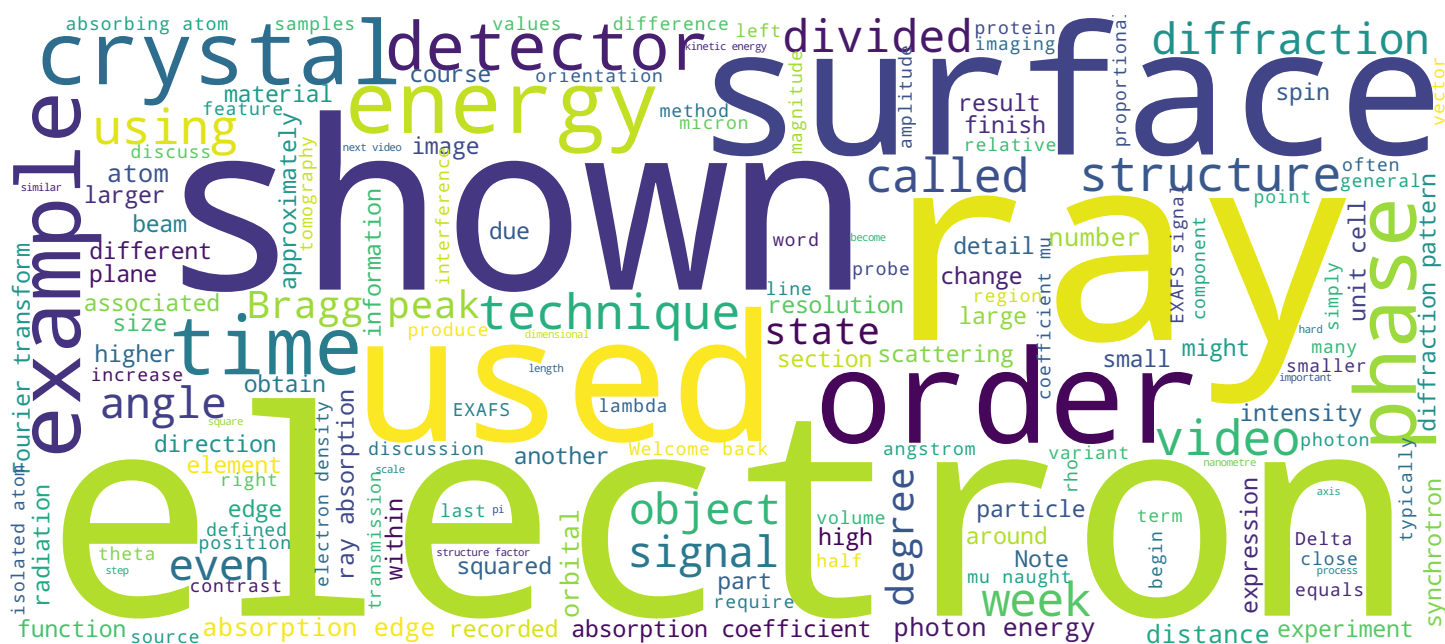


Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



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Video



Contents and objectives of this video



- Introductory remarks
- Rules of thumb
- Extracting the EXAFS signal

Welcome back to a discussion of the last of the X-ray absorption techniques covered in this course, namely, extended X-ray absorption fine structure spectroscopy. After some introductory remarks, we will consider simple rules of thumb associated with EXAFS and how one goes about extracting the EXAFS signal from an absorption spectrum.

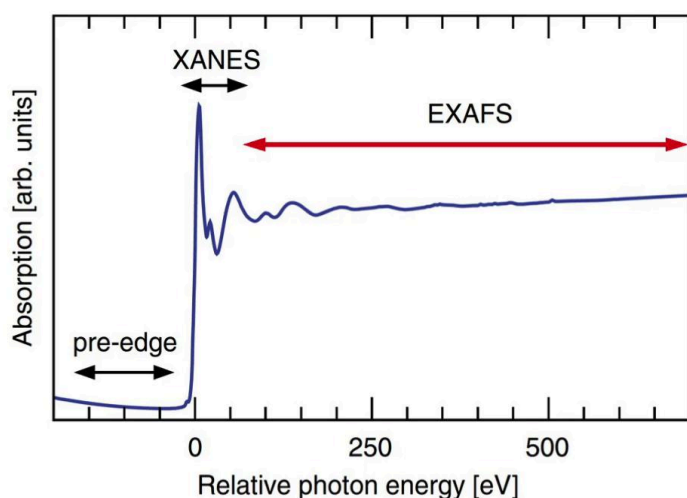
Notes

Summary



0m 05s

EXAFS – introductory comments



- ca. 50 – 1000 eV above absorption edge
- $\lambda_e \sim 1.5 - 0.4 \text{ \AA}$
- IMFP $\sim 5 - 20 \text{ \AA}$
 - Probes immediate neighbourhood around absorbing atom
 - Single-scattering dominates
- Oscillations due to interference of backscattered electron cloud with outgoing photoelectron wavefunction
- Sensitivity down to ca. 50 ppm

Extended X-ray absorption fine structure signal refers to the oscillations in the X-ray absorption coefficient starting at approximately 50 electronvolts above an absorption edge, and extending all the way up to several hundred electronvolts, or even at one kiloelectronvolt. If we remember our equation for the de Broglie wavelength, we see that EXAFS produces electron wave functions with wavelengths of the order of 0.4 to one and a half angstroms, similar to, if slightly smaller, than interatomic distances.

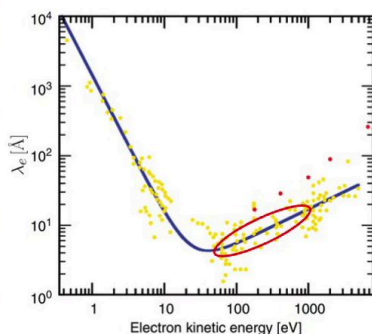
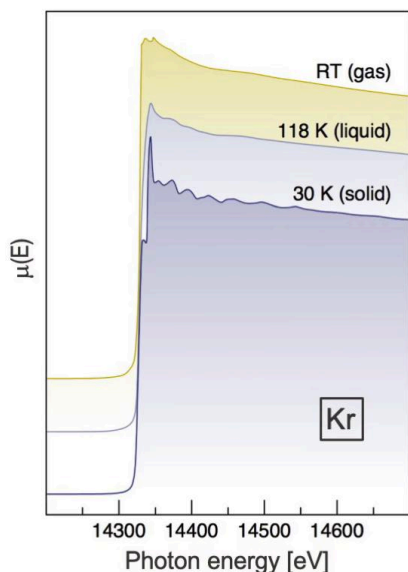
Notes

Summary



0m 27s

EXAFS – introductory comments



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Q. Wang *et al.*, Phys. Rev. B **72** 092202 (2005)

The inelastic mean free path of electrons in this range is short, of the order of a few angstroms, hence EXAFS only probes the immediate neighborhood of the absorbing atom. Moreover, single scattering dominates, making modelling simpler. EXAFS is therefore an important technique in non-crystalline solids and liquids, as it yields information of the short-range structure. It is much used for investigating liquids, clusters, biological materials, low-concentration impurities down to 10 parts per million, and catalysts, although it can also be used for well-ordered structures. Now, consider the graph on the left showing the EXAFS spectra for krypton above its K-edge. The absorption coefficient of an isolated atom, μ_0 , varies almost monotonically and smoothly with wave vector or energy above the absorption edge. In the liquid state, however, the absorption coefficient, μ , is modulated by the so-called EXAFS function, χ , because of interference with backscattered waves. As a solid, the EXAFS modulation is even more pronounced, as the interference is enhanced by the krypton being crystalline.

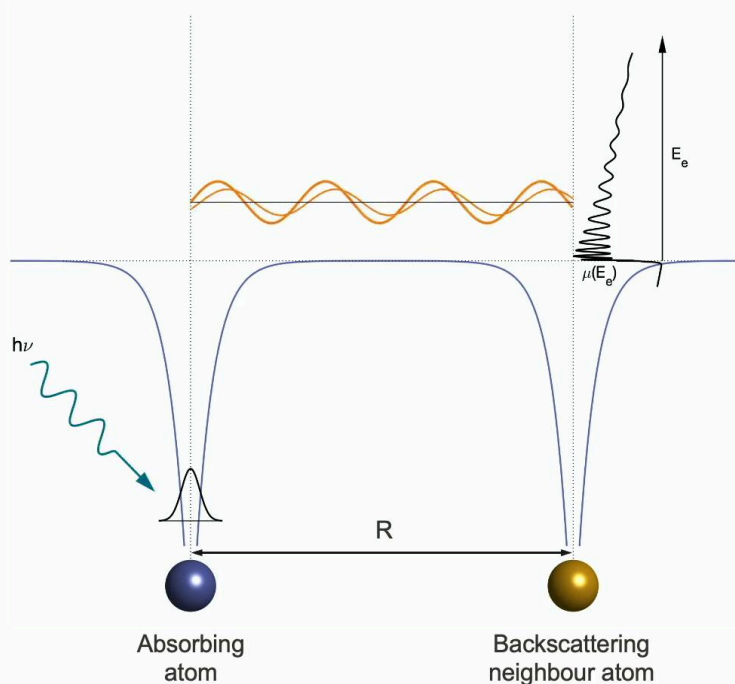
Notes

Summary



1m 06s

EXAFS – introductory comments



- ca. 50 – 1000 eV above absorption edge
- $\lambda_e \sim 1.5 - 0.4 \text{ \AA}$
- IMFP $\sim 5 - 20 \text{ \AA}$
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 - Single-scattering dominates
- **Oscillations due to interference of backscattered electron cloud with outgoing photoelectron wavefunction**
- Sensitivity down to ca. 50 ppm

EXAFS is caused by single backscattering events by nearest neighbour atoms of the outgoing photoelectron produced through X-ray absorption. The back scattered waves interfere with the original photoelectron wave, which results in a change in the electron density at the absorbing atom. Because the de Broglie wavelength decreases with increasing photoelectron energy, the phase between the outgoing wave and backscattered wave at the absorbing atom will change. As a consequence, this leads to a modulation of the absorption strength, $\mu(E_e)$, as the photon energy is scanned. This is the EXAFS signal.

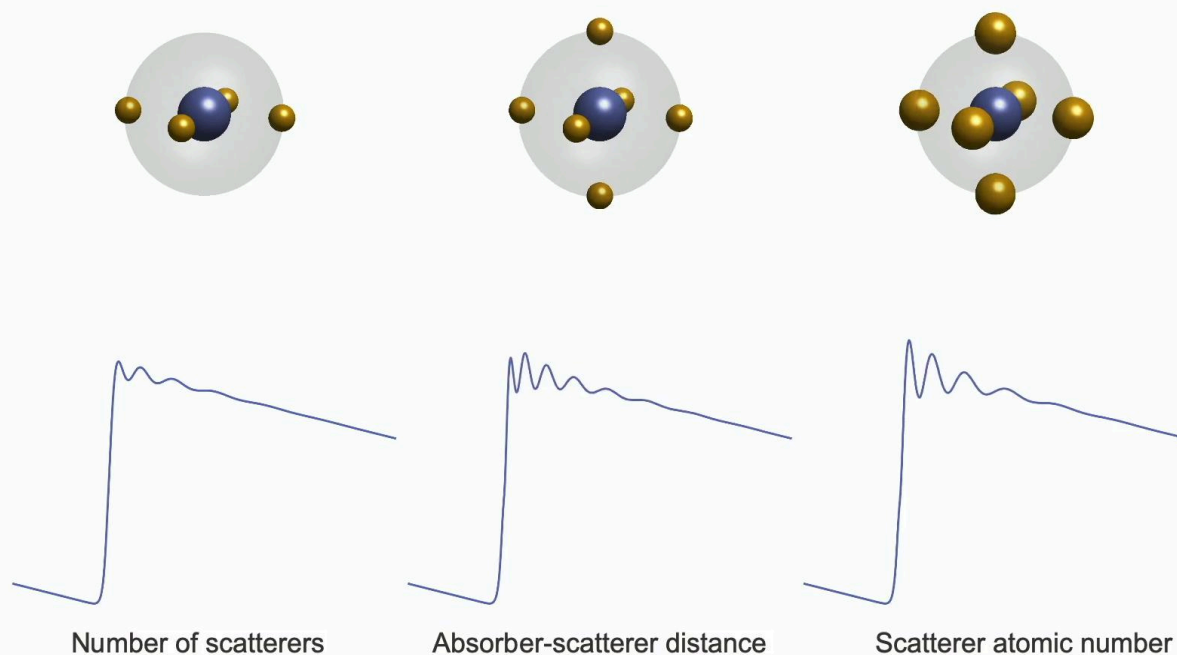
Notes

Summary



2m 32s

The EXAFS signal – rules of thumb



The most important parameters, in addition to the atomic absorption coefficient, μ , are the electron wavelength, λ_e , which is inversely proportional to the square root of the photoelectron's kinetic energy, the number of nearest neighbours, the distance r between the absorbing atom and neighbouring atoms, and the strength of the backscattering from the neighbouring atoms. These three rules of thumb are shown schematically here. The EXAFS oscillatory signal increases with the number of neighbours in a given shell. The oscillation period dilates with decreasing shell radius, and this signal also increases with the scattering amplitude of the scattering atoms, which is closely related to their atomic number.

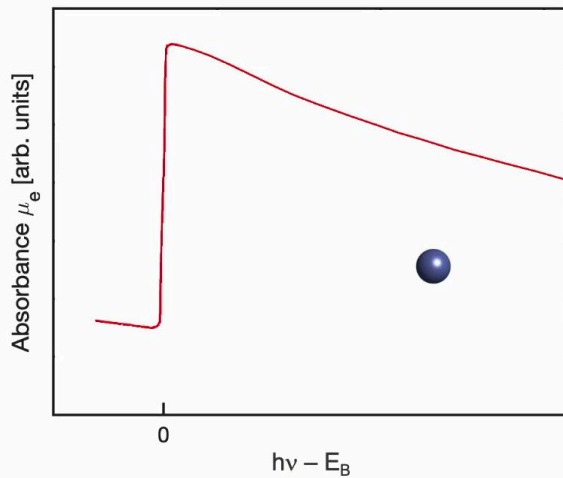
Notes

Summary



3m 17s

The EXAFS signal quantitatively



- Isolated atom
 - $\mu_0(h\nu)$
 - Featureless except absorption edge

Consider first the absorption coefficient of an isolated atom, μ_0 , which varies monotonically and smoothly with wavevector or energy above the absorption edge.

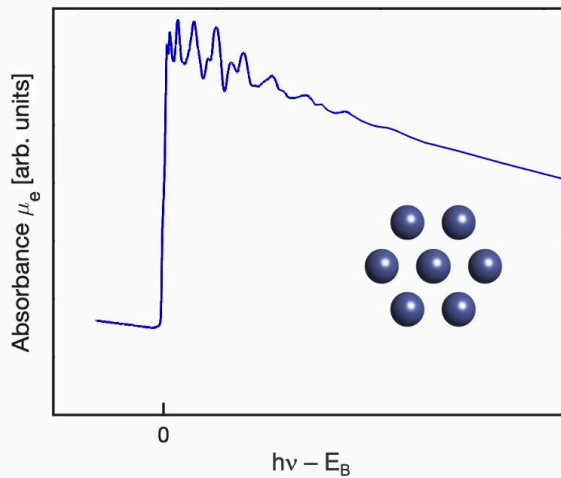
Notes

Summary



4m 07s

The EXAFS signal quantitatively



- Isolated atom
 - $\mu_0(h\nu)$
 - Featureless except absorption edge
- In environment of surrounding scattering atoms
 - Modulated absorption due to interference between outgoing and backscattered electron waves

$$\mu(k_e) = \mu_0(k_e) [1 + \chi(k_e)]$$

$$\chi(k_e) = \frac{\mu(k_e) - \mu_0(k_e)}{\mu_0(k_e)}$$

In condensed matter, however, the absorption coefficient μ_K , is modulated by the EXAFS function $\chi(k_e)$ as a function of photon energy or wavevector. More commonly, the absorption coefficient μ and the EXAFS function are expressed in terms of the photoelectron's de Broglie wavevector, k_e . Rearranging this expression, we obtain $\chi(k_e)$ of k_e is equal to $\mu(k_e) - \mu_0(k_e)$ divided by $\mu_0(k_e)$. $\chi(k_e)$ is therefore, an expression of the effect of an isolated atom's absorption characteristics caused by it no longer being isolated.

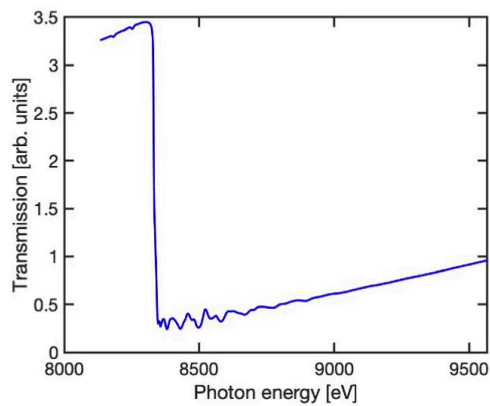
Notes

Summary



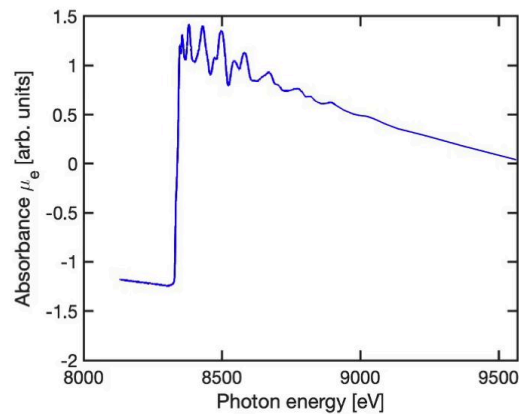
4m 20s

Converting transmission to absorbance



$$Tr = I/I_0 = \exp(-\mu z)$$

$$\ln \left(\frac{1}{Tr} \right) \propto \mu$$



We finish this first of two videos on EXAFS by going step by step through the process of extracting the EXAFS signal, starting with the transmission spectra. The transmission is simply the transmitted intensity divided by the incident intensity, which we have argued both in the first part of the course and also earlier this week to be equal to the exponent of minus μz . Therefore, the natural logarithm of the reciprocal transmission is proportional to μ .

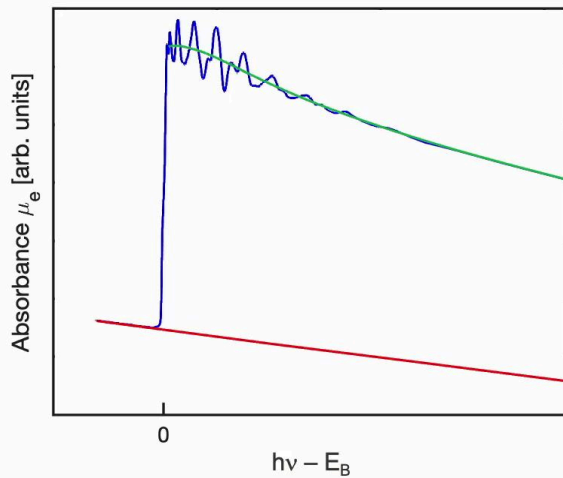
Notes

Summary



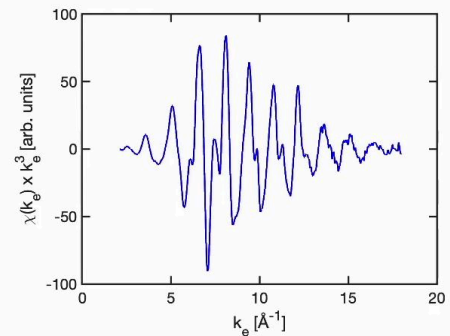
5m 06s

Extracting the EXAFS signal



- Extracting $\chi(k_e)$
 - Linear fit **pre-edge** and subtract from $\mu(k_e)$
 - Fit data above **absorption edge** to a polynomial and subtract this too
 - Convert $h\nu$ to k_e using

$$k_e [\text{\AA}^{-1}] = 0.512 \sqrt{(h\nu - E_B)[\text{eV}]}$$



We then need to remove both the background signal and a smooth polynomial fit for μ_0 , the absorption spectrum for the isolated atom above the absorption edge. We then convert the abscissa from the photon energy to k_e , using our regular expression for this. This yields an oscillatory function that is very weak for high values of k_e . The trick is now to weight the function by multiplying it by k_e cubed, or sometimes k_e squared.

Notes

Summary



5m 38s

In the next video...



With this massaged data, we move to the final video of this week, where we look in detail at the EXAFS signal. We'll finish with a brief description of variants of EXAFS, notably EDXAS and QEXAFS.

Notes

Summary



6m 15s