Lecture 3

Dynamics

3.1 Introduction

Having described the states and the observables of a quantum system, we shall now introduce the rules that determine their time evolution.

In classical mechanics, the state of a single particle system is described by the *classical trajectory*, i.e. by the knowing the position of the particle as a function of time: $x(t)$. [1]

The time-dependence of the position is described by Newton's law:

$$f = ma \,, \tag{3.1}$$

where $a(t) = d^2x(t)/dt^2$ is the acceleration of the system, and f is the external force acting on it.

Newton's law is a dynamic equation, relating the time evolution of the state of the system to the force acting on it. It is a second order differential equation, which can be solved (at least in principle) once we know the initial condition for the position and the velocity of the particle at some given time t_0.

As discussed in the previous chapter, in quantum mechanics the concept of classical trajectory cannot be defined, and the state of the system is described by the wave function. In this lecture we describe the quantum analogue of Newton's law, i.e. the equation that describes the time evolution of the wave function.

3.2 Schrödinger equation

3.2.1 Equation of motion

The time evolution of a quantum state is dictated by Schrödinger's equation:

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t)}\,, \tag{3.2}$$

where $\hat{H} = \hat{T} + \hat{V}$ is the Hamiltonian operator. Eq. (3.2) replaces Newton's equation of classical mechanics. [2]

The operator $\hat{H}$ is obtained from the classical Hamiltonian, by replacing the position and momentum with the corresponding operators $\hat{X}$ and $\hat{P}$ in Cartesian coordinates.

Schrödinger's equation states that the Hamiltonian operator determines the time shifts of the wave function, i.e. $\hat{H} = i\hbar\frac{\partial}{\partial t}$. Similarly, the momentum operator determines the space

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[1]If the particle evolves in more than one space dimension, then the position is identified by a vector $\underline{x}(t)$.

[2]It was introduced by the Austrian physicist Erwin Schrödinger in 1926, following the wave-particle duality suggested by de Broglie.

translations - remember that $\hat{P} = -i\hbar\frac{\partial}{\partial x}$. In a four-dimensional Minkowski space-time this correspondence can be written as a four-vector relation:

$$\hat{P}_\mu = i\hbar\frac{\partial}{\partial x^\mu} \,. \tag{3.3}$$

It is interesting to note that special relativity can be easily "embedded" in the rules of quantum mechanics! The Standard Model of particle physics, which describes the interactions between the fundamental constituents of matter very successfully, is based on this fact. This will become more clear when you study quantum field theory.

A digression on Schrödinger's equation Let us discuss briefly a heuristic explanation of the identification $\hat{H} = i\hbar\frac{\partial}{\partial t}$ by considering a one-dimensional plane wave

$$\Psi(x,t) = \text{const} \times e^{-i(\omega t - kx)} \,. \tag{3.4}$$

The plane wave describes e.g. the propagation of monochromatic light. Applying the operator $i\hbar\frac{\partial}{\partial t}$ we obtain:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hbar\omega\Psi(x,t) = h\nu\Psi(x,t) \quad (\omega = 2\pi\nu)\,, \tag{3.5}$$

which is precisely the energy of the photon.

Moreover we know that probabilities must be normalized to one. The mathematical translation of this property is that:

$$\int dx\Psi(x,t)^*\Psi(x,t) = 1\,, \quad \text{for all } t\,. \tag{3.6}$$

Hence the derivative with respect to time of the integral above must vanish:

$$\int dx \left[\left(\frac{\partial}{\partial t}\Psi(x,t)^*\right)\Psi(x,t) + \Psi(x,t)^*\left(\frac{\partial}{\partial t}\Psi(x,t)\right) \right] = 0\,; \tag{3.7}$$

the latter equation shows that $\frac{\partial}{\partial t}$ must be represented by an anti-Hermitean operator. The Hamiltonian $\hat{H}$ is the operator associated to the energy of the system and therefore is hermitean. This explains the factor of i that appears in Schrödinger's equation, it is necessary to connect $\frac{\partial}{\partial t}$ to an Hermitean operator. Finally the factor $\hbar$ is needed on dimensional grounds. Other numerical factors – e.g. factors of 2, π, etcetera – cannot be derived by these simple arguments, but are explained by the heuristic derivation above.

Time evolution using Dirac notation If we use Dirac's notation to represent the quantum states by kets, Schrödinger's equation becomes:

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \,. \tag{3.8}$$

The equation above simply states that the time-evolution of the vector $|\Psi(t)\rangle$ is generated by acting on the vector with the operator $\hat{H}$.

3.2.2   Eigenstates of the Hamiltonian

Let us consider a time-independent Hamiltonian:

$$\hat{H} = \hat{H}(\hat{X}, \hat{P}),\tag{3.9}$$

where there is no explicit dependence on time.

    The time evolution for an energy eigenstate can be worked out easily. Schrödinger's equation becomes simply:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = E\Psi(x,t).\tag{3.10}$$

Integrating Eq. (3.10) with respect to time:

$$\Psi(x,t) = \psi_E(x)\exp\left[-\frac{i}{\hbar}Et\right],\tag{3.11}$$

where $\psi_E(x)$ is the spatial wavefunction corresponding to the eigenvalue E.

    Such states are known as *stationary states* because the associated probability density is independent of time:

$$
\begin{aligned}
|\Psi_E(x,t)|^2 \equiv \Psi_E^*(x,t)\Psi_E(x,t) &= \psi_E^*(x)\exp\{iEt/\hbar\}\psi_E(x)\exp\{-iEt/\hbar\}\\
&= |\psi_E(x)|^2.
\end{aligned}
$$

Likewise, the expectation value of any operator is also independent of time:

$$\langle\Psi_E(t)|\hat{O}|\Psi_E(t)\rangle = \int dx\,\Psi_E(x,t)^*\hat{O}\Psi_E(x,t)\tag{3.12}$$

$$= \int dx\,\psi_E(x)^*e^{iEt/\hbar}\hat{O}e^{-iEt/\hbar}\psi_E(x)\tag{3.13}$$

$$= \int dx\,\psi_E(x)^*e^{iEt/\hbar}e^{-iEt/\hbar}\hat{O}\psi_E(x)\tag{3.14}$$

$$= \int dx\,\psi_E(x)^*\hat{O}\psi_E(x)\tag{3.15}$$

$$= \langle\Psi_E(0)|\hat{O}|\Psi_E(0)\rangle.\tag{3.16}$$

    Note that *formally* we can write the solution of the Schrödinger equation as:

$$|\Psi(t)\rangle = \exp\left[-\frac{i}{\hbar}\hat{H}t\right]|\Psi(0)\rangle,\tag{3.17}$$

even for a state that is not an eigenstate of the energy. However in this case $\exp\left[-\frac{i}{\hbar}\hat{H}t\right]$ is a complicated operator. It can be written explicitly using a Taylor expansion:

$$\exp\left[-\frac{i}{\hbar}\hat{H}t\right] = \sum_n\frac{1}{n!}\left(\frac{-i}{\hbar}\right)^n\hat{H}^nt^n.\tag{3.18}$$

When applied to an eigenstate of the energy it turns out to be a simple complex phase!! You will see some examples in problem sheet 2.

The eigenvalue equation

$$\boxed{\hat{H}\psi_n(x) = E_n\psi_n(x)} \tag{3.19}$$

yields the eigenvalues E_n, i.e. all the possible values of the energy of the system, and the stationary states $\psi_n(x)$. Eq. (3.19) is often referred to as *time-independent Schrödinger equation.*

Using the explicit definition of $\hat{H}$ in Eq. (1.35), we can write the time-independent Schrödinger equation as a second order differential equation:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]u_n(x) = E_n u_n(x). \tag{3.20}$$

Eigenvalues and eigenstates are found by looking for normalizable solutions of the differential equation, taking into account the appropriate boundary conditions. Note that some authors use the notation $\{u_n(x)\}$ for the eigenfuncitons of the energy. We are going to use this convention below.

3.2.3 General restrictions on $\Psi(x,t)$

We see from the form of Eq. (3.20) that its solutions have to satisfy a number of properties:

1. $\Psi(x,t)$ must be a single-valued function of x and t.

2. $\Psi(x,t)$ must be a continuous function of x and t.

3. $\frac{\partial\Psi}{\partial x}(x,t)$ must be a continuous function of x.

There is an exception to this set of rules.

1. Restriction 3 does not apply when the potential energy function $V(x)$ has infinite discontinuities e.g. the 'particle-in-a-box' problem met in Physics 2, for which

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

We shall see see later a detailed description of this system.

3.2.4   Example: the quantum harmonic oscillator

In order to give a concrete example of solutions of the Schrödinger equation, let us review the quantum harmonic oscillator.

Remember that the harmonic oscillator is of paramount importance in physics, because every system close to the minimum of the potential is described by a quadratic potential, i.e. it behaves like a harmonic oscillator.

Classically, the equation of motion for a particle of mass m, subject to a restoring force proportional to the displacement, x, is

$$m\ddot{x} = -k\,x \tag{3.21}$$

where the constant of proportionality, k, is usually called the spring constant. This has oscillatory solutions of angular frequency $\omega = \sqrt{k/m}$. We can obtain the energy equation by writing

$$\ddot{x} = v\frac{\mathrm{d}v}{\mathrm{d}x}, \tag{3.22}$$

and integrating to give

$$\tfrac{1}{2}mv^2 + \tfrac{1}{2}kx^2 = E, \tag{3.23}$$

so that the potential energy function, V, is given by

$$V(x) = \tfrac{1}{2}kx^2 = \tfrac{1}{2}m\omega^2 x^2. \tag{3.24}$$

The evolution of the position of the oscillator as a function of time $x(t)$ is shown in Fig. 3.1 for two different values of ω. The total energy of the oscillator is $E = \tfrac{1}{2}m\omega^2 L^2$, where L is the maximum amplitude of the oscillations. The larger the amplitude of the oscillations, the larger the energy of the system. In the case depicted in Fig. 3.1 the amplitude $L = 1$ for both curves.

For the quantum harmonic oscillator, the time-independent Schrödinger equation is thus

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \tfrac{1}{2}m\omega^2 x^2 \right] u_n(x) = E_n u_n(x). \tag{3.25}$$

We will not discuss the details of the solution of this differential equation, although you may have already seen it in a mathematical methods course and/or book. In any case we will develop a much more elegant method to find its solutions in a later lecture. It suffices to say that acceptable solutions only arise for certain values of the total energy i.e. the energy is *quantised*.

The energy eigenvalues are as follows:

$$E_n = (n + \tfrac{1}{2})\hbar\omega \quad n = 0,\, 1,\, 2,\, 3,\, \ldots \infty \tag{3.26}$$
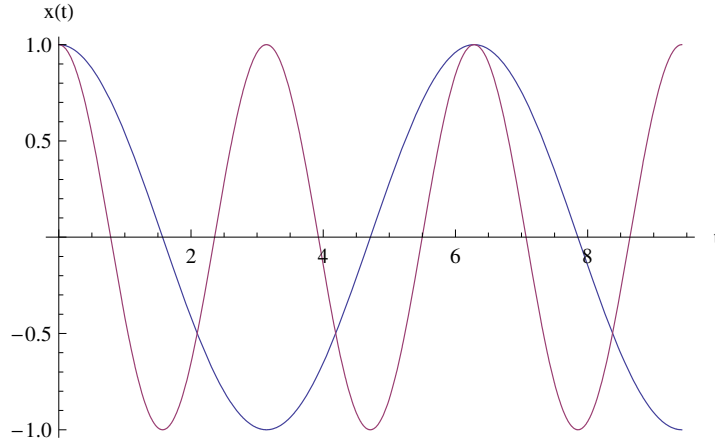
Figure 3.1: Classical trajectory of the harmonic oscillator for $\omega = 1$ (blue curve), and $\omega = 2$ (red curve).

The state of lowest energy, or *ground state*, is labelled by $n = 0$ and has an energy $\frac{1}{2}\hbar\omega$ rather than zero.

The corresponding eigenfunctions may be written as

$$u_n(x) = C_n \exp\{-\alpha^2 x^2/2\}\, H_n(\alpha x) \tag{3.27}$$

where C_n is a normalisation constant, $\alpha^2 \equiv m\omega/\hbar$ and $H_n(\alpha x)$ are polynomials of degree n, known as *Hermite polynomials*. They satisfy the orthogonality relation

$$\int_{-\infty}^{\infty} \exp\{-s^2\} H_m(s) H_n(s)\, \mathrm{d}s = 2^n \sqrt{\pi}\, n!\, \delta_{mn}\,, \tag{3.28}$$

implying that the energy eigenfunctions are orthogonal (orthonormal with an appropriate choice of the constant, C_n).

The first few Hermite polynomials are

$$\begin{aligned} H_0(s) &= 1 & H_2(s) &= 4s^2 - 2 \\ H_1(s) &= 2s & H_3(s) &= 8s^3 - 12s \end{aligned} \tag{3.29}$$

Note that the polynomials, and hence the energy eigenfunctions, are alternately even and odd functions, i.e. are of either even or odd parity. If we introduce a *parity operator*, $\hat{\mathcal{P}}$, whose action on a function, $f(x)$, is defined by

$$\hat{\mathcal{P}}\, f(x) = f(-x)\,, \tag{3.30}$$

so that the eigenvalues of $\hat{\mathcal{P}}$ are ± 1 only, corresponding to the even and odd functions

$$f_+(x) \equiv \tfrac{1}{2}[f(x) + f(-x)] \quad \text{and} \quad f_-(x) \equiv \tfrac{1}{2}[f(x) - f(-x)]. \tag{3.31}$$

You can readily check that:

$$\hat{\mathcal{P}}\, u_n(x) = (-1)^n\, u_n(x), \tag{3.32}$$

and we say that the parity is $(-1)^n$.

The probability density to find the oscillator at a given position x is $|u_n(x)|^2$. The probability densities for the first five levels are shown in Fig. 3.2. Note that for higher values of the energy, we get a larger probability to find the oscillator at larger values of x.
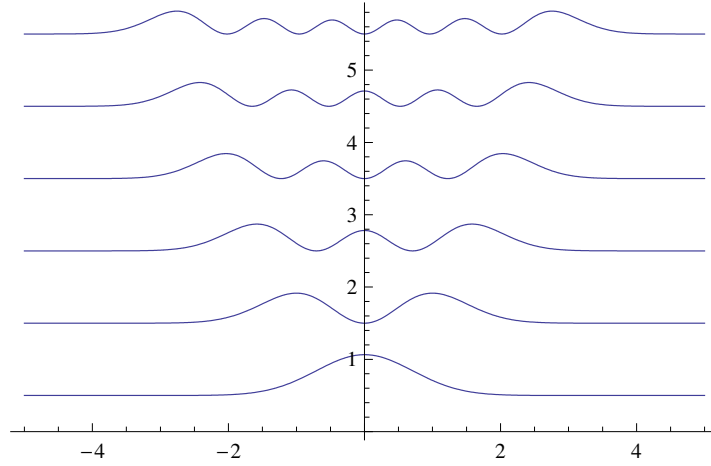

Figure 3.2: Probability to find the oscillator at x for the first five levels of the harmonic oscillator for $\alpha = 1$. Each curve is shifted upwards by $n + \frac{1}{2}$ to improve the readability of the plot.

In order to quantify the last sentence we can compute the average position, and the fluctuations of the position. The expectation value of the position of the quantum harmonic oscillator is given by:

$$\langle x \rangle_n = \int_{-\infty}^{+\infty} dx\, x\, \left| C_n \exp\{-\alpha^2 x^2/2\}\, H_n(\alpha x) \right|^2. \tag{3.33}$$

You can easily convince yourself that $\langle x \rangle = 0$, because the integrand is always an *odd* function of x. This is what we would have naively expected, since the system is symmetric under parity. The quantum oscillator is equally likely to be to the left or to the right of the origin at $x = 0$.

It is more interesting to compute the mean square deviation $\langle x^2 \rangle$, which measures the amplitude of the oscillations. You can compute the integrals explicitly for the first few Hermite polynomials, or simply look up the answer in a table of integrals:

$$\langle x^2 \rangle_n = (n + \frac{1}{2}) \frac{1}{\alpha^2} \,. \tag{3.34}$$

Once again this is the quantitative expression of our intuitive understanding from classical mechanics: the larger the energy, the larger the oscillations!!

3.2.5 Expansion in stationary states

Given the expansion of the wave function at $t = 0$ in the $\{u_n(x)\}$ basis:

$$\Psi(x,0) = \sum_n a_n u_n(x), \quad a_n = \langle u_n | \Psi(0) \rangle \,, \tag{3.35}$$

we can express the evolved wave function at time t as:

$$\Psi(x,t) = \sum_n a_n e^{-iE_n t/\hbar} u_n(x) \,. \tag{3.36}$$

If the Hamiltonian does not depend explicitly on time, then the energy levels E_n are constant in time:

$$\frac{d}{dt} E_n = \frac{d}{dt} \langle \Psi_n(x,t) | \hat{H} | \Psi_n(x,t) \rangle = \frac{d}{dt} \int dx \, \Psi_n(x,t)^* \hat{H} \Psi_n(x,t)$$
$$= \frac{1}{i\hbar} \int dx \, \Psi_n(x,t)^* \left[\hat{H}, \hat{H} \right] \Psi_n(x,t) = 0 \tag{3.37}$$

An observable such that:

$$\frac{d}{dt} \langle \Psi(t) | \hat{O} | \Psi(t) \rangle = 0 \,, \tag{3.38}$$

for *any* state $\Psi(x,t)$ is called a *conserved observable*.

A time-independent operator is conserved if and only if $\left[\hat{H}, \hat{O} \right] = 0$.

This is a consequence of the equation that determines the time-dependence of a matrix element:

$$i\hbar \frac{d}{dt} \langle \Psi(t) | \hat{O} | \Psi(t) \rangle = \langle \Psi(t) | \left[\hat{O}, \hat{H} \right] | \Psi(t) \rangle \,. \tag{3.39}$$

The proof of this result is left as an exercise in problem sheet 2.

3.3   Summary

Let us conclude this chapter by summarizing the main concepts introduced in this lecture.

- Time-dependent Schrödinger equation.

- Eigenstates of the Hamiltonian. Time-independent Schrödinger equation. Physical characterization of the stationary states.

- First properties of the solutions of the Schrödinger equation.

- The harmonic oscillator. Analytic solution, comparison between the quantum, and the classical behaviours.

- Completeness of the energy eigenstates. Expansion in stationary states.