Chapter 2

Theoretical Framework for NEXAFS

This chapter is concerned with basic concepts and theories that form the foundation for the Near-Edge X-ray Absorption Fine Structure or NEXAFS. We begin the chapter with x-ray sources and interactions of x-rays with matter. Thereafter, we describe the x-ray absorption spectroscopy (XAS) in detail.

2.1 X-ray sources

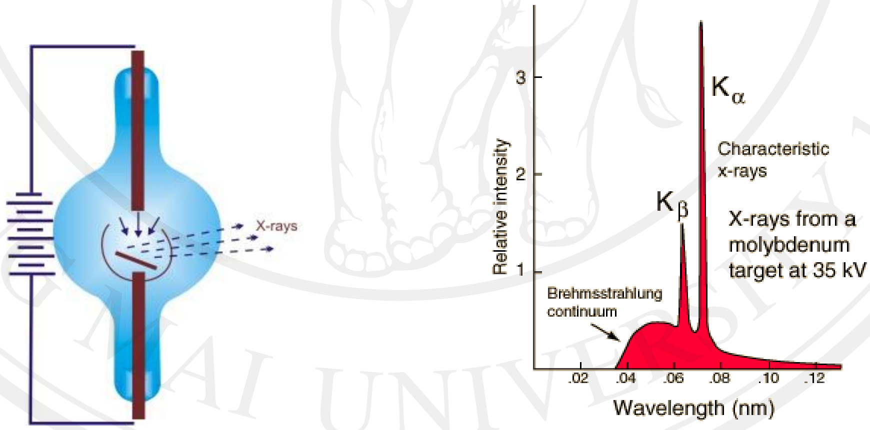
We will describe briefly about the 2 classes of x-ray sources; conventional source and synchrotron radiation sources.

2.1.1 Conventional X-ray sources

A conventional equipment for production of x-rays is an x-ray tube as shown in Figure 2.1(a) [9]. Inside an x-ray tube, which is a vacuum tube, there is an emitter, either a filament or a cathode as an electron source and an anode to collect the electrons. Thus a flow of electrical current, known as the beam, is established through the tube. A high voltage power source is connected across cathode and anode to accelerate the electrons. Electrons from the cathode collide with the tungsten (and sometimes molybdenum or copper) target deposited on the anode. There are two different atomic processes that can produce x-ray photons in the x-ray tube. One is emission from heavily accelerated of high energy charge particles called **Bremsstrahlung**. The other is emission from electron transition to the innermost energy level in the atoms called **K-shell emission**. They can both occur in heavy atoms like tungsten. About 1% of the energy generated is emitted/radiated, perpendicular to the path of the electron beam, as x-rays which form a typical spectrum shaped like a hump topped by several spikes as shown in Figure 2.1(b). The

X-ray spectrum depends on the anode material and the accelerating voltage. The hump is Bremsstrahlung radiation emitted by electrons as they are decelerated by their impact on a metal disk. Since the electrons undergo different degrees of deceleration in the metal, they give off different levels of energy in the form of x-rays, resulting the continuous spectrum, as the hump. The highest energy in the spectrum corresponds to the shortest wavelength in the beam. This maximum energy results from a high-speed electron being slowed to a full stop, converting all of its kinetic energy into radiation.

The spikes result from characteristic radiation. These rays are emitted when electrons are knocked out of their shells in a target atom, and the resulting vacancies are filled by other electrons. Characteristic radiation is not continuous, because target electrons from outer shells give off very specific amounts of energy as they drop into vacancies in lower-level (inner) shells.



(a) **(b)**

Figure 2.1: (a) schematic diagram of x-ray tube and (b) its spectrum [9].

2.1.2 Synchrotron radiation

The most important machine which generates x-rays as well as other electromagnetic radiations for scientific research is a synchrotron. The synchrotron is a large machine that accelerates electrons to almost the speed of light. As the electrons are deflected through magnetic fields they create extremely bright radiation.

Figure 2.2 shows a structure diagram of a synchrotron light source. Electrons are generated in the center (electron gun) and accelerated to 99.9997% of the speed of light by the linear accelerator (linac). The electrons are then transferred to the booster ring, where they are increased in energy. They are then transferred to the outer storage ring. The electrons are circulated around the storage ring by a series of magnets separated by straight sections. As the electrons are deflected through the magnetic field created by the magnets, they give off electromagnetic radiation, called synchrotron radiation. The radiation is emitted in a narrow cone in the forward direction, at a tangent to the electron's orbit. The radiation is unique in its intensity and brilliance and it can be generated across the range of the electromagnetic spectrum: from infrared to x-rays.

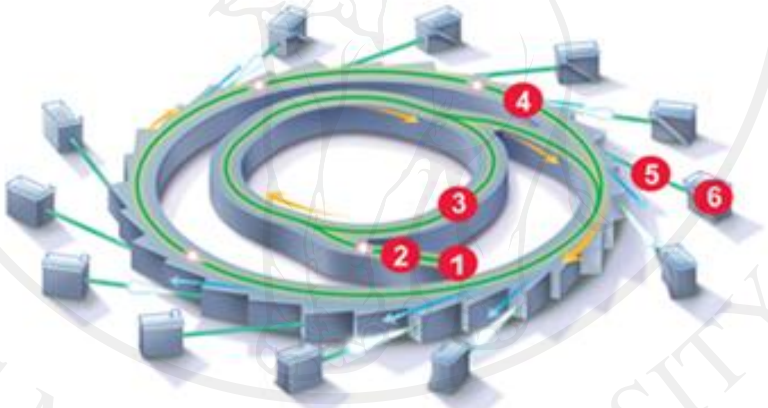
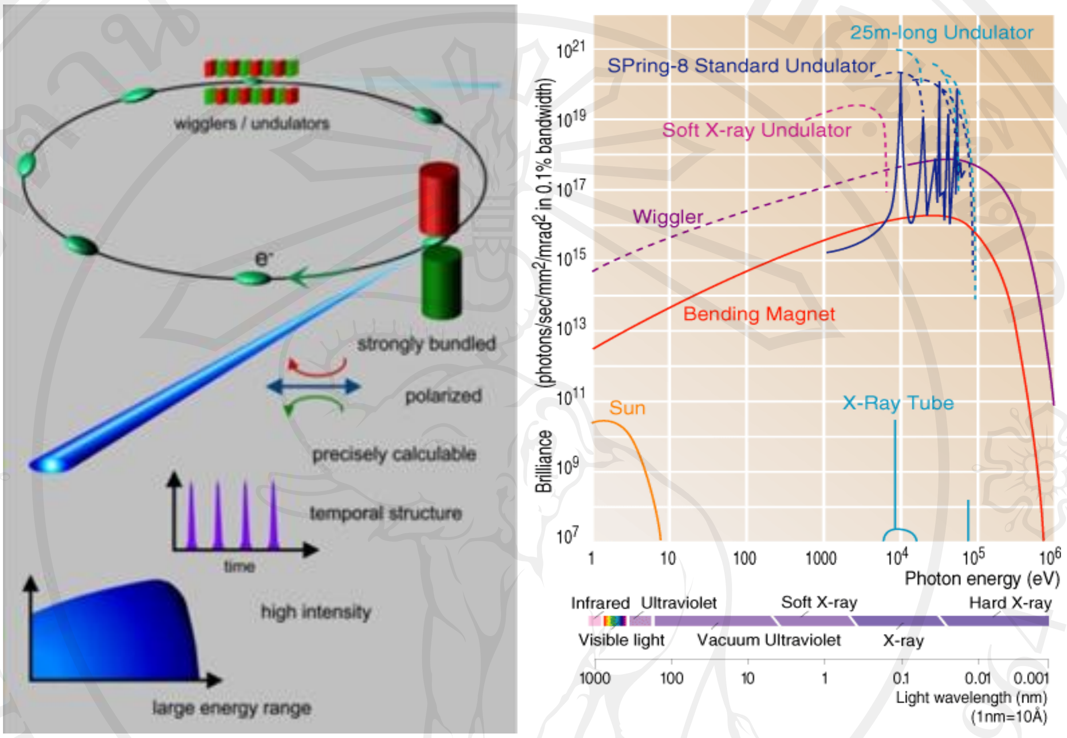


Figure 2.2: Structure diagram of synchrotron light source [10]:
1. electron gun, 2. Linac, 3. booster ring, 4. storage ring, 5. Beamline, 6. end station.

The diagram in Figure 2.3(a) shows the generation of synchrotron radiation while Figure 2.3(b) shows spectra of synchrotron radiation. At each deflection of the electron path a beam of light is produced. The effect is similar to the sweeping of a search light. The radiation is then channelled down beamlines to endstations where it is used for research.



(a) **(b)**

Figure 2.3: (a) Generation of synchrotron radiation and (b) its spectra [11].

2.2 X-ray Interaction with Matters

X-ray interactions are important in diagnostic examinations and in scientific research for many reasons. For example, the selective interaction of x-ray photons with the structure of the human body produces the image; the interaction of photons with the receptor converts an x-ray image into one that can be viewed or recorded. For scientists, they interest in radiation and particles produces by the interaction of x-rays and matter which those provide information about nature of the matter they were studied. Since the quantum energies of x-ray photons are much too high to be absorbed in electron transitions between states for most atoms, they can interact with an electron only by knocking it completely out of the atom. That is, all x-rays are classified as **ionizing radiation.** This can occur by giving all of the energy to an electron (photoionization) or by giving part of the energy to the electron and the remainder to a lower energy photon which is called **Compton scattering**. The schematic diagrams in Figure 2.4 show x-ray ionization and emission processes in an atom.

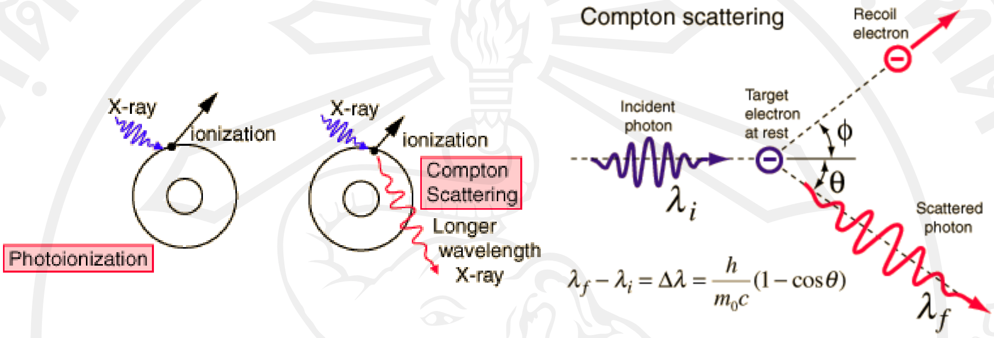


Figure 2.4: X-ray ionization and emission processes in isolated atoms [12].

Since the x-rays have high energy, the electrons in which x-rays can knock it out of atom are deeply level electrons called core electrons. A term “core hole” was introduced to call a situation of loss of core electron in an atom, showing in Figure 2.5(a). An atom with core hole is extremely unstable. The life time of the core hole is of the order of 10^{-15} s or 1 fs. There are two major decay processes: fluorescence and Auger. In fluorescence (Figure 2.5(b)), another electron of the atom fills the core hole. This process can only occur if the energy of the electron is higher than the core hole.

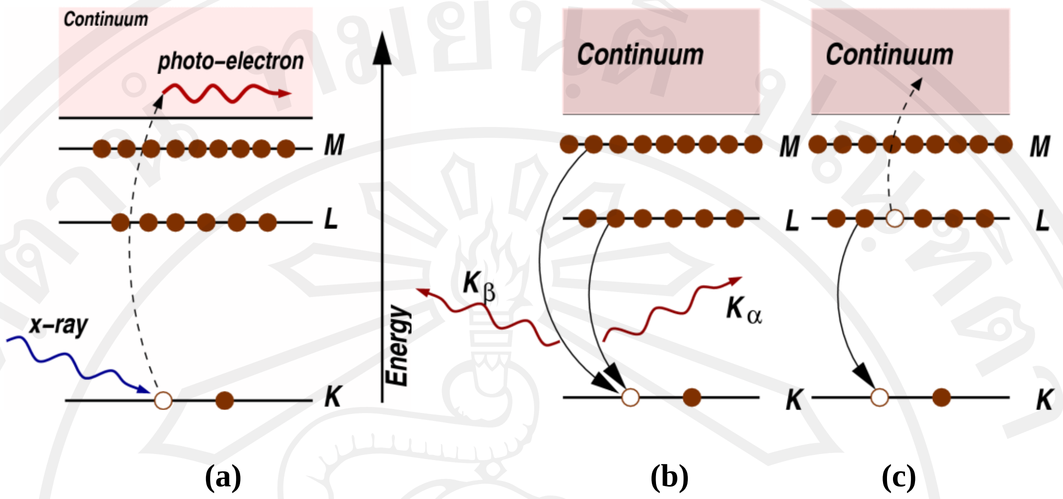


Figure 2.5: (a) Photoelectric effect of core-level electron, (b) decay of the excited state by x-ray fluorescence, and (c) decay of the excited state by Auger effect [13].

In other words, a shallow core electron can fill a deep core hole. Also a valence electron can fill a core hole. The energy difference between these two states is released as electromagnetic radiation. In most cases, this will be x-rays, but very shallow level will release ultraviolet radiation or light. The second process is Auger decay,shown in Figure 2.5(c). When an electron from the 2p shell drops to fill a vacancy formed by 1s shell ionization, the resulting x-ray photon with energy $E_{2p} - E_{1s}$ may excite a third electron, for example, anther 2p electron. Such a process can be denoted as a 1s2p2p Auger process. The probability of Auger electron production increases as the difference between the energy states of the shell decreases. Light elements are more susceptible to the formation of Auger electrons by multiple ionizations. Thus the proportion of radiation emitted at characteristic wavelengths is lower than for heavier elements. Relationship between fluorescence yield and Auger yield and the atomic number of target atoms is shown in Figure 2.6.

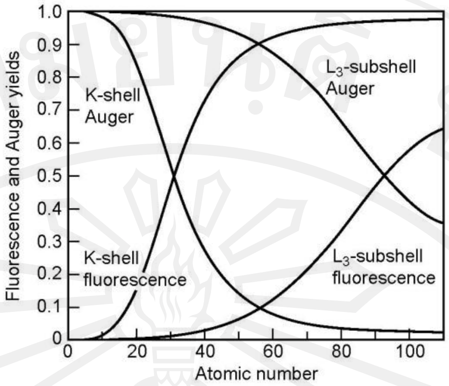


Figure 2.6: Fluorescence and Auger yield relate to atomic number of target atoms [14].

2.3 X-ray Absorption Spectroscopy (XAS)

Several ways to do the analysis based on the absorption of x-ray by individual atoms had grown strong in the past few decades. Besides complementing the other crystallographic techniques, the analysis of materials by their characteristic x-ray absorption “fingerprints” has several decided advantages. For example, the local atomic environment can be determined separately for each type of atom in a chemical compound, and the material does not need an ordered structure. Atoms in an amorphous materials or biological molecules can then be investigated. The information can be obtained for each type of atom separately by tuning the x-ray energy to coincide with the absorption edges of just one type of atom at a time.

This information about the geometrical arrangements around an atom can be found in the fine structures at the absorption edge of an x-ray absorption spectrum. X-ray Absorption Spectroscopy (XAS) provides information about the nature of the empty molecular orbitals of the absorbing atom. The number of empty molecular orbitals and their energy positions are characteristic for different chemical species. XAS is therefore a technique for identifying different molecular species.

2.3.1 X-ray absorption coefficient vs photon energy

When a beam of monochromatic x-ray goes through a matter, it loses its intensity due to interaction with the atoms in the material. For an homogeneous medium, the x-ray intensity drops exponentially with and transmitted intensity is

$$I = I_0 e^{-\rho \mu d} \tag{2.1}$$

Where I and I_0 are the transmitted and the incident x-ray intensities respectively, ρ is the mass density, μ is the absorption coefficient and d is the thickness of the sample. The absorption coefficient will decrease smoothly with higher energy, except for certain photon energies, as shown in Figure 2.7. When the photon energy reaches the critical value for a core electron transition, the absorption coefficient increases abruptly. These abrupt increases in absorption occur whenever the incident photon has just enough energy to promote a core electron to an unoccupied valence level or into the continuum (leave the atom). The probability to eject an electron is largest when the photon energy is sufficient for the transition process. After each absorption edge the absorption coefficient will continue to decrease with increasing photon energy [1].

The loss in intensity can also be expressed in terms of the photoabsorption cross-section, σ_{abs} by the following expression:

$$I = I_0 e^{-n_a \sigma_{abs} d} \tag{2.2}$$

where I and I_0 are the transmitted and the incident x-ray intensities, n_a is the atomic density and d is the thickness of the sample. The difference between the two expressions, (2.1) and (2.2) is that (2.1) is a macroscopic description of the photoabsorption process and involve atoms in a particular solid material or molecular form, while (2.2) is a microscopic description of the same process but for single isolated atoms. One benefit in the microscopic description is the possibility to separate the contributions of the various atomic subshells [14].

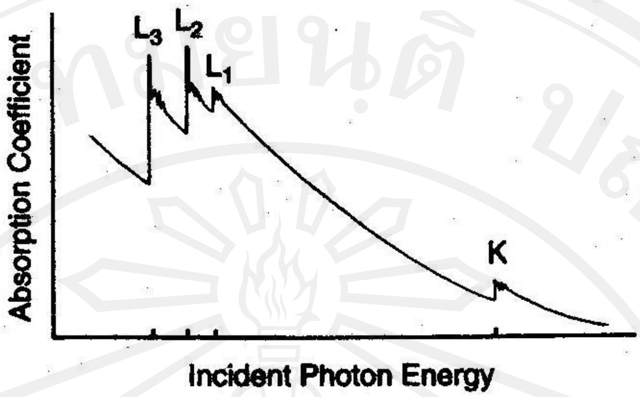


Figure 2.7: X-ray absorption [15].

2.3.2 X-ray absorption measurements

XAS measure the energy dependence of the x-ray absorption coefficient μ(E) at and above the absorption edge of a selected element. A schematic of experimental setup shown in Figure 2.8.

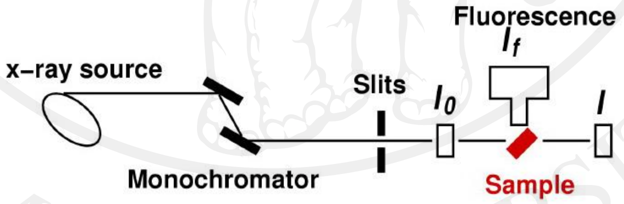


Figure 2.8: Schematic diagram of x-ray absorption experiment [16].

The absorption coefficient μ(E) can be measured in two ways, transmission mode and fluorescent mode. In transmission mode, the absorption is measured directly by measuring what is transmitted through the sample. Intensity of x-rays before (I_0) and after (I) pass a sample is measured at a certain value of photon energy *E*. The x-ray photon energy *E* is scanned by rotates the monochromator. Then we got μ(E) (2.1):

$$\mu(E) \propto -\ln(I/I_0). \tag{2.3}$$

In fluorescence mode, the re-filling deep core hole is detected. Typically, the fluorescent x-ray intensity (I_f) is measured, but sometimes emitted electron can be measured. Since fluorescence is proportional to absorption events, so

$$\mu(E) \propto I_f / I_0 . \tag{2.4}$$

X-rays intensity can also be measured by an ionization chamber. The ionization chamber is filled with an inert gas (e.g. N_2). When an x-ray beam enter a chamber, gas molecules absorbs the x-rays, ejecting electrons and ions, which ionize more gas molecules. Number of electrons and ions generated depend on x-ray energy and intensity. A voltage applied across the chamber collect the electrons, giving a total current. An x-ray absorption spectrum as shown in Figure 2.9 can be obtained from a measurement in fluorescent mode by plotting I_f / I_0 or μ on the vertical axis and incident energy on the horizontal axis.

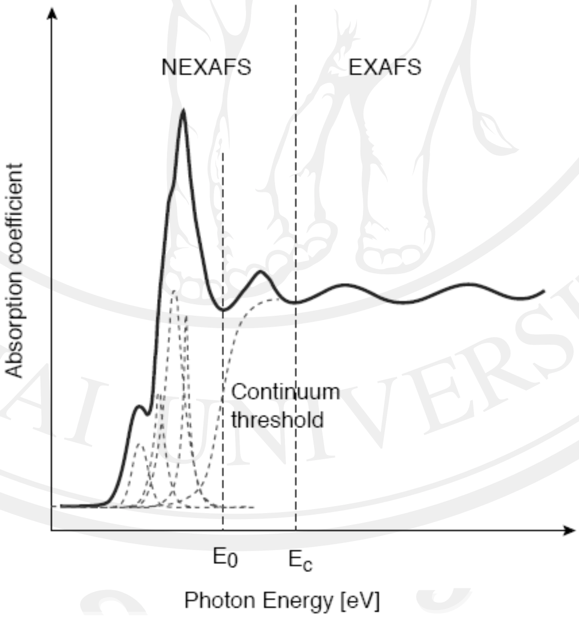


Figure 2.9: In an x-ray absorption edge there are discrete structure from core electron transition (dotted line) superimposed. The photon ionization energy (E0) is the threshold energy the ptotoelectron need to have escape into continuum and Ec is the critical energy value for EXAFS [3].

2.3.3 X-ray absorption spectrum and the absorption edge

In an x-ray absorption spectrum, as shown in Figure 2.9, there are three distinguishable parts: the low-energy NEXAFS (Near Edge X-ray Absorption Fine Structure) region with discrete structure from core electron transitions superimposed, the NEXAFS region with multiple scattering processes in the continuum (between E_0 and E_c), and the EXAFS (Extended X-ray Absorption Fine Structure) region with single scattering processes at higher energies.

The absorption edge structure often consists of discrete absorption bands superimposed on the steeply rising continuum absorption edge. These discrete absorption bands are caused by transitions of core electrons to discrete bound valence levels. The absorption edges that are of most interest are the K-edge (1s – 3p), followed by the three L-edges: L1-edge (2s – 5p), L2-edge ($2p_{1/2}$ – $5d_{3/2}$) and L3-edge ($2p_{3/2}$ – $5d_{5/2}$) [17]. These edges are element specific and shifts to higher energies when the atomic number increases. Since the core levels depend on the element and its chemical environment, they also show chemical specificity. X-ray absorption spectroscopy is therefore not only an element specific technique, but it is also sensitive to the immediate environment of the absorbing atom.

X-ray energy range of 3 – 30 keV results in accessibility of K-edges from roughly chlorine to silver. The L-edge of elements from molybdenum through the actinides also falls within this energy range. Radiation in the range of 0.1 – 3 keV will make it possible to do XAS studies of the lower atomic number elements such as carbon, nitrogen and oxygen. The availability of third generation synchrotron sources now allows the routine performance of XAS investigations using K absorption edges occurring even above 30 keV. Measurements made at absorption edges in the energy range 40 keV to 90 keV have successfully been accomplished. That means that XAS spectrum at K-edge of lead (88.0 keV) has been measured.

2.3.4 X-ray absorption processes

Electrons can be treated as either a particle or a wave, and to understand the different phenomenon of XAS the emitted photoelectrons need to be treated as a wave. The wavelength λ and the momentum p of an electron are related by the de

Broglie equation,

$$\lambda = \frac{h}{p}, \tag{2.5}$$

where h is the Planck's constant. By defining the magnitude of wave vector k of the electron as

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{\lambda}. \tag{2.6}$$

Then the kinetic energy of an electron is

$$E_k = \tfrac{1}{2} m v^2 = \frac{p^2}{2m} = \left(\frac{h}{2\pi}\right)^2 \frac{k^2}{2m}. \tag{2.7}$$

For an emitted photoelectron the kinetic energy is given by

$$E_k = E - E_0 = h\nu - E_0 \tag{2.8}$$

when E is the energy of the incident x-ray and E_0 is the threshold energy which the photoelectron needs to have in order to escape into the continuum. The x-ray energy is quantized with Planck's constant h and the frequency ν.

An expression of the wave vector for the emitted photoelectron as a function of the incident photon energy hν becomes

$$k = \sqrt{\left(\tfrac{2\pi}{h}\right)^2 2m(h\nu - E_0)} \tag{2.9}$$

Equation (2.9) indicates that there are three types of excited photoelectrons, described in Figure 2.10. The first type is the excited photoelectron which does not have enough energy to leave the absorbing atom and k from (2.9) is invalid (usually referred to as k = 0). That electron will do a transition to one of the unoccupied valence states. These transitions will give rise to edge peaks, i.e. peaks before the continuum threshold (ionization threshold) located at the energy value E_0. This energy value E_0 is the threshold energy the photoelectron needs to have if it will escape into the continuum (leave the atom). The second type of excited photoelectrons has energy enough to escape into the continuum therefore $k > 0$. However, the kinetic energy of the photoelectrons are low (10 – 40 eV), and the excited photoelectrons are strongly backscattered by the neighboring atoms. When the incoming x-ray has the critical energy value E_c, the wave vector of the photoelectron will have the critical value k_c =

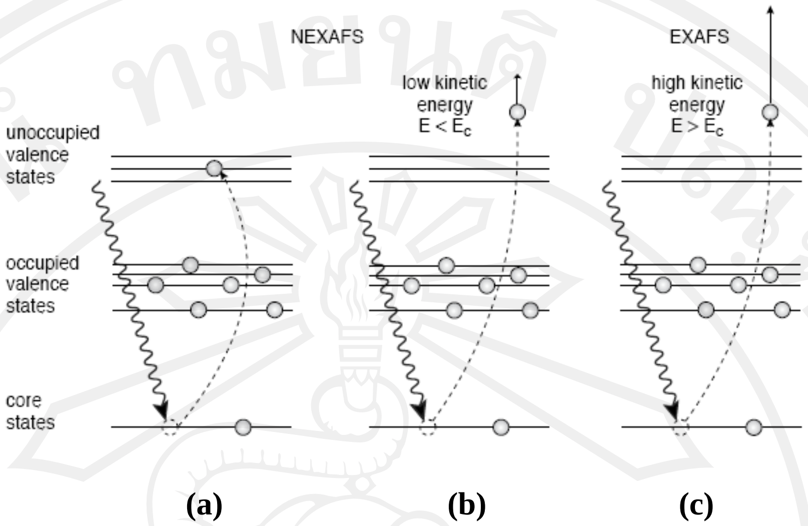


Figure 2.10: There are three types of excited photoelectrons: (a) Low-energy NEXAFS when $E = E_0$, (b) NEXAFS when $E_0 < E < E_c$ and (c) EXAFS when $E > E_c$. [3].

2/*R*. The photoelectron wave will then have a wavelength same as the distance to the closest of the neighboring atoms, see Figure 2.11. Actually, the photoelectron will be part of a multiple scattering process and involve several neighboring atoms, see Figure 2.12(a). All of these scattering pathways will contribute to the fine structure near the absorption edge. An excited photoelectron, with high kinetic energy, will then be weakly backscattered by only one of the neighbor atoms, and hence a single scattering process will occur, see Figure 2.1(b). A single scattering process will give rise to fine structures ~50 – 1000 eV after the absorption edge (EXAFS), while multiple scattering process will give rise to fine structures ~10 – 50 eV after the edge (NEXAFS).

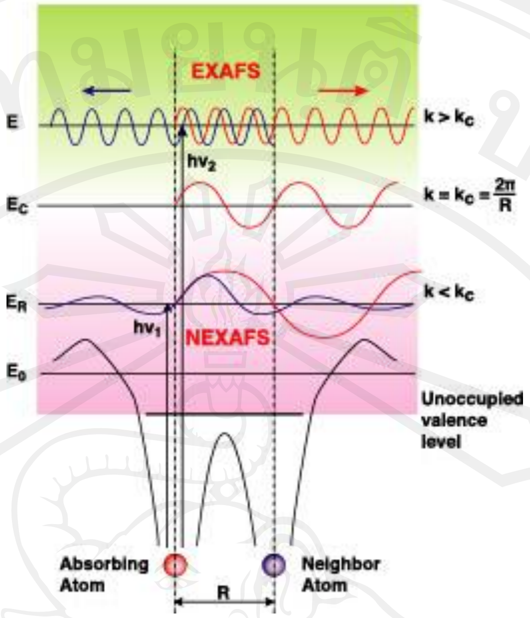
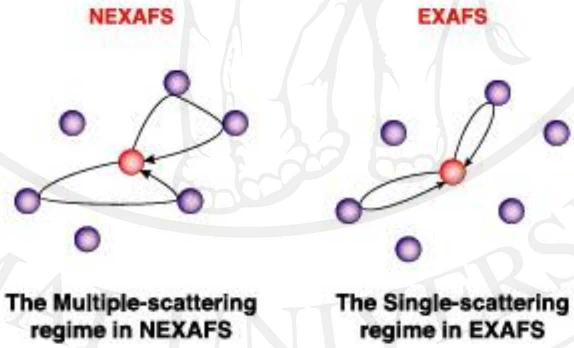


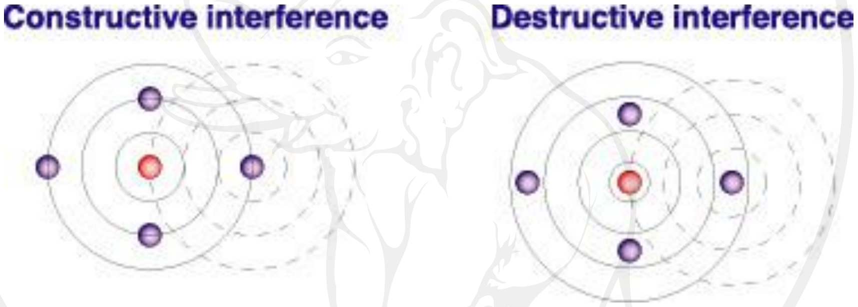
Figure 2.11: Excitation in a diatomic molecule (excitations at low energies: NEXAFS region and excitations at high energies: EXAFS region). When $k = k_c = 2/R$, the NEXAFS merge into EXAFS [1]



(a) (b)

Figure 2.12: Photoelectron scattering processes [1].

The probability that a core electron will absorb an x-ray photon depends on both the initial and the final states of the atom. If the core electron is excited to the continuum, the initial state corresponds to the ground-state atom and the final state includes both the ionized atom and the photoelectron wave. If the absorbing atom has a neighboring atom, the outgoing photoelectron wave will be backscattered, thereby producing an incoming electron wave. The final state is then the sum of the outgoing and all the incoming waves, one from each neighboring atom. Depending on the wavelength of the photoelectron and the length of the scattering pathway, the scattered wave can interfere constructively or destructively with the photoelectron wave at the absorbing atom, see Figure 2.13. This interference will affect the absorption cross section, since the cross section is proportional to the matrix element $<\Psi_i| r |\Psi_f>$, where $<\Psi_i|$ and $|\Psi_f>$ represent the initial and final states of the system, respectively, and r is the distance between the absorbing atom and the neighboring atom. The interference between the outgoing and the incoming waves give rise to a sinusoidal variation of the absorption coefficient μd versus the photon energy E of EXAFS and is described more in detail in [1].



(a) **(b)**

Figure 2.13: The photoelectron wave (solid circles) can be backscattered from the neighboring atoms (dotted circles) and interfere with the photoelectron wave at the absorbing atom. Depending on the wavelength of the photoelectron and the length of the scattering pathway, the scattered wave can interfere constructively or destructively with the photoelectron wave at the absorbing atom [18].

In summary, the analysis of the edge region (NEXAFS) is essentially a spectroscopy. The position , the edge and the assignment of peaks near or on the edge give information about oxidation state, covalency (increasing ligand character of metal d orbitals), molecular symmetry of the site, and thereby coordination number. The EXAFS provides direct, local structural information about the atomic neighborhood of the element being probed (usually a metal). The information content consists of numbers of ligands (coordination number), the identity of the ligand atoms, and precise radial distances. It can be particularly informative when there are other metals in the atomic neighborhood of the metal being probed (as in clusters).

2.4 NEXAFS Applications

Common applications of NEXAFS can be categorized as the following [1].

- The determination of local geometry of atomic arrangements in complex systems by analysis of multiple-scattering resonances and core excitons.
- The determination of the effective atomic charge on the absorbing atom.
- The determination of local electronic structure in metallic systems.

2.5 NEXAFS Interpretation

The interpretation of NEXAFS is complicated by the fact that there is not a simple analytic (or even physical) description of NEXAFS. It has been reported that the edge position and shape is sensitive to formal valence state, ligand type, and coordination environment [2]. There is a long practice of correlating formal charge state with absorption edge shifts [19]. Therefore, a common application of NEXAFS is to use the shift of the edge position to determine the valence state. However, it has also been suggested that edge shift can be driven solely by bond length. Thus, it is difficult to experimentally distinguish between the direct correlation (formal-charge → edge-shift) and the indirect one (formal-charge → bond distance → edge-shift). Pre-edge transitions are often found in transition metal NEXAFS spectra which can be used as an indicator of local site symmetry and orbital occupancy. The heights and positions of pre-edge peaks can also be reliably used to empirically determine oxidation states and coordination chemistry. These approaches of assigning formal valence state based on edge features and as a fingerprinting technique make NEXAFS somewhat easy to crudely interpret, even if a complete physical understanding of all spectral features is not available.

The edges often show strong peaks at the top of the edge. The existence of a sharp intense absorption band indicates the final state electron is highly confined by the potential that it sees. This can be due to empty bound atomic states of the right symmetry for a dipole allowed transition. Suppose you have a free atom that has a bound but empty *p* symmetry state. This will show up as an intense peak at the absorption edge. If that atom were placed into a material, the tails of its attractive potential would be truncated by the attractive potential of the neighboring atoms, allowing the final state electron wave to leak out of the confining central atom potential, which would broaden the bound state into a resonance. The sharp peak at the edge would be smoothed out and suppressed, at least as far as the central atom absorption μ_o is concerned.

It is often useful to fit an unknown spectrum to a linear combination of known spectra. For many systems, such analysis based on linear combinations of known spectra from “model compounds” is sufficient to tell ratios of valence states and/or phases. More sophisticated linear algebra techniques such as Principle Component Analysis and Factor Analysis can (and are) also be applied to NEXAFS spectra.

For NEXAFS, precise and accurate calculations/interpretation of all spectral features are still difficult, time-consuming, and not always reliable. This situation is improving through the quantitative analyses of NEXAFS using ab initio calculations. Such calculations would help explain which bonding orbitals and/or structural characteristics give rise to certain spectral features.