X-ray Absorption Spectroscopy

A short course

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Course Objective

To familiarize students/researchers with the principles, practices and applications of XAFS techniques for materials analysis.

References:

J. Stöhr, NEXAFS Spectroscopy (Springer, 1992)

D. Koningsberger & R. Prins, (eds), X-ray Absorption Spectroscopy: Principles, Applications and Techniques of EXAFS, SEXAFS and XANES (Wiley, 1988)

T.K. Sham (ed) Chemical Applications of Synchrotron Radiation (World Scientific, 2002)

Frank de Groot and Akio Kotani, Core Level Spectroscopy of Solids (Taylor & Francis CRC press, 2008)

Relevant questions to be addressed

- What is XAS and XAFS ?
- What is synchrotron radiation ?
- How to make XAFS measurements ?
- How to analyze XAFS Data ?
- What information can XAFS provide ?

Course outline

- Introduction: materials and the interaction of light with materials
- XAFS spectroscopy - the near edge
- XAFS spectroscopy - the extended region (EXAFS)

What is X-ray absorption spectroscopy (XAS)?

- X-ray interacts with all electrons in matter when its energy exceeds the binding energy of the electron.
- X-ray excites or ionizes the electron to a previously unoccupied electronic state (bound, quasi bound or continuum). The study of this process is **XAS**
- Since the binding energy of core electrons is **element specific**, XAS is element and core level specific (e.g. Si K-edge at 1840 eV is the 1s electronic excitation threshold of silicon)

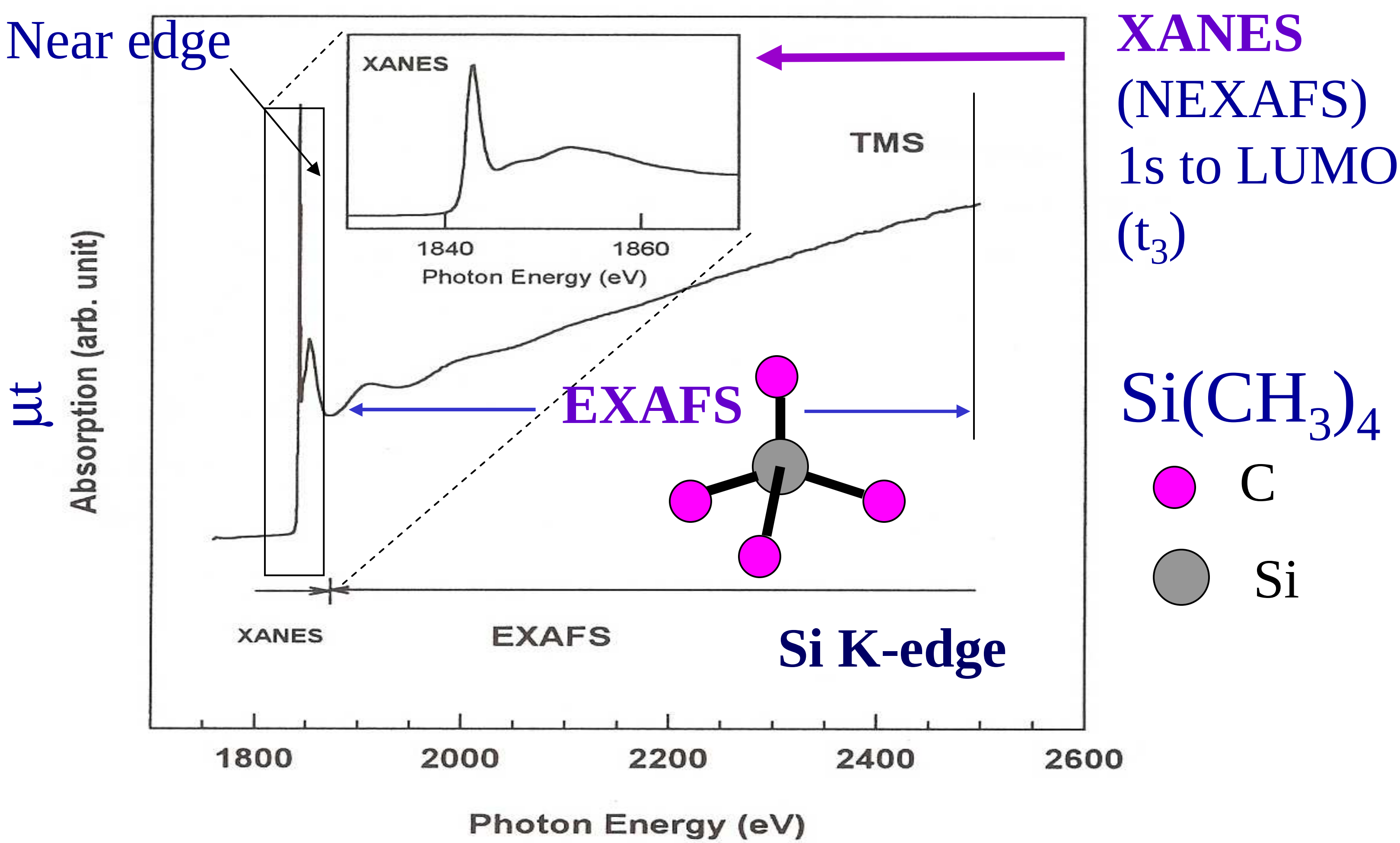
What is X-ray absorption fine structures (XAFS) ?

As core electron is excited with $h\nu \geq$ the threshold (E_o), it is excited to a final state defined by the **chemical environment**, which modulates the absorption coefficient relative to that of a free atom. This **modulation** is known the **XAFS**,

- XAFS contains all the information about the local structure and bonding of the absorbing atom
- XAFS study requires a **tunable X-ray source** – synchrotron radiation

Note: **XAS** and **XAFS** are often used interchangeably, XAS is a general term, XAFS is specific to the modulation of the absorption coefficient by the chemical environment

What does XAFS look like?

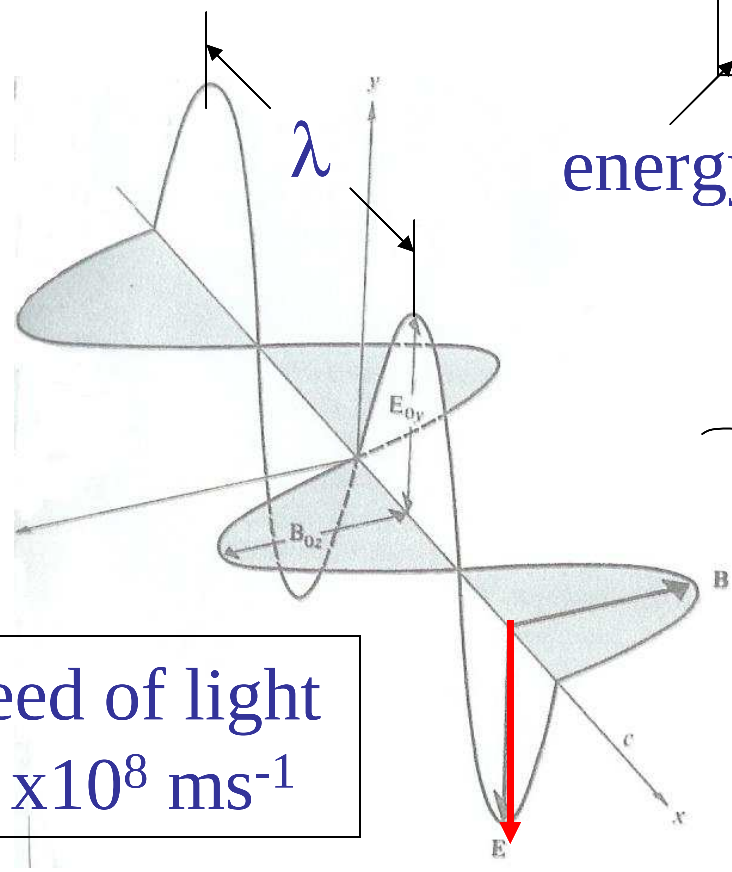


Part I

- Light
- Materials
- Synchrotron radiation
- Interaction of light with matter

Probing matter with SR, versatile *light*

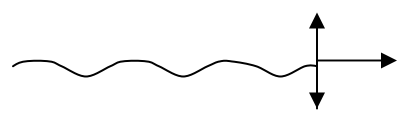
What is ***light*** ? (particle carries a packet of energy)



$$E = h\nu = hc/\lambda$$

energy → E; frequency(s^{-1}) → ν

E vector (polarization)



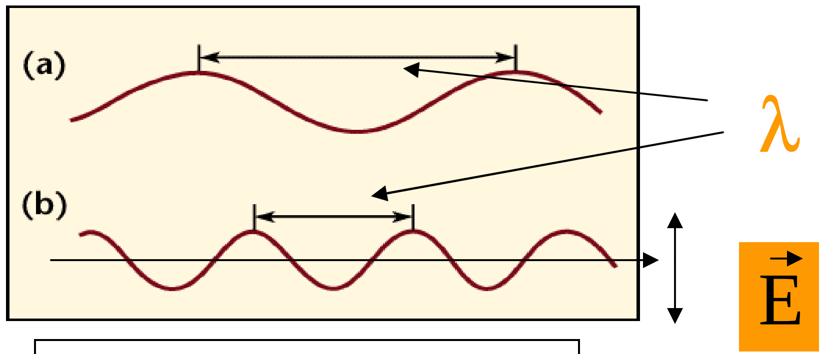
c: speed of light

$c = 3 \times 10^{8}\ ms^{-1}$

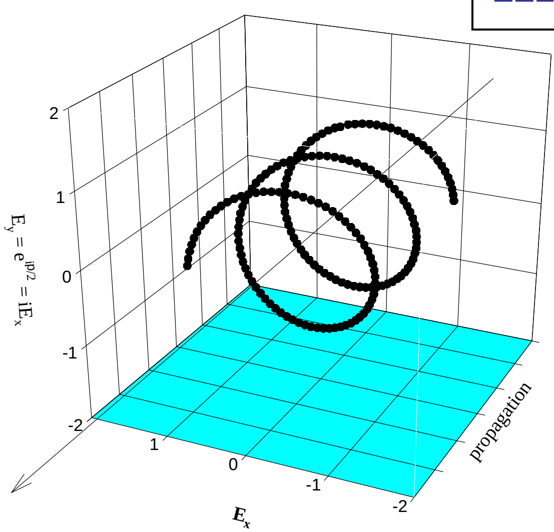
h: Planck's constant

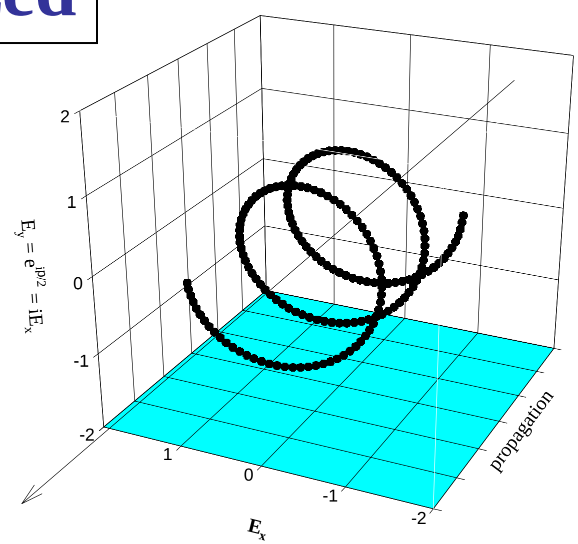
$h = 6.626 \times 10^{-34}$ Js

Light is a particle (photon) with spin = 1 and behaves like a wave



linear polarized

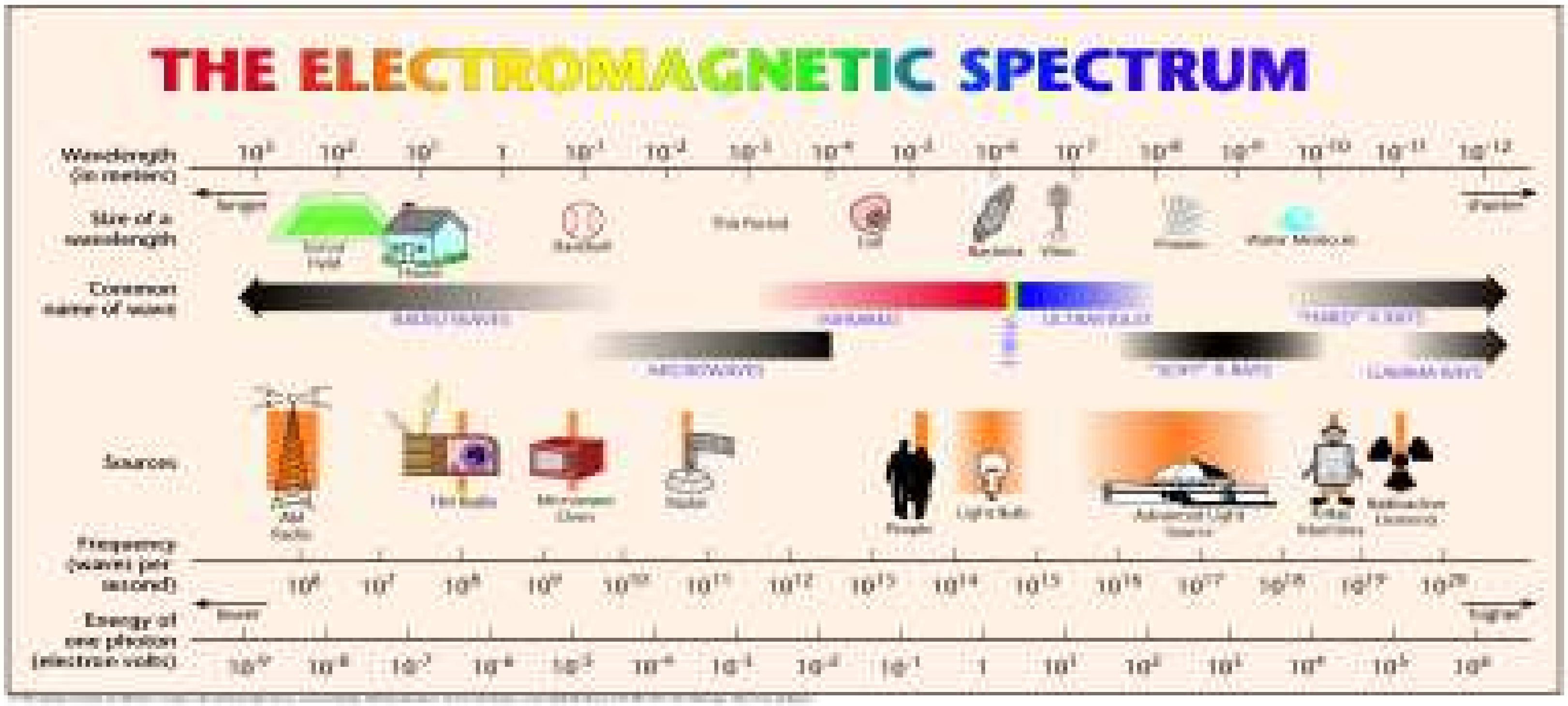




circular polarized light

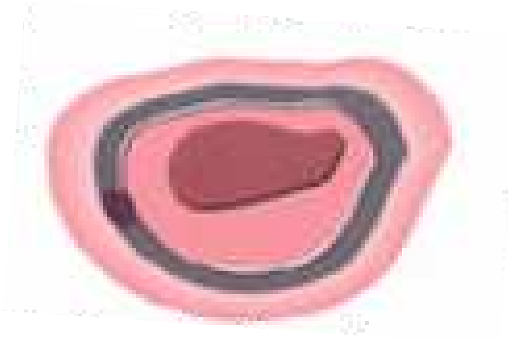
Electromagnetic wave spectrum

$\lambda(Å) = 12398.5/E(eV)$

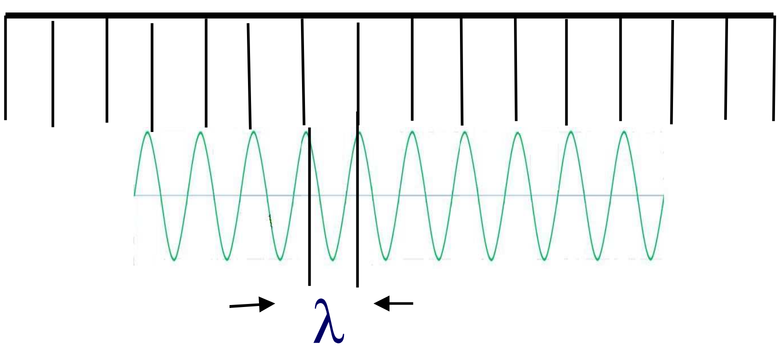


Light sees object with dimension comparable to its wavelength

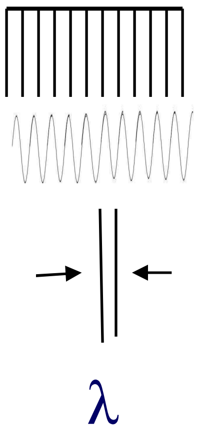
“Rulers” for small sizes: Photons and Electrons



Cell



Water molecule



Synchrotron radiation: photons with tunable wavelength, λ (10^4 nm – 10^{-3} nm)

What is synchrotron radiation?

- **When an electron traveling at nearly the speed of light in an orbit, it emits a *continuum* of *electromagnetic radiation*** *tangential* **to the orbit**

Synchrotron light

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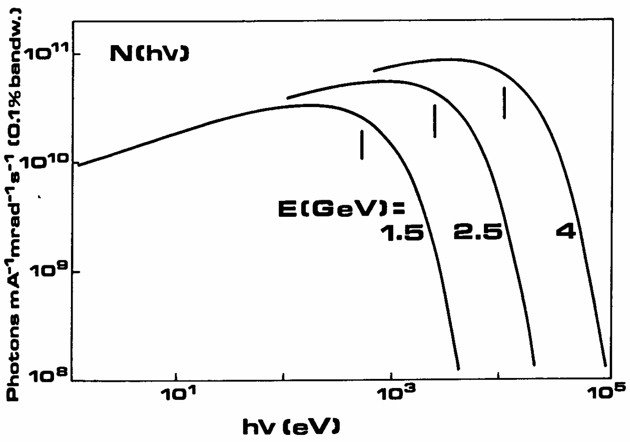
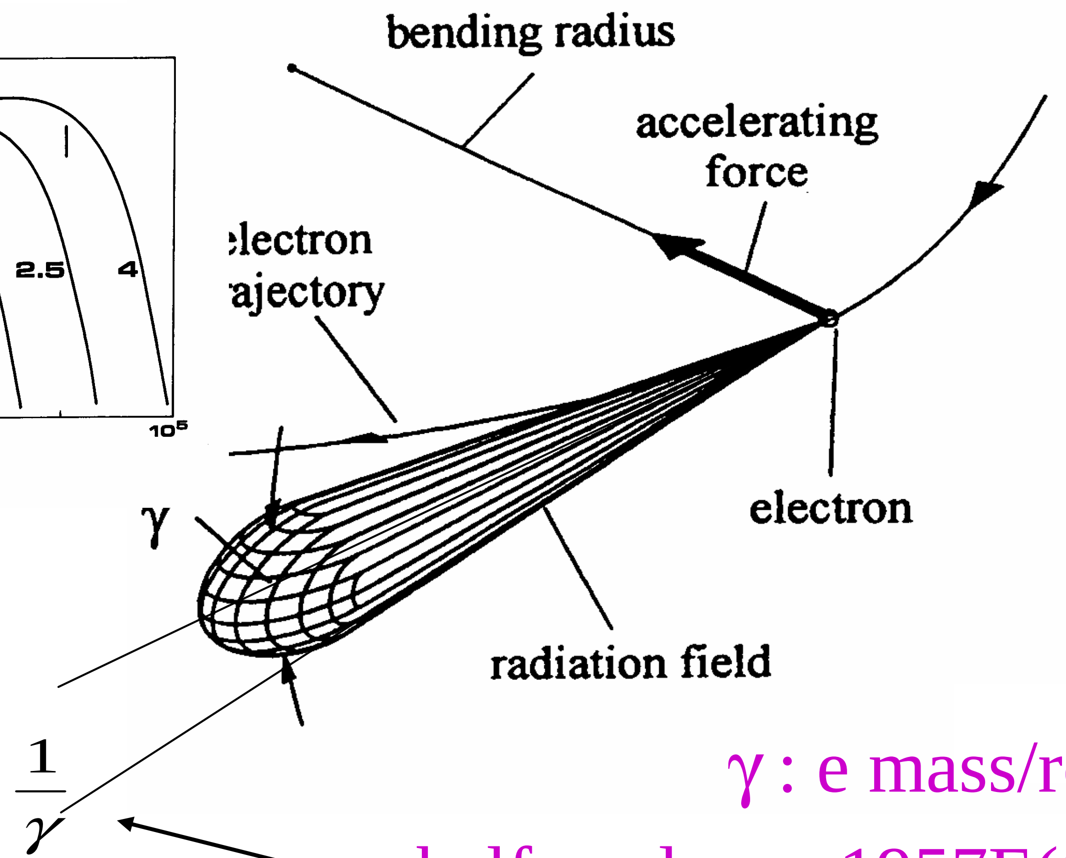
Radiation Pattern: Spatial distribution





γ : e mass/rest mass

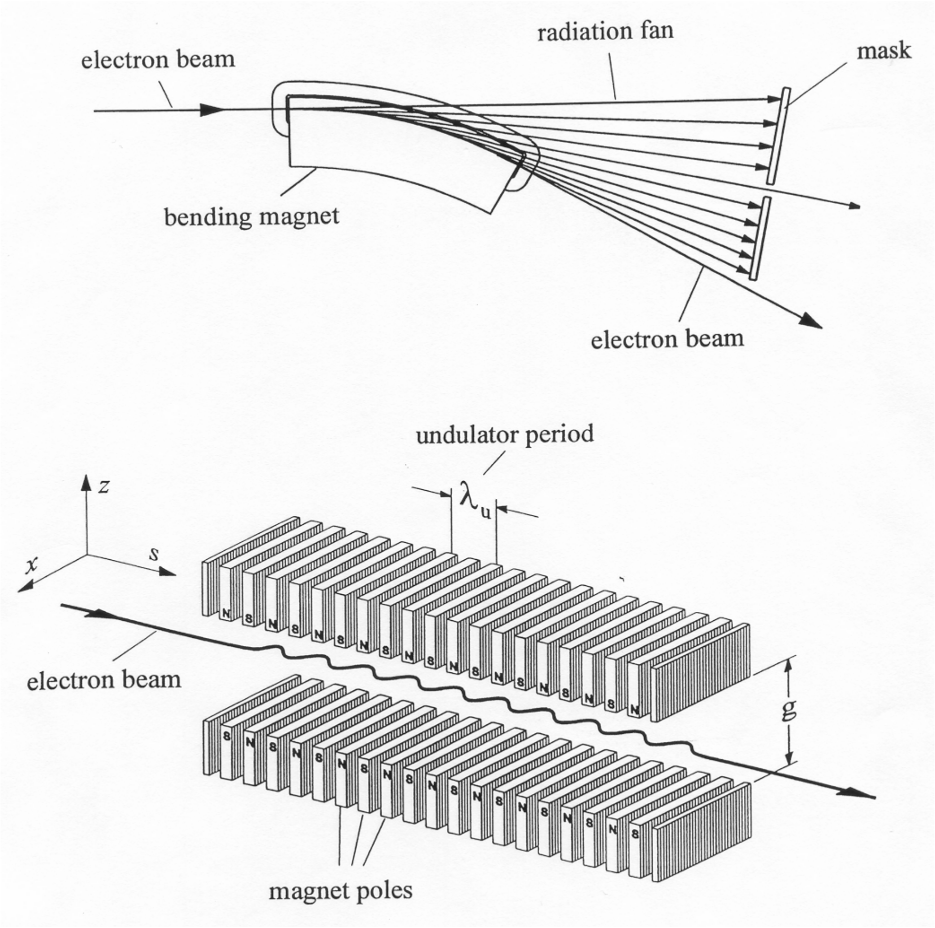
half angle, γ ~1957E(GeV)

At APS, E = 7.0 GeV

1/γ = 0.073 mrad = 0.0041°

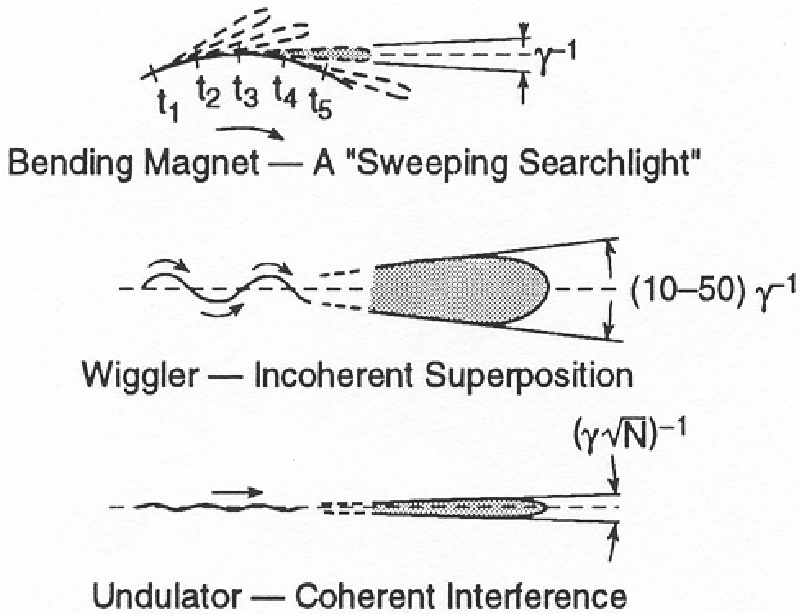
→ highly collimated source

Bending Magnet and Insertion Device

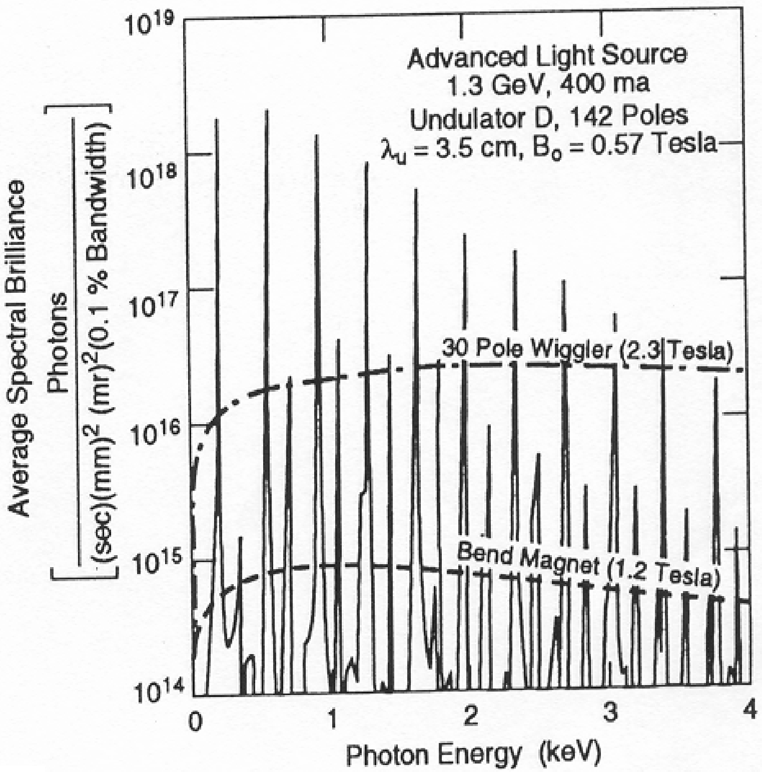


Third generation sources, e.g. APS, ALS, CLS etc are insertion device based sources

Spatial distribution

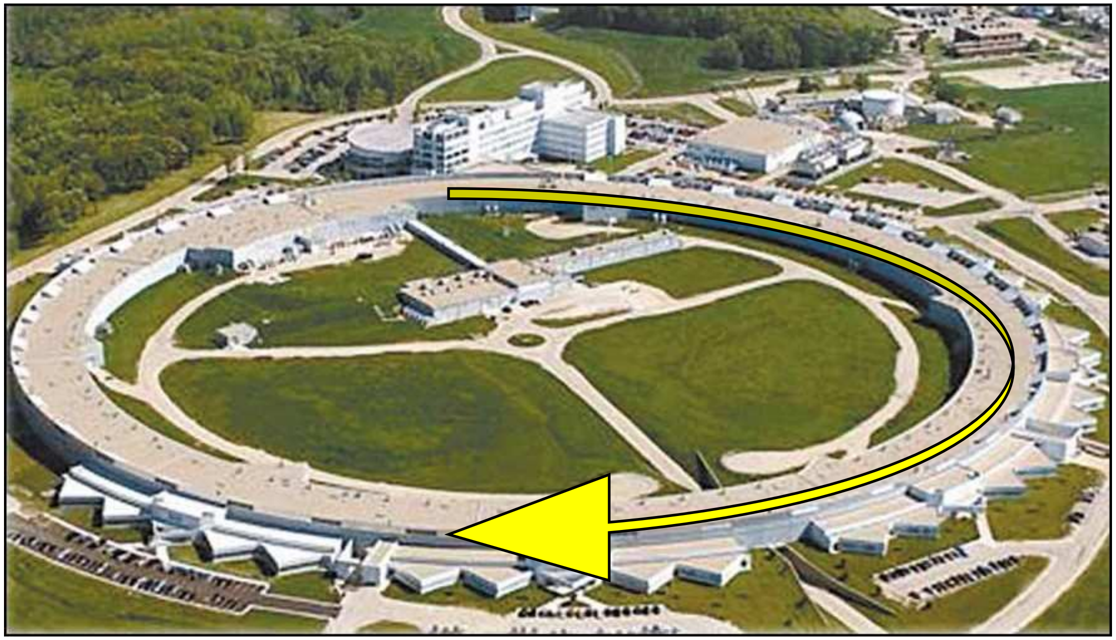


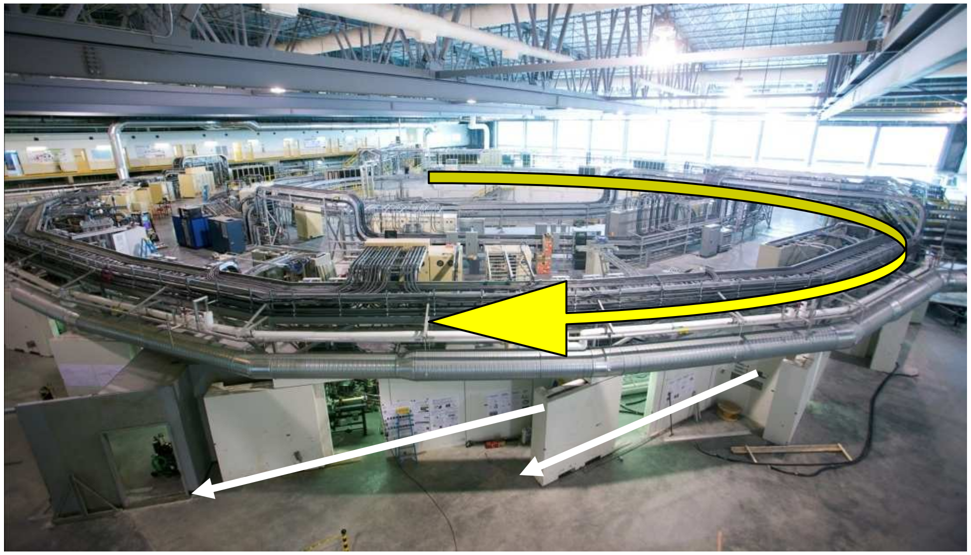
Spectral distribution



Third Generation Light Sources

The 7.0 GeV Advanced Photon Source (APS)





The 2.9 GeV Canadian Light Source (CLS)

Synchrotron radiation properties

- **Tunability (IR to hard x-rays,** element specific**)**
- **Brightness (highly collimated,** micro/nano beam**)**
- **Polarization (linear, circular, tunable,** dichroism**)**
- **Time structure (short pulse,** dynamics**)**
- **Coherence (undulator,** partial**; FEL, ~** full, imaging**)**

Materials: matter with desired functionalities

General considerations

- Materials can be classified by

a) phase: gas, liquid and solid
b) properties: metal, semiconductor, insulator, etc.
c) composition: pure substance, composite
d) functionalities: biomaterials, nanomaterials, LED materials, superconductor, soft matter etc.

- Issues in materials analysis

a) morphology
b) structure
c) bonding (electronic structure)

Materials Properties

- Material properties are determined by the electronic structure of the material
- The electronic structure is determined by the behavior of the electron in its environment, technically the ***potential*** set up by the nuclei and other electrons (structure and bonding) as well as the boundary conditions
- Surface/Interface and proximity effects

Properties of electrons

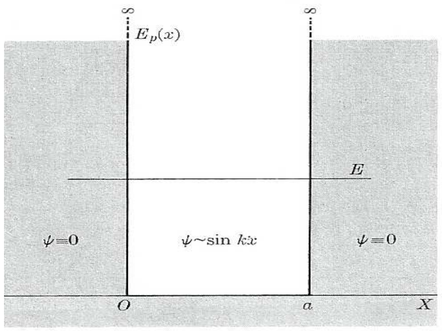
- Smallest charge particle that carries a negative charge
- Exhibits wave behavior $\lambda = h/p$ (de Broglie)
- Posses a spin of ½ (fermions, exchange interaction)
- Absorbs light when it is bound by a ***potential***

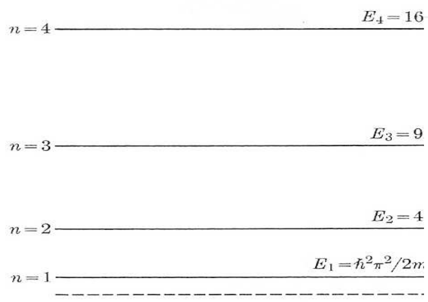
  (Free electron does not absorb light)

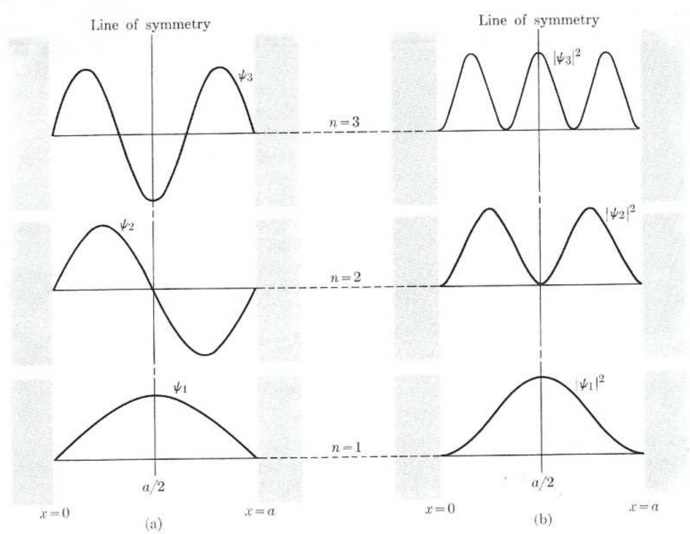
Potentials (electrostatic)

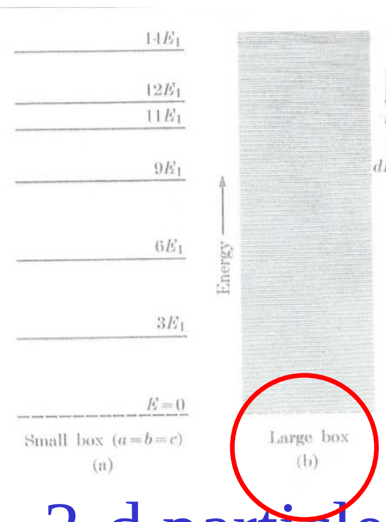
- Particle in a box
- Atom: coulomb (asymptote) plus centrifugal (non zero angular momentum, potential barrier)
- Molecule: molecular potential (all nuclei, all electrons)
- Solid: periodic potential (crystals)
- Potential supports discrete energy states (core/valence levels in atoms and molecules) and closely spaced states (bands in solids, polymers, nanostructures)
- Synchrotron spectroscopy studies transitions between occupied and unoccupied states, these transitions are strongly influenced by the local environment, therefore XAFS probes the local environment.

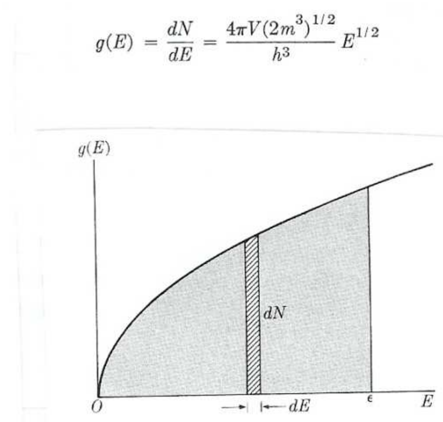
Potentials and electronic states





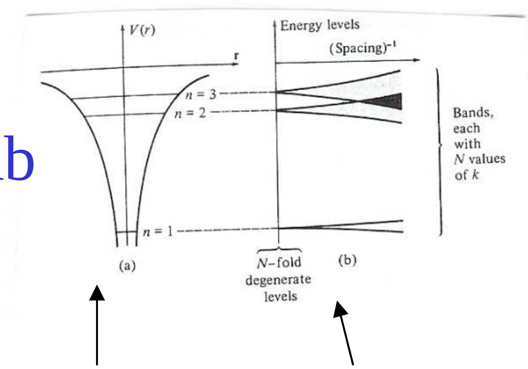






3-d particle in a box (cube)

coulomb

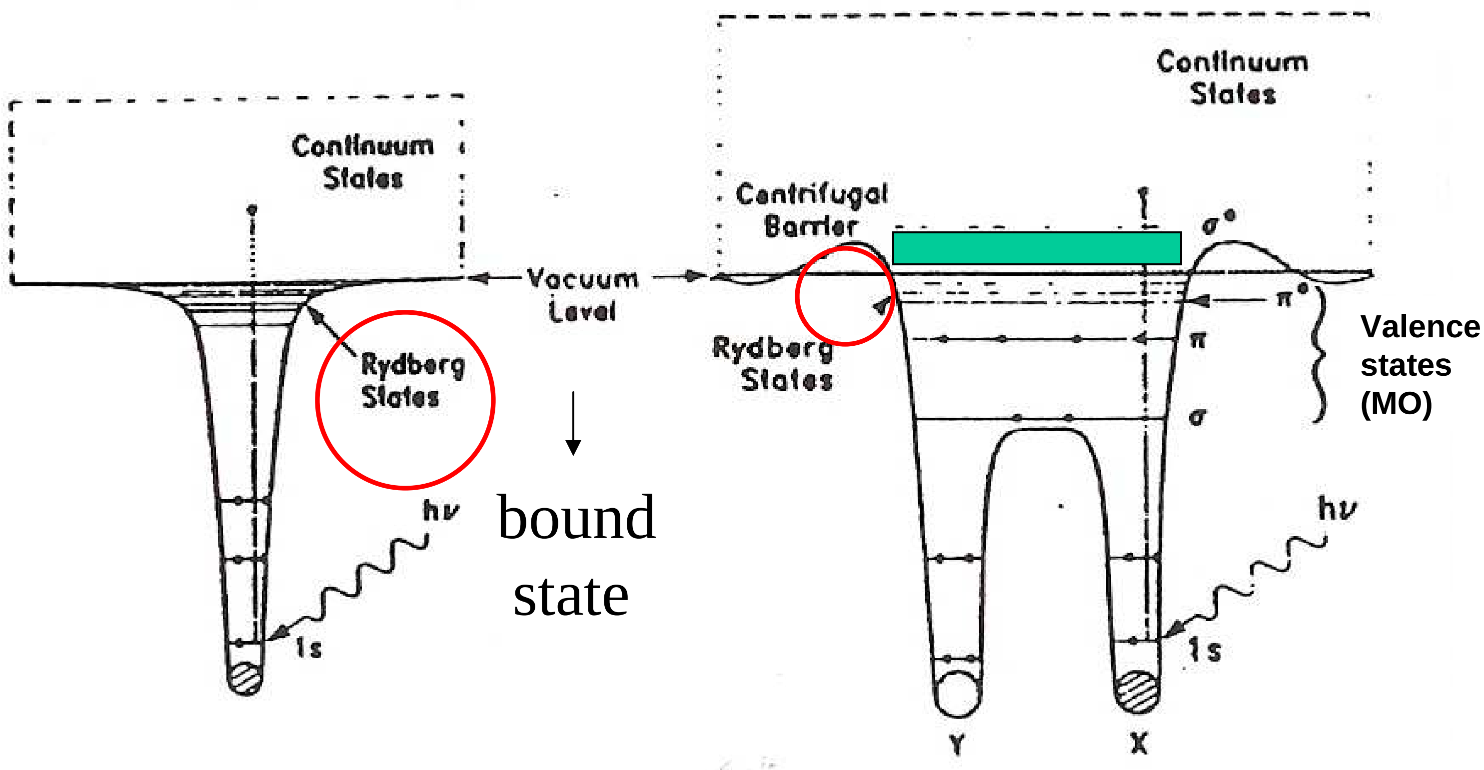


1-d particle in a box

Single atom N atoms (solid)

electronic states are quantized

Potential in diatomic molecule



free atom

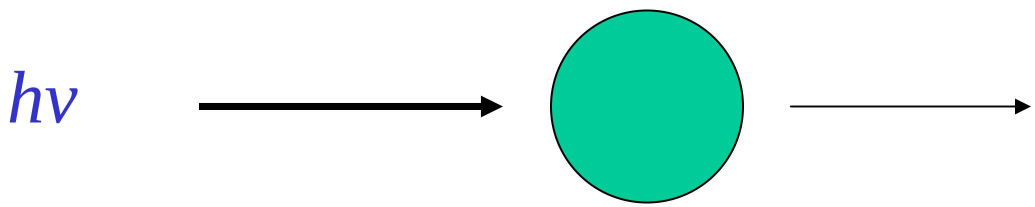
unsaturared diatomic molecule (e.g. double bonds, C=O, O=O, etc.)

Interaction of light with matter

- Scattering (elastic and inelastic)
- **Absorption** (annihilation of the photon)
- Scattering and absorption are taking place simultaneously
- Magnitude of interaction, scattering amplitude /absorption cross-sections (coefficient) depends on whether or not the photon energy is close to the absorption threshold

Atomic scattering factors

- The interaction of light and atom for photons in the energy range of VUV to soft and hard x-rays (> 30 eV) can be expressed in terms of their **scattering factor in the forward scattering position** (θ = 0)



$$f(0) = f_1 + i f_2$$

Refractive index

Scattering (Z)

Absorption coefficient

How does light interact with matter?

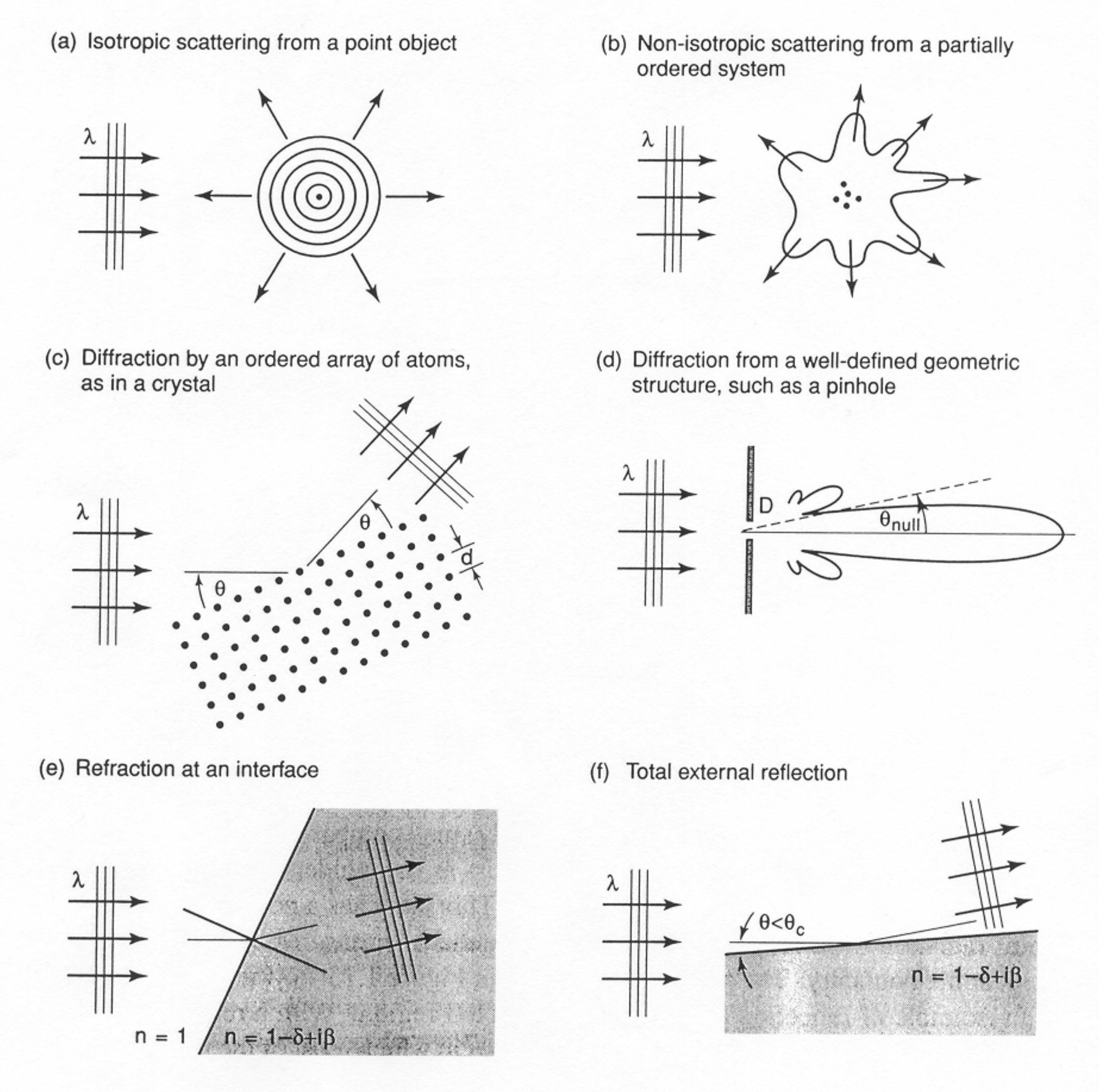
- **Scattering** (momentum/energy transfer)
  - elastic scattering
  - inelastic
- **Absorption** (annihilation of the photon)

photoabsorption	**XAFS**	
photoemission	**XPS, Auger**	De-excitation spectroscopy
fluorescence	**XES**	
luminescence	**XEOL**	

(A brace groups Auger, XES and XEOL under "De-excitation spectroscopy".)

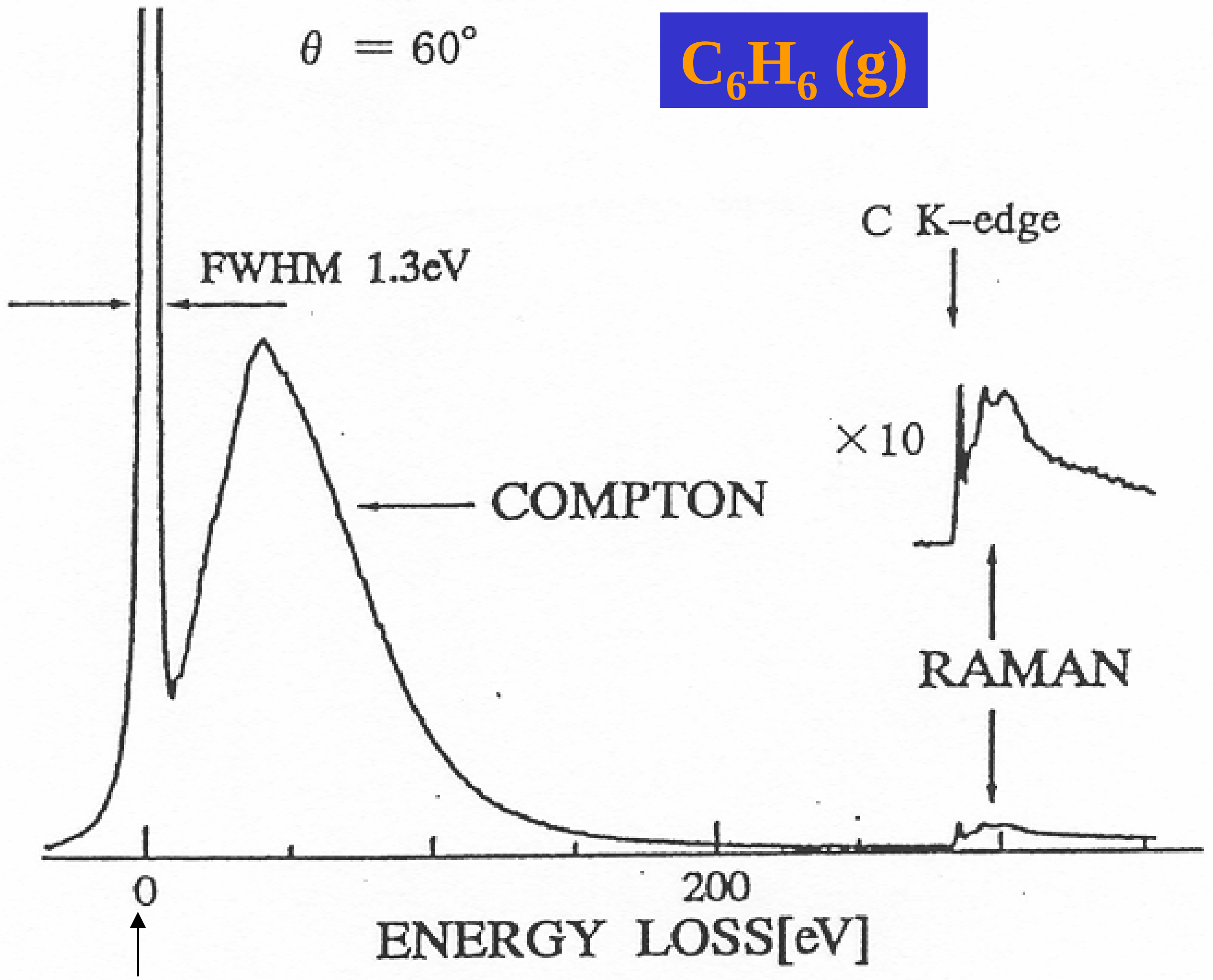
- **Resonance (e.g resonant X-ray scattering/emission)**

Some examples of scattering



"Soft X-Rays and Extreme Ultraviolet Radiation: Principles and Applications" D. Atwood Cambridge University press (1999)

Inelastic X-ray scattering



Elastic peak at 7072 eV

Udagawa et al. J. de Phys. Coll. IV/C2, 347 (1997) 2002

The overall picture

Absorption and scattering occur simultaneously

- Above and in the vicinity of an ***absorption edge*** absorption dominates

1s	K-edge		
2s	L_1-edge	2p $_{3/2,1/2}$	$L_{3,2}$-edge
3s	M_1-edge	3p $_{3/2.1/2}$	M $_{3,2}$-edge
.		3d $_{5/2,3/2}$	M $_{4,5}$-edge

- Far away from an absorption edge scattering is more important

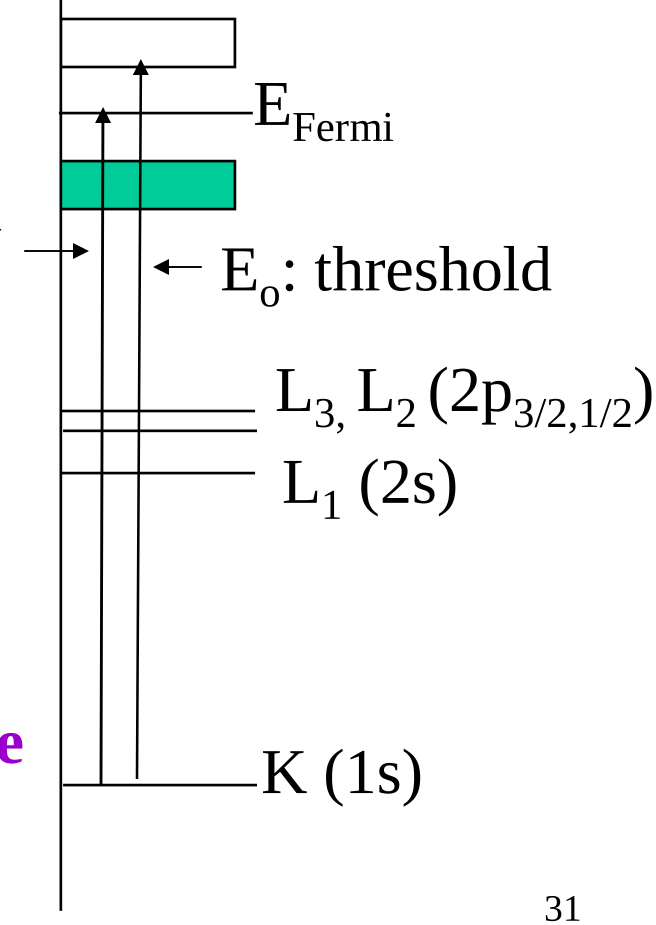
X-ray properties of elements

Silicon (Si) Z = 14

Electron Binding Energies (eV)

- **L_3: 99.8**
- **L_2: 100.4**
- **L_1: 149.7**
- **K: 1838.9**

BE: binding energy



Electron Level Widths (eV)

- **L_3: 0.014**
- **L_2: 0.015**
- **L_1: 1.030**
- **K: 0.480**

$$\Delta E \cdot \Delta t \leq \hbar/2\pi$$

Lifetime of the core hole

The refractive index

$$n = 1 - \delta + i\beta$$
$$= 1 - (n_a r_e \lambda^2/2\pi)\,(f_1^0 - i f_2^0)$$

δ : **related to scattering (f_1^0)**

β: **related to absorption (f_2^0)**

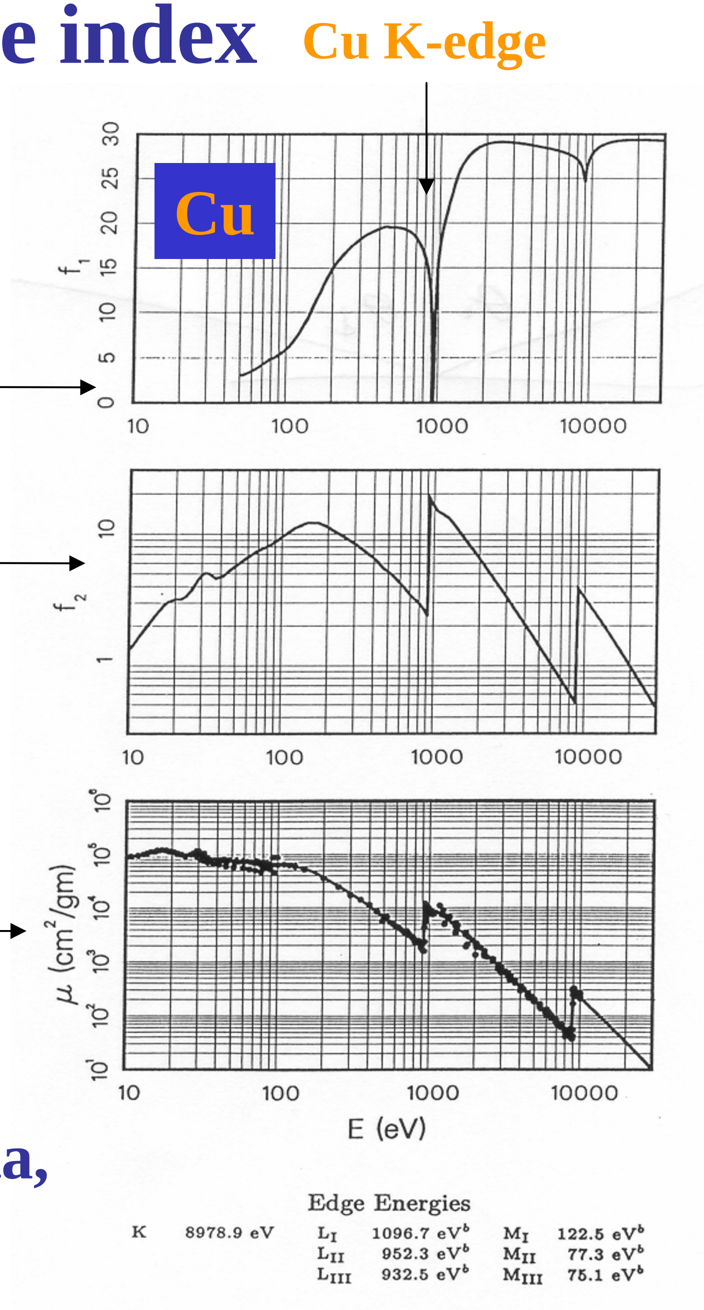
linear absorption coefficient

$\mu = \sigma \cdot \rho$ (cm^{-1})

σ = mass absorption (cm^2/gm)

ρ = density (gm-cm^{-3})

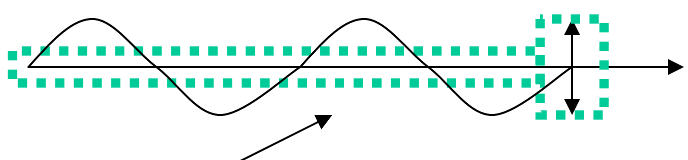
Henke et al. Atomic Data, Nucl. Data, 54, 181(1993)



The absorption process → spectroscopy

Photoabsorption is a transition process between quantum states. It excites a core/valence electron into a previously unoccupied ***bound states***, ***quasi bound states*** (excitation) or into the ***continuum*** (ionization, photoelectric effect).

A photon can be regarded as an **oscillating hammer** of which the oscillating electric field acts as a perturbation to the system (*the hammer knocks the electron out of the core orbital*)



Transition probability, partial and total absorption cross sections

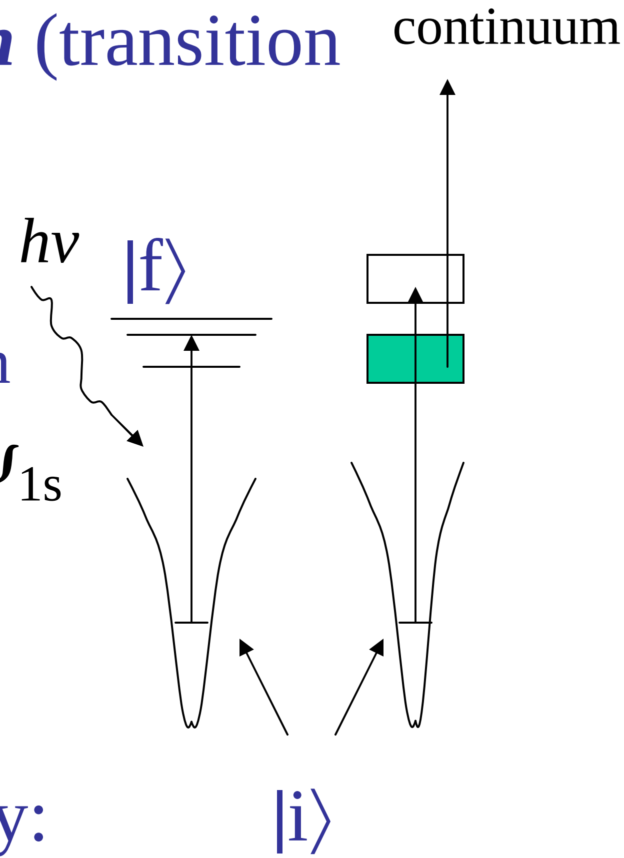
• Transition probability from a core level (partial absorption cross section) depends on the energy and symmetry of the initial and final states and the photon energy. Spectroscopy implication $\rightarrow$ ***intensity***

• At a given photon energy, all electrons in an atom with threshold energy less than the photon energy can be excited; the **total absorption cross section** is the **sum of all the partial absorption cross sections** of all levels involved a particular core level (1s, 2s etc.)

The ***partial absorption cross-section*** (transition probability) σ, can be expressed as

$$\sigma \propto |\langle i|\boldsymbol{\varepsilon}\cdot\mathbf{r}|f\rangle|^2 \rho(E_f)$$

Time-dependent perturbation



|i⟩: the initial state wave-function, e.g. ψ_{1s}

ε: electric vector of the synchrotron

r : the electric dipole vector

|f⟩ : the final state wave-function,

$\rho(E_f)$: the densities of states (occupancy: bands, unoccupied molecular orbitals and continuum states).

This expression is known as the Fermi’s golden rule.

Dipole selection rules are requirements of the angular momentum characteristic of the initial and final state for allowed transitions

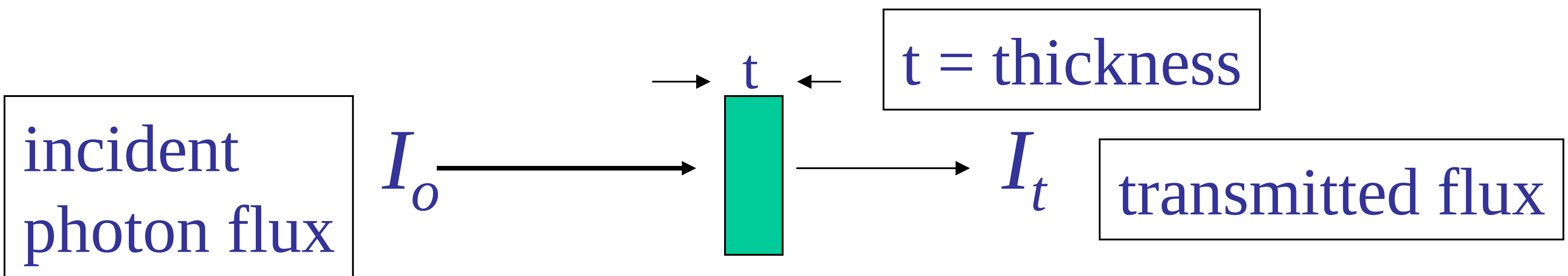
$$\Delta l = \pm 1, \Delta j = \pm 1, 0.$$

Thus, K (1s) and L_1 (2s) shell $(\ell = 0)$ absorption probes final states of p character and

$L_{3,2}$ shell ($2p_{3/2,1/2}$) $(\ell = 1,\ s = 1/2,\ j = 3/2, 1/2)$ probes final states with d and s character, in general p to d transition is a dominant process

Mass absorption coefficient

Mass absorption cross section is often expressed in barn/atom or cm^2/g; (1 barn = 10^{-24} cm^2)



$$I_t = I_o e^{\mu t}, \quad \mu t = ln\left(\frac{I_o}{I_t}\right), \quad \mu = \sigma\rho$$

absorption coefficient (cm^{-1})

mass absorption cross section (cm^2/g)

density (g/cm^3)

Note: μ or σ is a function of photon energy

Useful parameters

Transmission: % of incident photons transmitted for a given thickness of a uniform sample:

E.g. the transmission of 1000 eV photon through a 1 micron (10^{-4} cm) graphite film(normal incidence) is

$$transmission = \frac{I_t}{I_o} = e^{-\mu t} = e^{-0.363} = \cancel{0.886} = 69.6\%$$

$$\mu = \sigma\rho = (2.298 \times 10^3 cm^2 / g) \times (1.58 g / cm^3)$$

$$= 3.6308 \times 10^3 cm^{-1}$$

mass abs. coeff. density of graphite

$$\mu t = 3.6308 \times 10^3 cm^{-1} \times 10^{-4} cm = 0.368$$

Useful parameters

One-absorption length (*hv*): the thickness of the sample t_1, such that $\mu t = 1$ or $t_1 = 1/\mu$

E.g. the one absorption length of graphite at 1000 eV is

$$\mu = \sigma\rho = 3.36 \times 10^3 cm^{-1}$$

$$t_1 = 1/\mu = 1/3.63 \times 10^3 cm^{-1} = 2.98 \mu m$$

$$\frac{I_t}{I_o} = e^{-\mu t} = e^{-1} = 0.368$$

One absorption length corresponds to 37% transmission, 63% absorption

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One absorption length

This is also known as the 1/e attenuation length or simply **attenuation length** by which the incident photon flux has been attenuated to 1/e = 0.368 or 36.8 % of its intensity.

One absorption length is often used as an optimum length for the thickness of the sample in XAFS measurement for best signal to noise ratio

Representative absorption coefficients and one-absorption lengths.

Element	**Density**	**Energy**	**Mass abs. Coeff.**	**One-abs. length**
	(g/cm^3)	**(eV)**	**(cm^2/g)**	**(µm)**
Si	2.33	1840 (K)	3.32×10^3	1.3
		100 ($L_{3,2}$)	8.6×10^4	0.05
		30 (VB)	1.4×10^4	0.28
C(graphite)	1.58	300 (K)	4.01×10^4	0.16
		30 (VB)	1.87×10^5	0.034
Au		12000 (L_3)	1.796×10^2	2.88

↑ This provides info. about sampling depth

X-ray absorption is ideal for materials analysis, here is why

- Each element has its set of absorption edges (energy) and decay channels characteristic of the element
- Excitation channel specific (multi dimensional info)

  dipole selection rules, symmetry
- Sensitive to chemical environment (molecular potential)
- Tunability, high brightness, microbeam, polarization, time structure etc. provide many unprecedented capabilities for materials analysis

The absorption characteristics and the periodic table of the elements

low z elements: all levels are accessible with VUV (vacuum UV, 30 – 1000 eV) and soft X-rays (1000 – 5000 eV). In this region, absorption is the dominant process (measurement in high vacuum environment)

high z elements: deeper core levels are only accessible with hard X-rays (5000 eV to 40 keV). (measurements can be made in the ambient atmosphere)

Sources of information will be discussed below

The X-ray data booklet are provided in handouts

X-ray Reference Data

- X-ray data booklet (http://xdb.lbl.gov/)
- X-ray calculator (http://www-cxro.lbl.gov/)
- Mass absorption table (McMaster et al, 1969)
  (web: search for UCRL-50174)
- Photoionization cross section table (Yeh and Lindu)
- Radiative and radiationless yield table (Krause)

selected data from the X-ray booklet

1.1 Electron Binding Energy

1.2 X-ray Emission Energy

1.3 Fluorescence Yield for K and L Shells

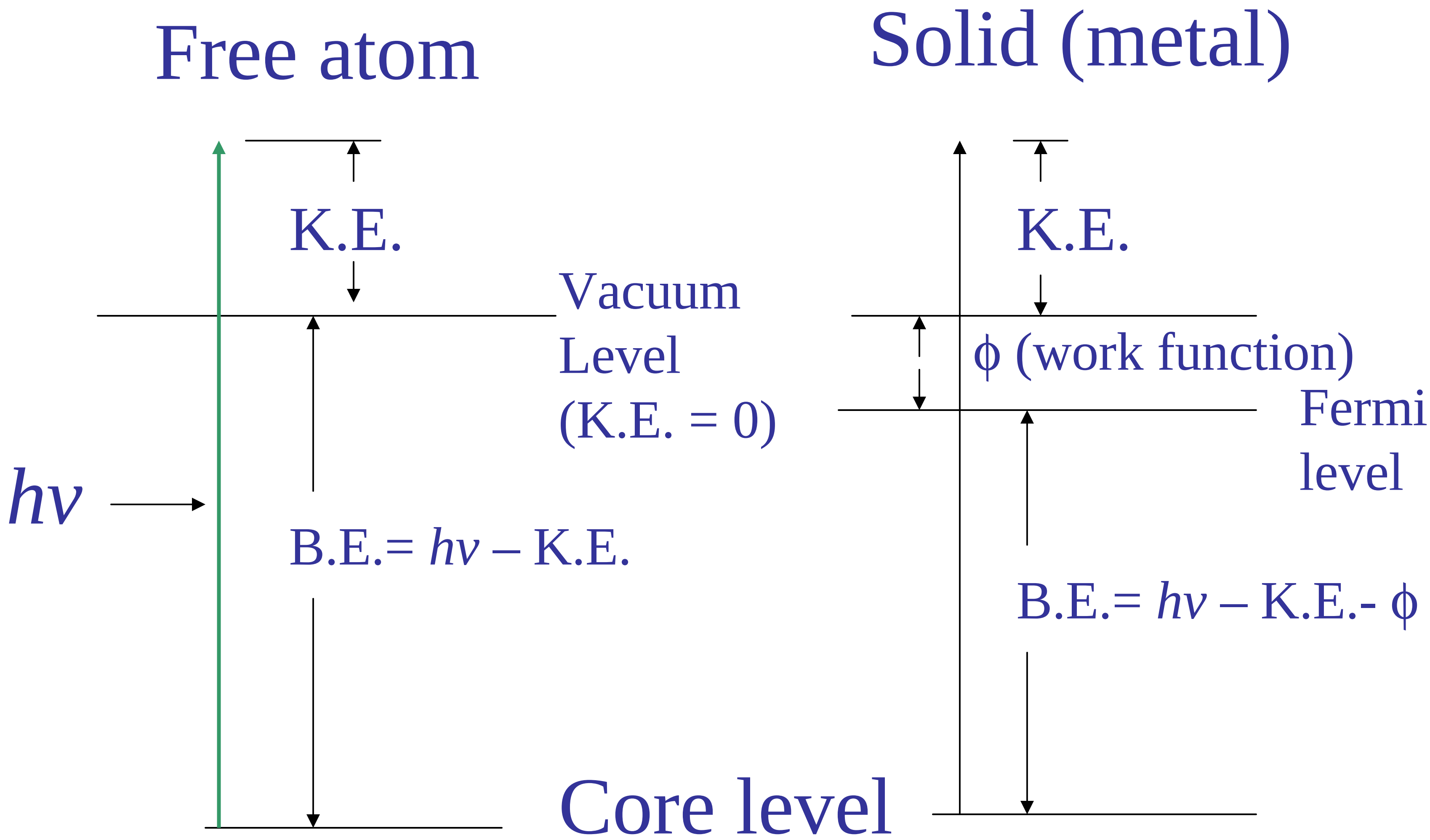
1.4 Principal Auger Electron Energies

1.5 Subshell Photoionization Cross Sections

1.6 Mass Absorption Coefficients

1.7 Atomic Scattering Factor

X-ray Binding Energy Table



Theory: RHF one electron energy, ε_i , i, core level of interest

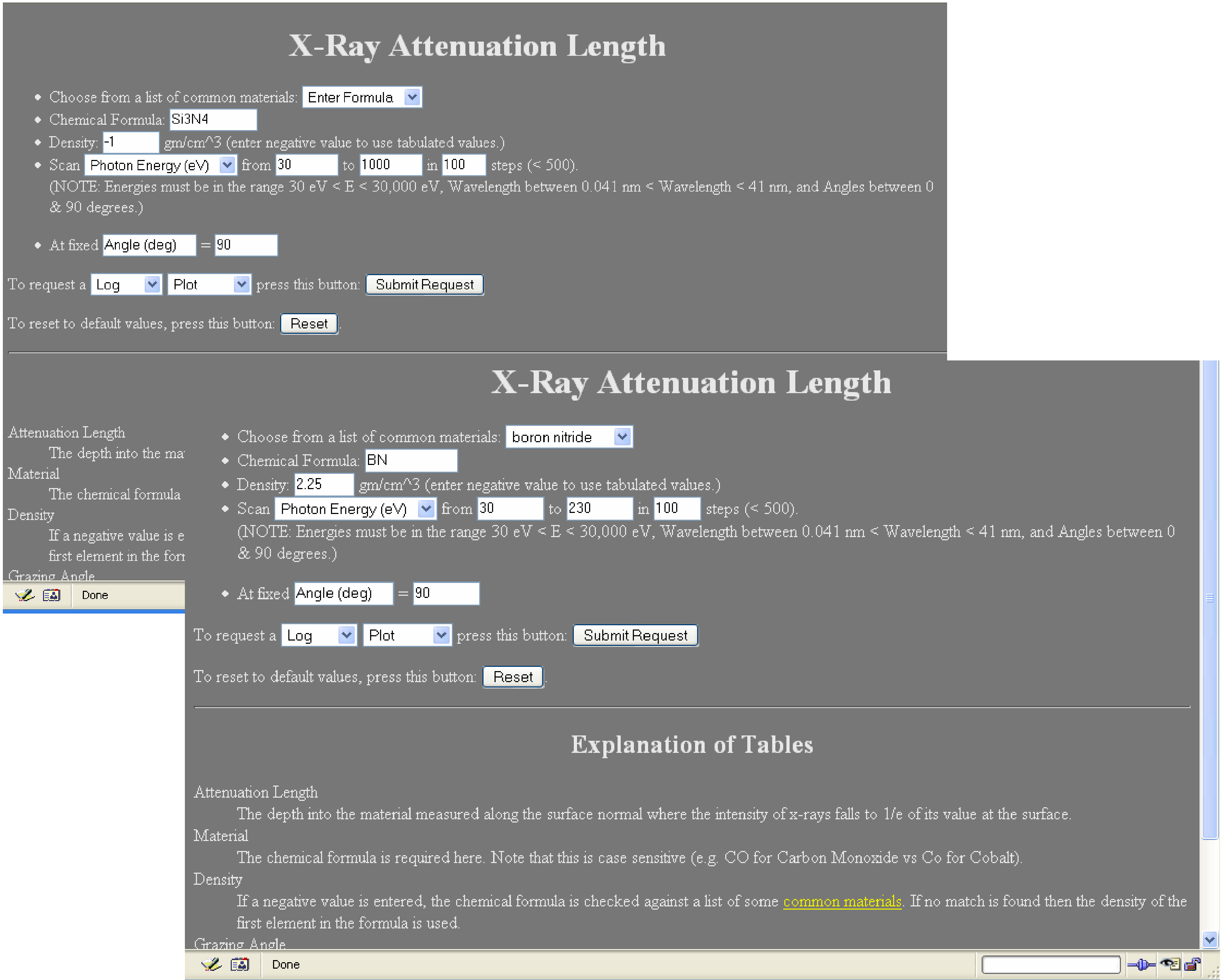
Calculation of X-ray absorption coefficient

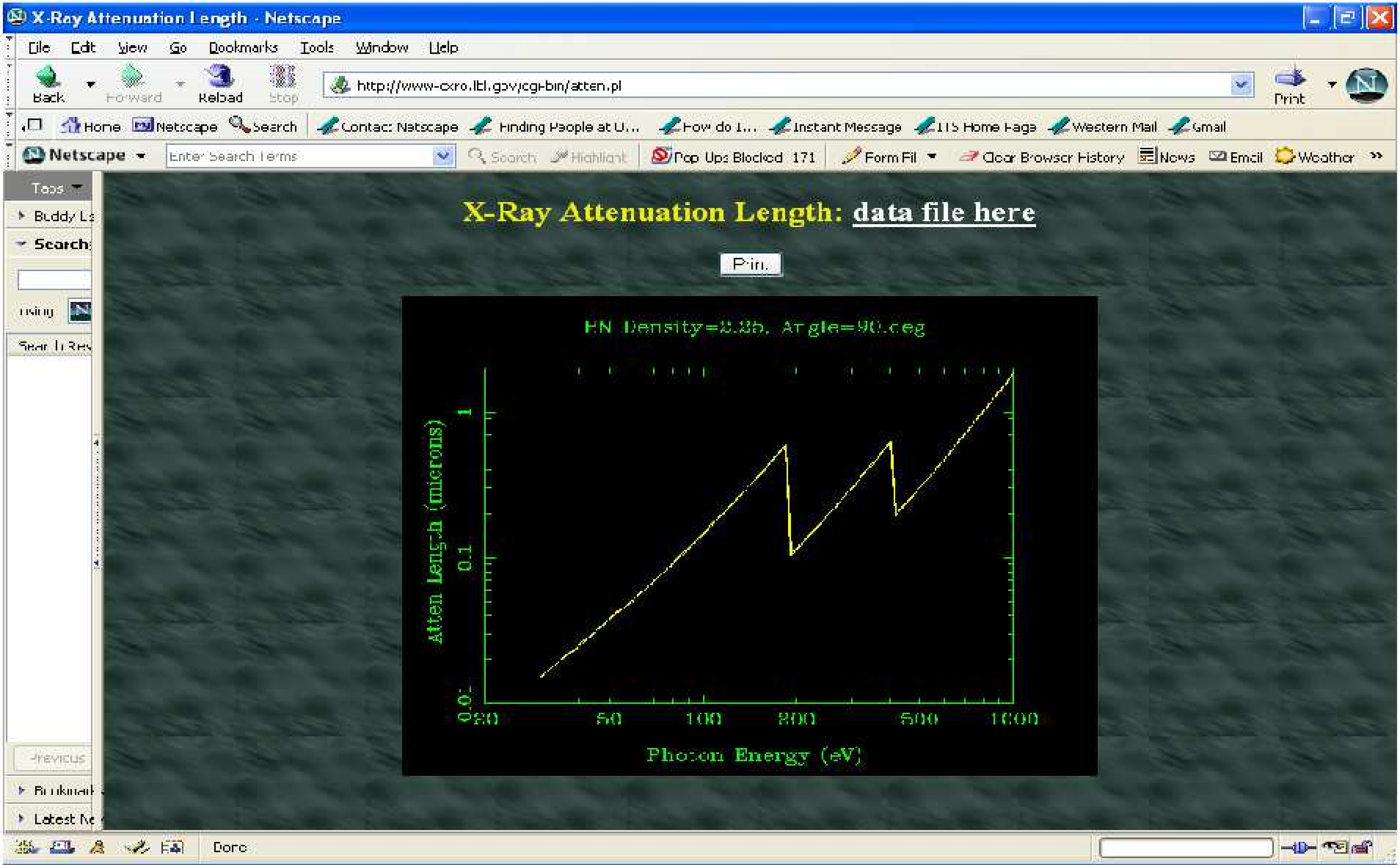
- The following web site http://henke.lbl.gov/optical_constants/ can be used to calculate absorption and related parameters based on **atomic cross-sections** (free atom! without the modulation by the chemical environment)

The X-ray calculator

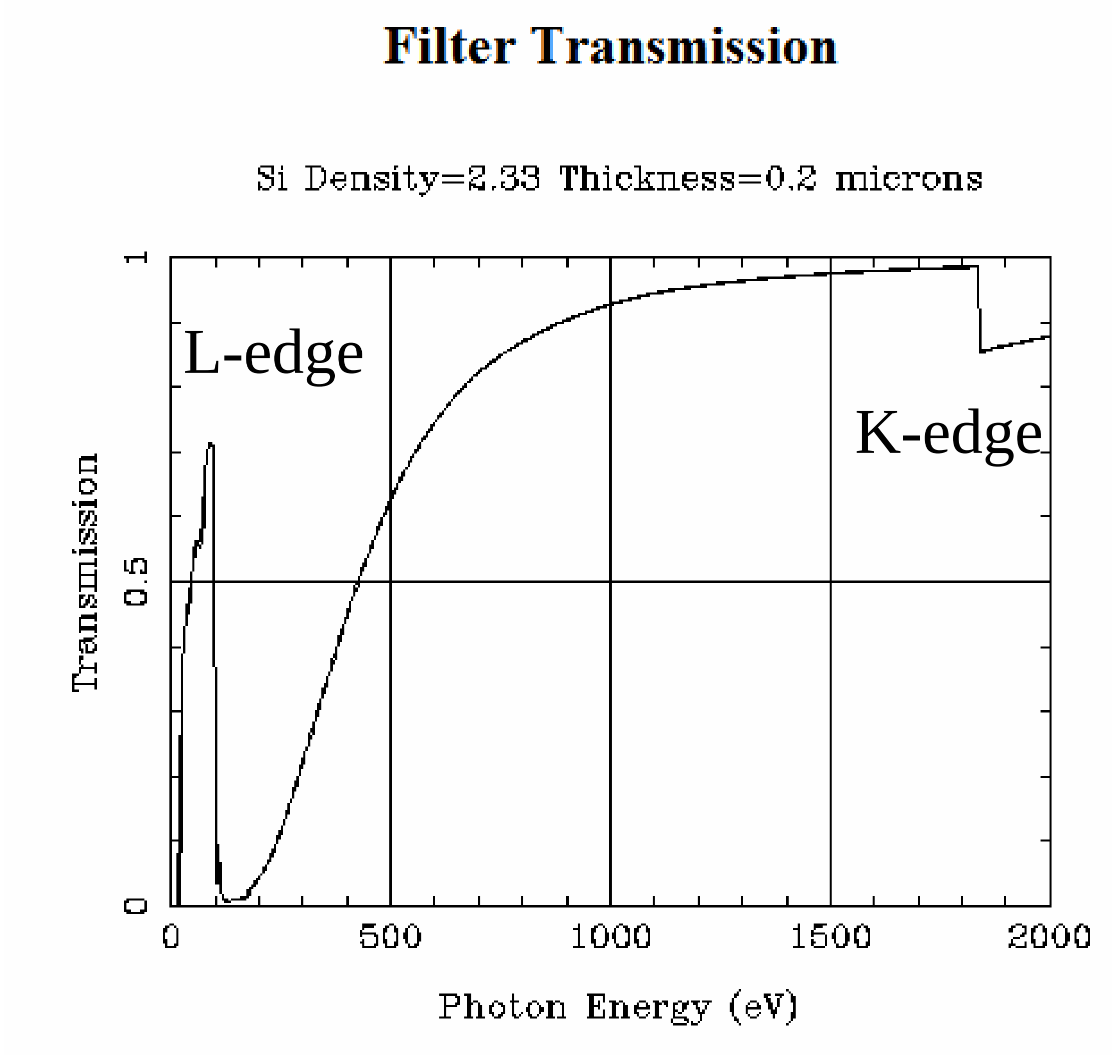
1. Go to the web: http://www-cxro.lbl.gov/
2. Click "x-ray tools" on the left panel
3. Click on " x-ray interaction with matter calculator" you will find the content of information from which
   x-ray properties of elements,
   attenuation length,
   transmission of gas and solid
   are most relevant to x-ray spectroscopy.

Exercise: Use the calculator to calculate the x-ray properties of the materials relevant to your research


X-Ray Attenuation Length
Choose from a list of common materials: Enter Formula
Chemical Formula: Si3N4
Density: -1 gm/cm^3 (enter negative value to use tabulated values.)
Scan Photon Energy (eV) from 30 to 1000 in 100 steps (< 500).
(NOTE: Energies must be in the range 30 eV < E < 30,000 eV, Wavelength between 0.041 nm < Wavelength < 41 nm, and Angles between 0 & 90 degrees.)
At fixed Angle (deg) = 90
To request a Log Plot press this button: Submit Request
To reset to default values, press this button: Reset.
Done
X-Ray Attenuation Length
Choose from a list of common materials: boron nitride
Chemical Formula: BN
Density: 2.25 gm/cm^3 (enter negative value to use tabulated values.)
Scan Photon Energy (eV) from 30 to 230 in 100 steps (< 500).
(NOTE: Energies must be in the range 30 eV < E < 30,000 eV, Wavelength between 0.041 nm < Wavelength < 41 nm, and Angles between 0 & 90 degrees.)
At fixed Angle (deg) = 90
To request a Log Plot press this button: Submit Request
To reset to default values, press this button: Reset.
Explanation of Tables
Attenuation Length
The depth into the material measured along the surface normal where the intensity of x-rays falls to 1/e of its value at the surface.
Material
The chemical formula is required here. Note that this is case sensitive (e.g. CO for Carbon Monoxide vs Co for Cobalt).
Density
If a negative value is entered, the chemical formula is checked against a list of some common materials. If no match is found then the density of the first element in the formula is used.
Done

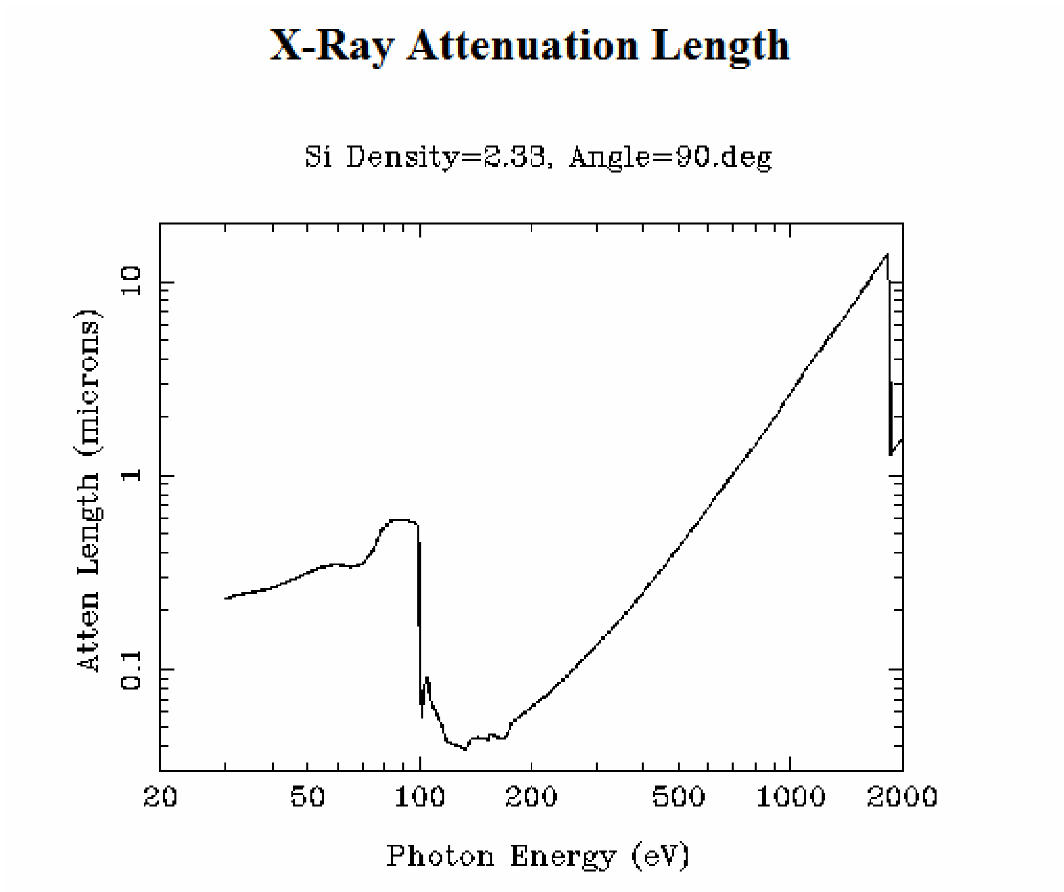

X-Ray Attenuation Length - Netscape
File Edit View Go Bookmarks Tools Window Help
http://www-cxro.lbl.gov/cgi-bin/atten.pl
X-Ray Attenuation Length: data file here
Print
Atten Length (microns)
1
0.1
0.01
20
50
100
200
500
1000
Photon Energy (eV)
Done

Example: Si



Filter Transmission
Si Density=2.33 Thickness=0.2 microns
Transmission
0
0.5
1
0
500
1000
1500
2000
Photon Energy (eV)
L-edge
K-edge

The attenuation length of Si



The attenuation length consideration is important in determining the thickness of the specimen in the XAFS measurements

What happens after absorption?

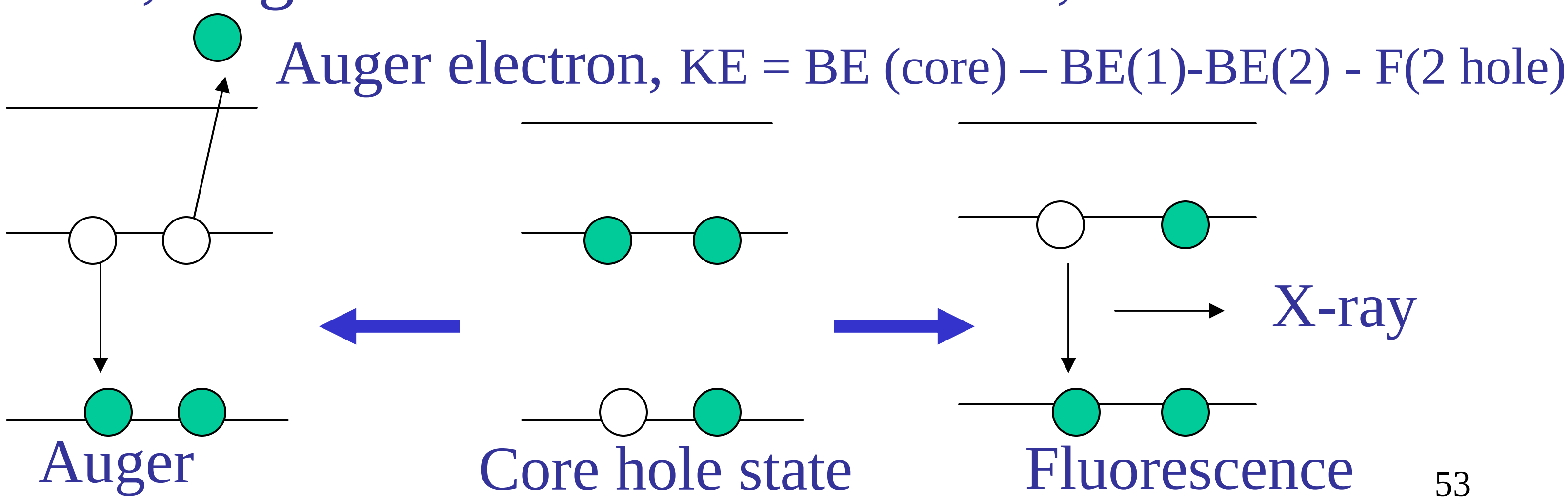
De-excitation of an atom with a core hole

Corehole decays via two primary processes:

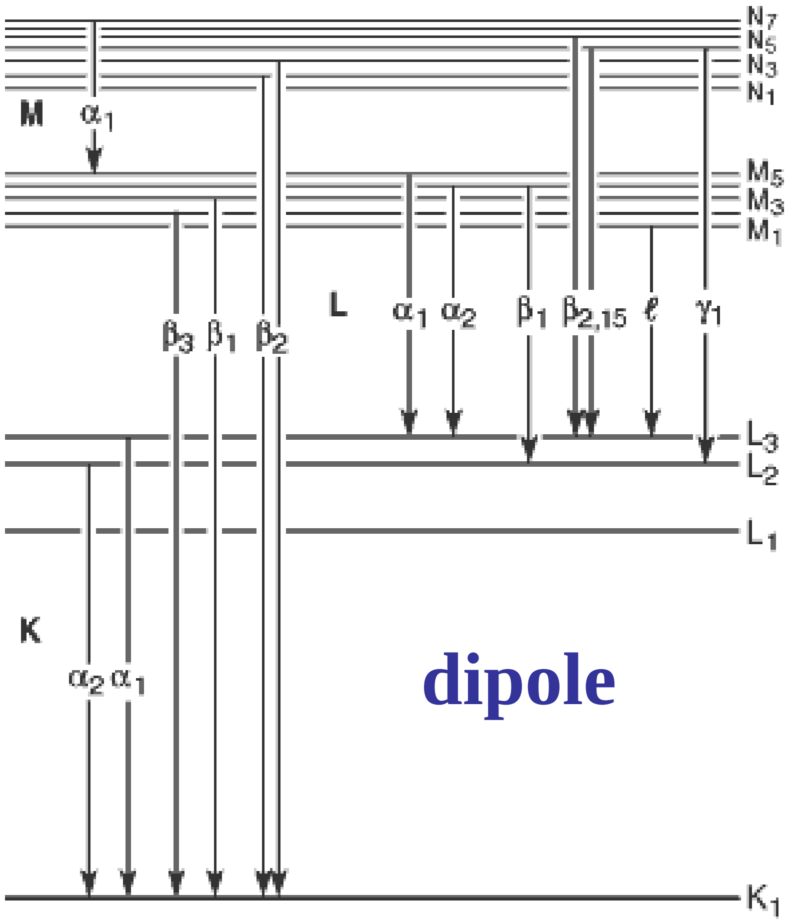
• **Auger** (electron channel, favorable route for shallow core levels, low z-elements)

• **X-ray Fluorescence** (photon channel, favorable route for deep core levels)

• Subsequent processes include cascade, defect formation, fragmentation of the molecule, luminescence

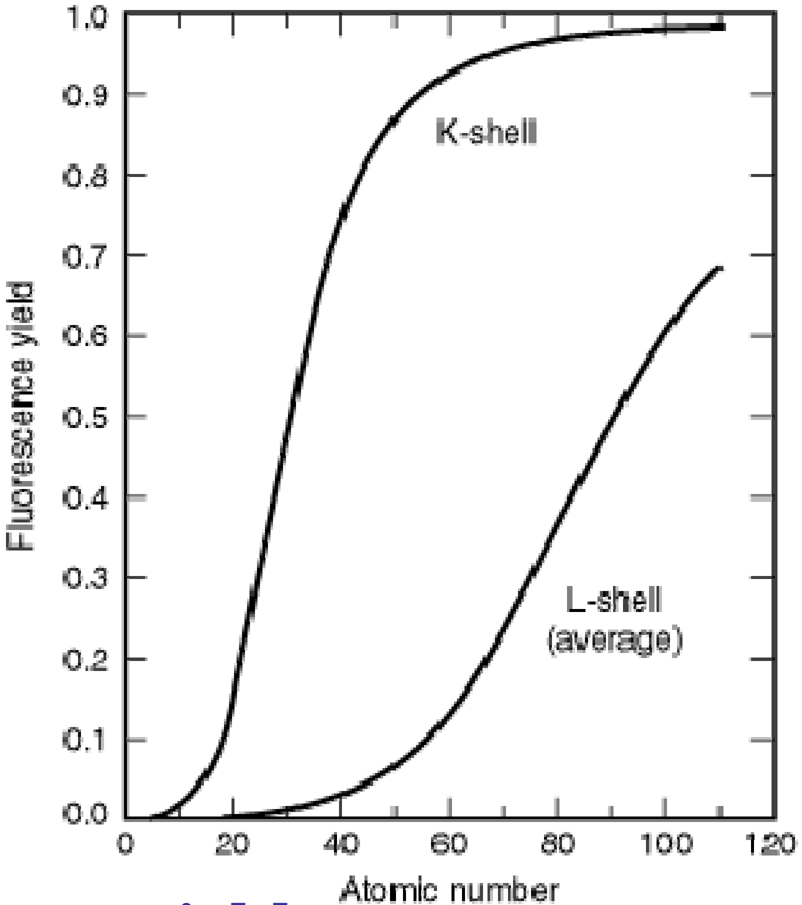


X-ray emission lines



dipole

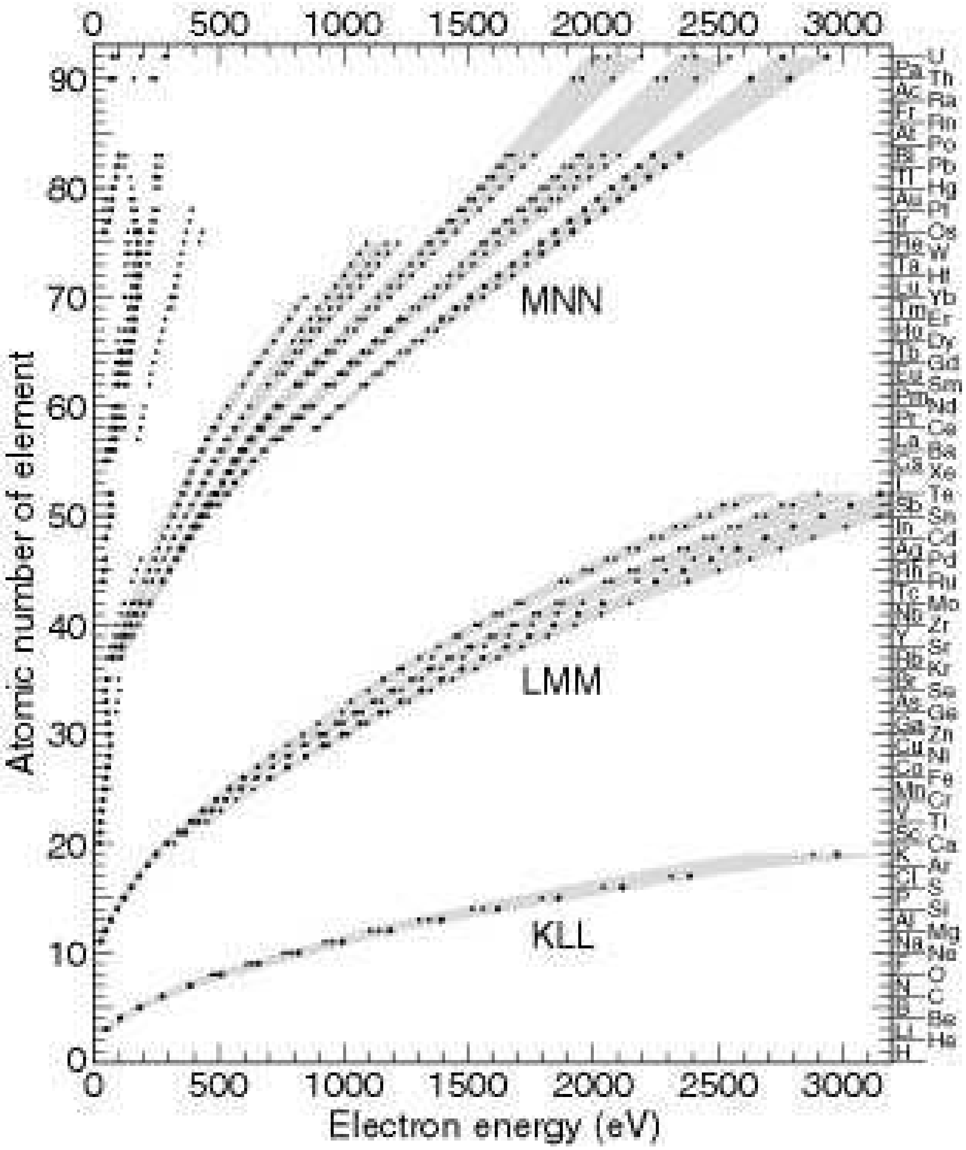
Fluorescence yield for K & L shells*



***Auger yield = 1- fluorescence yield**

Auger electron energies

KLL means the Auger process involves one L shell electron fills the 1s hole, the other L shell electron is ejected



LMM means the Auger process involves one M shell electron fills the 2s/2p hole, the other M shell electron is ejected