

Lab 1 – Module α_1
Electron Energy Levels

OBJECTIVES

- ✓ Review electronic structure concepts
- ✓ Learn principles of x-ray photoelectron spectroscopy
- ✓ Investigate electron energy levels in various solids

SUMMARY OF TASKS

- 1) Obtain XPS core and valence band spectra for all samples
- 2) Compare valence band spectra of metals, semiconductors and insulators
- 3) Estimate the band gaps for oxide and semiconductor samples
- 4) Determine scaling of electron energies with atomic number

BACKGROUND

Electronic Shells and Atomic Orbitals

As we have learned in 3.012, electrons orbiting the nucleus of an atom take on discrete energy values, specified by solutions to the Schrödinger equation. For the hydrogen atom [1]:

$$E_n = -\frac{\mu e^4}{2(4\pi\epsilon_0\hbar n)^2} = \frac{-13.60eV}{n^2} \text{ where } n = 1, 2, 3\dots \quad (1)$$

where μ is the reduced mass, e is the electron charge, ϵ_0 is the free space permittivity, and the integer n is the principal quantum number, which specifies the electronic shell.

For a hydrogen-like atom with a single electron and a nucleus having Z protons, the energy eigenvalues are modified to [2]:

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0\hbar n)^2} = \frac{-13.60Z^2 eV}{n^2} \quad (2)$$

As one might expect, raising the nuclear charge causes the electron to be bound more tightly, lowering the energy. **One task of this lab is to test the scaling relationship $E_n \sim Z^2$ for multielectron atoms using our XPS data.**

The wave function solutions of the Schrödinger equation quantify the probability distribution of the electron as a function of its distance from the nucleus. From equation (2) we see that $n=1$ is the lowest energy state (most negative). For higher electronic shells, the electron density is concentrated further from the nucleus (Fig. 1).

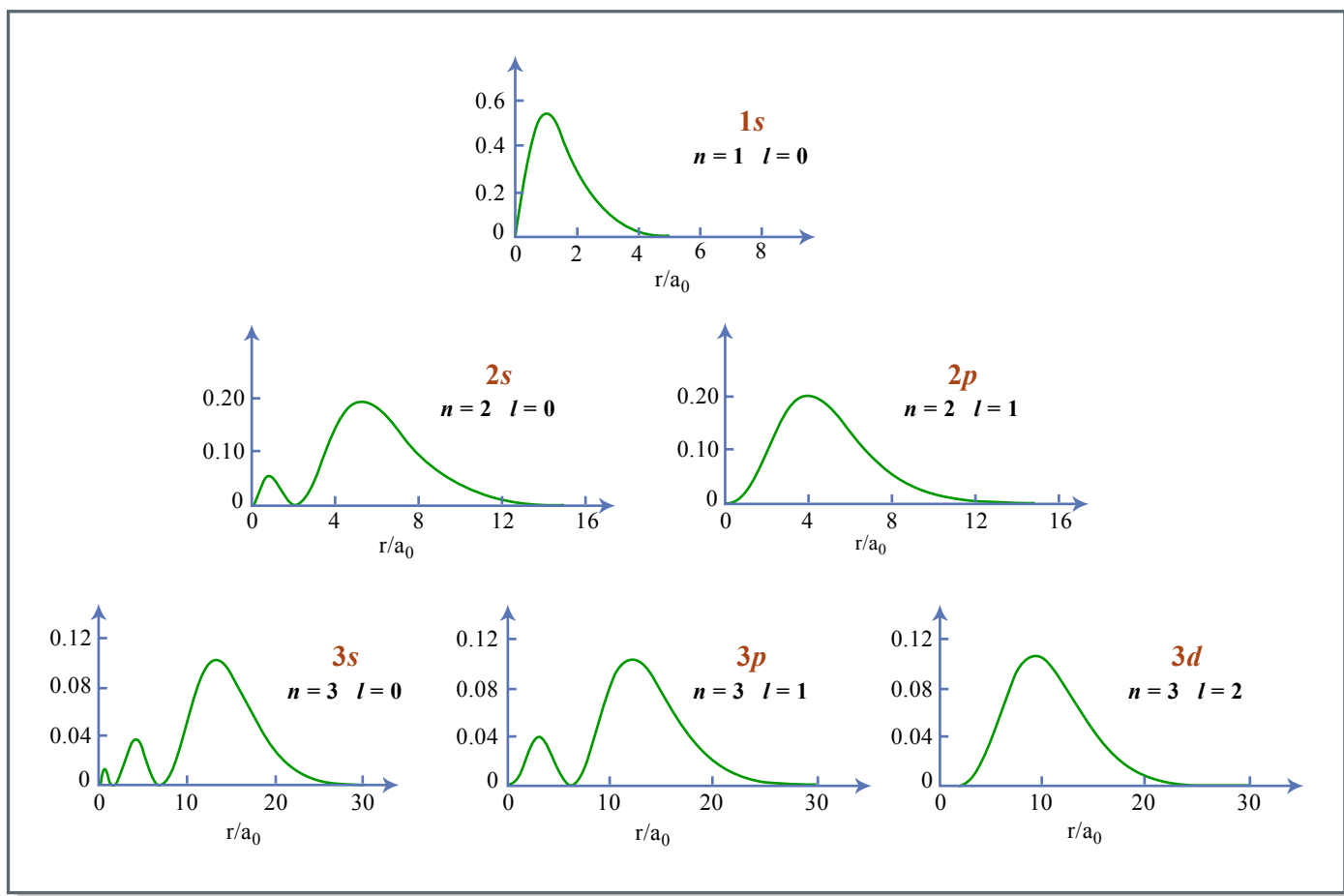


Figure 1. Radial electron density distribution for atomic orbitals in hydrogen-like atom .

Figure by MIT OCW.

For atoms with more than one electron, the Schrödinger equation can be solved only by approximation. In multi-electron atoms, electrons fill atomic orbitals of successive electronic shells. Electronic states are specified by the quantum numbers n , l , m , and m_s (principal, angular momentum, magnetic and spin), which have the allowed values shown in Fig. 2.

$$n = 0, 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, n-1$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

$$m_s = \pm 1/2$$

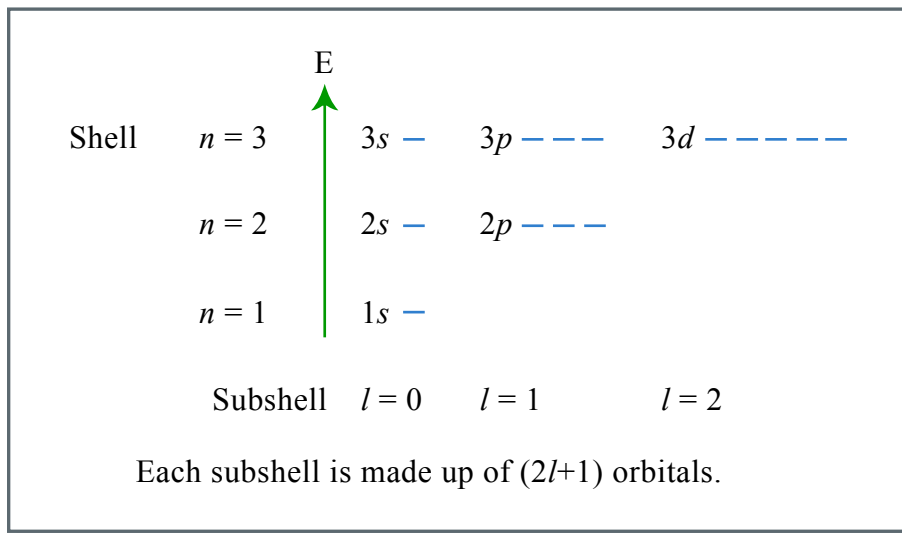


Figure 2. Schematic of electronic shells, subshells and orbitals.

Figure by MIT OCW.

Addition of electrons to a hydrogen-like system of fixed nuclear charge will modify the binding energy of the residing electron—with the addition of electrons, the first electron becomes less tightly bound to the nucleus due to screening of the nuclear charge. The binding energy of electrons in multi-electron atoms can be approximately calculated by a method known as the Hartree-Fock method [2].

Electronic States in Solids

What happens when atoms are packed together as condensed matter? We can connect the particle-in-a-box model discussed in 3.012 to electronic states observed in a solid,

by envisioning electrons as trapped in a box of finite width and depth that might be associated with the lattice spacing and nuclear charge, respectively. The finite potential causes the wave functions to “leak” out the sides of the box [4]. The resulting overlap between wave functions for electrons on adjacent atoms in the solid gives rise to the formation of energy “bands” rather than single values from a given atomic orbital. For lower energy states (low n values corresponding to core electronic states), electrons are still very localized within the box, as illustrated in Fig. 3 below. For the outermost occupied atomic orbitals (the valence band), substantial overlap of electron wave functions gives rise to chemical bonds.

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See <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/pbox.html#c1>

Figure 3. Comparison of wavefunctions within a box of infinite (left) and finite (right) potential (from [5]).

The energy gap between the valence band (composed of the highest occupied orbitals) and the conduction band (composed of the lowest unoccupied orbitals) observed in semiconductor and insulating materials is referred to as the *band gap* of a material, E_g . For electrons to bridge the gap and contribute to conduction they must be supplied with sufficient energy. If excitations across the band gap can be achieved at elevated temperatures, the material is classified as a semiconductor. Insulating materials have wider band gaps that cannot be breached by heating.

For metals, by contrast, the valence and conduction bands overlap, causing these materials to be electronically conductive even at absolute zero temperature, as seen in Fig. 4. The Fermi level, E_F , characterizes the top of the occupied energy level at

absolute zero. For metals, E_F resides in the conduction band, while in insulators and undoped semiconductors, $E_F = E_g/2$ [6]. **In our lab we will make use of this relationship to estimate the band gaps of insulators and semiconductors from our XPS valence band spectra.**

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See <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html>

Figure 4. Comparison of energy bands for electronic (a) insulators, (b) semiconductors and (c) conductors (from [7]).

X-ray Photoelectron Spectroscopy (XPS)

Direct measurement of electron binding energies in atoms and molecules can be made using the technique of photoelectron spectroscopy [8,9]. Photoelectron spectroscopy is based on the photoelectric effect, discovered by J.J. Thompson in 1899 and explained by Einstein in 1905, who was later awarded the Nobel prize for his work. In X-ray Photoelectron Spectroscopy (XPS), also called Electron Spectroscopy for Chemical Analysis (ESCA), x-rays irradiated on a sample result in the ejection of secondary electrons (photoelectrons) from the sample near surface (0.5-10 nm) with characteristic energies. Analysis of the photoelectron energies can provide quantitative information about the elemental composition of the sample as well as its bonding environment [8,9].

An XPS instrument typically uses a monochromatic x-ray source with photon energy given by:

$$E = h\nu = \frac{hc}{\lambda} \quad (3)$$

To eject an electron from the surface of a material, a photon must have energy larger than the binding energy of the electron, E_B . The excess energy of the photon is transferred to the ejected electron as kinetic energy (Fig. 5):

$$E_{kin} = h\nu - E_B \quad (4)$$

By measuring the value of the kinetic energy of photoelectrons, the electron binding energy can be determined. Since binding energies are characteristic of an element, XPS can be used to determine elements present in a material.

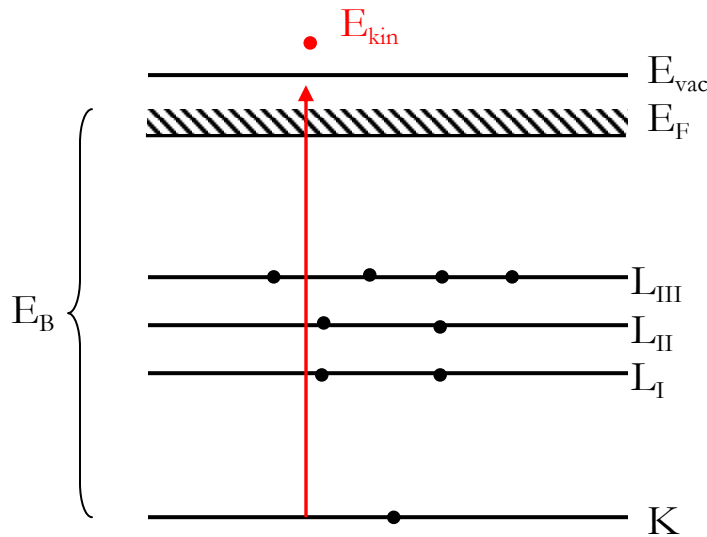


Figure 5. Photons of sufficient energy can eject electrons from core energy levels in atoms near the surface of a material.

Note that XPS is intrinsically a surface-sensitive technique, because to identify the electron's binding energy, it must escape the sample surface without undergoing an inelastic collision that would cause it to lose kinetic energy. For the same reason, XPS is performed in a high vacuum environment. Electrons able to escape the surface are collected through a lens and passed through an energy analyzer to determine the spectral range of electron energies (Fig. 6).

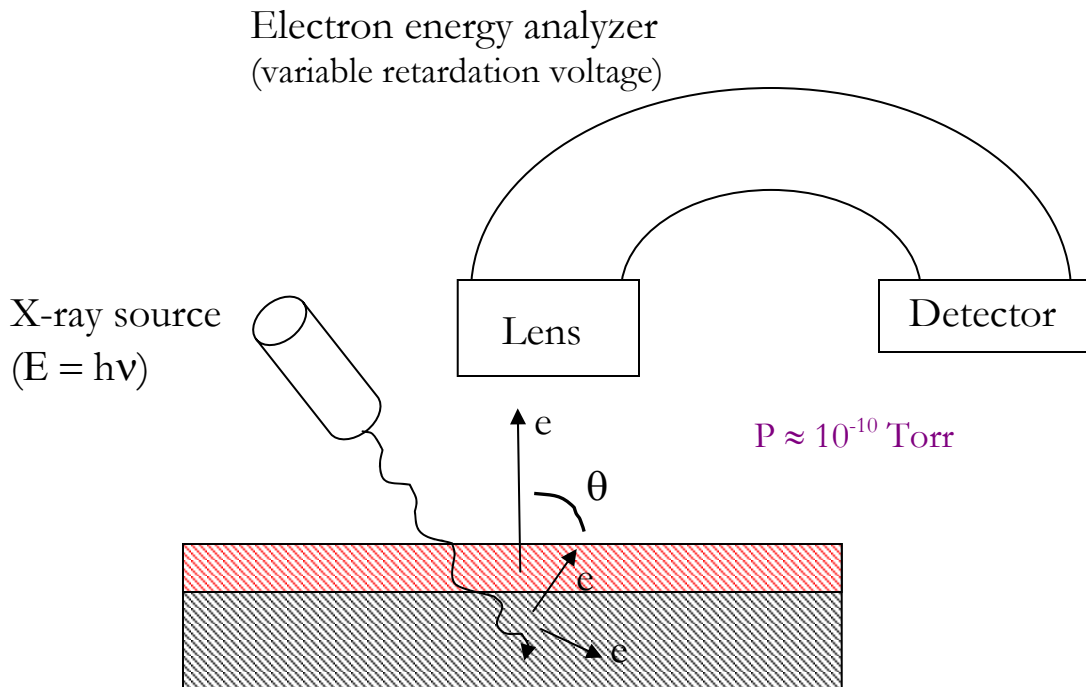


Figure 6. Schematic illustration of an XPS experiment. The kinetic energy of electrons ejected from the surface is analyzed to deduce its binding energy.

An XPS spectrum plots the number of electron counts vs. the electron binding energy calculated from eq. 4. Core electron states are observed at high binding energies, along with Auger electrons, as shown for a surface modified fluoropolymer in Fig. 7.

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Graph of Intensity vs. Binding Energy from Adem, E. et al.
 "Surface characterization of a binary grafting of Aac/NIPAAm onto poly(tetrafluoroethylene) (PTFE)."
Nucl. Instr. Meth. Phys. Res. B 234, 471 (2005)

Figure 7. XPS low resolution spectrum for a hydrophilic polymer coating grafted onto poly(tetrafluoroethylene) (from ref. [10]).

Auger electrons are created when electrons drop from a higher electronic shell to a lower one in order to fill the hole created by an ejected electron, and lower the energy of the atom. Excess energy from this process can result in the emission of a second electron from a higher energy shell, called an Auger electron, which also exhibits as characteristic kinetic energy, related to the energy levels of the three electrons.

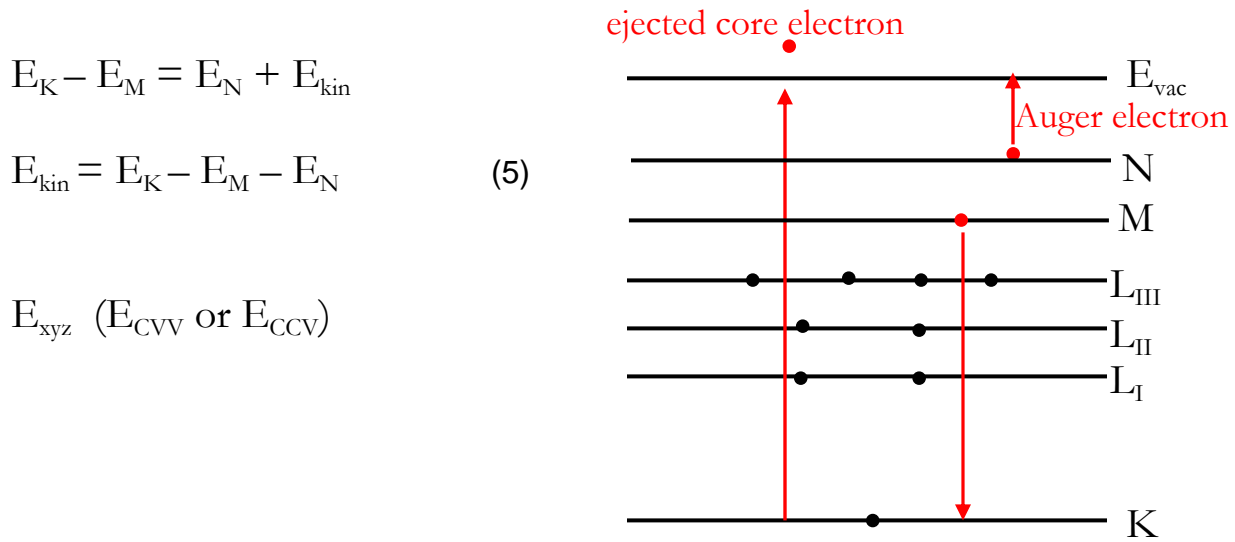


Figure 8. Schematic of Auger emission process.

Along with measuring core and Auger electron energies, XPS can be used to measure the band gaps of dielectric materials from certain satellite peaks of core electron peaks. Satellites are small peaks found at higher binding energies that arise due to the transfer of some of the photoelectron's kinetic energy to a secondary process—such as exciting an electron across the band gap:

$$E_{kin,sat} = h\nu - E_B - E_g \quad (5)$$

The band gap is then the energy difference between the measured binding energy of the core state and the lowest energy where satellite electrons are observed. For oxide materials, the band gap can be measured from an observed satellite off the O 1s peak, as illustrated in Fig. 9 [11]. **In our lab, we will employ this approach to obtain a measure for the band gap of our oxide sample.**

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Source: Petry, J., W. Vandervorst and T. Conrad. "The band structure of ALCVD AlZr- and AlHf-oxides as measured by XPS." *Mater. Sci. Eng. B* 109, 56 (2004).

Figure 9. Determination of E_g for oxides using the O 1s peak. The band gaps is measured from the center of the O 1s to the point where the satellite slope extrapolates to baseline (from [11]).

Valence Band Spectra

Photoelectron spectroscopy can also be a powerful tool for examination of the valence band electron energies [12-15]. Often instruments for this purpose use ultraviolet light sources for photoemission [9]. Figure 10 illustrates the ultraviolet photoelectron spectroscopy (UPS) spectrum from polyethylene, $-(CH_2-CH_2)_n-$, along with the density of states calculated for heptane using Hartree-Fock methods [12]. Peaks in the 5-12 eV range are associated with electrons contributed from the C 2p orbitals, while those in the 12-21 eV arise from C 2s orbitals.

On examining Fig. 10, we can observe that the valence band begins at an energy value several electron volts below zero binding energy ($E_B=0$ is equated with the Fermi level [14,16]). This indicates that polyethylene is an insulating material—a large band gap is present between the valence and conduction bands.

How might we expect the valence band spectrum to change for a semiconductor? For a metal? For an alkali halide crystal? **In our lab we will compare the valence band spectra for these various classes of materials.**

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Source: Ono, M., and E. Morikawa. "Ultraviolet photoelectron spectroscopy study of synchrotron radiation-degraded polyethylene ultrathin films." *J. Phys. Chem. B* 108, 1894 (2004).

Fig. 10. UPS spectrum and calculated density of states for polyethylene (from [12]).

Experimental

Materials: Al₂O₃, ZnS, KBr, Au, graphite, Si

Instrument: Kratos Axis Ultra, Al K_α monochromated source

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