Introductory Quantum Theory - 6CCM332A

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Chapter 1

Concepts from Classical Physics and Early Quantum Mechanics

Classical physics consists of two main theories, Newton's mechanics and Maxwell's electromagnetism.

Concept 1.0.1. (Newton's mechanics)
This branch of classical physics deals with the motion of particles under the influence of forces. Their position $\vec{x}(t)$ can be computed using Newton's Second Law:

$$\frac{d}{dt}(m\dot{\vec{x}}) = \vec{F} \tag{1.1}$$

This is typically written as $\vec{F} = -\vec{\nabla}V$ where V is some potential.

Newton's Second Law has many equivalent formulations:

- Euler-Lagrange equations from $L := T - V$ where $T = \frac{m}{2}\dot{\vec{x}}^2$
- Hamilton equations: $\dot{p} = -\frac{\partial H}{\partial q}, \dot{q} = \frac{\partial H}{\partial p}$
- Poisson brackets: $\dot{p} = \{p, H\}, \dot{q} = \{q, H\}, H = T + V$

Concept 1.0.2. (Maxwell's Theory of Electromagnetism)
This branch of classical physics descrbes electric and magnetic fields, $\vec{E}(t, \vec{x})$ and $\vec{B}(t, \vec{x})$, as induced by electric charges.
The theory is governed by Maxwell's equations:

- $\vec{\nabla} \cdot \vec{E} = 4\pi\rho$
- $\vec{\nabla} \cdot \vec{B} = 0$
- $\vec{\nabla} \times \vec{E} + \frac{1}{c}\frac{\partial \vec{B}}{\partial t} = 0$
- $\vec{\nabla} \times \vec{B} - \frac{1}{c}\frac{\partial \vec{E}}{\partial t} = \frac{4\pi}{c}\vec{j}$

where ρ is the electric charge density, $\vec{j}$ is the electric current density and c is the speed of light.

1.1 Early Quantum Mechanical Ideas

Observation 1.1.1 (1860s)**.** *Hot Hydrogen gas emits light. A spectral analysis reveals that only a discrete set of wavelengths are emitted.*

Observation 1.1.2 (1900)**.** *Black body radiation (in hot coal for example) occurs in discrete packages denoted **quanta of energy**. The physicist Max Planck presents the spectral density of such radiation. It is found that the energy of the radiation satisfies $E = \hbar\omega$. Where $\hbar = 1 \times 10^{-34} Js$ is **Planck's constant** and ω is the wavelength of the radiation.*

Observation 1.1.3 (1905)**.** *When UV light is shone against certain materials, electrons are emitted. The physicist Albert Einstein explains this effect using the assumption that light is a stream of particles with energy $E = \hbar\omega$ and momentum $p = \hbar k$.*

Observation 1.1.4 (1911)**.** *The physicist Ernest Rutherford's experiments suggest that atoms consist of a positively charged nucleus and of negatively charged electrons orbiting around it under the influence of the Coulomb Force. According to Maxwell's theory, the electrons' acceleration must cause them to give off electromagnetic radiation. This would cause them to lose energy and fall into the nucleues. This implies that, according to classical physics, atoms are unstable which is a contradiction to the fact that matter composed of atoms exists and is stable.*

Observation 1.1.5 (1913)**.** *The physicist Niels Bohr supplements Rutherford's model by postulating that only certain electronic orbits are permitted. In specific, electrons can only orbit where their orbital angular momentum is quantised: $mvr = n\hbar, n \in \mathbb{N}$. This agrees with the experiments from the 1860s.*

Observation 1.1.6 (1924)**.** *The physicist Louis de Broglie postulates that particles can behave like waves and vice versa. This is known as **wave-particle duality**. We can therefore associate a frequency* $\omega = \frac{E}{\hbar}$ *and wave number* $k = \frac{p}{\hbar}$ *to a particle with energy* E *and momentum* p*.*

Observation 1.1.7. *The physicists Clinton Davisson and Lest Germer devise an analogue of the double slit experiment for electrons. An interference pattern, just like that with light, is obtained with wavelength that fits de Broglie's formulae. Hence, very small particles can show wave-like behaviour.*

Chapter 2

The Schrödinger equation

This equation was formulated by Erwin Schrödinger in 1925. It governs non-relativistic Quantum Mechanics in a similar way to how Newton's Second Law governs non-relativistic classical mechanics. It cannot be derived but it results from de Broglie's postulates.

2.1 Setting up the equation

We begin by noting de Broglie's postulates. A particle of energy E and momentum p can be viewed as a wave with frequency $\omega = \frac{E}{\hbar}$ and wavelength $\lambda = \frac{2\pi\hbar}{p}$. This gives us a wave number of $k = \frac{2\pi}{\lambda} = \frac{p}{\hbar}$.

We can now describe a plane wave with these observations:

$$\Psi(x,t) = Ce^{i(kx-\omega t)}$$

Clearly, $E\Psi(x,t) = \hbar\omega\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$ and $p\Psi(x,t) = -i\hbar\frac{\partial}{\partial x}\Psi(x,t)$. We can now use the relation $E = \frac{p^2}{2m}$ we can see that $\Psi(x,t)$ satisfies $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$.

We can now generalise the above formulation by considering a potential function V. The total energy is thus $E = \frac{p^2}{2m} + V$. Following a similar path as before, we get

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\Psi(x,t) \tag{2.1}$$

the Schrödinger equation.

2.2 Properties of the Schrödinger Equation

Property 2.2.1. $\Psi(x,t) = e^{i(kx-\omega t)}$ *is not a solution if* $V \neq 0$. *A solution* $\Psi(x,t)$ *to the Schrödinger equation is still referred to as a wave function.*

Property 2.2.2. *The Schrödinger equation can easily be extended to three dimensional space via the following equation:*

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{x},t) = \left(-\frac{\hbar^2}{2m}\Delta + V(\vec{x},t)\right)\Psi(\vec{x},t)$$

where $\Delta = \vec{\nabla}\cdot\vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ *is the* ***Laplacian*** *operator.*

Property 2.2.3. *The related momentum is now a linear differential operator acting on a wave function* Ψ*:*

$$\hat{p} = i\hbar\frac{\partial}{\partial x}$$

The position is still given by $\hat{x} = x$ *which acts on a wave function by multiplication.*
It is easy to see that

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

This is an example of non-commutativity of quantum mechanical observables.
We also define $H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\Delta + V$ *as the* ***Hamilton*** *operator.*

Property 2.2.4. *The Schrödinger equation, being a partial differential equation, satifies the superposition principle.*
If ψ_1 *and* ψ_2 *are solutions of* $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = H\Psi(x,t)$ *then* $\alpha_1\psi_1+\alpha_2\psi_2, \forall\, \alpha_1,\alpha_2 \in \mathbb{C}$ *is also a solution.*

Property 2.2.5. *The Schrödinger equation is first order in* $\frac{\partial}{\partial t}$ *and hence* $\Psi(\vec{x},0)$ *can be determined from* $\Psi(\vec{x},t=0)$.
If V *is time independent then* $\Psi(\vec{x},t) = e^{-\frac{i}{\hbar}tH}\Psi(\vec{x},0)$.

Property 2.2.6. *Assume $V = V(\vec{x})$ is a time-independent potential function. Using seperation of variables, set:*

$$\Psi(\vec{x}, t) = \psi(\vec{x}) f(t)$$

We can now substitute this into the Schrödinger equation to get:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} (\psi(\vec{x}) f(t)) &= \left(-\frac{\hbar^2}{2m} \Delta + V(\vec{x}) \right) (\psi(\vec{x}) f(t)) \\ \implies i\hbar\, \psi(\vec{x}) \frac{\partial}{\partial t} f(t) &= f(t) \left(-\frac{\hbar^2}{2m} \Delta + V(\vec{x}) \right) \psi(\vec{x}) \\ \implies i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) &= \frac{1}{\psi(\vec{x})} \left(-\frac{\hbar^2}{2m} \Delta + V(\vec{x}) \right) \psi(\vec{x}) \end{aligned}$$

Now the left hand side is a function of only t and the right hand side is a function of only x. This must mean that both sides are equal to a constant, say E. We therefore have the two equations

$$i\hbar \frac{d}{dt} f(t) = E f(t) \tag{2.2}$$

$$H\psi(\vec{x}) = E\psi(\vec{x}) \tag{2.3}$$

The first is a first order differential equation with solution

$$f(t) = f(0) e^{-\frac{i}{\hbar} E t}$$

The second equation is a second order differential equation. if $\psi(\vec{x})$ is a solution to this equation then

$$\Psi(\vec{x}, t) = f(0) \psi(\vec{x}) e^{-\frac{i}{\hbar} E t}$$

is a solution to the original time-dependent Schrödinger equation.
*Equation (2.3) is referred to as the **time-independent** Schrödinger equation. It is an eigenvalue equation for the operator H with eigenfunction $\psi(\vec{x})$ and eigenvalue E.*
If $\{\psi_n\}_{n \in N}$ is a collection of wave functions with indexing set N that satisfy $H\psi_n = E_n \psi_n$ for all $n \in N$ then

$$\Psi(\vec{x}, t) = \sum_{n \in N} f(0) c_n \psi_n(\vec{x}) e^{-\frac{i}{\hbar} E_n t}$$

solves the time-dependent Schrödinger equation for all $c_n \in \mathbb{C}$.

2.3 Probabilistic Interpretation

Definition 2.3.1. *Let $\Psi(\vec{x},t)$ be a wave function describing a quantum mechanical particle. Then*

$$\rho(\vec{x},t) = |\Psi(\vec{x},t)|^2 = \Psi(\vec{x},t)^*\Psi(\vec{x},t)$$

is the ***probability density*** *of finding the particle at the position $\vec{x}$ and time t.*

Definition 2.3.2. *Let $\Psi(\vec{x},t)$ be a wave function and $\rho(\vec{x},t)$ its corresponding probability density. Then $\Psi(\vec{x},t)$ is said to be* ***normalised*** *if*

$$\int_{\mathbb{R}^3} \rho(\vec{x},t)\; d^3x = 1$$

Remark. *Any wave function that satisfies the Schrödinger equation is normalisable. Indeed, if $\psi(\vec{x},t)$ is a non-normalised solution for the Schrödinger equation then $c\,\psi(\vec{x},t)$ is also a solution for all $c \in \mathbb{C}$. We can hence choose C such that the wave function is normalised.*

Proposition 2.3.3. *Let $\Psi(\vec{x},t)$ be a wave function describing a quantum mechanical particle. Then the associated proability density $\rho(\vec{x},t)$ satisfies the following conservation law*

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

where $\vec{j} = \frac{i\hbar}{2m}(\Psi\vec{\nabla}\Psi^* - \Psi^*\vec{\nabla}\Psi)$.

Proof.

$$\begin{aligned}
\frac{\partial}{\partial t}\rho(\vec{x},t) &= \frac{\partial}{\partial t}\Psi(\vec{x},t)^*\Psi(\vec{x},t) \\
&= \frac{\partial}{\partial t}(\Psi(\vec{x},t)^*)\Psi(\vec{x},t) + \Psi(\vec{x},t)^*\frac{\partial}{\partial t}(\Psi(\vec{x},t)) \\
&= \frac{i}{\hbar}H^*(\Psi(\vec{x},t)^*)\Psi(\vec{x},t) - \frac{i}{\hbar}\Psi(\vec{x},t)^*H(\Psi(\vec{x},t)) \\
&= \frac{i}{\hbar}\left[H^*(\Psi(\vec{x},t)^*)\Psi(\vec{x},t) - \Psi(\vec{x},t)^*H(\Psi(\vec{x},t))\right] \\
&= \frac{i}{\hbar}\left[\left\{-\frac{\hbar^2}{2m}\Delta\Psi(\vec{x},t)^* + V^*\Psi(\vec{x},t)^*\right\}\Psi(\vec{x},t)\right.
\end{aligned}$$

$$
\begin{aligned}
&- \Psi(\vec{x},t)^* \left\{ -\frac{\hbar^2}{2m}\Delta\Psi(\vec{x},t) + V\Psi(\vec{x},t) \right\} \Big] \\
&= \frac{i}{\hbar}\left[-\frac{\hbar^2}{2m}\Delta\Psi(\vec{x},t)^*\Psi(\vec{x},t) + \frac{\hbar^2}{2m}\Delta\Psi(\vec{x},t)\Psi(\vec{x},t)^* \right] \\
&= \frac{i\hbar}{2m}\left[-\Psi(\vec{x},t)\Delta\Psi(\vec{x},t)^* + \Psi(\vec{x},t)^*\Delta\Psi(\vec{x},t) \right] \\
&= \frac{i\hbar}{2m}\vec{\nabla}\cdot\left[-\Psi(\vec{x},t)\vec{\nabla}\Psi(\vec{x},t)^* + \Psi(\vec{x},t)^*\vec{\nabla}\Psi(\vec{x},t) \right] \\
&= -\vec{\nabla}\cdot\vec{j}
\end{aligned}
$$

where we have used the fact that $V(\vec{x}) = V(\vec{x})^*$ □

Remark. *The above conservation law is referred to as the* ***continuity equation*** *and also arises in Maxwell's theory of electromagnetism. We see through calculus that*

$$\frac{d}{dt}\int_W \rho \, d^3x = -\oint \vec{j}\cdot d\vec{S}$$

This shows us that probability is conserved. It can leak out of W but can neither be created nor destroyed.

Definition 2.3.4. *We define the vector space $L^2(X)$ to be the set of functions*

$$L^2(X) = \left\{ \psi : X \to \mathbb{C} \,\middle|\, \int_X \psi(x)^*\psi(x)\, dx < \infty \right\}$$

where X is a measure space such as $\mathbb{R}$ or $\mathbb{R}^3$.

Definition 2.3.5. *We define a scalar product $\langle\cdot,\cdot\rangle$ on $L^2(X)$ by the following function*

$$
\begin{aligned}
&\langle\cdot,\cdot\rangle : L^2(X)\times L^2(X) \to \mathbb{C} \\
&\qquad (\psi(x),\phi(x)) \mapsto \langle\psi(x),\phi(x)\rangle = \int_X \psi(x)^*\phi(x)\, dx
\end{aligned}
$$

Definition 2.3.6. *Let $A : L^2(\mathbb{R}) \to L^2(\mathbb{R})$ be a linear operator and $\psi_1, \psi_2 : \mathbb{R} \to \mathbb{C}$ functions. Then A is called self-adjoint if*

$$\langle\psi_1, A\psi_2\rangle = \langle A\psi_1, \psi_2\rangle \;\forall\, \psi_1,\psi_2 \in L^2(\mathbb{R})$$

Definition 2.3.7. *Let Ψ be a wave function and A a linear self-adjoint operator. We define the* ***expectation value of A acting on Ψ*** *to be*

$$\langle A\rangle_\Psi := \langle \Psi, A\Psi\rangle = \int_{\mathbb{R}}^3 \Psi(\vec{x},t)^* A\Psi(\vec{x},t)\ d^3x$$

Proposition 2.3.8. *Let Ψ be a wave function and A linear self adjoint operator. Then the expectation value of A acting on Ψ is a real number.*

Proof.

$$\langle A\rangle_\Psi = \langle \Psi, A\Psi\rangle = \langle A\Psi, \Psi\rangle = \langle \Psi, A\Psi\rangle^* = \langle A\rangle_\Psi$$

□

2.4 Ehrenfest's Theorem

Proposition 2.4.1. *Let Ψ be a wave function. Then the expection of the position operator $\hat{x}$ on Ψ satisfies the classical physics relation between velocity and momentum*

$$m\frac{d}{dt}\langle \hat{x}\rangle_\Psi = \langle \hat{p}\rangle_\Psi$$

Proof. We prove the proposition for one space dimension. The proof for 3 space dimentions is analogous.

$$\begin{aligned}
m\frac{d}{dt}\langle \hat{x}\rangle_\Psi &= m\frac{d}{dt}\int_{\mathbb{R}} \Psi^* x \Psi\ dx \\
&= m\int_{\mathbb{R}} x\frac{d}{dt}\left(\Psi^*\Psi\right)\ dx \\
&= m\int_{\mathbb{R}} x\left(\frac{d}{dt}(\Psi^*)\Psi + \frac{d}{dt}(\Psi)\Psi^*\right)\ dx \\
&= m\int_{\mathbb{R}} x\left\{\frac{i}{\hbar}H^*(\Psi^*)\Psi - \frac{i}{\hbar}H(\Psi)\Psi^*\right\}\ dx \\
&= m\int_{\mathbb{R}} x\left\{\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi^* + V^*\Psi^*\right)\Psi - \left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V\Psi\right)\Psi^*\right\}\ dx \\
&= m\int_{\mathbb{R}} \frac{ix}{\hbar}\left\{\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi^* + V^*\Psi^*\right)\Psi - \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V\Psi\right)\Psi^*\right\}\ dx
\end{aligned}$$

$$
\begin{aligned}
&= m \int_{\mathbb{R}} \frac{ix}{\hbar} \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi^* \Psi + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi \Psi^* \right\} \, dx \\
&= \int_{\mathbb{R}} \frac{i\hbar x}{2} \left\{ -\frac{\partial^2}{\partial x^2} \Psi^* \Psi + \frac{\partial^2}{\partial x^2} \Psi \Psi^* \right\} \, dx \\
&= \frac{i\hbar}{2} \int_{\mathbb{R}} x \left\{ -\Psi \frac{\partial^2}{\partial x^2} \Psi^* + \Psi^* \frac{\partial^2}{\partial x^2} \Psi \right\} \, dx \\
&= \frac{i\hbar}{2} \int_{\mathbb{R}} x \left\{ \Psi^* \frac{\partial^2}{\partial x^2} \Psi - \Psi \frac{\partial^2}{\partial x^2} \Psi^* \right\} \, dx \\
&= \frac{i\hbar}{2} \int_{\mathbb{R}} x \frac{\partial}{\partial x} \left\{ \Psi^* \frac{\partial}{\partial x} \Psi - \Psi \frac{\partial}{\partial x} \Psi^* \right\} \, dx \\
&= \frac{i\hbar}{2} \left[x \left\{ \Psi^* \frac{\partial}{\partial x} \Psi - \left(\frac{\partial}{\partial x} \Psi^* \right) \Psi \right\} \right]_{-\infty}^{\infty} - \frac{i\hbar}{2} \int_{\mathbb{R}} \Psi^* \frac{\partial}{\partial x} \Psi - \Psi \frac{\partial}{\partial x} \Psi^* \, dx
\end{aligned}
$$

Now since Ψ is normalisable, we have that

$$
\begin{aligned}
&\int_{\mathbb{R}} |\Psi|^2 < \infty \\
&\implies |\Psi|^2 \sim \frac{1}{x^{1+\varepsilon}} \text{ as } |x| \to \infty, \text{ for some } \varepsilon > 0 \in \mathbb{R} \\
&\implies |\Psi| \sim x^{\frac{-(1+\varepsilon)}{2}} \text{ as } |x| \to \infty, \text{ for some } \varepsilon > 0 \in \mathbb{R} \\
&\implies \frac{\partial}{\partial x} |\Psi| \sim \frac{-(1+\varepsilon)}{2} x^{\frac{-(3+\varepsilon)}{2}} \text{ as } |x| \to \infty, \text{ for some } \varepsilon > 0 \in \mathbb{R} \\
&\implies |\Psi| \frac{\partial}{\partial x} |\Psi| \sim \frac{-(1+\varepsilon)}{2} x^{\frac{-(4+\varepsilon)}{2}} \text{ as } |x| \to \infty, \text{ for some } \varepsilon > 0 \in \mathbb{R} \\
&\implies x |\Psi| \frac{\partial}{\partial x} |\Psi| \sim \frac{-(1+\varepsilon)}{2} x^{-(1+\delta)} \text{ as } |x| \to \infty, \text{ for some } \delta > 0 \in \mathbb{R}
\end{aligned}
$$

Now since $lim_{x \to \infty} x^{-(1+\delta)} = 0$, we have that $x\Psi \frac{\partial}{\partial x} \Psi^*$ and $x\Psi^* \frac{\partial}{\partial x} \Psi$ both converge to zero. Hence the first integral in the last line of the result above vanishes and we are left with

$$
\begin{aligned}
m \frac{d}{dt} \langle \hat{x} \rangle_\Psi &= -\frac{i\hbar}{2} \int_{\mathbb{R}} \Psi^* \frac{\partial}{\partial x} \Psi - \Psi \frac{\partial}{\partial x} \Psi^* \, dx \\
&= \frac{i\hbar}{2} \int_{\mathbb{R}} \Psi \frac{\partial}{\partial x} \Psi^* - \Psi^* \frac{\partial}{\partial x} \Psi \, dx \\
&= \frac{1}{2} \int_{\mathbb{R}} \Psi (i\hbar \frac{\partial}{\partial x} \Psi^*) - \Psi^* \left(i\hbar \frac{\partial}{\partial x} \Psi \right) \, dx
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\int_{\mathbb{R}} \left(\Psi^*(-i\hbar\frac{\partial}{\partial x}\Psi)\right)^* - \Psi^*\left(i\hbar\frac{\partial}{\partial x}\Psi\right)\ dx \\
&= \frac{1}{2}\int_{\mathbb{R}} \left(\Psi^*\left(\frac{i}{\hbar}\frac{\partial}{\partial x}\Psi\right)\right)^* + \Psi^*\left(\frac{i}{\hbar}\frac{\partial}{\partial x}\Psi\right)\ dx \\
&= \frac{1}{2}\int_{\mathbb{R}} \left(\Psi^*\left(\hat{p}\Psi\right)\right)^* + \Psi^*\left(\hat{p}\Psi\right)\ dx \\
&= \frac{1}{2}\left[\int_{\mathbb{R}} \left(\Psi^*\left(\hat{p}\Psi\right)\right)^*\ dx + \int_{\mathbb{R}}\Psi^*\left(\hat{p}\Psi\right)\ dx\right] \\
&= \frac{1}{2}\left[\langle\Psi,\hat{p}\Psi\rangle^* + \langle\Psi,\hat{p}\Psi\rangle\right] \\
&= \frac{1}{2}\left[\langle\hat{p}\rangle_\Psi^* + \langle\hat{p}\rangle_\Psi\right] \\
&= \langle\hat{p}\rangle_\Psi
\end{aligned}
$$

where we have used the fact that the expectation value of a self-adjoint operator is real. □

Proposition 2.4.2. *Let Ψ be a wave function. Then the expectation value of the position operator on Ψ satisfies Newton's Second Law*

$$m\frac{d}{dt^2}\langle\hat{x}\rangle_\Psi = \langle -\frac{\partial}{\partial x}V\rangle_\Psi$$

Proof. We prove the proposition for one space dimension. The proof for 3 space dimentions is analogous.

$$
\begin{aligned}
m\frac{d}{dt^2}\langle\hat{x}\rangle_\Psi &= \frac{d}{dt}\langle\hat{p}\rangle_\Psi \\
&= \frac{d}{dt}\int_{\mathbb{R}}\Psi^*\hat{p}\Psi\ dx \\
&= \frac{d}{dt}\int_{\mathbb{R}}\Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\ dx \\
&= \int_{\mathbb{R}}\frac{\partial}{\partial t}\Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi\ dx \\
&= \int_{\mathbb{R}}\frac{\partial}{\partial t}\Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi\ dx \\
&= \int_{\mathbb{R}}\left(\frac{\partial}{\partial t}\Psi^*\frac{\partial}{\partial x}\Psi + \Psi^*\frac{\partial}{\partial x}\left(\frac{\partial}{\partial t}\Psi\right)\right)\ dx
\end{aligned}
$$

$$= \int_{\mathbb{R}} \left[\left(-i\hbar \frac{\partial}{\partial t} \Psi^* \right) \frac{\partial}{\partial x} \Psi - \Psi^* \frac{\partial}{\partial x} \left(i\hbar \frac{\partial}{\partial t} \Psi \right) \right] \, dx$$
$$= \int_{\mathbb{R}} \left[\frac{\partial}{\partial x} \Psi \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V^* \right) \Psi^* - \Psi^* \frac{\partial}{\partial x} \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right) \Psi \right] \, dx$$
$$= \int_{\mathbb{R}} \left[\frac{-\hbar^2}{2m} \frac{\partial \Psi}{\partial x} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{\partial \Psi}{\partial x} V \Psi^* + \frac{-\hbar^2}{2m} \Psi^* \frac{\partial^3 \Psi}{\partial x^3} - \Psi^* \frac{\partial (V\Psi)}{\partial x} \right] \, dx$$
$$= \int_{\mathbb{R}} \left[\frac{-\hbar^2}{2m} \left(\frac{\partial \Psi}{\partial x} \frac{\partial^2 \Psi^*}{\partial x^2} - \Psi^* \frac{\partial^3 \Psi}{\partial x^3} \right) + \cancel{\frac{\partial \Psi}{\partial x} V \Psi^*} - \Psi^* \frac{\partial V}{\partial x} \Psi - \cancel{\Psi^* \frac{\partial \Psi}{\partial x} V} \right] \, dx$$
$$= \frac{\hbar^2}{2m} \left(\underbrace{\int_{\mathbb{R}} \frac{\partial \Psi}{\partial x} \frac{\partial^2 \Psi^*}{\partial x^2} \, dx}_{A} - \underbrace{\int_{\mathbb{R}} \Psi^* \frac{\partial^3 \Psi}{\partial x^3} \, dx}_{B} \right) - \int_{\mathbb{R}} \Psi^* \frac{\partial V}{\partial x} \Psi \, dx$$

We can now integrate the term A by parts

$$\int_{\mathbb{R}} \frac{\partial \Psi}{\partial x} \frac{\partial^2 \Psi^*}{\partial x^2} \, dx = \cancelto{0}{\left[\frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} \right]_{-\infty}^{\infty}} - \int_{\mathbb{R}} \frac{\partial^2 \Psi}{\partial x^2} \frac{\partial \Psi^*}{\partial x} \, dx$$
$$= - \cancelto{0}{\left[\frac{\partial^2 \Psi}{\partial x^2} \Psi^* \right]_{-\infty}^{\infty}} + \int_{\mathbb{R}} \frac{\partial^3 \Psi}{\partial x^3} \Psi^* \, dx$$

where we have used a similar analytical process as the previous proposition's proof to show that the boundary terms vanish. We hence see that A cancels with B, leaving

$$m \frac{d}{dt^2} \langle \hat{x} \rangle_\Psi = - \int_{\mathbb{R}} \Psi^* \frac{\partial V}{\partial x} \Psi \, dx$$
$$= \int_{\mathbb{R}} \Psi^* \left(- \frac{\partial V}{\partial x} \Psi \right) \, dx$$
$$= \left\langle \Psi^*, \left(- \frac{\partial V}{\partial x} \Psi \right) \right\rangle$$
$$= \left\langle - \frac{\partial V}{\partial x} \right\rangle_\Psi$$

□

2.5 Uncertainity and the connection between eigenvalues and measurements

Definition 2.5.1. *Let Ψ be a wave function and A a linear operator acting on Ψ. We define the* ***uncertainty*** $(\Delta A)_\Psi$ *of a measurement of A to be*

$$(\Delta A)_\Psi = \sqrt{\langle (A - \langle A \rangle_\Psi)^2 \rangle_\Psi}$$

Proposition 2.5.2. *Let Ψ be a wave function and A a self-adjoint linear operator on Ψ. Then the uncertainty of the measurement of A acting on Ψ vanishes if and only if Ψ is an eigenfunction of A.*

Proof.

$$0 = (\Delta A)_\Psi^2 = \langle (A - \langle A \rangle_\Psi)^2 \rangle_\Psi = \langle \Psi, (A - \langle A \rangle_\Psi)^2 \Psi \rangle$$

Now note from previous results that

$$(A - \langle A \rangle_\Psi)^* = A^* - \langle A \rangle_\Phi^* = A - \langle A \rangle_\Phi$$

Hence

$$\begin{aligned}
\langle \Psi, (A - \langle A \rangle_\Psi)^2 \Psi \rangle &= \int_{\mathbb{R}} \Psi^* (A - \langle A \rangle_\Psi)^2 \Psi \, dx \\
&= \int_{\mathbb{R}} \Psi^* (A - \langle A \rangle_\Psi)^* (A - \langle A \rangle_\Psi) \Psi \, dx \\
&= \int_{\mathbb{R}} ((A - \langle A \rangle_\Psi) \Psi)^* (A - \langle A \rangle_\Psi) \Psi \, dx \\
&= \langle (A - \langle A \rangle_\Psi) \Psi, (A - \langle A \rangle_\Psi) \Psi \rangle
\end{aligned}$$

Returning to the original assumption we see that

$$\begin{aligned}
\langle (A - \langle A \rangle_\Psi) \Psi, (A - \langle A \rangle_\Psi) \Psi \rangle = 0 &\iff (A - \langle A \rangle_\Psi) \Psi = 0 \\
&\iff A\Psi = \langle A \rangle_\Psi \Psi
\end{aligned}$$

Therefore the uncertainty vanishes if and only if Ψ is an eigenfunction of A with eigenvalue $\langle A \rangle_\Psi$. □

Remark. *It is obvious that if there is no uncertainty in the measurement then there is no deviation from the expected value $\langle A \rangle_\Psi$. By the above, it follows that if there is no uncertainty in the measurement, the measured value of the operator A acting on Ψ is an eigenvalue of the operator A acting on Ψ.*

Chapter 3

Examples

3.1 Free Schrödinger equation: wave packets

Let us consider a free particle under the influence of the zero potential: $V = 0$. The Schrödinger equation thus reduces to the **free** Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$$

Since the Hamilton operator is not time-dependent, we can consider solutions to the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = E\Psi(x)$$

From a previous section, we know that the solutions to the time-independent equation are

$$\psi_k(x) \sim e^{ikx} \quad \text{where } k \in \mathbb{R}$$

Hence the solution to the original Schrödinger equation is

$$\Psi_k(x,t) \sim e^{ikx - i\omega_k t}$$

where $E_k = \frac{\hbar^2 k^2}{2m} = \omega_k \hbar$.

These represent plane waves which are not normalisable. However we can consider superpositions over k by taking the Fourier transform of the wave function which will give us a normalisable wave function

$$\Psi(x,t) = \frac{1}{2\pi}\int e^{i(kx-\omega_k t)}\hat{\Psi}(k)\ dk$$

We refer to each $\hat{\Psi}(k)$ as a **wave packet**.

We now consider the Gaussian wave packet

$$\hat{\Psi}(k) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-a^2(k-k_0)^2}$$

The contribution of each **k-mode** peaks at k_0 with a spread $\sim \frac{1}{a^2}$. Inserting into $\Psi(x,t)$, we see that

$$\Psi(x,t) = \frac{1}{2\pi}\int e^{i(kx-\omega_k t)}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-a^2(k-k_0)^2}\ dk$$

3.2 Particle in a box

We consider a particle confined to the interval $0 \leq x \leq l$ moving freely inside. The probability of finding the particle outside the interval must be 0 hence we seek solutions of the free Schrödinger equation with $\Psi(x) = 0$ for $x < 0$ and $x > l$.
Since the Schrödinger equation is a differential equation, we require that Ψ be continuous and differentiable. This sets a constraint of $\Psi(0) = \Psi(l) = 0$. We will use the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = E\Psi(x)$$

The general solution to $\Psi(x)$ dependents on the sign of E.

$\underline{E = 0}$

If E = 0, the general solution is of the form $\psi(x) = A + Bx$ where $A, B \in \mathbb{C}$. The constraint $\psi(0) = 0$ implies that $A = 0$ and $\psi(l) = 0$ implies that $B = 0$. Now, $\psi(x) = 0$ is not a normalisable solution hence it is impossible for $E = 0$.

$\underline{E < 0}$

If $E < 0$, the general solution is of the form

$$\psi(x) = Acosh\left(\sqrt{\frac{2m|E|}{\hbar^2}}x\right) + Bsinh\left(\sqrt{\frac{2m|E|}{\hbar^2}}x\right)$$

The constraint $\psi(0) = 0$ implies that $A = 0$ and we are left with

$$\psi(x) = Bsinh\left(\sqrt{\frac{2m|E|}{\hbar^2}}x\right)$$

The second constraint $\psi(l) = 0$ implies that $B = 0$. This is because the hyperbolic sine is non-zero everywhere except $x = 0$, forcing $B = 0$.
This solution is again impossible to normalise hence it is not possible for $E < 0$.

$\underline{E > 0}$

If $E > 0$, the general solution is of the form

$$\psi(x) = Acos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + Bsin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

The constraint $\psi(0) = 0$ implies that $A = 0$ and we are left with

$$\psi(x) = Bsin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

Now the constraint $\psi(l) = 0$ implies that

$$\begin{aligned}
&\sqrt{\frac{2mE}{\hbar^2}}l = n\pi \\
&\implies \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{l^2} \\
&\implies 2mE = \frac{\hbar^2 n^2\pi^2}{l^2} \\
&\implies E = \frac{\hbar^2 n^2\pi^2}{2ml^2}
\end{aligned}$$

where we have used the fact that the left hand side is strictly positive meaning we can discard the negative solutions of the sine wave. We refer to the discreteness of the energy by the **quantisation of energy** and we label each individual energy level by E_n. Each $n = 1, 2, 3, \ldots$ is referred to as a **quantum number**.

We therefore have a solution of

$$\psi_n(x) = B sin(\frac{n\pi x}{l})$$

We must now normalise this state:

$$\begin{aligned}
1 &= \int_{\mathbb{R}} |\psi(x)|^2 \, dx \\
&= |B|^2 \int_0^l sin^2\left(\frac{n\pi x}{l}\right) \, dx \\
&= \frac{|B|^2}{2} \int_0^l 1 - cos\left(\frac{2n\pi x}{l}\right) \, dx \\
&= \frac{l|B|^2}{2} \\
&\implies B = \sqrt{\frac{2}{l}}
\end{aligned}$$

Hence our final solution is

$$\psi_n(x) = \sqrt{\frac{2}{l}} \, sin\left(\frac{n\pi x}{l}\right)$$

We can combine this with the time solution found in a previous section to obtain a solution to the time-dependent Schrödinger equation:

$$\Psi_n(x,t) = \sqrt{\frac{2}{l}} \, sin\left(\frac{n\pi x}{l}\right) e^{-\frac{i}{\hbar}E_n t}$$

We shall now look at the expectation values of the position and momentum operators.

$$
\begin{aligned}
\langle \hat{x} \rangle_{\Psi_n} &= \int_{\mathbb{R}} \Psi_n^* x \Psi_n \, dx \\
&= \frac{2}{l} \int_0^l x sin^2 \left(\frac{n\pi x}{l} \right) \, dx \\
&= \frac{1}{l} \int_0^l x - x cos \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{1}{l} \left[\frac{x^2}{2} \right]_0^l + \frac{1}{l} \int_0^l x cos \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{l}{2} + \frac{1}{2n\pi} \left[x sin \left(\frac{2n\pi x}{l} \right) \right]_0^l - \frac{1}{l} \int_0^l sin \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{l}{2} + \cancelto{0}{\frac{1}{l} \left[cos \left(\frac{2n\pi x}{l} \right) \right]_0^l} \\
&= \frac{l}{2}
\end{aligned}
$$

Hence we expect to find the particle at the middle of the interval.

$$
\begin{aligned}
\langle \hat{x}^2 \rangle_{\Psi_n} &= \int_{\mathbb{R}} \Psi_n^* x^2 \Psi_n \, dx \\
&= \frac{1}{l} \int_0^l x^2 - x^2 cos \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{1}{l} \left[\frac{x^3}{3} \right]_0^l - \frac{1}{l} \int_0^l x^2 cos \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{l^2}{3} - \cancelto{0}{\frac{1}{2n\pi} \left[x^2 sin \left(\frac{2n\pi x}{l} \right) \right]_0^l} + \frac{1}{n\pi} \int_0^l x sin \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{l^2}{3} - \frac{l}{2n^2\pi^2} \left[x cos \left(\frac{2n\pi x}{l} \right) \right]_0^l + \frac{l}{n^2\pi^2} \int_0^l cos \left(\frac{2n\pi x}{l} \right) \, dx \\
&= \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2} + \cancelto{0}{\frac{l^2}{4n^3\pi^3} \left[sin \left(\frac{2n\pi x}{l} \right) \right]_0^l} \\
&= \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}
\end{aligned}
$$

We can now calculate the uncertainty of the position operator acting on Ψ_n:

$$\begin{aligned}(\Delta\hat{x})^2_{\Psi_n} &= \langle\hat{x}^2\rangle_{\Psi_n} - \langle\hat{x}\rangle^2_{\Psi_n}\\ &= \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2} - \frac{l^2}{4}\\ &= \frac{l^2}{12} - \frac{l^2}{2n^2\pi^2}\end{aligned}$$

The expectation value of the momentum operator (and its square) can also be calculated:

$$\begin{aligned}\langle\hat{p}\rangle_{\Psi_n} &= \int_{\mathbb{R}} \Psi_n^* \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_n \, dx\\ &= \frac{-i\hbar n\pi}{l}\int_0^l sin^2\left(\frac{n\pi x}{l}\right) cos\left(\frac{n\pi x}{l}\right) sin\left(\frac{n\pi x}{l}\right) \, dx\\ &= \frac{-i\hbar n\pi}{2l}\int_0^l sin^2\left(\frac{n\pi x}{l}\right) sin\left(\frac{2n\pi x}{l}\right) \, dx\\ &= \frac{-i\hbar n\pi}{2l}\int_0^l \left[1 - 2cos\left(\frac{2n\pi x}{l}\right)\right] sin\left(\frac{2n\pi x}{l}\right) \, dx\\ &= \frac{-i\hbar n\pi}{4l}\int_0^l sin\left(\frac{2n\pi x}{l}\right) \, dx + \frac{i\hbar n\pi}{4l}\int_0^l cos\left(\frac{2n\pi x}{l}\right) sin\left(\frac{2n\pi x}{l}\right) \, dx\\ &= \cancelto{0}{\frac{i\hbar}{8}\left[cos\left(\frac{2n\pi x}{l}\right)\right]_0^l} + \frac{i\hbar n\pi}{8l}\int_0^l sin\left(\frac{4n\pi x}{l}\right) \, dx\\ &= \cancelto{0}{-\frac{i\hbar n\pi}{32l}\left[cos\left(\frac{4n\pi x}{l}\right)\right]_0^l}\\ &= 0\end{aligned}$$

We therefore expect the particle to have vanishing momentum.

$$\begin{aligned}\langle\hat{p}^2\rangle_{\Psi_n} &= \int_{\mathbb{R}} \Psi_n^* \left(-\hbar^2\frac{\partial^2}{\partial x^2}\right)\Psi_n \, dx\\ &= -\frac{4n\pi\hbar^2}{l^2}\int_0^l sin^2\left(\frac{n\pi x}{l}\right)\frac{\partial}{\partial x}\left[cos\left(\frac{n\pi x}{l}\right) sin\left(\frac{n\pi x}{l}\right)\right] \, dx\\ &= -\frac{2n\pi\hbar^2}{l^2}\int_0^l sin^2\left(\frac{n\pi x}{l}\right)\frac{\partial}{\partial x}\left[sin\left(\frac{2n\pi x}{l}\right)\right] \, dx\end{aligned}$$

$$
\begin{aligned}
&= -\frac{4n^2\pi^2\hbar^2}{l^3}\int_0^l sin^2\left(\frac{n\pi x}{l}\right) cos\left(\frac{2n\pi x}{l}\right)\ dx \\
&= -\frac{2n^2\pi^2\hbar^2}{l^3}\int_0^l \left[1 - cos\left(\frac{2n\pi x}{l}\right)\right] cos\left(\frac{2n\pi x}{l}\right)\ dx \\
&= -\frac{2n^2\pi^2\hbar^2}{l^3}\int_0^l cos\left(\frac{2n\pi x}{l}\right)\ dx + \frac{n^2\pi^2\hbar^2}{l^2}\int_0^l cos^2\left(\frac{2n\pi x}{l}\right)\ dx \\
&= \cancelto{0}{-\frac{n\pi\hbar^2}{l^2}\left[sin\left(\frac{2n\pi x}{l}\right)\right]_0^l} + \frac{2n^2\pi^2\hbar^2}{l^3}\int_0^l cos^2\left(\frac{2n\pi x}{l}\right)\ dx \\
&= \frac{n^2\pi^2\hbar^2}{l^3}\int_0^l cos\left(\frac{4n\pi x}{l}\right) + 1\ dx \\
&= \cancelto{0}{\frac{n\pi\hbar^2}{4l^2}\left[sin\left(\frac{4n\pi x}{l}\right)\right]_0^l} + \frac{n^2\pi^2\hbar^2}{l^3}[x]_0^l\ dx \\
&= \frac{n^2\pi^2\hbar^2}{l^2}
\end{aligned}
$$

We can now calculate the uncertainity of the momentum operator acting on Ψ

$$
\begin{aligned}
(\Delta\hat{p})^2_{\Psi_n} &= \langle\hat{p}^2\rangle_{\Psi_n} - \langle\hat{p}\rangle^2_{\Psi_n} \\
&= \frac{n^2\pi^2\hbar^2}{l^2}
\end{aligned}
$$

Observation 3.2.1. *The uncertainties of the position and momentum operators satisfy Heisenberg's uncertainity principle (to be covered later):*

$$
\begin{aligned}
(\Delta\hat{x})_{\Psi_n}(\Delta\hat{p})_{\Psi_n} &= \sqrt{\frac{l^2}{12} - \frac{l^2}{2n^2\pi^2}}\frac{n\pi\hbar}{l} \\
&= n\pi\hbar\sqrt{\frac{2n^2\pi^2 - 12}{24n^2\pi^2}} \\
&= \frac{n\pi\hbar}{2}\sqrt{\frac{n^2\pi^2 - 6}{3n^2\pi^2}} \\
&= \frac{\hbar}{2}\sqrt{\frac{n^2\pi^2 - 6}{3}} \\
&\geq \frac{\hbar}{2}
\end{aligned}
$$

Observation 3.2.2. *The classical expectation value of the position agrees with the quantum mechanical one. Since, a priori, we do not know the position of the particle in the box, all values are equally likely and we have:*

$$\langle x \rangle_{class} = \frac{1}{l} \int_0^l x \, dx = \frac{l}{2} = \langle \hat{x} \rangle_{\Psi_n}$$

where $\frac{1}{l}$ *is the normalisation factor. The classical expectation value of the square of the position does not agree however:*

$$\langle x^2 \rangle_{class} = \frac{1}{l} \int_0^l x^2 \, dx = \frac{l^2}{3}$$

We see that $\langle \hat{x}^2 \rangle_{\Psi_n}$ *approaches this value as* $n \to \infty$*. This is suggestive of the* ***correspondence principle*** *where we expect classical physics to emerge from quantum mechanics for large quantum numbers.*

3.3 Potential barrier

We now consider the case of paticles approaching a potential barrier from the left. The potential barrier is described by

$$V(x) = \begin{cases} 0 & \text{if } x < 0 \\ V_0 & \text{if } x \geq 0 \end{cases}$$

where V_0 is some real constant.

In classical mechanics, we would expect particles satisfying $E_{kin} < V_0$ to be reflected at $x = 0$ and to pass through the barrier if $E_{kin} > V_0$. There would be no mixing between the two states.
In quantum mechanics, there is a very different picture as we shall see.

We want to solve the time-independent Schrödinger equation for two situations:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) = E\Psi(x) \qquad \text{for } x < 0 \tag{3.1}$$

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) = (E - V_0)\Psi(x) \qquad \text{for } x \geq 0 \tag{3.2}$$

We require $\Psi(x)$ and $\frac{\partial\Psi(x)}{\partial x}$ to be both continuous.

The general solution to (3.1) is

$$\Psi_1(x) = Ae^{ikx} + Be^{-ikx}$$

where $k = \frac{1}{\hbar}\sqrt{2mE}$. The first term of $\Psi_1(x)$ represents a plane wave coming in from the left and the second term represents reflected plane waves.
The general solution to (3.2) is

$$\Psi_2(x) = Ce^{ilx} + De^{-ilx}$$

where $l = \frac{1}{\hbar}\sqrt{2m(E - V_0)}$

$\underline{E > V_0}$
We can assume that for $x \geq 0$, there are no particles coming from the right, thus we can set $D = 0$.
We now apply the conditions of continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = 0$:

$$\begin{aligned}
\Psi_1(0) = \Psi_2(0) &\implies A + B = C \\
\Psi_1'(0) = \Psi_2'(0) &\implies k(A - B) = lC = l(A + B) \\
\implies B = A\frac{k-l}{k+l}, C = A\frac{2k}{k+l}
\end{aligned}$$

We will now consider the probability current associated with the system. Recall from a previous section that the probability current j is

$$j(x) = \frac{\hbar}{2mi}\left(\Psi(x)^*\frac{\partial}{\partial x}\Psi(x) - \Psi(x)\frac{\partial}{\partial x}\Psi(x)^*\right)$$

We define the **transmission current** j_t to be the probability current related to the number of particles that get through the barrier

$$\begin{aligned}
j_t(x) &= \frac{\hbar}{2mi}\left(ilC^*e^{-ilx}Ce^{ilx} + ilCe^{ilx}C^*e^{-ilx}\right) \\
&= \frac{l\hbar|C|^2}{m}
\end{aligned}$$

We define the **reflection current** j_r to be the probability current related to the number of particles that are reflected at $x = 0$

$$\begin{aligned}
j_r(x) &= \frac{\hbar}{2mi}\left(-ikB^*e^{ikx}Be^{-ikx} - ikBe^{-ikx}B^*e^{ikx}\right) \\
&= -\frac{k\hbar|B|^2}{m}
\end{aligned}$$

We define the **incoming current** j_{in} to be the probability current related to the number of particles that are coming from the left

$$\begin{aligned} j_{in}(x) &= \frac{\hbar}{2mi}\left(ikA^*e^{-ikx}Ae^{ikx} + ikAe^{ikx}Ae^{-ikx}\right) \\ &= \frac{k\hbar|A|^2}{m} \end{aligned}$$

We can now define two useful quantities, the **reflection coefficient** R and the **transmission coefficient** R:

$$\begin{aligned} R &:= \left|\frac{j_r}{j_{in}}\right| \\ T &:= \left|\frac{j_t}{j_{in}}\right| \end{aligned}$$

It is easy to show that $R + T = 1$. In the example we have been studying, we have that

$$\begin{aligned} R &= \left(\frac{k-l}{k+l}\right)^2 \\ T &= \frac{|4kl|}{(k+l)^2} \end{aligned}$$

We now see that in this case, even though $E > V_0$, there is a non-vanishing probability that a quantum mechanical particle will be reflected at the barrier. This is a stark difference from classical mechanics.

$\underline{E < V_0}$ In this case, the solution for (3.2) is

$$\Psi_2(x) = C'e^{-l'x} + D'e^{l'x}$$

where $l' = \frac{1}{\hbar}\sqrt{2m(V_0 - E)}$.
We can once again set $D' = 0$ so we are left with

$$\Psi_2(x) = C'e^{-l'x}$$

The continuity conditions of Ψ and Ψ' imply that $A+B = C'$ and $k(A-B) = -l'C'$. This gives us

$$\begin{aligned} B &= A\frac{k-il'}{k+il'} \\ C' &= A\frac{2k}{k+il'} \end{aligned}$$

We see that $C \neq 0$ hence there is a non-zero probability of finding a quantum mechanical particle beyond the barrier, despite the fact that $E < V_0$. This is an example of the **tunneling** effect.

3.4 Potential well

We will now look at an example of a system involving a potential well described by

$$V(x) = \begin{cases} -V_0 & \text{if } -l \leq x \leq l \\ 0 & \text{if } |x| > l \end{cases}$$

for some real constant $V_0 > l$.
We see that since $V(x) = V(-x)$ and $\frac{\partial^2}{\partial x^2} = \frac{\partial^2}{\partial(-x)^2}$, the Hamilton operator $\hat{H}$ is invariant under $x \mapsto -x$. This implies that if $\psi(x)$ satisfies $\hat{H}\psi(x) = E\psi(x)$ then so does $\psi(-x)$. Therefore $\psi_{ev}(x) := \frac{1}{2}(\psi(x) + \psi(-x))$ and $\psi_{odd}(x) := \frac{1}{2}(\psi(x) - \psi(-x))$ are also both solutions of the Schrödinger equation, We can therefore look for even and odd solutions seperately. We restrict ourselves to the case of even functions for the moment and distinguish two cases:

$\underline{-V_0 < E < 0}$ This case represents the bound state particles - in other word, particles in a bounded region of space. Substituting the potential into the time-independent Schrödinger equation, we have that

$$\psi''(x) = \begin{cases} k_{out}^2\psi(x) & \text{if } |x| > l \\ -k_{in}^2\psi(x) & \text{if } |x| \leq l \end{cases}$$

where $k_{out} = \frac{1}{\hbar}\sqrt{-2mE}$ and $k_{in} = \frac{1}{\hbar}\sqrt{2m(E + V_0)}$ It follows that the solution is

$$\psi(x) = \begin{cases} Ae^{K_{out}x} & \text{if } x < -l \\ B\cos(k_{in}x) & \text{if } |x| \leq l \\ Ae^{-k_{out}x} & \text{if } x > l \end{cases}$$

Now, the continuity of $\psi(x)$ and $\psi'(x)$ at $x = -l$ implies that

$$Ae^{-k_{out}l} = B\cos(k_{in}l)$$
$$Ak_{out}e^{-k_{out}l} = Bk_{in}\sin(k_{in}l)$$

Dividing the first equation by the second, we have that

$$k_{out} = k_{in}\tan(k_{in}l) \tag{3.3}$$

In addition, from the definition of k_{out} and k_{in} we have that

$$\begin{aligned} k_{out}^2 + k_{in}^2 &= \frac{1}{\hbar^2}(-2mE + 2mE + 2mV_0) \\ &= \frac{2m}{\hbar^2}V_0 \end{aligned} \tag{3.4}$$

From graph of Equation (3.4) is simply a circle. Taking the intersection of this graph and that of Equation (3.3) (in the $K_{out} - K_{in}$ plane), we see that there are only finitely many solutions for k_{out} and k_{in}. This implies that there are only finitely many values that the energy of the bound states can take. In other words, the energy for the bound states are quantised.

3.5 Particle in a delta potential

Consider a potential $V(x) = -V_0\delta(x)$ where V_0 is a positive real constant and δ is the delta 'function' (distribution) defined by

$$\int_{-\infty}^{\infty} f(x)\delta(x)\, dx = f(0)$$

We want to solve the time-independent Schrödinger equation for this potential with the extra condition that the solution is continuous everywhere.
Now, $\delta(x)$ behaves like an infinitely high peak concentrated at $x = 0$. Hence we can assume that $\delta(x) = 0$ for $x \neq 0$. We have the following for the Shrödinger equations away from $x = 0$:

$$\frac{-h^2}{2m}\frac{\partial^2}{\partial x^2}\psi_I(x) = E\psi_I(x) \qquad \text{for } x < 0 \tag{3.5}$$

$$\frac{-h^2}{2m}\frac{\partial^2}{\partial x^2}\psi_{II}(x) = E\psi_{II}(x) \qquad \text{for } x < 0 \tag{3.6}$$

The general solutions to Equations (3.5) and (3.6) are as follows

$$\begin{aligned} \psi_I(x) &= Ae^{ikx} + Be^{-ikx} \\ \psi_{II}(x) &= Ce^{ikx} + De^{-ikx} \end{aligned}$$

where $k^2 = \frac{2mE}{\hbar^2}$ and A, B, C, D are some complex constants. We now consider only the case where $E < 0$ for normalisable solutions:

$\underline{E < 0}$ If $E < 0$ then k is imaginary. Take $k = iK$ for some positive real constant K. We require normalisable wave functions so we must have that

$\psi_I(x) \to 0$ for $x \to -\infty$ and $\psi_{II}(x) \to 0$ for $x \to \infty$. The general solutions are in the form

$$\psi_I(x) = Ae^{-Kx} + Be^{Kx}$$
$$\psi_{II}(x) = Ce^{-Kx} + De^{Kx}$$

We see that in order for these equations to be normalisable, we must have that $A = D = 0$. Now the requirement of continuity at $x = 0$ means that $\lim_{\varepsilon\to 0} \psi_I(\varepsilon) = \lim_{\varepsilon\to 0} \psi_{II}(\varepsilon)$ (we require the use of limits as these functions are not defined at 0). This is only true if $B = C$.
Now we consider the Schrödinger equation including the point $x = 0$

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) - V_0\delta(x)\psi(x) = E\psi(x)$$

Rearranging to isolate the derivative it follows that

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{-2mE}{\hbar^2}\psi(x) - \frac{2mV_0}{\hbar^2}\delta(x)\psi(x)$$

Integrating both sides with respect to x between $-\varepsilon$ and ε (for some real constant ε) and then applying the fundamental theorem of calculus yields

$$\psi'(\varepsilon) - \psi'(-\varepsilon) = \frac{-2mE}{\hbar^2}\int_{\varepsilon}^{\varepsilon} \psi(x)\, dx - \frac{2mV_0}{\hbar^2}\int_{\varepsilon}^{\varepsilon} \psi(x)\delta(x)\, dx \tag{3.7}$$

From previous analysis of the general solution, we know that $\psi(0) = B$. Combining this with the definition of the delta function, Equation (3.7) becomes

$$\psi'(\varepsilon) - \psi'(-\varepsilon) = \frac{-2mE}{\hbar^2}\int_{\varepsilon}^{\varepsilon} \psi(x)\, dx - \frac{2mBV_0}{\hbar^2}\, dx \tag{3.8}$$

We can also see that

$$\begin{aligned}\psi'(\varepsilon) - \psi'(-\varepsilon) &= \frac{\partial}{\partial x}\Psi_{II}(x)\bigg|_{x=\varepsilon} - \frac{\partial}{\partial x}\Psi_I(x)\bigg|_{x=-\varepsilon} \\ &= -BKe^{-K\varepsilon} - BKe^{K\varepsilon}\end{aligned}$$

Now taking the limit $\varepsilon \to 0$ of Equation (3.8) with the above, we are left with

$$-2BK = -\frac{-2mBV_0}{\hbar^2}$$

this implies that $K = \frac{mV_0}{\hbar^2}$. Now since $K = ik$, we have that

$$\frac{mV_0}{\hbar^2} = ik$$
$$\frac{m^2V_0^2}{\hbar^4} = -k^2$$
$$\frac{m^2V_0^2}{\hbar^4} = -\frac{2mE}{\hbar^2}$$
$$E = -\frac{mV_0^2}{2\hbar^2}$$

We see that the delta potential admits one bound state (solution with normalisable wave function) with energy $E = -\frac{mV_0^2}{2\hbar^2}$.

Chapter 4

General Formulation of Quantum Mechanics

4.1 Hilbert spaces

Definition 4.1.1. *Let V be a vector space over $\mathbb{C}$. We define a* ***scalar product*** $\langle \cdot, \cdot \rangle$ *on V to be a map* $\langle \cdot, \cdot \rangle : V \times V \to \mathbb{C}$ *satisfying the following axioms:*

1. $\langle x, y \rangle = \langle y, x \rangle^*$
2. $\langle x, \lambda y + \mu z \rangle = \lambda \langle x, y \rangle + \mu \langle x, z \rangle$
3. $\langle x, x \rangle \geq 0$ *with equality if and only if* $x = 0$

where $x, y, z \in V$ and $\lambda \in \mathbb{C}$.

Definition 4.1.2. *Let V be a vector space equipped with a scalar product $\langle \cdot, \cdot \rangle$. We define an* ***orthonormal basis*** *to be a basis $\{\psi_i\}_{i \in I}$ with $\langle \psi_i, \psi_j \rangle = \delta_{ij}$ for all $i, j \in I$.*

Remark. *Let V be a vector space $\{\psi_i\}_{i \in I}$ be an orthonormal basis of V. Let $x, y \in V$. Then we can express x and y in terms of the basis as follows:*

$$\sum_{i \in I} \alpha_i \psi_i, \quad y = \sum_{j \in J} \beta_j \psi_j$$

where $\alpha_i, \beta_i \in \mathbb{C}$. It follows that

$$\langle x, y \rangle = \sum_{i,j} \alpha_i^* \beta_j \langle \psi_i, \psi_j \rangle = \sum_{i,j} \alpha_i^* \beta_j \delta_{ij} = \sum_i \alpha_i^* \beta_i$$

Definition 4.1.3. *Let V be a vector space and* $\{\psi_i\}_{i\in I} \subseteq V$ *a sequence. We say that* $\{\psi_i\}_{i\in I}$ ***converges*** *to* $\psi \in V$ *if* $\lim_n ||\psi_n - \psi|| = 0$.

Definition 4.1.4. *Let V be a vector space and* $\{\psi_n\}_{n\in\mathbb{N}} \subseteq V$ *a sequence. We say that* $\{\psi_n\}_{n\in\mathbb{N}}$ *is a* ***Cauchy sequence*** *if*

$$\forall\, \varepsilon > 0, \exists\, n \in \mathbb{N}\ s.t\ ||\psi_n - \psi_m|| < \varepsilon\ \forall\, n, m \in \mathbb{N}$$

Let V be a vector space. We say that V is **complete** if every Cauchy sequence in V converges.

Definition 4.1.5. *Let V be a vector space over* $\mathbb{C}$ *that is complete and equipped with a scalar product. Then we say that V is a* ***Hilbert space*** *and we denote it by* $\mathcal{H}$.

Definition 4.1.6. *Let* $\mathcal{H}$ *be a Hilbert space. We say that* $\mathcal{H}$ *is* ***seperable*** *if it has a countable basis.*

Example 4.1.7. $\mathcal{H} = \mathbb{C}^N$ *with the standard scalar product*

$$\langle x, y\rangle = \sum_{i=1}^{N} x_i^* y_i$$

Example 4.1.8.

$$\mathcal{H} = l^2 := \left\{ (a_1, a_2, \dots) \;\middle|\; a_i \in \mathbb{C}, \sum_{i=1}^{\infty} |a_i|^2 < \infty \right\}$$

with the scalar product

$$\langle a, b\rangle := \sum_{i=1}^{\infty} a_i^* b_i$$

Example 4.1.9.

$$\mathcal{H} = L^2(\mathbb{R}^d) = \left\{ f : \mathbb{R}^d \to \mathbb{C} \;\middle|\; \int_{\mathbb{R}^d} |f(x)|^2\, d^d x < \infty \right\}$$

with the scalar product

$$\langle f, g\rangle := \int_{\mathbb{R}^d} f^*(x) g(x)\, d^d x$$

$L^2(\mathbb{R}^d)$ is seperable. For example, with $d = 1$, the functions

$$\psi_m(x) := x^m e^{-x^2}$$

with $m \in \mathbb{N}$ form a basis for $L^2(\mathbb{R})$

Definition 4.1.10. *Let V be a vector space over the complex numbers. The* ***dual space*** *of V is*

$$V := \{f : V \to \mathbb{C} \,|\, f \text{ is linear and continuous w.r.t the metric on } V\}$$

Any vector $\psi \in V$ gives an element $L_\psi \in V^*$.

Example 4.1.11. *Let V be a vector space and V^* its dual. Let $\psi\phi, \in V$ and consider the function $L_\psi(\phi) := \langle \psi, \phi \rangle$. It is indeed linear since $\langle \cdot, \cdot \rangle$ is linear in the second argument. We can also see that if $L_\psi \neq L_\phi$ if $\psi \neq \phi$. It follows that V injects into its dual space.*
If $V = \mathcal{H}$ is a Hilbert space then it can be shown that any $L \in \mathcal{H}$ is of the form $L = L_\phi$ for some $\phi \in \mathcal{H}$ and hence $\mathcal{H} \cong \mathcal{H}^*$.
We note that the map $\phi \to L_\phi$ is anti-linear:

$$L_{\alpha_1\psi_1 + \alpha_2\psi_2} = \alpha_1^* L_{\psi_1} + \alpha_2^* L_{\psi_2}$$

$\forall\, \alpha_i \in \mathbb{C}, \forall\, \psi_i \in \mathcal{H}$

Notation 4.1.12. *Let $\mathcal{H}$ be a Hilbert space and $\psi, \phi \in \mathcal{H}$. We rewrite $\langle \psi, \psi \rangle$ as $\langle \psi | \psi \rangle$ and seperate the scalar product into two seperate entities $\langle \psi | \in \mathcal{H}^*$ (**bra**) and $| \phi \rangle \in \mathcal{H}$ (**ket**). This is referred to as **Dirac's bra-ket notation**.*

Remark. *Dirac's notation allows us to write down objects such as $|\phi\rangle \langle\psi|$ and determine what they do easily. $(|\phi\rangle \langle\psi|) |x\rangle = |\phi\rangle \langle\phi|x\rangle$. Hence $|\phi\rangle \langle\psi|$ is just a linear map from $\mathcal{H} \to \mathcal{H}$.*

4.2 Linear operators

Definition 4.2.1. *Let $\mathcal{H}$ be a Hilbert space. A* ***linear operator*** *is a map $A : \mathcal{H} \to \mathcal{H}$ where $A(\lambda x + \mu y) = \lambda Ax + \mu Ay \;\forall\, x, y \in \mathcal{H}, \forall\, \lambda, \mu \in \mathbb{C}$.*

Definition 4.2.2. *Let $\mathcal{H}$ be a Hilbert space and A a linear operator on $\mathcal{H}$. The* ***adjoint*** *of A is the linear operator $A^\dagger$ defined by*

$$\langle x, A^\dagger y \rangle = \langle Ax, y \rangle$$

for all $x, y \in \mathcal{H}$.

Definition 4.2.3. *Let $\mathcal{H}$ be a Hilbert space and A a linear operator on $\mathcal{H}$. We say that A is **self-adjoint** if $A = A^\dagger$.*

Definition 4.2.4. *Let $\mathcal{H}$ be a Hilbert space and A a linear operator on $\mathcal{H}$. We say that A is **unitary** if $UU^\dagger = U^\dagger U = 1_{\mathcal{H}}$*

Proposition 4.2.5. *Let $\mathcal{H}$ be a Hilbert space and A a self adjoint operator. Then $U = e^{iA}$ is unitary.*

Proof. It suffices to show that $U^\dagger = U^{-1}$. First consider e defined as a power series. Then

$$U^\dagger = \left(e^{iA}\right)^\dagger = e^{(iA)^\dagger} = e^{-iA^\dagger} = e^{-iA} = U^{-1}$$

as required. □

Definition 4.2.6. *Let $\mathcal{H}$ be a Hilbert space. We define the **othogonal complement** of ψ in $\mathcal{H}$ to be the set*

$$\psi^\perp := \{\varphi \in \mathcal{H} \mid \langle \varphi, \psi \rangle = 0\}$$

Remark. *For a self adjoint operator, we have that $A\psi^\perp \subseteq \psi^\perp$*

Example 4.2.7. *$\mathcal{H} = \mathbb{C}^N$ equipped with the standard inner product. The linear operators are $N \times N$ matrices A over $\mathbb{C}$ where $A^\dagger = (A^T)^*$.*

Example 4.2.8. *Let $\mathcal{H}$ be any Hilbert space and $|\psi\rangle \in \mathcal{H}$ a normalised vector (i.e $\langle \psi|\psi\rangle = 1$). Then $P_\psi := |\psi\rangle \langle \psi|$ is a self adjoint operator with $P_\psi^2 = P_\psi$. It is referred to as a **projection operator**.*

Example 4.2.9. *$\mathcal{H} = L^2(\mathbb{R})$. An example of a linear operator on this space is the **parity operator** P defined by $(P\psi)(x) = \psi(-x)$. It is self adjoint and unitary.*
The position operator $\hat{x}$ defined by $(\hat{x}\psi)(x) = x\psi(x)$. We can see that it is only defined (and hence self-adjoint) for certain elements of $\mathcal{H}$. Indeed, $\langle \psi_1|x\psi_2\rangle = \langle x\psi_1|\psi_2\rangle$. But $\psi \in L^2(\mathbb{R})$ does not imply that $\hat{x}\Psi \in L^2(\mathbb{R})$.
We also face the same problem with the momentum operator $\hat{p}\psi(x) = \frac{h}{i}\frac{\partial}{\partial x}\psi(x)$. We require that ψ be differentiable almost everywhere and for it and its derivative to be square integrable.

Remark. *Further to the previous example, we also note that the eigenvectors of such operators may not be in $L^2(\mathbb{R})$. For example, $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ has eigenfunctions $\psi_k(x) = e^{ikx}$ for some real constant k. This is not a square integrable function.*

Theorem 4.2.10. *(Spectral Theorem)*
Let $\mathcal{H}$ be a Hilbert space. Let $A : \mathcal{H} \to \mathcal{H}$ be a self adjoint operator. Then there exists an orthonormal basis $\psi_1, \dots, \psi_N$ of $\mathcal{H}$ made up of eigenvectors of A. In that basis, $A = \sum_n a_n |\psi_n\rangle \langle\psi_n|$ where a_n are the eigenvalues of A0

Proposition 4.2.11. *Let $\mathcal{H}$ be a Hilbert space and A a self adjoint operator on $\mathcal{H}$ with eigenvalues a_i for $1 \leq i \leq n$. Let $|\psi\rangle \in \mathcal{H}$ be a normalisable state. Furthermore, let $\{\psi_m\}$ be an orthonormal basis for $\mathcal{H}$. Then the expectation value $\langle A \rangle_\psi$ can be given by:*

$$\langle A \rangle_\psi = \sum_l |c_l|^2 a_l$$

where the c_i are the $\{\psi_m\}$-coordinates of $|\psi\rangle$ and the summation index l runs over the set of eigenvalues of A.

Proof. We can express $|\psi\rangle$ in terms of the orthonormal basis as follows:

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

for some $c_n \in \mathbb{C}$. We therefore have that

$$\begin{aligned}\langle A \rangle_\psi &= \langle \psi | A\psi \rangle \\ &= \sum_{n,m} c_n^* c_m \langle \psi_n | A\psi_m \rangle\end{aligned}$$

Applying the spectral theorem yields

$$\begin{aligned}
\langle A\rangle_\psi &= \sum_{n,m,l} c_n^* c_m \langle\psi_n| a_l |\psi_l\rangle \langle\psi_l|\psi_m\rangle \\
&= \sum_{n,m,l} c_n^* c_m a_l \langle\psi_n|\psi_l\rangle \langle\psi_l|\psi_m\rangle \\
&= \sum_{n,m,l} c_n^* c_m a_l \delta_{nl}\delta_{ml} \\
&= \sum_{l} c_l^* c_l a_l \\
&= \sum_{l} |c_l|^2 a_l
\end{aligned}$$

□

Remark. *This allows us the refine the interpretation of the expectation value. $\langle A\rangle_\psi$ is the mean value and the probability of obtaining the result a_l when measuring A, in a system of state ψ, is given by $|c_l|^2$.*
We can also formulate this in terms of projection operators. Let $A = \sum_n a_n |\psi_n\rangle\langle\psi_n|$ be a self adjoint operator with eigenvalues a_n and $|\psi_n\rangle$ an orthonormal basis of eigenstates. For a given eigenvalue a of A, we define the projection operator onto the a-eigenspace of A by:

$$\begin{aligned}
&P_a^A : \mathcal{H} \to \mathcal{H} \\
&P_a^A = \sum_{m \ s.t \ A|\psi_m\rangle = a|\psi_m\rangle} |\psi_m\rangle\langle\psi_m|
\end{aligned}$$

Then the probability of finding a when measuring A, if the system is in the state $|\psi\rangle$ is

$$p(a) = \langle\psi, P_a^A \psi\rangle$$

Proposition 4.2.12. *Let $\mathcal{H}$ be a Hilbert space and A and B self-adjoint operators on $\mathcal{H}$. Then $AB = BA$ if and only if there exists an orthonormal basis $|\psi_n\rangle$ of $\mathcal{H}$ consisting of common eigenvectors of A and B.*

Proof. We prove only the forward direction. Let $A\psi = a\psi$ were ψ is an eigenvector of A and a its corresponding eigenvalue. We have that $AB\psi =$

$BA\psi = aB\psi$. Therefore $B\psi$ is again an A-eigenvector with the same eigenvalue as ψ. It follows that B maps the a-eigenspace of A into itself. We can hence find an orthonormal basis of B-eigenvectors inside the a-eignspace as required. □

4.3 Axioms of Quantum Mechanics

We shall now formulate Quantum Mechanics in a more abstract fashion using the following axioms:

1. The state of a quantum mechanical system is described by normalised elements ψ of a Hilbert space $\mathcal{H}$
2.
   - Measurable quantities are described by self-adjoint operators $A : \mathcal{H} \to \mathcal{H}$
   - The only possible measurements of A are eigenvalues a of A
   - If the system is in the state ψ, the probability of finding a as a result of measuring A is $p(a) = \langle \psi, P_a^A \psi \rangle$ where $P_a^A : \mathcal{H} \to \mathcal{H}$ is the projection onto the a-eigenspace of A.
   - Immediately after a measurement of A that results in a, the system is in an eigenstate ψ_a of A. This is known as the **collapse of the wave function**.
3. The time evolution of the system is determined by the Hamliltonian operator H where $i\hbar \frac{\partial}{\partial t}\psi(t) = H\psi(t)$

4.4 Heisenberg's Uncertainty Relation

Notation 4.4.1. *Let A and B be two objects that can be multiplied together. Their* ***commutator*** *is denoted $[A, B]$ and is equal to $AB - BA$.*

Lemma 4.4.2. *Let A and B two self adjoint operators. Then $C := -i[A, B]$ is also a self adjoint operator.*

Proof. Consider a normalised state ψ. We want to show that $\langle \psi, C\psi \rangle = \langle C\psi, \psi \rangle$. We have that

$$\begin{aligned} \langle \psi, C\psi \rangle &= \langle \psi, -i(AB - BA)\psi \rangle \\ &= \langle \psi, -iAB + iBA)\psi \rangle \\ &= -i \langle \psi, AB\psi \rangle + i \langle \psi, BA\psi \rangle \end{aligned}$$

Now, since A and B are both self adjoint, we have that

$$\begin{aligned} \langle \psi, C\psi \rangle &= -i \langle A\psi, B\psi \rangle + i \langle B\psi, A\psi \rangle \\ &= -i \langle BA\psi, \psi \rangle + i \langle AB\psi, \psi \rangle \\ &= i \langle (AB - BA)\psi, \psi \rangle \\ &= \langle -i(AB - BA)\psi, \psi \rangle \\ &= \langle C\psi, \psi \rangle \end{aligned}$$

as required. □

Theorem 4.4.3. *Let A and B be two observables and ψ a normalised state. Then*

$$(\triangle A)_\psi (\triangle B)_\psi \geq \frac{1}{2} \left| \langle [A, B] \rangle_\psi \right|$$

Proof. Let $C := -i[A, B]$. Then by the previous lemma, C is self adjoint. Now set $a := A - \langle A \rangle_\psi$ and $b := B - \langle B \rangle_\psi$. Then it can easily be checked that $C = -i[a, b]$. Now,

$$\begin{aligned} (\triangle A)^2_\psi (\triangle B)^2_\psi &= \langle (A - \langle A \rangle_\psi)^2 \rangle_\psi \langle (B - \langle B \rangle)^2 \rangle_\psi \\ &= \langle a^2 \rangle_\psi \langle b^2 \rangle \psi \\ &= \langle \psi, a^2\psi \rangle \langle \psi, b^2\psi \rangle \\ &= \langle a\psi, a\psi \rangle \langle b\psi, b\psi \rangle \end{aligned}$$

Applying the Cauchy-Schwarz inequality yields

$$(\triangle A)^2_\psi (\triangle B)^2_\psi \geq | \langle a\psi, b\psi \rangle |^2$$

It is easily checked that a and b are themselves self-adjoint. Therefore

$$\begin{aligned}(\triangle A)^2_\psi (\triangle B)^2_\psi &\geq |\left\langle \psi, ab\psi \right\rangle|^2 \\ &= \left| \left\langle \psi, \frac{1}{2}(ab+ba) + \frac{1}{2}(ab-ba)\psi \right\rangle \right|^2\end{aligned}$$

We now note that $ab - ba = [a, b] = iC$ and thus

$$(\triangle A)^2_\psi (\triangle B)^2_\psi \geq \left| \frac{1}{2} \left\langle \psi, (ab+ba)\psi \right\rangle + \frac{i}{2} \left\langle \psi, C\psi \right\rangle \right|^2$$

We can again show that $ab+ba$ is a self adjoint operator and hence, by Proposition 2.3.8, both scalar products in the above inequality are real numbers. Thefore

$$\begin{aligned}(\triangle A)^2_\psi (\triangle B)^2_\psi &\geq \frac{1}{4}|\left\langle \psi, (ab+ba)\psi \right\rangle|^2 + \frac{1}{4}|\left\langle \psi, C\psi \right\rangle|^2 \\ &\geq \frac{1}{4}|\left\langle [A, B] \right\rangle_\psi|^2\end{aligned}$$

as required. □

Chapter 5

Further Examples

5.1 The Harmonic Oscillator

In this section we consider a quantum mechanical system with a Hamiltonian given by

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

where ω is some constant with unit s^{-1}. This Hamiltonian describes a harmonic oscillator. In classic treatments, a potential of $V = \frac{1}{2}kx^2$ leads to a force $F = -kx$ - Hooke's law for mass attached to a spring. Solutions are given by $x(t) = x_0 \cos(\omega t - \varphi_0)$ for some constants x_0, φ_0. The total energy $E = E_{kin} + E_{pot} \geq 0$ is conserved but it otherwise arbitrary.

Now treating the system quantum mechanically, we will find the **energy spectrum**. This is given by the eigenvalues of $\hat{H}$. Since the potential diverges for $x \to \pm\infty$, we will always have that the energy E of the system satifies $E < V(\infty)$ and $E < V(-\infty)$. Hence all states will be bounded states (energy is bounded to some finite interval; as opposed to **scattering states**). This implies that all eigenstates $|\psi\rangle$ of $\hat{H}$ are normalisable.

Proposition 5.1.1. *Consider the position operator $\vec{x}$ and the momentum operator $\vec{p}$. These operators satisfy the following relations:*

1. $\hat{x}^\dagger = \hat{x}$
2. $\hat{p}^\dagger = \hat{p}$
3. $[\hat{x}, \hat{p}] = i\hbar$

Proof. Let $|\psi\rangle$ be a normalised state.

Part 1 We need to show that $\langle\psi|\hat{x}\psi\rangle = \langle\hat{x}\psi|\psi\rangle$. Indeed

$$\begin{aligned}
\langle\psi|\hat{x}\psi\rangle &= \int_{\mathbb{R}^3} \psi^* x\psi \; d^3x \\
&= \int_{\mathbb{R}^3} (x^*\psi)^*\psi \; d^3x \\
&= \int_{\mathbb{R}^3} (x\psi)^*\psi \; d^3x \\
&= \langle\hat{x}\psi|\psi\rangle
\end{aligned}$$

Part 2 We need to show that $\langle\psi|\hat{p}\psi\rangle = \langle\hat{p}\psi|\psi\rangle$. We shall only consider the integral over one dimension for simplicity:

$$\begin{aligned}
\langle\psi|\hat{x}\psi\rangle &= \int_{\mathbb{R}} \psi^* \hat{p}\psi \; dx \\
&= \int_{\mathbb{R}} \psi^* i\hbar \frac{\partial}{\partial x}\psi \; dx \\
&= i\hbar \left([\psi^*\psi]_{\infty}^{\infty} - \int_{\mathbb{R}} \left[\frac{\partial}{\partial x}\psi*\right] \psi \; dx \right) \\
&= \frac{i}{\hbar} \left(\cancelto{0}{[|\psi|^2]_{\infty}^{\infty}} - \int_{\mathbb{R}} \left[\frac{\partial}{\partial x}\psi*\right] \psi \; dx \right) \\
&= \int_{\mathbb{R}} \left[i\hbar \frac{\partial}{\partial x}\psi*\right] \psi \; dx \\
&= \langle\hat{p}\psi|\psi\rangle
\end{aligned}$$

Part 3 We have that

$$\begin{aligned}
\langle\psi|[\hat{x},\hat{p}]\psi\rangle &= \langle\psi|\hat{x}\hat{p}\psi\rangle - \langle\psi|\hat{p}\hat{x}\psi\rangle \ dx \\
&= -i\hbar\int_{\mathbb{R}} \psi^* x \frac{\partial}{\partial x}\psi \ dx + i\hbar\int_{\mathbb{R}} \psi^* \frac{\partial}{\partial x}(x\psi) \ dx \\
&= -i\hbar\int_{\mathbb{R}} \psi^* x \frac{\partial}{\partial x}\psi \ dx + i\hbar\int_{\mathbb{R}} \psi^* (\psi + x\psi') \ dx \\
&= i\hbar\int_{\mathbb{R}} \psi^*\psi \ dx \\
&= i\hbar\,\langle\psi|\psi\rangle \ dx \\
&= i\hbar
\end{aligned}$$

□

Definition 5.1.2. *We define the* ***annihilation operator*** *(or* ***lowering operator****) a to be*

$$a := i\left(\frac{1}{2\hbar m\omega}\right)^{\frac{1}{2}}\hat{p} + \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\hat{x}$$

and the ***creation operator*** $a^\dagger$ *to be*

$$a^\dagger := \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\hat{x} - i\left(\frac{1}{2\hbar m\omega}\right)^{\frac{1}{2}}\hat{p}$$

which is just the adjoint of a.

Proposition 5.1.3. *The annilation and creation operators a and $a^\dagger$ satisfy the relation $[a, a^\dagger] = 1$.*

Proof. We have that

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

□

Remark. *From the above proof, we see that $a^\dagger a = -\frac{1}{2} + \frac{1}{\hbar\omega}\left(\frac{m\omega^2}{2}\hat{x}^2 + \frac{\hbar^2}{2m}\hat{p}^2 \right) = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2}$. It thus follows that we can write the Hamiltonian for the harmonic oscillator as*

$$\hat{H} = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right)$$

*Therefore the eigenvalues (and therefore the energies) of $\hat{H}$ can be determined if we know the eigenvalues of $N := a^\dagger a$, the **number operator**.*

Proposition 5.1.4. *The eigenvalues of the number operator $N = a^\dagger a$ are all real and positive.*

Proof. It is obvious that $N = a^\dagger a$ is self adjoint therefore its eigenvalues are all real by Proposition 2.3.8. Now let $N |\psi_\nu\rangle = \nu |\psi_\nu\rangle$ for some $\nu \in \mathbb{R}$ and $|\psi_\nu\rangle \neq 0$. Then $\nu \langle \psi_\nu | \psi_\nu \rangle = \langle \psi_\nu | N\psi_\nu \rangle = \langle \psi_\nu | a^\dagger a \psi_\nu \rangle = \langle a\psi_\nu | a\psi_n \rangle \geq 0$ where in the last equality we have used the fact that the scalar product of a vector with itself is always greater than or equal to 0. □

Proof. Such self adjoint operators with non-negative eigenvalues are called **positive operators**. □

Lemma 5.1.5. *The number, annihilation and creation operators satisfy the two relations* $[N, a^\dagger] = a^\dagger$ *and* $[N, a] = -a$.

Proof. We have that

$$[N, a^\dagger] = a^\dagger a a^\dagger - a^\dagger a^\dagger a = a^\dagger(aa^\dagger - a^\dagger a) = a^\dagger[a, a^\dagger] = a^\dagger$$
$$[N, a] = a^\dagger a a - a a^\dagger a = (a^\dagger a - a a^\dagger)a = -[a, a^\dagger] = -a$$

□

Theorem 5.1.6. *The set of eigenvalues of the number operator is exactly* $\mathbb{N} \cup \{0\}$.

Proof. Assume that $|\psi_\nu\rangle$ is a normalised eigenstate of N with eigenvalue ν. By the previous lemma, we have that

$$\begin{aligned} Na\,|\psi_\nu\rangle &= ([N, a] + aN)\,|\psi_\nu\rangle \\ &= (-a + aN)\,|\psi_\nu\rangle \\ &= -a\,|\psi_\nu\rangle + a\nu\,|\psi_\nu\rangle \\ &= (\nu - 1)a\,|\psi_\nu\rangle \end{aligned}$$

Hence either $a\,|\psi_\nu\rangle = 0$ or $a\,|\psi_\nu\rangle$ is an eigenstate of N with eigenvalue of $\nu - 1$.
By a similar approach to the above, the previous lemma also implies that

$$Na^\dagger\,|\psi_\nu\rangle = (\nu + 1)a^\dagger\,|\psi_\nu\rangle$$

Therefore, either $a^\dagger\,|\psi_\nu\rangle = 0$ or $a^\dagger\,|\psi_\nu\rangle$ is an eigenstate of N with eigenvalue $\nu + 1$.
Continuining as above, it follows that

$$\begin{aligned} Na^2\,|\psi_\nu\rangle &= (\nu - 2)a^2\,|\psi_\nu\rangle \\ &\vdots \\ Na^k\,|\psi_\nu\rangle &= (\nu - k)a^k\,|\psi_\nu\rangle \end{aligned}$$

Now consider the norms of these eigenstates, we have that

$$
\begin{aligned}
||\psi_\nu||^2 &= \langle \psi_\nu | \psi_\nu \rangle = 1 \\
||a\psi_\nu||^2 &= \langle a\psi_\nu | a\psi_\nu \rangle = \langle \psi_\nu | a^\dagger a \psi_\nu \rangle = \langle \psi_\nu | N\psi_\nu \rangle = \langle \psi_\nu | \nu\psi_\nu \rangle = \nu \langle \psi_\nu | \psi_\nu \rangle = \nu \\
||a^2\psi_\nu||^2 &= \langle a^2\psi_\nu | a^2\psi_\nu \rangle = \langle \psi_\nu | a^\dagger a^\dagger a a \psi_\nu \rangle = \langle \psi_\nu | a^\dagger N a \psi_\nu \rangle \\
&= \langle \psi_\nu | a^\dagger (\nu - 1) a \psi_\nu \rangle = (\nu - 1) \langle \psi_\nu | N\psi_\nu \rangle = \nu(\nu - 1) \\
&\vdots \\
||a^k\psi_\nu||^2 &= \nu(\nu - 1)\dots(\nu - k + 1)
\end{aligned}
$$

It is clear that, given large k, this expression will be negative unless $\nu \in \mathbb{N} \cup \{0\}$. But this is not possible since $||\psi||^2 \geq 0$ for any normalised ψ. Hence the set of allowed eigenvalues ν of N is exactly $\mathbb{N} \cup \{0\}$. □

Remark. *From this proof, it follows that the only allowed eigenvalues of the Hamiltonian are* $E_\nu = \hbar\omega \left(\nu + \frac{1}{2}\right)$.

We have therefore determined all possible energies of the quantum harmonic oscillator - we indeed find that energy is once again quantised.

Now assume that the eigenstate ψ_0, with the lowest possible eigenvalue such that $\nu = 0$, exists (the so-called **ground state**). We have that $N\psi_0 = 0$ and $||\psi_0||^2 = 1$. We can construct higher level eigenstates using the creation operator $a^\dagger$. From the previous proof, we have the following:

$$
\begin{aligned}
N(a^\dagger)^k |\psi_0\rangle &= k(a^\dagger)^k |\psi_0\rangle \\
||(a^\dagger)^k\psi_0||^2 &= k(k-1)\dots 2 \cdot 1 = k!
\end{aligned}
$$

for $k = 0, 1, \dots$. We can hence apply a normalising factor $\frac{1}{\sqrt{n!}}$ and write

$$
\psi_n = \frac{1}{\sqrt{n!}}(a^\dagger)^n\psi_0
$$

We therefore have $N\psi_n = n\psi_n$ for $n = 0, 1, \dots$.

We note that if $n = 0$ then the energy for the Harmonic oscillator is $E_0 = \frac{1}{2}\hbar\omega > 0$. This suggests that quantum oscillations can never be completely stopped - even in vacuum.

Now, since N is a self adjoint operator, the eigenstates ψ_n form an orthonormal basis. We can thus find the matrix elements of $a^\dagger$:

$$(a^\dagger)_{nm} = \langle\psi_n| a^\dagger |\psi_m\rangle = \sqrt{m+1}\,\langle\psi_n|\psi_{m+1}\rangle = \sqrt{m+1}\delta_{n,m+1}$$

To find the matrix elements of a, we use the definition of $[a, a^\dagger]$ and N:

$$\begin{aligned}
&[a, a^\dagger]\psi_n = \psi_n \\
&\implies aa^\dagger\psi_n - a^\dagger a\psi_n = \psi_n \\
&\implies a\sqrt{n+1}\psi_{n+1} - N\psi_n = \psi_n \\
&\implies \sqrt{n+1}a\psi_{n+1} - n\psi_n = \psi_n \\
&\implies \sqrt{n+1}a\psi_{n+1} = \psi_n(n+1) \\
&\implies a\psi_{n+1} = \frac{1}{\sqrt{n+1}}\psi_n
\end{aligned}$$

Using this, we find that

$$(a)_{nm} = \langle\psi_n| a |\psi_m\rangle = \sqrt{m}\delta_{n,m-1}$$

We cam immediately see that $a^\dagger$ is the adjoint of a and $N = a^\dagger a = diag(0, 1, 2\ldots)$. We also have the following formulations for the momentum and position operator (as infinite matrices):

$$\begin{aligned}
(\hat{p})_{n,m} &= i\sqrt{\frac{\hbar m\omega}{2}}\left(\sqrt{n}\delta_{n,m+1} - \sqrt{n+1}\delta_{n,m-1}\right) \\
(\hat{x})_{n,m} &= \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\delta_{n,m+1} + \sqrt{n+1}\delta_{n,m-1}\right)
\end{aligned}$$

It now suffices to find the explicit form of the ground state ψ_0. We can then express all eigenstates in terms of this function.

Obviously, ψ_0 should satisfy $a\psi_0 = 0$. We have that

$$\begin{aligned}
a &= \frac{1}{\sqrt{2}}\left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}\hat{x} + i\left(\frac{1}{\hbar m\omega}\right)\hat{p}\right] \\
&= \frac{1}{\sqrt{2}}\left(\frac{1}{x_0}\hat{x} + x_0\frac{\partial}{\partial x}\right)
\end{aligned}$$

where $x_0 = \sqrt{\frac{\hbar}{m\omega}}$. Now we use the change of variables $\xi = \frac{x}{x_0}$ to get

$$\left(\xi + \frac{\partial}{\partial \xi}\right)\psi_0(\xi) = 0$$

This has solution

$$\psi_0(\xi) = Ae^{-\frac{\xi^2}{2}}$$

for some constant A. By normalising this state, we arrive at

$$\psi_0(\xi) = \frac{1}{\pi^{1/4}}e^{-\frac{\xi^2}{2}}$$

which is just a Gauss curve. Now using the formula we obtained earlier for the higher excited states, it follows that

$$\psi_n(\xi) = \frac{1}{n!2^n\sqrt{\pi}}\left(\xi - \frac{\partial}{\partial \xi}\right)^n e^{-\frac{\xi^2}{2}}$$

5.2 Two-state systems

Example 5.2.1. *Consider the Hamiltonian given by the matrix*

$$H = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

where $E_1 \neq E_2$ are some real constants. The eigenstates are given by

$$|e_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$|e_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

with $H|e_j\rangle = E_j|e_j\rangle$ for $j = 1, 2$. Now consider the observable (self adjoint operator)

$$S = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Through some easy linear algebra, we find the normalised eigenstates of this observable to be

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}(|e_1\rangle + |e_2\rangle)$$
$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}(|e_1\rangle - |e_2\rangle)$$

with $S|\psi_1\rangle = |\psi_1\rangle$ *and* $S|\psi_2\rangle = -|\psi_2\rangle$.
We note that since H *and* S *do not commute, Proposition 4.2.12 implies that there is no orthonormal basis consisting of common eigenstates of* H *and* S.

Recall that if $\tilde{\psi}$ *satisfies the time independent Schrödinger equation* $H\tilde{\psi} = E\tilde{\psi}$, *then a solution of the full time-dependent Schrödinger equation* $i\hbar\frac{\partial\psi(t)}{\partial t} = H\psi(t)$ *is given by*

$$\psi(t) = \tilde{\psi}e^{-\frac{i}{\hbar}Et}$$

where we have assumed that the potential is time independent.
Now if $\tilde{\psi}_1, \tilde{\psi}_2, \ldots$ *is an orthonormal basis of* $\mathcal{H}$ *consisting of* H*-eigenstates, satisfying* $H\tilde{\psi}_n = E_n\tilde{\psi}_n$, *we have that for an aribtrary state* $\psi \in \mathcal{H}$

$$\psi = \psi(t=0) = \sum_n c_n(t=0)\tilde{\psi}_n$$

for some $c_n \in \mathbb{C}$. *At time* t, *the state therefore becomes*

$$\psi(t) = \sum_n c_n(t=0)e^{-\frac{i}{\hbar}E_n t}\tilde{\psi}_n$$

We see that in general, the state ψ *evolves in a non-trivial manner. The coefficients* $c_n(t)$ *depend on* t. *We illustrate this in the following example.*

Assume that that time $t = 0$, S *is measured and the resulting eigenvalue is* 1. *We know, by the axioms of quantum mechanics, that the system collapses into the corresponding eigenstate* $|\psi_1\rangle$. *Hence at time* $t = 0$, *the probability* $P_{t=0}(S = 1)$ *to find* $S = 1$ *is* 1 *and* $P_{t=0}(S = -1) = 0$.
Now, $\psi_{t=0} = \frac{1}{\sqrt{2}}e_1 + \frac{1}{\sqrt{2}}e_2$. *Through the above description of time evolution of linear combinations of energy eigenstates, we have that*

$$\psi(t) = \frac{1}{\sqrt{2}}e^{\frac{-i}{\hbar}E_1 t}e_1 + \frac{1}{\sqrt{2}}e^{\frac{-i}{\hbar}E_2 t}e_2$$

If we measure S again, at a time $t > 0$, the probability of finding $S = 1$ and $S = -1$ are

$$\begin{aligned}
P_t(S=1) = |\langle \psi_1 | \psi(t) \rangle|^2 &= \left| \left\langle \frac{1}{\sqrt{2}} e_1 + \frac{1}{\sqrt{2}} e_2 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_1 t} e_1 + \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_2 t} e_2 \right\rangle \right|^2 \\
&= \left| \left\langle \frac{1}{\sqrt{2}} e_1 + \frac{1}{\sqrt{2}} e_2 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_1 t} e_1 \right\rangle + \left\langle \frac{1}{\sqrt{2}} e_1 + \frac{1}{\sqrt{2}} e_2 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_2 t} e_2 \right\rangle \right|^2 \\
&= \left| \left\langle \frac{1}{\sqrt{2}} e_1 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_1 t} e_1 \right\rangle + \left\langle \frac{1}{\sqrt{2}} e_2 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_1 t} e_1 \right\rangle \right. \\
&\quad \left. + \left\langle \frac{1}{\sqrt{2}} e_1 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_2 t} e_2 \right\rangle + \left\langle \frac{1}{\sqrt{2}} e_2 \,\middle|\, \frac{1}{\sqrt{2}} e^{\frac{-i}{\hbar} E_2 t} e_2 \right\rangle \right|^2 \\
&= \left| \frac{1}{2} e^{\frac{-i}{\hbar} E_1 t} \langle e_1 | e_1 \rangle + \cancelto{0}{\frac{1}{2} e^{\frac{-i}{\hbar} E_1 t} \langle e_2 | e_1 \rangle} + \cancelto{0}{\frac{1}{2} e^{\frac{-i}{\hbar} E_2 t} \langle e_1 | e_2 \rangle} + \frac{1}{2} e^{\frac{-i}{\hbar} E_2 t} \langle e_2 | e_2 \rangle \right|^2 \\
&= \frac{1}{4} \left| e^{\frac{-i}{\hbar} E_1 t} + e^{\frac{-i}{\hbar} E_2 t} \right|^2
\end{aligned}$$

Now through some simple algebra, we can see that that the substitution $U = \frac{E_1 - E_2}{2\hbar} t$ gives us

$$\begin{aligned}
P_t(S=1) &= \cos^2(U) \\
&= \cos^2\left(\frac{E_1 - E_2}{2\hbar} t \right)
\end{aligned}$$

$$\begin{aligned}
P_t(S=-1) &= 1 - \cos^2\left(\frac{E_1 - E_2}{2\hbar} t \right) \\
&= \sin^2\left(\frac{E_1 - E_2}{2\hbar} t \right)
\end{aligned}$$

We see that if we wait a while before measuring again, it is no longer certain that we will find $S = 1$ again. Therefore if the system is not in an energy eigenstate after the first measurement at $t = 0$, it will evolve away from the state that it collapsed into.

Example 5.2.2. *Now we switch our view to several non-commuting observables. Let the Hamiltonian $H = 0$ (implying there is no time evolution).*

Consider the three self adjoint operators $S_j := \frac{\hbar}{2}\sigma_j$ for $j = 1, 2, 3$ where

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

*are the **Pauli matrices** satisfying the commutation relation $[S_j, S_k] = i\hbar\epsilon_{jkl}S_l$. The Heisenberg uncertainty relation implies that we cannot have a state in which both the measurements of S_1 and S_3 can be predicted with certainity. Consider $S_3 = \frac{\hbar}{2}\sigma_3$. Obviously the eigenstates are*

$$e_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, e_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

with corresponding eigenvalues $\frac{\hbar}{2}$ and $\frac{-\hbar}{2}$.
Now assume that the system is in the state $|\psi\rangle = |e_1\rangle$ (for example, after an S_3 measurement that produced $\frac{\hbar}{2}$). Now measure S_1. This also has eigenvalues $\pm\frac{\hbar}{2}$ but with eigenstates

$$\psi_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \psi_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Therefore the outcomes of the measurement have probabilities

$$|\langle\psi_+|e_1\rangle|^2 = \left|\frac{1}{\sqrt{2}}\langle(1,1)|(1,0)\rangle\right|^2 = \frac{1}{2}|\langle\psi_+|e_1\rangle|^2 = 1 - \frac{1}{2} = \frac{1}{2}$$

Therefore we cannot say anything about the outcome of the measurement of S_1 after we have made an S_3 measurement. If we measure S_3 again, we will find the same probabilities as above: measuring S_1 has destroyed all information that came from the previous S_3 measurement.

5.3 Angular momentum

Definition 5.3.1. *Consider a classical Newtonian system. Then the **angular momentum** $\vec{L}$ of a body is defined to be*

$$\vec{L} = \vec{x} \times \vec{p}$$

where $\vec{x}$ is the body's position and $\vec{p}$ is its momentum.

Remark. *The above definition is an important one and we should expect a similar quantity to arise in quantum mechanics. The angular momentum is used, in classical mechanics, to compute the orbits of planets in the solar system under the influence of the force of gravity and their angular momentum is conserved. We have the analogous situation in quantum mechanics where electrons orbit around the nucleus of a Hydrogen atom under the influence of the Coulomb potential. The quantum mechanical equivalent of the angular momentum is also conserved in this case.*

Definition 5.3.2. *Consider a Hilbert space $\mathcal{H}$ and the canonical operators $\hat{x}$ and $\hat{p}$ acting on $\mathcal{H}$. We define the* ***angular momentum*** *$\vec{L}$ to be the three dimensional vector with coordinates given by*

$$L_j = \epsilon_{jkl} x_k p_l$$

where x_i and p_i are understood to be the position and momemntum operators projected onto the i^{th} coordinate.

Proposition 5.3.3. *The angular momentum satisfies the following commutation relation*

$$[L_j, L_k] = i\hbar \epsilon_{jkl} L_l$$

Proof. We have that

$$\begin{aligned} [L_j, L_k] &= L_j L_k - L_k L_j \\ &= \epsilon_{jab} x_a p_b \epsilon_{kcd} x_c p_d - \epsilon_{kcd} x_c p_d \epsilon_{jab} x_a p_b \\ &= \epsilon_{jab} \epsilon_{kcd} (x_a p_b x_c p_d - x_c p_d x_a p_b) \\ &= \epsilon_{jab} \epsilon_{kcd} [x_a p_b, x_c p_d] \end{aligned}$$

Now we use the relation $[ab, c] = a[b, c] + [a, c]b$. Applying this we get

$$\begin{aligned} [L_j, L_k] &= \epsilon_{jab} \epsilon_{kcd} (x_a [p_b, x_c p_d] + [x_a, x_c p_d] p_b) \\ &= \epsilon_{jab} \epsilon_{kcd} ([x_c p_d, x_a] p_b + x_a [x_c p_d, p_b]) \\ &= \epsilon_{jab} \epsilon_{kcd} ((x_c [p_d, x_a] + [x_c, x_a] p_d) p_b + x_a (x_c [p_d, p_b] + [x_c, p_b] p_d)) \\ &= \epsilon_{jab} \epsilon_{kcd} (x_c [p_d, x_a] p_b + x_a [x_c, p_b] p_d) \\ &= -i\hbar \epsilon_{jab} \epsilon_{kcd} (\delta_{da} x_c p_b - \delta_{cb} x_a p_d) \\ &= -i\hbar \epsilon_{jdb} \epsilon_{kcd} x_c p_b + i\hbar \epsilon_{jab} \epsilon_{kbd} x_a p_d \end{aligned}$$

$$
\begin{aligned}
&= i\hbar\epsilon_{djb}\epsilon_{kcd}x_c p_b + i\hbar\epsilon_{jab}\epsilon_{kbd}x_a p_d \\
&= i\hbar\epsilon_{djb}\epsilon_{dkc}x_c p_b + i\hbar\epsilon_{bja}\epsilon_{bdk}x_a p_d \\
&= i\hbar(\delta_{jk}\delta_{bc} - \delta_{jc}\delta_{bk})x_c p_b + i\hbar(\delta_{jd}\delta_{ak} - \delta_{jk}\delta_{ad})x_a p_d \\
&= i\hbar(x_b p_b \delta_{jk} - x_j p_k + x_k p_j - \delta_{jk}x_d p_d)
\end{aligned}
$$

Renaming $b \to d$, we see that the two δ_{jk} terms cancel and we are left with

$$
\begin{aligned}
[L_j, L_k] &= i\hbar(x_k p_j - x_j p_k) \\
&= i\hbar\epsilon_{kjl}L_l
\end{aligned}
$$

as required. □

Remark. *We see that the three components of the angular momentum satisfy the same commutation relation as the matrices S_j introduced in the previous chapter. This suggests some sort of relation between the two. Indeed, we shall see that S_j describe the **spin** of a particle which can be interpeted (but is not the same as) the rotation of a particle around its axis.*

Proposition 5.3.4. *The eigenvalues of the operator L_i are given by $\hbar m$ for $m \in \mathbb{Z}$. In other words, the L_i-angular momentum is quantised.*

Proof. We shall only consider the L_3 case for simplicity. By definition, we have that

$$
\begin{aligned}
L_3 &= x_1 p_2 - x_2 p_1 \\
&= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad (5.1)
\end{aligned}
$$

where we have used the variables $x_1 = x, x_2 = y, x_3 = z$. For convenience, we shall switch to the spherical coordinates

$$
\begin{aligned}
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi \\
z &= r\cos\theta
\end{aligned}
$$

where r is a real positive constant, $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$. We can rewrite these transformations as follows

$$r = \sqrt{x^2 + y^2 + z^2} \tag{5.2}$$

$$\theta = \arctan\left(\frac{x^2 + y^2}{r^2}\right) \tag{5.3}$$

$$\phi = \arctan\left(\frac{y}{x}\right) \tag{5.4}$$

We need to find the partial derivatives $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial x}$ in terms of these coordinates. By the chain rule, we have that

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi} \tag{5.5}$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \tag{5.6}$$

Obviously from the definition of r we get that

$$\frac{\partial r}{\partial y} = \frac{y}{r}, \frac{\partial r}{\partial x} = \frac{x}{r}$$

Now,

$$\begin{aligned}
\frac{\partial \theta}{\partial y} &= \frac{\partial}{\partial y}\left(\frac{x^2 + y^2}{r^2}\right)\frac{1}{1 + \left(\frac{x^2+y^2}{r^2}\right)^2} \\
&= \frac{2y}{r^2}\frac{r^4}{r^4 + (x^2 + y^2)^2} \\
&= \frac{2yr^2}{r^4 + (x^2 + y^2)^2}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \theta}{\partial x} &= \frac{\partial}{\partial x}\left(\frac{x^2 + y^2}{r^2}\right)\frac{1}{1 + \left(\frac{x^2+y^2}{r^2}\right)^2} \\
&= \frac{2x}{r^2}\frac{r^4}{r^4 + (x^2 + y^2)^2} \\
&= \frac{2xr^2}{r^4 + (x^2 + y^2)^2}
\end{aligned}$$

and

$$\begin{aligned}\frac{\partial\phi}{\partial y} &= \frac{\partial}{\partial y}\left(\frac{y}{x}\right)\frac{1}{1+\left(\frac{y}{x}\right)^2}\\ &= \frac{1}{x}\frac{x^2}{x^2+y^2}\\ &= \frac{x}{x^2+y^2}\end{aligned}$$

$$\begin{aligned}\frac{\partial\phi}{\partial x} &= \frac{\partial}{\partial x}\left(\frac{y}{x}\right)\frac{1}{1+\left(\frac{y}{x}\right)^2}\\ &= \frac{-y}{x^2}\frac{x^2}{x^2+y^2}\\ &= \frac{-y}{x^2+y^2}\end{aligned}$$

Inserting these partial derivatives into Equations (5.5) and (5.6) gives us

$$\begin{aligned}\frac{\partial}{\partial y} &= \frac{y}{r}\frac{\partial}{\partial r} + \frac{2yr^2}{r^4+(x^2+y^2)^2}\frac{\partial}{\partial\theta} + \frac{x}{x^2+y^2}\frac{\partial}{\partial\phi}\\ \frac{\partial}{\partial x} &= \frac{x}{r}\frac{\partial}{\partial r} + \frac{2xr^2}{r^4+(x^2+y^2)^2}\frac{\partial}{\partial\theta} + \frac{-y}{x^2+y^2}\frac{\partial}{\partial\phi}\end{aligned}$$

Now inserting these into Equation (5.1), we have

$$\begin{aligned}L_3 = -i\hbar\Bigg(&\frac{xy}{r}\frac{\partial}{\partial r} + \frac{2xyr^2}{r^4+(x^2+y^2)^2}\frac{\partial}{\partial\theta} + \frac{x^2}{x^2+y^2}\frac{\partial}{\partial\phi}\\ &- \frac{xy}{r}\frac{\partial}{\partial r} - \frac{2xyr^2}{r^4+(x^2+y^2)^2}\frac{\partial}{\partial\theta} + \frac{y^2}{x^2+y^2}\frac{\partial}{\partial\phi}\Bigg)\end{aligned}$$

We now assume that there exists an eigenfunction ψ of L_3 with eigenvalue

$\hbar m$ with $m \in \mathbb{R}$. We have that

$$\begin{aligned} &L_3\psi = \hbar m\psi \\ &-i\hbar\frac{\partial}{\partial\phi}\psi(r,\theta,\phi) = \hbar m\psi(r,\theta,\phi) \\ &\frac{\partial}{\partial\phi}\psi(r,\theta,\phi) = im\psi(r,\theta,\phi) \end{aligned}$$

This is a first order differential equation with solution

$$\psi(r,\theta,\phi) = \psi(r,\theta,0)e^{im\phi}$$

Now note that the transformation $\phi \to \phi + 2\pi$ leaves x, y and z invariant meaning $\psi(r,\theta,\phi) = \psi(r,\theta,\phi+2\pi)$. This implies that $e^{im\phi} = e^{im(\phi+2\pi)}$. But this is only true if $m \in \mathbb{Z}$. Hence the eigenvalues of L_3 are quantised. $\square$

Chapter 6

Symmetries and the Heisenberg Picture of Time Evolution

6.1 Symmetries

Let $\mathcal{H}$ be a Hilbert space consisting of states of a quantum mechanical system and assume that the operator $Q : \mathcal{H} \to \mathcal{H}$ induces a symmetry on the system. Obviously Q should satisfy the following:

- Q should be invertible otherwise the symmetry would not be be able to be undone and thus information could be lost.

- $|\langle Q\psi, Q\phi\rangle|^2 = |\langle \psi, \phi\rangle|^2$ for all $\psi, \phi \in \mathcal{H}$ as $|\langle \psi, \phi\rangle|^2$ determines probability which must be conserved.

Definition 6.1.1. *Let $\mathcal{H}$ be a Hilbert space and $U : \mathcal{H} \to \mathcal{H}$ an operator. We say that U is* ***unitary*** *if $UU^\dagger = U^\dagger U = 1_{\mathcal{H}}$. In other words, the adjoint of U is the inverse of U. Equivalently, we have that if U is unitary then $\langle U\psi, U\phi\rangle = \langle \psi, \phi\rangle$ for all $\psi, \phi \in \mathcal{H}$.*

Definition 6.1.2. *Let $\mathcal{H}$ be a Hilbert space and $U : \mathcal{H} \to \mathcal{H}$ an operator. We say that U is* ***anti-unitary*** *if $\langle U\psi, U\phi\rangle = \langle \psi, \phi\rangle^*$.*

Remark. *Let Q be a an operator and $Q^{-1} = Q^\dagger e^{i\alpha}$ for some $\alpha \in \mathbb{R}$ then Q also satisfies both requirements of a symmetry. We say that Q is* ***unitary up to a phase****.*

Theorem 6.1.3. *(Wigner's Theorem) Let $\mathcal{H}$ be a Hilbert space and Q an operator on $\mathcal{H}$ satisfying the assumptions for a symmetry. Then Q is either unitary or anti-unitary up to a phase.*

We now examine the effect of unitary operators on observables and states. Let $\mathcal{H}$ be a Hilbert space, $U : \mathcal{H} \to \mathcal{H}$ a unitary operator and $A : \mathcal{H} \to \mathcal{H}$ an observable. Let $|\psi\rangle \to |\psi_U\rangle := U|\psi\rangle$ and $A \to A_U := UAU^\dagger$. Then

$$(A_U)^\dagger = (UAU^\dagger)^\dagger = U^{\dagger\dagger}A^\dagger U^\dagger = UAU^\dagger = A_U$$

therefore U preserves the self adjointness of A. We also have that

$$\langle \psi_U, A_U \phi_U\rangle = \langle U\psi, UAU^\dagger U\phi\rangle = \langle \psi, U^\dagger UA\phi\rangle = \langle \psi, A\phi\rangle$$

Hence expectation values $\langle \psi, A\psi\rangle$ and general matrix elements $\langle \psi, A\phi\rangle$ are invariant under the symmetry induced by U. We can also see that the eigenvalues of A_U are the same as those of A:

$$A|\psi\rangle = a|\psi\rangle \iff UAU^\dagger U|\psi\rangle = aU|\psi\rangle \iff A_U|\psi_U\rangle = a|\psi_U\rangle$$

Example 6.1.4. *Let $B : \mathcal{H} \to \mathcal{H}$ be a self adjoint operator and $S \in \mathbb{R}$. Then $U_S := e^{(iSB)}$ is unitary. Obviously, we have that*

$$B = i\left(\frac{d}{ds}U_S\right)\Big|_{S=0}$$

*This is called the **generator** of the continuous symmetry U_S.*

Example 6.1.5. *The parity operator P is also a unitary operator.*

In classical mechanics, we employed changes of coordinates which left the overall system invariant. One would want to investigate similar phenomenae in quantum mechanics. For the Hilbert space $\mathcal{H} = L^2(\mathbb{R})^3$ and a change of coordinates $\vec{x} \to \vec{x}' = F(\vec{x})$ we want to find a unitary operator $U_F : \mathcal{H} \to \mathcal{H}$ such that $(U_F\psi)(F(\vec{x})) = \psi(x)$ for some $\psi \in \mathcal{H}$. In other words, we require that $(U_F\psi)(x) = \psi(F^{-1}(\vec{x}))$.

Proposition 6.1.6. *Consider the translation $F(\vec{x}) = T_{\vec{a}}(\vec{x}) := \vec{x}+\vec{a}$ for some constant $\vec{a} \in \mathbb{R}^3$. Then the unitary operator corresponding to this translation leaving a wave function ψ invariant is*

$$U_{T_{\vec{a}}} = e^{\frac{-i}{\hbar}\vec{a}\cdot\vec{p}}$$

Proof. We have that

$$U_{T_{\vec{a}}}\vec{\psi}(\vec{x}) = \psi(U_{T_{\vec{a}}}^{-1}(\vec{x})) = \psi(\vec{x} - \vec{a})$$

Now Taylor expanding the right hand side, we get that

$$\begin{aligned} U_{T_{\vec{a}}}\vec{\psi}(\vec{x}) &= \psi(\vec{x}) - \vec{a} \cdot (\vec{\nabla}\psi)(\vec{x}) - \frac{1}{2}a_k a_l \frac{\partial}{\partial x_k}\frac{\partial}{\partial x_l}\psi(\vec{x}) + \dots \\ &= (1 - \vec{a} \cdot (\vec{\nabla}) - \frac{1}{2}a_k a_l \frac{\partial}{\partial x_k}\frac{\partial}{\partial x_l} + \dots)\psi(\vec{x}) \\ &= e^{-\vec{a}\cdot\vec{\nabla}}\psi(\vec{x}) \end{aligned}$$

Now the definition of angular momentum $\vec{p} = \frac{\hbar}{i}\vec{\nabla}$ yields

$$U_{T_{\vec{a}}}(\vec{x}) = e^{-\frac{i}{\hbar}\vec{a}\cdot\vec{p}}\psi(\vec{x})$$

as required. □

Proposition 6.1.7. *Consider the transformation $\vec{x} \to F(\vec{x}) = R\vec{x}$ for some rotation matrix $R \in SO(3)$ through an angle $\vec{\theta}$. Then the unitary operator corresponding to this rotation leaving a wave function ψ invariant is*

$$U_{R_{\vec{\theta}}} = e^{-\frac{i}{\hbar}\vec{\theta}\cdot\vec{L}}$$

where L is understood to be the angular momentum operator.

Proof. For simplicity we shall only prove the theorem for a rotation through an angle θ around the z axis. The rotation matrix for this case is given by

$$R_\theta = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

We now consider R_θ to induce an infinitesimal rotation on the system. In such a case, we can take the limit as $\theta \to 0$ and we get

$$R_3 \simeq 1_3 + \begin{pmatrix} 0 & -\theta & 0 \\ \theta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \mathcal{O}(\theta^2)$$

Applying this to the position vector $\vec{x}$ we have that

$$R_\theta \vec{x} = \vec{x} + \theta \begin{pmatrix} -x_2 \\ x_1 \\ 0 \end{pmatrix} + \mathcal{O}(\theta^2)$$

Therefore

$$(U_{R_\theta}\psi)(\vec{x}) = \psi(R_\theta^{-1}\vec{x}) = \psi(R_{-\theta}\vec{x}) \simeq \psi(\vec{x} - \theta(-x_2))$$

Now Taylor expanding the right hand side gives us

$$\begin{aligned}(U_{R_\theta}\psi)(\vec{x}) &\simeq \psi(\vec{x}) - \theta(-x_2)\frac{\partial}{\partial x_2}\psi(\vec{x}) - \theta x_1 \frac{\partial}{\partial x_2}\psi(\vec{x}) \\ &= \psi(\vec{x}) - \theta\left(x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_2}\right)\psi(\vec{x}) \\ &= \psi(\vec{x}) - \frac{i}{\hbar}\theta(x_1p_2 - x_2p_1)\psi(\vec{x}) \\ &= \psi(\vec{x}) - \frac{i}{\hbar}\theta L_3\psi(\vec{x})\end{aligned}$$

Hence for infinitessimal θ, we have

$$U_{R_\theta} = 1_3 - \frac{i}{\hbar}\theta L_3$$

Now consider θ to be a a finite angle (as opposed to infinitessimal). Obviously we can build up theta by considering it to be the sum of infinitessimal angles. In other words, we write

$$\theta = \frac{\theta}{N} + \frac{\theta}{N} + \cdots + \frac{\theta}{N}$$

and take the limit $N \to \infty$. But this is just the same as applying $U_{R_{\frac{\theta}{N}}}$ N times and taking the limit $N \to \infty$:

$$\begin{aligned}U_{R_\theta} &= \left(1_3 - \frac{i}{\hbar}\frac{\theta}{N}L_3\right)^N \\ &= e^{-\frac{i}{\hbar}\theta L_3}\end{aligned}$$

where we have used the well known limit definition of the exponential function. □

Definition 6.1.8. *Consider a quantum mechanical system with the Hamilton operator $\hat{H}$. Consider a unitary operator U (or an observable B). Then U (B) is called a* ***symmetry*** *if $[\hat{H}, U] = 0$ ($[\hat{H}, B] = 0$).*

Remark. $[\hat{H}, B] = 0 \implies [e^{iSB}, \hat{H}] = 0$

Example 6.1.9. *$H = \frac{p^2}{2m}$ commutes with $\hat{p}_k$ and $\hat{L}_k$. Hence translations and rotations are symmetries of a free particle.*

Example 6.1.10. *$H - \frac{\vec{p}^2}{2m} + \frac{m\omega^2}{2}\vec{x}^2$ commutes with $\hat{L}$. Hence rotations are symmetries of the 3-dimensional harmonic oscillator.*

Proposition 6.1.11. *Let $\hat{H}$ be a time independent Hamiltonian and B a time independent observable commuting with $\hat{H}$. Then*

- *the expectation values of B are time-independent*
- *if $|\psi(0)\rangle$ is an eigenstate of B with eigenvalue λ at time $t = 0$ then $|\psi(t)\rangle = e^{-\frac{i}{\hbar}tH}|\psi(0)\rangle$ is an eigenstate of B with eigenvalue λ at time t*

Proof. We shall only prove the first part.

Part 1 Using the Schrödinger equation, we have that

$$\begin{aligned}
\frac{d}{dt}\langle B\rangle_\psi &= \frac{d}{dt}\langle \psi(t), B\psi(t)\rangle \\
&= \left\langle \frac{\partial}{\partial t}\psi(t), B\psi(t)\right\rangle + \left\langle \psi(t), B\frac{d}{dt}\psi(t)\right\rangle \\
&= \left\langle \frac{1}{i\hbar}H\psi(t), B\psi(t)\right\rangle + \left\langle \psi(t), B\frac{i}{i\hbar}\psi(t)\right\rangle \\
&= \left\langle \psi(t), -\frac{1}{i\hbar}HB\psi(t)\right\rangle + \left\langle \psi(t), \frac{1}{i\hbar}BH\psi(t)\right\rangle \\
&= \left\langle \psi(t), -\frac{1}{i\hbar}HB\psi(t) + \frac{1}{i\hbar}BH\psi(t)\right\rangle \\
&= \left\langle \psi(t), \frac{1}{i\hbar}(BH\psi(t) - HB\psi(t))\right\rangle \\
&= \frac{1}{i\hbar}\langle [B, H]\rangle_\psi \\
&= 0
\end{aligned}$$

□

Example 6.1.12. *An example of a discrete symmetry that is implemented by an anti-unitary operator is the time reversal map $t \to -t$. Assume the Hamiltonian $\hat{H}$ is t-independent and real. Let $\psi \in L^2(\mathbb{R})^3$ a wave function and define*

$$\begin{aligned} Q_T &: \mathcal{H} \to \mathcal{H} \\ \psi(x,t) &\mapsto \psi(x,-t)^* \end{aligned}$$

Then we observe the following (letting $\tilde{t} = -t$):

- *ψ satisfies the Schrödinger equation if and only if $Q_T\psi$ satisfies the Schrödinger equation:*

$$\begin{aligned} \hbar\partial_t\psi(t) = H\psi(t) &\iff (i\hbar\partial_t\psi(t))^* = (H\psi(t))^* \\ &\iff -i\hbar\partial_t\psi(t)^* = H\psi(t)^* \\ &\iff i\hbar\partial_{\tilde{t}}\psi(-\tilde{t})^* = H\psi(-\tilde{t})^* \\ &\iff i\hbar\partial_{\tilde{t}}(Q_T\psi)(\tilde{t}) = H(Q_T\psi)(\tilde{t}) \end{aligned}$$

- *$\hat{H}$ commutes with Q_T:*

$$HQ_T\psi(t) = H\psi(-t)^* = (H\psi)^*(-t) = Q_T H\psi(t)$$

- *Q_T satisfies $\langle Q\psi, Q\psi\rangle = \langle\psi,\psi\rangle^*$*

Remark. *Such an operator is the only important example of an anti-unitary operator in quantum mechanics as any other anti-unitary operator can be expressed as $Q_T U$ for some unitary operator U.*

6.2 Heisenberg Picture of Time Evolution

We have so far been considering the Schrödinger picture where $\psi(t) \in \mathcal{H}$ are time-dependent states and $A : \mathcal{H} \to \mathcal{H}$ are observables (usually time independent) - this system is governed by the Schrödinger equation. Thanks to the Schrödinger equation, time evolution can be viewed as a symmetry of the system since scalar products of states evolving according to the Schrödinger equation don't change with time:

$$\begin{aligned} \frac{d}{dt}\langle\psi(t),\phi(t)\rangle &= \left\langle \frac{\partial}{\partial d}\psi(t),\phi(t)\right\rangle + \left\langle \phi(t),\frac{\partial}{\partial t}\phi(t)\right\rangle \\ &= \frac{i}{\hbar}\left(\langle H\psi(t),\phi(t)\rangle - \langle\psi(t),H\psi(t)\rangle\right) \\ &= 0 \end{aligned}$$

where we have used the fact that the Hamilton operator is self adjoint. Hence $\langle\psi(t),\phi(t)\rangle = \langle\psi(t_0),\phi(t_0)\rangle$. Hence we expect to find a unitary operator $U(t,t_0)$ such that

$$\psi(t) = U(t,t_0)\phi(t_0)$$

for all t, t_0 and ϕ. This operator satisfies the Schrödinger equation. In addition, it satisfies $U(t,t_0)^\dagger = U(t_0,t)$ and $U(t_0,t_0) = 1_{\mathcal{H}}$. If $\hat{H}$ is time independent then we have that

$$U(t,t_0) = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}$$

(if $\hat{H}$ is time dependent then it is given by $e^{-\frac{i}{\hbar}\int_{t_0}^{t}\hat{H}(\tau)\,d\tau}$).
We use U to pass from the Schrödinger picture to the Heisenberg picture where states are time independent and observables are usually t dependent.

Notation 6.2.1. *We denote a state ψ and observable A in the Schrödinger picture by ψ_S and A_S. Analogously, we denote them ψ_H and A_H in the Heisenberg picture.*

Definition 6.2.2. *Let ψ_S and A_S denote a state and observable in the Schrödinger picture. Then we define*

$$\begin{aligned} &\psi_H := U^\dagger(t,t_0)\psi_s(t) \\ &A_H(t,t_0) := U^\dagger(t,t_0)A_sU(t,t_0) \end{aligned}$$

in the Heisenberg picture.

Remark. *The commutation relations of observables are invariant: $[A_S,B_S] = C_S \iff [A_H(t,t_0),B_H(t,t_0)] = C_H(t,t_0)$. We also see that if the Hamiltonian in the Schrödinger picture is time independent then $\hat{H}_H = \hat{H}_S$ since $U(t,t_0)$ commutes with $\hat{H}_S$.*

Proposition 6.2.3. *Consider a state ψ in the Schrödinger picture ψ_S and in the Heisenberg picture ψ_H. Then*

$$\langle A_S \rangle_{\psi_S(t)} = \langle A_H(t, t_0) \rangle_{\psi_H}$$

In other words, expectation values of observables are invariant.

Proof. We have that

$$\begin{aligned}
\langle A_S \rangle_{\psi_S(t)} &= \langle \psi_S(t), A_S \psi_S(t) \rangle \\
&= \langle U(t, t_0)\psi_S(t_0), A_S U(t, t_0)\psi_s(t_0) \rangle \\
&= \langle \psi_H(t_0), (U(t, t_0)^\dagger A_S U(t, t_0))\psi_H(t_0) \rangle \\
&= \langle \psi_H(t_0), A_H(t, t_0)\psi_H(t_0) \rangle \\
&= \langle A_H(t, t_0) \rangle_{\psi_H}
\end{aligned}$$

□

Theorem 6.2.4. *Let A_S be an observable in the Schrödinger picture and A_H the observable in the Heisenberg picture. Then these two observables satisfy the following differential equation:*

$$\frac{d}{dt} A_H(t) = \frac{i}{\hbar}[\hat{H}, A_H] + \left(\frac{\partial}{\partial t} A_S \right)_H$$

This is known as ***Heisenberg's equation of motion****.*

Proof. Writing $A_H(t) := A_H(t, t_0)$, we have that

$$\begin{aligned}
i\hbar \frac{d}{dt} A_H(t) &= i\hbar (U^\dagger(t, t_0) A_S U(t, t_0)) \\
&= \left(i\hbar \frac{d}{dt} U^\dagger \right) A_S U + U^\dagger A_S \left(i\hbar \frac{\partial}{\partial t} U \right) + U^* \left(\frac{\partial}{\partial t} A_S \right) U \\
&= -U^\dagger \hat{H} A_S U + U^\dagger A_S \hat{H} U + i\hbar U^* \left(\frac{\partial}{\partial t} A_S \right) U \\
&= -U^\dagger \hat{H} U U^\dagger A_S U + U^\dagger A_S U U^\dagger \hat{H} U + i\hbar U^* \left(\frac{\partial}{\partial t} A_S \right) U \\
&= -\hat{H} A_H + A_H \hat{H} + i\hbar U^* \left(\frac{\partial}{\partial t} A_S \right) U \\
&= -[\hat{H}, A_H] + i\hbar U^* \left(\frac{\partial}{\partial t} A_S \right) U
\end{aligned}$$

Dividing through by $i\hbar$, we arrive at the desired result. □

Remark. *The Heisenberg equation of motion confirms our previous statements about conserved quantities. If A has no explicit time dependence in the Schrödinger picture then A is convserved if and only if it commutes with the Hamiltonian.*

Example 6.2.5. *Consider again the harmonic oscillator with Hamiltonian $H = \hbar\omega\left(a^\dagger + \frac{1}{2}\right)$ where $[a, a^\dagger] = 1$ and $\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}}(a + a^\dagger)$ is the position operator. $H, a, a^\dagger$ and $\hat{x}$ are all explicitly time independent operators in the Schrödinger equation.*
We now change to the Heisenberg picture using $U(t, t_0)$ and setting $t = 0$. We denote $U(t) := U(t, 0)$ and first compute the following:

$$\begin{aligned}
Ha &= \hbar\omega(N + \frac{a}{2}) \\
&= \hbar\omega(\frac{a}{2} + [N, a] + aN) \\
&= a\hbar\omega(N + \frac{1}{2}) - a\hbar\omega \\
&= a(H - \hbar\omega) \\
&\implies H^n a = a(H - \hbar\omega)^n \\
&\implies e^{\lambda H} a = a e^{\lambda(H - \hbar\omega)}
\end{aligned}$$

for some λ. We can therefore calculate the operators in the Heisenberg picture as follows:

$$\begin{aligned}
a(t) = U(t)^\dagger a U(t) &= e^{\frac{i}{\hbar}tH} a e^{-\frac{i}{\hbar}tH} \\
&= a e^{\frac{i}{\hbar}tH - \frac{i}{\hbar}t\hbar\omega} e^{-\frac{i}{\hbar}tH} \\
&= e^{-it\omega} a
\end{aligned}$$

$$a^\dagger(t) = (a(t))^\dagger = e^{i\omega t} a^\dagger$$

$$H(t) = e^{\frac{i}{\hbar}tH} H e^{-\frac{i}{\hbar}tH} = H$$

$$\begin{aligned}
\hat{x} &= U^\dagger(t)\hat{x}U(t) \\
&= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} (a(t) + a^\dagger(t)) \\
&= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} (e^{-i\omega t} a + e^{i\omega t} a^\dagger)
\end{aligned}$$

We will now calculate the expectation value of $\hat{x}(t)$ *in the time independent state* $|\psi\rangle = \frac{1}{\sqrt{2}}(|\psi_n\rangle + |\psi_{n+1}\rangle)$ *where* $|\psi_n\rangle$ *is a normalised eigenstate of* N *with eigenvalue* $n \in \mathbb{N} \cup \{0\}$*. We shall use, from previous results, that* $a\,|\psi_{n+1}\rangle = \sqrt{n+1}\,|\psi_n\rangle$ *and* $a^\dagger\,|\psi_n\rangle = \sqrt{n+1}\,|\psi_{n+1}\rangle$*. We have that*

$$\begin{aligned}
\langle \hat{x}(t)\rangle_\psi &= \langle \psi, \hat{x}\psi\rangle \\
&= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \left(\frac{1}{\sqrt{2}}\right)^2 \left(\langle \psi_n, a(t)\psi_{n+1}\rangle + \langle \psi_{n+1}, a^\dagger(t)\psi_n\rangle\right) \\
&= \frac{1}{2}\left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \left(e^{-i\omega t}\sqrt{n+1}\,\langle \psi_n, \psi_n\rangle + e^{i\omega t}\sqrt{n+1}\,\langle \psi_{n+1}, \psi_{n+1}\rangle\right) \\
&= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \cos\omega t
\end{aligned}$$

which looks very similar to the position at time t *of the harmonic oscillator in the classical setting.*