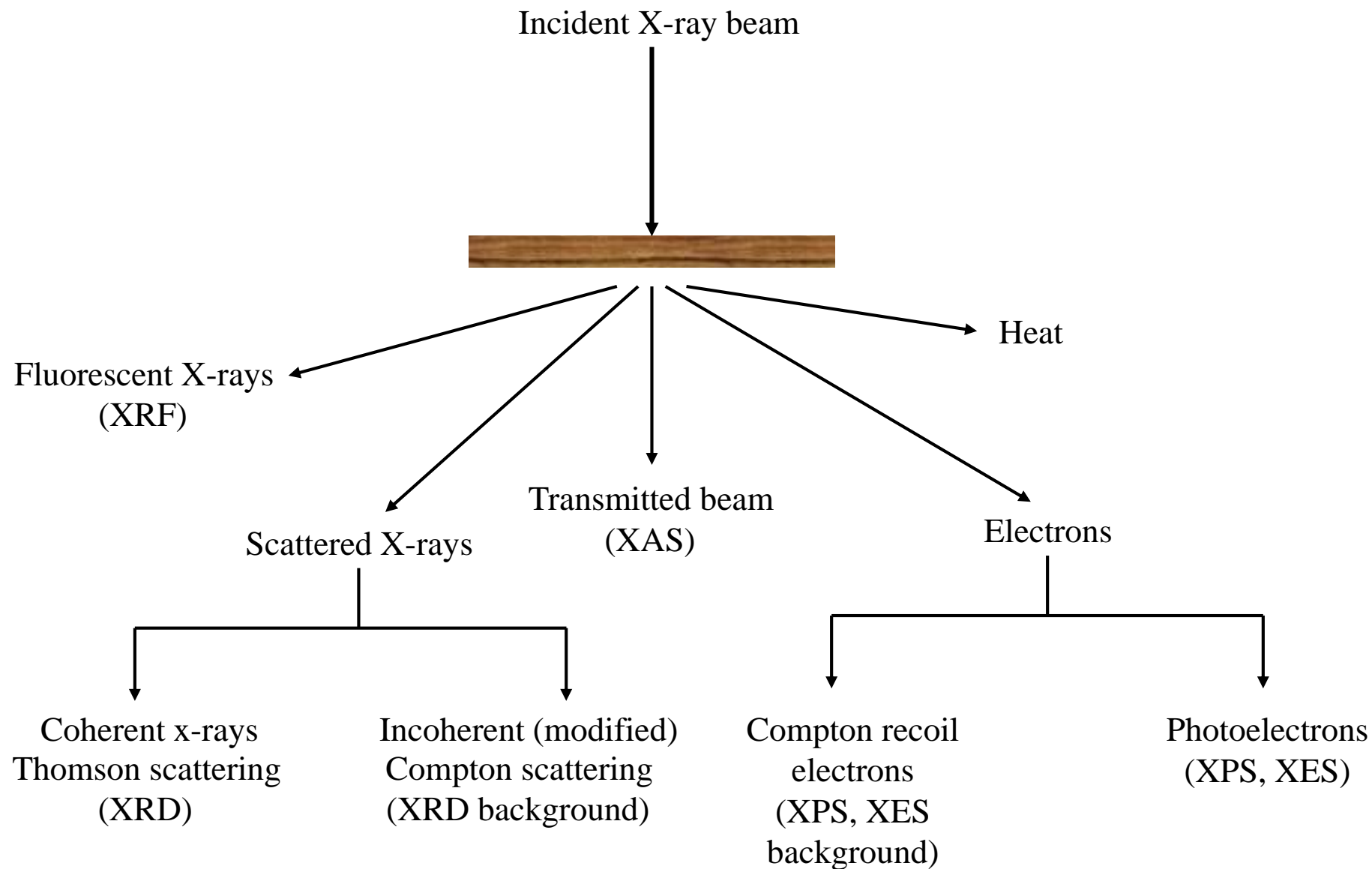


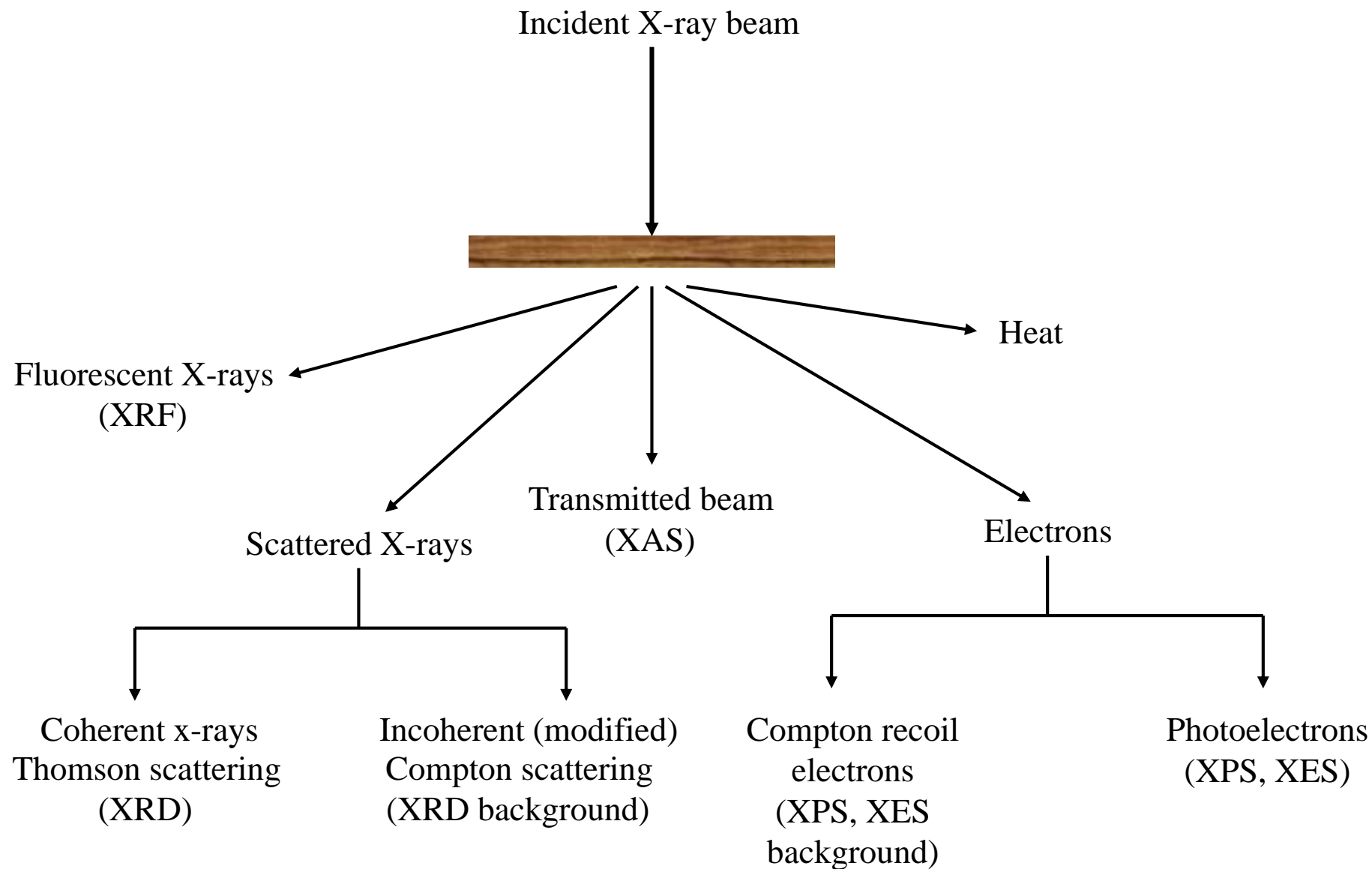
X-ray Absorption Spectroscopy

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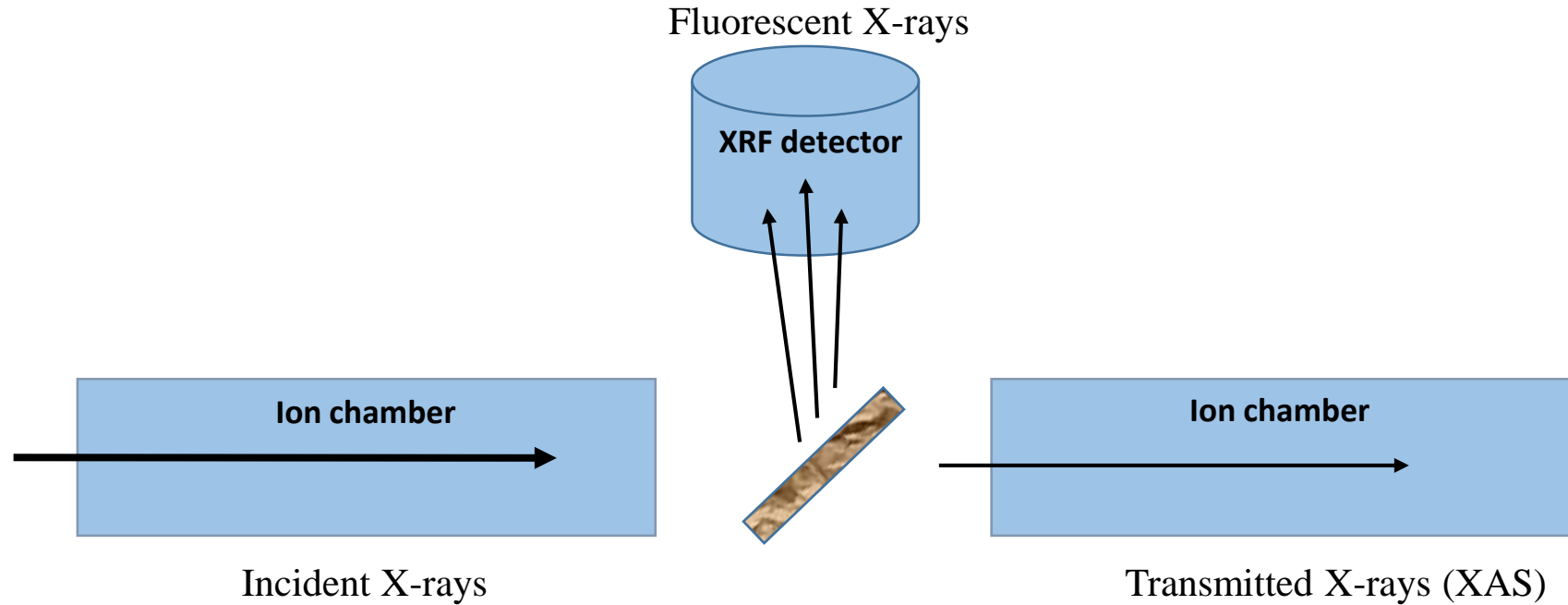
Interaction of X-rays with matter



Interaction of X-rays with matter



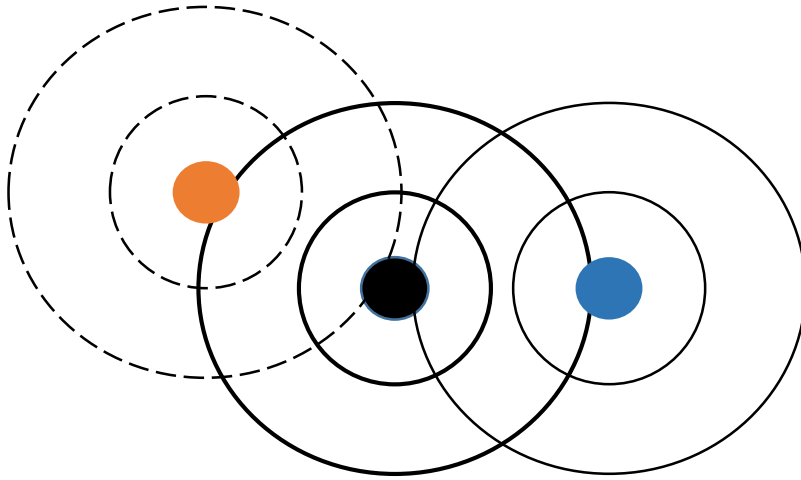
X-ray Absorption Spectroscopy



- Requires x-rays over a range of frequencies.
- Such x-rays are usually derived from synchrotron sources as they are easily tunable.

- Excitation of core-electrons into higher unoccupied energy states
- Extremely sensitive to chemical state and local environment
- Contains information about type of bond, bond strength, bond length, nearest neighbor atom, disorder, etc.

Main Idea



Photoelectron from atom (black) being scattered by two neighboring atoms. Circular rings represent constant phase wavefronts.

- These spectra are a result of quantum interference of the photoelectron (produced by x-ray absorption) scattered by neighboring atoms.

$$\textit{Kinetic energy} = E_{x\text{-ray}} - E_{\textit{binding}}$$

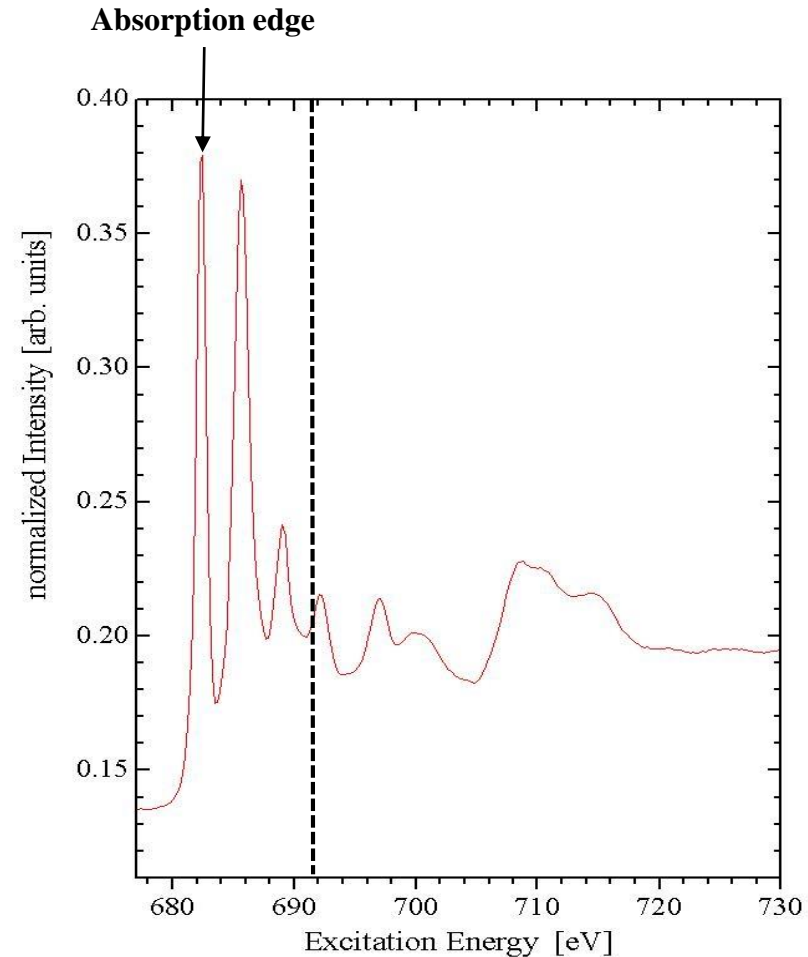
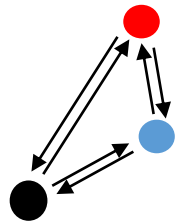
- As the wavelength of the incident x-rays changes, the KE of photoelectron also changes. This causes variation in the wavelength of photoelectrons.
- Change in wavelength causes change in phase of the photoelectron scattered by neighbor atoms.
- Thus, interfering waves go in and out of phase causing an interference pattern which depends on the local arrangement of atoms.

A typical X-ray Absorption Spectrum

XANES

X-ray Absorption Near Edge Structure

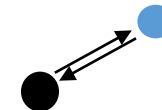
- Long wavelength electrons
- Multiple-scattering paths
- Sensitive to symmetry of neighboring atoms, valence, band structure, etc.

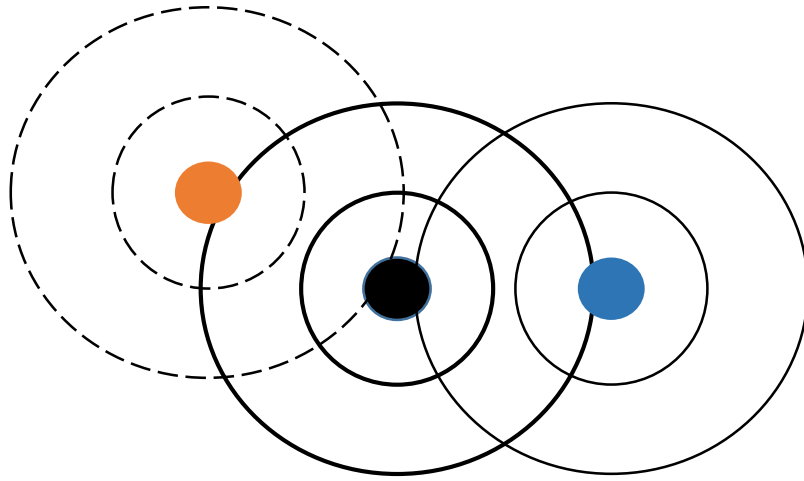


EXAFS

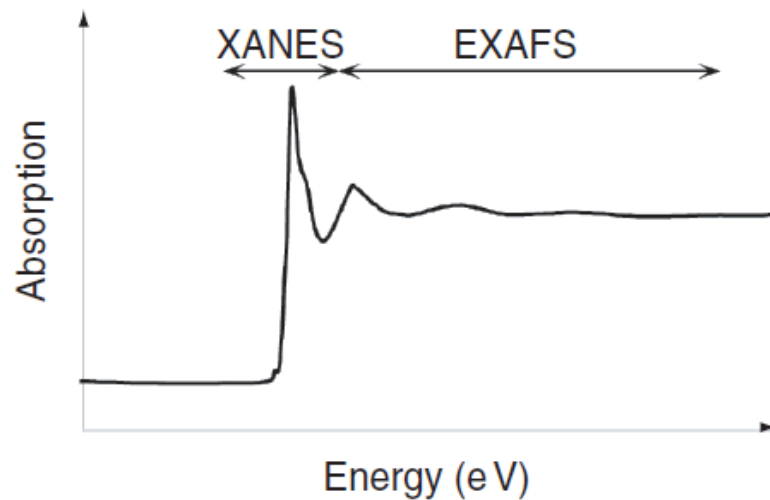
Extended X-ray Absorption Fine Structure

- ~20 – 30 eV past the edge
- Shorter wavelength electrons
- Dominated by single-scattering paths
- Sensitive to immediate local environment (nearest neighbors).





Photoelectron from atom (black) being scattered by two neighboring atoms. Circular rings represent constant phase wavefronts.



XANES

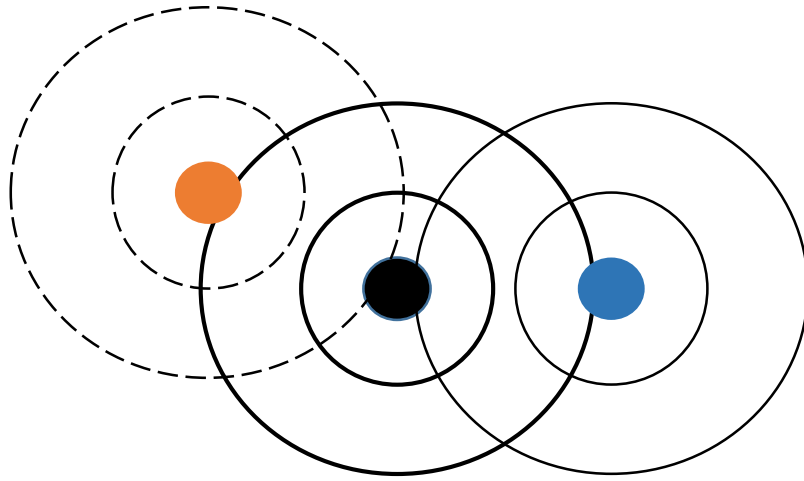
X-ray Absorption Near Edge Structure

$$\text{Kinetic energy} = E_{x\text{-ray}} - E_{\text{binding}}$$

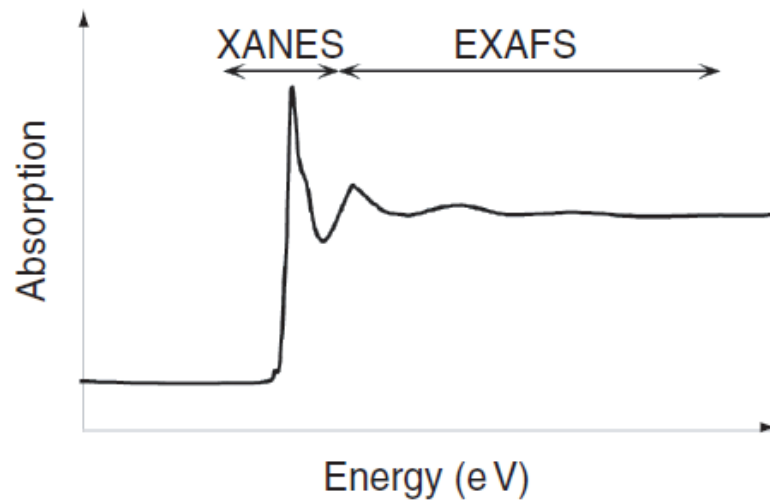
Less kinetic energy \rightarrow long wavelength

Long wavelengths \rightarrow interference dominated by multiple-scattering (from many neighboring atoms).

Hence, many scattering paths have to be accounted for. This complicates the quantitative analysis.



Photoelectron from atom (black) being scattered by two neighboring atoms. Circular rings represent constant phase wavefronts.



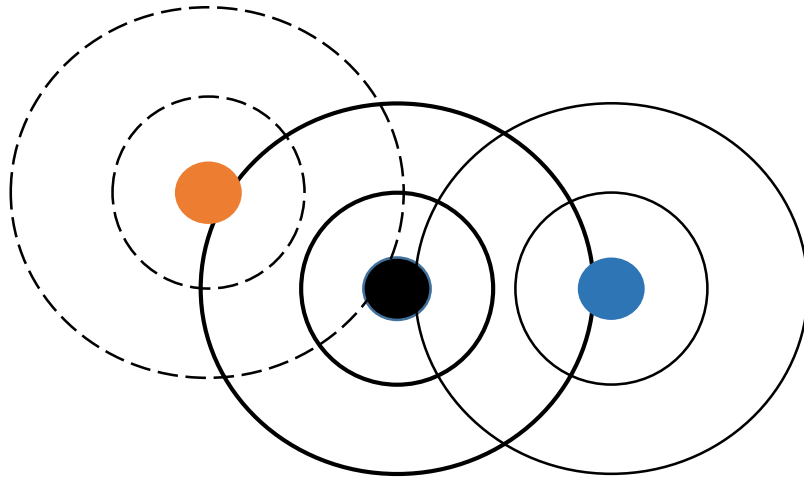
XANES

X-ray Absorption Near Edge Structure

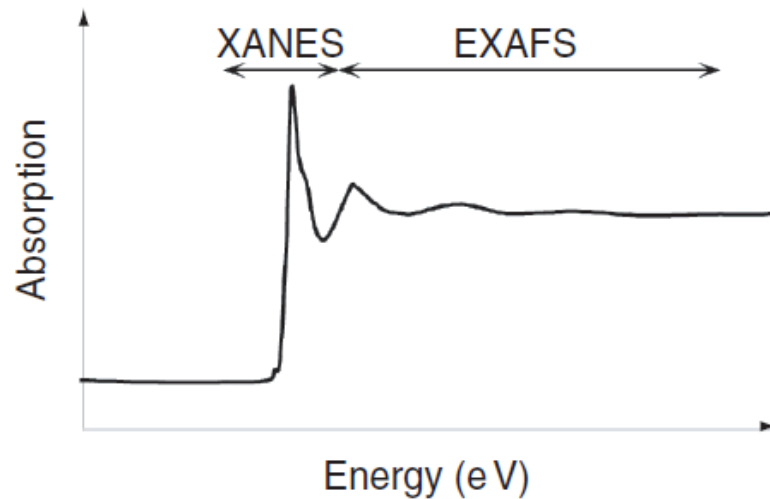
However,

Multiple-scattering makes near-edge spectra sensitive to symmetry of neighboring atomic arrangements.

- ➔ Can be used as an indicator to the kind of bond symmetry such as tetrahedral or octahedral.
- ➔ This also makes it an indicator for valence in certain systems.
- ➔ Also used in electronic band structure calculations since band structure calculations also involve multiple-scattering paths of electrons in a solid similar to XANES.



Photoelectron from atom (black) being scattered by two neighboring atoms. Circular rings represent constant phase wavefronts.



EXAFS

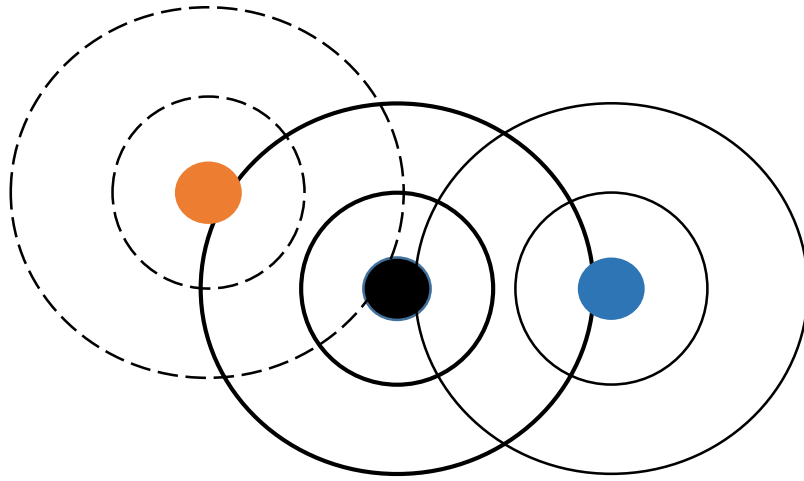
Extended X-ray Absorption Fine Structure

Increase in *Kinetic energy* ($E_{x\text{-ray}} - E_{\text{binding}}$) results in photoelectrons with shorter de Broglie, comparable to inter-atomic distances.

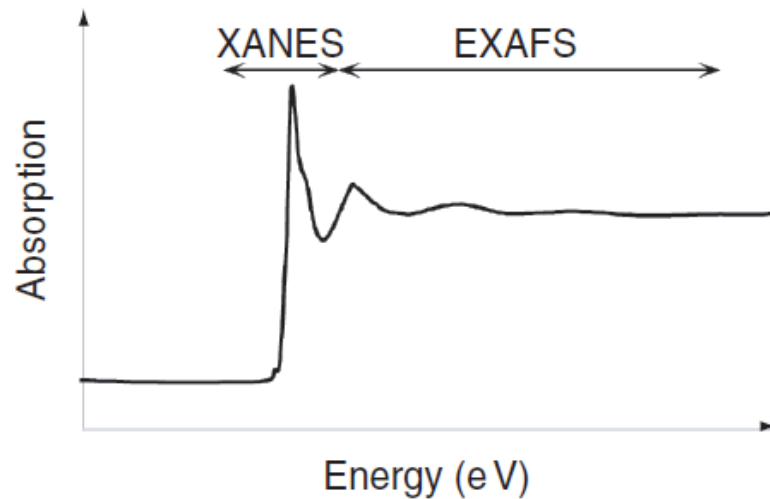
In EXAFS, amplitude of scattered photoelectrons falls off as $1/R^2$ where R is the absorber-scatterer distance.

Other factors such as inelastic losses, thermal fluctuations, mean free path and multiple scatterers contribute significantly to further dampening of interference.

For this reason, scattering is mostly limited to atoms/ions in the vicinity of the absorber ($\sim 0.5\text{nm}$).



Photoelectron from atom (black) being scattered by two neighboring atoms. Circular rings represent constant phase wavefronts.

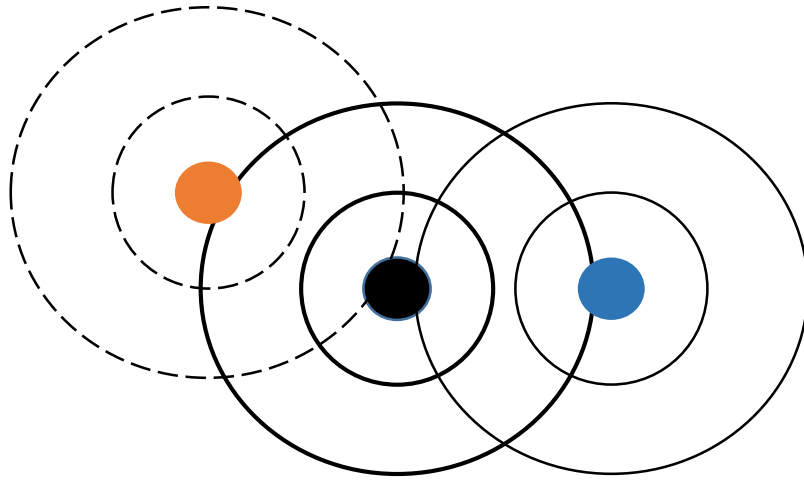


EXAFS

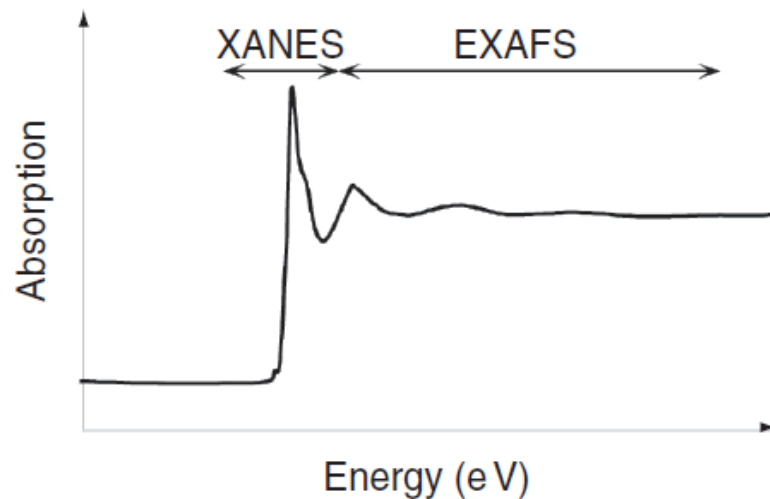
Extended X-ray Absorption Fine Structure

The phase and amplitude of backscattered photoelectrons depend on factors such as the type of bonding atom, any change in surrounding potential due to disorders, initial and final states of atoms, etc.

Thus, numerical analysis of EXAFS yields information about the immediate local environment surrounding the absorber atom/ion.



Photoelectron from atom (black) being scattered by two neighboring atoms. Circular rings represent constant phase wavefronts.



Summary

XAFS involves analysis of photoelectron scattering by surrounding atoms/ion.

Unlike x-rays, these scatterings are observable over a short range. This makes XAFS suitable for probing local environment around the absorber.

The complex nature of scattering necessitates extensive use numerical analysis and modelling to extract any information about the material.

XAFS can provide information about:

- Chemical state of an atom/ion in a matrix,
- Symmetry of atoms in the vicinity of the atom/ion under study,
- Electronic band structure,
- Nature of bonding and bond length,
- Disorder and defects

References

1. *X-ray Absorption Spectroscopy* by J. E. Penner-Hahn, University of Michigan, Ann Arbor, MI, USA
2. *Elements of X-ray Diffraction* by B. D. Cullity
3. *Solid State Physics* by Ashcroft and Mermin
4. *Characterization of Materials* by Elton N. Kaufmann