Quantum Mechanics

Cambridge University Mathematical Tripos: Part IB

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Contents

1 Historical introduction

1.1 Timeline

- (1801–3) Particles were shown to have wave-like properties using Young's double slit experiment.
- (1862–4) Electromagnetism was conceived by Maxwell. Light was discovered to be an electromagnetic wave.
- (1897) Discovery of the electron by Thomson.
- (1900) The Planck law was discovered, which explains black-body radiation.
- (1905) The photoelectric effect was discovered by Einstein.
- (1909) Wave-light interference patterns were shown to exist with only one photon recorded at a time.
- (1911) Rutherford created his atomic model.
- (1913) Bohr created his atomic model.
- (1923) The Compton experiment showed x-ray scattering off electrons.
- (1923–4) De Broglie discovered the concept of wave-particle duality.
- (1925–30) The theory of quantum mechanics emerged at this time.
- (1927–8) The diffraction experiment was carried out with electrons.

1.2 Particles and waves in classical mechanics

In classical mechanics, a point-particle is an object with energy and momentum in an infinitesimally small point of space. Therefore, a particle is determined by the three-dimensional vectors $\mathbf{x}, \mathbf{v} = \dot{\mathbf{x}}$. The motion of a particle is governed by Newton's second law,

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

Solving this equation involves determination of $\mathbf{x}, \dot{\mathbf{x}}$ for all $t > t_0$, once initial conditions $\mathbf{x}(t_0), \dot{\mathbf{x}}(t_0)$ are known.

Waves are classically defined as any real- or complex-valued function with periodicity in time and/or space. For instance, consider a function f such that $f(t + T) = f(t)$, which is a wave with period T. The frequency ν is defined to be $\frac{1}{T}$, and the angular frequency ω is defined as $2\pi\nu = \frac{2\pi}{T}$. Suppose we have a function in one dimension obeying $f(x+\lambda) = f(x)$. This has wavelength λ and wave number $k = \frac{2\pi}{\lambda}$.

Consider $f(x) = \exp(\pm ikx)$. In three dimensions, this becomes $f(x) = \exp(\pm i\mathbf{k} \cdot \mathbf{x})$. This is called a 'plane wave'; the one-dimensional wave number k has been transformed into a three-dimensional wave vector $\mathbf{k}$. λ is now defined as $\frac{2\pi}{|k|}$.

The wave equation in one dimension is

$$\frac{\partial^2 f(x,t)}{\partial t^2} - c^2 \frac{\partial^2 f(x,t)}{\partial x^2} = 0; \quad c \in \mathbb{R}$$

The solutions to this equation are

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

where $\omega = ck; \lambda = \frac{c}{\nu}$. The two conditions are known as the dispersion relations. $A_{\pm}$ is the amplitude of the waves.

In three dimensions,

$$\frac{\partial^2 f(\mathbf{x},t)}{\partial t^2} - c^2\nabla^2 f(\mathbf{x},t) = 0; \quad c \in \mathbb{R}$$

The solution is

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

where $\omega = c|\mathbf{k}|; \lambda = \frac{c}{\nu}$.

Note. Other kinds of waves are solutions to other governing equations, provided that another dispersion relation $\omega(\mathbf{k})$ is given. Also, for any governing equation linear in f, the superposition principle holds: if f_1, f_2 are solutions then so is $f_1 + f_2$.

1.3 Black-body radiation

Several experiments have shown that light behaves with some particle-like characteristics. For example, consider a body heated at some temperature T. Any such body will emit radiation. The simplest body to study is called a 'black-body', which is a totally absorbing surface. The intensity of light emitted by a black body was modelled as a function of the frequency. The classical prediction for the spectrum of emitted radiation was that as the frequency increased, the intensity would also increase. A curve with a clear maximum point was observed. Planck's law was found to be the equation of this curve, which can be derived from the equation $E = \hbar\omega$ involving the Planck constant, instead of the classical energy equation $E = k_B T$ involving the Boltzmann constant. This then implies that light was 'quantised' into particles.

1.4 Planck's constant

The Planck constant is $h \approx 6.61 \times 10^{-34}\,\mathrm{J\,s}$. The reduced Planck constant is $\hbar = \frac{h}{2\pi}$. Quantum mechanics typically uses the reduced Planck constant over the normal Planck constant. The dimensionality of h is energy multiplied by time, or position multiplied by momentum.

1.5 Photoelectric effect

Consider a metal surface in a vacuum, which is hit by light with angular frequency ω. When the radiation hits the surface of the metal, electrons were emitted. Classically, we would expect that:

(i) Since the incident light carries energy proportional to its intensity, increasing the intensity we should have sufficient energy to break the bonds of the electrons with the atoms of the metal.

(ii) Since the intensity and frequency are independent, light of any ω would eventually cause electrons to be emitted, given a high enough intensity.

(iii) The emission rate should be constant.

In fact, the experiment showed that

(i) The maximum energy $E_{\max}$ of emitted electrons depended on ω, and not on the intensity.

(ii) Below a given threshold $\omega_{\min}$, there was no electron emission.

(iii) The emission rate increased with the intensity.

Einstein's explanation for this phenomenon was that the light was quantised into small quanta, called photons. Photons each carry an energy $E = \hbar\omega$. Each photon could liberate only one electron. Thus,

$$E_{\max} = \hbar\omega - \phi$$

where ϕ is the binding energy of the electron with the metal. The higher the intensity, the more photons hit the metal. This implies that more electrons will be scattered.

1.6 Compton scattering

X-rays were emitted towards a crystal, scattering free electrons. The X-ray should then be deflected by some angle θ. Classically, for a given θ we would expect that the intensity as a function of ω would have a maximum at ω_0, the frequency of the incoming X-rays. This is because we would not expect ω to change much after scattering an electron. However, there was another peak at ω', which was dependent on the angle θ. In fact, considering the photon and electron as a relativistic system of particles, we can derive (from IA Dynamics and Relativity),

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

where $\mathbf{p}$ is the initial momentum and $\mathbf{q}$ is the final momentum. Assuming $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$,

$$|\mathbf{p}| = \hbar|\mathbf{k}| = \hbar\frac{\omega}{c}; \quad |\mathbf{q}| = \hbar|\mathbf{k}'| = \hbar\frac{\omega'}{c}$$

Hence,

$$\frac{1}{\omega} = \frac{1}{\omega'} + \frac{\hbar}{mc}(1 - \cos\theta)$$

So the frequency of the outgoing X-ray should have an angular frequency which is shifted from the original. The expected peak was actually caused by X-rays simply not interacting with the electrons.

1.7 Atomic spectra

The Rutherford scattering experiment involved shooting α particles at some thin gold foil. Most particles travelled through the foil, some were slightly deflected, and some were deflected completely back. This indicated that the gold foil was mostly comprised of vacuum and there was a high density of positive charge within the atom. Electrons would orbit around the nucleus. However, there were problems with this model:

(i) If the electrons in orbits moved, they would radiate and lose energy. However if the electrons were static, they would simply collapse and fall into the nucleus.

(ii) This model did not explain the atomic spectra, the observed frequencies of light absorbed or emitted by an atom when electrons change energy levels.

The spectra had frequency

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

where R_0 is the Rydberg constant, approximately $1 \times 10^7\ \mathrm{m}^{-1}$. Bohr theorised that the electron orbits themselves are quantised, so L (the orbital angular momentum) is an integer multiple of $\hbar$; $L_n = n\hbar$. First, the quantisation of L implies the quantisation of v and r. Indeed, given that $L \equiv m_e v r$, we have that v is quantised: $v_n = \frac{n\hbar}{m_e r}$. Further, by the Coulomb force, $F = \frac{e^2}{4\pi\varepsilon^2}\frac{1}{r^2}\mathbf{e}_r = m_e a_r \mathbf{e}_r$ where a_r is the radial acceleration. Then $\frac{e^2}{4\pi\varepsilon^2}\frac{1}{r^2} = m_e\frac{v^2}{r} \implies r = r_n = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}n^2$. The coefficient on n^2 is known as the Bohr radius. Immediately then the energy levels E of the atom can be shown to be quantised, since

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

giving

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

The ground energy level is at $n = 1$, giving

$$E_1 = -13.6\,\mathrm{eV}$$

The excited states are E_n for $n > 1$. The energy emitted when descending from E_n to E_1 are the spectral lines:

$$\Delta E = \hbar\omega$$

The Bohr model gives

$$\omega_{mn} = \frac{\Delta E_{mn}}{\hbar} = 2\pi c\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

which agrees with the Rydberg constant R_0 defined earlier.

2 Wavefunctions

2.1 Wave-like behaviour of particles

De Broglie hypothesised that any particle of any mass is associated with a wave with

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

This hypothesis made sense of the quantisation of electron angular momentum; if the electron lies on a circular orbit then $2\pi r = n\lambda$ where λ is the wavelength of the electron. However,

$$p = \hbar k = \hbar\frac{2\pi}{\lambda} \implies L = m_e v r = pr = \hbar\frac{2\pi}{\lambda}\frac{n\lambda}{2\pi} = n\hbar$$

Hence the angular momentum must be quantised. The electron diffraction experiment showed that this hypothesis was true, by showing that electrons behaved sufficiently like waves. Interference patterns were observed with $\lambda = \frac{2\pi}{|\mathbf{k}|} = \frac{2\pi k}{|\mathbf{p}|}$ compatible with the De Broglie hypothesis.

2.2 Probabilistic interpretation of wavefunctions

In classical mechanics, we can describe a particle with $\mathbf{x}, \dot{\mathbf{x}}$ or $\mathbf{p} = m\dot{\mathbf{x}}$. In quantum mechanics, we need the state ψ described by $\psi(\mathbf{x}, t)$ called the wavefunction.

Remark. Note that the state is an abstract entity, while $\psi(\mathbf{x}, t)$ is the representation of ψ in the space of $\mathbf{x}$. In some sense, $\psi(\mathbf{x}, t)$ is the complex coefficient of ψ in the continuous basis of $\mathbf{x}$. In other words, $\psi(\mathbf{x}, t)$ is ψ in the $\mathbf{x}$ representation. In this course, we always work in the $\mathbf{x}$ representation.

Definition. A wavefunction is a function $\psi(\mathbf{x}, t) : \mathbb{R}^3 \to \mathbb{C}$ that satisfies certain mathematical properties (defined later) dictated by its physical interpretation. t is considered a fixed external parameter, so it is not included in the function's type.

The physical interpretation of a wavefunction is called Born's rule. The probability density for a particle to be at some point $\mathbf{x}$ at t is given by $|\psi(\mathbf{x}, t)|^2$. We write the probability density as ρ, hence $\rho(\mathbf{x}, t)\,\mathrm{d}V$ is the probability that the particle lies in some small volume V centred at $\mathbf{x}$. Now, since the particle must be somewhere, the wave function must be *normalisable*, or *square-integrable* in $\mathbb{R}^3$:

$$\int_{\mathbb{R}^3} \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)\,\mathrm{d}V = \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2\,\mathrm{d}V = N \in (0, \infty)$$

Since we want the total probability to be 1, we must normalise the wavefunction by defining

$$\overline{\psi}(\mathbf{x}, t) = \frac{1}{\sqrt{N}}\psi(\mathbf{x}, t) \iff \int_{\mathbb{R}^3} \left|\overline{\psi}(\mathbf{x}, t)\right|^2 \mathrm{d}V = 1$$

Hence, $\rho(\mathbf{x}, t) = \left|\overline{\psi}(\mathbf{x}, t)\right|^2$ really is a probability density. From now, we will not use the bar for denoting normalisation, since normalisation is evident from context.

2.3 Bases and equivalence classes

In linear algebra, we consider vectors in some vector space such as $\mathbb{R}^n$. In quantum mechanics, we instead consider states in a space of wave functions. The analogous concept to vector components is to represent a state ψ in an infinite-dimensional x axis basis $\psi(x, t)$. Note that if two wavefunctions differ by a constant phase, that is, $\exists \alpha \in \mathbb{R}$ such that

$$\widetilde{\psi}(x, t) = e^{i\alpha}\psi(x, t)$$

then the states are equivalent in terms of probability, since the probability density is given by the norm of ψ, not its angle. We can think of states as arrays in the vector space of wavefunctions. We can then describe the equivalence class $[\psi]$ as the set of all functions ϕ such that $\phi = \lambda\psi$, for some $\lambda \in \mathbb{C} \setminus \{0\}$, since we must retain the condition that ϕ is normalisable.

2.4 Hilbert spaces

In quantum mechanics, we are interested in the functional space of square-integrable functions on $\mathbb{R}^3$, which is a type of *Hilbert space* and denoted $\mathcal{H}$.

Remark. Since the set of wavefunctions form a vector space, $\psi_1, \psi_2 \in \mathcal{H}$ implies that $\psi = \lambda_1\psi_1 + \lambda_2\psi_2 \in \mathcal{H}$ for constants $\lambda_1, \lambda_2 \in \mathbb{C}$ provided this ψ is nonzero. For waves, this is the well-known superposition principle. Note that this exact formulation of linearity is unique to quantum mechanics; for example, in classical mechanics, two solutions to Newton's equations may not be combined into a new solution by taking their sum.

Proposition. If $\psi_1(x,t), \psi_2(x,t)$ are normalisable, then $\psi = \lambda_1\psi_i(x,t) + \lambda_2\psi_2(x,t)$ is also normalisable.

Proof. Recall the inequality

$$2|z_1||z_2| \leq |z_1|^2 + |z_2|^2$$

Then we can show

$$\begin{aligned}\int_{\mathbb{R}^3} |\lambda_1\psi_1 + \lambda_2\psi_2|^2 \,\mathrm{d}V &= \int_{\mathbb{R}^3} \left(|\lambda_1\psi_1| + |\lambda_2\psi_2|\right)^2 \mathrm{d}V \\ &= \int_{\mathbb{R}^3} \left(|\lambda_1\psi_1|^2 + 2|\lambda_1\psi_1||\lambda_2\psi_2| + |\lambda_2\psi_2|^2\right) \mathrm{d}V \\ &= \int_{\mathbb{R}^3} \left(2|\lambda_1\psi_1|^2 + 2|\lambda_2\psi_2|^2\right) \mathrm{d}V < \infty\end{aligned}$$

so the norm is non-infinite. □

2.5 Inner product

We define the inner product between two wavefunctions to be

$$\langle\psi, \phi\rangle = \int_{\mathbb{R}^3} \psi^\star \phi \,\mathrm{d}V$$

The following statements hold.

(i) $\langle\psi, \phi\rangle$ exists for all wave functions $\psi, \phi \in \mathcal{H}$;

(ii) $\langle\psi, \phi\rangle^\star = \langle\phi, \psi\rangle$;

(iii) the inner product is antilinear in the first entry, and linear in the second entry; and

(iv) for continuous ψ, $\langle\psi, \psi\rangle = 0$ is true if and only if ψ is identically zero.

We prove the first statement, since the others are obvious from the definition. By the Cauchy–Schwarz inequality,

$$\begin{aligned}\int_{\mathbb{R}^3} |\psi|^2 \,\mathrm{d}V &\leq N_1; \\ \int_{\mathbb{R}^3} |\phi|^2 \,\mathrm{d}V &\leq N_2; \\ \therefore \int_{\mathbb{R}^3} |\psi\phi| \,\mathrm{d}V &\leq \sqrt{\int_{\mathbb{R}^3} |\psi|^2 \,\mathrm{d}V \cdot \int_{\mathbb{R}^3} |\phi|^2 \,\mathrm{d}V} < \infty\end{aligned}$$

2.6 Normalisation

Definition. We define the norm of a wavefunction to be $\|\psi\| \equiv \langle \psi, \psi \rangle$. A wavefunction ψ is *normalised* if $\|\psi\| = 1$.

Definition. A set of wavefunctions $\{\psi_n\}$ is *orthonormal* if $\langle \psi_m, \psi_n \rangle = \delta_{mn}$. A set of wavefunctions $\{\psi_n\}$ is *complete* if for any $\psi \in \mathcal{H}$, we can write

$$\psi = \sum_n \lambda_n \psi_n$$

for $\lambda_n \in \mathbb{C}$.

Proposition. If $\{\psi_n\}$ is a complete and orthonormal basis of $\mathcal{H}$, then

$$\phi = \sum_{k=0}^{n} c_k \psi_k$$

where

$$c_k = \langle \psi_k, \phi \rangle$$

Proof. Suppose we can write ϕ in this form. Then,

$$\begin{aligned} \langle \psi_n, \phi \rangle &= \left\langle \psi_n, \sum_m c_m \psi_m \right\rangle \\ &= \sum_m c_m \langle \psi_n, \psi_m \rangle \\ &= \sum_m c_m \delta_{mn} \\ &= c_n \end{aligned}$$

□

Remark. If ϕ is the desired outcome of a measurement for a particle described by ψ, then the probability of observing ϕ given ψ at some time t is

$$|\langle \psi, \phi \rangle|^2 = \left| \int_{\mathbb{R}^3} \psi^\star \phi \, \mathrm{d}V \right|^2$$

2.7 Time-dependent Schrödinger equation

Definition. The evolution of the wavefunction over time is given by the *time-dependent Schrödinger equation (TDSE)*,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi$$

where $U = U(x)$ is a real potential energy term.

Remark. This equation is a first-order differential equation in t. Contrast this to Newton's second law, which is a second-order differential equation in t. This implies that we only need a single initial condition $\psi(x, t_0)$ to determine all future behaviour.

Remark. Note the asymmetry between the spatial and temporal components: there is only a first derivative in time but a second derivative in space. This implies that this equation is incompatible with relativity, where time and space must be treated equitably.

One way to conceptualise the TDSE is by letting ψ be some wave defined by

$$\psi(x,t) = \exp[i(k \cdot x - \omega t)]$$

Then, the De Broglie hypothesis ($k = p/\hbar, \omega = E/m$) implies that

$$\psi(x,t) = \exp\left[\frac{i}{\hbar}\left(p \cdot x - \frac{p^2}{2m}t\right)\right]$$

which is a solution to the TDSE.

2.8 Normalisation and time evolution

Because of the TDSE, we can show that the norm N of a wavefunction ψ is independent of t.

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

Now, note that

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{\partial}{\partial t}\langle\psi^\star, \psi\rangle = \psi^\star \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^\star}{\partial t}$$

The TDSE then gives

$$\begin{aligned}
\frac{\partial \psi}{\partial t} &= \frac{i\hbar}{2m}\nabla^2\psi^2 + \frac{i}{k}U\psi; \\
\frac{\partial \psi^\star}{\partial t} &= -\frac{i\hbar}{2m}\nabla^2\psi^2 - \frac{i}{k}U\psi^\star \\
\therefore \frac{\partial|\psi|^2}{\partial t} &= \nabla \cdot \left[\frac{i\hbar}{2m}(\psi^\star \nabla\psi - \psi\nabla\psi^\star)\right]
\end{aligned}$$

Finally,

$$\int_{\mathbb{R}^3} \frac{\partial|\psi|^2}{\partial t}\,\mathrm{d}V = \int_{\mathbb{R}^3} \nabla \cdot \left[\frac{i\hbar}{2m}(\psi^\star \nabla\psi - \psi\nabla\psi^\star)\right] = 0$$

since $\psi, \psi^\star$ are such that $|\psi| \to 0$ as $|x| \to \infty$.

2.9 Conserved probability current

We have proven that the normalisation of wavefunctions are constant in time. Hence, we can derive the probability conservation law:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot J = 0; \quad J(x,t) = \frac{-i\hbar}{2m}(\psi^\star \nabla\psi - \psi\nabla\psi^\star)$$

This is the conserved probability current.

3 Observables and operators

3.1 Expectation and operators

Given the wavefunction, we would like to extract some information about the particle it represents.

Definition. An *observable* is a property of the particle that can be measured.

Definition. An *operator* is any linear map $\mathcal{H} \to \mathcal{H}$ such that

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

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

In quantum mechanics, each observable is represented by an operator acting on the state ψ. Each measurement is represented by an expectation value of the operator. In comparison, in linear algebra we would often use a linear transformation for a similar purpose. Once we have a basis for a linear transformation, we have a matrix. In quantum mechanics, we use the x basis, so we can write

$$\widetilde{\psi} = (\hat{O})(x, t)$$

Example. Consider the class of finite differential operators

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

This includes, for example, position, momentum, and energy.

Example. A translation is an operator:

$$s_a : \psi(x) \mapsto \psi(x - a)$$

Example. The parity operator is

$$P : \psi(x) \mapsto \psi(-x)$$

3.2 Dynamical observables

In general, to calculate the expectation value of an observable, we place the operator between $\psi^\star$ and ψ and integrate over the whole space. From the probabilistic interpretation of the Born rule, the position of the particle can be interpreted as

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

Hence, we can write the coefficient x as the operator $\hat{x}$. Now, consider the momentum. By considering the time-dependent Schrödinger equation with $U = 0$, and then integrating by parts,

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

So the operator $\hat{p}$ is $-i\hbar \frac{\partial}{\partial x}$. Given x and p, we can write many classical dynamical observables. The classical notion is written in parentheses. The symbol $\mapsto$ is used instead of equality since we are representing the observable in the x basis.

$$\begin{aligned}
& \hat{x} \mapsto x \\
& \hat{p} \mapsto -i\hbar \frac{\partial}{\partial x} \\
\left(T = \frac{p^2}{2m} \right) \quad & \hat{T} \mapsto \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \\
& \hat{U} \mapsto U(\hat{x}) = U(x)
\end{aligned}$$

3.3 Hamiltonian operator

The total energy is

$$E = T + U$$

given by the Hamiltonian operator

$$\hat{H} = \hat{T} + \hat{U}$$

In one dimension,

$$\hat{H} \mapsto \frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x)\psi$$

In three dimensions,

$$\hat{H} \mapsto \frac{-\hbar^2}{2m} \nabla^2 \psi + U(x)\psi$$

We can now represent the time-dependent Schrödinger equation in a more compact form:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

We can now prove that for a particle in a potential $U(x) \neq 0$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p\rangle = -\left\langle\frac{\partial U}{\partial x}\right\rangle$$

3.4 Time-independent Schrödinger equation

From the time-dependent version of the equation,

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

we can try a solution of the form

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

Then, we can find

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

Then, dividing by $T\chi$,

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

Since the left and right hand sides depend only on x and t respectively but are equal, they must be equal to a separation constant $E \in \mathbb{R}$. Solving for time,

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

If E were complex, T would diverge. Solving for space, we have the time-independent Schrödinger equation as follows.

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

Explicitly,

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

This is an eigenvalue equation for $\hat{H}$; we wish to find the eigenvalues for $\hat{H}$ in the x basis. Note that the factorised solution $\psi = T\chi$ is just a particular class of solutions for the time-dependent Schrödinger equation. However, it can be shown that any solution to the time-dependent equation can be written as a linear combination of the time-independent equation solutions.

4 One-dimensional solutions to the Schrödinger equation

4.1 Stationary states

Definition. With the ansatz $\psi(x,t) = \chi(x)T(t)$, we have found a particular class of solutions

of the time-independent Schrödinger equation:

$$\psi(x,t) = \chi(x)e^{-\frac{iEt}{\hbar}}$$

where $\chi(x)$ are the eigenfunctions of $\hat{H}$ with eigenvalue E. Such solutions are called stationary states.

Note,

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

This explains the naming of the states as 'stationary', as their probability density is independent of time. Now, suppose E is quantised. Then, the general solution to the system is

$$\psi(x,t) = \sum_{n=1}^{N} a_n \chi_n(x) e^{-\frac{iE_n t}{\hbar}}$$

where N can be finite or infinite. In principle, we can also have a continuous energy state $E_\alpha, \alpha \in \mathbb{R}$. We can still use the same idea:

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

Note that $|a_n|^2$ and $A(\alpha)\,\mathrm{d}\alpha$ give the probability of measuring the particle energy to be E_n or E_α.

4.2 Infinite potential well

We define

$$U(x) = \begin{cases} 0 & \text{for } |x| \le a \\ \infty & \text{for } |x| > a \end{cases}$$

For $|x| > a$, we must have $\chi(a) = 0$. Otherwise, $\chi \cdot U = \infty$. This gives us a boundary condition, $\chi(\pm a) = 0$. For $|x| \le a$, we seek solutions of the form

$$-\frac{\hbar^2}{2m}\chi''(x) = E\chi(x); \quad \chi(\pm a) = 0$$

Equivalently,

$$\chi''(x) + k^2\chi(x) = 0; \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

Since $E > 0$,

$$\chi(x) = A\sin kx + B\cos kx$$

Imposing boundary conditions,

$$A\sin ka + B\cos ka = 0; \quad A\sin ka - B\cos ka = 0$$

Suppose $A = 0$, giving $\chi(x) = B\cos kx$. Then, imposing boundary conditions, $\chi_n(x) = B\cos k_n x$ where $k_n = \frac{n\pi}{2a}$, and n are odd positive integers. These are even solutions.

Alternatively, suppose $B = 0$. In this case, $\chi(x) = A\sin kx$. Thus, $\chi_n(x) = A\sin k_n x$ where $k_n = \frac{n\pi}{2a}$, and n are even nonzero positive integers. These provide odd solutions.

We can also determine the normalisation constants by defining that the eigenfunctions of the Hamiltonian are normalised to unity. Thus,

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

Hence, the general solution is given by the eigenvalues

$$E_n = \frac{\hbar^2}{2n} k_n^2 = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

and eigenfunctions

$$\chi_n(x) = \sqrt{\frac{1}{a}} \begin{cases} \cos\left(\frac{n\pi x}{2a}\right) & \text{if } n \text{ odd} \\ \sin\left(\frac{n\pi x}{2a}\right) & \text{if } n \text{ even} \end{cases}$$

Remark. Note that unlike classical mechanics, the ground state energy is not zero. Note also that χ_n have $(n+1)$ nodes in which $\rho(x) = 0$. When $n \to \infty$, $\rho_n(x)$ tends to a constant, which is like in classical mechanics. Eigenfunctions of the Hamiltonian in this case were either odd or even; we can in fact prove that this is the case in general.

Proposition. If we have a system of non-degenerate eigenstates ($E_i \neq E_j$), then if $U(x) = U(-x)$ the eigenfunctions of $\hat{H}$ must be either odd or even.

Proof. The time-independent Schrödinger equation is invariant under $x \mapsto -x$ if U is even. Hence, if $\chi(x)$ is a solution with eigenvalue E, then $\chi(-x)$ is also a solution. Since we have a non-degenerate solution, $\chi(-x) = \chi(x)$ hence the solutions must be the same up to a normalisation factor. For consistency, $\chi(x) = \chi(-(-x)) = \alpha\chi(-x) = \alpha^2\chi(x)$. Hence $\alpha = \pm 1$, so χ is either odd or even. □

4.3 Finite potential well

We define

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

Classically, if $E < U_0$, the particle has insufficient energy to escape the well. We will only consider eigenstates with $E < U_0$ here, but we will find that it is possible in quantum mechanics to escape the well with positive probability. We will search for even functions only, odd functions can be solved independently. If $|x| \leq a$,

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

Equivalently,

$$\chi''(x) + k^2\chi(x) = 0; \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

The solution becomes

$$\chi(x) = A\sin kx + B\cos kx \implies \chi(x) = B\cos kx$$

since we are only looking for even solutions. In the region $|x| > a$,

$$-\frac{\hbar^2}{2m}\chi''(x) + U_0\chi(x) = E\chi(x)$$

giving

$$\chi''(x) - \overline{k}^2\chi(x) = 0; \quad \overline{k} = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

This yields exponential solutions:

$$\chi(x) = Ce^{\overline{k}x} + De^{-\overline{k}x}$$

Imposing the normalisability constraints, for $x > a$ we have $C = 0$, and for $x < -a$ we have $D = 0$. Imposing even parity, $C = D$ when nonzero. Thus,

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

Now we must impose continuity of $\chi(x)$ and its derivative at $x = \pm a$. First,

$$Ce^{-\overline{k}a} = B\cos(ka)$$

The other gives

$$-\overline{k}Ce^{-\overline{k}a} = -kB\sin(ka)$$

From the ratio of both constraints,

$$k\tan(ka) = \overline{k}$$

From the definition of $k, \overline{k}$,

$$k^2 + \overline{k}^2 = \frac{2mU_0}{\hbar^2}$$

We will define some rescaled variables for convenience: $\xi = ka, \eta = \overline{k}a$. Rewriting,

$$\xi\tan\xi = \eta; \quad \xi^2 + \eta^2 = r_0^2; \quad r_0 = \frac{2mU}{\hbar}$$

This may be solved graphically. The eigenvalues of the system correspond to the points of intersection between the two equations. There are always a finite number of possible intersections, regardless of the value of r_0. The eigenvalues are

$$E_n = \frac{\hbar^2}{2na^2}\xi_n^2; \quad \xi \in \{\xi_1, \ldots, \xi_n\}; \quad n = 1, \ldots, p$$

When $U_0 \to \infty$, $r_0 \to \infty$. At this point, there are an infinite amount of intersections, so the eigenvalues of the Hamiltonian become that of the infinite well. Further $\chi(x)$ tends to the eigenfunctions of the infinite well. Note that the $\chi_n(x)$ have some positive region outside the well. We can use the unused condition above to write C in terms of B, and then we can use the normalisation condition to find B.

4.4 Free particles

A free particle is under no potential. The time-independent Schrödinger equation is

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

This has solutions

$$\chi_k(x) = Ae^{ikx}; \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

The complete solution, adding $T(t)$, is thus

$$\psi_k(x,t) = \chi_k(x)e^{-iE_k t/\hbar} = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}$$

which are called De Broglie plane waves. This is not a solution since

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

which diverges. In general, any non-bound solution is non-normalisable. This is true since $\int_{-\infty}^{\infty} |\chi(x)|^2\,\mathrm{d}x < \infty$ requires $\lim_{R\to\infty} \int_{|x|>R} |\chi(x)|\,\mathrm{d}x = 0$. So, to solve the free particle system, we will build a linear combination of plane waves χ to yield a normalisable solution. This is called the Gaussian wavepacket. Alternatively, we can simply ignore the problem of normalisability, and change the interpretation of $\chi_n(x)$.

4.5 Gaussian wavepacket

Due to the superposition principle, we can take a continuous linear combination of the ψ_k functions.

$$\psi(x,t) = \int_0^{\infty} A(k)\psi_k(x,t)\,\mathrm{d}k$$

We can construct a suitable $A(k)$ such that ψ is normalisable. Choosing

$$A(k) = A_{\mathrm{GP}}(k) = \exp\Big[-\frac{\sigma}{2}(k-k_0)^2\Big]; \quad k_0 \in \mathbb{R}, \sigma \in \mathbb{R}^+$$

produces a solution called the Gaussian wavepacket. Substituting into the above,

$$\psi_{\mathrm{GP}}(x,t) = \int_0^{\infty} \exp\Big[-\frac{\sigma}{2}(k-k_0)^2\Big]\psi_k(x,t)\,\mathrm{d}k = \int_0^{\infty} \exp[F(k)]\,\mathrm{d}k$$

$$F(k) = -\frac{\sigma}{2}(k-k_0)^2 + ikx - i\frac{\hbar k^2}{2m}t$$

We can rewrite this as

$$F(k) = -\frac{1}{2}\left(\sigma + \frac{i\hbar t}{m}\right)k^2 + (k_0\sigma + ix)k - \frac{\sigma}{2}k_0^2$$

We define further

$$\alpha \equiv \sigma + \frac{i\hbar t}{m}; \quad \beta = k_0\sigma + ix; \quad \delta = -\frac{\sigma}{2}k_0^2$$

Completing the square,

$$F(k) = -\frac{\alpha}{2}\left(k - \frac{\beta}{\alpha}\right)^2 + \frac{\beta^2}{2\alpha} + \delta$$

We arrive at the solution

$$\psi_{\mathrm{GP}}(x,t) = \exp\left[\frac{\beta^2}{2\alpha} + \delta\right] \int_{-\infty}^{\infty} \exp\left[-\frac{\alpha}{2}\left(k - \frac{\beta}{\alpha}\right)^2\right] \mathrm{d}k$$

Under a change of variables $\tilde{k} = k - \frac{\beta}{\alpha}, u = \mathrm{Im}(\frac{\beta}{\alpha})$,

$$\psi_{\mathrm{GP}}(x,t) = \exp\left[\frac{\beta^2}{2\alpha} + \delta\right] \int_{\infty - iu}^{\infty - iu} \exp\left[-\frac{\alpha}{2}\tilde{k}\right] \mathrm{d}\tilde{k}$$

We arrive at the usual Gaussian integral:

$$I(a) = \int_{-\infty}^{\infty} \exp\left[-ax^2\right] \mathrm{d}x = \sqrt{\frac{\pi}{2}}$$

giving

$$\psi_{\mathrm{GP}}(x,t) = \sqrt{\frac{2\pi}{\alpha}} \exp\left[\frac{\beta^2}{2\alpha} + \delta\right] = \sqrt{\frac{2\pi}{\alpha}} \exp\left[-\frac{\sigma}{2} \frac{\left(x - \frac{\hbar k_0}{m} t\right)^2}{\left(\sigma^2 + \frac{\hbar^2 t^2}{m^2}\right)}\right]$$

We define $\overline{\psi}_{\mathrm{GP}}$ to be the normalised Gaussian wavefunction, so $\overline{\psi}_{\mathrm{GP}} = C\psi_{\mathrm{GP}}$. We can find that

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

This is a wavefunction whose probability density distribution resembles a Gaussian e^{-x^2} term, with a maximum point at

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_{\mathrm{GP}}^{\star} x \psi_{\mathrm{GP}} \, \mathrm{d}x = \int_{-\infty}^{\infty} x \rho_{\mathrm{GP}} \, \mathrm{d}x = \frac{\hbar k_0}{m} t$$

and a width of

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

The physical interpretation is that the uncertainty of the particle's position grows with time. In this case, we can find

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_{\mathrm{GP}}^{\star} i\hbar \frac{\partial}{\partial x} \psi_{\mathrm{GP}} \, \mathrm{d}x = \hbar k_0$$

which is constant. The uncertainty in the momentum can be found to be

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \frac{\hbar}{\sqrt{\frac{1}{2}\left(\sigma + \frac{\hbar^2 t^2}{m\sigma}\right)}}$$

Thus,

$$\Delta x \Delta p = \frac{\hbar}{2}$$

We can find for a single plane wave that

$$\Delta x = \infty; \quad \Delta p = 0$$

4.6 Beam interpretation

We can choose to ignore the normalisation problem and take the plane waves as the eigenfunctions of the Hamiltonian:

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

Instead of $\chi_k(x)$ describing a single particle, we can interpret it as a beam of particles with momentum $p = \hbar k$ and $E = \frac{\hbar^2k^2}{2m}$ with probability density

$$\rho_k(x) = \left|\chi_k(x)e^{-\frac{i\hbar^2k^2}{2m}t}\right|^2 = |A|^2$$

which here is interpreted as a constant average density of particles. The probability current is given by

$$J_k(x,t) = -\frac{i\hbar}{2m}\left(\psi_k^\star\frac{\partial\psi_k}{\partial x} - \psi_k\frac{\partial\psi_k^\star}{\partial x}\right) = -\frac{i\hbar}{2m}|A|^2 2ik = |A|^2\frac{\hbar k}{m} = |A|^2\underbrace{\frac{p}{m}}_{\text{velocity}}$$

This is interpreted as the average flux of particles.

4.7 Scattering states

We wish to investigate what happens when a particle, or beam of particles, is thrown onto a potential $U(x)$. In this case, suppose we have a step function

$$U(x) = \begin{cases} U_0 & \text{if } 0 \le x < a \\ 0 & \text{otherwise} \end{cases}$$

and a Gaussian wavepacket which is centred at $x_0 \ll 0$ moving in the $+x$ direction, towards the spike in potential. As $t \gg 0$, we end up with a probability density given by two wavepackets; one will be moving left from the spike and one will have cleared the spike and continues moving to the right.

Definition. The reflection coefficient R is

$$R = \lim_{t\to\infty}\int_{-\infty}^{0}|\psi_{\text{GP}}(x,t)|^2\,\mathrm{d}x$$

which is the probability for the particle to be reflected. The transmission coefficient is

$$T = \lim_{t\to\infty}\int_{0}^{\infty}|\psi_{\text{GP}}(x,t)|^2\,\mathrm{d}x$$

By definition, $R + T = 1$.

In practice, working with Gaussian packets is mathematically challenging, although not impossible. The beam interpretation, by allowing us to use non-normalisable stationary state wavefunctions, greatly simplifies the computation.

4.8 Scattering off potential step

Consider a potential

$$U(x) = \begin{cases} 0 & \text{if } x \leq 0 \\ U_0 & \text{if } x > 0 \end{cases}$$

We want to solve

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

We split the problem into two regions: $x \leq 0, x > 0$. For $x \leq 0$, the TISE becomes

$$\chi_k''(x) + k^2\chi_k(x) = 0; \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

The solution is

$$\chi(x) = Ae^{ikx} + Be^{-ikx}$$

This is a superposition of two beams; the beam of incident particles Ae^{ikx} and the beam of reflected particles Be^{-ikx} which are travelling in the opposite direction. In the region $x > 0$, we have

$$\chi_{\bar{k}}''(x) + \bar{k}^2\,\chi_{\bar{k}}(x) = 0; \quad \bar{k} = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}$$

where $\bar{k}$ is real if $E > U_0$, and $\bar{k}$ is pure-imaginary if $E < U_0$. Therefore, for $E > U_0$ we have

$$\chi_{\bar{k}}(x) = Ce^{i\bar{k}x} + De^{-i\bar{k}x}$$

which is a beam of particles moving towards the right and an incident beam of particles from the right moving towards the left. Since no such incident beam exists, we can set $D = 0$. If $E < U_0$, the solution is

$$\bar{k} \equiv i\eta \implies \chi_{\bar{k}}(x) = Ce^{-\eta x} + De^{\eta x}$$

$D \neq 0$ would give infinite values of $\chi_{\bar{k}}(x)$ as $x \to \infty$. In either case, the eigenfunctions are

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

By imposing the boundary conditions, specifically the continuity of χ, we can determine the constants.

$$A + B = C; \quad ikA - ikB = i\bar{k}C$$

which gives

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

We can view these solutions in terms of particle flux.

$$J_k(x,t) = -\frac{i\hbar}{2m}\left(\psi_k^\star\frac{\partial\psi_k}{\partial x} - \psi_k\frac{\partial\psi_k^\star}{\partial x}\right)$$

If $E > U_0$, we find

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

The incident flux is $\frac{\hbar k}{m}|A|^2$, the reflected flux is $\frac{\hbar k}{m}|B|^2$, and the transmitted flux is $\frac{\hbar k}{m}|C|^2$. We can define

$$R = \frac{J_{\text{ref}}}{J_{\text{inc}}} = \frac{|B|^2}{|A|^2} = \left(\frac{k-\overline{k}}{k+\overline{k}}\right)^2$$

We can also define

$$T = \frac{J_{\text{trans}}}{J_{\text{inc}}} = \frac{k|C|^2}{\overline{k}|A|^2} = \frac{4k\overline{k}}{(k+\overline{k})^2}$$

We can check that our original interpretation makes sense; for example, $R+T=1$, and $E \to U_0, \overline{k} \to 0$ implies $T \to 0, R \to 1$. If $E \to \infty$, $T \to 1$ and $R \to 0$. If $E < U_0$,

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

since $\chi_{\overline{k}}^- = \chi_{\overline{k}}^\star$. Here, $T = 0$ but $\chi_{\overline{k}}^-(x) \neq 0$.

4.9 Scattering off a potential barrier

Consider the potential

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

When $E < U_0$, we define

$$k = \sqrt{\frac{2mE}{\hbar^2}} > 0; \quad \eta = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} > 0$$

The solution is then

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

since we can normalise the incoming flux to one. The boundary conditions are that $\chi(x) = \chi'(x)$ are both continuous at $x = 0, x = a$. This gives four conditions, which are enough to solve the problem. $\chi(x)$ and its derivative at zero give

$$1 + A = B + C; \quad ik - ikA = -\eta B + \eta C$$

and the continuity at a gives

$$Be^{-\eta a} + Ce^{\eta a} = De^{ika}; \quad -\eta Be^{-\eta a} + \eta Ce^{\eta a} = ikDe^{ika}$$

Solving the system gives

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

The transmitted flux is $j_{\text{tr}} = \frac{\hbar k}{m}|D|^2$ and the incident flux is $j_{inc} = \frac{\hbar k}{m}$. Hence, the transmission coefficient is $T = |D|^2$. This is

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

If we take the limit as $U_0 \gg E$, we have $\eta a \gg 1$. Then

$$T \to \frac{16k^2\eta^2}{(\eta^2+k^2)^2}\exp[-2\eta a] \propto \exp\left[-\frac{2a}{k}\sqrt{2m(U_0-E)}\right]$$

So the probability decreases exponentially with the width of the barrier.

4.10 Harmonic oscillator

Consider a parabolic potential

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

where k is an elastic constant and $\omega = \sqrt{\frac{k}{m}}$ is the angular frequency of the harmonic oscillator. Classically, we find the solution $x = A\cos\omega t + B\sin\omega t$. This gives a continuous energy spectrum. The TDSE gives

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

Since this is a bound system, we will have a discrete set of eigenvalues. The potential is symmetric so the eigenfunctions are odd or even. We will make the change of variables

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

which reformulates the TDSE as

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

We will start by considering the solution for $\varepsilon = 1$. In this case, $E = \frac{\hbar\omega}{2}$. The solution in this case is

$$\chi_0(\xi) = \exp\left[-\frac{\xi^2}{2}\right]$$

So the first eigenfunction, χ_0, is known in terms of x, given by

$$\chi_0(x) = A\exp\left[-\frac{m\omega}{2\hbar}x^2\right]; \quad E_0 = \frac{\hbar\omega}{2}$$

To find the other eigenfunctions, we will take the general form

$$\chi(\xi) = f(\xi)\exp\left[-\frac{\xi^2}{2}\right]$$

This works because we know we have a bound solution and χ must tend to zero quickly as ξ tends to infinity, due to the differential equation in terms of ξ, ε. Using the above ansatz for χ in the Schrödinger equation,

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

Note that if $\varepsilon = 1$, a solution is $f = 1$. We can find a power series solution to this differential equation, with $\xi = 0$ as a regular point.

$$f(\xi) = \sum_{n=0}^{\infty} a_n\xi^n$$

We find

$$\xi \frac{\mathrm{d}f}{\mathrm{d}\xi} = \sum_{n=0}^{\infty} n a_n \xi^n; \quad \frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} = \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} = \sum_{n=0}^{\infty} (n+1)(n+2) a_{n+2} \xi^n$$

Comparing coefficients of ξ^n,

$$(n+1)(n+2)a_{n+2} - 2n a_n + (\varepsilon - 1)a_n = 0$$

Hence,

$$a_{n+2} = \frac{2n - \varepsilon + 1}{(n+1)(n+2)} a_n$$

Since the function must be either even or odd, exactly one of a_0 and a_1 must be zero.

Proposition. If the series for f does not terminate, χ is not normalisable.

Proof. Suppose the series does not terminate. We will consider the asymptotic behaviour as $n \to \infty$.

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

But this is the same asymptotic behaviour as the function $g(\xi)$ given by

$$g(\xi) = \exp\left[\xi^2\right] = \sum_{m=0}^{\infty} \frac{\xi^{2m}}{m!} = \sum_{n=0}^{\infty} b_n \xi^n$$

with

$$b_n = \begin{cases} \frac{1}{m!} & n = 2m \\ 0 & n = 2m+1 \end{cases}$$

So asymptotically,

$$\frac{b_{n+2}}{b_n} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n}{2}+1\right)!} = \frac{2}{n+2} \to \frac{2}{n}$$

Hence χ would have a form asymptotically equal to

$$\chi(\xi) \sim \exp\left[\frac{\xi^2}{2}\right]$$

Hence $\chi(\xi)$ would be not normalisable. □

Hence f must be a polynomial. So there exists N such that $a_{N+2} = 0$ and $a_N \neq 0$. So for this value,

$$2N - \varepsilon + 1 = 0 \implies \varepsilon = 2N + 1$$

By the definition of ε,

$$E_N = \left(N + \frac{1}{2}\right)\hbar\omega$$

In particular, $E_{N+1} - E_N = \hbar\omega$. The eigenfunctions are

$$\chi_N(\xi) = f_N(\xi) \exp\left[-\frac{\xi^2}{2}\right]$$

with the property that

$$\chi_N(-\xi) = (-1)^N \chi_N(\xi)$$

$$\begin{aligned} f_0(\xi) &= 1 \\ f_1(\xi) &= \xi \\ f_2(\xi) &= 1 - 2\xi^2 \\ f_3(\xi) &= \xi - \frac{2}{3}\xi^3 \\ &\vdots \end{aligned}$$

5 Operators and measurements

5.1 Hermitian operators

Definition. The *Hermitian conjugate* of an operator $\hat{A}$ is written $\hat{A}^\dagger$, and is defined such that

$$\langle \hat{A}^\dagger \psi_1, \psi_2 \rangle = \langle \psi_1, \hat{A}\psi_2 \rangle$$

where $\psi_1, \psi_2 \in \mathcal{H}$.

We can verify that for $a_1, a_2 \in \mathbb{C}$,

(i) $(a_1\hat{A}_1 + a_2\hat{A}_2)^\dagger = a_1^\star \hat{A}_1^\dagger + a_2^\star \hat{A}_2^\dagger$;

(ii) $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$

Definition. A *Hermitian operator* is a linear operator $\hat{O} : \mathcal{H} \to \mathcal{H}$ such that

$$\hat{A}^\dagger = \hat{A}$$

Equivalently,

$$\langle \hat{A}\psi_1, \psi_2 \rangle = \langle \psi_1, \hat{A}\psi_2 \rangle$$

Example. The familiar operators $\hat{x}$, $\hat{p}$ are Hermitian.

$$\begin{aligned} \langle \hat{x}\psi_1, \psi_2 \rangle &= \int_{\mathbb{R}^3} (x\psi_1)^\star \psi_2 \, \mathrm{d}V \\ &= \int_{\mathbb{R}^3} \psi_1^\star x \psi_2 \, \mathrm{d}V \\ &= \langle \psi_1, \hat{x}\psi_2 \rangle \end{aligned}$$

For $\hat{p}$, integrating by parts, we have

$$\begin{aligned}\langle \hat{p}\psi_1, \psi_2\rangle &= \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x}\psi_1\right)^{\star} \psi_2 \,\mathrm{d}x \\ &= i\hbar \int_{-\infty}^{\infty} \frac{\partial \psi_1^{\star}}{\partial x}\psi_2 \,\mathrm{d}x \\ &= -i\hbar \int_{-\infty}^{\infty} \psi_1^{\star} \frac{\partial \psi_2}{\partial x} \,\mathrm{d}x \\ &= \langle \psi_1, \hat{p}\psi_2\rangle\end{aligned}$$

Theorem. The eigenvalues of a Hermitian operator are real.

Proof. Let $\hat{A}$ be a Hermitian operator, and ψ a normalised eigenfunction with eigenvalue a.

$$\langle \psi, \hat{A}\psi\rangle = \langle \psi, a\psi\rangle = a\langle \psi, \psi\rangle = a$$

Since $\hat{A}$ is Hermitian,

$$\langle \psi, \hat{A}\psi\rangle = \langle \hat{A}\psi, \psi\rangle = \langle a\psi, \psi\rangle = a^{\star}\langle \psi, \psi\rangle = a^{\star}$$

Hence $a = a^{\star}$ so $a \in \mathbb{R}$. □

Theorem. Let $\hat{A}$ be a Hermitian operator, and ψ_1, ψ_2 normalised eigenfunctions with distinct eigenvalues a_1, a_2. Then ψ_1, ψ_2 are orthogonal.

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

$$\langle \hat{A}\psi_1, \psi_2\rangle = a_1\langle \psi_1, \psi_2\rangle$$

But also,

$$\langle \psi_1, \hat{A}\psi_2\rangle = a_2\langle \psi_1, \psi_2\rangle$$

These two values must be the same, so $\langle \psi_1, \psi_2\rangle = 0$. □

Theorem. The discrete and continuous set of eigenfunctions of any Hermitian operator form a complete orthogonal basis for the Hilbert space. This theorem is stated without proof.

Corollary. Every solution of the time-dependent Schrödinger can be written as a superposition of stationary states.

$$\psi(x,t) = \sum_{n=1}^{\infty} a_n \chi_n(x) e^{-iE_n t/\hbar}; \quad a_n = \langle \chi_n, \psi\rangle$$

In the continuous case,

$$\psi(x,t) = \int_{\Delta_\alpha} A(\alpha)\chi_\alpha(x) e^{-iE_n t/\hbar}\,\mathrm{d}\alpha; \quad A(\alpha) = \langle \chi_\alpha, \psi\rangle$$

5.2 Postulates of quantum mechanics

The following postulates are used to interpret measurements in quantum systems.

(i) Any observable O is represented by a Hermitian operator $\hat{O}$.

(ii) The possible outcomes of O are the eigenvalues of $\hat{O}$. Since $\hat{O}$ is Hermitian, we can only ever observe real values.

(iii) Let $\hat{O}$ have a discrete set of normalised eigenfunctions $\{\psi_i\}$ with distinct eigenvalues $\{\lambda_i\}$. Let ψ be a state, written in terms of the eigenfunctions of $\hat{O}$.

$$\psi = \sum a_i \psi_i$$

Suppose we measure O on a particle in the state ψ. Then, the probability that O takes value λ_i is

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

(iv) The above postulate can be generalised to the case where $\hat{O}$ has degenerate eigenvalues. Let $\{\psi_i\}$ be a discrete set of normalised eigenfunctions with not necessarily distinct eigenvalues $\{\lambda_i\}$. If $\{\psi_i\}_{i\in I}$ is a complete set of orthonormal eigenfunctions with the same eigenvalue λ, then

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

(v) We can verify from the postulates above that the sum of all probabilities is unity.

$$\sum_i |a_i|^2 = \sum_i \langle a_i\psi_i, a_i\psi_i\rangle = \sum_i \sum_j \langle a_i\psi_i, a_j\psi_j\rangle = \langle \psi, \psi\rangle = 1$$

(vi) If O is measured on a state ψ at time t, and the outcome is λ_i, then the wavefunction instantaneously 'collapses' into the measured state after the measurement.

$$\psi \mapsto \psi_i$$

This is called the *projection postulate*.

(vii) If $\hat{O}$ has degenerate eigenfunctions all with eigenvalue λ, then instead we find

$$\psi \mapsto \sum_{i\in I} a_i\psi_i$$

So in this case, the wavefunction collapses to a linear combination of the eigenfunctions that give this eigenvalue.

5.3 Expectation of operators

Definition.

$$\psi = \sum_i a_i\psi_i = \sum_i \langle \psi_i, \psi\rangle \psi_i$$

The *projector* operator projects ψ onto a specific eigenfunction.

$$\hat{P}: \psi \mapsto \langle \psi_i, \psi \rangle \psi_i$$

Definition. The expectation value of an observable $\hat{O}$ on a state ψ is

$$\begin{aligned}
\langle O \rangle_\psi &= \sum_i \lambda_i \mathbb{P}(O = \lambda_i) \\
&= \sum_i \lambda_i |\langle \psi_i, \psi \rangle|^2 \\
&= \left\langle \sum_i \langle \psi_i, \psi \rangle \psi_i, \sum_j \lambda_j \langle \psi_j, \psi \rangle \psi_j \right\rangle \\
&= \langle \psi, \hat{O}\psi \rangle
\end{aligned}$$

5.4 Commutators

Definition. The *commutator* of two operators $\hat{A}$ and $\hat{B}$ is the operator given by

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

We observe the following properties of the commutator.

(i) $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$;

(ii) $[\hat{A}, \hat{A}] = 0$;

(iii) $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$;

(iv) $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$;

Example. The commutator $[\hat{x}, \hat{p}]$ in one dimension is given by, for every $\psi \in \mathcal{H}$,

$$\begin{aligned}
\hat{x}\hat{p}\psi &= x\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x) = -i\hbar x\frac{\partial \psi}{\partial x} \\
\hat{p}\hat{x}\psi &= \left(-i\hbar\frac{\partial}{\partial x}\right)x\psi(x) = -i\hbar\psi - i\hbar x\frac{\partial \psi}{\partial x} \\
\therefore [\hat{x}, \hat{p}]\psi &= i\hbar\psi
\end{aligned}$$

Hence,

$$[\hat{x}, \hat{p}] = i\hbar\hat{I}$$

where $\hat{I}$ is the identity operator. This specific commutator is known as the canonical commutator relation.

5.5 Simultaneously diagonalisable operators

Definition. Hermitian operators $\hat{A}$ and $\hat{B}$ are said to be *simultaneously diagonalisable* if there exists a complete basis of joint eigenfunctions $\{\psi_i\}$ such that $\hat{A}\psi_i = \lambda_i\psi_i$ and $\hat{B}\psi_i = \mu_i\psi_i$ for $\lambda_i, \mu_i \in \mathbb{R}$.

Theorem. Hermitian operators $\hat{A}$ and $\hat{B}$ are simultaneously diagonalisable if and only if $\left[\hat{A}, \hat{B}\right] = 0$.

Proof. Suppose $\hat{A}$ and $\hat{B}$ are simultaneously diagonalisable. Then, by definition, there exists a complete basis $\{\psi_i\}$ with eigenvalues λ_i, μ_i for $\hat{A}, \hat{B}$. Now, for any element ψ_i of this basis, the commutator is

$$\left[\hat{A}, \hat{B}\right]\psi_i = \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i = \hat{A}\mu_i\psi_i - \hat{B}\lambda_i\psi_i = \mu_i\hat{A}\psi_i - \lambda_i\hat{B}\psi_i = \lambda_i\mu_i\psi_i - \mu_i\lambda_i\psi_i = 0$$

Let ψ be an arbitrary function in the Hilbert space $\mathcal{H}$. Then by linearity,

$$\left[\hat{A}, \hat{B}\right]\psi = \sum_i c_i\left[\hat{A}, \hat{B}\right]\psi_i = 0$$

Conversely, suppose that the commutator is zero. Let ψ_i be an eigenfunction of $\hat{A}$ with eigenvalue λ_i. Then, since the commutator is zero, we have

$$0 = \left[\hat{A}, \hat{B}\right]\psi_i = \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i \implies \hat{A}\left(\hat{B}\psi_i\right) = \lambda_i\left(\hat{B}\psi_i\right)$$

Hence, $\hat{B}$ maps the eigenspace E_i of $\hat{A}$ with eigenvalue λ_i into itself. So $\hat{B}|_{E_i}$ is a Hermitian operator on E_i. Since this holds for any eigenfunction and eigenvalue, we can find a complete basis of simultaneous eigenfunctions of $\hat{A}$ and $\hat{B}$. □

5.6 Uncertainty

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

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

where

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

The two definitions are equivalent:

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

Lemma. $(\Delta_\psi A)^2 \geq 0$, and $\Delta_\psi A = 0$ if and only if ψ is an eigenfunction of $\hat{A}$.

Proof. Since $\hat{A}$ is Hermitian,

$$\begin{aligned}(\Delta_\psi A)^2 &= \left\langle \left(\hat{A} - \langle \hat{A} \rangle_\psi \hat{I}\right)^2 \right\rangle_\psi \\ &= \left\langle \psi, \left(\hat{A} - \langle \hat{A} \rangle_\psi \hat{I}\right)^2 \psi \right\rangle \\ &= \left\langle \left(\hat{A} - \langle \hat{A} \rangle_\psi \hat{I}\right)\psi, \left(\hat{A} - \langle \hat{A} \rangle_\psi \hat{I}\right)\psi \right\rangle \\ &= \left\| \left(\hat{A} - \langle \hat{A} \rangle_\psi \hat{I}\right)\psi \right\|\end{aligned}$$

Let $\phi = \left(\hat{A} - \langle \hat{A} \rangle_\psi \hat{I}\right)\psi$. The norm of any function is non-negative, so the square uncertainty is non-negative. Now, suppose this norm $\|\phi\|$ is zero. Then, $\phi = 0$. Hence,

$$\hat{A}\psi = \langle \hat{A} \rangle_\psi \psi$$

so it is an eigenfunction of $\hat{A}$. If ψ is conversely an eigenfunction of $\hat{A}$ with eigenvalue a, then

$$\langle \hat{A} \rangle_\psi = \langle \psi, \hat{A}\psi \rangle = a\|\psi\| = a$$

Further,

$$\langle \hat{A}^2 \rangle_\psi = \langle \psi, \hat{A}^2\psi \rangle = a^2$$

Hence,

$$\left(\Delta_\psi A\right)^2 = a^2 - a^2 = 0$$

□

5.7 Schwarz inequality

Theorem. Let $\psi, \phi \in \mathcal{H}$. Then,

$$|\langle \psi, \phi \rangle|^2 \leq \langle \phi, \phi \rangle \langle \psi, \psi \rangle$$

and

$$|\langle \psi, \phi \rangle|^2 = \langle \phi, \phi \rangle \langle \psi, \psi \rangle \iff \exists a \in \mathbb{C}, \phi = a\psi$$

Proof. For all $a \in \mathbb{C}$, we have

$$0 \leq \langle \phi - a\psi, \phi - a\psi \rangle$$

In particular, let

$$a = \frac{\langle \psi, \phi \rangle}{\langle \psi, \psi \rangle}$$

Then,

$$0 \leq \langle \phi, \phi \rangle - \frac{2|\langle \psi, \phi \rangle|^2}{\langle \psi, \psi \rangle} + \frac{|\langle \psi, \phi \rangle|^2}{\langle \psi, \psi \rangle} = \langle \phi, \phi \rangle - \frac{|\langle \psi, \phi \rangle|^2}{\langle \psi, \psi \rangle}$$

Hence,

$$|\langle\psi,\phi\rangle|^2 \leq \langle\psi,\psi\rangle\langle\phi,\phi\rangle$$

Equality holds if and only if $\phi - a\psi = 0$. □

5.8 Generalised uncertainty theorem

Theorem. Let A and B be observables, and $\psi \in \mathcal{H}$. Then

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

Proof.

$$(\Delta_\psi A)^2 = \left\langle\left(\hat{A} - \langle\hat{A}\rangle_\psi \hat{I}\right)\psi, \left(\hat{A} - \langle\hat{A}\rangle_\psi \hat{I}\right)\psi\right\rangle$$

Defining $\hat{A}' = \hat{A} - \langle\hat{A}\rangle_\psi \hat{I}$ and $\hat{B}' = \hat{B} - \langle\hat{B}\rangle_\psi \hat{I}$,

$$(\Delta_\psi \hat{A}')^2 = \langle\hat{A}'\psi,\hat{A}'\psi\rangle$$

and analogously for $\hat{B}'$. Now,

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

Since $\hat{A}'$ is Hermitian,

$$(\Delta_\psi \hat{A}')(\Delta_\psi \hat{B}') \geq |\langle\psi,\hat{A}'\hat{B}'\psi\rangle|$$

By definition, $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ and let the anticommutator be $\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$. If $\hat{A}'$ and $\hat{B}'$ are Hermitian,

$$[\hat{A}',\hat{B}']^\dagger = -[\hat{A}',\hat{B}']$$

and

$$\{\hat{A}',\hat{B}'\}^\dagger = \{\hat{A}',\hat{B}'\}$$

So the anticommutator is Hermitian. Now, we can write

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

Hence,

$$\begin{aligned}(\Delta_\psi \hat{A}')(\Delta_\psi \hat{B}') &\geq \left|\left\langle\psi,\left(\frac{1}{2}[\hat{A}',\hat{B}'] + \frac{1}{2}\{\hat{A}',\hat{B}'\}\right)\psi\right\rangle\right| \\ &= \left|\left\langle\psi,\frac{1}{2}[\hat{A}',\hat{B}']\psi\right\rangle + \left\langle\psi,\frac{1}{2}\{\hat{A}',\hat{B}'\}\psi\right\rangle\right|\end{aligned}$$

We can prove that $\langle\psi,\{\hat{A}',\hat{B}'\}\psi\rangle \in \mathbb{R}$. Since the anticommutator is Hermitian,

$$\langle\psi,\{\hat{A}',\hat{B}'\}\psi\rangle = \langle\{\hat{A}',\hat{B}'\}\psi,\psi\rangle = \langle\psi,\{\hat{A}',\hat{B}'\}\psi\rangle^*$$

Analogously we can prove that $\langle\psi,[\hat{A}',\hat{B}']\psi\rangle \in i\mathbb{R}$.

$$\langle\psi,[\hat{A}',\hat{B}']\psi\rangle = \langle[\hat{A}',\hat{B}']^*\psi,\psi\rangle = -\langle\psi,[\hat{A}',\hat{B}']\psi\rangle^*$$

Hence,

$$\begin{aligned}
(\Delta_\psi \hat{A}')^2 (\Delta_\psi \hat{B}')^2 &\geq \left| \left\langle \psi, \frac{1}{2}[\hat{A}', \hat{B}']\psi \right\rangle + \left\langle \psi, \frac{1}{2}\{\hat{A}', \hat{B}'\}\psi \right\rangle \right|^2 \\
&= \frac{1}{4}|\langle \psi, [\hat{A}', \hat{B}']\psi \rangle|^2 + \frac{1}{4}|\langle \psi, \{\hat{A}', \hat{B}'\}\psi \rangle|^2 \\
&\geq \frac{1}{4}|\langle \psi, \{\hat{A}', \hat{B}'\}\psi \rangle|^2 \\
\therefore (\Delta_\psi \hat{A}')^2 (\Delta_\psi \hat{B}')^2 &\geq \frac{1}{4}|\langle \psi, \{\hat{A}, \hat{B}\}\psi \rangle|^2
\end{aligned}$$

□

5.9 Consequences of uncertainty relation

(i) $\left[\hat{A}, \hat{B}\right] = 0$ implies that there exists a joint set of eigenfunctions which is a complete basis of $\mathcal{H}$. In particular, $\hat{A}$ and $\hat{B}$ can be measured simulaneously with arbitrary precision. For instance, we can measure E, $\left|\overline{L}\right|$ and L_z simultaneously for an electron on a hydrogen atom.

(ii) We cannot simultaneously measure position and momentum of a particle with arbitrary precision. In particular,

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

This is Heisenberg's uncertainty principle.

5.10 States of minimal uncertainty

The Gaussian wavepacket was a state of minimal uncertainty:

$$\Delta_\psi x \Delta_\psi p = \frac{\hbar}{2}$$

We would like to analyse the conditions for a state ψ to have minimal uncertainty.

Lemma. ψ is a state of minimal uncertainty if and only if

$$\hat{x}\psi = ia\hat{p}\psi$$

for some $a \in \mathbb{R}$. A non-example is the De Broglie plane waves.

Lemma. The condition for the above lemma to hold is that

$$\psi(x) = ce^{-bx^2}; \quad b, c \in \mathbb{R}, b > 0, c \neq 0$$

The Gaussian wavepacket is an example of this form.

5.11 Ehrenfest theorem

Theorem. The time evolution of a Hermitian operator $\hat{A}$ is governed by

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

In this course, we will not see any operators with time dependence, so the last term will not be needed.

Proof.

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

The time-dependent Schrödinger equation gives

$$\left(i\hbar\frac{\partial\psi}{\partial t}\right)^\star = (\hat{H}\psi)^\star \implies -i\hbar\frac{\partial\psi^\star}{\partial t} = \psi^\star\hat{H}^\star = \psi^\star\hat{H}$$

Hence,

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

□

Example. Let $\hat{A} = \hat{H}$. Then,

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

This corresponds to the classical notion of conservation of energy.

Example. Let $\hat{A} = \hat{p}$. First, note

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

Hence,

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

This corresponds exactly to Newton's second law,

$$\dot{p} = -\frac{\mathrm{d}U}{\mathrm{d}x}$$

Example. Let $\hat{A} = \hat{x}$. We have

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

Hence,

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

which aligns with the classical equation

$$\dot{x} = \frac{p}{m}$$

6 Three-dimensional solutions to the Schrödinger equation

6.1 Time-independent Schrödinger equation in spherical polar coordinates

For a spherically symmetric potential in $\mathbb{R}^3$, the time-independent Schrödinger equation is

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

Recall that the Laplacian operator can be expanded in spherical polar coordinates as

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]\right)\chi(x) + U(x)\chi(x) = E\chi(x)$$

where

$$x = r\cos\phi\sin\theta; \quad y = r\sin\phi\sin\theta; \quad z = r\cos\theta$$

Definition. A *spherically symmetric potential* is a potential U which depends only on r.

We search for the particular solutions of the time-dependent Schrödinger equation with spherically symmetric potential that are radial eigenfunctions. If $\chi(r)$ is a function of r alone,

$$\nabla^2\chi(r) = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\chi(r))$$

Hence,

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

This is equivalent to

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

The normalisation condition is

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

The eigenfunctions $\chi(r)$ must converge to zero sufficiently fast as $r \to \infty$ in order to be normalisable. To solve the time-independent Schrödinger equation, we will define

$$\sigma(r) = r\chi(r)$$

Then,

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

This is defined for $r \geq 0$. The normalisation condition here is

$$\int_0^\infty |\sigma(r)|^2 \,\mathrm{d}r < N; \quad \sigma(0) = 0; \quad \sigma'(0) < \infty$$

The conditions at zero force χ to be defined and have finite derivative at zero. To solve the equation for σ, we solve on $\mathbb{R}$ and search for odd solutions $\sigma^{(-)}$, so

$$\sigma^{(-)}(-r) = -\sigma^{(-)}(r)$$

6.2 Spherically symmetric potential well

Consider the potential well given by

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

where $a, U_0 > 0$. The time-independent Schrödinger equation is

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

We search for odd-parity bound states, so $0 < E < U_0$. Let

$$k = \sqrt{\frac{2mE}{\hbar^2}}; \quad \overline{k} = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

The solution for σ is

$$\sigma(r) = \begin{cases} A\sin(kr) & r \leq a \\ Be^{-\overline{k}r} & r > a \end{cases}$$

The continuity condition at $r = a$ can be imposed to find $A\sin ka = Be^{-\overline{k}a}$. The continuity of the derivative gives $kA\cos ka = -\overline{k}Be^{-\overline{k}a}$. Therefore,

$$-k\cot(ka) = \overline{k}; \quad k^2 + \overline{k}^2 = \frac{2mU_0}{\hbar^2}$$

Hence,

$$-\xi \cot \xi = \eta; \quad \xi^2 + \eta^2 = r_0^2$$

where $\xi = ka$ and $\eta = \bar{k}a$, and $r_0 = a\sqrt{2mU_0/\hbar}$. If $r_0 < \frac{\pi}{2}$, we have no solutions because $\xi \geq 0$. Equivalently, there are no solutions if

$$U_0 < \frac{\pi^2 \hbar^2}{8ma^2}$$

7 Solution to hydrogen atom

7.1 Radial wavefunction of hydrogen atom

The hydrogen atom is comprised of a nucleus and a single electron. The nucleus has a positive charge and the electron has a negative charge. We will model the proton to be stationary at the origin. The Coulomb force experienced by the electron is given by

$$F = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2} = -\frac{\partial U}{\partial r} \implies U = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Since zero potential is achieved only at infinity, we search for bound states with $E < 0$. We will search for the radial symmetric eigenfunctions. We have

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

We define

$$\nu^2 = -\frac{2mE}{\hbar^2} > 0; \quad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2} > 0$$

The Schrödinger equation becomes

$$\chi''(r) + \frac{2}{r}\chi'(r) + \left(\frac{\beta}{r} - \nu^2\right)\chi(r) = 0$$

Asymptotically as $r \to \infty$, we can see that $\chi'' \sim \nu^2\chi$. Since $\nu^2 > 0$, this yields solutions that asymptotically behave similarly to $e^{-r\nu}$, where the positive exponential solution is not applicable due to the normalisation condition. For $r = 0$, the eigenfunction should be finite. We will consider an ansatz educated by the asymptotical behaviour. Suppose

$$\chi(r) = f(r)e^{-\nu r}$$

and we solve for $f(r)$. The Schrödinger equation is

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

This is a homogeneous linear ordinary differential equation with a regular point at $r = 0$. Suppose there exist series solutions.

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

We can differentiate and find

$$f'(r) = \sum_{n=0}^{\infty} a_n(c+n)r^{c+n-1}; \quad f''(r) = \sum_{n=0}^{\infty} a_n(c+n)(c+n-1)r^{c+n-2}$$

Hence,

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

By comparing coefficients of the lowest power of r,

$$a_0c(c-1)+2a_0c=0 \implies a_0c(c+1)=0 \implies c=-1,0$$

The solution $c=-1$ implies $\chi(r)\sim\frac{1}{r}$ which is invalid at $r=0$. So we require $c=0$. Then the power series becomes

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

Comparing coefficients of equal powers of r,

$$a_nn(n+1)+a_{n-1}(-2\nu n+2\nu+\beta-2\nu)=0$$

Hence, we arrive at the recurrence relation

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

Suppose this series were infinite. Asymptotically, the behaviour of $f(r)$ is determined by $\frac{a_n}{a_{n-1}}\sim\frac{2\nu}{n}$. We can compare this behaviour to the asymptotic behaviour of $g(r)=e^{2\nu r}$. In this case, the series expansion with coefficients b_n satisfies

$$b_n=\frac{(2\nu)^n}{n!} \implies \frac{b_n}{b_{n-1}}=\frac{2\nu}{n}$$

Hence, asymptotically $f(r)\sim e^{2\nu r}$ if the series does not terminate. Since $\chi(r)=f(r)e^{-\nu r}$, we have $\chi(r)\sim e^{\nu r}$ which is not normalisable. Hence the series is finite. So there exists an integer $N>0$ such that $a_N=0$ and $a_{N-1}\neq 0$. This implies $2\nu N-\beta=0$ hence $\nu=\frac{\beta}{2N}$. Substituting ν^2 and β, we find

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

So the eigenvalues are equivalent to those found in the Bohr model. We now wish to find the radial eigenfunctions. Note, $\frac{\beta}{2\nu}=N$ hence we can substitute and find

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

This recursion can be used to find the coefficients of the polynomial $f_N(r)$.

$$\begin{aligned}f_1(r)&=1\\f_2(r)&=1-\nu r\\f_3(r)&=1-2\nu r+\frac{2}{3}\nu^2r^2\end{aligned}$$

These are called the Laguerre polynomials of order $N-1$ (for example, the first order Laguerre polynomial is f_2). We can then multiply the Laguerre polynomials by $e^{-\nu r}$ and normalise over $\mathbb{R}^3$ to find the normalised eigenfunctions $\chi_N(r)$. For example,

$$\chi_1(r) = \frac{\nu^{3/2}}{\sqrt{\pi}} = \frac{1}{\sqrt{\pi}}\left(\frac{e^2 m_e}{4\pi\varepsilon_0\hbar^2}\right)^{3/2} e^{-\nu r}$$

Recall that the Bohr model implied that the ground state has radius a_0, known as the Bohr radius, given in terms of ν by $a_0 = \frac{1}{\nu}$. Using quantum mechanics, we instead find

$$\begin{aligned}
\langle r\rangle_{\chi_1} &= \int_{\mathbb{R}^3} \chi_1^\star(r) r \chi_1(r)\,\mathrm{d}V \\
&= \int_0^{2\pi} \mathrm{d}\phi \int_{-1}^{1} \mathrm{d}\cos\theta \int_0^\infty \frac{\nu^3}{\pi} r^3 e^{-2\nu r}\,\mathrm{d}r \\
&= 4\pi\frac{\nu^3}{\pi}\int_0^\infty r^3 e^{-2\nu r}\,\mathrm{d}r \\
&= \frac{3}{2}a_0
\end{aligned}$$

We have verified with physical experiments that this larger expected radius is physically accurate.

7.2 Angular momentum

Recall that classically the angular momentum L is given by

$$L = x \times p$$

Spherically symmetric potentials conserve classical angular momentum:

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

Solving classical problems in this way allows us to reduce a three-dimensional problem into a two-dimensional problem, by considering motion on the plane $L\cdot x = 0$. Then we reduce to one dimension by considering $\hat{e}_r$. In quantum mechanics, we can do an analogous simplification.

Definition. In quantum mechanics, the angular momentum is given by

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

In Cartesian coordinates, this reduces to

$$\hat{L}_i = -i\hbar\varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}$$

Each component $\hat{L}_i$ is a Hermitian operator. Note,

$$\begin{aligned}[\hat{L}_1, \hat{L}_2]\psi(x_1, x_2, x_3) &= -\hbar^2\Bigg[\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)\left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right) \\ &\quad - \left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right)\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)\Bigg]\psi \\ &= -\hbar^2\left[x_2\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_2}\right]\psi \\ &= -i\hbar\hat{L}_3\psi\end{aligned}$$

Hence the commutator $\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k$ is nonzero for $i \neq j$. In particular, we cannot measure each component of the angular momentum simultaneously.

Definition. The *total angular momentum* is

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

We can find that $\left[\hat{L}^2, \hat{L}_i\right] = 0$, so we can measure both the total angular momentum and a specific component of angular momentum simultaneously. For a spherically symmetric potential, given by $\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{r})$, we can find

$$\left[\hat{H}, \hat{L}^2\right] = \left[\hat{H}, \hat{L}_i\right] = 0$$

7.3 Commutativity of angular momentum operators

The set $\left\{\hat{H}, \hat{L}^2, \hat{L}_i\right\}$ commutes pairwise. By convention, we choose $i = 3$ to extract the z component of the angular momentum. Hence,

(i) We can find joint eigenstates of the three operators, and such eigenstates can be chosen to form a basis for the Hilbert space $\mathcal{H}$.

(ii) The corresponding eigenvalues $|L|, L_z, E$ can be measured simultaneously to an arbitrary precision.

(iii) The set of operators is maximal; there exists no operator (other than a linear combination of the above) that commutes with all three.

7.4 Joint eigenfunctions of angular momentum

We search for joint eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$. We will write $\hat{L}$ in spherical coordinates. In Cartesian coordinates,

$$\hat{L} = -i\hbar x \cdot \nabla$$

Hence,

$$\hat{L}_3 = -i\hbar\frac{\partial}{\partial\phi}; \quad \hat{L}^2 = -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

Now we search for eigenfunctions of these operators.

$$\hat{L}^2 Y(\theta, \phi) = \lambda Y(\theta, \phi); \quad \hat{L}_3 Y(\theta, \phi) = \hbar m Y(\theta, \phi)$$

Solving the equation in $\hat{L}_3$,

$$-i\hbar\frac{\partial}{\partial\phi}Y(\theta,\phi) = \hbar m Y(\theta,\phi)$$

We can find solutions of the form $Y(\theta,\phi) = y(\theta)x(\phi)$. We find

$$-i\hbar y(\theta)x'(\phi) = \hbar m y(\theta)x(\phi)$$

Hence $y(\theta)$ is arbitrary, and further

$$-i\hbar x'(\phi) = \hbar m x(\phi) \implies x(\phi) = e^{im\phi}$$

Given that the wavefunctions must be single-valued on $\mathbb{R}^3$, we must have $x(\phi)$ invariant under the choice of $\phi = \phi + 2\pi k$. Hence m must be an integer. Since this must also be an eigenfunction of $\hat{L}^2$, we have further

$$-\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{\partial^2}{\partial\phi^2}\right][y(\theta)x(\phi)] = \lambda y(\theta)x(\phi)$$

Hence, substituting $x(\phi) = e^{im\phi}$, we find

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

This is the associate Legendre equation. The solutions of $y(\theta)$ are the associate Legendre functions.

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

where the P_ℓ are the Legendre polynomials. Since the ordinary Legendre polynomials are of degree ℓ, we must have $|m| \leq \ell$ to obtain a nonzero solution. This corresponds to the classical notion that $|L_z| \leq |L|$ for a physical solution. The eigenvalues of $\hat{L}^2$ are

$$\lambda = \ell(\ell+1)\hbar^2$$

with $\ell \in \{0, 1, 2, \dots\}$. Thus,

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

The Y functions are called the spherical harmonics. The parameters ℓ, m are known as the quantum numbers of the eigenfunction; ℓ is the total angular momentum quantum number and m is the azimuthal quantum number. Examples of normalised eigenfunctions are

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

All spherical harmonics can be shown to be orthogonal.

7.5 Full solution to hydrogen atom

The time-independent Schrödinger equation for the hydrogen atom is

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

Writing the Laplacian in spherical polar coordinates,

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

Hence,

$$\hat{L}^2=\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\phi^2}\right]\implies -\hbar^2\nabla^2=-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r+\frac{\hat{L}^2}{r^2}$$

Thus we can rewrite the TISE as

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

Since $\hat{L}^2,\hat{L}_3,\hat{H}$ are a maximal set of pairwise commuting operators, we know that the eigenfunctions of the Hamiltonian χ must also be eigenfunctions of $\hat{L}^2,\hat{L}_3$. Hence,

$$\chi(r,\theta,\phi)=R(r)Y_{\ell,m}(\theta,\phi)$$

Since χ is an eigenfunction of $\hat{L}^2$,

$$\hat{L}^2(R(r)Y_{\ell,m}(\theta,\phi))=R(r)\hbar^2\ell(\ell+1)Y_{\ell,m}(\theta,\phi)$$

Substituting into the TISE, we find

$$\begin{aligned}&-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}\right)Y_{\ell,m}(\theta,\phi)+\frac{\hbar^2}{2m_er^2}\ell(\ell+1)R(r)Y_{\ell,m}(\theta,\phi)-\frac{e^2}{4\pi\varepsilon_0 r}R(r)Y_{\ell,m}(\theta,\phi)\\&=ER(r)Y_{\ell,m}(\theta,\phi)\end{aligned}$$

Cancelling the spherical harmonic,

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}\right)+\underbrace{\left(\frac{\hbar^2}{2m_er^2}\ell(\ell+1)-\frac{e^2}{4\pi\varepsilon_0 r}\right)}_{U_{\text{eff}}=\text{ effective potential}}R(r)=ER(r)$$

This is an equation for the radial part of the solution. We have already solved this equation for $\ell=0$ to find $\chi(r)$, the radial wavefunction. Note that the azimuthal quantum number does not appear in the effective potential, giving a degeneracy of order at least $2\ell+1$. We define

$$\nu^2=-\frac{2m_eE}{\hbar^2}>0;\quad \beta=\frac{e^2m_e}{2\pi\varepsilon_0\hbar^2}$$

Hence,

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

The asymptotic limit is as before in the radial case, since the angular velocity dependence is suppressed by $\frac{1}{r^2}$. We have $R'' - \nu^2 R \to 0$ hence $R \propto e^{-\nu r}$ in the limit. We let $R(r) = g(r)e^{-\nu r}$. Then,

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

Expanding in power series,

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

Substituting and comparing the lowest power of r,

$$a_0[\sigma(\sigma-1) + 2\sigma - \ell(\ell+1)] = 0 \implies \sigma(\sigma+1) = \ell(\ell+1)$$

Hence, $\sigma = \ell$ or $\sigma = -\ell - 1$. If $\sigma = -\ell - 1$, we have $R(r) \sim \frac{1}{r^{\ell+1}}$ which cannot be the solution, so $\sigma = \ell$. Thus,

$$g(r) = r^\ell \sum_{n=0}^{\infty} a_n r^n$$

We can evaluate the recurrence relation between the coefficients as before to find

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

which gives

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

If $\ell = 0$ this yields the result for the radial solution. Unless the series terminates, it is possible to show that R diverges. Hence g must be a polynomial with first zero coefficient $a_{n_{\max}}$. Here,

$$2\nu(n_{\max} + \ell) - \beta = 0$$

We define $N = n_{\max} + \ell$, so $2\nu N - \beta = 0$ giving $\nu = \frac{\beta}{2N}$. Note that $N > \ell$ since $n_{\max} > 0$. We can then find the energy level to be

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

which is an identical energy spectrum as we found before when not considering angular momentum (using the Bohr model). For each E_N, we have $N = n_{\max} + \ell$ so there can be $\ell = 0, \dots, N-1$ and $m = -\ell, \dots, \ell$. Hence, the degeneracy of the solution for each N is

$$D(N) = \sum_{\ell=0}^{N-1} \sum_{m=-\ell}^{\ell} 1 = N^2$$

So the degeneracy increases quadratically with the energy level. For example, for $N = 2$ there are four possible eigenfunctions with the same energy. The eigenfunctions are now dictated by three quantum numbers.

$$\chi_{N,\ell,m}(r,\theta,\phi) = R_{N,\ell}(r)Y_{\ell,m}(\theta,\phi) = r^\ell g_{N,\ell}(r) e^{-\frac{\beta r}{2N}} Y_{\ell,m}(\theta,\phi)$$

where $g_{N,\ell}$ is a polynomial of degree $N-\ell-1$ defined by the recurrence relation

$$a_k = \frac{2\nu}{k}\frac{k+\ell-N}{k+2\ell+1}a_{n-1}$$

These are the generalised Laguerre polynomials, often written

$$g_{N,\ell}(r) = L_{N-\ell-1}^{2\ell+1}(2r)$$

The quantum number $N \in \{0, 1, \dots\}$ is known as the *principal* quantum number.

7.6 Comparison to Bohr model

In the Bohr model, the energy levels were predicted accurately. Further, the maximum of the radial probability corresponds to the orbits found in the Bohr model:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(\left|\chi_{N,0,0}(r)\right|^2 r^2\right) = 0$$

The classical trajectory, and the assumption about the angular momentum $L^2 = N^2\hbar^2$, were incorrect. The angular momentum found in quantum mechanics is $L^2 = \ell(\ell+1)\hbar^2$, which corresponds closely with the Bohr model for large ℓ.

7.7 Other elements of the periodic table

The above solution does not hold for other elements of the periodic table. Generalising to a nucleus with charge $+ze$ and z orbiting electrons, we could model this as

$$\chi(x_1, \dots, x_z) = \chi(x_1)\dots\chi(x_N); \quad E = \sum_{j=1}^{N} e_j$$

This approximation can be acceptable for small z, but diverges very quickly from the true solution as z increases, due to the electron-electron interactions and the Pauli exclusion principle.