

IB Quantum Mechanics

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October 30, 2022

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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:

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

2.3.1 Properties of the Inner Product

(i) $(\psi, \phi) = (\phi, \psi)^*$,

(ii) It is antilinear in the first entry, and linear in the second entry:

$$\begin{aligned} (a_1\psi_1 + a_2\psi_2, \phi) &= a_1^*(\psi_1, \phi) + a_2^*(\psi_2, \phi), \\ (\psi, a_1\phi_1 + a_2\phi_2) &= a_1(\psi, \phi_1) + a_2(\psi, \phi_2). \end{aligned}$$

(iii) The inner product of $\psi \in \mathcal{H}$ with itself is non-negative:

$$(\psi, \psi) = \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 d^3x > 0.$$

Definition 2.5. The norm of the wavefunction ψ is the real number $\|\psi\| = \sqrt{(\psi, \psi)}$. We say ψ is normalized if $\|\psi\| = 1$.

Definition 2.6. Two wavefunctions $\psi, \phi \in \mathcal{H}$ are orthogonal if $(\psi, \phi) = 0$, and a set of wavefunctions $\{\psi_n\}$ is orthonormal if

$$(\psi_m, \psi_n) = \delta_{mn}.$$

Definition 2.7. A set of wavefunctions $\{\psi_n\}$ is complete if all $\phi \in \mathcal{H}$ can be written as a linear combination of the $\{\psi_n\}$:

$$\phi = \sum_{n=0}^{\infty} c_n \psi_n.$$

Lemma 2.1. *If $\{\psi_n\}$ form a complete orthonormal basis of \mathcal{H} , then $c_n = (\psi_n, \phi)$.*

Proof:

$$\begin{aligned} (\psi_n, \phi) &= \left(\psi_n, \sum_{m=0}^{\infty} c_m \psi_m \right) \\ &= \sum_{m=0}^{\infty} c_m (\psi_n, \psi_m) = \sum_{m=0}^{\infty} c_m \delta_{mn} \\ &= c_n. \end{aligned}$$

2.4 Time-dependent Schrödinger Equation

The first postulate of quantum mechanics that we have encountered is Born's rule:

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

The second is the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t}(\mathbf{x}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}, t) + U(\mathbf{x}) \psi(\mathbf{x}, t).$$

Here $U(\mathbf{x}) \in \mathbb{R}$ is the potential. Looking at the equation, we spot the following:

- There is a first derivative in time: once $\psi(x, t_0)$ is known, then we know $\psi(x, t)$ at all times.
- There is an asymmetry in time and space. This implies the TDSE is a non-relativistic equation.

Heuristically, this comes from the observation of electron diffraction, which leads to the thought that electrons behave like waves. Thus, we can think of a function

$$\psi(\mathbf{x}, t) \propto \exp[i(\mathbf{k} \cdot \mathbf{x} - \omega t)]$$

that describes the dynamics of the electron. From De Broglie, we get

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

For a free particle, we get

$$E = \frac{|\mathbf{p}|^2}{2m} \implies \omega = \frac{|\mathbf{p}|^2}{2m\hbar} = \frac{\hbar}{2m} |\mathbf{k}|^2.$$

The dispersion relation for a particle-wave is

$$\omega \propto |\mathbf{k}|^2.$$

For a light-wave, as the energy equation is different, we get

$$\omega \propto |\mathbf{k}|.$$

From dimensional analysis, we see that the wave equation must have a single derivative with respect to time, and a double derivative with respect to space.

To apply the Schrödinger equation, we need to ensure the wavefunction remains normalized throughout time. Hence we look at the following properties:

(i) The squared integral

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

is independent of time.

Proof: We have

$$\frac{d\mathcal{N}}{dt} = \frac{d}{dt} \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 d^3x = \int_{\mathbb{R}^3} \frac{\partial}{\partial t} |\psi(\mathbf{x}, t)|^2 d^3x.$$

But the partial derivative

$$\frac{\partial}{\partial t} (\psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t)) = \psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \psi.$$

From the TDSE and its conjugate,

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \frac{i\hbar}{2m} \nabla^2 \psi - i \frac{U}{\hbar} \psi, \\ \frac{\partial \psi^*}{\partial t} &= -\frac{i\hbar}{2m} \nabla^2 \psi^* + i \frac{U}{\hbar} \psi^* \\ \implies \frac{\partial}{\partial t} (\psi^* \psi) &= \nabla \cdot \left[\frac{i\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) \right] \\ \implies \frac{d\mathcal{N}}{dt} &= \int_{\mathbb{R}^3} \nabla \cdot \left[\frac{i\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) \right] = 0, \end{aligned}$$

because ψ, ψ^* are such that $|\psi|, |\psi^*| \rightarrow 0$ as $|\mathbf{x}| \rightarrow \infty$.

(ii) The probability is conserved with respect to time:

$$\frac{\partial \rho}{\partial t}(\mathbf{x}, t) + \nabla \cdot \mathbf{J} = 0,$$

where

$$\mathbf{J}(\mathbf{x}, t) = -\frac{i\hbar}{2m} [\psi^* \nabla \psi - \psi \nabla \psi^*].$$

2.5 Expectation Values and Operators

We have seen that all information is stored within the wavefunction, but we want to know how to extract information from ψ .

Definition 2.8. An observable is any property of the particle described by ψ that can be measured.

2.5.1 Heuristic Interpretation

Suppose we want to measure the position of a particle. The expectation is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi(x, t)|^2 dx = \int_{-\infty}^{\infty} \psi^*(x, t) x \psi(x, t) dx.$$

Hence the operator with respect to x is

$$\mathcal{O}_x \rightarrow \hat{x} \rightarrow x.$$

The expectation value of an observable is the mean of an infinite series of measurements performed on particles on the same state. Performing the same measurement on one particle will collapse the wavefunction, and subsequent measurements will give the same result.

As time goes on $\langle x \rangle$ will change. Thus we might be interested in knowing the momentum. Using our usual definition of momentum as mass times velocity, we get

$$\begin{aligned} \langle p \rangle &= m \frac{d\langle x \rangle}{dt} = m \frac{d}{dt} \int_{-\infty}^{\infty} \psi^* x \psi dx = m \int_{-\infty}^{\infty} x \frac{\partial}{\partial t} (\psi^* \psi) dx \\ &= \frac{i\hbar m}{2m} \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) dx \\ &= -\frac{i\hbar}{2} \int_{-\infty}^{\infty} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) dx \\ &= -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx = \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx. \end{aligned}$$

Hence we can see the operator $\hat{x} = x$ represents position, and the operator $\hat{p} = -i\hbar \partial / \partial x$ represents momentum.

2.5.2 Hermitian Operators

In a \mathbb{C}^n linear map, we generally have $w = Tv$, where T is a complex matrix of size n . In quantum mechanics, the linear maps are from $\mathcal{H} \rightarrow \mathcal{H}$, given by $\hat{O} : \psi \rightarrow \tilde{\psi}$.

Definition 2.9. An operator \hat{O} is any linear map $\mathcal{H} \rightarrow \mathcal{H}$ such that

$$\hat{O}(a_1\psi_1 + a_2\psi_2) = a_1\hat{O}\psi_1 + a_2\hat{O}\psi_2,$$

with $a_1, a_2 \in \mathbb{C}$, $\psi_1, \psi_2 \in \mathcal{H}$.

Some examples of operators are:

- Finite differential operators, given by

$$\sum_{n=0}^N p_n(x) \frac{\partial^n}{\partial x^n}.$$

- Translation operators

$$S_a : \psi(x) \rightarrow \psi(x - a).$$

- Parity operator

$$P : \psi(x) \rightarrow \psi(-x).$$

Definition 2.10. The Hermitian conjugate \hat{O}^\dagger of an operator \hat{O} is the operator such that

$$(\hat{O}^\dagger\psi_1, \psi_2) = (\psi_1, \hat{O}\psi_2).$$

We can verify that

- $(a_1\hat{A}_1 + a_2\hat{A}_2)^\dagger = a_1^*\hat{A}_1^\dagger + a_2^*\hat{A}_2^\dagger$,
- $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$.

Definition 2.11. An operator \hat{O} is Hermitian if

$$\hat{O} = \hat{O}^\dagger \iff (\hat{O}\psi_1, \psi_2) = (\psi_1, \hat{O}\psi_2).$$

All physics quantities in quantum mechanics are represented by Hermitian operators.

Example 2.1.

(i) $\hat{x} : \psi(x, t) \rightarrow x\psi(x, t)$ is Hermitian as

$$\int_{-\infty}^{\infty} (x\psi_1)^* \psi_2 \, dx = \int_{-\infty}^{\infty} \psi_1^* x \psi_2 \, dx.$$

(ii) $\hat{p} : \psi(x, t) \rightarrow -i\hbar \frac{\partial \psi}{\partial x}(x, t)$ is Hermitian as

$$\begin{aligned} (\hat{p}\psi_1, \psi_2) &= \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \psi_1}{\partial x} \right)^* \psi_2 \, dx = i\hbar \int_{-\infty}^{\infty} \frac{\partial \psi_1^*}{\partial x} \psi_2 \, dx \\ &= i\hbar [\psi_1^* \psi_2]_{-\infty}^{\infty} - i\hbar \int_{-\infty}^{\infty} \psi_1^* \frac{\partial \psi_2}{\partial x} \, dx \\ &= \int_{-\infty}^{\infty} \psi_1^* \left(-i\hbar \frac{\partial \psi_2}{\partial x} \right) \, dx = (\psi_1, \hat{p}\psi_2). \end{aligned}$$

(iii) Kinetic energy

$$\hat{T} : \psi(x, t) \rightarrow \frac{\hat{p}^2}{2m} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}(x, t).$$

(iv) Potential energy

$$\hat{U} : \psi(x, t) \rightarrow U(\hat{x})\psi(x, t) = U(x)\psi(x, t).$$

(v) Total energy

$$\hat{H} : \psi(x, t) \rightarrow (\hat{T} + \hat{U})\psi(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \psi(x, t).$$

Theorem 2.3. *The eigenvalues of Hermitian operators are real.*

Proof: Let \hat{A} be a hermitian operator with eigenvalue a , eigenfunction $\|\psi\| = 1$. Then

$$(\psi, \hat{A}\psi) = (\psi, a\psi) = a(\psi, \psi) = a,$$

but since \hat{A} is Hermitian, this equals

$$(\hat{A}\psi, \psi) = (a\psi, \psi) = a^*(\psi, \psi) = a^*.$$

So $a^* = a$, and $a \in \mathbb{R}$.

Theorem 2.4. *If \hat{A} is a Hermitian operator, and ψ_1, ψ_2 are normalised eigenfunctions of \hat{A} with distinct eigenvalues a_1, a_2 , then ψ_1, ψ_2 are orthogonal.*

Proof: We have $\hat{A}\psi_1 = a_1\psi_1$, $\hat{A}\psi_2 = a_2\psi_2$. Then

$$\begin{aligned} a_1(\psi_1, \psi_2) &= a_1^*(\psi_1, \psi_2) = (a_1\psi_1, \psi_2) = (\hat{A}\psi_1, \psi_2) \\ &= (\psi_1, \hat{A}\psi_2) = (\psi_1, a_2\psi_2) = a_2(\psi_1, \psi_2). \end{aligned}$$

Since $a_1 \neq a_2$, we get $(\psi_1, \psi_2) = 0$.

Theorem 2.5. *The discrete (or continuous) set of eigenfunctions of any Hermitian operator together form a complete orthonormal basis of \mathcal{H} , so*

$$\psi(x, t) = \sum_{i \in I} c_i \psi_i(x, t).$$

2.5.3 Expectation values and operators

So far, we have seen every quantum observable is represented by a Hermitian operator \hat{O} . We define the following postulates for the operators:

1. The possible outcomes of a measurement of the observable O are the eigenvalues of \hat{O} .
2. If \hat{O} has a discrete set of normalized eigenfunctions $\{\psi_i\}$ with distinct eigenvalues $\{\lambda_i\}$, the measurement of O on a particle described by ψ has probability

$$\mathbb{P}(O = \lambda_i) = |a_i|^2,$$

where $\psi = \sum a_i \psi_i$.

3. If $\{\psi_i\}$ are the set of orthonormal eigenfunctions of \hat{O} , and $\{\psi_i\}_{i \in I}$ is the complete set of orthonormal eigenfunctions with eigenvalue λ , then

$$\mathbb{P}(O = \lambda) = \sum_{i \in I} |a_i|^2.$$

Indeed, if ψ is normalized, we can check

$$\sum_{i=1}^N |a_i|^2 = \sum_{i=1}^N (a_i \psi_i, a_i \psi_i) = \sum_{i,j=1}^N (a_i \psi_i, a_j \psi_j) = (\psi, \psi) = 1.$$

4. The projection postulate: If O is measured on ψ at time t and the outcome of the measurement of λ_i , the wavefunction of ψ instantaneously becomes ψ_i . If \hat{O} has degenerate eigenvalues with the same eigenvalue, the wavefunction becomes

$$\psi = \sum_{i \in I} a_i \psi_i.$$

Definition 2.12 (Projection Operator). Given $\psi = \sum a_i \psi_i = \sum (\psi_i, \psi) \psi_i$, define

$$\hat{P}_i : \psi \mapsto (\psi_i, \psi) \psi_i.$$

We can now define the expectation value of an observable measured on state ψ :

$$\begin{aligned} \langle O \rangle_\psi &= \sum_i \lambda_i \mathbb{P}(O = \lambda_i) = \sum_i \lambda_i |a_i|^2 = \sum_i \lambda_i |(\psi_i, \psi)|^2 \\ &= \left(\sum_i (\psi_i, \psi) \psi_i, \sum_j \lambda_j (\psi_j, \psi) \psi_j \right) = (\psi, \hat{O} \psi) \\ &= \int \psi^*(x, t) \hat{O} \psi(x, t) dx. \end{aligned}$$

The expectation satisfies linearity:

$$\langle a\hat{A} + b\hat{B} \rangle_\psi = a\langle \hat{A} \rangle_\psi + b\langle \hat{B} \rangle_\psi.$$

Remark.

- The physics implication of the projection postulate is that if O is measured twice, the outcome of the second measurement is the same as the first with probability 1, if the difference between measurement times is small.

- Born's rule says if $\phi(\mathbf{x}, t)$ is the state that gives the desired outcome on a measurement on a state $\psi(\mathbf{x}, t)$, the probability of such an outcome is given by

$$|(\psi, \phi)|^2 = \left| \int_{-\infty}^{\infty} \psi^*(x, t) \phi(x, t) dx \right|^2.$$

2.6 Time-independent Schrödinger equation

Recall the one-dimensional time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t}(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}(x, t) + U(x)\psi(x, t) = \hat{H}\psi(x, t).$$

We try separation of variables:

$$\psi(x, t) = T(t)\chi(x).$$

Substituting, this gives

$$i\hbar \frac{\partial T}{\partial t}(t)\chi(x) = T(t)\hat{H}\chi(x).$$

Dividing by $T(t)\chi(x)$, we get

$$\frac{1}{T(t)} i\hbar \frac{\partial T(t)}{\partial t} = \frac{\hat{H}\chi(x)}{\chi(x)} = E.$$

Solving for time, we get

$$\frac{1}{T(t)} i\hbar \frac{\partial T(t)}{\partial t} = E \implies T(t) = e^{-iEt/\hbar}.$$

The time-independent Schrödinger equation is the equation for $\chi(x)$:

$$\hat{H}\chi(x) = E\chi(x) \iff -\frac{\hbar^2}{2m} \frac{\partial^2 \chi(x)}{\partial x^2} + U(x)\chi(x) = E\chi(x).$$

Note that the time-independent Schrödinger equation is an eigenvalue equation for the \hat{H} operator, and the eigenvalues of \hat{H} are all possible outcomes for the measurement of the energy of the state ψ .

2.7 Stationary states

We have find a particular solution to the time-dependent Schrödinger equation

$$\Psi(x, t) = \chi(x)e^{-iEt/\hbar}.$$

Definition 2.13. These solutions are called **stationary states**.

This is because the probability distribution of these states satisfies

$$\rho(x, t) = |\Psi(x, t)|^2 = |\chi(x)|^2,$$

meaning they are independent of time.

Due to completeness of eigenfunctions, applying this to $\hat{O} = \hat{H}$ gives the following result.

Theorem 2.6. *Every solution of the time-dependent Schrödinger equation can be written as a linear combination of stationary states.*

For systems with a discrete set of eigenvalues of \hat{H} , namely, $E_n = E_1, E_2, \dots$, then

$$\psi(x, t) = \sum_n a_n \chi_n(x) e^{-iE_n t/\hbar}.$$

For systems with a continuous set of eigenvalues of \hat{H} ,

$$\psi(x, t) = \int_{\Delta} A(\alpha) \chi_{\alpha}(x) e^{-iE_{\alpha} t/\hbar} d\alpha.$$

Here, the probability of measuring the energy to be $E_n = E(\alpha)$ is $|a_n|^2$ in the discrete case, or $|A(\alpha)|^2 d\alpha$ in the continuous case.

Consider a system with only two energy eigenvalues $E_1 \neq E_2$. Then we can write the state ψ as a combination

$$\psi(x, t) = a_1 \chi_1(x) e^{-iE_1 t/\hbar} + a_2 \chi_2(x) e^{-iE_2 t/\hbar}.$$

Then this gives $\psi(x, 0) = a_1 \chi_1(x) + a_2 \chi_2(x)$. If $a_1 = 0$, then $\psi(x, t) = a_2 \chi_2(x) e^{-iE_2 t/\hbar}$, which implies ψ is a stationary state.

If $a_1 \neq 0$ and $a_2 \neq 0$, then

$$\begin{aligned} |\psi(x, t)|^2 &= |a_1 \chi_1 e^{-iE_1 t/\hbar} + a_2 \chi_2 e^{-iE_2 t/\hbar}|^2 \\ &= a_1^2 |\chi_1|^2 + a_2^2 |\chi_2|^2 + 2a_1 a_2 \chi_1(x) \chi_2(x) \cos\left(\frac{(E_1 - E_2)t}{\hbar}\right). \end{aligned}$$

Hence ψ is not a stationary state.

3 4-Dimension Solutions of Schrödinger Equation

The time-independent Schrödinger equation is

$$\begin{aligned}\hat{H}\chi(x) &= E\chi(x), \\ -\frac{\hbar^2}{2m}\chi''(x) + U(x)\chi(x) &= E\chi(x).\end{aligned}$$

We want to solve the TISE for 3 cases:

1. Bound states;
2. Free particles;
3. Scattering states.

3.1 Bound States

3.1.1 Infinite potential well

Consider the potential function

$$U(x) = \begin{cases} 0 & |x| \leq a, \\ +\infty & |x| > a, \end{cases}$$

For $|x| > a$, we must have $\chi(x) = 0$, otherwise $U \cdot \chi = \infty$. Hence we have boundary conditions $\chi(\pm a) = 0$.

For $|x| \leq a$, we look for solutions of

$$\begin{cases} -\frac{\hbar^2}{2m}\chi''(x) = E\chi(x), \\ \chi(\pm a) = 0. \end{cases}$$

This has solutions $\chi(x) = A \sin(kx) + B \cos(kx)$, where $k = \sqrt{2mE/\hbar^2}$. Using the boundary conditions, we get $A \sin(ka) = B \cos(ka) = 0$.

- (i) $A = 0$ and $\cos(ka) = 0$, so $k_n = n\pi/(2a)$ for odd integers n .
- (ii) $B = 0$ and $\sin(ka) = 0$, so $k_n = n\pi/(2a)$ for even integers n .

We can determine A and B by requiring normalization of the electron:

$$\int_{-a}^a |\chi_n(x)|^2 dx = 1 \implies A = B = \sqrt{\frac{1}{a}}.$$

Remark. (i) The ground state χ_1 has nonzero energy.

(ii) As $n \rightarrow \infty$, $|\chi_n(x)|^2$ approaches a constant.

Proposition 3.1. *If the quantum system has non-degenerate eigenstates, then if $U(x) = U(-x)$, the eigenfunctions of \hat{H} are either odd or even.*

Proof: If $U(x) = U(-x)$, then the TISE is invariant under $x \mapsto -x$. Hence if $\chi(x)$ is a solution with eigenvalue λ , $\chi(-x)$ is also a solution with eigenvalue λ and $\chi(-x) = \alpha\chi(x)$.

Hence $\chi(x) = \chi(-(-x)) = \alpha^2\chi(x)$, so $\alpha^2 = 1$. Hence either $\alpha = 1$, and χ is even, or $\alpha = -1$, and χ is odd.

3.1.2 Finite Potential Well

Consider the more physical problem of a finite potential well:

$$U(x) = \begin{cases} 0 & |x| \leq a, \\ U_0 & |x| > a. \end{cases}$$

Consider $E > 0$ and $E < U_0$. We look for odd and even eigenfunctions.

(i) For even parity bounded states, $\chi(-x) = \chi(x)$, so we solve

$$\begin{cases} -\frac{\hbar^2}{2m}\chi''(x) = E\chi(x) & |x| \leq a, \\ -\frac{\hbar^2}{2m}\chi''(x) = (E - U_0)\chi(x) & |x| > a. \end{cases}$$

The first equation gives $\chi''(x) + k^2\chi(x) = 0$, where $k = \sqrt{2mE/\hbar^2}$, and so $\chi(x) = A\sin(kx) + B\cos(kx)$. But $A = 0$, since χ is even, so $\chi(x) = B\cos(kx)$.

The second equation gives $\chi''(x) - \bar{k}^2\chi(x) = 0$, with $\bar{k} = \sqrt{2m(U_0 - E)/\hbar^2}$. Then $\chi(x) = ce^{+\bar{k}x} + De^{-\bar{k}x}$. Imposing normalisability, we get $c = 0$ for $x > a$ and $d = 0$ for $x < -a$. Then, imposing evenness, we get

$$\chi(x) = \begin{cases} Ce^{\bar{k}x} & x < -a, \\ B\cos(kx) & |x| \leq a, \\ Ce^{-\bar{k}x} & x > a. \end{cases}$$

Continuity of χ and χ' at $x = \pm a$ implies

$$ce^{-\bar{k}a} = B\cos(ka),$$

$$-\bar{k}ce^{-\bar{k}a} = -kB \sin(ka).$$

This gives $k \tan(ka) = \bar{k}$, and $k^2 + \bar{k}^2 = (2mU_0)/\hbar^2$. Let $\xi = ka, \eta = \bar{k}a$. Then we have $\xi \tan \xi = \eta$ and $\xi^2 + \eta^2 = r_0^2$.

The eigenvalues of the Hamiltonian correspond to the points of intersection of these graphs.

As $U_0 \rightarrow \infty$, we get the same result for the infinite potential well.

(ii) The odd part is found in the example sheets.

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