University of Babylon
College of Science
Department of Chemistry
Course No. Chsc 424

Undergraduate Studies
Physical chemistry
Fourth year - Semester 2
Credit Hour: 3 hrs.
Scholar units: three units

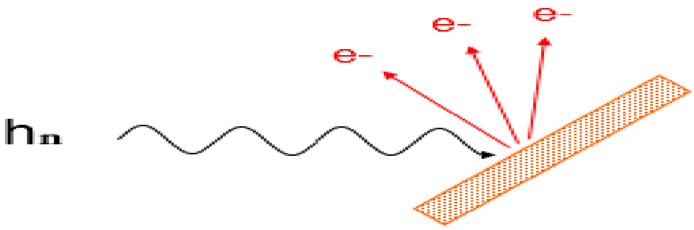
Lectures of Quantum mechanics
Second Semester, Scholar year 2017-2018
Prof. Dr. Abbas A-Ali Draea

Lecture No. Ten: Photoemission Spectroscopy

1-Introudction.
2- Types of photoemission spectroscopy.
3-Physical principle.

1-Introudction.

Photoemission spectroscopy (PES), also known as photoelectron spectroscopy, refers to energy measurement of electrons emitted from solids, gases or liquids by the photoelectric effect. In order to determine the binding energies of electrons in a substance by this phenomena. The term refers to various techniques, depending on whether the ionization energy is provided by an X-ray photon, an EUV photon(Ultraviolet photon) . Regardless of the incident photon beam, however, all photoelectron spectroscopy revolves around the general theme of surface analysis by measuring the ejected electrons. Ionization occurs when matter interacts with light of sufficient energy (Heinrich Hertz, 1886) as in following diagram.



Since E_{hn} = electron kinetic energy + electron binding energy

In a PES experiment monochromatic light is directed onto a sample. The emitted photoelectrons are discriminated with respect to their kinetic energy and, depending on the information desired, other observables like emission direction or spin, before they are detected and counted. The principle is sketched in figure 1, left, for an angle-resolved experiment on a single crystal.

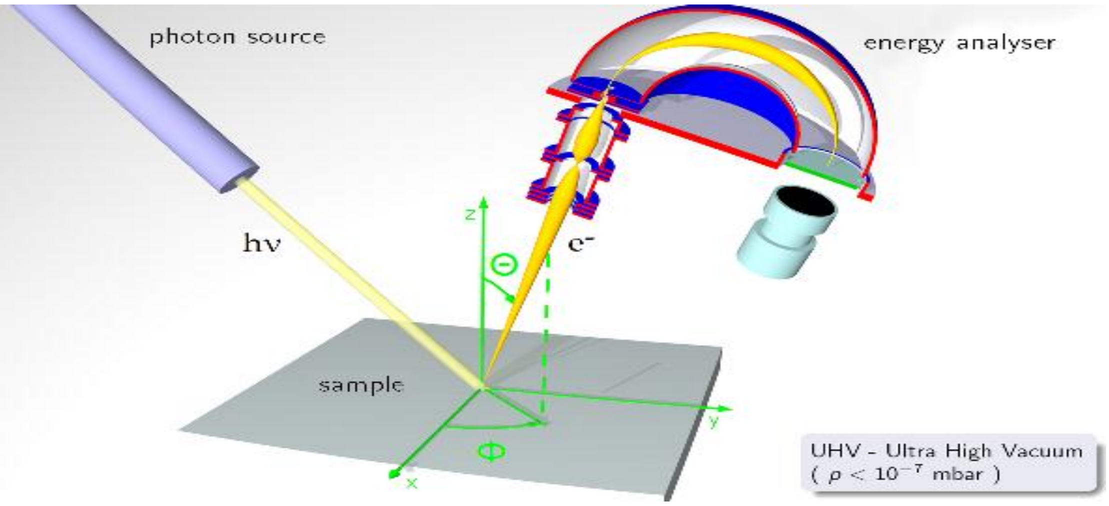


Figure 1: Principle of angle-resolved photoelectron spectroscopy.

Can be inserted main point on Photoelectron spectroscopy as follow:

- Photoelectron spectroscopy uses this phenomenon to learn about the electronic structure of matter.
- If electromagnetic radiation present is in resonance with the energy spacing between different states (electronic, vibrational, rotational, etc) of matter, radiation will be absorbed and transitions will occur.

- The radiation that is transmitted through the sample is measured, and spectrum can be reported as either transmittance or absorbance of radiation.

2- Types of photoemission spectroscopy:

They found several types are:

- X-ray photoelectron spectroscopy (XPS) was developed in 1957 and is used to study the energy levels of atomic core electrons, primarily in solids. Referred to the technique as "electron spectroscopy for chemical analysis" (ESCA), since the core levels have small chemical shifts depending on the chemical environment of the atom that is ionized, allowing chemical structure to be determined. XPS is sometimes referred to as PESIS (photoelectron spectroscopy for inner shells), whereas the lower-energy radiation of UV light is referred to as PESOS (outer shells) because it cannot excite core electrons.

- Ultraviolet photoelectron spectroscopy (UPS) is used to study valence energy levels and chemical bonding, especially the bonding character of molecular orbitals. The method was developed originally for gas-phase molecules in 1962, later technique is modified the technique and used a UV laser to excite the sample, in order to measure the binding energy of electrons in gaseous molecular clusters.
- Two-photon photoelectron spectroscopy (2PPE) extends the technique to optically excited electronic states through the introduction of a pump-and-probe scheme.
- Extreme-ultraviolet photoelectron spectroscopy (EUPS) lies in between XPS and UPS. It is typically used to assess the valence band structure. Compared to XPS, it gives better energy resolution, and compared to UPS, the ejected electrons are faster.

3-Physical principle:

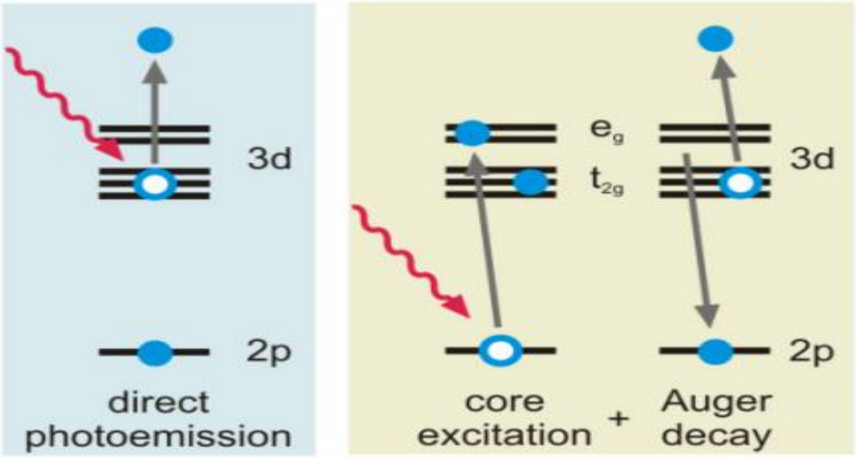
The physics behind the PES technique is an application of the photoelectric effect. The sample is exposed to a beam of UV or XUV light inducing photoelectric ionization. The energies of the emitted photoelectrons are characteristic of their original electronic states, and depend also on vibrational state and rotational level. For solids, photoelectrons can escape only from a depth on the order of nanometers, so that it is the surface layer which is analyzed.

Because of the high frequency of the light, and the substantial charge and energy of emitted electrons, photoemission is one of the most sensitive and accurate techniques for measuring the energies and shapes of electronic states and molecular and atomic orbitals. Photoemission is also among the most sensitive methods of detecting substances in trace concentrations, provided the sample is compatible with ultra-high vacuum and the analyte can be distinguished from background.

Typical PES (UPS) instruments use helium gas sources of UV light, with photon energy up to 52 eV (corresponding to wavelength 23.7 nm). The photoelectrons that actually escaped into the vacuum are collected, energy resolved, slightly retarded and counted, which results in a spectrum of electron intensity as a function of the measured kinetic energy. Because binding energy values are more readily applied and understood, the kinetic energy values, which are source dependent, are converted into binding energy values, which are source independent. This is achieved by applying Einstein's relation:

$$E_k = h\nu - E_B$$

The hν term of this equation is due to the energy (frequency) of the UV light that bombards the sample. Photoemission spectra are also measured using synchrotron radiation sources. The binding energies (E_B) of the measured electrons are characteristic of the chemical structure and molecular bonding of the material. By adding a source monochromator and increasing the energy resolution of the electron analyzer, peaks appear with full width at half maximum (FWHM) less than 5–8 meV. Following sketch represent the mechanism.



Sketch of the direct PES and the Auger-like channel which quantum mechanically interfere in PES.