IB Quantum Mechanics

Ishan Nath, Michaelmas 2022

Based on Lectures by Prof. Maria Ubiali

April 3, 2023

Contents

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 $\mathbf{v} = \dot{\mathbf{v}} = \frac{d}{dt}\mathbf{x}$. 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 $\omega \to \infty$. 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 $h \approx 6.6 \cdot 10^{-34}$Joule $\times$ 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

$$v = \frac{L}{m_0 r} \implies v_n = n\frac{\hbar}{m_e r}.$$

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

$$E_n = \frac{1}{2}m_e v_n^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_n} = -\frac{e^2}{8\pi\varepsilon_0 a_0}\frac{1}{n^2} = -\frac{e^4 m_e}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} = \frac{E_1}{n^2}.$$

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

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

  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

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

- The linear map $V \to V$ represented by a matrix T becomes the linear maps between $L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$, 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. $\psi(\mathbf{x}, t) : \mathbb{R}^3 \to \mathbb{C}$ 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,* $\rho(\mathbf{x}, t)\, \mathrm{d}V$ *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

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

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

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

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

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

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

$$\begin{aligned}
\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \,\mathrm{d}^3x &= \int_{\mathbb{R}^3} |\alpha_1\psi_1(\mathbf{x},t) + \alpha_2\psi_2(\mathbf{x},t)|^2 \,\mathrm{d}^3x \\
&\leq \int_{\mathbb{R}^3} (|\alpha_1\psi_1(\mathbf{x},t)| + |\alpha_2\psi_2(\mathbf{x},t)|)^2 \,\mathrm{d}^3x \\
&= \int_{\mathbb{R}^3} (|\alpha_1\psi_1(\mathbf{x},t)|^2 + |\alpha_2\psi_2(\mathbf{x},t)|^2 + 2|\alpha_1\psi_1||\alpha_2\psi_2|) \,\mathrm{d}^3x \\
&\leq \int_{\mathbb{R}^3} 2|\alpha_1\psi_1(\mathbf{x},t)|^2 + 2|\alpha_2\psi_2(\mathbf{x},t)|^2 \,\mathrm{d}^3x \\
&= 2|a_1|^2\mathcal{N}_1 + 2|a_2|^2\mathcal{N}_2 < \infty.
\end{aligned}$$

2.3 Inner Product

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

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

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:

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

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:

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

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:

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

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 believe 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

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

is independent of time.

Proof: We have

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

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,

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

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

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

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

where the probability current is

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

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

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

Hence the operator with respect to x is

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

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

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

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 $\mathcal{H} \to \mathcal{H}$, given by $\hat{O} : \psi \to \tilde{\psi}$.

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

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

- Parity operator

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

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

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

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

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

(iii) Kinetic energy

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

(iv) Potential energy

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

(v) Total energy

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

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

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

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 $\psi = \sum a_i \psi_i = \sum (\psi_i, \psi)\psi$, 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:

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

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 om a measurement on a state $\psi(\mathbf{x}, t)$, the probability of such an outcome is given by

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

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

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

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 (Hamiltonian), 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, $E_n = E_1, E_2, \ldots$, 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 $\hat{H}$,

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

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

$$\psi(x,t) = a_1\chi_1(x)e^{-iE_1t/\hbar} + a_2\chi_2(x)e^{-iE_2t/\hbar}.$$

This gives $\psi(x,0) = a_1\chi_1(x) + a_2\chi_2(x)$. If $a_1 = 0$, then $\psi(x,t) = a_2\chi_2(x)e^{-iE_2t/\hbar}$, which implies ψ is a stationary state.

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

$$\begin{aligned}|\psi(x,t)|^2 &= |a_1\chi_1 e^{-iE_1t/\hbar} + a_2\chi_2 e^{-iE_2t/\hbar}|^2 \\ &= a_1^2|\chi_1^2| + a_2^2|\chi_2|^2 + 2a_1a_2\chi_1(x)\chi_2(x)\cos\left(\frac{(E_1-E_2)t}{\hbar}\right).\end{aligned}$$

Hence ψ is not a stationary state.

3 4D Solutions of Schrödinger Equation

The time-independent Schrödinger equation is

$$\hat{H}\chi(x) = E\chi(x),$$

$$-\frac{\hbar^2}{2m}\chi''(x) + U(x)\chi(x) = E\chi(x).$$

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

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

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 a.

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

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

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

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

(ii) As $n \to \infty$, $|\chi_n(x)|^2$ 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:

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

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

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

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

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

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

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

3.1.3 Harmonic Oscillator

Consider the harmonic oscillator, which models many physical situations.

$$U(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2.$$

Here, we say k is the elastic constant and $\omega = \sqrt{k/m}$ is the angular frequency of the harmonic oscillator. In classical mechanics, we model this system as $\ddot{x}(t) = -\omega^2x(t)$, so

$$x(t) = A\sin(\omega t) + B\cos(\omega t),$$

with $T = 2\pi/\omega$ being the period. In quantum mechanics, we have the Schrödinger equation

$$-\frac{\hbar^2}{2m}\chi''(x) + \frac{1}{2}m\omega^2x^2\chi(x) = E\chi(x).$$

We expect to have a discrete set of eigenvalues, with either even or odd eigenfunctions. Defining the variables

$$\xi^2 = \frac{m\omega}{\hbar}x^2, \quad \varepsilon = \frac{2E}{\hbar\omega},$$

under a change of variables, our equation becomes

$$-\frac{\mathrm{d}^2\chi(\xi)}{\mathrm{d}\xi^2} + \xi^2\chi(\xi) = \varepsilon\chi(\xi).$$

We solve this by starting from a particular solution $\varepsilon = 1$, which corresponds to $E_0 = \hbar\omega/2$. Then,

$$\chi_0(\xi) = -e^{-\xi^2/2}.$$

Hence we have found an eigenvalue $E_0 = \hbar\omega/2$. To find other eigenfunctions of $\hat{H}$, we take the function

$$\chi(\xi) = f(\xi)e^{-\xi^2/2}.$$

Then plugging in χ, we get f must satisfy

$$-\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} + 2\xi\frac{\mathrm{d}f}{\mathrm{d}\xi} + (1-\varepsilon)f = 0.$$

We can represent f as a power series: $f(\xi) = \sum a_n \xi^n$. Then,

$$\begin{aligned}
\xi\frac{\mathrm{d}f}{\mathrm{d}\xi} &= \sum_{n=0}^{\infty} n a_n \xi^n, \\
\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} &= \sum_{n=0}^{\infty} n(n-1)a_n\xi^{n-1} = \sum_{n=0}^{\infty}(n+1)(n+2)a_n\xi^n.
\end{aligned}$$

Plugging these values in, we get

$$\sum_{n=0}^{\infty}[(n+1)(n+2)a_{n+2} = 2na_n + (\varepsilon-1)a_n]\xi^n = 0 \implies a_{n+2} = \frac{(2n-\varepsilon+1)}{(n+1)(n+2)}.$$

Because of the parity of eigenfunctions, we either have $a_n = 0$ for odd n, giving $f(\xi) = f(-\xi)$, or $a_n = 0$ for even n, giving $f(\xi) = -f(-\xi)$.

Proposition 3.2. *If the series $\sum a_n\xi^n$ does not terminate, then the eigenfunction of $\hat{H}$ would not be normalisable.*

Proof: Suppose that the series does not terminate. We examine the behaviour of the series:

$$\frac{a_{n+2}}{a_n} \to \frac{2}{n}.$$

This has the same asymptotic behaviour as

$$y(\xi) = e^{\xi^2} = \sum_{m=0}^{\infty}\frac{\xi^{2m}}{m!} = \sum_{n=0}^{\infty} b_m\xi^m.$$

So if $e^{\xi^2/2}$ and $f(\xi)$ have the same asymptotic behaviour, then

$$\chi(\xi) \sim e^{\xi^2}\cdot e^{-\xi^2/2} = e^{\xi^2/2}.$$

However, this is non-normalisable.

Given that the series $\sum a_n\xi^n$ terminates, there must exist N such that $a_{N+2} = 0$, with $a_N \neq 0$, i.e. $\varepsilon = 2N + 1$.

Thus $E_N = (N + 1/2)\hbar\omega$. Note in particular $E_{N+1} - E_N = \hbar\omega$, and the eigenfunctions are $\chi(x) = f_N(\xi)e^{-\xi^2/2}$. Here, the polynomials f_N satisfy

$$f_N(\xi) = (-1)^N e^{\xi^2} \frac{\mathrm{d}^N}{\mathrm{d}\xi^N}(e^{-\xi^2}),$$

and are known as the Hermite polynomials.. The first few values are

N	E_N	$f_N(\xi)$
0	$\hbar\omega/2$	1
1	$3\hbar\omega/2$	ξ
2	$5\hbar\omega/2$	$(1 - 2\xi^2)$
3	$7\hbar\omega/2$	$(\xi - 2\xi^2/3)$

3.2 The Free Particle

We take the time-independent Schrödinger equation with $U \equiv 0$:

$$-\frac{\hbar^2}{2m}\chi''(x) = E\chi(x).$$

This has solutions

$$\chi(x) = e^{ikx},$$

where $k = \sqrt{2mE/\hbar^2}$, and the energy is then $\hbar^2k^2/2m$. Hence,

$$\psi_k(x) = \chi_k(x)e^{-iE_kt/\hbar} = \exp\left(i\left(kx - \frac{\hbar k^2}{2m}\right)\right).$$

However, this wavefunction is not square integrable, as

$$\int_{-\infty}^{\infty} |\phi_k(x,t)|^2 \,\mathrm{d}x = \int_{-\infty}^{\infty} 1 \,\mathrm{d}x = +\infty.$$

To resolve this, we have two options:

1. Build a linear superposition of non-normalisable states that is normalisable;
2. Ignore the problem but change the interpretation.

3.2.1 Gaussian Wavepacket

Here we will build a superposition of non-normalisable states to make a normalisable state. Take

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k)\psi_k(x,t) \,\mathrm{d}k.$$

A possible option is the *Gaussian wavepacket*:

$$A(k) = A_{GP}(k) = \exp\left[-\frac{\sigma}{2}(k-k_0)^2\right],$$

where σ is positive and $k_0 \in \mathbb{R}$.

Substituting these values,

$$\begin{aligned}
\psi_{GP}(x,t) &= \int_{-\infty}^{\infty} \exp\left[-\frac{\sigma}{2}(k-k_0)^2 + ikx - \frac{i\hbar k^2}{2m}\right] \mathrm{d}k \\
&= \int_{-\infty}^{\infty} \left[-\frac{1}{2}\alpha k^2 + \beta k + \delta\right] \mathrm{d}k \\
&= \int_{-\infty}^{\infty} \left[-\frac{\alpha}{2}\left(k - \frac{\beta}{\alpha}\right)^2 + \frac{\beta^2}{2\alpha} + \delta\right] \mathrm{d}k \\
&= \exp\left[\frac{\beta^2}{2\alpha} + \delta\right] \int_{-\infty}^{\infty} \exp\left[-\frac{\alpha}{2}\left(k - \frac{\beta}{\alpha}\right)^2\right] \mathrm{d}k \\
&= \exp\left[\frac{\beta^2}{2\alpha} + \delta\right] \int_{-\infty-iu}^{\infty-iu} \exp\left(-\frac{\alpha}{2}\tilde{k}^2\right) \mathrm{d}k \\
&= \sqrt{\frac{2\pi}{\alpha}} \exp\left[\frac{\beta^2}{2\alpha} + \delta\right].
\end{aligned}$$

Now β^2 has a real factor of $-x^2$, hence ψ_{GP} is normalisable to $\bar{\psi}_{GP}$. Hence

$$\rho_{GP}(x,t) = |\bar{\psi}_{GP}(x,t)|^2 = \sqrt{\frac{\sigma}{\pi(\sigma^2 + \frac{\hbar^2 t^2}{m^2})}} \exp\left[\frac{\sigma(x - \frac{\hbar k_0}{m}t)^2}{\sigma^2 + \frac{\hbar^2 t^2}{m^2}}\right].$$

The centre of the distribution is $\langle x \rangle_{\psi_{GP}}$, which is

$$\langle x \rangle_{\psi_{GP}} = \int_{-\infty}^{\infty} \bar{\psi}^*_{GP}(x,t) x \bar{\psi}^*_{GP}(x,t)\, \mathrm{d}x = \int_{-\infty}^{\infty} x \rho_{GP}(x,t)\, \mathrm{d}x = \frac{\hbar k_0}{m} t.$$

Here $\hbar k_0/m$ can be though of as the velocity of the particle. The error of the position of the particle is

$$\Delta x = \sqrt{\langle x^2 \rangle_{\psi_{GP}} - \langle x \rangle^2_{\psi_{GP}}} = \sqrt{\frac{1}{2}\left(\sigma + \frac{\hbar^2 t^2}{m^2 \sigma}\right)}.$$

Physically, this means the longer the particle is left to travel, the more uncertain we are about its position. We can also calculate the momentum

$$\langle p \rangle_{\psi_{GP}} = \int_{-\infty}^{\infty} \bar{\psi}^*_{GP}(x,t) \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \bar{\psi}_{GP}(x,t)\right) \mathrm{d}x = \hbar k_0,$$

which we expect given the velocity of the particle. The error of the momentum is

$$\Delta p = \sqrt{\langle p^2\rangle_{\psi_{GP}} - \langle p\rangle^2_{\psi_{GP}}} = \frac{\hbar}{\sqrt{2\sigma}}.$$

We see that at $t = 0$, $\Delta x \cdot \Delta p = \hbar/2$, and in fact this is minimal.

The Gaussian wavepacket is a state of minimum uncertainty at $t = 0$. Other $A(k)$ may give a normalisable state, but if you compute $\Delta x \cdot \Delta p$ the value will be greater than $\frac{\hbar}{2}$.

For the De Broglie wave $\psi_k(x,t)$, we have $\Delta x = \infty$ and $\Delta p = 0$.

3.2.2 Beam Interpretation

In the following, we ignore the normalisation problem, and take $\chi_k = e^{ikx}$ as an eigenfunction of $\hat{H}$, so

$$\psi_k(x,t) = Ae^{ikx}e^{-i\frac{\hbar^2k^2}{2m}t},$$

but instead of $\chi_n(x)$ describing a single particle, they describe a beam of particles with

$$P_n = \hbar k, \quad E_k = \frac{\hbar^2 k^2}{2m},$$

and probability density

$$\rho_k(x,t) = |A|^2,$$

representing the constant average density of particles. We can compute the probability current as

$$\begin{aligned} j_k(x,t) &= -\frac{i\hbar}{2m}\left(\psi_k^*\frac{\partial\psi_k}{\partial x} - \psi_k\frac{\partial\psi_k^*}{\partial x}\right) \\ &= |A|^2\frac{\hbar k}{m} = |A|^2\frac{p}{m}, \end{aligned}$$

the average flux of particles.

3.3 Scattering States

Suppose we have a free particle, thrown at a potential barrier, between 0 and a. Typically, if $E > U_0$, the particle will make it over, otherwise it will be reflected. For quantum states, this is more complicated.

Definition 3.1. The probability that the particle is reflected is given by the reflection coefficient
$$R = \lim_{t\to\infty} \int_{-\infty}^{0} |\psi_{GP}(x,t)|^2 \,\mathrm{d}x.$$

Similarly, the probability that the particle is transmitted is given by the transmission coefficient
$$T = \lim_{t\to\infty} \int_{0}^{\infty} |\psi_{GP}(x,t)|^2 \,\mathrm{d}x.$$
From construction, $R + T = 1$.

It is possible to solve scattering problems using the Gaussian wavepacket, however the beam interpretation gives the same results for R and T, and it easier, hence we will use it.

3.3.1 Scattering off Potential Step

Consider the potential
$$U(x) = \begin{cases} 0 & x \leq 0, \\ U_0 & x > 0. \end{cases}$$
To find $\chi_k(x)$, we solve the time-independent Schrödinger equation on both regions:
$$-\frac{\hbar^2}{2m}\chi_k''(x) + U(x)\chi_k(x) = E\chi_k(x).$$

- On $x \leq 0$, $U \equiv 0$, so the TISE becomes
$$\chi_k''(x) + K^2\chi_k(x) = 0,$$
where $k = \sqrt{2mE/\hbar^2} > 0$. We know the general solution is
$$\chi_k(x) = Ae^{ikx} + Be^{-ikx}.$$

- For $x > 0$, $U(x) = U_0$, so
$$\chi_{\bar{k}}''(x) + \bar{k}^2\chi_{\bar{k}}(x) = 0,$$
where $\bar{k} = \sqrt{2m(E-U_0)/\hbar^2}$. If $E > U_0$, then
$$\chi_{\bar{k}}(x) = Ce^{i\bar{k}x} + De^{i\bar{k}x}.$$
Now $D = 0$, since initially there is no beam coming from the right.

  If $E < U_0$, we get
$$\chi_{\bar{k}}(x) = Ce^{-\nu x} + De^{\nu x}.$$
Similarly, $D = 0$, otherwise $\chi_{\bar{k}}$ diverges.

We look at the case when $E \geq U_0$. Putting the solutions together,

$$\chi_{k,\bar{k}}(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x \leq 0, \\ Ce^{i\bar{k}x} & x > 0. \end{cases}.$$

We impose the continuity of $\chi(x)$ and $\chi'(x)$ to get

$$\begin{cases} A + B = C \\ ikA - ikB = i\bar{k}C \end{cases}.$$

Hence, we get

$$B = \frac{k - \bar{k}}{k + \bar{k}}A, \quad C = \frac{2k}{k + \bar{k}}A.$$

In terms of the particle flux $J(x,t)$, we get

$$J(x,t) = \begin{cases} \frac{\hbar k}{m}(|A|^2 - |B|^2) & x < 0, \\ \frac{\hbar \bar{k}}{m}|C|^2 & x \geq 0. \end{cases}$$

Hence we have incoming, reflected and transmitted flux

$$j_{inc}(x) = \frac{\hbar k}{m}|A|^2, \quad j_{ref}(x) = \frac{\hbar k}{m}\left(\frac{k - \bar{k}}{k + \bar{k}}\right)^2 |A|^2, \quad j_{tr} = \frac{\hbar \bar{k}}{m}\frac{4k^2}{(k + \bar{k})^2}|A|^2.$$

Hence we can calculate the reflection and transmission coefficients

$$R = \frac{j_{ref}}{j_{inc}} = \frac{|B|^2}{|A|^2} = \left(\frac{k - \bar{k}}{k + \bar{k}}\right)^2,$$

$$T = \frac{j_{tr}}{j_{inc}} = \frac{|C|^2}{|A|^2}\frac{\bar{k}}{k} = \frac{4k\bar{k}}{(k + \bar{k})^2}.$$

Note $R + T = 1$, as $E \to U_0$, then $\bar{k} \to 0$ so $T \to 0$ and $R \to 1$, and as $E \to \infty$, $T \to 1$ and $R \to 0$.

Now we can look at the case when $E < U_0$. Then, we can calculate

$$j_{in} = \frac{\hbar k}{m}|A|^2, \quad j_{tr} = 0, \quad j_{ref}(x,t) = \frac{\hbar k}{m}|B|^2.$$

Hence $R = 1$ and $T = 0$, but $\chi_{\bar{k}}(x) \neq 0$ for all $x > 0$.

3.3.2 Scattering off Potential Barrier

Consider the potential

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

We consider when $E < U_0$, then let $k = \sqrt{2mE/\hbar^2} > 0$, $\eta = \sqrt{2m(U_0 - E)/\hbar^2} > 0$. The solution of the TISE is

$$\chi(x) = \begin{cases} e^{ikx} + Ae^{-ikx} & x \leq 0, \\ Be^{-\nu x} + Ce^{\nu x} & 0 < x < a, \\ De^{ikx} + E^{-ikx} & x \geq a. \end{cases}$$

Now $E = 0$ as there are no incoming waves from the right. The continuity of χ, χ' at $x = 0, a$ gives four equations, from which we can solve for A, B, C and D:

$$\begin{cases} 1 + A = B + C, \\ ik - ikA = -\eta B + \eta C, \\ Be^{-\eta a} + Ce^{\eta a} = De^{ika}, \\ -\eta Be^{-\eta a} + \eta Ce^{\eta a} = ikDe^{ika}. \end{cases}$$

Solving, we can find

$$D = -\frac{4i\eta k}{(\eta - ik)^2 \exp[(\eta + ik)a] - (\eta + ik)^2 \exp[-(\eta - ik)a]}.$$

Hence the transmission coefficient is

$$T = |D|^2 = \frac{4k^2\eta^2}{(k^2 + \eta^2)^2 \sinh^2(\eta a) + 4k^2\eta^2}.$$

Taking the limit $U_0 \gg E$, then $\eta a \gg 1$, so

$$T \to \frac{16k^2\eta^2}{(\eta^2 + k^2)^2} e^{-2\eta a}.$$

4 Simultaneous Measurements

4.1 Commutators

Definition 4.1. The *commutator* of two operators $\hat{A}$, $\hat{B}$ is the operator $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.

The commutator has the properties:

- $[\hat{A},\hat{B}] = -[\hat{B},\hat{A}]$;
- $[\hat{A},\hat{A}] = 0$;
- $[\hat{A},\hat{B}\hat{C}] = [\hat{A},\hat{B}]\hat{C} + \hat{B}[\hat{A},\hat{C}]$;
- $[\hat{A}\hat{B},\hat{C}] = \hat{A}[\hat{B},\hat{C}] + [\hat{A},\hat{C}]\hat{B}$.

Example 4.1.

We compute $[\hat{x},\hat{p}]$ in one dimension. Take $\psi \in \mathcal{H}$. Then

$$\hat{x}\hat{p}\psi = x\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x) = -i\hbar x\frac{\partial\psi}{\partial x}(x),$$

$$\hat{p}\hat{x}\psi = -i\hbar\frac{\partial}{\partial x}(x\psi(x)) = -i\hbar\psi(x) - i\hbar x\frac{\partial\psi}{\partial x}(x),$$

$$\implies [\hat{x},\hat{p}]\psi = i\hbar\psi, \quad [\hat{x},\hat{p}] = i\hbar\hat{I}.$$

Definition 4.2. Two Hermitian operators $\hat{A}$ and $\hat{B}$ are simultaneously diagonalizable in $\mathcal{H}$ if there exists a complete basis of joint eigenfunctions $\{\psi_i\}$ such that

$$\hat{A}\psi_i = a_i\psi_i, \quad \hat{B}\psi_i = b_i\psi_i.$$

Theorem 4.1. *Two Hermitian operators $\hat{A}$ and $\hat{B}$ are simultaneously diagonalizable if and only if $[\hat{A},\hat{B}] = 0$.*

Proof: If $\hat{A}$, $\hat{B}$ are simultaneously diagonalizable then there exists a set of joint eigenfunctions $\{\psi_i\}$ which are a complete basis of x. Now,

$$[\hat{A},\hat{B}]\psi_i = \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i = (a_ib_i - a_ib_i)\psi_i = 0.$$

Take $\psi \in \mathcal{H}$. Then we can write it as a sum of ψ_i, so

$$[\hat{A},\hat{B}]\psi = \sum c_i[\hat{A},\hat{B}]\psi_i = 0.$$

Now if $[\hat{A}, \hat{B}] = 0$ and ψ_i is an eigenfunction of $\hat{A}$ with eigenvalue a_i, then

$$0 = [\hat{A}, \hat{B}]\psi_i = \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i = \hat{A}\hat{B}\psi_i - a_i\hat{B}\psi_i$$

$$\implies \hat{A}(\hat{B}\psi_i) = a_i(\hat{B}\psi_i).$$

Thus $\hat{B}$ maps the eigenspace E_i of eigenfunctions of $\hat{A}$ with eigenvalues a_i into itself, so $\hat{B}|_{E_i}$ is a Hermitian operator on E_i, and we can diagonalize it.

Since this holds for all eigenspaces E_i of $\hat{A}$, we can find a complete basis of simultaneous eigenfunctions of $\hat{A}$ and $\hat{B}$.

4.2 Heisenberg's Uncertainty Principle

Definition 4.3. The uncertainty in a measurement of an observable A on a state ψ is defined as

$$\Delta_\psi A = \sqrt{(\Delta_\psi A)^2},$$

where

$$(\Delta_\psi A)^2 = \langle (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})^2 \rangle_\psi = \langle \hat{A}^2 \rangle_\psi - (\langle \hat{A} \rangle_\psi)^2.$$

Note these two definitions are equivalent, as

$$\begin{aligned}
\langle (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})^2 \rangle_\psi &= \int_{\mathbb{R}^3} \psi^* (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})^2 \psi \, \mathrm{d}^3 x \\
&= \int_{\mathbb{R}^3} \psi^* \hat{A}^2 \psi \, \mathrm{d}^3 x + (\langle \hat{A} \rangle_\psi)^2 \int_{\mathbb{R}^3} \psi^* \psi \, \mathrm{d}^3 - 2\langle \hat{A} \rangle_\psi \int_{\mathbb{R}^3} \psi^* \hat{A} \psi \, \mathrm{d}^3 x \\
&= \langle \hat{A} \rangle_\psi^2 - (\langle \hat{A} \rangle_\psi)^2.
\end{aligned}$$

Lemma 4.1. $(\Delta_\psi A)^2 \geq 0$, *with equality if and only if* ψ *is an eigenfunction of* A.

Proof:

$$\begin{aligned}
(\Delta_\psi A)^2 &= \langle (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})^2 \rangle_\psi \\
&= (\psi, (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})^2 \psi) = ((\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})\psi, (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})\psi) \\
&= (\phi, \phi) \geq 0.
\end{aligned}$$

Now we prove that $(\Delta_\psi A)^2 = 0 \iff \phi = 0$. Indeed, if $(\Delta_\psi A)^2 = 0$, then $(\phi, \phi) = 0$, so $\hat{A}\psi = \langle \hat{A} \rangle_\psi \psi$.

Alternatively, if ψ is an eigenfunction of $\hat{A}$ with real eigenvalue $a \in \mathbb{R}$, then $\langle \hat{A} \rangle_\psi = (\psi, \hat{A}\psi) = a(\psi, \psi) = a$, and similarly $\langle \hat{A}^2 \rangle_\psi = a^2$.

Then $(\Delta_\psi A)^2 = \langle \hat{A}^2 \rangle_\psi - (\langle \hat{A} \rangle_\psi)^2 = 0$.

Lemma 4.2. *If $\psi, \phi \in \mathcal{H}$, then $|(\psi, \phi)|^2 \leq (\psi, \psi)(\phi, \phi)$, with equality if and only if $\phi = a\psi$ for some $a \in \mathbb{C}$.*

This is the Schwarz inequality.

Theorem 4.2 (Generalized Uncertainty Theorem)**.** *If A and B are observables, then*

$$(\Delta_\psi A)(\Delta_\psi B) \geq \frac{1}{2}|(\psi, [\hat{A}, \hat{B}]\psi)|.$$

Proof: Note $(\Delta_\psi A)^2 = ((\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})\psi, (\hat{A} - \langle \hat{A} \rangle_\psi \hat{I})\psi)$, and similarly for B.

Define $\hat{A}' = \hat{A} - \langle \hat{A} \rangle_\psi \hat{I}$, $\hat{B}' = \hat{B} - \langle \hat{B} \rangle_\psi \hat{I}$. Then, using the Schwarz inequality,

$$(\Delta_\psi A)^2 (\Delta_\psi B)^2 \geq |(\hat{A}'\psi, \hat{B}'\psi)|^2 = |(\psi, \hat{A}'\hat{B}'\psi)|^2.$$

Define $\{\hat{A}', \hat{B}'\} = \hat{A}'\hat{B}' + \hat{B}'\hat{A}'$, the anti-commutator. Then this is symmetric, so we can write

$$\hat{A}'\hat{B}' = \frac{1}{2}([\hat{A}', \hat{B}'] + \{\hat{A}', \hat{B}'\}).$$

Note under the Hermitian conjugate, $[\hat{A}', \hat{B}']$ flips sign, whereas $\{\hat{A}', \hat{B}'\}$ stays the same. Hence $(\psi, [\hat{A}', \hat{B}']\psi)$ is purely imaginary and $(\psi, \{\hat{A}', \hat{B}'\}\psi)$ is real. So,

$$(\Delta_\psi A)^2 (\Delta_\psi B)^2 = \frac{1}{4}(|(\psi, [\hat{A}', \hat{B}']\psi)|^2 + |(\psi, \{\hat{A}', \hat{B}'\}\psi)|^2).$$

Dropping the anti-commutator term and taking the square roots gives our result.

4.2.1 Consequences of the Uncertainty Theorem

We have shown that $[\hat{A}, \hat{B}] = 0 \iff$ we can simultaneously diagonalize A and B. But this is if and only if A and B can be measured simultaneously to arbitrary precision on a given state.

Moreover, if we take $\hat{A} = \hat{x}$, $\hat{B} = \hat{p}$, then what we recover is *Heisenberg's Uncertainty principle*

$$(\Delta_\psi x)(\Delta_\psi p) \geq \frac{\hbar}{2}.$$

Note if $\psi = \psi_{GP}$, then at $t = 0$, we have equality in the above. This is due to the following two lemmas:

Lemma 4.3. *ψ is a state of minimal uncertainty if and only if $\hat{x}\psi = ia\hat{p}\psi$, for $a \in \mathbb{R}$.*

From this, we can deduce the following:

Lemma 4.4. *Minimal uncertainty occurs if and only if*

$$\psi(x) = Ce^{-kx^2},$$

for $c \in \mathbb{C}$, and $k \in \mathbb{R}^+$.

4.3 Ehrenfest Theorem

We look at the Ehrenfest theorem, which tells us the evolution of the operators over time.

Theorem 4.3 (Ehrenfest theorem)**.** *The expectation value of a Hermitian operator $\hat{A}$ evolves according to*

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{A}\rangle_\psi = \frac{i}{\hbar}\langle [\hat{H}, \hat{A}]\rangle_\psi + \left\langle \frac{\partial \hat{A}}{\partial t}\right\rangle_\psi.$$

Proof: We will integrate over parts:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{A}\rangle_\psi &= \frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty} \psi^* \hat{A}\psi \,\mathrm{d}x = \int_{-\infty}^{\infty} \frac{\partial}{\partial t}(\psi^*\hat{A}\psi)\,\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\left(\frac{\partial \psi^*}{\partial t}\hat{A}\psi + \psi^*\frac{\partial \hat{A}}{\partial t}\psi + \psi^*\hat{A}\frac{\partial \psi}{\partial t}\right)\mathrm{d}x \\
&= \frac{i}{\hbar}\int_{-\infty}^{\infty}\psi^*(\hat{H}\hat{A} - \hat{A}\hat{H})\psi\,\mathrm{d}x + \left\langle \frac{\partial \hat{A}}{\partial t}\right\rangle_\psi \\
&= \frac{i}{\hbar}\langle [\hat{H}, \hat{A}]\rangle_\psi + \left\langle \frac{\partial \hat{A}}{\partial t}\right\rangle_\psi
\end{aligned}$$

Example 4.2.

1. If we take $\hat{A} = \hat{H}$, then $[\hat{H}, \hat{H}] = 0$ and since $\hat{H}$ doesn't depend on

time,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{H}\rangle_\psi = 0.$$

2. Take $\hat{A} = \hat{p}$. Then,

$$\begin{aligned}
[\hat{H},\hat{p}]\psi &= \left[\frac{\hat{p}^2}{2m} + U(\hat{x}), \hat{p}\right]\psi = [U(\hat{x}),\hat{p}]\psi \\
&= U(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t) - \left(-i\hbar\frac{\partial}{\partial x}\right)(U(x)\psi(x,t)) \\
&= -i\hbar U(x)\frac{\partial\psi}{\partial x}(x,t) + i\hbar U(x)\frac{\partial\psi}{\partial x}(x,t) + i\hbar\frac{\partial U}{\partial x}\psi(x,t) \\
&= i\hbar\frac{\partial U}{\partial x}\psi(x,t).
\end{aligned}$$

Hence we get

$$\frac{\mathrm{d}\langle\hat{p}\rangle_\psi}{\mathrm{d}t} = \frac{i}{\hbar}\langle[\hat{H},\hat{p}]\rangle_\psi = -\langle\frac{\partial U}{\partial X}\rangle_\psi.$$

This is the quantum mechanics equivalent of Newton's second law.

3. If we let $\hat{A} = \hat{x}$, then

$$\begin{aligned}
[\hat{H},\hat{x}] &= \left[\frac{\hat{p}^2}{2m} + U(\hat{x}), \hat{x}\right] = \frac{1}{2m}[\hat{p}^2,\hat{x}] \\
&= \frac{1}{2m}(\hat{p}[\hat{p},\hat{x}] + [\hat{p},\hat{x}]\hat{p}) \\
&= -\frac{i\hbar}{m}\hat{p}.
\end{aligned}$$

So this gives

$$\frac{\mathrm{d}\langle\hat{x}\rangle_\psi}{\mathrm{d}t} = \frac{i}{t}\langle[\hat{H},\hat{x}[\rangle_\psi = \frac{\langle\hat{p}\rangle_\psi}{m},$$

which is the quantum mechanics reformulation of $p = mv$, i.e. momentum is velocity times mass.

4.4 Harmonic Oscillator Revisited

Remember the Hamiltonian of the harmonic oscillator is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2,$$

where $k = m\omega^2$ is the elastic function. To find the eigenvalues and eigenfunctions of $\hat{H}$, we rewrite

$$\begin{aligned}\hat{H} &= \frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x}) + \frac{i\omega}{2}[\hat{p}, \hat{x}] \\ &= \frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x}) + \frac{\hbar\omega}{2}\hat{I}\end{aligned}$$

Definition 4.4. We define the linear operators

$$\hat{a} = \frac{1}{\sqrt{2m}}(\hat{p} - im\omega\hat{x}), \qquad \hat{a}^\dagger = \frac{1}{\sqrt{2m}}(\hat{p} + im\omega\hat{x}).$$

Then we can rewrite the Hamiltonian as

$$\hat{H} = \hat{a}^\dagger\hat{a} + \frac{\hbar\omega}{2}\hat{I}.$$

We can compute the value

$$\begin{aligned}[\hat{a}, \hat{a}^\dagger] &= \frac{1}{2m}[\hat{p} - im\omega\hat{x}, \hat{p} + im\omega\hat{x}] \\ &= -\frac{im\omega}{2m}[\hat{x}, \hat{p}] + \frac{im\omega}{2m}[\hat{p}, \hat{x}] \\ &= \hbar\omega\hat{I}.\end{aligned}$$

This lets us compute

$$\begin{aligned}[\hat{H}, \hat{a}] &= [\hat{a}^\dagger\hat{a}, \hat{a}] = -\hbar\omega\hat{a}, \\ [\hat{H}, \hat{a}^\dagger] &= \hbar\omega\hat{a}^\dagger.\end{aligned}$$

Suppose χ is an eigenfunction of $\hat{H}$ with eigenvalue E. We consider the energy of $(\hat{a}\chi)$:

$$\begin{aligned}\hat{H}(\hat{a}\chi) &= [\hat{H}, \hat{a}]\chi + \hat{a}\hat{H}\chi = -\hbar\omega\hat{a}\chi + E\hat{a}\chi \\ &= (E - \hbar\omega)\hat{a}\chi,\end{aligned}$$

so $(\hat{a}\chi)$ is an eigenfunction of $\hat{H}$ with eigenvalue $(E - \hbar\omega)$, and similarly $(\hat{a}^\dagger\chi)$ is an eigenfunction of $\hat{H}$ with eigenvalue $(E + \hbar\omega)$.

By induction, we can prove that $(\hat{a}^n\chi)$ is an eigenfunction with eigenvalue $(E - n\hbar\omega)$, and $(\hat{a}^{\dagger n}\chi)$ is an eigenfunction with eigenvalue $(E + n\hbar\omega)$.

Using the fact that the energies are non-zero, there exist an eigenfunction χ_0 such that $\hat{a}\chi_0 = 0$. Finding χ_0,

$$\begin{aligned}
\frac{1}{\sqrt{2m}}(\hat{p} - im\omega\hat{x})\chi_0 &= 0, \\
-i\hbar\frac{\partial\chi_0}{\partial x} - im\omega x\chi_0 &= 0, \\
\chi_0(x) &= Ce^{-m\omega x^2/2\hbar},
\end{aligned}$$

which is a Gaussian. The excited states with $E > E_0$ are the given by

$$\begin{aligned}
\chi_n = (a^\dagger)^n\chi_0 &= \frac{1}{(\sqrt{2m})^n}(\hat{p} + im\omega\hat{x})^n\chi_0 \\
&= \frac{C}{(\sqrt{2m})^n}\left(-i\hbar\frac{\partial}{\partial x} + im\omega x\right)^n e^{-m\omega^2/2\hbar},
\end{aligned}$$

with eigenvalues

$$E_n = \frac{\hbar\omega}{2} + n\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\omega.$$

5 3D Solutions of the Schrödinger Equation

5.1 TISE for Spherically Symmetric Potentials

In three dimensions, the TISE is

$$-\frac{\hbar^2}{2m}\nabla^2\chi(\mathbf{x}) + U(\mathbf{x})\chi(\mathbf{x}) = E\chi(\mathbf{x}).$$

Here, we have replaced the double derivative with the Laplacian operator ∇^2.

- In Cartesian coordinates (x, y, z), the Laplacian is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

- In spherical coordinates (r, θ, ϕ), we have

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right].$$

Definition 5.1. A spherically symmetric potential satisfies

$$U(\mathbf{x}) = U(r, \theta, \phi) = U(r).$$

We start by looking at even, spherically symmetric stationary states $\chi(r, \theta, \phi) = \chi(r)$. The TISE becomes

$$-\frac{\hbar^2}{2mr}\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\chi(r)) + U(r)\chi(r) = E\chi(r),$$

which we can write as

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\chi}{\mathrm{d}r}\right) + U(r)\chi = E\chi.$$

The normalisation condition for χ says

$$\int_{\mathbb{R}^3} |\chi(r, \theta, \phi)|^2\,\mathrm{d}V < \infty \iff \int_0^\infty |\chi(r)|^2 r^2\,\mathrm{d}r < \infty.$$

Hence the eigenfunction $\chi(r)$ must go to 0 sufficiently fast as $r \to \infty$, and behave well at $r \to 0$.

We can solve the TISE by defining $\sigma(r) = r\chi(r)$. Then, in terms of σ, the TISE becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\sigma}{\mathrm{d}r^2} + U(r)\sigma = E\sigma.$$

This is just the one-dimensional TISE, defined only on $\mathbb{R}^+$, and with the usual normalisation conditions

$$\int_0^\infty |\sigma(r)|^2 \,\mathrm{d}r < \infty.$$

If χ is to be defined, we must have $\sigma(0) = 0$ and $\sigma'(0)$ finite. Indeed, if $\sigma(r) \sim a \neq 0$ as $r \to 0$, then $\hat{H}$ is not Hermitian.

Proof: For $\hat{H}$ to be Hermitian, we need $(\phi, \hat{H}\chi) = (\hat{H}\phi, \chi)$. This is

$$\begin{aligned}(\phi, \hat{H}\chi) &= \int_0^\infty r^2\phi(r)\hat{H}\chi(r)\,\mathrm{d}r = -\frac{\hbar^2}{2m}\int_0^\infty \phi\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\chi}{\mathrm{d}r}\right)\mathrm{d}r \\ &= -\frac{\hbar^2}{2m}\left[r^2\phi\frac{\mathrm{d}\chi}{\mathrm{d}r} - r^2\chi\frac{\mathrm{d}\phi}{\mathrm{d}r}\right] - \frac{\hbar^2}{2m}\int_0^\infty \frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\phi}{\mathrm{d}r}\right)\chi\,\mathrm{d}r.\end{aligned}$$

Note the last term is simply $(\hat{H}\phi, \chi)$. Now if $\phi(r) \sim B \neq 0$ as $r \to 0$, then $\chi(r) \sim \frac{A}{r}$ with $A \neq 0$. So,

$$r^2\phi\frac{\mathrm{d}\chi}{\mathrm{d}r} - r^2\chi\frac{\mathrm{d}\phi}{\mathrm{d}r} \not\to 0,$$

as $r \to 0$.

Then, we can solve over the entirety of $\mathbb{R}$ by letting $U(-r) = U(r)$, and look for odd solutions to the TISE.

Example 5.1.

Take the spherically symmetric potential well

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

where a, U_0 are positive. We solve for odd σ:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\sigma}{\mathrm{d}r^2} + U(r)\sigma = E\sigma.$$

We look for odd parity bound states with $0 \leq E \leq U_0$. Then, letting

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \qquad \bar{k} = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}},$$

we find odd solutions

$$\sigma(r) = \begin{cases} A\sin(kr) & |r| \leq a, \\ Be^{-\bar{k}r} & r > a, \\ -Be^{\bar{k}r} & r < -a. \end{cases}$$

The boundary conditions imply continuity of $\sigma(r)$ and $\sigma'(r)$ at $r = a$, so

$$\begin{cases} A\sin ka = Be^{-\bar{k}a}, \\ kA\cos ka = -\bar{k}Be^{-\bar{k}a}. \end{cases}$$

This gives two equations

$$-k\cot(ka) = \bar{k}, \qquad k^2 + \bar{k}^2 = \frac{2mU_0}{\hbar^2}.$$

Substituting $\zeta = ka$, $\eta = \bar{k}a$, we get $\eta = -\zeta\cot\zeta$ and $\eta^2 + \zeta^2 = r_0^2$. (insert picture)

Now if $r_0 < \frac{\pi}{2}$, then there are no solutions.

Compared to the same equation in one-dimension, there are two differences:

1. Below a given threshold for U_0, there are no bound states in three dimensions.
2. Our solution looks like

$$\chi(r) = \begin{cases} a\frac{\sin(kr)}{r} & r < a, \\ B\frac{e^{-\bar{k}r}}{r} & r \geq a. \end{cases}$$

5.2 Angular Momentum

In classical mechanics, we have an important quantity $\mathbf{L} = \mathbf{x} \times \mathbf{p}$, the *angular momentum*. This is conserved for spherically symmetric potentials, as

$$\frac{\mathrm{d}\mathbf{L}}{\mathrm{d}t} = \dot{\mathbf{x}} \times \mathbf{p} + \mathbf{x} \times \dot{\mathbf{p}} = 0.$$

This has important corollaries: in dynamics and relativity, we saw the conservation of angular momentum could take a three-dimensional problem (the two-body problem), to a one-dimensional problem.

Definition 5.2. The *angular momentum operator* is defined by

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = -i\hbar \mathbf{x} \times \nabla.$$

In Cartesian coordinates, this can be expressed as

$$\hat{L}_i = \varepsilon_{ijk} \hat{x}_j \hat{p}_k = -i\hbar \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}.$$

Then $\hat{L}_i$ satisfies the following properties:

- $\hat{L}_i$ is Hermitian.
- $[\hat{L}_i, \hat{L}_j] \neq 0$ for $i \neq j$. Hence, different components of $\mathbf{L}$ cannot be determined simultaneously. In fact, we can prove

$$[\hat{L}_i, \hat{L}_j] = i\hbar \varepsilon_{ijk} \hat{L}_k.$$

Proof:

$$\begin{aligned}
[\hat{L}_1, \hat{L}_2]\chi(\mathbf{x}) &= -\hbar^2 \left[\left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) \right. \\
&\qquad \left. - \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) \left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \right] \chi(\mathbf{x}) \\
&= -\hbar^2 \left(x_2 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_2} \right) \chi(\mathbf{x}) \\
&= i\hbar \hat{L}_3 \chi(\mathbf{x}).
\end{aligned}$$

Definition 5.3. We define the *total angular momentum operator* $\hat{L}^2$ as

$$\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2.$$

The total angular momentum satisfies the following properties:

- $[\hat{L}^2, \hat{L}_1] = 0$.
- For $U(r)$, $[\hat{L}^2, \hat{H}] = [\hat{L}_i, \hat{H}] = 0$.

Proof:

$$\begin{aligned}
[\hat{L}_i, \hat{x}_j] &= [\varepsilon_{imn}\hat{x}_m\hat{p}_n, \hat{x}_j] = \varepsilon_{imn}[\hat{x}_m\hat{p}_n, \hat{x}_j] \\
&= \varepsilon_{imn}(\hat{x}_m \underbrace{[\hat{p}_n, \hat{x}_j]}_{-i\hbar\delta_{nj}} + \underbrace{[\hat{x}_m, \hat{x}_j]}_{0} \hat{p}_n) \\
&= -i\hbar\varepsilon_{imj}\hat{x}_m = i\hbar\varepsilon_{ijm}\hat{x}_m, \\
[\hat{L}_i, \hat{x}_j^2] &= [\hat{L}_i, \hat{x}_j]\hat{x}_j + \hat{x}_j[\hat{L}_i, \hat{x}_j] \\
&= i\hbar\varepsilon_{ijm}(\hat{x}_m\hat{x}_j + \hat{x}_j\hat{x}_m) = 0.
\end{aligned}$$

This proves that $[\hat{L}_i, U(r)] = 0$, as $U(r)$ is simply $U(\sqrt{\hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2})$. Similarly, we can prove

$$\begin{aligned}
[\hat{L}_i, \hat{p}_j] &= i\hbar\varepsilon_{ijm}\hat{p}_m, \\
[\hat{L} - i, \hat{p}^2] &= 0, \\
\implies [\hat{L}_i, \hat{H}] &= 0, \\
[\hat{L}^2, \hat{H}] &= 0.
\end{aligned}$$

We have the following observations:

1. We can find joint eigenstates of the three operators $\{\hat{H}, \hat{L}^2, \hat{L}_i\}$ which form a basis of $\mathcal{H}$.
2. The eigenvalues of the three operators can be simultaneously measured at an arbitrary precision.
3. This set of operators is *maximal*, meaning we cannot construct another operator (other than $\hat{I}$) that commutes with all three.

To find joint eigenfunction of, say $\hat{L}^2$ and $\hat{L}_3$, we can write $\hat{\mathbf{L}}$ in spherical coordinates:

$$\begin{aligned}
\hat{L}_3 &= -i\hbar\frac{\partial}{\partial\phi}, \\
\hat{L}^2 &= -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right].
\end{aligned}$$

Now, we look for joint eigenfunctions $Y(\theta, \phi) = y(\theta)X(\phi)$. Then, as it is an eigenfunction of $\hat{L}_3$,

$$\begin{aligned}
-i\hbar\left(\frac{\partial}{\partial\phi}X(\phi)\right)y(\theta) &= \hbar m X(\phi)y(\theta), \\
\implies X(\phi) &= e^{im\phi}.
\end{aligned}$$

As the wave-function is single-valued in $\mathbb{R}^3$, $X(\phi)$ must be invariant under $\phi \to \phi + 2\pi$. Hence, $m \in \mathbb{Z}$. Now, as $y(\theta)e^{im\phi}$ is an eigenfunction of $\hat{L}^2$, we find

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial y}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}y = -\frac{\lambda}{\hbar^2}y.$$

This is the associated Legendre equation, and it has solution

$$y(\theta) = P_{l,m}(\cos\theta) = (\sin\theta)^{|m|}\frac{\mathrm{d}^{|m|}}{\mathrm{d}(\cos\theta)^{|m|}}P_l(\cos\theta).$$

Because $P_l(\cos\theta)$ is a polynomial is $\cos\theta$ of degree l, we need $-l \leq m \leq l$. This gives eigenvalues $\lambda = \hbar^2 l(l+1)$.

Combining these, the joint eigenfunctions are

$$Y_{l,m}(\theta,\phi) = P_{l,m}(\cos\theta)e^{im\phi}.$$

Then the eigenvalue of $\hat{L}^2$ is $\hbar^2 l(l+1)$, and the eigenvalue of $\hat{L}_3$ is $m\hbar$.

Here, l and m are quantum numbers that characterise the total angular momentum (as l), and the azimuthal number, which is the z-component of angular momentum (as m). We write out the first few spherical harmonics:

$$\begin{aligned}
Y_{0,0}(\theta,\phi) &= \frac{1}{\sqrt{4\pi}}, && l=0, m=0,\\
Y_{1,0}(\theta,\phi) &= \sqrt{\frac{3}{4\pi}}\cos\theta, && l=1, m=0,\\
Y_{1,\pm1}(\theta,\phi) &= \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\hbar i\phi}, && l=1, m=\pm1.
\end{aligned}$$

All the spherical harmonics are orthonormal.

5.3 The Hydrogen Atom

Consider a nucleus of a hydrogen atom, consisting of a proton p with charge $+e$, and electron e^{-1} with charge $-e$, at a radius of r from the proton.

We model the atom by letting the proton be stationary at the origin. The force provided by the proton (the Coulomb force) is given by

$$\begin{aligned}
F_{coulomb}(r) &= -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2} = -\frac{\partial U_{coulomb}}{\partial r},\\
U_{coulomb}(r) &= -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}.
\end{aligned}$$

This force, and hence the potential, is spherically symmetric. The Schrödinger equation is

$$-\frac{\hbar^2}{2m_e}\nabla^2\chi(r,\theta,\phi) - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\chi(r,\theta,\phi) = E\chi(r,\theta,\phi).$$

In spherical coordinates, we can write

$$\begin{aligned} -\hbar^2\nabla^2 &= \frac{-\hbar^2}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{r^2\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\phi^2}\right) \\ &= -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{L}^2}{r^2}. \end{aligned}$$

If we put this in the TDSE,

$$-\frac{\hbar^2}{2m_e}\frac{1}{r}\left(\frac{\partial^2}{\partial r^2}r\chi\right) + \frac{\hat{L}^2}{2m_e r^2}\chi - \frac{e^2}{4\pi\varepsilon_0 r}\chi = E\chi.$$

Now, notice that eigenfunctions of $\hat{H}$ are also eigenfunctions of $\hat{L}^2$ and $\hat{L}_3$, so χ must also be an eigenfunction of $\hat{L}^2$, $\hat{L}_3$. Hence, if we write $\chi(r,\theta,\phi) = R(r)Y_{l,m}(\theta,\phi)$, then we get

$$-\frac{\hbar^2}{2m_e}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right)Y + \frac{\hbar^2}{2m_e r^2}l(l+1) + RY - \frac{e^2}{4\pi\varepsilon_0}RY = ERY.$$

We can divide by Y, and end up with a one-dimensional equation for the radial part:

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left(-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2m_e r^2}\right)R = ER,$$

which is in the form of a TISE.

5.3.1 Spherically Symmetric Solutions

We first look at the solutions where $l = 0$. Then $Y_{0,0}(\theta,\phi) = (4\pi)^{-1/2}$. We solve in terms of the rescaled variables

$$\nu^2 = -\frac{2mE}{\hbar^2} > 0, \qquad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2}.$$

Then R satisfies

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \left(\frac{\beta}{r} - \nu^2\right)R = 0.$$

Remark.

(i) The asymptotic behaviour (as $r \to \infty$) is determined by

$$\frac{\mathrm{d}^2 R}{\mathrm{d}r^2} - \nu^2 R = 0 \implies R(r) \sim e^{\pm r\nu}.$$

We must have $R(r) \sim e^{-r\nu}$, by normalisability.

(ii) At $r = 0$, the eigenfunction has to be finite.

By our observation in (i), we write $R(r) = f(r)e^{-\nu r}$. Then, we get that f satisfies

$$f''(r) + \frac{2}{r}(1 - \nu r)f'(r) + \frac{1}{r}(\beta - 2\nu)f(r) = 0.$$

This is a homogeneous linear ODE with a regular point at $r = 0$, so we may write it as a power series. Let

$$f(r) = r^c \sum_{n=0}^{\infty} a_n r^n.$$

Then,

$$\sum_{n=0}^{\infty}\left[a_n(c+n)(c+n-1)r^{c+n-2} + \frac{2}{r}(1-\nu r)a_n(c+n)r^{c+n-1} + (\beta - 2\nu)r^{c+n-1}\right] = 0.$$

The lowest power of r has coefficient

$$a_0 c(c-1) + 2a_0 c = 0 \implies c = 0, c = -1.$$

If $c = -1$, then $\chi \sim Ar^{-1}$ near $r = 0$, hence is not normalisable. So we must have $c = 0$. Then, for $n \geq 1$, we find

$$\sum_{n=1}^{\infty}[a_n n(n+1) + a_{n-1}(\beta - 2\nu n)]r^{n-2} = 0,$$

which recursively gives

$$a_n = \frac{2\nu n - \beta}{n(n+1)} a_{n-1}.$$

Now we would like to say that these terms eventually die off, as in the case for the Hermite polynomials.

Proposition 5.1. *If $f(r) = \sum a_n r^n$ is infinite, then $R(r)$ is not normalisable.*

Proof: The asymptotic behaviour of $f(r)$ is determined by the ratio of the coefficients, which is

$$\frac{a_n}{a_{n-1}} \to \frac{2\nu}{n}.$$

This satisfies the same asymptotic behaviour as

$$g(r) = e^{2\nu r} = \sum_{n=0}^{\infty} \frac{(2\nu)^n}{n!} r^n.$$

Now, if asymptotically $f(r) \sim e^{2\nu r}$, then $R(r) = f(r)e^{-\nu r} \sim e^{\nu r}$, which is not normalisable. Hence, the series must terminate.

Therefore, there exists $N > 0$ such that $a_N = 0$, and $a_{N-1} \neq 0$. Thus,

$$2\nu N - \beta = - \implies \nu = \frac{\beta}{2N}.$$

Substituting in ν and β, we get that the energies are

$$E_N = -\frac{e^4 m_e}{32\pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{N^2},$$

which is identical to the Bohr atom.

To find the eigenfunctions $R_N(r)$, we can substitute $2N\nu = \beta$, to find that

$$\frac{a_n}{a_{n-1}} = -2\nu \frac{N-n}{n(n+1)}.$$

This can be used inductively to find R_N.

N	$R_N(r)$
1	$A_1 e^{-\nu r}$
2	$A_2(1 - \nu r)e^{-\nu r}$
3	$A_3(1 - 2\nu r + \frac{2}{3}\nu^2 r^2)e^{-\nu r}$

In general, $R_N(r) = L_N(\nu r)e^{-\nu r}$, where L_N are the *Laguerre polynomials*.

5.3.2 Asymmetric Solutions

We look at the general case, when $l \geq 0$. Then again, we have TISE

$$\frac{\mathrm{d}^2 R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \left(\frac{\beta}{r} - 2\nu - \frac{l(l+1)}{r^2}\right)R = 0.$$

Looking at the asymptotic behaviour, we again write $R(r) = f(r)e^{-\nu r}$. Then

$$f'' + \frac{2}{r}(1 - \nu r)f' + \left(\frac{\beta}{r} - 2\nu - \frac{l(l+1)}{r^2}\right)f = 0.$$

If we write f as

$$f(r) = r^\sigma \sum_{n=0}^{\infty} a_n r^n.$$

The lowest power coefficient is $r^{\sigma-2}$, which has coefficient

$$\sigma(\sigma+1) - l(l+1) = 0 \implies \sigma = -l-1, \sigma = l.$$

However $\sigma = -l-1$ gives $R \sim r^{-l-1}$ around $r = 0$, which is not integrable, so we must have

$$f(r) = r^l \sum_{r=0}^{\infty} a_n r^n.$$

This gives recursive formula

$$a_n = \frac{2\nu(n+l) - \beta}{n(n+2l-1)} a_{n-1}.$$

As before, this is not normalisable unless there exists $n_{max} > 0$ such that $a_{n_{max}} = 0$, and $a_{n_{max}-1} \neq 0$. Hence

$$2\nu \underbrace{(n_{max} + l)}_{N} = \beta = 0 \implies 2\nu N - \beta = 0 \implies \nu = \frac{\beta}{2N}.$$

Again the energy values are

$$E_N = -\frac{e^4 m_e}{32\pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{N^2}.$$

However, the degeneracy, which is the number of eigenstates with same eigenvalue, is larger. If $N = n_{max} + l$, then we can take any $0 \leq l \leq N-1$ and any $-l \leq m \leq l$. This gives N^2 possible eigenstates.

The eigenfunctions can then be written as

$$\chi_{N,l,n}(r,\theta,\phi) = R_{N,l}(r)Y_{l,m}(\theta,\phi) = r^l f_{N,l}(r)e^{-\nu r}Y_{l,m}(\theta,\phi).$$

Now $f_{N,l}(r)$ is a polynomial of degree $N-l-1$, with coefficients

$$a_k = \frac{2\nu}{k}\frac{k+l-N}{k+2l+1}.$$

These are known as the *generalized Laguerre polynomials*. The eigenstates are defined by the quantum numbers

$$\begin{aligned} N &= 0, 1, 2, \ldots, && \text{principal quantum numbers,} \\ l &= 0, \ldots, N-1, && \text{total angular momentum,} \\ m &= -l, \ldots, l, && \text{azimuthal quantum numbers.} \end{aligned}$$

Hence, while the Bohr model accurately predicted the energies of the eigenstates, the quantization of the angular momentum was not correct, as $L^2 = l(l+1)\hbar^2$, for any $l < N$.

Index