

IB Quantum Mechanics

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1 Historical Introduction

1.1 Particles and Waves in Classical Mechanics

These are the basic concepts of particle mechanics. We begin by looking at particles.

Definition 1.1. A point particle is an object carrying energy E and momentum p in an infinitesimally small point of space.

A particle is defined by its position \mathbf{x} and velocity $\mathbf{v} = \dot{\mathbf{x}} = \frac{d}{dt}\mathbf{x}$. From Newton's second law, we have

$$\mathbf{F}(\mathbf{x}(t), \dot{\mathbf{x}}(t)) = m\ddot{\mathbf{x}}(t).$$

Solving this determines $\mathbf{x}(t), \dot{\mathbf{x}}(t)$ for all t once the initial conditions $\mathbf{x}(t_0), \dot{\mathbf{x}}(t_0)$ are known.

Particles do not interfere with each other.

Definition 1.2. A wave is any real or complex-valued function with periodicity in time or space.

If we take a function of time t , such that $f(t + T) = f(t)$, where T is the period, then $\nu = 1/T$ is the frequency, and the angular frequency is $\omega = 2\pi\nu = 2\pi/T$. Examples of such functions are $f(t) = \sin \omega t, \cos \omega t, e^{i\omega t}$.

If we take a function of space x , such that $f(x + \lambda) = f(x)$, where λ is the wave length, then $k = 2\pi/\lambda$ is the wave number. Some examples are $f(x) = \cos \omega x, \sin \omega x, e^{i\omega x}$.

In one dimension, an EM wave obeys the equation

$$\frac{\partial^2 f(x, t)}{\partial t^2} - c^2 \frac{\partial^2 f(x, t)}{\partial x^2} = 0,$$

where $c \in \mathbb{R}$. This has solutions

$$f_{\pm}(x, t) = A_{\pm} \exp(\pm ikx - i\omega t),$$

provided that the wavelength and frequency are related by $\omega = ck$ or $\lambda\nu = c$. Here A_{\pm} is the amplitude of the wave, and $\omega = ck$ is the dispersion relation.

In three dimensions, an EM wave obeys the equation

$$\frac{\partial^2 f(\mathbf{x}, t)}{\partial t^2} - c^2 \nabla^2 f(\mathbf{x}, t) = 0.$$

Here we need $f(x, t_0)$ and $\frac{df}{dt}(x, t_0)$ to determine a unique solution. The periodic solutions are

$$f(\mathbf{x}, t) = A \exp(i\mathbf{k} \cdot \mathbf{x} - i\omega t),$$

where $\omega = c|\mathbf{k}|$.

Remark.

- (i) Other kind of waves arise as solution of other governing equations provided a different dispersion relation.
- (i) If the governing equation is linear, the superposition principle holds, stating if f_1, f_2 are solutions, then $f = f_1 + f_2$ is a solution.

1.2 Particle-like behaviour of waves

1.2.1 Black-body radiation

When a body is heated at temperature T , it radiates light at different frequencies. The classical prediction is that $E = k_B T$, where E is the energy of the wave and k_B is the Boltzmann constant. This gives

$$I(\omega) \propto k_B T \frac{\omega^2}{\pi^2 c^3}.$$

This diverges as $\omega \rightarrow \infty$. Planck's model stated

$$I(\omega) \propto \frac{\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1}.$$

Here $\hbar = h/2\pi$ is the reduced Planck constant, with $h \approx 6.6 \cdot 10^{-34} \text{Joule} \times \text{sec}$. This only makes sense if $E = \hbar \omega$.

1.2.2 Photoelectric effect

The photoelectric effect is a result of an experimental phenomena, where light hitting a metal surface caused electrons to emit from the surface.

This experiment took place as the intensity I and angular frequency ω of the incident light changed.

The classical expectation is as follows:

- (i) Since the energy of the incident light is proportional to I , as I increases, there will be enough energy to break the bonds of the electrons with the atoms.

- (ii) The emission rate should be constant as I increases.

The experiment drew a number of surprising facts:

1. Below ω_{min} , there was not electron emission.
2. The maximum energy of the electrons depended on ω and not I .
3. The emission rate increased as I increased.

In 1905, Einstein developed Planck's idea to explain this phenomena.

- Light was quantized in small quanta, called photons.
- Each photon carries $E = \hbar\omega$, $p = \hbar k$.
- The phenomenon of electron emission comes from scattering of a single photon off of a single electron.

Then for the electron to leave, we must have

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

where ϕ is the binding energy of the electron with the metal atoms. Then moreover,

$$E_{max} = \hbar\omega_{max} - \phi.$$

Finally, as I increases, there is a greater number of photons, so this leads to a higher electron emission rate.

1.2.3 Compton scattering

In 1923, Compton studied X-rays scattering off free electrons. Here, the binding energy of the electrons was much smaller than the incoming energy, so the electrons were essentially free.

The expectation was that, given an X-ray of frequency ω , the resulting frequency ω' after the impact would follow a Gaussian centred at ω . This could be done by analysing the intensity of the outgoing light.

The result was a very narrow Gaussian centred around ω , but there also was another peak at another frequency φ .

In fact, we can find that the angle of the outgoing X-ray via

$$2 \sin^2 \frac{\theta}{2} = \frac{mc}{|q|} - \frac{mc}{|p|},$$

where p, q are the momenta of the ingoing and outgoing photons. Then, since $p = \hbar k$ and $q = \hbar k'$, we get

$$|p| = \hbar k = \hbar \frac{\omega}{c}, \quad |q| = \hbar \frac{\omega'}{c}, \quad \frac{1}{\omega'} = \frac{1}{\omega} + \frac{\hbar}{mc}(1 - \cos \theta).$$

1.3 Atomic Spectra

In 1897, Thompson formulated the plum-pudding model, where the atom has uniformly distributed charge.

In 1909, Rutherford conducted the gold foil experiment, showing the majority of the atom was vacuum. This resulted in the Rutherford model. However, this did not work because:

- (i) If the electron moves on a circular orbit, it would radiate.
- (ii) The electrons would collapse on the nucleus due to the Coulomb force.
- (iii) The model did not explain the measured spectra.

In 1913, Bohr explained these problems by assuming the electron orbits around the nucleus are quantized so that the orbital angular momentum L takes discrete values

$$L_n = n\hbar.$$

Proposition 1.1. *If L is quantized, then r, v, E are quantized.*

Proof: Since $L = m_e v r$, this implies

$$v = \frac{L}{m_e r} \implies v_n = n \frac{\hbar}{m_e r}.$$

The Coulomb Force shows

$$F = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2} = m_e \frac{v^2}{r}.$$

This gives

$$r = r_n = n^2 \left(\frac{4\pi\epsilon_0}{m_e e^2} \hbar^2 \right) = n^2 a_0,$$

where a_0 is the Bohr radius.

As a result of the quantization of the radius and velocity, the energy is also quantized. The energy is

$$E_n = \frac{1}{2}m_e v_n^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_n} = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2} = -\frac{e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2}.$$

Here E_1 is the lowest possible energy state, or ground state, of the Bohr atom.

The energy emitted by transition from the m -th to the n -th orbital is $E_{mn} = E_m - E_n$. Using $E_{mn} = \hbar\omega_{mn}$, we get

$$\omega_{mn} = 2\pi c R_0 \left(\frac{1}{n^2} - \frac{1}{m^2} \right),$$

where R_0 agrees with the Rydberg constant.

1.4 Wave-like Behaviour of Particles

In 1923, De Broglie hypothesised that any particles of any mass can be associated with a wave having

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

In 1927, Davisson and Germer scattered electrons off of crystals. The interference pattern was consistent with the De Broglie hypothesis.

2 Foundation of Quantum Mechanics

Quantum mechanics is founded in linear algebra:

- The vector \mathbf{v} in LA becomes the state ψ in QM.
- The bases $\{e_i\}$ in LA becomes the bases \mathbf{x} in QM.
- The coordinate representation

$$\mathbf{v} \rightarrow \begin{pmatrix} v_1 \\ \vdots \\ v_n \end{pmatrix}$$

becomes the wavefunction $\psi(\mathbf{x}, t)$.

- The vector space V becomes the wavefunction space $L^2(\mathbb{R}^3)$.
- The inner product $\langle -, - \rangle$ becomes the inner product

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

- The linear map $V \rightarrow V$ represented by a matrix T becomes the linear maps between $L^2(\mathbb{R}^3) \rightarrow L^2(\mathbb{R}^3)$, given by operators \hat{O} .

2.1 Wavefunctions and Probabilistic Interpretation

In classical mechanics, the dynamics of a particle is determined by \mathbf{x} and $\dot{\mathbf{x}}$. In quantum mechanics, we have a similar idea.

Definition 2.1. ψ is the state of the particle.

Definition 2.2. $\psi(\mathbf{x}, t) : \mathbb{R}^3 \rightarrow \mathbb{C}$ is a complex-valued function satisfying mathematical properties dictated by physical interpretation.

Proposition 2.1 (Born's rule). *The probability density for a particle to sit at \mathbf{x} at given time t is $\rho(\mathbf{x}, t) \propto |\psi(\mathbf{x}, t)|^2$. Then, $\rho(\mathbf{x}, t) dV$ is the probability that the volume sits in a small volume centred around \mathbf{x} , which is proportional to the squared modulus of $\psi(\mathbf{x}, t)$.*

- (i) Because the particle has to be somewhere, the wavefunction has to be normalisable (or square-integrable) in \mathbb{R}^3 , so

$$\int_{\mathbb{R}^3} \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) d^3x = \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 d^3x = \mathcal{N} < \infty,$$

with $\mathcal{N} \in \mathbb{R}$ and $\mathcal{N} \neq 0$.

- (ii) Because the total probability has to be 1, we consider the normalised wavefunction

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

Then we have

$$\int_{\mathbb{R}^3} |\bar{\psi}(\mathbf{x}, t)|^2 d^3x = 1,$$

so $\rho(\mathbf{x}, t) = |\bar{\psi}(\mathbf{x}, t)|^2$. We often write wavefunctions as ψ , and then normalise at the end.

- (iii) If $\tilde{\psi}(\mathbf{x}, t) = e^{i\alpha} \psi(\mathbf{x}, t)$ with $\alpha \in \mathbb{R}$, then $|\tilde{\psi}(\mathbf{x}, t)|^2 = |\psi(\mathbf{x}, t)|^2$, so ψ and $\tilde{\psi}$ are equivalent states.

The state ψ corresponds to rays in the vector space, which are equivalence classes of wavefunctions under the equivalence relation $\psi_1 \sim \psi_2 \iff \psi_1 = e^{i\alpha} \psi_2$.

2.2 Hilbert Space

Definition 2.3. The set of all square-integrable functions in \mathbb{R}^3 is called a Hilbert space \mathcal{H} or $L^2(\mathbb{R}^3)$.

Theorem 2.1. If $\psi_1(\mathbf{x}, t), \psi_2(\mathbf{x}, t) \in \mathcal{H}$, then $\psi(\mathbf{x}, t) = \alpha_1 \psi_1(\mathbf{x}, t) + \alpha_2 \psi_2(\mathbf{x}, t) \in \mathcal{H}$.

Proof: Since $\psi_1, \psi_2 \in \mathcal{H}$, we can say

$$\int_{\mathbb{R}^3} |\psi_1(\mathbf{x}, t)|^2 d^3x = \mathcal{N}_1, \quad \int_{\mathbb{R}^3} |\psi_2(\mathbf{x}, t)|^2 d^3x = \mathcal{N}_2.$$

Note the triangle inequality: if $z_1, z_2 \in \mathbb{C}$, then $|z_1 + z_2| \leq |z_1| + |z_2|$. Let $z_1 = \alpha_1 \psi_1(\mathbf{x}, t)$, $z_2 = \alpha_2 \psi_2(\mathbf{x}, t)$. Then

$$\begin{aligned} \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 d^3x &= \int_{\mathbb{R}^3} |\alpha_1 \psi_1(\mathbf{x}, t) + \alpha_2 \psi_2(\mathbf{x}, t)|^2 d^3x \\ &\leq \int_{\mathbb{R}^3} (|\alpha_1 \psi_1(\mathbf{x}, t)| + |\alpha_2 \psi_2(\mathbf{x}, t)|)^2 d^3x \\ &= \int_{\mathbb{R}^3} (|\alpha_1 \psi_1(\mathbf{x}, t)|^2 + |\alpha_2 \psi_2(\mathbf{x}, t)|^2 + 2|\alpha_1 \psi_1| |\alpha_2 \psi_2|) d^3x \\ &\leq \int_{\mathbb{R}^3} 2|\alpha_1 \psi_1(\mathbf{x}, t)|^2 + 2|\alpha_2 \psi_2(\mathbf{x}, t)|^2 d^3x \\ &= 2|\alpha_1|^2 \mathcal{N}_1 + 2|\alpha_2|^2 \mathcal{N}_2 < \infty. \end{aligned}$$

2.3 Inner Product

Definition 2.4. Define the inner product in \mathcal{H} as

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

Theorem 2.2. *If $\psi, \phi \in \mathcal{H}$, then the inner product exists.*

Proof: Let the square integrals of ψ and ϕ be \mathcal{N}_1 and \mathcal{N}_2 , respectively. Then, we use the Schwarz inequality as follows:

$$\begin{aligned} |(\psi, \phi)| &= \left| \int_{\mathbb{R}^3} \psi^*(\mathbf{x}, t) \phi(\mathbf{x}, t) \, d^3x \right| \\ &\leq \sqrt{\int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \, d^3x} \cdot \sqrt{\int_{\mathbb{R}^3} |\phi(\mathbf{x}, t)|^2 \, d^3x} \\ &= \sqrt{\mathcal{N}_1 \mathcal{N}_2} < \infty. \end{aligned}$$

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