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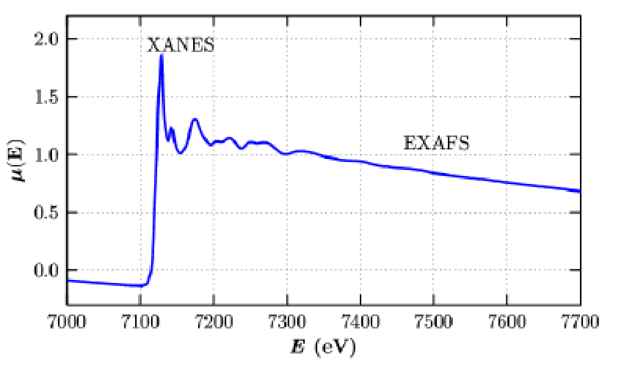
XAFS: X-ray Absorption Fine-Structure

Summary

- **Basic Principles:**
  - **X-ray absorption and fluorescence**
  - **Simple theoretical description**
- **Experiment Design:**
  - **Transmission v. Fluorescence modes**
  - **Fluorescence detectors**
- **Data Analysis:**
  - **EXAFS Analysis: near neighbor *R*, *N*, and atomic species**
  - **XANES Analysis: formal valence and coordination chemistry**

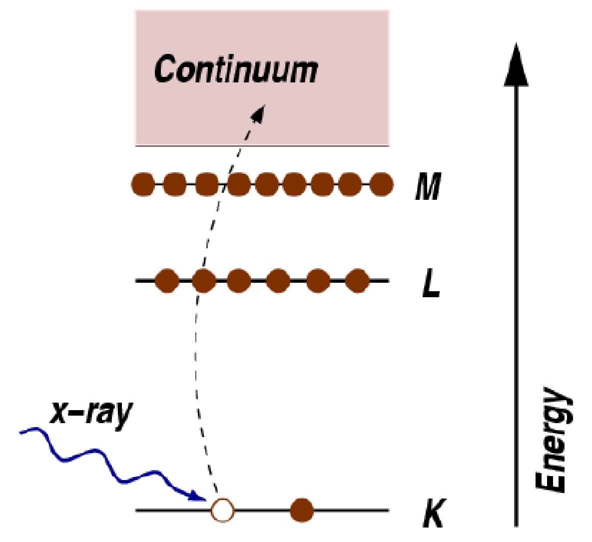
What is XAFS?

- **X-ray Absorption Fine-Structure (XAFS) is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge. XAFS is also referred to as X-ray Absorption Spectroscopy (XAS) and is broken into 2 regimes:**
  - **XANES X-ray Absorption Near-Edge Spectroscopy**
  - **EXAFS Extended X-ray Absorption Fine-Structure which contain related, but slightly different information about an element's local coordination and chemical state.**
- **Fe *K*-edge XAFS for FeO:**
- ***XAFS Characteristics*:**
- **• local atomic coordination**
- **• chemical / oxidation state**
- **• applies to any element**
- **• works at low concentrations**
- **• minimal sample requirements**



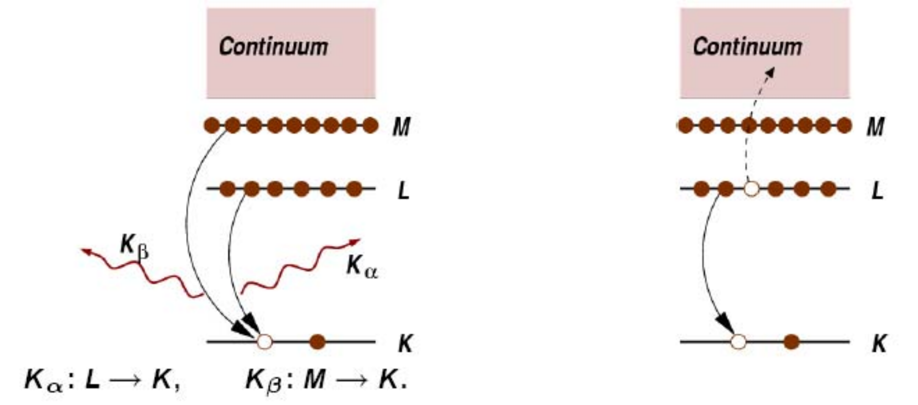
X-ray Absorption

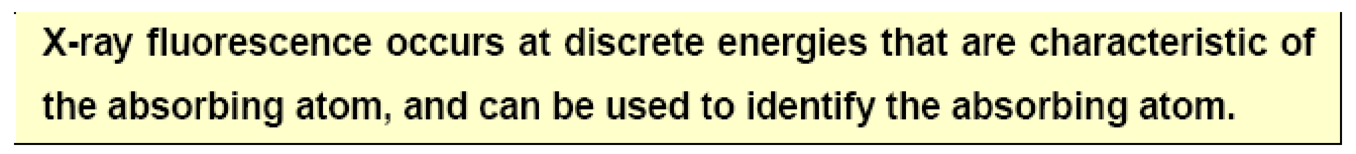
- **X-rays (light with wavelength $0.03<\lambda<12$ Å or energy $1<E<500$ keV) are absorbed by all matter through the *photo-electric effect***
- **An x-ray is absorbed by an atom, promoting a core-level electron (*K*, *L*, or *M* shell) out of the atom and into the continuum. The atom is left in an *excited state* with an empty electronic level (a *core hole*). The electron ejected from the atom is called the *photo-electron*.**



X-ray Fluorescence

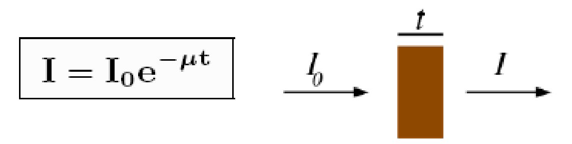
- **When x-rays are absorbed by the photo-electric effect, the excited core-hole will relax back to a “ground state” of the atom. A higher level core electron drops into the core hole, and a *fluorescent x-ray* or *Auger electron* is emitted.**
- ***X-ray Fluorescence*: An x-ray with energy = the difference of the corelevels is emitted.**
- ***Auger Effect*: An electron is promoted into the continuum from another corelevel.**




X-ray fluorescence occurs at discrete energies that are characteristic of the absorbing atom, and can be used to identify the absorbing atom.

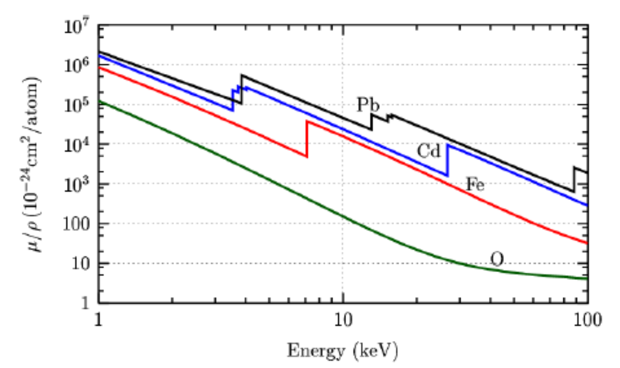
The X-ray Absorption Coefficient: μ

- The intensity of an x-ray beam as it passes through a material of thickness t is given by the *absorption coefficient* μ:

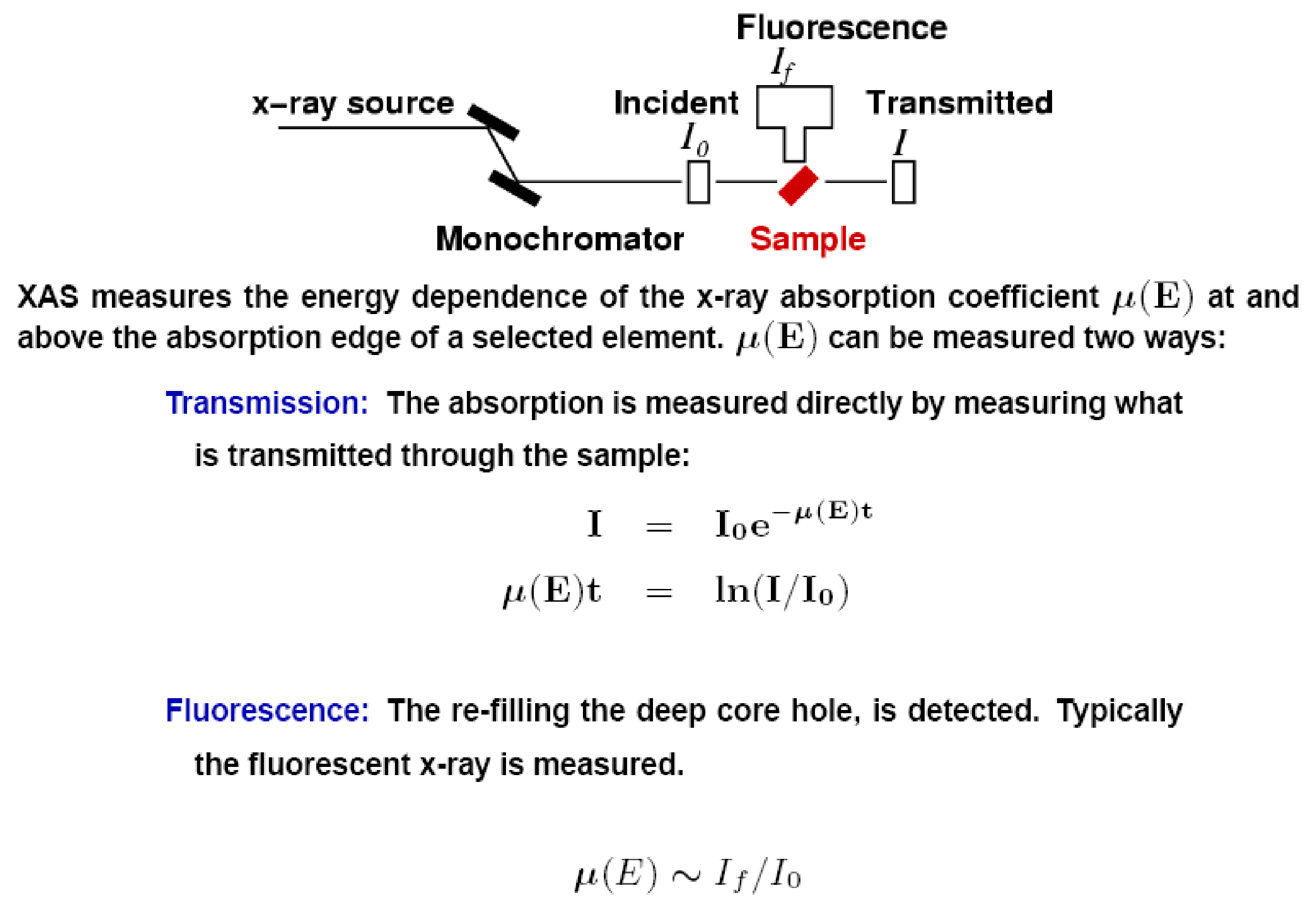


$$\boxed{I = I_0 e^{-\mu t}}$$

- where I_0 is the x-ray intensity hitting the material, and I is the intensity transmitted through the material.



X-ray Absorption Measurements



XAS measures the energy dependence of the x-ray absorption coefficient $\mu(\mathrm{E})$ at and above the absorption edge of a selected element. $\mu(\mathrm{E})$ can be measured two ways:

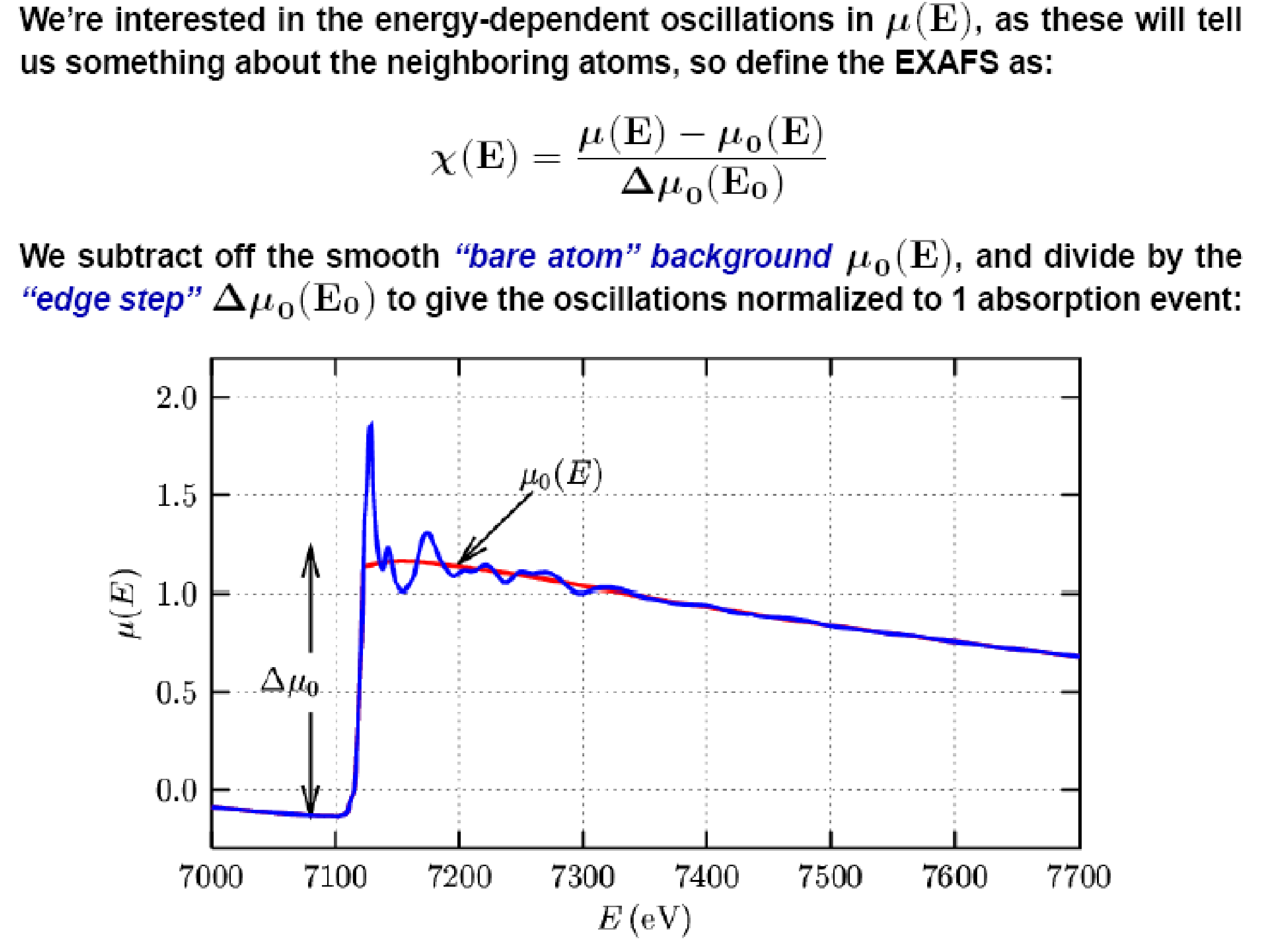
Transmission: The absorption is measured directly by measuring what is transmitted through the sample:

$$\begin{aligned} \mathrm{I} &= \mathrm{I_0 e^{-\mu(E)t}} \\ \mu(\mathrm{E})\mathrm{t} &= \ln(\mathrm{I}/\mathrm{I_0}) \end{aligned}$$

Fluorescence: The re-filling the deep core hole, is detected. Typically the fluorescent x-ray is measured.

$$\mu(E) \sim I_f/I_0$$

X-ray Absorption Fine Structure



We're interested in the energy-dependent oscillations in $\mu(\mathrm{E})$, as these will tell us something about the neighboring atoms, so define the **EXAFS** as:

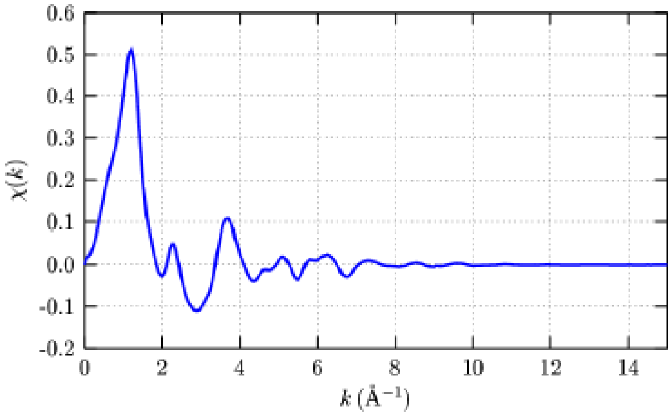
$$\chi(\mathrm{E}) = \frac{\mu(\mathrm{E}) - \mu_0(\mathrm{E})}{\Delta\mu_0(\mathrm{E}_0)}$$

We subtract off the smooth *"bare atom" background* $\mu_0(\mathrm{E})$, and divide by the *"edge step"* $\Delta\mu_0(\mathrm{E}_0)$ to give the oscillations normalized to 1 absorption event:

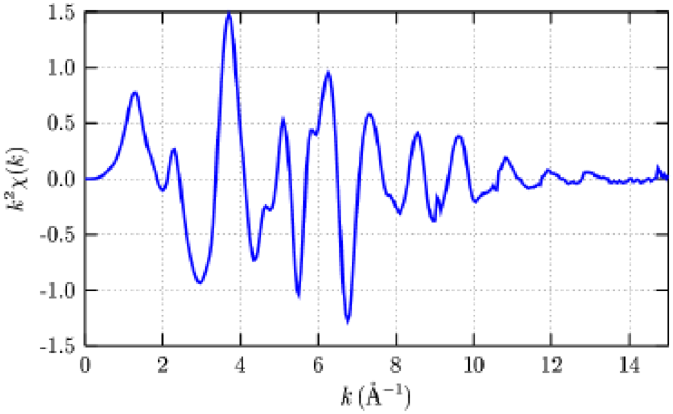
EXAFS: $\chi(k)$

It's convenient to think of the XAFS in terms of *photo-electron wavenumber* k:

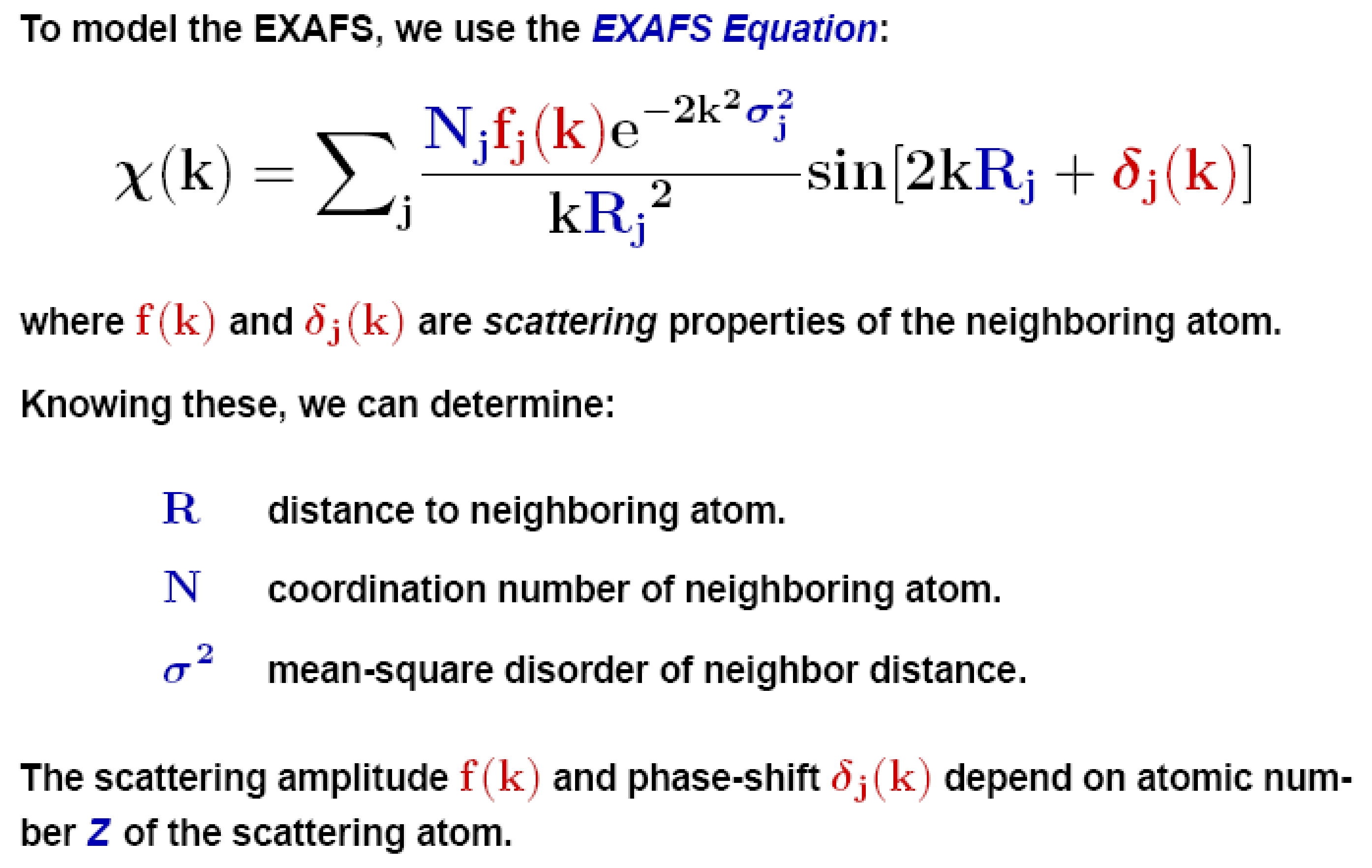
$\mathrm{k} = \sqrt{\frac{2\mathrm{m}(\mathrm{E}-\mathrm{E}_0)}{\hbar^2}}$ rather than x-ray energy, so that we have $\chi(\mathrm{k}) = \chi(\mathrm{k}[\mathrm{E}])$:



$\chi(\mathrm{k})$ is often shown weighted by k^2 or k^3 to amplify the oscillations at high-k:



The EXAFS Equation



To model the EXAFS, we use the ***EXAFS Equation***:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$

where $f(k)$ and $\delta_j(k)$ are *scattering* properties of the neighboring atom.

Knowing these, we can determine:

R distance to neighboring atom.

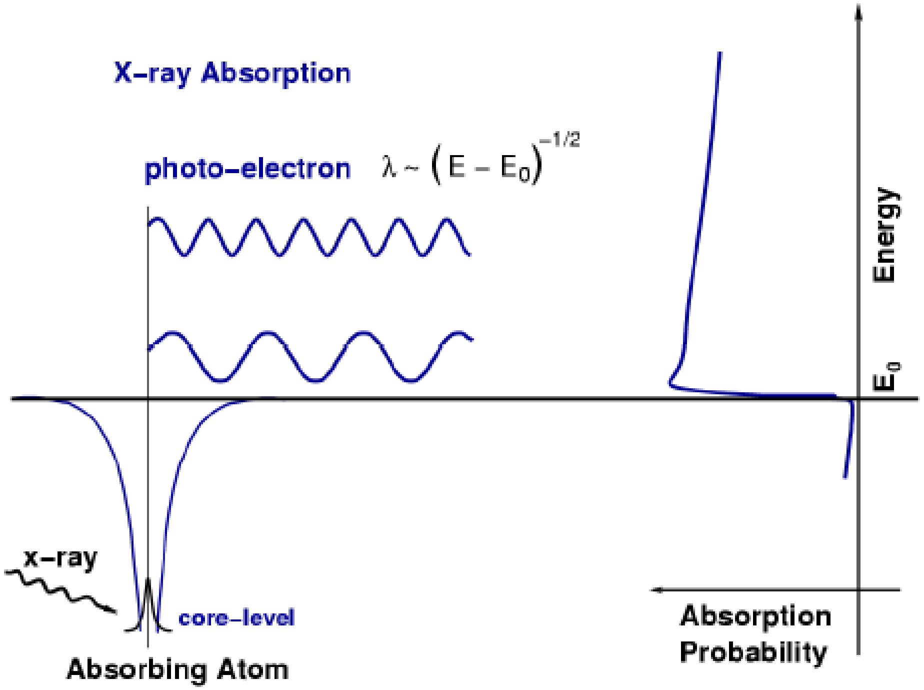
N coordination number of neighboring atom.

σ^2 mean-square disorder of neighbor distance.

The scattering amplitude $f(k)$ and phase-shift $\delta_j(k)$ depend on atomic number ***Z*** of the scattering atom.

XAFS Theory: X-ray Absorption by a Free Atom

An atom absorbs and x-ray of energy E, destroying a core electron with energy $\mathrm{E_0}$ and creating a photo-electron with energy $(\mathrm{E} - \mathrm{E_0})$. The core level is eventually filled, and a fluorescence x-ray or an Auger electron is ejected from the atom.



x-ray absorption needs an available state for the photo-electron to go into:

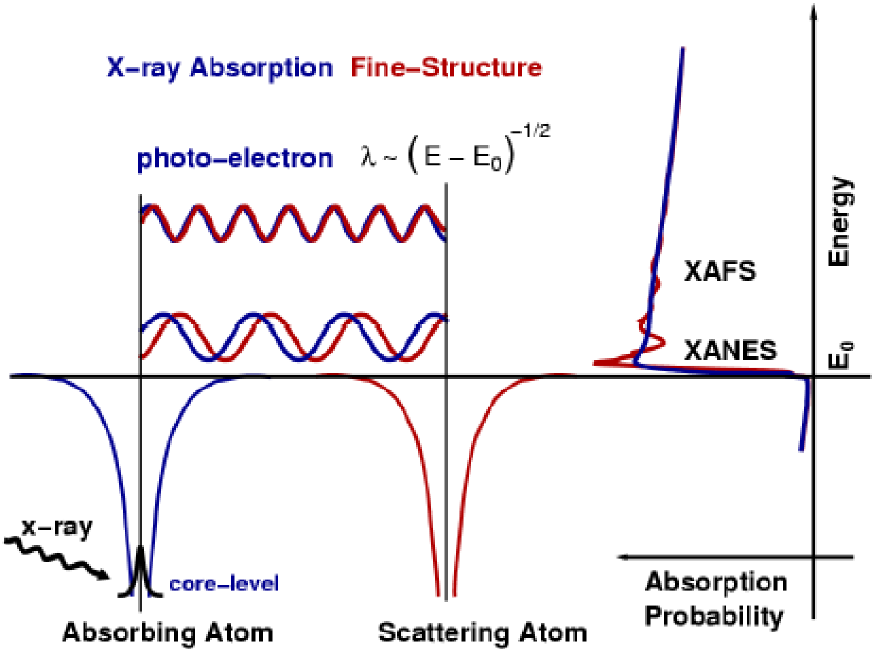
No available state:
No absorption

Once the x-ray energy is large enough to promote a core-level to the continuum, there is a sharp increase in absorption.

For an isolated atom, $\mu(\mathrm{E})$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

X-ray Absorption with Photo-Electron Scattering

With another atom nearby, the ejected photo-electron can *scatter* from a neighboring atom and return back to the absorbing atom.



When this happens, the photo-electron scattered back will interfere with itself.

μ depends on the presence of an electron state with energy $(E - E_0)$ and at the absorbing atom.

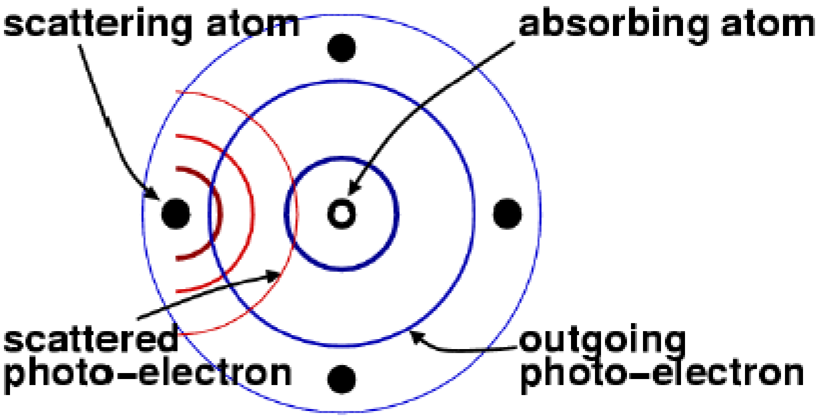
The amplitude of the back-scattered photo-electron *at the absorbing atom* will oscillate with energy, causing oscillations in $\mu(E)$.

The XAFS oscillations are an interference effect due to the presence of neighboring atoms.

The EXAFS Equation: simple description

Starting with $\chi \sim \psi_{\text{scatt}}(0)$, we can build a simple model for the EXAFS from the photo-electron as:

1. leaving the absorbing atom
2. scattering from the neighbor atom
3. returning to the absorbing atom

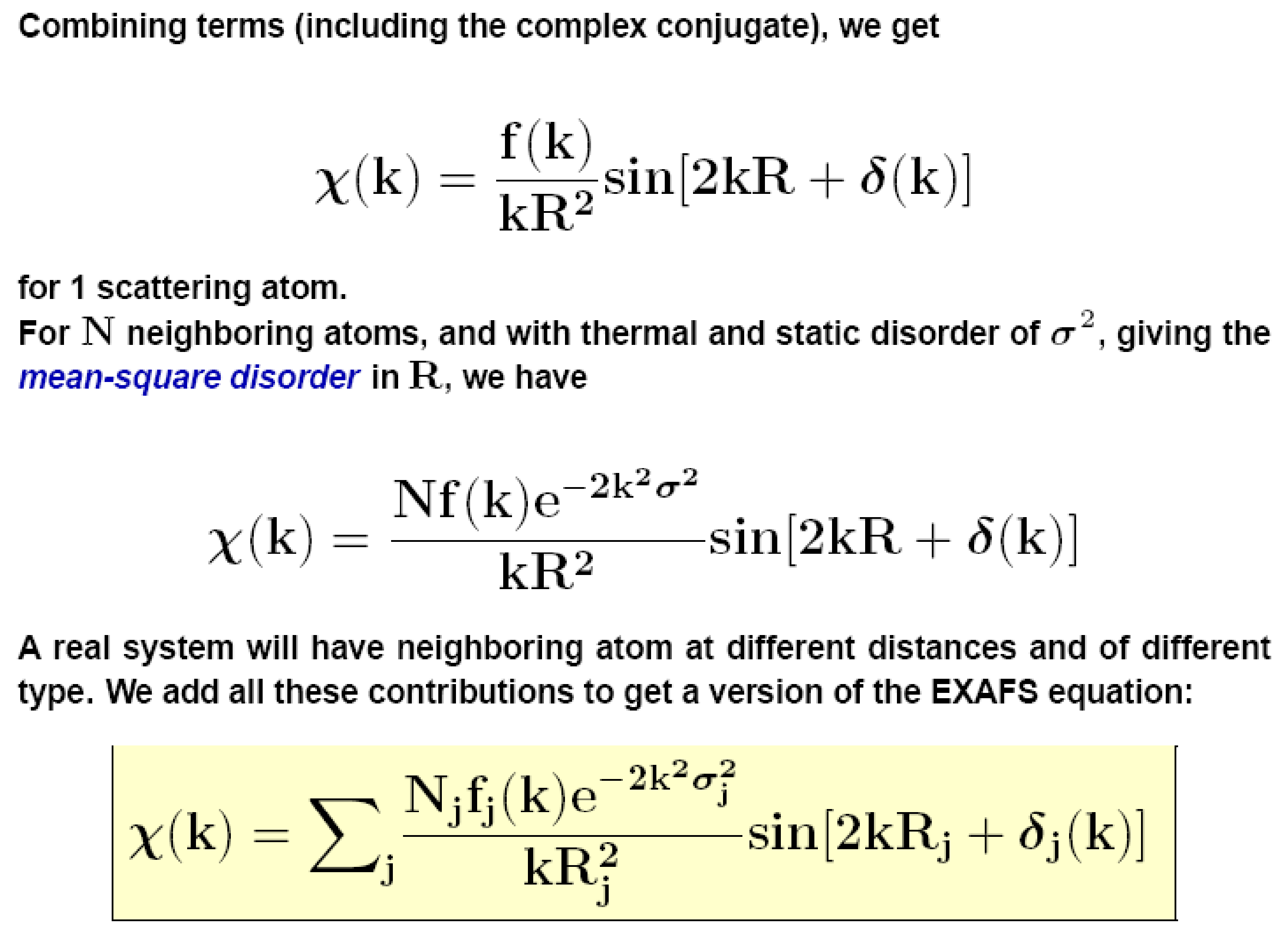


With spherical wave e^{ikr}/kr for the propagating photo-electron, and a scattering atom at a distance $r = R$, we get

$$\chi(k) = \frac{e^{ikR}}{kR}\left[2kf(k)e^{i\delta(k)}\right]\frac{e^{ikR}}{kR} + C.C.$$

where the neighboring atom gives the amplitude $f(k)$ and phase-shift $\delta(k)$ to the scattered photo-electron.

Development of the EXAFS Equation



Combining terms (including the complex conjugate), we get

$$\chi(k) = \frac{f(k)}{kR^2}\sin[2kR + \delta(k)]$$

for 1 scattering atom.
For N neighboring atoms, and with thermal and static disorder of σ^2, giving the *mean-square disorder* in R, we have

$$\chi(k) = \frac{Nf(k)e^{-2k^2\sigma^2}}{kR^2}\sin[2kR + \delta(k)]$$

A real system will have neighboring atom at different distances and of different type. We add all these contributions to get a version of the EXAFS equation:

$$\boxed{\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2}\sin[2kR_j + \delta_j(k)]}$$

The Photo-Electron Mean-Free Path

Getting to

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

we used a spherical wave for the photo-electron: e^{ikr}/kr. The photo-electron can also scatter *inelastically*, and may not be able to get back the absorbing atom.

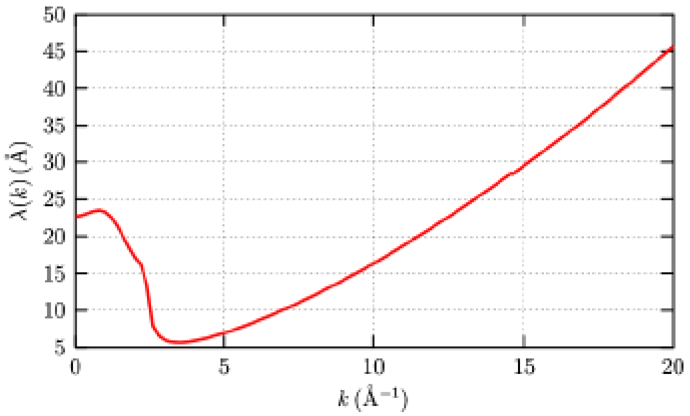
Using a damped wave-function: $\boxed{e^{ikr}e^{-r/\lambda(k)}/kr}$

where $\lambda(k)$ is the photo-electron's *mean free path*, the EXAFS equation becomes:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

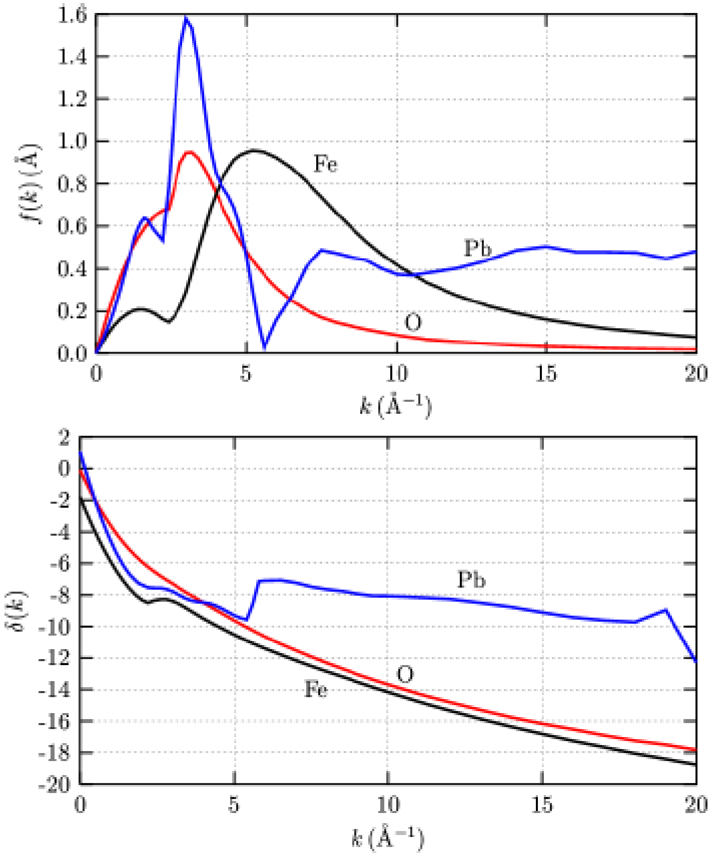
The mean-free-path is $<$ 25 Å for much of the EXAFS range.

λ and the R^{-2} term make EXAFS a *local atomic probe*.



Scattering Amplitude and Phase-Shift

The scattering amplitude $f(k)$ and phase-shift $\delta_j(k)$ depend on atomic number.



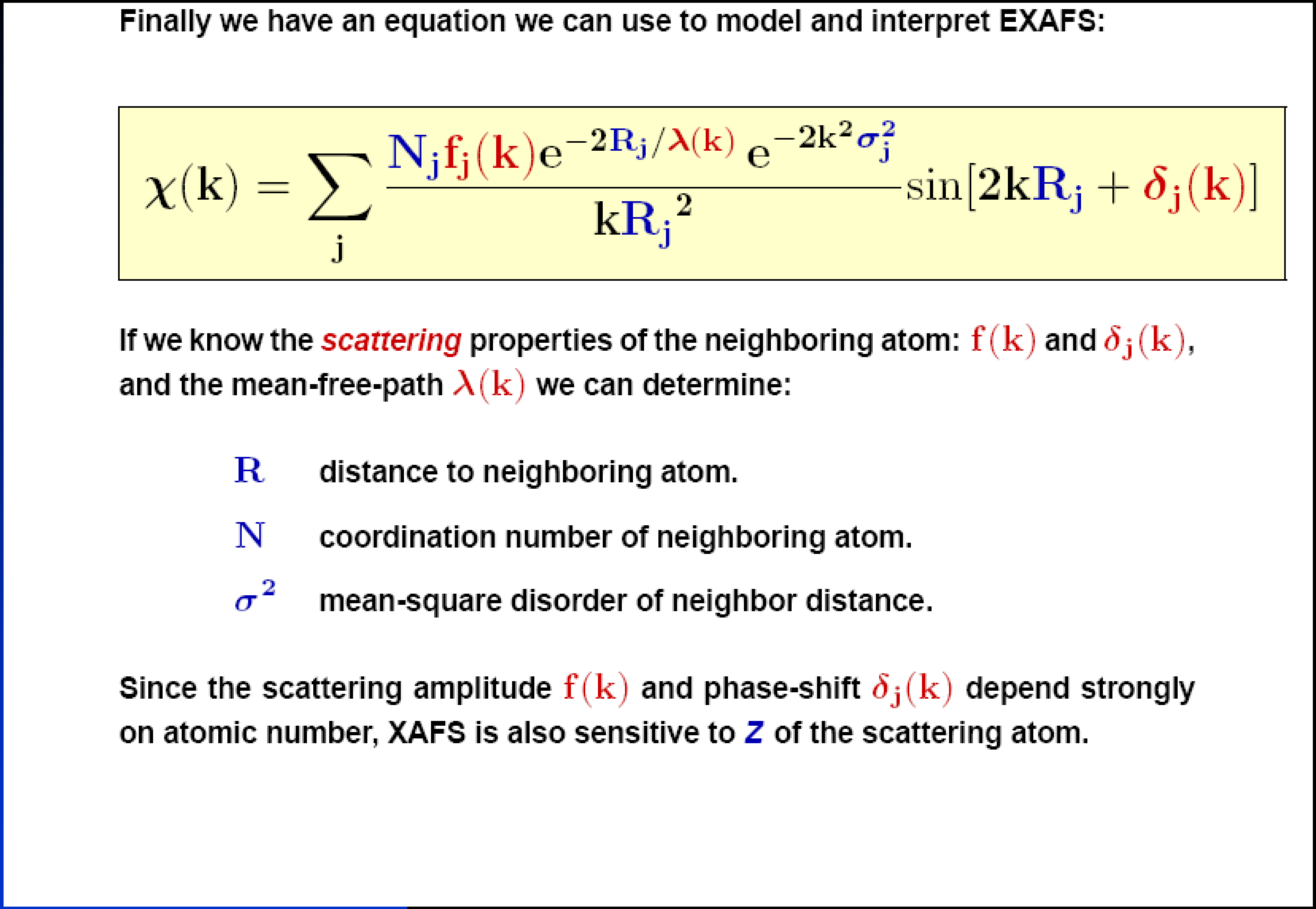
The scattering amplitude $f(k)$ peaks at different k values and extends to higher-k for heavier elements. For very heavy elements, there is structure in $f(k)$.

The phase shift $\delta_j(k)$ shows sharp changes for very heavy elements.

These scattering functions can be accurately calculated, and used in the EXAFS modeling.

Z can usually be determined to with 5 or so. Fe and O can be distinguished, but Fe and Mn cannot be.

The EXAFS Equation



Finally we have an equation we can use to model and interpret **EXAFS**:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)}\, e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$

If we know the *scattering* properties of the neighboring atom: $f(k)$ and $\delta_j(k)$, and the mean-free-path $\lambda(k)$ we can determine:

R	distance to neighboring atom.
N	coordination number of neighboring atom.
σ^2	mean-square disorder of neighbor distance.

Since the scattering amplitude $f(k)$ and phase-shift $\delta_j(k)$ depend strongly on atomic number, XAFS is also sensitive to *Z* of the scattering atom.

X-ray Absorption Measurements: Experimental Design

- **Important points to consider for measuring XAFS are:**
  - ***Monochromatic x-rays:*** **Need x-rays with a small energy spread or bandwidth:** $\Delta E<1$ **eV at 10keV.**
  - ***Linear Detectors:*** **The XAFS (k) is small, so we need a lotof photons (ie, a synchrotron) and detectors that are very linear in x-ray intensity (ion chambers).**
  - ***Well-aligned Beam:*** **The x-ray beam hitting the detectors has to be the same hitting the sample.**
  - ***Homogeneous sample:*** **For transmission measurements, we need a sample that is of uniform and appropriate sample thickness of nearly 2 absorptionlengths. It should be free from pinholes. If a powder, the grains should be very fine-grained (absorption length) and uniform.**

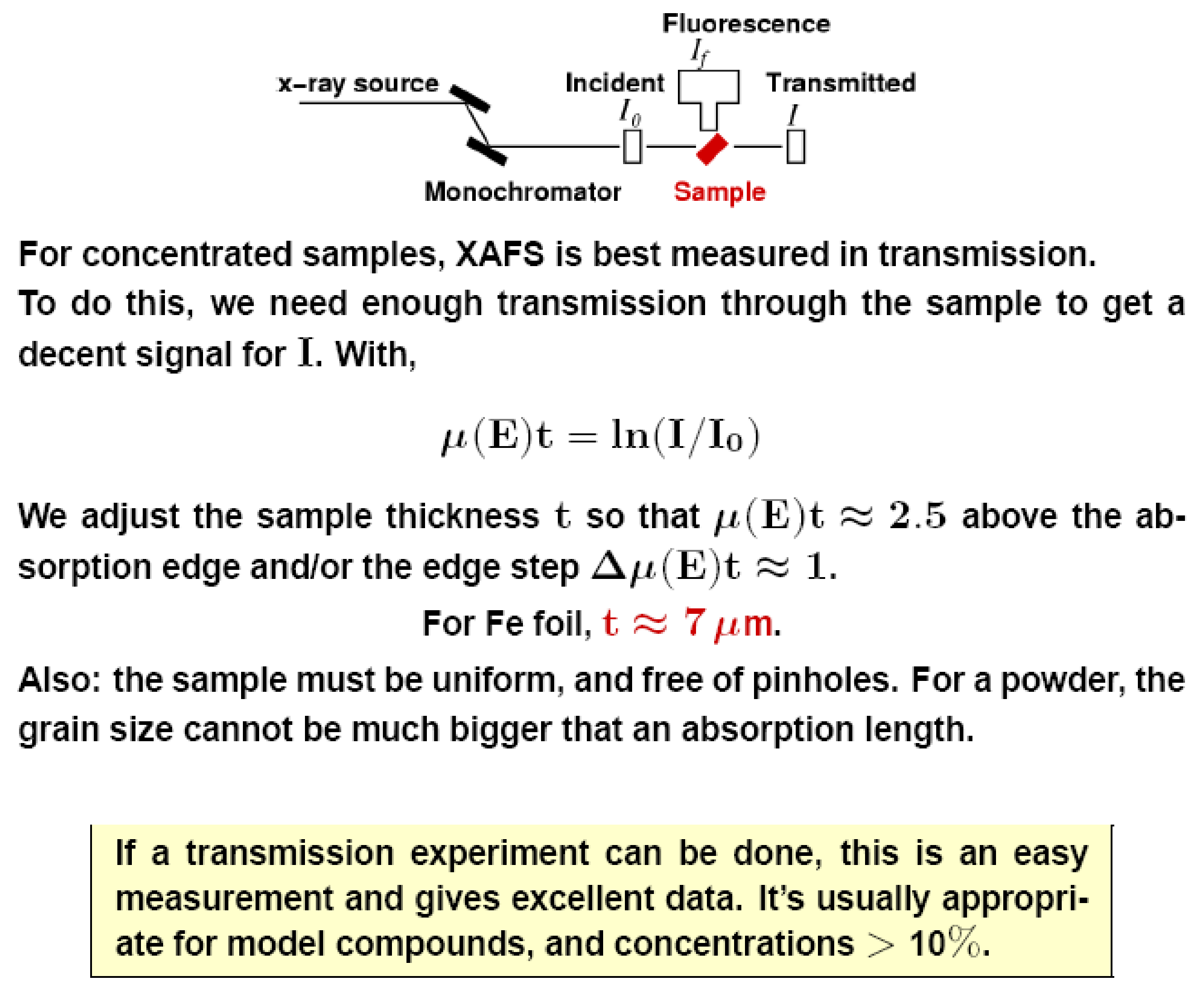
X-ray Absorption Measurements: The Experiment

- ***Energy Scanning*** **The beamline needs to deliver monochromatic x-rays that are tunable so we can scan energy across the absorption edge. We'll scan from 200 eV below to 800 eV above the Fe K-edge, like this:**

Region	**Starting Energy (eV)**	**Ending Energy (eV)**	**Step Size (eV)**
Pre-edge	**-200**	**-20**	**5.0**
XANES	**-20**	**+30**	**0.5**
EXAFS	**+30**	**800**	**0.05 $Å^{-1}$**

- **Notes: all values relative to a nominal value of the edge energy. In the EXAFS region, it's common to step in *k* rather than energy. *Counting Statistics:* The EXAFS is a fairly small signal, so for good data $\mu(E)$ should have a noise level of about 10^{-3}. That means we need to collect at least 10^6 photons.**
- ***Transmission*** **: Fluxes at synchrotrons are > 10^8 photons/sec. Count rate is not much of an issue.**
- ***Fluorescence*** **: May be a concern, especially when concentrationsare very low.**

X-ray Absorption Measurements: Transmission



For concentrated samples, **XAFS** is best measured in transmission.

To do this, we need enough transmission through the sample to get a decent signal for I. With,

$$\mu(\mathrm{E})\mathrm{t} = \ln(\mathrm{I}/\mathrm{I}_0)$$

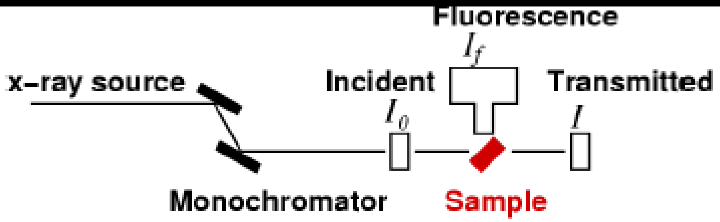
We adjust the sample thickness t so that $\mu(\mathrm{E})\mathrm{t} \approx 2.5$ above the absorption edge and/or the edge step $\Delta\mu(\mathrm{E})\mathrm{t} \approx 1$.

For Fe foil, $\mathrm{t} \approx 7\,\mu\mathrm{m}$.

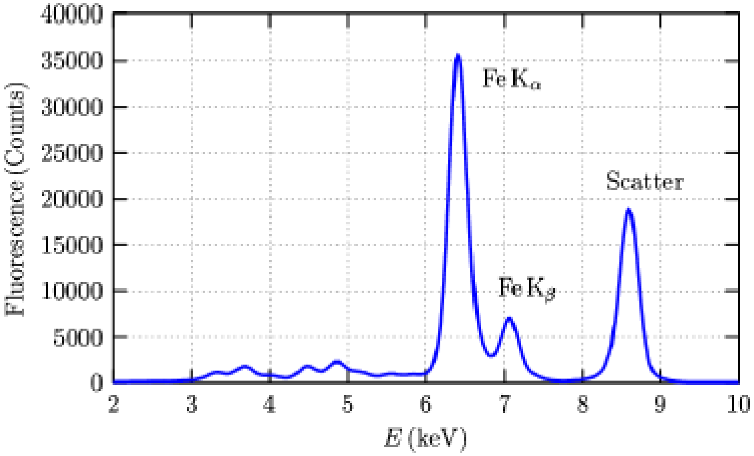
Also: the sample must be uniform, and free of pinholes. For a powder, the grain size cannot be much bigger that an absorption length.

> If a transmission experiment can be done, this is an easy measurement and gives excellent data. It's usually appropriate for model compounds, and concentrations $> 10\%$.

X-ray Absorption Measurements: Fluorescence



For thick samples or lower concentrations (down to the ppm level), monitoring the x-ray fluorescence is the preferred measurement.

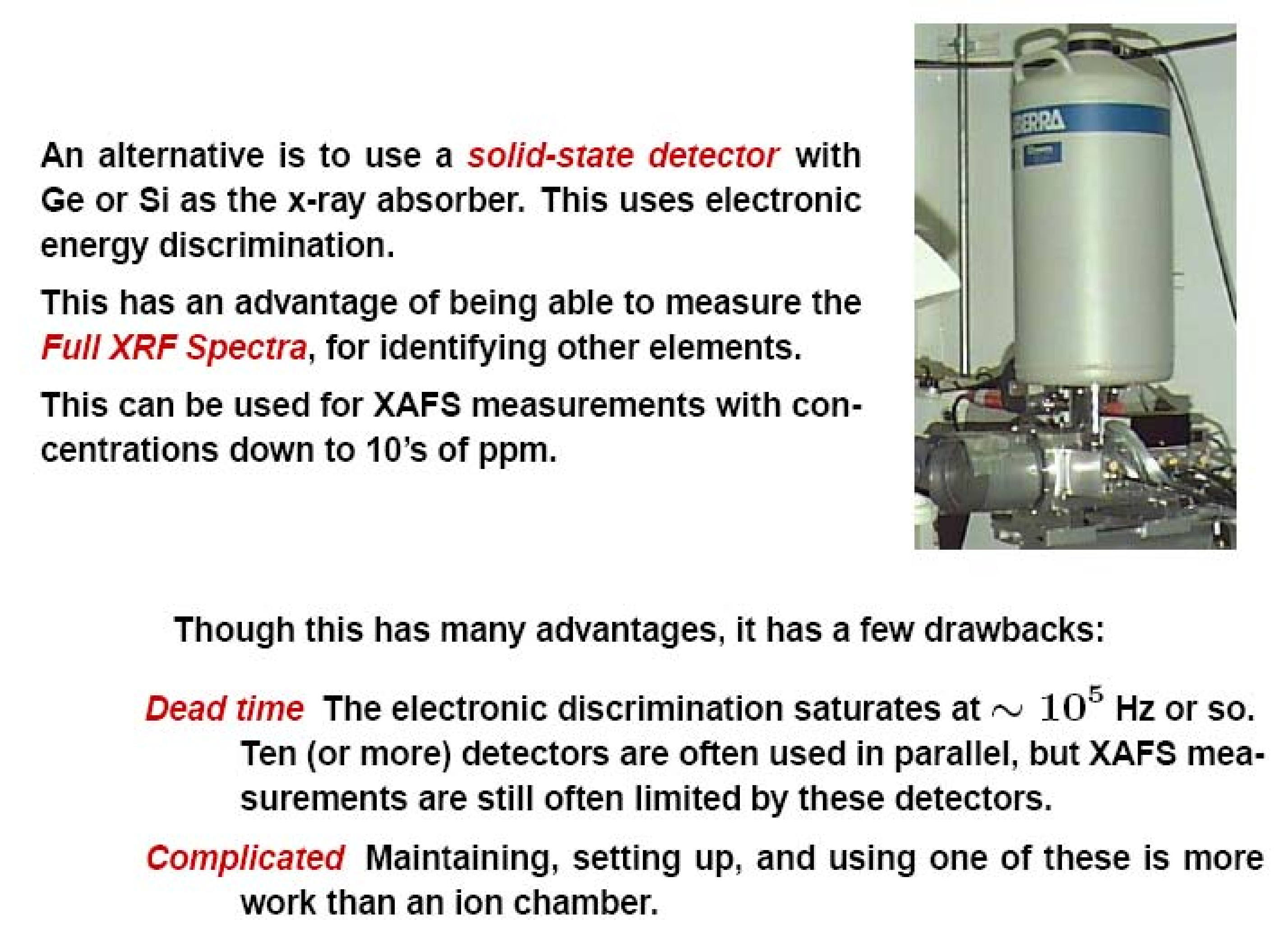


The x-rays emitted from the sample will include the fluorescence line of interest (here, both Fe K_α and Fe K_β) as well as *scattered* x-rays, and other fluorescence lines (here, Ca, Ti, and V).

There are both *elastically scattered* (at the same energy as the incident beam), and *inelastically scattered* (Compton effect) x-rays.

In many cases the scatter or other fluorescence lines will dominate the fluorescence spectra.

Fluorescence Measurements: Solid-State Detectors



An alternative is to use a *solid-state detector* with Ge or Si as the x-ray absorber. This uses electronic energy discrimination.

This has an advantage of being able to measure the *Full XRF Spectra*, for identifying other elements.

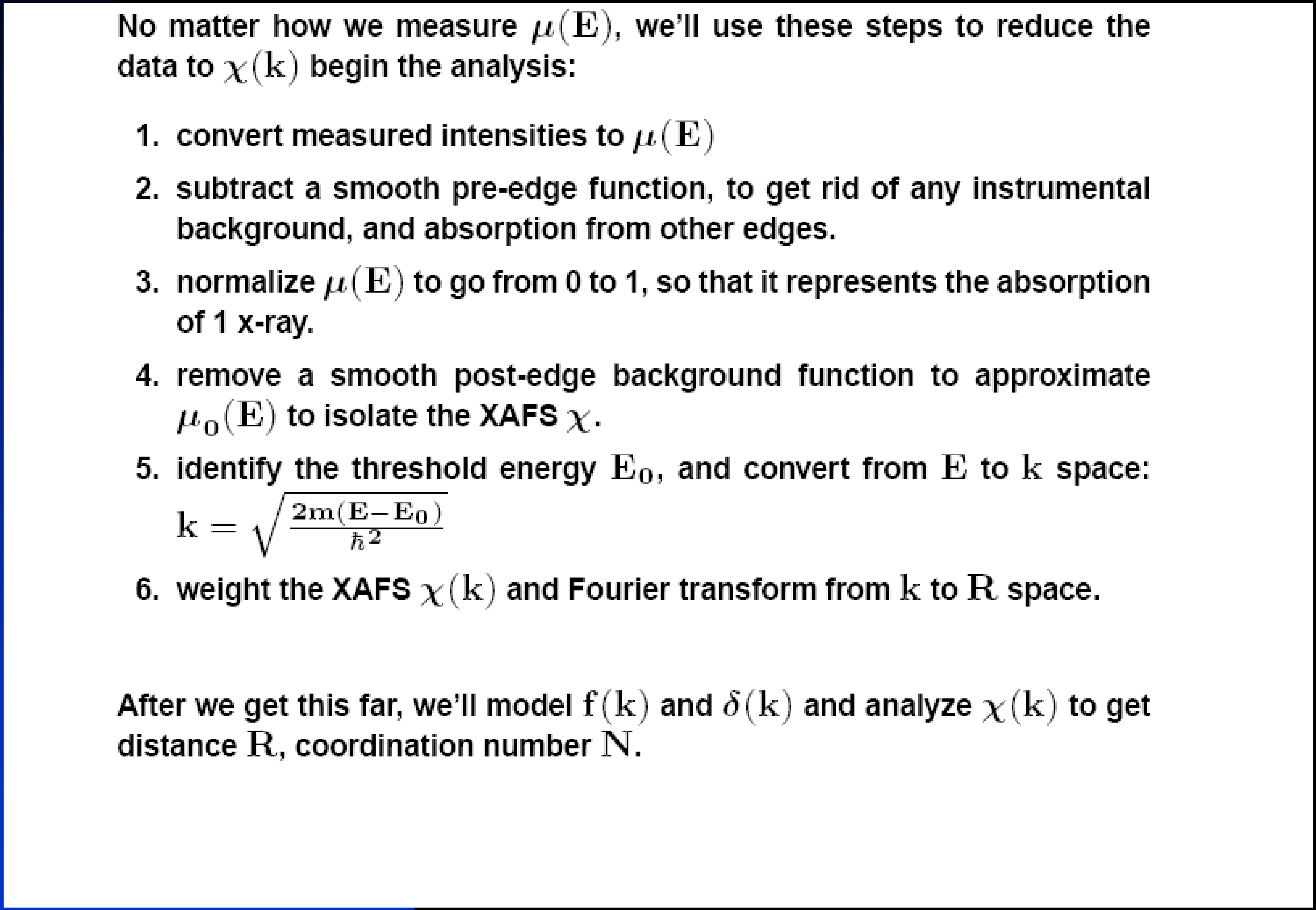
This can be used for XAFS measurements with concentrations down to 10's of ppm.

Though this has many advantages, it has a few drawbacks:

Dead time The electronic discrimination saturates at $\sim 10^5$ Hz or so. Ten (or more) detectors are often used in parallel, but XAFS measurements are still often limited by these detectors.

Complicated Maintaining, setting up, and using one of these is more work than an ion chamber.

Data Reduction: Strategy



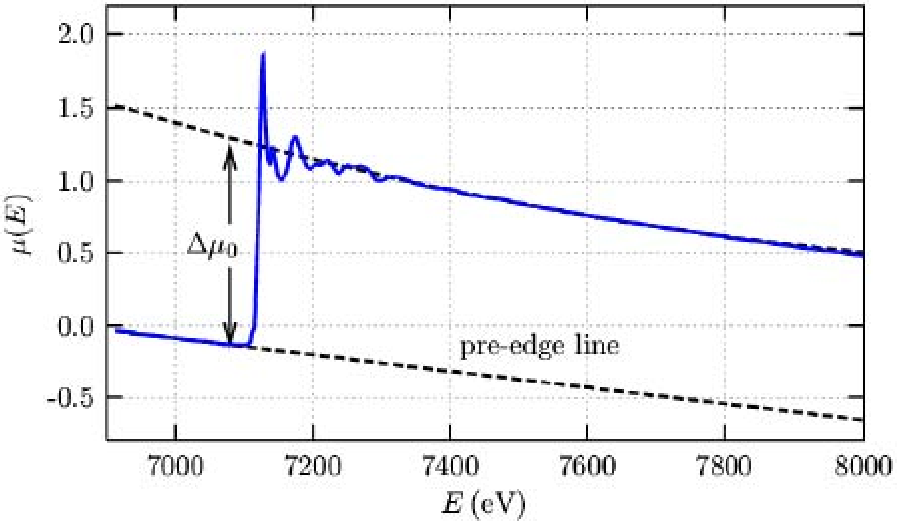
No matter how we measure $\mu(E)$, we'll use these steps to reduce the data to $\chi(k)$ begin the analysis:

1. convert measured intensities to $\mu(E)$
2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
3. normalize $\mu(E)$ to go from 0 to 1, so that it represents the absorption of 1 x-ray.
4. remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS χ.
5. identify the threshold energy E_0, and convert from E to k space: $k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$
6. weight the XAFS $\chi(k)$ and Fourier transform from k to R space.

After we get this far, we'll model $f(k)$ and $\delta(k)$ and analyze $\chi(k)$ to get distance R, coordination number N.

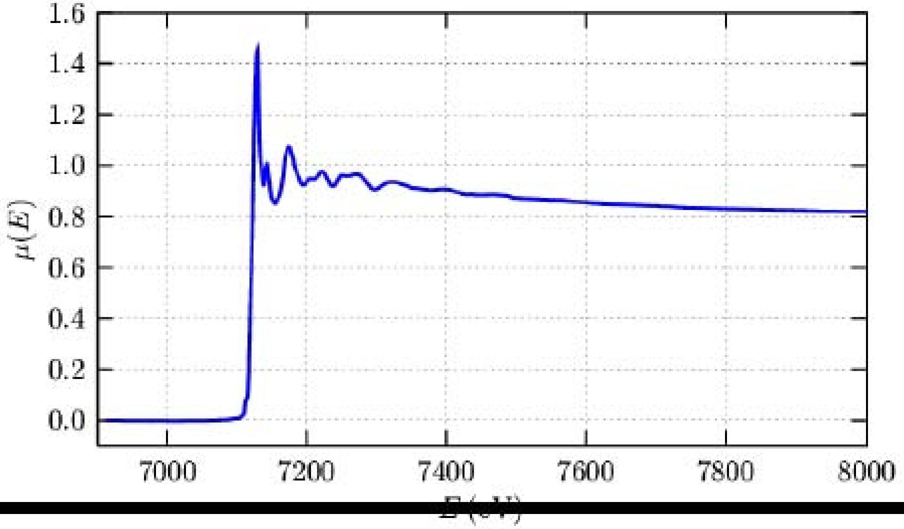
Data Reduction: Pre-Edge Subtraction, Normalization

Starting with $\mu(\mathrm{E})$ data for Fe_2O_3, the data reduction goes like this:



Pre-Edge Subtraction

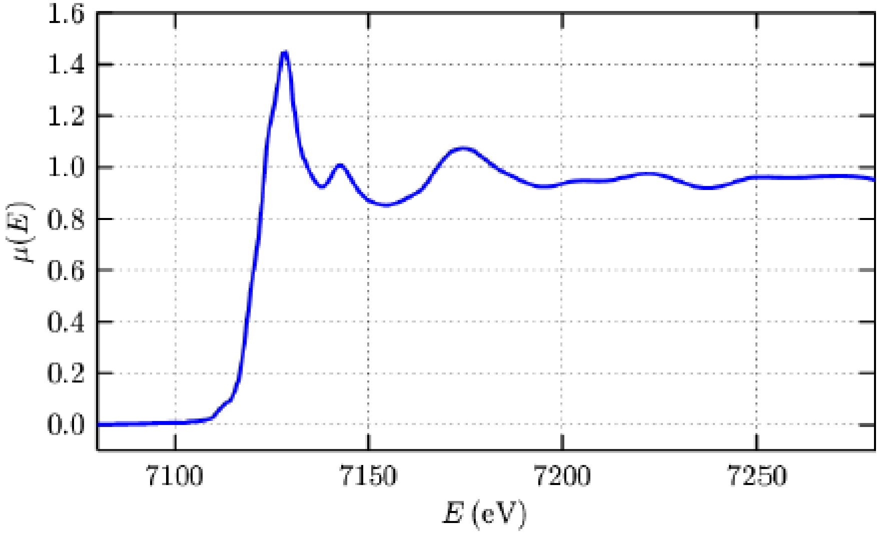
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

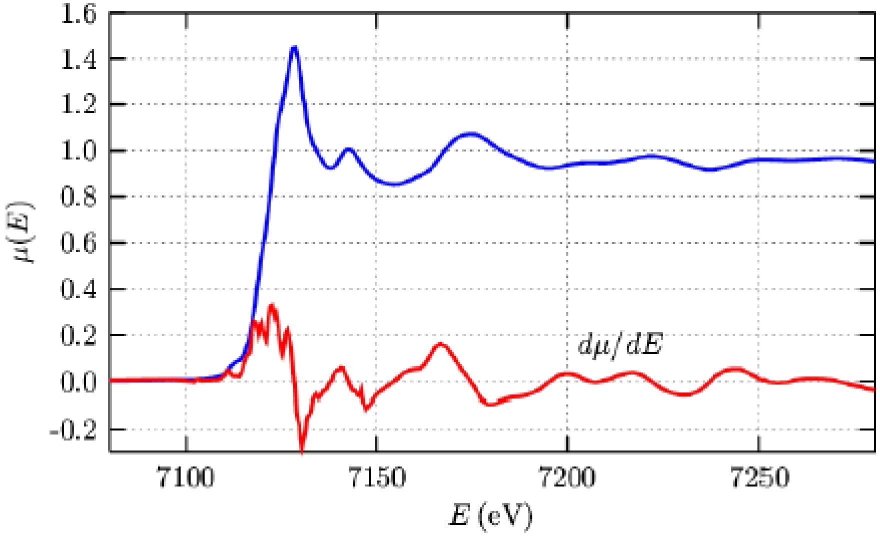
We estimate the *edge step*, $\Delta\mu_0(\mathrm{E}_0)$ by extrapolating a simple fit to the above $\mu(\mathrm{E})$ to the edge. We normalize by this value to get the absorption from 1 x-ray.

Data Reduction: Normalized XANES and E_0



XANES

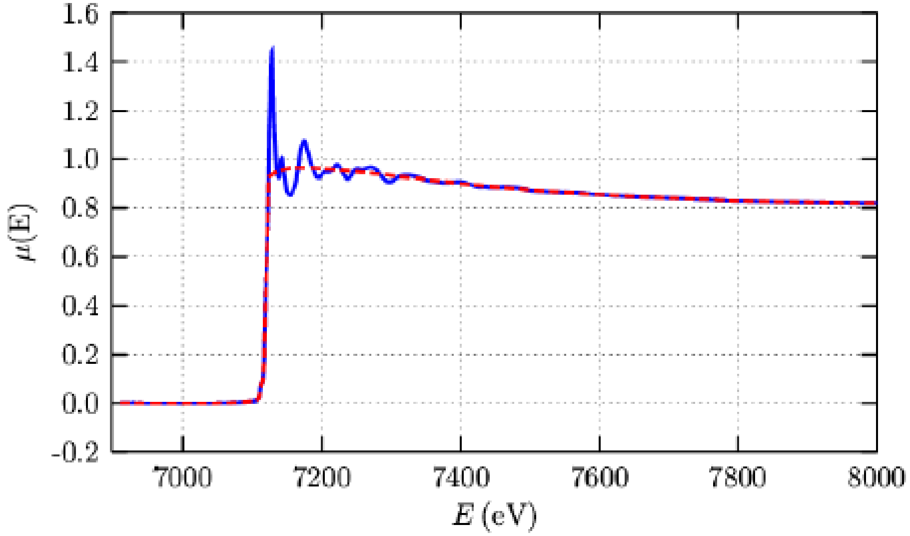
The XANES portion (below) shows a fairly rich spectral structure. We'll come back to this for XANES analysis.



Derivative

We can select E_0 roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we'll keep in mind that we may need to refine this value later on.

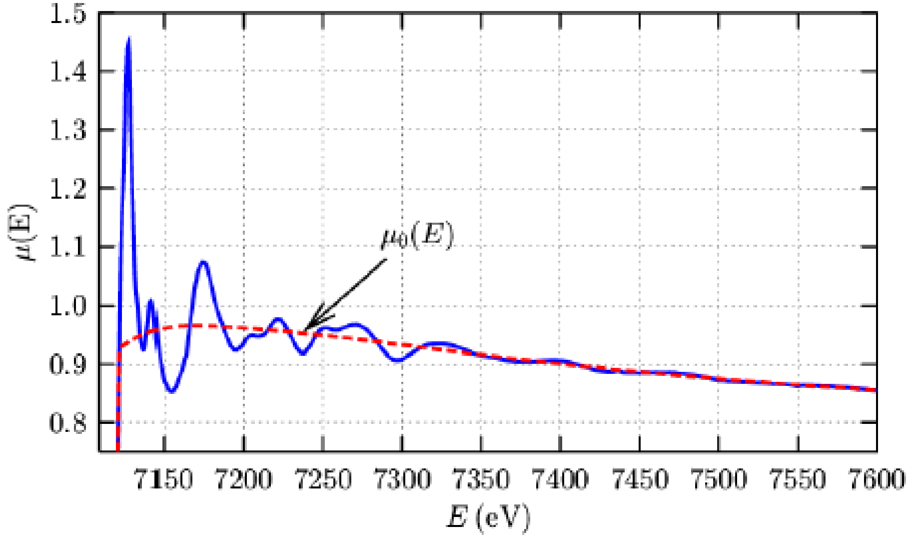
Data Reduction: Post-Edge Background Subtraction



Post-Edge Background

We don't have a measurement of $\mu_0(\mathrm{E})$ (the absorption coefficient without neighboring atoms).

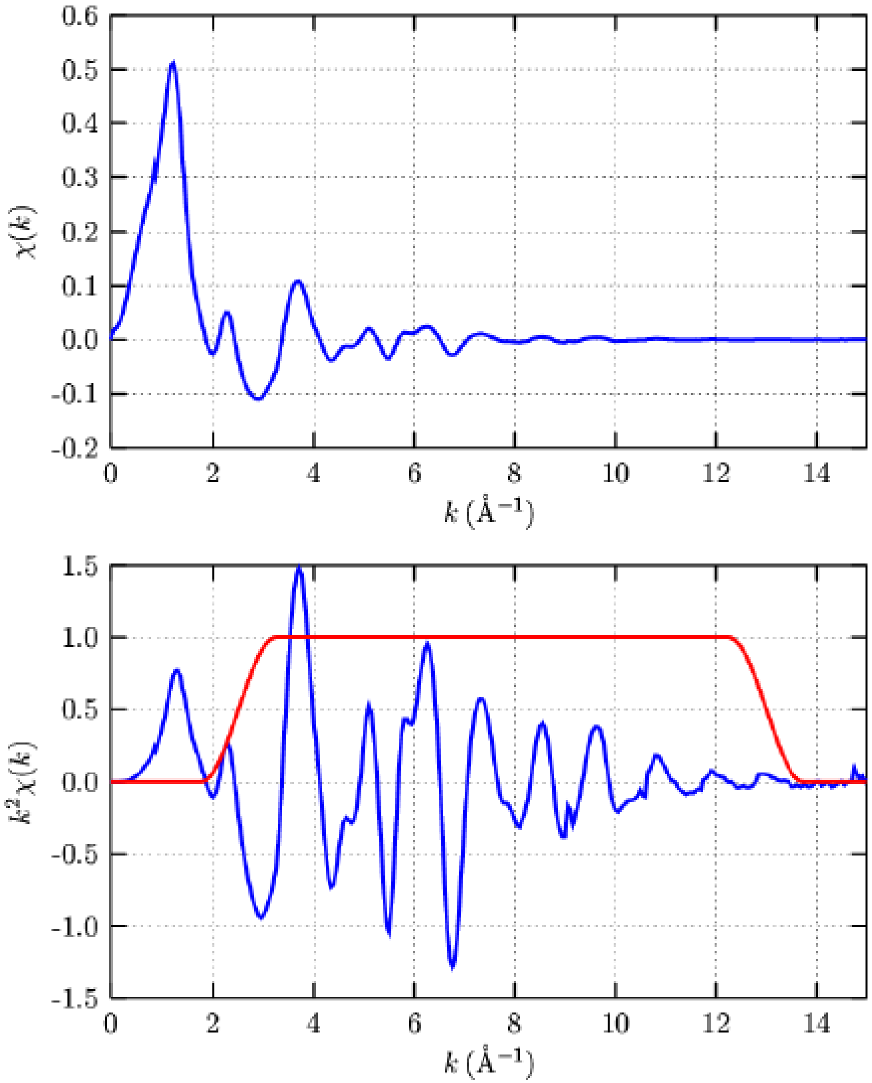
We approximate $\mu_0(\mathrm{E})$ by an adjustable, smooth function: a ***spline***.



This can be somewhat dangerous – a flexible enough spline could match the $\mu(\mathrm{E})$ and remove all the EXAFS!

We want a spline that will match the ***low frequency*** components of $\mu_0(\mathrm{E})$.

Data Reduction: $\chi(k)$, k-weighting



$\chi(\mathrm{k})$

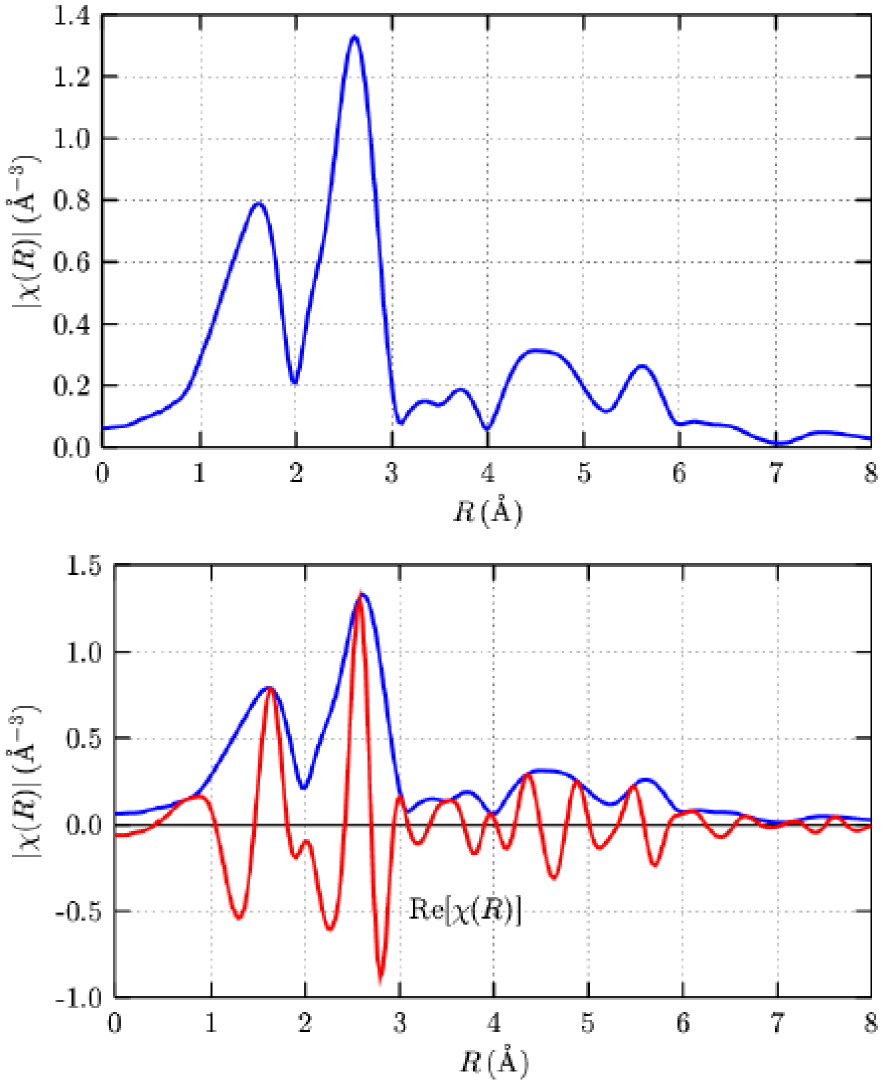
The raw EXAFS $\chi(\mathrm{k})$ usually decays quickly with k, and difficult to assess or interpret by itself.

It is customary to weight the higher-k portion of the spectra by multiplying by k^2 or k^3.

k-weighted $\chi(\mathrm{k})$: $\mathrm{k}^2\chi(\mathrm{k})$

$\chi(\mathrm{k})$ is composed of sine waves, so we'll Fourier Transform from k to R-space. To avoid "ringing", we'll multiply by a *window function*.

Fourier Transform: χ(R)



$\chi(\mathrm{R})$

The Fourier Transform of $\mathrm{k}^2\chi(\mathrm{k})$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe-Fe.

The Fe-O distance in FeO is 2.14Å, but the first peak is at 1.6Å. This shift in the first peak is due to the ***phase-shift***, $\delta(\mathrm{k})$: $\sin[2\mathrm{kR} + \delta(\mathrm{k})]$.

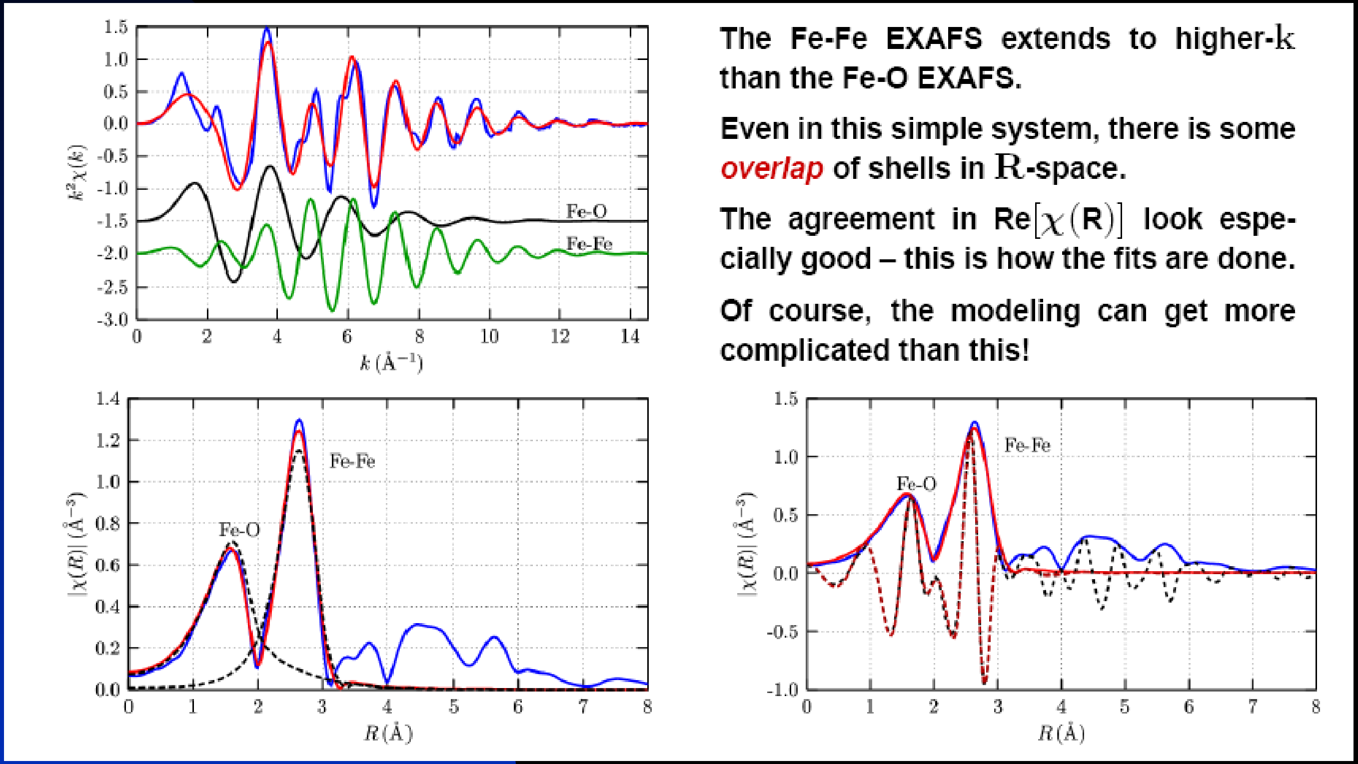
A shift of -0.5Å is typical.

$\chi(\mathrm{R})$ is complex:

The FT makes $\chi(\mathrm{R})$ complex. Usually only the amplitude is shown, but there are really oscillations in $\chi(\mathrm{R})$.

Both real and imaginary components are used in modeling.

EXAFS Analysis: two shell model of FeO

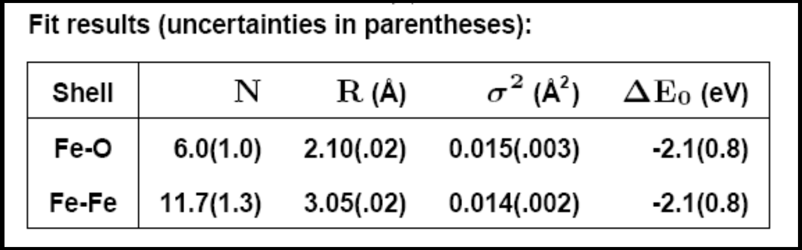


The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.

Even in this simple system, there is some *overlap* of shells in R-space.

The agreement in Re$[\chi(R)]$ look especially good – this is how the fits are done.

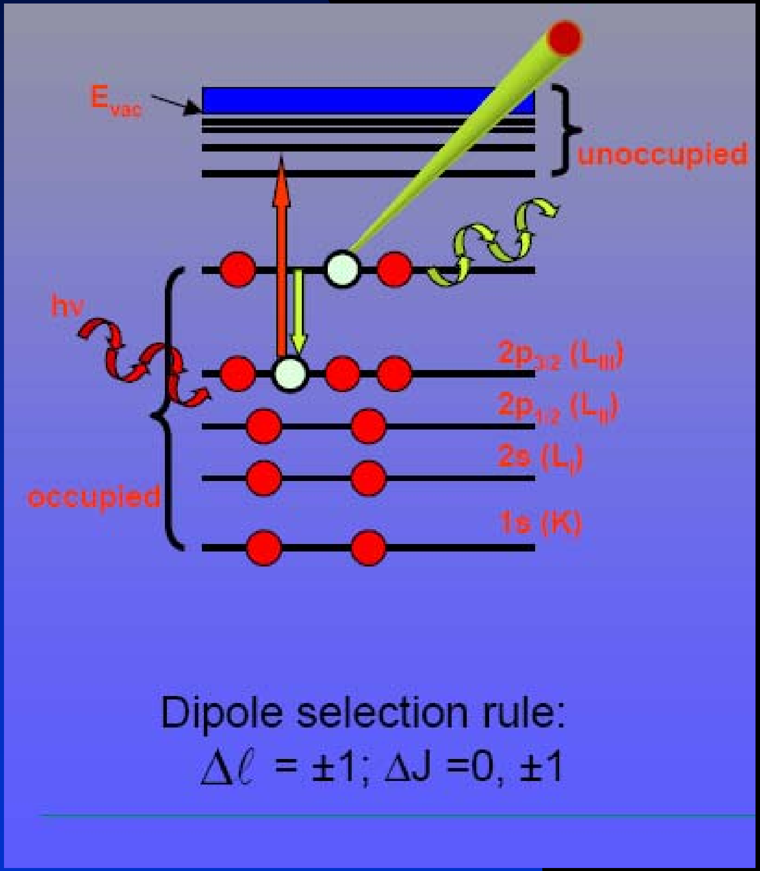
Of course, the modeling can get more complicated than this!



Fit results (uncertainties in parentheses):

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

XANES: X-ray Absorption Near Edge Structure



Dipole selection rule:
$\Delta\ell = \pm1$; $\Delta J = 0, \pm1$

At photoelectron kinetic energies with wavelengths near the first interatomic distance:

- Discrete transitions to unpopulated states
- XANES is a probe of the density of empty electron states projected onto the phtoabsorber

At higher XANES energies:

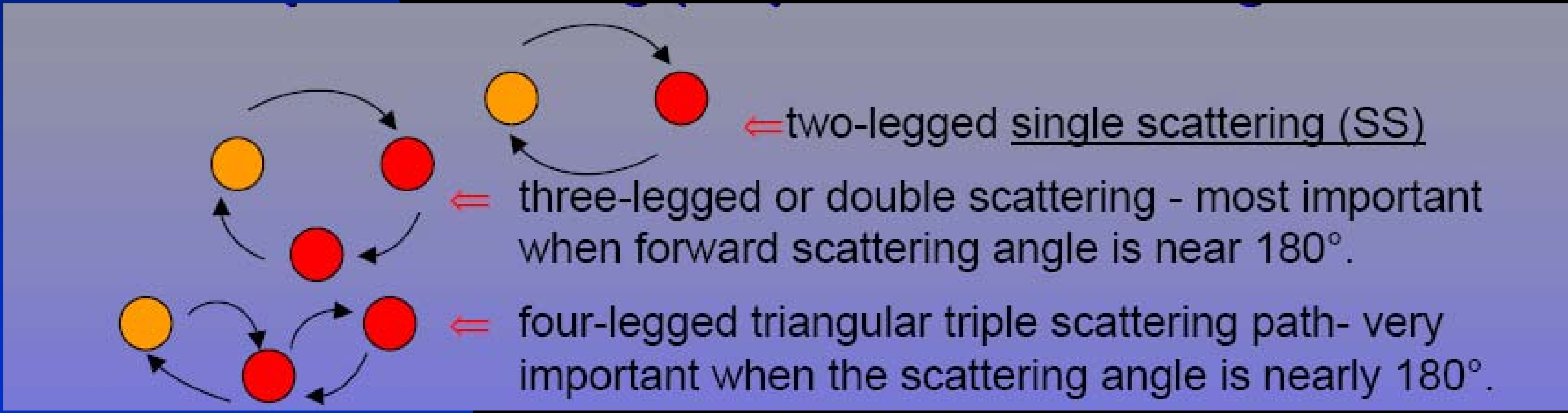
- The multiple scattering phenomenon dominates
- XANES is a probe for high order correlation functions

XANES: fingerprinting

- Despite large advances in the past years, predictive XANES calculations are not satisfactory.
- Interpretation is still qualitative by comparison to known,
  - reference spectra (“fingerprint”) or
  - theoretically calculated spectra (e.g., multiple scattering or band structure calculations).
- XANES features and their intensity and energy position are dependent on a number of factors including
  - •absorbing atom valence
  - •coordination geometry
  - •orbital occupancy
  - •electronegativityof coordinating atoms
  - •interatomicdistances•orientation (for anisotropic samples)

Multiple scattering (MS) in the XAFS regime

- **In addition to SS in EXAFS, oscillations from MS of the photoelectron can be observed in EXAFS - mostly at low k•**
- **MS is most likely along atoms with a collinear arrangement (“lensing” or “focussing” effect)•**
- **MS peaks are never found in the FT spectrum at distances shorter than the second coordination shell**
- **A simple assumption is that the rel. mean square displacement is additive - paths longer than triple scattering paths are rare**

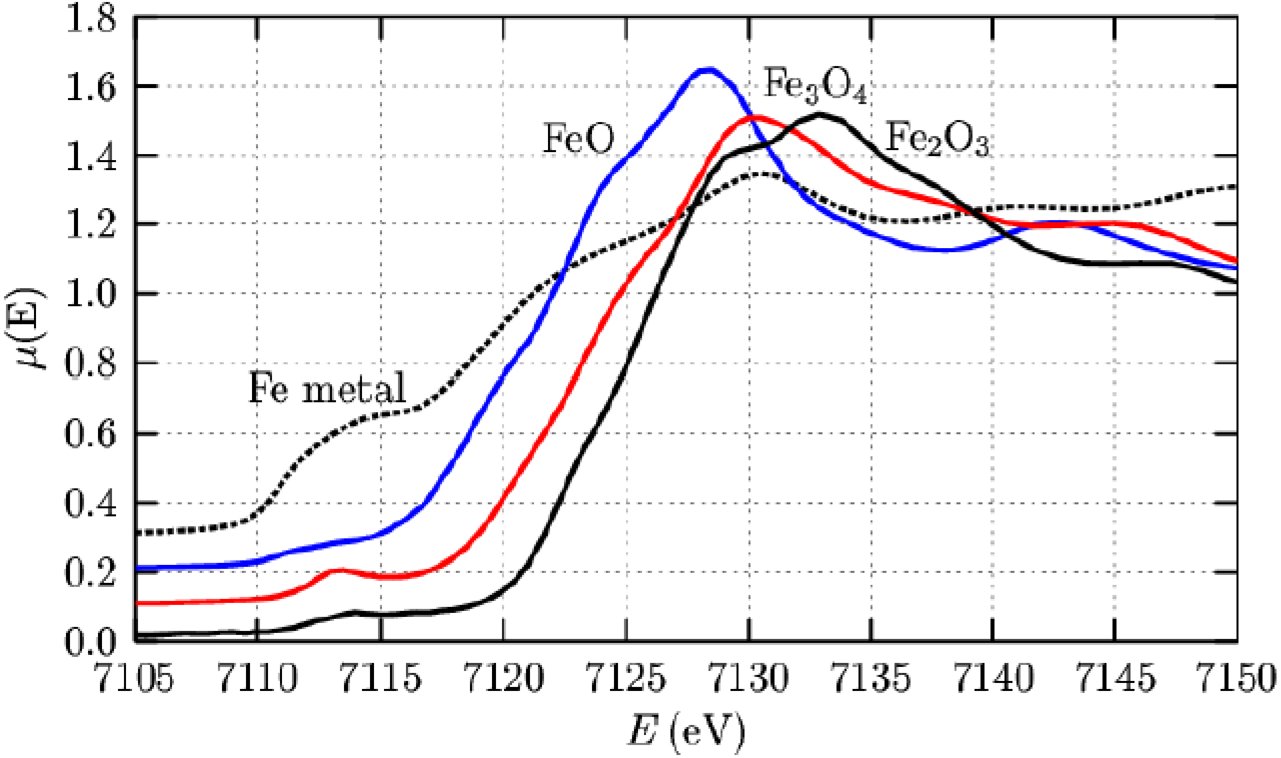


⇐two-legged <u>single scattering (SS)</u>

⇐ three-legged or double scattering - most important when forward scattering angle is near 180°.

⇐ four-legged triangular triple scattering path- very important when the scattering angle is nearly 180°.

XANES Analysis: Oxidation State



XANES for Fe oxides and metal. **The shift of the edge position can be used to determine the valence state.**

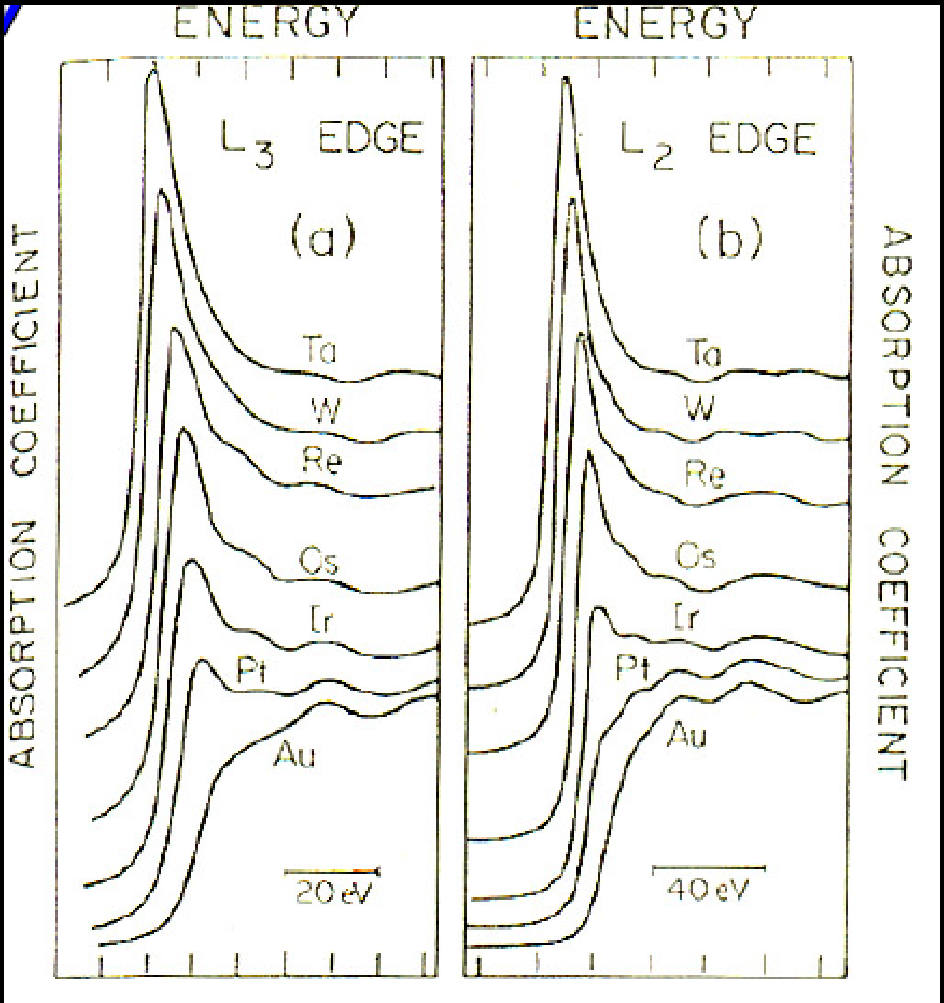
The heights and positions of pre-edge peaks can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

XANES: orbital occupancy

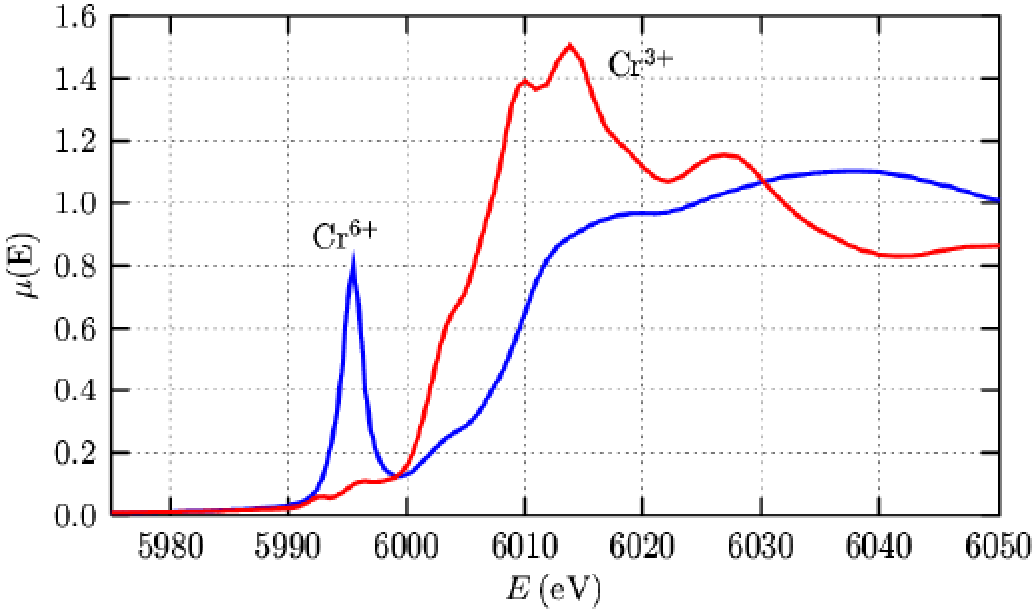
L3,2 edge white line areas are a measure of 5d-band holes.

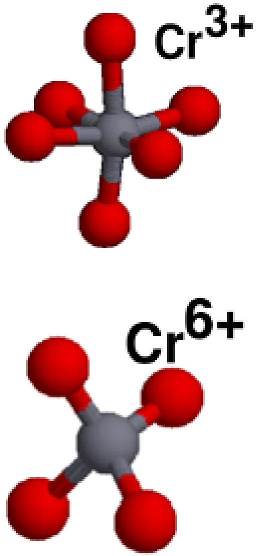
Ta	**5d^3**
W	**5d^4**
Re	**5d^5**
Os	**5d^6**
Ir	**5d^7**
Pt	**5d^{10}**
Au	**5d^{10}**

L3,2 WL intensity decreases as d-orbtials are filled



XANES Analysis: Oxidation State and Coordination Chemistry





The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

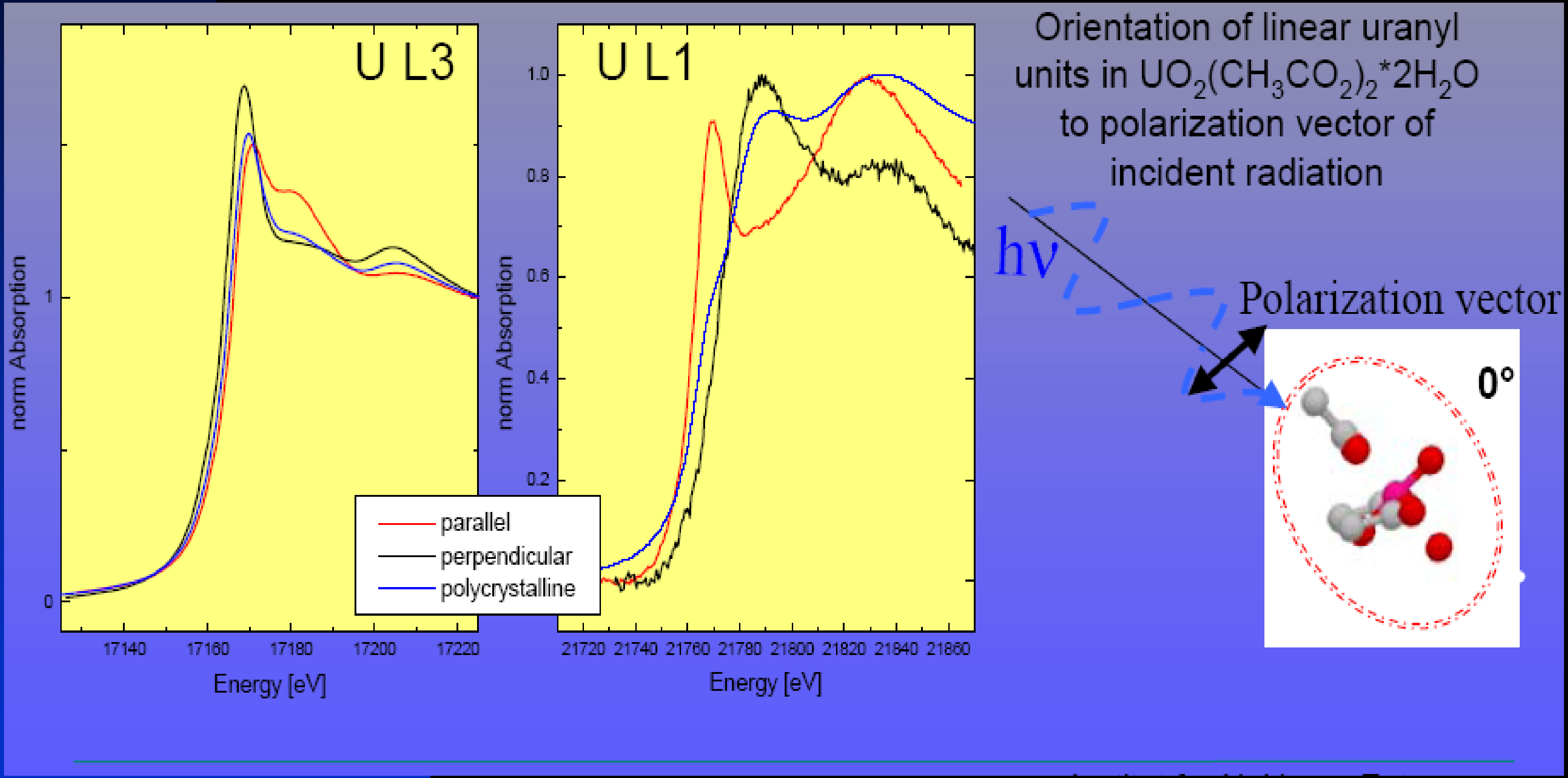
For ions with partially filled d shells, the p-d hybridization changes dramatically as *regular octahedra* distort, and is very large for *tetrahedral* coordination.

This gives a dramatic *pre-edge peak* – absorption to a localized electronic state.

Polarized XAFS -
U L_{III} and L_I edge XANES features of oriented samples

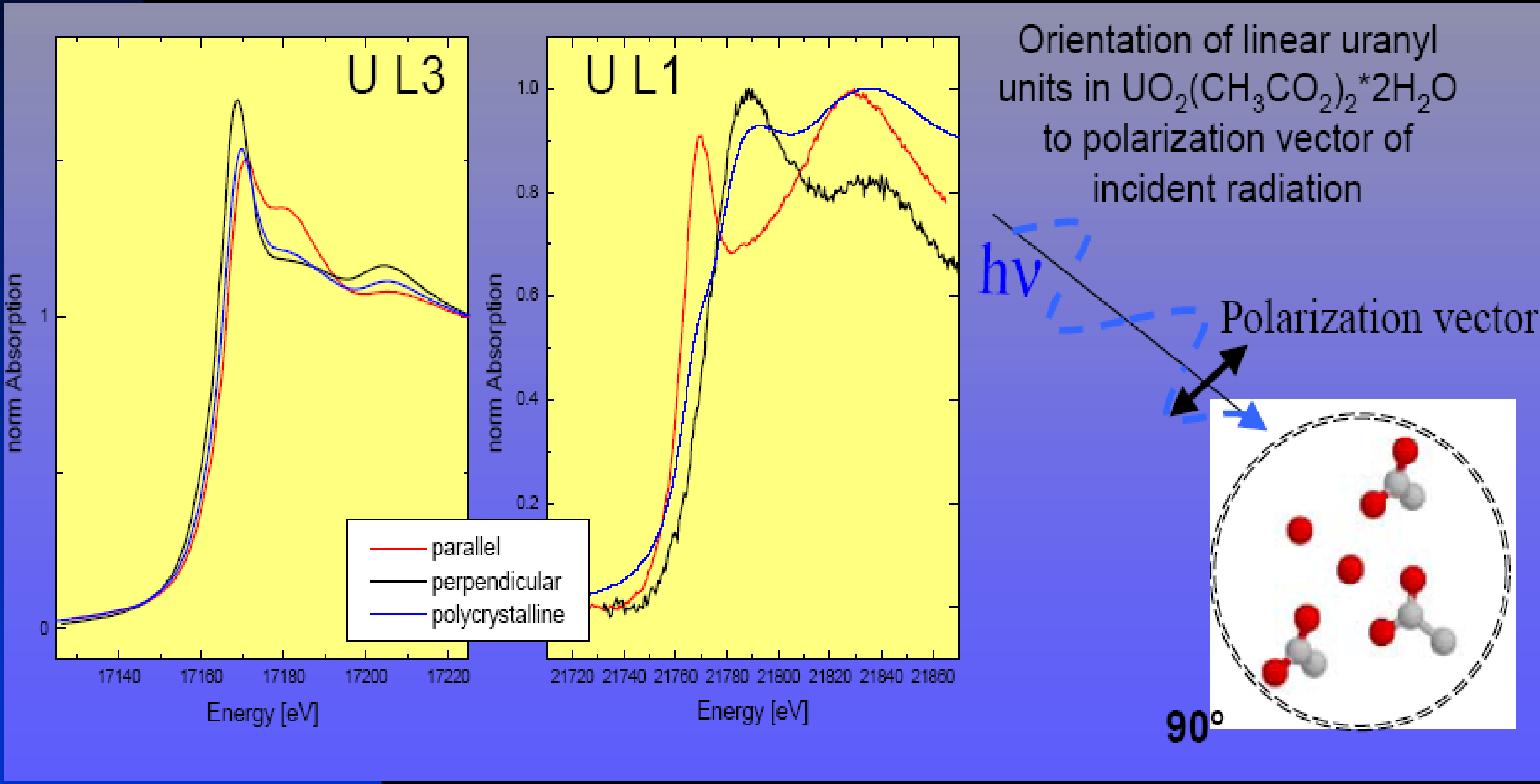
- The linear uranyl ($O=U=O^{2+}$) cation exhibits striking variations in its XAFS spectra as a function of orientation relative to the incident radiation's polarization vector.
  - Changes in U L_{III} XANES edge features: white line (2p→6d (6s) transition), 10eV feature (scattering on O*ax*), and 35eV feature (scattering on L*eq*)
  - U L_I XANES polarization dependency is more dramatic, due to the higher orientation of p-like final states.

Polarized XAFS -- U L_{III} and L_I edge XANES of oriented $UO_2(CH_3CO_2)_2{*}2H_2O$



Orientation of linear uranyl units in $UO_2(CH_3CO_2)_2{*}2H_2O$ to polarization vector of incident radiation

Polarized XAFS -- U L_{III} and L_I edge XANES of oriented $UO_2(CH_3CO_2)_2*2H_2O$



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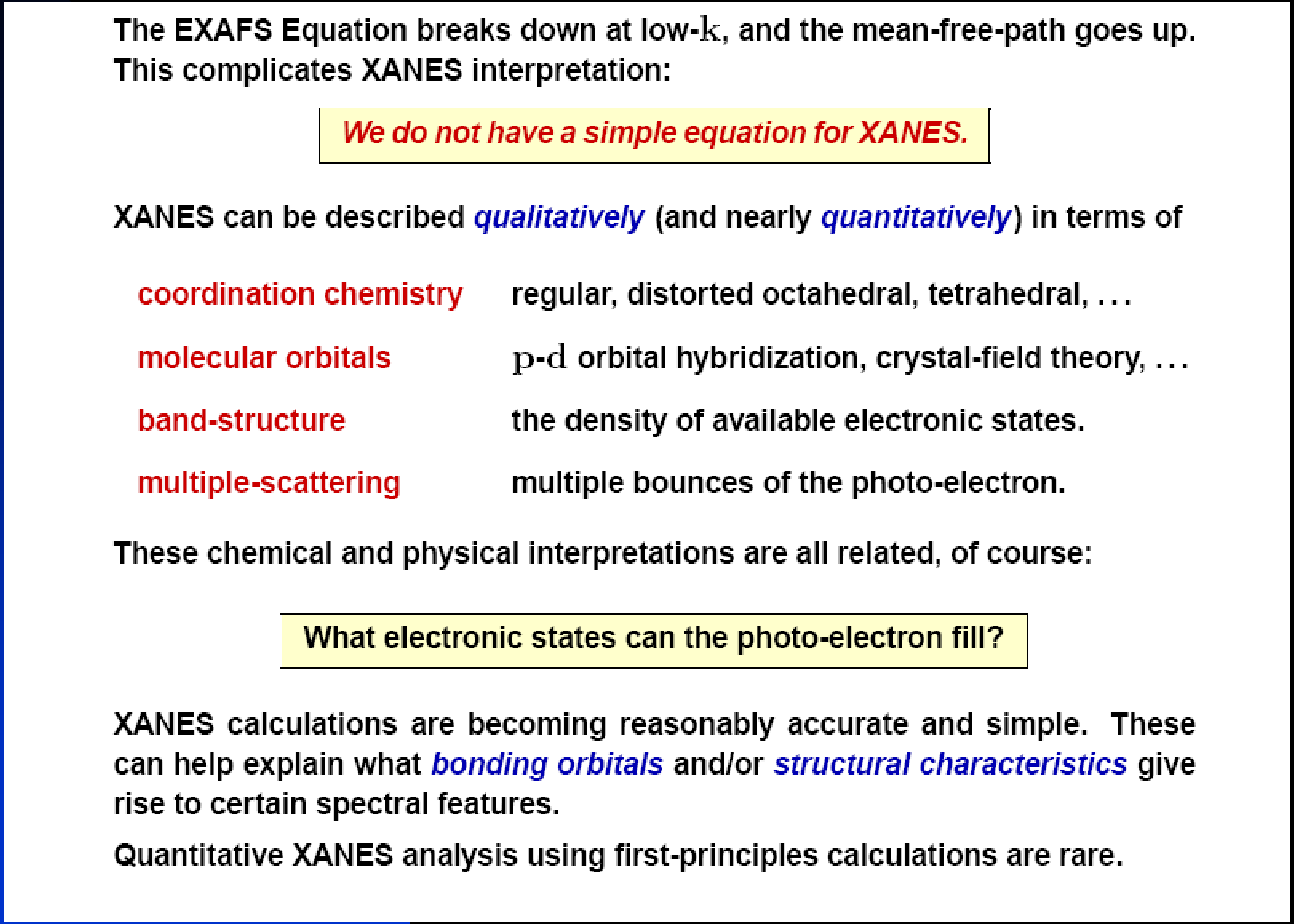
XANES Interpretation



The EXAFS Equation breaks down at low-k, and the mean-free-path goes up. This complicates XANES interpretation:

We do not have a simple equation for XANES.

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of

coordination chemistry	regular, distorted octahedral, tetrahedral, . . .
molecular orbitals	p-d orbital hybridization, crystal-field theory, . . .
band-structure	the density of available electronic states.
multiple-scattering	multiple bounces of the photo-electron.

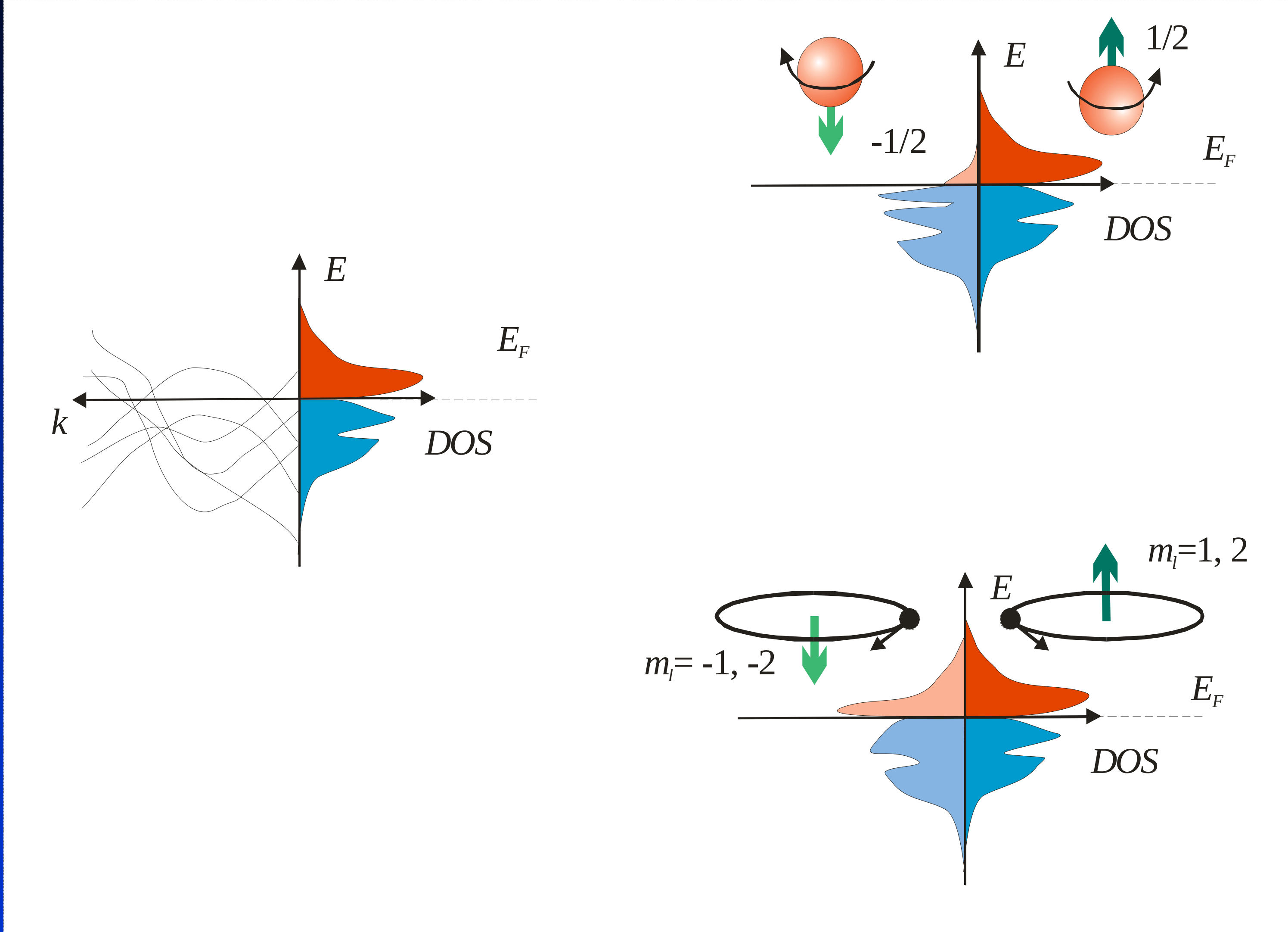
These chemical and physical interpretations are all related, of course:

What electronic states can the photo-electron fill?

XANES calculations are becoming reasonably accurate and simple. These can help explain what *bonding orbitals* and/or *structural characteristics* give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are rare.

XMCD: X-Ray Magnetic Circular Dichroism



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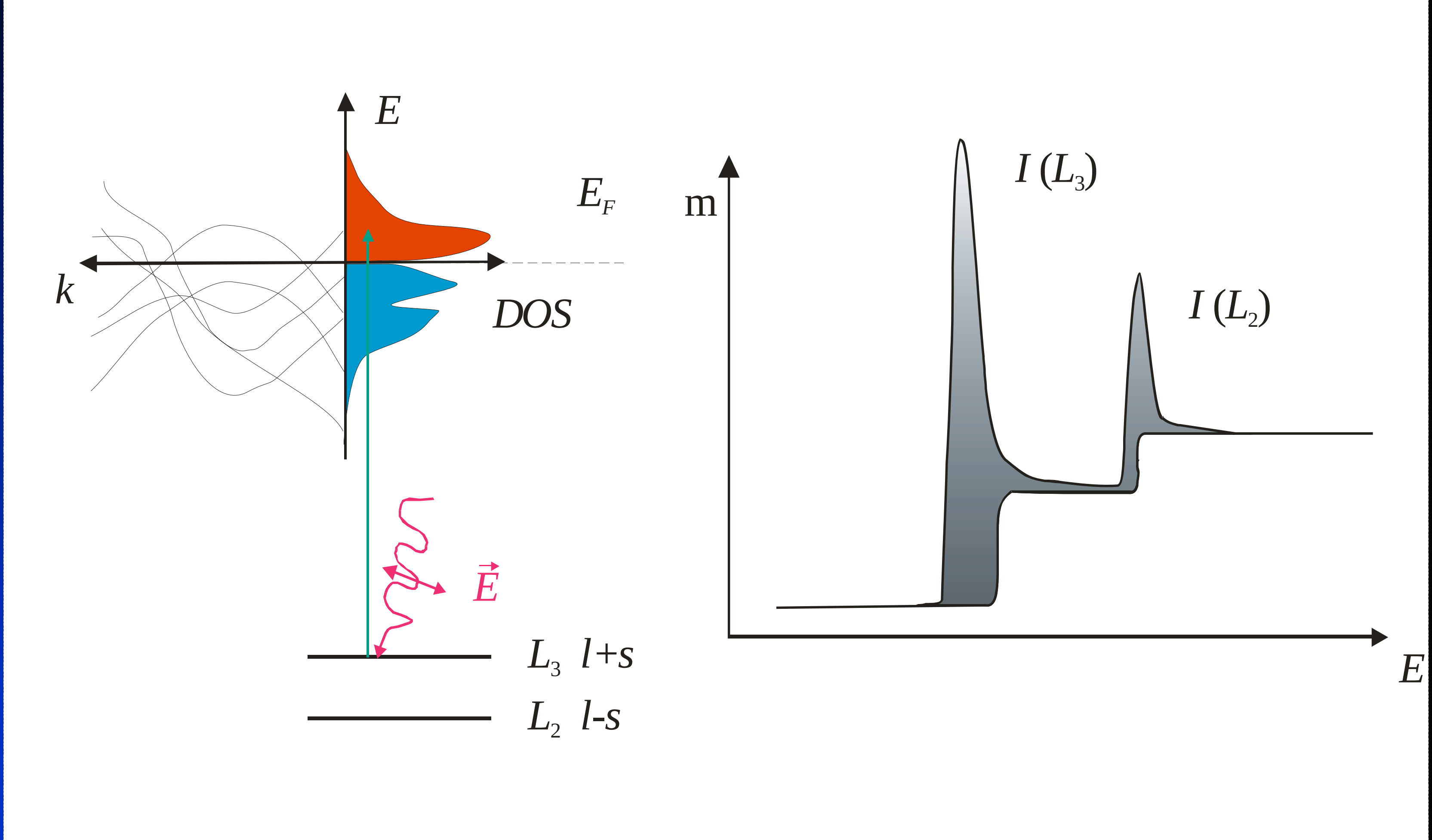

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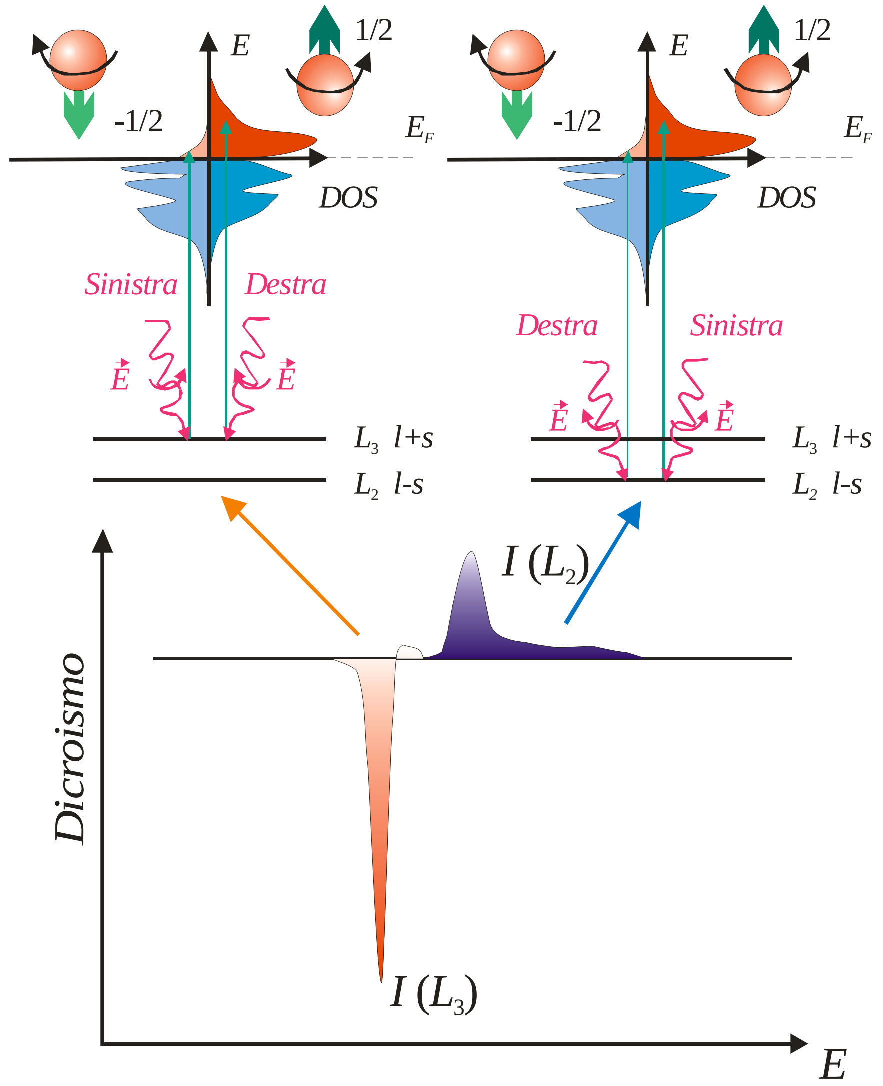

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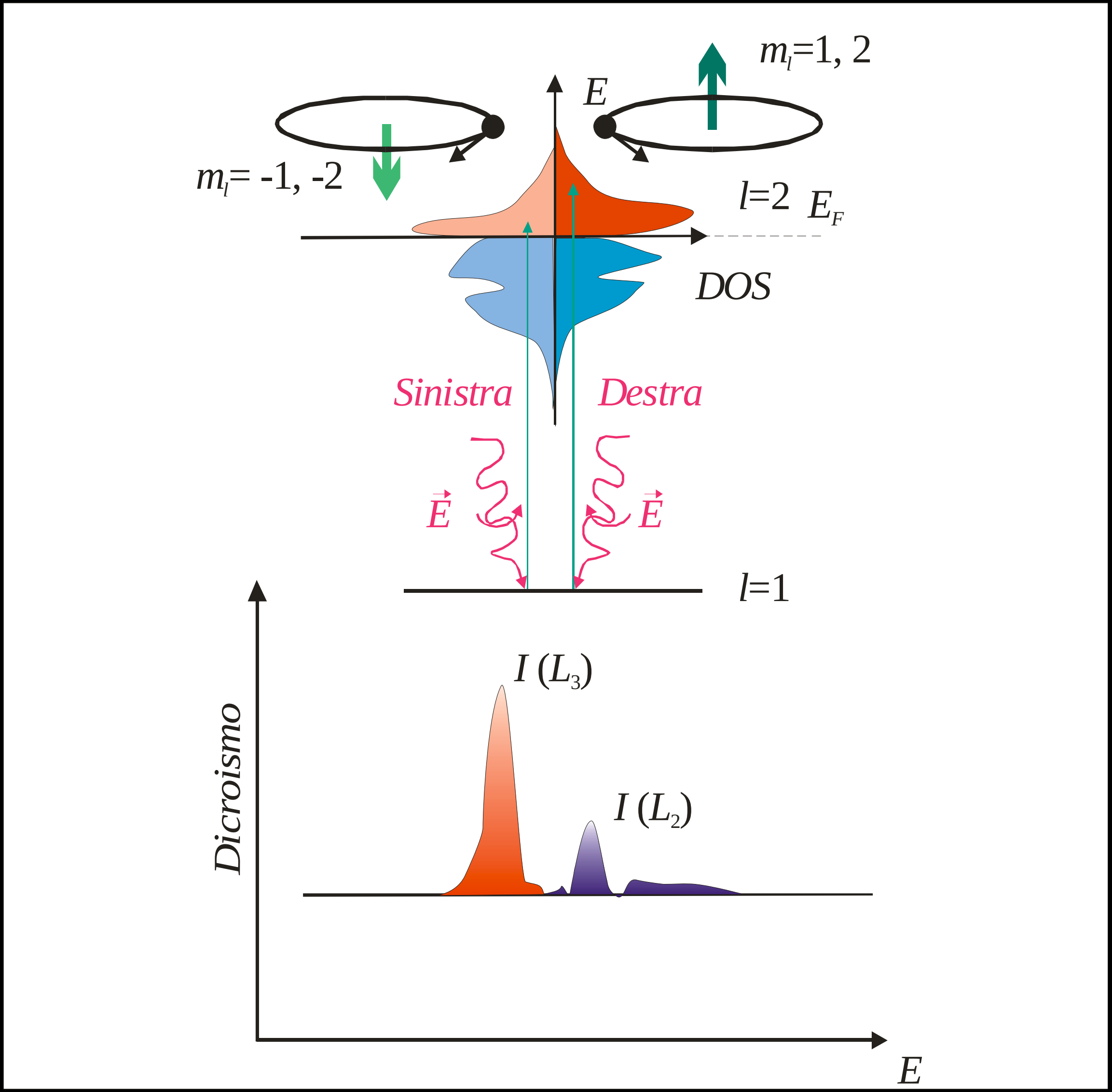
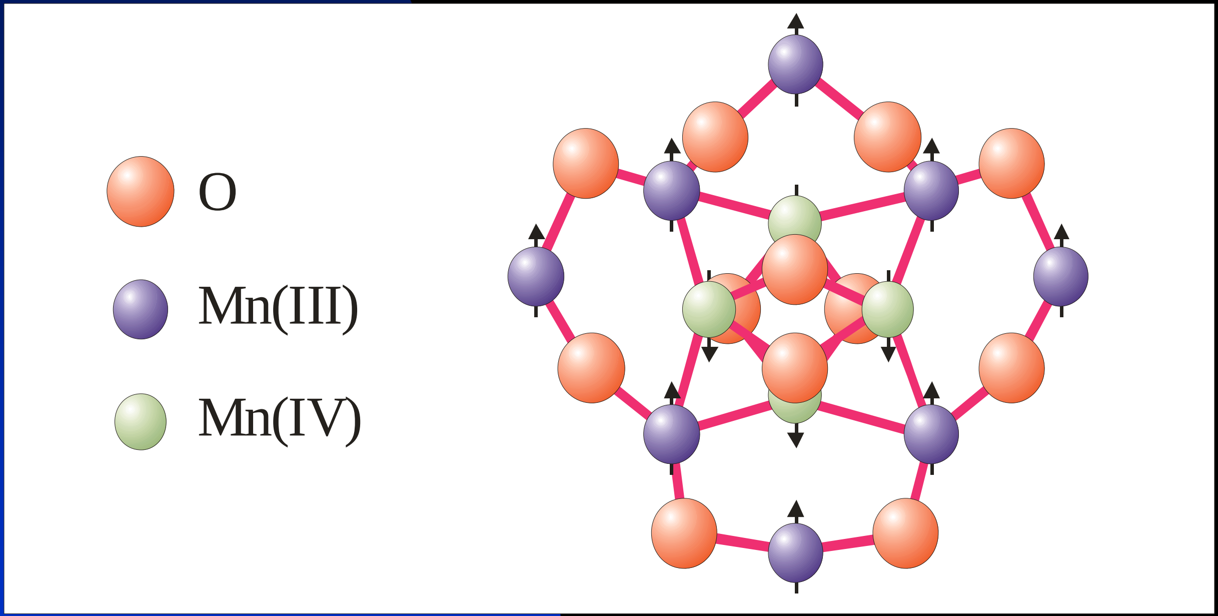


Regole di sommazione

- Lo spin s viene eliminato se si sommano gli integrali del segnale dicroico sulle soglie L_{III} (l+s) ed L_{II} (l-s): l » I(L_{III})+I(L_{II})
- Per eliminare il momento angolare l occorre tenere conto della degenerazione: s = I(L_{III})-2I(L_{II})

Esempio: Mn12Ac



- Secondo la teoria dei gruppi, il momento angolare orbitale è nullo (si dice che è quenchiato dal campo cristallino)

Esempio: Mn12Ac