Unit III : Introduction to Quantum Mechanics

Basics of Quantum Mechanics
- Quantum Point of View -

- Quantum particles can act as both particles and waves ➔ WAVE-PARTICLE DUALITY
- Quantum state is a conglomeration of several possible outcomes of measurement of physical properties ➔ Quantum mechanics uses the language of PROBABILITY theory (random chance)
- An observer cannot observe a microscopic system without altering some of its properties. Neither one can predict how the state of the system will change.
- QUANTIZATION of energy is yet another property of "microscopic" particles.

Basics of Quantum Mechanics
- Heisenberg Uncertainty Principle -

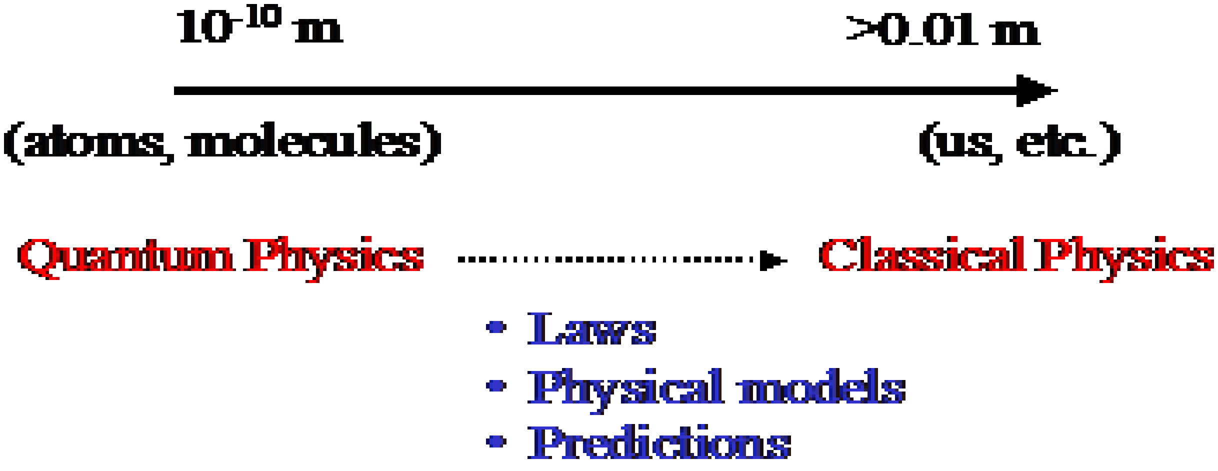
- One cannot unambiguously specify the values of particle's position and its momentum for a microscopic particle, i.e.

$$\Delta x(t_0) \cdot \Delta p_x(t_0) \geq \frac{1}{2} \frac{h}{2\pi}$$

- Position and momentum are, therefore, considered as incompatible variables.
- The Heisenberg uncertainty principle strikes at the very heart of the classical physics => the particle trajectory.

- The Correspondence Principle -

When Quantum physics is applied to macroscopic systems, it must reduce to the classical physics. Therefore, the nonclassical phenomena, such as uncertainty and duality, must become undetectable. Niels Bohr codified this requirement into his Correspondence principle:



- Laws
- Physical models
- Predictions

- Particle-Wave Duality -

- The behavior of a "microscopic" particle is very different from that of a classical particle:
  - ➔ in some experiments it resembles the behavior of a classical wave (not localized in space)
  - ➔ in other experiments it behaves as a classical particle (localized in space)
- Corpuscular theories of light treat light as though it were composed of particles, but can not explain DIFRACTION and INTERFERENCE.
- Maxwell's theory of electromagnetic radiation can explain these two phenomena, which was the reason why the corpuscular theory of light was abandoned.

- Waves as particles:

  - Max Plank work on black-body radiation, in which he assumed that the molecules of the cavity walls, described using a simple oscillator model, can only exchange energy in quantized units.

  - 1905 Einstein proposed that the energy in an electromagnetic field is not spread out over a spherical wavefront, but instead is localized in individual clumbs - quanta. Each quantum of frequency n travels through space with speed of light, carrying a discrete amount of energy and momentum =photon => used to explain the photoelectric effect, later to be confirmed by the *x*-ray experiments of Compton.

- Particles as waves

  - Double-slit experiment, in which instead of using a light source, one uses the electron gun. The electrons are diffracted by the slit and then interfere in the region between the diaphragm and the detector.

  - Aharonov-Bohm effect

Time Dependent Schrodinger Eq.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V(x,y,z)\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

$$\Psi(x,y,z,t) = e^{-iEt/\hbar}\psi(x,y,z)$$

$$V=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{\sqrt{x^2+y^2+z^2}}$$

Wave Equation!

Time Independent Schrodinger Eq.

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

$$V=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{\sqrt{x^2+y^2+z^2}}$$

Energy of the electron

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2n^2\hbar^2} \qquad n = 1, 2, 3, \ldots$$

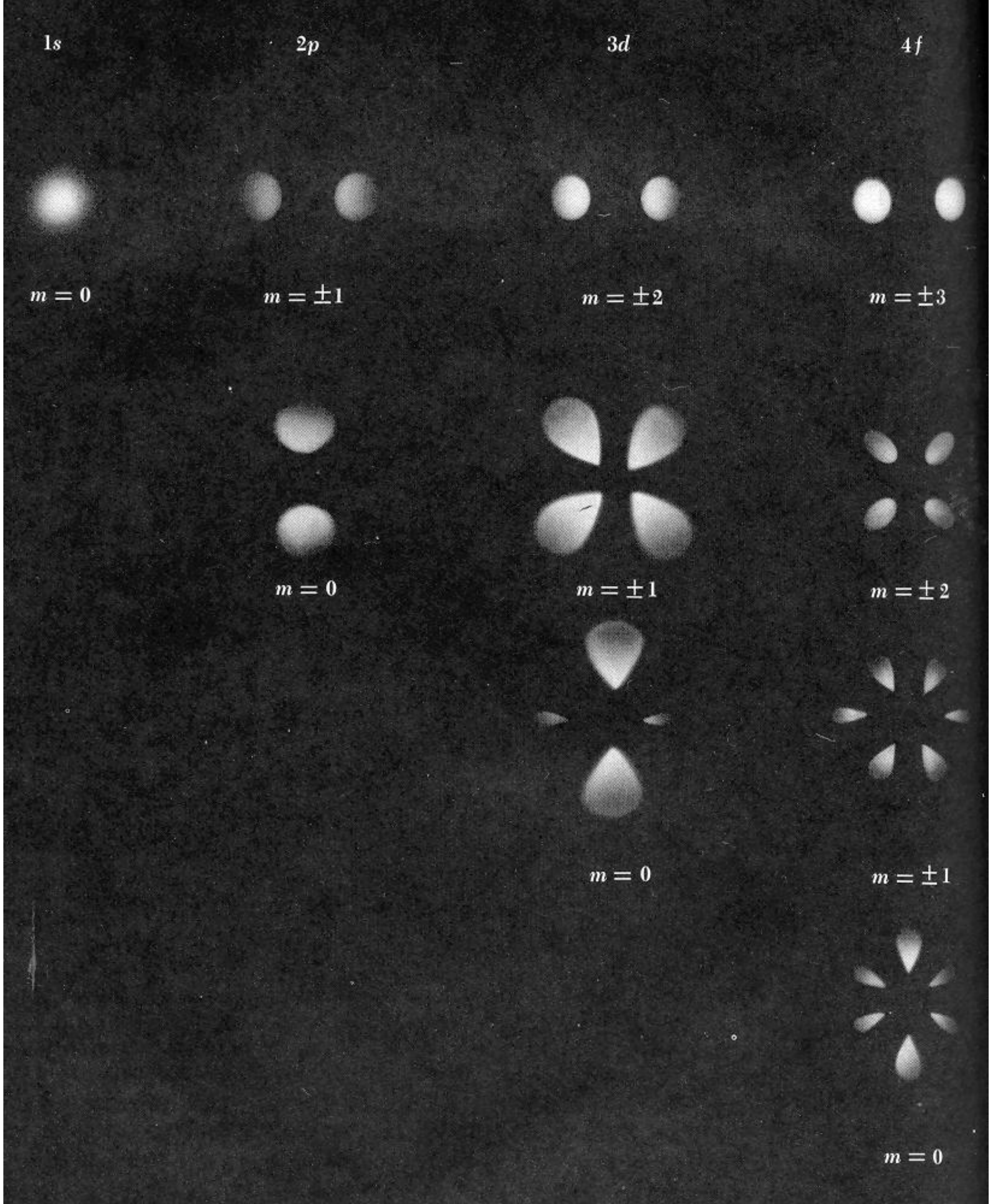
Energy is related to the Principle Quantum number, n.

This gives 3 of the 4 quantum numbers, the last one is the spin quantum number, s, either +½ or – ½.

Wave Functions

Probability to find an electron

$$|\Psi|^2 = \Psi\Psi^*,$$



Energy of the electron

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2n^2\hbar^2} \qquad n = 1, 2, 3, \ldots$$

The Born interpretation of wave function

- A wave function gives **the probability** of finding the particle at a certain location.
- This is the most commonly misunderstood concept in quantum chemistry.
- It is a mistake to think of a particle spreading like a cloud according to the wave function. Only **its probability density** does.

- **What is a wave function?**
- It has all the dynamical information about the particle.
- More immediately, it has the information about the location of the particle.

Max Born

- The square of the wave function $|\Psi|^2$ at a point is proportional to the probability of finding the particle at that point.

$$|\Psi|^2 = \Psi^* \Psi \geq 0$$

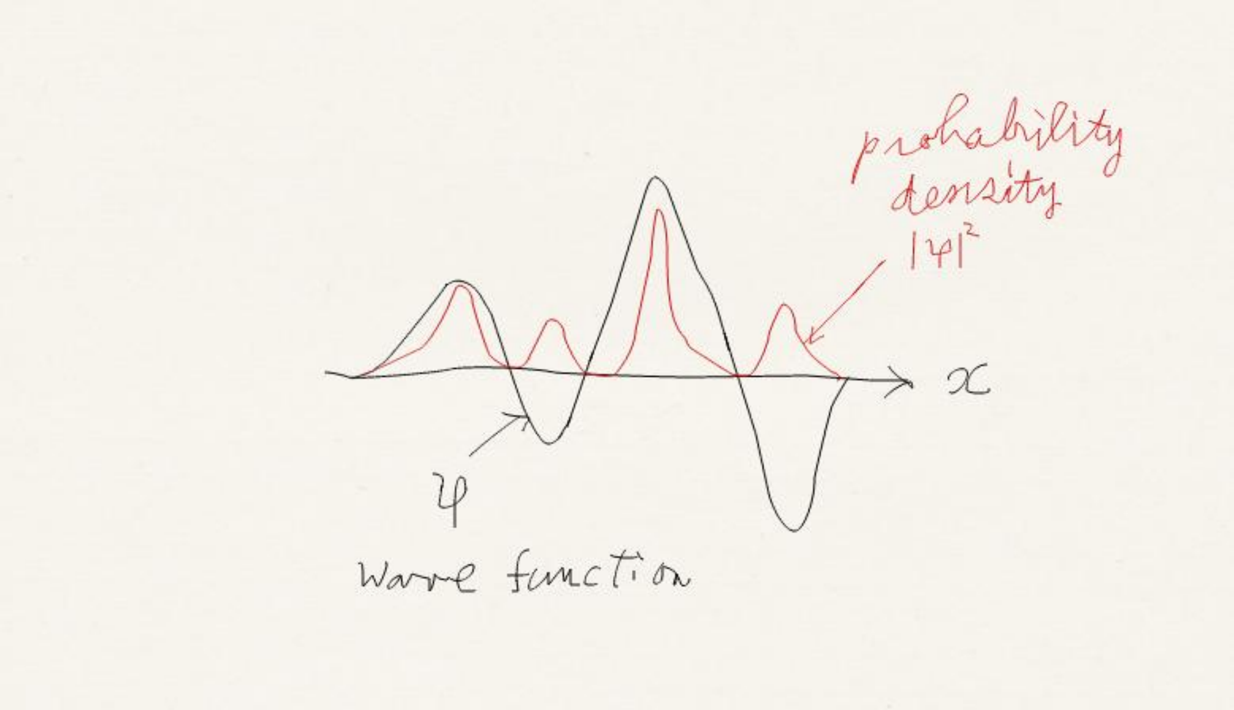
Always real, non-negative

Complex conjugate of Ψ

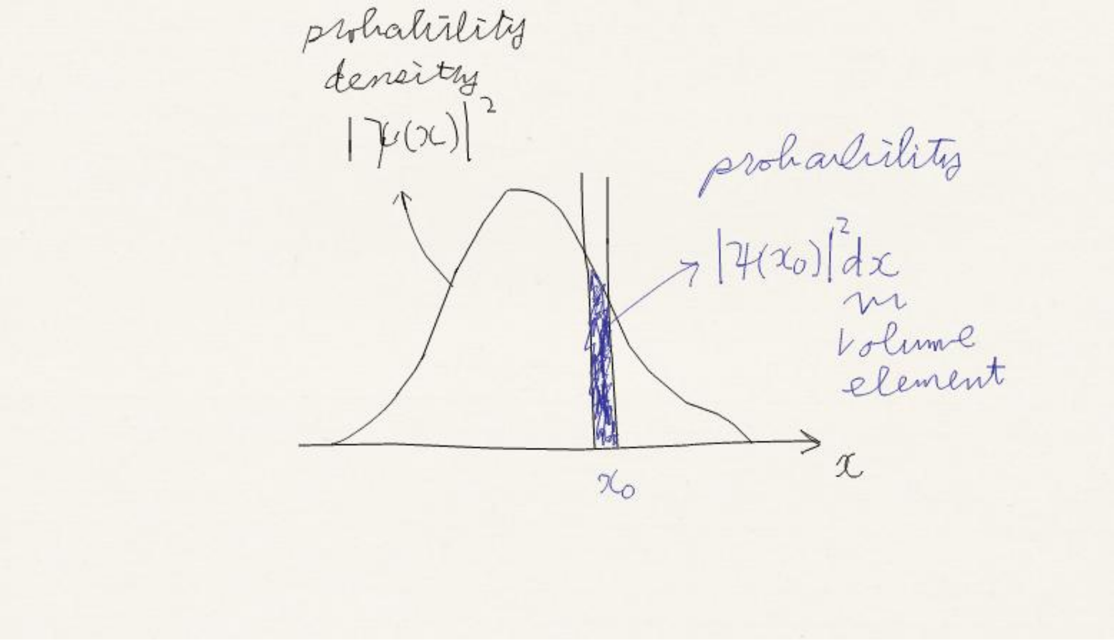
$$|a+bi|^2 = (a+bi)^*(a+bi) = (a-bi)(a+bi)$$

$$= a^2 - b^2 i^2 = a^2 + b^2 \geq 0$$

- A wave function is in general complex.
- But $|\Psi|^2$ is always real, non-negative.



- One-dimension: if the wave function of a particle has the value Ψ at point *x*, the probability of finding the particle between *x* and *x+dx* is proportional to $|\Psi|^2 dx$.



The Born interpretation

- Three-dimension: the probability of finding the particle in an infinitesimal volume $d\tau = dx\,dy\,dz$ at point $\boldsymbol{r}$ is proportional to $|\Psi(\boldsymbol{r})|^2\,d\tau$.
- $|\Psi(\boldsymbol{r})|^2$ is the **probability density**.

The Born interpretation

- It is a mistake to think that a particle spreads like a cloud or a mist with density proportional to $|\Psi|^2$. (Such an interpretation was seriously considered in physics but was dismissed.)

Future Scope and relevance to industry

- This dual nature is utilized in solar power technology. Incoming sunlight is concentrated by mirrors and lenses that rely on the wave-like properties of light. Once inside a solar cell, however, this focused light collides with electrons in a particle-like way, thus freeing the electrons to create an electric current.
- Qunatum dots and wires can be used in opto-electronic devices.
- Research based on various properties of Qunatum dots

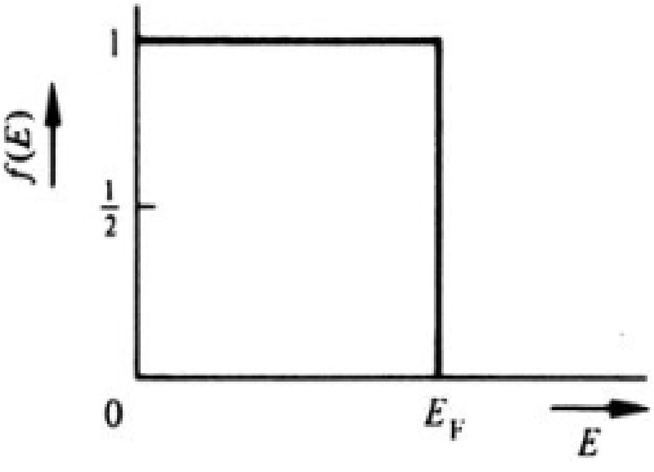
Classical free electron theory: Drude-Lorentz theory

- Metals consist of large number of free electrons that behaves like a molecules of perfect gas.
- Assembly of free electrons in a metal: free electron gas
- Random motion of free electron gas: speed is function of temperature, no practical contribution to conductivity
- On application of external field, random motion is modified, e- have some drift velocity
- All valence electrons can absorb energy. Average K.E.= 3/2 KT
- Follows Maxwell-Boltzman statistics
- Potential is uniform everywhere inside the crystal
- P.E. of electron inside the metal is neglected. Therefore, Total Energy= K.E.

Failure of Classical free electron theory

- Could not explain heat capacity of free electron gas
- Could not explain paramagnetic susceptibility of free elelctrons
- Could not explain variation in electrical conductivity with temperature
- Could not explain Wiedemann-Frenz law
- Could not explain long mean free path at low temperatures

Fermi-Dirac Statistics: Occupation Probability



(a) $T \to 0$ K