# Quantum Chemistry

## Course code: 18CYB101J

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| | Course Learning Outcome (CLO) |
|---|---|
| CLO 1 | Analyze atomic, molecular orbitals of organic, inorganic molecules to identify structure, bonding, molecular energy levels |
| CLO 2 | Utilize the principles of spectroscopic technique in analyzing the structure and properties of molecules |
| CLO 3 | Rationalize bulk properties using thermodynamic considerations and periodic properties of elements |
| CLO 4 | Utilize the concepts of thermodynamics in understanding thermodynamically driven chemical reactions |
| CLO 5 | Perceive the importance of stereochemistry in synthesizing organic molecules applied in pharmaceutical industries |
| CLO 6 | Utilize concepts in chemistry for technological advancement based on electronic, atomic and molecular level modification |

# Quantum Chemistry

- Branch of chemistry deals with application of quantum mechanics to chemical systems

- Understanding electronic structure and molecular dynamics

1. **Wave particle duality**

2. **Heisenberg's uncertainty principle**

3. **Postulates of quantum mechanics**

**Classical mechanics:** Formulated by Sir Isaac Newton

Obeyed by macroscopic particles such as planets and rigid bodies

However, **microscopic particles** such as electrons, protons, atoms and molecules do not obey Newtonian dynamics

**Reason: Wave-particle duality**

Hence there is need of quantum mechanics (or wave mechanics)
Key feature: Quantization of energy and angular momentum

The laws of quantum mechanics were formulated in 1925 by
**M. Born, W. Heisenberg and P. Jordan and**
**in 1926 by E. Schrodinger**

| **Classical mechanics** | **Quantum mechanics** |
| --- | --- |
| ❖ Deals with large objects | deals with small objects like electrons, atoms |
| ❖ Energy changes is continuous | discrete/quantized |
| ❖ Newtonian Equation | Schrodinger Equation |
| ❖ Deterministic | probabilistic |

# Quantum theory of radiation

The energy distribution in black body radiation could not be explained by classical mechanics.

The correct expression was derived by **Planck** on the basis of quantum theory of radiation.

1. Radiant energy is emitted or absorbed discontinuously in the form of tiny bundles of energy known as quanta.

2. Each quantum is associated with a definite amount of energy ($E = h\upsilon$) where E is energy in Joules, $\upsilon$ is the frequency of radiation

3. A body can emit or absorb energy in only in whole number multiples of quantum, i.e., $1h\upsilon$, $2h\upsilon$, …., $nh\upsilon$

Energy in fractions of quantum can not be lost or absorbed. This is known as **quantization of energy**.

# Photoelectric Effect: Wave –Particle Duality

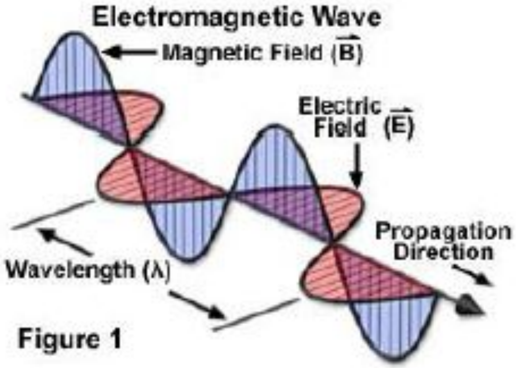
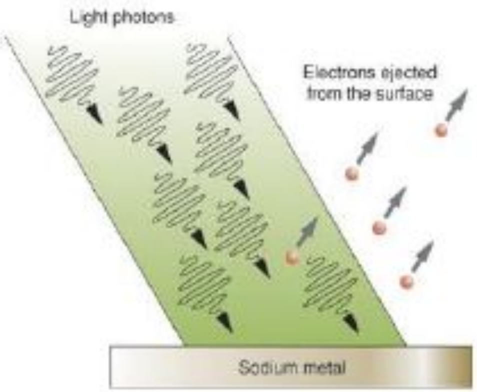


Figure 1

**Electromagnetic Radiation**

$$E = E_0 Sin(kx - \omega t)$$

Wave energy is related to Intensity
I $\propto E^2{}_o$ and is independent of ω




Einstein borrowed Planck's idea that ΔE=hν and proposed that radiation itself existed as small packets of energy (Quanta)now known as PHOTONS

$$E_P = h\nu = KE_M + \phi = \frac{1}{2}mv^2 + \phi$$

$\phi$ = Energy required to remove electron from surface

# Laws of quantum mechanics

**Matrix mechanics**

**German Physicists M. Born, W. Heisenberg**

**and P. Jordan (in 1925)**

**Wave mechanics**

**Schrodinger (in 1926)**

# Dual nature of Matter

- Initially, the properties of matter were explained based on its particle nature.

- Later on, it was experimentally found out that matter also possess the properties of a wave. Hence, the matter is said to possess dual nature, i.e., particle as well as a wave.

Properties of Matter

**Particle nature**

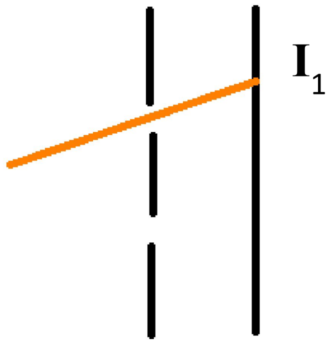
e.g., **Einsteins photoelectric effect, Compton effect**

**Wave nature**

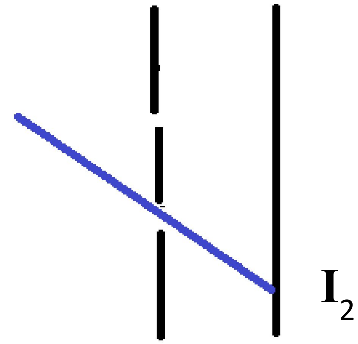
**Huygens, Maxwell**

# Particle nature

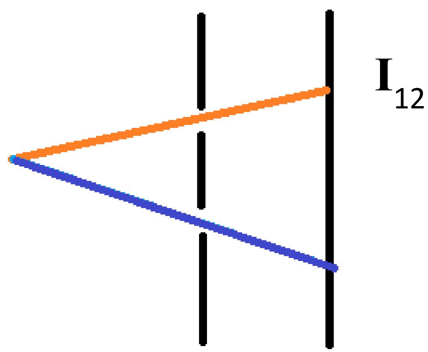
**Example: Bullets**

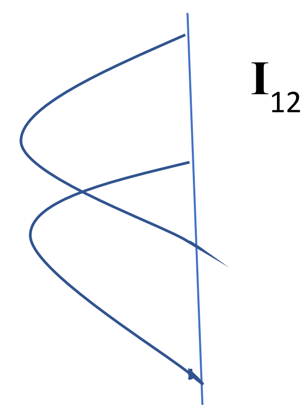



(1st slit)




(2nd slit)




$$I_{12} = I_1 + I_2$$

# With waves, how to get Intensity?

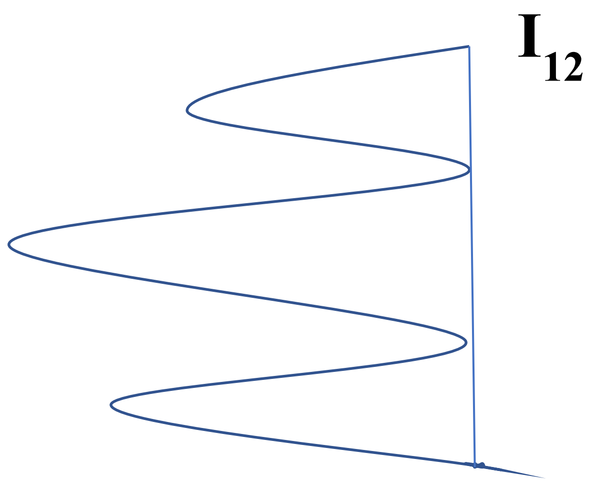
**Intensity, I depends on displacement$^2$**

$I_1 \; \alpha \; \psi_1^{\,2}$

$I_2 \; \alpha \; \psi_2^{\,2}$

$I_{12} \; \alpha \; \psi_{12}^{\,2}$ (but $I_{12} \neq I_1 + I_2$)

$\Psi_{12} = \Psi_1 + \Psi_2$



# Particle and wave character (dual character) of electron

Einstein in 1905 had suggested that light has a dual character, as wave and also as particle.

de Broglie proposed that matter also has a dual character, as wave and as particle.
de Broglie was awarded the Physics Nobel prize in 1929.

He derived the expression for calculating the wave length ($\lambda$) of a particle of mass (m) moving with velocity (u) as:

$$\boxed{\lambda = h / m.u}$$

The de Broglie hypothesis of wave character of electron received 1st experimental support from **C. J. Davisson and L. H. Germer**. They found that the impact of electrons resulted in diffraction patterns, which were similar to X-rays under similar conditions.
**The experiment gave direct evidence for wave character of electrons.**

# Heisenberg's Uncertainty principle

**This principle states that both the momentum and position of a particle cannot be determined simultaneously.**

**Mathematically,** it can be expressed as**:**

$$\boxed{\Delta x \, \Delta P \geq (h / 4\pi)}$$

where **$\Delta x$** represents the Uncertainty in position,
and **$\Delta P$** represents the Uncertainty in momentum.

- ❖ Thus, if the position of a particle is specified precisely, then it is impossible to predict about its momentum and,

- ❖ If the momentum is known, then it is impossible to predict about the location of particle.

# Heisenberg's uncertainty principle

► It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

► If the momentum of a particle is specified precisely, it is impossible to predict the location of the particle.

► If the position of a particle is specified exactly, then we can say nothing about its momentum.

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

**Classical mechanics allows us to predict the exact paths taken by the particles of the system and tells us where they will be at a future time.**

**In contrast, quantum mechanics gives the probabilities of finding the particles at various locations in space.**

# Postulates of quantum mechanics

1. The physical state of a system at time **t** is described by the wave function $\psi$ (x,t), which contains all accessible physical information about the system in that state

Wavefunction $\psi(x,t)$ □ position and time probability amplitude

2. The wave function and its first and second derivatives $d\psi(x,t)/dx$ and $d^2\psi(x,t)/dx$ are continuous, finite and single valued for all values of x.
   Also, the wave function is normalized, i.e.,
   $\int_{-\infty}^{\infty} \psi^* (x,t)\, \psi (x,t) = 1$
   where $\psi^*$ is the complex conjugate of $\psi$

3. A physically observable quantity can be represented by a Hermitian operator.

An operator $\hat{A}$ is said to be Hermitian if it satisfies the following condition:

$$\int \psi_i^* \hat{A} \psi_j dx = \int (\psi_j (\hat{A} \psi_i)^* dx$$

where $\psi_i$ and $\psi_j$ are the wave functions representing the physical states of the quantum system, i.e., a particle, an atom or a molecule

4. The allowed values of an observable A are the eigen values, ai, in the operator equation $\hat{A} \psi_i = a_i \psi_i$
where $\hat{A}$ is the operator for the observable, $\psi_i$ is an eigen function of $\hat{A}$ with eigenvalue $a_i$

In other words, measurement of the observable A yields the eigen value $a_i$

5. The average value, <A> of an observable A, corresponding to the operator $\hat{A}$
Is obtained from the relation

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, dx$$

where the function $\psi$ is assumed to be normalized

6. The wave function $\psi$ (x, t) is a solution of the time dependent equation

$$\hat{H} \psi (x, t) = i\hbar \, (d\psi (x,t)/dt)$$

where $\hat{H}$ is the Hamiltonian operator of the system

# Schrodinger's philosophy

**PARTICLES can be WAVES**
**and WAVES can be PARTICLES**

**New theory is required to explain the behavior of electrons, atoms and molecules**

**Should be Probabilistic, not deterministic (non-Newtonian) in nature**

**Wavelike equation for describing sub/atomic systems**

# Schrödinger wave equation

► The position of a particle is distributed through space like the amplitude of a wave.

► In quantum mechanics, a wavefunction describes the motion and location of a particle.

$$\psi \quad \Psi$$

► A wavefunction is just a mathematical function which may be large in one region, small in others and zero elsewhere.

$$\sin x \quad or \quad e^{-x}$$

# Schrödinger Wave Equation

- Erwin Schrodinger, in 1926, gave a wave equation to describe the behavior of electron waves in atoms and molecules.

- The discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions, $\psi$, which are related to the probability of finding electrons at various places around the nucleus

$$d^2\psi/dx^2 + d^2\psi/dy^2 + d^2\psi/dz^2 + (8\pi^2 m\,(E-V)/h^2)\psi = 0$$

or, $[- h^2/8\pi^2 m\,(d^2\psi/dx^2 + d^2\psi/dy^2 + d^2\psi/dz^2)] + V\psi = E\psi$

or, $[- h^2/8\pi^2 m\,(d^2/dx^2 + d^2/dy^2 + d^2/dz^2) + V]\psi = E\psi$

This is the well known **Schrödinger wave equation** proposed in 1926. Schrödinger shared the 1933 Physics Nobel Prize with Dirac for the discovery of new productive forms of atomic theory.

Thank

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