

CH107: Physical Chemistry

- **Quantum Mechanics in Chemistry:**

- Hydrogen atom: orbitals

- Multielectron atoms: Spin orbital

- Molecules: Molecular orbitals

Instructor (D3):

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CH 107 2022 Course Information

**Classes on Mondays (9:30 am), Tuesday (10:30 am)
and Thursdays (11:30 am)**

Tutorials on Wednesdays 2 pm

Attendance, marks change and course related issues:

**Course Secretary: Ms. Charine
Central Facility, Chemistry Department**

Email: charine@chem.iitb.ac.in

Phone: (022)2576 4159

CH 107: Division 3

Tutorial venue and Teaching Assistants Wednesdays: 2 – 3 pm

D3/T1	LT-206	-Shobhna Kapoor
D3/T2	LT-301	-Sarthak (BS)
D3/T3	LT-302	-Manas (BS)
D3/T4	LT-303	-Kamal Majee
D3/T5	LT-304	-Bhawna
D3/T6	LT-305	-Arkaprabha
D3/T7	LT-305	-Somesh
D3/T8	IC1	-Amrita Manna
D3/T9	IC2	-Pooja Sharma

CH 107 schedule and evaluation scheme

Duration	Half-semester (~8 weeks)
Quiz	18 Jan 2023
End-Semester Exam	to be declared

Evaluation Scheme

Mini quiz during tutorials	8 Marks
Home Assignments	6 Marks
Quiz	12 Marks
End-Semester Exam	24 Marks
Passing Marks	?

Topics for 2022-2023

- **Origin of Quantization** Week 1
Postulates of Quantum Mechanics
Particle in a Potential Well
- **Electronic Structure in Atoms** Week 2-4
Hydrogen atom
Multi-electronic atoms
- **Chemical Bonding** Week-5-6
Molecular Orbital Theory
Energetics/Electronic structure of homonuclear diatomics
Heteronuclear diatomics and polyatomics, hybridization

CH 107: Text books

- Physical Chemistry – I.N. Levine, 5th Ed.
- Physical Chemistry – P.W. Atkins 2nd Ed.
- Physical Chemistry: Molecular Approach - McQuarrie and Simon
- Fundamentals of molecular spectroscopy – Banwell and McCash

Important Websites:

CH107 Course Material for 2013 and previous year's power-point slides:

www.chem.iitb.ac.in/academics/menu.php

<http://vod.cdeep.iitb.ac.in/> (Previous years lectures)

All materials will be uploaded on IITB Moodle

<http://moodle.iitb.ac.in>

Why should you study Physical Chemistry?

Use the laws of physics and apply to chemistry

Deeper understanding of physical processes/mechanisms
and get insights on how things work the way they do!

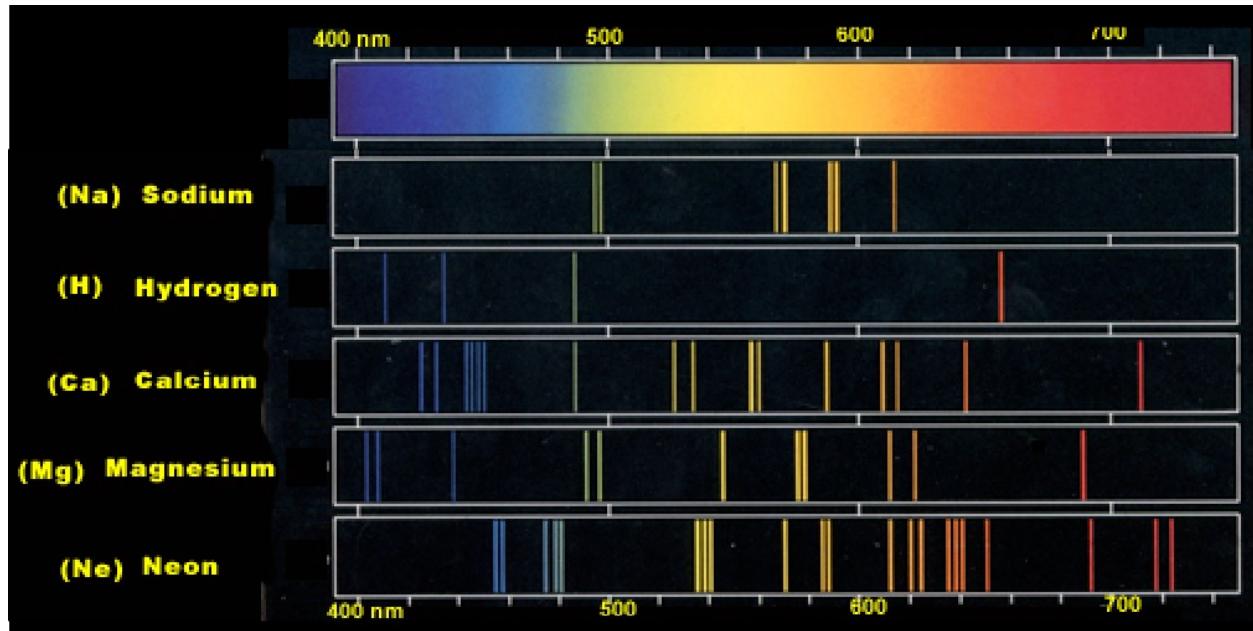
**Bridge between novel molecules (materials) prepared by
synthetic chemists and their potential applications.**

<https://www.acs.org/content/acs/en/careers/college-to-career/areas-of-chemistry/physical-chemistry.html>

- Biotechnology and healthcare
- Energy Science – “Solar Energy” conversion
- Wall Street, Law Firms and Venture Capitals
- Nanoelectronics/Nanotechnology: Molecular Electronics

Recapitulation

Atomic Spectra



Balmer Series

410.1 nm

$$434.0 \text{ nm} \quad \frac{1}{\lambda} = R_{\infty} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

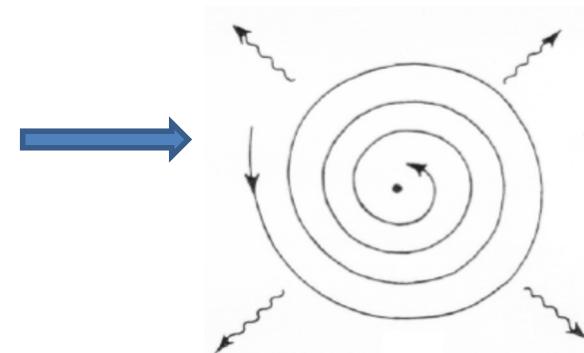
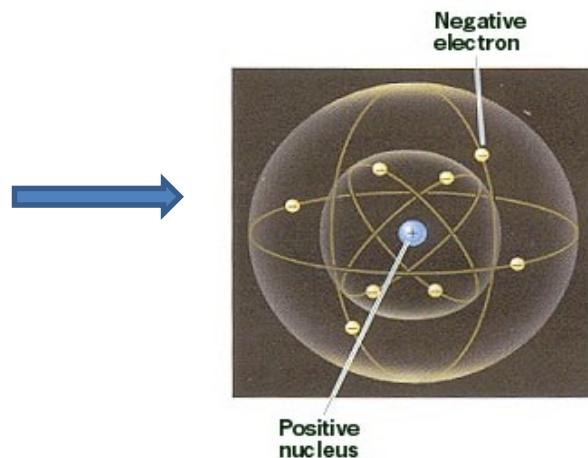
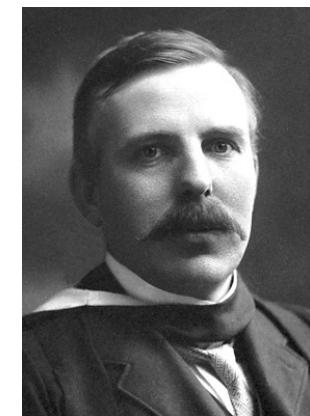
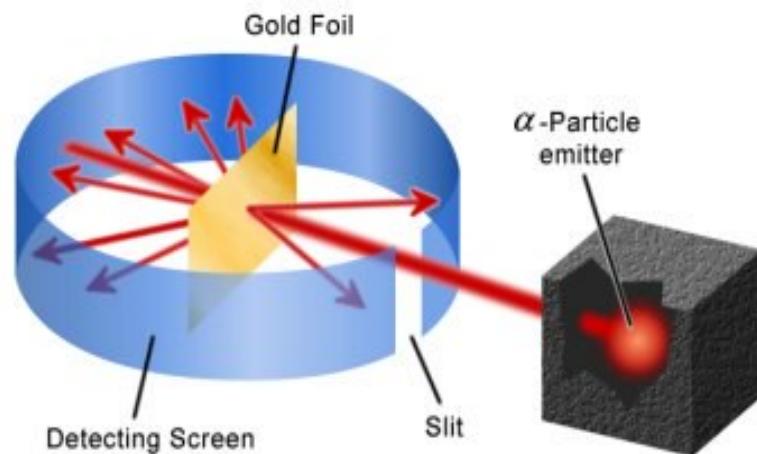
486.1 nm

$$656.2 \text{ nm} \quad R_{\infty} = 1.09678 \times 10^7 \text{ m}^{-1}$$

The Rydberg-Ritz Combination Principle states that the spectral lines of any element include frequencies that are either the sum or the difference of the frequencies of two other lines.

“ R_{∞} is the most accurately measured fundamental physical constant”

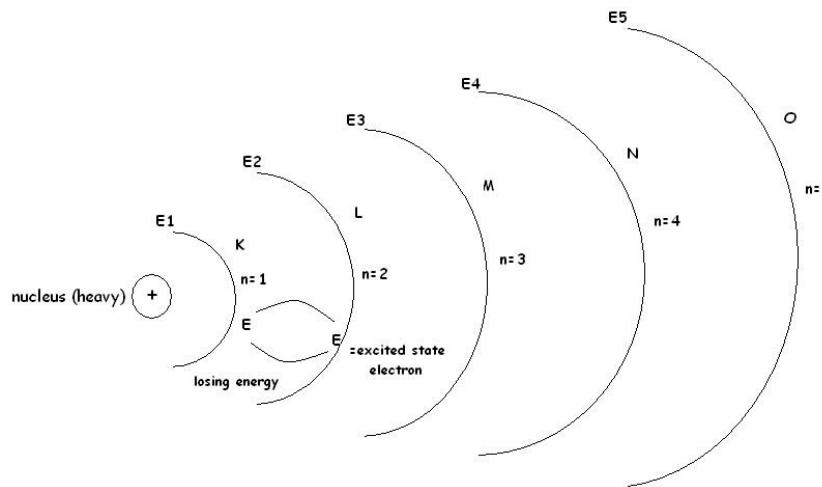
Rutherford Model of Atom



Planetary model of atoms with central positively charged nucleus and electrons going around

Classical electrodynamics predicts that such an arrangement emits radiation continuously and is unstable

Bohr Phenomenological Model of Atom



Electrons rotate in circular orbits around a central (massive) nucleus, and obeys the laws of classical mechanics.

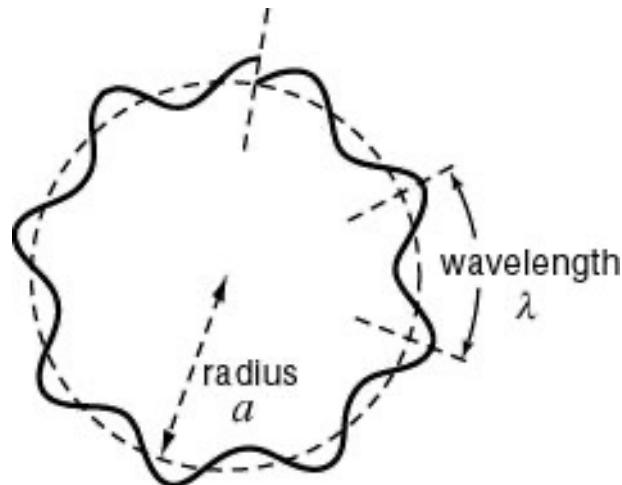
Allowed orbits are those for which the electron's angular momentum equals an integral multiple of $\hbar/2\pi$ i.e. $m_e v r = nh/2\pi$

Energy of H-atom can only take certain discrete values: “Stationary States”

The Atom in a stationary state does not emit electromagnetic radiation

When an atom makes a transition from one stationary state of energy E_a to another of energy E_b , it emits or absorbs a photon of light: $E_a - E_b = \hbar\nu$

Bohr Model of Atom

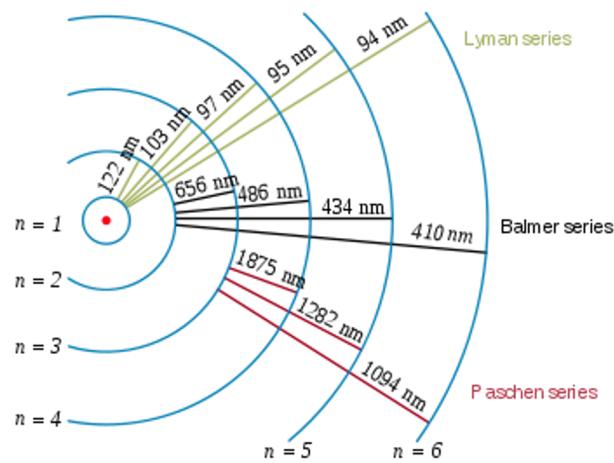


Angular momentum quantized

$$mvr = \frac{nh}{2\pi} \quad n=1,2,3,\dots$$
$$(2\pi r = n\lambda)$$

Energy expression

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \cdot \frac{1}{n^2}$$



Spectral lines

$$\Delta E = \frac{m_e e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = h\nu \quad n_i, n_f = 1, 2, 3, \dots$$

Explains Rydberg formula

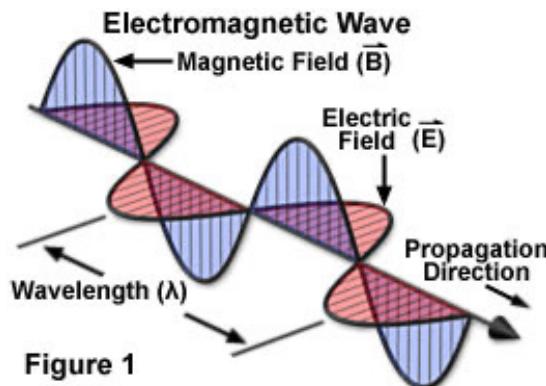
$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^2} = 1.09678 \times 10^{-2} \text{ nm}^{-1}$$

Ionization potential of H atom 13.6 eV

We are talking about electron in an atom, so is it a particle or wave?

Emergence of wave-particle duality

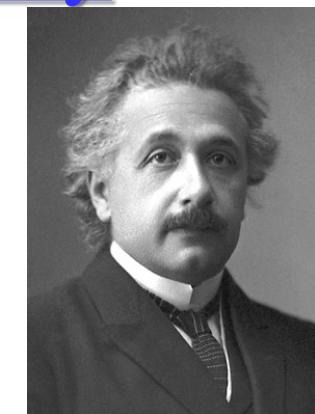
Photoelectric Effect: Wave –Particle Duality



Electromagnetic Radiation

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

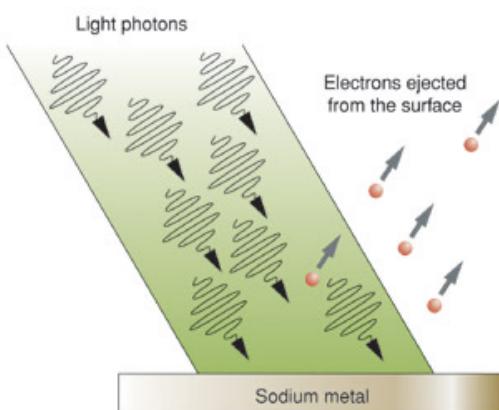
Wave energy is related to Intensity
 $I \propto E^2 o$ and is independent of ω



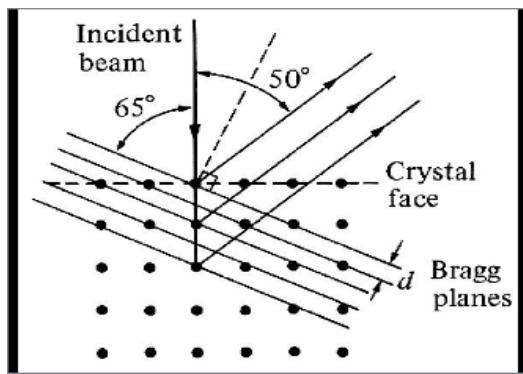
Einstein borrowed Planck's idea that $\Delta E = hv$ and proposed that radiation itself existed as small packets of energy (Quanta) now known as PHOTONS

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

ϕ = Energy required to remove electron from surface



Diffraction of Electrons : Wave –Particle Duality



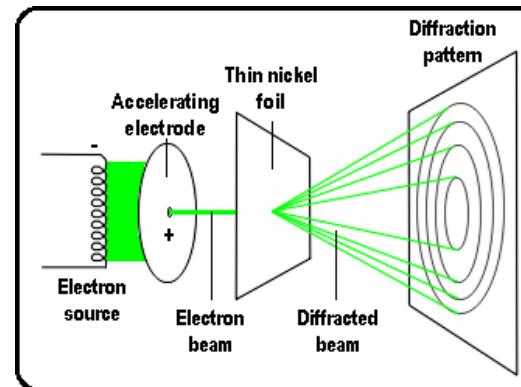
Davisson-Germer Experiment

A beam of electrons is directed onto the surface of a nickel crystal. Electrons are scattered, and are detected by means of a detector that can be rotated through an angle θ . When the Bragg condition $m\lambda = 2ds\sin\theta$ was satisfied (d is the distance between the nickel atom, and m an integer) constructive interference produces peaks of high intensity

Diffraction of Electrons : Wave –Particle Duality

G. P. Thomson Experiment

Electrons from an electron source were accelerated towards a positive electrode into which was drilled a small hole. The resulting narrow beam of electrons was directed towards a thin film of nickel. The lattice of nickel atoms acted as a diffraction grating, producing a typical diffraction pattern on a screen



de Broglie Hypothesis: Mater waves



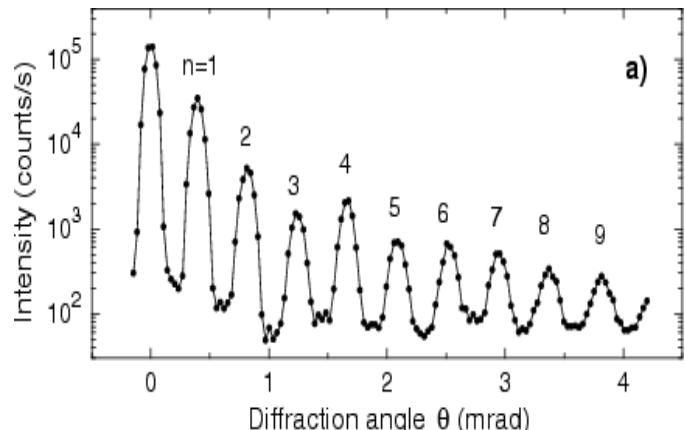
Since **Nature** likes **symmetry**,
Particles also should have **wave-like** nature

De Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Electron moving @ 10^6 m/s

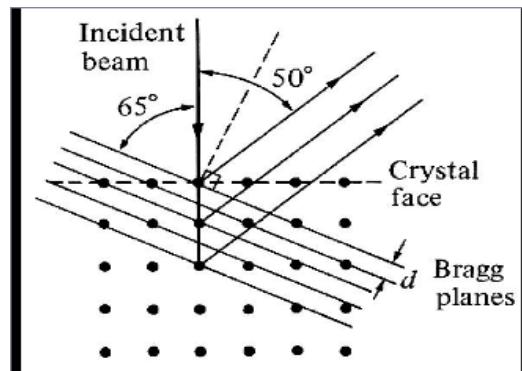
$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34} \text{ J s}}{9.1 \times 10^{-31} \text{ Kg} \times 1 \times 10^6 \text{ m/s}} = 7 \times 10^{-10} \text{ m}$$



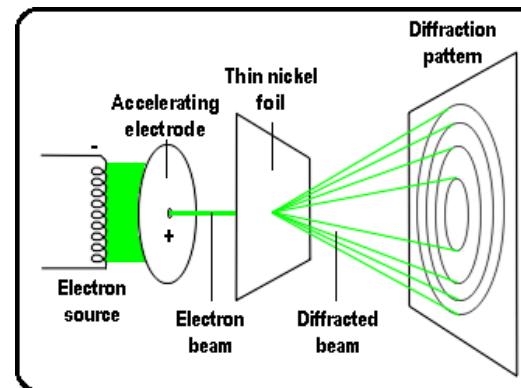
He-atom scattering

Diffraction pattern of He atoms at the speed 2347 m s^{-1} on a silicon nitride transmission grating with 1000 lines per millimeter. Calculated de Broglie wavelength $42.5 \times 10^{-12} \text{ m}$ de Broglie wavelength too small for macroscopic objects

Diffraction of Electrons : Wave –Particle Duality



The wavelength of the electrons was calculated, and found to be in close agreement with that expected from the De Broglie equation



Interference Pattern of Electrons : Wave –Particle Duality

Double Slit Experiment

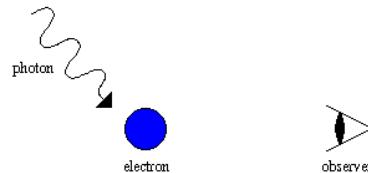


Uncertainty Principle

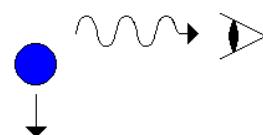


Measurement Problem in Quantum Mechanics

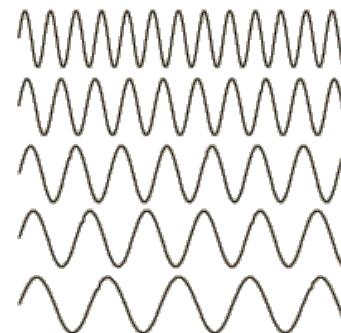
before observation



after observation

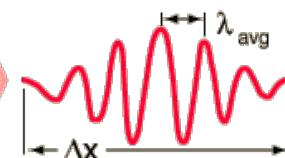


Precisely determined momentum



A sine wave of wavelength λ implies that the momentum p is precisely known: $p = \frac{h}{\lambda}$.
But the wavefunction and the probability of finding the particle $\psi^*\psi$ is spread over all of space. p precise
 x unknown

Adding several waves of different wavelength together will produce an interference pattern which begins to localize the wave.



but that process spreads the momentum values and makes it more uncertain. This is an inherent and inescapable increase in the uncertainty Δp when Δx is decreased.

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

Uncertainty principle

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{4\pi}$$

I have shown that exactly 20,308 more people used the Heisenberg Uncertainty Principle today than yesterday.



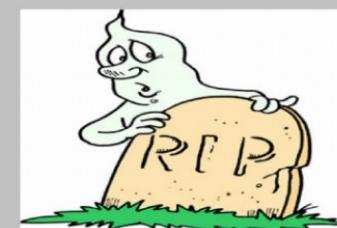
So in other words, you have no idea how many people used it today.



Correct.



HERE LIES
HEISENBERG



Uncertainty Principle in ACTION!!!



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

Schrodinger's philosophy



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

A concoction of

$$E = T + V = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V$$

$E = h\nu = \hbar\omega$ Wave is Particle

$\lambda = \frac{h}{p} = \hbar k$ Particle is Wave

*let me start with
classical wave equation*

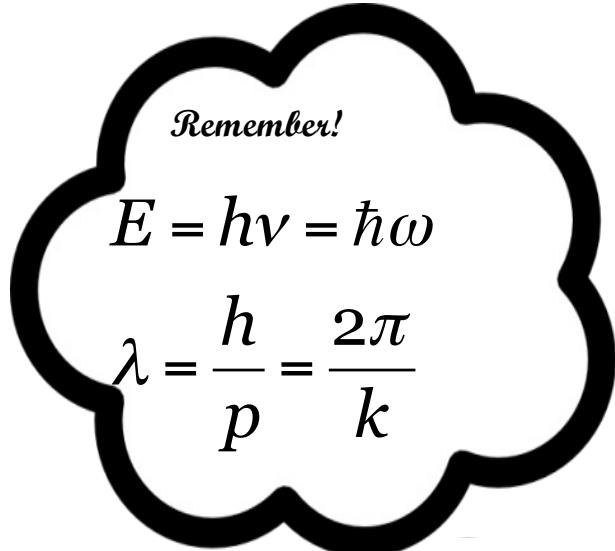


Schrodinger's philosophy

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2} \quad \text{Classical Wave Equation}$$

$\Psi(x,t)$ = Amplitude

$\Psi(x,t) = Ce^{i\alpha}$; Where $\alpha = 2\pi \left(\frac{x}{\lambda} - vt \right)$ is the phase



$$\alpha = 2\pi \left(\frac{x}{\lambda} - vt \right) = \frac{x \cdot p - E \cdot t}{\hbar}$$

Schrodinger's philosophy

$$\Psi(x,t) = Ce^{i\alpha} \quad \text{and} \quad \alpha = \frac{x \times p - E \times t}{\hbar}$$

$$\frac{\partial \Psi(x,t)}{\partial t} = iCe^{i\alpha} \times \frac{\partial \alpha}{\partial t} = i \times \Psi(x,t) \times \frac{\partial \alpha}{\partial t} = i \times \Psi(x,t) \times \left(\frac{-E}{\hbar} \right)$$

$$\boxed{\frac{-\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = E \times \Psi(x,t)}$$

$$\frac{\partial \Psi(x,t)}{\partial x} = iCe^{i\alpha} \times \frac{\partial \alpha}{\partial x} = i \times \Psi(x,t) \times \frac{\partial \alpha}{\partial x} = i \times \Psi(x,t) \times \left(\frac{p_x}{\hbar} \right)$$

$$\boxed{\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x} = p_x \times \Psi(x,t)}$$

Schrodinger Equation

In classical mechanics \hat{H} represents total energy

We can therefore write

$$\hat{H}\psi = W\psi \quad \text{as} \quad \hat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \cdot \psi(x)$$

Schrodinger equation is an eigenvalue equation

There can be many solutions $\psi_n(x)$ each corresponding to different energy E_n

Laws of Quantum Mechanics

The mathematical description of Quantum mechanics is built upon the concept of an operator

Classical Variable

Position, x

Momentum, $p_x = mv$

Kinetic Energy, $T_x = \frac{p_x^2}{2m}$

Kinetic Energy, $T = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$

Potential Energy, $V(x)$

QM Operator

\hat{x}

$$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} = -i\hbar \frac{d}{dx}$$

$$\hat{T}_x = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\hat{T} = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$\hat{V}(x)$

Laws of Quantum Mechanics

1. The state of a system is completely specified by a wave- function $\Psi(r,t)$.
2. To every observable in classical mechanics, there corresponds a linear operator in quantum mechanics
3. In measurement of observable associated with operator A , *only values that will be observed* are the (real) *eigenvalues of A, which satisfy the eigenvalue eq.*

$$\hat{A} \cdot \Psi_n = a_n \cdot \Psi_n$$

Ψ_n are the eigenfunctions of the system and a_n are corresponding eigenvalues

If the system is in state Ψ_k , a measurement on the system will yield an eigenvalue a_k

Laws of Quantum Mechanics

Only real eigenvalues will be observed, which will specify a number corresponding to the classical variable

If $\Psi(x) = \sin(cx)$

$$\frac{d}{dx} \Psi(x) = c \cdot \cos(cx)$$

$$\frac{d^2}{dx^2} \Psi(x) = -c^2 \cdot \sin(cx) = -c^2 \cdot \Psi(x)$$

If $\Psi(x) = e^{\alpha x}$

There may be, and typically are, many eigenfunctions for the same QM operator!

$$\frac{d}{dx} \Psi(x) = \alpha \cdot e^{\alpha x}$$

$$\frac{d^2}{dx^2} \Psi(x) = \alpha^2 \cdot e^{\alpha x} = \alpha^2 \cdot \Psi(x)$$

Laws of Quantum Mechanics

4. All the eigenfunctions of Quantum Mechanical operators are “Orthogonal”

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \langle \psi_m | \psi_n \rangle = 0 \quad \text{for } m \neq n$$

Laws of Quantum Mechanics

5. The average value of the observable corresponding to operator \hat{A} is

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\nu$$

From classical correspondence we can define average values for a distribution function $P(x)$

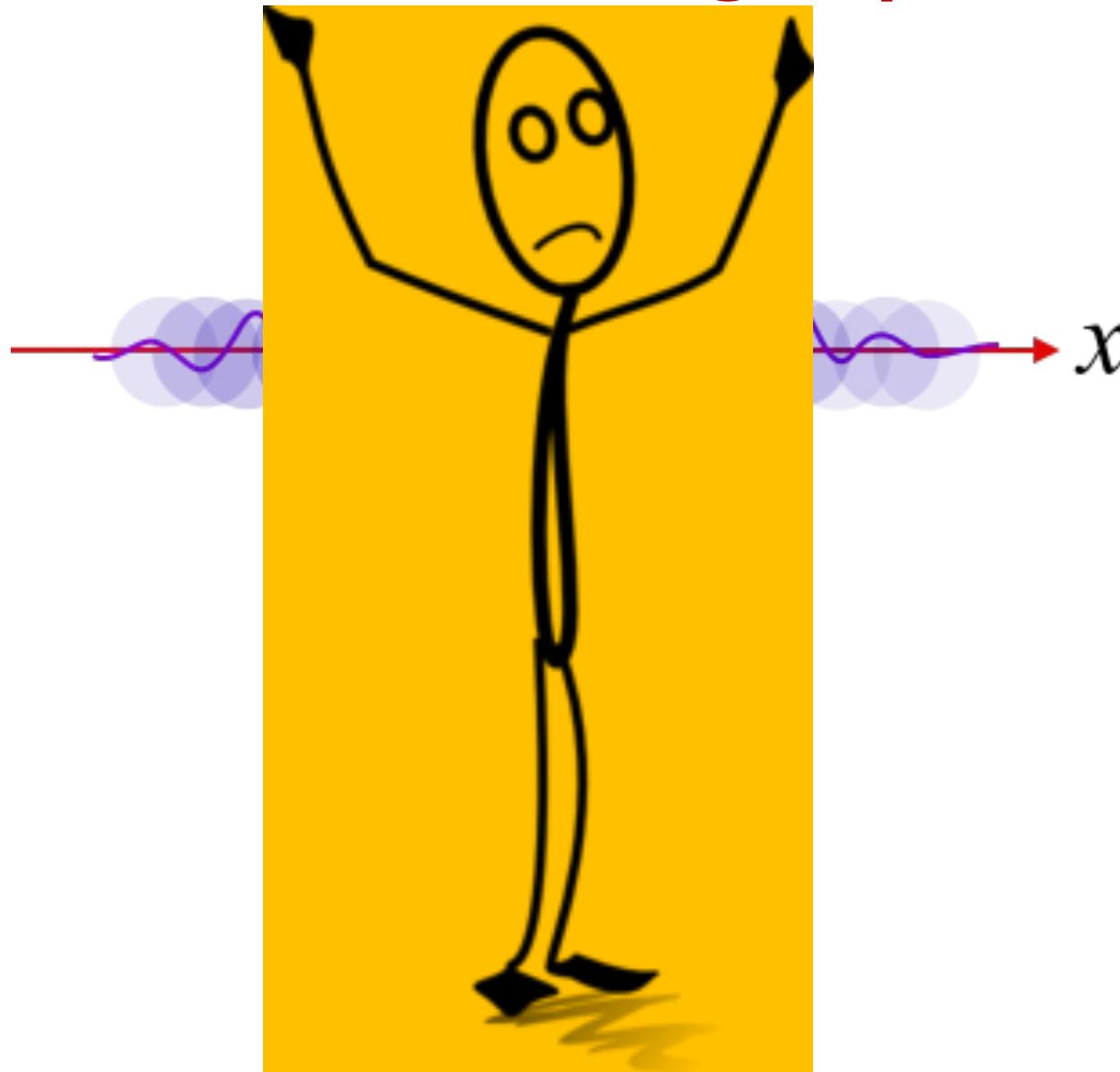
$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) \cdot dx \text{ and } \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \cdot dx$$

$\langle a \rangle$ corresponds to the average value of a classical physical quantity or observable , and \hat{A} represents the corresponding Quantum mechanical operator

$$\langle a \rangle = \int_{-\infty}^{+\infty} \hat{A} \cdot P(x) dx = \int_{-\infty}^{+\infty} \hat{A} \cdot |\Psi|^2 dx \underset{\text{all space}}{\approx} \int \Psi^* \hat{A} \Psi dx = \langle \Psi | \hat{A} | \Psi \rangle$$

What can you get from solving the Schrodinger
Equation?

What is the meaning of $\psi(x,t)$?



Born Interpretation



Classical wave equation:

$\Psi(x,t)$ = Amplitude and $|\Psi(x,t)|^2$ = Intensity

Quantum mechanical system:

- The state is completely specified by a wavefunction $\Psi(x,t)$, which can be complex
- All possible information can be derived from $\Psi(x,t)$
- Intensity is equivalent to Probability (density).
- $|\Psi(x,t)|^2 = P(x)$

Born Interpretation



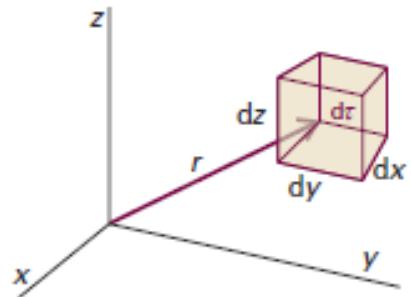
Probability density

$$P(x) = |\Psi(x, t)|^2 = \Psi^*(x, t) \cdot \Psi(x, t)$$

Probability

$$P(x_a \leq x \leq x_a + dx) = |\Psi(x, t)|^2 dx = \Psi^*(x_a, t) \cdot \Psi(x_a, t) dx$$

Probability in 3-dimensions



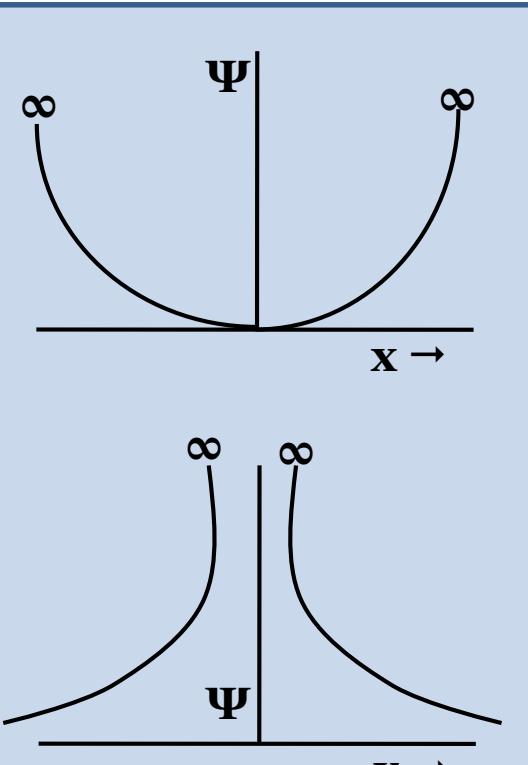
$$\begin{aligned} P(x_a \leq x \leq x_a + dx, y_a \leq y \leq y_a + dy, z_a \leq z \leq z_a + dz) \\ &= \Psi^*(x_a, y_a, z_a, t') \cdot \Psi(x_a, y_a, z_a, t') dx dy dz \\ &= |\Psi(x_a, y_a, z_a, t')|^2 d\tau \end{aligned}$$

6. Normalization of Wavefunction

Since $\Psi^*\Psi d\tau$ is the probability, the total probability of finding the particle somewhere in space has to be unity

$$\iiint_{\text{all space}} \Psi^*(x, y, z) \cdot \Psi(x, y, z) dx dy dz \\ = \int_{\text{all space}} \Psi^* \Psi d\tau = \langle \Psi | \Psi \rangle = 1$$

If function diverges, i.e. $\rightarrow \infty$: Ψ can not be normalized, and therefore is NOT an acceptable wave function.



Unacceptable wavefunction

Ψ must vanish at $\pm\infty$, or more appropriately at the boundaries and **Ψ** must be finite

Restrictions on wavefunction

ψ must be a solution of the Schrodinger equation

ψ must be normalizable: ψ must be finite and $\rightarrow 0$ at boundaries/
 $\pm\infty$

Ψ must be a continuous function of x,y,z

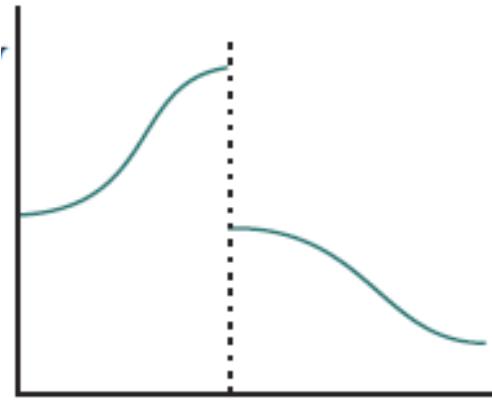
$d\Psi/dq$ must be must be continuous in q

Ψ must be single-valued

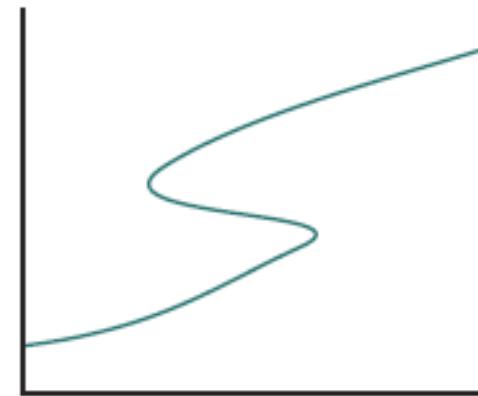
Ψ must be quadratically-intergrable
(square of the wavefunction should be integrable)

[Origin of quantization](#)

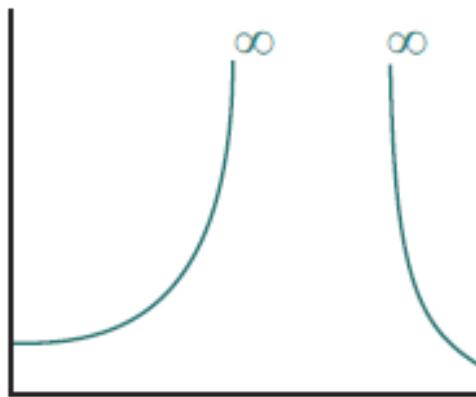
Restrictions on wavefunction



Unacceptable because
 ψ is not continuous



Unacceptable because
 ψ is not single-valued



Unacceptable because
 ψ goes to infinity

Essence of Quantum Mechanics

- **Not deterministic:** Can not precisely determine many parameters in the system, but Ψ can provide all the information (spatio-temporal) of a system.
- Only **average values** and **probabilities** can be obtained for classical variables, now in new form of “operators”.
- Total energy is conserved, but **quantization** of energy levels come spontaneously from **restriction** on wave function or **boundary condition**
- Final outputs tally very well with experimental results, and does not violate Classical mechanics for large value of mass.

Quantum Mechanics

Examples of Exactly Solvable Systems

1. Free Particle
2. Particle in a Square-Well Potential
3. Hydrogen Atom

