

**PHY 301**

**QUANTUM MECHANICS LECTURE NOTES**

**TOPIC 1**

**by**

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## **Chapter 1**

### **Fundamental Axioms of Quantum Theory**

#### **Learning Objectives:**

By the end of this topic you should be able to:-

- i. Describe the early experimental discoveries that led to the formulation of quantum mechanics.
- ii. Outline the basic postulates of quantum mechanics.
- iii. Define a wavefunction and explain its admissible characteristics.
- iv. Obtain, from first principles the Schrödinger equations in one and three dimensions
- v. Obtain expectation values of dynamical variables.

### **1.1 Historical Basis of Quantum Mechanics**

Before we discuss the salient mathematical axioms of quantum mechanics it is important for us to review some experimental dilemma that led to the development of quantum theory.

In physics and other sciences we are interested in collating experimental evidence, looking for patterns, trends and relationships between variables, which will lead to a ‘theory’. Development of the theory might involve the derivation (from empirical

data) of laws or relationships between the variables. These laws or relationships are then used to make additional predictions, which can be tested against further experimental observations.

We can adopt a similar approach for quantum theory but unfortunately quantum mechanics features equations that involve mathematical rules that are quite unfamiliar. More importantly, some of the implications are non-intuitive and lead to surprising conclusions.

Look at the following quotes from some of the founders of quantum theory:

*"If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet"*

-Neils Bohr

*"I think it safe to say that no one understands quantum mechanics".*

-Richard Feynman

We can introduce quantum theory by considering observations that could not be explained by classical mechanics. In many cases various quantization 'rules' were proposed to explain these experimental observations but these did not have any classical justification.

In what follows we discuss briefly some 'unexplained' observations or dilemmas which could not be accounted for by classical physics but found acceptance within the realms of quantum theory.

### **1.1.1 Black-Body Radiation**

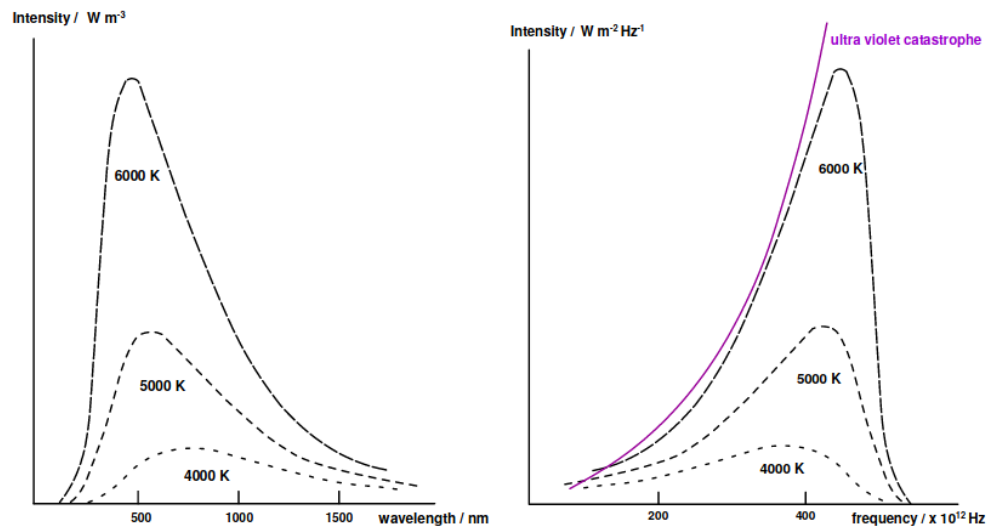
Towards the end of the nineteenth century there was interest in the frequencies (or wavelengths) emitted by a 'black body' when the temperature is increased. When an object is heated it can radiate large amounts of energy as infrared radiation.

Measurements were made of the intensity of the light emitted at different frequencies (or wavelengths) by such objects. In addition measurements were made at different temperatures. In order to improve the experiment and avoid any reflections of the ra-

diation, a cavity was used with a small hole, which emits the radiation: a black body. (A surface that absorbs all wavelengths of electromagnetic radiation is also the best emitter of electromagnetic radiation at any wavelength. Such an ideal surface is called a black body. The continuous spectrum of radiation it emits is called black-body radiation.)

It was found that the amount of black-body radiation emitted at any frequency depends only on the temperature, not the actual material.

Graphs of specific intensity against wavelength (or frequency) are shown in Figure 1.1.



**Figure 1.1: Graphs of specific intensity against wavelength (or frequency)**

As the temperature increases, each maximum shifts towards the higher frequency (shorter wavelength).

Attempts to obtain theoretically the correct black-body graph using classical mechanics failed. Wien obtained an equation that 'fitted' observations at high frequencies (low wavelengths). Later Lord Rayleigh obtained an equation that 'fitted' at low frequencies but tended off to infinity at high frequencies (see line on the above frequency graph). This divergence was called the ultraviolet catastrophe.

In 1900 Planck looked at the two equations and produced a 'combined' relationship,

which gave excellent agreement with the experimental curve. However, initially this relationship could not be derived from first principles.

Planck studied his relationship and the theory involved and noticed that he could resolve the problem by making the assumption that the absorption and emission of radiation by the oscillators could only take place in ‘jumps’ given by:

$$E = nhf \quad (1.1)$$

where  $E$  is energy,  $f$  is frequency,  $h$  is a constant and  $n = 0, 1, 2, 3, \dots$

### 1.1.2 Photoelectric effect

In 1887 Hertz observed that a spark passed between two plates more often if the plates were illuminated with ultraviolet light. Later experiments gave the unexpected results we are familiar with, namely:

- a the non-emission of electrons with very bright but low frequency radiation on a metal surface, e.g. very bright red light, and
- b the increase in the speed of the emitted electron with frequency but not with intensity. Increasing the intensity only produced more emitted electrons.

These results were unexpected because energy should be able to be absorbed continuously from a wave. An increase in the intensity of a wave also means an increase in amplitude and hence a larger energy.

The puzzle was why energy is not absorbed from a continuous wave, e.g. any electromagnetic radiation, in a cumulative manner. It should just take more time for energy to be absorbed and an electron emitted but this does not happen. Einstein proposed that electromagnetic radiation is emitted and absorbed in small packets. The energy of each packet is given by:

$$E = hf \quad (1.2)$$

where E is the energy of a ‘packet’ of radiation of frequency f.

This proposal also explained why the number of electrons emitted depended on the irradiance of the electromagnetic radiation and why the velocity of the emitted electrons depended on the frequency.

### 1.1.3 Models of the atom

Rutherford’s scattering experiment indicated that the majority of the mass of the atom was in a small nucleus, with the electrons ‘somewhere’ in the atomic space.

Using classical mechanics, an electron in an orbit could stay in that orbit, the central force being balanced by electrostatic attraction. However, the electron has a negative charge and hence it should emit radiation, lose energy and spiral into the nucleus.

Our current theory is insufficient. Why do the electrons ‘remain in orbit’? Do they in fact ‘orbit’?

In the late nineteenth century attempts were made to introduce some ‘order’ to the specific frequencies emitted by atoms. Balmer found, by trial and error, a simple formula for a group of lines in the hydrogen spectra as:

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (1.3)$$

where  $\lambda$  is the wavelength, R the Rydberg constant, n is an integer 2, 3, 4,...

Other series were then discovered, eg Lyman with the first fraction 1/12 and Paschen with the first fraction 1/32. However, this only worked for hydrogen and atoms with

one electron, eg ionized helium, and moreover did not provide any theoretical reason why the formula should work.

In 1913 Bohr introduced the idea of energy levels. Each atom has some internal energy due to its structure and internal motion but this energy cannot change by any variable amount, only by specific discrete amounts. Any particular atom has a specific set of energy levels. Different elements each have their own set of levels. Experimental evidence of the day provided agreement with this idea and energy level values were obtained from experimental results. Transitions between energy levels give the characteristic line spectra for elements.

In order to solve the problem that an electron moving in a circular orbit should continuously emit radiation and spiral into the nucleus, Bohr postulated that an electron can circulate in certain permitted, stable orbits without emitting radiation. He made the assumption that the normal electromagnetic phenomena did not apply at the atomic scale! Furthermore he made an intuitive guess that angular momentum is quantized. (It is said that he noticed that the units of Planck's constant ( $\text{Js}$ ) are the same as those of angular momentum ( $\text{kgm}^2\text{s}^{-1}$ ).) The allowed orbit, of radius  $r$ , of an electron must have angular momentum of an integral multiple of  $h/2\pi$ :

$$mvr = \frac{nh}{2\pi} \quad (1.4)$$

where  $n$  is an integer 1, 2, 3,...

Thus for any specific orbit  $n$  we can calculate the radius of that orbit given the tangential speed or vice versa.

For the hydrogen atom with a single electron, mass  $m_e$  revolving around a proton (or more correctly around the centre of mass of the system), we can assume the proton is stationary since it is 2000 times bigger. Hence, equating the electrostatic force and centripetal force  $mev^2/r$ :



$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{r_n^2} = \frac{m_e V_n^2}{r_n} \quad \text{where } \epsilon_0 \text{ is the permittivity of free space} \quad (1.5)$$

for the  $n^{\text{th}}$  orbit.

Equations 1.4 and 1.5 can be solved simultaneously to give

$$r_n = \epsilon_0 \frac{n^2 h^2}{\pi m_e e^2} \quad \text{and} \quad V_n = \frac{1}{\epsilon_0} \frac{e^2}{2\pi h} \quad (1.6)$$

for the  $n^{\text{th}}$  orbit.

Calculating  $r_1$  for the radius of the first Bohr orbit uses data given in assessments, namely  $h, m_e, e, \epsilon_0$  and gives  $r_1 = 5.3 \times 10^{-11} \text{ m}$ .

These equations give the values of the radii for the non-radiating orbits for hydrogen and the value of  $n$  was called the quantum number of that orbit.

### 1.1.4 De Broglie wavelength

We use the word ‘particle’ to describe localised phenomena that transport mass and energy, and the word ‘wave’ to describe delocalized (spread out) phenomena that carry energy but no mass.

Experimental observations seem to suggest that both electromagnetic radiation and electrons can behave like particles and like waves. They exhibit both wave phenomena, such as interference and diffraction, and particle phenomena, for example photons causing electron emission in the photoelectric effect or electron ‘billiard ball type’ collisions.

An electron can show wave-like phenomena. In the mid 1920s G P Thomson, in Aberdeen, bombarded a thin metal with an electron beam and obtained a diffraction ring. In 1927 Davisson and Germer directed a beam of electrons onto the surface of a nickel crystal and observed the reflected beam. They had expected to see diffuse reflection since even this smooth surface would look ‘rough’ to the tiny electrons.

To their surprise, they observed a similar pattern to X-ray diffraction from a surface. Thomson and Davisson were awarded the Nobel Prize in 1937 for demonstrating the wave-like properties of electrons. (Thomson's father, J J Thomson, won the Nobel Prize in 1906 for discovering the electron as a particle.)

In 1923 de Broglie suggested that since light had particle-like properties, perhaps nature was dualistic and particles had wave-like properties. From relativity theory, the energy of a particle with zero rest mass, eg a photon, is given by  $E = pc$  and we know that  $E = hf$ , hence  $p = h/\lambda$ .

Thus the wave and particle are related through its momentum.

For a particle  $p = mv$  and for a wave  $p = h/\lambda$ , giving a relationship  $mv = h/\lambda$  or:

$$\lambda = \frac{h}{p} \quad (1.7)$$

Thus we can calculate the de Broglie wavelength of a particle of velocity  $v$ .

### 1.1.5 Specific heat of solids

In solids, the atoms vibrate about their equilibrium positions in their lattice sites.

Based on the law of equipartition of energy, the average energy of a simple harmonic oscillator is  $kT$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature.

An atom can vibrate about three mutually perpendicular directions giving the average energy of the atom as  $3 kT$ . Then the energy per gram atom is  $3NkT=3RT$ ,  $N$  being the Avogadro's number and  $R$ , the gas constant. This leads to a value of  $C_v = 3R$ , which is known as the Dulong-Petit law. At ordinary temperatures, solids generally obey this relation, which is based on classical theory. However, when the temperature is lowered the specific heat decreases and goes to zero when  $T \rightarrow 0K$ . Thus, the classical ideas failed to explain the variation of specific heat of solids with temperature.