

# PX2132: Introductory Quantum Mechanics

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These notes accompany the course videos; details of derivations will appear here, but the videos should also be watched for surrounding explanation.

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## Books

All the information relevant to this course appears in a condensed form in the accompanying notes. The online videos provide further detail. There is no course textbook, but the notes provide references to the following books when helpful (all are freely available online):

- J. Binney and D. Skinner, *The Physics of Quantum Mechanics*  
[<https://www-thphys.physics.ox.ac.uk/people/JamesBinney/QBhome.htm>]
- P. A. M. Dirac, *The Principles of Quantum Mechanics*  
[[archive.org/details/in.ernet.dli.2015.177580](https://archive.org/details/in.ernet.dli.2015.177580)]
- R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*  
[[feynmanlectures.caltech.edu](http://feynmanlectures.caltech.edu)]

While later editions of the first two books are available for a price, references should be assumed to be made to these free editions. The following books are available as eBooks for free through Cardiff University library and will also be referred to:

- D. J. Griffiths, *Introduction to Quantum Mechanics* (Cambridge University Press, 2nd edition)
- S. Weinberg, *Lectures on Quantum Mechanics* (Cambridge University Press, 2nd edition, 2015).

Other books which you may wish to consult, but which will not be referred to directly in the course:

- A. I. M. Rae and J. Napolitano, *Quantum Physics* (Routledge, 6th edition, 2015) ISBN 9781482299182
- J. J. Sakurai and J. Napolitano, *Modern Quantum Mechanics* (Cambridge University Press, 2nd edition, 2017) ISBN 978-1-108-42241-3
- L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics Volume 3 - Quantum Mechanics: Non-Relativistic Theory* (Pergamon Press, Third edition, 1977) ISBN 0080291406
- S. Gasiorowicz, *Quantum Physics* (Wiley, 3rd edition, 2003) ISBN 978-0471057000
- A. P. French and E. Taylor, *An Introduction to Quantum Physics* (W. W. Norton & Company, 1978) ISBN 0393091066
- R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles* (Wiley and Sons, 2nd edition, 1985) ISBN 978-0471873730.

## List of definitions

**The canonical commutation relation**  $[\hat{x}, \hat{p}] = i\hbar\hat{1}$

**Dirac notation** the notation  $|\psi\rangle$  for complex vectors. Also called bra-ket notation, with  $\langle\phi|$  the ‘bra’,  $|\psi\rangle$  the ‘ket’, and  $\langle\phi|\psi\rangle$  a bracket.

**Expectation value**  $\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle$ . The mean value of an operator measured by a given state.

**First quantization** a wave-like description of quantum objects:  $\psi(x)$ .

**The Hamiltonian** the energy operator.  $\hat{H} = \hat{p}^2/2m + \hat{V}$ ;  $\hat{H}\psi(x) = -\hbar^2\psi''/2m + V(x)\psi$ .

**The Heisenberg picture** the description of quantum states as time independent, and operators as time dependent.

**The Heisenberg uncertainty principle**  $\sigma_{\hat{A}}\sigma_{\hat{B}} \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right|$  where  $\sigma_{\hat{A}}$  denotes the standard deviation of operator  $\hat{A}$ .

**Hilbert space** a linear vector space with an inner product and square-normalisable vectors

**Hermiticity**  $\hat{A} = \hat{A}^\dagger$  where  $\hat{A}^\dagger = \hat{A}^{*T}$ . For differential operators:  $\int_{-\infty}^{\infty} \varphi(x)^* (\hat{A}\psi(x)) dx = \int_{-\infty}^{\infty} (\hat{A}\varphi(x))^* \psi(x) dx$ .

**Ladder operators** an operator which raises or lowers the quantum number of a state it acts on. Also called creation/annihilation operators or raising and lowering operators.

**Normalisation** the prefactor on a wavefunction ensuring that the total probability to find the particle is one.

**The number operator** in the harmonic oscillator, the operator whose eigenstates are the energy eigenstates and whose eigenvalues are the level of the state.

**Orthonormality** orthogonal and normalised. If a set of states is orthonormal the inner product of any state with itself is 1 and the inner product between any two different states is zero.

**The probability density**  $\rho$  integrated over a region of space, this gives the probability to find the particle in that region.  $\rho(x, t) dx = |\psi(x, t)|^2 dx$  is the probability to find the particle between  $x$  and  $x + dx$  at time  $t$ .

**The probability current density**  $j$  the current density associated with a flow of probability:

$$j(x, t) = \frac{i\hbar}{2m} \{\psi\nabla\psi^* - \psi^*\nabla\psi\}.$$

**The probability amplitude** the complex number associated to each point in space by the wavefunction  $\psi$ .

**Quantum numbers** eigenvalues of operators which commute with the Hamiltonian; expectation values which do not change in time.

**The Schrodinger picture** the description of quantum states as time dependent, and operators as time independent.

**Second quantisation** a particle-like description of quantum objects in terms of ladder operators.

**Stationary states** energy eigenstates. So called as their probability densities are time independent.

**Superposition** summing solutions to the TDSE to get a new solution to the TDSE

**The time dependent schroedinger equation**  $i\hbar\partial_t|\psi\rangle = \hat{H}|\psi\rangle$ , or in the position basis  $i\hbar\dot{\psi} = \hat{H}\psi$ . Abbreviated TDSE.

**The time independent schroedinger equation**  $\hat{H}|\psi\rangle = E|\psi\rangle$ , or in the position basis  $\hat{H}\psi(x) = E\psi(x)$ . Abbreviated TISE.

**The wavefunction**  $\psi$  a function which assigns a complex number to each point in space. The modulus square is the probability density  $\rho$ .

# 1 Introduction

## Videos:

- V1.0: Introduction to the course
- V1.1: History of quantum mechanics
- V1.2: The Schrödinger equation
- V1.3: Plane waves
- V1.4: Amplitudes and probabilities
- V1.5: Two slit demo

## Topics:

- recap of vectors, matrices, and differential equations
- the experimental necessity of quantum mechanics: Compton scattering, de Broglie relation  $p = h/\lambda = \hbar k$ ; single particle interference; photoelectric effect and  $E = hf = \hbar\omega$
- the time-dependent Schrodinger equation (TDSE)
- the time-independent Schrodinger equation (TISE)
- the wavefunction
- probability density
- probability current density
- general boundary conditions.

## For the exam you should be able to:

- understand and apply  $p = \hbar k$ ,  $E = \hbar\omega$
- write down the TDSE and TISE
- derive the TISE from the TDSE using separation of variables
- deduce the time dependence of a solution to the TISE
- state the Born rule
- state the meaning of the probability density and to calculate it for a given wavefunction
- derive the continuity equation for the local conservation of probability
- derive the probability current density and calculate it for a given wavefunction
- state the two boundary conditions which always apply to the wavefunction.

## 1.1 The Schrödinger equation

The time-dependent Schrödinger equation (TDSE) is

$$\boxed{i\hbar\partial_t\psi(\mathbf{x},t) = \hat{H}\psi(\mathbf{x},t)} \quad (1)$$

where

$$\partial_t\psi(\mathbf{x},t) = \left(\frac{\partial\psi(\mathbf{x},t)}{\partial t}\right)_{\mathbf{x}} \quad (2)$$

and  $(\cdot)_{\mathbf{x}}$  indicates that  $\mathbf{x}$  is held constant. Here,  $\hbar$  is the reduced Planck's constant,  $\mathbf{x}$  is position,  $t$  is time, and  $i$  is the imaginary unit. Getting some idea for the meaning of the mysterious wavefunction  $\psi$  is the content of this entire course. The Hamiltonian operator  $\hat{H}$ , which has dimensions of energy, is defined to be

$$\hat{H}\psi(\mathbf{x},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x})\right)\psi(\mathbf{x},t) \quad (3)$$

where  $m$  is the mass of the particle,  $V(\mathbf{x})$  is the potential confining the particle, and

$$\nabla = \begin{pmatrix} \partial_x \\ \partial_y \\ \partial_z \end{pmatrix} \quad (4)$$

is the gradient operator (I have used the simpler notation  $\partial_x = (\partial/\partial x)_{y,z,t}$  here).

The TDSE is a second-order partial differential equation. The equation is separable using the substitution  $\psi(\mathbf{x},t) = \phi(\mathbf{x})T(t)$ :

$$\begin{aligned} i\hbar\phi(\mathbf{x})\frac{dT(t)}{dt} &= T(t)\hat{H}\phi(\mathbf{x}) \\ \downarrow \\ i\hbar\frac{1}{T(t)}\frac{dT(t)}{dt} &= \frac{1}{\phi(\mathbf{x})}\hat{H}\phi(\mathbf{x}) \end{aligned} \quad (5)$$

where the derivatives are now total derivatives. Since the relation holds for all  $\mathbf{x}$  and  $t$  both sides must be equal to a constant which we will suggestively call  $E$ . We can assume  $E$  is real for now; we will prove this later. This gives two equations. The first is **the time-independent Schrödinger equation (TISE)**:

$$\frac{1}{\phi(\mathbf{x})}\hat{H}\phi(\mathbf{x}) = E$$

↓



$$\hat{H}\phi(\mathbf{x}) = E\phi(\mathbf{x}). \quad (6)$$

The second gives the time evolution of the wavefunction:

$$\begin{aligned} i\hbar \frac{1}{T(t)} \frac{dT(t)}{dt} &= E \\ \downarrow \\ T(t) &= \exp(-iEt/\hbar) T(0) \\ \downarrow \end{aligned}$$

$$\psi(\mathbf{x}, t) = \psi(\mathbf{x}, 0) \exp(-iEt/\hbar). \quad (7)$$

We will focus on the 1D case in which  $\nabla = \partial/\partial x = \partial_x$  unless otherwise stated, but the generalisation is straightforward.

## 1.2 General boundary conditions

The following boundary conditions apply to all the cases of physical interest in the TISE:

$$\begin{aligned} \text{(i)} \quad \phi(\mathbf{x}) &\text{ is continuous} \\ \text{(ii)} \quad \nabla\phi(\mathbf{x}) &\text{ is continuous except possibly at infinite discontinuities in } V(\mathbf{x}). \end{aligned} \quad (8)$$

These follow from the fact that the TISE is second-order in spatial derivatives, and we never consider potentials which are too pathological (we can have infinite potentials and discontinuous potentials, and even derivatives of discontinuities, but nothing worse). A useful condition for cases when (ii) does not apply is that  $\psi = 0$  in continuous regions where  $V = \infty$ .

## 1.3 Probability density

The meaning of the wavefunction  $\psi$  is debated. What can be said for certain is that  $|\psi(x, t)|^2 dx$  gives the probability to find the particle between  $x$  and  $x + dx$  at time  $t$ . This is called the Born rule. The quantity

$$\rho(x, t) = |\psi(x, t)|^2 \quad (9)$$

is called the *probability density*. Since the particle must exist somewhere we have that

$$\int_{-\infty}^{\infty} \rho(x, t) dx = 1. \quad (10)$$

The overall probability to find the particle somewhere is always 1, no matter what happens, so **probability is globally conserved**.

#### 1.4 Probability current density

Consider how the probability density  $\rho(\mathbf{x}, t)$  changes with respect to time (it's no harder to consider three dimensions, so we will for generality):

$$\begin{aligned} \partial_t \rho(x, t) &= \partial_t |\psi|^2 = \psi^* \partial_t \psi + \psi \partial_t \psi^* \\ &= \frac{1}{i\hbar} \{ \psi^* (i\hbar \partial_t \psi) - \psi (-i\hbar \partial_t \psi^*) \} \\ &\quad \downarrow \text{TDSE} \\ &= \frac{i\hbar}{2m} \{ \psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \} \\ &= \frac{i\hbar}{2m} \nabla \cdot \{ \psi^* \nabla \psi - \psi \nabla \psi^* \}. \end{aligned}$$

This gives us a **continuity equation for conservation of probability**:

$$\partial_t \rho(\mathbf{x}, t) = -\nabla \cdot \mathbf{j}(\mathbf{x}, t) \quad (11)$$

where

$$\mathbf{j}(\mathbf{x}, t) = \frac{i\hbar}{2m} \{ \psi \nabla \psi^* - \psi^* \nabla \psi \} \quad (12)$$

is the **probability current density**. The physical meaning is that **probability is locally conserved**. This is a stronger statement than global conservation. It says that if the probability is going to decrease in one region of space, it must flow out of that region, like a fluid. If a quantity were globally but not locally conserved, it could decrease in one region and increase in a disconnected region simultaneously. For example, when you shuffle cards, the number of red cards in the pack is conserved globally but not locally.

## 2 Scattering and tunnelling

### Videos:

- V2.1a–V2.1d: Scattering from a potential step
- V2.2: Quantum tunnelling
- V3.3: Evanescent waves demo

### Topics:

- plane waves
- recovering  $p = \hbar k$  and  $E = \hbar\omega$  from the Schrödinger equation
- scattering from a potential step
- tunnelling and barrier penetration
- scanning tunnelling microscopes.

### For the exam you should be able to:

- write down the form of a plane wave
- use this form to show the Schrödinger equation is compatible with  $p = \hbar k$  and  $E = \hbar\omega$
- state the forms of the TISE in regions of constant potential
- find the transmission and reflection amplitudes for scattering from a potential step
- find the probability current densities for scattering from a potential step
- find the probabilities of transmission and reflection from a potential step
- explain the steps necessary to solve scattering from a potential barrier of finite width
- explain the physical significance of quantum tunnelling
- explain the relevance to scanning tunnelling spectroscopy and microscopy

### For the exam you will not be required to:

- rote learn any solutions
- solve explicitly for the amplitudes associated with the finite-width barrier

## 2.1 TISE: solutions in regions of constant potential

In regions of constant potential there are three forms of solution, all of which have counterparts in classical waves:

$$\text{travelling waves (plane waves): } \phi(x) = a \exp(ikx) + b \exp(-ikx) \quad (13)$$

$$\text{standing waves: } \phi(x) = a \cos(kx) + b \sin(kx) \quad (14)$$

$$\text{evanescent waves: } \phi(x) = a \exp(\kappa x) + b \exp(-\kappa x). \quad (15)$$

The coefficients  $a$  and  $b$  can be complex in general. The forms above assume  $k$  and  $\kappa$  are real. In fact any one of the three options is already completely general if we allow complex wavevectors. Nevertheless, it is often simpler to choose the appropriate form of solution using physical intuition. Standing waves are relevant if leftgoing and rightgoing travelling waves appear in the region with equal amplitude (useful for bound states); evanescent waves are relevant if the particle's energy is less than the potential in the region.

## 2.2 Solving the Schrödinger Equation

Despite having some abstract interpretational questions surrounding it, quantum mechanics has survived because it gives phenomenally accurate predictions. The process of obtaining predictions in quantum mechanics is the process of solving the TDSE. This is always done in the same way.

- First, we specify the problem. The only thing that changes between problems is the potential  $V(x)$ . It always helps to draw the potential.
- Next, we solve the TISE, which is entirely specified by the potential. The solutions to the TISE are wavefunctions with known energies. These special wavefunctions are really important, because of Eq 7. If we know all the wavefunctions with known energies we can deduce any other possible wavefunction, including how it changes in time. Solving the TISE is the hard part of solving the TDSE. To solve the TISE we do the following.
  - We write down a reasonable guess for the solutions. For regions of constant potential these guesses are above.
  - We substitute the guesses into the TISE.
  - We obtain expressions for the energy  $E$  in terms of the wavevector  $k$  in each region.
  - We use the general boundary conditions to patch together the solutions in different regions, and to constrain the free parameters in the trial solutions.
- Finally, with this information, we can straightforwardly add the time dependence to the solutions we have found. This gives the desired set of solutions to the TDSE (what we wanted). By adding these solutions together we can make any possible solution to the TDSE.

Often in these notes we will not bother getting the time dependence back out, as doing so is always the same. But it's the solutions to the TDSE we really want. I heard this put nicely once: Schrödinger won the Nobel prize for writing down the TDSE, not the TISE. The TISE is just a means to solving the TDSE. This is easy to forget since in practice we spend all our time solving the TISE, as it's the hard part of the problem.

### 2.3 Plane waves

A trivial example is given by the potential  $V(x) = 0$ . Here we find the general solutions

$$\begin{aligned}\phi(x) &= a_{\pm} \exp(\pm ikx) \\ T(t) &= T(0) \exp(-iEt/\hbar)\end{aligned}\tag{16}$$

for real  $k$ . The time dependent wave function is

$$\psi(x, t) = \phi(x) T(t) = a_{\pm} \exp(\pm ikx - iEt/\hbar)\tag{17}$$

for a possibly complex  $a_{\pm}$ . These correspond to plane waves propagating in the  $\pm x$  directions. Comparing to the general form of a plane wave solution

$$\psi(x, t) = a_{\pm} \exp(\pm ikx - i\omega t),\tag{18}$$

which should hopefully be familiar from other courses, we see that

$$E = \hbar\omega.\tag{19}$$

This is Einstein's relation relating the energy of a particle to its angular frequency. Substituting Eq 18 into the TISE, Eq. 6, we find that

$$E = \frac{\hbar^2 k^2}{2m}.\tag{20}$$

Equating this to the non-relativistic expression for the kinetic energy

$$E = \frac{p^2}{2m}\tag{21}$$

we find the de Broglie relation

$$p = \hbar k.\tag{22}$$

### 2.4 Scattering from a potential step

Consider the potential

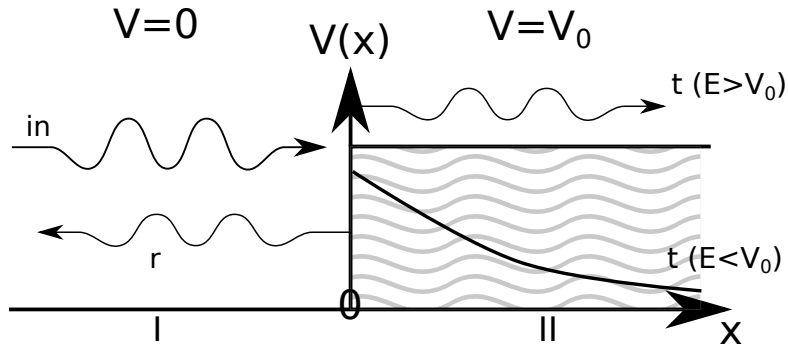


Figure 1: The potential step defined in Eq. 23, with schematic solutions indicated.

$$V(x) = \begin{cases} 0, & x < 0 \text{ (region I)} \\ V_0, & x \geq 0 \text{ (region II)}. \end{cases} \quad (23)$$

This is shown schematically in Fig. 23. The picture draws an intuitive analogy with gravitational potential. But the particle really lives along a 1D line, and the potential would generally be electrostatic. Assume a particle is incident on the step from the left.

To find the wavefunction which solves the TISE we can solve the TISE in regions *I* and *II* and match them using the the general boundary conditions of Eq. 8. From the solution of the TISE we can always obtain the full solution to the TDSE straightforwardly using Eq. 7. We will return to this later. For now we will focus on solving the TISE.

### 2.4.1 Region *I*

For  $x < 0$  we have the general solution

$$\begin{aligned} \phi_I(x) &= a_I \exp(ik_I x) + b_I \exp(-ik_I x) \\ E &= \frac{\hbar^2 k_I^2}{2m}. \end{aligned} \quad (24)$$

where  $k_I$  are real. There is no reason to assume the leftgoing and rightgoing amplitudes are the same, so standing waves would not be appropriate. The energy of the particle is greater than that of the (zero) potential in this region, so we expect wave-like solutions rather than evanescent solutions. The expression for  $E$  in terms of  $k_I$  is again found by substituting the form of  $\phi$  into the TISE. Here  $a_I$  corresponds to the rightmoving ingoing wave, and  $b_I$  the leftmoving reflected wave. This wavefunction is unphysical as it cannot be normalised; a more physical solution would involve summing up plane waves to form a wave packet of finite extent. Without loss of generality we can choose to set  $a_I = 1$  and  $b_I = r$ , the reflection amplitude:

$$\phi_I(x) = \exp(ik_I x) + r \exp(-ik_I x). \quad (25)$$

### 2.4.2 Region II: $E > V_0$

Assuming  $E > V_0$  we have the general solution

$$\begin{aligned}\phi_{II}(x, t) &= a_{II} \exp(ik_{II}x) + b_{II} \exp(-ik_{II}x) \\ E - V_0 &= \frac{\hbar^2 k_{II}^2}{2m}.\end{aligned}\quad (26)$$

Since the energy  $E$  is the same in Eqs 24 and 26 we have

$$k_I^2 = k_{II}^2 + \frac{2mV_0}{\hbar^2}.\quad (27)$$

Physically we know that  $b_{II} = 0$ , because this term corresponds to a left-going wave. But the wave entered from the left, so must be purely right-going. Rename  $a_{II} = t$  the transmission amplitude:

$$\phi_{II}(x) = t \exp(ik_{II}x).\quad (28)$$

Now we can use the general boundary conditions (i) and (ii) which are always true (Eq 8). Boundary condition (i) gives:

$$\begin{aligned}\phi_I(0) &= \phi_{II}(0) \\ \downarrow \\ 1 + r &= t.\end{aligned}\quad (29)$$

Boundary condition (ii):

$$\begin{aligned}\phi'_I(0) &= \phi'_{II}(0) \\ \downarrow \\ k_I(1 - r) &= k_{II}t.\end{aligned}\quad (30)$$

Combining with Eq. 29 we have:

$$r = \frac{k_I - k_{II}}{k_I + k_{II}}\quad (31)$$

$$t = \frac{2k_I}{k_I + k_{II}}.\quad (32)$$

These are the probability amplitudes for reflection and transmission. Their meaning is obscure in exactly the same way that the meaning of  $\psi$  is obscure; but they can be used to establish the

probability for reflection and transmission, which we will do shortly. First let's consider the case  $E < V_0$ .

### 2.4.3 Region II: $E < V_0$

Assuming  $E > V_0$  we instead have the solution

$$\begin{aligned}\phi_{II}(x) &= a_{II} \exp(\kappa x) + b_{II} \exp(-\kappa x) \\ E - V_0 &= -\frac{\hbar^2 \kappa^2}{2m}.\end{aligned}\tag{33}$$

We know on physical grounds that  $a_{II} = 0$ . We can rename  $b_{II} = t$ .

$$\phi_{II}(x) = t \exp(-\kappa x).\tag{34}$$

Boundary condition (i):

$$\begin{aligned}\phi_I(0) &= \phi_{II}(0) \\ &\downarrow \\ 1 + r &= t\end{aligned}\tag{35}$$

as before (Eq. 29). From Eqs. 24, 33

$$k_I^2 = -\kappa^2 + \frac{2mV_0}{\hbar^2}.\tag{36}$$

Boundary condition (ii):

$$\begin{aligned}\phi'_I(0) &= \phi'_{II}(0) \\ &\downarrow \\ ik_I(1 - r) &= -\kappa t.\end{aligned}\tag{37}$$

Therefore combining with Eq. 35 we have:

$$r = \frac{k_I - i\kappa}{k_I + i\kappa}\tag{38}$$

$$t = \frac{2k_I}{k_I + i\kappa}.\tag{39}$$

Note that the same result can be achieved more simply by substituting  $k_{II} \rightarrow i\kappa$  into the results for  $E > V_0$ .



#### 2.4.4 Probability fluxes

Now to extract some physically measurable quantity from the results. The probability that the particle is reflected by the step,  $R$ , is given by the ratio of reflected probability current density  $j_R$  to incident probability current density  $j_{in}$ :

$$R = \left| \frac{j_R}{j_{in}} \right| \quad (40)$$

where the probability current density is defined in Eq. 12. Similarly the probability that the particle is transmitted by the step,  $T$ , is given by the ratio of transmitted probability current density  $j_T$  to incident probability current density  $j_{in}$ :

$$T = \left| \frac{j_T}{j_{in}} \right|. \quad (41)$$

First consider the case  $E > V_0$ . Using Eq 7 to establish the time dependence of the wavefunctions we have

$$\psi_{in}(x, t') = \exp(-iEt'/\hbar) \exp(ik_I x) \quad (42)$$

$$\psi_R(x, t') = r \exp(-iEt'/\hbar) \exp(-ik_I x) \quad (43)$$

$$\psi_T(x, t') = t \exp(-iEt'/\hbar) \exp(-ik_{II} x) \quad (44)$$

where  $t'$  has been used to indicate time in order to avoid confusion with the transmission probability amplitude  $t$ . Using the expression for the probability current density in terms of the wavefunction (Eq 12) gives

$$j_{in} = \frac{\hbar k_I}{m} \quad (45)$$

$$j_R = \frac{\hbar(-k_I)}{m} |r|^2 \quad (46)$$

$$j_T = \frac{\hbar k_{II}}{m} |t|^2 \quad (47)$$

where the negative sign in  $j_R$  is because  $j$  is a vector quantity. The probability of reflection and transmission is then

$$R = |r|^2 \quad (48)$$

$$T = \frac{k_{II}}{k_I} |t|^2. \quad (49)$$

Substituting the forms of  $r$  and  $t$  found above gives

$$R = \left| \frac{k_I - k_{II}}{k_I + k_{II}} \right|^2 \quad (50)$$

$$T = \frac{k_{II}}{k_I} \left| \frac{2k_I}{k_I + k_{II}} \right|^2. \quad (51)$$

It is straightforward to verify that

$$R + T = 1. \quad (52)$$

This is just a statement of the conservation of probability. For  $E < V_0$  we have

$$\psi_{in}(x, t') = \exp(-iEt'/\hbar) \exp(ik_I x) \quad (53)$$

$$\psi_R(x, t') = r \exp(-iEt'/\hbar) \exp(-ik_I x) \quad (54)$$

$$\psi_T(x, t') = t \exp(-iEt'/\hbar) \exp(-\kappa x) \quad (55)$$

and so

$$j_{in} = \frac{\hbar k_I}{m} \quad (56)$$

$$j_R = \frac{\hbar(-k_I)}{m} |r|^2 \quad (57)$$

$$j_T = 0. \quad (58)$$

The probability of reflection and transmission is now

$$R = 1 \quad (59)$$

$$T = 0. \quad (60)$$

The particle is reflected with certainty. It nevertheless has an amplitude to be detected within the barrier. This is a manifestation of some of the magic of quantum mechanics. Even though the particle is certainly reflected from the barrier, if you look for it in the barrier you may find it. For a measurement to locate the particle in the barrier, it would need to provide enough energy for that event to occur. The additional energy would have to be provided by the measurement itself. You can think of it as the measurement device changing the potential so that the potential step has a finite width, beyond which  $E < V_0$  again. We will consider this situation next.

## 2.5 Quantum tunnelling

Now consider the potential

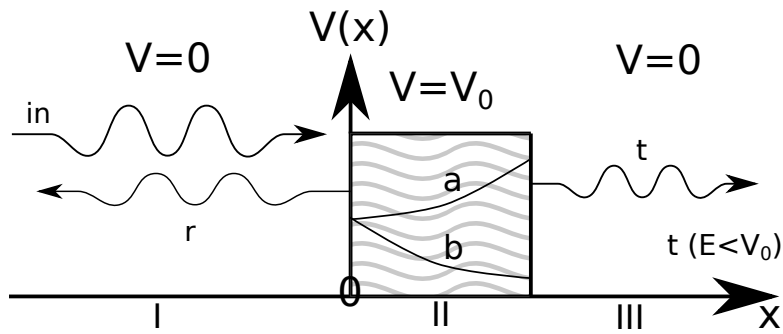


Figure 2: The potential barrier of Eq. 61. Schematic solutions; those in region II assume  $E < V_0$ .

$$V(x) = \begin{cases} 0, & x < 0 \text{ (region I)} \\ V_0, & 0 \leq x < L \text{ (region II)} \\ 0, & x \geq L \text{ (region III)}. \end{cases} \quad (61)$$

This is shown in Fig. 2.

We can no longer neglect the increasing solution in region II. While we therefore have two extra unknowns, we also have two extra boundary conditions, giving four in total:

$$(i) \quad \phi_I(0) = \phi_{II}(0) \quad (62)$$

$$(ii) \quad \phi'_I(0) = \phi'_{II}(0) \quad (63)$$

$$(iii) \quad \phi_{II}(L) = \phi_{III}(L) \quad (64)$$

$$(iv) \quad \phi'_{II}(L) = \phi'_{III}(L). \quad (65)$$

We know that  $k_I = k_{III}$  since the potentials are the same in these regions:

$$k_I = k_{III} \triangleq k \quad (66)$$

and substituting into the TISE gives

$$k = \frac{\sqrt{2mE}}{\hbar}. \quad (67)$$

As before, we must treat the cases  $E > V_0$  and  $E < V_0$  separately.

### 2.5.1 $E > V_0$

The wavefunctions in the various regions are:

$$\phi_I(x) = \exp(ikx) + r \exp(-ikx) \quad (68)$$

$$\phi_{II}(x) = a \exp(ik'x) + b \exp(-ik'x) \quad (69)$$

$$\phi_{III}(x) = t \exp(ikx). \quad (70)$$

where the wavevector in region  $II$  is defined to be  $k'$ :

$$k_{II} \triangleq k' \quad (71)$$

$$k' = \frac{\sqrt{2m(E - V_0)}}{\hbar}. \quad (72)$$

Applying the boundary conditions we have

$$(i) \quad 1 + r = a + b \quad (73)$$

$$(ii) \quad 1 - r = \frac{k'}{k} (a - b) \quad (74)$$

$$(iii) \quad a \exp(ik'L) + b \exp(-ik'L) = t \exp(ikL) \quad (75)$$

$$(iv) \quad \frac{k'}{k} (a \exp(ik'L) - b \exp(-ik'L)) = t \exp(ikL). \quad (76)$$

These are four coupled linear equations in four unknowns, and can be solved by standard methods. There is no especially elegant way to do so. If you work through the problem, which is beyond the scope of this course (but do-able), you can solve for the probability of transmission:

$$T = \frac{4E(E - V_0)}{4E(E - V_0) + V_0^2 \sin^2 \left( L\sqrt{2m(E - V_0)}/\hbar \right)}. \quad (77)$$

Note that when  $k'L = n\pi$  for integer  $n$ , there is perfect 'resonant transmission',  $T = 1$ ,  $R = 0$ . The particle passes through the barrier as if it weren't there.

### 2.5.2 $E < V_0$

The wavefunction regions  $I, III$  are unchanged, and that in region  $II$  is:

$$\phi_{II}(x) = a \exp(\kappa x) + b \exp(-\kappa x). \quad (78)$$

We can simply take the results of the  $E > V_0$  case and substitute  $k' \rightarrow -i\kappa$ . Substituting the expressions for  $k$  and  $\kappa$ :

$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2\left(L\sqrt{2m(V_0 - E)}/\hbar\right)}. \quad (79)$$

Resonant transmission is no longer possible. But the result is nevertheless remarkable. The particle has a probability to be found on the opposite side of the barrier to where it started, even though the potential of the barrier is larger than the energy of the particle. This is quantum tunnelling.

### 3 Bound states (I)

**Videos:**

- V3.1: The infinite potential well
- V3.2: Normalisation
- V3.3: Stationary states
- V3.4: Orthonormality of eigenstates
- V3.5: Fourier decomposition

**Topics:**

- The infinite potential well (particle in a box)
- energy eigenvalues and eigenfunctions
- the Born rule
- normalisation of wavefunctions
- orthogonality of eigenstates
- energy eigenstates as stationary states
- complete orthonormal bases.

**For the exam you should be able to:**

- solve for the energy eigenstates and eigenvalues of the infinite potential well (particle in a box)
- explain the physical relevance of normalisation
- normalise a given wavefunction
- explain the relevance of the orthogonality of eigenstates
- demonstrate the orthogonality of given wavefunctions
- explain what is meant by energy eigenstates being stationary states and to prove this mathematically
- explain the significance of sets of eigenstates forming complete orthonormal bases
- explain the significance of expectation values of observable quantities (observables)
- find the expectation values of powers of position and momentum for a given wavefunction

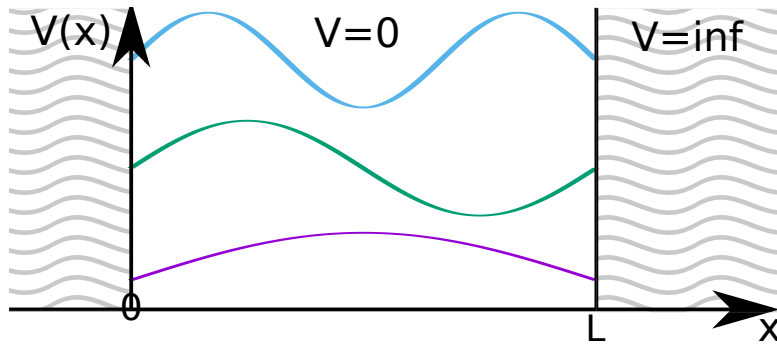


Figure 3: The infinite potential well. Snapshots of the real parts of the first few energy eigenfunctions are shown, offset vertically for clarity (see video V3.1).

### 3.1 The 1D infinite potential well

Consider the following potential:

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & \text{otherwise.} \end{cases} \quad (80)$$

This is the infinite potential well, or particle in a box. Note again that it's not really a well, although it looks like that in the picture. It's a 1D line, with an infinitely large potential everywhere except a region in the middle. The particle is therefore confined to the region of zero potential. This is shown in Fig. 3. Inside the well the TISE is

$$-\frac{\hbar^2}{2m} \frac{d^2\phi(x)}{dx^2} = E\phi(x). \quad (81)$$

The general solutions are now standing waves:

$$\phi(x) = a \cos(kx) + b \sin(kx). \quad (82)$$

You can see this from the symmetry of the problem. If you did not, and used travelling solutions, that would work just as well, and you would find that the solutions had equal amplitudes for leftgoing and rightgoing parts. Since the infinite potential restricts the particle's location to within the 'well', the infinite potential acts as a boundary condition enforcing

$$(i) \phi(0) = 0 \quad (83)$$

$$(ii) \phi(L) = 0. \quad (84)$$

Using these conditions gives

$$(i) a = 0 \quad (85)$$

$$(ii) \sin(kx) = 0 \quad \therefore k = \frac{n\pi}{L}, \quad n \in \mathbb{Z}. \quad (86)$$

The first is straightforward: put  $x = 0$  into Eq 82. Once this is done you only have

$$\phi(x) = b \sin(kx). \quad (87)$$

Now use condition (ii) to find the second constraint. You need sine waves which fit in the well to give zero amplitude at either end. There are an infinite number of solutions:

$$\phi_n(x) = b_n \sin(k_n x) \quad (88)$$

where

$$k_n = \frac{n\pi}{L} \quad (89)$$

and substituting into the TISE gives the corresponding energy eigenvalues

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \quad (90)$$

with  $n$  any positive integer. The first few are shown in Fig. 3. The solutions  $\phi_n$  are called energy eigenstates:  $\phi_1$  is called the ground state wavefunction,  $\phi_2$  the first excited state, and so on. They are states of definite energy: if the energy of  $\phi_n$  is measured,  $E_n$  will be found with probability 1.

### 3.2 Normalisation

While the position of the particle cannot be predicted with certainty, we know that the particle must exist somewhere, and so the probability density integrated over all of space must be one. In general, in 1D, we therefore have that

$$1 = \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx \quad (91)$$

**the normalization of the wavefunction.** In the specific case of the infinite well we have that

$$1 = \int_0^L |\psi|^2 dx. \quad (92)$$

This condition allows us to find the coefficient  $b_n$  in Eq. 88:



$$\begin{aligned}
 1 &= \int_0^L \left| b_n \sin\left(\frac{n\pi x}{L}\right) \right|^2 dx \\
 &\downarrow \\
 |b_n| &= \sqrt{\frac{2}{L}}.
 \end{aligned} \tag{93}$$

Therefore the normalised eigenfunctions are

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{94}$$

up to an arbitrary complex prefactor of magnitude 1. This arbitrary prefactor is called the global phase of the wavefunction, and is meaningless by itself as it can never be observed. The differences in phases between two wavefunctions can, however, be detected, as we saw in the video of the two-slit experiment.

### 3.3 Stationary states

Recall that we can always reconstruct the time dependence of the wavefunction from the time-independent solution using Eq. 7. In the case of the infinite well we have

$$\psi_n(x, t) = \exp(iE_n t/\hbar) \phi_n(x) = \sqrt{\frac{2}{L}} \exp\left(\frac{i\hbar n^2 \pi^2 t}{2mL^2}\right) \sin\left(\frac{n\pi x}{L}\right). \tag{95}$$

In the specific case that  $\phi_n(x)$  is an energy eigenfunction, the time evolution only affects the complex phase, not the magnitude of the solution. **Energy eigenfunctions are stationary states**, meaning the observable probability density  $|\psi|^2$  does not vary with time:

$$|\psi_n(x, t)|^2 = |\phi_n(x)|^2 = \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right). \tag{96}$$

### 3.4 Expectation values

Using the probability density we can find the average values  $\langle \mathcal{O} \rangle$  of observables  $\mathcal{O}$ . An observable is a quantity which can actually be observed in an experiment. In probability theory averages are sometimes called expectation values. For example, the expectation value of the outcome of a die roll is  $\frac{1}{6} \sum_{i=1}^6 i = 3.5$ , the average value of the faces. The name carries over to quantum mechanics, where the expectation value can be found using

$$\boxed{\langle \hat{\mathcal{O}} \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \mathcal{O}(x) \psi(x, t) dx.} \tag{97}$$

For example, the expected value of position is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi(x)|^2 dx \tag{98}$$

and the expected value of the squared-position is

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 |\psi(x)|^2 dx. \quad (99)$$

The expected position of the particle in the ground state of the infinite potential well is given by

$$\begin{aligned} \langle x \rangle &= \int_0^L x |\psi_1(x, t)|^2 dx \\ &= \int_0^L x |\phi_1(x)|^2 dx \\ &= \frac{2}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= L/2. \end{aligned}$$

If you prepare the particle in its ground state then measure its location, then repeat this process of preparation and measurement many times, the resulting average will tend to half way across the well.

## 4 Bound states (II)

### Videos:

- V4.1: Quantum superposition
- V4.2: The finite potential well

### Topics:

- Quantum superposition
- Schrodinger's cat
- the measurement problem
- the finite potential well.

### For the exam you should be able to:

- explain the principle of quantum superposition
- calculate properties of superposed states
- decompose a given wavefunction into a superposition of energy eigenstates
- find the time dependence of a given spatial wavefunction
- justify the forms of the wavefunctions solving the TISE for the finite potential well
- explain the steps involved in solving the TISE in the finite potential well
- prove that there is at least one bound state in any finite potential well

### For the exam you will not be required to:

- provide a full solution for the finite potential well

## 4.1 Quantum superposition

**Quantum mechanics is linear.** This means that any sum of solutions to the TDSE is also a solution. This is the principle of wave superposition, familiar for example from the classical wave equation. If two wavefunctions each individually solve the TDSE, any linear combination of them also solves it.

However, this is not true for the TISE. Solutions to the TISE are energy eigenfunctions. They are stationary states. The sum of two stationary states is never itself stationary. Consider for example the energy eigenfunctions corresponding to the lowest two energies in the infinite potential well. These are stationary states, as seen from the time independence of their probability densities:

$$|\psi_1(x, t)|^2 = \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) \quad (100)$$

$$|\psi_2(x, t)|^2 = \frac{2}{L} \sin^2\left(\frac{2\pi x}{L}\right). \quad (101)$$

But now consider the probability density of the sum of these wavefunctions:

$$|\psi_1(x, t) + \psi_2(x, t)|^2 = \frac{2}{L} \left( \sin^2\left(\frac{\pi x}{L}\right) + \sin^2\left(\frac{2\pi x}{L}\right) + 2 \cos\left(\frac{3\hbar\pi^2 t}{2mL^2}\right) \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) \right). \quad (102)$$

This is time dependent. As an aside, note that the combined state  $\psi_1(x, t) + \psi_2(x, t)$  is also no longer correctly normalized. This can be fixed straightforwardly.

## 4.2 Measurement

If a measurement of energy is performed on a superposition of energy eigenstates

$$\varphi(x) = \sum_n a_n \phi_n(x) \quad (103)$$

one of the energies  $E_n$  will be found. After this measurement the wavefunction will be changed to the corresponding eigenstate  $\phi_n$ . The probability of finding state  $\phi_n$  is given by  $|a_n|^2$  before the measurement. After the measurement it is 1. The process of changing the wavefunction is not built into the mathematics of the Schrodinger equation. You just have to write down a new wavefunction by hand.

These statements are well-tested experimentally, but their philosophical interpretation is debated. Understanding what happens when measurements are performed on quantum systems is called the measurement problem, and is a major open problem in physics and philosophy.

The interpretation with the least philosophical baggage is probably the Copenhagen interpretation. But it achieves its lack of baggage by simply declaring that certain questions should not be asked. In the Copenhagen interpretation the process of measurement literally causes the wavefunction

to change abruptly. The mechanism is left a mystery. This process is termed the collapse of the wavefunction.

Everybody agrees with the maths of quantum mechanics, and I will focus on the maths in these notes. For the sake of getting on with things I will refer to wavefunction collapse, but you can imagine your preferred interpretation instead.

### 4.3 Complete orthonormal basis

In general, the set of normalised energy eigenfunctions form a *complete orthonormal basis*. Mathematically, this means that

$$\int_{-\infty}^{\infty} \phi_n^*(x) \phi_m(x) dx = \delta_{nm} \quad (104)$$

where the Kronecker delta is defined through

$$\delta_{nm} = \begin{cases} 1, & n = m \\ 0, & n \neq m \end{cases}. \quad (105)$$

A consequence of this is that any function  $\varphi(x)$  which matches the same boundary conditions can be constructed as a sum of energy eigenstates

$$\varphi(x) = \sum_n a_n \phi_n(x). \quad (106)$$

This is a very important result. Essentially it is the reason we can consider the TISE and use it to solve the TDSE, even for wavefunctions which are not themselves energy eigenstates. The process is analogous to writing a vector as a sum of basis vectors. This analogy is explored in depth later in the course. The complex coefficients  $a_n$  can be found using

$$a_n = \int_{-\infty}^{\infty} \phi_n^*(x) \varphi(x) dx. \quad (107)$$

We can, as always, include the time dependence:

$$\varphi(x) = \sum_n a_n \phi_n(x) \quad (108)$$

$$\downarrow \quad (109)$$

$$\psi(x, t) = \sum_n a_n \phi_n(x) \exp(-iE_n t/\hbar). \quad (110)$$

### 4.4 The finite potential well

Consider the potential:

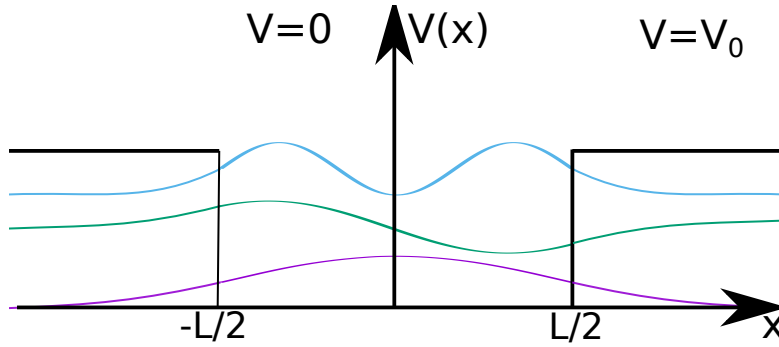


Figure 4: The finite potential well. In this case the potential  $V_0$  is such that three bound states exist. The real parts of the wavefunctions are sketched offset in energy.

$$V(x) = \begin{cases} V_0, & x < -L/2 \text{ (region I)} \\ 0, & -L/2 \leq x \leq L/2 \text{ (region II)} \\ V_0, & x > L/2 \text{ (region III)}. \end{cases} \quad (111)$$

There are two differences to the infinite potential well in Eq 81. First, the well has been placed symmetrically about the origin. This doesn't change anything, and the infinite well could just as easily have been specified in this way. Second, the particle now has a probability to exist within the boundary region, and only a finite number of energy eigenstates will exist within the well (bound states with  $E < V_0$ ). This makes the problem much harder. In fact, it cannot be solved exactly and analytically. It must instead be solved numerically. But we can still build intuition analytically. We must solve the TISE in each region then match the solutions using the boundary conditions at the connecting points.

### Region II

Within the well the general solution is the same as that of the infinite well before boundary conditions are applied. As the edges of the well are now symmetrical about the origin it is convenient to write the general solution in terms of odd (sine) and even (cosine) functions:

$$\phi_{II}(x) = a \sin(kx) + b \cos(kx) \quad (112)$$

$$E = \frac{\hbar^2 k^2}{2m}. \quad (113)$$

### Regions I, III

Assuming  $E < V_0$  we have the general solution

$$\phi(x) = c \exp(\kappa x) + d \exp(-\kappa x) \quad (114)$$

$$E - V_0 = -\frac{\hbar^2 \kappa^2}{2m} \quad (115)$$

for real  $\kappa$ . Normalizability requires that the wavefunction tend to zero at  $x = \pm\infty$ , which means only the solutions which decay away from the well are relevant:

$$\phi_I(x) = c \exp(\kappa x) \quad (116)$$

$$\phi_{III}(x) = d \exp(-\kappa x). \quad (117)$$

### Solution

We have four unknown quantities and four boundary conditions:

$$(i) \quad \phi_I(-L/2) = \phi_{II}(-L/2) \quad (118)$$

$$(ii) \quad \phi'_I(-L/2) = \phi'_{II}(-L/2) \quad (119)$$

$$(iii) \quad \phi_{II}(L/2) = \phi_{III}(L/2) \quad (120)$$

$$(iv) \quad \phi'_{II}(L/2) = \phi'_{III}(L/2). \quad (121)$$

It is convenient to consider the even and odd solutions separately. Inspired by the solutions for the infinite well, we see that:

$$\text{even } \phi: \quad a = 0 \quad (122)$$

$$d = c \quad (123)$$

$$\text{odd } \phi: \quad b = 0 \quad (124)$$

$$d = -c. \quad (125)$$

The relative size of the two coefficients is easily fixed with one of the boundary conditions. The overall normalisation can be fixed in the usual way. As in the infinite well, only discrete energy eigenvalues exist at certain values of  $E$ . Unlike the infinite well, there are now a finite number of eigenvalues, and the eigenfunctions are not orthogonal to one another and do not form a complete set of states.

In the infinite well the wavefunctions had to vanish at the ends of the well, giving a constraint on the possible wavevectors. In the finite well the wavevectors are still constrained, but now they are only constrained by requiring the wavefunctions to remain continuous between the two regions (the general boundary conditions in Eq 8). These give equations relating  $k$  and  $\kappa$ , as follows:

$$\text{even } \phi: \quad \left. \begin{array}{l} (i) \quad c \exp(-\kappa L/2) = b \cos(kL/2) \\ (ii) \quad \kappa c \exp(-\kappa L/2) = kb \sin(kL/2) \end{array} \right\} \frac{\kappa}{k} = \tan(kL/2) \quad (126)$$

Figure 5: Graphical solutions for the bound state energies in Eq. 129.

$$\text{odd } \phi: \left. \begin{array}{l} (i) \quad c \exp(-L/2) = -a \sin(kL/2) \\ (ii) \quad \kappa c \exp(-L/2) = ka \cos(kL/2) \end{array} \right\} \frac{\kappa}{k} = -\cot(kL/2). \quad (127)$$

These are transcendental equations and cannot be solved analytically. Using the expressions for  $k$  and  $\kappa$  in terms of  $E$  (Eqs. 113 and 115) reveals that solutions exist whenever

$$\sqrt{\frac{V_0 - E}{E}} = \begin{cases} \tan\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{even } \phi \\ -\cot\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{odd } \phi. \end{cases} \quad (128)$$

Continuing to treat odd and even separately, squaring both sides and rearranging gives

$$E = \begin{cases} V_0 \cos^2\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{even } \phi \\ V_0 \sin^2\left(\frac{L}{\hbar}\sqrt{\frac{mE}{2}}\right), & \text{odd } \phi. \end{cases} \quad (129)$$

Some solutions are shown graphically in Fig. 5. There is always at least one even solution even for arbitrarily weak  $V_0$ .



## 5 Finite-dimensional Hilbert spaces

### Videos:

- V5.1: Complex vectors
- V5.2: Hermitian matrices
- V5.3a–V5.3c: Spin-1/2
- V5.4: Polarisation demo

### Topics:

- Complex vectors and matrices
- Dirac notation
- Hermitian matrices: eigenvalues and eigenvectors, properties
- complete orthonormal bases, resolution of the identity
- Spin-1/2: Stern-Gerlach experiment, Pauli matrices, commutation relations

### For the exam you should be able to:

- work with complex vectors and matrices
- employ Dirac notation for complex vectors
- state and derive the properties of Hermitian matrices of use in quantum mechanics
- describe spin-1/2 particles using a 2-dimensional Hilbert space

For the purposes of this course we can define a Hilbert space to be a linear vector space with an inner product, in which all vectors are square-integrable. We will see in lecture 7 wavefunctions obey these properties. In fact we've been dealing with the difficult case until now – we've been working with infinite dimensional Hilbert spaces without knowing it. The easier case is that of finite-dimensional Hilbert spaces. A simple example is the set of states associated with the spin of a spin-1/2 particle such as an electron.

Measuring the spin of an electron along a chosen direction always returns the value either  $+\hbar/2$  or  $-\hbar/2$ . The fact that the results take quantized values rather than a continuous range of values is a clear instance of the 'quantum' part of quantum mechanics: quantum means discrete.

Before looking at spin-1/2 in more detail it will be necessary to look at some properties of (finite-dimensional) complex vectors and matrices.

## 5.1 Complex vectors and matrices

Quantum mechanics is linear algebra: vectors and matrices, but also functions, which can be thought of as infinite-dimensional vectors. Specifically, the vectors live in a complex vector space. A vector space is not a complicated idea. It is just the space in which the vectors live. For 2D vectors this is the 2D plane. There are 10 axioms which define something to be a linear vector space. For example, adding two vectors should give another vector. All the axioms are intuitive and familiar. A Hilbert space additionally has an inner product, which is a generalisation of the dot product for vectors. Again, this should be familiar: all the vectors we are used to seeing can have dot products taken between them. The fancy terminology of vector spaces, inner product spaces, and Hilbert spaces, is just a way to make precise the things we would be doing anyway. The final property we need is that if a vector in quantum mechanics represents a quantum state, it had better be normalised. Together these conditions tell us we have a 'Hilbert space'  $\mathcal{H}$ .

A convenient notation for complex vectors, formerly denoted  $\mathbf{v}$ , has them written  $|v\rangle$ :

$$\mathbf{v} = |v\rangle = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \vdots \\ v_N \end{pmatrix} \quad (130)$$

where  $v_i$  are the complex scalar elements of the  $N$ -dimensional vector  $|v\rangle$ . The Hermitian conjugate (complex conjugate transpose) of the vector is then written  $\langle v|$ :

$$\mathbf{v}^\dagger = (|v\rangle)^\dagger = (|v\rangle)^{*T} = \langle v| = \left( v_1^*, v_2^*, v_3^*, \dots, v_N^* \right). \quad (131)$$

We generally refer to this as Dirac notation, after its inventor Paul Dirac. Dirac himself referred to it as bra-ket notation, where vectors  $|\psi\rangle$  are referred to as 'kets' and their Hermitian conjugates  $\langle\psi|$  are referred to as 'bras'. The notation implies the existence of the inner product (dot product),

so that

$$\mathbf{u}^\dagger \mathbf{v} = \langle u|v \rangle = \left( u_1^*, u_2^*, u_3^*, \dots, u_N^* \right) \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \vdots \\ v_N \end{pmatrix} = \sum_i^N u_i^* v_i. \quad (132)$$

This is then a bra-ket, *i.e.* bracket. It is a complex scalar, because a  $1 \times N$  matrix (row vector) multiplied by an  $N \times 1$  matrix (column vector) is a  $1 \times 1$  matrix (scalar). From Eq. 132 it can be seen that another convenience of the notation follows:

$$\langle v|u \rangle = (\langle u|v \rangle)^* \quad (133)$$

sometimes written

$$(\langle u|v \rangle)^* = \overline{\langle u|v \rangle}. \quad (134)$$

Similarly, we can define the outer product (tensor product) as a ket-bra:

$$\mathbf{v} \mathbf{u}^\dagger = |v\rangle\langle u| = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ \vdots \\ v_N \end{pmatrix} \left( u_1^*, u_2^*, u_3^*, \dots, u_N^* \right) = \begin{pmatrix} v_1 u_1^* & v_1 u_2^* & v_1 u_3^* & \dots & v_1 u_N^* \\ v_2 u_1^* & & & & \\ v_3 u_1^* & & & & \\ \vdots & & & \ddots & \\ v_N u_1^* & & & & v_N u_N^* \end{pmatrix} \quad (135)$$

this is an  $N \times N$  complex matrix. Matrices are ‘operators’ in vectors, meaning a matrix can act on a vector to give a different vector. This is built in to Dirac notation:

$$(|v\rangle\langle u|) |w\rangle = |v\rangle\langle u|w\rangle = \langle u|w\rangle |v\rangle \quad (136)$$

*i.e.* the matrix  $|v\rangle\langle u|$  acts on vector  $|w\rangle$  to give vector  $|v\rangle$  multiplied by scalar  $\langle u|w\rangle$ . A useful identity which holds for any complete set of orthonormal vectors  $|e_i\rangle$  is the **resolution of the identity**:

$$\mathbb{I} = \sum_i |e_i\rangle\langle e_i| \quad (137)$$

where  $\mathbb{I}$  is the identity matrix. This allows us to write any vector into the basis  $|e_i\rangle$ :

$$|v\rangle = \mathbb{I}|v\rangle = \sum_i |e_i\rangle\langle e_i|v\rangle = \sum_i (\langle e_i|v\rangle) |e_i\rangle. \quad (138)$$

For example, since

$$|e_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |e_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (139)$$

span the space of two-dimensional vectors, we can write any two-dimensional vector as

$$|v\rangle = \sum_{i=1}^2 (\langle e_i|v\rangle) |e_i\rangle = v_1|e_1\rangle + v_2|e_2\rangle, \quad (140)$$

and the resolution of the identity holds:

$$\sum_{i=1}^2 |e_i\rangle\langle e_i| = |e_1\rangle\langle e_1| + |e_2\rangle\langle e_2| \quad (141)$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad (142)$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad (143)$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \checkmark \quad (144)$$

## 5.2 Hermitian matrices

Important for quantum mechanics are **Hermitian matrices**, those matrices equal to their Hermitian conjugates:

$$M = M^\dagger. \quad (145)$$

These have many important and physically-relevant properties.

### Hermitian operators have real eigenvalues.

Denote the eigenvector with eigenvalue  $\lambda_n$  by the convenient notation  $|n\rangle$ :

$$M|v_n\rangle = \lambda_n|v_n\rangle. \quad (146)$$

Taking the Hermitian conjugate we have

$$\begin{aligned} (M|v_n\rangle)^\dagger &= (\lambda_n|v_n\rangle)^\dagger \\ &\downarrow \\ \langle v_n|M^\dagger &= \langle v_n|\lambda_n^*. \end{aligned} \quad (147)$$

Therefore

$$\langle v_n | M - M^\dagger | v_n \rangle = (\lambda_n - \lambda_n^*) \langle v_n | v_n \rangle \quad (148)$$

because we can act right with  $M$  using Eq. 146 and left with  $M^\dagger$  using Eq. 147. Since

$$\langle v_n | v_n \rangle = ||n||^2 > 0 \quad (149)$$

(i.e. the square modulus of a vector is always strictly greater than zero) we see that

$$M = M^\dagger \Rightarrow \lambda = \lambda^* \quad (150)$$

i.e. Hermitian operators have real eigenvalues  $\square$

### The normalised eigenvectors of Hermitian matrices are orthonormal.

Begin again with Eq. 146. Consider this object:

$$\langle v_m | M - M^\dagger | v_n \rangle = (\lambda_n - \lambda_m) \langle v_m | v_n \rangle \quad (151)$$

where the equality follows from acting  $M$  to the right and  $M^\dagger$  to the left as before. Assuming no two eigenvalues are degenerate, i.e.  $\lambda_n \neq \lambda_m \forall m \neq n$ , we have that

$$M = M^\dagger \Rightarrow \langle v_m | v_n \rangle = 0. \quad (152)$$

Furthermore, assuming we always normalise our eigenvectors correctly,

$$\langle v_n | v_n \rangle = 1 \quad (153)$$

and so we have the stronger condition

$$\langle v_n | v_m \rangle = \delta_{nm} \quad (154)$$

with  $\delta_{nm}$  the Kronecker delta.  $\square$

In fact the eigenvectors of a Hermitian matrix form a complete orthonormal basis for the vector space (Hilbert space) in which they live. This means that we can use them to resolve the identity:

$$\mathbb{I} = \sum_n |v_n\rangle\langle v_n| \quad (155)$$

Acting on this expression with  $M$  shows that any Hermitian operator can be written as the sum of its eigenvalues multiplied by outer products formed from their respective eigenvectors:

$$M = \sum_n \lambda_n |v_n\rangle\langle v_n|. \quad (156)$$

In fact, you can look at the resolution of the identity as a special case of this, since the identity matrix is Hermitian with eigenvalue 1 for every vector. Therefore any complete orthonormal basis can be used to construct the identity.

### 5.3 Spin-1/2

Reference: Feynman III Chapter 5

#### 5.3.1 Mathematical structure

A simple example of matrices in action in quantum mechanics is provided by spin-1/2 particles (of which electrons are an example). Spin is intrinsic angular momentum. Classically you might think of it as analogous to the angular momentum of the Earth spinning about its axis, but it is inherently quantum in nature and has no good classical analogue.

In the *Stern Gerlach experiment* a beam of spin-1/2 silver atoms is directed through a magnetic field gradient (directed along  $z$ ). This accelerates the atoms according to the  $z$ -projection of their spins. Silver atoms were used originally as these have spin but are charge neutral. Electrons would receive an additional unhelpful redirection owing to their charges.

Classically we would expect a continuous range of deflections. Measuring the Earth's intrinsic angular momentum along a continuous range of directions will return a continuous range of values, with a maximum when measuring parallel to the axis of rotation and zero when measuring perpendicular to this axis. The silver atoms were instead found to deflect in one of two directions, a clear demonstration of quantization. For spin- $n$  particles there are  $2n + 1$  directions.

Some key observations are these:

- measurement of spin along any chosen direction yields either  $+\hbar/2$  or  $-\hbar/2$
- subsequent measurements along the same direction, without other measurements in between, will consistently return the same result
- if the spin is known along  $z$ , a measurement along any perpendicular direction is completely ambiguous, with 50% probability for each of  $\pm\hbar/2$
- therefore, even though repeated measurements along  $z$  yield the same result, if a measurement along  $x$  is performed, a subsequent re-measurement of  $z$  will give a 50% probability of either result  $\pm\hbar/2$ .

This sequence of observations gets to the heart of quantum weirdness. Quantum mechanics is not magic for the sake of magic; it is the simplest explanation we know of which can explain the behaviour of the world on the smallest scales.

The observations above suggest the following mathematical structure. The state of the spin- $1/2$  particle should be represented by vectors with two eigenvalues,  $\pm\hbar/2$ . Since there are two eigenvalues there should be two eigenvectors which span a two-dimensional complex vector space. The observable quantities associated with spin measurements should be  $2 \times 2$  Hermitian matrices with these eigenvalues. Defining  $\hat{S}_i$  to be the operator corresponding to the observable spin along direction  $i$ , we have:

$$\hat{S}_i|\uparrow\rangle_i = +\frac{\hbar}{2}|\uparrow\rangle_i, \quad i \in \{x, y, z\} \quad (157)$$

$$\hat{S}_i|\downarrow\rangle_i = -\frac{\hbar}{2}|\downarrow\rangle_i. \quad (158)$$

There should be three such matrices, one for each perpendicular direction, and they should not commute. Their lack of commutation should be such that an eigenvector of one operator should have equal amplitudes to be either eigenvector of either other operator. For example:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \exp(i\alpha) (|\uparrow_z\rangle + \exp(i\beta)|\downarrow_z\rangle) \quad (159)$$

where  $\alpha$  is a real number corresponding to an unmeasurable global phase, and  $\beta$  is a real number corresponding to an unspecified relative phase. Similar relations must hold between the other eigenvectors. One consistent choice is as follows:

$$\hat{S}_i = \frac{\hbar}{2}\sigma_i \quad (160)$$

with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (161)$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (162)$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (163)$$

These are called the Pauli matrices. For this choice we have

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (164)$$

$$|\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (165)$$

and, for example,

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (|\uparrow_z\rangle + |\downarrow_z\rangle). \quad (166)$$

The different matrices do not commute, as required:

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k \quad (167)$$

where Einstein summation notation has been assumed (*i.e.* there is an implicit sum over index  $k$ ) and  $\epsilon_{ijk}$  is the Levi-Civita symbol defined by

$$\epsilon_{ijk} = \begin{cases} 0, & \text{any of } i, j, k \text{ equal} \\ 1, & ijk = 123 \text{ or cyclic permutations} \\ -1, & ijk = 321 \text{ or cyclic permutations.} \end{cases} \quad (168)$$

### 5.3.2 Measurements

To work out what happens when a state is prepared with a definite state of spin in one direction but is then measured in a different direction, we have to decompose the vector into the relevant basis. For example, say a state is prepared with spin up along  $x$ :

$$|\psi\rangle = |\uparrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \quad (169)$$

This state is then measured in the  $z$  direction. To work out the possible outcomes and their relative amplitudes we should write the state in the  $z$ -basis:

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (|\uparrow_z\rangle + |\downarrow_z\rangle). \quad (170)$$

The probability for measuring  $|\uparrow_z\rangle$  is given by the square magnitude of the coefficient of  $|\uparrow_z\rangle$ :  $1/2$ . Mathematically, the probability amplitude for finding the state  $|\uparrow_z\rangle$  upon performing a measurement in the  $z$  direction for a state  $|\uparrow_x\rangle$  is

$$\langle\uparrow_z|\uparrow_x\rangle. \quad (171)$$

In this case,



$$\langle \uparrow_z | \uparrow_x \rangle = \langle \uparrow_z | \cdot \frac{1}{\sqrt{2}} (| \uparrow_z \rangle + | \downarrow_z \rangle) \rangle \quad (172)$$

$$= \frac{1}{\sqrt{2}} (\langle \uparrow_z | \uparrow_z \rangle + \langle \uparrow_z | \downarrow_z \rangle) \quad (173)$$

$$= \frac{1}{\sqrt{2}} (1 + 0) \quad (174)$$

and the corresponding probability for measuring  $| \uparrow_z \rangle$  in a  $z$ -measurement of state  $| \uparrow_x \rangle$  is

$$| \langle \uparrow_z | \uparrow_x \rangle |^2 = 1/2. \quad (175)$$

In general we can say that:

the amplitude for measuring state  $| \varphi \rangle$  when a state is prepared as  $| \psi \rangle$  is

$$\langle \varphi | \psi \rangle \quad (176)$$

and the corresponding probability is

$$| \langle \varphi | \psi \rangle |^2. \quad (177)$$

We can also consider repeated measurements by passing the particle along multiple Stern Gerlach apparatuses with different orientations. By blocking off one of the two output paths of each apparatus we can select spins with a chosen orientation along a chosen direction.

To find the amplitude for a state initially prepared spin-up-in- $z$  to pass a filter for spin-down-in- $y$  then spin-up-in- $x$ , and to finally be measured spin-down-in- $z$ , we need to evaluate

$$\begin{aligned} & (\text{amplitude for } \downarrow_z \text{ given initially } \uparrow_x) \cdot (\text{amplitude for } \uparrow_x \text{ given initially } \downarrow_y) \cdot (\text{amplitude for } \downarrow_y \text{ given initially } \uparrow_z) \\ & \langle \downarrow_z | \uparrow_x \rangle \quad \cdot \quad \langle \uparrow_x | \downarrow_y \rangle \quad \cdot \quad \langle \downarrow_y | \uparrow_z \rangle \end{aligned} \quad (178)$$

and so on. Each condition is required to be true independently so we multiply the probability amplitudes. Probability amplitudes in quantum mechanics play the role of probabilities in classical probability theory: it is the amplitudes which are multiplied or added rather than the probabilities. Consider a state initially spin up along  $z$  which is then passed through an  $x$ -oriented Stern Gerlach apparatus, but the two possible beams are recombined before measuring along  $z$  again. Then we must add the amplitudes for the two possibilities in the intermediate  $x$  state, because both are accepted:

$$\langle \uparrow_z | \uparrow_x \rangle \cdot \langle \uparrow_x | \uparrow_z \rangle + \langle \uparrow_z | \downarrow_x \rangle \cdot \langle \downarrow_x | \uparrow_z \rangle. \quad (179)$$

But if we accept both intermediate states we haven't made an intermediate measurement, so we don't expect the state to be changed and the overall amplitude should be 1 (the amplitude for a

state prepared spin-up-in- $z$  to be measured spin-up-in- $z$ ). This is born out mathematically, as we can rewrite the expression as:

$$\langle \uparrow_z | (| \uparrow_x \rangle \langle \uparrow_x | + | \downarrow_x \rangle \langle \downarrow_x |) | \uparrow_z \rangle \quad (180)$$

$$= \langle \uparrow_z | \mathbb{I} | \uparrow_z \rangle \quad (181)$$

$$= \langle \uparrow_z | \uparrow_z \rangle = 1. \quad (182)$$

The second line follows because  $| \uparrow_x \rangle$  and  $| \downarrow_x \rangle$  together form a complete orthonormal basis for the set of 2D complex vectors, which must be true because they are the full set of non-degenerate eigenvectors of a Hermitian matrix  $\hat{S}_x$ . You can also check this explicitly:

$$| \uparrow_x \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad | \downarrow_x \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (183)$$

$$| \uparrow_x \rangle \langle \uparrow_x | + | \downarrow_x \rangle \langle \downarrow_x | = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} (1, 1) + \frac{1}{2} \begin{pmatrix} 1 \\ -1 \end{pmatrix} (1, -1) \quad (184)$$

$$= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (185)$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (186)$$

While a simple mathematical result, the physical interpretation is quite profound. Preparing a state of definite spin-up-in- $z$  we pass the particle through an intermediate  $x$ -oriented Stern Gerlach apparatus which measures the spin in the  $x$ -direction. The two possible paths followed by the particle are separated macroscopically; you could put your finger in the gap between them. A measurement along  $x$  would randomise the result of a measurement along  $z$ . But because we erase the information about the  $x$ -measurement before measuring along  $z$  (by recombining the possible beams), the initial  $z$  information remains intact. This is even though a classical particle would take one beam or the other. This is an example of a quantum eraser experiment. It shows that there is a fundamental difference between a quantum superposition with two possible outcomes, versus a classical probability with two known outcomes (such as tossing a coin). Exactly how the quantum situation is explained falls to a matter of interpretation.

### 5.3.3 Expectation values

The expected value of a given observable for a given state is simply given by the expectation value of the corresponding operator in that state. For example, the expected value of the spin in the  $i$  direction, of state  $|\psi\rangle$ , is

$$\langle \hat{S}_i \rangle = \langle \psi | \hat{S}_i | \psi \rangle. \quad (187)$$

If we prepare a state of spin up in  $z$ , the expectation value of the  $\hat{S}_z$  operator is

$$\langle \uparrow_z | \hat{S}_z | \uparrow_z \rangle = \langle \uparrow_z | \frac{\hbar}{2} | \uparrow_z \rangle = \frac{\hbar}{2} \quad (188)$$

as expected since it is an eigenstate. We could have found this using matrices:

$$\langle \uparrow_z | \hat{S}_z | \uparrow_z \rangle = (1, 0) \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}.$$

On the other hand,

$$\langle \uparrow_z | \hat{S}_x | \uparrow_z \rangle = (1, 0) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0. \quad (189)$$

This makes sense as a measurement of the spin in the  $x$ -direction of an eigenstate of spin in the  $z$ -direction has an equal probability of coming out  $+\hbar/2$  or  $-\hbar/2$ .

## 6 Matrix Mechanics

### Videos:

- V6.1: Operators and observables
- V6.2: The Heisenberg uncertainty principle
- V6.3: The Heisenberg picture
- V6.4: Conserved quantities

### Topics:

- $\hat{p}$  and  $\hat{x}$  operators
- canonical commutation relations
- complete sets of states
- quantum numbers
- the Heisenberg uncertainty principle
- the Heisenberg and Schrodinger pictures
- the Heisenberg equations of motion
- Ehrenfest's theorem.

### For the exam you should be able to:

- state the canonical commutation relations
- find the commutators of given operators
- explain the significance of operators commuting
- state the Heisenberg uncertainty principle
- show that given wavefunctions obey the uncertainty principle
- explain what is meant by the Heisenberg and Schrodinger pictures
- deduce the Heisenberg equation of motion
- state Ehrenfest's theorem and explain its physical significance
- discuss the correspondence principle
- deduce Ehrenfest's theorem from the Heisenberg equation of motion
- state the meaning of a conserved quantity

- show that the observable quantity associated to a given operator is conserved
- explain the meaning of quantum numbers.

**For the exam you will not be required to:**

- derive the Heisenberg uncertainty principle.

## 6.1 Operators and observables

Observable quantities are represented in quantum mechanics by Hermitian operators. Operators are denoted with hats  $\hat{O}$ . For finite-dimensional Hilbert spaces operators are just Hermitian matrices. When dealing with wavefunctions we are dealing with infinite-dimensional Hilbert spaces (Lecture 7). In this case operators are represented by differential operators such as  $-i\hbar\nabla$ . This mathematical structure was chosen by Heisenberg based on experimental observations.

First, real eigenvalues are required because we measure real numbers in experiment, and Hermitian operators have real eigenvalues. Second, different Hermitian matrices need not commute; if two matrices commute it is possible to find simultaneous eigenvectors for them, and the observables corresponding to both operators can be known simultaneously. But this need not be the case in quantum mechanics. For example, we have the position operator  $\hat{x}$ . This has an infinite number of orthonormal eigenvectors  $|x\rangle$ . The eigenvalues  $x$  are the possible positions of the particle:

$$\hat{x}|x\rangle = x|x\rangle. \quad (190)$$

We have the momentum operator  $\hat{p}$  with eigenvectors  $|p\rangle$ :

$$\hat{p}|p\rangle = p|p\rangle. \quad (191)$$

The operators  $\hat{x}$  and  $\hat{p}$  do not commute. In fact we have the **canonical commutation relation**

$$[\hat{x}, \hat{p}] = i\hbar\hat{\mathbb{I}} \quad (192)$$

where  $\hat{\mathbb{I}}$  is the identity operator which has eigenvalue 1 for any state. When dealing with matrices it is the identity matrix. Because these operators do not commute, no state is able to simultaneously be an eigenstate of both. The canonical commutation relation encodes the experimental observation that it is not possible to have simultaneous knowledge of a particle's position and momentum.

The energy operator is already familiar. It is the Hamiltonian appearing in the Schrödinger equation:

$$\hat{H}|n\rangle = E_n|n\rangle. \quad (193)$$

The energy receives contributions from the kinetic  $\hat{T}$  and potential  $\hat{V}$  terms. Being observable, each gets its own operator:

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + \hat{V}. \quad (194)$$

In the special case of a free particle we can drop the potential term. In this case we have that

$$\hat{H} = \frac{\hat{p}^2}{2m} \quad (195)$$

and in this case the Hamiltonian commutes with the momentum operator:

$$\text{free particle: } [\hat{H}, \hat{p}] = 0. \quad (196)$$

When two operators commute it is possible to find simultaneous eigenvectors for them. Dirac notation is very convenient for such cases, allowing us to write things such as

$$\hat{H}|p, n\rangle = E_n|p, n\rangle \quad (197)$$

$$\hat{p}|p, n\rangle = p|p, n\rangle. \quad (198)$$

## 6.2 The Heisenberg Uncertainty Principle

**Proof: Griffiths 3.5.1**

Define the uncertainty  $\sigma_{\hat{A}}$  in an observable  $\hat{A}$  as the standard deviation:

$$\sigma_{\hat{A}} = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}. \quad (199)$$

For any two operators  $\hat{A}$  and  $\hat{B}$  we have the (generalized) **Heisenberg Uncertainty Principle**:

$$\sigma_{\hat{A}}\sigma_{\hat{B}} \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right|. \quad (200)$$

For example, from Eq. 192 we have the uncertainty relation between  $\hat{x}$  and  $\hat{p}$ :

$$\sigma_x\sigma_p \geq \frac{\hbar}{2}. \quad (201)$$

Again, the maths is clear and undisputed. The physical interpretation comes down to your personal preference, until an experiment is deduced to distinguish the possible options.

## 6.3 The Heisenberg and Schrödinger pictures

Until now we have been working in the **Schrödinger picture**: time-independent operators  $\hat{A}_S$  (S for Schrödinger) and time-dependent states  $|\psi_S(t)\rangle$ , where

$$|\psi_S(t)\rangle = \exp\left(-i\hat{H}t/\hbar\right) |\psi_S(0)\rangle. \quad (202)$$

Here the state  $|\psi\rangle$  has not been assumed to be an energy eigenstate; if it is, the expression reduces to the usual form

$$|\psi_S(t)\rangle = \exp(-iEt/\hbar) |\psi_S(0)\rangle. \quad (203)$$

The **Heisenberg picture** takes the opposite approach: time-independent states  $|\psi_H\rangle$  (H for Heisenberg) are acted on by time-dependent operators  $\hat{A}_H(t)$ , where

$$\hat{A}_H(t) = \exp\left(i\hat{H}t/\hbar\right) \hat{A}_S \exp\left(-i\hat{H}t/\hbar\right). \quad (204)$$

While Schrödinger operators can have their own explicit time dependence, for example if the potential is changing with time, we will not consider such cases in this course. The Schrödinger and Heisenberg pictures are completely equivalent and make all the same predictions. They are equivalent to active and passive transformations: operators map between states  $|\psi\rangle$  in the Hilbert space, and the question of time dependence is simply whether the states or operators are changing. In particular, amplitudes are the same in both pictures:

$$\begin{aligned} \langle \varphi_S(t) | \hat{A}_S | \psi_S(t) \rangle &= \langle \varphi_S(0) | \exp\left(i\hat{H}t/\hbar\right) \hat{A}_S \exp\left(-i\hat{H}t/\hbar\right) | \psi_S(0) \rangle \\ &= \langle \varphi_H | \exp\left(i\hat{H}t/\hbar\right) \hat{A}_S \exp\left(-i\hat{H}t/\hbar\right) | \psi_H \rangle \\ &= \langle \varphi_H | \hat{A}_H(t) | \psi_H \rangle. \end{aligned} \quad (205)$$

Here we made the arbitrary choice

$$|\psi_H\rangle = |\psi_S(0)\rangle; \quad (206)$$

other options are just changed by an unmeasurable global phase.

## 6.4 The Heisenberg equation of motion

Taking the derivative of Eq. 204 with respect to time gives the Heisenberg equation of motion

$$\boxed{i\hbar \frac{d\hat{A}_H(t)}{dt} = [\hat{A}_H(t), \hat{H}].} \quad (207)$$

This equation fulfils the role of the TDSE in the Heisenberg picture.

## 6.5 Conserved quantities

The observable quantity  $A$  associated with operator  $\hat{A}$  is conserved if and only if

$$A \text{ is conserved iff } \frac{d\langle \psi | \hat{A} | \psi \rangle}{dt} = 0 \quad \forall |\psi\rangle. \quad (208)$$

Note that this statement is independent of picture. It follows that

$$\boxed{A \text{ is conserved iff } [\hat{A}, \hat{H}] = 0.} \quad (209)$$

Take the trivial but important example of  $\hat{A} = \hat{\mathbb{I}}$ , the identity operator:



$$[\hat{\mathbb{I}}, \hat{H}] = 0 \quad (210)$$

$$\therefore \frac{d\langle\psi|\psi\rangle}{dt} = 0 \quad (211)$$

the conservation of probability. This was used in Eq. 12 to define the probability current.

## 6.6 Ehrenfest's theorem

In the Heisenberg picture states  $|\psi_{\text{H}}\rangle$  are time independent, so sandwiching Eq. 207 between states gives

$$\begin{aligned} i\hbar\langle\psi_{\text{H}}|\frac{d\hat{A}_{\text{H}}(t)}{dt}|\psi_{\text{H}}\rangle &= \langle\psi_{\text{H}}|[\hat{A}_{\text{H}}(t), \hat{H}]|\psi_{\text{H}}\rangle \\ &\downarrow \\ i\hbar\frac{d\langle\psi_{\text{H}}|\hat{A}_{\text{H}}(t)|\psi_{\text{H}}\rangle}{dt} &= \langle\psi_{\text{H}}|[\hat{A}_{\text{H}}(t), \hat{H}]|\psi_{\text{H}}\rangle. \end{aligned}$$

Noting that both sides of the expression are again independent of picture, we have Ehrenfest's theorem:

$$\boxed{i\hbar\frac{d\langle\hat{A}\rangle}{dt} = \langle[\hat{A}, \hat{H}]\rangle} \quad (212)$$

This is key in demonstrating that quantum mechanics matches classical predictions on average, meaning that classical quantities relate to expectation values. In particular, we have

$$m\frac{d\langle\hat{x}\rangle}{dt} = \langle\hat{p}\rangle \quad (213)$$

which shows that the classical equation  $p = mv$  is obeyed by quantum systems when classical  $p$  and  $x$  are replaced by the expectation values of their quantum operators, and

$$\frac{d\langle\hat{p}\rangle}{dt} = -\langle\nabla V(\hat{x})\rangle. \quad (214)$$

This resembles Newton's second law, but not quite: the expectation value is taken over all  $\langle\nabla V(\hat{x})\rangle$ , while the expression would need to read  $\nabla V(\langle\hat{x}\rangle)$  for Newton's second law to be obeyed by the expectation values of position and momentum. Nevertheless, Ehrenfest's theorem lends weight to the 'correspondence principle', that classical mechanics is returned in the limit of large quantum numbers: if the standard deviation  $\sqrt{\langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2}$  around the mean  $\langle\hat{x}\rangle$  is small, i.e. the particle is sharply localised, the approximation  $\langle\nabla V(\hat{x})\rangle \approx \nabla V(\langle\hat{x}\rangle)$  is better, and classical mechanics is approximately returned by expectations values. Since  $\hat{x}$  and  $\hat{H}$  do not commute, a wavepacket well-localised in  $\hat{x}$  necessarily requires more contribution from higher energy levels in the superposition

of energy eigenstates.

## 6.7 Quantum numbers

Two Hermitian matrices can share a set of eigenvectors if and only if they commute. Therefore the observable quantities associated with different operators can be known simultaneously if and only if the corresponding operators commute. We call a set of observables which can be known simultaneously **quantum numbers**. In general the observable properties we wish to refer to are those independent of time. Partly the reason is that time-dependent quantities will vary quickly and appear as their average values in experiments with finite resolution. Since time-independent expectation values require the operator to commute with the Hamiltonian, it is usual to take the energy as one of the observables, and therefore the quantum numbers of a particle are the observable properties associated with the set of operators which commute with the Hamiltonian. Mathematically the requirement for an observable to be a good quantum number is that the quantity is conserved:

$$\frac{d\langle\hat{Q}\rangle}{dt} = 0 \quad (215)$$

where  $\hat{Q}$  is the operator associated to the observable. From Ehrenfest's theorem we therefore have that

$$\langle[\hat{Q}, \hat{H}]\rangle = 0 \quad (216)$$

and so

$$[\hat{Q}, \hat{H}] = 0. \quad (217)$$

Therefore, for an observable to be a good quantum number in a given quantum system, the corresponding operator must commute with the Hamiltonian. Note that the Hamiltonian always commutes with itself, and so energy is always a good quantum number. Note also that just because the quantum system admits a given observable as a good quantum number does not mean that all states of the system have this quantity well defined.

As an example of a set of quantum numbers, consider the electron in the Hydrogen atom (see lecture 10). This can be assigned the following quantum numbers simultaneously:

$$\text{energy: } \hat{H}|n\rangle = E_n|n\rangle \quad (218)$$

$$\text{squared total angular momentum: } \hat{L}^2|l\rangle = \hbar^2 l(l+1)|l\rangle \quad (219)$$

$$\text{z-projection of angular momentum: } \hat{L}_z|m\rangle = \hbar m|m\rangle \quad (220)$$

$$\text{spin: } \hat{S}|s = \pm\rangle = \pm \frac{\hbar}{2}|s = \pm\rangle \quad (221)$$

and therefore we can write certain states of the electron in the Hydrogen atom, unambiguously, as  $|n, l, m, s\rangle$  where the letters label the quantum numbers. We have, for example,

$$\hat{H}\hat{L}_z|n, l, m, s\rangle = \hat{L}_z\hat{H}|n, l, m, s\rangle = E_n\hbar m|n, l, m, s\rangle. \quad (222)$$

## 7 Quantum mechanics

### Videos:

- V7.1: Infinite dimensional Hilbert spaces
- V7.2: Fourier transforms
- V7.3: Differential operators
- V7.4: The postulates of quantum mechanics
- V7.5: Schrödinger's cat demo

### Topics:

- Functions as infinite-dimensional vectors: examples of operators
- Equivalence of Schrödinger, Heisenberg, and Dirac notations
- expectation values
- wavefunction overlap
- The postulates of quantum mechanics
- interpretations of quantum mechanics

### For the exam you should be able to:

- work with functions as elements of a vector space, including taking inner products
- state the forms of the operators  $\hat{H}$ ,  $\hat{V}$ ,  $\hat{p}$ , and  $\hat{x}$  in the position basis
- confirm the Hermiticity of given differential operators in the position basis

### For the exam you will not be required to:

- recount details of different interpretations of quantum mechanics
- understand the dead cat.

## 7.1 Infinite-dimensional Hilbert spaces

Functions  $f(x)$ , including complex functions, obey all the axioms of linear vector spaces, and can be thought of as infinite-dimensional vectors. Recall Eq. 137, the resolution of the identity, which tells us that for a complete set of orthonormal vectors  $\{|e_i\rangle\}$  we have:

$$\mathbb{I} = \sum_i |e_i\rangle\langle e_i|.$$

The position eigenstates  $\{|x\rangle\}$  form a complete orthonormal basis for an infinite-dimensional vector space. The resolution of the identity can be written

$$\mathbb{I} = \int_{-\infty}^{\infty} |x\rangle\langle x| dx \quad (223)$$

or in three dimensions

$$\mathbb{I} = \iiint_{-\infty}^{\infty} |\mathbf{x}\rangle\langle \mathbf{x}| d^3\mathbf{x}. \quad (224)$$

This is consistent with the Born rule for the probability  $P(x)$ :

$$P(x) = |\langle x|\psi\rangle|^2 \quad (225)$$

and the fact that the total probability to find the particle is 1:

$$\mathbb{I} = \int_{-\infty}^{\infty} |x\rangle\langle x| dx \quad (226)$$

↓

$$\langle \psi|\mathbb{I}|\psi\rangle = \int_{-\infty}^{\infty} \langle \psi|x\rangle\langle x|\psi\rangle dx \quad (227)$$

↓

$$\langle \psi|\psi\rangle = 1 = \int_{-\infty}^{\infty} P(x) dx. \quad (228)$$

Note that it's fine to pull  $|\psi\rangle$  through the integral, as it is not itself a function of  $x$ . We will return to this in section 7.7.

## 7.2 Bases

A useful trick, the infinite-dimensional generalisation of Eq. 156, is to act the  $\hat{x}$  operator on Eq. 223, using

$$\hat{x}|x\rangle = x|x\rangle \quad (229)$$

to give the representation of the position operator in the position basis:

$$\hat{x} = \int_{-\infty}^{\infty} x|x\rangle\langle x|dx. \quad (230)$$

The momentum eigenstates  $\{|p\rangle\}$  also form a complete orthonormal basis for the same space, and we also have

$$\mathbb{I} = \int_{-\infty}^{\infty} |p\rangle\langle p|dp \quad (231)$$

and

$$\hat{p} = \int_{-\infty}^{\infty} p|p\rangle\langle p|dp.$$

The energy eigenstates solving the TISE form complete orthonormal bases:

$$\hat{H}|n\rangle = E_n|n\rangle \quad (232)$$

and we can similarly define

$$\mathbb{I} = \sum_n |n\rangle\langle n| \quad (233)$$

and

$$\hat{H} = \sum_n E_n |n\rangle\langle n|.$$

Just as we can project a vector into the basis  $\{|e_i\rangle\}$  using Eq. 137, we can project an infinite dimensional vector  $|f\rangle$  into the position basis:

$$|f\rangle = \mathbb{I}|f\rangle = \int_{-\infty}^{\infty} |x\rangle\langle x|f\rangle dx = \int_{-\infty}^{\infty} (\langle x|f\rangle) |x\rangle dx \quad (234)$$

where

$$\langle x|f\rangle = f(x). \quad (235)$$

This returns a complex scalar for each position  $x$ , and is simply the complex function  $f(x)$  as the notation suggests. The space of functions is equipped with an inner product:

$$\langle f|g\rangle = \int_{-\infty}^{\infty} f(x)^* g(x) dx \quad (236)$$

proven using the resolution of the identity, Eq. 223:

$$\langle f|g\rangle = \langle f|\mathbb{I}|g\rangle = \int_{-\infty}^{\infty} \langle f|x\rangle \langle x|g\rangle dx = \int_{-\infty}^{\infty} f(x)^* g(x) dx. \quad (237)$$

Normalisable functions plus this inner product therefore form a Hilbert space.

### 7.3 The Fourier transform

Just as we are free to choose any orthonormal basis for finite-dimensional vector spaces, we are free to do so with infinite-dimensional spaces. For example, we can equally-well project our kets into the momentum basis:

$$\langle p|f\rangle = f(p). \quad (238)$$

To convert a function written in the position basis,  $f(x)$ , to the same function written in the momentum basis,  $f(p)$ , we would usually use the Fourier transform. This gives us a consistency condition. Starting from Eq. 238 and inserting a complete set of position states:

$$f(p) = \langle p|f\rangle \quad (239)$$

$$= \int_{-\infty}^{\infty} \langle p|x\rangle \langle x|f\rangle dx \quad (240)$$

$$= \int_{-\infty}^{\infty} \langle p|x\rangle f(x) dx \quad (241)$$

and therefore

$$f(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(-ipx/\hbar) f(x) dx \quad (242)$$

where we see

$$\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(-ipx/\hbar). \quad (243)$$

The inverse Fourier transform follows naturally:

$$f(x) = \langle x|f\rangle \quad (244)$$

$$= \int_{-\infty}^{\infty} \langle x|p\rangle \langle p|f\rangle dp \quad (245)$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp(ipx/\hbar) f(p) dp \quad (246)$$

with

$$\langle x|p\rangle = (\langle p|x\rangle)^* \quad (247)$$

where the general result of Eq. 133 has been used.

## 7.4 Operators in the position basis

The non-commuting operators in Heisenberg's matrix mechanics all have equivalents in Schrödinger's wave mechanics. Working in the position basis they become differential operators. Writing them in three dimensional space for generality:

$$\hat{x} \rightarrow \mathbf{x} \quad (248)$$

$$\hat{\mathbf{p}} \rightarrow -i\hbar\nabla \quad (249)$$

$$\hat{H} = \frac{1}{2m}\hat{\mathbf{p}}^2 + \hat{V} \rightarrow -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}). \quad (250)$$

For example, the canonical commutation relation of Eq. 192 becomes:

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

as required.

## 7.5 Expectation values of operators

The expectation value of operator  $\hat{A}$ , denoted  $\langle\hat{A}\rangle$ , in state  $|\psi\rangle$  is given by

$$\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle \quad (251)$$

which is another convenience of Dirac notation. For example, we can evaluate the expectation value of the position operator using

$$\hat{x} = \int x|x\rangle\langle x|dx \quad (252)$$

to give



$$\langle \hat{x} \rangle = \langle \psi | \hat{x} | \psi \rangle \quad (253)$$

$$= \langle \psi | \left( \int x |x\rangle \langle x| dx \right) | \psi \rangle \quad (254)$$

$$= \int x \langle \psi | x \rangle \langle x | \psi \rangle dx \quad (255)$$

$$= \int x |\psi(x)|^2 dx \quad (256)$$

which agrees with the wave mechanics expression of Eq. 97 (in that earlier expression, operators were assumed projected into the position basis). Similarly, by acting  $\hat{x}$  on Eq. 252 we find

$$\hat{x}^2 = \int x^2 |x\rangle \langle x| dx \quad (257)$$

and so

$$\langle \hat{x}^2 \rangle = \int x^2 |\psi(x)|^2 dx. \quad (258)$$

## 7.6 Hermiticity of differential operators

Hermiticity is obvious in the matrix representation. For example:

$$\hat{p} = \int p |p\rangle \langle p| dp = \hat{p}^\dagger. \quad (259)$$

However, some care has to be taken when working in a particular basis, because, naively, we might think that  $(-i\hbar\partial_x)^\dagger = i\hbar\partial_x$ . But this cannot be true, as  $-i\hbar\partial_x$  is the momentum operator, and momentum is a physical observable and therefore is represented by a Hermitian operator. Therefore  $(-i\hbar\partial_x)^\dagger = -i\hbar\partial_x$ . Instead, working in the position basis, the Hermitian conjugate of an operator  $\hat{A}$  is defined as:

$$\int_{-\infty}^{\infty} \varphi(x)^* (\hat{A}^\dagger \psi(x)) dx \triangleq \int_{-\infty}^{\infty} (\hat{A} \varphi(x))^* \psi(x) dx \quad (260)$$

for arbitrary  $\varphi(x)$ ,  $\psi(x)$ . Therefore the condition for Hermiticity of operator  $\hat{A}$  is:

$$\text{Hermiticity: } \int_{-\infty}^{\infty} \varphi(x)^* (\hat{A} \psi(x)) dx = \int_{-\infty}^{\infty} (\hat{A} \varphi(x))^* \psi(x) dx \quad (261)$$

where  $\varphi(x)$ ,  $\psi(x)$  are normalisable, requiring them to vanish at  $x = \pm\infty$ . For example, the position operator trivially satisfies this:

$$\int_{-\infty}^{\infty} \varphi(x)^* (x\psi(x)) dx = \int_{-\infty}^{\infty} (x\varphi(x))^* \psi(x) dx. \quad (262)$$

The momentum operator is also Hermitian:

$$\begin{aligned} \int_{-\infty}^{\infty} \varphi(x)^* (-i\hbar \partial_x \psi(x)) dx &= [\varphi(x)^* (-i\hbar \psi(x))]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} (-i\hbar \partial_x \varphi(x)^*) \psi(x) dx \\ &= \int_{-\infty}^{\infty} (-i\hbar \partial_x \varphi(x))^* \psi(x) dx \end{aligned}$$

where integration by parts was used, and the boundary terms disappear because  $\varphi(x)$  and  $\psi(x)$  are required to vanish at  $x = \pm\infty$ .

## 7.7 Basis-independent TDSE

The time dependent Schrödinger equation in its most general form is

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \quad (263)$$

which avoids specifying a basis (position, momentum *etc.*) for the ket  $|\psi(t)\rangle$ . The usual position-dependent wavefunction is then given by projecting into the position basis:

$$\psi(x, t) = \langle x | \psi(t) \rangle. \quad (264)$$

Note that while we must project into the position basis, or the momentum basis, we do not need to perform a similar operation for time:  $|\psi(t)\rangle$  is simply labelled by its time. Non-relativistic quantum mechanics treats time as privileged. To treat position and time on an equal footing, a necessary condition for including relativistic effects, we must use quantum field theory, which is beyond the scope of this course.

## 7.8 The Postulates of Quantum Mechanics

Long overdue, perhaps, we are now in a position to state the axioms of quantum mechanics. These completely define what it is we do in quantum mechanics.

1. States of a system are represented by normalized kets  $|\psi\rangle$  in a complex Hilbert space  $\mathcal{H}$ .
2. Observable quantities are represented by Hermitian operators in  $\mathcal{H}$ .
3. All such Hermitian operators  $\hat{A}$  are assumed to possess a complete set of orthogonal eigenstates:  $\hat{A}|a_n\rangle = a_n|a_n\rangle$ .
4. The fundamental probability postulate for measurement is:
  - (a) the possible results of a measurement of  $\hat{A}$  are  $a_n$ ;
  - (b) after measurement of  $\hat{A}$  on state  $|\psi\rangle$  with result  $a_n$  the resulting state is  $|a_n\rangle$ ;
  - (c) the probability for this to happen is  $|\langle a_n | \psi \rangle|^2$  (the Born rule).

5. In the absence of measurement states evolve unitarily in time according to the TDSE:

$$i\hbar\partial_t|\psi(t)\rangle = \hat{H}|\psi(t)\rangle.$$

## 8 The quantum harmonic oscillator

### Videos:

- V8.1: The quantum harmonic oscillator
- V8.2: Ladder operators
- V8.3: The number operator
- V8.4: Second quantisation

### Topics:

- converting the quantum harmonic oscillator (QHO) TISE to Hermite's equation
- solution with Hermite polynomials
- raising and lowering (ladder) operators
- ladder operator commutation relations
- Energy eigenstates and eigenvalues of the QHO
- Second quantization

### For the exam you should be able to:

- work with Hermite polynomials, checking properties such as orthogonality
- find the commutators between the raising and lowering (ladder) operators, and with the Hamiltonian
- demonstrate that these commutation relations lead to an infinite ladder of equally-spaced energy eigenvalues
- justify the normalisation of the ladder operators
- deduce the ground state of the QHO from the existence of a bottom rung of the ladder
- explain the concepts of first and second quantization.

### For the exam you will not be required to:

- rote learn the form of the Hermite polynomials
- rote learn the form of the ladder operators.

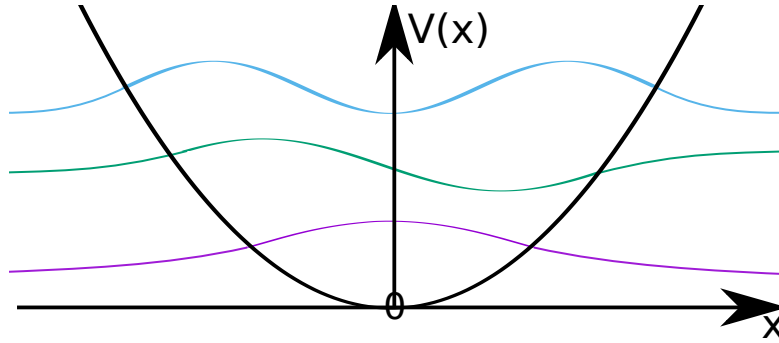


Figure 6: The quantum harmonic oscillator potential  $V(x) = \frac{1}{2}m\omega^2x^2$  and first few eigenstates.

A very important problem is the quantum harmonic oscillator:

$$\hat{V} = \frac{1}{2}m\omega^2\hat{x}^2. \quad (265)$$

This is the quantum version of the simple harmonic oscillator in 1D. The TISE reads:

$$-\frac{\hbar^2}{2m} \frac{d^2\phi_n(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\phi_n(x) = E_n\phi_n(x). \quad (266)$$

The potential is shown in Fig. 6.

There are two main approaches to solving the problem. The first is a continuation of the methods we've seen earlier in the course, solving the differential equations directly. The second method is far more elegant, and generalises to many other problems. It uses operators. We will see them in turn.

## 8.1 Hermite polynomials

It is convenient to rescale using  $x = \alpha y$ :

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2\phi_n(y)}{dy^2} + \frac{1}{2}m\omega^2\alpha^2y^2\phi_n(y) = E_n\phi_n(y) \quad (267)$$

and selecting

$$\alpha^2 = \frac{\hbar}{m\omega} \quad (268)$$

gives

$$\frac{1}{2} \left( -\frac{d^2\phi_n(y)}{dy^2} + y^2\phi_n(y) \right) = \epsilon_n\phi_n(y) \quad (269)$$

where

$$\epsilon_n \triangleq \frac{E_n}{\hbar\omega}. \quad (270)$$

Eq. 269 is a second order ODE. Substitute

$$\phi_n(y) = H_n(y) \exp\left(-\frac{y^2}{2}\right) \quad (271)$$

to reduce Eq. 269 to

$$H_n(y)'' - 2yH_n(y)' + (2\epsilon - 1)H_n(y) = 0. \quad (272)$$

This is known as Hermite's equation. It can be solved with Frobenius series to yield  $H_n(y)$ , the Hermite polynomials for  $n \geq 1$ :

$$H_n(y) = (-1)^n \exp(y^2) \frac{d^n}{dy^n} \exp(-y^2) \quad (273)$$

(where  $H_0 = 1$ ) with energy eigenvalues

$$\epsilon_n = n + 1/2 \quad (274)$$

for integer  $n \geq 0$ . Returning to the original scaling we have

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right). \quad (275)$$

## 8.2 Ladder operators

However, there is a far more elegant method. Returning to the original scaling of the TISE

$$\hat{H}|n\rangle = \left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\right)|n\rangle = E_n|n\rangle \quad (276)$$

define non-Hermitian operators

$$\hat{a}^\dagger \triangleq \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega}\hat{p}\right) \quad (277)$$

implying

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega}\hat{p}\right). \quad (278)$$

This gives

$$\hat{a}^\dagger\hat{a} = \frac{m\omega}{2\hbar} \left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2} + \frac{i}{m\omega}(\hat{x}\hat{p} - \hat{p}\hat{x})\right). \quad (279)$$

The term in nested parentheses is just the commutator

$$[\hat{x}, \hat{p}] = i\hbar\mathbb{1} \quad (280)$$

giving

$$\hat{a}^\dagger \hat{a} = \frac{m\omega}{2\hbar} \hat{x}^2 + \frac{\hat{p}^2}{2\hbar m\omega} - \frac{1}{2} \hat{\mathbb{I}}$$

and so

$$\hbar\omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \hat{\mathbb{I}} \right) = \hat{H}. \quad (281)$$

Therefore the TISE can be written

$$\hat{H}|n\rangle = \hbar\omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right) |n\rangle = E_n |n\rangle. \quad (282)$$

### 8.2.1 Commutation relations

The commutator of the operators is

$$[\hat{a}, \hat{a}^\dagger] = \frac{m\omega}{2\hbar} \left[ \hat{x} + \frac{i}{m\omega} \hat{p}, \hat{x} - \frac{i}{m\omega} \hat{p} \right] \quad (283)$$

$$= -\frac{i}{\hbar} [\hat{x}, \hat{p}] \quad (284)$$

and so

$$[\hat{a}, \hat{a}^\dagger] = 1 \quad (285)$$

The commutator of the operators with the Hamiltonian is therefore:

$$[\hat{H}, \hat{a}^\dagger] = \left[ \hbar\omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \hat{\mathbb{I}} \right), \hat{a}^\dagger \right] \quad (286)$$

$$= \hbar\omega (\hat{a}^\dagger \hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a}^\dagger \hat{a}) \quad (287)$$

$$= \hbar\omega \hat{a}^\dagger [\hat{a}, \hat{a}^\dagger] \quad (288)$$

giving

$$[\hat{H}, \hat{a}^\dagger] = \hbar\omega \hat{a}^\dagger. \quad (289)$$

Similarly,

$$[\hat{H}, \hat{a}] = -\hbar\omega \hat{a}. \quad (290)$$

### 8.2.2 Energy eigenstates and eigenvalues

Using Eq. 289 we can see the effect of  $\hat{a}^\dagger$  on the TISE of Eq. 282:

$$\hat{H}|n\rangle = E_n|n\rangle \quad (291)$$

↓

$$\hat{a}^\dagger \hat{H}|n\rangle = E_n \hat{a}^\dagger |n\rangle \quad (292)$$

↓

$$\left( \hat{H} \hat{a}^\dagger - [\hat{H}, \hat{a}^\dagger] \right) |n\rangle = E_n \hat{a}^\dagger |n\rangle \quad (293)$$

↓

$$\left( \hat{H} \hat{a}^\dagger - \hbar\omega \hat{a}^\dagger \right) |n\rangle = E_n \hat{a}^\dagger |n\rangle \quad (294)$$

and the final result

$$\boxed{\hat{H} (\hat{a}^\dagger |n\rangle) = (E_n + \hbar\omega) (\hat{a}^\dagger |n\rangle).} \quad (295)$$

That is, if  $|n\rangle$  is an eigenstate of the harmonic oscillator with eigenvalue  $E_n$ , then  $\hat{a}^\dagger |n\rangle$  is an eigenstate with eigenvalue  $E_n + \hbar\omega$ . Repeating the process  $m$  times we find

$$\hat{H} \left( (\hat{a}^\dagger)^m |n\rangle \right) = (E_n + m\hbar\omega) \left( (\hat{a}^\dagger)^m |n\rangle \right). \quad (296)$$

This tells us that the energy levels are evenly spaced, and that

$$(\hat{a}^\dagger)^m |n\rangle \propto |n+m\rangle. \quad (297)$$

Similarly, we find

$$\hat{H} (\hat{a} |n\rangle) = (E_n - \hbar\omega) (\hat{a} |n\rangle). \quad (298)$$

We call  $\hat{a}^\dagger$  the raising operator, and  $\hat{a}$  the lowering operator. Collectively we call them ladder operators, as they move the state up or down the rungs of an energy ladder with evenly spaced rungs. While there exist an infinite number of rungs, the energies do not stretch down to negative energies. To see this, first note that

$$|\hat{a}|n\rangle|^2 \geq 0 \quad (299)$$

because the thing on the left, whatever it is, is the square modulus of something, and that is always  $\geq 0$ . Expanding it out we have



$$\langle n | \hat{a}^\dagger \hat{a} | n \rangle \geq 0 \quad (300)$$

$$\langle n | \frac{1}{\hbar\omega} \hat{H} - \frac{1}{2} | n \rangle \geq 0 \quad (301)$$

$$\langle n | \frac{1}{\hbar\omega} E_n - \frac{1}{2} | n \rangle \geq 0 \quad (302)$$

$$E_n \geq \frac{\hbar\omega}{2}. \quad (303)$$

Therefore there is a lowest-energy state, a lowest rung to the ladder. This is the ground state which we denote  $|0\rangle$ . This is just a convenient label for a ket. It is not the number zero. You can think of it as shorthand for  $|\psi_{n=0}\rangle$ . The ground state has the property that

$$\hat{a}|0\rangle = 0 \quad (304)$$

where the right hand side really is the number 0, so that any further action of lowering operators continues to return 0. To find the energy of the ground state we can work in the position basis using the definition of the lowering operator from Eq. 278:

$$\sqrt{\frac{m\omega}{2\hbar}} \left( \hat{x} + \frac{i}{m\omega} \hat{p} \right) |0\rangle = 0 \quad (305)$$

↓

$$\left( x + \frac{\hbar}{m\omega} \frac{d}{dx} \right) \phi_0(x) = 0. \quad (306)$$

This is a first order linear ODE which has the solution

$$\phi_0(x) \propto \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \quad (307)$$

Inserting this into the TISE of Eq. 266 gives

$$E_0 = \frac{\hbar\omega}{2}. \quad (308)$$

This is the **ground state energy**, also called the **zero-point energy**.

Combining the results, we see that

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

for integer  $n$ . Defining the ‘number operator’

$$\hat{n} \triangleq \hat{a}^\dagger \hat{a} \quad (309)$$

we see that

$$\hat{n}|n\rangle = n|n\rangle. \quad (310)$$

### 8.2.3 Normalization

We have that

$$\langle n|\hat{n}|n\rangle = n \quad (311)$$

↓

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = n \quad (312)$$

↓

$$\|\hat{a}|n\rangle\|^2 = n \quad (313)$$

↓

$$\|\hat{a}|n\rangle\| = \sqrt{n}. \quad (314)$$

Therefore, since

$$\hat{a}|n\rangle \propto |n-1\rangle$$

and

$$\langle n-1|n-1\rangle = 1 \quad (315)$$

we have

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle. \quad (316)$$

Similarly,

$$|\hat{a}^\dagger|n\rangle|^2 = \langle n|\hat{a}\hat{a}^\dagger|n\rangle = \langle n|\hat{n} + [\hat{a}, \hat{a}^\dagger]|n\rangle = n + 1 \quad (317)$$

and so

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \quad (318)$$

By induction we can also see that

$$\frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle = |n\rangle. \quad (319)$$

### 8.3 Second quantization

- Equation 319 tells us we can create the  $n^{\text{th}}$  excited state of the harmonic oscillator by acting  $n$  raising operators on the ground state.
- Since all rungs of the ladder are evenly spaced with spacing  $\hbar\omega$ , we can also interpret the  $n^{\text{th}}$  excited state as the presence of  $n$  identical particles each of energy  $\hbar\omega$ .
- Solving the TDSE for the wavefunction of a quantum system we call ‘first quantization’. It is the realisation that classical particles exhibit wave-like properties in a quantum description. We call the process of rewriting a problem in terms of ladder operators ‘second quantization’. It is the realisation that classical waves gain particle-like properties in a quantum description. The descriptions are equivalent.
- It turns out that in order to consistently include relativistic effects into quantum mechanics, you must allow the number of particles to vary. The result is quantum field theory. This treats particles as excitations of quantum fields which permeate all of space; to create a particle at position  $x$  you act a raising operator  $\hat{a}_x^\dagger$  on the vacuum state of no particles.
- For this reason we also call the raising and lowering operators the ‘creation and annihilation operators’: they create and annihilate particles in a second-quantised description.
- The fact that we can fit multiple particles into the same state identifies  $\hat{a}^\dagger$  as the creation operator of a *boson*.

In summary: the state  $|n\rangle$  can be thought of as the  $n^{\text{th}}$  excited state of the harmonic oscillator. In first-quantised language,  $\langle x|n(t)\rangle = \psi_n(x, t)$ ; this is a stationary state with energy  $(n + 1/2)\hbar\omega$ . But since this is equal to  $\frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^n|0\rangle$  it can equally well be thought of as  $n$  independent bosonic particles, each with energy  $\hbar\omega$ , sat in the harmonic potential. The fact that the total energy is not  $n\hbar\omega$ , but instead  $(n + 1/2)\hbar\omega$ , is due to the vacuum (state  $|0\rangle$ ) itself, which contains 0 particles) having its own energy. This is the ‘zero point energy’ of the harmonic oscillator.

## 9 The Schrödinger equation in three dimensions

### Videos:

- V9.1: The 3D infinite potential well
- V9.2: The 3D quantum harmonic oscillator
- V9.3: Angular momentum
- V9.4: Angular momentum ladder operators

### Topics:

- 3D infinite potential well
- 3D quantum harmonic oscillator
- polar co-ordinates
- angular momentum
- commutation relations for angular momentum operators
- $\hat{L}_z$  and  $\hat{L}^2$  as a maximal set of commuting operators
- angular momentum ladder operators

### For the exam you should be able to:

- solve the TISE/TDSE for the 3D infinite potential well
- solve the TISE/TDSE for the 3D quantum harmonic oscillator
- state the form of the angular momentum operator
- derive the position-basis form of the angular momentum operator in cartesian co-ordinates
- derive the position-basis form of  $\hat{L}_z$  in polar co-ordinates
- find the commutation relations between the x, y, and z-projections of the angular momentum operator
- show that  $\hat{L}^2$  commutes with all three of  $\hat{L}_{x,y,z}$
- find the commutation relations between the angular momentum raising and lowering operators  $\hat{L}_{\pm}$
- use the commutation relations between  $\hat{L}_{\pm}$  to deduce the existence of a ladder of states with different  $\hat{L}_z$  eigenvalues.

### For the exam you will not be required to:

- rote learn the form of  $\nabla^2$  in spherical polar co-ordinates.

## 9.1 TISE in three dimensions

Nothing fundamentally difficult happens when considering full three dimensional problems compared to 1D problems. But certain observable properties, such as angular momentum, only have meaning in dimensions greater than one. In this lecture we will see how to handle them.

### 9.1.1 Cubic box

Consider the infinite potential well in three dimensions where

$$\mathbf{r} = (x, y, z) \quad (320)$$

$$V(\mathbf{r}) = \begin{cases} 0, & 0 < \{x, y, z\} < a \\ \infty, & \text{otherwise.} \end{cases} \quad (321)$$

Inside the box the TISE reads

$$-\frac{\hbar^2 \nabla^2}{2m} \phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}} \phi_{\mathbf{n}}(\mathbf{r}) \quad (322)$$

$$-\frac{\hbar^2}{2m} (\partial_x^2 + \partial_y^2 + \partial_z^2) \phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}} \phi_{\mathbf{n}}(\mathbf{r}) \quad (323)$$

where  $\mathbf{n} = (n_x, n_y, n_z)$  just assigns an independent integer to each direction. This is separable into three second order ODEs using

$$\phi_{\mathbf{n}}(\mathbf{r}) \triangleq X_{n_x}(x) Y_{n_y}(y) Z_{n_z}(z) \quad (324)$$

$$E_{\mathbf{n}} \triangleq E_{n_x}^x + E_{n_y}^y + E_{n_z}^z \quad (325)$$

giving

$$-\frac{\hbar^2}{2m} \left( \frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} \right) = E_{n_x}^x + E_{n_y}^y + E_{n_z}^z. \quad (326)$$

We simply have three independent copies of the 1D infinite potential well. We can define three separate TISEs:

$$\hat{H}^x X_{n_x}(x) \triangleq \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) X_{n_x}(x) = E_{n_x}^x X_{n_x}(x) \quad (327)$$

and the same for  $y$  and  $z$ . Solving as before we find

$$X_{n_x}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \quad (328)$$

$$E_{n_x}^x = \frac{\hbar^2 n_x^2 \pi^2}{2ma^2} \quad (329)$$

and overall we have

$$\phi_{\mathbf{n}}(\mathbf{r}) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \quad (330)$$

$$E_{\mathbf{n}} = \frac{\hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2). \quad (331)$$

Since the Hamiltonians in each direction commute:

$$[\hat{H}^i, \hat{H}^j] = 0, \quad \{i, j\} \in \{x, y, z\} \quad (332)$$

we can define a set of time-independent quantum numbers

$$\hat{H}|n_x, n_y, n_z\rangle = E_{n_x, n_y, n_z}|n_x, n_y, n_z\rangle \quad (333)$$

or

$$\hat{H}|\mathbf{n}\rangle = E_{\mathbf{n}}|\mathbf{n}\rangle \quad (334)$$

where

$$\langle \mathbf{r} | \mathbf{n} \rangle = \phi_{\mathbf{n}}(\mathbf{r}). \quad (335)$$

### Degeneracy

Something new which we did not see in 1D is that multiple different energy eigenstates can now have the same energy. The ket is labelled by the three independent integers. While the ground state  $|1, 1, 1\rangle$  is unique, with energy  $E_{(1,1,1)} = 3\hbar^2/2ma^2$ , higher excited states are degenerate, with  $E_{1,1,2} = E_{1,2,1} = E_{2,1,1}$ .

However, the eigenkets still form an orthonormal basis:

$$\langle m_x, m_y, m_z | n_x, n_y, n_z \rangle = \delta_{n_x m_x} \delta_{n_y m_y} \delta_{n_z m_z} \quad (336)$$

which can be seen explicitly, for example, by inserting a complete set of position states:

$$\langle m_x, m_y, m_z | n_x, n_y, n_z \rangle = \iiint \langle m_x, m_y, m_z | \mathbf{x} \rangle \langle \mathbf{x} | n_x, n_y, n_z \rangle dx dy dz \quad (337)$$

$$= \frac{8}{a^3} \iiint \sin\left(\frac{m_x \pi x}{a}\right) \sin\left(\frac{m_y \pi y}{a}\right) \sin\left(\frac{m_z \pi z}{a}\right) \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) dx dy dz \quad (338)$$

$$= \left(\frac{2}{a} \int \sin\left(\frac{m_x \pi x}{a}\right) \sin\left(\frac{n_x \pi x}{a}\right) dx\right) \cdot (x \rightarrow y) \cdot (x \rightarrow z) \quad (339)$$

$$= \delta_{n_x m_x} \delta_{n_y m_y} \delta_{n_z m_z}. \quad (340)$$

### 9.1.2 3D Harmonic oscillator

In precisely the same manner, the 3D harmonic oscillator can be separated into three 1D harmonic oscillators:

$$\hat{H} \phi_{\mathbf{n}}(\mathbf{r}) = \left(-\frac{\hbar^2 \nabla^2}{2m} + \frac{1}{2} m \omega^2 \hat{\mathbf{r}}^2\right) \phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}} \phi_{\mathbf{n}}(\mathbf{r}) \quad (341)$$

with energy eigenvalues

$$E_{\mathbf{n}} = \hbar \omega \left(n_x + n_y + n_z + \frac{3}{2}\right). \quad (342)$$

We can define ladder operators in each cartesian direction separately:

$$\hat{a}_x^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega} \hat{p}_x\right) \quad (343)$$

$$\hat{a}_y^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{y} - \frac{i}{m\omega} \hat{p}_y\right) \quad (344)$$

$$\hat{a}_z^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{z} - \frac{i}{m\omega} \hat{p}_z\right) \quad (345)$$

and number operators

$$\hat{n}_x = \hat{a}_x^\dagger \hat{a}_x \quad (346)$$

*etc.* so that

$$\hat{H} |n_x, n_y, n_z\rangle = \hbar \omega \left(\hat{n}_x + \hat{n}_y + \hat{n}_z + \frac{3}{2}\right) |n_x, n_y, n_z\rangle. \quad (347)$$

## 9.2 Angular momentum

### 9.2.1 Cartesian co-ordinates

Classically, angular momentum is defined to be

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \quad (348)$$

In quantum mechanics we promote observables to operators, so that

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \quad (349)$$

or in the position basis

$$\hat{\mathbf{L}} = -i\hbar \hat{\mathbf{r}} \times \nabla. \quad (350)$$

Note that angular momentum has the same dimensions as  $\hbar$ . In cartesian co-ordinates we have

$$\hat{\mathbf{L}} = -i\hbar \begin{pmatrix} \hat{y}\partial_z - \hat{z}\partial_y \\ \hat{z}\partial_x - \hat{x}\partial_z \\ \hat{x}\partial_y - \hat{y}\partial_x \end{pmatrix}. \quad (351)$$

Checking the commutation relations we find

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k \quad (352)$$

where  $\epsilon_{ijk}$  is the Levi-Civita symbol and Einstein summation notation is assumed (*i.e.* there is an implicit sum over  $k \in \{1, 2, 3\}$ ). Since no two operators commute, it is not possible to have simultaneous knowledge of the angular momentum along any two directions. From the Heisenberg uncertainty principle of Eq. 200 we see that

$$\sigma_{\hat{L}_i} \sigma_{\hat{L}_j} \geq \frac{\hbar}{2} |\langle \hat{L}_k \rangle|.$$

However, the squared angular momentum

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (353)$$

commutes with all three:

$$[\hat{L}_i, \hat{L}^2] = 0. \quad (354)$$

The maximal set of commuting operators is  $\hat{L}^2$  and one of  $\hat{L}_i$ . The physical observable associated with the operator  $\hat{L}^2$  is the square of the angular momentum.

### 9.2.2 Spherical polar co-ordinates

In spherical polar co-ordinates



$$\mathbf{r} = (r, \theta, \phi) \quad (355)$$

we have that

$$\hat{L}_z = -i\hbar\partial_\phi.$$

This is particularly simple compared to  $\hat{L}_x$  and  $\hat{L}_y$ . For this reason we choose our co-ordinates so that  $\hat{z}$  lies along whatever direction is of interest, and use  $\hat{L}^2$  and  $\hat{L}_z$  as our maximal commuting set.

Expanding  $\nabla^2$  gives the TISE:

$$\hat{H}\psi(\mathbf{r}, t) = \left( -\frac{\hbar^2}{2mr^2}\partial_r(r^2\partial_r) + \frac{1}{2mr^2}\hat{L}^2 + V(r, \theta, \phi) \right) \psi(\mathbf{r}, t) = E\psi(\mathbf{r}, t) \quad (356)$$

where the squared angular momentum operator is

$$\hat{L}^2\psi(\mathbf{r}, t) = -\hbar^2 \left( \frac{1}{\sin(\theta)}\partial_\theta(\sin(\theta)\partial_\theta) + \frac{1}{\sin^2(\theta)}\partial_\phi^2 \right) \psi(\mathbf{r}, t). \quad (357)$$

This can also be found from Eq. 350.

### 9.2.3 Angular momentum ladder operators

Consider the operators

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y. \quad (358)$$

Using Equation 352 the commutator with  $\hat{L}_z$  can be seen to be

$$[\hat{L}_\pm, \hat{L}_z] = \mp\hbar\hat{L}_\pm. \quad (359)$$

By the reasoning applied to the energy raising and lowering operators of the harmonic oscillator, we see that  $\hat{L}_\pm$  are raising and lowering (ladder) operators for the  $z$ -projection of angular momentum. It is conventional to denote the eigenstates of  $\hat{L}_z$  as  $|m\rangle$ , where  $m$  is an integer unrelated to the mass of the particle:

$$\hat{L}_z|m\rangle = \hbar m|m\rangle. \quad (360)$$

The fact that the eigenvalues of  $\hat{L}_z$  take integer values will be derived explicitly in Lecture 10. Assuming it for now, we find that

$$\hat{L}_\pm \hat{L}_z |m\rangle = \hbar m \hat{L}_\pm |m\rangle \quad (361)$$

$$\left( \hat{L}_z \hat{L}_\pm + [\hat{L}_\pm, \hat{L}_z] \right) |m\rangle = \hbar m \hat{L}_\pm |m\rangle \quad (362)$$

$$\left( \hat{L}_z \hat{L}_\pm \mp \hbar \hat{L}_\pm \right) |m\rangle = \hbar m \hat{L}_\pm |m\rangle \quad (363)$$

$$\hat{L}_z \left( \hat{L}_\pm |m\rangle \right) = \hbar (m \pm 1) \left( \hat{L}_\pm |m\rangle \right) \quad (364)$$

that is, if  $|m\rangle$  is an eigenstate of  $\hat{L}_z$  with eigenvalue  $\hbar m$ , then  $\hat{L}_\pm |m\rangle$  is an eigenstate with eigenvalue  $\hbar (m \pm 1)$ , as required. Since

$$\left[ \hat{L}_i, \hat{L}^2 \right] = 0 \quad (365)$$

we also have that

$$\left[ \hat{L}_\pm, \hat{L}^2 \right] = 0 \quad (366)$$

and the operators do not affect the total angular momentum, only its projection along a given direction. Thinking physically we see that there must therefore be both a top and bottom rung to the ladder of eigenvalues  $\hbar m$ , and that

$$-l \leq m \leq l. \quad (367)$$

## 10 The hydrogen atom

### Videos:

- V10.1: Spherically symmetric potentials: angular equation
- V10.2: Spherically symmetric potentials: radial equation
- V10.3: The hydrogen atom

### Topics:

- the TISE in spherical polar co-ordinates
- separating into radial and angular equations
- separating the angular equation into the azimuthal and polar equations
- solution of the azimuthal equation using associated Legendre polynomials
- solution of the angular equation using spherical harmonics
- rewriting the radial equation as the 1D TDSE with a centrifugal barrier term
- the TISE for the electron in the hydrogen atom
- solution to the radial equation by reduction to La Guerre's equation
- quantum numbers of the electron in the hydrogen atom

### For the exam you should be able to:

- separate the TISE in spherical polar co-ordinates into radial, azimuthal, and polar parts (given the TISE itself)
- rewrite the radial equation of the TISE for a spherically-symmetric potential as a 1D TISE with centrifugal barrier term
- explain the origin of the quantum numbers of the electron in the hydrogen atom
- state the origin of atomic line spectra
- recount the basic idea of the Bohr model of the atom

### For the exam you will not be required to:

- rote learn the forms of the spherical harmonics (although you should have a basic familiarity with them)
- learn detailed properties of the associated Legendre equation or La Guerre's equation
- rote learn the solutions to the TISE for the hydrogen atom.

The solution of the TDSE for the hydrogen atom proved the usefulness of quantum mechanics. The results are phenomenally accurate. The absolute full solution is a bit too laborious for this course, so we will only see an overview of the key ideas. We will, however, see the full solution, neglecting higher-order corrections.

## 10.1 Spherically-symmetric potentials

The TDSE is always separable into time and space co-ordinates. In the special case of a spherically-symmetric potential  $V = V(r)$  it additionally becomes separable into ODEs for the radial part, and the angular parts:

$$\psi(\mathbf{r}, t) \triangleq T(t) \varphi(\mathbf{r}) \quad (368)$$

$$\varphi(\mathbf{r}) \triangleq T(t) R(r) Y(\theta, \phi). \quad (369)$$

Inserting into Eq. 356 gives

$$\frac{1}{Y(\theta, \phi)} \hat{L}^2 Y(\theta, \phi) = 2mr^2 (E - V(r)) + \frac{\hbar^2}{R(r)} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R(r). \quad (370)$$

Both sides are therefore equal to a constant as usual. Defining this constant to be  $\hbar^2 k^2$  gives

$$\text{radial equation: } \frac{\hbar^2}{R(r)} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R(r) + 2mr^2 (E - V(r)) = \hbar^2 k^2 \quad (371)$$

$$\text{angular equation: } \hat{L}^2 Y(\theta, \phi) = \hbar^2 k^2 Y(\theta, \phi). \quad (372)$$

### 10.1.1 Angular equation

The angular equation reads:

$$-\hbar^2 \left( \frac{1}{\sin(\theta)} \partial_\theta (\sin(\theta) \partial_\theta) + \frac{1}{\sin^2(\theta)} \partial_\phi^2 \right) Y(\theta, \phi) = \hbar^2 k^2 Y(\theta, \phi) \quad (373)$$

re-arranging,

$$-\partial_\phi^2 Y(\theta, \phi) = k^2 \sin^2(\theta) Y(\theta, \phi) + \sin(\theta) \partial_\theta (\sin(\theta) \partial_\theta) Y(\theta, \phi). \quad (374)$$

This is again separable: substituting

$$Y(\theta, \phi) = P(\cos(\theta)) F(\phi) \quad (375)$$

gives

$$\frac{\sin(\theta)}{P(\cos(\theta))} \frac{d}{d\theta} \left( \sin(\theta) \frac{dP(\cos(\theta))}{d\theta} \right) + k^2 \sin^2(\theta) P(\cos(\theta)) = -\frac{1}{F(\phi)} \frac{d^2 F(\phi)}{d\phi^2}. \quad (376)$$

We again set both sides equal to a constant. It is traditional to name this constant  $m^2$  which causes an unfortunate confusion with the mass  $m$ .

### Polar equation

The polar part is solved by

$$F(\phi) = \exp(\pm im\phi). \quad (377)$$

The observable probability density  $|F|^2$  should be single-valued, requiring

$$F(\phi + 2\pi) = F(\phi) \quad (378)$$

and so

$$\exp(2\pi im) = 1. \quad (379)$$

This requires  $m$  to be an integer. Note that  $F_m(\phi)$  is an eigenstate of  $\hat{L}_z$ :

$$\hat{L}_z F_m(\phi) = -i\hbar \partial_\phi F_m(\phi) = \hbar m F_m(\phi). \quad (380)$$

The integer  $m$  is called the ‘magnetic quantum number’; it is the observable corresponding to the measurement of the angular momentum projected along the  $z$ -axis.

### Azimuthal equation

The azimuthal equation

$$\sin(\theta) \frac{d}{d\theta} \left( \sin(\theta) \frac{dP(\cos(\theta))}{d\theta} \right) + k^2 \sin^2(\theta) P(\cos(\theta)) = m^2 P(\cos(\theta)) \quad (381)$$

is known as the associated Legendre equation. It is solved by the ‘associated Legendre polynomials’  $P_l^m(\cos(\theta))$  where  $k^2 = l(l+1)$  for  $l$  any positive integer: it is called the ‘orbital quantum number’, or ‘azimuthal quantum number’. The equation was known and studied long before quantum mechanics came along (hence the confusion with the symbol  $m$ ). It is known from the study of the equation that the values of  $m$  must be limited to the range

$$-l \leq m \leq l, \quad l \in \mathbb{Z}. \quad (382)$$

### Solution to the angular equation

Combining the results of the polar and azimuthal parts we have that

	$m = -2$	$-1$	$0$	$1$	$2$
$l = 0$			$\frac{1}{2\sqrt{\pi}}$		
$1$		$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin(\theta)\exp(-i\phi)$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos(\theta)$	$-Y_1^{-1*}$	
$2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2(\theta)\exp(-2i\phi)$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin(2\theta)\exp(-i\phi)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2(\theta) - 1)$	$-Y_2^{-1*}$	$Y_2^{-2*}$

Table 1: The first few spherical harmonics  $Y_l^m(\theta, \phi)$ .

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi) \quad (383)$$

$$\hat{L}_z Y_l^m(\theta, \phi) = \hbar m Y_l^m(\theta, \phi) \quad (384)$$

where

$$Y_l^m(\theta, \phi) = \mathcal{N} P_l^m(\cos(\theta)) \exp(\pm im\phi) \quad (385)$$

are the ‘spherical harmonics’ ( $\mathcal{N}$  is a normalization). They are orthonormal:

$$\int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\phi Y_l^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) = \delta_{ll'} \delta_{mm'} \quad (386)$$

and form a complete orthonormal basis for functions on the surface of a sphere:

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_{lm} Y_l^m(\theta, \phi) \quad (387)$$

for complex scalars  $f_{lm}$ . The first few spherical harmonics are given in Table 1.

Note that we can write this using Dirac notation:

$$\hat{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle \quad (388)$$

$$\hat{L}_z |l, m\rangle = \hbar m |l, m\rangle \quad (389)$$

where

$$\langle \theta, \phi | l, m \rangle = Y_l^m(\theta, \phi). \quad (390)$$

### 10.1.2 Radial equation

Substituting Eq. 383 into the radial equation of Eq. 371 gives

$$\left( -\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right) R_l(r) = ER_l(r). \quad (391)$$

It is convenient to define

$$R_l(r) \triangleq \frac{\chi_l(r)}{r} \quad (392)$$

which gives

$$-\frac{\hbar^2}{2m} \frac{d^2 \chi_l(r)}{dr^2} + V_{eff}(r) \chi_l(r) = E \chi_l(r) \quad (393)$$

where

$$V_{eff}(r) \triangleq V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \quad (394)$$

Eq. 393 is simply the 1D TISE with a modified potential term given in Eq. 394. The additional contribution built into  $V_{eff}$  is called the centrifugal barrier term.

### 10.1.3 Solution and normalization

Substituting Eq. 383 back into Eq. 356 we find that, **for spherically-symmetric potentials, the TISE reduces to:**

$$\hat{H} \varphi_{l,m}(\mathbf{r}) = \left( -\frac{\hbar^2}{2mr^2} \partial_r (r^2 \partial_r) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right) \varphi_{l,m}(\mathbf{r}) = E \varphi_{l,m}(\mathbf{r}) \quad (395)$$

with

$$\varphi_{l,m}(\mathbf{r}) = R_l(r) Y_l^m(\theta, \phi). \quad (396)$$

In spherical polar co-ordinates we have the Jacobian  $r^2 \sin(\theta)$ ; given that

$$\iiint |\varphi(\mathbf{r})|^2 d^3 \mathbf{r} = 1 \quad (397)$$

$$\downarrow \quad (398)$$

$$\int_0^\infty r^2 |R(r)|^2 dr \int_0^\pi \sin(\theta) |P_l^m(\theta)|^2 d\theta \int_0^{2\pi} |F_m(\phi)|^2 d\phi = 1 \quad (399)$$

it is convenient to choose a normalization such that

$$\int_0^\infty r^2 |R_l(r)|^2 dr = 1 \quad (400)$$

$$2\pi \int_0^\pi \sin(\theta) |P_l^m(\theta)|^2 d\theta = 1. \quad (401)$$

The reason we have any choice is that it is only the full wavefunction  $\psi(\mathbf{r}, t)$  which must be normalised; how we divvy the normalisation up among the separate parts is up to us.

## 10.2 The hydrogen atom

The TISE governing the electron in the Hydrogen atom is

$$\hat{H}\varphi(\mathbf{r}) = \left( -\frac{\hbar^2 \nabla^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} \right) \varphi(\mathbf{r}). \quad (402)$$

Note that the potential is negative, giving an infinite ladder of negative energy bound states. The potential is spherically symmetric, and so we can use the separable form

$$\varphi_{l,m}(\mathbf{r}) = r^{-1} \chi_l(r) Y_l^m(\theta, \phi). \quad (403)$$

From Eq. 393 the radial equation is then

$$-\frac{\hbar^2}{2m} \frac{d^2 \chi_l(r)}{dr^2} - \frac{e^2}{4\pi\epsilon_0 r} \chi_l(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \chi_l(r) = E \chi_l(r).$$

Defining the quantities

$$a_0 \triangleq \frac{4\pi\epsilon_0 \hbar^2}{me^2} \quad (\text{the Bohr radius}) \quad (404)$$

$$\rho \triangleq \frac{r}{a_0} \quad (405)$$

$$\lambda^2 \triangleq -\frac{2mEa_0^2}{\hbar^2} \quad (406)$$

and redefining  $\chi_l(a_0\rho) \rightarrow \chi_l(\rho)$  since  $\chi$  is not yet known, the equation reduces to

$$\frac{d^2 \chi_l(\rho)}{d\rho^2} - \left( \lambda^2 - \frac{2}{\rho} + \frac{l(l+1)}{\rho^2} \right) \chi_l(\rho) = 0. \quad (407)$$

For  $\rho \gg 1$  the normalizable solution is

$$\chi_l(\rho) \underset{\lim_{\rho \rightarrow \infty}}{\propto} \exp(-\lambda\rho) \quad (408)$$

and for  $\rho \ll 1$

$$\chi_l(\rho) \underset{\lim_{\rho \rightarrow 0}}{\propto} \rho^{l+1}. \quad (409)$$

This motivates the substitution

$$\chi_l(\rho) = \rho^{l+1} \exp(-\lambda\rho) F(2\lambda\rho) \quad (410)$$

for a function  $F(2\lambda\rho)$  to be found. Substituting into Eq. 407 along with

$$y = 2\lambda\rho \quad (411)$$

gives



$$yF''(y) + F'(y)(2(l+1) - y) - \left(l + 1 - \frac{1}{\lambda}\right)F(y) = 0 \quad (412)$$

which is LaGuerre's equation, whose solutions are LaGuerre polynomials  $L_{n-l-1}^{2l+1}(y)$  (which again form a complete orthonormal basis), with  $n > 0$  an integer called the 'principal quantum number'. The energy eigenvalues, substituting back into Eq. 402, are

$$E_n = \frac{-\hbar^2}{2ma_0^2n^2}. \quad (413)$$

This matches the Rydberg formula, and the Bohr model. Overall the solutions are

$$\varphi_{n,l,m}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \exp\left(-\frac{r}{na_0}\right) \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta, \phi). \quad (414)$$

Note that the result is labelled by three integers: these form a set of quantum numbers which can be known simultaneously. It is convenient to define the ket  $|n, l, m\rangle$  such that

$$\langle r, \theta, \phi | n, l, m \rangle = \varphi_{n,l,m}(r, \theta, \phi) \quad (415)$$

in which case we have the following results:

$$\hat{H}|n, l, m\rangle = E_n|n, l, m\rangle \quad (416)$$

$$\hat{L}^2|n, l, m\rangle = \hbar^2 l(l+1)|n, l, m\rangle \quad (417)$$

$$\hat{L}_z|n, l, m\rangle = \hbar m|n, l, m\rangle \quad (418)$$

where

$n > 0$  the principal quantum number

$0 \leq l < n$  the azimuthal quantum number, or orbital quantum number

$-l \leq m \leq l$  the magnetic quantum number ( $z$ -projection of orbital angular momentum).

The set of quantum numbers is completed by the spin quantum number  $s = \pm 1/2$  which we saw in section 5.

### 10.2.1 The Bohr model

Eq. 413 accurately predicts the energy levels of the Hydrogen atom. A much easier way to derive the energy eigenvalues is the Bohr quantisation condition. The reasoning is wrong, but the result is correct. Both this model and the correct Schrödinger equation were attempts to explain the same experimental observations, after all.

Bohr postulated the following:

- (i) Electrons travel along circular orbits (he notes in his paper that elliptical orbits would give the same results).
- (ii) The angular momentum of the electron along these orbits is an integer multiple of  $\hbar$ .
- (iii) The electron can only gain or lose energy via transitions from one orbit to another.

These conditions can be useful in obtaining rough estimates for the energy levels of Hydrogen-like systems.