

# **X-ray Absorption Spectroscopy: The extended region**

XAS: X-ray Absorption

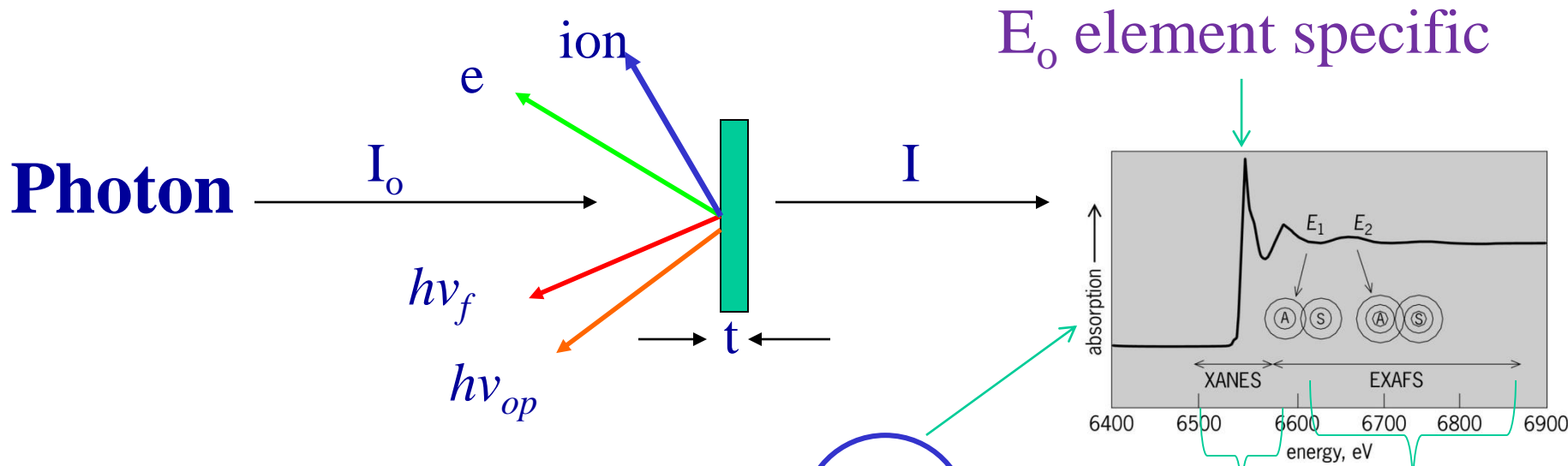
XAFS: X-ray Absorption Fine Structures

XANES: X-ray Absorption Near Edge Structures

NEXAFS: Near Edge X-ray Absorption Fine  
Structure

***EXAFS***: Extended X-ray Absorption Fine  
Structures

# X-ray absorption spectroscopy



**Transmission:**  $I = I_0 e^{-\mu t}$ ;  $\mu t = \ln(I_0 / I)$

Absorption across an edge

bonding symmetry structure local

**Yield spectroscopy:**

$$\mu t \propto Y(h\nu)$$


$$\mu t = f(h\nu) \cdot Y(h\nu)$$

# What does $\mu(h\nu)$ measure across an edge?

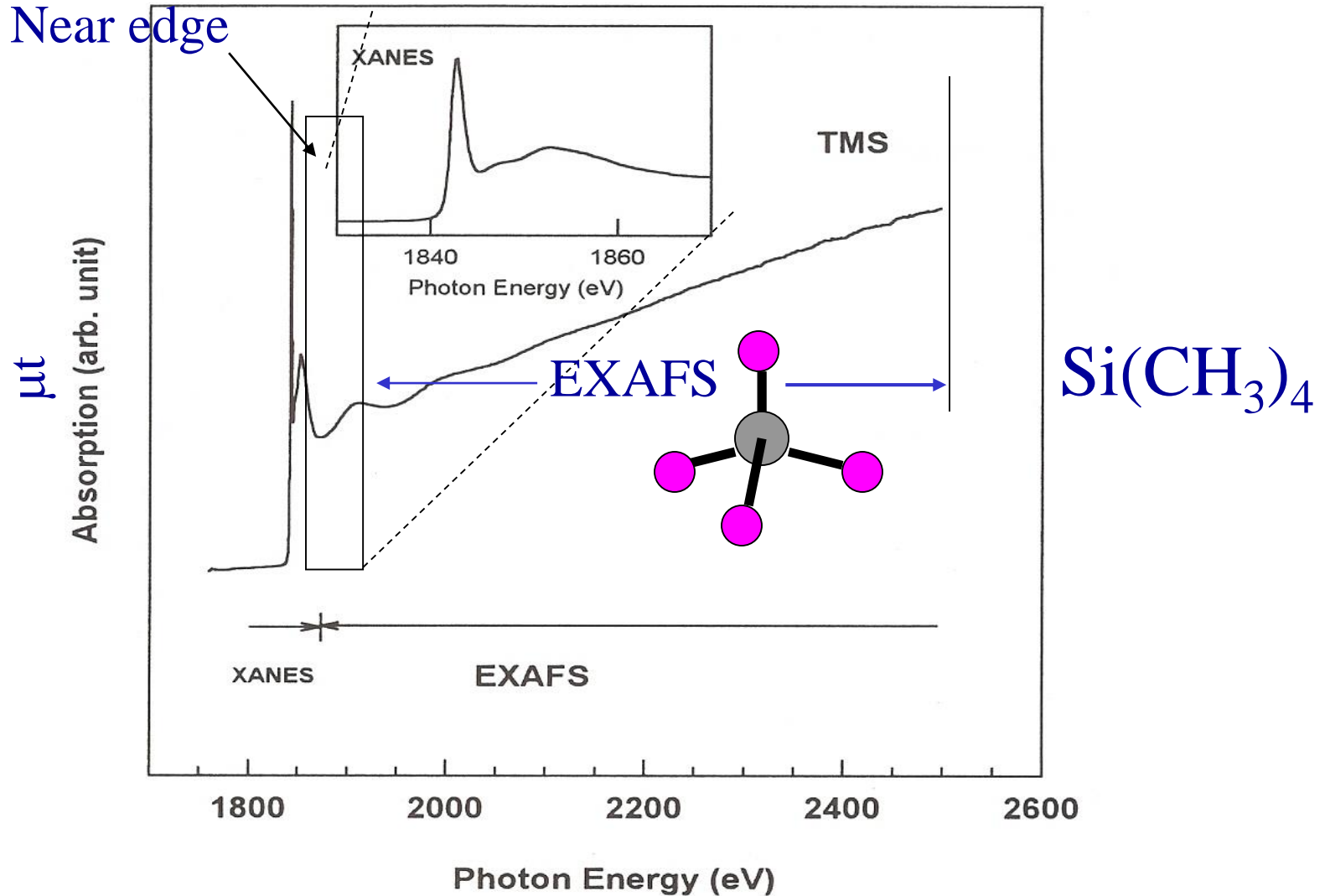
The modulation in  $\mu$  above the edge is the **XAFS**, it contains information about the structure and bonding of the absorbing atom in a chemical environment

**Edge jump:** threshold of the core excitation

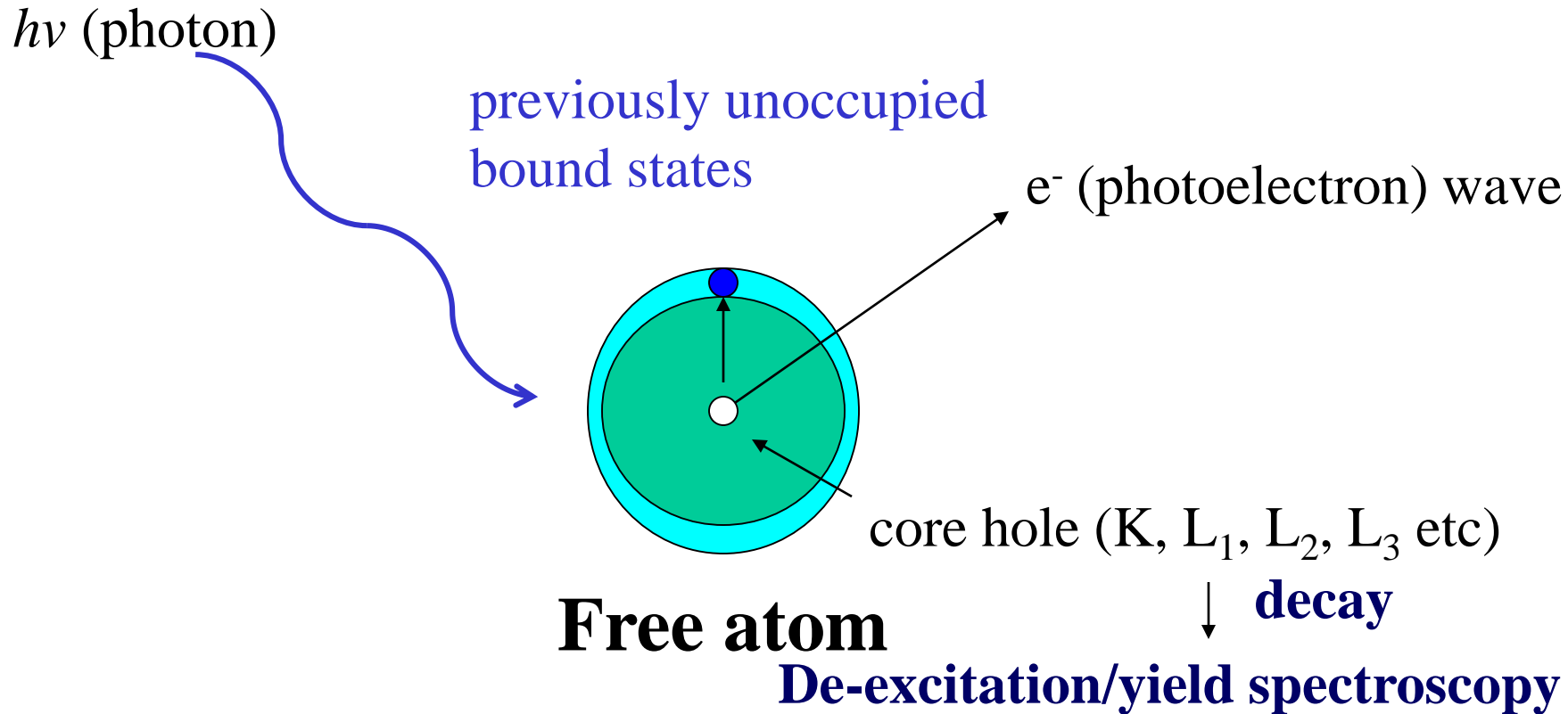
**Near edge region:** core to bound and quasi bound state transition – multiple scattering effect dominates

 ***Extended region above the threshold:*** core to continuum transition, single scattering dominates, interference of outgoing and backscattering waves

# What is XAFS?



# Origin of XAFS

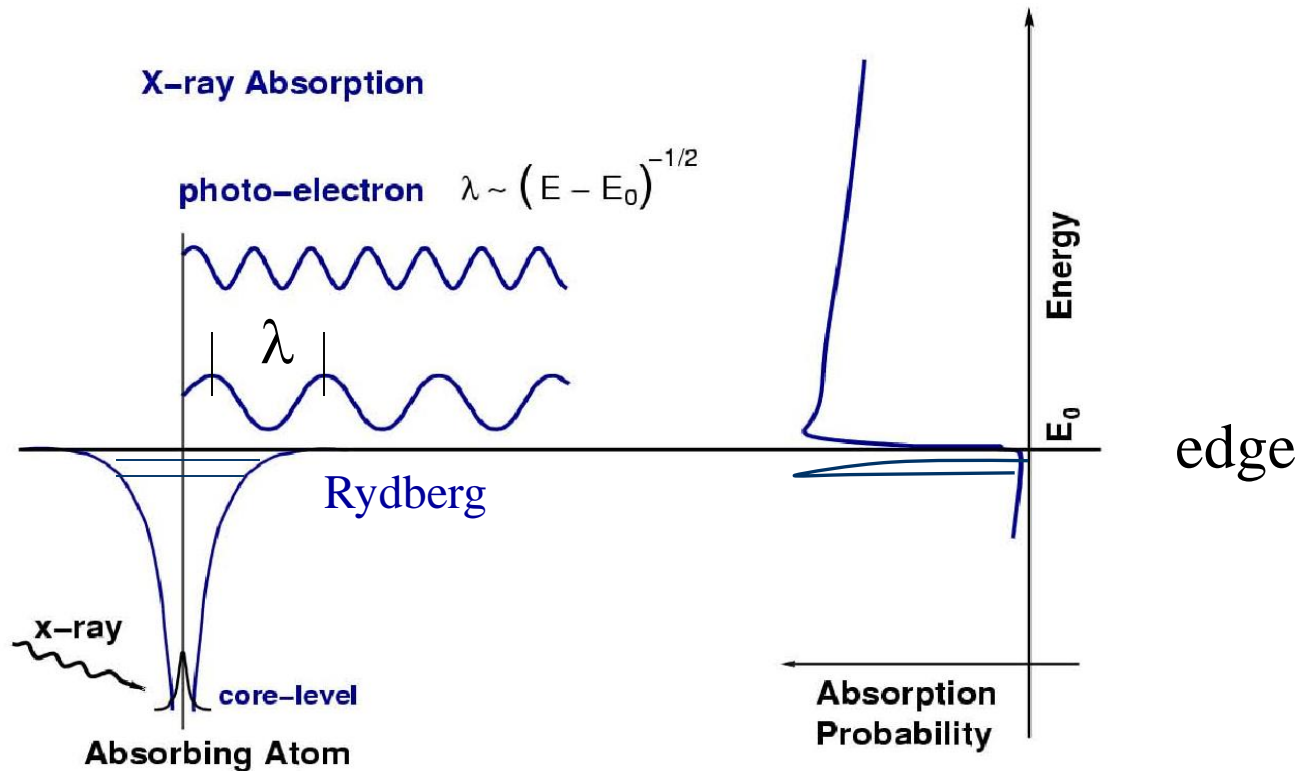


$h\nu \geq$  threshold energy of the core electron (binding energy)

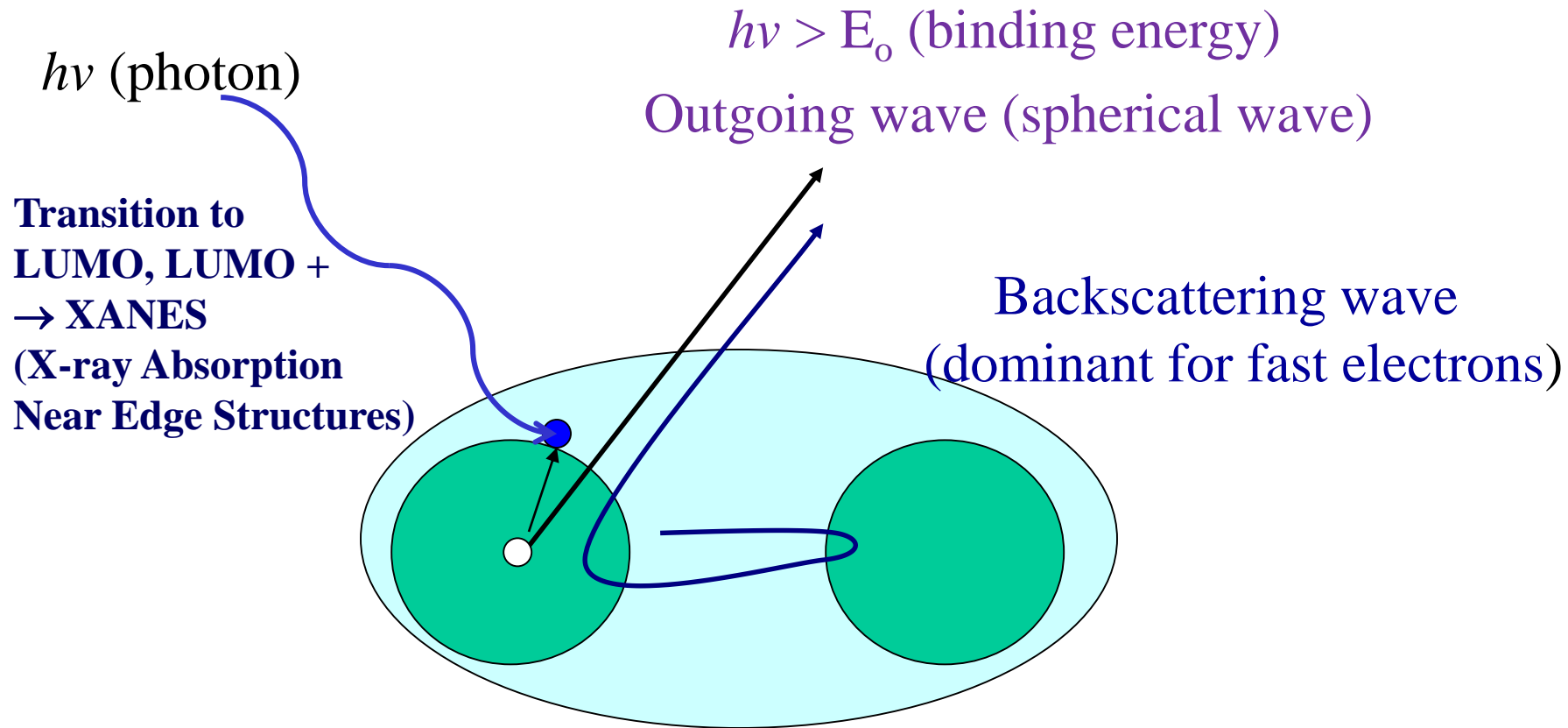
Selection rule: electric dipole

# Origin of EXAFS

$e^-$  with  $KE > 0$  propagates as a wave with  $k \sim (KE)^{1/2}$ . If it does not encounter another atom in the vicinity, the  $\mu(h\nu)$  varies monotonically as a function of photon energy



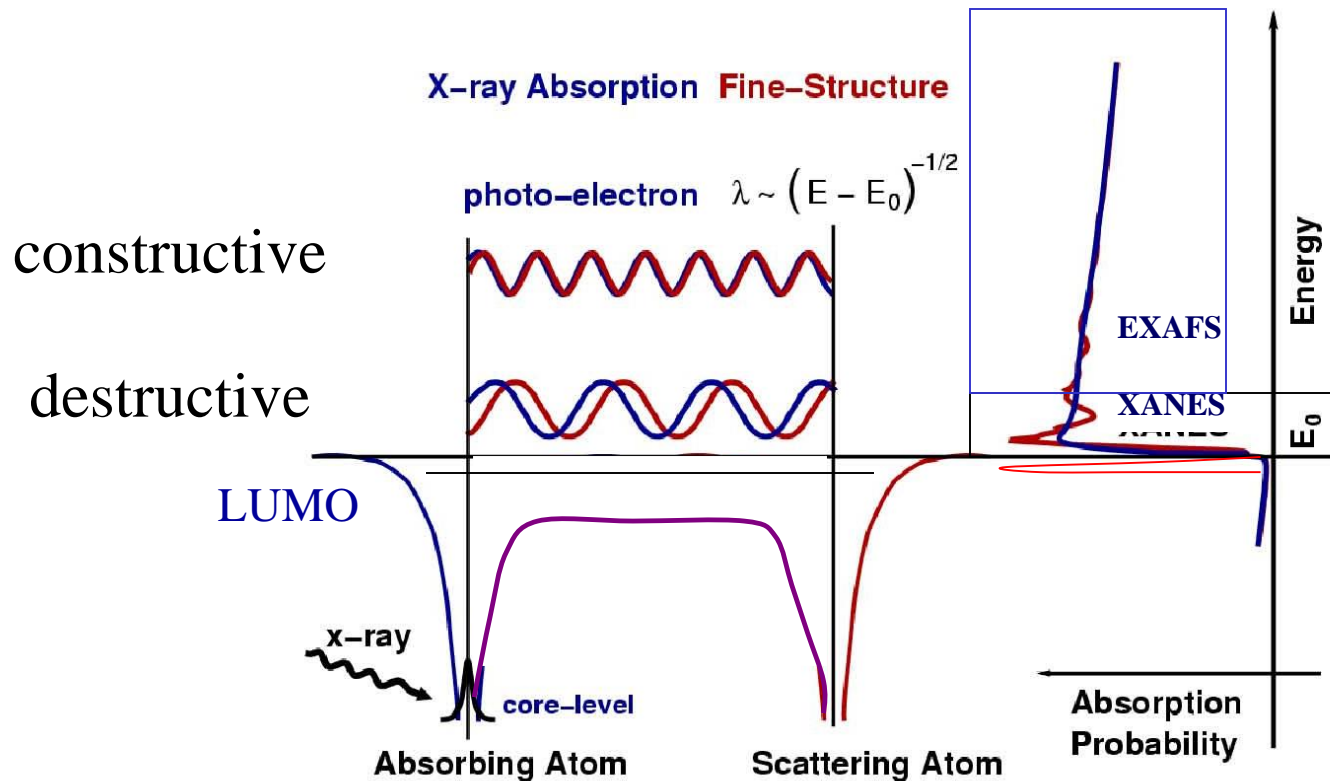
# Diatomic molecule



If the outgoing and backscattered waves are in phase, the interference is constructive, if they are out of phase, the interference is destructive

# Origin of EXAFS

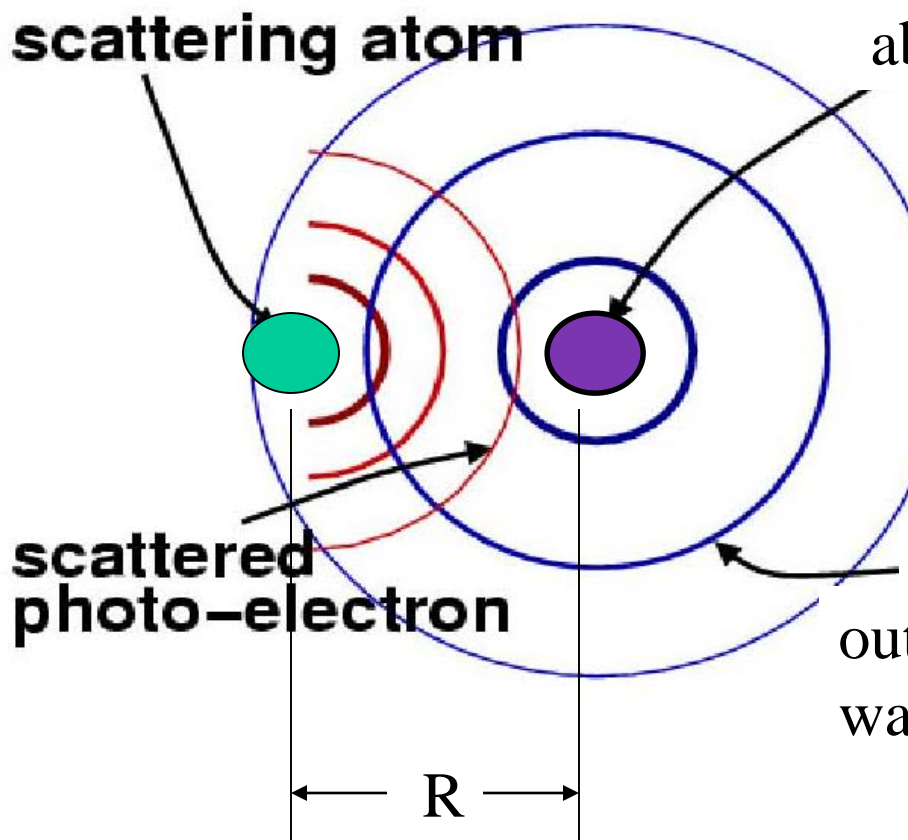
The forward and backscattered waves will interfere **constructively** and **destructively** at the absorbing atom, producing oscillations in  $\mu(h\nu) \rightarrow$  EXAFS



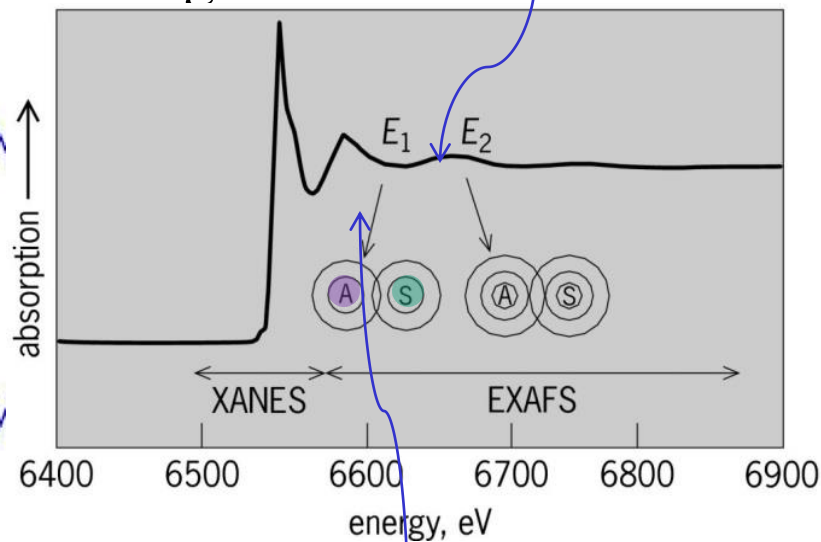


The interference modulates  $\mu$ . Thus  $\mu$  depends on  $\lambda$  of the outgoing wave, the electronic structure (amplitude of the scattering atom and the phase shift of both atoms) and the inter-atomic distance ( $R$ )

constructive interference  
yields a maximum



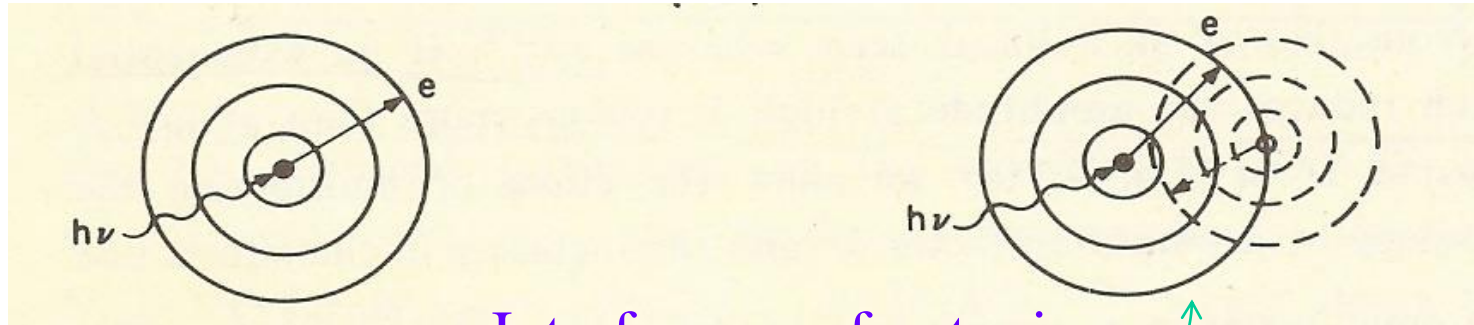
absorbing atom



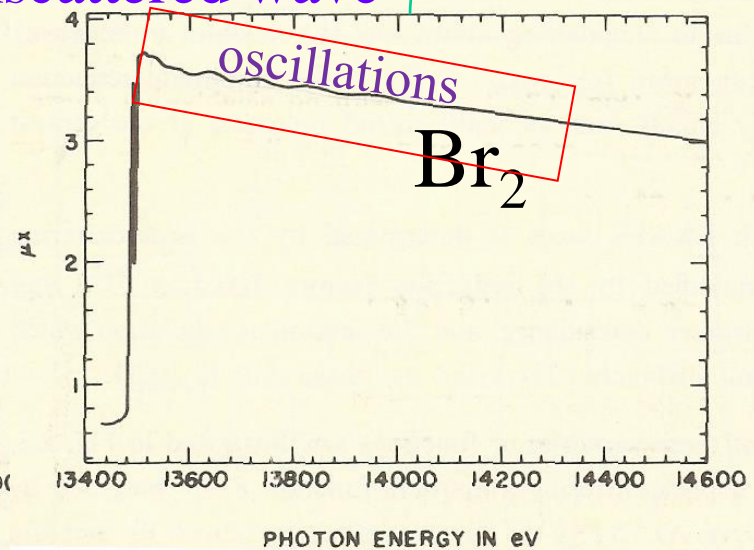
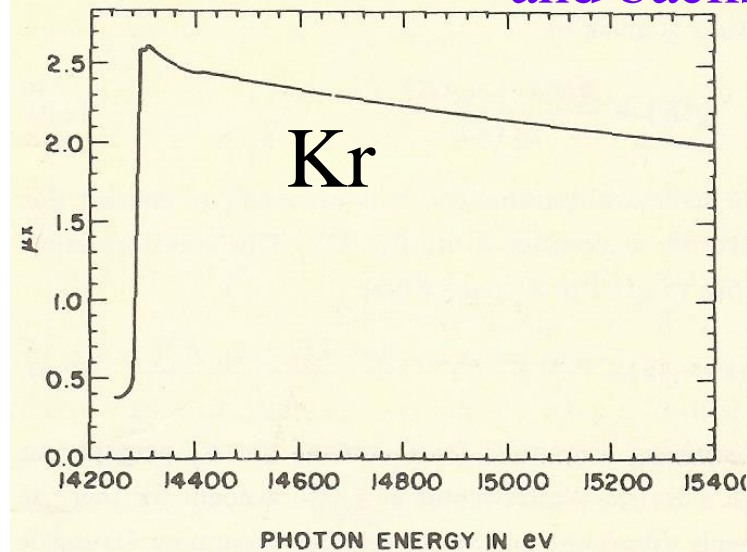
outgoing  $e^-$   
wave

destructive interference  
yields a minimum

EXAFS: 
$$\chi(k) = \frac{\mu_{sample} - \mu_{atom}}{\mu_{atom}}$$



Interference of outgoing  
and backscattered wave

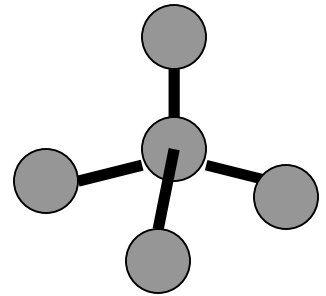
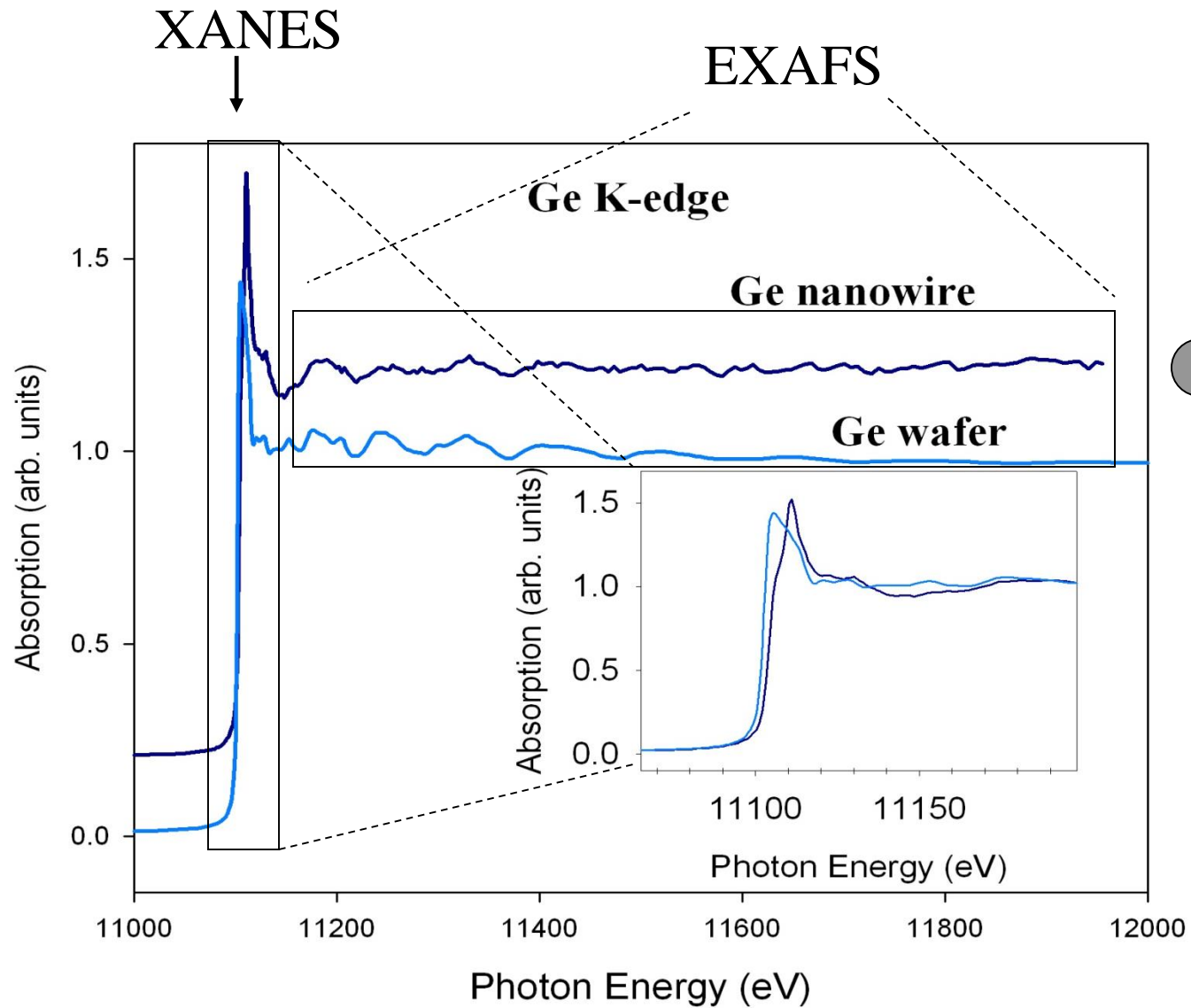


Brian M. Kincaid, "Synchrotron Radiation Studies of K-Edge X-ray Photo-absorption Spectra: Theory and Experiment", *Stanford University*, 1975; Advisor: S. Doniach

# EXAFS: the modern view

- EXAFS is the **oscillations in  $\mu$**  beyond the XANES region
- The oscillations arise from the interference of the *outgoing* and the *backscattered* electron wave which modulates the absorption coefficient (no neighboring atom, no EXAFS)
- Single scattering pathway dominates at high  $k$  (energy)
- The **thermal motion modifies** the amplitude of the EXAFS
- It is a short range phenomenon ( $\sim 4 \text{ \AA}$ ) (IMFP of electrons)
- It works for **disorder systems** (liquid, amorphous materials)
- EXAFS is **additive** - all absorber-scattering atom pairs contribute to EXAFS additively
- The **phase** and **amplitude** are **transferable for chemically similar systems**; they are also separable by **Fourier Transform**
- Theoretical phases and amplitudes are often used in analysis; they can be generated in the FEFF code developed by J.J. Rehr of the University of Washington

# EXAFS of medium and high Z atoms



# Conversion of kinetic energy $E - E_0$ to wave vector $k$

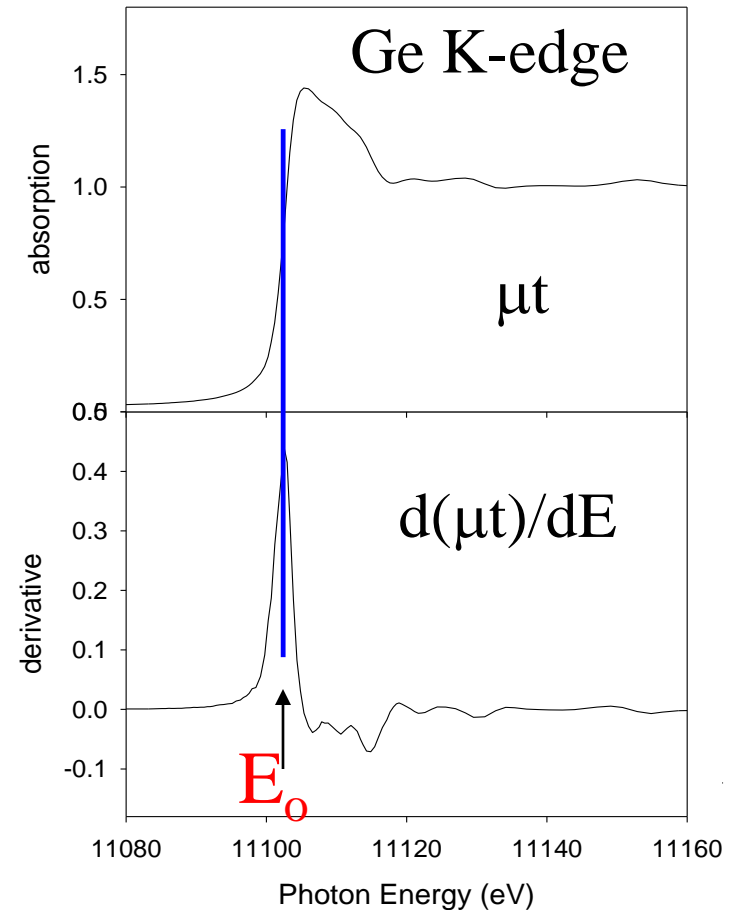
$$k(\text{\AA}^{-1}) = \frac{2\pi}{\lambda} = \sqrt{(2m/\hbar^2)(E - E_0)} = \sqrt{0.263\Delta E(\text{eV})}$$

$$k = 0.513\sqrt{\Delta E}$$

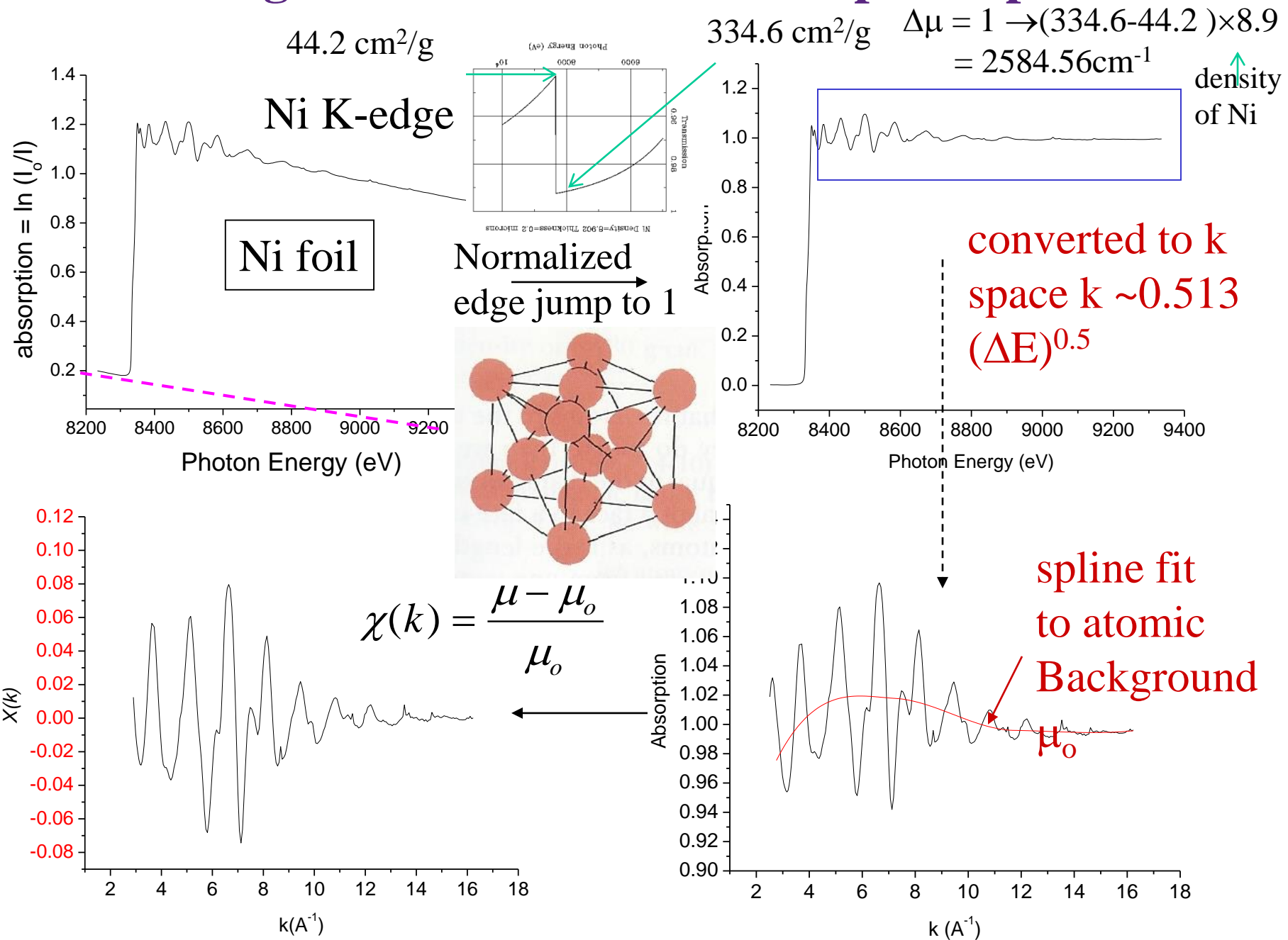
Where  $E_0$  is the threshold energy (usually the point of inflection of the edge jump),  $E$  is the photon energy.

Thus 50 eV above the threshold corresponds to a  $k$  value of  $3.63 \text{\AA}^{-1}$

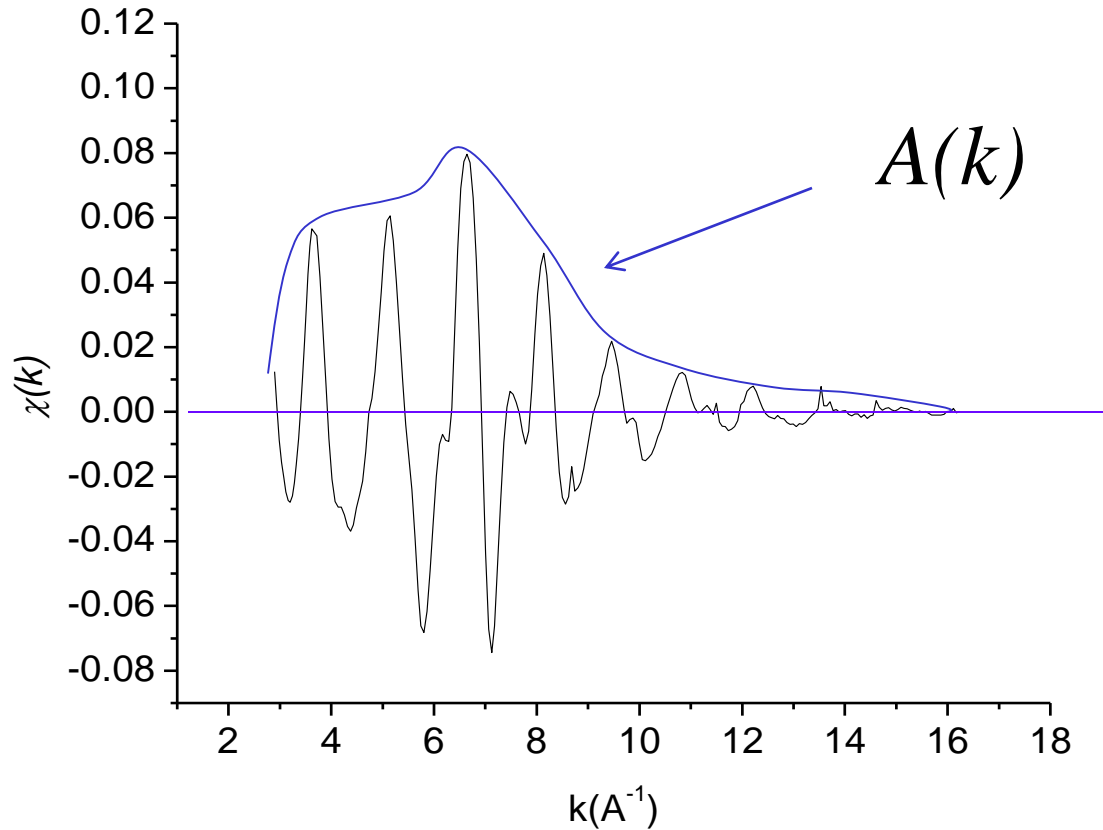
$k = 2 \text{\AA}^{-1}$  corresponds to 15.2 eV above threshold



# Extracting EXAFS data from absorption spectrum



# The EXAFS formula



$$\chi(k) = \sum_j \left[ \frac{N_j S_0^2 f(k, \theta) e^{-2R_j/\lambda_e(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \right] \sin[2kR_j + \phi(k)]$$
$$= A(k)\Phi(k)$$

# EXAFS formula and relevant parameters

## The EXAFS equation

$$\chi(k) = \sum_j \left[ \frac{N_j S_0^2 f(k, \theta) e^{-2R_j/\lambda_e(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \right] \sin[2kR_j + \phi(k)]$$

$= A(k)\Phi(k)$

amplitude

phase

$N_j$ : coordination number of atom type  $j$ , e.g.  $\text{TiCl}_4$ ,  $N_{\text{Cl}} = 4$

$S_0^2$ : amplitude reduction term (shake-up, shake-off loss)

$f(\theta, k)$ : atomic scattering amplitude, e.g.  $f(\pi, k)$  for single scattering

$e^{-2R_j/\lambda_e(k)}$ ,  $e^{-2k^2\sigma_j^2}$  : amplitude damping terms due to electron

escape depth  $\lambda_e$  and mean displacement due to thermal motion  $\sigma_j$ ,

$R_j$  : interatomic distance,  $\phi(k) = 2\delta_a(k) + \delta_b(k)$  : phase function with contributions from the absorber  $\delta_a(k)$  and the backscatterer  $\delta_b(k)$



# Relationship between $\mu(E)$ and $\chi(k)$ : A simplified EXAFS equation

We recall  $\mu(E) \propto \left| \langle \psi_i | \hat{H}' | \psi_f \rangle \right|^2$

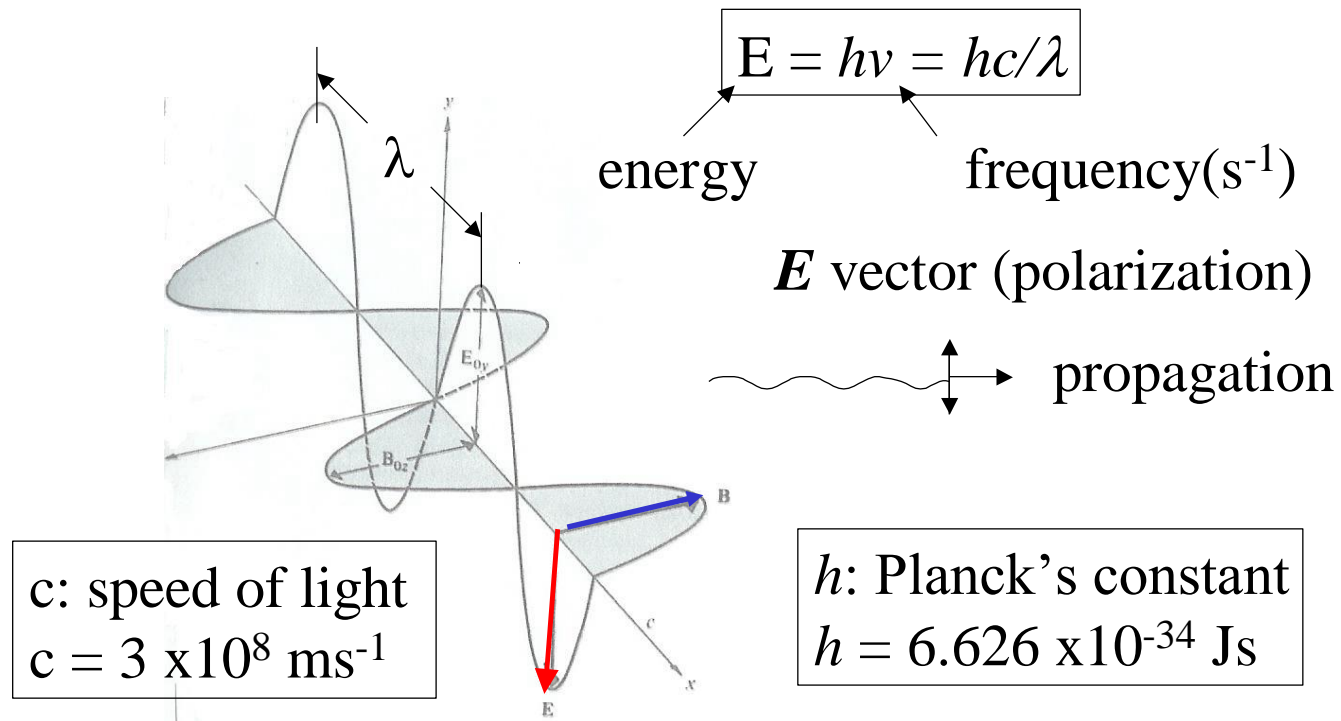
$\langle \psi_i | = \langle i |$  Initial state wavefunction,  
describing the core electron

$\hat{H}'$  Interaction,  $H' = e^{kr} \sim 1$  (dipole)

$|\psi_f \rangle = |f \rangle$  Final state wavefunction  
describing the photoelectron,  
sensitive to **chemical environment**

↑  
where all the actions are

*Footnote* : interaction of light with a bound electron in an atom



**E** field interacts with electron charge,

**B** field interacts with magnetic dipole moment

For a plane wave  $B$  and  $E$  have equal strength in free space

Which interaction is more important?

## Footnote, cont'

### **E field** interacts with electron charge

The interaction energy  $U \propto e \cdot V = e \int E dr$

distance  
potential  
electric field

Interaction energy  $\sim eEa_o$  *If we take the radius of the atom as  $a_o =$  Bohr's radius*

### **B field** interacts with magnetic dipole moment

The interaction energy  $U \sim (e\hbar/mc) \cdot B$

magnetic field  
gyromagnetic ratio:  
magnetic dipole moment /angular momentum

## Relative strength of magnetic/electric interaction

$$\frac{U_{mag}}{U_{elect}} = \frac{\frac{e\hbar}{mc} B}{eEa_o} = \frac{\hbar B}{mcEa_o}$$

Since

$$a_o = \frac{e^2}{mc} \cdot \frac{1}{\alpha^2}$$

And fine structure constant  $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$

$$\frac{U_{mag}}{U_{elect}} \approx \frac{\hbar B}{mcE} \frac{mc^2}{e^2} \alpha^2 \approx \alpha = \frac{1}{137}$$

Electric interaction is more than two orders of magnitude stronger than the magnetic interaction

# Dipole approximation

The photon field in the electromagnetic wave is a plane wave

$$A = \{ A_o e^{i(k \cdot r - \omega t)} \}_{real}$$

If the wavelength is larger than the diameter of the atom, the  $e^{ikr}$  term can be replaced with 1 in the expansion (small atom approx.)

$$e^{ikr} = 1 + i(k \cdot r) + \frac{1}{2!} (ik \cdot r)^2 + \frac{1}{3!} (ik \cdot r)^3 + \dots$$

The term  $(k \cdot r)^n$  is called electric  $2^{(n+1)}$  pole and magnetic  $2^n$  -pole transition. E.g.:  $n = 0$ , electric dipole and magnetic monopole,  $n = 1$ , electric quadrupole and magnetic dipole etc.

# Dipole approximation

The interaction Hamiltonian

$$H' = \frac{e}{mc} \vec{A} \cdot \vec{P}$$

vector potential · momentum

Same as  $(\epsilon \cdot r)$  discussed earlier

can be replaced with

$$H' = \frac{e}{mc} A_o P \cos \omega t$$

Time dependent  
perturbation

## Final state in EXAFS

$$|\psi_f\rangle = |f\rangle = |f_0 + f_{scatt}\rangle$$

free atom      neighboring atom

$$\mu(E) \propto |\langle \psi_i | \hat{H}' | \psi_f \rangle|^2 = |\langle i | \hat{H}' | f_0 + f_{scatt} \rangle|^2$$

Expanding  $\mu$  we get

$$\mu(E) = |\langle i | \hat{H}' | f_0 \rangle|^2 + (1 + \frac{\langle i | \hat{H}' | f_{scatt} \rangle \langle f_0 | \hat{H}' | i \rangle^*}{|\langle i | \hat{H}' | f_0 \rangle|^2} + \text{complex conjugate})$$

This is the only term that is sensitive to the environment

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

$$\chi(E) \propto \langle i | \hat{H}' | f_{scatt} \rangle \approx \langle i | f_{scatt} \rangle$$

$$\chi(E) \propto \langle i | \hat{H}' | f_{scatt} \rangle \approx \langle i | f_{scatt} \rangle$$

EXAFS involves the *change* in the photoelectron wavefunction due to back scattering.

Since the initial state is localized spatially ( $\delta$  function), We have

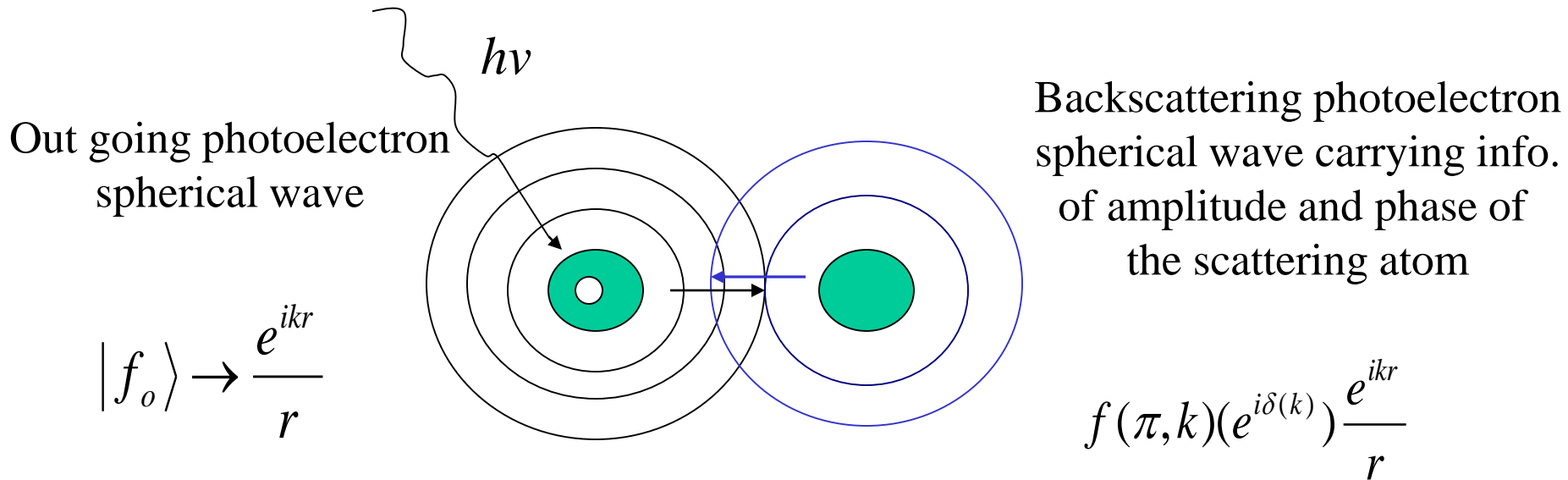
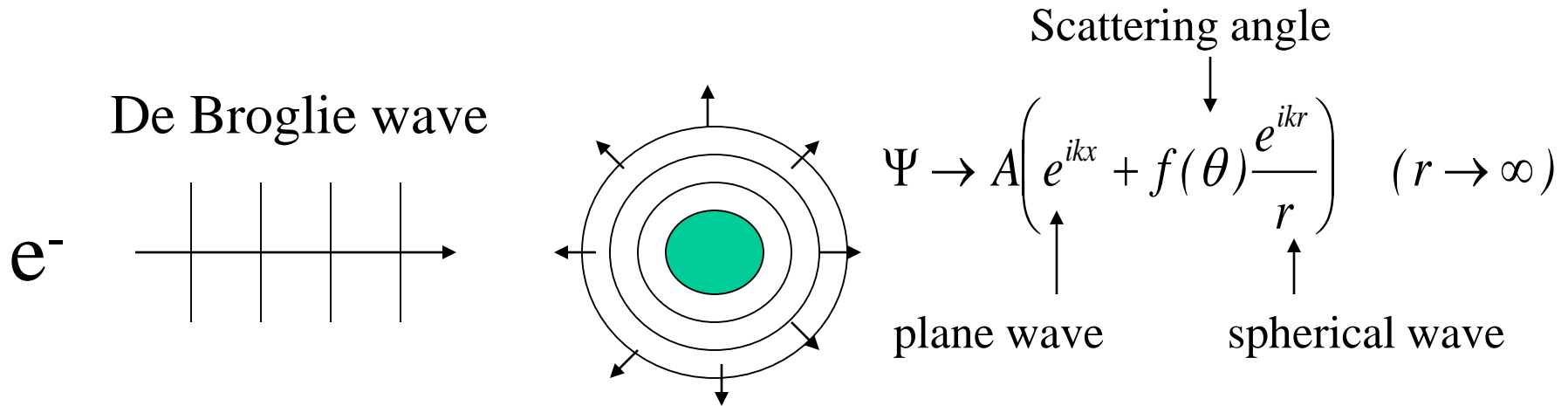
$$\chi(E) \approx \int \delta(r) \psi_{scatt}(r) dr \sim \psi_{scatt}(0)$$

initial ↓      ↓  $\Delta\psi_{final}$  at  $r \sim 0$   
scattering ↑      ↓  
 Vanishes if there is no neighboring atom

Thus EXAFS is the modulation of the photoelectron wavefunction at the absorbing atom resulting from its backscattering from neighboring atoms



# EXAFS of a diatomic molecule



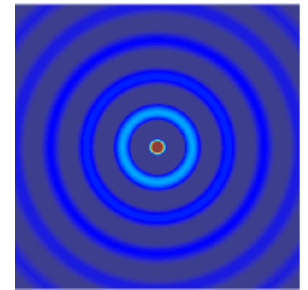
Since  $\chi(E) \sim \psi_{scatt}(0)$

We can build a simple model to account for EXAFS by considering the following events

[ref. Newville, XAFS workshop

[http://cars9.uchicago.edu/xafs\\_school/](http://cars9.uchicago.edu/xafs_school/)]

- outgoing photoelectron (spherical wave)
- scattering of the electron wave by the neighboring atom
- returning of the backscattered wave to the absorbing atom



For the spherical photoelectron wave,  $e^{ikr}/kr$ , with a neighboring atom at a distance  $R$ , we get

$$\chi(k) \propto \frac{e^{ikR}}{kR} \cdot \boxed{2k \cdot f(\pi, k) \cdot (e^{i\delta(k)})} \cdot \frac{e^{ikR}}{kR} + c.c.$$

amplitude      phase-shift

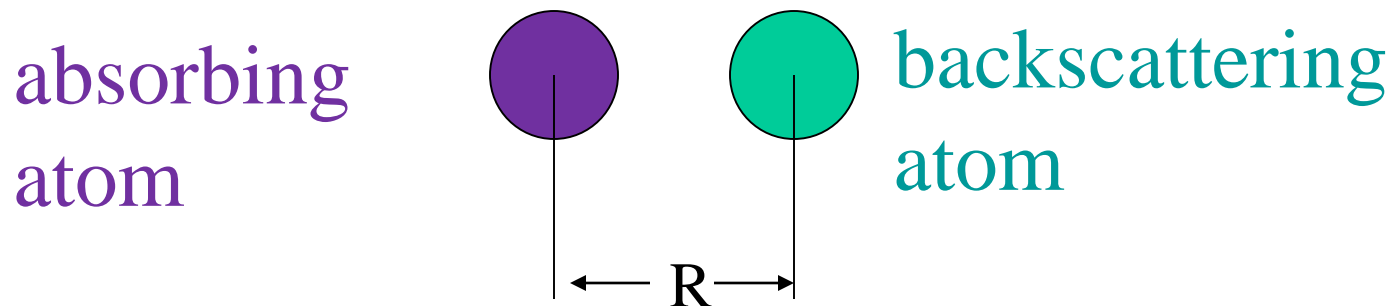
# The EXAFS of an atom in a diatomic molecule is

$$\chi(k) = -\text{Im} \left[ \frac{f(\pi, k) \cdot e^{i(2kR + \delta(k))}}{kR^2} \right]$$

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

amplitude for 180°  
backscattering

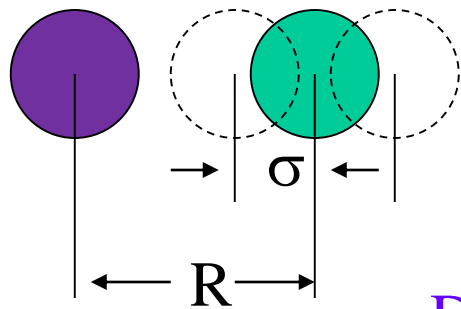
phase shift has both  
absorbing and back-  
scattering atom  
contributions



# the Debye-Waller (DW) factor

Since the molecule vibrates, leading to an instantaneous variation of the bond length, the effect is represented by the **mean square displacement,  $\sigma^2$** , an amplitude damping term, the Debye-Waller (DW) factor,

$$e^{-2k^2\sigma^2}$$



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

← DW term

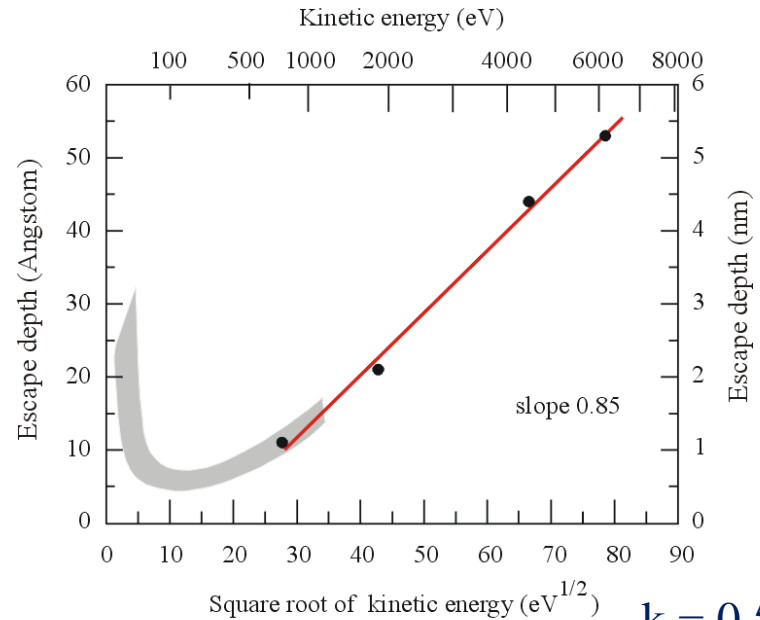
DW = 1 when  $\sigma = 0$ , when  $\sigma > 0$ , DW < 1, thus vibration contributes to the damping of the amplitude

# For a multi-atom system with coordination number $N_j$

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

We next consider the **inelastic scattering** of the photoelectron, the escape depth,  $\lambda(k)$  contributing to a amplitude loss,  $e$

$$e^{-2R_j / \lambda(k)}$$



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

Free mean path term

The last term to consider is the **manybody effect** term associated with **shake-up** and **shake-off**, contributing to amplitude loss. This is to be distinguished from the inelastic loss, which takes place after the electron has left the atom. This term is often denoted as “ $S_o^2$ ”

$$S_o^2 = \left| \left\langle \Phi_f^{N-1} \mid \Phi_o^{N-1} \right\rangle \right|^2$$

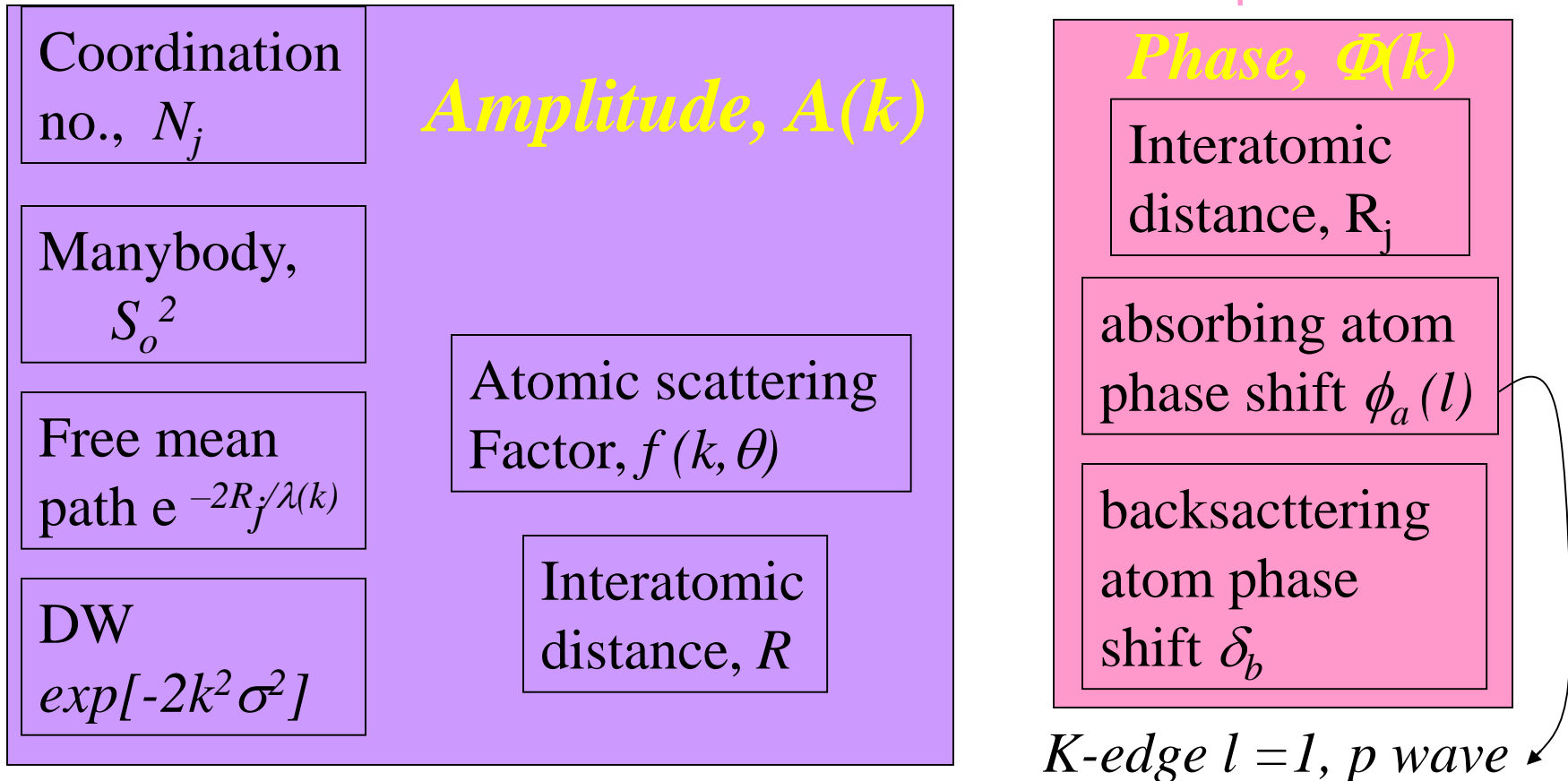
fully relaxed                      un-relaxed

$S_o^2 = 1$  in the absence of manybody effect (single particle approximation); in reality, it has a constant in  $k$  for modest  $k$  values, ranging from 0.7 ~ 0.9 (depending on the chemical environment)

For more detailed information visit the following site and download course materials from the 2009 XAFS workshop  
[http://cars9.uchicago.edu/xafs\\_school/](http://cars9.uchicago.edu/xafs_school/)

# Summary: The EXAFS formula

$$\chi(k) = \sum_j \left[ \frac{N_j S_0^2 f(k, \theta) e^{-2R_j/\lambda_e(k)} e^{-2k^2 \sigma_j^2}}{kR_j^2} \right] \sin[2kR_j + \phi(k)]$$





# The behavior of EXAFS parameters in k space

The phase  $\Phi(k) = \sin[2kR_j + \phi(k)]$

For K, L<sub>1</sub> edge

$$\phi_{ab}(k) = \phi_a^\ell(k) + \phi_b(k) - \pi, \quad \ell = 1, \text{ } p \text{ wave } (\Delta\ell = 1, \text{ dipole})$$

For L<sub>3,2</sub> edge

$$\phi_{ab}(k) = \phi_a^\ell(k) + \phi_b(k) \quad \ell = 2,0 \text{ } (\Delta\ell = \pm 1, \text{ dipole})$$

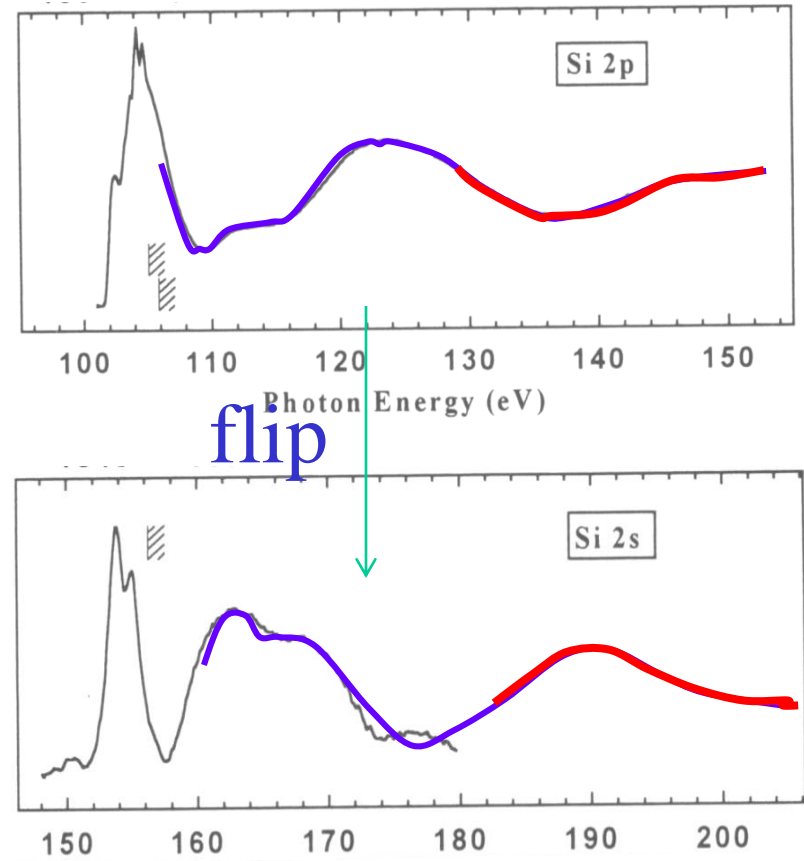
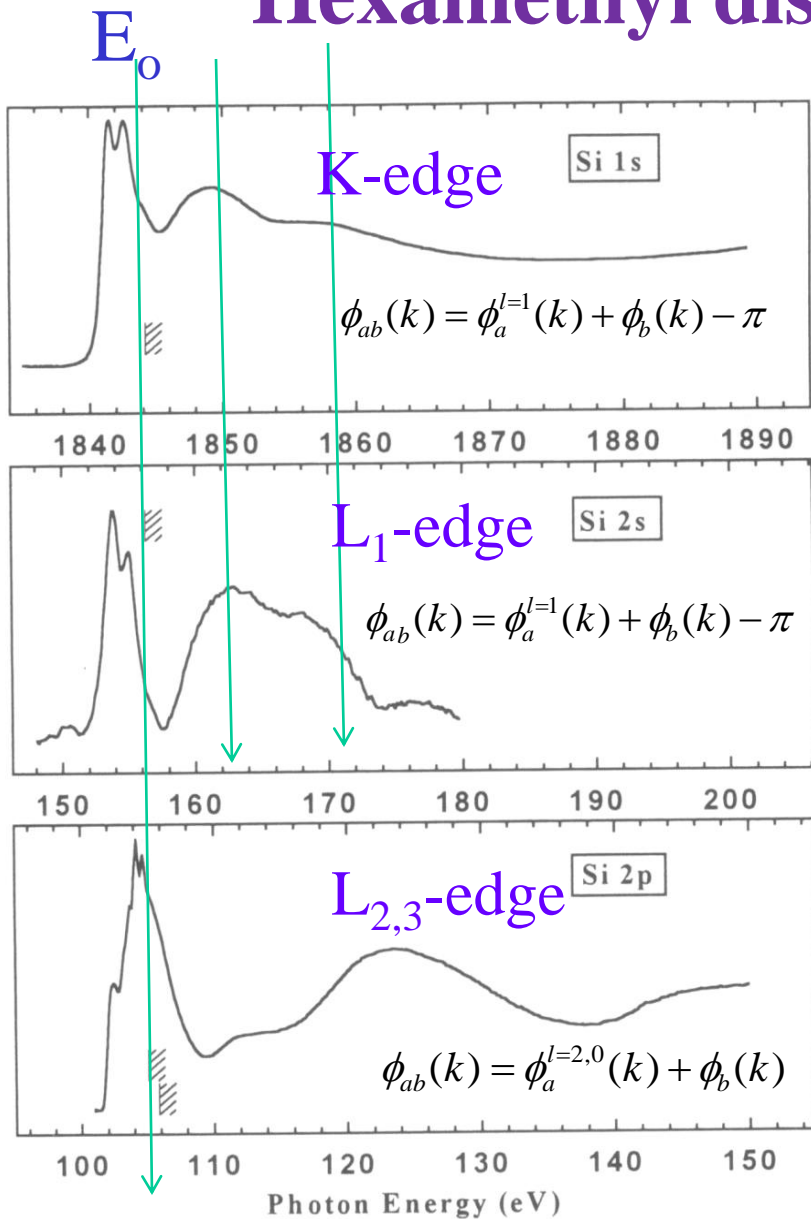
$\phi_{ab}$  : Phase function of the absorber-backscatterer

$\phi_a^\ell$  ; Phase shift of the outgoing e<sup>-</sup> from the absorbing atom

$\phi_b$  : Phase shift of the neighboring atom

Note: the phase shift difference between K and L<sub>3</sub>-edge is  $\pi$

# Hexamethyl disilane, Si K & L-edge



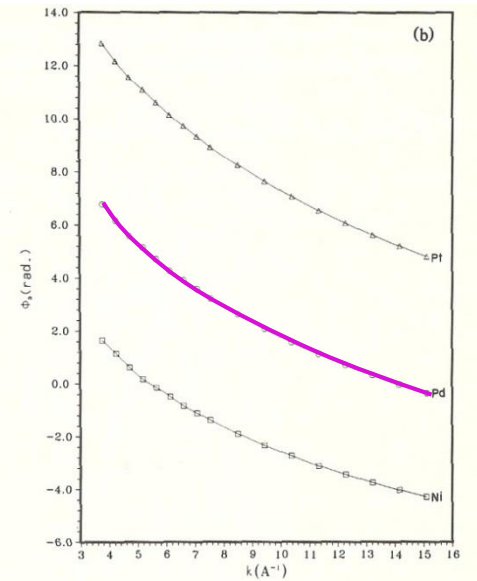
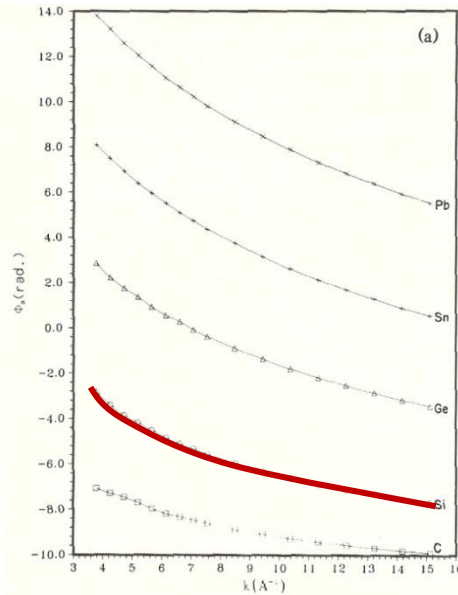
Max  $\rightarrow$  Min,  
 phase shifted by  $\pi$

# Theoretical phase functions

## Absorbing atom

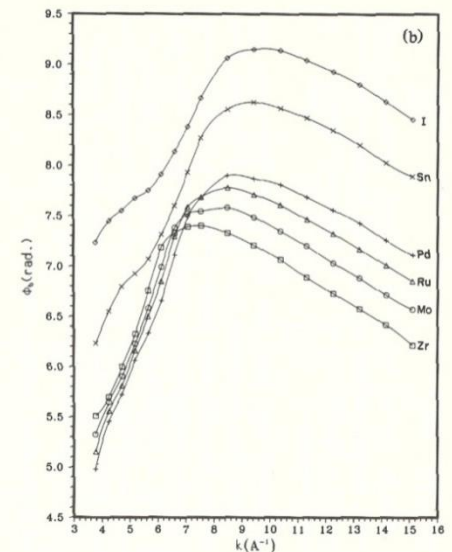
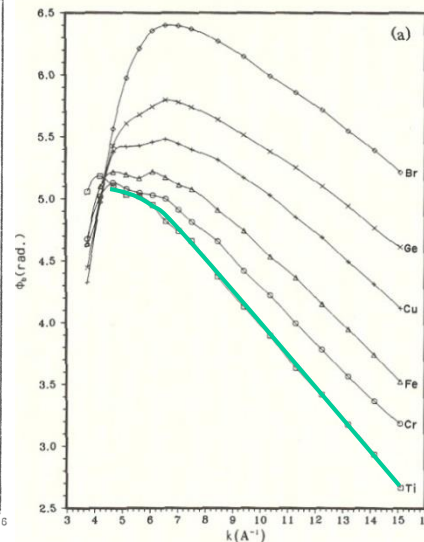
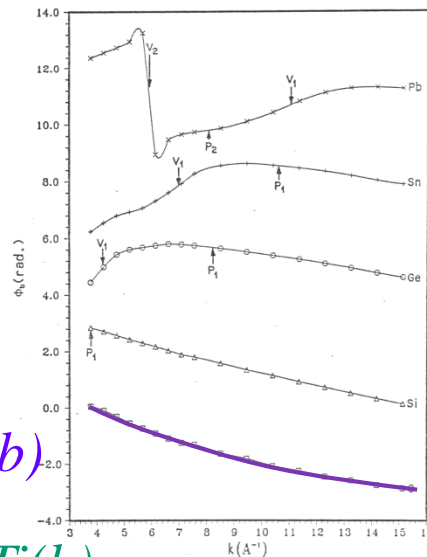
phase-shifts  $\phi_a l$   
for the K-edge,  $\longrightarrow$   
 $l = 1$ , p - wave

For low and medium  $z$   
elements,  $\phi_{ab} = \alpha + \beta k$   
is a good approximation



## Backscattering

Atom phase  
shifts  $\phi_b$   $\longrightarrow$

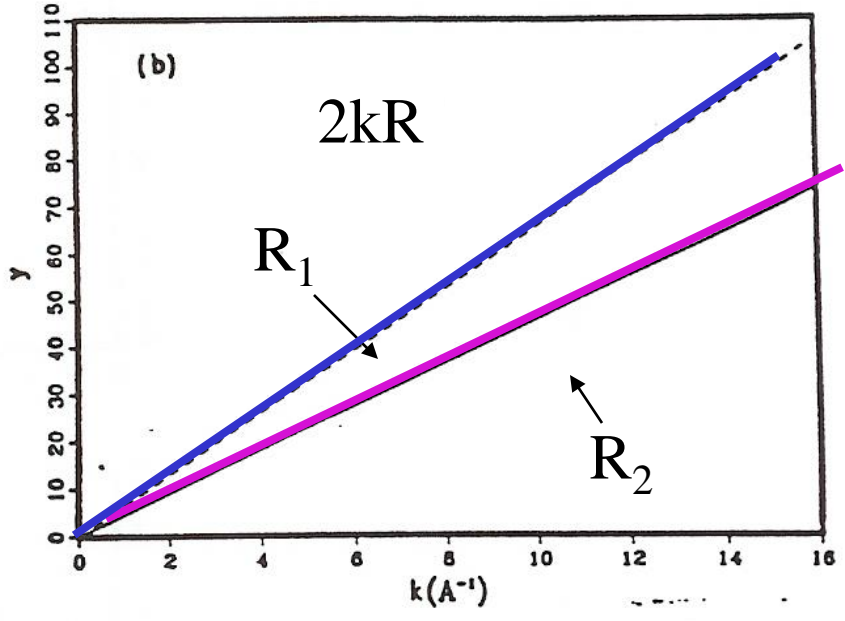
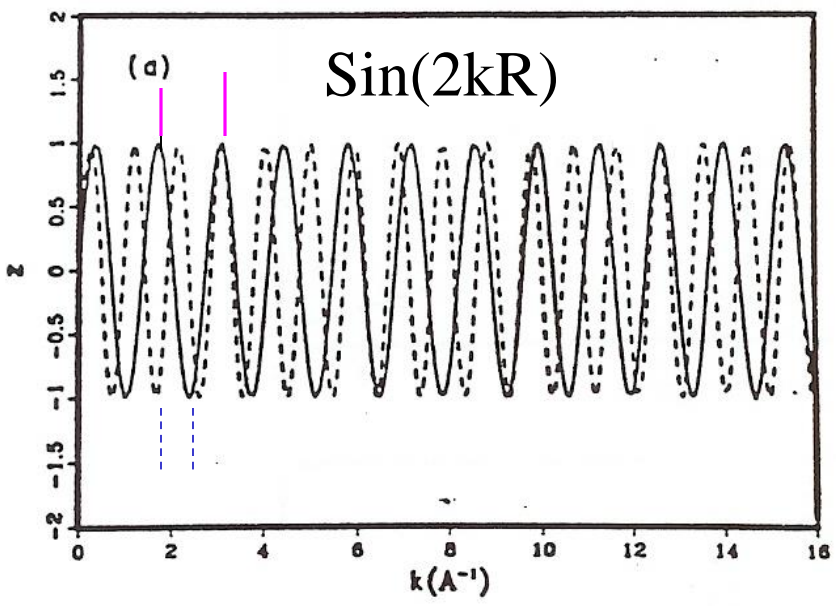


$$\phi_{Si-C} = \phi_{Si(a)} + \phi_{C(b)}$$

$$\phi_{Pd-Ti} = \phi_{Pd(a)} + \phi_{Ti(b)}$$

0

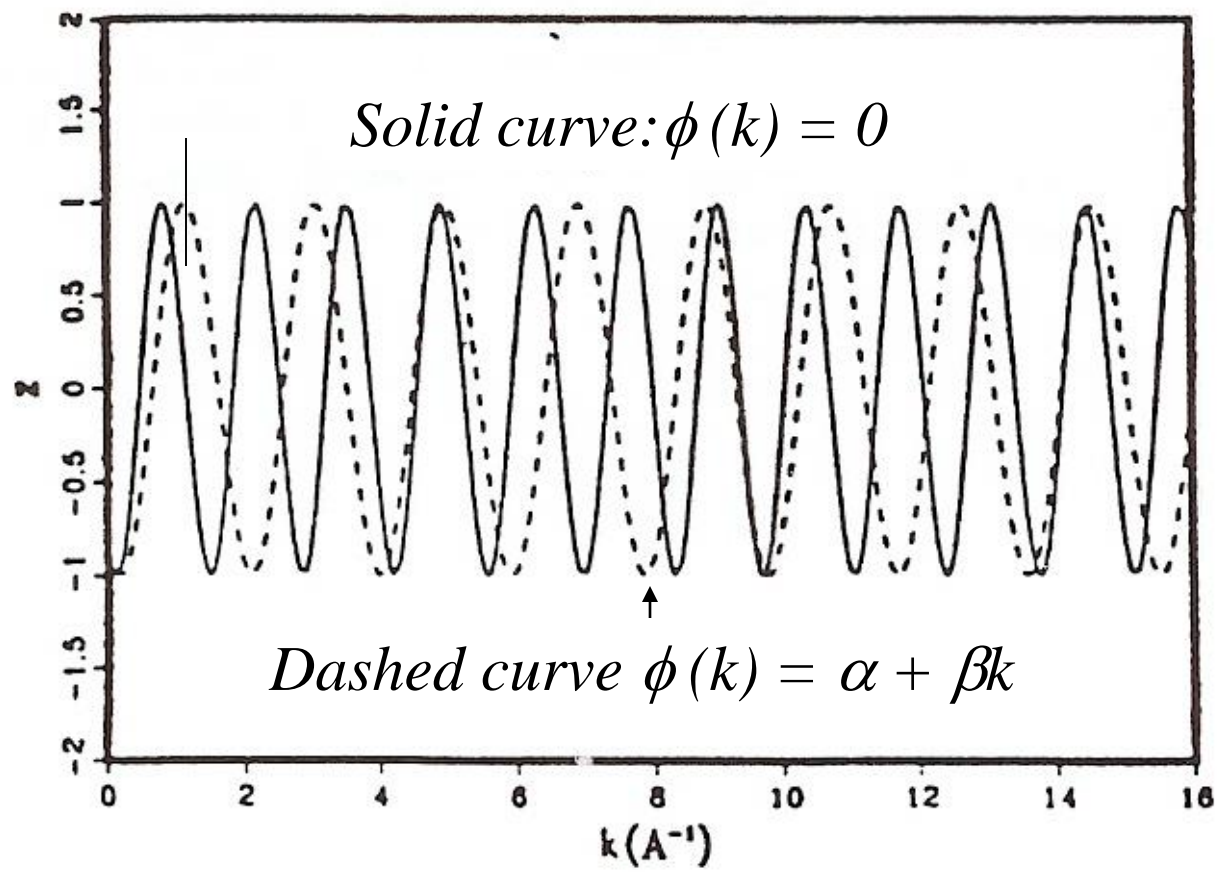
$$\Phi(k) = \sin[2kR_j + \phi(k)]$$



The larger the  $R$ , the shorter the period in  $k$  space

$$\Phi(k) = \sin[2kR_j + \phi(k)]$$

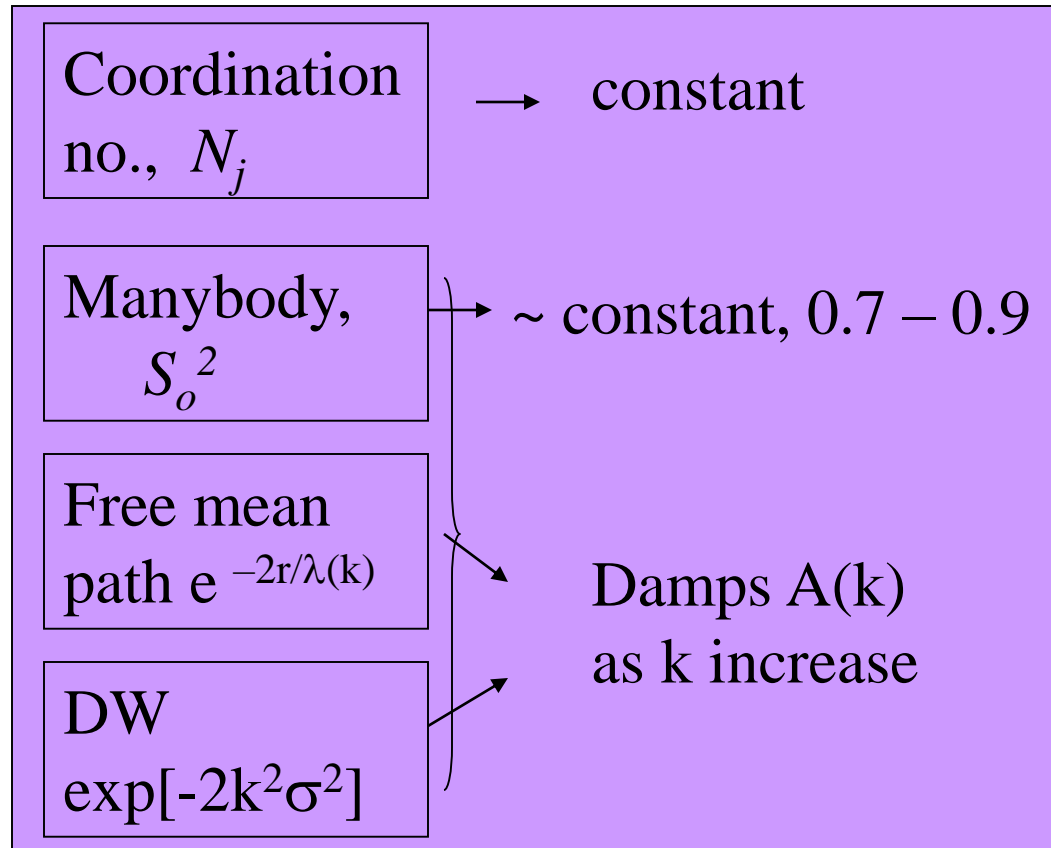
When  $\phi(k) \sim \alpha + \beta k$  is included, the separation between oscillation maximum increases in  $k$



# The behavior of EXAFS parameters in k space

Amplitude,  $A(k) =$  Atomic scattering  
Factor,  $f(k, \theta)$  ← Element  
specific

modified by ↑

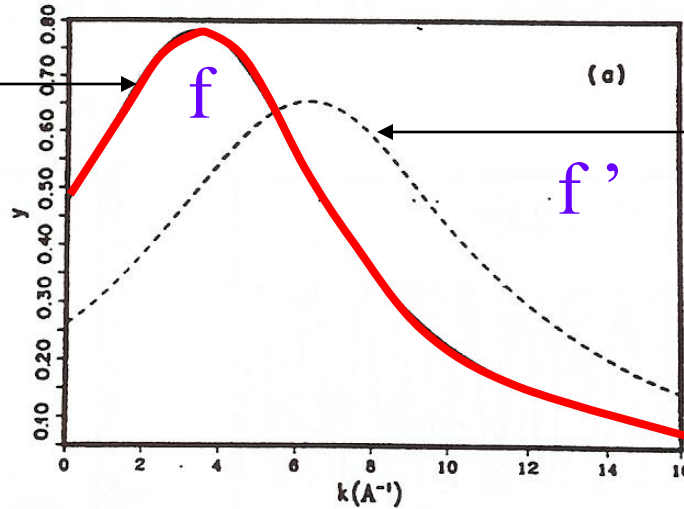


# Atomic scattering factor, $f(k, \theta)$

$$\chi(k) = f(k, \pi) \sin[2kR_j + \phi(k)]$$

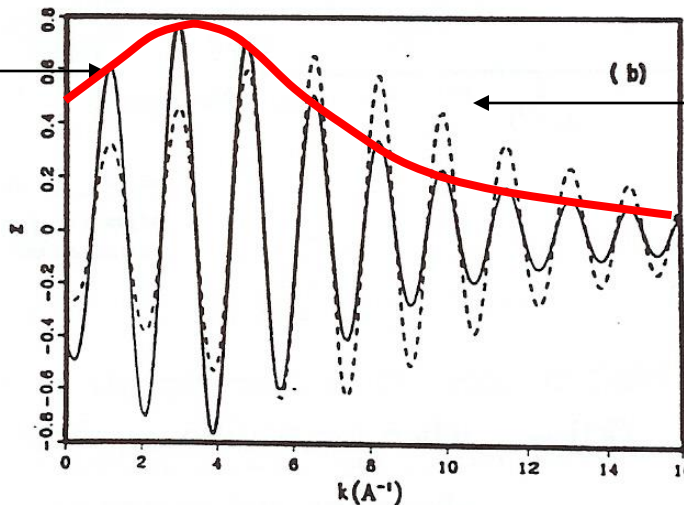
Backscattering  
( $\theta = \pi$ ) amplitude  
With max in the  
low k region

$$f(k, \pi) \cdot \sin[2kR + \phi(k)]$$



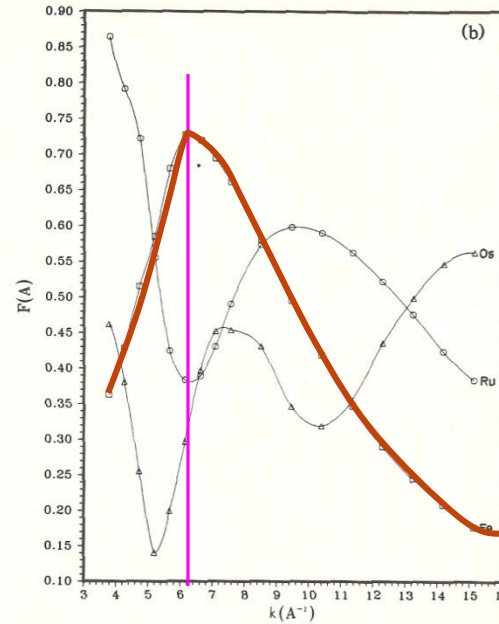
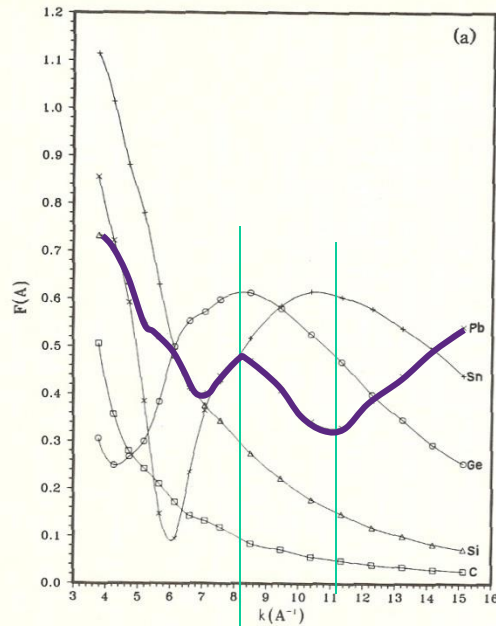
Backscattering  
( $\theta = \pi$ ) amplitude  
With max in the  
medium k region

$$f'(k, \pi) \cdot \sin[2kR + \phi(k)]$$



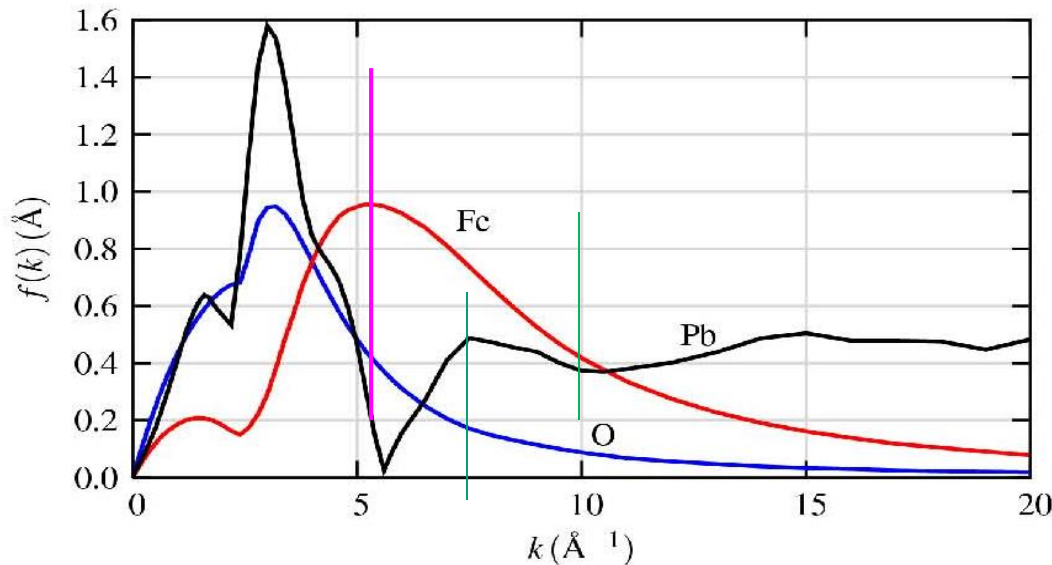
# Theoretical backscattering amplitude, $f(k, \pi)$

B.K. Teo and P.A. Lee J. Amer. Chem. Soc. 101 2815(1979)



166

Teo and Lee (old data) produce qualitatively the same shape of  $A(k)$  but the max/min occurs at higher  $k$

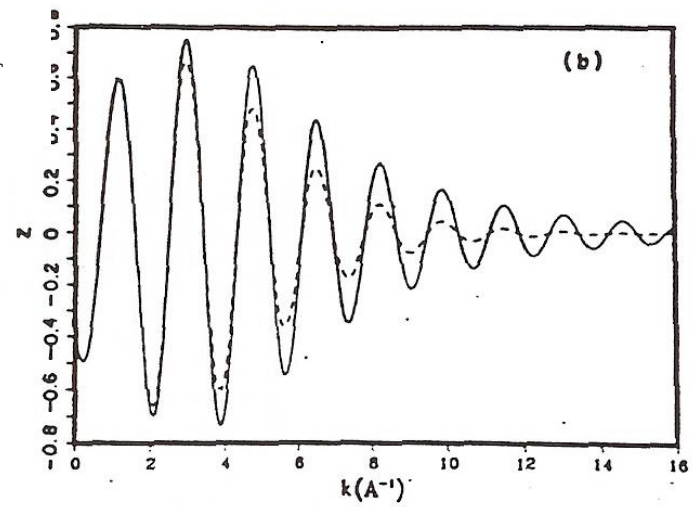
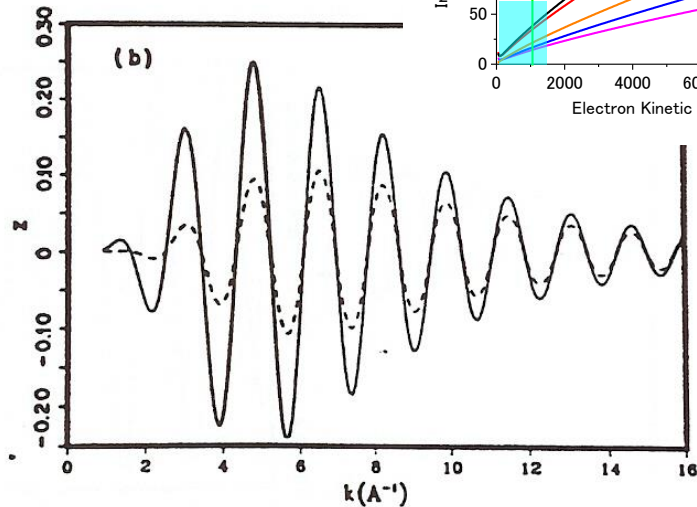
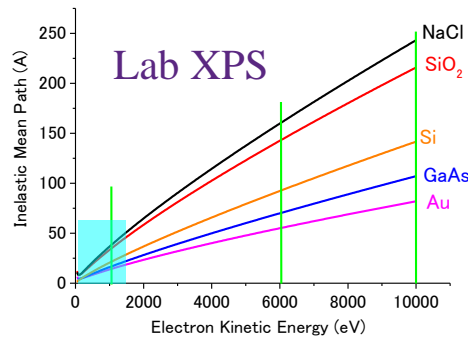
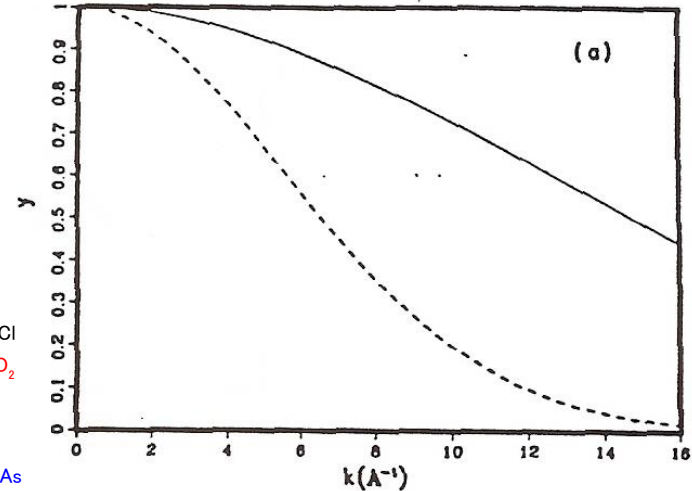
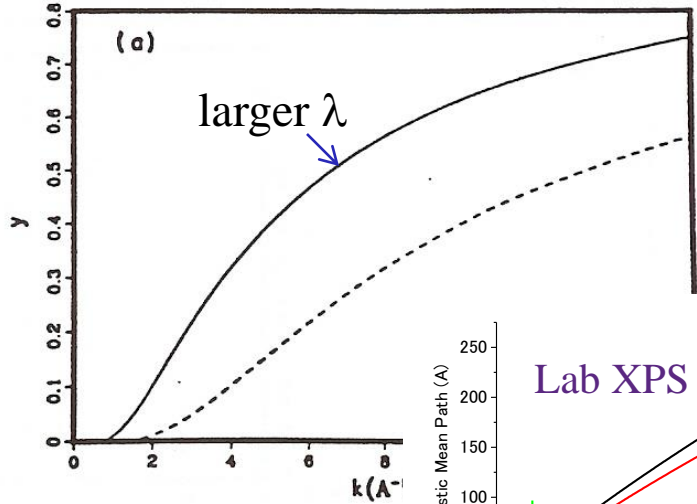


FEFF  
developed by  
J.J. Rehr,  
(best calculation)



$$f(k, \theta) e^{-2R_j/\lambda_e(k)} \sin[2kR_j + \phi(k)]$$

$$f(k, \theta) e^{-2k^2\sigma^2} \sin[2kR_j + \phi(k)]$$



Damps the  $A(k)$  more significantly in low  $k$     Damps the  $A(k)$  more significantly in high  $k$

# XAFS measurements

- Transmission
- Total electron yield (vacuum)
- Partial electron yield (vacuum)
- Ion yield (vacuum)
- Fluorescence yield
- Photoluminescence yield
- Photoconductivity (dielectric liquid)

Yield  
(soft x-ray)

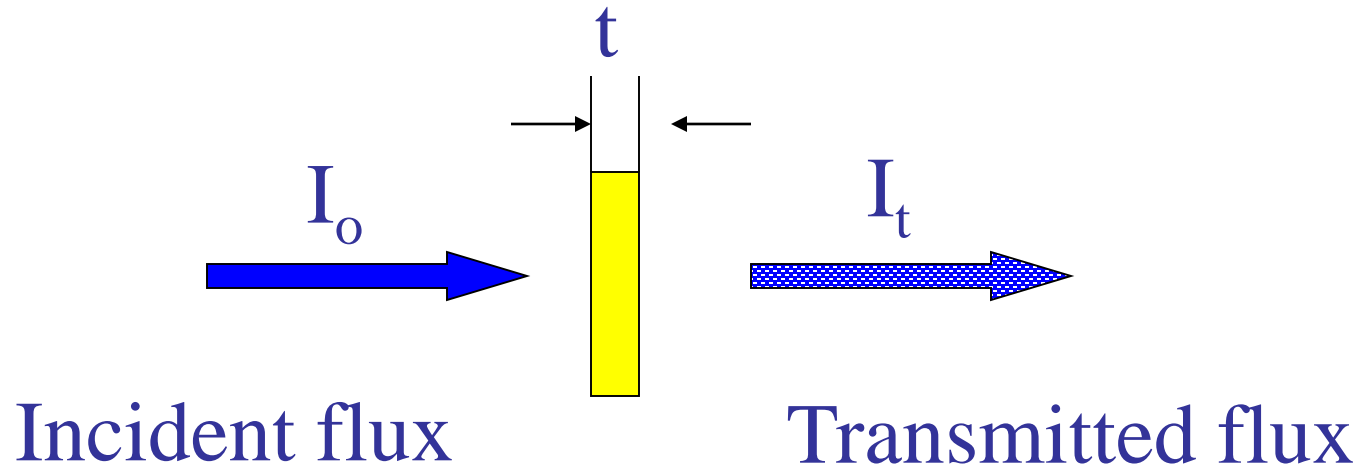
Assumption: Yield  $\propto \mu t$  (not always the case)

$$Yield = f(h\nu)I_o(1 - e^{-\mu t})$$

For a thin sample:

$$Yield = f(h\nu)I_o[1 - (1 - \mu t + \frac{1}{2!}(\mu t)^2 + \dots)] \propto \mu t$$

# Transmission



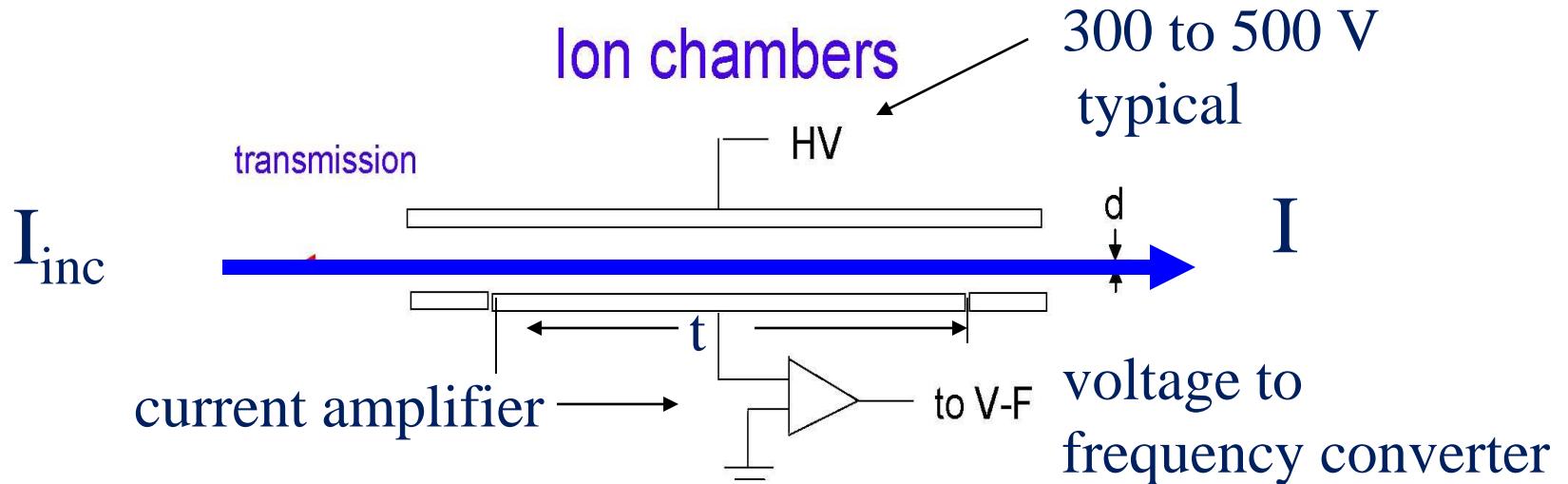
## Beer-Lambert law

Transmission  $I_t = I_o e^{-\mu t}$

Absorption  $I_a = I_o - I_t = I_o (1 - e^{-\mu t})$

$$\mu t = \ln \left( \frac{I_o}{I_t} \right) \quad \text{To be measured}$$

# X-ray detectors



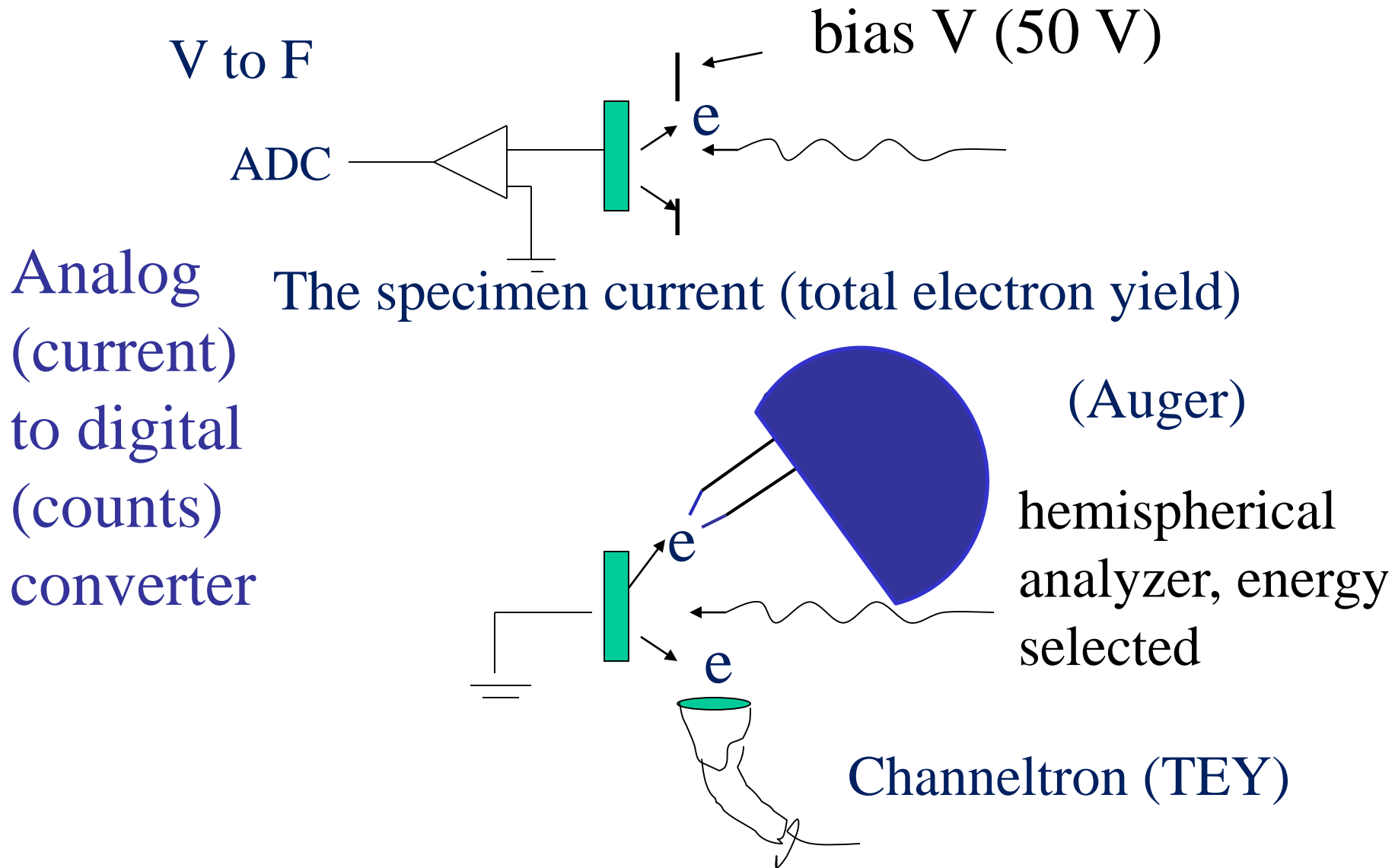
An Ion chamber is filled with inert gas ( He, Ar, N<sub>2</sub> etc. ). The absorption of x-rays produces ion pairs, typically, it requires ~30 eV (**W value**) to produce 1 ion pair at 1 atm pressure (e.g. 27 eV for Ar and 33 eV for N<sub>2</sub>). Thus for Ar, a 2700eV photon produces 100 ion pairs. The flux  $I$  emerging from an Ar ion chamber is

$$I(\text{photons / s}) = iw(\text{Ar}) \frac{e^{-\mu(\text{Ar})t}}{eE(h\nu)(1 - e^{-\mu(\text{Ar})t})}$$

Labels for the equation:

- $I$ : current
- $w(\text{Ar})$ : photon energy
- $e^{-\mu(\text{Ar})t}$ : exponential decay factor
- $eE(h\nu)$ : photon energy
- $1 - e^{-\mu(\text{Ar})t}$ : absorption factor

# Electron yield detectors



# **X-ray Fluorescence yield**

## **Nondispersive**

- Scintillation counter
- Ion chamber (Lytle detector) (with filters)

## **Moderate energy resolution**

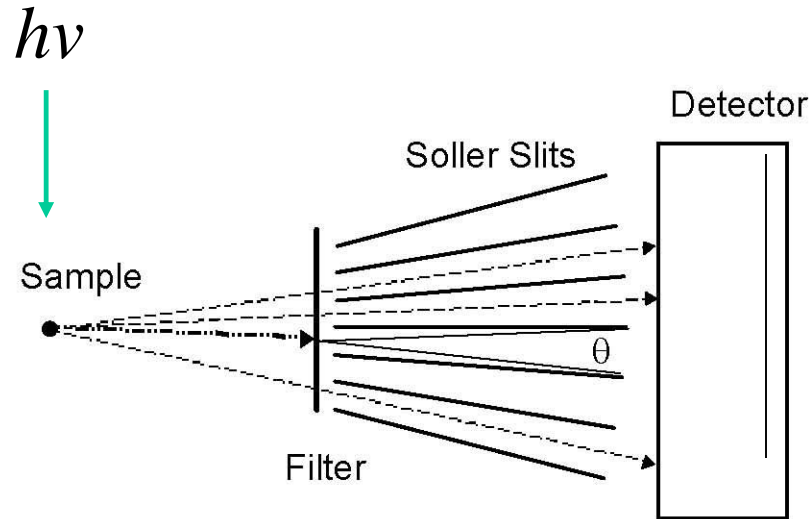
Solid state detectors (Ge, Si)

## **High energy resolution**

WDX detector (crystal monochromator)

# Filter-slits (Stern-Heald or Lytle detector)

see Stern and Heald, RSI 50, 1579 (1979)

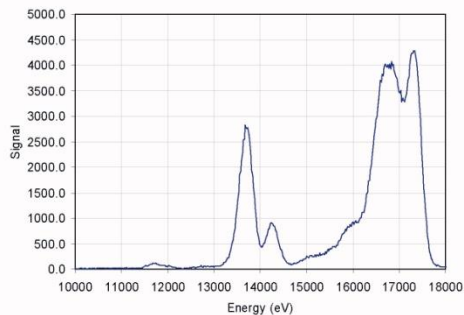


- Large solid angle (large  $N_f$ )
- Unlimited count rate
- Moderate reduction in background –  $N_b$  still problem
- Little rejection of lower energy fluorescence lines
- Near practical limits
- Works best for K edges above 4 keV

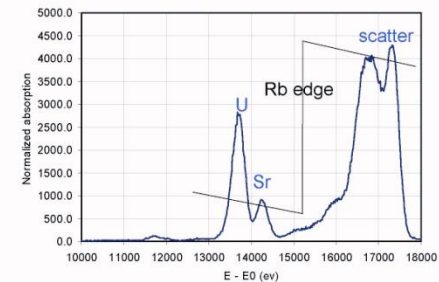
# Multi-element solid state

- Resolution (fwhm) 200-300 eV
- Individual element limited to few  $\times 10^5$
- Background or lower energy fluorescence lines can saturate countrate
- Standard arrays limited to about 30 elements

Typical spectrum- U contaminated Sediment



Filter can reduce the background in fluorescence measurement



Problem Rb fluorescence can enter the detector



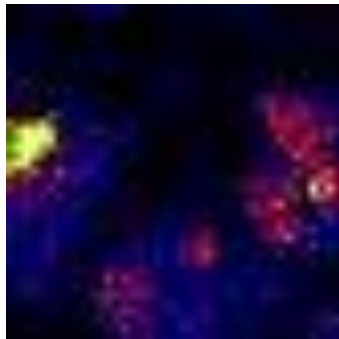
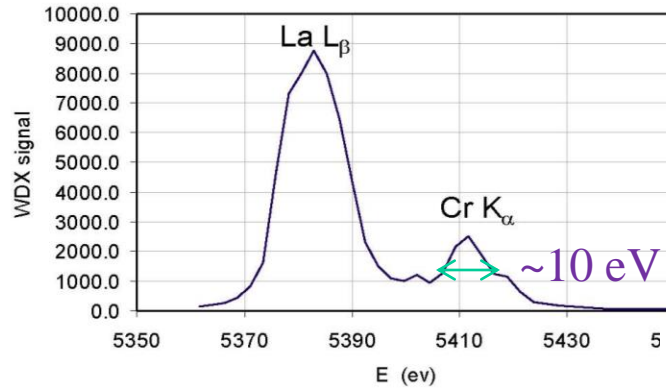
# WDX detector (Rowland circle)

Very good energy resolution and background discrimination

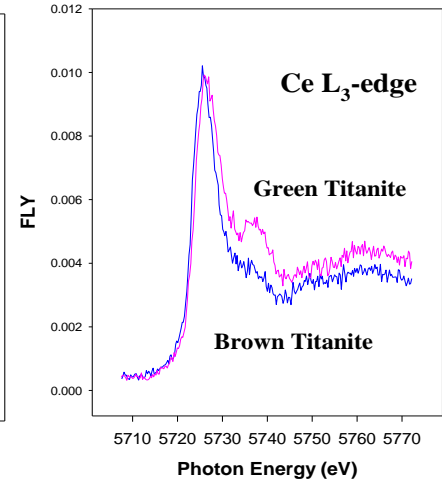
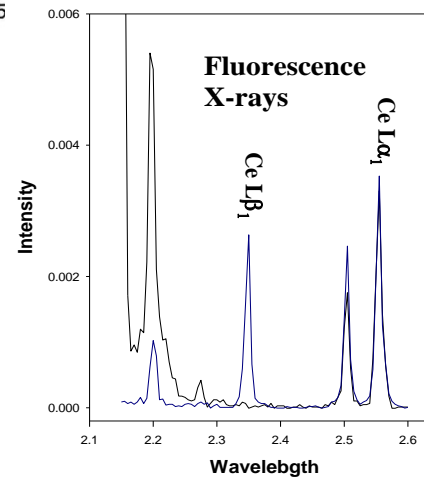
Poor collection efficiency



20 nm Cr doped  $\text{TiO}_2$  on  $\text{LaAlO}_3$



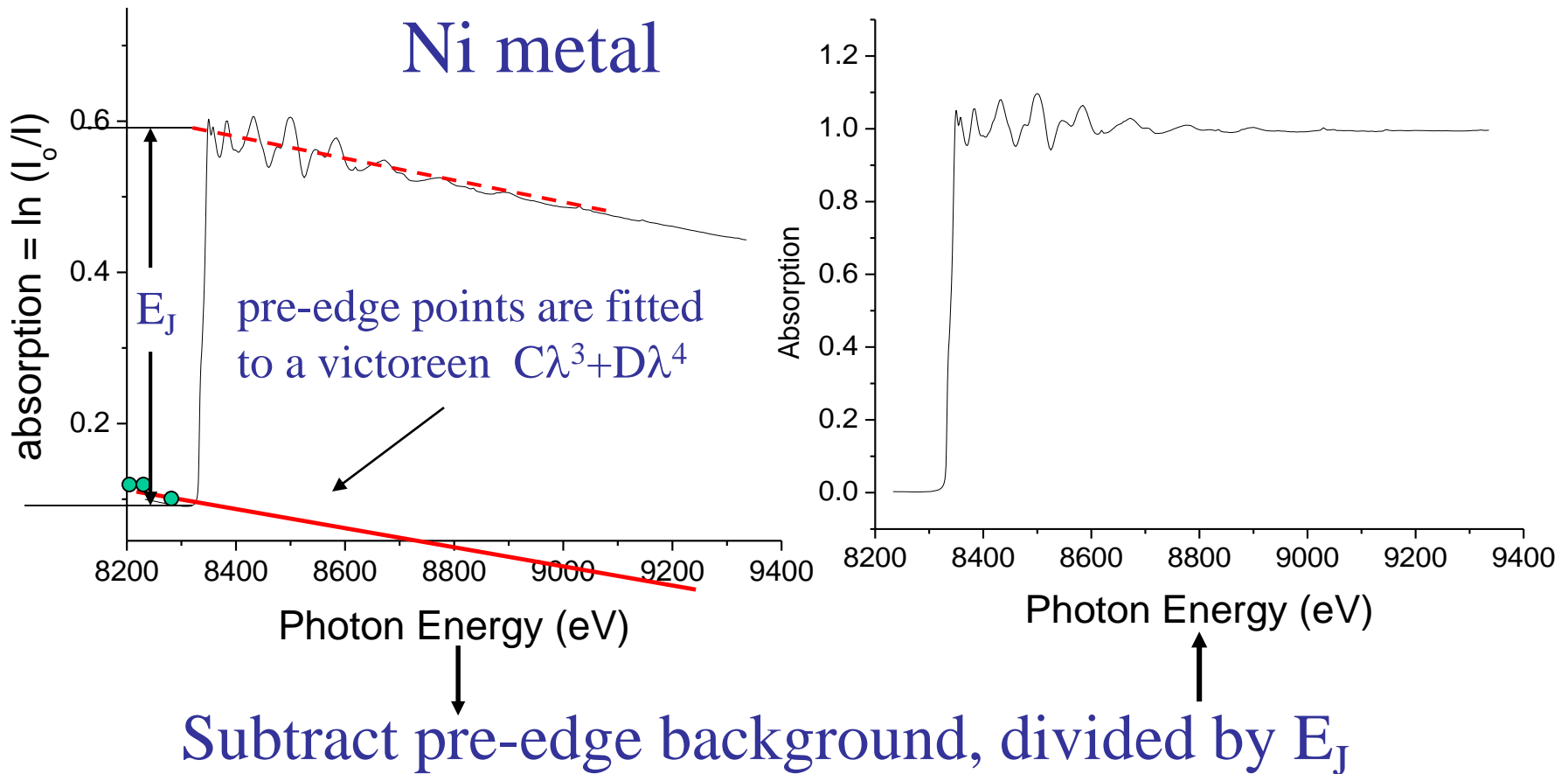
Ce in Titanite



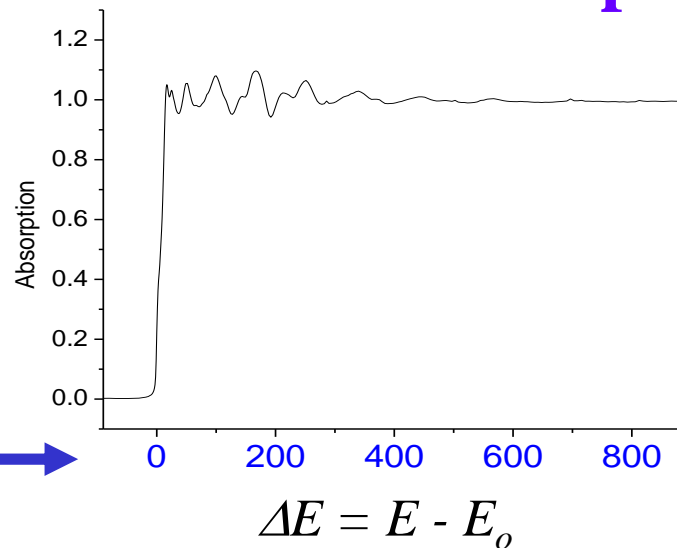
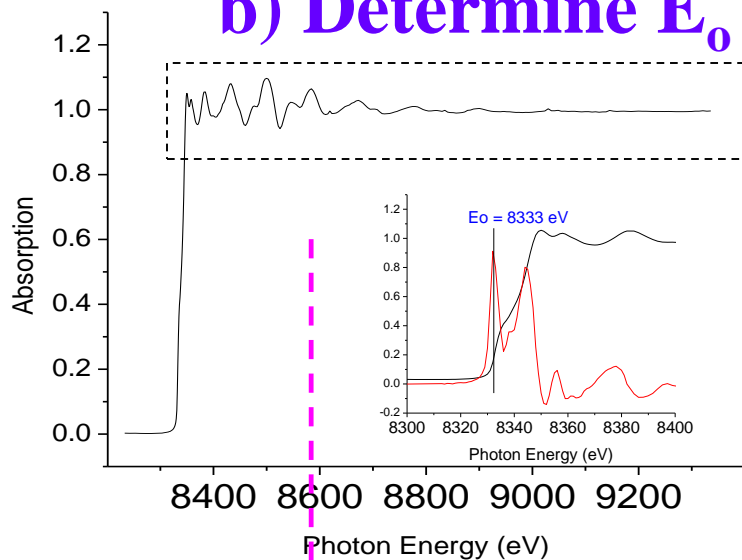
# EXAFS Analysis

I. Data reduction: extract EXAFS  $\chi$  from the absorption  $\mu$

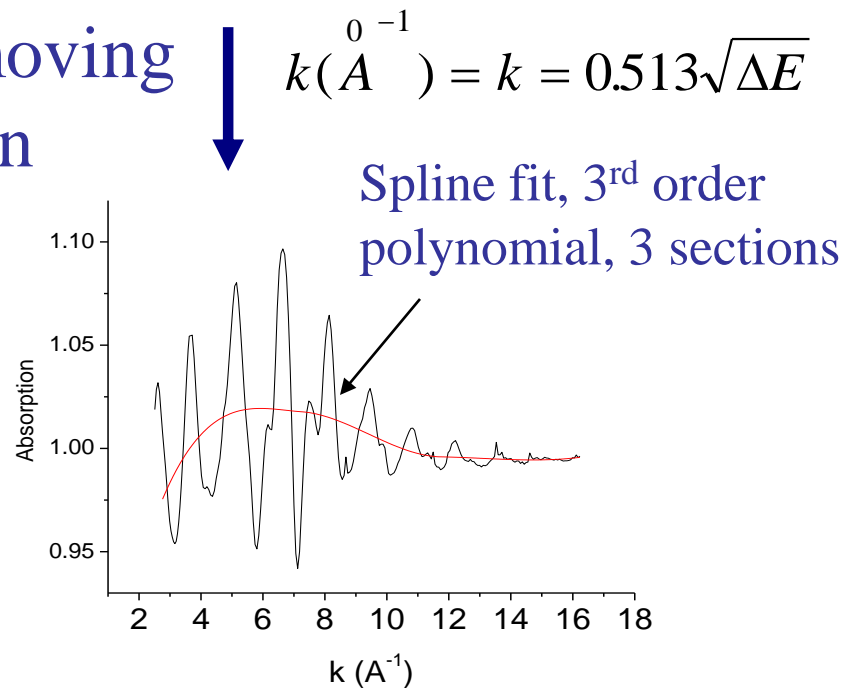
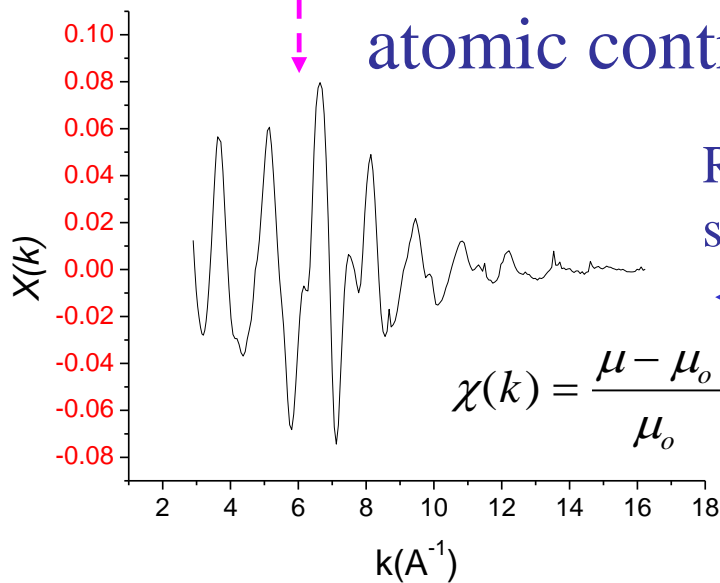
a) Pre-edge background removal



## b) Determine $E_0$ and convert data to k space

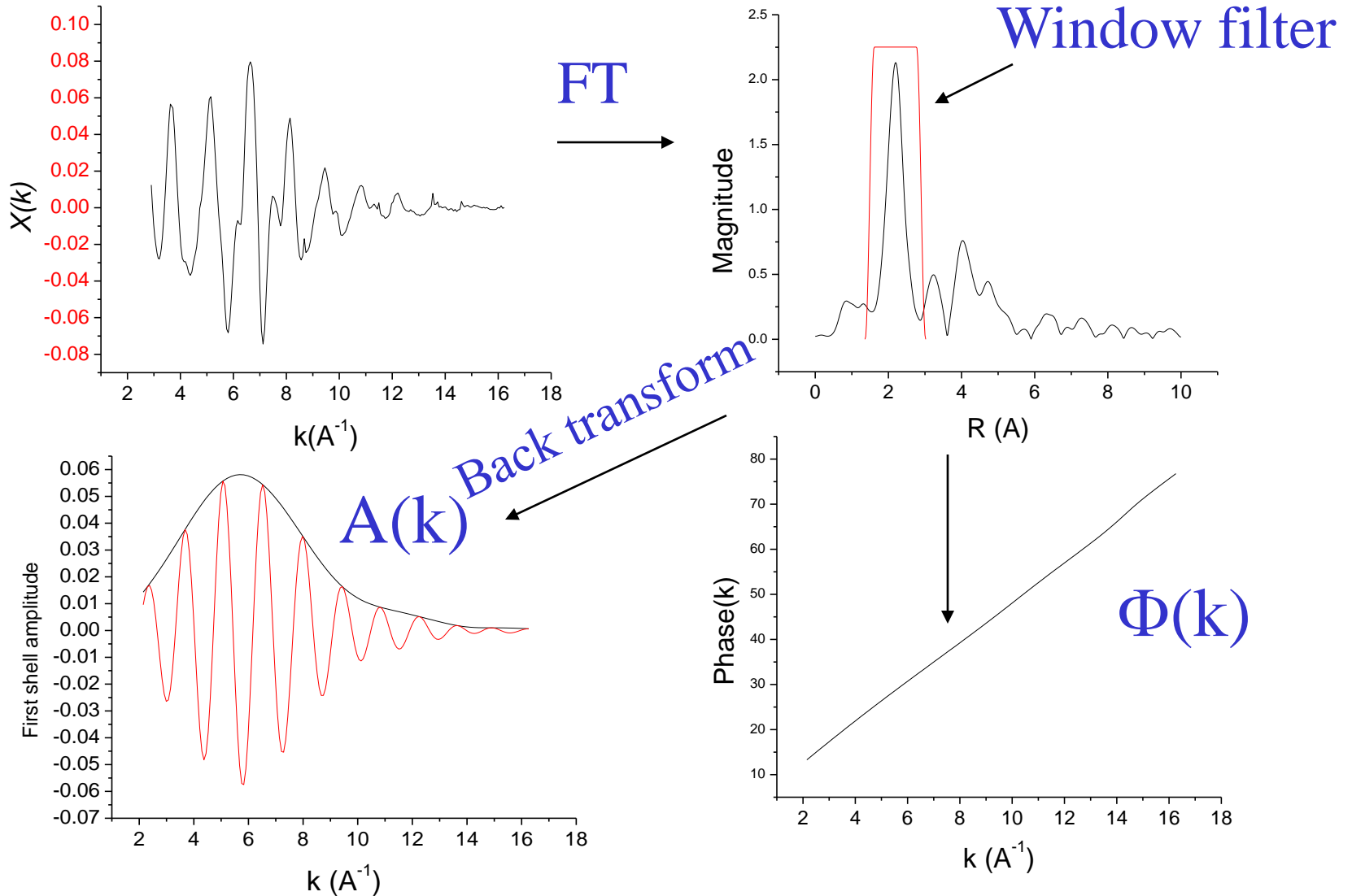


## c) Get $\chi(k)$ by removing atomic contribution



# II. Data Analysis:

## a) Separation of amplitude and phase



# Fourier Transform in EXAFS

$$\chi(k) = \sum_j A_j(k) \sin[(2kr_j + \phi(k))]$$

Consider the Fourier transform of EXAFS

$$\begin{aligned} FT[\chi(k)] &= \int \chi(k) e^{-2ikr_j} dk \\ &= \sum_j \int A_j(k) \sin[2kr_j + \phi_j(k)] e^{-2ik_j r} dk \\ &= \sum_j FT[\chi_j(k)] \end{aligned}$$

Consider the FT of one single shell

$$FT[\chi_j(k)] = FT\{A_j(k) \sin[2kr_j + \phi_j(k)]\}$$

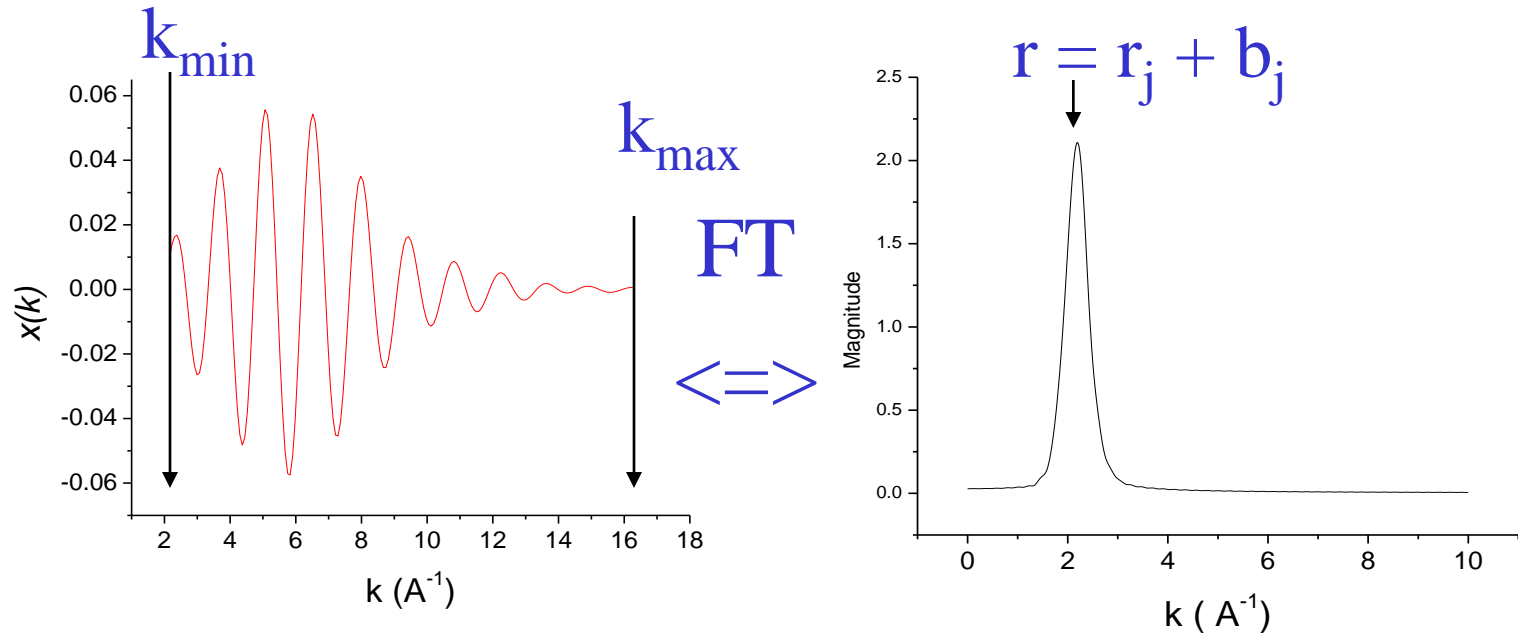
amplitude

phase

# In k space, A(k) is convoluted in the oscillatory behavior of the phase so that

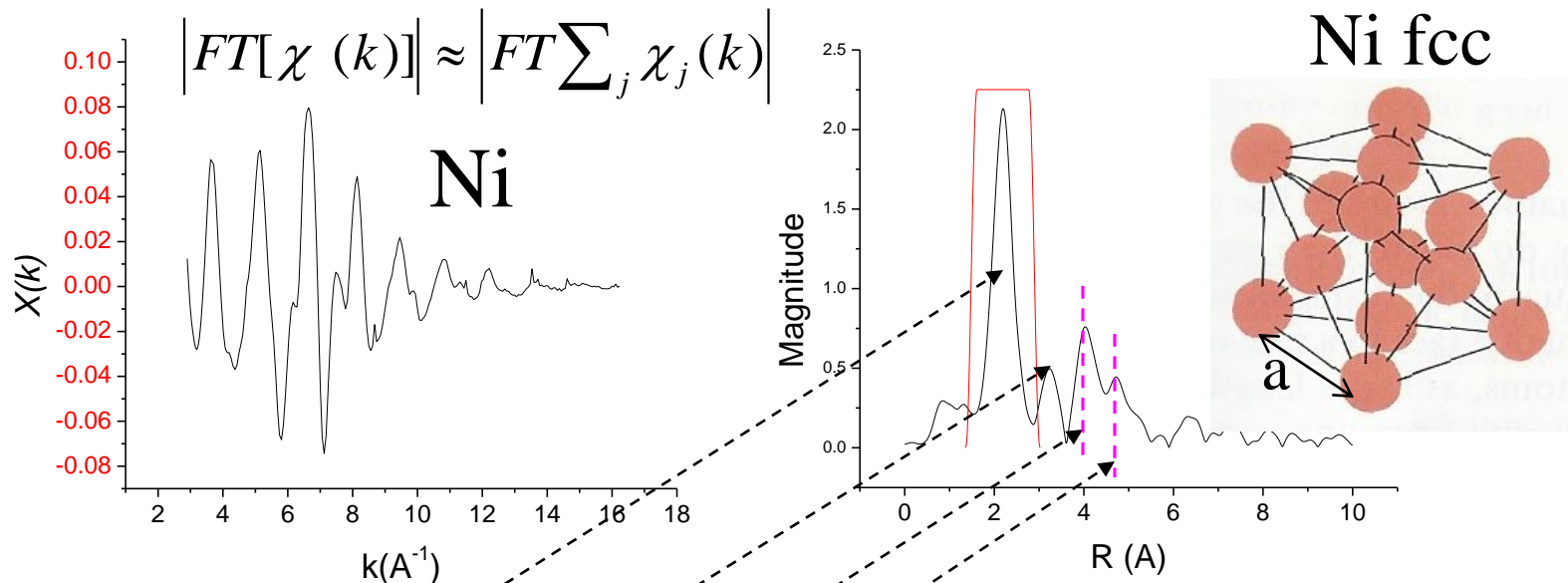
$$FT[\chi_j(k)] \propto FT\{\sin[2kr_j + \phi_j(k)]\}, \quad \phi(k) \approx \alpha + \beta k \approx a_j + 2b_j k$$

$$|FT[\chi_j(k)]| \approx \left| \frac{\sin(r_j - r + b_j)(k_{\max} - k_{\min})}{2(r_j - r + b_j)} \right| \quad \text{for } r > 0$$



The r space peak position is shorter than the real  $r_j$  ( $b \sim -0.2$  to  $-0.3 \text{ \AA}$ ); this is often referred to as the phase-shift uncorrected value

# For multi-shells

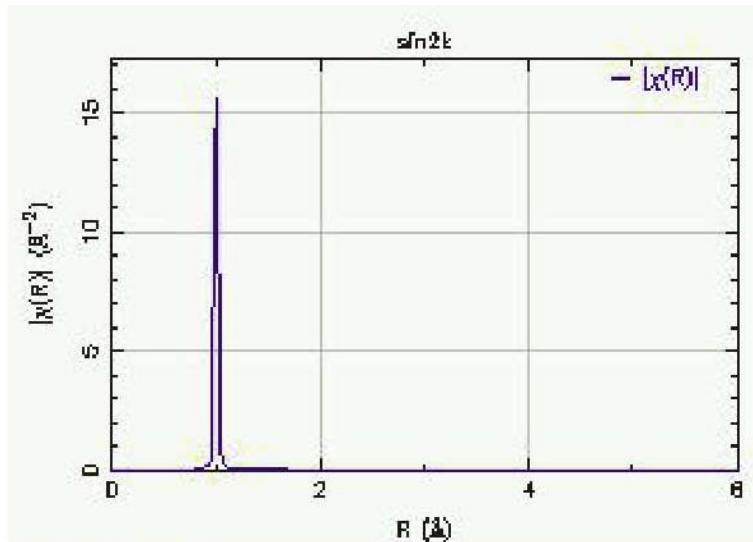
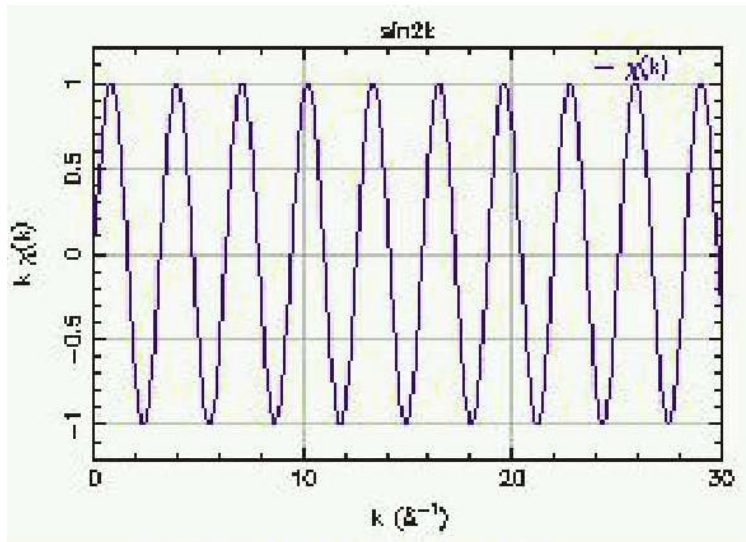


	FCC		BCC		Diamond		HCP	
Shell	Atom	Distance	Atom	Distance	Atom	Distance	Atom	Distance
1 <sup>st</sup>	12	$1/\sqrt{2}$	8	$\sqrt{3}/2$	4	$\sqrt{3}/4$	6	$\sqrt{1/3+b}/4$
2 <sup>nd</sup>	6	1	6	1	12	$\sqrt{2}/2$	6	1
3 <sup>rd</sup>	24	$\sqrt{6}/2$	12	$\sqrt{2}$	12	$\sqrt{11}/4$	6	$\sqrt{4/3+b}/4$
4 <sup>th</sup>	12	$\sqrt{2}$	24	$\sqrt{11}/2$	6	1	2	$\sqrt{b}$

Distance in unit of a,  $b = (c/a)^2$

# $k^n$ weighting and filtering

FT is a frequency filter for an infinite sine wave the FT is a  $\delta$  function (localized)

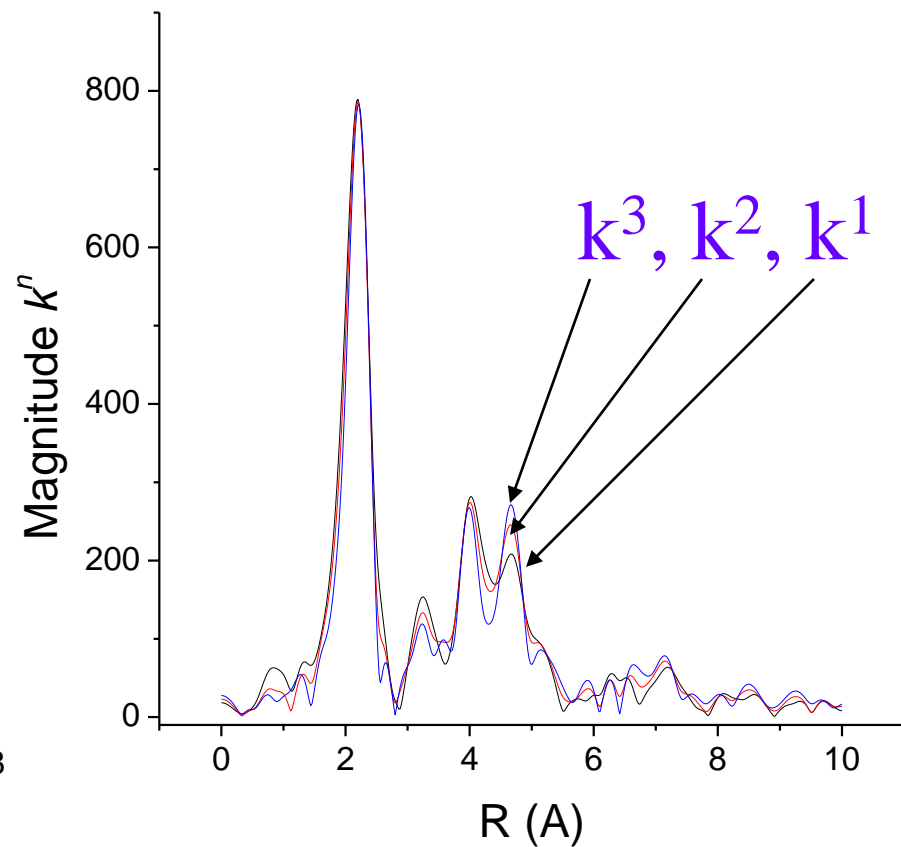
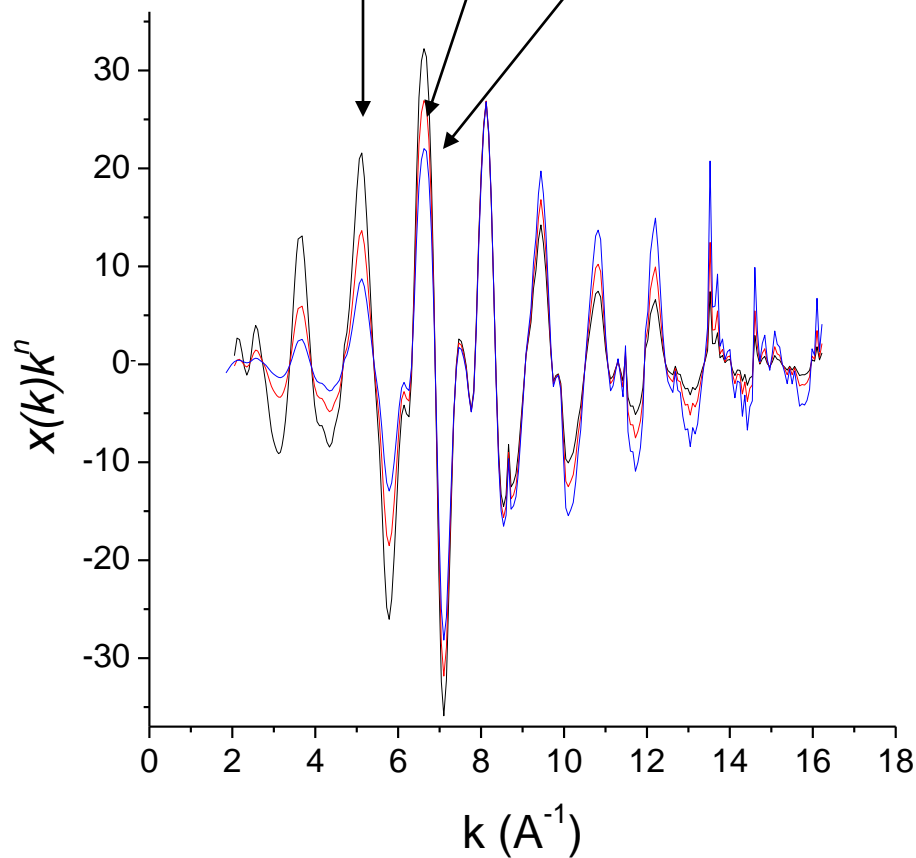


EXAFS is not an infinite sine function but a sum of discrete sine waves, FT yields a broadened, sometimes distorted peak,  $k^n$  weighting and filtering are often used to improve the quality of the analysis

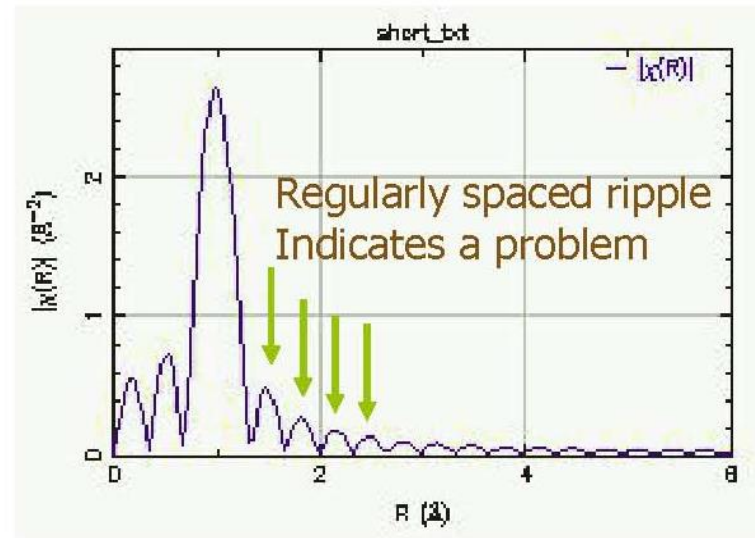
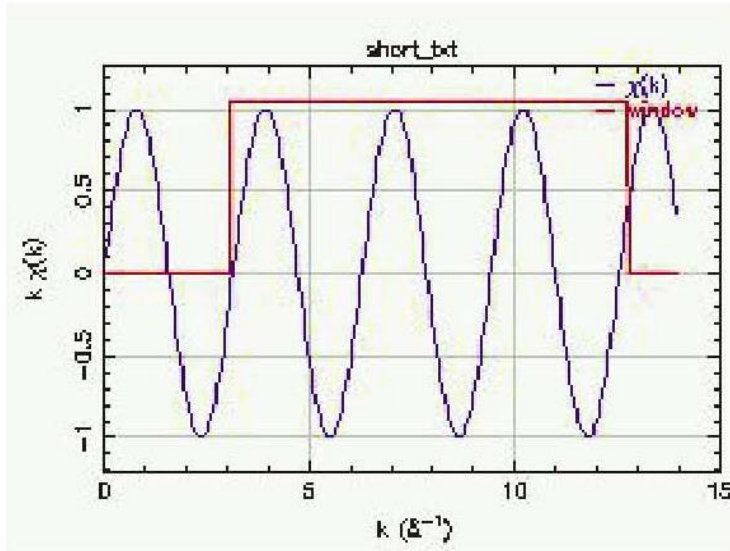


# $k^n$ weighting ( $n = 0 - 3$ )

$k^1, k^2, k^3$



# Filtering window



Discrete FT leads to leakage in R space (side lobes), proper window selection can suppress side lobes and distortion

We often use a filter window in the back transform

Windows often used are

Rectangle

Hamming

Hanning etc.

# Methods in EXAFS analysis

## Phase difference and log ratio method:

Effective when we are interested in the difference in bond length between two closely related systems such as bulk-nano structures, metal ions in solution and metal oxides with different oxidation states, Let

$$\Phi(k') = 2k'r + \phi(k')$$

be the phase of the unknown and the phase of the model compound is

$$\Phi(k)_m = 2kr_m + \phi_m(k)$$

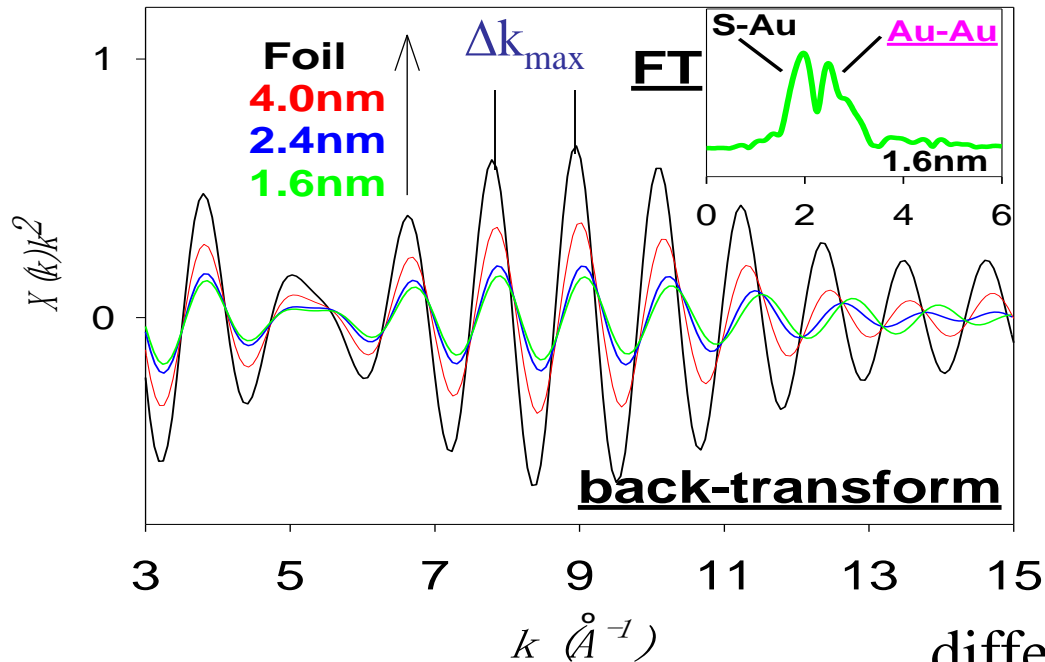
And  $k'$  is an adjustable parameter then

$$\Phi(k') - \Phi_m(k) = 2k'r - 2kr_m + \phi(k') - \phi_m(k)$$

Bt adjusting  $E_o$  of  $k'$  until  $\phi(k') - \phi_m(k) = 0$

*The bond length difference can be obtained from the slope of  $\Delta\Phi$*

Alternatively, we can consider the difference in adjacent maximum of the oscillations in k space



$$\chi(k) = A(k, r)\Phi(k, r)$$

$$\Phi(k) = \sin \phi(k)$$

$$= \sin[(2r + \beta)k + \alpha]$$

difference between adjacent maximum

$$\frac{\partial \phi}{\partial k} = 0 \rightarrow \Delta k_{\max} = \frac{2\pi}{(2r + \beta)}$$

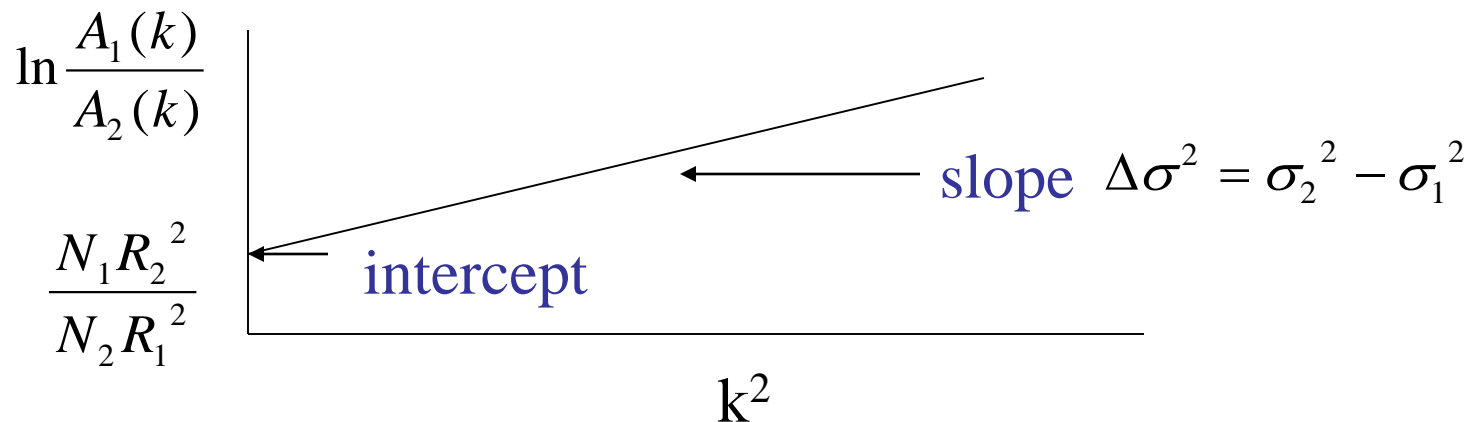
Find  $\beta$  from model compound

# Amplitude log ratio

$$\chi(k) = \sum_j \left[ \frac{N_j S_0^2 f(k, \theta) e^{-2R_j/\lambda_e(k)} e^{-2k^2 \sigma_j^2}}{k R_j^2} \right] \sin[2kR_j + \phi(k)]$$

For two closely related samples, we assume that in  $A(k)$  everything is the same except  $N$ ,  $R$  and  $\sigma$ , then we have

$$\ln \frac{A_1(k)}{A_2(k)} \approx \ln \frac{N_1 R_2^2}{N_2 R_1^2} + 2k^2 (\sigma_2^2 - \sigma_1^2)$$



# Beating method

When atomic shells are close to each other, the beating of the two waves produces minima in the total amplitude  $A(k)$  and “kinks” in the the total phase. The position of the beat nodes satisfies

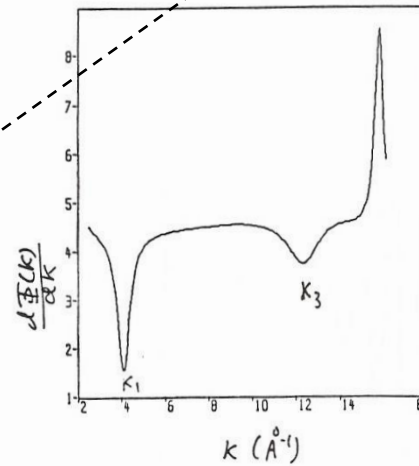
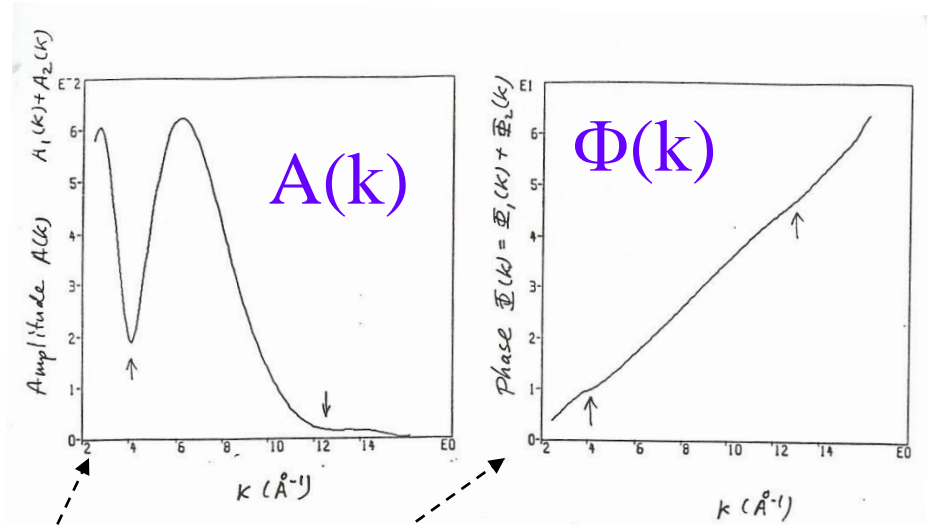
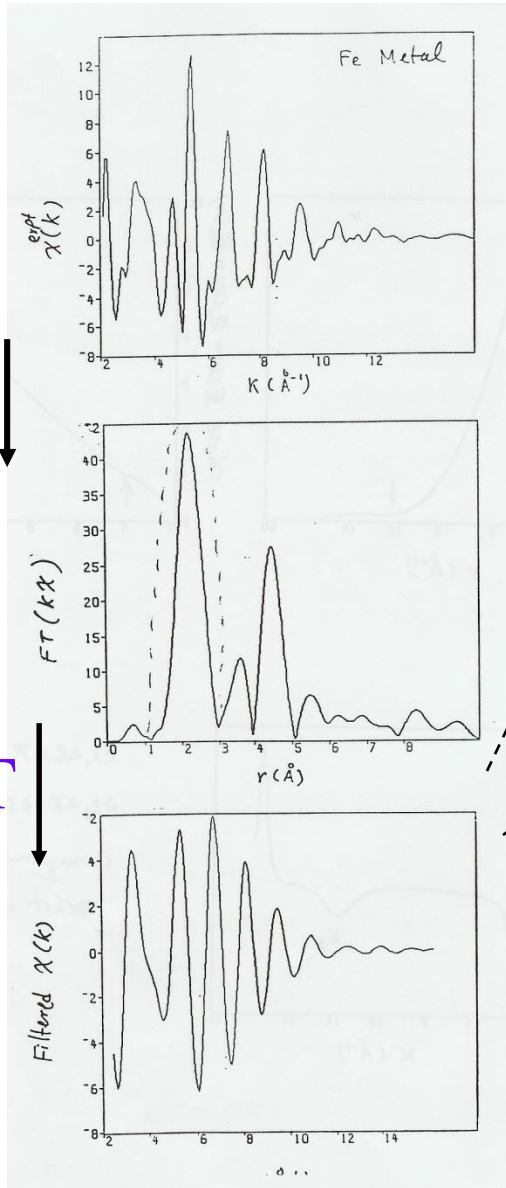
$$2k_n \Delta R + \phi_1 - \phi_2 \approx n\pi, \quad n = 1, 3, \dots$$

Since the phase for different shells is the same we have

$$2k_n \Delta R \approx n\pi, \quad n = 1, 3, \dots$$

bcc Fe, the first and second shell is very close,  $\Delta R = 0.385 \text{ \AA}$

FT



$$2k_1\Delta R = \pi,$$

$$\Delta R = 0.385 \text{ \AA}$$

$$2k_3\Delta R = 3\pi,$$

$$\Delta R = 0.381 \text{ \AA}$$

$$2k_n\Delta R \approx n\pi, \quad n = 1, 3, \dots$$

# Curve fitting

Useful parameters can be obtained by fitting the data to the following equation

$$\chi(k) = \sum_j \left[ \frac{N_j S_0^2 f(k, \theta) e^{-2R_j/\lambda_e(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \right] \sin[2kR_j + \phi(k)]$$

There are many codes to perform fitting analysis. Details will not be discussed in this course. Typically, theoretical amplitude and phase (FEFF) or experimental data of standards are used for the fitting. More details can be obtained from web site references.

Several useful sites can be linked from

<http://publish.uwo.ca/~tsham/>

Click on “link” then “spectroscopy”



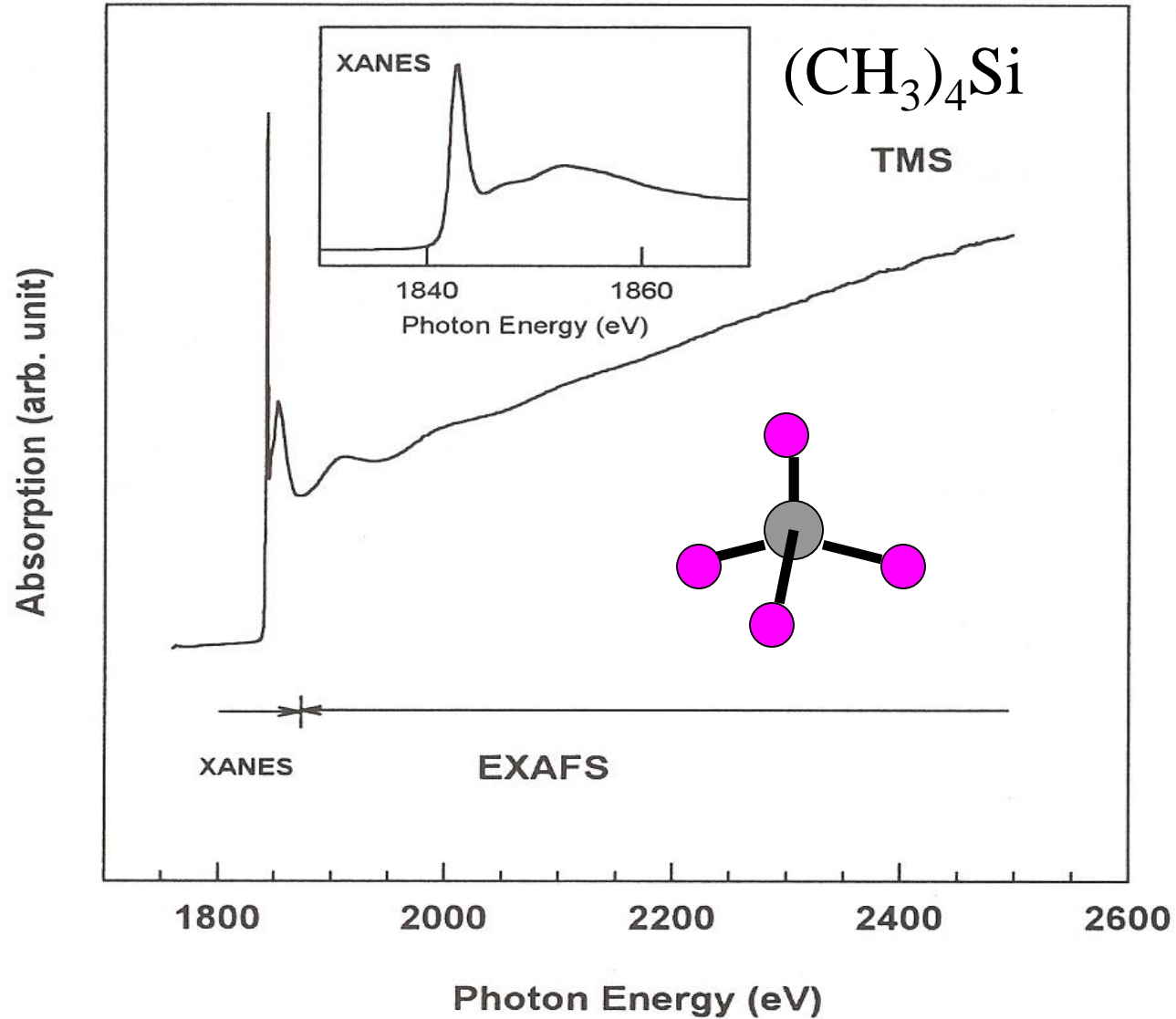
# **Data analysis computer codes**

**Ban:** Dos based, good for preliminary examination of data

**Athena:** Window based contemporary version (public domain, by Bruce Ravel of NIST) (recommended)

**Winxas:** Commercial soft ware

# EXAFS: Other Examples



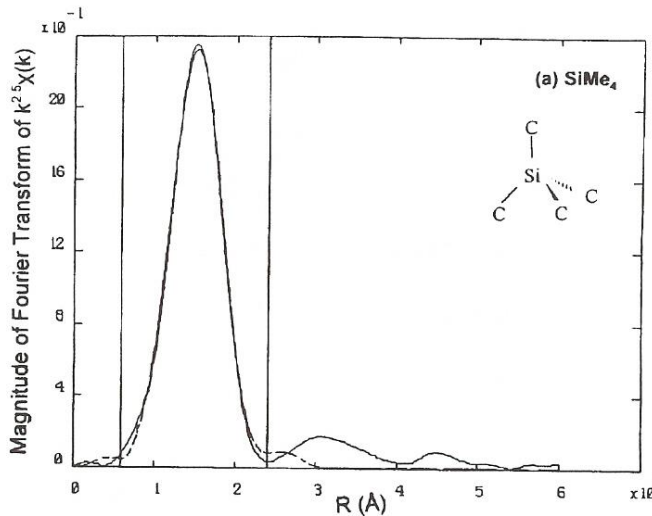
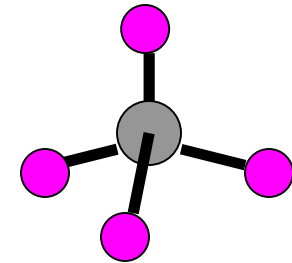
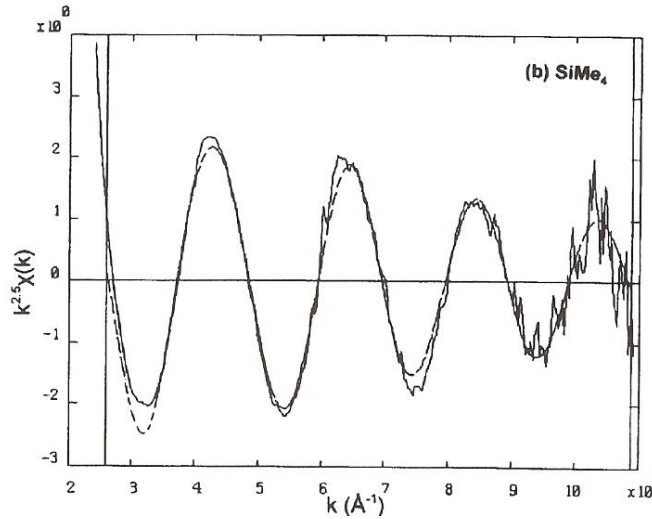
# Identical backscattering atoms

Si-C bond  
single sinusoidal  
Curve in k space

FT

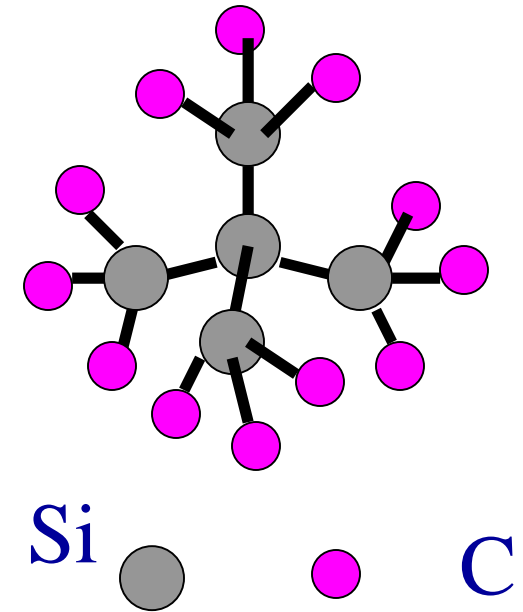
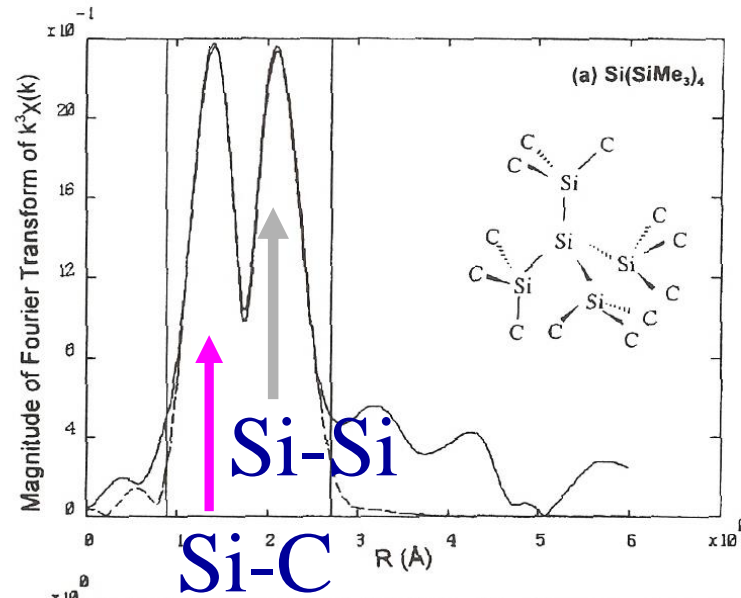


Single  
bond  
length

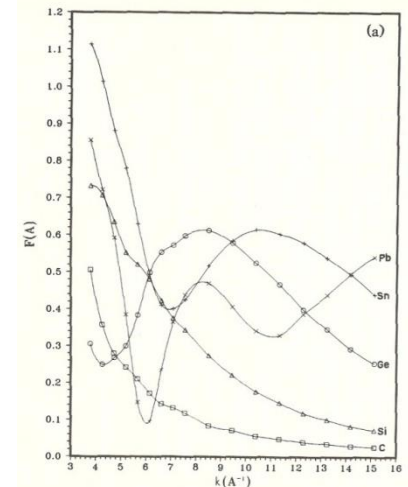
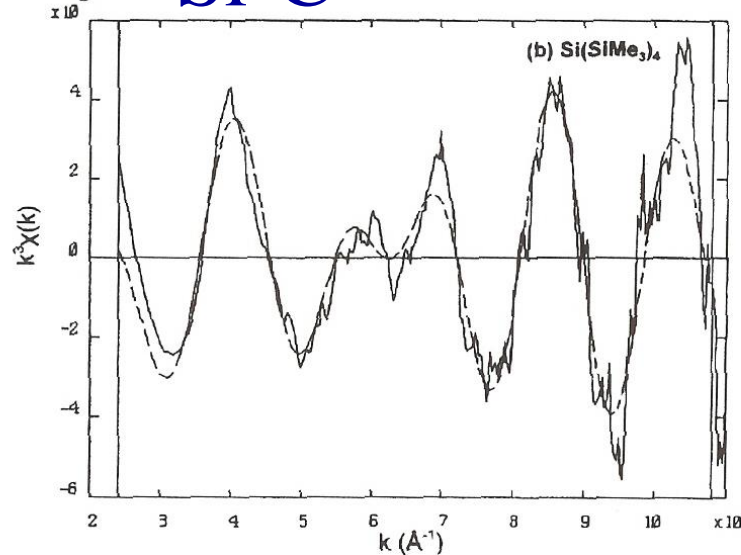


# Two types of backscattering atoms

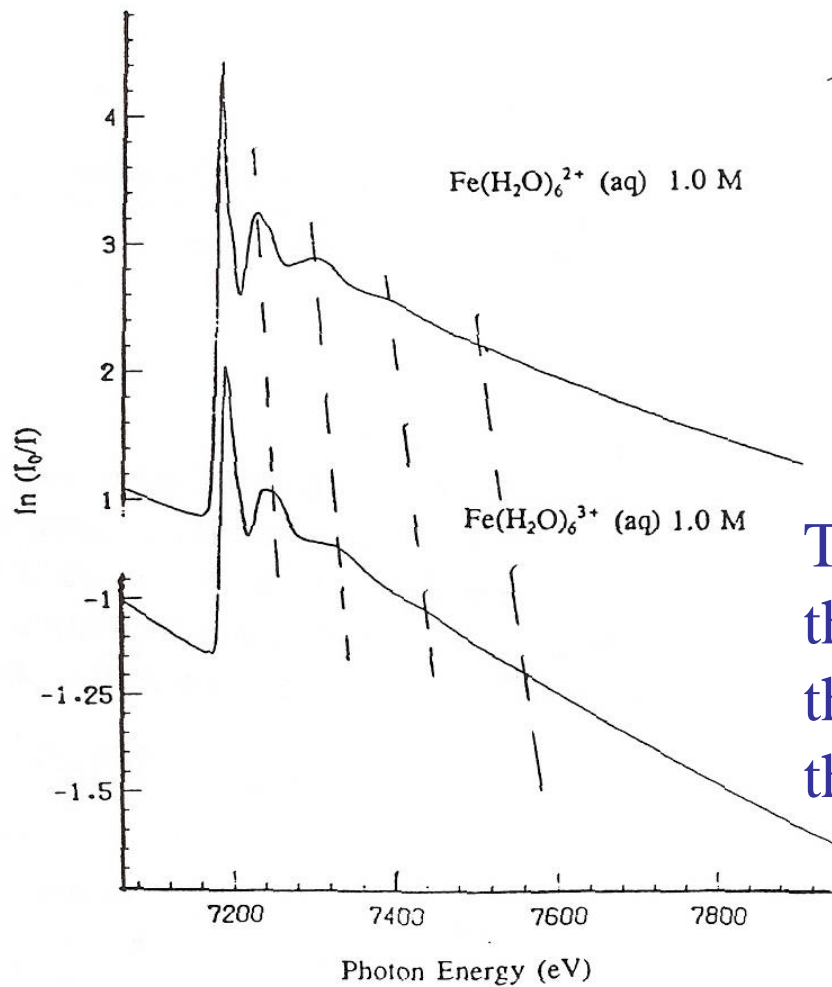
FT shows  
two peaks  
associated  
**Si-C** and  
**Si-Si** bonds



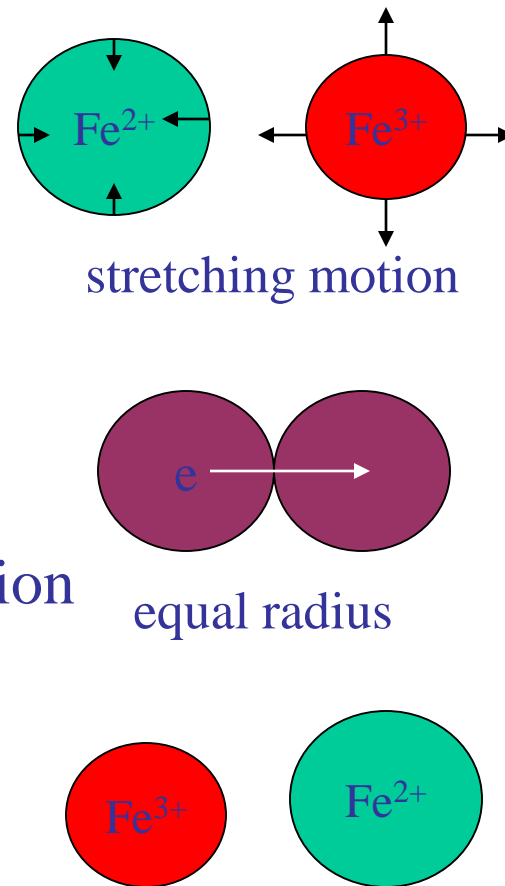
Beating of  
two sine waves  
is apparent



# Electron exchange reactions (nuclear tunneling)



The bigger  
the separation  
the shorter  
the bond

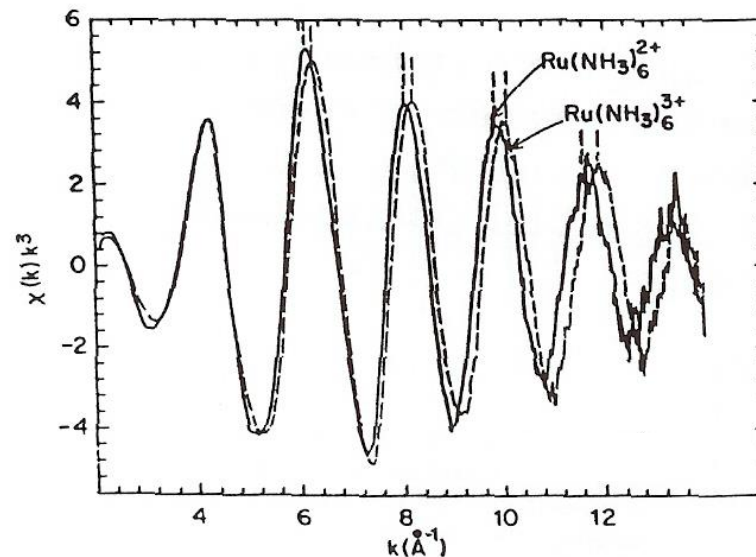
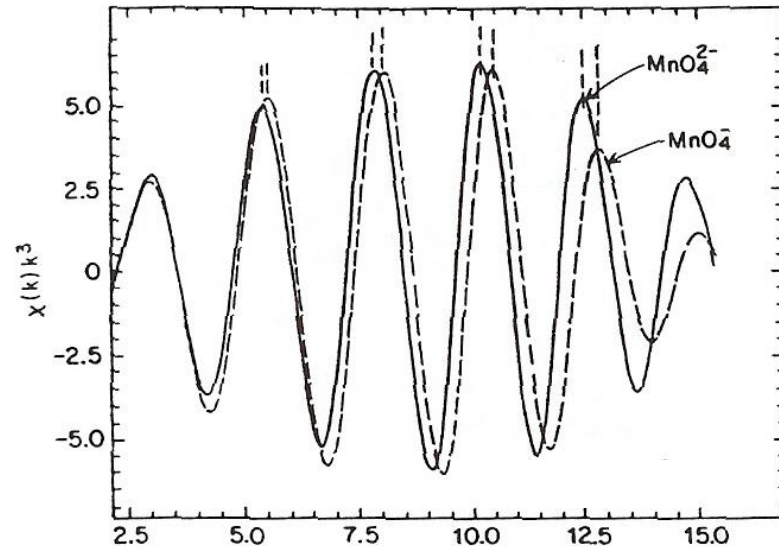


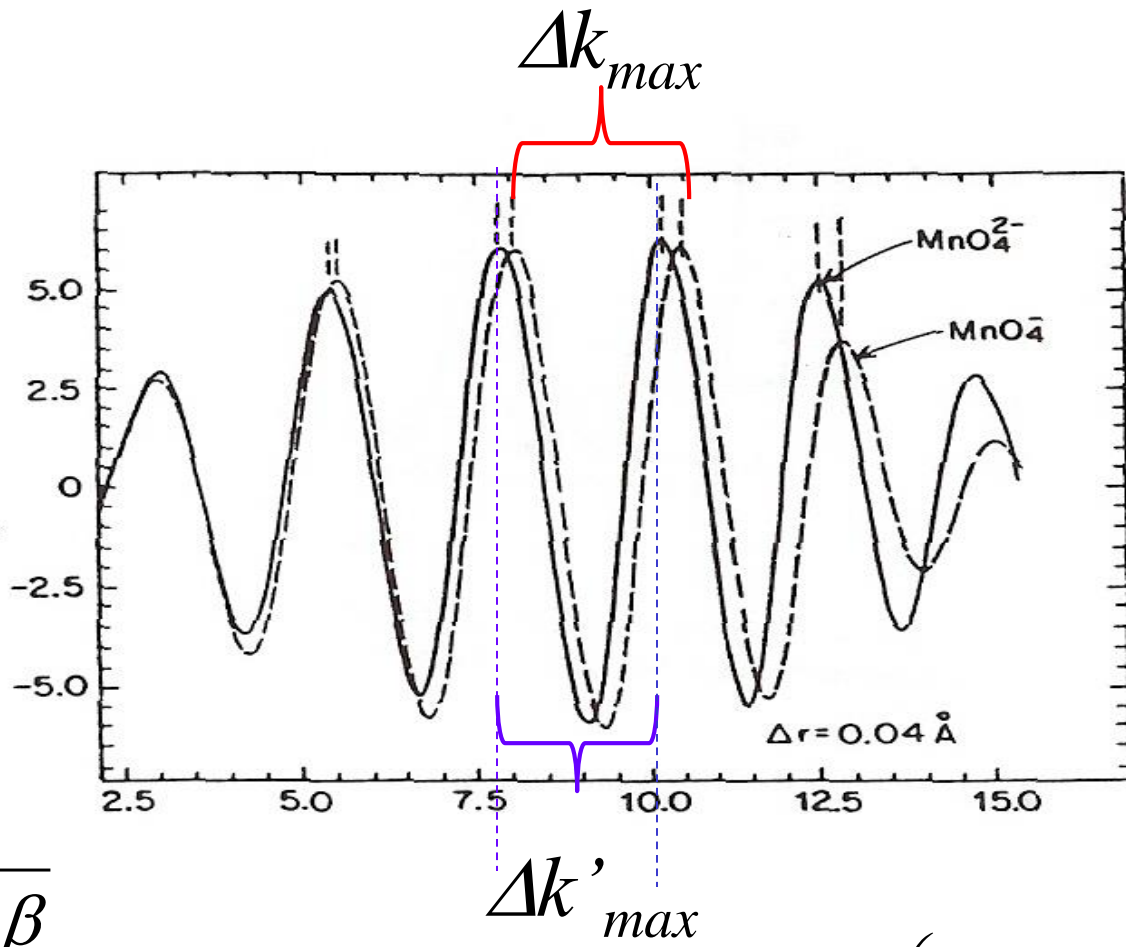
# EXAFS of other electron exchange pairs

Qualitatively, we can predict which complex has a longer bond from the progressive mismatching of the oscillation maximum

$$\frac{\partial \phi}{\partial k} = 0 \rightarrow \Delta k_{\max} = \frac{2\pi}{(2r + \beta)}$$

accurate  $\Delta R$





From one max to the next, the phase changes by  $2\pi$

$$\Delta k_{\max} = \frac{2\pi}{2r + \beta}$$

$$2r + \beta = \frac{2\pi}{\Delta k_{\max}}$$

$$2r' + \beta = \frac{2\pi}{\Delta k'_{\max}}$$

$$\Delta k'_{\max}$$

$$2(r' - r) + (\beta - \beta) = 2\pi \left( \frac{1}{\Delta k'_{\max}} - \frac{1}{\Delta k_{\max}} \right)$$

$$\Delta r \propto \left( \frac{1}{\Delta k'_{\max}} - \frac{1}{\Delta k_{\max}} \right)$$