PH502: Quantum Physics
Lecture Notes

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Contents

Part I

Lecture Notes

1 Qubits

This section covers

- 2-state systems

Suggested reading (all references are from the module's official reading list):

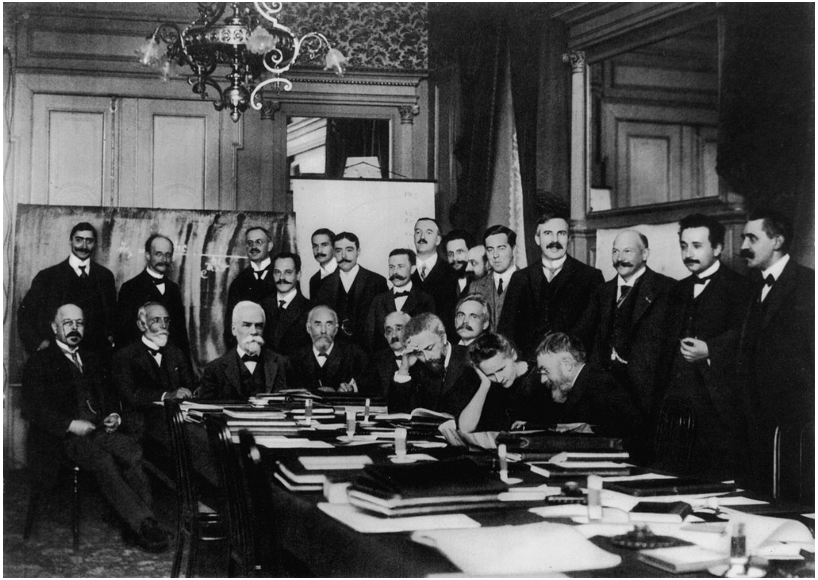
- **Bransden & Joachain Chap. 5**
- **Zettili Chaps. 2-3**
- Feynmann Lectures in Physics Vol. 3 Chap. 1 + Chap. 8
- Rae Chap. 4
- Chester Caps. 1-3

You saw last year that there is a need for a new theory, going beyond Classical Physics: Quantum Physics.

Quantum Physics can be quite counter-intuitive, so it is good to encapsulate the theory in some **postulates**.

The postulates tell us what the theory says at a very basic level. Some of that is counter-intuitive. The idea is that we accept those postulates for the time being, and then deduce other things from them. Over time an intuition develops which replaces our ordinary, "everyday" intuition (which doesn't help in a quantum world).

Quantum Physics is not easy to learn: it gave these guys a headache! [1st Solvay Conference, 1911]



To make learning the postulates easier we will develop the quantum theory initially for the simplest kind of physical system we could think of: a **2-state system**.

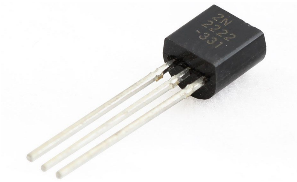
In this section we will explain what such simple system might consist of; deduce, for a particularly simple example, its classical behaviour; and describe without proof its (rather different!) quantum behaviour.

In latter sections we will introduce the postulates and derive the behaviour described here from those postulates.

Later in the course we will generalise and apply the postulates to other systems.

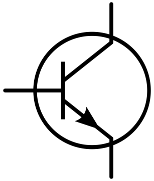
A classical 2-state system can be used as a "**bit**": if we use a state to represent "0" and another state to represent "1", we can use a string of 2-state systems to encode classical information, e.g. 110101 represents the number 53 in binary code.[1]

Present-day computing technology is based on bits implemented through electronic devices such as transistors:[2]



Quantum physics is necessary to understand the workings of the transistor.

Once we know how it works, though, it becomes just an electronic component in a circuit that can be described using the laws of Classical Physics:



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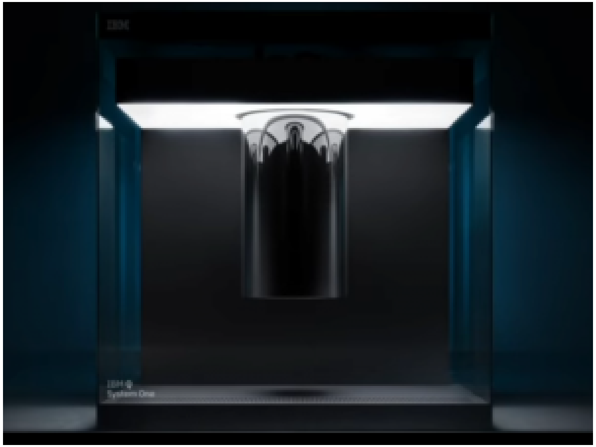
[1] $53 = 1 \times 2^5 + 1 \times 2^4 + 0 \times 2^3 + 1 \times 2^2 + 0 \times 2^1 + 1 \times 2^0$.

[2] Transistor image from https://electrosome.com (accessed 29/Sep/2019).

We are now at the start of a revolution in the way we process information. This is due to the advent of **quantum computing** which is based not on bits, but on"**qubits**": quantum 2-state systems.

Here is a photograph of the IBM Q System One, the first commercial quantum computer, unveiled in January 2019:



Unlike bits, qubits behave in a way that is**essentially quantum-mechanical**.

In 2015, CO_2 emissions from data centres overtook the airline industry.

Quantum computers may be the key to much more energy-efficient information processing.

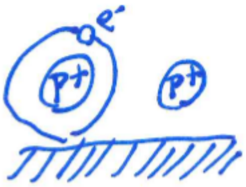
Thus, the study of 2-state systems is not just purely academic.

1.1 2-state systems

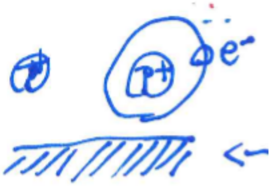
A 2-state system is a system that, at some coarse-grained level of description, can only be in one of two states.

Examples of 2-state systems:

- A classical capacitor: the two states are
  - charged = 1
  - empty = 0
- A single-electron (quantum) capacitor:
  - 1 electron
  - 0 electrons
- The electron in an H_2^+ ion. This molecule has two protons. The two states correspond to the electron being on the left proton or the right proton:

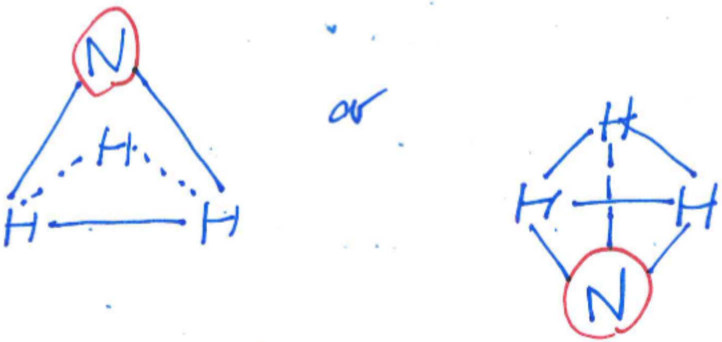


or



We have to assume that the molecule is"clamped" to some substrate i.e. the protons don't move and only the electron can do so.

- The ammonia (NH_3) molecule. Here the two states correspond to the Nitrogen atom being above or below the plan defined by the three Hydrogen atoms:

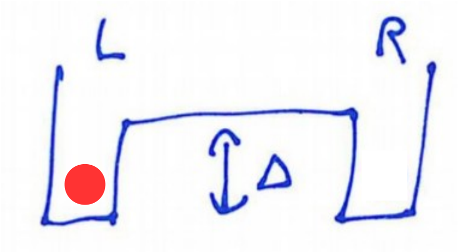
  

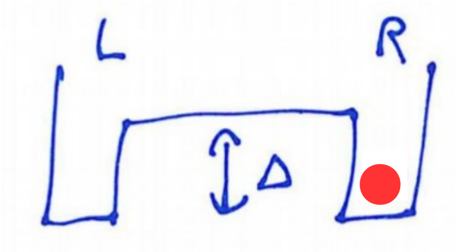
  This is the basis of the MASER (Microwave Amplification by Stimulated Emission of Radiation - the precursor of the LASER).

  There is an excellent discussion of two-state systems using the ammonia molecule as the chief example in Feynmann Vol. 3.

- A superconducting flux qubit. The two states correspond to left- and righ-circulating close-loop currents. Superconductors have the advantage that they can behave quantum-mechanically even on the scale of everyday objects, hence their use in quantum computers.

- A particle that can be in one of two boxes. Here one state corresponds to the particle being in the left-hand box and another state to the right-hand one.





or

The last example may seem a bit academic but it can be realised with current technologies - for example for electrons in engineered nano-structures or for atoms in magneto-optical traps (also, the clamped H_2^+ ion can also be considered to be an example of the particle in two boxes). We will focus on this example in what follows but most of what we will say will be valid quite generally for any 2-state system.

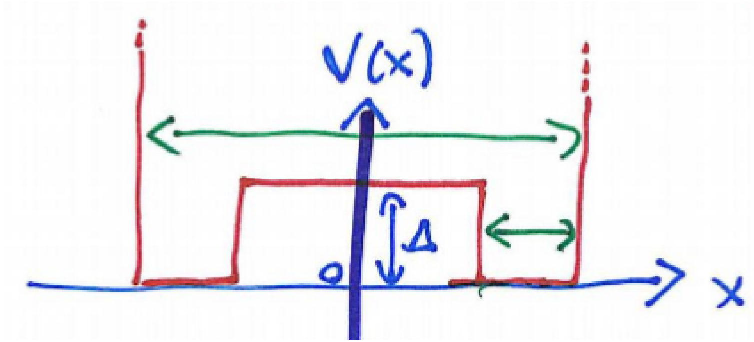
Question:

What is a two-state (or two-level) system?

1.2 Classical 2-state system

Let's see first what we expect from our system in the classical situation. The model can be described by the potential

$$V(x)=\begin{cases}0 & \text{within the boxes}\\ \Delta & \text{within the barrier}\\ \infty & \text{everywhere else}\end{cases} \tag{1.1}$$

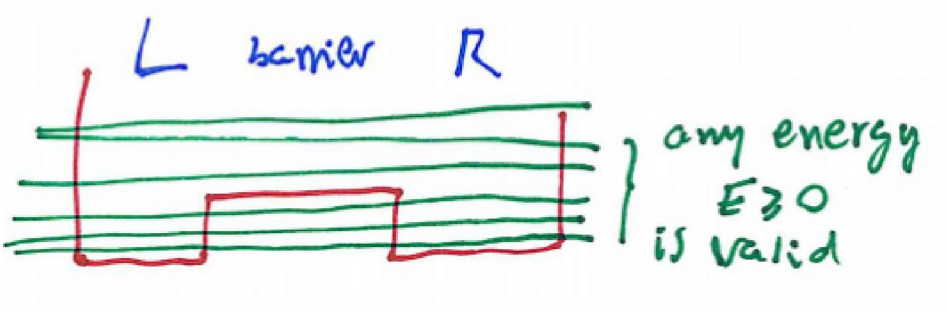


The allowed trajectories for the particle given its energy$E$ are given by solving the equation for conservation of energy:

$$\frac{p^2}{2m}+V(x)=E \tag{1.2}$$

Here$x$ is the particle's position and$p$ is its momentum.

The first thing to note is that this equation has solutions for any energy $E \geq 0$ i.e. there is a **continuuum spectrum** of possible energies.



If x is in the left box (L) or the right box (R) we have $V(x) = 0$ and therefore Eq. (1.2) yields

$$\frac{p^2}{2m} = E \Rightarrow p = \pm\sqrt{2mE}. \tag{1.3}$$

For any positive energy ($E > 0$), this means the particle moves with constant momentum either to the right ($p > 0$) or to the left ($p < 0$). For $E = 0$ the particle is sitting still. For $E < 0$ this is not a solution.

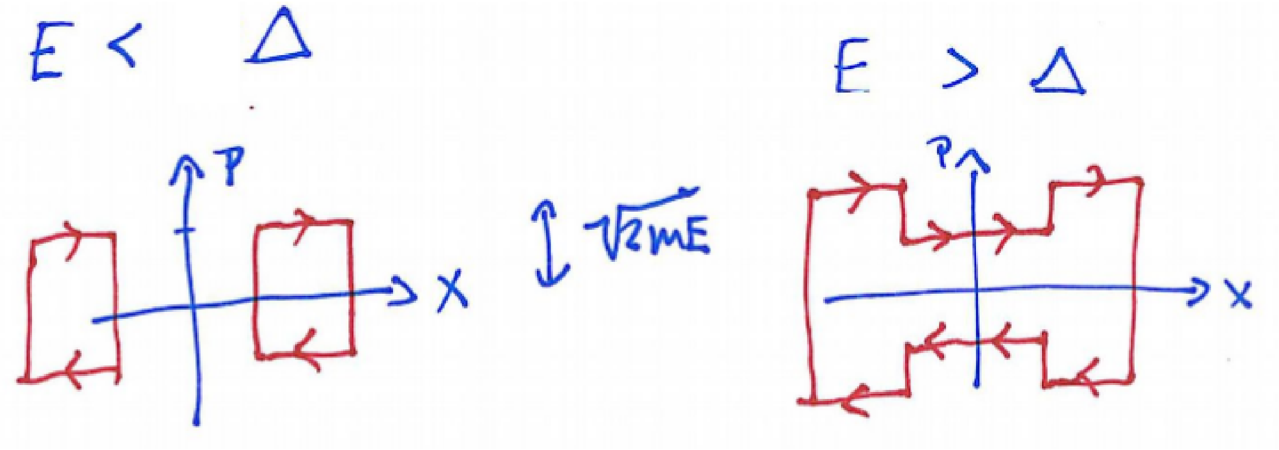
If x is in the barrier region we have

$$\frac{p^2}{2m} + \Delta = E \Rightarrow p = \pm\sqrt{2m(E - \Delta)}. \tag{1.4}$$

Again, the particle moves leftward or rightward with constant momentum, although for a given energy $E > \Delta$ this is a smaller momentum than it had when it was in one of the boxes: when the particle enters the box, it is slowed down y the barrier energy Δ. If $E < \Delta$ then the particle does not have enough energy to penetrate the barrier so it bounces back into the box. This is seen in Eq. (1.4) in that for $E < \Delta$ it yields an imaginary value of p i.e. there are no solutions in the barrier region for such low energies.

Finally, for x outside the above ranges (i.e. neither in the boxes or in the barrier region) the potential is infinity and therefore there are no solutions.

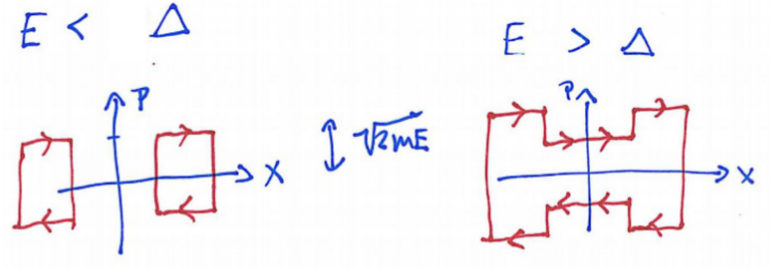
The following phase-space diagrams summarise the particle's motion depending on its energy:



For low energies ($0 \leq E \leq \Delta$) the particle bounces back and forth between the walls of either the L box or the R box, depending on the initial conditions (i.e. the initial value of$x$ and$p$ at time$t = 0$). For higher energies ($E > \Delta$) the particle oscillates between one box and the other, moving more slowly as it traverses the intermediate, barrier region.

Exercise: Classical two-box particle trajectories

Consider the two phase-space diagrams from the previous page:



Use them as your starting point, deduce different plots showing position *vs* time and momentum *vs* time for $E < \Delta$ and for $E > \Delta$. Assume that the particle starts somewhere inside the right-hand side box moving towards the right.

Faced with such system experimentally, here are a few things we could always do, at least in principle:

1. We could **measure** the position x, energy E and direction of travel (the sign of p) at any given time independently and without **perturbing** the system.
2. The above measurements could be carried out in any **order** and could determine the sought values with **certainty**.
3. Once x, E, and $\mathrm{sign}\,(p)$ are known at $t = 0$, the state of the system is completely determined, allowing us to **predict** future values of those variables at any subsequent times.

As we shall see shortly, none of the above three statements hold for a quantum system. Moreover, the energy is not a continuum either.

Assignment: tackle Problem5.

Note: This problem is optional. It is a more realistic description of a classical two-state system, so it further illustrates the preceding discussion.

Before moving on to discuss what the quantum version of our "toy model" does, let us consider in more detail the case when the energy $E < \Delta$. The magnitude of the particle's momentum$|p|$ is then constant and the particle stays in the box where it was found at time $t = 0$ for all $t > 0$. If we adopt a coarse-grained description of the particle's position where we only say whether it is on the L box or the R box, then for such low energies the position of the particle is constant: if it is found in L, it will remain in L, and vice versa, as it does not have enough energy to overcome the barrier between the two boxes. This is also not correct in the quantum case.

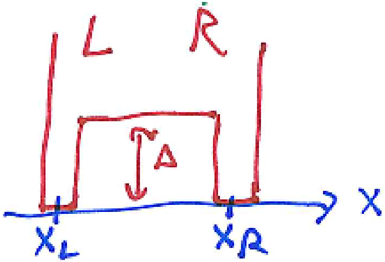
Exercise: Classical two-state period

How long does it take for the particle to move from the left-hand box to the right-hand box? Assume $E \gtrsim \Delta$ so the velocity in the barrier region is much less than inside the boxes, so that time spent in the boxes can be negelcted. The time is $T/2$, where T is the preiod with which the particle oscillates between the two boxes.

1.3 Quantum 2-state system

We now describe what happens in a quantum system that behaves according to the laws of Quantum Physics. In this section we will do this descriptively; in latter sections we will introduce a few simple principles (the Postulates) from which that behaviour can be deduced.

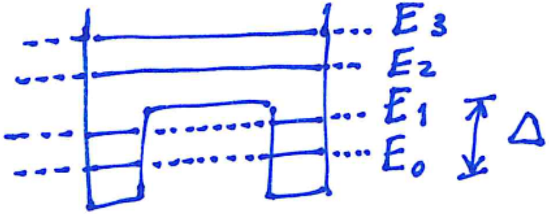
As before, we consider a simple 2-state system consisting of a particle that can be in one of two boxes, separated by an energy barrier:



In a quantum system, just as in a classical system, we can always **measure** the energy E and position$x$ of the particle.

As in the classical case, **energy is conserved**: if I measure the energy$E$ and find a given valueE_n subsequent measurements of energy will always yield the same value.

The first difference we find with the classical case is that the **energy is quantised**: only certain values $E_0, E_1, E_2, ...$ are allowed.



The details of how many energy values are allowed within a certain energy range depend on parameters of the system: barrier height Δ, and the distance between the two boxes, etc.

Let us assume $E < \Delta$, so the particle has zero probability (at least from a classical point of view) of being found in the barrier region.

Let us also take a **coarse-grained** view of the variable x and say that all we are interested in is whether the particle is in the L box or the R box:

$$x \approx x_L \text{ or } x \approx x_R \tag{1.5}$$

For simplicity, let us focus on the case where there are only **two energies** lower than the energy barrier:

$$E_0, E_1 < \Delta \, , \; E_2, E_3, ... > \Delta$$

We will assume the energy of the particle always takes one of these two values. This is called a **two-level system** (or two energy-level system). Clasically-speaking, this is the boring situation, where the particle is stuck in one of the boxes. The quantum case, however, is more interesting...

We now come to another, even more stark difference between the classical and quantum cases called **quantum tunnelling**:

- We recall that in the classical case for $E < \Delta$ the particle is "trapped" in one of the boxes.
- In the quantum case, if we measure x and find, for example, x_L, subsequent measurements of x will yield x_L with certainty only if carried out **immediately** after the first measurement.
- If we instead wait a finite time $t > 0$ before the second measurement is carried out then we can find *either* x_L *or* x_R. In other words, sometimes the particle appears to have "tunnelled" through the barrier, even though it did not have enough energy to do so!

A further difference with the classical case is that the process is **probabilistic** i.e after a known time t we can not know for certain whether the particle will be found at x_L or at x_R. Even if we repeat the experiment again in exactly the same initial conditions, with the same measurements carried out at exactly the same times, the values of t at which the particle will be found at x_L and x_R will vary. There is an intrinsic **uncertainty** in the particle's position.

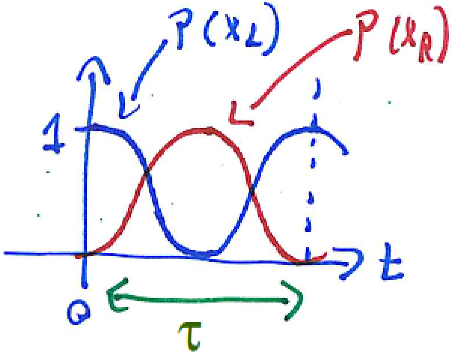
Question: normalisation

Suppose that by repeatedly carrying out the same experiment with our quantum 2-level system we find that at the end of the expeirment the particle is found on the left %62 of the time, on averge. How often will it be found on the right?

Not everything is totally random, though. We can record the statistical frequency with which the particle is found at x_L andx_R at different times, over many identical experiments, and work out the corresponding **probabilities**, $P(x_L)$ and $P(x_R)$. We find that they depend on time in a reproducible way —so the probabilities themselves can be predicted with **certainty**.

Specifically, if $x = x_L$ at $t = 0$, then the time evolution of $P(x_L)$ and $P(x_R)$ is given by harmonic functions (a sin and a cosine) with **period**

$$\tau = \frac{h}{E_1 - E_0}. \tag{1.6}$$



Note that τ depends on the energy difference $E_1 - E_0$ and on Planck's constant h.

Exercise: Planck's constant

Look up Planck's constant, h. Show that the units of the LHS and RHS of Eq. (1.6) are the same.

Assignment: tackle Problem 6.

The last special feature about the quantum problem is that **measurement unavoidably perturbs the system**:

- Suppose we measure the energy and find the value E_0. Subsequent measurements of the energy still yield the value E_0 (see above).
- Suppose we then measure x. We get x_L or x_R with 50% probability. Let us assume that we get x_L.
- Suppose we then measure the energy again. This time we can obtain E_0 or E_1, with 50% probability for each energy value. After the energy is measured, however, the position becomes uncertain once more.

Thus, measuring one property (in our example, x) alters the probability distribution for another (in our example, E): when E is fixed, x is completely uncertain; when x is fixed (i.e. immediately after it's measured) E becomes completely uncertain. This is an instance of **Heisenberg's uncertainty principle.**

(The more common instance of the Heisenberg Uncertinaty Principle refers to the position and momentum of a particle that is moving freely in a vacuum.)

Summary table: Comparison of classical and quantum behaviour (particle in two boxes, $E < \Delta$)

Classical	Quantum
• Energy, position can be measured with certainty.	• Energy, position can be measured with certainty. (Meaning if we measure the same quantity twice, with no delay between measurements, we obtain the same result.)
• Allowed energy values vary continuously. (We focused on the case $E < \Delta$.)	• Energy values are quantised. (We focused on the case $E_0 < E_1 < \Delta < E_3 < E_4 < \ldots$ and $E = E_0$ or E_1: the 2-level system.)
• Energy and position both conserved. (If particle is found at x_L, it remains at x_L.)	• Energy is conserved: measurement of energy yields $E = E_0$ at some time (say, $t = 0$) then subsequent measurements of energy yield $E = E_0$ for all $t > 0$. In contrast, position is not conserved: following a measurement finding $x = x_L$ at $t = 0$, subsequent measurements at $t > 0$ yield sometimes x_L and sometimes x_R – called quantum tunnelling.
• Energy, position can be predicted with certainty.	• The actual values x takes at $t > 0$ are uncertain i.e. cannot be predicted before the measurement takes place. However, their probability distribution is well-defined and evolves in time in a predictable way [period $\tau = h/(E_1 - E_0)$]. • The uncertainties in x and E are related: a measurement of E makes x uncertain while measurement of x makes E uncertain. This is called Heisenberg's uncertainty principle.

Exercise: Classical or Quantum?

You are tasked with evaluating whether a certain device works by using quanutm physics or it can be considered classical. Which of the following features can *only* be compatible with quantum behaviour. Assume that the system can be described by a particle-in-two-boxes model like the one we have been cosnidering (either the classical or the quantum version).

- The energy stored in the device is always one of a series of discrete values.
- Sometimes you find the particle in one of the boxes, but when you check again you find it in a different box.
- The energy soterd in the device is always below a certain limiting value.
- The particle oscillates periodically between the L and R boxes.
- Repeated measurements of the energy always yield the same value, however when you measure position subsequent measurtements of energy can yield different values.

2 Quantum States

This section covers

- Bras and kets.
- Eigenstates and Eigenvalues; Superposition Principle; Probability Amplitudes; Change of basis; Operators.

We now start to describe the postulates of Quantum Mechanics from which the behaviours that we described before can be deduced.

For the time being we will give our postulates for a 2-level system and use this simple case for all our examples. The generalisation of the postulates to more complex situations will come later.

A $\boxed{\text{box}}$ will signal the introduction of each new postulate. Later on we will use it to denote any important result.

2.1 Eigenstates and eigenvalues

States with where a given observable (i.e. measurable property) takes a fixed, well-defined value are called **eigenstates** of that property. The value the property takes is called the **eigenvalue**.Such eigenstate isdenoted by

$$|\text{value of the property}\rangle$$

This is called a“ket” and it is part of Paul Dirac’s“bra-ket” notation, which we will use throughout.

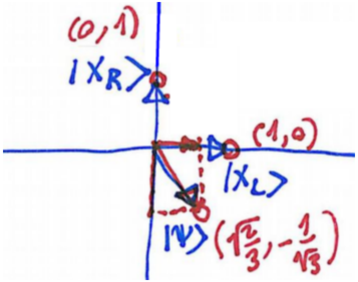
Here are a few examples of kets which denote eigenstates of different properties:

Eigenstates of position	Eigenvalue
$\|x_L\rangle$	x_L
$\|x_R\rangle$	x_R
Eigenstates of energy	
$\|E_0\rangle$	E_0
$\|E_1\rangle$	E_1

2.2 Superposition principle

The eigenstates of a given property can be taken as basis unit vectors of an abstract space: the **Hilbert space**.

For example, $|x_L\rangle$ and $|x_R\rangle$ can be used as the basis unit vectors defining a 2-dimensional Hilbert space:



Now comes our first postulate:

$$\boxed{\text{Every possible state of the system is represented by a point in the Hilbert space.}}$$

In the picture,

- $(1,0)$ represents $|x_L\rangle$;
- $(0,1)$ represents $|x_R\rangle$;
- $\left(\sqrt{2/3}, -1/\sqrt{3}\right)$ represents $|\psi\rangle = \sqrt{\frac{2}{3}}|x_L\rangle - \frac{1}{\sqrt{3}}|x_R\rangle$.

Nomenclature:

- $\langle x_L|\psi\rangle = \sqrt{2/3}$ is the“projection” of $|\psi\rangle$ onto $|x_L\rangle$;
- $\langle x_L|\psi\rangle = -1/\sqrt{3}$ is the“projection” of $|\psi\rangle$ onto $|x_R\rangle$.

2.3 Probability amplitudes

Now, what does it mean when a state $|\psi\rangle$ has finite projection onto two states with different values of the same property?

The projection $\langle x_L|\psi\rangle$ is also called the**probability amplitude** that if the particle is in the state $|\psi\rangle$ a measurement of its position x will find it at x_L. Likewise $\langle x_R|\psi\rangle$ is called the probability amplitude that it finds it at x_R. The corresponding **probabilities** are given by

$$\boxed{\begin{array}{rcl} P(x_L) & = & |\langle x_L|\psi\rangle|^2 \\ P(x_R) & = & |\langle x_R|\psi\rangle|^2 \end{array}}$$

This is valid for any state $|\psi\rangle$ in the Hilbert space.

So a state with projections onto more than one basis vector is one with finite probability of more than one value of the corresponding property.

For our particular example

$$\begin{array}{rcl} \langle x_L|\psi\rangle = \sqrt{\frac{2}{3}} & \Rightarrow & P(x_L) = \frac{2}{3} \approx 67\% \text{ probability} \\ \langle x_R|\psi\rangle = -\sqrt{\frac{1}{3}} & \Rightarrow & P(x_L) = \frac{1}{3} \approx 33\% \text{ probability} \end{array}$$

Evidently

$$P(x_L) + P(x_R) = 2/3 + 1/3 = 100\% \text{ probability}$$

since in our model the particle can only be on the Left or on the Right.

More generally the set of amplitudes

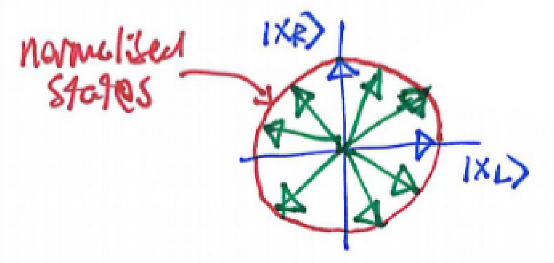
$$\begin{pmatrix} \langle x_L|\psi\rangle \\ \langle x_R|\psi\rangle \end{pmatrix}$$

are called the **state vector** or, equivalently, the **wave function** of the system in the state $|\psi\rangle$.[3]

The state vectors must be **normalised**:

$$\sum_{x=x_L,x_R} P(x) = 1 \Rightarrow |\langle x_L|\psi\rangle|^2 + |\langle x_R|\psi\rangle|^2 = 1$$

Thus, not every point in the Hilbert space corresponds to a possible state of the system:



Assignment: tackle Problem7.

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[3] From here onwards we will write state vectors as 2×1 matrices$\begin{pmatrix} * \\ * \end{pmatrix}$ rather than 1×2 matrices$(*, *)$.

2.4 Change of basis (= change of representation)

We now discuss changes of basis, also called changes of representation.

This is not an additional postulate –it is merely a consequence of the previous two.

Take an arbitrary state e.g.

$$|\psi\rangle = \sqrt{\frac{2}{3}}|x_L\rangle - \frac{1}{\sqrt{3}}|x_R\rangle. \tag{2.1}$$

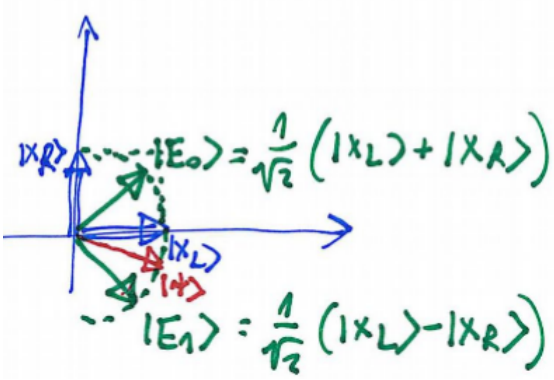
The corresponding state vector is $\begin{pmatrix} \sqrt{2/3} \\ -1/\sqrt{3} \end{pmatrix}$ in the $\{|x_L\rangle, |x_R\rangle\}$ basis. This gives the probabilities $P\left(x_L\right)$ and $P\left(x_R\right)$ that a measurement of$x$ will yield the values x_L or x_R, respectively.

What if we measure energy, E? What are the corresponding probabilities $P\left(E_0\right)$ and $P\left(E_1\right)$?

Write the energy eigenstates in terms of position eigenstates e.g.

$$|E_0\rangle = \frac{1}{\sqrt{2}}\left(|x_L\rangle + |x_R\rangle\right) \tag{2.2}$$

$$|E_1\rangle = \frac{1}{\sqrt{2}}\left(|x_L\rangle - |x_R\rangle\right) \tag{2.3}$$



From (2.2,2.3) we deduce

$$|x_L\rangle = \frac{1}{\sqrt{2}}\left(|E_0\rangle + |E_1\rangle\right) \tag{2.4}$$

$$|x_R\rangle = \frac{1}{\sqrt{2}}\left(|E_0\rangle - |E_1\rangle\right) \tag{2.5}$$

Substitute (2.4,2.5) in (2.1) to express $|\psi\rangle$ in terms of$\{|E_0\rangle, |E_1\rangle\}$:

$$\begin{aligned} |\psi\rangle &= \sqrt{\frac{2}{3}}|x_L\rangle - \frac{1}{\sqrt{3}}|x_R\rangle \\ &= \sqrt{\frac{2}{3}}\left[\frac{1}{\sqrt{2}}\left(|E_0\rangle + |E_1\rangle\right)\right] - \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}\left(|E_0\rangle - |E_1\rangle\right)\right] \\ &= \frac{1}{\sqrt{3}}|E_0\rangle + \frac{1}{\sqrt{3}}|E_1\rangle - \frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}|E_0\rangle + \frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}|E_1\rangle \\ \Rightarrow |\psi\rangle &= \frac{1}{\sqrt{3}}\left(1 - \frac{1}{\sqrt{2}}\right)|E_0\rangle + \frac{1}{\sqrt{3}}\left(1 + \frac{1}{\sqrt{2}}\right)|E_1\rangle, \end{aligned} \tag{2.6}$$

i.e. state vector of$|\psi\rangle$ is

$$\begin{array}{l} \begin{pmatrix} \sqrt{2/3} \\ -1/\sqrt{3} \end{pmatrix} \text{ in } \{|x_L\rangle, |x_R\rangle\} \text{ basis;} \\ \frac{1}{\sqrt{3}}\begin{pmatrix} 1 - 1/\sqrt{2} \\ 1 + 1/\sqrt{2} \end{pmatrix} \text{ in } \{|E_0\rangle, |E_1\rangle\} \text{ basis.} \end{array} \tag{2.7}$$

Assignment: tackle Problem8.

2.5 Complex amplitudes

We now note an important consequence of the SE (3.11): since it involves the imaginary unit$i \equiv \sqrt{-1}$ the amplitudes of probability

$$\begin{aligned} A(t) &= \langle x_L | \psi(t) \rangle \\ B(t) &= \langle x_R | \psi(t) \rangle \end{aligned}$$

are in general complex numbers, each with a**magnitude**and a**phase.**

This means the Hilbert space has to be generalised to allow for**complex coordinates**.

This requires us to generalise the**projection**operation as an**inner product**:

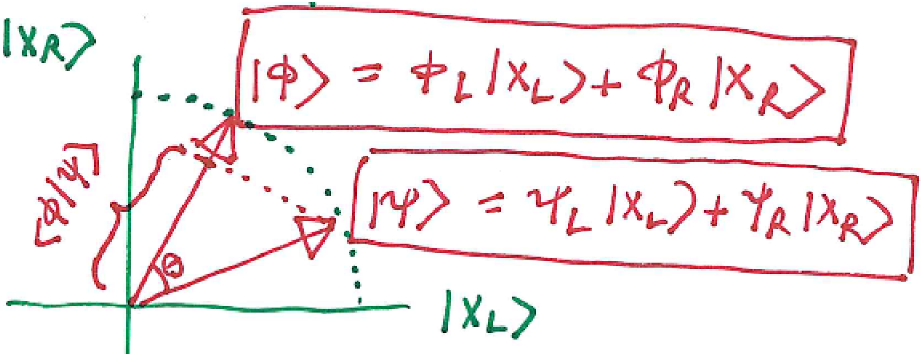
Given two states

$$\begin{aligned} |\phi\rangle &= \phi_L |x_L\rangle + \phi_R |x_R\rangle && (2.8) \\ |\psi\rangle &= \psi_L |x_L\rangle + \psi_R |x_R\rangle && (2.9) \end{aligned}$$

the**projection** of$|\psi\rangle$ onto$|\phi\rangle$ i.e. the**bra-ket**, or**inner product**,$\langle\phi|\psi\rangle$ is defined as

$$\boxed{\langle\phi|\psi\rangle \equiv \begin{pmatrix} \phi_L^* & \phi_R^* \end{pmatrix} \begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = \phi_L^* \psi_L + \phi_R^* \psi_R}. \qquad (2.10)$$

When the amplitudes of probability$\phi_L, \phi_R, \psi_L, \psi_R$ are all real, this is the same as a projection in the usual, geometric sense:

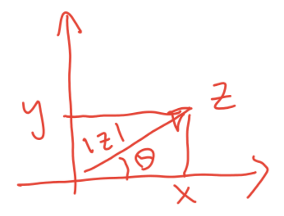


$$\langle\phi|\psi\rangle \equiv \phi_L\psi_L + \phi_R\psi_R \text{ for real amplitudes.}$$

This is a particular case of the inner product (2.10) but is not valid in general.

More generally we are dealing with**complex numbers**:

A quick recap: complex numbers



$$
\begin{aligned}
\text{If } z &= x + iy \text{ with } x, y \text{ real} \\
\text{then } z &= |z|\, e^{i\theta} \\
&\ \text{where } |z| = \sqrt{x^2+y^2} \text{ is the } \textbf{magnitude}\text{, or } \textbf{modulus} \text{ of } z \\
&\ \text{and } \theta \text{ is its } \textbf{phase} \\
\text{We then have } x &= |z| \cos\theta \\
\text{and } y &= |z| \sin\theta. \\
\text{The } \textbf{complex conjugate} \text{ of } z \text{ is } z^* &= x - iy = |z|\, e^{-i\theta}. \\
\text{We thus have } |z|^2 = x^2 + y^2 &= z^* z, \text{ which offers a practical way to calculate} \\
&\ \text{the squared modulus to obtain probabilities.} \\
\text{The } \textbf{real part} \text{ of } z \text{ is } \mathcal{R}(z) &= x \text{ and can be obtained using } \mathcal{R}(z) = \frac{1}{2}(z + z^*). \\
\text{The } \textbf{imaginary part} \text{ of } z \text{ is } \mathcal{I}(z) &= y \text{ and can be obtained using } \mathcal{I}(z) = \frac{1}{2i}(z - z^*).
\end{aligned}
$$

Example: Given the two states

$$\begin{aligned} |\psi\rangle &= \frac{1}{\sqrt{2}}\left(|x_L\rangle + |x_R\rangle\right) \\ |\phi\rangle &= \frac{1}{\sqrt{2}}\left(|x_L\rangle + i|x_R\rangle\right) \end{aligned}$$

compute the projections/inner products$\langle\phi|\psi\rangle$ and$\langle\psi|\phi\rangle$.

Solution:

The state vectors in position basis are

$$|\psi\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ and } |\phi\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix},$$

therefore

$$\begin{aligned} \langle\psi|\phi\rangle &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1^* & 1^* \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ i \end{pmatrix} = \frac{1}{2}(1+i)\,; \\ \langle\phi|\psi\rangle &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1^* & i^* \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & -i \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2}(1-i)\,.\,\blacksquare \end{aligned}$$

Note$\langle\psi|\phi\rangle \neq \langle\phi|\psi\rangle$ i.e. the inner product is **not commutative**.

However, in our example

$$\boxed{\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*}. \tag{2.11}$$

This is **true in general**: inner product reversal is equivalent to complex conjugation.

Assignment: tackle Problem 9.

This allows us to easily **reverse a change of basis**.

For instance, take the transoformation from eigenstates of energy to eigenstates of position in the example on page 29, Eqs. (2.4,2.5):

$$|x_L\rangle = \frac{1}{\sqrt{2}}\left(|E_0\rangle + |E_1\rangle\right) \text{ and } |x_R\rangle = \frac{1}{\sqrt{2}}\left(|E_0\rangle - |E_1\rangle\right).$$

From it we can read off the projections

$$\langle E_0|x_L\rangle = \frac{1}{\sqrt{2}};\ \langle E_1|x_L\rangle = \frac{1}{\sqrt{2}};\ \langle E_0|x_R\rangle = \frac{1}{\sqrt{2}};\ \langle E_1|x_R\rangle = -\frac{1}{\sqrt{2}}. \tag{2.12}$$

Using Eq. (35) we can deduce

$$\langle x_L|E_0\rangle = \frac{1}{\sqrt{2}};\ \langle x_L|E_1\rangle = \frac{1}{\sqrt{2}};\ \langle x_R|E_0\rangle = \frac{1}{\sqrt{2}};\ \langle x_R|E_1\rangle = -\frac{1}{\sqrt{2}} \tag{2.13}$$

from which the inverse of Eqs. (2.4,2.5) follows:

$$|E_0\rangle = \frac{1}{\sqrt{2}}\left(|x_L\rangle + |x_R\rangle\right) \text{ and } |E_1\rangle = \frac{1}{\sqrt{2}}\left(|x_L\rangle - |x_R\rangle\right) \tag{2.14}$$

Assignment: tackle Problem 10.

2.6 Bras, kets and completeness

We now derive some further consequences of the definition of the inner product.

The definition of the inner product for two arbitrary states$|\phi\rangle$, $|\psi\rangle$, Eqs. (2.8-2.10), suggests that we define the bra$\langle\phi|$ corresponding to a ket$|\phi\rangle$ in terms of the bras of the basis states as follows:

$$\boxed{\langle\phi| = \phi_L^*\langle x_L| + \phi_R^*\langle x_R|}\,. \tag{2.15}$$

In effect using this definition the expression$\langle\phi|\psi\rangle$ naturally leads to the correct form of the inner product:

$$\begin{aligned}
\langle\phi|\psi\rangle &= \left(\phi_L^*\langle x_L| + \phi_R^*\langle x_R|\right)\left(\psi_L|x_L\rangle + \psi_R|x_R\rangle\right) \\
&= \phi_L^*\psi_L \underbrace{\langle x_L|x_L\rangle}_{=1} + \phi_R^*\psi_L \underbrace{\langle x_R|x_L\rangle}_{=0} + \phi_R^*\psi_L \underbrace{\langle x_R|x_L\rangle}_{=0} + \phi_R^*\psi_R \underbrace{\langle x_R|x_R\rangle}_{=1} \\
&= \phi_L^*\psi_L + \phi_R^*\psi_R,
\end{aligned}$$

where in the$2^{\underline{\text{nd}}}$ line we have used linearity and in the $3^{\underline{\text{rd}}}$ that$\{|x_L\rangle, |x_R\rangle\}$ is a basis for our Hilbert space.

Using bras and kets we can express the**completeness relation:**

$$\boxed{\begin{array}{c}|x_L\rangle\langle x_L| + |x_R\rangle\langle x_R| = 1\\ \text{completeness relation}\\ \text{for position eigenstates}\\ \text{(2-state system)}\end{array}} \tag{2.16}$$

Proof:

Let$|\psi\rangle = A|x_L\rangle + B|x_R\rangle$ be an arbitrary state.

Let us apply the operator$|x_L\rangle\langle x_L| + |x_R\rangle\langle x_R|$ from the left:

$$\begin{aligned}\left(|x_L\rangle\langle x_L| + |x_R\rangle\langle x_R|\right)|\psi\rangle &= |x_L\rangle\underbrace{\langle x_L|\psi\rangle}_{=A} + |x_R\rangle\underbrace{\langle x_R|\psi\rangle}_{=B}\\ &= A|x_L\rangle + B|x_R\rangle\\ &= |\psi\rangle\end{aligned}$$

so multiplying by$|x_L\rangle\langle x_L| + |x_R\rangle\langle x_R|$ does nothing to the state,Q.E.D.■

Exactly the same applies to the basis vectors of any other representation, e.g.

$$\boxed{\begin{array}{c}|E_0\rangle\langle E_0| + |E_1\rangle\langle E_1| = 1\\ \\ \text{completeness relation}\\ \text{for energy eigenstates}\end{array}} \tag{2.17}$$

The completeness relation can be used to obtain the inner product: given two states

$$\begin{aligned} |\phi\rangle &= \phi_L|x_L\rangle + \phi_R|x_R\rangle \text{ and} \\ |\psi\rangle &= \psi_L|x_L\rangle + \psi_R|x_R\rangle\,, \end{aligned}$$

the projection of$|\psi\rangle$ on$|\phi\rangle$ is

$$\begin{aligned} \langle\phi|\psi\rangle &= \langle\phi|\left(|x_L\rangle\langle x_L| + |x_R\rangle\langle x_R|\right)|\psi\rangle \\ &= \langle\phi|\left(|x_L\rangle\langle x_L|\psi\rangle + |x_R\rangle\langle x_R|\psi\rangle\right) \\ &= \underbrace{\langle\phi|x_L\rangle}_{=\langle x_L|\phi\rangle^*}\langle x_L|\psi\rangle + \underbrace{\langle\phi|x_R\rangle}_{=\langle x_R|\phi\rangle^*}\langle x_R|\psi\rangle \\ &= \phi_L^*\psi_L + \phi_R^*\psi_R, \end{aligned}$$

which is exactly the definition of the inner product (2.10).

Likewise, if the decompositions of the same states in the energy basis are

$$\begin{aligned} |\phi\rangle &= \phi_0|E_0\rangle + \phi_1|E_1\rangle \text{ and} \\ |\psi\rangle &= \psi_{10}|E_0\rangle + \psi_1|E_1\rangle\,, \end{aligned}$$

respectively, then

$$\begin{aligned} \langle\phi|\psi\rangle &= \langle\phi|\left(|E_0\rangle\langle E_0| + |E_1\rangle\langle E_1|\right)|\psi\rangle \\ &= \phi_0^*\psi_0 + \phi_1^*\psi_1. \end{aligned}$$

This shows that**the definition of the inner product is basis-independent:**

$$\boxed{\langle\phi|\psi\rangle = \phi_L^*\psi_L + \phi_R^*\psi_R = \phi_0^*\psi_0 + \phi_1^*\psi_1}\,.$$

In fact, it is not a definition, but simply a consequence of the completeness relations which are in turn consequences of the superposition principle.

So we now know how to change basis (representation) from eigenstates of one property to eigenstates of another property, but *how do we know which are the eigenstates and eigenvalues of a given property*?

2.7 Operators

For every measurable property (e.g. position x or energy E) there is a **linear operator** defined in the system's Hilbert space:

$$\text{states of the system} \overset{operator}{\rightarrow} \text{states of the system}$$

The eigenstates and eigenvalues of the property are those of the corresponding operator.

For example, the operator for position x is denoted $\hat{x}$ and has the following properties:

- Linearity:

$$\hat{x}\left(A|\psi\rangle + B|\phi\rangle\right) = A\hat{x}|\psi\rangle + B\hat{x}|\phi\rangle \tag{2.18}$$

- Eigenstates and eigenvalues:

$$\begin{aligned} \hat{x}|x_L\rangle &= x_L|x_L\rangle && (2.19) \\ \hat{x}|x_R\rangle &= x_R|x_R\rangle && (2.20) \end{aligned}$$

For example,the operator for energy E is denoted $\hat{H}$ and obeys:

- Linearity:

$$\hat{H}\left(A|\psi\rangle + B|\phi\rangle\right) = A\hat{H}|\psi\rangle + B\hat{H}|\phi\rangle \tag{2.21}$$

- Eigenstates and eigenvalues:

$$\hat{H}|E_0\rangle = E_0|E_0\rangle \tag{2.22}$$

$$\hat{H}|E_1\rangle = E_1|E_1\rangle \tag{2.23}$$

2.8 Action of operators on arbitrary states

From the action of an operator on its eigenstates we can work out how it acts on any other state.

- For example, if we know $|\psi\rangle$ in terms of $|x_L\rangle$ and $|x_R\rangle$ then we know how $\hat{x}$ acts on $|\psi\rangle$:

$$\begin{aligned} |\psi\rangle &= A|x_L\rangle + B|x_R\rangle \qquad (2.24) \\ \Rightarrow \hat{x}|\psi\rangle &= \hat{x}\left(A|x_L\rangle + B|x_R\rangle\right) \\ &= A\underbrace{\hat{x}|x_L\rangle}_{=x_L|x_L\rangle} + B\underbrace{\hat{x}|x_{LR}\rangle}_{=x_R|x_R\rangle} \\ \Rightarrow \hat{x}|\psi\rangle &= Ax_L|x_L\rangle + Bx_R|x_R\rangle. \qquad (2.25) \end{aligned}$$

In terms of the state vectors in the position basis/representation,

$$\hat{x}\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} Ax_L \\ Bx_R \end{pmatrix} = \begin{pmatrix} x_L & 0 \\ 0 & x_R \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} \qquad (2.26)$$

i.e. the action of the operator $\hat{x}$ on state vectors in the position representation is described by the diagonal **matrix**

$$\hat{x} = \begin{pmatrix} x_L & 0 \\ 0 & x_R \end{pmatrix}. \qquad (2.27)$$

- Similarly if we know $|\psi\rangle$ in terms of $|E_0\rangle$ and $|E_1\rangle$ then we know how $\hat{H}$ acts on $|\psi\rangle$:

$$\begin{aligned} |\psi\rangle &= C|E_0\rangle + D|E_1\rangle && (2.28) \\ \Rightarrow \hat{H}|\psi\rangle &= CE_0|E_0\rangle + DE_1|E_1\rangle. && (2.29) \end{aligned}$$

  Thus in the energy basis/representation,

$$\hat{H}\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix}\begin{pmatrix} C \\ D \end{pmatrix} \tag{2.30}$$

  so the matrix representing $\hat{H}$ in the energy basis is

$$\hat{H} = \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix}. \tag{2.31}$$

In general, the operator corresponding to any observable takes the form of a **diagonal matrix** whose non-zero elements are the eigenvalues of that observable **in the basis of eigenstates of that observable**.

What if we want$|\psi\rangle$ in one basis e.g.

$$|\psi\rangle = \psi_L|x_L\rangle + \psi_R|x_R\rangle \tag{2.32}$$

and want to find the effect of another operatore.g.$\hat{H}|\psi\rangle$?

- Option 1 (quite tedious):**change basis** of$|\psi\rangle$ [Subsec. 2.4]

  $$\{|x_L\rangle, |x_R\rangle\} \rightarrow \{|E_0\rangle, |E_1\rangle\}\,, \tag{2.33}$$

  then apply$\hat{H}$, then transform back.

- Option 2 (much better!): we want$\hat{H}|\psi\rangle$ in basis$\{|x_L\rangle, |x_R\rangle\}$. Compute amplitudes

  $$\left\langle x_L|\hat{H}|\psi\right\rangle\,,\, \left\langle x_R|\hat{H}|\psi\right\rangle. \tag{2.34}$$

Let's do the latter. Substituting Eq. (2.32),

$$\begin{aligned}\left\langle x_L|\hat{H}|\psi\right\rangle &= \langle x_L|\hat{H}\left(\psi_L|x_L\rangle+\psi_R|x_R\rangle\right)\\ &= \langle x_L|\left(\psi_L\hat{H}|x_L\rangle+\psi_R\hat{H}|x_R\rangle\right)\\ &= \langle x_L|\psi_L\hat{H}|x_L\rangle+\langle x_L|\psi_R\hat{H}|x_R\rangle\\ &= \psi_L\langle x_L|\hat{H}|x_L\rangle+\psi_R\langle x_L|\hat{H}|x_R\rangle \qquad (2.35)\end{aligned}$$

Here we used that

1. $\hat{H}$ is linear and
2. the projection operation$\langle x_L|\ldots$ is linear.

Similarly

$$\left\langle x_R|\hat{H}|\psi\right\rangle=\psi_L\langle x_R|\hat{H}|x_L\rangle+\psi_R\langle x_R|\hat{H}|x_R\rangle \qquad (2.36)$$

Thus in the$\{|x_L\rangle,|x_R\rangle\}$ basis

$$\hat{H}|\psi\rangle=\left(\begin{array}{c}\left\langle x_L\middle|\hat{H}\middle|\psi\right\rangle\\ \left\langle x_R\middle|\hat{H}\middle|\psi\right\rangle\end{array}\right)=\left(\begin{array}{cc}\left\langle x_L\middle|\hat{H}\middle|x_L\right\rangle & \left\langle x_L\middle|\hat{H}\middle|x_R\right\rangle\\ \left\langle x_R\middle|\hat{H}\middle|x_L\right\rangle & \left\langle x_R\middle|\hat{H}\middle|x_R\right\rangle\end{array}\right)\left(\begin{array}{c}\psi_L\\ \psi_R\end{array}\right),$$

so the matrix representing$\hat{H}$ in the position basis is

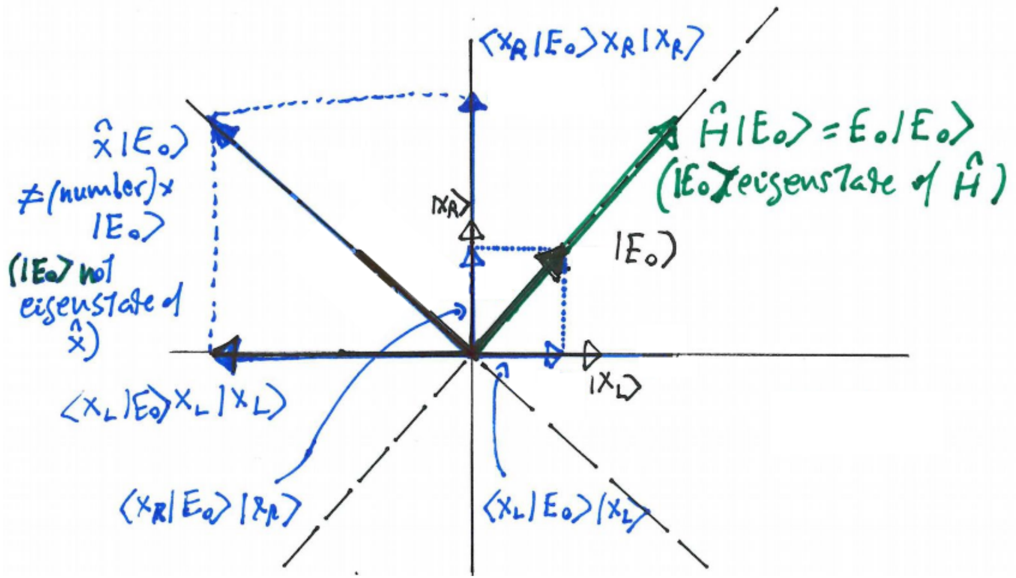
$$\hat{H}=\left(\begin{array}{cc}\left\langle x_L\middle|\hat{H}\middle|x_L\right\rangle & \left\langle x_L\middle|\hat{H}\middle|x_R\right\rangle\\ \left\langle x_R\middle|\hat{H}\middle|x_L\right\rangle & \left\langle x_R\middle|\hat{H}\middle|x_R\right\rangle\end{array}\right) \qquad (2.37)$$

Graphical interpretation of the action of an operator in the Hilbert space:

Eigenstates of a property are only **shortened**, **lengthened**, and/or **reversed** under the action of the corresponding operator. Any **rotation** means that the state is not an eigenstate of that property.

E.g. take $|E_0\rangle$ which is an eigenstate of $\hat{H}$ but not of $\hat{x}$. Compare $\hat{H}|E_0\rangle$ to $\hat{x}|E_0\rangle$:

$$\begin{aligned} \hat{H}|E_0\rangle &= E_0|E_0\rangle && (2.38)\\ \hat{x}|E_0\rangle &= \hat{x}\left(\langle x_L|E_0\rangle|x_L\rangle + \langle x_R|E_0\rangle|x_R\rangle\right) \\ &= \langle x_L|E_0\rangle\hat{x}|x_L\rangle + \langle x_R|E_0\rangle\hat{x}|x_R\rangle \\ &= \langle x_L|E_0\rangle x_L|x_L\rangle + \langle x_R|E_0\rangle x_R|x_R\rangle && (2.39) \end{aligned}$$



2.9 Quantisation

We now discuss how to find what values a property can take i.e. how observables are**quantised**.

As we will see quantisation follows from the postulates introduced above (i.e. not a new postulate).

Since the allowed values of a property are the eigenvalues of the corresponding operator, knowing how the operator acts on arbitrary states allows us to find the permissible (i.e. quantised) values of the property. How? By solving the the**eigenvalue problem.**

Example: Suppose a two-state system with Hamiltonian

$$\hat{H} = \begin{pmatrix} 0 & -T \\ -T & 0 \end{pmatrix} \tag{2.40}$$

in the$\{|x_L\rangle, |x_R\rangle\}$ basis.

$T > 0$ is an unspecified parameter which must be an**energy**e.g.$T = 1$eV.

What are the allowed values of the energy?

Solution:

1. Write the eigenvalue problem:

$$\hat{H}|E_n\rangle = E_n|E_n\rangle. \tag{2.41}$$

2. Write the energy eigenstate$|E_n\rangle$ in the position basis:

$$|E_n\rangle = A_n|x_L\rangle + B_n|x_R\rangle. \tag{2.42}$$

3. Re-write (2.41) as a**matrix eigenvalue problem**:

$$\begin{pmatrix} 0 & -T \\ -T & 0 \end{pmatrix}\begin{pmatrix} A_n \\ B_n \end{pmatrix} = E_n \begin{pmatrix} A_n \\ B_n \end{pmatrix}. \tag{2.43}$$

4. Find the roots of the**characteristic polynomial:**

$$\begin{aligned} \left|\begin{pmatrix} 0 & -T \\ -T & 0 \end{pmatrix} - E_n \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right| &= 0 \qquad (2.44) \\ \Rightarrow \left|\begin{pmatrix} -E_n & -T \\ -T & -E_n \end{pmatrix}\right| &= 0 \\ \Rightarrow E_n^2 - T^2 &= 0 \end{aligned}$$

The two solutions$E_n = \pm T$ are the**eigenvalues of the energy**:

$$\begin{aligned} E_0 &= -T \text{ ground state energy;} \qquad (2.45) \\ E_1 &= +T \text{ excited state energy.} \qquad (2.46) \end{aligned}$$

■

Example: what are the corresponding eigenstates? Express them in the position basis.

In the energy basis, by definition

$$|E_0\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } |E_1\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.47}$$

In position basis, each energy eigenstate$|E_n\rangle$ will have some unknown componentsA_n, B_n:

$$|E_n\rangle = A_n|x_L\rangle + B_n|x_R\rangle = \begin{pmatrix} A_n \\ B_n \end{pmatrix}. \tag{2.48}$$

We want to determine the amplitudesA_n, B_n $(n = 0, 1)$:

1. Go back tot he**eigenvalue problem**(2.43) substituting the**known values of the energy**(2.45,2.46):

$$\begin{aligned} \begin{pmatrix} 0 & -T \\ -T & 0 \end{pmatrix}\begin{pmatrix} A_n \\ B_n \end{pmatrix} &= \mp T\begin{pmatrix} A_n \\ B_n \end{pmatrix} \text{ for } n = \begin{cases} 0 \\ 1 \end{cases} \\ \Rightarrow \begin{pmatrix} -TB_n \\ -TA_n \end{pmatrix} &= \begin{pmatrix} \mp TA_n \\ \mp TB_n \end{pmatrix} \Rightarrow \begin{cases} -TB_n &= \mp TA_n \\ -TA_n &= \mp TB_n \end{cases} \Rightarrow \begin{cases} B_n &= \pm A_n \\ A_n &= \pm B_n \text{ (redundant)} \end{cases} \end{aligned} \tag{2.49}$$

   i.e.

$$B_n = \pm A_n. \tag{2.50}$$

   This does not determine overall size of the amplitudes, only their**relative size and sign**.

2. To find absolute size use**normalisation**:

$$|A_n|^2 + |B_n|^2 = 1. \tag{2.51}$$

Assuming$A_n > 0$ (real)[4][5]

$$A_n^2 + B_n^2 = 1. \tag{2.52}$$

Substituting (2.50) we get

$$A_n^2 + A_n^2 = 1 \Rightarrow A_n = 1/\sqrt{2}. \tag{2.53}$$

3. Substituting (2.53) and (2.50) back into (2.48) we arrive at the**solutions**

Energy	State
$E_0 = -T$	$\vert E_0\rangle = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$ in position basis $= \frac{1}{\sqrt{2}}\left(\vert x_L\rangle + \vert x_R\rangle\right)$
$E_1 = +T$	$\vert E_1\rangle = \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$ in position basis $= \frac{1}{\sqrt{2}}\left(\vert x_L\rangle - \vert x_R\rangle\right)$

■

Assignment: tackle Problem11.

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[4] Amplitudes of probability**can be complex**; we will see this later on in the module.

[5] We could have assumedA_n have any other phase e.g.$A_n = -|A_n|$(negative) or$A_n = |A_n|\, e^{i\theta}$ for any other phaseθ. It doesn't matter as long as the**relative**phase betweenA_n andB_n is consistent with (2.50). This is because probabilities depend on the squared magnitude$|A_n|^2$ which does not change with the sign, or phase, ofA_n.

2.10 Hermitian and self-adjoint operators

Measurements yield real numbers so although amplitudes of probability are complex numbers, eigenvalues must be real.

E.g.

- Energy:$\hat{H}|E\rangle = E|E\rangle$ with$E$ real;
- Position:$\hat{x}|x\rangle = x|x\rangle$ with$x$ real.

Operators whose eigenvalues are real are called**Hermitian**,

therefore

$$\boxed{\text{All operators representing observables must be } \textbf{Hermitian}.}$$

Given an operatore.g. $\hat{H}$ its**adjoint**$\hat{H}^\dagger$ is defined by

$$\boxed{\left\langle \psi \left| \hat{H}^\dagger \right| \phi \right\rangle = \left\langle \phi \left| \hat{H} \right| \psi \right\rangle^*} \tag{2.54}$$

for every pair of states$|\psi\rangle, |\phi\rangle$.

An operatore.g. is**self-adjoint**if

$$\hat{H} = \hat{H}^\dagger. \tag{2.55}$$

In that case its matrix

$$\hat{H} = \begin{pmatrix} H_{1,1} & H_{1,2} \\ H_{2,1} & H_{2,2} \end{pmatrix}$$

in**any basis**has the property

$$H_{n,m} = H^*_{m,n} \tag{2.56}$$

i.e. its transpose is the same as its complex conjugate or, equivalently,

$$H_{1,1} \text{ and } H_{2,2} \quad \text{are} \quad \text{real} \tag{2.57}$$

$$\text{and } H_{2,1} \quad = \quad H^*_{1,2}. \tag{2.58}$$

Theorem:(not proven)

$$\boxed{\text{An operator is self-adjoint if and only if it is Hermitian}}.$$

As a direct consequence, all operators describing observables are self-adjoint.

2.11 Expectation values

The **expectation value**$\langle\hat{x}\rangle$ of an **observable** such as position x in a given **state** (e.g. $|\psi\rangle = A|x_L\rangle + B|x_R\rangle$) is the average value of$x$ obtained after many measurements always with the system prepared in the same intitial state $|\psi\rangle$.

The expectation value is evidently given by

$$\begin{aligned} \langle\hat{x}\rangle &= x_L\,|A|^2 + x_R\,|B|^2 \qquad (2.59)\\ \text{i.e. } \langle\hat{x}\rangle &= x_L\,|\langle x_L|\psi\rangle|^2 + x_R\,|\langle x_R|\psi\rangle|^2 \qquad (2.60)\end{aligned}$$

It is thus easy to calculate an expectation value if we know the **probabilities** of various measurement outcomes.

Assignment: tackle Problem12.

It is trivial to show that the definition in Eq. (2.59) is, in matrix form,

$$\boxed{\langle\hat{x}\rangle = \underset{\substack{\text{bra } \langle\psi| \text{ in}\\ \text{position basis}}}{\begin{pmatrix} A^* & B^* \end{pmatrix}} \underset{\substack{\text{matrix of } \hat{x} \text{ in}\\ \text{position basis}}}{\begin{pmatrix} x_L & 0 \\ 0 & x_R \end{pmatrix}} \underset{\substack{\text{ket } |\psi\rangle \text{ in}\\ \text{position basis}}}{\begin{pmatrix} A \\ B \end{pmatrix}}.} \qquad (2.61)$$

The expectation value can also be expressed compactly using bra-kets:

$$\boxed{\begin{array}{c} \langle\hat{x}\rangle = \langle\psi\,|\hat{x}|\,\psi\rangle \\ \\ \text{expectation value} \\ \text{of position } x \end{array}} \qquad (2.62)$$

Proof:

$$\begin{aligned}
\langle\psi\,|\hat{x}|\,\psi\rangle &= \langle\psi|\hat{x}|\left(A|x_L\rangle + B|x_R\rangle\right) \\
&= A\langle\psi|\ \underbrace{\hat{x}|x_L\rangle}_{=x_L|x_L\rangle} + B\langle\psi|\ \underbrace{\hat{x}|x_R\rangle}_{=x_R|x_R\rangle} \\
&= = x_L A \ \underbrace{\langle\psi|x_L\rangle}_{=\langle x_L|\psi\rangle^*=A^*} + x_R B \ \underbrace{\langle\psi|x_R\rangle}_{=\langle x_R|\psi\rangle^*=B^*} = x_L\left|A\right|^2 + x_R\left|B\right|^2 \ \underline{\text{Q.E.D.}} \ \blacksquare
\end{aligned}$$

Bra-kets allow us to compute the expetation value using any other basis e.g. energy:

$$\begin{aligned}
\langle\hat{x}\rangle &= \langle\psi|\hat{x}|\psi\rangle \\
\text{[insert completeness relation, twice]} &= \langle\psi|\overbrace{\left(|E_0\rangle\langle E_0| + |E_1\rangle\langle E_1|\right)}^{1=}\hat{x}\overbrace{\left(|E_0\rangle\langle E_0| + |E_1\rangle\langle E_1|\right)}^{1=}|\psi\rangle \\
&= (\underbrace{\langle\psi|E_0\rangle}_{=\langle E_0|\psi\rangle^*}\langle E_0| + \underbrace{\langle\psi|E_1\rangle}_{=\langle E_1|\psi\rangle^*}\langle E_1|)\hat{x}(|E_0\rangle\langle E_0|\psi\rangle + |E_1\rangle\langle E_1|\psi\rangle)
\end{aligned}$$

$$\Rightarrow \boxed{\langle\hat{x}\rangle = \underset{\substack{\text{bra } \langle\psi| \text{ in} \\ \text{energy basis}}}{\begin{pmatrix} \langle E_0|\psi\rangle^* & \langle E_1|\psi\rangle^* \end{pmatrix}} \underset{\substack{\text{matrix of } \hat{x} \text{ in} \\ \text{energy basis}}}{\begin{pmatrix} \langle E_0|\hat{x}|E_0\rangle & \langle E_0|\hat{x}|E_1\rangle \\ \langle E_1|\hat{x}|E_0\rangle & \langle E_1|\hat{x}|E_1\rangle \end{pmatrix}} \underset{\substack{\text{ket } |\psi\rangle \text{ in} \\ \text{energy basis}}}{\begin{pmatrix} \langle E_0|\psi\rangle \\ \langle E_1|\psi\rangle \end{pmatrix}}.} \tag{2.63}$$

One can therefore calculate an expectation value directly from state vectors and operator matrices, as an alternative to using the straight definition.

Assignment: tackle Problem13.

2.12 Gauge freedom

One consequence of everything we've seen so far (not a new postulate) is that changing the the**overall phase**of the wave function,

$$|\psi\rangle \to |\psi\rangle e^{i\alpha}, \tag{2.64}$$

does*not*affect**expectation values**such as

$$\begin{aligned} \langle\psi\,|\hat{x}|\,\psi\rangle &\qquad \text{(position)}, \\ \left\langle\psi\left|\hat{H}\right|\psi\right\rangle &\qquad \text{(energy)}, \\ &\qquad \text{etc.} \end{aligned} \tag{2.65}$$

<u>Why?</u> Because probabilities are unaffected:[6]

$$\begin{aligned} |\langle x_L|\psi\rangle|^2 &= \langle x_L|\psi\rangle^* \langle x_L|\psi\rangle & (2.66) \\ &\to \left(\langle x_L|\psi\rangle\, e^{i\alpha}\right)^* \left(\langle x_L|\psi\rangle\, e^{i\alpha}\right) & (2.67) \\ &= \langle x_L|\psi\rangle^*\, e^{-i\alpha}\, \langle x_L|\psi\rangle\, e^{i\alpha} & (2.68) \\ &= |\langle x_L|\psi\rangle|^2\,, & (2.69) \end{aligned}$$

therefore all statistical averages like (2.60) will be unchanged,<u>Q.E.D.</u>■

---

[6] Remember that for any angleα the phase factor$\left(e^{i\alpha}\right)^* = (\cos\alpha + i\sin\alpha)^* = \cos\alpha - i\sin\alpha = e^{-i\alpha}$.

3 State Evolution

This section covers

- The Schrodinger equation. Stationary states. Completeness. Expectation values. Collapse of the state vector.

3.1 Time-evolution (1): the Schrödinger Equation

A general state$|\psi\rangle$will be time-dependent:$|\psi(t)\rangle$.

Its time-evolution is given by**the Schrödinger equation (SE):**

$$\boxed{i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle}. \tag{3.1}$$

Here

- $i \equiv \sqrt{-1}$ (the imaginary unit);
- $\hbar \equiv h/2\pi$ (Planck's constant,$h \approx 6.62607004 \times 10^{-34}$ J s, divided by 2π);
- $\hat{H} = \hat{E}$ (the Hamiltonian operator).

This is one of the most important**postulates** of Quantum Mechanics.

The energy operator is thus a special one as it determines how system evolve in time. That's why it gets its own name ("Hamiltonian").

Let us write

$$|\psi(t)\rangle = A(t)\,|x_L\rangle + B(t)\,|x_R\rangle \tag{3.2}$$

i.e.

$$|\psi(t)\rangle = \begin{pmatrix} A(t) \\ B(t) \end{pmatrix} \text{ in the } \{|x_L\rangle, |x_R\rangle\} \text{ basis.} \tag{3.3}$$

In this representation the position eigenstates$|x_L\rangle, |x_R\rangle$ are taken to be static and the time-dependence of$|\psi(t)\rangle$ is encapsulated in the time-evolution of the corresponding amplitudes of probability

$$\begin{aligned} A(t) &= \langle x_L|\psi(t)\rangle\,; \qquad (3.4)\\ B(t) &= \langle x_R|\psi(t)\rangle\,. \qquad (3.5) \end{aligned}$$

Let us re-write the SE (3.1) as a differential equation for$A(t)$ and$B(t)$:

1. The LHS is

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle &= i\hbar\frac{\partial}{\partial t}\left[A(t)\,|x_L\rangle + B(t)\,|x_R\rangle\right] \\ &= \left[i\hbar\frac{\partial}{\partial t}A(t)\right]|x_L\rangle + \left[i\hbar\frac{\partial}{\partial t}B(t)\right]|x_R\rangle \\ &= \begin{pmatrix} i\hbar\frac{\partial}{\partial t}A(t) \\ i\hbar\frac{\partial}{\partial t}B(t) \end{pmatrix} \text{ in the } \{|x_L\rangle, |x_R\rangle\} \text{ basis.} \qquad (3.6) \end{aligned}$$

2. The RHS

$$\begin{aligned} \hat{H}|\psi(t)\rangle &= \hat{H}\left[A(t)\,|x_L\rangle + B(t)\,|x_R\rangle\right] \\ &= A(t)\,\hat{H}|x_L\rangle + B(t)\,\hat{H}|x_R\rangle \qquad (3.7) \end{aligned}$$

To write this as a vector in the$\{|x_L\rangle, |x_R\rangle\}$ basis we need the projections onto$|x_L\rangle$ and$|x_R\rangle$:

$$\begin{aligned}
\left\langle x_L \left| \hat{H} \right| \psi(t) \right\rangle &= \langle x_L| \left[A(t)\,\hat{H}|x_L\rangle + B(t)\,\hat{H}|x_R\rangle\right] \\
&= A(t)\,\langle x_L|\hat{H}|x_L\rangle + B(t)\,\langle x_L|\hat{H}|x_R\rangle \text{ and} \qquad (3.8) \\
\left\langle x_R \left| \hat{H} \right| \psi(t) \right\rangle &= \langle x_R| \left[A(t)\,\hat{H}|x_L\rangle + B(t)\,\hat{H}|x_R\rangle\right] \\
&= A(t)\,\langle x_R|\hat{H}|x_L\rangle + B(t)\,\langle x_R|\hat{H}|x_R\rangle, \text{ respectively.} \qquad (3.9)
\end{aligned}$$

Thus the RHS is

$$\begin{aligned}
\hat{H}|\psi(t)\rangle &= \begin{pmatrix} A(t)\,\langle x_L|\hat{H}|x_L\rangle + B(t)\,\langle x_L|\hat{H}|x_R\rangle \\ A(t)\,\langle x_R|\hat{H}|x_L\rangle + B(t)\,\langle x_R|\hat{H}|x_R\rangle \end{pmatrix} \\
&= \begin{pmatrix} \langle x_L|\hat{H}|x_L\rangle & \langle x_L|\hat{H}|x_R\rangle \\ \langle x_R|\hat{H}|x_L\rangle & \langle x_R|\hat{H}|x_R\rangle \end{pmatrix} \begin{pmatrix} A(t) \\ B(t) \end{pmatrix} \text{ in the } \{|x_L\rangle, |x_R\rangle\} \text{ basis.} \qquad (3.10)
\end{aligned}$$

3. We now equate the expressions obtained in (3.6) and (3.10):

$$\boxed{i\hbar\frac{\partial}{\partial t}\begin{pmatrix} A(t) \\ B(t) \end{pmatrix} = \begin{pmatrix} \langle x_L|\hat{H}|x_L\rangle & \langle x_L|\hat{H}|x_R\rangle \\ \langle x_R|\hat{H}|x_L\rangle & \langle x_R|\hat{H}|x_R\rangle \end{pmatrix} \begin{pmatrix} A(t) \\ B(t) \end{pmatrix}}, \qquad (3.11)$$

which is the SE in the$\{|x_L\rangle, |x_R\rangle\}$ basis.

As we see the equation involves the matrix representing$\hat{H}$ in that basis. An analogous expression is valid in any other basis.

3.2 Stationary states

Recall the Schrödinger Equation

$$\boxed{i\hbar\frac{\partial}{\partial t}|\psi\left(t\right)\rangle=\hat{H}|\psi\left(t\right)\rangle} \qquad (3.1)$$

features the Hamiltonian operator$\hat{H}$. This makes eigenstates of the energy special.

Consider arbitrary state$|\psi(t)\rangle$. Let us expand

$$|\psi\left(t\right)\rangle=\psi_0\left(t\right)|E_0\rangle+\psi_1\left(t\right)|E_1\rangle \tag{3.12}$$

where$|E_0\rangle,|E_1\rangle$ are the (time-independent) eigenstates of the energy:

$$\begin{aligned}\hat{H}|E_n\rangle &= E_n|E_n\rangle \\ n &= 0,1\end{aligned} \tag{3.13}$$

Obtaining the time-evolution of$|\psi(t)\rangle$ is the same as obtaining that of the probability amplitudes$\psi_0\left(t\right),\psi_1\left(t\right).$

Let's put the Schrödinger equation in terms of the energy-basis probability amplitudes:

1. Put (3.12) into (3.1):

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left[\psi_0\left(t\right)\left|E_0\right\rangle+\psi_1\left(t\right)\left|E_1\right\rangle\right] &= \hat{H}\left[\psi_0\left(t\right)\left|E_0\right\rangle+\psi_1\left(t\right)\left|E_1\right\rangle\right] \\ \Rightarrow\left[i\hbar\frac{\partial}{\partial t}\psi_0\left(t\right)\right]\left|E_0\right\rangle+\left[i\hbar\frac{\partial}{\partial t}\psi_1\left(t\right)\right]\left|E_1\right\rangle &= \psi_0\left(t\right)\hat{H}|E_0\rangle+\psi_1\left(t\right)\hat{H}|E_1\rangle \\ \left[\text{using (3.13)}\right] &= \left[\psi_0\left(t\right)E_0\right]\left|E_0\right\rangle+\left[\psi_1\left(t\right)E_1\right]\left|E_1\right\rangle \end{aligned}$$

2. For the LHS on the second line to equate the RHS on the third line we must have the amplitudes of the two energy eigenstates to be the same:

$$i\hbar\frac{\partial}{\partial t}\psi_0\left(t\right) = \psi_0\left(t\right)E_0 \tag{3.14}$$

$$i\hbar\frac{\partial}{\partial t}\psi_1\left(t\right) = \psi_1\left(t\right)E_1 \tag{3.15}$$

   i.e.

$$\boxed{\begin{array}{c} i\hbar\frac{\partial}{\partial t}\left(\begin{array}{c}\psi_0\left(t\right)\\ \psi_1\left(t\right)\end{array}\right)=\left(\begin{array}{cc}E_0 & \\ & E_1\end{array}\right)\left(\begin{array}{c}\psi_0\left(t\right)\\ \psi_1\left(t\right)\end{array}\right) \\ \\ \text{Schrödiner Equation in energy basis} \end{array}} \tag{3.16}$$

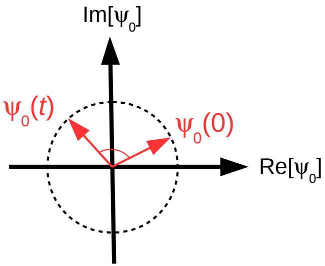
Note the equations for$\psi_0\left(t\right)$ and $\psi_1\left(t\right)$ are **decoupled**.

Let us now solve these equations:

$$(3.14) \Rightarrow \frac{\partial}{\partial t}\psi_0(t) = -i\frac{E_0}{\hbar}\psi_0(t) \tag{3.17}$$

$$|\psi_1(t)|^2 = |\psi_1(0)|^2 \Rightarrow \psi_0(t) = \psi_0(0)\, e^{-i\frac{E_0}{\hbar}t} \tag{3.18}$$

i.e. the time-evolution of $\psi_0(t)$ is just a **multiplication by a phase factor** $e^{-iE_0 t/\hbar}$:



This means the **probability** of measuring energy E_0 is **constant**:

$$\boxed{|\psi_0(t)|^2 = |\psi_0(0)|^2}. \tag{3.19}$$

Likewise

$$(3.15) \Rightarrow \psi_1(t) = \psi_1(0)\, e^{-i\frac{E_1}{\hbar}t} \tag{3.20}$$

$$\Rightarrow \boxed{|\psi_1(t)|^2 = |\psi_1(0)|^2}. \tag{3.21}$$

Consequences:

- If initial state is an eigenstate of the **energy**e.g.

$$\left.\begin{array}{rcl}\psi_0\left(0\right) & = & 1\\ \psi_1\left(0\right) & = & 0\end{array}\right\} \Rightarrow \text{initial state is } |\psi\left(0\right)\rangle = |E_0\rangle$$

  then the time-evolution just changes the overall phase,

$$|\psi\left(t\right)\rangle = e^{-i\frac{E_0}{\hbar}t}|\psi\left(0\right)\rangle$$

  Gauge freedom [Subsec.2.12] then implies that all measurable properties stay the same.

  In other words, $\boxed{\text{energy eigenstates are stationary}}$.

- If we know the energy eigenstates [i.e. the solutions to Eq. (3.13)] then it is straight-forward to compute the time-evolution of any given initial state$|\psi\left(0\right)\rangle$:

  1. Find amplitudes in energy basis:

$$\begin{aligned}\psi_0\left(0\right) &= \left\langle E_0|\psi\left(0\right)\right\rangle, & (3.22)\\ \psi_1\left(0\right) &= \left\langle E_1|\psi\left(0\right)\right\rangle. & (3.23)\end{aligned}$$

  2. The time-evolved states is given by

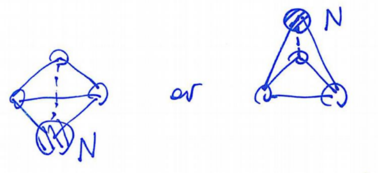
$$|\psi\left(t\right)\rangle = \psi_0\left(t\right)|E_0\rangle + \psi_1\left(t\right)|E_1\rangle, \tag{3.24}$$

     where

$$\begin{aligned}\psi_0\left(t\right) &= \psi_0\left(0\right)e^{-i\frac{E_0}{\hbar}t}; & (3.25)\\ \psi_1\left(t\right) &= \psi_1\left(0\right)e^{-i\frac{E_1}{\hbar}t}. & (3.26)\end{aligned}$$

Example: the ammonia molecule (NH_3)[7]

This has two equivalent configurations, one with the Nitrogen atom above the plane defined by the Hydrogens and another one with the Nitrogen below the Hydrogens:



We we call these two states$|\blacktriangle\rangle$ and $|\blacktriangledown\rangle$, respectively.

The stationary states (i.e. the energy eigenstates) are known to be

$$|E_0\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ and } |E_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ in the } \{|\blacktriangle\rangle, |\blacktriangledown\rangle\} \text{ basis.}$$

How does the state$|\blacktriangle\rangle$ evolve in time?

---

[7] For a much more extensive treatment, see Feynmann in the module's reading list.

Solution:

The intial state is

$$|\psi(0)\rangle = |\blacktriangle\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ in the } \{|\blacktriangle\rangle, |\blacktriangledown\rangle\} \text{ basis.}$$

Follow the two-step process outlined above.

Step 1:

$$\begin{aligned} \langle E_0|\psi(0)\rangle &= \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)^* \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}1 + \frac{1}{\sqrt{2}}0 = \frac{1}{\sqrt{2}} \\ \langle E_1|\psi(0)\rangle &= \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}\right)^* \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}1 - \frac{1}{\sqrt{2}}0 = \frac{1}{\sqrt{2}} \\ \therefore |\psi(0)\rangle &= \frac{1}{\sqrt{2}}|E_0\rangle + \frac{1}{\sqrt{2}}|E_1\rangle \end{aligned}$$

Step 2:

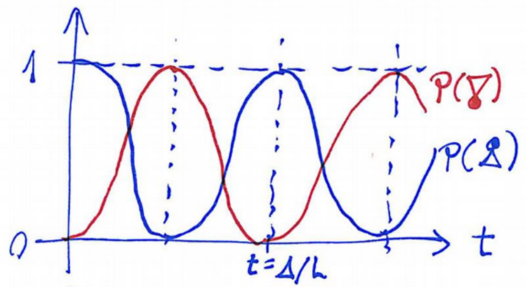
$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{\sqrt{2}}e^{-i\frac{E_0}{\hbar}t}|E_0\rangle + \frac{1}{\sqrt{2}}e^{-i\frac{E_1}{\hbar}t}|E_1\rangle \\ &= \frac{1}{2}e^{-i\frac{E_0}{\hbar}t}\begin{pmatrix} 1 \\ 1 \end{pmatrix} + \frac{1}{2}e^{-i\frac{E_1}{\hbar}t}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ in the } \{|\blacktriangle\rangle, |\blacktriangledown\rangle\} \text{ basis} \\ &= \frac{1}{2}\begin{pmatrix} e^{-i\frac{E_0}{\hbar}t} + e^{-i\frac{E_1}{\hbar}t} \\ e^{-i\frac{E_0}{\hbar}t} - e^{-i\frac{E_1}{\hbar}t} \end{pmatrix} \text{ in the } \{|\blacktriangle\rangle, |\blacktriangledown\rangle\} \text{ basis} \end{aligned}$$

Now substitute$E_0 = -\Delta/2, E_1 = +\Delta/2$ to obtain[8]

$$|\psi(t)\rangle = \begin{pmatrix} \cos\left(\frac{\Delta}{2\hbar}t\right) \\ i\sin\left(\frac{\Delta}{2\hbar}t\right) \end{pmatrix} \text{ in the } \{|\blacktriangle\rangle, |\blacktriangledown\rangle\} \text{ basis } \blacksquare$$

So the amplitudes of probability for the N to be above or below the three H's both vary harmonically. It is most illustrative to look at the actual probabilities that the N will be above or below, respectively:

$$\begin{aligned} P_{\blacktriangle}(t) &= |\langle\blacktriangle|\psi(t)\rangle|^2 = \cos^2\left(\frac{\Delta}{2\hbar}t\right) \\ P_{\blacktriangledown}(t) &= |\langle\blacktriangledown|\psi(t)\rangle|^2 = \sin^2\left(\frac{\Delta}{2\hbar}t\right) \end{aligned}$$



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[8] We've used the well-known relations

$$\begin{aligned} e^{i\alpha} + e^{-i\alpha} &= 2\cos\alpha \\ e^{i\alpha} - e^{-i\alpha} &= 2i\sin\alpha \end{aligned}$$

Thus the molecule oscillates harmonically between the two configurations: initially it is certainly▲, then the probability of▼ increases until it a▼ configuration becomes certain, after which then the probability of▲ starts to increase again and so on, with**period**

$$\tau = \frac{h}{\Delta} \text{ i.e. } \boxed{\tau = \frac{h}{E_1 - E_0}}. \quad (1.6)$$

This is the result we quoted without proof in Subsec. 1.3. Well, here is the proof![9]

Assignment: tackle Problem14.

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[9] The reader who strives for more generality may want to note that the result stems from the fact that the initial state was an equal superposition of two energy eigenstates with energiesE_1 andE_0. It does not relay on any of the details of the particualr problem we were considering.

3.3 Collapse of the state vector

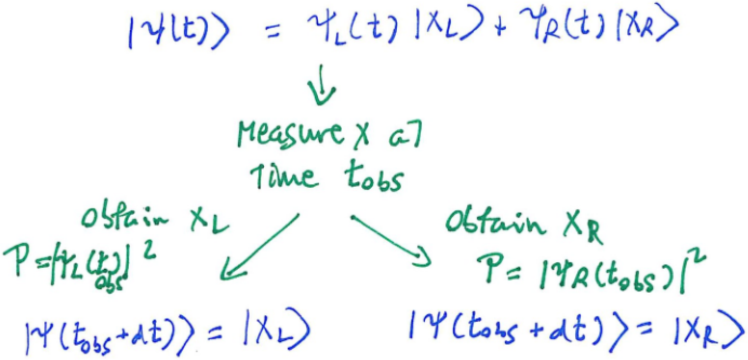
This is one of our final postulates.

Take system in arbitrary state$|\psi\rangle$. Measure property e.g. position$x$. Suppose we obtain valuex_L. Then

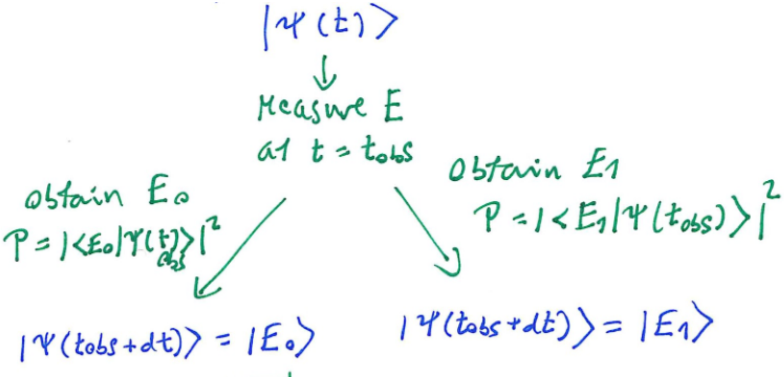
Immediately after the
measurement the system is in the state$|x_L\rangle$.

The wave function has“collapsed”:

The collapse of the wave function is consistent with the result obtained in the measurement:

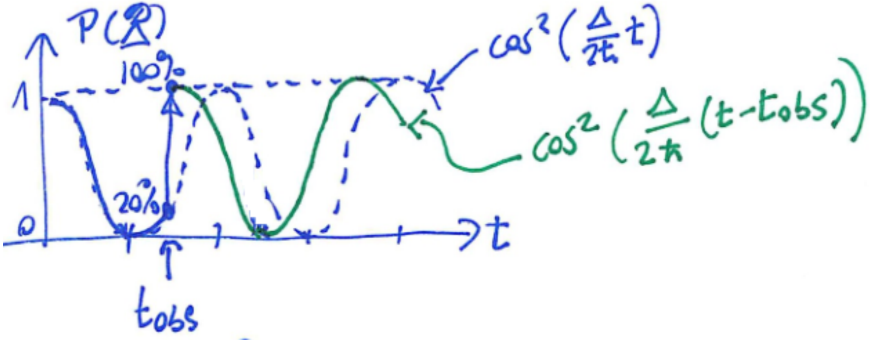


It does not matter which property we are measuring - e.g. an energy measurement of the energy leads to an energy eigenstate:



Note a consequence of wave function collapse is that, after a measurement, we become **certain** of the measured property but this may imply **uncertainty** of some other property, e.g. if we measure energy and get E_0 we are certain to be in the state $|E_0\rangle$ but this state may have an uncertain position e.g. $50\% x_L$, $50\% x_R$. This connects with our discussion of the Heisenberg Uncertainty Principle on page 19.

Wave function collapse applies also to time-dependent states - e.g. an observation of the position of the N atom in an ammonia molecule at time $t_{\rm obs}$ could modify the plot on page 64 thus (assuming the measurement yields ▲):



Thus measurement introduces an additional, non-linear dynamics on top of that given by the Schrödinger equation which is linear and applies while the system is not being observed.

Assignment: tackle Problem 15.

4 Wave Functions

This section covers

- The wavefunction. Probability density.
- Solutions of the Schrodinger equation for simple physical systems with constant potentials: Free particles. Particles in a box. Classically allowed and forbidden regions.

4.1 Three states

Suppose a quantum system with 3 different states,e.g. a particle can be in one of 3 boxes at$x = x_L, x_M, x_R$:

States can be represented by 3-component vectors. Operators decribing observables are3×3 matrices.

In our example a state$|\psi\rangle$ would be represented by a three-component vector,

$$|\psi\rangle = \begin{pmatrix} \psi_L \\ \psi_M \\ \psi_R \end{pmatrix}, \tag{4.1}$$

where $\psi_L \equiv \langle x_L|\psi\rangle$,$\psi_M \equiv \langle x_M|\psi\rangle$, and $\psi_R \equiv \langle x_R|\psi\rangle$ are the amplitudes of probability to find the particle in the left (L), middle (M) and right (R) boxes, respectively. These amplitudes will be subject to a normalisation condition of the form

$$|\psi_L|^2 + |\psi_M|^2 + |\psi_R|^2 = 1. \tag{4.2}$$

The Hamiltonian will be the matrix

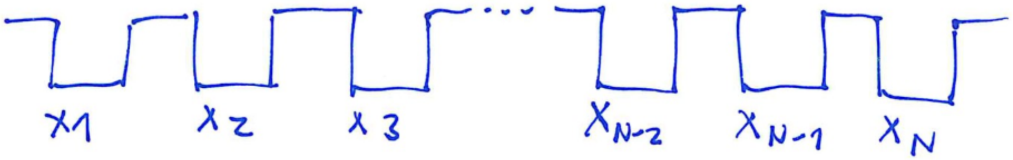
$$\hat{H} = \begin{pmatrix} H_{L,L} & H_{L,M} & H_{L,R} \\ H_{M,L} & H_{M,M} & H_{M,R} \\ H_{R,L} & H_{R,M} & H_{R,R} \end{pmatrix} \tag{4.3}$$

where the matrix elements $H_{L,L} \equiv \left\langle x_L|\hat{H}x_L\right\rangle$, $H_{L,L} \equiv \left\langle x_L|\hat{H}x_L\right\rangle$, etc.

For any 3-state system, $\hat{H}$ will in general have 3 eigenstates $|E_0\rangle, |E_1\rangle, |E_2\rangle$ with 3 corresponding eigenvalues E_0, E_1, E Two or more of these eigensates may be **degenerate**, i.e. the sates may be different but with the same eigenvalue e.g. $E_0 = E_1 < E_2$.

4.2 Many states

We could have many more possible states, e.g. a particle which has available N different boxes:



The the Hilbert space becomes N-dimensional! States are repsented by N-dimensional vectors

$$|\psi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix} \tag{4.4}$$

where the $n^{\underline{\text{th}}}$ amplitude is given by $\psi_n = \langle x_n|\psi\rangle$.

Normalisation implies $\sum_{n=1}^{N} |\psi_n|^2 = 1$.

Operators are represented by $N \times N$ matrices with N eigenstates and up to[10] N eigenvalues.

---

[10] We write "up to" because two or more distinct eigenstates could be degenerate, i.e. share the same eigenvalue.

The state vector for$|\psi\rangle$ can be seen as a function$\psi\left(x_n\right)$ assigning to each allowed valuex_n of the measured property$x$ and amplitude of probability$\langle x_n|\psi\rangle$:

$$\begin{aligned} x_1 &\to \psi_1 = \langle x_1|\psi\rangle \equiv \psi\left(x_1\right) \\ x_2 &\to \psi_2 = \langle x_2|\psi\rangle \equiv \psi\left(x_2\right) \\ &\dots \\ x_N &\to \psi_N = \langle x_N|\psi\rangle \equiv \psi\left(x_N\right) \end{aligned} \tag{4.5}$$

$\psi\left(x_n\right)$ is the"wave function" of state$|\psi\rangle$ in the position representation.

Matrices that are diagonal in a given basis that be viewed as multiplication<u>e.g.</u> in position basis,

$$\hat{x} = \begin{pmatrix} x_1 & & & \\ & x_2 & & \\ & & \ddots & \\ & & & x_N 0 \end{pmatrix} \tag{4.6}$$

$$\therefore \hat{x}|\psi\rangle = \begin{pmatrix} x_1 & & & \\ & x_2 & & \\ & & \ddots & \\ & & & x_N 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix} = \begin{pmatrix} x_1\psi_1 \\ x_2\psi_2 \\ \vdots \\ x_N\psi_N \end{pmatrix} \tag{4.7}$$

which can be written

$$\hat{x}\psi\left(x_n\right) = x_n\psi\left(x_n\right) \tag{4.8}$$

i.e. we multiply the function$\psi\left(x\right)$ by$x$.

4.3 A continuum

What if x (or some other variable) can change continuously?

In this case it no longer makes sense to talk about a state vector however we still can talk about a**wave function**:

$$x \to \psi(x) = \langle x|\psi\rangle$$

The normalisation condition is now an integral:

$$\int_0^L dx\ |\psi(x)|^2 = \int_0^L dx\ |\psi(x)|^2 = 1$$

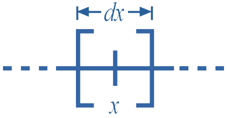
Note the wave function has**dimensions**:

$$[dx] = \text{Length} \Rightarrow \left[|\psi(x)|^2\right] = 1/\text{Length} \Rightarrow [\psi(x)] = 1/\sqrt{\text{Length}}$$

C.f. to state vectors which are dimensionless!

$\psi(x)$ is a probability **density** per unit length:

$$|\psi(x)|^2\, dx = \text{probability of finding particle within } dx \text{ of } x$$



For example, consider the wave function

$$\psi\left(x\right)=A\sin\left(\frac{\pi x}{L}\right)$$

What is the normalisation constant A?

We require

$$1=\int_0^L dx\left|\psi\left(x\right)\right|^2=A^2\int_0^L dx\ \sin\left(x\pi/L\right)^2$$

We now introduce the change of variables

$$y\equiv\frac{\pi x}{L}\Rightarrow dy=\frac{\pi}{L}dx\Rightarrow dx=\frac{L}{\pi}dy.$$

Thus we have

$$1=A^2\frac{L}{\pi}\int_0^\pi dy\ \sin^2 y$$

Now we notice that the integral on the RHS is made up of two identical contributions, one from$y = 0 \ldots \pi/2$ and another one from$y = \pi/2 \ldots \pi$:

$$1 = \int_0^L$$

$$= A^2$$

We thus can write

$$\int_0^\pi dy\, \sin^2 y = 2 \int_0^{\pi/2} dy\, \sin^2 y$$

and recognise the integral on the RHS as a particular instance of

$$\int_0^{\pi/2} \sin^m x\, dx = \frac{m-1}{m} \int_0^{\pi/2} \sin^{m-2} x\, dx$$

from the standard formula sheet (taking $m = 2$), giving

$$\int_0^{\pi/2} dy\, \sin^2 y = \frac{1}{2} \int_0^{\pi/2} dx = \frac{\pi}{4}.$$

Thus

$$1 = A^2 \frac{L}{\cancel{\pi}} 2 \frac{\cancel{\pi}}{4} \Rightarrow \boxed{A = \sqrt{\frac{2}{L}}} \Rightarrow \text{ the wave function is } \psi\left(x\right) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right).$$

Assignment: tackle Problem16.

4.4 Operators in a continuum

For a continuum of possible states, operators are not matrices, but general operations carried out on the functions in that basis.

For example in position representation

$$\hat{x}\psi\left(x\right)=x\psi\left(x\right)\ \text{(because } \hat{x} \text{ is diagonal in the position basis)} \tag{4.9}$$

$$\text{and}\hat{p}\psi\left(x\right)=\frac{\hbar}{i}\frac{\partial}{\partial x}\psi\left(x\right)\ \text{ i.e. } \underbrace{\boxed{\hat{p}=\frac{\hbar}{i}\frac{\partial}{\partial x}}}_{\text{momentum operator in pos. basis}} \tag{4.10}$$

The above expression of the momentum operator int he position basis is our **7th postulate** of Quantum Mechanics.

Knowing $\hat{x}$ and $\hat{p}$ in the position basis allows us to construct any operator, such as the Hamiltonian $\hat{H}$, of a quantum system from that of its classical counterpart. E.g.

$$H_{\text{classical}}=\frac{p^2}{2m}+V\left(x\right)\Rightarrow\hat{H}=\frac{\hat{p}^2}{2m}+V\left(\hat{x}\right)\Rightarrow\boxed{\hat{H}=\frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2+V\left(x\right)} \tag{4.11}$$

Assignment: tackle Problem 17.

The **completeness relation** (Eq. (2.16), can be generalised to a continuum of position eigenstates:

$$\boxed{\begin{array}{c}\int dx|x\rangle\langle x| = 1\\ \text{completeness relation}\\ \text{for position eigenstates}\\ \text{(1D continuum)}\end{array}}. \tag{4.12}$$

This works for any other operator too, e.g. $\int dp|p\rangle\langle p| = 1$.

We use this to generalise our **expectation value** formula (2.63):

- Consider an operator representing an observable property, expressed in a given basis. For instance, the momentum operator$\hat{p}$expressed in the position basis$x$ [Eq. (4.10)].
- The espectation value of the property in question in a state$|\psi\rangle$ whose wave function in that basis is$\langle x|\psi\rangle = \psi\left(x\right)$ can be ontained using

$$\boxed{\left\langle \psi\left|\hat{p}\right|\psi\right\rangle = \int dx\,\psi\left(x\right)^{*}\hat{p}\psi\left(x\right)}. \tag{4.13}$$

Proof: this is analogous to the matrix expression (2.63), valid for a discrete, two-state system (note also that in that case we were computing the expectation value of$x$, not$p$). The proof is also analogous: we want to show that the above expression is the same as

$$\left\langle \psi\left|\hat{p}\right|\psi\right\rangle = \int dp\,P_{\psi}\left(p\right)p,$$

where$P_{\psi}\left(p\right) = \left|\langle p|\psi\rangle\right|^{2}$ is the proabability that, in the state$|\psi\rangle$, a measurement of momentum will yield the value$p$. Indeed

$$\begin{aligned}
\left\langle \psi\left|\hat{p}\right|\psi\right\rangle &= \langle\psi|\hat{p}|\overbrace{\int dp|p\rangle\langle p|}^{1=}\psi\rangle = \int dp\langle p|\psi\rangle\langle\psi|\underbrace{\hat{p}|p\rangle}_{=p|p\rangle} \\
&= = \int dp\langle p|\psi\rangle\underbrace{\langle\psi|p\rangle}_{=\langle p|\psi\rangle^{*}}p\int dp\left|\langle p|\psi\rangle\right|^{2}p,\ \underline{\text{Q.E.D.}}
\end{aligned}$$

4.5 Free particle: plane waves

Consider a particle moving freely in one dimension:

The Hamiltonian is, in position representation,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V \tag{4.14}$$

where the potential energy V is *constant* (independent of x).

The position-representation wave function $\psi(x)$ of a stationary state with energy E is found by solving the time-independent Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\psi(x) = E\psi(x) \Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = (E - V)\psi(x) \tag{4.15}$$

This is solved by taking $\psi(x)$ equal to

$$\underbrace{\boxed{\psi_k(x) = Ae^{ikx}}}_{\textbf{planewave}\text{ with wave vector }k} \tag{4.16}$$

$$\text{with } \underbrace{\boxed{E = \frac{\hbar^2 k^2}{2m} + V}}_{\text{energy of plane wave}} \tag{4.17}$$

Plane wave states $|k\rangle$ with wave functions $\langle x|k\rangle \equiv \psi_k(x)$ are **eigenstates of momentum**:

$$\hat{p}\psi_k(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}Ae^{ikx} = \hbar k Ae^{ikx} = \hbar k\psi_k(x) \Rightarrow \boxed{\hat{p}\psi_k(x) = p\psi_k(x)} \tag{4.18}$$

$$\text{with momentum } \boxed{p = \hbar k} \tag{4.19}$$

Eq. (4.19) is another form of the **de Broglie wave-particle duality** equation: substituting $k = 2\pi/\lambda$ and $\hbar = h/2\pi$,

$$p = \frac{h}{2\pi}\frac{2\pi}{\lambda} \Rightarrow \boxed{p = \frac{h}{\lambda}} \tag{4.20}$$

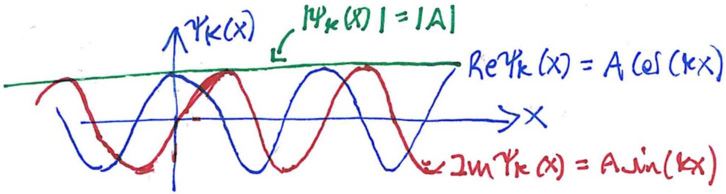
- Note plane wave states are **2-fold degenerate**:

$$\left.\begin{array}{r}\text{Plane wave state } |k\rangle \text{ with momentum } +\hbar k \\ \text{Plane wave state } |-k\rangle \text{ with momentum } -\hbar k\end{array}\right\} \text{same energy } E=\frac{\hbar^2k^2}{2m}+V \tag{4.21}$$

  One of these states is moving to the **left** ($p > 0$) and the other to the **right** ($p < 0$).

- The **probability density** at x is

$$|\psi_k(x)|^2 = \left|Ae^{ikx}\right|^2 = |A|^2 \text{ (constant)} \tag{4.22}$$



  This is consistent with the **Heisenberg uncertainty principle** $\Delta x \Delta p \gtrsim \hbar$: as these are momentum eigenstates, $\Delta p = 0 \Rightarrow \Delta x = \infty$.

- Finally, how do we **normalise** a plane wave? Note that $\int_{-\infty}^{\infty} dx\ |\psi_k(x)|^2 = |A|^2 \int_{-\infty}^{\infty} dx = \infty$ (!!!) The "trick" is to define a *very large* region of length L in which the particle can be found. Then the normalisation condition becomes

$$\int_0^L dx\ |\psi_k(x)|^2 = |A|^2 L = 1 \Rightarrow \boxed{|A| = \frac{1}{\sqrt{L}}} \tag{4.23}$$

  Objection: if the particle is confined to move within $0 \leq x \leq L$, then it is not free!

  Response: sure. Plane waves are an **idealisation**.

4.6 Particle in a box

Suggested reading (all references are from the module's official reading list):

- **Bransden & Joachain Secs. 4.1 to 4.6.**
- **Zettili Secs. 4.1 to 4.7.**

Assume particle in a 1D continuum with Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{4.24}$$

where the potential

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq L \\ \infty & \text{otherwise.} \end{cases} \tag{4.25}$$

This defines a"box" from 0 to$L$ where the particle is confined.

Outside the box we have$E = \infty$ therefore the stationary wave function

$$\psi(x) = 0 \text{ for } x < 0 \text{ or } x > L. \tag{4.26}$$

Inside the box$\psi(x)$ the potential is zero so the time-independent Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x) \tag{4.27}$$

This is the Schrödinger equation for a plane wave.

There are two degenerate solutions for the given energy:

$$\psi(x) = Ae^{ikx} \text{ and } Be^{-ikx} \tag{4.28}$$

with

$$\frac{\hbar^2 k^2}{2m} = E. \tag{4.29}$$

Any linear comnbination can therefore be a solution:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \tag{4.30}$$

We now introduce a**new postulate**applying to continuum wave functions:

$$\boxed{\psi(x) \text{ must be continuous}}$$

Thus

$$\begin{aligned} \psi(0) = 0 \Rightarrow A + B = 0 \quad \text{(i)} \\ \psi(L) = 0 \Rightarrow Ae^{ikL} + Be^{-ikL} = 0 \quad \text{(ii)} \end{aligned} \tag{4.31}$$

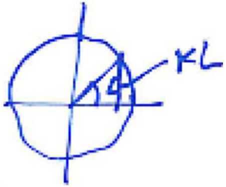
Now from (i) we obtain

$$\psi(x) = A\left(e^{ikx} - e^{-ikx}\right) \Rightarrow \psi(x) = 2iA\sin(kx) \tag{4.32}$$

and from (i) and (ii) we obtain

$$\begin{aligned} A\left(e^{ikL} - e^{-ikL}\right) = 0 &\Rightarrow 2iA\sin(kL) = 0 \\ &\Rightarrow \sin(kL) = 0 \end{aligned}$$

Now, the anglesα for which$\sin(\alpha) = 0$ are$0, \pi$,and multiples thereof. In this case the angle iskL:



$$\Rightarrow \boxed{kL = n\pi,\ n = \pm 1, \pm 2, \pm 3, \ldots}$$

So only some values of the wave number$k$ are allowed. It is quantised.

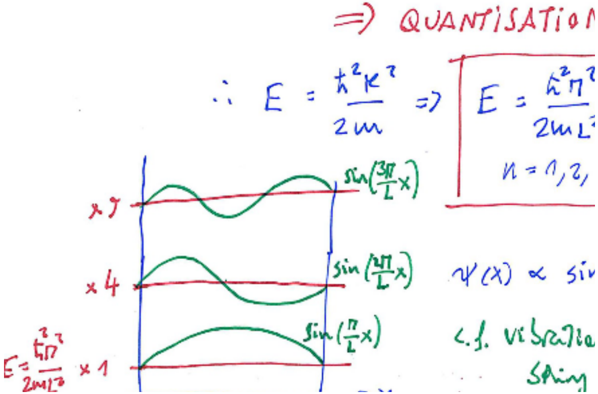
This illustrates an important feature of Quantum Mechanics:

$$\boxed{\text{CONFINEMENT} \Rightarrow \text{QUANTISATION}}$$

Once the wave number$k$ is quantised, so is the energy$E$:

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow \boxed{E = \frac{\hbar^2\pi^2}{2mL^2} n^2,\ n = 1, 2, 3, \ldots}$$

Note $\psi(x) \propto \sin\left(\frac{n\pi x}{L}\right)$ – c.f. vibrations on a string!



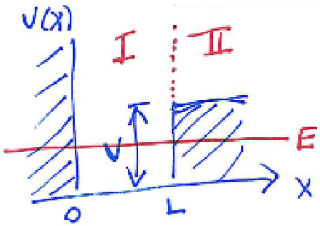
$$\text{Normalisation:} \quad \int_0^L dx \, |\psi(x)|^2 = 1 \Rightarrow |A| = \ldots \text{(see Problems)}$$

Assignment: tackle Problem18.

4.7 Classically-allowed and forbidden regions: the "leaky" box

Let's see what happens when one of the walls of our box is not totally impenetrable i.e. the height of the energy barrier that a classical particle would have to vercome to exit the box is finite:

$$V(x) = \begin{cases} \infty & \text{if } x < 0 \\ 0 & \text{if } 0 \leq x \leq L \\ V & \text{if } x > L \end{cases} \tag{4.33}$$



Let us assume the energy E of the particle obeys $0 < E < V$:

Where can the particle be?

Classically,

- Region I is **allowed** but
- Region II is **forbidden**: $E = p^2/2m + \cancel{V} < \cancel{V} \Rightarrow p^2 < 0 \Rightarrow p$ imaginary (not allowed)

Let us now solve the **quantum** problem:

- Region I: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi\left(x\right) = E\psi\left(x\right) \Rightarrow \psi\left(x\right) = \psi_I\left(x\right)$ where

$$\psi_I\left(x\right) = Ae^{ikx} + Be^{-ikx} \tag{4.34}$$

$$\text{with } E = \frac{\hbar^2 k^2}{2m} \left[\Rightarrow k = \frac{1}{\hbar}\sqrt{2mE}\right] \tag{4.35}$$

[in Eq. (4.35) we have ignored the negative solution without loss of generality].

- Region II: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi\left(x\right) = \left(E-V\right)\psi\left(x\right) \Rightarrow \psi\left(x\right) = \psi_{II}\left(x\right)$ where

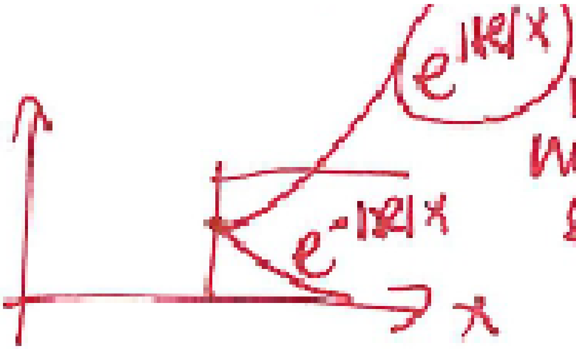
$$\psi_{II}\left(x\right) = Ce^{i\kappa x} + De^{-i\kappa x} \tag{4.36}$$

$$\text{with } E = \frac{\hbar^2 \kappa^2}{2m} + V \left[\Rightarrow \kappa = \frac{1}{\hbar}\sqrt{2m\left(E-V\right)}\right] \tag{4.37}$$

We now note that $E - V < 0 \Rightarrow \kappa = i\left|\kappa\right|$ (imaginary) with $\left|\kappa\right| = \frac{1}{\hbar}\sqrt{2m\left|E-V\right|}$ (real positive). Then $\psi_{II}\left(x\right)$ is a sum of two exponentials,

$$\psi_{II}\left(x\right) = Ce^{-\left|\kappa\right|x} \cancel{+ De^{\left|\kappa\right|x}}, \tag{4.38}$$

and we have crossed the second term because it represents an exponential growth of probability of finding the particle as we probe deeper into the classically-forbidden region, which makes no physical sense (and is not normalisable):



not normalizable

$\Downarrow$

not physical

$\psi(x)$ must be **continuous** at $x = 0$:

$$0 = \psi_I(0) = A + B \Rightarrow B = -A \Rightarrow \psi_I(x) = A\left(e^{-ikx} - e^{-ikx}\right)$$
$$\Rightarrow \psi_I(x) = 2iA\sin(kx) \tag{4.39}$$

$\psi(x)$ must also be **continuous** at $x = L$:

$$\psi_I(L) = \psi_{II}(L) \Rightarrow 2iA\sin(kL) = Ce^{-|\kappa|L} \tag{4.40}$$

We now introduce a **new postulate**:

$$\boxed{\boxed{\text{If } V(x) \text{ is finite, then } \frac{d\psi(x)}{dx} \text{ must be continuous}}} \tag{4.41}$$

What this means is that the wave function must not only lack any jumps in value, but must also be **smooth** (the exception is when the potential jumps to infinity, which is why this postulate did not apply for the box with impenetrable walls, or to the leaky box at $x = 0$).

At $x = 0$ the potential is finite so the new postulate does not apply, however it does at $x = L$:

$$\left.\frac{d\psi_I(x)}{dx}\right|_{x=L} = \left.\frac{d\psi_{II}(x)}{dx}\right|_{x=L} \Rightarrow 2iA\cos(kL)\,k = Ce^{-|\kappa|L}(-|\kappa|) \tag{4.42}$$

Combining Eqs. (4.40) and (4.42) we get a relation between k and κ:

$$\frac{\cancel{2iA}\sin(kL)}{\cancel{2iA}\cos(kL)\,k} = \frac{\cancel{Ce^{-|\kappa|L}}}{\cancel{Ce^{-|\kappa|L}}(-|\kappa|)} \Rightarrow \tan(kL) = -\frac{k}{|\kappa|} \tag{4.43}$$

Both k and κ are related to the energy E *via* Eqs. (4.35,4.37):

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \kappa^2}{2m} + V \Rightarrow \underbrace{\kappa^2}_{=-|\kappa|^2} = k^2 - \frac{2mV}{\hbar^2} \Rightarrow |\kappa| = \sqrt{\frac{2mV}{\hbar^2} - k^2} \tag{4.44}$$

Combining the last two equations we obtain

$$\tan(kL) = -\frac{k}{\sqrt{\frac{2mV}{\hbar^2} - k^2}} \tag{4.45}$$

Eqs. (4.35,4.44,4.45) can be written

$$\tilde{E} = \tilde{k}^2 \tag{4.46}$$

$$|\tilde{\kappa}| = \sqrt{\tilde{V} - \tilde{k}^2} \tag{4.47}$$

$$\tan\left(\tilde{k}\right) = -\frac{\tilde{k}}{\sqrt{\tilde{V} - \tilde{k}^2}} \tag{4.48}$$

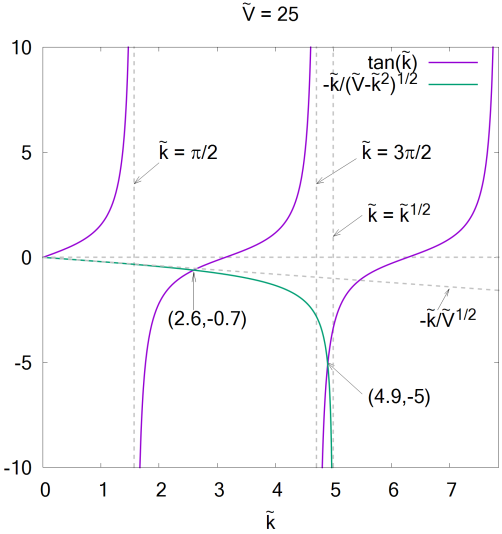
where we have defined dimensionless expressions for the energy, barrier height, wave vector and decay rate by using energy scale $\hbar^2/2mL^2$ and length scale L as the units:

$$\tilde{E} \equiv \left(\frac{\hbar^2}{2mL^2}\right)^{-1} E;\ \tilde{V} \equiv \left(\frac{\hbar^2}{2mL^2}\right)^{-1} V;\ |\tilde{\kappa}| \equiv |\kappa|\, L;\ \tilde{k} \equiv kL \tag{4.49}$$

For a given barrier height $\tilde{V}$ Eq. (4.48) gives the wave vector $\tilde{k}$ and then we can use (4.47) and (4.46) to find the decay rate $|\kappa|$ and energy E.

Eq. (4.48) is a **transcedental** equation that must be solved graphically and/or numerically.

Here's an example ($\tilde{V} = 25$):



The solutions are where the green and purple curves cross.

Since the green curve diverges at $\tilde{k} = \sqrt{\tilde{V}} = 5$, there are only two such crossings [the $k = 0$ solution is not physical].

- First crossing:

$$\tilde{k} \approx 2.6 \Rightarrow k \approx 2.6 L^{-1}$$

$$\Rightarrow \tilde{E} \approx 2.6^2 \approx 6.8 \Rightarrow E = \frac{\hbar^2}{2mL^2}\tilde{E} = \frac{V}{\tilde{V}}\tilde{E} \approx \frac{V}{25}6.8 \approx 0.27V$$

$$\text{and } |\tilde{\kappa}| = \sqrt{\tilde{V} - \tilde{k}^2} \approx \sqrt{25 - 2.6^2} \approx\Rightarrow |\kappa| \approx 4.3L^{-1}$$

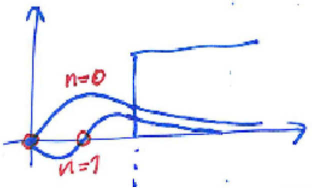
- Second crossing:

$$\tilde{k} \approx 4.91 \Rightarrow k \approx 4.91L$$

$$\Rightarrow \tilde{E} \approx 4.91^2 \approx 24.1 \Rightarrow E = \frac{\hbar^2}{2mL^2}\tilde{E} = \frac{V}{\tilde{V}}\tilde{E} \approx \frac{V}{25}24.1 \approx 0.96V$$

$$\text{and } |\tilde{\kappa}| = \sqrt{\tilde{V} - \tilde{k}^2} \approx \sqrt{25 - 4.91^2} \approx\Rightarrow |\kappa| \approx 0.94L^{-1}$$

Thus both k and κ are finite and the two parts of the wave function combine to give somethign that looks like the partcile-in-a-box solutions, except for this "leaky" box there is some exponentially-decaying amplitude of probability to find the particle in the classically-forbidden Region II:



Note in particular that the ground state has $n = 0$ nodes and the excited state has $n = 1$ nodes, as expected.

For this example there are no higher-energy bound states as the next allowd energy would have $E > V$ and would be allowed classically to escape the box (we have only looked for solutions with $E < V$).

In order to determine the wave function quantitatively, we need to find a relationship betweeen the coefficients A and C. This is provided by

$$2iA\cos(kL)\,k = Ce^{-|\kappa|L}\left(-|\kappa|\right) \Rightarrow 2iA = -\frac{|\kappa|\,L\,e^{-|\kappa|L}}{kL\,\cos(kL)}C$$

which can be used to write (89) in the form

$$\psi_I(x) = -C\frac{|\kappa|\,L\,e^{-|\kappa|L}}{kL\,\cos(kL)}\sin(kx) \tag{4.50}$$

Thus once we know kL and $|\kappa|\,L$ both $\psi_I(x)$ and $\psi_{II}(x)$ are now written in terms of the single coefficient C, which allows us to plot the wave function.

Determining the last coefficient C requires **normalisation**:

$$\int_0^\infty dx\ |\psi(x)|^2 = 1 \Rightarrow \int_0^L dx\ |\psi_I(x)|^2 + \int_L^\infty dx\ |\psi_{II}(x)|^2 = 1. \tag{4.51}$$

Substituting (87) and (93) the normalisation condition becomes

$$|C|^2\left\{\frac{e^{-2|\kappa|L}}{\cos^2(kL)}\int_0^L \sin^2(kx) + \int_0^\infty dxe^{-2|\kappa|x}\right\} = 1$$

To do the first integral on the RHS, change variables:$kx \equiv \beta \Rightarrow dx = d\beta/k$:

$$\int_0^L dx \sin^2(kx) = \frac{1}{k}\int_0^{kL} d\beta \sin^2\beta = \frac{1}{k}\int_0^y d\beta \sin^2\beta = \frac{1}{2k}(y - \sin y \cos y)$$

where we have used the definition$y \equiv kL$ and the standard integral$\int_0^y d\beta \sin^2\beta = \frac{1}{2}(y - \sin y \cos y)$.

The other integral is simply done:

$$\int_0^\infty dx e^{-2|\kappa|x} = -\frac{1}{2|\kappa|}\underbrace{\left[e^{-2|\kappa|x}\right]_0^\infty}_{=0-1} = \frac{1}{2|\kappa|}.$$

Thus[11]

$$|C|^2\left\{\frac{e^{-2|\kappa|L}}{\cos^2(kL)}\frac{1}{2k}\left[kL-\sin(kL)\cos(kL)\right]+\frac{1}{2|\kappa|}\right\}=1$$

$$\Rightarrow |C|=\sqrt{\frac{e^{-2|\kappa|L}}{\cos^2(kL)}\frac{1}{2k}\left[kL-\sin(kL)\cos(kL)\right]+\frac{1}{2|\kappa|}}$$

Assignment: tackle Problem19.

---

[11] Proof:

$$\int_0^y d\beta\sin^2\beta=\int_{\beta=0}^{\beta=y}\underbrace{d\beta\sin\beta}_{=-d\cos\beta}\sin\beta=-\left\{\underbrace{\left[\cos\beta\sin\beta\right]_{\beta=0}^{\beta=y}}_{=\cos y\sin y-\cos 0\underbrace{\sin 0}_{=0}}-\underbrace{\int_{\beta=0}^{\beta=y}\underbrace{d(\sin\beta)}_{=\cos\beta d\beta}\cos\beta}_{=\int_{\beta=0}^{\beta=y}\cos^2\beta d\beta}\right\}$$

$$=-\cos y\sin y+\int_{\beta=0}^{\beta=y}\underbrace{\cos^2\beta}_{=1-\sin^2\beta}d\beta=-\cos y\sin y+\underbrace{\int_0^y d\beta}_{=y}-\int_0^y d\beta\sin^2\beta$$

Taking the last intergal on the RHS to the LHS,

$$2\int_0^y d\beta\sin^2\beta=-\cos y\sin y+y\Rightarrow\int_0^y d\beta\sin^2\beta=\frac{1}{2}\left(y-\cos y\sin y\right).$$

5 Simple Harmonic Oscillator

Suggested reading (all references are from the module's official reading list):

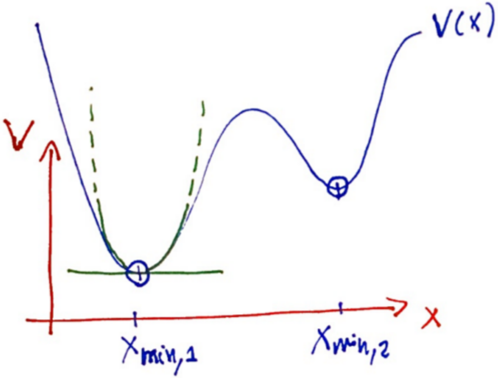
- **Bransden & Joachain (2nd Edition), Sec. 4.7 (see also Sec. 5.6, Eqs. [5.188-...] for an alternative treatment of the same topic).**

This section covers

- The simple harmonic oscillator. Atomic vibrations.

5.1 Harmonic oscillator potentials

Consider a particle moving in one dimension in some potential energy landscape, given by a function$V(x)$:



It is natural for the particle to come to rest near one of the potential energy minima,$x = x_{\min,1}$ or$x_{\min,2}$. Small perturbations will let the particle explore the potential energy landscape*near*the minimum$x = x_{\min}$. To describe such motion one can carry out a Taylor expansion,

$$V(x) = V(x_{\min}) + V'(x_{\min})(x - x_{\min}) + \frac{1}{2}V''(x_{\min})(x - x_{\min})^2 + o(x - x_{\min})^3, \tag{5.1}$$

and cut it to the lowest non-trival order (green dashed line):

$$V(x) \approx V(x_{\min}) + V'(x_{\min})(x - x_{\min}) + \frac{1}{2}V''(x_{\min})(x - x_{\min})^2. \tag{5.2}$$

If we measure potential energy and position from their values at the minimim

$$x_{\text{min}} \equiv 0, V\left(x_{\text{min}}\right) \equiv 0 \tag{5.3}$$

then this is equivalent to approximating$V\left(x\right)$ by

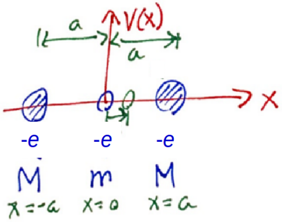
$$\boxed{V_{\text{SHO}}\left(x\right) = \frac{1}{2}kx^2} \tag{5.4}$$

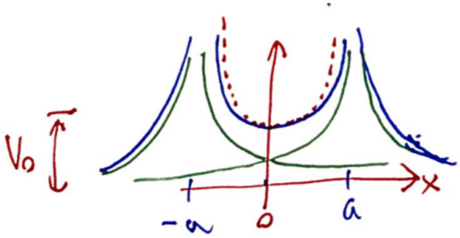
Simple Harmonic Oscillator

where

$$k = \left.\frac{\partial^2 V}{\partial x^2}\right|_{x=0}. \tag{5.5}$$

Example: consider an electron (with charge$-e$) moving along a one-dimensional channel and sitting between two negative ions with charges$-e$ each (all three charges with the same sign):





Find the harmonic potential that best describes the electron near its point of stable equilibrium.

Solution: The Coulomb potential felt by the electron is given by

$$V\left(x\right) = \frac{1}{4\pi\epsilon_0}\frac{\left(-e\right)^2}{\left|x-a\right|} + \frac{1}{4\pi\epsilon_0}\frac{\left(-e\right)^2}{\left|x+a\right|} = \frac{e^2}{4\pi\epsilon_0}v\left(x\right) \text{ with } v\left(x\right) = \frac{1}{\left|x-a\right|} + \frac{1}{\left|x+a\right|} \tag{5.6}$$

Near$x = 0$ the function$V(x)$ has a minumum and therefore can be approximated by a simple harmonic oscillator. To show this we need to carry out the following Taylor expansion:

$$v(x) \approx v(0) + v'(0)\, x + \frac{1}{2} v''(0)\, x^2 \tag{5.7}$$

We use that for$|x| < a$ we have$|x - a| = a - x$, $|x + a| = x + a$ whence

$$v(x) = \frac{1}{a-x} + \frac{1}{a+x}, \tag{5.8}$$

$$v'(x) = \frac{-1}{(a-x)^2}(-1) - \frac{1}{(a+x)^2} = \frac{1}{(a-x)^2} - \frac{1}{(a+x)^2}, \text{ and} \tag{5.9}$$

$$v''(x) = \frac{-1}{(a-x)^4} 2(a-x)(-1) + \frac{1}{(a+x)^2} 2(a+x) = 2\left[\frac{1}{(a-x)^3} + \frac{1}{(a+x)^3}\right]. \tag{5.10}$$

Substituting$x = 0$,

$$v(0) = \frac{2}{a}; \tag{5.11}$$

$$v'(0) = 0 \text{ as we expected } (x = 0 \text{ is a potential energy minimum}); \text{ and} \tag{5.12}$$

$$v''(0) = \frac{4}{a^{3.}} \tag{5.13}$$

Thus

$$v(x) \approx \frac{2}{a} + \frac{2}{a^3} x^2 \tag{5.14}$$

whence

$$V(x) \approx \text{const.} + \frac{1}{2} k x^2 \text{ with } \boxed{k = \frac{e^2}{\pi \epsilon_0 a^3}} \blacksquare \tag{5.15}$$

More generally, any potential$V(x)$ can be approximated by$V_{\mathrm{SHO}}(x)$ near a local potential energy minmum if we choose the“spring constant”k appropriately. Rather conveniently, the resulting problem can be solved exactly. These two facts, taken together, give the SHO paramount importance.

Assignment: Problem20.

5.2 Harmonic oscillator frequency and classical turning points

Classically, the SHO potential$V_{\mathrm{SHO}}(x) = \frac{1}{2}kx^2$ [Eq. (5.4)] leads to a force

$$F(x) = -\frac{\partial V(x)}{\partial x} = -\frac{1}{2}k\frac{\partial x^2}{\partial x} \Rightarrow \underbrace{\boxed{F(x) = -kx}}_{\text{Hooke's law}} \tag{5.16}$$

This is the well-known restoring force of a spring with spring constant$k$.

As we know from first-year Physics the solutions of the classical equation of motion

$$F = m\,d^2x/dt^2 \tag{5.17}$$

leads to simple harmonic motion:

$$x(t) = l\cos(\omega t + \phi)\,,\ \text{where} \tag{5.18}$$

- l is the amplitude of the oscillations i.e. how far the particle gets from the potential energy minimum;
- ϕ is their phase (i.e. it determines the initial value of$x$ for a given amplitude);
- andω is the angular frequency of the oscillations.

A andϕ are set by the initial conditions, whileω is fixed and given by

$$\boxed{\omega = \sqrt{\frac{k}{m}}} \quad \begin{array}{c}\text{frequency of simple}\\ \text{harmonic oscillator}\end{array} \tag{5.19}$$

Exercise (revision): Problem21.

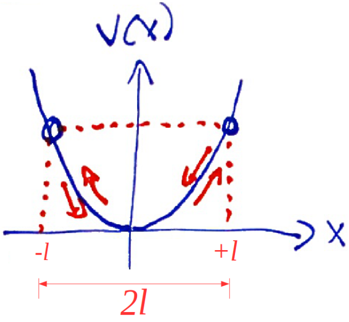
It is customary to use Eq. (5.19) re-write the SHO potential (5.4) in terms of its characteristic frequency:

$$V_{\mathrm{SHO}}(x) = \frac{1}{2} m \omega^2 x^2. \tag{5.20}$$

The **energy** of a classical SHO is

$$E = \underbrace{\frac{p^2}{2m}}_{K} + \underbrace{\frac{1}{2} m \omega^2 x^2}_{U} \tag{5.21}$$

Given the energy E, the particle will oscillate between two **turning points** located at a certain distance l from the origin:



At the turning points the kinetic energy $K = 0$ therefore

$$E = U = \frac{1}{2} m \omega^2 l^2 \tag{5.22}$$

$$\Rightarrow l = \sqrt{\frac{2E}{m\omega^2}} \tag{5.23}$$

5.3 Stationary states: energies and wave functions

To obtain the quantum **Hamiltonian** we replace in the energy equation (5.21) the momentum p and position x with the corresponding **operators**. If we write the operators in **position representation** we obtain

$$\hat{H} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + \frac{1}{2}m\omega^2 x^2 \tag{5.24}$$

which is a particular case of Eq. (4.11) corresponding to the potential in Eq. (5.4).

The **time-independent Schrödinger equation** $\hat{H}|n\rangle = E_n|n\rangle$ takes the form

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right]\psi_n(x) = E_n\psi_n(x) \tag{5.25}$$

where

$$\psi_n(x) = \langle x|n\rangle \tag{5.26}$$

is the position-representation wave function of the $n^{\underline{\text{th}}}$ stationary state, $|n\rangle$, with energy E_n.

We will know **everything** about the SHO potential if we can solve Eq. (5.25).

As we will see it is very useful to introduce the following characteristic **energy scale**:

$$\boxed{E_0 \equiv \frac{\hbar\omega}{2}} \quad \begin{array}{c}\text{characteristic energy scale}\\ \text{of a quantum SHO}\end{array} \tag{5.27}$$

The distance from the origin of the classical turning points corresponding to that energy yields, *via* (5.23), a corresponding **length scale**:

$$\boxed{l_0 = \sqrt{\frac{\hbar}{m\omega}}} \quad \begin{array}{c}\text{characteristic length scale}\\ \text{of a quantum SHO}\end{array} \tag{5.28}$$

Define dimensionless **rescaled variables** that measure energy and position in units of E_0 and l_0, respectively:

$$\begin{array}{rll}\text{Rescaled energy:} & \lambda_n \equiv & E_n/E_0; \\ \text{Rescaled length:} & \xi \equiv & x/l_0.\end{array} \tag{5.29}$$

The stationary Schrödinger equation (5.25) takes the form

$$\frac{\partial^2}{\partial\xi^2}\varphi_n(\xi) + \left(\lambda_n - \xi^2\right)\varphi_n(\xi) = 0 \tag{5.30}$$

where we have defined the ξ-dependent wave function

$$\varphi_n(\xi) \equiv \psi_n(l_0\xi). \tag{5.31}$$

Assignment: Prove this [Problem 22].

Let us now impose the following **physical constraint:**

$$\psi_n(x) \to 0 \text{ as } x \to \infty. \tag{5.32}$$

We know this **must be true** because as $x \to \infty$ the potential $V_{\text{SHO}}(x) \to \infty$ therefore a particle with finite energy E cannot be found at infinity.

This suggests we write

$$\varphi_n(\xi) = \underbrace{N_n}_{\substack{\text{normalisation}\\ \text{factor}}} \quad \underbrace{e^{-\xi^2/2}}_{\substack{\text{Gaussian}\\ \text{decay}}} \quad \underbrace{H_n(\xi)}_{\substack{\text{arbitrary}\\ \text{function}}} \quad . \tag{5.33}$$

There's no loss of generality because $H_n(x)$ is an **arbitrary function**. However if we find solutions where $H_n(x)$ does not grow faster than $e^{\xi^2/2}$, we are done.

Substituting (5.33) in the time-independent Schrödinger equation (5.30) we obtain

$$\frac{\partial^2}{\partial \xi^2} H_n(\xi) - 2\xi \frac{\partial}{\partial \xi} H_n(\xi) + (\lambda_n - 1) H_n(\xi) = 0 \tag{5.34}$$

This is the equation that we have to solve.

We can make use of a bit of**mathematical knowledge:**

A bit of mathematical knowledge: The Hermite Equation

The differential equation

$$\frac{\partial^2}{\partial \xi^2} H(\xi) - 2\xi \frac{\partial}{\partial \xi} H(\xi) + (\lambda - 1) H(\xi) = 0 \tag{5.35}$$

admits solutions with polynomial form inξ if, and only ifλ is equal to

$$\lambda = 2n + 1, \text{ where } n = 0, 1, 2, 3, \ldots \tag{5.36}$$

For each value of$n$ the solution$H(\xi)$ equals

$$H(\xi) = (-1)^n e^{\xi^2} \left(\frac{\partial}{\partial \xi}\right)^n e^{-\xi^2} \text{ where } \left(\frac{\partial}{\partial \xi}\right)^0 \equiv 1. \tag{5.37}$$

The stationary states of the quantum SHO are therefore given by the**quantum number**

$$\boxed{n = 0, 1, 2, 3, \ldots}. \tag{5.38}$$

The corresponding**energies**are

$$E_n = E_0 \lambda_n \Rightarrow \boxed{E_n = \hbar\omega\left(\frac{1}{2} + n\right)}. \tag{5.39}$$

Note that

- The energy levels are**equally spaced** with energy difference

  $$\Delta E = E_{n+1} - E_n = \hbar\omega.$$

  This is seen for example in**vibrational spectra**of molecules.

- The lowest possible energy is not zero, as in the classical case, but

  $$E_0 = \hbar\omega/2.$$

  This is called the**zero-point energy** and is an intrinsically quantum effect.

Assignment: tackle Problem23.

Finally, the**wave functions** are

$$\psi_n\left(x\right) = \varphi_n\left(x/l_0\right) \Rightarrow \boxed{\psi_n\left(x\right) = N_n e^{-\left(x/l_0\right)^2/2} H_n\left(x/l_0\right)}, \tag{5.40}$$

where$H_n\left(\xi\right)$ is the$n$<u>th</u> Hermite polynomial [given by Eq. (5.37)].

The**normalisation factor**N_n is determined, as usual, by requiring that$\int_{-\infty}^{\infty} dx \left|\psi_n\left(x\right)\right|^2 = 1$. Using the following mathematical result for Hermite polynomials:

$$\int_{-\infty}^{\infty} d\xi\, e^{-\xi^2} H_n\left(\xi\right)^2 = \sqrt{\pi}2^n n! \tag{5.41}$$

one can show that

$$\boxed{N_n = \frac{1}{\sqrt{l_0\sqrt{\pi}2^n n!}}}. \tag{5.42}$$

Let us work out the two simplest**examples**:

<u>Example:</u> SHO ground state ($n = 0$):

Energy:$E_0 = \frac{\hbar\omega}{2}$.

Hermite polynomial:$H_0\left(\xi\right) = \underbrace{\left(-1\right)^0}_{=1} e^{\xi^2} \underbrace{\left(\frac{\partial}{\partial\xi}\right)^0}_{=1} e^{-\xi^2} = e^{\xi^2} e^{-\xi^2} = 1.$

$\Rightarrow$Wave function:$\psi_0\left(x\right) = N_0 e^{-\left(x/l_0\right)^2/2} H_0\left(x/l_0\right) = N_0 e^{-\left(x/l_0\right)^2/2} = N_0 e^{-\frac{x^2}{2l_0^2}} \left[= N_0 e^{-\frac{x^2 m\omega}{2\hbar}}\right]$

Normalisation factor:$N_0 = \frac{1}{\sqrt{l_0\sqrt{\pi}2^0 0!}} = \frac{1}{\sqrt{l_0\sqrt{\pi}}}.\blacksquare$

<u>Example:</u> SHO ground state ($n = 1$):

Energy:$E_0 = \frac{3}{2}\hbar\omega$.

Hermite polynomial:$H_1\left(\xi\right) = \left(-1\right)^1 e^{\xi^2} \frac{\partial}{\partial\xi} e^{-\xi^2} = -e^{\xi^2} e^{-\xi^2}\left(-2\xi\right) = 2\xi.$

$\Rightarrow$Wave function:$\psi_1\left(x\right) = N_1 e^{-\left(x/l_0\right)^2/2} H_1\left(x/l_0\right) = N_1 e^{-\left(x/l_0\right)^2/2} 2\xi = N_1 e^{-\frac{x^2}{2l_0^2}} \frac{2x}{l_0} \left[= N_1 e^{-\frac{x^2 m\omega}{2\hbar}} 2\sqrt{\frac{m\omega}{\hbar}} x\right]$

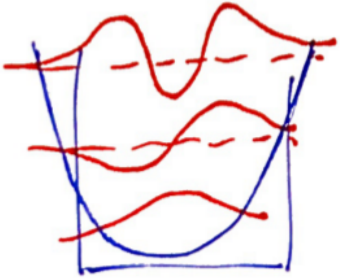
Normalisation factor:$N_1 = \frac{1}{\sqrt{l_0\sqrt{\pi}2^1 1!}} = \frac{1}{\sqrt{2l_0\sqrt{\pi}}}.\blacksquare$

The next two states are left as an exercise:

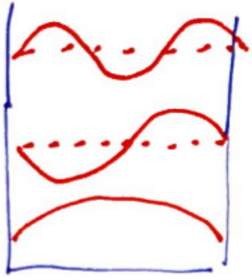
Assignment: tackle Problem24.

In general, we find that the $n^{\underline{\text{th}}}$ stationary wave function has n nodes (changes of sign), just like the particle-in-a-box wave functions:

Ground state, 1st excited state, and 2nd excited state ...



... for a simple harmonic oscillator [Subsect. 5.3].



... for a particle in a box [Subsec. 4.6].

This is a **universal feature** for quantum particles moving in one dimension.[12]

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[12] It is worth noting also the differences:

- Firstly, the quantum number we use to count SHO states runs from 0 for the ground state, to 1 for the 1st excited state, 2 for the second excited state, and so on. In contrast, for the particle-in-a-box we used 1 for the ground state, 2 for the 1st excited state, etc. So wereas for the SHO n is the number of nodes, for the particle-in-a-box $n-1$ is the number of nodes.
- Secondly, wereas the particle-in-a-box wave functions become exactly zero abruptly at the edges of the box, the SHO wave functions tend to zero smoothly and asymptotically at $x \to \pm\infty$. Thus while the number of nodes, i.e. changes of sign of the wave function, is the same in both cases, the number of zeros is not: the partilce-in-a-box wave functions have two additional zeros, compared to the SHO ones.

We have so far stated our results**without proof**. To conclude, we will show explicitly,**by substitution**,that our wave functions and energies solve the TI Schrödinger equation for the simplest case,$n = 0$:

1. Substitute the wave function$\psi(x) = Ae^{-\frac{x^2}{2l^2}}$ into the time-independent Schrödinger equation (5.25):

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\cancel{A}e^{-\frac{x^2}{2l^2}} + \frac{1}{2}m\omega^2x^2\cancel{A}e^{-\frac{x^2}{2l^2}} = E\cancel{A}e^{-\frac{x^2}{2l^2}}$$

2. The first term on the LHS involves

$$\frac{\partial^2}{\partial x^2}e^{-\frac{x^2}{2l^2}} = \frac{\partial}{\partial x}\left(e^{-\frac{x^2}{2l^2}}\frac{-\cancel{2}x}{\cancel{2}l^2}\right) = e^{-\frac{x^2}{2l^2}}\frac{-x}{l^2}\frac{-x}{l^2} + e^{-\frac{x^2}{2l^2}}\frac{-1}{l^2} = \frac{1}{l^2}\left(\frac{x^2}{l^2} - 1\right)e^{-\frac{x^2}{2l^2}},$$

   thus the equation becomes

$$\frac{-\hbar^2}{2m}\frac{1}{l^2}\left(\frac{x^2}{l^2} - 1\right)\cancel{e^{-\frac{x^2}{2l^2}}} + \frac{1}{2}m\omega^2x^2\cancel{e^{-\frac{x^2}{2l^2}}} = E\cancel{e^{-\frac{x^2}{2l^2}}}$$

3. We now put all the terms involving$x$ on one side of the equation and those not involving$x$ on the other side:

$$\left(\frac{-\hbar^2}{2m}\frac{1}{l^4} + \frac{1}{2}m\omega^2\right)x^2 = E - \frac{\hbar^2}{2m}\frac{1}{l^2}$$

4. Since the RHS does not depend on$x$, the LHS must not depend on$x$ either. The only way this can be true is if

$$\frac{-\hbar^2}{\cancel{2}m}\frac{1}{l^4} + \frac{1}{\cancel{2}}m\omega^2 = 0 \Rightarrow l = \sqrt{\frac{\hbar}{m\omega}}$$

5. That makes the LHS equal to zero, so the RHS must equal zero too:

$$E - \frac{\hbar^2}{2m}\frac{1}{l^2} = 0 \Rightarrow E = \frac{\hbar^2}{2m}\frac{1}{l^2} = \frac{\hbar^{\cancel{2}}}{2\cancel{m}}\frac{\cancel{m}\omega}{\cancel{\hbar}} = \frac{\hbar\omega}{2}, \text{ Q.E.D.}$$

Assignment: tackle Problem25.

Assignment: tackle Problem26.

6 Quantum tunneling

Suggested reading

- **Bransden and Joachain Sections 3.2, 4.2 and 4.3.**
- Rae Section 2.5.

This section covers

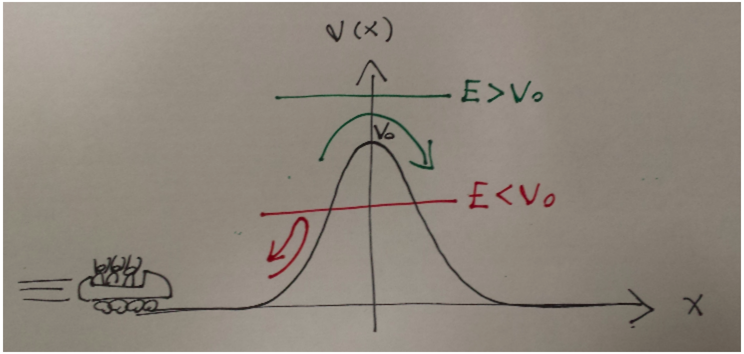
- Reflection and transmission of particles incident onto a potential barrier. Probability flux. Tunnelling of particles.

6.1 What is quantum tunnelling?

This topic deals with one of those suprising aspects of quantum systems: their ability to“tunnel” between states that would normally be separated by an insurmountable**energy barrier**. To explain what we mean by quantum tunnelling, we have to discuss first what we mean by an energy barrier, both in the classical and quantum descriptions of matter.

Energy barriers in Classical Mechanics

Imagine, for example, a large“hill” on a roller-coaster:

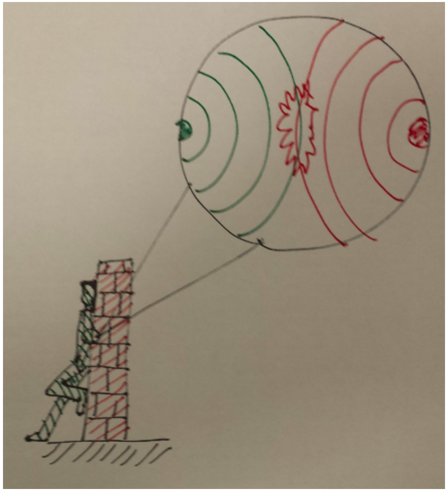


The car comes with some energy,E. Initially, this is in the form of kinetic energy,$E = p^2/2m$ (where$m$ is the mass of the car,$p = mv$ is its momentum, where$v$ is the velocity). This then gets partially converted to potential energy,$V(x)$, as the car climbs up the hill (the car does not have any source of energy: roller-coaster cars usually do not have an engine, they are pulled up the first hill by an external mechanism and then they are let go). The hill represents a barrier that the car has to overcome. If the hill has height$h$, the potential energy of the train when it reached the top is$mgh \equiv V_0$, where$g \approx 9.8\,\mathrm{ms}^{-1}$ is the acceleration due to gravity.

There are two distinct options:

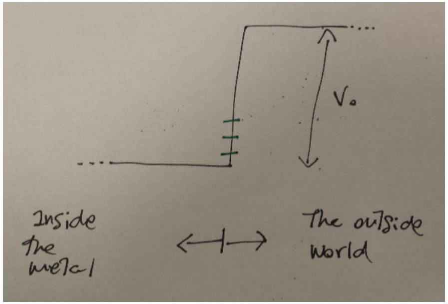
- If the train has energy$E > V_0$, then when it reaches the top of the barrier it will still be moving to the right, albeit with reduced velocity (so as to keep the total energy,$E = p^2/2m + V(x)$, constant) and so it will overcome the barrier and continue on the other side.
- In contrast, if the energy is$E < V_0$, then before the car reaches the top of the hill all its kinetic energy will have been converted to potential energy, and conservation of energy will prevent it from advancing further. The car will reverse its motion and go back the way it came.

Barriers like these occur everywhere. I can lean against a wall withouut falling because the electrons in the outler layers of my molecules are electrostacially-repelled by those in the bricks or concrete the wall is made of. This is a huge energy barrier, much bigger than the force my weight exerts on the wall when I lean on it. It would be very surprising if I suddenly fell to the opposite side of the wall.



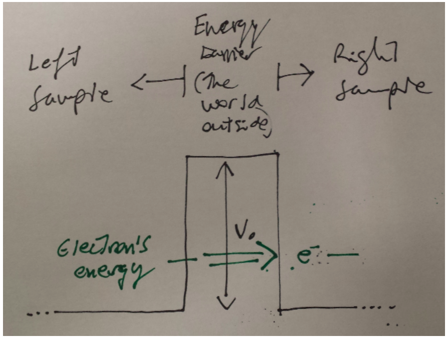
Energy barriers in Quantum Mechanics

Energy barriers also exist in the microscopic world. For example, the electrons in a material, even when they can move freely around the sample (as in a metal), cannot easily get out of it, because their potential energy is lower inside the material than outside it, due to the attraction extered by the postiviely-charge atomic nuclei:



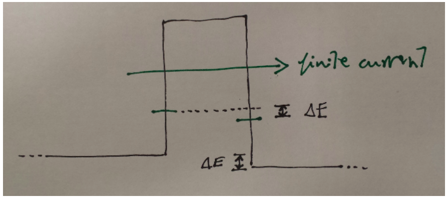
However, unlike classical particles, electrons can overcome this barrier, even when their energy is lower than the barrier itself. This is called**quantum-mechanical“tunnelling”** and it has been verified extensively. Indeed, it forms the basis of the**Scanning Tunnelling Microscope (STM)**, an experimental technique that we have mentioned before in this course.

To be more concrete, let us imagine that a second sample is brought in close proximity with the original one:

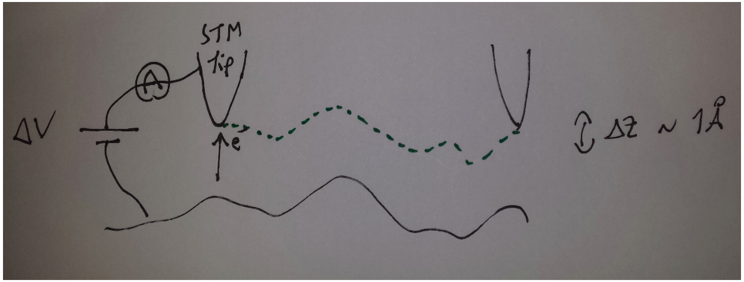


The two samples have a finite separation$a$, and therefore it is impossible, classically speaking, for an electron to thet from the left-hand sample to the righ-hand one unless its energy$E > V_0$, the height of the barrier. But all the electrons in either sample were at an energy$E < V_0$ to begin with so none of them can make it. Yet experimentally we find that electrons do have a finite probability to tunnel across the barrier.

In fact, if a small potential energy difference is introduced between the two samples (for example, by connecting them to opposite poles of a battery) then we find that the slightly increased probability to tunnel in one of the two directions leads to a net current flowing towards the sample with the higher voltage (i.e. the lower potential energy of negatively-charged electrons). This is in spite of the fact that none of the electrons have enough energy to overcome the barrier.



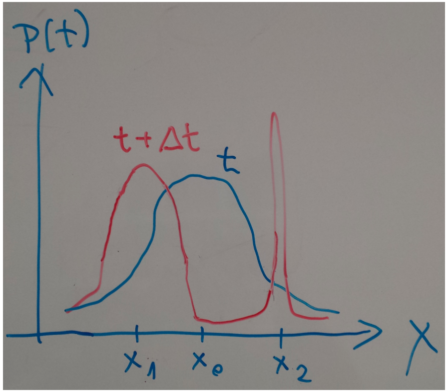
In STM, the sample on the left would be of the material under investigation, and the sample on the right would be a metallic tip which is the crucial element of the scanning tunnelling microscope. The tip is brought close to the surface of the sample and kept at a constant potential energy difference with the sample. This leads to a detectable current of electrons between the sample and the tip. This current depends on the potential energy difference but also on the distance between the tip and the surface of the sample. The tip is then scans the surface, and its height is varied precisely to keep the current constant. Recording these heights variations gives a very accurate topographical map of the surface (with precision of order of 1 Angstrom = 0.1 nm).



6.2 Probability current

Motion in Quantum Mechanics

In order to understand**tunnelling**we need to understand**motion**in quantum mechanics. This is not straightforward. Whereas in classical mechanics a particle has a well-defined position,x, and therefore it is evident that its motion is just given by the time-dependent function$x(t)$, in quantum mechanics the particle has a**probability distribution**$P(x,t)$of being at different positions$x$ at different times$t$. Consider the following time-evolution of the probability of finding a particle at a given position$x$ from one distribution$P(x,t)$ at time$t$ to a different one,$P(x,t+\Delta t)$, a finite timeΔt later:



At time$t$, the particle could be said to be somewhere nearx_0. After the timeΔt as elapsed, the probability for the particle to be found in that region remains finite, but smaller, and the highest probabilities to find the particle are nearx_1 and nearx_2. Has the particle moved to the left, to the right, or both?

Even if we measure, at time$t + \Delta t$, the actual position of the particle, we still cannot answer the above question. Suppose that when we carry out the measurement we find it nearx_1. Does this mean that the particle moved to the left? We don't know, because at the earlier time$t$, the probability that the particle would be found to the left ofx_1 was also finite, so it could have moved to the right between$t$ and$t + \Delta t$. In order to find out where the particle was at time$t$, we would have had to measure its actual position at that time, but then we would have destroyed the probability distribution we started with (the wave function would have collapsed to a completely localised one, see Subsection3.3,Collapse of the state vector). The time-evolution of the probability distribution would then have been entirely different.

The continuity equation

Fortunately, it turns out that motion of quantum particles can be conceptualised by introducing the idea of a **probabilitycurrent** or **probability flux**. This concept is entirely analogous to the current of water in a pipe or of electrons in a wire. So instead of talking about where the particle is moving from and to, we will discuss the direction and strength of the probability of finding the particle somewhere, and how it changes with time.

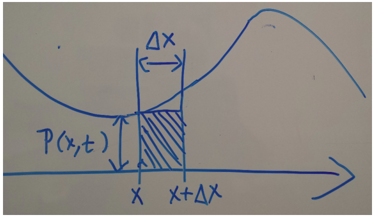
Suppose, specifically, that a particle can move along the$x$ axis. Let us assume that we know the time-evolution of its probability distribution,$P(x,t)$. This gives the probability$\Delta N(x,t)$ that at time$t$ the particle is found between$x$ and$x + \Delta x$. If the intervalΔx is very small, this is given by[13]

$$\Delta N(x,t) = P(x,t)\,\Delta x. \tag{6.1}$$

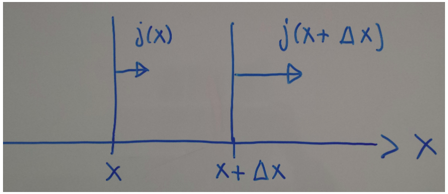
---

[13] More generally, ifΔx were sizable, then the probability in question would have to be calculated through the integral$\int_x^{x+\Delta x} dx'\,P(x',t)$. In the limit when$\Delta x$ is very small we can assume that$P(x',t)$ does not very perceptibly within the domain of integration and approximate this by$P(x,t)\int_x^{x+\Delta x} dx' = P(x,t)\,[x']_{x'=x}^{x'=x+\Delta x} = P(x,t)\,\Delta x$.

The key now is to think of$P\left(x,t\right)$ as the density of a fluid. Of course, we only have one particle, but you can imagine carrying out exactly the same experiment many times and averaging the results to obtain something equivalent to what you would have with a fluid of many non-interacting particles. On everage there will be$P\left(x,t\right)\Delta x$ particles between$x$ andΔx at any given time$t$ (since we are dealing with a single particle in total, this number is between 0 and 1).



Now let us define the current$j\left(x,t\right)$ as the rate at which particles are, on average, moving through the single point$x$ at any given time$t$ (from left to right if$j\left(x,t\right)>0$, and from the right to the left if$j\left(x,t\right)<0$, by convention). Then evidently the number of particles in our chosen interval will remain constant if$j\left(x,t\right)=j\left(x+\Delta x,t\right)$, i.e. if the rate at which particles enter the interval from the left is the same as the rate at which they leave it to the right. More generally if the currents coming in from the left and going out to the right are not equal, then the number of particles in our interval suffers a net change:



Mathematically, the rate at which the probability to find the particle between x and $x + \Delta x$ changes, is given by the derivative $\partial \Delta N (x,t) / \partial t$. This rate is evidently the difference between $j(x,t)$ and $j(x + \Delta x, t)$:

$$\frac{\partial \Delta N (x,t)}{\partial t} = \underbrace{j(x,t)}_{\text{arriving}} - \underbrace{j(x+\Delta x, t)}_{\text{leaving}}. \tag{6.2}$$

Substituing Eq. (6.1) we obtain

$$\frac{\partial P(x,t)}{\partial t}\Delta x = j(x,t) - j(x+\Delta x, t) \tag{6.3}$$

$$\Rightarrow \frac{\partial P(x,t)}{\partial t} = \frac{j(x+\Delta x, t) - j(x,t)}{\Delta x} \tag{6.4}$$

whence

$$\Rightarrow \boxed{\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x} j(x,t)}. \tag{6.5}$$

This is called the **continuity equation** and it holds for classical fluids (e.g., running water) if we take $P(x,t)$ to represent the density of the fluid and also for probability distributions of quantum particles. It is based on very general arguments.

More generally, probability distributions may occur in three dimensions. Then the current density is a vector, $\mathbf{j}(\mathbf{r},t)$, giving the magnitude **and direction** of probability flow, and whose value is defined for each location in space, $\mathbf{r} = (x,y,z)$, and of course for each time t. Similarly, the probability density depends on $\mathbf{r}$ and t. The the continuity equation then takes the form

$$\boxed{\frac{\partial P(\mathbf{r},t)}{\partial t} = -\nabla_{\mathbf{r}} \cdot \mathbf{j}(\mathbf{r},t)}. \tag{6.6}$$

We can integrate both sides of this equation over a given **volume** V to put the rate of change of the total probability of finding the particle inside that volume,

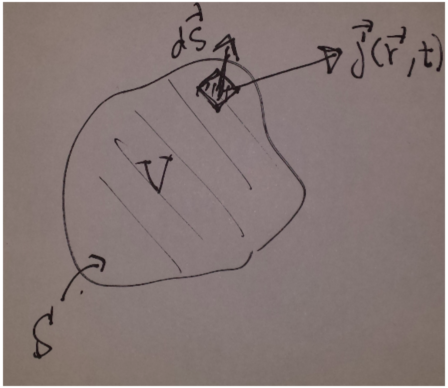
$$N\left(\mathbf{r},t\right)\equiv\int_V d^3\mathbf{r}P\left(\mathbf{r},t\right), \tag{6.7}$$

in terms of the **probability current flux** through the **surface** S delimiting that volume:

$$\boxed{\frac{\partial}{\partial t}N\left(\mathbf{r},t\right)} \quad = \quad \int_V d^3\mathbf{r}\frac{\partial P\left(\mathbf{r},t\right)}{\partial t}=-\int_V d^3\mathbf{r}\nabla_{\mathbf{r}}\cdot\mathbf{j}\left(\mathbf{r},t\right) \tag{6.8}$$

$$\boxed{=} \quad \boxed{-\int_S \mathbf{j}\left(\mathbf{r},t\right)\cdot d\mathbf{s}}, \tag{6.9}$$

where in the last line we have invoked **Gauss' theorem** and $d\mathbf{s}$ is an area element on the surface S.



From wave functions to probability current densities

In the foregoing we have described, by means of the continuity equation, the variation in time of the probability distribution in terms of a probability current, however we have not established how that probability current could be calculated, or what for it would have. The nice thing about this in QM is that the**Schrödinger equation**actually gives us the time-evolution of the probability distribution. We can then compare to the continuity equation to deduce what the current must be.

In a time-dependent state$|\Psi(t)\rangle$ the amplitude of probability for finding the particle near$x$ is$\langle x|\Psi(t)\rangle$, and the corresponding probability distribution is given by

$$P(x,t) = |\langle x|\Psi(t)\rangle|^2 \ . \tag{6.10}$$

The derivative of$P(x,t)$ with respect to time is given by

$$\begin{aligned}\frac{\partial}{\partial t}P(x,t) &= \frac{\partial}{\partial t}|\langle x|\Psi(t)\rangle|^2 = \frac{\partial}{\partial t}\left(\langle x|\Psi(t)\rangle^* \langle x|\Psi(t)\rangle\right) &(6.11)\\ &= \langle x|\Psi(t)\rangle \frac{\partial}{\partial t}\langle x|\Psi(t)\rangle^* + \langle x|\Psi(t)\rangle^* \frac{\partial}{\partial t}\langle x|\Psi(t)\rangle &(6.12)\end{aligned}$$

The derivatives with respect to time$t$ of the amplitude$\langle x|\Psi(t)\rangle$ and of its complex conjugate$\langle x|\Psi(t)\rangle^*$ follow from the Schrödinger equation: [Eq. (3.1)]

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

Indeed, projecting both sides of this equation onto position$x$ we obtain

$$i\hbar\frac{\partial}{\partial t}\langle x|\Psi(t)\rangle = \langle x|\hat{H}|\Psi(t)\rangle. \tag{6.13}$$

Taking the complex conjugate of both terms of the last equation we obtain

$$-i\hbar\frac{\partial}{\partial t}\langle x|\Psi(t)\rangle^* = \langle x|\hat{H}|\Psi(t)\rangle^*. \tag{6.14}$$

Putting these two results back into (6.12) we obtain

$$\frac{\partial}{\partial t}P(x,t) = \frac{i}{\hbar}\left[\langle x|\Psi(t)\rangle\langle x|\hat{H}|\Psi(t)\rangle^* - \langle x|\Psi(t)\rangle^*\langle x|\hat{H}|\Psi(t)\rangle\right] \tag{6.15}$$

Thus if we compute the bra-ket$\langle x|\hat{H}|\Psi(t)\rangle$ we can have an expression for$\partial P/\partial t$ in terms of the state of the system.

Let us now assume a simple Hamiltonian of the form of Eq. (4.11),

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + V(\hat{x})\left[= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + V(x) \text{ in position representation}\right].$$

The first term is the kinetic energy and the second term is a position-dependent potential energy. The bra-ket we are after is$\langle x|\hat{H}|\Psi(t)\rangle$. This is the position-representation wave function of the state obtained by applying the Hamiltonian$\hat{H}$ to the time-dependent state$|\Psi(t)\rangle$. This can be obtained by applying the position-representation of$\hat{H}$ to the position-representation wave function corresponding to the state$|\Psi(t)\rangle$ i.e.$\langle x|\Psi(t)\rangle$:

$$\langle x|\hat{H}|\Psi(t)\rangle = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\langle x|\Psi(t)\rangle. \tag{6.16}$$

We can now plug this result back into (6.15) to obtain

$$\begin{aligned}\frac{\partial}{\partial t}P\left(x,t\right) &= \frac{i}{\hbar}\left\{\left\langle x|\Psi\left(t\right)\right\rangle\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right]\left\langle x|\Psi\left(t\right)\right\rangle^*\right.\\ &\qquad\left.-\left\langle x|\Psi\left(t\right)\right\rangle^*\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)\right]\left\langle x|\Psi\left(t\right)\right\rangle\right\} \qquad (6.17)\end{aligned}$$

Evidently the terms involving$V\left(x\right)$ cancel, so we are left with

$$\frac{\partial}{\partial t}P\left(x,t\right) = \frac{i}{\hbar}\left\{-\left\langle x|\Psi\left(t\right)\right\rangle\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\langle x|\Psi\left(t\right)\right\rangle^*+\left\langle x|\Psi\left(t\right)\right\rangle^*\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\langle x|\Psi\left(t\right)\right\rangle\right\} \qquad (6.18)$$

$$= \frac{\hbar}{2mi}\left\{\left\langle x|\Psi\left(t\right)\right\rangle\frac{\partial^2}{\partial x^2}\left\langle x|\Psi\left(t\right)\right\rangle^*-\left\langle x|\Psi\left(t\right)\right\rangle^*\frac{\partial^2}{\partial x^2}\left\langle x|\Psi\left(t\right)\right\rangle\right\} \qquad (6.19)$$

$$= -\frac{\partial}{\partial x}\left\{\frac{\hbar}{2mi}\left[\left\langle x|\Psi\left(t\right)\right\rangle^*\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle-\left\langle x|\Psi\left(t\right)\right\rangle\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle^*\right]\right\} \qquad (6.20)$$

The LHS of the first line is the LHS of the continuity equation (6.5). Comparing the RHS on the last line to the RHS of (6.5) shows that indeed the continuity equation is obeyed if we choose the probability current to be given by

$$\boxed{j\left(x,t\right)=\frac{\hbar}{2mi}\left[\left\langle x|\Psi\left(t\right)\right\rangle^*\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle-\left\langle x|\Psi\left(t\right)\right\rangle\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle^*\right]}. \qquad (6.21)$$

current $j\left(x,t\right)$ in terms of the wave function $\left\langle x|\Psi\left(t\right)\right\rangle$

Note that the RHS of Eq. (6.21) can be re-written as

$$\frac{\hbar}{2m}\left\{\frac{1}{i}\left\langle x|\Psi\left(t\right)\right\rangle^{*}\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle+\left[\frac{1}{i}\left\langle x|\Psi\left(t\right)\right\rangle^{*}\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle\right]^{*}\right\},$$

leading to[14]

$$\boxed{j\left(x,t\right)=\Re\left[\left\langle x|\Psi\left(t\right)\right\rangle^{*}\frac{1}{m}\frac{\hbar}{i}\frac{\partial}{\partial x}\left\langle x|\Psi\left(t\right)\right\rangle\right]}\quad. \tag{6.22}$$

current $j\left(x,t\right)$ in terms of the wave function $\left\langle x|\Psi\left(t\right)\right\rangle$ (alternative form)

This admits a suggestive interpretation if we notice that$(\hbar/i)\,\partial/\partial x$ gives the action of the momentum operator in position representation and that$1/m$ times the momentum gives the velocity. So in some sense$j\left(x,t\right)$ could be interpreted as describing an actual flow of particles at position$x$ and time$t$. However notice that this last equation is not really the expectation value of an operator. Indeed, the position and the momentum cannot have well-defined values simulaneously, of course. So the intepretation we just gave is just a semi-classical picture and must be used with caution. In general it is best to stick to the description of$j\left(x,t\right)$ as giving the current of probability, as above.

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[14] $\Re\left(\ldots\right)$ stands for the real part of$(\ldots)$, i.e.$\Re\left(\ldots\right)=\frac{1}{2}\left[\left(\ldots\right)+\left(\ldots\right)^{*}\right]$

Some consequences of Eq. (6.21) [or, equivalently, (6.22)]:

- If the time-dependent wave function $\langle x|\Psi(t)\rangle$ is **real** then there is no probability flow:

$$j(x,t) = 0. \tag{6.23}$$

- Let us now consider the probability current in a **stationary state** [Subsec. 3.2] i.e. one with the form

$$|E_n(t)\rangle = e^{-\frac{i}{\hbar}E_n t}|E_n(0)\rangle,$$

where $|E_n(0)\rangle$ is an eigenstate of $\hat{H}$, with eigenvalue E_n. Substituing this for $|\Psi(t)\rangle$ in Eq. (6.21) we obtain

$$\boxed{j(x,t) = \frac{\hbar}{2mi}\left[\langle x|E_n(0)\rangle^* \frac{\partial}{\partial x}\langle x|E_n(0)\rangle - \langle x|E_n(0)\rangle \frac{\partial}{\partial x}\langle x|E_n(0)\rangle^*\right]}. \tag{6.24}$$

Note that the time-dependent factors $e^{-\frac{i}{\hbar}E_n t}, e^{\frac{i}{\hbar}E_n t}$ completely cancel out, i.e. the probability current is **time-independent** in a stationary state.

- We also note that if the real-space wave function of a stationary state is **real at $t = 0$**, $\langle x|E_n(0)\rangle = \langle x|E_n(0)\rangle^*$, then we again obtain

$$j(x,t) = 0 \text{ for all } t, \tag{6.25}$$

even though the time-dependent wave is not real (because it has the phase factor $e^{-\frac{i}{\hbar}E_n t}$). So, for example, the stationary states of a **particle in a box** [Subsec. 4.6], show **no probability current**.

- In contrast, the **stationary states of a free particle** in empty space, given by plane waves [Subsec. 4.5] do have a **finite probability current**. In one dimension the time-independent part of such plane waves is given by Eqs. (4.16,4.23): $\langle x|k\rangle = \frac{1}{\sqrt{L}}e^{ikx}$, where k is the wave vector and L is the nominal length to which the particles are confined. Substituting this into (6.24) yields

  $$\boxed{j\left(x,t\right) = \frac{1}{L}\frac{\hbar k}{m} \text{ for a plane wave in 1D}}. \tag{6.26}$$

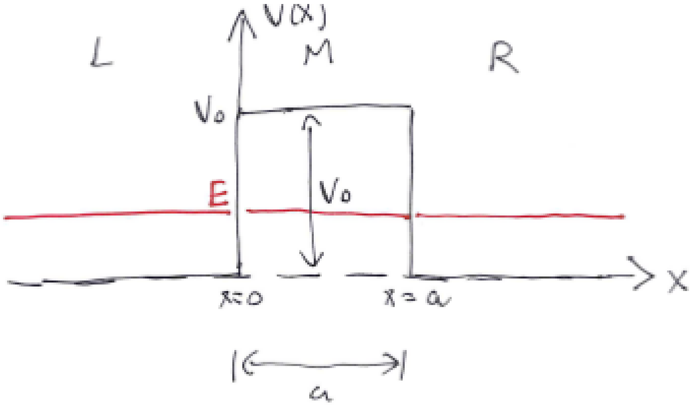
  This makes sense: $\hbar k$ is the momentum, and therefore $\hbar k/m$ is the velocity, so we are just obtaining the velocity with which the particle is moving, normalised by the length L.

  It might seem a bit puzzling that a state in which a particle is moving uniformly in a certain direction is stationary - however, the point is that the probability distribution itself, in this case, remains uniform, i.e. the particle always has the same probability of being anywhere, and this does not change in time. This situation is analogous to a uniform-density fluid where as many particles enter a given region per unit time as leave it, so the amount of fluid in the region remains constant.

Assignment: Problem 27.

6.3 Reflection and transmission through a barrier

Consider particle with energy E in presence of barrier of height $V_0 > E$:



Classically, particle cannot get through barrier. Let us see what happens in quantum mechanics.

Let us obtain the stationary states $|E(0)\rangle$ i.e. solutions to the time-independent Schrödinger equation.

We can then obtain the probability current density $j(x)$ using Eq. (6.24).[15]

---

[15] We write $j(x)$ instead of $j(x,t)$ because as we saw above for stationary states this quantity is time-independent.

In terms of position-representation wave functions$\psi\left(x\right)\equiv\left\langle x|E\left(0\right)\right\rangle$ the equation giving the current is

$$j\left(x,t\right)=\frac{\hbar}{2mi}\left[\psi\left(x\right)^{*}\frac{\partial}{\partial x}\psi\left(x\right)-\psi\left(x\right)\frac{\partial}{\partial x}\psi\left(x\right)^{*}\right]. \tag{6.27}$$

The Schrödinger equation takes the form

$$\left[-\frac{\hbar^{2}}{2m}\frac{\partial^{2}}{\partial x^{2}}+V\left(x\right)\right]\psi\left(x\right)=E\psi\left(x\right). \tag{6.28}$$

The potential is

$$V\left(x\right)=\begin{cases}0 & \text{if } x<0 \text{ (L)}\\ V_{0} & \text{if } 0\leq x\leq a \text{ (M)}\\ 0 & \text{if } x>a \text{ (R)}\end{cases} \tag{6.29}$$

Therefore

$$\text{in regions L,R:} -\frac{\hbar^{2}}{2m}\frac{\partial^{2}}{\partial x^{2}}\psi\left(x\right)=E\psi\left(x\right) \tag{6.30}$$

$$\text{i.e. } \psi''\left(x\right)=-k^{2}\psi\left(x\right) \text{ with } k^{2}=\frac{2mE}{\hbar^{2}} \tag{6.31}$$

$$\text{in region M:} \left(-\frac{\hbar^{2}}{2m}\frac{\partial^{2}}{\partial x^{2}}+V_{0}\right)\psi\left(x\right)=E\psi\left(x\right) \tag{6.32}$$

$$\text{i.e. } \psi''\left(x\right)=+\kappa^{2}\psi\left(x\right) \text{ with } \kappa^{2}=\frac{2m\left(V_{0}-E\right)}{\hbar^{2}} \tag{6.33}$$

Thus in L,R the solutions are linear combinations ofe^{ikx} ande^{-ikx} while in M they are linear combinations of$e^{\kappa x}$ and$e^{-\kappa x}$:

$$\psi\left(x\right)=\begin{cases}A_Le^{ikx}+B_Le^{-ikx} & \text{if } x<0 \text{ (L)}\\ A_Me^{\kappa x}+B_Me^{-\kappa x} & \text{if } 0\leq x\leq a \text{ (M)}\\ A_Re^{ikx}+B_Re^{-ikx} & \text{if } x>a \text{ (R)}\end{cases} \tag{6.34}$$

We now impose continuity of the wave function...

$$\psi\left(x=0^-\right)=\psi\left(x=0^+\right)\Rightarrow\boxed{A_L+B_L=A_M+B_M} \tag{6.35}$$

$$\psi\left(x=a^-\right)=\psi\left(x=a^+\right)\Rightarrow\boxed{A_Me^{\kappa a}+B_Me^{-\kappa a}=A_Re^{ika}+B_Re^{-ika}} \tag{6.36}$$

...and of its first derivative...

$$\psi'\left(x=0^-\right)=\psi'\left(x=0^+\right)\Rightarrow\boxed{ikA_L-ikB_L=\kappa A_M-\kappa B_M} \tag{6.37}$$

$$\psi'\left(x=a^-\right)=\psi'\left(x=a^+\right)\Rightarrow\boxed{A_M\kappa e^{\kappa a}-B_M\kappa e^{-\kappa a}=A_Rike^{ika}-B_Rike^{-ika}} \tag{6.38}$$

...which leaves us with**4 equations** [Eqs. (6.35-6.38)] to determine**6 unkowns** $[A_L,B_L,A_M,B_M,A_R,B_R]$.

To obtain additional equations we need to impose **boundary conditions at infinity.**

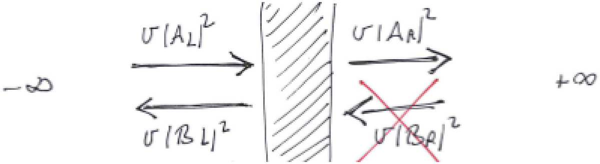
Let us first compute the **current** in the L and R regions: substituting (6.34) in (6.27),

$$j\left(x\right)=\begin{cases}\frac{\hbar k}{m}\left(\left|A_L\right|^2-\left|B_L\right|^2\right) & \text{for } x<0 \text{ (L)}\\ \frac{\hbar k}{m}\left(\left|A_R\right|^2-\left|B_R\right|^2\right) & \text{for } x>0 \text{ (R)}\end{cases} \tag{6.39}$$

Note $\hbar k/m = p/m = v$, the velocity of the particle, so the above equation reads

$$j\left(x\right)=\begin{array}{c}\text{velocity}\\ \text{of particle}\end{array}\times\left[\begin{array}{ccc}\text{probability} & & \text{probability}\\ \text{particle} & - & \text{particle}\\ \text{going right} & & \text{going left}\end{array}\right] \tag{6.40}$$

We now impose the additional boundary conditions:



- The net flow into the barrier from $x=-\infty$ must equal the net away from the barrier towards $x=+\infty$:

$$\boxed{\frac{\hbar \cancel{k}}{\cancel{m}}\left(\left|A_L\right|^2-\left|B_L\right|^2\right)=\frac{\hbar \cancel{k}}{\cancel{m}}\left(\left|A_R\right|^2-\left|B_R\right|^2\right)} \tag{6.41}$$

- There is no source of particles at $x=\infty$:

$$v\left|B_R\right|^2=0\Rightarrow\boxed{B_R=0} \tag{6.42}$$

Now we have **6 equations** [Eqs. (6.35-6.38) and (6.41-6.42)] **for 6 unkowns** [$A_L, B_L, A_M, B_M, A_R, B_R$]!

We are rally interested in the**reflection and transmission coefficients**

$$R \equiv \frac{|B_L|^2}{|A_L|^2} \tag{6.43}$$

$$T \equiv \frac{|A_R|^2}{|A_L|^2} \tag{6.44}$$

These give the fraction of incoming particles that get reflected from and transmitted through the barrier, respectively.

Note that

- $R + T = 1$ always;
- classically, for$E < V_0$ we should have$R = 1, T = 0$.

Solving Eqs. (6.35-6.38) and (6.41-6.42) forB_L/A_L andA_R/A_L we obtain[16]

$$\frac{B_L}{A_L} = \frac{(k^2+\kappa^2)\left(e^{2ka}-1\right)}{e^{2\kappa a}(k+i\kappa)^2-(k-i\kappa)^2} \Rightarrow R = \left[1+\frac{4E(V_0-E)}{V_0^2\sinh^2(\kappa a)}\right]^{-1} \tag{6.45}$$

$$\frac{A_R}{A_L} = \frac{4ik\kappa e^{-ika}e^{\kappa a}}{e^{2\kappa a}(k+i\kappa)^2-(k-i\kappa)^2} \Rightarrow T = \left[1+\frac{V_0^2\sinh^2(\kappa a)}{4E(V_0-E)}\right]^{-1} \tag{6.46}$$

---

[16] The algebra is left as an exercise. See Bransden & Joachain, Section 4.4 (4th Edition).

Note that the expression for$T$ can be easily obtained form the expression for$R$ by demanding$R+T=1$. Indeed defining

$$A \equiv \frac{4E\left(V_0-E\right)}{V_0^2\sinh^2\left(\kappa a\right)} \tag{6.47}$$

allows us to recast (6.45,6.46) in the form

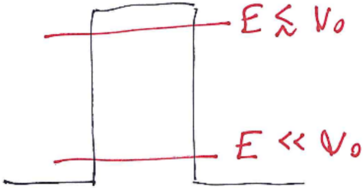
$$R=\left[1+A\right]^{-1} \tag{6.48}$$

$$T=\left[1+1/A\right]^{-1}. \tag{6.49}$$

From this it is easy to show that

$$R+T=\left[1+A\right]^{-1}+\left[\left(A+1\right)/A\right]^{-1}=\left(1+A\right)/\left(A+1\right)=1.$$

It is illustrative to consider the following limiting cases of the particle's energy:



- Much less than the height of the barrier:

$$E \ll V_0 \Rightarrow \begin{cases} T \approx 0; \\ R \approx 1. \end{cases} \tag{6.50}$$

In this case the particle is always reflectedm, which coincides with the classical result $(R = 1, T = 0)$.

- Just below the height of the barrier:

$$E \lesssim V_0 \Rightarrow \begin{cases} T \approx 1; \\ R \approx 0. \end{cases} \tag{6.51}$$

In this case the particle is*always transmitted*, in start contradiction with the classical prediction!

For intermediate energies, the probabilities of transmission and reflection are both finite - so the classical result is only recovered in the$E \ll V_0$ limit.

Proof of Eqs. (6.50,6.51):

We write

$$\kappa^2 = \frac{2m\,(V_0 - E)}{\hbar^2} \Rightarrow \kappa a = \sqrt{\frac{V_0 - E}{\hbar^2/2ma^2}}$$

and note that when $E \ll V_0$ we have $\kappa a \to \infty$ while when $E \lesssim V_0$ we have $\kappa a \to 0$.

In the first case, $\sinh \kappa a = \frac{1}{2}\left(e^{\kappa a} - e^{-\kappa a}\right) \to \infty$ so $A \to 0$ and therefore using (6.48,6.49) we get $R = 1, T = 0$.

In the second case, $\sinh \kappa a = \frac{1}{2}\left(e^{\kappa a} - e^{-\kappa a}\right) \to \frac{1}{2}\,(1 - 1) = 0$ and so we have $A \to \infty$ leading to $R = 0, T = 1$.

Assignment: Problem28.

7 Perturbation Theory

Suggested reading (all references are from the module's official reading list):

- **Zettili Subsection 9.2.1.**

This section covers

- Perturbation theory.

7.1 Formalism

Until now, we have assumed that, whatever the system we were dealing with, it was possible to solve the corresponding stationary Schrödinger equation,

$$\boxed{\hat{H}|n\rangle = E_n|n\rangle}, \tag{7.1}$$

exactly. However, on many occassions this is just not possible, and approximation methods are required. Here we will discuss what is arguably one of the most important approximation schemes, namely**time-independent perturbation theory**. This is useful when we*do*know how to solve exactly the Shcrödinger equation

$$\boxed{\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle}, \tag{7.2}$$

for certain Hamiltonian,$\hat{H}_0$, to which has been added a**perturbation**,$\lambda\hat{H}_1$. The full Hamiltonian is

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1 \tag{7.3}$$

and for it we do not know how to solve Eq. (7.1), which takes the form

$$\boxed{\left(\hat{H}_0 + \lambda \hat{H}_1\right) |n\rangle = E_n |n\rangle}, \tag{7.4}$$

The parameterλ is some dimensionless quantity that tells us whether the perturbation is large or small compared to the unperturbed Hamiltonian,$\hat{H}_0$.

The central idea of perturbation theory is to assume that we are dealing with a**small perturbation**,

$$\lambda \ll 1, \tag{7.5}$$

and exploit this to find an approximate solution to Eq. (7.1) which is a slightly modified version of Eq. (7.2). We will assume a**time-independent** Hamiltonian and also that all the stationary states of the unperturbed Hamiltonian are**non-degenerate** (i.e. each energy corresponds to only one state).

The method starts by assuming that the energies and the corresponding stationary states can be expressed as a sum of many terms, each of which will become negligible faster as the perturbation becomes smaller (i.e. asλ becomes small):

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \tag{7.6}$$

$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \dots \tag{7.7}$$

The whole of perturbation theory is predicated on this simple and intuitive assumption. Substituting these two expansions in (7.4) we obtain

$$\begin{aligned} &\left(\hat{H}_0 + \lambda \hat{H}_1\right) \left(\left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \dots\right) \\ &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\right) \left(\left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \dots\right) \end{aligned} \tag{7.8}$$

The key step now is to recognise the LHS and RHS of this equation are both polynomials inλ and that therefore we can group the terms on the in the same power ofλ. Then we have

$$
\begin{aligned}
\hat{H}_0 \left|n^{(0)}\right\rangle &= E_n^{(0)} \left|n^{(0)}\right\rangle && (7.9)\\
\hat{H}_0 \left|n^{(1)}\right\rangle + \hat{H}_1 \left|n^{(0)}\right\rangle &= E_n^{(0)} \left|n^{(1)}\right\rangle + E_n^{(1)} \left|n^{(0)}\right\rangle && (7.10)\\
\hat{H}_0 \left|n^{(2)}\right\rangle + \hat{H}_1 \left|n^{(1)}\right\rangle &= E_n^{(0)} \left|n^{(2)}\right\rangle + E_n^{(1)} \left|n^{(1)}\right\rangle + E_n^{(2)} \left|n^{(0)}\right\rangle && (7.11)\\
\vdots \quad & \quad \vdots && (7.12)\\
\hat{H}_0 \left|n^{(j)}\right\rangle + \hat{H}_1 \left|n^{(j-1)}\right\rangle &= E_n^{(0)} \left|n^{(j)}\right\rangle + E_n^{(1)} \left|n^{(j-1)}\right\rangle + \ldots + E_n^{(j)} \left|n^{(0)}\right\rangle && (7.13)
\end{aligned}
$$

The first of the above equations comes from equating theλ-independent terms and is obviously just our unperturbed Schrödinger's equation, (7.2). The other equations correspond to higher and higher orders inλ and can be used to obtain better and better approximations.

Let's first assume thatλ is not negligible, but is small enough that all but the linear terms in (7.6,7.7) can be neglected. Let's compute the first correction to the energy,$\lambda E_n^{(1)}$. We use Eq. (7.10). Let us project both sides of that equation on the$n$$\underline{\text{th}}$ unperturbed state,$|n^{(0)}\rangle$:

$$
\left\langle n^{(0)}\right| \hat{H}_0 \left|n^{(1)}\right\rangle + \left\langle n^{(0)}\right| \hat{H}_1 \left|n^{(0)}\right\rangle = \left\langle n^{(0)}\right| E_n^{(0)} \left|n^{(1)}\right\rangle + \left\langle n^{(0)}\right| E_n^{(1)} \left|n^{(0)}\right\rangle . \tag{7.14}
$$

The first term on the LHS of this equation can now be simplified as follows:

$$
\begin{aligned}
\left\langle n^{(0)}\right| \hat{H}_0 \left|n^{(1)}\right\rangle &= \left\langle n^{(1)}\right| \hat{H}_0 \left|n^{(0)}\right\rangle^* && (7.15)\\
&= \left\langle n^{(1)}\right| E_0^{(0)} \left|n^{(0)}\right\rangle^* && (7.16)\\
&= E_0^{(0)} \left\langle n^{(1)}|n^{(0)}\right\rangle^* && (7.17)\\
&= E_0^{(0)} \left\langle n^{(0)}|n^{(1)}\right\rangle , && (7.18)
\end{aligned}
$$

where we have used (7.2) and the fact that all energies are real. This is evidently equal to the first term on the RHS, so those two terms cancel. The second term on the RHS, on the other hand, is just

$$\left\langle n^{(0)}\right| E_n^{(1)} \left|n^{(0)}\right\rangle = E_n^{(1)} \left\langle n^{(0)}|n^{(0)}\right\rangle = E_n^{(1)}, \tag{7.19}$$

therefore we are left with

$$\boxed{E_n^{(1)} = \left\langle n^{(0)}\right| \hat{H}_1 \left|n^{(0)}\right\rangle}. \tag{7.20}$$

This is an extremely important result in perturbation theory: it tells us that when a perturbation is added to the Hamiltonian of a quantum system, to first order the change in the energy of each of its stationary states is just the epxectation value of the perturbation in the corresponding unperturbed state.

One can continue in the same spirit to obtain the second-order correction to the energy:

$$\boxed{E_n^{(2)} = \sum_{l\neq n} \frac{\left|\langle l^{(0)}|\hat{H}_1 \left|n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_l^{(0)}}}. \tag{7.21}$$

To summarise, the energy expansion (7.6) takes the form

$$\boxed{\boxed{E_n = E_n^{(0)} + \lambda \left\langle n^{(0)}\right| \hat{H}_1 \left|n^{(0)}\right\rangle + \lambda^2 \sum_{l\neq n} \frac{\left|\langle l^{(0)}|\hat{H}_1 \left|n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_l^{(0)}} + \dots}} \tag{7.22}$$

Assignment: Problem29.

Addendum (advanced): Proof of Eq. (7.21)

Let us assume that theλ^2 terms are important as well —that is, we are looking for a second-order approximation now. We now use Eq. (7.11). Like before, we project on$|n^{(0)}\rangle$ and obtain

$$\left\langle n^{(0)}\right|\hat{H}_0\left|n^{(2)}\right\rangle+\left\langle n^{(0)}\right|\hat{H}_1\left|n^{(1)}\right\rangle=\left\langle n^{(0)}\right|E_n^{(0)}\left|n^{(2)}\right\rangle+\left\langle n^{(0)}\right|E_n^{(1)}\left|n^{(1)}\right\rangle+\left\langle n^{(0)}\right|E_n^{(2)}\left|n^{(0)}\right\rangle \tag{7.23}$$

As before, the first terms on the LHS and the RHS cancel and the last term on the RHS is just$E_n^{(2)}$. Solving for that quantity, we obtain

$$E_n^{(2)}=\left\langle n^{(0)}\right|\left(\hat{H}_1-E_n^{(1)}\right)\left|n^{(1)}\right\rangle. \tag{7.24}$$

Unfortunately, this expression now involves the first-order corrections to the state$|n^{(0)}\rangle$,$|n^{(1)}\rangle$, which we have not yet obtained. So whereas the first-order correction to the energy could be obtained using the unperturbed states, the second-order correction to the energy requires a first-order correction to the state. To obtain this, let us use the fact that the unperturbed stationary states form a complete set to expand the first-order perturbation in them:

$$|n^{(1)}\rangle=\sum_m|m^{(0)}\rangle\langle m^{(0)}|n^{(1)}\rangle. \tag{7.25}$$

Plugging this into the first-order equation (7.10) we obtain

$$\hat{H}_0\sum_m|m^{(0)}\rangle\langle m^{(0)}|n^{(1)}\rangle+\hat{H}_1\left|n^{(0)}\right\rangle=E_n^{(0)}\sum_m|m^{(0)}\rangle\langle m^{(0)}|n^{(1)}\rangle+E_n^{(1)}\left|n^{(0)}\right\rangle. \tag{7.26}$$

With some re-arranging, and using the unperturbed SE to eliminate the operator form the first term on the LHS,

$$\left(E_m^{(0)}-E_n^{(0)}\right)\sum_m|m^{(0)}\rangle\langle m^{(0)}|n^{(1)}\rangle+\left(\hat{H}_1-E_n^{(1)}\right)\left|n^{(0)}\right\rangle=0. \tag{7.27}$$

We now project on$|l^{(0)}\rangle$ and get

$$\left(E_l^{(0)}-E_n^{(0)}\right)\langle l^{(0)}|n^{(1)}\rangle+\langle l^{(0)}|\left(\hat{H}_1-E_n^{(1)}now\right)\left|n^{(0)}\right\rangle=0 \tag{7.28}$$

$$\Rightarrow\left(E_l^{(0)}-E_n^{(0)}\right)\langle l^{(0)}|n^{(1)}\rangle+\langle l^{(0)}|\hat{H}_1\left|n^{(0)}\right\rangle-E_n^{(1)}\delta_{l,n}=0. \tag{7.29}$$

Here we have used repeatedly that$\langle l^{(0)}|m^{(0)}\rangle = \delta_{l,m}$. For$l = n$, the above equation is the same as (7.20). For$l \neq n$, it yields

$$\boxed{\langle l^{(0)}|n^{(1)}\rangle = \frac{\langle l^{(0)}|\hat{H}_1\,|n^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}}} \text{ for all } l \neq n. \tag{7.30}$$

This yields the amplitdues of the first-order corrections to the stationary states in the unperturbed energy representation. All we need is to compute the matrix elements of the perturbation in the unperturbed basis. The procedure we have used to obtain these amplitudes is called the**Rayleigh-Schrödinger method**. The method is only valid if these amplitudes turn out to be small —otherwise, the perturbation is important and the expansion (7.7) cannot be cut off. Specifically, our method will also fail if the unperturbed Hamiltonian,$\hat{H}_0$, has two or more degenerate states,$|n^{(0)}\rangle$, $|l^{(0)}\rangle$, because then their energy difference$E_n^{(0)} - E_l^{(0)}$ in the denominator vanishes, making the amplitude$\langle l^{(0)}|n^{(1)}\rangle$ diverge.

Armed with these first-order corrections to the probability amplitudes, we can now evaluate the second-order correction to the energy. First, we apply the completeness relation to (7.24)

$$\begin{aligned} E_n^{(2)} &= \left\langle n^{(0)}\right| \left(\hat{H}_1 - E_n^{(1)}\right) \sum_l |l^{(0)}\rangle\langle l^{(0)} \left| n^{(1)}\right\rangle & (7.31) \\ &= \sum_l \langle n^{(0)}|\hat{H}_1|l^{(0)}\rangle\langle l^{(0)}|n^{(1)}\rangle - E_n^{(1)}\langle n^{(0)} \left| n^{(1)}\right\rangle & (7.32) \end{aligned}$$

We now note that the term in the summation on the RHS corresponding to$l = n$ cancels exactly the second term on the RHS, by virtue of (7.20). We thus have just

$$E_n^{(2)} = \sum_{l\neq n} \langle n^{(0)}|\hat{H}_1|l^{(0)}\rangle\langle l^{(0)}|n^{(1)}\rangle. \tag{7.33}$$

We now plug in (7.30) to find

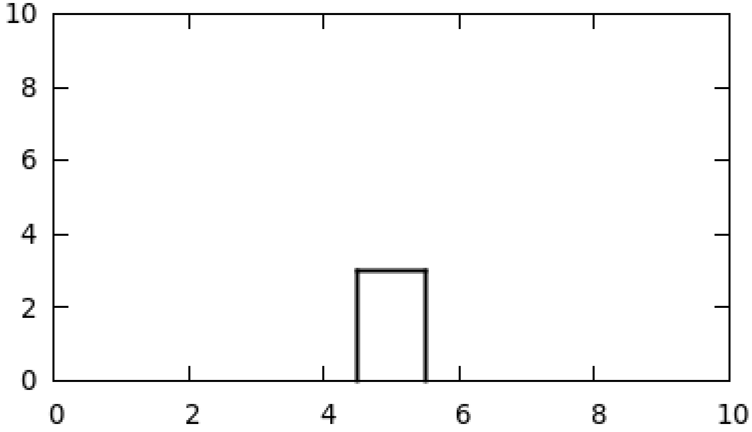
$$E_n^{(2)} = \sum_{l\neq n} \left\langle n^{(0)}\right| \hat{H}_1|l^{(0)}\rangle \frac{\langle l^{(0)}|\hat{H}_1\,|n^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}}, \tag{7.34}$$

from which Eq. (7.21) follows.

7.2 Applications

Example: a dimple in the middle of a well. Suppose we have an infinite square well going from $x = 0$ to $x = L$ and we create a small, thin barrier in the middle, in the form of a small step potential

$$\lambda V(x) = \lambda \begin{cases} V_0 & \text{if } |x - L/2| < \delta/2, \\ 0 & \text{otherwise.} \end{cases} \tag{7.35}$$



We are going to assume that, if λ is small, the small barrier will not make a big difference (it will be a small perturbation). We will also assume that δ is small compared to L (this is not necessary for perturbation theory to be applicable, it just makes the calculation easier —see below). The question is: how does this change, i.e. adding this small energy barrier in the middle of the potential well, the energy of the ground state?

To lowest order, the energy in the ground state is

$$E_1 = E_1^{(0)} + \lambda E_1^{(1)} \tag{7.36}$$

where

$$E_1^{(0)} = \frac{\hbar^2 \pi^2}{2mL^2} \tag{7.37}$$

(from Dr. Mountjoy's notes, Section 3.1). The first-order correction is given by Eq. (7.20), above:

$$\lambda E_1^{(1)} = \left\langle 1^{(0)} \right| \lambda \hat{H}_1 \left| 1^{(0)} \right\rangle, \tag{7.38}$$

where we have substituted$|1^{(0)}\rangle$ for the zeroth-order ground state. To evaluate this, we need to write it in some particular representation. Since we are given the potential$V(x)$ in the position representation, let us use that basis. Using the completeness relation for a continuum of position eigenstates, Eq. (4.12), we can re-write (7.38) as

$$\lambda E_1^{(1)} = \int dx \int dx' \langle 1^{(0)}|x\rangle\langle x|\lambda\hat{H}_1|x'\rangle\langle x'|1^{(0)}\rangle. \tag{7.39}$$

We have now put everything in terms of the matrix elements of$\lambda\hat{H}_1$ in position representation,

$$\langle x|\lambda\hat{H}_1|x'\rangle = V(x)\langle x|x'\rangle = V(x)\,\delta(x-x'), \tag{7.40}$$

and the corresponding ground state wavefunction,

$$\psi(x) \equiv \langle x|\psi\rangle = B\sin\left(\frac{n\pi}{L}x\right) = B\sin\left(\frac{\pi}{L}x\right)$$

[see Subsec. 4.6:Particle in a box; take$n = 1$ for the ground state]

Thus

$$\begin{aligned}
\lambda E_1^{(1)} &= \int dx\langle 1^{(0)}|x\rangle V\left(x\right)\langle x|1^{(0)}\rangle \\
&= \int_0^L dxV\left(x\right)\left|\langle x|1^{(0)}\rangle\right|^2 \\
&= \int_{L/2-\delta/2}^{L/2+\delta/2} dx\lambda V_0\left|B\right|^2\sin^2\left(\frac{\pi}{L}x\right) \\
&= \lambda V_0\left|B\right|^2\int_{L/2-\delta/2}^{L/2+\delta/2} dx\sin^2\left(\frac{\pi}{L}x\right) \\
&\approx \lambda V_0\left|B\right|^2\delta\sin^2\left(\frac{\pi}{2}\right) \\
&= \lambda V_0\left|B\right|^2\delta. \qquad (7.41)
\end{aligned}$$

where in the ante-penultimate line we have assumed that$\delta \ll L$ (thin barrier) so we can neglect the change of$\sin^2\left(\frac{\pi}{L}x\right)$ with$x$ within$\delta/2$ of$x=0$.

Finally, we need the normalisation factor$|B|^2$, which is obtained from

$$\begin{aligned}
\int dx \left|\langle x|1^{(0)}\rangle\right|^2 &= 1 \qquad (7.42)\\
\Rightarrow \int_0^L dx \left|B\sin\left(\frac{\pi}{L}x\right)\right|^2 &= 1\\
\Rightarrow |B|^2 &= \left[\int_0^L dx\ \sin^2\left(\frac{\pi}{L}x\right)\right]^{-1}\\
&= \left[\frac{L}{\pi}\int_0^{\pi} d\xi\ \sin^2(\xi)\right]^{-1}\\
&= \left[\frac{2L}{\pi}\int_0^{\pi/2} d\xi\ \sin^2(\xi)\right]^{-1} \qquad (7.43)
\end{aligned}$$

Now we use the famous integral

$$\int_0^{\pi/2} \sin^m x\, dx = \frac{m-1}{m}\int_0^{\pi/2} \sin^{m-2} x\, dx \tag{7.44}$$

with$m = 2$:

$$\begin{aligned}
\left|\langle x|1^{(0)}\rangle\right|^2 |B|^2 &= \left[\frac{2L}{\pi}\frac{1}{2}\int_0^{\pi/2} dx\right]^{-1}\\
&= \left[\frac{2L}{\pi}\frac{1}{2}\frac{\pi}{2}\right]^{-1}\\
&= \frac{2}{L}. \qquad (7.45)
\end{aligned}$$

Hence our final result is

$$\lambda E^{(1)} = \lambda V_0 \frac{2\delta}{L} \tag{7.46}$$

so the energy is

$$E_1 \approx \frac{\hbar^2 \pi^2}{2mL^2} + z\lambda V_0 \frac{\delta}{L}. \blacksquare \tag{7.47}$$

Assignment: Problem30.

Assignment: Problem31.

Part II

Problems

The following problems are intended to aid your understanding of the material in the lecture notes. Each problem is closely-related to one of the lectures. The shaded boxes in the lecture notes tell you when you should be attempting each of the problems. It is crucial that you attempt the problems as we progress.

1. Revision: vectors (PH311).[17]

A quick recap: vectors

Consider the two-dimensional plane. Let $\mathbf{u}_1$ and $\mathbf{u}_2$ be the unit vectors pointing along the horizontal and vertical directions, respectively. $\mathbf{u}_1$ and $\mathbf{u}_2$ form a **basis** which means that any other vector $\mathbf{v}$ can be written in the form $\mathbf{v} = a\mathbf{u}_1 + b\mathbf{u}_2$. We say that $\mathbf{v} = (a, b)$ is the expression in Cartesian coordinates of the vector $\mathbf{v}$ in the $\mathbf{u}_1, \mathbf{u}_2$ basis. By definition the Cartesian coordinates of the basis vectors themselves are $\mathbf{u}_1 = (1, 0)$ and $\mathbf{u}_2 = (0, 1)$. The dot product of two vectors $\mathbf{v} = a\mathbf{u}_1 + b\mathbf{u}_2$ and $\mathbf{w} = c\mathbf{u}_1 + d\mathbf{u}_2$ is given by $\mathbf{v}.\mathbf{w} = ac + bd$. The norm of $\mathbf{v}$ is $|\mathbf{v}| = \sqrt{a^2 + b^2}$. This all generalises stright-forwardly to higher dimensions e.g. if we have 3 basis vectors (three dimensions) then a vector has three components a, b, c and its norm is $\sqrt{a^2 + b^2 + c^2}$.

(a) Consider the following vectors expressed in the $\{\mathbf{u}_1, \mathbf{u}_2\}$ basis:

- $\mathbf{p} = (3, -1)$
- $\mathbf{q} = (-1/2, -2)$
- $\mathbf{r} = (1, 1)$

i. Draw a diagram showing the positions of $\mathbf{u}_1, \mathbf{u}_2, \mathbf{p}, \mathbf{q}$, and $\mathbf{r}$ on the plane.

ii. Calculate the following linear combinations. Express your results in Cartesian coordinates in the $\{\mathbf{u}_1, \mathbf{u}_2\}$ basis:

- $\mathbf{p} + \mathbf{q}$

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[17] This is a *revision* problem. It will not be assessed.

- $\mathbf{p}-\mathbf{q}$
- $\mathbf{p}-2\mathbf{q}+\mathbf{r}/2$

iii. Calculate the norms of$\mathbf{u}_1, \mathbf{u}_2, \mathbf{p}, \mathbf{q},$ and $\mathbf{r}$.

(b) The basis vectors$\mathbf{u}_1, \mathbf{u}_2$ are orthogonal ($\mathbf{u}_1.\mathbf{u}_2$=0) and normalised ($|\mathbf{u}_1|^2 = |\mathbf{u}_2|^2 = 1$). Check that the same is true for the vectors

$$\mathbf{w}_1 = \frac{1}{\sqrt{2}}(1,1)$$
$$\mathbf{w}_2 = \frac{1}{\sqrt{2}}(1,-1)$$

and therefore they can be also be used as a basis.

(c) Add to your diagram the vectors$\mathbf{w}_1$ and$\mathbf{w}_2$ showing the new axes they define on the plane.

(d) Use the expression of$\mathbf{p}$ in Cartesian coordinates, given above, to write$\mathbf{p}$ as a linear combination of$\mathbf{u}_1$ and $\mathbf{u}_2$. Now similarly write the basis vectors$\mathbf{u}_1, \mathbf{u}_2$ themselves as slinear combinations of the new basis vectors$\mathbf{w}_1, \mathbf{w}_2$. Substitute into the expression for$\mathbf{p}$ to deduce a new formula giving$\mathbf{p}$ as a linear combination of$\mathbf{w}_1$ and$\mathbf{w}_2$. From this, deduce the Cartesian expression of$\mathbf{p}$ in the new basis.

(e) The dot product of a vector with a basis vector is called a“projection”. Calculate the projections$\mathbf{w}_1.\mathbf{p}$ and$\mathbf{w}_2.\mathbf{p}$ and compare them to the Cartesian-coordinate expression of$\mathbf{p}$ in the$\mathbf{w}_1, \mathbf{w}_2$ basis obtained above. Explain, using a diagram, why this is called a“projection”.

2. Revision: Matrices (PH311).[18]

A quick recap: matrices

- Linear operations with matrices (addition, multiplication by a scalar, i.e. by a number, and combinations of those) are carried out just like with vectors, by combining the equivalent elements of each matrix individually.

- The transpose of a2×2 matrix$\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ is$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^T = \begin{pmatrix} a & c \\ b & d \end{pmatrix}$. More generally, for a matrix of arbitrary dimensions$I\times J$ with elements$a_{i,j}$ $(i = 1,2,\ldots,I$ is the row index and$j = 1,2,\ldots,J$ is the column index), the tranpose is given by$a^T_{i,j} = a_{j,i}$. If, in addition to transposing the matrix, we take the complex conjugate, that is called the adjoint matrix, denoted by a“dagger”$\dagger$:$a^\dagger_{i,j} = a^{T*}_{i,j} = a^*_{j,i}$.

- The elements of a matrix$\mathbf{M}$ that equals the product of two others matrices$\mathbf{A}$ and$\mathbf{B}$,$\mathbf{M} = \mathbf{A}.\mathbf{B}$, are given by$m_{i,j} = \sum_l a_{i,l}b_{l,j}$, where the elements of$\mathbf{A}$ and$\mathbf{B}$ are given by$a_{i,j}$ and$b_{i,j}$, respectively. Thus, the product of a matrix with dimensions$I\times L$ with another of dimensions$L\times J$ gives a matrix with dimensions$I\times J$. Note that the number or columns of the first matrix must equal the number of rows of the second matrix, otherwise the product is not well-defined.

(a) Consider the following2×2 matrices:

- $\mathbf{A} = \begin{pmatrix} 1 & 2 \\ 2 & 4 \end{pmatrix}$

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[18] This is a*revision*problem. It will not be assessed.

- $\mathbf{B} = \begin{pmatrix} 1 & 1/2 \\ 1/2 & -1 \end{pmatrix}$
- $\mathbf{C} = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$

What property do all these matrices have in common? (hint: try transposing them and see what you get).

(b) Calcuate the linear combination $\mathbf{X} = \mathbf{A} - 2\mathbf{B}$.

(c) Calculate the matrix product $\mathbf{Y} = \mathbf{B}.\mathbf{C}$.

3. Revision: determinants (from PH311).[19]

A quick recap: determinants

The determinant of a (square)$N \times N$matrix$\mathbf{A}$ with elements$a_{i,j}$ is

$$|\mathbf{A}| = \sum_P \mathrm{sign}\,(P) \prod_{i=1}^{N} a_{i,P_i}$$

where the sum is over all the permutations$P_{1,}P_2, \ldots, P_N$ of$1, 2, \ldots, N$ and$\mathrm{sign}\,(P)$ denotes the sign of the permutation. For2×2 and3×3 matrices this gives, respetcively,

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = aei + bfg + dhc - ceg - bdi - fha.$$

(a) Calculate the determinants of the matrices$\mathbf{A}, \mathbf{B}, \mathbf{C}$ given in Problem2.

(b) Calculate the determinant of

$$\begin{pmatrix} 1 & 2 & i \\ 2 & 0 & -i \\ -i & i & 2 \end{pmatrix}.$$

---

[19] This is a *revision* problem. It will not be assessed.

4. Revision: vectors and matrices (from PH311).[20]

A quick recap: vectors and matrices

- A row vector(a, b) can be considered as a1×2 matrix. Its transposition$(a, b)^T = \begin{pmatrix} a \\ b \end{pmatrix}$ is a column vector, or2×1 matrix. The same goes for vectors with larger number of components (in higher dimensions).

- A particular case of matrix multiplication is when the first matrix$\mathbf{M}$ is an$N \times N$ (square) matrix and the second matrix$\mathbf{x}$ is an$N \times 1$ matrix (a column vector). Then the product$\mathbf{M}.\mathbf{x} = \mathbf{y}$ gives a new$N-$row column vector. We say$\mathbf{y}$ is the rewsult of*applying*the matrix$\mathbf{M}$ to the vector$\mathbf{x}$.

- The column vector$\mathbf{x}$ is said to be an*eigenvector*of the matrix$\mathbf{M}$ if$\mathbf{M}.\mathbf{x} = \lambda \mathbf{x}$ for some scalarλ (a scalar is a real or complex number).

- The characteristic polynomial of a matrix$\mathbf{M}$ of dimensions$N \times N$ is the$|\mathbf{M} - \lambda \mathbf{1}|$, where$\lambda$ is a free variable and$\mathbf{1} = \begin{pmatrix} 1 & & \\ & \ddots & \\ & & 1 \end{pmatrix}$ is the$N \times N$ identity matrix.

- The eigenvalues of$\mathbf{M}$ are the roots of its characteristic polynomial, i.e. the values ofλ for which$|\mathbf{M} - \lambda \mathbf{1}| = 0$.

---

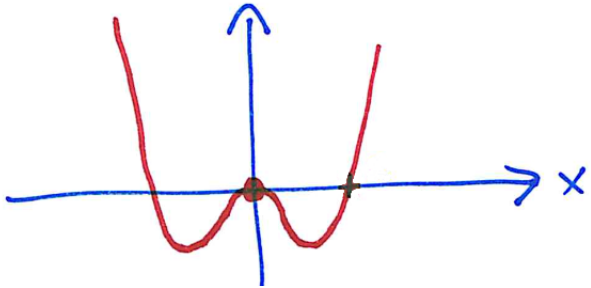
[20] This is a *revision* problem. It will not be assessed.

(a) Apply the matrix$\mathbf{C}$ in Problem2 to each of the vectors$\mathbf{p}, \mathbf{q}, \mathbf{r}$ in Problem1 to obtain new vectors$\mathbf{p}', \mathbf{q}', \mathbf{r}'$. Is any of them and eigenvector of$\mathbf{C}$?

(b) Find all the eigenvalues of each of the matrices$\mathbf{A}, \mathbf{B},$ and $\mathbf{C}$ in Problem2 by solving for the roots of their characteristic polynomials. Are your resuls for$\mathbf{C}$ consistent with what you obtained in the previous section?

5. [21]Sketch the possible orbits in phase space (i.e. the space of momentum$p$ and position$x$) of a particle moving in the following potential (see figure):

$$V(x) = -ax^2 + \frac{b}{4}x^4$$



Do this by solving the equation

$$\frac{p^2}{2m} + V(x) = E$$

for different values of the energy,E.

Give ranges of values of E over which the particle is localised on either side of the barrier and able to overcome it and move between the L and R sides of its accessible space, respectively.

Express your result as a function of the parameter$a > 0$.

---

[21] This is an*advanced*problem. It will not be assessed. Attempt this problem only after you are confident with the other problems covered so far.

Hints: *Inspection of the figure in combination with the above condition will tell you that for low values of the energy there are no solutions; for higher energies, but below certain threshold there are solutions in two disconnected regions of space: one with negative x and another one with positive x; and for higher energies there are solutions spanning a range of x going from negative to positive values.*

You can now sketch the orbits in phase space, i.e. in a p vs x plot. The disconnected orbits correspond to the particle being localised, depending on the initial conditions, either on the L or R side ($x < 0$ and $x > 0$, respectively). The higher-energy solutions correspond to a particle able to overcome the barrier and moving freely between L and R.

To find the energy thresholds to go from one behaviour to another you need to first find the stationary points of $V(x)$ by demanding $dV/dx = 0$ and then determine the value of $V(x)$ at those points. You can also check which stationary points are maxima or minima by computing the sign of d^2V/dx^2.

6. Eq. (1.6) describes quite generally the time evolution of a two-state quantum system. Given two energy levels available to the system, E_0 and E_1, the equation gives the period of oscillation of some other measurable property, such as the box the particle is in (in the one-particle-in-two-boxes example we dealt with in the lectures). Suppose a quantum system emits radiation by oscillating between two such states. Calculate the energy level difference necessary to produce radiation of the following wavelengths:

   (a) 1 pm (gamma rays);

   (b) 1 nm (soft X-rays);

   (c) 1 μm (visible light);

   (d) 500 m (medium frequency microwaves);

   (e) 80 km (Verly Low Frequency radio waves).

   Hint: *one way to tackle this is to use the speed of light in a vacuum, c, to convert the wavelength to a frequency, then from the frequency obtain the period of oscillation* τ *and solve for* $E_1 - E_0$.

7. A particle is in a linear superposition of two states with energies E_0 and E_1:

$$|\phi\rangle = A|E_0\rangle + \frac{A}{\sqrt{3-\epsilon}}|E_1\rangle$$

where $A > 0$ and $0 < \epsilon < 3$.

(a) What is the value of A? Express your answer as a function of ϵ.

(b) Use your expression to plot A vs ϵ.

(c) Show by a diagram the location of the state $|\phi\rangle$ on the Hilbert space, using $|E_0\rangle$ and $|E_1\rangle$ as the basis vectors, for $\epsilon = 0, 1,$ and 2.

Hint: *use the normalisation condition* $P(E_0) + P(E_1) = 1$.

8. A magnetic particle can have its magnetisation pointingup $|\uparrow\rangle$ or down $|\downarrow\rangle$. The eigenstates of the energy are

$$\begin{aligned} |E_0\rangle &= \frac{1}{\sqrt{2}}|\uparrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle \\ |E_1\rangle &= \frac{1}{\sqrt{2}}|\uparrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\rangle \end{aligned}$$

The particle is in a linear superposition

$$|\phi\rangle = A|E_0\rangle + \frac{A}{\sqrt{3}}|E_1\rangle$$

with $A > 0$.

(a) What is the value of A?

(b) What is the state vector in the $\{|E_0\rangle, |E_1\rangle\}$ basis?

(c) What is the state vector in the $\{|\uparrow\rangle, |\downarrow\rangle\}$ basis?

9. Consider the states

$$\begin{aligned} |\psi\rangle &= \frac{1}{\sqrt{2}}\left(e^{i\alpha}|x_L\rangle + |x_R\rangle\right) \\ |\phi\rangle &= \frac{1}{\sqrt{2}}\left(i|x_L\rangle + |x_R\rangle\right) \end{aligned}$$

where α is a real number. Compute the following quantities:

(a) $\langle\phi|\psi\rangle$

(b) $\langle\psi|\phi\rangle$

(c) $|\langle\psi|\phi\rangle|^2$

Hint:*for any complex numberz,*$|z|^2 = z^* z$.

10. A quantum communication channel uses superpositions of photon states with vertical polarisation $|\updownarrow\rangle$ and horizontal polarisation $|\leftrightarrow\rangle$. Individual qubits are transmitted using the states $|0\rangle, |1\rangle$ given by the following superpositions of polarised states:

$$
\begin{aligned}
|0\rangle &= \frac{1}{\sqrt{2}}\left(|\updownarrow\rangle + e^{i\pi/4}|\leftrightarrow\rangle\right) \\
|1\rangle &= \frac{1}{\sqrt{2}}\left(-i|\updownarrow\rangle + |\leftrightarrow\rangle\right)
\end{aligned}
$$

Invert these relations two write $|\updownarrow\rangle$ and $|\leftrightarrow\rangle$ in terms of $|0\rangle$ and $|1\rangle$ and use your result to write the state

$$
|\Phi\rangle = \frac{1}{2}\left(\sqrt{1}|\updownarrow\rangle + i\sqrt{3}|\leftrightarrow\rangle\right)
$$

explictly as a linear superposition of $|0\rangle$ and $|1\rangle$.

Hint: *to invert the basis transformation, use the given form to deduce the four projections of* $|0\rangle$,$|1\rangle$ onto $|\updownarrow\rangle$,$|\leftrightarrow\rangle$. *Then, use the fact the inverting the order of an inner product is the same as taking its complex conjugate to deduce the inverse relation.*

11. A qubit can be in one of two states

$$|0\rangle \text{ or } |1\rangle.$$

The Hamiltonian is given by

$$\hat{H} = \begin{pmatrix} 0 & -\Omega \\ -\Omega & 2\Omega/\sqrt{3} \end{pmatrix} \text{ in the } \{|0\rangle, |1\rangle\} \text{ basis,}$$

where the parameter Ω is an experimentally-controllable energy scale.

(a) Find the eigenvalues of the energy, E_+ and E_- ($E_- < E_+$).

(b) Find the ground state energy eigenvector

$$|E_-\rangle = \begin{pmatrix} A \\ B \end{pmatrix}$$

in the $\{|0\rangle, |1\rangle\}$ basis.

You may assume $A > 0$.

Hint:*Derive theg ratio A/B, then require normalisation.*

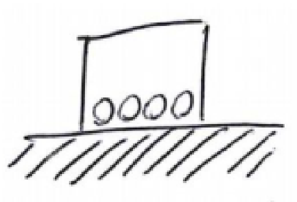
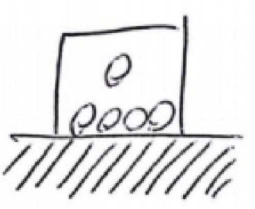
(c) A measurement of the energy of our qubit produces the lower value, E_-. What is the probability of finding the qubit in the state $|1\rangle$ straight after this measurement?

12. **Expectation values from probabilities.** A quantum system has 4 possible energy eigenstates $|E_1\rangle, |E_2\rangle, |E_3\rangle, |E_4\rangle$. The energy of the $n^{\underline{\text{th}}}$ eigenstate is known to be given by $E_n = \hbar\omega n$ for $n = 1, 2, 3, 4$. The system is in the following linear superposition of energy eigenstates:

$$|\psi\rangle = \frac{1}{2\sqrt{2}}\left(|E_1\rangle - i\frac{5}{2}|E_2\rangle + \frac{\sqrt{3}}{2}|E_4\rangle\right) .$$

What is the expectation value of the energy? Use the definition of expectation value, Eq. (2.60), to deduce your answer.

13. **Expectation values from operator matrices.** A "quantum dot" nanostructure acts as a single-electron capacitor that can have two charge states:

"empty" state	"charged" state
	
Charge Q $\vert 0\rangle$	Charge $Q+e$ $\vert e\rangle$

Let $\hat{C}$ be the charge operator with eigenstates $|0\rangle$ and $|e\rangle$:

$$\begin{aligned} \hat{C}|0\rangle &= Q|0\rangle; \\ \hat{C}|e\rangle &= (Q+e)\,|e\rangle. \end{aligned}$$

In terms of $\{|0\rangle, |e\rangle\}$, the two eigenstates of the energy are

$$|E_-\rangle = \frac{1}{2}\left(-|0\rangle + \sqrt{3}|e\rangle\right) \tag{7.48}$$

$$|E_+\rangle = \frac{1}{2}\left(\sqrt{3}|0\rangle + |e\rangle\right) \tag{7.49}$$

(a) Obtain the matrix

$$\begin{pmatrix} \left\langle E_- \middle| \hat{C} \middle| E_- \right\rangle & \left\langle E_- \middle| \hat{C} \middle| E_+ \right\rangle \\ \left\langle E_+ \middle| \hat{C} \middle| E_- \right\rangle & \left\langle E_+ \middle| \hat{C} \middle| E_+ \right\rangle \end{pmatrix}$$

that describes $\hat{C}$ in the energy basis $\{|E_-\rangle, |E_+\rangle\}$.

Hint: to calculate each of the four matrix elements, say $\left\langle E_- \middle| \hat{C} \middle| E_+ \right\rangle$, first write $\langle E^-|$ as a row vector, $\hat{C}$ as a matrix and $|E+\rangle$ as a column vector, all in the same basis, then simply calculate the product:

$$\underbrace{\langle E_-|}_{(1\times 2\ \mathit{matrix})} \quad \underbrace{\hat{C}}_{(2\times 2\ \mathit{matrix})} \quad \underbrace{|E_+\rangle}_{(2\times 1\ \mathit{matrix})} \qquad = \mathit{a\ number.}$$

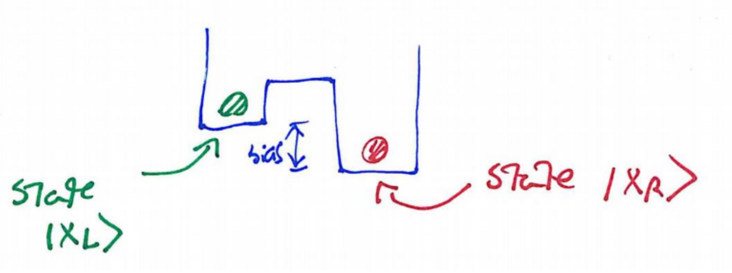
This is easy if we work in the charge basis.

(b) Using the above result, calculate the expectation value $\left\langle \psi \middle| \hat{C} \middle| \psi \right\rangle$ of the excess charge in the quantum dot when it is in the state

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left[\cos(\alpha)\, |E_-\rangle + \sin(\alpha)\, |E_+\rangle\right]$$

where α is a real number.

14. A biased double quantum dot can hold an electron on the LEFT ($x = x_L$) or the RIGHT ($x = x_R$):



The two eigenstates of the energy are

$$\begin{aligned} |E_0\rangle &= \frac{1}{\sqrt{3}}|x_L\rangle + \sqrt{\frac{2}{3}}|x_R\rangle \\ |E_1\rangle &= \sqrt{\frac{2}{3}}|x_L\rangle - \frac{1}{\sqrt{3}}|x_R\rangle \end{aligned}$$

The corresponding energy eigenvalues are E_0 and $E_1 = E_0 + \Delta E$ (with $\Delta E > 0$), respectively.

At $t = 0$ the electron is in the state $|x_L\rangle$.

What is the *earliest time* $\tau > 0$ at which a measurement of the electron's position will yield x_L or x_R with 50% probability? Express your result as a function of ΔE.

Hints: Compute the probability $P_R(t) = |\langle x_R|\psi(t)\rangle|^2$ *[or, equivalently,* $P_L(t) = |\langle x_L|\psi(t)\rangle|^2 = 1 - |\langle x_R|\psi(t)\rangle|^2$*] and solve the equation* $P_R(t) = 1/2$*. Because it is a trigonometric equation, there may be more than one solution, and you have to make sure you use the solution corresponding to the smallest value of* t*. It really helps if you plot* $P_R(t)$ *vs* t *to get a graphical view of what the solutions are and which the earliest one is.*

15. A particle has a magnetic moment that can only point up $|\uparrow\rangle$ or down $|\downarrow\rangle$.

At $t = 0$ the particle is in the $|\uparrow\rangle$ state.

For $t > 0$ the probability distribution for the magnetic moment direction evolves according to

$$\begin{aligned} P_\uparrow(t) &= \cos^2(\omega t) \\ P_\downarrow(t) &= \sin^2(\omega t) \end{aligned}$$

where ω is a known angular frequency.

At time $t = \tau$ $(0 < \tau < \pi/2\omega)$ a measurement of the particle's magnetic moment direction is carried out. The measurement indicates that the magnetic moment is again pointing up. A second measurement is carried out at a later time $t = \tau + \Delta t$.

- What is the probability that the second measurement will also show the magnetic moment to be pointing up?

Express your result as a function of the measurement delay Δt.

Hint: there's not much calculation involved. Just think carefully about what the measurement postulate implies for this problem.

16. Find the value of the constant $A > 0$ for the following state vectors/wave functions:

(a) Electron that can be at one of three sites x_1, x_2, x_3 with state vector

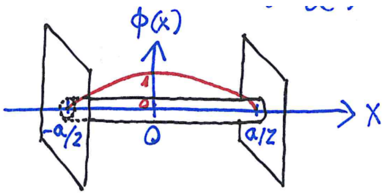
$$|\psi\rangle = \begin{pmatrix} 1/\sqrt{3} \\ i/\sqrt{4} \\ A \end{pmatrix}$$

(b) A photon moving along a straight, one-dimensional optical fibre with two mirrors at

$$x = -a/2 \text{ and } x = a/2$$

whose wave function is

$$\phi(x) = A\cos\left(\frac{\pi x}{a}\right)$$



Hint: In both cases, A is determined by enforcing normalisation.

17. **Continuum eigenfunctions.** Consider a free particle moving along the one-dimensional coordinate x. Check whether each of the following wave functions represent eigenstates of momentum, energy, or both. When the wave function is an eigenstate of one of the two observables, give the corresponding eigenvalue:

(a) $\psi\left(x\right) = Akx$

(b) $\phi\left(x\right) = A\cos\left(kx\right)$

(c) $\xi\left(x\right) = \frac{1}{\sqrt{2L}}\left[e^{ikx} + ie^{-ikx}\right]$

Hint: *you can use that for a free particle there is no interaction potential.*

18. Find the normalisation constant A in the wave function of a particle in a box,

$$\psi\left(x\right) = 2iA\sin\left(kx\right) \text{ where } k = \frac{\pi}{L}n,$$

as a function of n for $n = 2, 3, 4$.

19. Find k, κ, E for solutions to the "leaky box" problem with $E < V$ in the case when

$$\alpha = \frac{V}{\hbar^2/2mL^2} = 16.$$

Find the coefficients A and C determining the wave function

$$\psi(x) = \begin{cases} 2iA\sin(kx) & \text{if } 0 < x < L; \\ Ce^{-|\kappa|x} & \text{if } L < x < \infty. \end{cases}$$

Assume $C > 0$ (real and positive). Assume also that the length of the box, L, is known and give your results as functions of L.

20. Suppose an electron in a quantum dot is confined by a Gaussian-like potential

$$V(x) = -V_0 e^{-(x/\sigma)^2},$$

where x is the position of the electron along the symmetry axis of the nanostructure and V_0, σ are two known positive constants (with dimensions of energy and length, respectively).

(a) Find the SHO potential $V_{\text{SHO}}(x)$ that best approximates $V(x)$ near $x = 0$.

Hint: obtain the Taylor expansion of $V(x)$*, cutting it off at quadratic order in* x/σ*.*

(b) Plot $V_{\text{SHO}}(x)$ and $V(x)$ on the same graph, showing how they differ as$x$ becomes larger.

21. Substitute the formula in Eq. (5.18) for the time-evolution of the position of a harmonic oscillator, namely

$$x\left(t\right)=A\cos\left(\omega t+\phi\right),$$

in the corresponding classical equation of motion (5.17) to prove that it is a solution as long as ω obeys the relation in Eq. (5.19), that is, as long as the angular frequency of oscillations is given by

$$\omega=\sqrt{\frac{k}{m}}.$$

22. Substitute the definitions of the characteristic length and energy of a SHO [Eqs. (5.27,5.28)]

$$l_0 \equiv \sqrt{\frac{\hbar}{m\omega}}\ ,\ E_0 \equiv \frac{\hbar\omega}{2}$$

in the time-independent Schrödinger equation (5.25) to show it takes the form (5.30):

$$\frac{\partial^2}{\partial\xi^2}\varphi_n(\xi) + \left(\lambda_n - \xi^2\right)\varphi_n(\xi) = 0$$

where$\varphi_n(\xi) \equiv \psi_n(l_0\xi)$.

23. A gas containing hydroxide (OH^-) molecules has been an absorption line at wave number $1/\lambda = 3500\,\mathrm{cm}^{-1}$. This means that when photons with that wave number hit the molecule, they can be absorbed due to a transition between two successive energy levels of the molecule whose energy difference, ΔE, equals the energy of the photon. The two energy levels correspond to different vibrational states of the molecule. You may assume that the molecular vibrations can be described by the oscillating motion of the H^+ ion (i.e. a proton) around its equilbrium distance from the O^{2-} ion, which can be considered fixed (since its mass is much larger than that of the proton). You may assume that the two energy levels are consecutive.

   (a) Calculate the energy of photons absorbed in this line.

   Hint: use the speed of light to obtain the frequency of the light, then use Planck's equation giving the energy of a photon in terms of its frequency and Planck's constant.

   (b) Deduce the angular frequencyω of the effective harmonic oscillator potential in which the proton moves.

   Hint: use the equation obtained in the lectures for the energy difference between two consecutive energy levels of a SHO and equate it to the photon's energy. Solve for the harmonic oscillator frequency.

   (c) What pairs of vibrational states can be involved in the absorption of the photon?

24. Construct the $n = 2, 3$ solutions of the SHO (energy and wave functions). Compare them to the $n = 0, 1$ solutions obtained in the lectures, and put all four wave functions on the same plot, indicating the main differences.

25. Consider a particle of mass m confined to move along a straight line in a harmonic oscillator potential with angular oscillation frquency ω.The wave function

$$\psi\left(x\right)=Be^{-\frac{x^{2}}{2l^{2}}}x.$$

(a) Find the value of the normalisation constant B, as a function of$l$, by requiring that $\int_{-\infty}^{\infty}dx\,\left|\psi\left(x\right)\right|^{2}=1$.

(b) Show by substitution that this wave function corresponds to a stationary state of the particle, deriving a formula for the wave function parameter l and another one for the energy, both expressed as functions of m and ω.

(c) What is the probability that the particle is found between$-l$ and l? Compare your result to the case of a classical particle with the same energy.

26. Consider a simple harmonic oscillator. Let us denote by $|n\rangle$ its $n^{\underline{\text{th}}}$ stationary eigenstate, with energy $E_n = \hbar\omega\left(\frac{1}{2} + n\right)$. Let us assume that at $t = 0$ the system is in the state $|\Psi(0)\rangle \equiv \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$.

   (a) Write a computer code that plots the probability density $P(x,t) = |\langle x|\Psi(t)\rangle|^2$ as a function of position$x$ at any given time$t$.

   (b) Use your program to find the period with which the peak in the probability distribution oscillates from left to the right.

   (c) Compare your result to the classical period of oscillation of a simple harmonic oscillator.

27. A quantum particle is in a one-dimensional box potential (with infinitely high energy barrier at the edges of the box, $x = 0, L$). At time $t = 0$, the particle's state $|\psi\rangle$ is an equal superposition of the two lowest-energy stationary states, namely the ground state $|1\rangle$ and the first excited state $|2\rangle$, with equal phase for the two states: $|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$.

   (a) Find a formula for the probability density profile as a function of x at $t = 0$, $P(x, 0) = |\langle x|\psi\rangle|^2$. You will need the correctly-normalised particle-in-a-box stationary wave functions $\langle x|1\rangle$ and $\langle x|2\rangle$. Choose the normalisation factors to be real and such that the two stationary wave functions have the same sign on the left side of the box ($0 < x < L/2$).

   (b) Use a computer to plot the function $P(x, 0)$ obtained above.[22]

   (c) Find a numerical approximation to the valu x_{max} at which the probability density for finding the particle is maximum.

   (d) What is the current at $t = 0$, $j(x, 0)$?[22]

   (e) Find a formula for the time-dependent probability density profile, $P(x, t) = |\langle x|\psi(t)\rangle|^2$. You will need to make use of the particle-in-a-box energies, $E_n = n^2\hbar^2\pi^2/2mL^2$, which we derived in the lectures, to obtain the time dependence of each of the two components of the wave function: that corresponding to the ground state and that corresponding to the first excited state.

   (f) Make a plot (again, using a computer) showing how $P(x, t)$ changes as a function of time. You will see that the behaviour is periodic in time. Find the period (you can do this, for example, by

---

[22] The tools you use to complete parts27b,27c and27f is up to you. To create the plots, you could write a script in Python or Fortran, use a plotting program such as GNUplot, or even a chart on a spreadsheet. To find x_{max}, you could again write some code in a language of your choice, e.g. using the bisection method. Alternatively, some plotting programs like GNUplot allow you to place the cursor of the plot and read off the coordinates (which combined with zooming can give you quite an accurate reading of where two curves cross). You could even print the plot and use a ruler and a pencil - which is fine as far as the result is accurate to within 1% or so.

evaluating $P(x,t)$ at a fixed, arbitrary value of x for different times and seeing at what value of the time the probability density goes back to the value it had at $t=0$).[22]

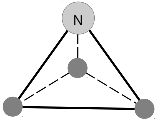
(g) Find an expression for the current in the centre of the box, $j\left(L/2,t\right)$ at arbitrary times t, using the time-dependent wave function which you obtained as part of part27e, above. Interpret your result in terms of the time-evolution of the probability distribution and find an analytical formula for the period.

28. In a future war, soldiers are equipped with guns that fire beams of positrons. They are also kitted out with suits that are reinforced with sheets made of a material designed to stop the positrons. Depending of the material used, the sheet can be made 1nm thick with a 1KeV high potential energy barrier for the positrons or 10nm thick with a 700eV high barrier. The positrons have energy equal to 600eV.

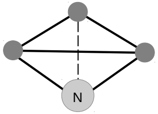
    (a) Calculate the transmission coefficient of each sheet to see which one is better.

    (b) What would the transmission coefficient be for a suit with both sheets, one on top of each other? (Assume that you can treat the two barriers as two consecutive, but independent tunneling problems).

29. The ammonia molecule (NH_3) can exist in one of two equivalent quantum states, $|a\rangle$ and $|b\rangle$, depending on whether the Nitrogen atom is, respectively, *a*bove or*b*elow the plane defined by the three Hydrogens:



$|a\rangle$



$|b\rangle$

Ignoring all other degrees of freedom, the Hamiltonian $\hat{H}_0$ can be written in terms of the parameters ϵ_0 and Δ (both of which are >0) by the following matrix:

$$\begin{pmatrix} \epsilon_0 & -\Delta \\ -\Delta & \epsilon_0 \end{pmatrix}$$

in the basis in which

$$|a\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } |b\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

An ammonia molecule is now placed in an externally-applied electric field which favours the state $|a\rangle$ over $|b\rangle$. The Hamiltonian is thus perturbed,

$$\hat{H}_0 \to \hat{H}_0 + \mathcal{E}\hat{H}_1,$$

where$\hat{H}_1$ is represented by the matrix

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and $\mathcal{E}$ is proportional to the electric field strength. Find the unperturbed stationary states of the system (specified by their state vectors) and their energies and compute the corrections to those energies using perturbation theory. Assume that $\mathcal{E}$ is small and that therefore we can compute the energies to second order in $\mathcal{E}$.

30. Show that the result (7.47) does not depend on the precise shape of the barrier as long as it is small, so we can use first-order parturbation theory, and the width is also small, $\delta \ll L$, by repeating the calculation for a Gaussian-shaped barrier,

$$\lambda V\left(x\right) = \lambda V_0 e^{-\left(\frac{x-L/2}{\delta}\right)^2}.$$

31. Consider the particle in a box perturbed by a small potential energy barrier as in the example on page144 of the lecture notes.

    (a) Compute the first-order approximations to the energies of the first excited state and the second excited state.

    (b) Interpret physically the results you obtain by examining a plot of the probability distribution $P(x)$ for the two unperturbed states.