

# CH 107 Week 0 and Week 1: Summary

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We started the CH 107 Lectures for this week by discussing the Wave Nature of Matter. We talked about the Uncertainty Principle (and how Bohr's Model did not account for it), and we talked about various electron diffraction experiments (such as the Davisson-Germer Experiment and the GP Thompson Experiment) which proved de Broglie's Hypothesis that matter could also exhibit Wave Properties. These experiments also showed that matter waves followed de Broglie's Law:

$$\lambda_{dB} = \frac{h}{p} \quad (1)$$

This explained why electrons showed only particle properties in most situations, and showed their wave nature only when interacting with objects of roughly the same size as their wavelengths, eg: Atomic Lattices.

We then discussed the Schrödinger Equation, where each particle was associated with a Wave Function  $\Psi(x, y, z, t)$ , which followed Schrödinger's Equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \quad (2)$$

We then applied separation of variables on this Equation and obtained:

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-\frac{iEt}{\hbar}} \quad (3)$$

where  $\psi(x, y, z)$  satisfies the Time Independent Schrödinger Equation:

$$\hat{H}\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \quad (4)$$

It was noticed that this was an eigenvalue equation for the Hamiltonian Operator  $\hat{H}$ , which represents the total Energy of the Particle. Therefore,  $\psi$  must be an energy eigenstate of the particle, with Energy  $E$ .

We then talked about the Born interpretation of the wave function  $\Psi$ . This states that the particle is completely represented by its Wave Function  $\Psi$ , which tells us all the information that we can know about the Particle.  $|\Psi|^2 = \Psi^*\Psi$  (the "Intensity" of the Wave Function), represents the Probability Density of the particle being measured to be at a particular position i.e., the Probability

that the particle is measured to be inside a volume  $V$ , is given by:

$$P = \iiint_V |\Psi|^2 d\tau$$

The Born interpretation follows from the Copenhagen Interpretation of Quantum Mechanics, which states that before measurement of the position, the particle does not have a position, and it is the process of measurement, which forces the particle to attain a fixed position, via a collapse of the wavefunction into a position eigenstate. Hence this theory, is inherently Probabilistic and Non-Deterministic. We also looked at the Realist and Agnostic Interpretations of Quantum Mechanics which were disproved by the experiments conducted by John Bell in 1964.

We also discussed operators, and how every observable in Quantum Mechanics is associated with an operator, which operates on the wave function and gives us information about that observable. eg: The position, momentum and energy operators are  $\hat{x} = x$ ,  $\hat{p} = -i\hbar\nabla$  and  $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m}\nabla^2 + V(x)$  respectively.

Eigenfunctions of this operator represent states of definite value of the observable, and on the measurement of the observable, the wave function collapses to one of these Eigenstates. The eigenvalues of these operators represent the allowed values of the observable. Since all physical observables are represented by Hermitian Operators, all the eigenvalues are real, and eigenfunctions corresponding to different eigenvalues are orthogonal, i.e.

$$\langle\psi_m|\psi_n\rangle = \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \delta_{mn} \quad (5)$$

where  $\delta_{mn}$  is the Kronecker Delta, which is 1, when  $m = n$ , and 0 otherwise. The expectation value of an observable represented by an operator  $\hat{Q}$ , is given by:

$$\langle\Psi|\hat{Q}\Psi\rangle = \int_{-\infty}^{\infty} \Psi^* \hat{Q}\Psi dx \quad (6)$$

We then looked at the conditions required for a Wave Function (a solution of the Schrödinger Equation) to be physically acceptable:

1. The Wave Function should be a single valued Function of the spatial coordinates and time.
2. The Wave Function should be continuous (at the most it may have removable discontinuities).
3. The Wave Function should be differentiable and its derivative should be continuous (except at points where the Potential diverges).
4. The Wave Function should go to 0 as the spatial coordinates tend to  $\infty$ , and the Wave Function should not diverge at any point (i.e., the Wave Function must be bounded).

5. The Wave Function must be Square Integrable (Normalisable). That is,  $\langle \Psi | \Psi \rangle = \int_{-\infty}^{\infty} |\Psi|^2 dx$  must be finite and non-zero. A physical Wave Function is always normalized ( $\langle \Psi | \Psi \rangle = 1$ ), as this represents the fact that the probability of the particle being found is always 1. Any square Integrable Wave Function is always Normalisable. This is because if  $\Psi$ , is a solution of the Schrödinger Equation, with  $\langle \Psi | \Psi \rangle = k$ , where  $k$  is a finite, positive real number, then  $\Psi' = A\Psi$ , is also a solution, where  $|A|^2 = \frac{1}{k}$ , satisfying  $\langle \Psi' | \Psi' \rangle = 1$ . This is because the Schrödinger Equation is a Linear Differential Equation. Note that, even if a solution of the Time Independent Schrödinger Equation is not normalisable, as long as it satisfies the other conditions mentioned above, we can take linear combinations of it to get a normalisable Wave Function satisfying the Time Dependent Schrödinger Equation.

These conditions can sometimes lead to the Quantization of Dynamical variables such as Energy.

We then solved the Schrödinger Equation for a One-Dimensional Free Particle. For the free particle, it turned out that the stationary states were given by:

$$\Psi(x, t) = Ae^{i(kx - \frac{\hbar k^2 t}{2m})} + Be^{-i(kx + \frac{\hbar k^2 t}{2m})} \quad (7)$$

This Wave Function is not normalisable, and hence cannot represent a physically realisable Wave Function, but, as mentioned earlier, Linear Combinations of this Wave Function can be made Normalisable.

Also note that here,

$$E = \frac{\hbar^2 k^2}{2m} \quad (8)$$

Therefore,  $E$  is continuous and not quantized.

We then considered a particle in an infinite Square Well, i.e., a Particle in a Box. We observed that, in one dimension, the stationary states were given by:

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{in^2\pi^2\hbar t}{2mL^2}} \quad (9)$$

where  $n$  is a positive integer. Note that, here:

$$\langle x \rangle = \langle \Psi_n | x | \Psi_n \rangle = \frac{L}{2} \quad (10)$$

and

$$\langle p \rangle = \langle \Psi_n | (-i\hbar \frac{\partial \Psi_n}{\partial x}) \rangle = 0 \quad (11)$$

We noticed that, here, the energy was given by:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad (12)$$

i.e, Energy is Quantized! It is also noticed, that the Ground State Energy is non-zero. This is guaranteed by Heisenberg's Uncertainty Principle, as if the

Energy were 0, the momentum of the particle would be precisely 0, and it's position would be precisely constant, thus  $\Delta x = \Delta p = 0$ , violating Heisenberg's Uncertainty Principle.

We then considered the Spectroscopy of this system, and found that:

$$\Delta E = \frac{hc}{\lambda} = \frac{(n_1^2 - n_2^2)h^2}{8mL^2} \quad (13)$$

We then considered the selection rule for allowed spectroscopic transitions, which came out to be:

$$\Delta n = 2k + 1 \quad (14)$$

(i.e.  $\Delta n$  must be odd ( $\Delta n = 1, 3, 5, \dots$ )) We applied this model to simple conjugated systems. It correctly predicted that as the length of the conjugation increased, the wavelength of absorption also increases. We then quantitatively, considered Hexatriene, which is a conjugated system of Length  $L = 0.73 \text{ nm}$ . On filling 6 electrons, we would fill 2 electrons in  $n = 1$ , 2 electrons in  $n = 2$ , and 2 electrons in  $n = 3$ . Therefore, the first allowed transition would be from  $n = 3$  to  $n = 4$ , which would have:

$$\lambda = \frac{8mL^2c}{h(n_f^2 - n_i^2)} \quad (15)$$

$$\lambda = \frac{8mL^2c}{7h} = 251 \text{ nm} \quad (16)$$

This is very close to the experimentally obtained value of 258 nm, and shows that the particle in a box is a good first approximation of linear conjugated systems.

We then considered the behaviour of Quantum Dots, which behave like Particles in Boxes. These also show colours, according to the relation:

$$\lambda = \frac{8mL^2c}{h(n_f^2 - n_i^2)} \quad (17)$$

We also solved the Schrödinger Equation for a Particle in a box for two and three dimensions, and obtained:

For two dimensions:

$$\Psi_{n_x n_y}(x, y, t) = \Psi_{n_x}(x, t) \Psi_{n_y}(y, t) \quad (18)$$

$$\Psi_{n_x n_y}(x, y, t) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) e^{-\frac{i\pi^2 \hbar t}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)} \quad (19)$$

and

$$E_{n_x n_y} = E_{n_x} + E_{n_y} \quad (20)$$

$$E_{n_x n_y} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) \quad (21)$$

For three dimensions:

$$\Psi_{n_x n_y n_z}(x, y, z, t) = \Psi_{n_x}(x, t) \Psi_{n_y}(y, t) \Psi_{n_z}(z, t) \quad (22)$$

$$\Psi_{n_x n_y n_z}(x, y, z, t) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) e^{-\frac{i \pi^2 \hbar t}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)} \quad (23)$$

and

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} \quad (24)$$

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (25)$$

Note that, while no degeneracy was possible in the one-dimensional case, degeneracy is possible in the two and three dimensional cases.

For example, for a cubical square box,  $\Psi_{211}$ ,  $\Psi_{121}$  and  $\Psi_{112}$  are all degenerate (they have the same Energy). This degeneracy occurs due to the extra symmetry that the system has got by making  $L_x = L_y = L_z$ .