QUANTUM MECHANICS

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AIMS, February 21, 2005

Abstract

These notes are based on a lecture course I gave to second and third year mathematics students at Oxford in years 1999–2002.

This is a mathematics course, and I am not assuming any knowledge of physics. The comments I will occasionally make about physics are there motivate some of the material, and (hopefully) make it more interesting.

The lectures will be self–contained but I need to assume some maths knowledge. In particular I would want you to be familiar with basic concepts of linear algebra (like matrices, eigenvectors, eigenvalues, and diagonalisation), and ordinary differential equations (second order linear ODEs, boundary conditions).

Contents

Chapter 1

The breakdown of classical mechanics

Black body radiation: radiation emitted in packets (*quanta*)

$$E = \hbar\omega, \tag{1.1}$$

where ω is a frequency and $\hbar = 1.0546 \times 10^{-34} Js = h/2\pi$ is a Planck's constant. (Planck 1900)

Einstein 1905: The quanta are feature of light. Photo-electric effect:[PICTURE] Experimental fact: increasing of frequency of light increased the energy of emitted electrons, but not their number. Increasing the flux (intensity) caused more electrons coming out with the same energy. Light is a stream of *photons* whose energy is proportional to the frequency $\omega = 2\pi c/\gamma$, where c is the speed of light and γ is the wavelength. 1900-1924 'Old quantum theory' (Compton's scattering, Nielst Bohr's (1913) hydrogen atom). De Broglie waves (1924): particles (*electrons*) behave like waves:

$$\mathbf{p} = \hbar\mathbf{k}, \tag{1.2}$$

where $\underline{\mathrm{k}}$ is a wave vector $|k| = 2\pi/\gamma$.

Particles in classical mechanics have well defined trajectories, that is a position, and a velocity is known at each instant of time. How one might observe these features?[PICTURE] To measure particles position one must hit its with a photon, but this photon will transfer its momentum to a particle, thus changing particles momentum (it applies only to small particles, eg. electrons). Consequences

- Measurement process modifies what is being measured
- No trajectories in quantum mechanics
- Indeterminism (linked to the wave properties of matter)

Need for a new theory.

Chapter 2

Schrödinger's Equation

Look for a wave equation satisfied by de Broglie 'matter wave'. The plane wave $\psi(\mathbf{x},t) = \exp(-i(\omega t - \mathbf{k}\cdot\mathbf{x})$ satisfies

$$i\hbar\frac{\partial\psi}{\partial t} = \hbar\omega\psi = E\psi, \qquad \frac{\hbar}{i}\nabla\psi = \hbar\mathbf{k}\psi = \mathbf{p}\psi.$$

Note the relationship between the observables (physical quantities which we want to measure) and differential operators acting on a wave function

$$E \longrightarrow i\hbar\frac{\partial}{\partial t}, \qquad \mathbf{p} \longrightarrow \frac{\hbar}{i}\nabla. \tag{2.1}$$

For a conservative dynamical system $H = p^2/2m + V(\underline{\mathrm{x}}) = E$. Use (2.1) to obtain

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{x})\psi \tag{2.2}$$

The *time dependent Schrödinger equation* (TDS) (1925) for a complex function $\psi = \psi(\mathbf{x},t)$ (valid also in one or two dimensions). There are solutions other than plane waves.

2.1 Separable solutions

Look for $\psi(\mathbf{x},t) = T(t)\Psi(\mathbf{x})$

$$i\hbar\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{\Psi}\Big(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi\Big)$$

$LHS = RHS$ =constant= E

$$i\hbar\frac{\mathrm{d}T}{\mathrm{d}t} = ET \longrightarrow T(t) = e^{-itE/\hbar}T(0),$$

and

$$-\hbar^2/2m\nabla^2\Psi + V\Psi = E\Psi, \tag{2.3}$$

which is the *time independent Schrödinger equation* (TIS). The *stationary states* are

$$\psi(\mathbf{x},t) = \Psi(\mathbf{x})T(0)e^{-itE/\hbar} = \psi(\mathbf{x},0)e^{-itE/\hbar}. \tag{2.4}$$

2.2 The Interpretation of the wave function

What is $\psi(\mathbf{x}, t)$? The most widely accepted is the (*Copenhagen*) interpretation in Max Born (1926):

- *The entire information about a quantum state (particle) is contained in the wave function. For a normalised wave function*

$$\rho(\mathbf{x}) = |\psi(\mathbf{x})|^2 = \overline{\psi}\psi \tag{2.5}$$

gives the probability density for the position of the particle.

So the probability that the particle moving on a line is in the interval (a, b) is given by

$$\int_b^a |\psi(x,t)|^2 \mathrm{d}x. \tag{2.6}$$

Remarks:

- Particle 'has to be somewhere', so

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x},t)|^2 \mathrm{d}^3\mathbf{x} = 1 \tag{2.7}$$

this is the *normalisation condition.*

- $\psi(\mathbf{x}, t)$ and $\psi(\mathbf{x}, t)e^{i\phi(\mathbf{x},t)}$ give the some information. The real function $\phi(\mathbf{x}, t)$ is called *the phase.*

- Both (2.2) and (2.3) are linear differential equations. Their solutions satisfy the *superposition principle*: If ψ_1 and ψ_2 are solutions then so is $c_1\psi_1 + c_2\psi_2$, for any $c_1, c_2 \in \mathbb{C}$ (so solutions form a complex vector space, later to be identified with a *Hilbert space.*)

- The general solution to (2.2) will not be separable, but will be of the form

$$\sum c_n \psi_n(\mathbf{x}, t), \tag{2.8}$$

where $\psi_n(\mathbf{x}, t) = \Psi_n(\mathbf{x})T_n(t)$ are stationary states given by (2.4).

- For each stationary state

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_n + V\Psi_n = E_n\Psi_n.$$

The probability of measuring the value E_n is $|c_n|^2$, and (from the Parceval's theorem, and (2.7)) [THINK ABOUT IT IN GENERAL]

$$\sum_n |c_n|^2 = 1.$$

- The mean position is given by

$$\langle \mathbf{r} \rangle = \int_{\mathbb{R}^3} \overline{\psi}\mathbf{r}\psi \mathrm{d}^3x$$

2.3 Conservation of probability

Assume the normalisation (2.7) at $t = 0$.

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x}, 0)|^2 \mathrm{d}^3\mathbf{x} = 1.$$

Is

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \mathrm{d}^3\mathbf{x} = 1 \qquad \text{for} \qquad t > 0 \ ?$$

The TDS equation (2.2) and its complex conjugations are

$$\begin{aligned} i\hbar\frac{\partial\psi}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{x})\psi, \\ -i\hbar\frac{\partial\overline{\psi}}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2\overline{\psi} + V(\mathbf{x})\overline{\psi}, \end{aligned}$$

where $V(\mathbf{x})$ is real.

$$\begin{aligned} \frac{\partial}{\partial t}\Big(|\psi(\mathbf{x}, t)|^2\Big) &= \frac{\partial\overline{\psi}}{\partial t}\psi + \overline{\psi}\frac{\partial\psi}{\partial t} \\ &= \Big(\frac{\hbar}{2im}\nabla^2\overline{\psi} - \frac{V}{i\hbar}\overline{\psi}\Big)\psi + \overline{\psi}\Big(-\frac{\hbar}{2im}\nabla^2\psi + \frac{V}{i\hbar}\psi\Big) \\ &= \frac{i\hbar}{2m}(\overline{\psi}\nabla^2\psi - \psi\nabla^2\overline{\psi}) = \frac{i\hbar}{2m}\nabla\cdot(\overline{\psi}\nabla\psi - \psi\nabla\overline{\psi}). \end{aligned}$$

Definition 2.3.1 *The probability current is*

$$\mathbf{j}(\mathbf{x}, t) = -\frac{i\hbar}{2m}(\overline{\psi}\nabla\psi - \psi\nabla\overline{\psi}). \tag{2.9}$$

So we have proved

Proposition 2.3.2 *If ψ is a solution to* (2.2) *then the probability density* (2.5) *and the probability current* (2.9) *satisfy the continuity equation*

$$\frac{\partial\rho}{\partial t} + div\mathbf{j} = 0. \tag{2.10}$$

We shall now use the divergence theorem and Proposition 2.3.2 to show that QM probability is conserved.

Proposition 2.3.3 *Suppose that $\mathbf{j}(\mathbf{x}, t)$ tends to 0 faster than $|\mathbf{x}|^{-2}$ as $|\mathbf{x}| \to \infty$. Then*

$$\int_{\mathbb{R}^3} \rho(\mathbf{x}, t)\mathrm{d}^3\mathbf{x}.$$

is independent of time.

Proof. Let B be a ball enclosed by a sphere $S_{|\mathbf{x}|}$ of radius $|\mathbf{x}|$. Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_B \rho(\mathbf{x},t)\mathrm{d}^3\mathbf{x} = \int_B \frac{\partial\rho(\mathbf{x},t)}{\partial t}\mathrm{d}^3\mathbf{x} = -\int_B \mathrm{div}\mathbf{j}\mathrm{d}^3\mathbf{x} = -\int_{S_{|\mathbf{x}|}} \mathbf{j}\cdot\mathrm{d}\mathbf{S}.$$

So if $\mathbf{j}(\mathbf{x},t)$ tends to 0 faster than $|\mathbf{x}|^{-2}$ the last integral tends to 0 as $|\mathbf{x}| \to \infty$, and so $\int_{\mathbb{R}^3}\rho(\mathbf{x},t)\mathrm{d}^3\mathbf{x}$ is independent of time.

□

Example. Consider a potential well

$$V(x) = \begin{cases} 0 & \text{for } x \in (0,a) \\ \infty & \text{otherwise.} \end{cases} \tag{2.11}$$

The equation (2.3) reduces to

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = E\Psi \qquad \text{for } x \in (0,a), \qquad \Psi = 0 \text{ otherwise.}$$

Solve the boundary value problem

$$\Psi(x) = \begin{cases} A\cosh(x\sqrt{2m|E|}/\hbar) + B\sinh(x\sqrt{2m|E|}/\hbar) & \text{if } E < 0 \\ A + Bx \qquad \text{if } E = 0 \\ A\cos(x\sqrt{2mE}/\hbar) + B\sin(x\sqrt{2mE}/\hbar) & \text{if } E > 0. \end{cases}$$

From $\Psi(0) = 0$ we have $A = 0$ in each case. From $\Psi(a) = 0$ we have $B = 0$ if $E \leqslant 0$ (so that $\Psi = 0$ in those cases), and

$$\frac{a\sqrt{2mE}}{\hbar} = n\pi \qquad \text{for } n \in \mathbb{Z} \qquad \text{if } E > 0.$$

So we have infinitely many nontrivial solutions parametrised by a positive integer (the sign can be absorbed in B)

$$\Psi_n(x) = B_n \sin\Big(\frac{n\pi x}{a}\Big), \qquad \text{and } E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}. \tag{2.12}$$

Remarks

- Equation (2.3) gave rise to an *eigenvalue problem*. Allowed energies are eigenvalues E_n corresponding to eigenvectors Ψ_n. If a given eigenvalue corresponds to only one eigenvector then it is called *non-degenerated*. Otherwise it is degenerated
- Energies of the system can take only discrete values, which is a purely quantum phenomenon.

Definition 2.3.4 *When the energies of a quantum system are discrete and bounded below, then the lowest possible energy state is called* the ground state *and the higher states are known as 1st, 2nd, ..., kth excited states. The integer parametrising discrete energies (or other observables) is called a quantum number.*

The normalisation condition (2.7) yields

$$\int_0^a {B_n}^2 \sin^2\Big(\frac{n\pi x}{a}\Big)\mathrm{d}x = 1, \qquad \text{so } B_n = \sqrt{\frac{2}{a}}.$$

The stationary states (2.4) are

$$\psi_n(x,t) = \sqrt{\frac{2}{a}} e^{-in^2\pi^2\hbar t/(2ma^2)} \sin\frac{n\pi x}{a}$$

and the general solution is given by (2.8). To determine c_n suppose that $\psi(x,0) = f(x)$. From (2.8)

$$f(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\frac{n\pi x}{a}, \qquad \text{so } c_n = \sqrt{\frac{2}{a}} \int_0^a f(x) \sin\frac{n\pi x}{a}\mathrm{d}x. \tag{2.13}$$

Look at Born's probabilistic interpretation:

$$|\psi_n(x,t)|^2 = \frac{2}{a}\sin^2\frac{n\pi x}{a} = \frac{1}{a}\Big(1 - \cos\frac{2n\pi x}{a}\Big).$$

What is a probability that a particle described by ψ_n is between 0 and x_0?

$$F_n(x_0) = \int_0^{x_0} \frac{1}{a}\Big(1 - \cos\frac{2n\pi x}{a}\Big)\mathrm{d}x = \Big(\frac{x_0}{a} - \frac{1}{2n\pi}\sin\frac{2n\pi x_0}{a}\Big).$$

The classical distribution would be $F(x_0) = x_0/a = \lim_{n\to\infty} F_n(x_0)$.

Definition 2.3.5 (Bohr's correspondence principle) *Quantum mechanical formulae approach those of the classical mechanics if the quantum number is large.*

Example 2.3.6 *Suppose that $\psi(x,0) = 1/\sqrt{a} = const$. Find a probability of measuring energy E_n.*

From (2.13)

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sqrt{\frac{1}{a}} \sin\frac{n\pi x}{a}\mathrm{d}x = \frac{\sqrt{2}}{n\pi}\Big[-\cos\frac{n\pi x}{a}\Big]_0^a = \frac{\sqrt{2}}{n\pi}[1 - (-1)^n]$$

So the probability of measuring E_n is 0 if n is even, and

$$\frac{8}{n^2\pi^2}$$

if is n is odd.

Chapter 3

Basic scattering theory (in one dimension)

The way physicists discover new elementary particles is by scattering experiments. Huge accelerators collide particles through targets, and by analysing the changes to momentas of scattered particles, a picture of a target is built. We shall look at some features of the scattering theory.

3.1 Free particle

Equation (2.3) with $V = 0$ yields

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = E\Psi.$$

With the definition $k = \sqrt{2mE}/\hbar$ the solution is

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{3.1}$$

and the stationary states (2.4) are

$$\psi(x,t) = \Psi(x)e^{-iEt/\hbar} = \underbrace{Ae^{i(kx-\omega t)}}_{\text{incoming wave}} + \underbrace{Be^{-i(kx+\omega t)}}_{\text{outgoing wave}}, \qquad \text{where } \omega = \frac{E}{\hbar}. \tag{3.2}$$

Convention: incoming=incident from the left.

Remarks

- If $B = 0$, then $\rho(x,t) = |\psi(x,t)|^2 = |A|^2$, so the probability of finding a particle in an interval L is (from (2.6)) $|A|^2L$. But

  $$\int_{\mathbb{R}} \rho(x,t)\mathrm{d}x = \infty,$$

  and the plane waves can not be normalised (one way to get around it is suggested in the problem one, sheet two). However it still makes sense to talk about relative probabilities of finding a particle in two intervals.

- The normalizable wave functions (like (2.12)) are called *bound states*. Other (like plane waves (3.2)) are *scattering states*.
- There are no restrictions on k (and so E) in (3.2). Therefore the energies are continuous.
- The probability current (2.9) for (3.2) is

$$j = \frac{\hbar}{2mi}\Big(\overline{\psi}\frac{\mathrm{d}\psi}{\mathrm{d}x} - \psi\frac{\mathrm{d}\overline{\psi}}{\mathrm{d}x}\Big) = \frac{\hbar k}{m}\Big(|A|^2 - |B|^2\Big), \tag{3.3}$$

where the factor $\hbar k/m$ can be identified (by the De Broglie formula (1.2)) with a velocity.

3.2 Reflection and transmission coefficients

In the example (2.11) the boundary conditions at ∞ determined the energy eigenvalues in $(0, a)$ (this led to a discrete spectrum). In the scattering theory the energy of a potential barrier determines energies of a quantum system at the large distances. [PICTURE] Regions where $V(x) = 0$ correspond to free particle (3.1)

$$\Psi(x) = \begin{cases} \Psi_L = & A_L e^{ik_L x} + B_L e^{-ik_L x}, \qquad \text{for } x \leqslant 0 \\ \Psi_V & \text{depends on } V(x), \qquad \text{for } x \in [0, a] \\ \Psi_R = & A_R e^{ik_R x}, \qquad \text{for } x > a \end{cases}$$

For a beam incident from the left define

Definition 3.2.1

$$\begin{aligned} \text{Reflection coefficient} &= \frac{|\text{reflected current}|}{|\text{incident current}|} = \frac{|B_L|^2}{|A_L|^2} = R \\ \text{Transmission coefficient} &= \frac{|\text{transmitted current}|}{|\text{incident current}|} = \frac{k_R|A_R|^2}{k_L|A_L|^2} = T \end{aligned} \tag{3.4}$$

We don't know Ψ in the interaction region. However, we can still say something:

Proposition 3.2.2 *For one-dimensional, time independent problems*

1. *The probability current is constant.*
2. *The sum of reflection and transmition coefficient is* 1.

Proof.

1. The continuity equation (2.10) reduces to $\mathrm{d}j/\mathrm{d}x = 0$, so that j is constant in regions L, V, and R. In fact $j_L = j_V = j_R$, which follows from the matching conditions: Ψ and $\mathrm{d}\Psi/\mathrm{d}x$ are continuous at $x = 0$ and $x = a$ (and in general, at the potential discontinuities), so that the probability current is well defined.
2. Equation (3.3) and the first part of this Proposition imply

$$k_L(|A_L|^2 - |B_L|^2) = k_R|A_R|^2.$$

The result follows if one divides the last formula by $k_L|A_L|$.

□

3.3 Examples

Potential Step [PICTURE]

$$V(x) = \begin{cases} 0 & \text{for } x < 0 \\ V_0 & \text{for } x \geqslant 0. \end{cases} \tag{3.5}$$

$$\Psi = \begin{cases} \Psi_L = & A_L e^{ik_L x} + B_L e^{-ik_L x}, & \text{for } x < 0, & \text{where} & k_L = \sqrt{2mE}/\hbar \\ \Psi_R = & A_R e^{ik_R x} + B_R e^{-ik_R x}, & \text{for } x > 0, & \text{where} & k_R = \sqrt{2m(E-V_0)}/\hbar. \end{cases}$$

Note that k_R may be real or imaginary. The matching conditions are

$$\begin{aligned} \Psi_L(0) &= \Psi_R(0) \longrightarrow A_L + B_L = A_R + B_R \\ \Psi'_L(0) &= \Psi'_R(0) \longrightarrow k_L(A_L - B_L) = k_R(A_R - B_R), \end{aligned}$$

which relates the waves on both sides of the potential jump

$$\begin{aligned} A_L &= \frac{1}{2k_L}\Big((k_L + k_R)A_R + (k_L - k_R)B_R\Big), \\ B_L &= \frac{1}{2k_L}\Big((k_L - k_R)A_R + (k_L + k_R)B_R\Big). \end{aligned}$$

Assume that the particle is incident from the left, and $E > V_0$. Now k_R is real and $B_R = 0$ (as no beam is coming from ∞. The reflection and transmition coefficients (scattering data) are given by

$$R = \frac{|B_L|^2}{|A_L|^2} = \frac{(k_L - k_R)^2}{(k_L + k_R)^2}, \qquad T = \frac{k_R |A_R|^2}{k_L |A_L|^2} = \frac{4k_L k_R}{(k_L + k_R)^2}.$$

3.4 Potential Barrier

[PICTURE]

$$V(x) = \begin{cases} V_0 > 0 & \text{for } x \in [0, a] \\ 0 & \text{otherwise.} \end{cases} \tag{3.6}$$

Consider an incoming beam of particles with energy $0 < E < V_0$. In classical mechanics the whole beam would be reflected. How about QM? In the regions 0 and 2 we have the free particle solutions (3.1). In the region 1 the wave function satisfies

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} - \tilde{k}^2\Psi = 0, \qquad \text{where} \qquad \tilde{k}^{=}\frac{\sqrt{2m(V_0 - E)}}{\hbar}.$$

Therefore we have

$$\Psi = \begin{cases} \Psi_0 = & A_0 e^{ikx} + B_0 e^{-ikx}, & \text{for } x \leqslant 0 & k = \sqrt{2mE}/h \\ \Psi_1 = & A_1 e^{\tilde{k}x} + B_1 e^{-\tilde{k}x}, & \text{for } x \in [0, a] & \\ \Psi_2 = & A_2 e^{ikx}, & \text{for } x > a & \end{cases}$$

$B_2 = 0$ as there are no incident particles coming from from ∞. Continuity of the wave function and its first derivatives gives four conditions on five constant

$$\begin{aligned}
\Psi_0(0) &= \Psi_1(0) & A_0 + B_0 &= A_1 + B_1 \\
\Psi_0{}'(0) &= \Psi_1{}'(0) & ik(A_0 - B_0) &= \tilde{k}(A_1 + B_1) \\
\Psi_1(a) &= \Psi_2(a) & A_1 e^{a\tilde{k}} + B_1 e^{-a\tilde{k}} &= A_2 e^{ika} \\
\Psi_1{}'(a) &= \Psi_2{}'(a) & \tilde{k}(A_1 e^{a\tilde{k}} - B_1 e^{-a\tilde{k}}) &= ikA_2 e^{ika}.
\end{aligned}$$

A simple algebra gives

$$\frac{A_2}{A_0} = \frac{4ik\tilde{k}e^{-ika}}{e^{\tilde{k}a}(k + i\tilde{k})^2 - e^{-\tilde{k}a}(k - i\tilde{k})^2}$$

so that the transmition coefficient (3.4) $T \neq 0$. This is a quantum phenomenon known as *tunnelling*. Classical particles with $E < V_0$ would not have enough energy to penetrate te barrier. Quantum particles can (because of their wave properties) tunnel through large barriers. This has many application (for example Scanning tunneling electron microscope, Nobel 1986).

3.5 Finite square well

[PICTURE]

$$V(x) = \begin{cases} 0 & \text{for } x \in (0, a) \\ V_0 > 0 & \text{otherwise.} \end{cases} \tag{3.7}$$

Case 1. $0 < E < V_0$ [Bound states.] In the region $x \in (0, a)$

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + k^2\Psi = 0, \qquad \text{where} \qquad k = \frac{\sqrt{2mE}}{\hbar}.$$

In the region $x \in (-\infty, 0] \cup [a, \infty)$

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} - \tilde{k}^2\Psi = 0, \qquad \text{where} \qquad \tilde{k} = \frac{\sqrt{2m(V_0 - E)}}{\hbar}.$$

This yields

$$\Psi = \begin{cases} \Psi_0 = A_0 e^{\tilde{k}x}, & \text{for } x \leqslant 0 \\ \Psi_1 = A_1 e^{ikx} + B_1 e^{-ikx}, & \text{for } x \in [0, a] \\ \Psi_2 = B_2 e^{-\tilde{k}x}, & \text{for } x > a \end{cases}$$

and $B_0 = A_2 = 0$ so that Ψ remains bounded for $|x| \to \infty$. We have four boundary conditions:

$$\begin{aligned}
A_0 - A_1 - B_1 &= 0 \\
\tilde{k}A_0 - ikA_1 + ikB_1 &= 0 \\
e^{ika}A_1 + e^{-ika}B_1 - e^{-\tilde{k}a}B_2 &= 0 \\
ike^{ika}A_1 - ike^{-ika}B_1 + \tilde{k}e^{-\tilde{k}a}B_2 &= 0
\end{aligned}$$

The determinant of the associated matrix must vanish for the nontrivial solutions to exists. This gives a condition for energy:

$$\det \begin{pmatrix} 1 & -1 & -1 & 0 \\ \tilde{k} & -ik & ik & 0 \\ 0 & e^{ika} & e^{-ika} & -e^{-\tilde{k}a} \\ 0 & ike^{ika} & -ike^{-ika} & \tilde{k}e^{-\tilde{k}a} \end{pmatrix} = 0$$

which yields

$$\tan ka = \frac{2k\tilde{k}}{k^2 - \tilde{k}^2}. \tag{3.8}$$

Remarks

- Since $0 < E < V_0$, there are only finitely many of states of the form (3.8). If $V_0 \to \infty$ we recover the result (2.12).
- The wave function (or the probability of finding a particle) is non zero in a classically forbidden region $x \in (-\infty, 0] \cup [a, \infty)$.

Case 2. $E > V_0$ [Scattering states.] In the region $x \in (0, a)$ equation (2.3) yields

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + k^2\Psi = 0, \qquad \text{where} \qquad k^2 = \frac{2mE}{\hbar^2} > 0.$$

In the region $x \in (-\infty, 0] \cup [a, \infty)$

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + \tilde{k}^2\Psi = 0, \qquad \text{where} \qquad \tilde{k}^2 = \frac{2m(E - V_0)}{\hbar^2} > 0.$$

So, in each region, we have a combination of exponents (two constants in each region). Six constants and four boundary conditions, so there are no restrictions on energy. We have *continuous spectrum.*

Chapter 4

The harmonic oscillator

In classical mechanics the harmonic oscillator is described by the potential $V = (1/2)m\omega^2 x^2$, which leads to the Newton equation

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -m\omega^2 x,$$

and the continuous energy spectrum.

The quantum harmonic oscillator (first solved by Heisenberg in 1925) is an important example, because many systems (eg. atoms in crystals) undergoing small disturbances behave like harmonic oscillators. The time independent Schrödinger equation (2.3) yields

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\Psi = E\Psi. \tag{4.1}$$

We shall adopt the following strategy:

1. Find the asymptotic behaviour ϕ of Ψ for large $|x|$,
2. make a substitution $\Psi = f\phi$,
3. solve an equation for f using a power series method (a1 differential equations).

First simplify: In terms of

$$z := x\sqrt{m\omega/\hbar}, \qquad \epsilon = E/\hbar\omega$$

equation (4.1) becomes

$$\Psi'' + (2\epsilon - z^2)\Psi = 0, \qquad \text{where} \qquad {}' = \frac{\mathrm{d}}{\mathrm{d}z}. \tag{4.2}$$

Step 1: For large z the function $\phi = \exp(-z^2/2)$ satisfies (4.2). Inspection

$$\phi' = -z\phi, \qquad \phi'' = -\phi + z^2\phi, \tag{4.3}$$

which is (4.2) with $\epsilon = 1/2$. For large z the multiple of z^2 dominates, so we neglect ϵ.
Step 2: Substitute $\Psi(z) = f(z)\phi(z)$ to (4.2)

$$f''\phi + 2f'\phi' + f\phi'' + (2\epsilon - z^2)f\phi = 0.$$

Use (4.3)

$$f''\phi - 2zf'\phi - f\phi + z^2 f\phi + 2\epsilon f\phi - z^2 f\phi = 0,$$

and put $2N := 2\epsilon - 1$ to obtain

$$f'' - 2zf' + 2Nf = 0. \tag{4.4}$$

This is the Hermite equation, well known in the 19th century mathematics.
Step 3: Solve (4.4) using a method of series solutions. The point $z = 0$ is regular, so take $f(z) = \sum_{n=0}^{\infty} a_n z^n$, which yields

$$\sum_{n=0}^{\infty} n(n-1)a_n z^{n-2} - 2\sum_{n=0}^{\infty} n a_n z^n + 2N\sum_{n=0}^{\infty} a_n z^n = 0.$$

This gives the recursion relation

$$a_{n+2} = \frac{2(n-N)}{(n+2)(n+1)} a_n. \tag{4.5}$$

All a_ns have the same sign (assume non-negative). For large n (4.5) yields

$$\frac{a_{n+2}}{a_n} = \frac{2}{n},$$

so f has a behaviour of $\exp(z^2) = \sum_{n=0}^{\infty} z^{2n}/n!$ for even n, or $z\exp(z^2)$ for odd n, and $\Psi = f\phi \sim \exp z^2/2$, which is not normalisable. **Conclusion:** The series must terminate for some n, so (from (4.5)) N must be a non-negative integer

$$N = \frac{E}{\hbar\omega} - \frac{1}{2} = n \in \mathbb{Z} \longrightarrow E = \Big(n + \frac{1}{2}\Big)\hbar\omega.$$

The corresponding $f(z)$ is a polynomial of degree n, known as *n-th Hermite polynomial*. We have proved

Proposition 4.0.1 *The energy levels of a harmonic oscillator with the potential* $(1/2)m\omega^2 x^2$ *are discrete, and given by*

$$E_n = \Big(n + \frac{1}{2}\Big)\hbar\omega, \qquad n = 0, 1, 2, \ldots \ . \tag{4.6}$$

The corresponding wave functions are

$$\Psi_n(x) = c_n H_n\Big(x\sqrt{\frac{m\omega}{\hbar}}\Big)\exp\Big(-\frac{m\omega x^2}{2\hbar}\Big), \tag{4.7}$$

where c_n are normalisation constants, and H_n are polynomials of degree n.

4.1 Hermite polynomials

Equation (4.4) with N integer is

$$H_n{}'' - 2zH_n{}' + 2nH_n = 0, \qquad n = 0, 1, \ldots . \tag{4.8}$$

This defines H_n up to a multiplicative constant, which is fixed by demanding that the coefficient of z^n in $H_n(z)$ is 2^n. The first few polynomials are

$$H_0(z) = 1, \qquad H_1(z) = 2z, \qquad H_2(z) = 4z^2 - 2, \qquad H_3(z) = 8z^3 - 12z, \ldots$$

From (4.5) it follows that H_n is even for even n, and odd for odd n. The general form of Hermite polynomials is given by

Proposition 4.1.1 *Let H_n be a polynomial of degree n which satisfies* (4.8)*, and is normalised by demanding that the coefficient of z^n in $H_n(z)$ is 2^n. Then*

$$H_n(z) = (-1)^n e^{z^2} \Big(\frac{\mathrm{d}}{\mathrm{d}z}\Big)^n e^{-z^2}. \tag{4.9}$$

Proof. Define a generating function

$$G(z, s) = \sum_{n=0}^{\infty} \frac{s^n}{n!} H_n(z)$$

so that

$$H_n(z) = \Big(\frac{\partial}{\partial s}\Big)^n G(z, s)|_{s=0}.$$

One can show (sheet 3, problem 4), that

$$G(z, s) = e^{-s^2+2sz}. \tag{4.10}$$

The last formula will give the general form of Hermite polynomials. Rewrite (4.10) as $G(z, s) = \exp(z^2) \exp[-(s - z)^2]$, and note that

$$\frac{\partial}{\partial s} \exp[-(s - z)^2] = -2(s - z) \exp[-(s - z)^2] = -\frac{\partial}{\partial z} \exp[-(s - z)^2].$$

Therefore

$$H_n(z) = (-1)^n e^{z^2} \Big(\frac{\partial}{\partial z}\Big)^n e^{-(s-z)^2}|_{s=0} = (-1)^n e^{z^2} \Big(\frac{\mathrm{d}}{\mathrm{d}z}\Big)^n e^{-z^2}.$$

□

We shall now use (4.9) to determine the normalisation constants c_n appearing in (4.7)

$$1 = \int_{-\infty}^{\infty} |\Psi_n|^2 \mathrm{d}x = \sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} |c_n|^2 [H_n(z)]^2 e^{-z^2} \mathrm{d}z = \sqrt{\frac{\hbar}{m\omega}} |c_n|^2 \int_{-\infty}^{\infty} (-1)^n H_n(z) \Big(\frac{\mathrm{d}}{\mathrm{d}z}\Big)^n e^{-z^2} \mathrm{d}z.$$

We integrate the last formula n times by parts, and note that $\exp(-z^2)$ vanishes at $\pm\infty$. This yields

$$1 = \sqrt{\frac{\hbar}{m\omega}} |c_n|^2 \int_{-\infty}^{\infty} e^{-z^2} \Big(\frac{\mathrm{d}}{\mathrm{d}z}\Big)^n H_n(z) \mathrm{d}z,$$

but $H_n(z)$ is a polynomial of nth degree, with the coefficient of z^n equal to 2^n. Therefore

$$1 = \sqrt{\frac{\hbar}{m\omega}}|c_n|^2 n! 2^n \int_{-\infty}^{\infty} e^{-z^2} \mathrm{d}z.$$

Finally

$$|c_n|^2 = \Big(\frac{m\omega}{\pi\hbar}\Big)^{1/2} \frac{1}{2^n n!}. \tag{4.11}$$

4.2 Correspondence with classical theory

From (4.6) the lowest possible energy of the oscillator is $\hbar\omega/2$. This is known as the *zero point energy* (in classical mechanics the lowest energy is zero, which corresponds to the particle being at rest at the origin. In QM this is not allowed by the uncertainty principle (Section (6.6)).

Let E_n be the total energy of the oscillator. For the classical oscillator the motion can take place only in those regions of space for which

$$V(x) = \frac{1}{2}m\omega^2 x^2 \leqslant E_n = \hbar\omega\Big(n + \frac{1}{2}\Big), \qquad \text{so} \qquad |x| \leqslant \sqrt{\frac{\hbar(2n+1)}{m\omega}}.$$

The probability of finding a particle in a classically forbidden region (i.e. outside the *turning points* $\pm\sqrt{\hbar(2n+1)/m\omega}$ is non-zero in QM [PICTURE]. The agreement between classical and quantum probability densities improves rapidly with increasing n.

4.3 2D oscillator

Consider the potential $V(x,y) = (1/2)m(\omega_1^2 x^2 + \omega_2^2 y^2)$. The Schrödinger equation (2.3) yields

$$-\frac{\hbar^2}{2m}\Big(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2}\Big) + \frac{1}{2}m(\omega_1^2 x^2 + \omega_2^2 y^2)\Psi = E\Psi.$$

Seek a solution of the form $\Psi(x,y) = f(x)g(y)$. The last equation (when divided by $\Psi(x,y)$)gives

$$-\frac{\hbar^2}{2m}\Big(\frac{f''}{f} + \frac{g''}{g}\Big) + \frac{1}{2}m(\omega_1^2 x^2 + \omega_2^2 y^2) = E,$$

and

$$-\frac{\hbar^2}{2m}f'' + \frac{1}{2}m\omega_1^2 x^2 f = E_1 f, \qquad -\frac{\hbar^2}{2m}g'' + \frac{1}{2}m\omega_2^2 y^2 g = E_2 g, \qquad E_1 + E_2 = E.$$

Solutions to the above equations are parametrised by non-negative integers, and are given by (4.7) and (4.6):

$$f_p(x) = \Big(\frac{m\omega_1}{\pi\hbar}\Big)^{1/4}\Big(\frac{1}{2^p p!}\Big)^{1/2} H_p\Big(x\sqrt{\frac{m\omega_1}{\hbar}}\Big)\exp\Big(-\frac{m\omega_1 x^2}{2\hbar}\Big), \qquad E_p = \hbar\omega_1\Big(p+\frac{1}{2}\Big),\ p = 0,1,...$$

$$g_q(y) = \Big(\frac{m\omega_2}{\pi\hbar}\Big)^{1/4}\Big(\frac{1}{2^q q!}\Big)^{1/2} H_q\Big(y\sqrt{\frac{m\omega_2}{\hbar}}\Big)\exp\Big(-\frac{m\omega_2 y^2}{2\hbar}\Big), \qquad E_p = \hbar\omega_2\Big(q+\frac{1}{2}\Big),\ q = 0,1,...$$

The total wave function and the energy levels are

$$\Psi_{pq}(x,y) = f_p(x)g_q(y), \qquad E_{pq} = \hbar\omega_1\Big(p+\frac{1}{2}\Big) + \hbar\omega_2\Big(q+\frac{1}{2}\Big).$$

A harmonic oscillator for which $\omega_1 = \omega_2 = \omega$ is called *isotropic*. In this case $E_{pq} = \hbar\omega(p+q+1) = \hbar\omega(N+1)$, where $N = p+q = 0, 1, ...,$ and Ψ_{pq}, Ψ_{qp} are linearly independent functions with the same energy. If, for example, $p = 0, q = 1$ then any linear combination $\alpha\Psi_{01} + \beta\Psi_{10}$ will have energy $E = \hbar\omega$, so we have 2D space of eigenfunctions with this energy.

Definition 4.3.1 *If the space of solutions to the TIS* (2.3) *with fixed energy has dimension* $k > 1$*, then the energy is* k*-fold degenerate (if the space is 1D, then the energy levels are non-degenerate).*

If N is fixed, then $p = 0, 1, ...N$, and $q = N - p$, and the Nth excited states have degeneracy $N+1$ (all combinations of Ψ_{pN-p}, $p = 0, ...N$ have this energy).
Remarks

- If the potential contains a cross term then we need to diagonalise it by an orthogonal transformation

$$\begin{aligned} V(x,y) &= \frac{1}{2}m\omega^2(ax^2 + 2bxy + cy^2) \\ &= \frac{1}{2}m\omega^2(x\ y)\begin{pmatrix} a & b \\ b & c \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} \longrightarrow \frac{1}{2}m\omega^2(X\ Y)\begin{pmatrix} A & 0 \\ 0 & C \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} \end{aligned}$$

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} \longrightarrow \frac{\partial^2\Psi}{\partial X^2} + \frac{\partial^2\Psi}{\partial Y^2},$$

  and use the results of the last section (here a, b, c, A, C are constant real numbers).

- In three (and more) dimensions proceed in a similar way: Transfer to normal coordinates, and separate variables to reduce the problem to independent $1D$ oscillators. The total energy will be the sum of their energies, and the wave function will be the product of their wave functions.

Chapter 5

The hydrogen atom

Ernesrt Rutherford [1911] (based on experiments): atoms are miniatures of solar systems. Electrons of charge $-e$ orbit heavy (fixed) nucleus of a positive charge Ze [PICTURE]. For a hydrogen atom we have one electron. Classically atoms should not exist: Moving electrons radiate the electromagnetic energy, and fall into a nucleus. The first QM explanation was given by Bohr [1913] (using ad-hoc assumptions), and latter by Pauli [1925]. This was one of the biggest successes of quantum theory.

Force acting on electron [PICTURE]

$$F(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r^2}.$$

The corresponding potential

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

(compare the Newtonian gravity, Mods TT), where r is the distance between the electron and nucleus, $\varepsilon_0 = const$ (dielectric constant of vacuum), and m is the mass of the electron. The 3D TIS is

$$-\frac{\hbar^2}{2m}\nabla^2\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi. \tag{5.1}$$

LECTURE 8

5.1 The energy spectrum of the hydrogen atom

We shall neglect the angular variables, and assume that the electron moves radially in the central potential. This will be sufficient to determine the energy levels. The full treatment involving the angular variables leads to spherical harmonics, and will be discussed in the course *Further Quantum Theory*. If $\Psi = \Psi(r)$, then (5.1) becomes

$$\frac{-\hbar^2}{2m}\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\Psi) - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi.$$

Define

$$R = r\Psi, \qquad \text{and} \qquad \alpha = \frac{4\pi\varepsilon_0\hbar^2}{Zme^2}, \tag{5.2}$$

and rewrite the last equation as

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}R + \frac{2}{\alpha r}R + \frac{2mE}{\hbar^2}R = 0. \tag{5.3}$$

We aim to solve this equation subject to the following boundary conditions:

- $\Psi = R/r$ is finite at $r = 0$, so $\lim_{r\to 0} R(r) = 0$,
- $\int_{\mathbb{R}^3} |\Psi(r)|^2 r^2 \mathrm{d}r$ is finite, so $\lim_{r\to\infty} R(r) = 0$.

Our strategy will be similar to the one we used to solve the harmonic oscillator.
Step 1: For large r the asymptotic behaviour is

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}R + \frac{2mE}{\hbar^2}R \simeq 0,$$

so the energy is negative (otherwise we would have the oscillatory solution contradicting the second boundary condition). With the definition $k^2 = -2mE/\hbar^2$ we have $R \simeq \exp(-kr)$, for large r.
Step 2: Set $R(r) = f(r)\exp(-kr)$. Equation (5.3) yields

$$k^2 e^{-kr} f - 2ke^{-kr}\frac{\mathrm{d}f}{\mathrm{d}r} + e^{-kr}\frac{\mathrm{d}^2 f}{\mathrm{d}r^2} + \frac{2}{\alpha r}e^{-kr} f - k^2 e^{-kr} f = 0.$$

Put $\rho = r/\alpha$. Then the last equation becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}\rho^2}f - 2k\alpha\frac{\mathrm{d}}{\mathrm{d}\rho}f + \frac{2}{\rho}f = 0. \tag{5.4}$$

Now $\rho = 0$ is a 'regular singular point', so look for a solution of the form

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

Equation (5.4) yields

$$\sum_{n=0}^{\infty}(n+c)(n+c-1)a_n\rho^{n+c-2} - 2k\alpha\sum_{n=0}^{\infty}(n+c)a_n\rho^{n+c-1} + 2\sum_{n=0}^{\infty}a_n\rho^{n+c-1}.$$

Setting $n = 0$ we obtain the indicial equation $c(c-1) = 0$. Its solutions differ by integer. We take $c = 1$ (because R/r must be finite at $r = 0$). The recurrence equation is

$$n(n+1)a_n = 2(k\alpha n - 1)a_{n-1}. \tag{5.5}$$

Now argue as for the harmonic oscillator. For large n

$$\frac{a_n}{a_{n-1}} \simeq \frac{2k\alpha}{n},$$

and f behaves like $\exp(2k\alpha\rho) = \exp(2kr)$ (so Ψ is not normalizable). Therefore the series must terminate, and

$$k\alpha n - 1 = 0, \qquad \text{for some} \qquad n = 1, 2, \ldots \ .$$

Recall that $k^2 = -2mE/\hbar^2$, so the energy levels are

$$E_n = \frac{-k^2\hbar^2}{2m} = -\frac{\hbar^2}{2m\alpha^2 n^2} = \frac{E_1}{n^2}. \tag{5.6}$$

The energies are negative because it is conventional to take $V = 0$ at ∞.

Definition 5.1.1 *The positive integer n is known as the principal quantum number.*

The radial wave function with principal quantum number n is

$$\Psi_n(r) = \frac{e^{-kr}}{r} f(r) = e^{-r/\alpha n}[a_0 + a_1(r/\alpha) + ..a_{n-1}(r/\alpha)^{(n-1)}] = e^{-r/\alpha n} L_n(r/\alpha), \tag{5.7}$$

where L_n is a polynomial of order $n-1$ [CHECK], called *the Laguerre polynomial.*

Example 5.1.2 *Let us normalise the ground state $\Psi_1(r) = a_0 \exp[-(r/\alpha)]$ (corresponding to $n = 1$)*

$$1 = \int_{\mathbb{R}^3} |\Psi_1(r)| r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = 4\pi|a_0|^2 \int_0^\infty r^2 e^{-2r/\alpha}\mathrm{d}r.$$

Instead of integrating it by parts we shall perform a simple trick (often used by Richard Feynman). Put $\beta = 2/\alpha$. Then

$$1 = 4\pi|a_0|^2 \frac{\mathrm{d}^2}{\mathrm{d}\beta^2} \int_0^\infty e^{-\beta r}\mathrm{d}r = 4\pi|a_0|^2 \frac{\mathrm{d}^2}{\mathrm{d}\beta^2}\Big[-\frac{1}{\beta}e^{-\beta r}\Big]_0^\infty = \frac{8\pi|a_0|^2}{\beta^3} = \pi|a_0|^2\alpha^3,$$

and

$$\Psi_1(r) = \frac{1}{\sqrt{\pi\alpha^3}} e^{-r/\alpha}, \tag{5.8}$$

where α is given by (5.2).

The probability of the electron being in the spherical shell between r and $r+\mathrm{d}r$ is $4\pi|\Psi_n(r)|^2 r^2 \mathrm{d}r$. The radial probability density for Ψ_1

$$r^2 e^{-2r/\alpha}$$

has a maximum at $r = \alpha$[PICTURE]. The constant α is therefore the most probable radial distance of the electron from the nucleus (if $Z = 1$ the number α is called *the Bohr radius*). The expectation value of r for the ground state is

$$< r >= 4\pi \int_0^\infty \overline{\Psi}_i r \Psi_1 r^2 \mathrm{d}r = \frac{3\alpha}{2}.$$

5.2 Physical predictions

- For large n we have $E_n \to 0$, the minimum energy to escape the nucleus. The case $E > 0$ corresponds to scattering states.

- Suppose that the electron jumps from level E_j to E_k $(k > j)$. This releases energy

$$E_j - E_k = E_{jk} = \Big(\frac{1}{j^2} - \frac{1}{k^2}\Big) E_1 = \hbar\omega_{jk}, \tag{5.9}$$

  (where we used the Planck law (1.1), and (5.6)), in the form of light (a photon). (For $j = 2$ frequencies (5.9) are in visible part of electro-magnetic spectrum, called the Balmer series. They have been measured, and provide an excellent experimental test of QM). If an electron absorbs a photon the reverse process occurs, and the electron can jump up a level (*excitation*). If an energy of an absorbed photon is large enough, the electron may escape from the atom. If an electron occurs in the state E_j, the photon must supply $-E_j$ (*ionization energy*).

- The 'solar system' analogy is not good. A 'cloud' is (the electron spreads over a whole atom, until measured).

Chapter 6

The mathematical structure of quantum theory

Imagine a thought experiment: Particle in a box[PICTURE]. We do not know where it is , so the wave function must be spread throughout the box. An impenetrable membrane in now inserted dividing the box into two disconnected chambers 1, and 2. Some of the wave is trapped in 1, some in 2, but the particle is only in one chamber. If an observation is made, and the particle is found in 1, then the wave in chamber 2 must disappear - there is a zero probability of finding a wave in 2. This is called *a collapse of the wave function* and will be discussed in Section 8. Before the observation

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

such that $\Psi_1 = 0$ in chamber 2, and $\Psi_2 = 0$ in chamber 1. We have

$$\int_{\text{chamber 1}} |\Psi_1|^2 \mathrm{d}V = 1 = \int_{\text{chamber 2}} |\Psi_2|^2 \mathrm{d}V.$$

The normalisation condition

$$1 = \int_{\text{box}} |\Psi|^2 \mathrm{d}V = \underbrace{|c_1|^2 + |c_2|^2}_{1} + 2\mathrm{Re}[\overline{c_1}c_2 \int_{\text{box}} \overline{\Psi_1}\Psi_2 \mathrm{d}V]$$

gives the orthogonality relation

$$\int_{\text{box}} \overline{\Psi_1}\Psi_2 \mathrm{d}V = 0.$$

This example generalizes to many (or infinitely many) chambers: Now

$$\Psi = \sum_n c_n \Psi_n, \tag{6.1}$$

where Ψ_n is a normalised wave function in chamber n and the summation is over all chambers. From the normalisation condition we deduce the orthogonality relations

$$\int_{\text{box}} |\Psi|^2 \mathrm{d}V = 1 \longrightarrow \int_{\text{box}} \overline{\Psi_m}\Psi_n \mathrm{d}V = \delta_{nm} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n, \end{cases} \tag{6.2}$$

where δ_{nm} is the Kronecker tensor. Analogies with the linear algebra of vectors (a1) are clear: Equation (6.1) is an expansion of a vector Ψ in an orthogonal basis Ψ_n, and equation (6.2) defines a scalar (or inner) product. The orthogonality reflects the exclusive property of measurement.

6.1 Hilbert spaces

Following Paul Dirac (19??) we shall denote the state vectors by

$$|\Psi\rangle \in \mathcal{H} \qquad \text{'ket' vectors, and} \qquad \langle\Phi| \in \mathcal{H}^* \qquad \text{'bra' vectors.}$$

Here $\mathcal{H}$ is a complex vector space with an inner product (*unitary space*), $\mathcal{H}^*$ is its dual. The (anti-)isomorphism between $\mathcal{H}$ and $\mathcal{H}^*$ is

$$|\Psi\rangle = \sum_N c_n|\Psi_n\rangle \sim \langle\Psi| = \sum_N \overline{c}_n\langle\Psi_n|, \qquad \text{where } c_n \in \mathbb{C}. \tag{6.3}$$

The scalar product is

$$(\langle\Phi|, |\Psi\rangle) \in \mathcal{H}^* \times \mathcal{H} \longrightarrow \underbrace{\langle\Phi|\Psi\rangle}_{\text{bra-ket}} \in \mathbb{C}. \tag{6.4}$$

The norm in $\mathcal{H}$ is defined by:

$$\|\Psi\|^2 = \langle\Psi|\Psi\rangle \qquad (= 1 \text{ for normalised states}). \tag{6.5}$$

The properties of the scalar product are

$$\langle\Phi|\Psi\rangle = \overline{\langle\Psi|\Phi\rangle} \tag{6.6}$$

$$\langle\Phi|(\alpha|\Psi\rangle + \beta|\Theta\rangle) = \alpha\langle\Phi|\Psi\rangle + \beta\langle\Phi|\Theta\rangle, \tag{6.7}$$

and they imply

$$(\langle\alpha\Phi| + \langle\beta\Omega|)|\Theta\rangle = \overline{\alpha}\langle\Phi|\Theta\rangle + \overline{\beta}\langle\Omega|\Theta\rangle,$$

for any $\alpha, \beta \in \mathbb{C}, |\Psi\rangle, |\Theta\rangle \in \mathcal{H}, \langle\Phi|, \langle\Omega| \in \mathcal{H}^*$. Note that the QM conventions are other way around to the algebraic conventions; The inner product is linear in a second variable and anti-linear in a first.

The vector space $\mathcal{H}$ is usually infinite. We shall assume that it is *complete* in the following sense: Whenever $\{|\Psi_n\rangle \in \mathcal{H}\}$ is a sequence of vectors, such that

$$\forall_{\varepsilon>0}\exists_{N_\varepsilon\in\mathbb{Z}}\||\Psi_n\rangle - |\Psi_m\rangle| < \varepsilon \qquad \text{for all } m, n > N_\varepsilon$$

than there exists a limit vector $|\Psi\rangle \in \mathcal{H}$, such that $\||\Psi_n\rangle - |\Psi\rangle| \longrightarrow 0$ (i.e. any Cauchy sequence in $\mathcal{H}$ is convergent).

Definition 6.1.1 *A Hilbert space is a complex inner product space which is complete.*

The state space is assumed to be a Hilbert space (strictly speaking a Hilbert space is 'to small' to contain the eigenstates of position and momentum operators. Instead, one uses a space of tempered distributions).

Example 6.1.2 $\mathcal{H} = L^2(\mathbb{R}^n)$ *(where* $n = 1, 2, 3$ *are important cases) is a space of complex-valued functions such that*

$$\|f\|^2 = \int_{\mathbb{R}^n} |f(x)|^2 \mathrm{d}^n x < \infty. \tag{6.8}$$

This example is very important in wave mechanics. In fact we used it in the first half of the course. The scalar product is given by

$$\langle f|g\rangle = \int_{\mathbb{R}^n} \overline{f} g \mathrm{d}^n x. \tag{6.9}$$

It is well defined as a consequence of (6.8)*.*

Example 6.1.3 $\mathcal{H} = \mathbb{C}^n$*. Let*

$$|f\rangle = \begin{pmatrix} f_1 \\ \vdots \\ f_n \end{pmatrix}, \qquad |g\rangle = \begin{pmatrix} g_1 \\ \vdots \\ g_n \end{pmatrix}, \qquad \text{where } f_i, g_i \in \mathbb{C}.$$

The scalar product is

$$\langle f|g\rangle = \sum_{i=1}^{n} \overline{f}_i g_i \in \mathbb{C}. \tag{6.10}$$

6.2 Linear operators

Observables in QM are described by certain linear transformations. Let $\hat{A} : \mathcal{H} \longrightarrow \mathcal{H}$ be a linear operator (transformation) on $\mathcal{H}$, i.e.

$$\hat{A}(\alpha|\Psi\rangle + \beta|\Phi\rangle) = \alpha\hat{A}|\Psi\rangle + \beta\hat{A}|\Phi\rangle \tag{6.11}$$

where $\alpha, \beta \in \mathbb{C}$. The linear operators (from now on called just operators) can be added and multiplied:

$$(\alpha\hat{A} + \beta\hat{B})|\Psi\rangle = \alpha\hat{A}|\Psi\rangle + \beta\hat{B}|\Psi\rangle, \qquad (\hat{A}\hat{B})|\Psi\rangle = \hat{A}(\hat{B}|\Psi\rangle).$$

Therefore they form *an associative algebra.* Note that an operator $\hat{A}$ may be defined only on a subspace $\mathcal{D}(\hat{A})$ of $\mathcal{H}$, called *the domain of* $\hat{A}$.

Definition 6.2.1 *The commutator of two operators* $\hat{A}, \hat{B}$ *is*

$$[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{6.12}$$

The commutators do not usually vanish, so operator algebras are *non-commutative.* Properties of commutators:

Proposition 6.2.2 *For operators all* $\hat{A}, \hat{B}, \hat{C}$*, the commutator satisfies*

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \tag{6.13}$$

$$[\alpha\hat{A} + \beta\hat{B}, \hat{C}] = \alpha[\hat{A}, \hat{C}] + \beta[\hat{B}, \hat{C}] \tag{6.14}$$

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C} \qquad \textit{(Leibnitz rule)} \tag{6.15}$$

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0 \qquad \textit{(Jacobi identity).} \tag{6.16}$$

Proof. Similar to identities for Poisson brackets.

□

Remark A vector space (for example of operators) equipped with bi-linear product satisfying (6.13), (6.14), and (6.16) is called *Lie algebra*.

Definition 6.2.3 *The adjoint of a linear operator $\hat{A}$ is the unique linear transformation $\hat{A}^*$ that satisfies*

$$(\langle\Phi|\hat{A}^*)|\Psi\rangle = \langle\Phi|(\hat{A}|\Psi\rangle) \tag{6.17}$$

for all $|\Psi\rangle, |\Phi\rangle \in \mathcal{D}(\hat{A})$. The operator is called self-adjoint (*or incorrectly* Hermitian *in the physics literature*) *if $\hat{A} = \hat{A}^*$.*

Remark. We shall usually rewrite formula (6.17) as $\langle\hat{A}^*\Phi|\Psi\rangle = \langle\Phi|\hat{A}\Psi\rangle$. Formulae (6.6,6.17) imply

$$\langle\Psi|\hat{A}^*\Phi\rangle = \langle\hat{A}\Psi|\Phi\rangle = \overline{\langle\Phi|\hat{A}\Psi\rangle}.$$

For self-adjoint operators it makes sense to write $\langle\Phi|\hat{A}|\Psi\rangle$.

Definition 6.2.4 *Let $|\Psi\rangle \neq 0$ be a vector such that*

$$\hat{A}|\Psi\rangle = a|\Psi\rangle \tag{6.18}$$

for some $a \in \mathbb{C}$. Then $|\Psi\rangle$ is called an eigen-vector and a is called an eigen-value of $\hat{A}$.

Example 6.2.5 *Let $\mathcal{H} = L^2(\mathbb{R}^n)$ be the Hilbert space from the Example* 6.1.2. *Now $|f\rangle = f(x_1, ..., x_n)$. Examples of operators are*

$$\hat{X}_1 f := x_1 f \qquad \hat{D}_1 f := \frac{\partial f}{\partial x_1}, \qquad \hat{1} f := f.$$

These are multiplication operator, differentiation operator, and identity operator respectively. There are many more examples. Note that

$$\hat{D}_1(\hat{X}_1 f) - \hat{X}_1(\hat{D}_1 f) = (\hat{D}_1(x_1))f, \qquad \textit{so} \qquad [\hat{D}_1, \hat{X}_1] = \hat{1}.$$

Example 6.2.6 *Let $\mathcal{H} = \mathbb{C}^n$ be the Hilbert space from the Example* 6.1.3.

$$\hat{A}|f\rangle = \begin{pmatrix} A_{11} & \dots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \dots & A_{nn} \end{pmatrix} \begin{pmatrix} f_1 \\ \vdots \\ f_n \end{pmatrix},$$

so linear operators are represented by $n \times n$ complex matrices. What is the matrix corresponding to $\hat{A}^*$? Let $|f\rangle, |g\rangle \in \mathbb{C}^n$. The formula

$$\langle\hat{A}^* f|g\rangle = \langle f|\hat{A}g\rangle$$

has the following matrix counterpart

$$\sum_{i,j}^{n} (\overline{A}^*_{ij}\overline{f}_j) g_i = \sum_{i,j}^{n} \overline{f}_i (A_{ij} g_j).$$

Changing i to j in the RHS, and comparing coefficients of $\overline{f_j}g_i$ we find that

$$A^* = \overline{A}^T \tag{6.19}$$

The matrix A^* is called a Hermitian conjugate *of A. Hermitian matrices are those for which $A^* = A$. In the finite-dimensional case the self-adjoint operators are represented by Hermitian matrices.*

6.3 Postulates of quantum mechanics

Wave mechanics of Schrödinger was preceded by a matrix mechanic of Heisenberg (1925). The general mathematical scheme containing both mechanics as special cases was later proposed by von-Neumann, Weyl, Wigner and others.

1. Each physical system is described by an element of a Hilbert space $\mathcal{H}$ (a state vector), which contains all information about the system.

2. Superposition principle. If $|\Psi_1\rangle$, and $|\Psi_2\rangle$ are state vectors then $\alpha|\Psi_1\rangle + \beta|\Psi_2\rangle$ (for $\alpha, \beta \in \mathbb{C}$) is also a possible state vector.

3. The observables (dynamical variables, like position, momentum, energy, ...) are represented by self-adjoint operators in $\mathcal{H}$.

4. The result of measuring an observable (corresponding to) $\hat{A}$ is one of the eigenvalues of $\hat{A}$. If a state vector is
$$|\Psi\rangle = \sum_n c_n|\Psi_n\rangle, \tag{6.20}$$
where $|\Psi_n\rangle$s are eigen-vectors of $\hat{A}$ (i.e, $\hat{A}|\Psi_n\rangle = a_n|\Psi_n\rangle$), then a measurement will give an eigen-value a_n with the probability $|c_n|^2$. After the measurement the state vector 'collapses' into one of the eigen-states $|\Psi_n\rangle$.

Consequence: Statistical aspect of QM. If we prepare many copies of the same state, and measure $\hat{A}$ at the same instant of time, the average answer will be $\sum_n a_n|c_n|^2$. Calculate

$$\hat{A}|\Psi\rangle = \sum_n a_n c_n|\Psi_n\rangle, \qquad \langle\Psi|\hat{A}\Psi\rangle = \sum_n c_n a_n\langle\Psi|\Psi_n\rangle.$$

The orthogonality of $|\Psi_n\rangle$, and equation (6.20) imply $\overline{c_n} = \langle\Psi|\Psi_n\rangle$. Therefore the expectation value of an observable $\hat{A}$ is a state $|\Psi\rangle$ is

$$E_\Psi(\hat{A}) = \frac{\langle\Psi|\hat{A}\Psi\rangle}{\langle\Psi|\Psi\rangle} \ (= \langle\hat{A}\rangle_\Psi). \tag{6.21}$$

The results of our measurement should be given by real numbers. For this to be consistent we have to prove

Proposition 6.3.1 *For every $|\Psi\rangle \in \mathcal{H}$ the expectation value E_Ψ has the following properties:*

1. $E_\Psi(\hat{1}) = 1$.

2. $E_\Psi(\hat{A})$ *is real for all self-adjoint operators* $\hat{A}$.

3. $E_\Psi(\alpha\hat{A} + \beta\hat{B}) = \alpha E_\Psi(\hat{A}) + \beta E_\Psi(\hat{B})$ *for all linear operators* $\hat{A}, \hat{B}$ *and all* $\alpha, \beta \in \mathbb{C}$.

Proof.

1.
$$E_\Psi(\hat{1}) = \frac{\langle\Psi|\Psi\rangle}{\langle\Psi|\Psi\rangle} = 1.$$

2. Since $\hat{A}$ is self-adjoint we have
$$E_\Psi(\hat{A}) = \frac{\langle\Psi|\hat{A}\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\hat{A}\Psi|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\overline{\langle\Psi|\hat{A}\Psi\rangle}}{\langle\Psi|\Psi\rangle} = \overline{E_\Psi(\hat{A})}.$$

3. Follows from (6.6), and the linearity of operators.

□

Remarks.

- If $|\Psi\rangle$ is an eigenvector of $\hat{A}$ with eigenvalue a, then
$$E_\Psi(\hat{A}) = \frac{\langle\Psi|a|\Psi\rangle}{\langle\Psi|\Psi\rangle} = a, \tag{6.22}$$
and Proposition (6.3.1) tells us that the eigenvalues of self-adjoint operators are real.

- Let $\hat{A}$ be self-adjoint, and let $\hat{A}|\Psi_1\rangle = a_1|\Psi_1\rangle$, $\hat{A}|\Psi_2\rangle = a_2|\Psi_2\rangle$, with $a_1 \neq a_2$. Then
$$\langle\hat{A}\Psi_1|\Psi_2\rangle - \langle\Psi_1|\hat{A}\Psi_2\rangle = 0 = (\overline{a_1} - a_2)\langle\Psi_1|\Psi_2\rangle$$
but $\overline{a_1} = a_1$ from the first remark, so $\langle\Psi_1|\Psi_2\rangle = 0$, i.e. $|\Psi_1\rangle$, and $|\Psi_2\rangle$ are orthogonal.

How does this abstract formulation relates to the Schrödinger equation? Take $\mathcal{H} = L^2(\mathbb{R}^3)$, and choose the *position representation*, that is $|\Psi\rangle = \Psi(x_1, x_2, x_3) \in L^2(\mathbb{R}^3)$.

Definition 6.3.2 *The position operators* $\hat{X}_j$*, and momentum operators* $\hat{P}_j, j = 1, 2, 3$ *are given by multiplication operators, and differentiation operators respectively* (*compare* (2.1)):
$$\hat{X}_j = x_j, \qquad \hat{P}_j = \frac{\hbar}{i}\frac{\partial}{\partial x_j} \;\; (or \;\; \hat{P} = -i\hbar\nabla). \tag{6.23}$$

The Hamiltonian operator, defined on twice-differentiable functions, is
$$\hat{H} = \frac{\sum_{j=1}^3 \hat{P}_j^2}{2m} + V(\hat{X}_j) = -\frac{\hbar^2}{2m}\nabla^2 + V(x_j) \tag{6.24}$$
corresponds to the energy observable.

Conclusion. The time independent Schrödinger equation (2.3) is just an assertion that $|\Psi\rangle$ is an eigen-state of $\hat{H}$ corresponding to eigenvalue E. Indeed,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \tag{6.25}$$

and (6.23, 6.24) imply (2.3).

Proposition 6.3.3 *The operators $\hat{X}_j$, and $\hat{P}_j$ defined by* (6.23) *are self-adjoint.*

Proof. We shall proof it in one dimension (the proof for $n = 3$ goes exactly the same).
Position : From Example 6.1.2

$$\langle \hat{X}\Phi|\Psi\rangle = \int_{\mathbb{R}} \overline{x\Phi(x)}\Psi(x)\mathrm{d}x = \int_{\mathbb{R}} \overline{\Phi(x)}x\Psi(x)\mathrm{d}x = \langle \Phi|\hat{X}\Psi\rangle.$$

Momentum: Use integration by parts

$$\langle \hat{P}\Phi|\Psi\rangle = \int_{\mathbb{R}} \overline{\frac{\hbar}{i}\frac{\mathrm{d}\Phi}{\mathrm{d}x}}\Psi\mathrm{d}x = -\frac{\hbar}{i}\Big([\overline{\Phi}\Psi]_{-\infty}^{\infty} - \int_{\mathbb{R}} \overline{\Phi}\frac{\mathrm{d}\Psi}{\mathrm{d}x}\mathrm{d}x\Big) = 0 + \int_{\mathbb{R}} \overline{\Phi}\frac{\hbar}{i}\frac{\mathrm{d}\Psi}{\mathrm{d}x}\mathrm{d}x = \langle \Phi|\hat{P}\Psi\rangle.$$

6.4 Time evolution in QM

Postulate 5: The state vector undergoes an unitary evolution; Write

$$|\Psi(t)\rangle = \hat{U}(t)|\Psi(0)\rangle, \tag{6.26}$$

where $\hat{U}(t)$ is an *unitary operator*, that is it satisfies $\hat{U}^*\hat{U} = \hat{1}$. Let $|\Theta\rangle$ be an eigenstate of $\hat{U}$, i.e. $\hat{U}|\Theta\rangle = u|\Theta\rangle$. Then

$$\hat{U}^*\hat{U}|\Theta\rangle = \overline{u}u|\Theta\rangle = |\Theta\rangle,$$

therefore $u = \exp(i\alpha)$, where $\alpha \in \mathbb{R}$. Put $\hat{U} = \exp(i\hat{\alpha})$, (the exponent is defined formally, by the Taylor expansion) and note that

$$\hat{U}^* = \exp[-i\hat{\alpha}^*)] = \hat{U}^{-1} = \exp[-i\hat{\alpha})]$$

$\hat{\alpha} = \hat{\alpha}^*$ and $\hat{\alpha}$ is self-adjoint. Differentiating (6.26) with respect to t yields

$$\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = i\Big(\frac{\mathrm{d}}{\mathrm{d}t}\hat{\alpha}(t)\Big)\exp[i\hat{\alpha}(t)]|\Psi(0)\rangle = \frac{1}{i\hbar}\hat{H}(t)|\Psi(t)\rangle,$$

where the Hamiltonian is defined by

$$\hat{H}(t) = -\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{\alpha}(t).$$

Therefore the state vector develops is time according to the abstract time-dependent Schrödinger equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle. \tag{6.27}$$

When $\hat{H}$ doesn't depend on time then the analysis simplifies, and the unitary evolution is given by $\hat{U}(t) = \exp[-it\hat{H}/\hbar]$, and (6.26) gives a formal solution to (6.27). Note that

$$\langle\Psi(t)|\Psi(t)\rangle = \langle\hat{U}(t)\Psi(0)|\hat{U}(t)\Psi(0)\rangle = \langle\Psi(0)|\hat{U}^*(t)\hat{U}(t)\Psi(0)\rangle = \langle\Psi(0)|\Psi(0)\rangle$$

which confirms the results of Proposition 2.3.3.

Proposition 6.4.1 *Let $\hat{A}(t)$ be an observable and let $|\Psi(t)\rangle$ be a normalized solution to the time dependent Schrödinger equation. Then*

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{A}(t)\rangle = \langle\frac{\partial}{\partial t}\hat{A}(t)\rangle + \frac{i}{\hbar}\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle. \tag{6.28}$$

Proof. Problem sheet 5.

□

If $\hat{A}$ doesn't explicitly depend on time, then the expectation value $\langle\hat{A}\rangle$ is conserved iff $\hat{A}$ commutes with the Hamiltonian. Then $\hat{A}$ is called a *conserved quantity*. Compare it with the known formula from classical mechanics

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \{H, f\}, \qquad \text{where} \qquad \{H, f\} = \sum_{i=1}^{3} \frac{\partial H}{\partial p_i}\frac{\partial f}{\partial x_i} - \frac{\partial H}{\partial x_i}\frac{\partial f}{\partial p_i},$$

and note the correspondence between classical Poisson brackets, and the commutators

$$\{H, f\} \longrightarrow \frac{i}{\hbar}[\hat{H}, \hat{f}].$$

6.5 Commutation relations and canonical quantisation

Explore the relation between the commutators and the Poisson brackets in classical mechanics. Take $\mathcal{H} = L^2(\mathbb{R})$, and recall that $\hat{P} = -i\hbar\mathrm{d}/\mathrm{d}x, \hat{X} = x$. We shall show that

$$[\hat{P}, \hat{X}] = -\hat{1}i\hbar. \tag{6.29}$$

Indeed, let $\Psi(x) \in L^2(\mathbb{R})$, then

$$\hat{P}\hat{X}\Psi = \hat{P}(\hat{X}\Psi) = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}(x\Psi) = -i\hbar\Psi - i\hbar x\frac{\mathrm{d}\Psi}{\mathrm{d}x} = -i\hbar\Psi + \hat{X}\hat{P}\Psi,$$

so $(\hat{P}\hat{X} - \hat{X}\hat{P})\Psi = -i\hbar\Psi$. Analogous result holds in three dimensions:

Proposition 6.5.1 *In three dimensions, the canonical commutation relations are*

$$\left[\hat{P}_j, \hat{X}_k\right] = -\delta_{jk}\hat{1}i\hbar, \qquad \left[\hat{X}_j, \hat{X}_k\right] = 0, \qquad \left[\hat{P}_j, \hat{P}_k\right] = 0. \tag{6.30}$$

Proof. The proof of the first relation is analogous to the derivation (6.29). The second relation is trivial, finally the third one holds because $\partial_j\partial_k = \partial_k\partial_j$, for $j, k = 1, 2, 3$.

□

Note the resemblance of the Poisson brackets relations

$$\{p_j, x_k\} = \delta_{jk}, \qquad \{x_j, x_k\} = 0, \qquad \{p_j, p_k\} = 0.$$

The idea of a quantisation: To quantise a classical system, each function f on a classical phase space (i.e. a function of positions and momentas) should be replaced by a self- adjoint operator $\hat{Q}(f)$ is such a way that Q is a linear map, $\hat{Q}(1) = \hat{1}$, and for any pair of functions f and g

$$[\hat{Q}(f), \hat{Q}(g)] = -i\hbar\hat{Q}(\{f, g\}) \tag{6.31}$$

(clearly works if p and x are replaced by (6.23) - *canonical quantisation*). It inspired the mathematics of the last 30 years. Because of the operator ordering problem it is not always possible quantise a given classical system without ambiguities.

6.6 The Heisenberg uncertainty Principle

Definition 6.6.1 *The dispersion of an operator $\hat{A}$ in the state $|\Psi\rangle$ is*

$$\Delta_\Psi(\hat{A}) = \sqrt{E_\Psi(\hat{A}^2) - [E_\Psi(\hat{A})]^2}. \tag{6.32}$$

Proposition 6.6.2 *Let $\hat{A}, \hat{B}$, and $\hat{C}$ be self-adjoint operators satisfying the commutation relations $[\hat{A}, \hat{B}] = i\hat{C}$. Then for any vector $|\Psi\rangle \in \mathcal{H}$*

$$E_\Psi(\hat{A}^2)E_\Psi(\hat{B}^2) \geqslant \frac{1}{4}E_\Psi(\hat{C})^2. \tag{6.33}$$

Proof. First calculate $\|(\hat{A} - is\hat{B})\Psi\|^2$ for $s \in \mathbb{R}$:

$$(\hat{A} - is\hat{B})^*(\hat{A} - is\hat{B}) = \hat{A}^2 - is[\hat{A}, \hat{B}] + s^2\hat{B}^2 = \hat{A}^2 + s\hat{C} + s^2\hat{B}^2.$$

Therefore

$$\begin{aligned}\langle(\hat{A} - is\hat{B})\Psi|(\hat{A} - is\hat{B})\Psi\rangle &= \langle\Psi|(\hat{A} - is\hat{B})^*(\hat{A} - is\hat{B})\Psi\rangle \\ &= E_\Psi(\hat{A}^2) + sE_\Psi(\hat{C}) + s^2E_\Psi(\hat{B}^2) \geqslant 0.\end{aligned}$$

The above quadratic expression is non-negative. As a polynomial in s, it has no real roots, or it has one repeated root. Therefore the discriminant satisfies

$$E_\Psi(\hat{C})^2 - 4E_\Psi(\hat{A}^2)E_\Psi(\hat{B}^2) \leqslant 0,$$

which gives (6.33).

□

LECTURE 13

Corollary 6.6.3 (The Heisenberg's Uncertainty Principle) *The dispersions of the position and momentum are related by*

$$\Delta_\Psi(\hat{P})\Delta_\Psi(\hat{X}) \geqslant \frac{\hbar}{2}. \tag{6.34}$$

Proof. Let

$$\hat{A} = \hat{P} - E_\Psi(\hat{P})\hat{1}, \qquad \hat{B} = \hat{X} - E_\Psi(\hat{X})\hat{1}.$$

Note that

$$E_\Psi(\hat{A}^2) = E_\Psi(\hat{P}^2 - 2E_\Psi(\hat{P})\hat{P} + E_\Psi(\hat{P})^2\hat{1}) = \Delta_\Psi(\hat{P})^2, \qquad E_\Psi(\hat{B}^2) = \Delta_\Psi(\hat{X})^2.$$

Then, since $\hat{1}$ commutes with all operators

$$[\hat{A}, \hat{B}] = [\hat{P}, \hat{X}] = -i\hbar\hat{1},$$

so that $\hat{C} = -\hbar\hat{1}$. Therefore (6.32) and Proposition 6.6.2 imply

$$\Delta_\Psi(\hat{P})^2\Delta_\Psi(\hat{X})^2 = E_\Psi(\hat{A}^2)E_\Psi(\hat{B}^2) \geqslant \frac{1}{4}\hbar^2,$$

and (6.34) follows on taking the positive square roots.

□

States for which (6.34) is an equality are called *minimal uncertainty states*. Implication of Heisenberg's principle: The greater accuracy with which we know the position of the particle, the less we know about its momentum. The Planck's constant determines the scale of quantum fuzziness.

6.7 Commuting observables and parity

Applying (6.34) to the case when $[\hat{A}, \hat{B}] = 0$ yields a trivial result

$$\Delta_\Psi(\hat{A})\Delta_\Psi(\hat{B}) \geqslant 0.$$

It is possible to achieve the lower bound if one or both dispersions vanish.

Proposition 6.7.1 *The dispersion of $\hat{A}$ in the state $|\Psi\rangle$ vanishes iff $\hat{A}|\Psi\rangle = a|\Psi\rangle$.*

Proof. Assume $\hat{A}|\Psi\rangle = a|\Psi\rangle$. From (6.22) $E_\Psi(\hat{A}) = a$, therefore

$$(E_\Psi(\hat{A})\hat{1} - \hat{A})|\Psi\rangle = 0. \tag{6.35}$$

We also have the identity

$$E_\Psi([E_\Psi(\hat{A})\hat{1} - \hat{A}]^2) = \Delta_\Psi(\hat{A})^2,$$

from which it is clear that $\Delta_\Psi(\hat{A}) = 0$ iff (6.35) is satisfied.

□

If $|\Psi\rangle$ is an eigenvector of both $\hat{A}$ and $\hat{B}$ then both observables can be measured precisely.

Proposition 6.7.2 *Let $\hat{A}$ and $\hat{B}$ be self-adjoint operators on the Hilbert space $\mathcal{H}$, and let $\mathcal{H}_A$, and $\mathcal{H}_B$ denote the subspaces spanned by eigenvectors of $\hat{A}$ and $\hat{B}$ respectively. Let $\mathcal{H}_{A,B}$ denote the span of vectors that are simultaneously eigenvectors for both $\hat{A}$ and $\hat{B}$. Then*

$$[\hat{A}, \hat{B}] = 0 \qquad \textit{implies} \qquad \mathcal{H}_{A,B} = \mathcal{H}_A \cap \mathcal{H}_B.$$

Proof. As in a1 algebra.

□

Remark. If $\mathcal{H}$ admits an orthonormal basis of eigenvectors for $\hat{A}$, then $\mathcal{H}_A = \mathcal{H}$, and $[\hat{A}, \hat{B}] = 0$ implies

$$\mathcal{H}_{A,B} = \mathcal{H} \cap \mathcal{H}_B = \mathcal{H}_B.$$

Therefore all eigenvectors of $\hat{B}$ are in span of vectors which are simultaneously eigenvectors of both operators. This motivates:

Definition 6.7.3 *The observables corresponding to commuting operators are said to be compatible, or simultaneously measurable.*

Example. Take $\mathcal{H} = L^2(\mathbb{R})$ and consider the one-dimensional wave mechanics. Define the parity operator by

$$\hat{\mathcal{P}}\Psi(x) := \Psi(-x). \tag{6.36}$$

For proofs of the following statements see sheet 6, question 1. Note that $\hat{\mathcal{P}}^2 = \hat{1}$, so the only possible eigenvalues of $\hat{\mathcal{P}}$ are 1 and -1. It easily follows that $\hat{\mathcal{P}}$ is self-adjoint. Consider a particle moving in a potential such that $V(x) = V(-x)$. It follows that $[\hat{\mathcal{P}}, \hat{H}] = 0$, and by Proposition 6.7.2 we can find eigenvectors of $\hat{H}$, which are also eigenvectors of $\hat{\mathcal{P}}$. Indeed, if $\hat{H}\Psi = E\Psi$, then

$$\Psi_+ := \frac{\Psi(x) + \Psi(-x)}{2}, \qquad \Psi_- := \frac{\Psi(x) - \Psi(-x)}{2}$$

satisfy the Schrödinger equation (with $V(x) = V(-x)$), and $\hat{\mathcal{P}}\Psi_+ = \Psi_+$, $\hat{\mathcal{P}}\Psi_- = -\Psi_-$.

Remark. Equation (6.28) implies that $\hat{\mathcal{P}}$ is a conserved quantity.

Chapter 7

The algebra of the harmonic oscillator

Can one use the algebraic methods developed in the last two Sections, to solve 'real QM problems'? We shall re-derive the results of Section 4, without referring to Schrödinger equation, and wave mechanics.

Proposition 7.0.4 *Let $\hat{A}$ be an operator such that*

$$[\hat{A}, \hat{A}^*] = \hat{1}. \tag{7.1}$$

The eigenvalues of an operator $\hat{N} = \hat{A}^*\hat{A}$ are non-negative integers.

Proof. We have

$$\hat{N}^* = (\hat{A}^*\hat{A})^* = \hat{A}^*(\hat{A}^*)^* = \hat{N},$$

so $\hat{N}$ is self adjoint and from Proposition 6.3.1 it follows that it has real eigenvalues. Calculate the commutators:

$$[\hat{N}, \hat{A}] = [\hat{A}^*\hat{A}, \hat{A}] = \hat{A}^*[\hat{A}, \hat{A}] + [\hat{A}^*, \hat{A}]\hat{A} = -\hat{A},$$
$$[\hat{N}, \hat{A}^*] = [\hat{A}^*\hat{A}, \hat{A}^*] = \hat{A}^*[\hat{A}, \hat{A}^*] + [\hat{A}^*, \hat{A}^*]\hat{A} = \hat{A}^*,$$

where we used the Leibniz rule (6.15) for commutators.

Assume that $\hat{N}$ has at least one eigenvector. Let $|n\rangle$ be an eigenvector of $\hat{N}$ corresponding to a real eigenvalue $n \in \mathbb{R}$ i.e. $\hat{N}|n\rangle = n|n\rangle$. We shall show that n is a non-negative integer, and that $\hat{N}$ has infinitely many eigen-vectors. Calculate

$$\hat{N}\hat{A}|n\rangle = ([\hat{N}, \hat{A}] + \hat{A}\hat{N})|n\rangle = -\hat{A}|n\rangle + n\hat{A}|n\rangle = (n-1)\hat{A}|n\rangle, \tag{7.2}$$

so either $\hat{A}|n\rangle = 0$, or $\hat{A}|n\rangle$ is an eigenvector of $\hat{N}$ with eigenvalue $(n-1)$. Similarly

$$\hat{N}\hat{A}^*|n\rangle = ([\hat{N}, \hat{A}^*] + \hat{A}^*\hat{N})|n\rangle = \hat{A}^*|n\rangle + n\hat{A}^*|n\rangle = (n+1)\hat{A}^*|n\rangle. \tag{7.3}$$

Either $\hat{A}^*|n\rangle = 0$, or $\hat{A}^*|n\rangle$ is an eigen-vector of $\hat{N}$ with eigen-value $(n+1)$. When is $\hat{A}|n\rangle = 0$?

$$\|\hat{A}|n\rangle\|^2 = \langle \hat{A}n|\hat{A}n\rangle = \langle n|\hat{A}^*\hat{A}|n\rangle = \langle n|\hat{N}|n\rangle = n\langle n|n\rangle = n\||n\rangle\|^2$$

The LHS is non-negative so $n \geqslant 0$, and

$$\hat{A}|n\rangle = 0, \qquad \text{iff} \qquad n = 0. \tag{7.4}$$

Now

$$\|\hat{A}^*|n\rangle\|^2 = \langle \hat{A}^* n|\hat{A}^* n\rangle = \langle n|\hat{A}\hat{A}^*|n\rangle = \langle n|\hat{1} + \hat{N}|n\rangle = (n+1)\langle n|n\rangle = (n+1)\||n\rangle\|^2,$$

so from (7.4) $\hat{A}^*|n\rangle$ is never 0.

Fix $n \neq 0$. Then $\hat{A}|n\rangle, \hat{A}^2|n\rangle, \hat{A}^3|n\rangle, ...$ are all eigen states of $\hat{N}$ with eigen-values $(n-1), (n-2), (n-3), ...$, unless one of them vanishes. This means that (for non-negative integer k) $\hat{A}^k|n\rangle = 0$ or $\hat{A}^k|n\rangle$ is an eigen-vector of $\hat{N}$ with an eigen-value $(n-k) \in \mathbb{R}$. If $k \geqslant n \geqslant k-1$ then $n - k \leqslant 0$, which is not allowed as an eigenvalue unless $\hat{A}^k|n\rangle = 0$ (from (7.4)), in which case $n - k = 0$, and

$$n = k, \qquad k = 0, 1, 2, ...$$

□

Remarks

- We have only assumed the commutation relations (7.1), and not the actual form of the operators $\hat{A}$, and $\hat{A}^*$.
- All non-negative integers are possible eigen-values. If $k \in \mathbb{Z}^+$ is and eigen-value, then we can get down to 0 applying $\hat{A}$ k times. Conversely, by applying $\hat{A}^*$ we can 'climb up', and construct eigen-states corresponding to all positive integers. This motivates the following definition:

Definition 7.0.5 *Operators $\hat{A}$, and $\hat{A}^*$ are known as respectively* lowering *(or* annihilation*), and* rising *(or* creation*) operators. The operator $\hat{N} = \hat{A}^*\hat{A}$ is known as the* number operator*.*

Proposition 7.0.6 *For normalised eigenvectors of $\hat{N}$ we have*

$$\hat{A}|n\rangle = \sqrt{n}|n-1\rangle, \qquad \hat{A}^*|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{7.5}$$

Proof. Recall that $\hat{N}|n\rangle = n|n\rangle$. By (7.2) $\hat{A}|n\rangle$ is an eigenvector of $\hat{N}$ with an eigenvalue $n-1$, so $\hat{A}|n\rangle = c_{n-1}|n-1\rangle$, and

$$1 = \langle n-1|n-1\rangle = \frac{1}{|c_{n-1}|^2}\langle n|\hat{A}^*\hat{A}|n\rangle = \frac{n}{|c_{n-1}|^2}.$$

Choose $c_{n-1} = \sqrt{n}$. Similarly

$$1 = \langle n+1|n+1\rangle = \frac{1}{|d_{n+1}|^2}\langle n|\hat{A}\hat{A}^*|n\rangle = \frac{1}{|d_{n+1}|^2}\langle n|([\hat{A}, \hat{A}^*] + \hat{A}^*\hat{A})|n\rangle = \frac{n+1}{|d_{n+1}|^2}$$

so $d_{n+1} = \sqrt{n+1}$.

□

LECTURE 15

7.1 The harmonic oscillator once again

Return to the one-dimensional harmonic oscillator with Hamiltonian

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{X}^2$$

where $\hat{P}$, and $\hat{X}$ are self adjoint operators satisfying $[\hat{P}, \hat{X}] = -i\hbar\hat{1}$. We *do not* want to refer to a particular representation (6.23). Define

$$\hat{a} = \frac{1}{\sqrt{2m\omega\hbar}}(\hat{P} - im\omega\hat{X}), \qquad \hat{a}^* = \frac{1}{\sqrt{2m\omega\hbar}}(\hat{P} + im\omega\hat{X}). \tag{7.6}$$

Calculate

$$\begin{aligned}\hat{a}^*\hat{a} &= \frac{1}{2m\omega\hbar}(\hat{P} + im\omega\hat{X})(\hat{P} - im\omega\hat{X}) = \frac{1}{2m\omega\hbar}\Big(\hat{P}^2 - im\omega[\hat{P}, \hat{X}] + m^2\omega^2\hat{X}^2\Big) \\ &= \frac{1}{\hbar\omega}(\hat{H} - \frac{1}{2}\hbar\omega\hat{1}).\end{aligned}$$

Therefore

$$\hat{H} = \hbar\omega\hat{a}^*\hat{a} + \frac{1}{2}\hbar\omega\hat{1}. \tag{7.7}$$

Proposition 7.1.1 *The eigenvalues of $\hat{H}$ are*

$$E_n = \Big(n + \frac{1}{2}\Big)\hbar\omega, \qquad n = 0, 1, 2, ... \tag{7.8}$$

Proof. Calculate the commutator

$$\begin{aligned}[\hat{a}, \hat{a}^*] &= \frac{1}{2m\omega\hbar}[\hat{P} - im\omega\hat{X}, \hat{P} + im\omega\hat{X}] \\ &= \frac{1}{2m\omega\hbar}\Big([\hat{P}, \hat{P}] + im\omega[\hat{P}, \hat{X}] - im\omega[\hat{X}, \hat{P}] + m^2\omega^2[\hat{X}, \hat{X}]\Big) = \frac{2im\omega[\hat{P}, \hat{X}]}{2m\omega\hbar} = \hat{1}.\end{aligned}$$

Operators $\hat{a}$, and $\hat{a}^*$ satisfy $[\hat{a}, \hat{a}^*] = 1$, which is (7.1), and (from Proposition 7.0.4) the eigenvalues of $\hat{a}^*\hat{a}$ are $n = 0, 1, ...$ Therefore the eigenvalues of $\hat{H}$ given by (7.7) are (7.8).

□

Let $\hat{N} = \hat{a}^*\hat{a}$, and $\hat{N}|n\rangle = n|n\rangle$ (as in 7.0.4). Equation (7.7) implies that

$$\hat{N}|n\rangle = \Big(\frac{\hat{H}}{\hbar\omega} - \frac{1}{2}\hat{1}\Big)|n\rangle = n|n\rangle, \longrightarrow \hat{H}|n\rangle = \hbar\omega\Big(\hat{N} + \frac{1}{2}\hat{1}\Big)|n\rangle = \hbar\omega\Big(n + \frac{1}{2}\Big)|n\rangle$$

and $|n\rangle$ is an eigenstate of $\hat{H}$ corresponding to energy (7.8). From (7.5)

$$\hat{a}^*|n\rangle = \sqrt{n+1}|n+1\rangle \longrightarrow |n\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^*)^n|0\rangle, \tag{7.9}$$

where $|0\rangle$ is a ground state corresponding to $E = \hbar\omega/2$. So far we didn't refer to the explicit form of $\hat{P}$, and $\hat{X}$. Now we shall use (6.23) to prove

Proposition 7.1.2 *Let $\mathcal{H} = L(\mathbb{R})$. In the position representation (6.23) the normalised eigenvector Ψ_n corresponding to an energy eigenvalue (7.8) is given by*

$$\frac{1}{\sqrt{n!}}\Big(\frac{m\omega}{\pi\hbar}\Big)^{1/4}\Big(\frac{\hbar}{2m\omega}\Big)^{n/2}\Big(\frac{\mathrm{d}}{\mathrm{d}x} - \frac{m\omega}{\hbar}x\Big)^n \exp\left[-(m\omega x^2)/(2\hbar)\right]. \tag{7.10}$$

Proof. From now on we shall replace $|n\rangle$ by Ψ_n. From (7.6, 6.23)

$$\hat{a} = \frac{1}{\sqrt{2m\omega\hbar}}(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x} - im\omega x), \qquad \hat{a}^* = \frac{1}{\sqrt{2m\omega\hbar}}(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x} + im\omega x).$$

From (7.4) $\hat{a}\Psi_0 = 0$, which yields

$$\frac{\partial\Psi_0}{\partial x} = -\frac{m\omega}{\hbar}x\Psi_0, \qquad \text{so} \qquad \Psi_0 = c_0 \exp\left[-(m\omega x^2)/(2\hbar)\right].$$

The constant c_0 is fixed by $\langle\Psi_0|\Psi_0\rangle = 1$ to be $(\frac{m\omega}{\pi\hbar})^{1/4}$ (see (4.11). The formula (7.10) follows from (7.9).

□

Chapter 8

Measurement and paradoxes

8.1 Measurement in quantum mechanics

In classical physics it is assumed that disturbances to the system during a measurement could be kept below any given level of tolerance. In QM this is not the case. Recall the fourth postulate of QM, and assume that we want to measure an observable $\hat{A}$ with discrete and non-degenerate spectrum, such that normalised eigenvectors $\hat{A}|\Phi_n\rangle = a_n|\Phi_n\rangle$ form an orthogonal basis for the Hilbert space. Consider the equation

$$|\Psi\rangle = \sum_n |\Phi_n\rangle\langle\Phi_n|\Psi\rangle = \sum_n \hat{\mathcal{P}}_n^A|\Psi\rangle,$$

Where $\hat{\mathcal{P}}_n^A := |\Phi_n\rangle\langle\Phi_n|$ is a projection operator. It can act both on bra, and ket vectors, and it projects the state vectors onto an eigenvector of $\hat{A}$, with an eigenvalue a_n. The relations

$$(\hat{\mathcal{P}}_n^A)^2 = |\Phi_n\rangle\langle\Phi_n|\Phi_n\rangle\langle\Phi_n| = \hat{\mathcal{P}}_n^A, \qquad (\hat{\mathcal{P}}_n^A)^* = \overline{|\Phi_n\rangle\langle\Phi_n|} = |\Phi_n\rangle\langle\Phi_n| = \hat{\mathcal{P}}_n^A$$

define a projection operator. The resolution of identity is given by

$$\hat{1} = \sum_n |\Phi_n\rangle\langle\Phi_n|.$$

The measurement of changes $|\Psi\rangle$ to $\hat{\mathcal{P}}_n^A|\Psi\rangle$. Unlike the unitary time evolution the measurement usually changes the norm of the wave function

$$|\Psi\rangle \longrightarrow \hat{\mathcal{P}}_n^A|\Psi\rangle$$

R process. Collapse of the wave function. Non-deterministic, non-unitary $\||\hat{\mathcal{P}}_n^A\Psi\rangle\|^2 \neq \||\Psi\rangle\|^2$.

Change of the wave function is *nonlocal*. The moment that the energy of a harmonic oscillator is measured to be $\hbar\omega/2$ the wave function is transmuted to a multiple of Ψ_0 throughout the entire universe. This contradicts the common sense, and the theory of relativity.

$$|\Psi(t_1)\rangle \longrightarrow |\Psi(t_2)\rangle$$

U process. Deterministic unitary evolution (6.26).

$$\begin{array}{ccc} \mathbf{U} & \longrightarrow & \mathbf{U} \\ & & \downarrow \ \mathbf{R} \\ & & \mathbf{U} \ \longrightarrow . \end{array}$$

The **R** process is not described by the standard formalism of Schrödinger equation. Does it really happen. Is **R** a change of our knowledge of the state, or is it a change in the state itself?

8.2 The Einstein–Rosen–Podolsky paradoxes

The conservation laws provide information about one part of entangled system in terms of another. The stationary atom decays into two parts [PICTURE]. Observables $x_A + x_B = const, p_A - p_B = const$ can be measured with an arbitrary precision as

$$[\hat{X}_A + \hat{X}_B, \hat{P}_A - \hat{P}_B] = 0$$

If one chooses to measure the momentum of B, and a position of A, then (by combining information, and using conservation laws), one should be able to give both the position and the momentum of B, beating the uncertainty principle.

One would expect that the measurement of A by should not depend on anything what has happened to B (the locality assumption).

Einstein (EPR 1935) used this paradox to support his opinion, that QM is incomplete. He claimed that any observable possesses an objectively existing value, which is determined by a state vector, and a set of hidden variables. His mistake (!) was to treat two particle separately. According to QM they are entangled, and form a sort of *biparticle*. The famous result John Bell showed that any theory which reproduces results of QM must posses some non-local features

8.3 Violation of Bell's inequalities

Let $\mathrm{P}(R \setminus S)$ be the probability of the event that R occurs but S does not.

Proposition 8.3.1 *For any events Q, R, and S we have*

$$\mathrm{P}(Q \setminus R) + \mathrm{P}(R \setminus S) \geqslant \mathrm{P}(Q \setminus S). \tag{8.1}$$

Proof. Any point $q \in (Q \setminus S)$ is either in R or not in R. In the first case it is in $(R \setminus S)$ and otherwise it is in $(Q \setminus R)$. Therefore $(Q \setminus S) \subseteq (Q \setminus R) \cup (R \setminus S)$ which implies (8.1).

□

Any theory based on local realism should satisfy (8.1).

Let $\mathcal{H} = \mathbb{C}^2$ be spanned by two orthogonal vectors $|\xi\rangle$,and $|\eta\rangle$ which represent vertical and horisontal polarisations respectively. A photon polarised at an angle θ to the vertical is described by

$$|\Psi(\theta)\rangle = |\xi\rangle \cos\theta + |\eta\rangle \sin\theta.$$

Each filter [PICTURE] act as measuring apparatus, and corresponds to a projection operator. After passing through vertically polarized filter, the particle is described by

$$|\xi\rangle\langle\xi|\Psi(\theta)\rangle = \cos\theta|\xi\rangle.$$

The probability of a photon passing through the filter is therefore $\cos^2\theta$.

Let r be a filter and let R denote the event that a photon passes through r. This event will occur with probability $\mathrm{P}(R)$. Let s be a second filter at an angle ϕ to r. Photon which has been transmitted by r will be transmitted by s with probability $\cos^2\phi$. The probability that a photon transmitted by r will not be transmitted by s is

$$\mathrm{P}(R \setminus S) = \mathrm{P}(R)(1-\cos^2\phi) = \mathrm{P}(R)\sin^2\phi. \tag{8.2}$$

Consider a third filter q, at angle θ to s and $\theta-\phi$ to r PICTURE, and let Q be the event that a photon passes through q. We similarly calculate that

$$\mathrm{P}(Q \setminus R) = \mathrm{P}(Q)\sin^2(\theta-\phi), \qquad \mathrm{P}(Q \setminus S) = \mathrm{P}(Q)\sin^2\theta.$$

The Bell inequality (8.1)

$$P(Q \setminus R) + P(R \setminus S) - P(Q \setminus S) \geqslant 0.$$

It is experimentally possible to arrange $\mathrm{P}(Q) = \mathrm{P}(R)$, and the last formula becomes

$$\sin^2(\theta-\phi) + \sin^2\phi - \sin^2\theta \geqslant 0.$$

Take $0 < \theta = 2\phi < \pi/2$. Then (8.2) yields

$$2\sin^2\phi - \sin^2 2\phi = 2\sin^2\phi - 4\sin^2\phi\cos^2\phi = 2\sin^2\phi(1-2\cos^2\phi) \geqslant 0$$

which is not true for small ϕ. We reach a contradiction, because $P(R \setminus S)$ and $P(Q \setminus S)$ in (8.2) are not independent. The measurement at q has affected the measurement at r.

A naive view would suggest that insertion of the middle filter must result in more photons being stopped. Assume that he particle passed through q. If the filter r is not there, the photon will pass to the region III with probability $\cos^2\theta$, which is zero if $\theta = \pi/2$ If we insert the middle filter back, the probability of getting to III will be

$$\cos^2(\theta-\phi)\cos^2\phi = \cos^2(\pi/2-\phi)\cos^2\phi = \sin^2\phi\cos^2\phi.$$

which is positive for most angles. Therefore the middle filter, gives a photon a better chance of passing to region III.

Imagine an atom which emits two identically polarized photons A, and B , traveling (by conservation of momentum) in opposite directions. We arrange for each photon to meet a polarizing filter r_A, and r_B at some large distant from the atom. The behavior of photons at filters must be corelated. But if r_A, and r_B are widely separated and the light signal communicating the result of measurement of A would arrive to r_B only after the measurement of B had occurred. So we would expect that the transmition of B by r_B should not depend on anything what has happened to A (the locality assumption).

But according to quantum theory the polarization state of A must change whenever B passes through a filter. We can choose to insert the filter B after photons left the atom. How does A know that we shall measure B.

Alain Aspect [1981] experimentally verified the violation of triangle inequalities. Probability that A passes through r_A changes if we measure B.

8.4 Schrödinger's cat

The EPR type paradoxes do not prove that the quantum theory is incomplete. They only teach us that the intuition we developed in the study of classical mechanic fails when applied to the quantum world. System which are far apart can be entangled together, and can not be considered separately. No contradiction - there is no way of using entanglement to send signals faster than light.

Another group of paradoxes is associated with collapse (reduction) of the wave function. The following one was given by Schrödinger (1935) as a reaction to the EPR paper.

Imagine a cat inside a closed black box with a vial of cyanide, and a radioactive atom which has a probability of $1/2$ of decaying in one hour. If the atom decays, then the cyanide is released, and the cat dies. If it does not decay, then the cyanide is not released, and the cat stays alive. The paradox arises, because the atom (as a microscopic object) must is described by laws of quantum theory. After one hour, and before it is observed the atom is in a superposition of being decayed and undecayed. The cat is corelated with the atom, and is in a superposition of being dead and alive

$$|\Psi_{\mathrm{CAT}}\rangle = \frac{1}{\sqrt{2}}\Big(|\mathrm{dead}\rangle + |\mathrm{alive}\rangle\Big) \tag{8.3}$$

But we do not observe cats in this state!

- **Many worlds** The reduction process doesn't exist. All changes in time are **U** processes, and take place according to a linear Schrödinger's equation. a measurement is made, the universe branches into many different worlds, in each of which just one of the measured outcomes occurs (Everett 1957). This point of view is popular in quantum cosmology.

- **Open system** Systems are never isolated. They interact with an outside world (measuring apparatus) by many different forces. The cat is therefore entangled with the environment (otherwise we couldn't observe it at all). Collapse of the wave function is an approximation to the unitary evolution. Problem: According to this interpretation all processes should be reversable in time. We don't see it (perhaps) because we don't live long enough. (decoherence).

- **Hidden variables** Any observable possesses an objectively existing value, which is determined by a state vector, and a set of (non-local) hidden variables. Compare problem 4 sheet 1.

Sheet One

1. A particle of mass m moves freely within the interval $[-a, a]$ on the x axis. Assume that the wave function vanishes for $|x| \geqslant a$, and show that the stationary states are of the form

$$\psi(x,t) = \begin{cases} \frac{1}{\sqrt{a}} \exp\left(-\frac{iE_n t}{\hbar}\right) \cos\left(\frac{n\pi x}{2a}\right) & \text{for odd } n \\ \frac{1}{\sqrt{a}} \exp\left(-\frac{iE_n t}{\hbar}\right) \sin\left(\frac{n\pi x}{2a}\right) & \text{for even } n \end{cases}$$

with energy levels E_n given by

$$E_n = \frac{n^2\pi^2\hbar^2}{8ma^2}.$$

Find a probability that the particle described by ψ_n lies between $-a$ and $x \in [-a, a]$. What happens to this probability when n becomes very large?

2. A particle moves within a ball of radius R in $\mathbb{R}^3$ under the influence of the constant potential $V_0 > 0$. Show that there are continuous wave functions of the form $\Psi(r)$ (independent of angles and vanishing at $r = R$) that satisfy the time independent Schrödinger's equation. Find the energy levels, and the mean position of the particle.

3. A particle in a one-dimensional potential well

$$V(x) = \begin{cases} 0 & \text{for } x \in (0, a) \\ \infty & \text{otherwise.} \end{cases}$$

is in a state described by the wave function $\Psi(x) = Ax(a - x)$, where A is a constant. By expanding the wave function in terms of separable solutions

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\Big(\frac{n\pi x}{a}\Big), \qquad n = 1, 2, ...$$

(see equation (3.15)) find the probability distribution for the different energies of the particle.

4. Show that the wave function

$$\psi(x,t) = a(x,t) exp\Big(\frac{iS(x,t)}{\hbar}\Big)$$

satisfies the time dependent Schrödinger equation if and only if the real functions a and S satisfy the coupled system of equations

$$\frac{\partial S}{\partial t} + \frac{|\nabla S|^2}{2m} + V = \frac{\hbar^2}{2m}\frac{\nabla^2 a}{a}, \tag{8.4}$$

$$\frac{\partial (a)^2}{\partial t} + \operatorname{div}\Big(\frac{a^2}{m}\nabla S\Big) = 0. \tag{8.5}$$

Remark. In the classical limit of quantum mechanics (when $\hbar^2$ is neglected), the first equation involves only S and is essentially equivalent to classical equations of motion of the particle. Can you see the interpretation of the second equation?

Figure 8.1: Emission of electrons from metals.

Sheet Two

1. 'Quantum theory in finite universe': A particle of mass m moves freely ($V = 0$) on a circle of circumference L. Consider a particle incident from the left, and use the fact that a normalised time-dependent wave function must be a single valued function of position (ie. $\Psi(x) = \Psi(x + L)$) to show that the energy levels are discrete. Find the energy levels. Take the limit $L \to \infty$ and interpret your results.

2. In studying the emission of electrons from metals, it is necessary to take into account that electrons with an energy sufficient to leave the metal may be reflected at the metal surface. This motivates the following problem: Consider a one dimensional model with a potential V which is equal to $-V_0$ for $x < 0$ and equal to 0 for $x > 0$ (outside the metal (Figure 1)). Determine the reflection coefficient at the metal surface for an electron with energy $E > 0$.

3. Calculate the reflection and transmition coefficients for a beam of particles of energy $E > V_0 > 0$ incident from $x = -\infty$ on the potential barrier

$$V(x) = \begin{cases} V_0 & \text{for } x \in [0, a] \\ 0 & \text{otherwise.} \end{cases}$$

   If $k^2 = 2mE/\hbar^2$ and $\tilde{k} = 2m(E - V_0)/\hbar^2$ are fixed find the values of a for which the transmition coefficient has its maximum and minimum values.

4. A beam with energy $\hbar^2 k^2/2m$ and density $|A|^2$ is incident from large positive values of x, parallel to x axis, on a potential barrier of the form

$$V(x) = \begin{cases} 0 & \text{if } x > a, \\ -V_0 & \text{if } 0 < x < a, \\ \infty & \text{if } x < 0, \end{cases}$$

   where $V_0 > 0$ is a constant. Show that the wave function for $x > a$ can be written as

$$\Psi(x) = A[\exp(-ikx) + \exp(i[kx + \phi])], \qquad \phi \in \mathbb{R} \qquad \text{and find} \quad \exp(i\phi).$$

Sheet Three

1. A particle of mass m moves in the rectangular box $0 < x < a, 0 < y < b, 0 < z < c$ under the influence of zero potential (assume $V = \infty$ outside this region). Show that the permitted energies of the system are

$$E_{qrs} = \frac{\hbar^2\pi^2}{2m}\Big(\frac{q^2}{a^2} + \frac{r^2}{b^2} + \frac{s^2}{c^2}\Big),$$

where q, r, s are positive integers. In case when $a = b = c$ find normalised wave functions corresponding to the energy $11\hbar^2\pi^2/2ma^2$.

2. A one-dimensional harmonic oscillator carries a charge e and is placed in a uniform electric field $\mathcal{E} = const$, so that the potential becomes

$$V(x) = \frac{1}{2}m\omega^2x^2 - e\mathcal{E}x.$$

Show that each energy level is reduced by $e^2\mathcal{E}^2/2m\omega^2$. What are the new wave functions? [Hint: replace x by a new variable].

3. A two dimensional harmonic oscillator has Hamiltonian

$$H = \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2}m\omega^2(5x^2 + 6xy + 5y^2)$$

Find the energy levels and calculate the associated degeneracy of the lowest three energy levels.

4. The Hermite polynomial $H_n(z)$ satisfies the differential equation

$$\frac{\mathrm{d}^2H_n}{\mathrm{d}z^2} - 2z\frac{\mathrm{d}H_n}{\mathrm{d}z} + 2nH_n = 0, \qquad n = 0, 1, ...$$

is defined so that the coefficient of z^n is 2^n. The generating function is defined by

$$G(z, s) = \sum_{n=0}^{\infty} \frac{H_n(z)s^n}{n!}.$$

Prove that

- $\frac{\mathrm{d}H_n}{\mathrm{d}z} = 2nH_{n-1}(z)$,
- $\frac{\partial G}{\partial z} = 2sG$, and $\frac{\partial^2 G}{\partial z^2} - 2z\frac{\partial G}{\partial z} + 2s\frac{\partial G}{\partial s} = 0.$

Deduce that $G(z, s) = \exp(-s^2 + 2sz)$.

Figure 8.2: Spherical potential well.

Sheet Four

1. Consider a particle in a spherical potential well (Figure 1)

$$V(r) = \begin{cases} -V & \text{for } r \in [0, a] \\ 0 & \text{otherwise,} \end{cases}$$

where $V > 0$ is a constant. Find the normalised wave function $\Psi = \Psi(r)$ and the condition for energy levels.

2. Use the polar coordinates to write the time independent Schrödinger equation for two-dimensional model of the hydrogen atom. By considering separable solutions $\Psi(r, \theta) = F(r)G(\theta)$, show that the energy levels are of the form $-\kappa/(2n+1)^2$, where κ a positive constant, and $n = 0, 1, 2, \ldots$. Find the degeneracy of each level.

3. In terms of the parabolic coordinates

$$u = r(1 - \cos\theta), \qquad v = r(1 + \cos\theta), \qquad w = \phi.$$

Schrödinger equation for the 3D hydrogen atom can be written as

$$-\frac{\hbar^2}{2m}\Big(\frac{4}{u+v}\Big[\frac{\partial}{\partial u}\Big(u\frac{\partial\Psi}{\partial u}\Big) + \frac{\partial}{\partial v}\Big(v\frac{\partial\Psi}{\partial v}\Big)\Big] + \frac{1}{uv}\frac{\partial^2\Psi}{\partial w^2}\Big) - \frac{e^2}{2\pi\epsilon_0(u+v)}\Psi = E\Psi.$$

By considering separable solutions $\Psi(u, v, w) = F(u)G(v)H(w)$ show that the bound states have energies

$$E_N = -\frac{1}{2N^2}\frac{e^2}{4\pi\epsilon_0\alpha},$$

where α is the Bohr radius and $N = 1, 2, \ldots$. What is the degeneracy of the energy level E_N?

Sheet Five

1. Show that if $\hat{A}$ is a linear operator on $\mathcal{H}$ such that

$$\langle\Psi|\hat{A}\Psi\rangle/\langle\Psi|\Psi\rangle$$

is real for all states $|\Psi\rangle$, then $\hat{A}$ must be self-adjoint.

Let (r,θ,ϕ) be spherical polar coordinates. Show that operator $-i\hbar\partial/\partial r$ is not self-adjoint on the wave functions, but $-i\hbar(\partial/\partial r + 1/r)$ is self-adjoint.

Let $\hat{A}$ and $\hat{B}$ be self-adjoint operators. Show that $i[\hat{B},\hat{A}]$ is also self-adjoint.

2. A quantum mechanical system with only three independent states is described by the Hilbert space $\mathcal{H} = \mathbb{C}^3$. The Hamiltonian operator is

$$\hat{H} = \hbar\omega \begin{pmatrix} 1 & 2 & 0 \\ 2 & 0 & 2 \\ 0 & 2 & -1 \end{pmatrix}$$

Find the eigenvalues, and the eigenvectors of $\hat{H}$. At time $t = 0$ the system is in the state

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

Find the state vector $|\Psi(t)\rangle$ at a subsequent time t. Let p_1, p_2 and p_3 denote the probabilities of observing the system in the states

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

respectively. Show that $0 \leqslant p_2 \leqslant 1/2$.

3. Let $\hat{A}, \hat{B}, \hat{C}$ be operators. Prove the Leibnitz rule, and the Jacobi identity:

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

Let $\hat{A}(t)$ be an observable and let $|\Psi(t)\rangle$ be a normalised solution to the time dependent Schrödinger equation. Show that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{A}(t)\rangle = \langle\frac{\partial}{\partial t}\hat{A}(t)\rangle + \frac{i}{\hbar}\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle.$$

4. A particle of mass m moves along the x axis under the influence of a potential $V(\hat{X}) = m\omega^2\hat{X}^2/2$. Show that

$$E_\Psi\Big(\frac{\hat{P}^2}{2m}\Big)E_\Psi\Big(V(\hat{X})\Big) \geqslant \Big(\frac{\hbar\omega}{4}\Big)^2.$$

Sheet Six

1. Take $\mathcal{H} = L^2(\mathbb{R})$ and consider the parity operator

$$\hat{\mathcal{P}}\Psi(x) := \Psi(-x).$$

Note that $\hat{\mathcal{P}}^2 = \hat{1}$, and deduce that the only possible eigenvalues of $\hat{\mathcal{P}}$ are 1 and -1. Show that $\hat{\mathcal{P}}$ is self-adjoint. Consider a particle moving in a potential such that $V(x) = V(-x)$. Show that $[\hat{\mathcal{P}}, \hat{H}] = 0$ and find eigenvectors of $\hat{H}$, which are also eigenvectors of $\hat{\mathcal{P}}$. Find the expectation value of the position operator for a system in a non-degenerate energy state.

2. The operator $\hat{B}$ satisfies the relations

$$\hat{B}^2 = 0, \qquad \hat{B}^*\hat{B} + \hat{B}\hat{B}^* = \hat{1}.$$

Let $\hat{W} := \hat{B}^*\hat{B}$. Find $[\hat{W}, \hat{B}^*]$ and $[\hat{W}, \hat{B}]$, and show that $\hat{W}$ is a self-adjoint projection, that is $\hat{W}^2 = \hat{W} = \hat{W}^*$. Obtain a matrix representation for $\hat{B}, \hat{B}^*$, and $\hat{W}$ in which $\hat{W}$ is diagonal.

3. A charged particle moving in the plane perpendicular to a magnetic field B has Hamiltonian

$$\hat{H} = \frac{1}{2m}\Big[\Big(\hat{P}_1 + \frac{1}{2}e\hat{X}_2 B\Big)^2 + \Big(\hat{P}_2 - \frac{1}{2}e\hat{X}_1 B\Big)^2\Big].$$

Show that the allowed energy eigenvalues are

$$\Big(n + \frac{1}{2}\Big)\frac{|eB|\hbar}{m}, \qquad n = 0, 1, 2, \ldots .$$

4. Show that if $\hat{H}|\Psi\rangle = E|\Psi\rangle$ then for any operator $\hat{A}$ we have $\langle\Psi|[\hat{H}, \hat{A}]\Psi\rangle = 0$. Suppose that $\hat{H} = \hat{T} + \hat{V}$, where $\hat{T} = \hat{P}^2/2m$ and $\hat{V} = k\hat{X}^N$, where $k \in \mathbb{C}$ is a constant.

   (a) By taking $\hat{A} = \hat{X}$ show that $E_\Psi(\hat{P}) = 0$.

   (b) By taking $\hat{A} = \hat{X}\hat{P}$ derive the virial theorem, $2E_\Psi(\hat{T}) = NE_\Psi(\hat{V})$.

   (c) Deduce that $E_\Psi(\hat{T}) = NE/(N+2)$, and find $\Delta_\Psi(\hat{P})$.

   (d) When $\hat{V} = m\omega^2\hat{X}^2/2$ show that

$$\Delta_\Psi(\hat{P})\Delta_\Psi(\hat{X}) = \frac{E}{\omega}.$$