University of Babylon

College of Sciences

Department of Chemistry

Course No. Chsc 424

Undergraduate Studies

Physical chemistry
Fourth-year - Semester 1
The scholar year 2024-2025

Lectures of

Quantum Mechanics of Chemistry

Prof. Dr. Abbas A-Ali Drea

sci.abbas.abid@uobabylon.edu.iq

Lecture No. 3:

The experimental foundation of Modern Quantum mechanics

Discovering of double character phenomena of electron behavior due to experiments and theoretical results to measure the wavelength of a travelling electron as a function of its momentum.

Quantum theory predicts a fundamental relation between ***momentum and wavelength***.

1- De Broglie experiment :(De Broglie Wave)

De Broglie postulated that the wavelength of objects (The wave-like properties of matter) was given by$\lambda = \frac{h}{p}$, where h is Planck's constant, and p = mv is the linear momentum.

De Broglie called the "phase wave". His hypothetical intrinsic particle periodic phenomenon is in phase with that phase wave. He noted the phase wave does not transfer energy.

While the concept of waves being associated with matter is correct, De Broglie did not leap directly to the final understanding of quantum mechanics with no missteps. There are conceptual problems with the approach that De Broglie took in his ***thesis*** that he was not able to resolve but he calculated the wavelength of an electron equal to 0.166nm.

2- Experiment of electron diffraction:

In 1927, however, Clinton Davisson and Lester Germer discovered experimental proof of the wave-like properties of matter particularly electrons.

They were studying electron reflection from a nickel target. That is, electrons were "diffracting" from the crystal planes much like light diffracts from a grating, leading to constructive and destructive interference. Electron diffraction is an extremely important tool used to study new materials.

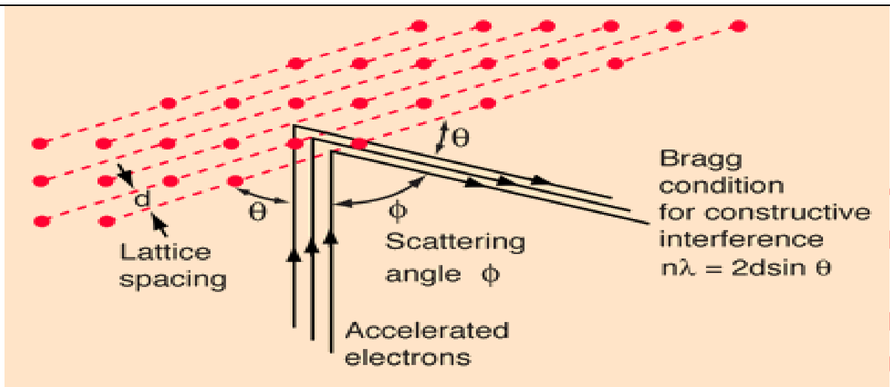


Figure 1: Electron Diffraction from atomic layers in a crystal.

Consider planes of atoms in a crystal as shown in Fig. 1, separated by distance d. Electron "waves" reflect from each of these planes. Since the electron is wave-like, the combination of the reflections from each interface will lead to an interference pattern. This is completely analogous to light interference. The de Broglie wavelength for the electron is given by: $\lambda = h/p$, where p can be calculated by knowing the energy of the electrons when they leave the "electron gun": $P^2/2m = e.V_a$ ------------(1)

Where Va is the accelerating potential. The condition for constructive interference is that the path length difference for the two waves shown in Fig. 3-1 is multiple of a wavelength. This leads to Bragg's Law: $n\lambda = 2d \sin\theta$ --------- (2)

Where n = 1, 2, is integer (n is the order of diffraction). In this experiment, only the first-order diffraction n = 1 is observed. Therefore, the intra-atomic distance in a crystal can be calculated by measuring the angle of electron diffraction and their wavelength (i.e. their momentum):

The following relation is derived from electron diffraction experiments. substituted wave length value into Brags law.

$$d = \frac{\lambda}{2\sin\theta} = \frac{h}{2\sin\theta \, . \sqrt{2e.me.Va}} --- (3)$$

where h is Planck's constant, e is the electronic charge, m_e is the electron's mass, and V_a is the accelerating voltage.

At last, the wavelength of the electron beam is 0.165nm but the same wavelength of the electron beam according to De Broglie is 0.166nm, this is very much closer between them and another provident to the failure of Bohr Theory.

3- Compton scattering:

Arthur Holly Compton discovered the Compton scattering phenomena. It is the inelastic scattering of a photon by a charged particle, usually an electron.

It results in a decrease in energy (increase in wavelength) of the photon (which may be an X-ray or gamma ray photon), called the **Compton Effect**.

Part of the photon's energy is transferred to the recoiling electron. Inverse Compton scattering exists, in which a charged particle transfers part of its energy to a photon.

The energy of the X-ray photon (≈17 keV) was much larger than the binding energy of the atomic electron, so the electrons could be treated as being free. The amount by which the light's wavelength changes is called the Compton shift. Compton scattering usually refers to the interaction involving only the electrons of an atom.

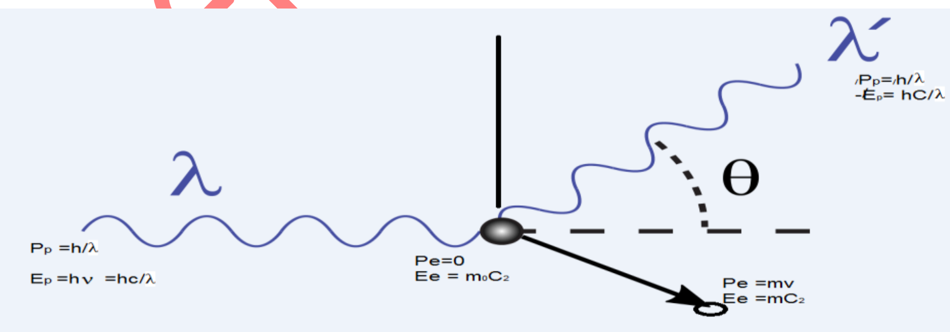


Figure 2. Diagram of Compton scattering phenomena.

Applying the conservation laws of energy, momentum and mass according to the axis.

The energy of photon before interference - Energy of photon after interference = Energy of electron after interference- Energy of electron before interference.

$$\frac{hc}{\lambda} - \frac{hc}{\lambda^{-}} = mc^2 - m_o c^2$$

The difference in Energy of photon = Difference in Energy of Electron

4- Photoelectric effect:

The photoelectric effect or *photoemission* is the production of electrons or other free carriers when light is shone onto a material. Electrons emitted in this manner can be called photoelectrons. According to classical electromagnetic theory, this effect can be attributed to the transfer of energy from light to an electron.

To make sense of the fact that light can eject electrons even if its intensity is low, Albert Einstein proposed that a beam of light is not a wave propagating through space, but rather a collection of discrete wave packets (photons), each with energy $h\nu$.

Photoemission can occur from any material, but **(Conditions of Photoemission)**

1-It is most easily observable from metals or other conductors because the process produces a charge imbalance, and if this charge imbalance is not neutralized by current flow (enabled by conductivity), the potential barrier to emission increases until the emission current ceases.

2-It is also usual to have the emitting surface in a vacuum since gases impede the flow of photoelectrons and make them difficult to observe.

3-Thin oxide layers on metal surfaces usually increase the energy barrier to photoemission if the metal has been exposed to oxygen, so most practical experiments and devices based on the photoelectric effect use clean metal surfaces in a vacuum.

4-photoelectron is an emitter into a solid rather than into a vacuum, the term internal photoemission is often used, and emission into a vacuum is distinguished as external photoemission.

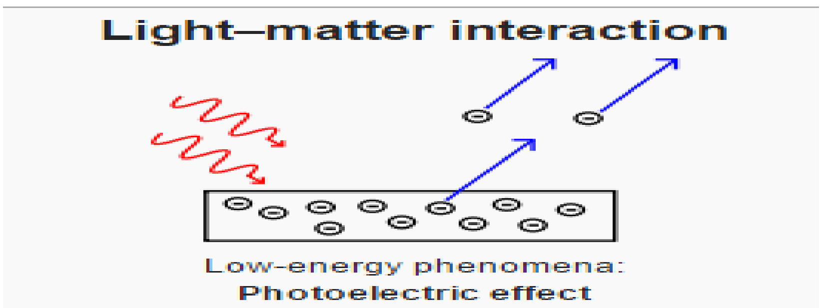


Figure: 4. Photoelectric effect (low energy phenomena).

3-5 Black body radiation:

Gustav Kirchhoff introduced the term black body radiation in 1860. Blackbody radiation is also called complete radiation temperature radiation or thermal radiation.

Blackbody radiation is the type of electromagnetic radiation within or surrounding a body in thermodynamic equilibrium with its environment. The radiation has a specific spectrum and intensity that depends only on the temperature of the body.

The thermal radiation spontaneously emitted by many ordinary objects can be approximated as blackbody radiation. A black body at room temperature appears black, as most of the energy it radiates is infrared and cannot be perceived by the human eye. Because the human eye cannot perceive colour at very low light intensities. When it becomes a little hotter, it appears dull red. As its temperature increases, further, it eventually becomes blue-white.

All normal matter emits electromagnetic radiation when it has a temperature above absolute zero. Conversely, all normal matter absorbs electromagnetic radiation to some degree. An object that absorbs all radiation falling on it, at all wavelengths, is called a black body. Simple mathematical relations are $E \alpha T$ and $E \alpha \nu$ or $E \alpha 1/\lambda$ therefore $T \alpha 1/\lambda$

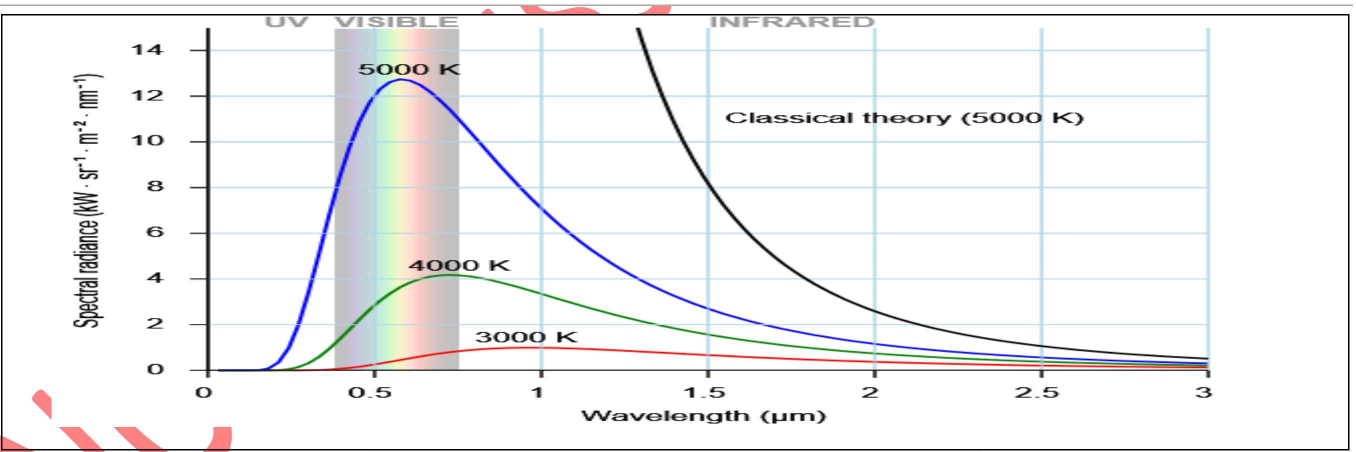


Figure 6. Black body radiation spectrum.

6- Uncertainty principles of Heisenberg:

Indeterminacy (uncertainty) principle, articulated (1927) by Werner Heisenberg.

The measuring of position and velocity cannot be done at the same time for any object, even in theory.

The concepts of exact position and exact velocity have no meaning in nature.

It is easy to measure both the position and the velocity of an automobile because the uncertainties implied by this principle for ordinary objects are too small values to be measurable (determinable).

The complete rule stipulates that the product of the uncertainties in position and velocity is equal to or greater than a tiny physical quantity, or constant (about 10^{-34} joule-second, the value of the quantity h (where h is Planck's constant). Only for the exceedingly small masses of atoms and subatomic particles does the product of the uncertainties become significant.

The uncertainty principle, developed by W. Heisenberg, is a statement of the effects of wave-particle duality on the properties of subatomic objects. Consider the concept of momentum in the wave-like microscopic world. The momentum of a wave is given by its wavelength. A wave packet like a photon or electron is a composite of many waves. Therefore, it must be made of many momentums. However, how can an object have many momentums?

$$\Delta x.\Delta P \geq \frac{h}{2\pi} \rightarrow \Delta x.\Delta v.m \geq \frac{h}{2\pi} \rightarrow \Delta x.\Delta v = \frac{h}{2\pi m} \rightarrow (x_2 - x_1).(v_2 - v_1) = \frac{h}{2\pi m}$$

From the final equation, the accuracy in position or velocity for the particle can be determined.

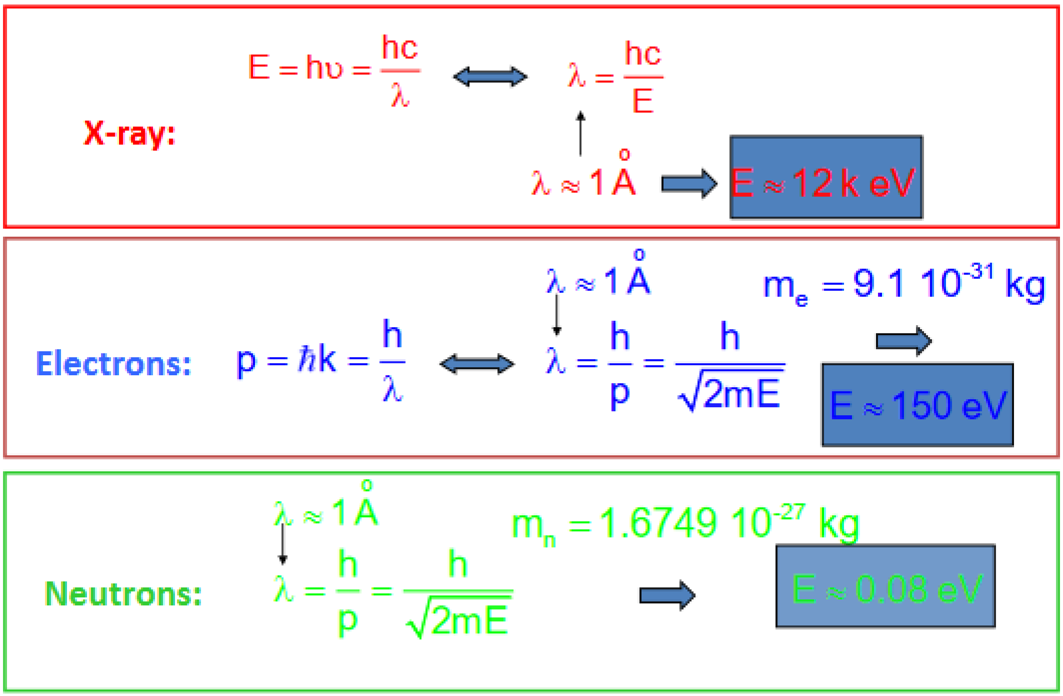
Applications:

Example:1

Estimate the energy kinetic differences between X-ray photon, electron and neutron at wavelength λ=1Å for each one.

Answer:

Energies X-ray, electrons and neutrons wave-particle



The kinetic energy of X-ray photon is larger than other species.

Exmple:2

Speed of projectile of a mass 1.0 gm is known to $1*10^{-6}$m.s^{-1}, calculate the minimum uncertainty in its position.

Answer: The uncertainty principle is $\Delta \boldsymbol{x}.\Delta \boldsymbol{P} \geq \frac{\boldsymbol{h}}{\boldsymbol{4\pi}}$

Estimation method of momentum $\Delta p = m\Delta v$ is the uncertainty in the speed then we can used equation of:

$$\Delta x = \frac{h}{4\pi}.\frac{1}{m.\Delta v} = \frac{1.055*10^{-34} J.s}{(1.0*10^{-3} Kg)*1*10^{-6} m.s^{-1}} = 5 * 10^{-26}\ m$$
