

# Quantum Mechanics

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# 1 Historical Introduction

## 1.1 Classical mechanics

Classical mechanics is based on two distinct concepts.

- (i) Particles - Point-like objects which have positions and velocities fully determined by Newton's second law as a function of time.  $m\ddot{x}(t) = F(x(t), \dot{x}(t))$ . Once  $x(t_0), \dot{x}(t_0)$  is known, the solution of the equation gives the position and velocity at all times. Particles can collide, scatter, but never interfere.
- (ii) Waves - Spread out objects which are functions of time and position. Periodic in  $t/x$ . Propagation is determined by the wave equation which is

$$\frac{\partial^2 f(x, t)}{\partial t^2} - c^2 \frac{\partial^2 f(x, t)}{\partial x^2} = \nu$$

We have solution  $f_{\pm}(x, t) = A_{\pm} \exp[i(kx - \omega t)]$ . And the solutions obey the dispersion relation  $\omega = ck$ . We have that  $\omega$  is the angular frequency related to  $\lambda$  (wavelength) by  $\nu = \frac{\omega}{2\pi}$  and  $\lambda = \frac{2\pi c}{\omega} = \frac{c}{\nu}$ . Waves interfere, causing constructive interference when in-phase and destructive interference when out of phase.

However we have some programs with classical mechanics.

- (i) Light behaving like particles
  - (a) Black body radiation (NE)
  - (b) Photoelectric effect
  - (c) Compton scattering (NE)
- (ii) Stability of atom
- (iii) Particles behaving like waves
  - (a) De Broglie Principle
  - (b) Electron diffraction

## 1.2 Photoelectric effect

This is the experiment when light hits a metal surface and causes electrons to be emitted. They used monochromatic radiation with fixed wavelength and changed the intensity of light and the wavelength. The classical expectation were:

- (i) Incident light carries  $E \propto I = |A|^2$ . They proposed that as the intensity increases there is enough energy to break the bond of the electron with the metal atoms, causing it to be released.
- (ii) The emission rate of the electrons should be constant over intensity past a certain point.

However what they actually observed was surprising.

- (i) Below given  $\omega$  there was no emission of electrons.
- (ii) The velocity (i.e. KE) depended on  $\omega$  not on  $I$ .
- (iii) The emission rate increased with intensity.

In 1905 Einstein used these observations to propose the following

- (i) Light comes in small quanta (now called photons).
- (ii) Each photon carries a small packet of energy,  $E$ .

$$E = \hbar\omega, \quad \mathbf{p} = \hbar\mathbf{k}$$

where

$$\hbar = \frac{h}{2\pi}$$

where  $h$  is the Planck constant.

- (iii) The interaction seen in the photoelectric effect was caused by each photon interacting with each photon in a *one-to-one* interaction. So we have that

$$\text{Kinetic energy of } e^- = \text{Kinetic energy of } \gamma - \text{binding energy of the metal}$$

we write this equation as

$$E_{min} = 0 = \hbar\omega_{min} - \phi.$$

So the kinetic energy of the electrons is directly proportion to  $\omega$ , not  $I$  which we expected in classical mechanics. Instead increasing the intensity increases the emission rate as we have more photons interacting with each electron.

### 1.3 Atomic spectra

In 1897 Thomson plum-pudding model purposed a uniform distribution of positive charge, with negatively charged electrons inside.

Later in 1908, Rutherford performed his gold foil experiment, showing Rutherford scattering (large angle scattering), hence proving that the atom was mostly empty space, and the positively charged part was concentrated at the centre of the atom. This couldn't work since the electrons would radiate energy in an orbit and the electrons would collapse on the nucleus. Also it didn't explain the spectra of light emitted by atoms in a set of discrete values of

$$w_{mn} = 2\pi c R_0 \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \quad n, m \in \mathbb{N}.$$

But in 1913 Bohr showed that the electron orbits are quantised so that the  $L$  (orbital angular model) takes only these values

$$L_n = n\hbar$$

So it was proposed that  $L$  was quantised hence so is  $r, v$ , and  $E$ .

*Proof.*  $\mathbf{L} = m_e \mathbf{v} \times \mathbf{r}$  so we have that

$$|\mathbf{L}| = L = M_e v r \implies v = \frac{L}{m_e r} \implies v_n = n \frac{\hbar}{m_e r}$$

$$\mathbf{F}^{\text{Coulomb}} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2} \mathbf{e}_r$$

and we know that

$$|\mathbf{F}^{\text{Coulomb}}| = m_e a_r$$

so

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2} = m_e \frac{v^2}{r} \implies r_h = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} n^2$$

so finally

$$r_0 = \frac{4\pi\epsilon_0}{m_e e^2} \hbar^2$$

similarly the energy is quantised since

$$E = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \implies E_n = -\frac{e^2}{8\pi\epsilon_0 r_0} \frac{1}{n^2}.$$

The lowest energy state is called the Ground level,  $E_1$  and the excited levels  $E_2, E_3, \dots$  get closer to each other as energy increases.

We have that

$$\omega_{mn} = \frac{\Delta E_{mn}}{\hbar} = 2\pi c \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$$

where  $\omega_{mn}$  is the angular frequency of light associated with an electron moving from energy state  $m$  to level  $n$ . This is the Bohr prediction from Rydberg constant  $R_0$ .

## 1.4 The wave-like behaviour of particles

In 1923 De Broglie hypothesised that each particle of any mass is associated with a wave having angular frequency,  $\omega$  given by

$$\omega = \frac{E}{\hbar}$$

. In 1927 this was observed by showing electron scattering off crystals which observed an interference pattern consistent with De Broglie's hypothesis.

## 2 Foundation of Quantum Mechanics

In quantum mechanics instead of a vector, we have a state represented by the letter  $\psi$ . The basis is a continuous basis  $\{\mathbf{x}\} \rightarrow \psi(\mathbf{x}, t)$ . Instead of a vector space  $\mathbb{C}^n$  we have a space of square-integrable functions,  $L^2(\mathbb{R}^3)$ . We define an inner product of two states,  $\psi, \phi \in L^2(\mathbb{R}^3)$  as

$$(\psi, \phi) = \int_{\mathbb{R}^3} \phi(\mathbf{x}, t) \psi(\mathbf{x}, t) d^3t.$$

An operator  $\hat{O}$  sends a state  $\psi$  to a state  $\phi$  as shown,

$$\phi = \hat{O}\psi.$$

### 2.1 Wave function and probabilistic interpretation

In classical mechanics  $\mathbf{x}$  and  $\dot{\mathbf{x}}$  determine the dynamics of a particle in a deterministic way.

However in quantum mechanics the state  $\psi(\mathbf{x}, t)$  determines the dynamics of particles in a probabilistic way.

**Definition.** (State of a particle) We say that  $\psi$  is the *state* of a particle, where  $\psi(\mathbf{x}, t)$  is the complex coefficient of  $\psi$  in the continuous basis of  $\mathbf{x}$  at a given time  $t$ . i.e.  $\psi(\mathbf{x}, t)$  is  $\psi$  in the  $\mathbf{x}$  representation and is called a wave function.

$$\psi(\mathbf{x}, t) : \mathbb{R}^3 \rightarrow \mathbb{C}$$

that satisfies mathematical properties dictated by its physical interpretation.

Born's rule or the probabilistic interpretation for a particle described by a state  $\psi$  to sit at  $\mathbf{x}$  at given time  $t$  is

$$\rho(\mathbf{x}, t) \propto |\psi(\mathbf{x}, t)|^2 = \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)$$

where

$$\rho(\mathbf{x}, t)dV = \text{probability that the particle sits in the some small volume } dV \text{ centered at } \mathbf{x}.$$

From this we get properties on  $\psi$  as follows:

- (i)  $\int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 d^3x = N \leq \infty$  with  $N \in \mathbb{R}$  and  $N \neq 0$ .
- (ii) Because the total probability has to be equal to 1 the wavefunction must be normalised to 1. So

$$\bar{\psi}(\mathbf{x}, t) = \frac{1}{\sqrt{N}}\psi(\mathbf{x}, t)$$

which integrates to 1 over  $\mathbb{R}^3$ , giving that  $\psi(\mathbf{x}, t) = |\bar{\psi}(\mathbf{x}, t)|^2$ .

*Remark.* Often we drop the  $\bar{\psi}$  notation and just write  $\psi$ , and normalise at the end.

If  $\tilde{\psi}(\mathbf{x}, t) = e^{i\alpha}\psi(\mathbf{x}, t)$  with  $\alpha \in \mathbb{R}$  then we have that

$$|\tilde{\psi}(\mathbf{x}, t)|^2 = |\psi(\mathbf{x}, t)|^2$$

so  $\psi$  and  $\tilde{\psi}$  are equivalent states.