Lecture Notes for Quantum Mechanics

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Niels Bohr (Nobel Prize in Physics 1922).

"If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet."

A visitor to Niels Bohr's country cottage, noticing a horse shoe hanging on the wall, teased Bohr about this ancient superstition. *Can it be true that you, of all people, believe it will bring you luck? Of course not*, replied Bohr, *but I understand it brings you luck whether you believe it or not.*

Contents

Some general remarks:

These notes aim to be self-contained. *Homework questions* are are placed at appropriate positions in the text, i.e. to work them out you will require only the preceeding material. Questions marked by a

star are optional. *Asides* give details on derivations we don't have time to go through in the lectures, or present material that goes beyond the core of the course. In some cases this material will be very useful for particular homework problems. *Exercises* are small problems that should be worked out after the lecture they pertain to. They are meant to ensure that you are continuously engaged with the course and not only the days immediately preceeding a tutorial.

This course aims to give an introduction to Quantum Mechanics. Let us start with some general context.

- QM is arguably humanity's greatest achievement. Actually, forget about the "arguably" part...

- Its understanding is the basis of much of our technological progress over the last 80 years.

- QM is intellectually challenging and only a minute fraction of humanity has any idea what it is about.

- We don't have an intuitive understanding of QM. As Richard Feyman famously said "Nobody understands quantum mechanics". An important addendum to this statement is that one naturally can not understand QM on a multitude of different levels, and the ultimate aim of this course is to elevate your ununderstanding to levels beyond your wildest imagination. Your ultimate goal should of course be to reach Feynman's level of ununderstanding...
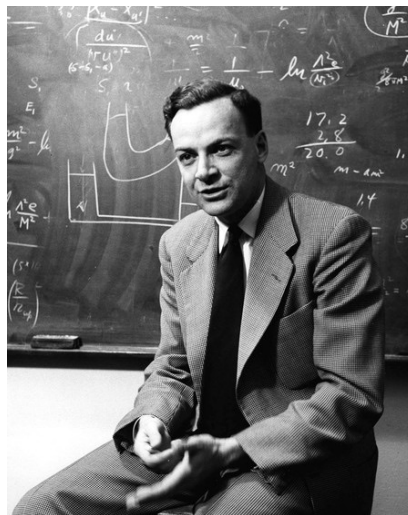
Figure 1: Richard Feynman (Nobel Prize in Physics 1965).

Part I
The Mathematical Structure of Quantum Mechanics

αγεωμετρητως μηδεις εισιτω Inscription on Plato's door.

QM is fundamentally different from Classical Mechanics in several ways:

- It does aim to provide a description of physical reality, but merely to make predictions for measurements. It is by its very design a *theory of measurement.*

- It accounts for the fact that measurements disturb the system; if the latter is small this is a large effect!

- QM is inherently probabilistic in nature: in general it cannot predict the outcome of a particular measurement exactly, but it rather provides a *probability distribution* for a set of possible outcomes.

  Examples of quantities that can be measured are energy, momentum, position, angular momentum. These are called *observables*. Measuring an observable can in general have many possible outcomes. These can be either *discrete* or *continuous*: position measurements will typically result in an outcome that various continuously in some interval $[a, b]$, but measuring energy will often result in a "quantized" set of outcomes E_1, E_2, ... Note that here and in the following we think of measurements in a rather abstract way and are not concerned with questions of experimental inaccuracies.

  The aim of QM is to provide *probability distributions* associated with measurements of observables

$$P(E_1), \; P(E_2), \ldots \qquad \sum_j P(E_j) = 1. \tag{1}$$

  These distributions give us a statistical understanding of what happens if we repeat a given experiment many times.

1   PROBABILITY AMPLITUDES AND QUANTUM STATES

1.1   PROBABILITY AMPLITUDES

A key aspect of QM is that probability enters in an unusual way. To stress this point let's recall that "classical" probabilities fulfil rules like

- If A,B are independent events with probabilities P(A) and P(B), then the probability for A *and* B is P(A and B)= P(A)P(B).

- If A,B are exclusive events with probabilities P(A) and P(B), then the probability for A *or* B is P(A or B)= P(A)+P(B).

QM works differently by construction. To understand why we follow Master Quantum Mechanic Richard Feynman's exquisite discussion (Feynman Lectures on Physics Vol 3) of double-slit thought experiments, which, incidentally, in German is of course a single word "Doppelspaltgedankenexperimente" – don't you just love it!

Feynman first considers the double-slit experiment for classical bullets. These can go through either slit,
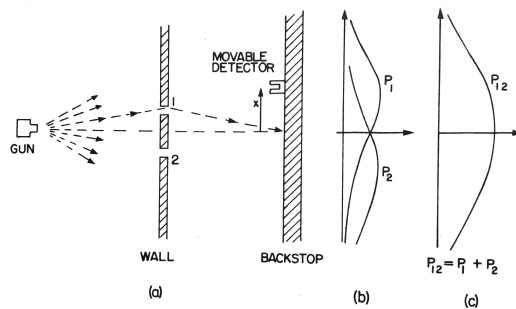
Figure 2: A double-slit experiment with indestructable bullets.

and the probability $P_{12}(x)$ of bullets arriving at position x on the detector screen is simply the sum of the probabilities $P_1(x)$ and $P_2(x)$ obtained by closing holes 2 and 1 respectively, i.e.

$$P_{12} = P_1 + P_2. \tag{2}$$

So for classical bullets we are dealing with classical probabilities.

Quantum mechanics works completely differently, as can be seen by repeating the double-slit experiment for electrons. What one observes is that electrons still reach the detector in "lumps", but now $P_{12}(x) \neq$
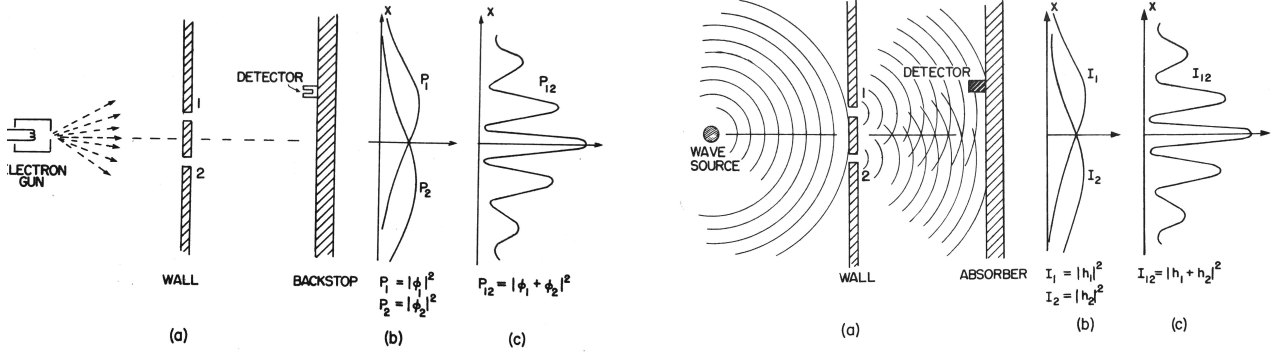
Figure 3: A double-slit experiment with (a) electrons and (b) waves.

$P_1(x) + P_2(x)$. Moreover, the observed probability distribution looks suspiciously like the interference pattern we would observe when conducting the experiment with waves! For waves we understand perfectly that intensities do not add, but instead we have

$$I_1 = |h_1|^2 , \quad I_2 = |h_2|^2 , \quad I_{12} = |h_1 + h_2|^2 , \tag{3}$$

where $h_{1,2}$ are the *amplitudes* of the waves. What the Doppelspaltgedankenexperiment shows is that electrons in some way behave like particles (lumpiness at detector) and in some ways like waves (interference)! This is called *particle-wave duality*.

The way to encode the baffling interference phenomenon into the fabric of QM is to postulate that the fundamental objects in QM are not probabilities, but *probability amplitudes A*.

Postulate 1: Probabilities from Probability Amplitudes

Probability amplitudes are complex numbers associated with the outcomes of measurements. The corresponding probabilities are obtained as

$$P(A) = |A|^2. \tag{4}$$

If there are several ways of arriving at a particular measurement outcome the associated probability amplitudes add.

This postulate allows us to understand why there is an interference pattern in out double-slit experiment for electrons. By Postulate 1 we have

$$P(x) = |\text{Probability amplitude to go from the electron gun to x}|^2 . \tag{5}$$

Clearly there are two paths from the gun G to position x on the screen. The electron could travel via slit 1 or via slit 2. Denoting the associated probability amplitudes by $A(1)$ and $A(2)$ respectively we have by our postulate

$$P(x) = |A(1) + A(2)|^2 , \tag{6}$$

because probability amplitudes add. Working this out we have

$$P(x) = |A(1)|^2 + |A(2)|^2 + \underbrace{2\text{Re}\left[A(1)A^*(2)\right]}_{\text{"Interference term"}}. \tag{7}$$

6

Expressing the complex amplitudes in terms of their magnitudes and phases $A(1) = \sqrt{P(1)}e^{i\phi(1)}$ we can rewrite this as

$$P(x) = P(1) + P(2) + 2\sqrt{P(1)P(2)}\cos\left(\phi(1) - \phi(2)\right). \tag{8}$$

This is clearly very different from the "classical" rule for adding probabilities for exclusive events! For $x \approx 0$ we have $P(1) \approx P(2)$ and therefore

$$P(x) \approx 2P(1)\left[1 + \cos\left(\phi(1) - \phi(2)\right)\right]. \tag{9}$$

The "classical" result would simply be $2P(1)$, while QM predicts a probability distribution that oscillates between 0 and $4P(1)$ as a consequence of "QM interference". Before we take leave of our double-slit experiments there is one more variation we need to consider. Now we position a light source behind the double
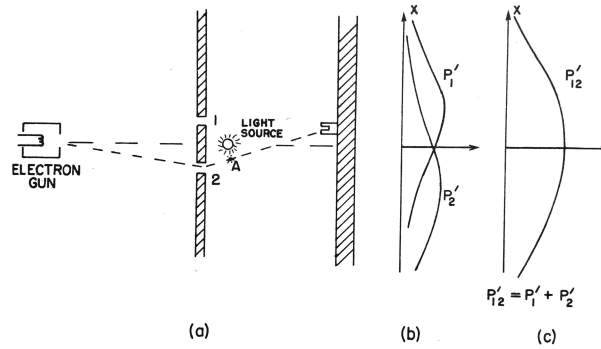
Figure 4: Double-slit experiments with electrons where we measure through which slit the electrons go.

slit, which allows us to measure through which slit the individual electrons go. In this experimental setup the interference disappears and probabilities add! If this does not give you goosebumps there is something seriously wrong with you! Our framework for QM will have to account for this bizarre interference-killing effect as well.

> **NB 1**
>
> The fundamental idea in QM is to associate probability amplitudes with measurement outcomes of given observables.

- Example 1: Let $E_0, E_1, \ldots$ be the possible outcomes of an energy measurement. With each energy we associate a complex probability amplitude $A(E_j)$ such that the probability for measuring E_j is $P(E_j) = |A(E_j)|^2$ and

$$\sum_j P(E_j) = 1. \tag{10}$$

- Example 2: Consider a position measurement in one dimension (like the one above). The possible outcomes are then real numbers in some interval $x \in [a, b]$. With each position x we associate a complex probability amplitude $\psi(x)$ such that $P(x) = |\psi(x)|^2$ and

$$\int_a^b dx \; P(x) = 1. \tag{11}$$

In this case the set of probability amplitudes can be viewed as a complex valued function.

1.2 Complete sets of amplitudes and quantum states

Knowing all amplitudes $A(E_j)$ provides us with a probabilistic description of repeated energy measurements in the following sense.

- Set up an experiment in a particular way. This fixes a particular set of probability amplitudes $\{A(E_0), A(E_1), \dots\}$.

- Measure the energy. The result is E_j Write the result down.

- Repeat the experiment many times (we imagine that we can set things up in precisely the same way each time). The ultimate result of our efforts is a *histogram* that gives probabilities $P(E_j)$ for the various observed measurement outcomes E_j. QM asserts that $P(E_j) = |A(E_j)|^2$.

- Changing our experimental setup would result in a different set of amplitudes $\{A'(E_0), A'(E_1), \dots\}$.

So far so good. The next step is a crucial one.

Definition 1 *A key aspect of QM is that specifying amplitudes for e.g. an energy measurement can provide enough information to obtain probabilistic descriptions of measurement outcomes of* any *other observable. Such sets of amplitudes are called* **complete**.

An efficient way of encoding the information contained in a complete set of amplitudes $\{A(E_0), A(E_1), \dots\}$ is to combine them into a *vector*

$$|\psi\rangle = (A(E_0), A(E_1), \dots). \tag{12}$$

We call this a *state* or *ket-state* using a terminology (and very clever notation) invented by P.A.M. Dirac.

Paul A.M. Dirac (Nobel Prize in Physics 1933).

"If you are receptive and humble, mathematics will lead you by the hand".

1.3 Dirac notation for complex linear vector spaces

It is easy to see that ket states form a complex linear vector space V. Addition of two kets is defined in terms of addition of the associated amplitudes

$$|\psi\rangle + |\phi\rangle = (A(E_0) + A'(E_0), A(E_1) + A'(E_1), \dots), \tag{13}$$

while multiplication by complex numbers is defined as

$$c|\psi\rangle = (cA(E_0), cA(E_1), \dots). \tag{14}$$

The vector space structure makes it clear that there are special states such that all amplitudes are zero except $A(E_j) = 1$. We denote these states by $|E_j\rangle$. By construction they are such that an energy measurement in a system described by the ket $|E_j\rangle$ returns the result E_j with probability 1. In other words they are *states of definite energy*. If $\{A(E_j)\}$ is a complete set of amplitudes these form a *basis* of V: any ket $|\psi\rangle$ can be expressed as a linear combination

$$|\psi\rangle = \sum_j \psi_j |E_j\rangle, \quad \psi_j \in \mathbb{C}. \tag{15}$$

1.3.1 DUAL ("BRA") STATES

Given a state $|\psi\rangle$ we want a quick way for extracting individual amplitudes. Mathematically speaking we are searching for linear maps

$$
\begin{aligned}
V &\longrightarrow \mathbb{C} \\
|\psi\rangle &\longrightarrow \psi_j
\end{aligned} \tag{16}
$$

such that $\alpha|\psi\rangle + \beta|\phi\rangle$ maps to $\alpha\psi_j + \beta\phi_j$. For finite dimensional linear vector spaces such maps form a linear vector space V^*, the *dual space*, of the same dimension as V. Dirac notations provide us with a very neat way of constructing a basis of V^*:

- Start with an orthonormal basis $B = \{|j\rangle\}$ of V.

- Define corresponding "bra" states $\langle j| \in V^*$ by specifying their action on B

$$
\langle n|j\rangle = \delta_{n,j} , \quad \text{"bra-ket" – Dirac's only joke.} \tag{17}
$$

- Extend this to general states $|\psi\rangle = \sum_j \psi_j |j\rangle$ by the rule

$$
\langle\psi| = \sum_j \psi_j^* \langle j| . \tag{18}
$$

In this way $\langle\psi|\phi\rangle$ turns into the usual scalar product for complex linear vector spaces

$$
\langle\psi|\phi\rangle = \sum_j \psi_j^* \phi_j = (\langle\phi|\psi\rangle)^* , \tag{19}
$$

and

$$
\langle\psi|\psi\rangle = \sum_j |\psi_j|^2 \geq 0 \quad \text{"Length" of } |\psi\rangle. \tag{20}
$$

NB 2

he length of state vectors in QM must always be 1, because probabilities must add up to 1.

1.4 ... AND BACK TO MEASUREMENTS

To describe the measurement of an observable A we express the ket $|\psi\rangle$ that describes our system as a linear combination of basis states that correspond to definite outcomes a_j

$$
|\psi\rangle = \sum_j \psi_j |a_j\rangle , \quad \psi_j = \langle a_j|\psi\rangle , \quad \sum_j |\psi_j|^2 = 1. \tag{21}
$$

The probability to obtain a_j in our measurement is

$$
|\psi_j|^2 = |\langle a_j|\psi\rangle|^2 \quad \text{"Born's rule."} \tag{22}
$$

An important question is what "state" a quantum mechanical system is in just after a particular observable has been measured. As QM deals with very small things measurements can greatly disturb the QM system, i.e. *change its QM state*. What should we expect? To be more precise let's start with a QM system described by the state $|\psi\rangle$, then measure the observable A and obtain the result a_j.

Figure 5: Max Born (Nobel Prize in Physics 1954) ... and his more famous granddaughter. Born is said to have thought that the Copenhagen interpretation of QM should really be called the Göttingen interpretation. He has a point...

Postulate 2: Projective nature of measurements

We expect that if we measure A again straight away, we will obtain the result a_j with certainty. This is only possible if the first measurement leaves the system in the state $|a_j\rangle$ – meaning that measurements are **projective**:

$$|\psi\rangle \longrightarrow \text{measure A, obtain result } a_j \Rightarrow \text{ system left in the state } |a_j\rangle.$$
(23)

1.5 ARBITRARINESS OF THE OVERALL PHASE

Let us now consider the two states $|\psi\rangle$ and $|\psi'\rangle = e^{i\alpha}|\psi\rangle$ where α is an arbitrary phase. According to the rules we have presented, there is no way of telling these two states apart through any quantum mechanical measurement! Indeed we have

$$|\psi'\rangle = e^{i\alpha}|\psi\rangle = \sum_j e^{i\alpha}\langle a_j|\psi\rangle \, |a_j\rangle.$$
(24)

Hence the possible measurement outcomes are again given by the set $\{a_j\}$ and the corresponding probabilities are

$$|\langle a_j|\psi'\rangle|^2 = |e^{i\alpha}\langle a_j|\psi\rangle|^2 = |\langle a_j|\psi\rangle|^2.$$
(25)

This tells us that $|\psi\rangle$ and $e^{i\alpha}|\psi\rangle$ *describe the same quantum mechanical state*. In the mathematical literature the states $e^{i\alpha}|\psi\rangle$, $\alpha \in \mathbb{R}$ are called a *ray*. In practice we will always fix the overall phase of quantum states in a convenient way.

Example 1: Atom in a double-well potential

As much of our discussion is necessarily rather abstract it is useful to explain how the new concepts work for a simple, but realistic example. Our example of choice will be a single atom confined by an external electromagnetic field (that couples to the atom's magnetic moment). This trapping works due to quantum mechanical effects, which means that we can't explain it at this point in the course. As we will see later in the course, atoms are in fact rather complicated quantum mechanical systems

themselves. However, there is an experimentally realizable regime, in which the only relevant degree of freedom associated with the atom is purely *motional*, i.e. the atom can move between local minima of the electromagnetic potential. The upshot is that, with respect to the relevant experimental probes, our simple QM system is characterized by two different probability amplitudes, associated with the atom sitting in the left and right potential well respectively, giving rise to the two quantum states $|1\rangle$ and $|2\rangle$

A general quantum state in this system is then of the form

$$|\psi\rangle = \alpha|1\rangle + \beta|2\rangle \ , \quad |\alpha|^2 + |\beta|^2 = 1. \tag{26}$$

If we prepare our system in the state $|\psi\rangle$ and then measure the position of the atom (e.g. by shining light on it), we find that with probability $|\alpha|^2$ ($|\beta|^2$) it is in the left (right) well. By this we mean that if we repeat the state-preparation and subsequent measurement procedure N times, we obtain a sequence of outcomes $RLLLRRRLRLLLRRLLLRRLLRLLLR...$, where R and L indicate that the atom was observed in the right/left well. Denoting by $N_{R,L}$ the numbers of R's and L's in our sequence, QM tells us that as N becomes large we have $N_R/N = |\alpha|^2$ and $N_L/N = |\beta|^2$.

Summary 1

1. QM systems are described by *quantum "ket" states* $|\psi\rangle$. These correspond to different ways of experimentally "setting up" the system. States that differ only by an overall phase factor describe the same physical situation and are to be identified.

2. Kets form a complex linear vector space V.

3. To each state $|\psi\rangle$ we can associate a complex valued linear map $\langle\psi|$. These "bra-vectors" form a linear vector space V^* of the same dimension as V.

4. To describe a measurement of an observable A we express the state $|\psi\rangle$ describing our system as a linear superposition of basis states that correspond to definite measurement outcomes a_j for A

$$|\psi\rangle = \sum_j \psi_j|a_j\rangle \ , \quad \psi_j = \langle a_j|\psi\rangle \ , \quad \sum_j |\psi_j|^2 = 1. \tag{27}$$

The probability to obtain a_j in our measurement is

$$|\psi_j|^2 = |\langle a_j|\psi\rangle|^2 \qquad \text{"Born's rule."} \tag{28}$$

5. After the measurement the system is left in the state $|a_j\rangle$ (if the outcome of the measurement was a_j).

1.1 What physical phenomenon requires us to work with probability amplitudes rather than with probabilities?

1.2 Given that $|\psi\rangle = e^{i\pi/5}|a\rangle + e^{i\pi/4}|b\rangle$, express $\langle\psi|$ as a linear combination of $\langle a|$ and $\langle b|$.

1.3 An electron can be in one of two potential wells that are so close that it can 'tunnel' from one to the other. Its state vector can be written

$$|\psi\rangle = a|A\rangle + b|B\rangle, \tag{29}$$

where $|A\rangle$ is the state of being in the first well and $|B\rangle$ is the state of being in the second well and all kets are correctly normalised. What is the probability of finding the particle in the first well given that: (a) $a = i/2$; (b) $b = e^{i\pi}$; (c) $b = \frac{1}{3} + i/\sqrt{2}$?

1.4 An electron can "tunnel" between potential wells that form a linear chain, so its state vector can be written as

$$|\psi\rangle = \sum_{n=-\infty}^{\infty} a_n|n\rangle, \tag{30}$$

where $|n\rangle$ is the state of being in the nth well, where n increases from left to right. Let

$$a_n = \frac{1}{\sqrt{2}}\left(\frac{-i}{3}\right)^{\frac{|n|}{2}} e^{in\pi}. \tag{31}$$

(a) What is the probability of finding the electron in the nth well?
(b) What is the probability of finding the electron in well 0 or anywhere to the right of it?

2 OPERATORS AND OBSERVABLES

In the lab we (i.e. our experimental colleagues) can *manipulate* quantum states, i.e. devise protocols that map states to other states. In our mathematical framework this is described by considering *linear operators* acting on V

$$\mathcal{O}: \quad V \longrightarrow V$$
$$|\psi\rangle \longrightarrow \mathcal{O}|\psi\rangle , \tag{32}$$

where $\mathcal{O}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha\mathcal{O}|\psi\rangle + \beta\mathcal{O}|\phi\rangle$. Dirac notation provides us with a very useful way of expressing operators. A general operator can be expressed in terms of basis states $|j\rangle$ and their dual states $\langle j|$ as follows:

- The object $|j\rangle\langle k|$ is a linear operator.
  Proof:
  $$|k\rangle\langle j|\left(\alpha|\psi\rangle + \beta|\psi\rangle\right) = |k\rangle\left(\alpha\langle j|\psi\rangle + \beta\langle j|\psi\rangle\right) = \underbrace{\alpha\langle j|\psi\rangle}_{\in\mathbb{C}}|k\rangle + \beta\langle j|\psi\rangle|k\rangle . \tag{33}$$

- The identity operator is
  $$\mathbf{1} = \sum_j |j\rangle\langle j|. \tag{34}$$

  Proof: Act with $\mathbf{1}$ on a general state $|\psi\rangle = \sum_k \psi_k|k\rangle$:
  $$\left[\sum_j |j\rangle\langle j|\right]|\psi\rangle = \sum_k \psi_k \sum_j |j\rangle\underbrace{\langle j|k\rangle}_{\delta_{j,k}} = \sum_k \psi_k|k\rangle = |\psi\rangle. \tag{35}$$

- A general operator A can be written in the form

$$A = \sum_{j,k} \langle j|A|k\rangle \; |j\rangle\langle k| \; .$$

(36)

the complex numbers $\langle j|A|k\rangle$ are called *matrix elements* of A in the basis $\{|j\rangle\}$.

Proof:

$$A = \mathbf{1}A\mathbf{1} = \Big(\sum_j |j\rangle\langle j|\Big)A\Big(\sum_k |k\rangle\langle k|\Big) \; .$$

(37)

> **NB 3**
>
> For finite dimensional linear vector spaces linear operators correspond to square matrices.

Like for matrices, a very useful way to characterize an operator is through its *eigenvalues* and *eigenvectors* ("eigenstates"). The eigenvalue equation for an operator $\mathcal{O}$ is

$$\mathcal{O}|o_j\rangle = o_j|o_j\rangle.$$

(38)

The eigenvalues $\{o_j\}$ form the *spectrum* of the operator $\mathcal{O}$. The most important operator in QM is the *Hamiltonian*, or energy operator. It is defined by

$$H = \sum_j E_j|E_j\rangle\langle E_j|,$$

(39)

where $|E_j\rangle$ are the quantum states introduced above that give result E_j with probability one when the energy is measured. The Hamiltonian fulfils by construction

$$H|E_j\rangle = E_j|E_j\rangle.$$

(40)

Hence the spectrum of the Hamiltonian is equal to the set of possible outcomes of energy measurements. This generalizes to other observables: with each observable we can associate an operator by

$$A = \sum_j a_j|a_j\rangle\langle a_j| \; ,$$

(41)

where $\{|a_j\rangle\}$ is a complete set of states that return the result a_j with probability one when the observable under consideration is measured. As the outcomes of the measurements we have in mind (energy, momentum, position etc) are real numbers the operators representing observables must be special.

2.1 Hermitian Operators

In QM observables are represented by *Hermitian* operators

$$A \text{ Hermitian} \Leftrightarrow (\langle\phi|A|\psi\rangle)^* = \langle\psi|A|\phi\rangle \; .$$

(42)

Hermitian operators have three crucial properties that we will use constantly in the following:

(H1) Their eigenvalues are real.

(H2) Eigenstates corresponding to different eigenvalues are orthogonal

$$\langle a_j|a_k\rangle = 0 \text{ if } a_j \neq a_k.$$

(43)

(H3) One can always construct an orthonormal basis of V from the eigenstates of a Hermitian operator.

Definition 2 *The Hermitian conjugate $B^\dagger$ of an operator B is defined by*

$$\langle\phi|B^\dagger|\psi\rangle = (\langle\psi|B|\phi\rangle)^* . \tag{50}$$

Hermitian operators fulfil $A = A^\dagger$. The following rules for taking Hermitian conjugates will be useful:

$$(A + B)^\dagger = A^\dagger + B^\dagger , \tag{51}$$
$$(cA)^\dagger = c^*A^\dagger , \tag{52}$$
$$(AB)^\dagger = B^\dagger A^\dagger . \tag{53}$$

Let us return to our example of an atom in a double-well potential. As discussed earlier, a basis of quantum states is provided by the two states shown below
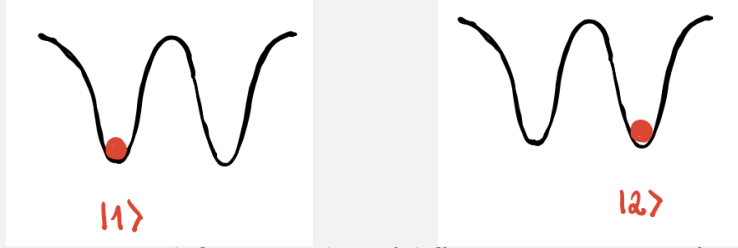
We can now define a number of different operators. In fact there are altogether 4 linearly independent operators in this system, namely

$$\hat{N}_1 = |1\rangle\langle 1| \ , \qquad \hat{N}_2 = |2\rangle\langle 2| \ ,$$
$$\hat{T}_R = |2\rangle\langle 1| \ , \qquad \hat{T}_L = |1\rangle\langle 2| \ . \tag{57}$$

The operators $\hat{N}_{1,2}$ are Hermitian and hence correspond to observables, while $\hat{T}_R^\dagger = \hat{T}_L$. We can however construct linear combinations $\hat{S} = \hat{T}_R + \hat{T}_L$ and $\hat{Y} = i[\hat{T}_R - \hat{T}_L]$ that are Hermitian operators. The physical meaning of the observables corresponding to $\hat{N}_{1,2}$ is easy to work out: they count the number of atoms in wells 1 and 2 respectively. Indeed, $|1\rangle$ and $|2\rangle$ are eigenstates of $\hat{N}_{1,2}$ and the corresponding eigenvalues are one and zero

$$\hat{N}_1|1\rangle = |1\rangle \ , \quad \hat{N}_1|2\rangle = 0 \ ,$$
$$\hat{N}_2|2\rangle = |2\rangle \ , \quad \hat{N}_2|1\rangle = 0 \ . \tag{58}$$

The operator $\hat{S}$ swaps the position of the atom and we therefore will call it swap operator

$$\hat{S}|1\rangle = |2\rangle \ , \quad \hat{S}|2\rangle = |1\rangle \ . \tag{59}$$

Its eigenvalues are ± 1 and the corresponding eigenstates are

$$\hat{S}|\pm\rangle = \pm|\pm\rangle \ , \qquad |\pm\rangle = \frac{|1\rangle \pm |2\rangle}{\sqrt{2}}. \tag{60}$$

Homework 2: OPERATORS

1.5 Let Q be the operator of an observable and let $|\psi\rangle$ be the state of our system.
(a) What are the physical interpretations of $\langle\psi|Q|\psi\rangle$ and $|\langle q_n|\psi\rangle|^2$, where $|q_n\rangle$ is the nth eigenket of the observable Q and q_n is the corresponding eigenvalue?
(b) What is the operator $\sum_n |q_n\rangle\langle q_n|$, where the sum is over all eigenkets of Q? What is the operator $\sum_n q_n|q_n\rangle\langle q_n|$?

1.6 Which of the following operators are Hermitian, given that $\hat{A}$ and $\hat{B}$ are Hermitian:
$\hat{A} + \hat{B}$; $c\hat{A}$; $\hat{A}\hat{B}$; $\hat{A}\hat{B} + \hat{B}\hat{A}$.
Show that in one dimension, for functions which tend to zero as $|x| \to \infty$, the operator $\partial/\partial x$ is not Hermitian, but $-i\hbar\partial/\partial x$ is. Is $\partial^2/\partial x^2$ Hermitian?

1.7 Given that $\hat{A}$ and $\hat{B}$ are Hermitian operators, show that $i[\hat{A}, \hat{B}]$ is a Hermitian operator.

1.8 Given that for any two operators $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$, show that

$$(\hat{A}\hat{B}\hat{C}\hat{D})^\dagger = \hat{D}^\dagger\hat{C}^\dagger\hat{B}^\dagger\hat{A}^\dagger.$$

2.2 COMMUTATORS AND COMPATIBLE OBSERVABLES

Definition 3 *The commutator of two operators A and B is*

$$[A, B] = AB - BA. \tag{61}$$

In QM commutators play an important role because of the following theorem.

Theorem 1 *Let A and B be two Hermitian operators. If $[A, B] = 0$ there exists a complete set of simultaneous eigenstates of the operators A and B, i.e.*

$$A|u_j\rangle = a_j|u_j\rangle , \quad B|u_j\rangle = b_j|u_j\rangle, \tag{62}$$

and $\{|u_j\rangle\}$ form a basis of the LVS on which A and B act.

Proof: One direction is simple: if A and B have a complete set of simultaneous eigenstates $|u_j\rangle$ we have

$$\langle u_j|[A, B]|u_k\rangle = (a_k b_k - b_k a_k)\langle u_j|u_k\rangle = 0, \tag{63}$$

which implies that the commutator is zero (because the $|u_j\rangle$ form a basis). Let's now turn to the other direction of the proof, i.e. let's assume $[A, B] = 0$ and show that this implies the existence of a complete set of simultaneous eigenstates. As A is Hermitian we know that is has a complete set of orthogonal eigenstates

$$A|a_j\rangle = a_j|a_j\rangle , \quad \langle a_j|a_k\rangle = \delta_{j,k}. \tag{64}$$

Now consider the matrix elements of the commutator in this basis

$$0 = \langle a_j|[A, B]|a_k\rangle = (a_j - a_k)\langle a_j|B|a_k\rangle \tag{65}$$

This tells us that if all eigenvalues a_j are different, we have $\langle a_j|B|a_k\rangle \propto \delta_{j,k}$, i.e. the eigenstates $|a_j\rangle$ of A are simultaneous eigenstates of B. The situation is a bit more complicated if some of the a_j are equal. Let us assume that n of the a_j are equal and let's label the eigenstates of A such they correspond to $a_1 = a_2 = \cdots = a_n = a$. Then

(i) Any linear combination $\sum_{j=1}^{n} \alpha_j|a_j\rangle$ is an eigenstate of A with eigenvalue a.

(ii) On the subspace spanned by $\{|a_1\rangle, \ldots, |a_n\rangle\}$ B is represented by Hermitian matrix $B_{jk} = \langle a_j|B|a_k\rangle$. Hence it can be diagonalized, i.e. we can construct eigenstates $|u_k\rangle$ of B by taking appropriate linear combinations of the $|u_k\rangle = \sum_{j=1}^{n} \beta_j^{(k)}|a_j\rangle$. These are simultaneous eigenstates of A by (i).

This generalizes straightforwardly to the case where we have several "degenerate" eigenvalues.

Even though all this Linear Algebra is of course very interesting in itself, you may be asking yourselves at this point what on earth this has to do with QM. As you may have guessed, it has to do with measurements! Let us consider two Hermitian operators A and B that correspond to two observables in an experiment. We know that the respective eigenstates of A and B can be used to construct an orthonormal basis of our linear vector space of quantum states

$$A|a_i\rangle = a_i|a_i\rangle, \quad B|b_i\rangle = b_i|b_i\rangle \Rightarrow |\psi\rangle = \sum_i \langle a_i|\psi\rangle \, |a_i\rangle = \sum_i \langle b_i|\psi\rangle \, |b_i\rangle. \tag{66}$$

Let us now make the following Gedankenexperiment: we first measure the observable corresponding to A, and then straight away measure the observable corresponding to B (without re-initializing our experiment). We want to compare this to the reverse order of measurements. Here we go:

- Measure A, then B

$$\begin{aligned} |\psi\rangle \quad &\longrightarrow \quad \text{measure A: } a_i \text{ with prob. } |\langle a_i|\psi\rangle|^2, \text{ system in state } |a_i\rangle \\ &\longrightarrow \quad \text{measure B: } b_j \text{ with prob. } |\langle b_j|a_i\rangle|^2 \text{ .} \end{aligned} \tag{67}$$

So the final outcome is a table of outcomes with associated probabilities

$$\text{outcome } (a_i, b_j) \text{ probability } |\langle a_i|\psi\rangle|^2 \, |\langle b_j|a_i\rangle|^2 \tag{68}$$

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- Measure B, then A

$$\begin{aligned}
|\psi\rangle \quad &\longrightarrow \quad \text{measure B: } b_j \text{ with prob. } |\langle b_j|\psi\rangle|^2, \text{ system in state } |b_j\rangle \\
&\longrightarrow \quad \text{measure A: } a_i \text{ with prob. } |\langle a_i|b_j\rangle|^2 \, .
\end{aligned} \tag{69}$$

So here the final outcome is a table

$$\text{outcome } (a_i, b_j) \text{ probability } |\langle b_j|\psi\rangle|^2 \, |\langle a_i|b_j\rangle|^2 \tag{70}$$

Clearly, the tables of measurement outcomes we obtain in the two ways will generally be different! That. Is. Deep. If the order of measurement does not matter, the observables corresponding to A and B are called *compatible*. As the order of measurement for two compatible observables does not matter and we always end up in a quantum state where both observables have a definite value, one could in principle set up an experiment that measures both observables *simultaneously*.

Theorem 2 *Two observables are compatible if and only if the commutator between the associated Hermitian operators vanishes*

$$[A, B] = 0. \tag{71}$$

Proof: If $[A, B] = 0$ there exists a basis of simultaneous eigenstates of A and B. Using this basis in the above consideration it is easy to see that the two outcomes are identical. On the other hand, if $[A, B] \neq 0$ there must be at least one eigenstate $|a_j\rangle$ of A that is not an eigenstate of B. As the state $|\psi\rangle$ above is arbitrary we can choose it to be $|a_j\rangle$. By considering the two sets of outcomes we see that they can only be equal if $|a_j\rangle$ is an eigenstate of B, giving a contradiction. This completes the proof.

Example 3: Atom in a double-well potential

As an explicit example let us see how sequential measurements work for our system of an atom in a double well potential. Let us consider measuring the observables corresponding to $\hat{N}_1$ and $\hat{S}$ when the system is prepared in the state $|\psi\rangle = |1\rangle$.

Homework 3: COMMUTATORS

1.9 Show that if there is a complete set of mutual eigenkets of the Hermitian operators $\hat{A}$ and $\hat{B}$, then $[\hat{A}, \hat{B}] = 0$. Explain the physical significance of this result.

1.10 Does it always follow that if a system is an eigenstate of $\hat{A}$ and $[\hat{A}, \hat{B}] = 0$ then the system will be in a eigenstate of $\hat{B}$? If not, give a counterexample.

1.11 Show that
(a) $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$
(b) $[\hat{A}\hat{B}\hat{C}, \hat{D}] = \hat{A}\hat{B}[\hat{C}, \hat{D}] + \hat{A}[\hat{B}, \hat{D}]\hat{C} + [\hat{A}, \hat{D}]\hat{B}\hat{C}$. Explain the similarity with the rule for differentiating a product.
(c) $[\hat{x}^n, \hat{p}] = i\hbar n \hat{x}^{n-1}$
(d) $[f(\hat{x}), \hat{p}] = i\hbar \frac{df}{dx}$ for any function $f(x)$.

1.12 Let A and B be two Hermitian operators. Prove that if $[A, B] = 0$ there exists a complete set of simultaneous eigenstates of the operators A and B, i.e.

$$A|u_j\rangle = a_j|u_j\rangle \, , \quad B|u_j\rangle = b_j|u_j\rangle, \tag{72}$$

and $\{|u_j\rangle\}$ form a basis of the LVS on which A and B act.

1.13 Prove that two observables are compatible if and only if the commutator between the associated Hermitian operators vanishes.

> **1.14** What does it mean to say that two operators commute? What is the significance of two observables having mutually commuting operators?
>
> Given that the commutator $[P, Q] \neq 0$ for some observables P and Q, does it follow that for all $|\psi\rangle \neq 0$ we have $[P, Q]|\psi\rangle \neq 0$?

2.3 Expectation Values

Definition 4 *The* **expectation value** *of an operator $\mathcal{O}$ in a quantum state $|\psi\rangle$ is defined as*

$$\langle\psi|\mathcal{O}|\psi\rangle . \tag{73}$$

Expectation values are hugely important in QM. To see why let us consider a Hermitian operator $A = A^\dagger$ associated with some observable. Any state can be written as linear combination of the eigenstates of A (why?)

$$|\psi\rangle = \sum_j \langle a_j|\psi\rangle \, |a_j\rangle. \tag{74}$$

Hence

$$\boxed{\langle\psi|A|\psi\rangle = \sum_j a_j|\langle a_j|\psi\rangle|^2.} \tag{75}$$

This expression has an important physical meaning: a_j are the outcomes of measuring the observable to which A corresponds, and $|\langle a_j|\psi\rangle|^2$ are the associated probabilities.

> **NB 4**
>
> So the expectation value gives the *average* over many measurements of our observable when the system is in the quantum state $|\psi\rangle$.

Let us now consider the expectation values

$$\langle\psi|A^n|\psi\rangle = \sum_j a_j^n|\langle a_j|\psi\rangle|^2. \tag{76}$$

These are nothing but the *moments of the probability distribution* associated with measuring the observable associated with A in the state $|\psi\rangle$! Nice.

3 Position and Momentum Representations

All animals are equal, but some are more equal than others. George Orwell.

The basic objects in QM are quantum states. In order to work with them we usually express them in some particular basis. Which choice is most convenient depends on the particular problem one is interested in. Having said this, some choices of basis are of particular importance.

3.1 Position Representation

This is obtained by working with probability amplitudes $\psi(x)$ for finding a particle at position x (in 1 dimension). In Dirac notation

$$|\psi\rangle = \int dx \, \psi(x) \, |x\rangle, \tag{77}$$

where $|x\rangle$ are quantum states in which a position measurement returns the result x with probability 1.

Definition 5 *The probability amplitude $\psi(x)$ is called a* wave function.

Now recall that we introduced bra-vectors to extract amplitudes from states. Here we want

$$\langle x'|\psi\rangle = \psi(x') = \int dx \ \psi(x) \ \langle x'|x\rangle. \tag{78}$$

This requires

$$\langle x'|x\rangle = \delta(x - x'), \tag{79}$$

where $\delta(x)$ is the *Dirac delta-function*. Indeed, a defining property of the delta-function is that (for all sufficiently well-behaved functions $f(x)$)

$$\int_{-\infty}^{\infty} dx \ f(x) \ \delta(x - x') = f(x'). \tag{80}$$

At this point students usually feel somewhat uncomfortable, because the scalar product of bras and kets involves a delta-function rather than a Kronecker delta. The reason for this is that x is a *continuous variable* and the same situation arises for other observables where the outcome of measurements can vary continuously. The resolution of the identity in terms of the states $|x\rangle$ reads

$$\mathbf{1} = \int dx \ |x\rangle\langle x|. \tag{81}$$

Check:

$$\mathbf{1}|\psi\rangle = \int dx \ |x\rangle\langle x|\psi\rangle = \int dx \ \psi(x) \ |x\rangle. \tag{82}$$

3.1.1   POSITION OPERATOR

Given a basis of states of definite position we can introduce the associated *position operator*

$$\boxed{\hat{x} = \int dx \ x \ |x\rangle\langle x|.}$$
$$\tag{83}$$

By construction the position operator has eigenstates $|x\rangle$ with eigenvalues x

$$\hat{x}|x'\rangle = \int dx \ x \ |x\rangle\langle x|x'\rangle = \int dx \ x \ |x\rangle \ \delta(x - x') = x'|x'\rangle. \tag{84}$$

It acts on general states as

$$\hat{x}|\psi\rangle = \int dx \ x \ |x\rangle\langle x|\psi = \int dx \ x\psi(x) \ |x\rangle \ , \tag{85}$$

i.e. *it multiplies the wave function by x.* By concatenating (84) we find

$$\hat{x}^n|x'\rangle = (x')^n|x'\rangle, \tag{86}$$

and therefore

$$\boxed{V(\hat{x})|x'\rangle = V(x')|x'\rangle \ ,}$$
$$\tag{87}$$

where $V(x)$ is a function that is to be understood in terms of its Taylor expansion around $x = 0$. For a QM particle moving in one dimension $V(\hat{x})$ would be the operator describing its *potential energy*. (Why?) We note that

$$\langle\psi|\hat{x}^n|\psi\rangle = \int dx \ |\psi(x)|^2 x^n \ , \tag{88}$$

so $\langle\psi|\hat{x}|\psi\rangle$ is the *average position* and $\langle\psi|\hat{x}^2|\psi\rangle - \langle\psi|\hat{x}|\psi\rangle^2$ the *variance* if we look at the histogram of many position measurements.

3.1.2 Position representation for other operators

An important question is how other operators look like in the position representation. For a general operator A we have

$$A = \mathbf{1} \, A \, \mathbf{1} = \int dx \, dx' \, |x\rangle\langle x'| \, \langle x|A|x'\rangle. \tag{89}$$

As usual in order to define the operator we require its matrix elements $\langle x|A|x'\rangle$. A particular important operator is the *momentum operator*. It is defined (in one dimension) as

$$\hat{p} = \int dp \, p \, |p\rangle\langle p|, \tag{90}$$

where $|p\rangle$ are states such that a momentum measurement returns the value p with certainty. In the position representation (see below for some motivation) one has

$$\boxed{\langle x|\hat{p}|x'\rangle = -i\hbar\frac{\partial}{\partial x} \, \delta(x - x').} \tag{91}$$

This gives

$$\boxed{\langle x|\hat{p}|\psi\rangle = \int dx'\langle x|\hat{p}|x'\rangle \, \psi(x') = -i\hbar\frac{\partial\psi(x)}{\partial x}.} \tag{92}$$

> **Aside 3:** Momentum operator
>
> At this point we have simply asserted that the position representation of the momentum operator is given by eqn (91). The justification will be given in Part III of the lectures, when we will consider translations in QM. The logic that underlies the identification of the momentum operator goes as follows. In classical mechanics momentum can be defined as the generator of translations. One then defines the momentum operator in quantum mechanics as the generator of translations in QM. This leads to (91).

3.2 Heisenberg Uncertainty Relation

Werner Heisenberg (Nobel Prize in Physics 1932).
"What we observe is not nature itself, but nature exposed to our method of questioning."

Heisenberg also gave an excellent definition of experts: *"An expert is someone who knows some of the worst mistakes that can be made in their subject, and how to avoid them."*

Let us consider the commutator $[\hat{x}, \hat{p}]$

$$\langle x|[\hat{x}, \hat{p}]|\psi\rangle = \langle x|\hat{x}\hat{p} - \hat{p}\hat{x}|\psi\rangle = -i\hbar x\frac{\partial\psi(x)}{\partial x} + i\hbar\frac{\partial}{\partial x}\big[x\psi(x)\big] = i\hbar\langle x|\psi\rangle. \tag{93}$$

As $|\psi\rangle$ is arbitrary this tells us that

$$\boxed{[\hat{x}, \hat{p}] = i\hbar.}$$

(94)

So momentum and position are *incompatible observables*! Now consider the variances for position and momentum measurements in the state $|\psi\rangle$

$$\langle\psi|(\hat{x} - x_0)^2|\psi\rangle \,, \quad \langle\psi|(\hat{p} - p_0)^2|\psi\rangle,$$

(95)

where $x_0 = \langle\psi|\hat{x}|\psi\rangle$ and $p_0 = \langle\psi|\hat{p}|\psi\rangle$. For general Hermitian operators $A = A^\dagger$ and $B = B^\dagger$ we have

$$2i\,\mathrm{Im}\langle\psi|AB|\psi\rangle = \langle\psi|[A, B]|\psi\rangle.$$

(96)

But the imaginary part of a complex number is always smaller than its magnitude and so

$$\mathrm{Im}\langle\psi|AB|\psi\rangle \leq |\langle\psi|AB|\psi\rangle|.$$

(97)

Next we use the Schwarz inequality, which in Dirac notations reads

$$|\langle\phi|\phi'\rangle| \leq \sqrt{\langle\phi|\phi\rangle\,\langle\phi'|\phi'\rangle}.$$

(98)

In the usual vector notation and for real vector spaces this reads $|\vec{a} \cdot \vec{b}| \leq ||\vec{a}||\,||\vec{b}||$, which is obviously true because $\vec{a} \cdot \vec{b} = ||\vec{a}||\,||\vec{b}||\cos\varphi$, where φ is the angle between the two vectors. Applying the Schwarz inequality to the states $B|\psi\rangle$ and $A|\psi\rangle$ on the rhight-hand-side of (97) and then using (96) we obtain

$$\frac{1}{2i}\langle\psi|[A, B]|\psi\rangle \leq \sqrt{\langle\psi|A^2|\psi\rangle\,\langle\psi|B^2|\psi\rangle}.$$

(99)

Finally we substitute $A = \hat{x} - x_0$, $B = \hat{p} - p_0$ and use $[A, B] = i\hbar$ to arrive at the *Heisenberg uncertainty relation*

$$\boxed{\frac{\hbar}{2} \leq \underbrace{\sqrt{\langle\psi|(\hat{x} - x_0)^2|\psi\rangle}}_{\Delta X}\underbrace{\sqrt{\langle\psi|(\hat{p} - p_0)^2|\psi\rangle}}_{\Delta P}.}$$

(100)

The physical content of the Heisenberg uncertainty relation is that the product of the variances of the QM probability distributions for position and momentum measurements must always be larger than $(\hbar/2)^2$. So if the state $|\psi\rangle$ is such that the variance of the position probability distribution is very small, i.e. we can determine the position very precisely, the variance of the probability distribution of momentum must be large enough to satisfy the inequality (100), i.e. very large. So, in a probabilistic sense, we can never know both the position and the momentum of a particle very precisely.

3.3 MOMENTUM REPRESENTATION

Momentum eigenstates fulfil $\hat{p}|p\rangle = p|p\rangle$. We can work out the corresponding wave functions by considering

$$\langle x|\hat{p}|p\rangle = -i\hbar\frac{\partial}{\partial x}\langle x|p\rangle = p\langle x|p\rangle.$$

(101)

This is a first order ODE with solution

$$\boxed{\langle x|p\rangle = A\,e^{\frac{i}{\hbar}px}.}$$

(102)

So the wave function of momentum eigenstates are *plane waves*! As $|\langle x|p\rangle|^2 = |A|^2$ is position independent a particle in a momentum eigenstates is equally likely to be found anywhere in space when its position is measured. The constant A is fixed by the normalization condition

$$\langle p|p'\rangle = \delta(p - p') \,,$$

(103)

which ensures that the resolution of the identity has the form

$$\mathbf{1} = \int dp \, |p\rangle\langle p|. \tag{104}$$

We have

$$\langle p|p'\rangle = \int dx \, \langle p|x\rangle\langle x|p'\rangle = \int dx \, |A|^2 e^{\frac{i}{\hbar}(p'-p)x} = |A|^2 \, 2\pi\hbar \, \delta(p-p'), \tag{105}$$

so $A = (2\pi\hbar)^{-1/2}$. The momentum representation is obtained by expressing states and operators in terms of a basis of momentum eigenstates

$$|\psi\rangle = \int_{-\infty}^{\infty} dp \, \langle p|\psi\rangle \, |p\rangle \;, \quad \mathcal{O} = \int dp \, dp' \langle p|\mathcal{O}|p'\rangle \, |p\rangle\langle p'|. \tag{106}$$

Using $|\psi\rangle = \int_{-\infty}^{\infty} dx \, \langle x|\psi\rangle \, |x\rangle = \int_{-\infty}^{\infty} dp \, \langle p|\psi\rangle \, |p\rangle$ we can relate the momentum and position representations

$$\langle p|\psi\rangle = \int_{-\infty}^{\infty} dx \, \psi(x) \, \frac{e^{-\frac{i}{\hbar}px}}{\sqrt{2\pi\hbar}} \;, \qquad \langle x|\psi\rangle = \int_{-\infty}^{\infty} dp \, \langle p|\psi\rangle \, \frac{e^{\frac{i}{\hbar}px}}{\sqrt{2\pi\hbar}}. \tag{107}$$

This is precisely the (inverse) *Fourier transformation* of the wave function!

3.4   Generalization to 3 Dimensions

In three spatial dimensions we use a basis of quantum states $|\vec{x}\rangle$ of definite position $\vec{x} = (x, y, z)$. These states fulfil the normalization condition

$$\langle \vec{x}|\vec{x}'\rangle = \delta^{(3)}(\vec{x} - \vec{x}') = \delta(x - x')\delta(y - y')\delta(z - z'). \tag{108}$$

The resolution of the identity is

$$\mathbf{1} = \int d^3\vec{x} \, |\vec{x}\rangle\langle\vec{x}|. \tag{109}$$

A general state can be written as a linear combination of these basis states

$$\boxed{|\psi\rangle = \int d^3\vec{x} \, \underbrace{\langle\vec{x}|\psi\rangle}_{\psi(\vec{x})} \, |\vec{x}\rangle.}$$

$$\tag{110}$$

Now we can define operators corresponding to each of the three components of position

$$\begin{aligned}
\hat{x} &= \int d^3\vec{x} \, x \, |\vec{x}\rangle\langle\vec{x}| \;, \\
\hat{y} &= \int d^3\vec{x} \, y \, |\vec{x}\rangle\langle\vec{x}| \;, \\
\hat{z} &= \int d^3\vec{x} \, z \, |\vec{x}\rangle\langle\vec{x}| \;.
\end{aligned} \tag{111}$$

By the same kind of argument as in the 1D case we have

$$V(\hat{x}, \hat{y}, \hat{z})|\vec{x}\rangle = V(x, y, z)|\vec{x}\rangle, \tag{112}$$

where $V(x, y, z)$ is to be understood in terms of its Taylor expansion around $(0, 0, 0)$. In D=3 we also have three components of momentum and can define the associated quantum states $|\vec{p}\rangle$, which return the result p_α with certainty when the α-component of momentum is measured ($\alpha = x, y, z$). Their normalization is as you may have already guessed

$$\langle \vec{p}|\vec{p}'\rangle = \delta^{(3)}(\vec{p} - \vec{p}') = \delta(p_x - p'_x)\delta(p_y - p'_y)\delta(p_z - p'_z). \tag{113}$$

Following our construction for D=1 we can define three Hermitian operators associated with the three components of momentum by

$$\hat{p}_\alpha|\vec{p}\rangle = p_\alpha|\vec{p}\rangle , \qquad \alpha = x, y, z \tag{114}$$

In the position representation we have

$$\langle\vec{x}|\hat{p}_\alpha|\vec{x}'\rangle = -i\hbar\frac{\partial}{\partial x_\alpha}\delta^{(3)}(\vec{x} - \vec{x}') , \qquad \alpha = x, y, z. \tag{115}$$

This implies that

$$\boxed{\langle\vec{x}|\hat{p}_\alpha|\psi\rangle = -i\hbar\frac{\partial}{\partial x_\alpha}\psi(\vec{x}) .} \tag{116}$$

4 Time Evolution in Quantum Mechanics

Newtonian mechanics is about equations of motion for physical quantities. The analogue in QM is time evolution of quantum states.

4.1 Time dependent Schrödinger equation and Ehrenfest's theorem

Postulate 3

The time evolution of quantum states is described by the **time-dependent Schrödinger equation**

$$\boxed{i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle,} \tag{117}$$

where H is the Hamiltonian of the system.

Erwin Schrödinger (Nobel Prize in Physics 1933).
"I insist upon the view that all is waves."

"I knew of Heisenberg's theory, of course, but I felt discouraged, not to say repelled, by the methods of transcendental algebra, which appeared difficult to me, and by the lack of visualizability." (Schrödinger in 1926)

The more I think about the physical portion of Schrödinger's theory, the more repulsive I find it. What Schrödinger writes about the visualizability of his theory is probably not quite right, in other words it's crap (in German "Mist")." (Heisenberg, writing to Pauli in 1926).

The associated equation for the bra-state is

$$\boxed{-i\hbar\frac{\partial}{\partial t}\langle\psi(t)| = \langle\psi(t)|H.} \tag{118}$$

The general rules are

$$\boxed{c|\psi\rangle \longrightarrow c^*\langle\psi| , \qquad A|\psi\rangle \longrightarrow \langle\psi|A^\dagger .} \tag{119}$$

To see what the bra-state corresponding to $A|\psi\rangle$ is we expand both the state and the operator in a basis

$$|\psi\rangle = \sum_j \psi_j |j\rangle \ , \quad A = \sum_{k,l} \langle k|A|l\rangle \ |k\rangle\langle l| \ . \tag{120}$$

Using $\langle l|j\rangle = \delta_{l,j}$ we then have

$$A|\psi\rangle = \sum_{k,l} \langle k|A|l\rangle \ \psi_l \ |k\rangle \ . \tag{121}$$

The associated bra state is

$$\sum_{k,l} (\langle k|A|l\rangle \ \psi_l)^* \ \langle k| = \sum_{k,l} (\langle k|A|l\rangle)^* \ \psi_l^* \ \langle k| = \sum_{k,l} \langle l|A^\dagger|k\rangle \ \psi_l^* \ \langle k| = \sum_l \psi_l^* \langle l|A^\dagger \sum_k |k\rangle\langle k| = \langle\psi|A^\dagger. \tag{122}$$

By combining the TDSEs for $|\psi(t)\rangle$ and $\langle\psi(t)|$ we obtain the evolution equation for the expectation values of (time-independent) operators

$$\boxed{-i\hbar\frac{\partial}{\partial t}\langle\psi(t)|\mathcal{O}|\psi(t)\rangle = \langle\psi(t)|[H,\mathcal{O}]|\psi(t)\rangle \ .}$$
$$\tag{123}$$

This is called *Ehrenfest's theorem*. As a first application of this equation let us consider a free QM particle with Hamiltonian $H = \hat{p}^2/(2m)$, i.e. only kinetic energy. Then

$$-i\hbar\frac{\partial}{\partial t}\langle\psi(t)|\hat{x}|\psi(t)\rangle = \frac{1}{2m}\langle\psi(t)|[\hat{p}^2,\hat{x}]|\psi(t)\rangle \ . \tag{124}$$

The commutator is worked out using a standard trick

$$[\hat{p}^2,\hat{x}] = \hat{p}^2\hat{x} - \hat{p}\hat{x}\hat{p} + \hat{p}\hat{x}\hat{p} - \hat{x}\hat{p}^2 = \hat{p}[\hat{p},\hat{x}] + [\hat{p},\hat{x}]\hat{p} = -2i\hbar\hat{p}. \tag{125}$$

This tells us that

$$m\frac{\partial}{\partial t}\langle\hat{x}\rangle = \langle\hat{p}\rangle. \tag{126}$$

This is precisely what we would expect classically (and shows that our definition of momentum operator is reasonable).

4.2   Time independent Schrödinger equation

The eigenvalue equation for the Hamiltonian is also known as the *time-independent Schrödinger equation*

$$\boxed{H|E_n\rangle = E_n|E_n\rangle \ .}$$
$$\tag{127}$$

As H is Hermitian we can obtain an orthonormal basis of energy eigenstates and hence write any state as linear combination

$$|\psi(t)\rangle = \sum_j \psi_j(t)|E_j\rangle \ . \tag{128}$$

Substituting this back into the TDSE we have

$$i\hbar\sum_j \frac{\partial\psi_j(t)}{\partial t}|E_j\rangle = \sum_j \psi_j(t)E_j|E_j\rangle. \tag{129}$$

Extracting the amplitudes for $|E_n\rangle$ by acting with $\langle E_n|$ we have

$$i\hbar\frac{\partial\psi_n(t)}{\partial t} = E_n\psi_n(t) \ . \tag{130}$$

This first order differential equation is easily solved

$$\psi_n(t) = \psi_n(0) e^{-\frac{i}{\hbar} E_n t} \ .$$ (131)

In Dirac notations

$$\boxed{|\psi(t)\rangle = \sum_n \langle E_n | \psi(0) \rangle \ e^{-\frac{i}{\hbar} E_n t} \ |E_n\rangle \ .}$$ (132)

> **NB 5**
>
> Given the solutions of the time-independent Schrödinger equation we can construct the solutions to the time-dependent Schrödinger equation for a given initial quantum state $|\psi(0)\rangle$ using (132). This is why the study of the TISE is so important!

For energy eigenstates themselves we have

$$\boxed{|E_n, t\rangle = e^{-\frac{i}{\hbar} E_n t} \ |E_n\rangle \ .}$$ (133)

So energy eigenstates only acquire a phase under time evolution. As a result the probabilities $|\langle x | E_n, t \rangle|^2$ to find a particle in an energy eigenstate at a given position x are time-independent. This is why energy eigenstates are also known as *stationary states*.

4.3   SCHRÖDINGER EQUATION IN THE POSITION REPRESENTATION

A key point is that we can express the TDSE in the position representation

$$i\hbar \frac{\partial}{\partial t} \langle x | \psi(t) \rangle = \langle x | H | \psi(t) \rangle.$$ (134)

This is very useful for Hamiltonians of the form

$$H = \underbrace{\frac{\hat{p}^2}{2m}}_{\text{kinetic energy}} + \underbrace{V(\hat{x})}_{\text{potential energy}} \ .$$ (135)

Given that

$$\langle x | \hat{p} | \psi(t) \rangle = -i\hbar \frac{\partial \psi(x,t)}{\partial x}$$ (136)

we have

$$\langle x | \hat{p}^2 | \psi(t) \rangle = \int dx' \ \langle x | \hat{p} | x' \rangle \langle x' | \hat{p} | \psi(t) \rangle = -\hbar^2 \int dx' \ \frac{\partial}{\partial x} \delta(x - x') \frac{\partial \psi(x',t)}{\partial x'} = -\hbar^2 \frac{\partial^2 \psi(x,t)}{\partial x^2} \ .$$ (137)

This gives

$$\langle x | H | \psi(t) \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \ .$$ (138)

Substituting this back into (134) we see that for Hamiltonians of the form (135) the TDSE can be represented as a *partial differential equation for the wave function*

$$\boxed{i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \ .}$$ (139)

Now you are starting to see where Schrödinger's view that "all is waves" comes from! The generalization to 3D is straightforward and we only quote the result

$$\boxed{i\hbar\frac{\partial\psi(\vec{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)\ .}$$

(140)

In the position representation the TISE reads

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

(141)

Here $\psi(x)$ are the wave functions of energy eigenstates. Many QM text approach the subject using the position representation on the Schrödinger equation as a starting point.

4.4 Probability Current

The probability density of finding a particle at position $\vec{x}$ at time t is according to Born's rule is

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

(142)

Taking the time derivative gives

$$\frac{\partial\rho(\vec{x},t)}{\partial t} = \psi^*(x,t)\frac{\partial\psi(\vec{x},t)}{\partial t} + \psi(x,t)\frac{\partial\psi^*(\vec{x},t)}{\partial t}\ .$$

(143)

We now use the TDSE for the wave function (140) and its complex conjugate to rewrite the right-hand side

$$\frac{\partial\rho(\vec{x},t)}{\partial t} = \frac{i\hbar}{2m}\left[\psi^*(x,t)\nabla^2\psi(\vec{x},t) - \psi(x,t)\nabla^2\psi^*(\vec{x},t)\right].$$

(144)

The right-hand side of this equation can be written as a divergence

$$\frac{\partial\rho(\vec{x},t)}{\partial t} = -\vec{\nabla}\cdot\vec{J}(\vec{x},t)\ ,$$

(145)

where $\vec{J}(\vec{x},t)$ is called *probability current*

$$\vec{J}(\vec{x},t) = \frac{i\hbar}{2m}\left[\psi(x,t)\vec{\nabla}\psi^*(\vec{x},t) - \psi^*(x,t)\vec{\nabla}\psi(\vec{x},t)\right].$$

(146)

Eqn (145) takes the form of a continuity equation that expresses the conservation of probability. Its integral form follows from the divergence theorem

$$\frac{d}{dt}\int_V d^3\vec{x}\ \rho(\vec{x},t) = -\int_V d^3\vec{x}\ \vec{\nabla}\cdot\vec{J}(\vec{x},t) = -\oint_{\partial V} d^2\vec{S}\cdot\vec{J}(\vec{x},t)\ ,$$

(147)

where ∂V is the boundary of the volume V. So the change in the probability for the particle to be found inside V is minus the integral over the volume's bounding surface of the probability flux out of the volume.

Homework 4: Time dependence and the Schrödinger equation

2.1 Write down the time-independent (TISE) and the time-dependent (TDSE) Schrödinger equations. Is it necessary for the wavefunction of a system to satisfy the TDSE? Under what circumstances does the wavefunction of a system satisfy the TISE?

2.2 Why is the TDSE first-order in time, rather than second-order like Newton's equations of motion?

2.3 A particle is confined in a potential well such that its allowed energies are $E_n = n^2 \mathcal{E}$, where $n = 1, 2, \ldots$ is an integer and $\mathcal{E}$ a positive constant. The corresponding energy eigenstates are $|1\rangle$, $|2\rangle$, $\ldots, |n\rangle, \ldots$ At $t = 0$ the particle is in the state

$$|\psi(0)\rangle = 0.2|1\rangle + 0.3|2\rangle + 0.4|3\rangle + 0.843|4\rangle.$$

(a) What is the probability, if the energy is measured at $t = 0$, of finding a number smaller than $6\mathcal{E}$?
(b) What is the mean value and what is the rms deviation of the energy of the particle in the state $|\psi(0)\rangle$?
(c) Calculate the state vector $|\psi\rangle$ at time t. Do the results found in (a) and (b) for time t remain valid for arbitrary time t?
(d) When the energy is measured it turns out to be $16\mathcal{E}$. After the measurement, what is the state of the system? What result is obtained if the energy is measured again?

2.4 A particle moves in the potential $V(\boldsymbol{x})$ and is known to have energy E_n. (a) Can it have well-defined momentum for some particular $V(\boldsymbol{x})$? (b) Can the particle simultaneously have well-defined energy and position?

2.5 Let $\psi(x, t)$ be the correctly normalized wave function of a particle of mass m and potential energy $V(x)$. Write down the expressions for the expectation values of (a) $\hat{x}$; (b) $\hat{x}^2$; (c) $\hat{p}_x$; (d) $\hat{p}_x^2$; (e) the energy.
What is the probability that the particle will be found in the interval (x_1, x_2)?

2.6 Consider a quantum mechanical particle with Hamiltonian

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

that is initially prepared in a state $|\psi(0)\rangle$. Using the TDSE show that the expectation value of an operator $\hat{Q}$ fulfils the following evolution equations

$$i\hbar \frac{d}{dt} \langle \psi(t)|\hat{Q}|\psi(t)\rangle = \langle \psi(t)|[\hat{Q}, H]|\psi(t)\rangle.$$

Consider the particular cases of the position and momentum operators and comment on the resulting equations

Part II
Wave Mechanics and Oscillators

Erwin with his psi can do
Calculations quite a few. Erich Hückel, freely translated by Felix Bloch.

5 WAVE MECHANICS

5.1 FREE PARTICLE IN ONE DIMENSION

Let us start with the case where our QM particle only has kinetic energy. Then the Hamiltonian is

$$H = \frac{\hat{p}^2}{2m} \ . \tag{148}$$

The TISE reads

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \ . \tag{149}$$

The solutions to this differential equation are the momentum eigenstates

$$u_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}px}, \tag{150}$$

where the energy is given by

$$E_p = \frac{p^2}{2m}. \tag{151}$$

In this case the energy eigenvalues are *not* quantized. Given the energy eigenstates we are now is a position to solve the time-dependent Schrödinger equation. We need to adjust our previous result

$$|\psi(t)\rangle = \sum_n \langle E_n|\psi(0)\rangle e^{-\frac{i}{\hbar}E_n t}|E_n\rangle \tag{152}$$

because the energy eigenvalues are continuous rather than discrete here. Using that the energy eigenstates are also momentum eigenstates we have

$$|\psi(t)\rangle = \int_{-\infty}^{\infty} dp \ \langle p|\psi(0)\rangle e^{-\frac{ip^2}{2m\hbar}t}|p\rangle. \tag{153}$$

The corresponding wave function is

$$\langle x|\psi(t)\rangle = \psi(x,t) = \int_{-\infty}^{\infty} \frac{dp}{\sqrt{2\pi\hbar}} \ \langle p|\psi(0)\rangle e^{-\frac{ip^2}{2m\hbar}t+\frac{i}{\hbar}px} \ . \tag{154}$$

Let us consider a state that at time $t = 0$ corresponds to a Gaussian wave packet

$$\psi(x,0) = \langle x|\psi(0)\rangle = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}}e^{-\frac{x^2}{4\sigma^2}+\frac{i}{\hbar}p_0 x} \ . \tag{155}$$

Going over to the momentum representation we have

$$\langle p|\psi(0)\rangle = \int dx \ \langle p|x\rangle\langle x|\psi(0)\rangle = \left[\frac{2\sigma^2}{\pi\hbar^2}\right]^{\frac{1}{4}} e^{-\frac{\sigma^2}{\hbar^2}(p-p_0)^2}. \tag{156}$$

This describes a superposition of momentum eigenstates with momenta centred around p_0 and probability amplitudes that become very small when $|p - p_0| \gg \frac{\hbar}{\sigma}$. Substituting this back into (154) and carrying out the integral (how?) we obtain

$$|\psi(x,t)|^2 = \frac{\sigma}{\sqrt{2\pi\hbar^4|b(t)|^4}}e^{-\frac{\sigma^2}{2\hbar^4|b(t)|^4}(x-p_0 t/m)^2} \ , \qquad \hbar^2 b^2(t) = \sigma^2 + \frac{i\hbar t}{2m} \ . \tag{157}$$

This describes a Gaussian wave packet moving with velocity p_0/m that *broadens* in time as

$$\sigma^2(t) = \sigma^2 + \left(\frac{\hbar t}{2m\sigma}\right)^2 \ . \tag{158}$$

We can understand this by noting that initially there is an uncertainty in momentum (as at time $t = 0$ we are dealing with a superposition of momentum eigenstates), which translates into an increasing uncertainty in position at later times.

5.2 Infinite square well

Let us consider a QM particle moving in a one-dimensional potential well

$$
V(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{else.} \end{cases}
\tag{159}
$$

The TISE for the wave function $\psi(x)$ reads

$$
-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x) \ .
\tag{160}
$$

As we are interested in finite E solutions the wave function must vanish at $x < 0$ and $x > a$. Continuity at $x = 0, a$ then imposes the boundary conditions

$$
\psi(0) = 0 = \psi(a).
\tag{161}
$$

In the interior of the potential we then have

$$
-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \ .
\tag{162}
$$

The general solution is

$$
\psi(x) = A\cos(kx) + B\sin(kx) \ , \quad E = \frac{\hbar^2 k^2}{2m}.
\tag{163}
$$

Imposing the boundary conditions gives $A = 0$ and the wave number k gets *quantized*

$$
k_n = \frac{\pi n}{a} \ , \quad n = 1, 2, 3, \ldots
\tag{164}
$$

The corresponding quantized energies are

$$
E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}.
\tag{165}
$$

Normalizing the wave functions by imposing

$$
\int_0^a dx |\psi(x)|^2 = 1 \ ,
\tag{166}
$$

we arrive at the following result for the energy eigenstates

$$
\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{a}x\right).
\tag{167}
$$

We note that the *overall phase* of the wave functions is arbitrary and we fix it to be equal to one. The lowest energy state is called the *ground state*. The wave functions $\psi_n(x)$ are either symmetric or antisymmetric
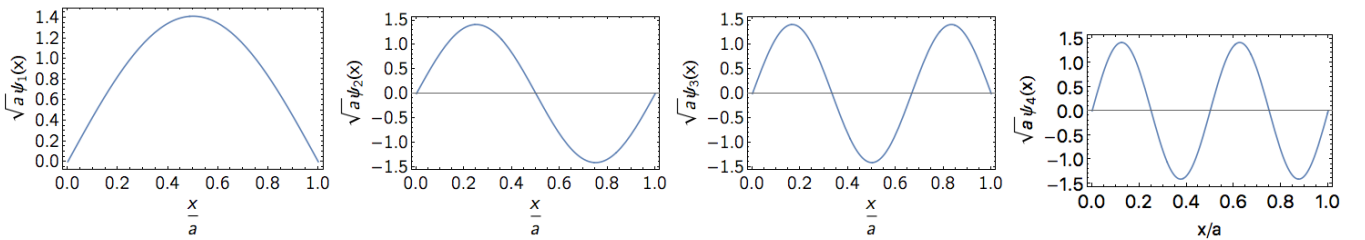
Figure 6: Wave functions for the 4 lowest energy states in the infinite square well potential.

under reflection around $x = a/2$.

5.3   FINITE SQUARE WELL

Let us now consider a particle moving in the potential

$$V(x) = \begin{cases} 0 & \text{if } |x| < a \\ V_0 & \text{if } |x| > a. \end{cases} \tag{168}$$

The TISE for the wave function $\psi(x)$ reads

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = [E - V(x)]\psi(x) . \tag{169}$$

Let us first consider the case $E < V_0$. In this case the solution of (169) is

$$\psi(x) = \begin{cases} A\cos(kx) + B\sin(kx) & \text{if } |x| < a , \\ Ce^{-\kappa x} + C'e^{\kappa x} & \text{if } x > a , \\ De^{\kappa x} + D'e^{-\kappa x} & \text{if } x < -a , \end{cases} \tag{170}$$

where

$$E = \frac{\hbar^2 k^2}{2m} = V_0 - \frac{\hbar^2 \kappa^2}{2m}. \tag{171}$$

Now we impose

- Normalizability

$$\int_{-\infty}^{\infty} dx \ |\psi(x)|^2 = 1 . \tag{172}$$

  This sets $C' = D' = 0$, i.e. imposes that the wave function vanishes at $x \to \pm\infty$.

- Continuity of $\psi(x)$ at $x = \pm a$, i.e. $\lim_{\epsilon \to 0} \psi(\pm a - \epsilon) = \lim_{\epsilon \to 0} \psi(\pm a + \epsilon)$

$$\begin{aligned} A\cos(ka) + B\sin(ka) &= Ce^{-\kappa a} , \\ A\cos(ka) - B\sin(ka) &= De^{-\kappa a} . \end{aligned} \tag{173}$$

- Continuity of $\psi'(x)$ at $x = \pm a$

$$\begin{aligned} Bk\cos(ka) - Ak\sin(ka) &= -C\kappa e^{-\kappa a} , \\ Bk\cos(ka) + Ak\sin(ka) &= D\kappa e^{-\kappa a} . \end{aligned} \tag{174}$$

Equations (173)and (174) have two types of solutions

(i) $B = 0$, $C = D$ and $k\tan(ka) = \kappa$, corresponding to *symmetric* wave functions $\psi(x) = \psi(-x)$.

(ii) $A = 0$, $C = -D$ and $k\cot(ka) = -\kappa$, corresponding to *antisymmetric* wave functions $\psi(x) = -\psi(-x)$.

The (anti)symmetry of energy eigenstates is a result of a *symmetry* of the problem under reflection around $x = 0$, i.e. $x \to -x$. This symmetry is called *parity*. Symmetric solutions are said to be *even* under the parity transformation (i.e. they map onto themselves), while antisymmetric solutions are *odd* under parity (i.e. they map onto minus themselves). What remains to be done is to solve the remaining equations for the wave numbers, e.g.

$$k\tan(ka) = \kappa = \sqrt{\frac{2mV_0}{\hbar^2} - k^2}. \tag{175}$$

We rewrite this slightly as

$$\tan(ka) = \sqrt{\frac{W^2}{k^2 a^2} - 1} , \quad W = \sqrt{\frac{2mV_0 a^2}{\hbar^2}}. \tag{176}$$
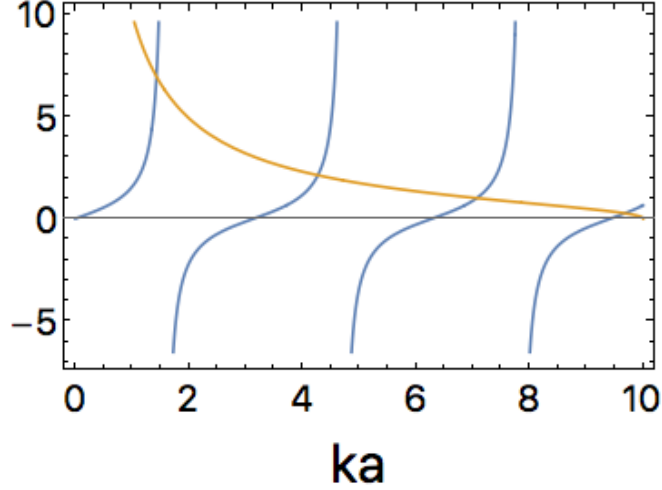
Figure 7: Solutions of eqn (176) for $W = 10$.

This equation does not have simple solutions, but we can understand the structure of solutions by plotting the two sides of the equation as functions of ka. This is done in Fig. 7. We see that for $W = 10$ there are 4 solutions to the equation. For larger values of W there will be more solutions, but there will always be at least one! We call these states *bound states*, because $|\psi(x)|^2$ drops off very quickly away from the square well, which means that the particle is most likely to be found inside the well. *So in one dimension a potential well will always have at least one bound state, no matter how small V_0 is.* Note however that the probability of finding the particle outside the well is not zero (as it would be classically for energies $E < V_0$)!

Let us now turn to the case $E > V_0$. Now the solutions to the TISE look like

$$
\psi(x) = \begin{cases} A\cos(kx) + B\sin(kx) & \text{if } |x| < a \ , \\ C\cos(Kx) + C'\sin(Kx) & \text{if } x > a \ , \\ D\cos(Kx) + D'\sin(Kx) & \text{if } x < -a \ , \end{cases} \tag{177}
$$

$$
E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 K^2}{2m} - V_0. \tag{178}
$$

In this case the wave functions will not vanish at $x \to \pm\infty$ and the spectrum of energies will be continuous.

5.4 SPLIT INFINITE SQUARE WELL

Next we consider a potential of the form

$$
\begin{aligned}
V(x) &= V_0\delta(x) + V_{\text{ISW}}(x) \ , \\
V_{\text{ISW}}(x) &= \begin{cases} 0 & \text{if } 0 < |x| < a/2 \\ \infty & \text{else.} \end{cases}
\end{aligned} \tag{179}
$$

The TISE reads

$$
-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \ . \tag{180}
$$

If $V_0 = 0$ we are dealing with an infinite square well, which is now symmetric around $x = 0$. The odd-parity energy eigenstates can be read off from our previous solution

$$
\psi_{2n}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi n}{a}x\right) \ , \qquad E_{2n} = \frac{\hbar^2\pi^2(2n)^2}{2ma^2} \ . \tag{181}
$$

31

As $\psi_{2n}(0) = 0$ these wave functions also fulfil the TISE (180) in presence of the additional delta-function potential!

Using that $V(x)$ vanishes away from $x = 0$ we conclude that the even-parity eigenstates must have wave functions of the form

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{if } 0 < x \leq a/2 , \\ Ae^{-ikx} + Be^{ikx} & \text{if } -a/2 \leq x < 0 . \end{cases} \tag{182}$$

The free parameters are fixed by noting that

- The wave functions must vanish at $\pm a/2$ for finite energy eigenstates, i.e. $\psi(\pm a/2) = 0$. This gives

$$B = -Ae^{ika} . \tag{183}$$

- The wave function must be continuous at $x = 0$. Our Ansatz fulfils this requirement.

- The derivative of the wave function at $x = 0$ is determined by integrating the TISE around $x = 0$

$$\int_{-\epsilon}^{\epsilon} dx \left[-\frac{\hbar^2 \psi''(x)}{2m} + V_0 \delta(x)\psi(x) - E\psi(x) \right] = 0 . \tag{184}$$

Using that the wave function is continuous at zero and taking the limit $\epsilon \to 0$ we obtain $\psi'(0^+) - \psi'(0^-) = \frac{2mV_0}{\hbar^2}\psi(0)$, which in turn implies

$$ik(A - B) = \frac{mV_0}{\hbar^2}(A + B) . \tag{185}$$

We see that the first derivative of the wave function is *discontinuous* at $x = 0$. This is a characteristic feature of delta-function potentials. If we regularize the delta function, e.g. by

$$\delta_\epsilon(x) = \frac{e^{-x^2/4\epsilon}}{\sqrt{4\pi\epsilon}}, \tag{186}$$

then the wave function and its derivative are continuous at $x = 0$. The discontinuity of the derivative arises only in the limit $\epsilon \to 0$. Substituting (183) leaves us with a quantization condition for k

$$k \cot(ka/2) = -\frac{mV_0}{\hbar^2} . \tag{187}$$

The most interesting case is when V_0 becomes very large. Then the right hand side of (187) is very large and k must be close to one of the singularities of $\cot(ka/2)$

$$k_{2n+1} \approx \frac{2n\pi}{a} - \frac{2n\pi}{a}\frac{2\hbar^2}{maV_0}. \tag{188}$$

For large V_0 our wave functions are thus approximately given by

$$\psi_{2n+1}(x) \approx \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi n}{a}|x|\right) , \qquad E_{2n+1} \approx \frac{\hbar^2\pi^2(2n)^2}{2ma^2} . \tag{189}$$

The corrections to the wave functions and energies are proportional to $1/V_0$. This implies that at large V_0 there are pairs of eigenstates with almost degenerate energies but opposite parities. Let us now prepare our system is the state corresponding to the wave function

$$\Psi(x, 0) = \frac{\psi_{2n}(x) - \psi_{2n+1}(x)}{\sqrt{2}}. \tag{190}$$

32

The probability density to find the particle at position x is

$$|\Psi(x,0)|^2 \approx \begin{cases} \frac{4}{a}\sin^2\left(\frac{2\pi n}{a}x\right) & \text{if } -\frac{a}{2} \le x \le 0 \\ 0 & \text{else.} \end{cases}$$
(191)

So to a very good approximation the particle is on the left hand side of the potential well. The time evolution of the system is given by the time-dependent Schrödinger equation. Using our general result

$$|\psi(t)\rangle = \sum_n \langle E_n|\psi(0)\rangle e^{-\frac{i}{\hbar}E_n t}|E_n\rangle \ ,$$
(192)

and going over to the position representation we have

$$\underbrace{\langle x|\psi(t)\rangle}_{\Psi(x,t)} = \sum_n \langle E_n|\psi(0)\rangle e^{-\frac{i}{\hbar}E_n t}\underbrace{\langle x|E_n\rangle}_{\psi_n(x)}.$$
(193)

For our particular choice of initial state this becomes

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left[e^{-\frac{i}{\hbar}E_{2n}t}\psi_{2n}(x) - e^{-\frac{i}{\hbar}E_{2n+1}t}\psi_{2n+1}(x)\right] \ .$$
(194)

Consider now the probability density to find the particle at position x at time $t^* = \pi\hbar/(E_{2n} - E_{2n+1})$. This is a late time as the splitting between the two energy levels is small. We have

$$|\Psi(x,t^*)|^2 = \frac{|\psi_{2n}(x) + \psi_{2n+1}(x)|^2}{2} \approx \begin{cases} \frac{4}{a}\sin^2\left(\frac{2\pi n}{a}x\right) & \text{if } 0 \le x \le \frac{a}{2} \\ 0 & \text{else.} \end{cases}$$
(195)

To a very good approximation the particle is now in the right hand side of the well! This is a purely quantum mechanical effect, which we refer to as *tunnelling* through a potential barrier.

5.5 Scattering of free particles

Next we consider a potential step

$$V(x) = \begin{cases} 0 & \text{if } |x| > a \\ V_0 & \text{if } |x| < a. \end{cases}$$
(196)

The corresponding TISE

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + [V(x) - E]\psi(x) = 0$$
(197)

is solved by considering the regions $x < -a$, $|x| < a$ and $x > a$ separately. For $E < V_0$ energy eigenstates are of the form

$$\psi(x) = \begin{cases} De^{ikx} + re^{-ikx} & \text{if } x < -a \\ Ae^{-\kappa x} + Be^{\kappa x} & \text{if } |x| < a \\ te^{ikx} + Ce^{-ikx} & \text{if } x > a \ , \end{cases}$$
(198)

where k and κ are related to the energy eigenvalue by

$$E = \frac{\hbar^2 k^2}{2m} = V_0 - \frac{\hbar^2\kappa^2}{2m}.$$
(199)

We see that the wave functions do not vanish at $\pm\infty$ and are not normalizable to one. We now specify solutions such that $C = 0$ and $D = 1$ as these have a nice physical interpretation. For $C = 0$ there is

no left-moving wave at $x > a$[1], and the wave functions can be interpreted as an incident plane wave with amplitude 1 that gets partially reflected by the barrier (re^{-ikx}) and partially transmitted (te^{ikx}).

The free parameters in (198) are fixed by the four requirements that the wave function and its first derivative are continuous at $x = \pm a$. This gives the following four equations for the four unknowns A, B, r, and t

$$
\begin{aligned}
e^{-ika} + re^{ika} &= Ae^{\kappa a} + Be^{-\kappa a} \,, \\
te^{ika} &= Ae^{-\kappa a} + Be^{\kappa a} \,, \\
ik[e^{-ika} - re^{ika}] &= \kappa[-Ae^{\kappa a} + Be^{-\kappa a}] \,, \\
ikte^{ika} &= \kappa[-Ae^{-\kappa a} + Be^{\kappa a}].
\end{aligned}
\tag{200}
$$

After some algebra we find

$$
\begin{aligned}
t &= \frac{2i\kappa k e^{-2ika}}{(k^2 - \kappa^2)\sinh(2\kappa a) + 2ik\kappa\cosh(2\kappa a)} \,, \\
r &= \frac{e^{-2ika}(\kappa^2 + k^2)\sinh(2\kappa a)}{(k^2 - \kappa^2)\sinh(2\kappa a) + 2ik\kappa\cosh(2\kappa a)}.
\end{aligned}
\tag{201}
$$

We note that

$$
|r|^2 + |t|^2 = 1,
\tag{202}
$$

which corresponds to the conservation of probability in the scattering interpretation mentioned above. A simple way of seeing that $|r|^2 + |t|^2 = 1$ is to consider the probability currents for $x < -a$ and $x > a$. We have

$$
J_{x<-a} = \frac{\hbar k}{m}[1 - |r|^2] \,, \qquad J_{x>a} = \frac{\hbar k}{m}|t|^2 \,.
\tag{203}
$$

These must be equal by conservation of probability (consider the integral form (147) of the continuity equation and take as the volume e.g. the interval $[-2a, 2a]$). The transmission probability is

$$
|t|^2 = \frac{4k^2\kappa^2}{4\kappa^2 k^2 + (k^2 + \kappa^2)^2\sinh^2(2\kappa a)} \,.
\tag{204}
$$

Transmission includes the possibility that the incoming particle failed to interact with the potential barrier. To isolate the possibility of scattering to occur we write the amplitude of the outgoing wave as $t = 1 + T$, where the 1 corresponds to the possibility of passing through undisturbed and T representing actual forward scattering. The total *scattering cross section* is defined as the sum of the probabilities for forwards and backwards scattering

$$
\sigma = |T|^2 + |r|^2 = |1 - t|^2 + |r|^2.
\tag{205}
$$

This is a good point to elaborate a bit more on continuity conditions for the derivative of the wave function. In our example the first derivative is continuous. Let us now however consider the limit $a \to 0$, $V_0 \to \infty$ such that $2aV_0 = V_\delta$ is kept fixed. Let us denote this limit as $\lim_\delta$. In this limit our potential is like a delta-function and hence no longer "nice" at $x = 0$. The derivative of the wave functions behaves as

$$
\begin{aligned}
\psi'(0^-) &= ik \lim_\delta(1 - r) = \frac{mV_\delta/\hbar^2}{ik - mV_\delta/\hbar^2} \,, \\
\psi'(0^+) &= ik \lim_\delta t = \frac{ik}{ik - mV_\delta/\hbar^2} \,.
\end{aligned}
\tag{206}
$$

So in the limit the first derivative is no longer continuous. Its jump at $x = 0$ is

$$
\psi'(0^+) - \psi'(0^-) = \frac{ik(2mV_\delta/\hbar^2)}{ik - mV_\delta/\hbar^2} = \frac{2mV_\delta}{\hbar^2}\psi(0).
\tag{207}
$$

---

[1] e^{ikx} corresponds to a right-moving wave as can be seen by including the time dependence imposed by the TDSE: $e^{ikx - i\frac{\hbar k^2}{2m}t}$. The points of constant phase can be seen to move rightwards.

5.6 RESONANT SCATTERING

Scattering experiments are widely used to probe the internal structure of atomic nuclei and "elementary" particles. We will now consider a toy model that explains how the structure of the scattering cross section reflects the existence of long-lived bound states inside the nucleus. To that end we consider particles moving in a one dimensional potential of the form

$$V(x) = V_\delta \left[\delta(x + a) + \delta(x - a) \right]. \tag{208}$$

We aim to construct finite energy eigenstates of the form

$$\psi(x) = \begin{cases} e^{ikx} + re^{-ikx} & \text{if } x < -a \\ Ae^{ikx} + Be^{-ikx} & \text{if } |x| < a \\ te^{ikx} & \text{if } x > a. \end{cases} \tag{209}$$

The energy of such a solution is

$$E(k) = \frac{\hbar^2 k^2}{2m}. \tag{210}$$

Such solutions can be interpreted in terms of a right-moving wave with unit amplitude that scatters off the potential and eventually generates a reflected left-moving wave at $x < -a$ and a transmitted right-moving wave at $x > a$. The wave functions (209) must fulfil the following conditions

- Continuity of the wave function at $x = \pm a$. This gives

$$\begin{aligned} e^{-ika} + re^{ika} &= Ae^{-ika} + Be^{ika} , \\ te^{ika} &= Ae^{ika} + Be^{-ika} . \end{aligned} \tag{211}$$

  These can be cast in matrix form

$$\underbrace{\begin{pmatrix} e^{-ika} & e^{ika} \\ e^{ika} & e^{-ika} \end{pmatrix}}_{M_1} \begin{pmatrix} A \\ B \end{pmatrix} = e^{ika} \begin{pmatrix} r \\ t \end{pmatrix} + e^{-ika} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{212}$$

- Jump discontinuity of the first derivatives at the positions of the delta-functions. These conditions are again obtained by integrating the TISE over infinitesimal intervals around $\pm a$, e.g.

$$\int_{a-\epsilon}^{a+\epsilon} dx \left[-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V_\delta \delta(x - a)\psi(x) - E\psi(x) \right] = 0 . \tag{213}$$

  This gives two equations

$$\begin{aligned} \psi'(a + 0) - \psi'(a - 0) &= \frac{2m}{\hbar^2} V_\delta \psi(a) , \\ \psi'(-a + 0) - \psi'(-a - 0) &= \frac{2m}{\hbar^2} V_\delta \psi(-a) . \end{aligned} \tag{214}$$

  These two equations can be written in matrix form as

$$\underbrace{\begin{pmatrix} (v_0 - ik)e^{-ika} & (v_0 + ik)e^{ika} \\ (v_0 + ik)e^{ika} & (v_0 - ik)e^{ika} \end{pmatrix}}_{M_2} \begin{pmatrix} A \\ B \end{pmatrix} = ike^{ika} \begin{pmatrix} r \\ t \end{pmatrix} - ike^{-ika} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \tag{215}$$

  where we have defined

$$v_0 = \frac{2mV_\delta}{\hbar^2}. \tag{216}$$

Eliminating A and B we can extract a system of equations for only r and t

$$\left[M_2 M_1^{-1} - ik \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right] \begin{pmatrix} r \\ t \end{pmatrix} = e^{-2ika} \begin{pmatrix} k \csc(2ka) \\ -ik - v_0 - k \cot(2ka) \end{pmatrix}. \tag{217}$$

The solution of this system is

$$
\begin{aligned}
t &= \frac{4k^2}{(2k + iv_0)^2 + e^{4ika} v_0^2} , \\
r &= \frac{v_0 [e^{-2ika}(v_0 - 2ik) - e^{2ika}(v_0 + 2ik)]}{(2k + iv_0)^2 + e^{4ika} v_0^2} .
\end{aligned} \tag{218}
$$

The total scattering cross section is defined as

$$\sigma = |t - 1|^2 + |r|^2 = 2 + \frac{4k^2 \left(-4k^2 - v_0^2 \cos(4ka) + v_0^2 \right)}{8k^4 + 4k^2 v_0^2 - v_0^2 \left(v_0^2 - 4k^2 \right) \cos(4ka) + 4k v_0^3 \sin(4ka) + v_0^4} . \tag{219}$$

We see that at certain values of k (and hence at particular energies) the cross section is strongly enhanced.
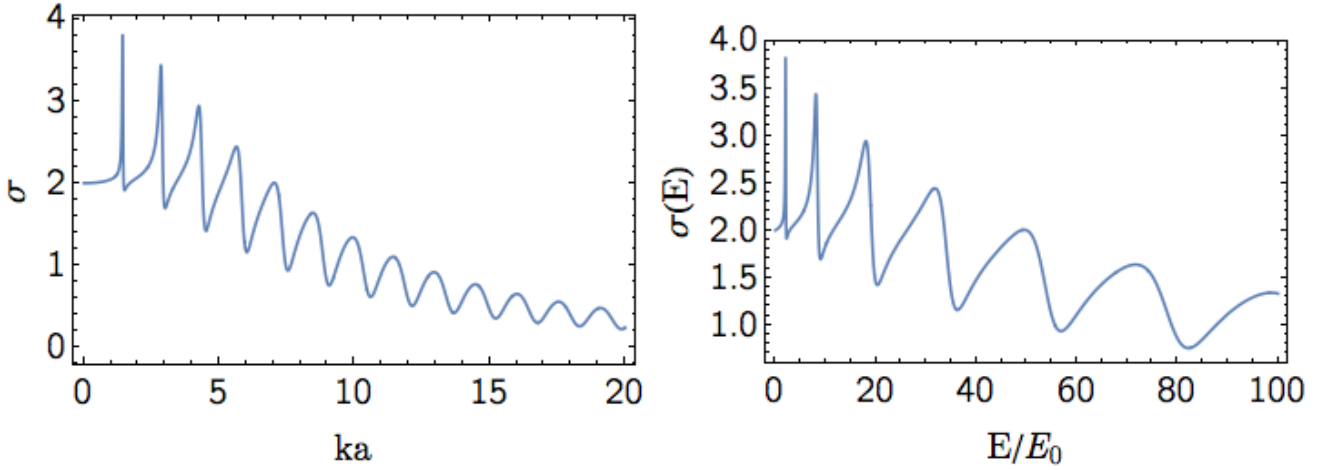
Figure 8: Left: Total scattering cross section σ as a function of ka for $v_0 a = 10$. Right: Total scattering cross section σ as a function of energy E for $v_0 a = 10$ ($E_0 = \hbar^2/(2ma^2)$).

To understand the origin of this phenomenon it is useful to consider the limit of an impenetrable delta-function potential $V_\delta \to \infty$. In this case we have $v_0 a \gg 1$ and the "resonances" occur at

$$k_n a \approx \frac{\pi n}{2} , \quad n = 1, 2, 3 \ldots \tag{220}$$

These correspond to energies

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{8ma^2}. \tag{221}$$

For very large values of V_δ we basically have a infinite square well (as the wave functions must vanish at $\pm a$). We already know that in the latter stationary states occur at energies, cf. (165)

$$E_n^{\text{ISW}} = \frac{\hbar^2 (\pi n)^2}{2m(2a)^2} = \frac{\hbar^2 (\pi n)^2}{8ma^2} , \tag{222}$$

where we have taken into account that the width of the well is $2a$. These are exactly the energies at which the total cross section has spikes! The interpretation is now clear: for special energies the cross section is large because the particle can get temporarily trapped between the barriers, until after some time it escapes

36

to the left or the right. We say that there is a long-lived bound state between the barriers at that energy. So the structure of the total cross section tells us about the energy levels of such long-lived bound states. Long-lived bound states are related to certain types of radioactive decay.

In the case where the peaks in the cross section are very narrow, it follows from our explicit expression for σ that they are approximately of the form

$$\sigma(E \approx E_R) \approx \text{const} + \frac{2(\Gamma/2)^2}{(\Gamma/2)^2 + (E - E_R)^2} \;, \tag{223}$$

where E_R is the energy at which the peak is centred. The form (223) is called *Breit-Wigner* cross section and is used widely to fit experimental data. It can be shown that the parameter Γ is inversely related to the time it takes for the particle to escape from inside the well.

Eugene Wigner (Nobel Prize in Physics 1963).
"Where in the Schrödinger equation do you put the joy of being alive?"

Wigner is also known for not being given tenure at Princeton University in the 1930ies.

Homework 5: WAVE MECHANICS

2.7 Particles move in the potential

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

Particles of mass m and energy $E > V_0$ are incident from $x = -\infty$. Show that the probability that a particle is reflected is

$$\left(\frac{k - K}{k + K}\right)^2,$$

where $k \equiv \sqrt{2mE}/\hbar$ and $K \equiv \sqrt{2m(E - V_0)}/\hbar$. Show directly from the time-independent Schrödinger equation that the probability of transmission is

$$\frac{4kK}{(k + K)^2}$$

and check that the flux of particles moving away from the origin is equal to the incident particle flux.

2.8 Show that the energies of bound, odd-parity stationary states of the square potential well

$$V(x) = \begin{cases} 0 & \text{for } |x| < a \\ V_0 > 0 & \text{otherwise} \end{cases},$$

are governed by

$$\cot(ka) = -\sqrt{\frac{W^2}{(ka)^2} - 1} \quad \text{where} \quad W \equiv \sqrt{\frac{2mV_0a^2}{\hbar^2}} \quad \text{and} \quad k^2 = 2mE/\hbar^2.$$

Show that for a bound odd-parity state to exist, we require $W > \pi/2$.

2.9 A free particle of energy E approaches a square, one-dimensional potential well of depth V_0 and width $2a$. Show that the probability of being reflected by the well vanishes when $Ka = n\pi/2$, where n is an integer and $K = (2m(E + V_0)/\hbar^2)^{1/2}$. Explain this phenomenon in physical terms.

2.10 A particle of energy E approaches from $x < 0$ a barrier in which the potential energy is $V(x) = V_\delta \delta(x)$. Show that the probability of its passing the barrier is

$$P_{\text{tun}} = \frac{1}{1 + (K/2k)^2} \quad \text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}}, \quad K = \frac{2mV_\delta}{\hbar^2}.$$

2.11 Given that the wavefunction is $\psi = A\mathrm{e}^{\mathrm{i}(kz-\omega t)} + B\mathrm{e}^{-\mathrm{i}(kz+\omega t)}$, where A and B are constants, show that the probability current density is

$$\boldsymbol{J} = v\big(|A|^2 - |B|^2\big)\,\hat{\boldsymbol{z}},$$

where $v = \hbar k/m$. Interpret the result physically.

2.12 Consider a free particle in one dimension with Hamiltonian

$$H = \frac{\hat{p}^2}{2m}. \tag{224}$$

Let the wave function of the particle at time $t = 0$ be a Gaussian wave packet

$$\psi(x,0) = \langle x|\psi(0)\rangle = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\frac{x^2}{4\sigma^2} + \frac{i}{\hbar}p_0 x}. \tag{225}$$

Show that in the momentum representation we have

$$\langle p|\psi(0)\rangle = \int dx \, \langle p|x\rangle\langle x|\psi(0)\rangle = \left[\frac{2\sigma^2}{\pi\hbar^2}\right]^{\frac{1}{4}} e^{-\frac{\sigma^2}{\hbar^2}(p-p_0)^2}. \tag{226}$$

Comment on the relation between the forms of the state in the position and momentum representations as a function of σ. By solving the TDSE show that the probability distribution function at time t can be written in the form

$$|\psi(x,t)|^2 = \frac{\sigma}{\sqrt{2\pi\hbar^2|b(t)|^2}} e^{-\frac{\sigma^2}{2\hbar^2|b(t)|^2}(x-p_0 t/m)^2}, \tag{227}$$

and derive the form of the function $b(t)$. Explain what happens physically to the particle as time evolves.

6 HARMONIC OSCILLATORS

The career of a young theoretical physicist consists of treating the harmonic oscillator in ever-increasing levels of abstraction. SIDNEY COLEMAN.

Harmonic oscillations are ubiquitous in Physics as they describe small excursions from points of equilibrium. QM harmonic oscillators are extremely important as they are the basic building blocks of relativistic Quantum Field Theories and the quantum theory of many-particle systems that describe solids.

The Hamiltonian for a one dimensional harmonic oscillator is

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2.$$
(228)

The corresponding TISE in the position representation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{m\omega^2}{2}x^2\psi(x) = E\psi(x).$$
(229)

One way of approaching the QM harmonic oscillator is to solve this differential equation by the Frobenius method. Here we will follow a different approach and employ operator methods. We start by introducing so called creation and annihilation operators by

$$
\begin{aligned}
a &= \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\omega\hbar}}\hat{p} \,, \\
a^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\omega\hbar}}\hat{p} \,.
\end{aligned}
$$
(230)

Here $a^\dagger$ is the Hermitian conjugate operator to a. Creation/annihilation operators fulfil the following commutation relations

$$\boxed{[a, a^\dagger] = -\frac{i}{2\hbar}[\hat{x}, \hat{p}] + \frac{i}{2\hbar}[\hat{p}, \hat{x}] = 1.}$$
(231)

The utility of these operators is that the Hamiltonian can be expressed in a simple way in terms of them. We have

$$a^\dagger a = \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{1}{2m\hbar\omega}\hat{p}^2 - \frac{i}{2\hbar}[\hat{p}, \hat{x}] \,,$$
(232)

which tells us that

$$\boxed{H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right).}$$
(233)

Here

$$\boxed{\hat{N} = a^\dagger a}$$
(234)

is referred to as the *number operator*. In order to proceed we will require the commutation relations of the creation/annihilation operators with the Hamiltonian (or equivalently the number operator)

$$[a, \hat{N}] = a \,, \qquad [a^\dagger, \hat{N}] = -a^\dagger.$$
(235)

These are established as follows

$$[a, \hat{N}] = aa^\dagger a - a^\dagger a a = [a, a^\dagger]a = a \,.$$
(236)

Now assume that we know an eigenstate $|E\rangle$ of H

$$H|E\rangle = E|E\rangle.$$
(237)

We will now show that both $a^\dagger|E\rangle$ and $a|E\rangle$ are eigenstates of H as well. Consider

$$Ha^\dagger|E\rangle = \left([H, a^\dagger] + a^\dagger H\right)|E\rangle = \left(\hbar\omega a^\dagger + a^\dagger E\right)|E\rangle = (E + \hbar\omega)\,a^\dagger|E\rangle.$$
(238)

That's a bingo: $a^\dagger|E\rangle$ is an eigenstate with energy $E + \hbar\omega$. Similarly we have

$$Ha|E\rangle = ([H, a] + aH)|E\rangle = (-\hbar\omega a + aE)|E\rangle = (E - \hbar\omega)\,a|E\rangle.$$
(239)

So $a|E\rangle$ is an eigenstate with energy $E - \hbar\omega$. Finally we consider the "length" $\langle E|a^\dagger a|E\rangle$ of the ket vector $a|E\rangle$

$$0 \leq \langle E|a^\dagger a|E\rangle = \langle E|\frac{H}{\hbar\omega} - \frac{1}{2}|E\rangle = \frac{E}{\hbar\omega} - \frac{1}{2}. \tag{240}$$

This tells us that the energy eigenvalues are bounded from below

$$E \geq \frac{\hbar\omega}{2}. \tag{241}$$

This means that there is an eigenstate with lowest energy E_0, which we denote by $|0\rangle$. Using (239) we have

$$Ha|0\rangle = (E_0 - \hbar\omega)a|0\rangle, \tag{242}$$

so either $a|0\rangle$ is an eigenstate with energy $E_0 - \hbar\omega$ or $a|0\rangle = 0$. The former is impossible because E_0 is by construction to lowest energy eigenvalue, so we must have

$$a|0\rangle = 0. \tag{243}$$

This in turn tell us that the ground state energy is

$$H|0\rangle = \frac{\hbar\omega}{2}|0\rangle \Rightarrow E_0 = \frac{\hbar\omega}{2}. \tag{244}$$

This is the first interesting result: the ground state energy of the QM harmonic oscillator is not zero, but $E_0 = \frac{\hbar\omega}{2}$. This is called the *zero-point energy*. Using (238) repeatedly we can construct eigenstates of the form

$$|n\rangle = \frac{1}{N_n}(a^\dagger)^n|0\rangle \ , \tag{245}$$

where N_n is a normalization constant. The energy of the states (245) is $E_n = E_0 + n\hbar\omega$ as each $a^\dagger$ adds an energy $\hbar\omega$ by virtue of (238), i.e.

$$\boxed{E_n = \hbar\omega\left(n + \frac{1}{2}\right).} \tag{246}$$

We now observe that

$$\begin{aligned}
[a, (a^\dagger)^n] &= a(a^\dagger)^n - (a^\dagger)^n a = [a, a^\dagger](a^\dagger)^{n-1} + a^\dagger[a, a^\dagger](a^\dagger)^{n-2} + (a^\dagger)^2[a, a^\dagger](a^\dagger)^{n-3} + \dots \\
&= n(a^\dagger)^{n-1},
\end{aligned} \tag{247}$$

which implies that

$$a|n\rangle = \alpha_n|n-1\rangle \ . \tag{248}$$

The constant α_n is most easily calculated by considering

$$\begin{aligned}
\langle n|a^\dagger a|n\rangle &= |\alpha_n|^2 \\
&= \langle n|\hat{N}|n\rangle = n.
\end{aligned} \tag{249}$$

Using that we can choose our normalization constants to be real we thus have

$$\boxed{a|n\rangle = \sqrt{n}|n-1\rangle.} \tag{250}$$

The analogous relation for the creation operator is

$$\boxed{a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle.} \tag{251}$$

It is established by noting that
$$a^\dagger |n\rangle = \beta_n |n+1\rangle \tag{252}$$

and then calculating
$$\langle n | a a^\dagger | n \rangle = |\beta_n|^2 = \langle n | \hat{N} + [a, a^\dagger] | n \rangle = n + 1. \tag{253}$$

Using (251) repeatedly we have
$$(a^\dagger)^n |0\rangle = \sqrt{n!} |n\rangle , \tag{254}$$

which gives the normalization constant
$$\boxed{N_n = \sqrt{n!}.} \tag{255}$$

Nice.

6.1 Ground state of the Quantum Harmonic Oscillator

We now turn to a more detailed analysis of the ground state and its properties. Our starting point is the fact the $|0\rangle$ is annihilated by a

$$a|0\rangle = 0 = \left[\sqrt{\frac{m\omega}{2\hbar}} \hat{x} + \frac{i}{\sqrt{2m\omega\hbar}} \hat{p} \right] |0\rangle. \tag{256}$$

In the position representation this becomes

$$
\begin{aligned}
0 &= \langle x | a | 0 \rangle = \langle x | \left[\sqrt{\frac{m\omega}{2\hbar}} \hat{x} + \frac{i}{\sqrt{2m\omega\hbar}} \hat{p} \right] |0\rangle \\
&= \int dx' \, \langle x | \left[\sqrt{\frac{m\omega}{2\hbar}} x + \frac{i}{\sqrt{2m\omega\hbar}} \hat{p} \right] |x'\rangle \langle x' | 0 \rangle \\
&= \sqrt{\frac{m\omega}{2\hbar}} \int dx' \, \underbrace{\langle x | \hat{x} | x' \rangle}_{x\delta(x-x')} \langle x' | 0 \rangle + \frac{i}{\sqrt{2m\omega\hbar}} \int dx' \, \underbrace{\langle x | \hat{p} | x' \rangle}_{-i\hbar \frac{d}{dx}\delta(x-x')} \langle x' | 0 \rangle \\
&= \left[\sqrt{\frac{m\omega}{2\hbar}} x + \frac{\hbar}{\sqrt{2m\omega\hbar}} \frac{d}{dx} \right] \underbrace{\langle x | 0 \rangle}_{\psi_0(x)} .
\end{aligned}
\tag{257}
$$

This is a first order differential equation for the ground state wave function $\psi_0(x)$. Its normalized solution is

$$\boxed{\psi_0(x) = \frac{1}{(2\pi\ell^2)^{\frac{1}{4}}} e^{-\frac{x^2}{4\ell^2}} , \qquad \ell = \sqrt{\frac{\hbar}{2m\omega}}.} \tag{258}$$

We see that the ground state wave function is a Gaussian centred around zero. Its energy $E_0 = \frac{\hbar\omega}{2}$ is larger than zero, in contrast to the lowest energy configuration of a classical harmonic oscillator. The existence of a zero-point energy is a direct consequence of the Heisenberg uncertainty relation. In order to have zero energy our quantum mechanical particle would need to have neither potential energy, i.e. be localized at $x = 0$, nor kinetic energy, i.e. have zero momentum. These two requirements cannot be met simultaneously because of the uncertainty relation.

We now turn to the calculation of ground state expectation values. We have

$$
\begin{aligned}
\langle 0 | \hat{x} | 0 \rangle &= \sqrt{\frac{\hbar}{2m\omega}} \langle 0 | a + a^\dagger | 0 \rangle = 0 , \\
\langle 0 | \hat{p} | 0 \rangle &= -i\sqrt{\frac{m\hbar\omega}{2}} \langle 0 | a - a^\dagger | 0 \rangle = 0 ,
\end{aligned}
\tag{259}
$$

where we have used that $a|0\rangle = 0 = \langle 0|a^\dagger$. This means that on average the particle in the ground state of our harmonic oscillator is located at $x = 0$ and has zero momentum. The variances are

$$\langle 0|\hat{x}^2|0\rangle = \frac{\hbar}{2m\omega}\langle 0|(a + a^\dagger)^2|0\rangle = \frac{\hbar}{2m\omega}\langle 0|aa^\dagger|0\rangle = \frac{\hbar}{2m\omega}\langle 0|[a, a^\dagger]|0\rangle = \frac{\hbar}{2m\omega} ,$$

$$\langle 0|\hat{p}^2|0\rangle = -\frac{m\hbar\omega}{2}\langle 0|(a - a^\dagger)^2|0\rangle = \frac{m\hbar\omega}{2}\langle 0|aa^\dagger|0\rangle = \frac{m\hbar\omega}{2}.$$

(260)

Putting everything together we have

$$\boxed{\Delta x \Delta p = \frac{\hbar}{2}.}$$

(261)

This means that the ground state of the harmonic oscillator saturates the Heisenberg uncertainty relation, i.e. it is a state of *minimal uncertainty*.

6.2 Excited states of the Quantum Harmonic Oscillator

We now turn to the wave functions for excited states. For the first excited state we have

$$\psi_1(x) = \langle x|1\rangle = \langle x|a^\dagger|0\rangle = \langle x|\left[\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\omega\hbar}}\hat{p}\right]|0\rangle$$

$$= \left[\frac{x}{2\ell} - \ell\frac{d}{dx}\right]\langle x|0\rangle$$

$$= \frac{1}{(2\pi\ell^2)^{\frac{1}{4}}}\frac{x}{\ell}e^{-\frac{x^2}{4\ell^2}} .$$

(262)

For the higher excited states we have the following *recurrence relation*

$$\psi_n(x) = \langle x|n\rangle = \frac{1}{\sqrt{n}}\langle x|a^\dagger|n - 1\rangle$$

$$= \frac{1}{\sqrt{n}}\left[\frac{x}{2\ell} - \ell\frac{d}{dx}\right]\underbrace{\langle x|n - 1\rangle}_{\psi_{n-1}(x)}.$$

(263)

Using this repeatedly we have

$$\psi_n(x) = \frac{1}{\sqrt{n!}}\left[\frac{x}{2\ell} - \ell\frac{d}{dx}\right]^n\psi_0(x) \equiv \frac{1}{\sqrt{n!}}f_n(x)\psi_0(x) ,$$

(264)

where $f_n(x)$ is some polynomial in x. Substituting (264) into (263) we obtain a recurrence relation for $f_n(x)$

$$f_n(x) = \frac{x}{\ell}f_{n-1}(x) - \ell f'_{n-1}(x) , \quad f_0(x) = 1 .$$

(265)

Comparing this with the recurrence relation of the so-called *Hermite polynomials* $H_n(z)$

$$H_n(z) = 2zH_{n-1}(z) - H'_{n-1}(z) , \quad H_0(z) = 1 ,$$

(266)

we conclude that

$$f_n(x) = \frac{1}{2^{n/2}}H_n\left(\frac{x}{\sqrt{2\ell}}\right).$$

(267)

This gives our final result

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{n!2^n}}H_n\left(\frac{x}{\sqrt{2\ell}}\right)\psi_0(x).}$$

(268)

The first few Hermite polynomials are

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

(269)

From the properties of the Hermite polynomials it follows that

- $\psi_{2n}(x)$ are even under parity $x \to -x$, i.e. $\psi_{2n}(-x) = \psi_{2n}(x)$.

- $\psi_{2n+1}(x)$ are odd under parity $x \to -x$, i.e. $\psi_{2n+1}(-x) = -\psi_{2n+1}(x)$.

- $\psi_n(x)$ has n nodes.

Expectation values in excited states of the harmonic oscillator can be calculated from the following

$$
\begin{aligned}
\langle n|a|n \rangle &= 0 , & \langle n|a^\dagger|n \rangle &= 0 , \\
\langle n|a^\dagger a|n \rangle &= n , & \langle n|aa^\dagger|n \rangle &= n+1 , & \langle n|(a^\dagger)^2|n \rangle = 0 = \langle n|a^2|n \rangle.
\end{aligned}
\tag{270}
$$

Using these we can easily show that

$$
\begin{aligned}
\langle n|\hat{x}|n \rangle &= 0 = \langle n|\hat{p}|n \rangle , \\
\langle n|\hat{x}^2|n \rangle &= \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right) , & \langle n|\hat{p}^2|n \rangle = \hbar m\omega\left(n+\frac{1}{2}\right)
\end{aligned}
\tag{271}
$$

The product of uncertainties is thus

$$
\Delta x \, \Delta p = \hbar\left(n + \frac{1}{2}\right) .
\tag{272}
$$

This tells us that only the ground state is a state of minimal uncertainty, and the uncertainties are larger in highly excited states.

6.3 What oscillates in the quantum harmonic oscillator?

Let us now consider a harmonic oscillator initially prepared in a state $|\psi(0)\rangle$

$$
|\psi(0)\rangle = \sum_{n=0}^{\infty} \underbrace{\langle n|\psi(0)\rangle}_{a_n} |n\rangle .
\tag{273}
$$

The TDSE tells us that at time t the state of the system will be

$$
|\psi(t)\rangle = \sum_{n=0}^{\infty} a_n \, e^{-i\omega t(n+\frac{1}{2})} |n\rangle .
\tag{274}
$$

The average position of our particle as a function of time is then given by the expectation value

$$
\langle \psi(t)|\hat{x}|\psi(t)\rangle = \sum_{n,m=0}^{\infty} a_m^* a_n e^{i\omega t(m-n)}\langle m|\hat{x}|n\rangle .
\tag{275}
$$

Matrix elements of the position operator are readily worked out using (250), (251) and $\hat{x} = \ell[a + a^\dagger]$

$$
\langle m|\hat{x}|n\rangle = \ell\left[\sqrt{n}\delta_{m,n-1} + \sqrt{n+1}\delta_{m,n+1}\right].
\tag{276}
$$

Substituting (276) into (275) we have

$$
\begin{aligned}
\langle \psi(t)|\hat{x}|\psi(t)\rangle &= \ell\sum_{n=1}^{\infty} \sqrt{n}\left[a_n a_{n-1}^* e^{-i\omega t} + a_{n-1}a_n^* e^{i\omega t}\right] \\
&= \sum_{n=1}^{\infty} b_n \cos(\omega t + a_n) ,
\end{aligned}
\tag{277}
$$

where $2\sqrt{n}\ell a_n^* a_{n-1} = b_n \exp(i\phi_n)$. Eqn (277) proves that if we prepare the harmonic oscillator in a generic initial state $|\psi(0)\rangle$ the expectation value of position oscillates with frequency ω. This is reassuring.

6.4 Quantum vs classical harmonic oscillator

The solution of the equations of motion for the classical harmonic oscillator is

$$x(t) = x_0 \sin(\omega t) \;, \quad E = \frac{m\omega^2}{2} x_0^2 \;. \tag{278}$$

Defining the probability density of finding the classical harmonic oscillator at position x by

$$P_{\rm cl}(x) dx = 2\frac{dt}{T} \;, \quad T = \frac{2\pi}{\omega} \;, \tag{279}$$

we have

$$P_{\rm cl}(x) = \frac{1}{\pi\sqrt{x_0^2 - x^2}} = \frac{1}{2\pi\ell\sqrt{\frac{E}{\hbar\omega} - \frac{x^2}{4\ell^2}}} \tag{280}$$

In Fig. 9 we compare $P_{\rm cl}(x)$ to the probability distribution of a quantum harmonic oscillator at the same energy $E_{100} = 100.5\hbar\omega$. We observe that the quantum mechanical probability is a strongly oscillatory func-
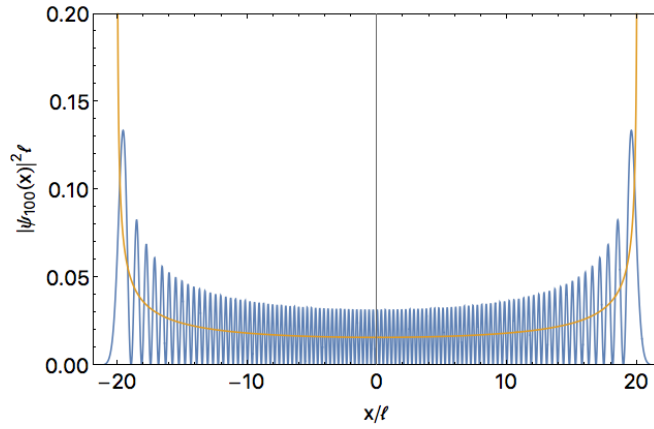
Figure 9: Probability distribution in a stationary state of the harmonic oscillator with $n = 100$.

tion with oscillations occurring on a length scale $\sim \ell/\sqrt{n}$. Averaging the quantum mechanical probability distribution over a very small range approaches the classical probability distribution in the large-n limit.

Aside 4: Coherent States

There are other states in the harmonic oscillator problem that are of great interest. Consider the eigenvalue equation for the annihilation operator

$$a|\alpha\rangle = \alpha|\alpha\rangle. \tag{281}$$

These are called *coherent states* for reasons that will become clear shortly. Recalling that

$$a = \frac{\hat{x}}{2\ell} + \frac{i\ell}{\hbar}\hat{p} \;, \tag{282}$$

we can turn (281) into a differential equation by going to the position representation

$$\begin{aligned}\langle x|a|\alpha\rangle &= \alpha\langle x|\alpha\rangle \\ &= \frac{x}{2\ell}\langle x|\alpha\rangle + \ell\frac{d}{dx}\langle x|\alpha\rangle. \end{aligned} \tag{283}$$

This is solved by

$$\Phi_\alpha(x) = \langle x|\alpha\rangle = \frac{1}{(2\pi\ell^2)^{1/4}} e^{-\frac{(x-2\ell\alpha)^2}{4\ell^2}} \;. \tag{284}$$

So the wave functions of coherent states are Gaussians centred at positions $2\ell\alpha$. We can express the coherent states in terms of the energy eigenstates (which after all form a basis) as follows. Using the eigenvalue equation together with (251) we obtain a recurrence relation

$$\langle n|a|\alpha\rangle = \alpha \ \langle n|\alpha\rangle = \sqrt{n+1}\langle n+1|\alpha\rangle. \tag{285}$$

This is solved by

$$\langle n|\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\langle 0|\alpha\rangle. \tag{286}$$

This provides us with the desired expansion in terms of energy eigenstates

$$|\alpha\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\langle 0|\alpha\rangle \ |n\rangle. \tag{287}$$

We note that coherent states are particular superpositions involving *all* energy eigenstates. We have

$$\langle 0|\alpha\rangle = \int_{-\infty}^{\infty} dx \ \Phi_\alpha(x)\Psi_0^*(x) = e^{-\frac{\alpha^2}{2}}. \tag{288}$$

What makes coherent states special is their time evolution. Using the expansion in terms of energy eigenstates we have

$$|\alpha,t\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\langle 0|\alpha\rangle \ e^{-\frac{i}{\hbar}E_n t}|n\rangle. \tag{289}$$

Using that $E_n = \hbar\omega(n+1/2)$ we have

$$
\begin{aligned}
|\alpha,t\rangle &= e^{-i\frac{\omega t}{2}} \sum_{n=0}^{\infty} \frac{\left(\alpha e^{-i\omega t}\right)^n}{\sqrt{n!}} \frac{\langle 0|\alpha e^{-i\omega t}\rangle}{\langle 0|\alpha e^{-i\omega t}\rangle}\langle 0|\alpha\rangle \ |n\rangle, \\
&= e^{-i\frac{\omega t}{2}} \frac{e^{-\alpha^2/2}}{e^{-(\alpha e^{-i\omega t})^2/2}}|\alpha e^{-i\omega t}\rangle \ ,
\end{aligned}
\tag{290}
$$

where we have used (288) for both $\langle 0|\alpha\rangle$ and $\langle 0|\alpha e^{-i\omega t}\rangle$. The corresponding wave functions are

$$\Phi_\alpha(x,t) = \Phi_{\alpha_t}(x)e^{-i\frac{\omega t}{2}} e^{-\frac{\alpha^2}{2}(1-e^{2i\omega t})}. \tag{291}$$

Here comes the joke: the probability density $|\Phi_\alpha(x,t)|^2$ of a coherent state looks like a Gaussian wave-packet that oscillates with frequency ω while *precisely retaining its shape*!

Aside 5: SOLVING THE SCHRÖDINGER EQUATION NUMERICALLY

Most Schrödinger equations cannot be solved exactly in the way we have done in our various examples. Therefore one typically resorts to numerical solutions. To be specific, let's consider the following example

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda\hat{x}^4 \equiv H_0 + \lambda\hat{x}^4 \ , \quad \lambda > 0. \tag{292}$$

Let's say that we are interested in determining the ground state wave function of this Hamiltonian. One way of doing this is to use our knowledge of the eigenstates of the harmonic oscillator part H_0

$$H_0|n\rangle = \hbar\omega(n+\frac{1}{2})|n\rangle. \tag{293}$$

Using that these states form an orthonormal basis of the space of quantum states we have

$$\mathbf{1} = \sum_{n=0}^{\infty} |n\rangle\langle n|, \tag{294}$$

and therefore

$$H = \mathbf{1}H\mathbf{1} = \sum_{n,m}\langle m|H|n\rangle \, |m\rangle\langle n|. \tag{295}$$

The eigenstates $|\psi_n\rangle$ of H can also be expressed in this basis

$$|\psi_n\rangle = \sum_{m}\langle m|\psi_n\rangle \, |m\rangle. \tag{296}$$

The matrix elements of the Hamiltonian in this basis are

$$\langle m|H|n\rangle \; = \hbar\omega(n+\frac{1}{2})\delta_{n,m} + \lambda\langle m|\hat{x}^4|n\rangle. \tag{297}$$

The matrix elements of the position operator can be determined either numerically by working out the integrals

$$\langle m|\hat{x}^4|n\rangle = \int_{-\infty}^{\infty} dx \, \left[\psi_m^{(0)}(x)\right]^* x^4 \psi_n^{(0)}(x), \tag{298}$$

where $\psi_n^{(0)}(x)$ are the harmonic oscillator wave functions, or by using our creation/annihilation operator algebra

$$\begin{aligned}
\langle m|\hat{x}^4|n\rangle \;\; &= \;\; \ell^4\langle m|(a+a^\dagger)^4|n\rangle \\
&= \;\; \ell^4\Big[\sqrt{n(n-1)(n-2)(n-3)}\delta_{m,n-4} + (4n-2)\sqrt{n(n-1)}\delta_{m,n-2} \\
&\quad + (6n^2+6n+3)\delta_{m,n} + \sqrt{(n+1)(n+2)}(4n+6)\delta_{m,n+2} \\
&\quad + \sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{m,n+4}\Big] \equiv \ell^4 V_{mn}.
\end{aligned} \tag{299}$$

The idea is now to *truncate* the sums in (295) by introducing a *cutoff* N. This turns H into an $(N+1) \times (N+1)$ matrix

$$H_{nm} = \hbar\omega\left[(n+\frac{1}{2})\delta_{n,m} + \underbrace{\frac{\lambda\ell^4}{\hbar\omega}}_{\mu} V_{nm}\right], \quad n,m = 0,\dots,N. \tag{300}$$

We now simply diagonalize the (dimensionless) matrix $H/(\hbar\omega)$ numerically and obtain approximate values for the energies and eigenstates of H. We increase the cutoff N until the ground state energy and wave function no longer change within our desired numerical accuracy. For example, taking $\mu = 0.1$ and $N = 10$ gives

$$E_0 \approx 0.668812\hbar\omega \, ,$$
$$|\psi_0\rangle \approx -0.986914|0\rangle + 0.160316|2\rangle - 0.0133936|4\rangle - 0.0086538|6\rangle + 0.0064238|8\rangle - 0.00223485|10\rangle. \tag{301}$$

Increasing the cutoff to $N = 20$ gives

$$\begin{aligned}
E_0 \;\; &\approx \;\; 0.668773\hbar\omega \, , \\
|\psi_0\rangle \;\; &\approx \;\; -0.986896|0\rangle + 0.160386|2\rangle - 0.0134396|4\rangle - 0.00875891|6\rangle + 0.00682899|8\rangle \\
&\quad - 0.00299289|10\rangle + 0.000832743|12\rangle - 0.0000103442|14\rangle - 0.000169943|16\rangle \\
&\quad + 0.000129011|18\rangle - 0.0000507885|20\rangle
\end{aligned} \tag{302}$$

You get the idea. In general we choose an appropriate basis of states in which to express our Hamiltonian of interest and carry out the analogous procedure.

3.1 After choosing units in which everything, including $\hbar = 1$, the Hamiltonian of a harmonic oscillator may be written $\hat{H} = \frac{1}{2}(\hat{p}^2 + \hat{x}^2)$, where $[\hat{x}, \hat{p}] = i$. Show that if $|\psi\rangle$ is a ket that satisfies $H|\psi\rangle = E|\psi\rangle$, then

$$\frac{1}{2}(\hat{p}^2 + \hat{x}^2)(\hat{x} \mp i\hat{p})|\psi\rangle = (E \pm 1)(\hat{x} \mp i\hat{p})|\psi\rangle.$$

Explain how this algebra enables one to determine the energy eigenvalues of a harmonic oscillator.

3.2 Given that $\hat{a}|n\rangle = \alpha|n-1\rangle$ and $E_n = (n + \frac{1}{2})\hbar\omega$, where the annihilation operator of the harmonic oscillator is

$$\hat{a} \equiv \frac{m\omega\hat{x} + i\hat{p}}{\sqrt{2m\hbar\omega}},$$

show that $\alpha = \sqrt{n}$. Hint: consider $|\hat{a}|n\rangle|^2$.

3.3 The pendulum of a grandfather clock has a period of $1\,\mathrm{s}$ and makes excursions of $3\,\mathrm{cm}$ either side of dead centre. Given that the bob weighs $0.2\,\mathrm{kg}$, around what value of n would you expect its non-negligible quantum amplitudes to cluster?

3.4 Show that the minimum value of $E(p, x) \equiv p^2/2m + \frac{1}{2}m\omega^2 x^2$ with respect to the real numbers p, x when they are constrained to satisfy $xp = \frac{1}{2}\hbar$, is $\frac{1}{2}\hbar\omega$. Explain the physical significance of this result.

3.5 How many nodes are there in the wavefunction $\langle x|n\rangle$ of the nth excited state of a harmonic oscillator?

3.6 Show that for a harmonic oscillator that wavefunction of the second excited state is $\langle x|2\rangle = \text{constant} \times (x^2/\ell^2 - 1)e^{-x^2/4\ell^2}$, where $\ell \equiv \sqrt{\hbar/2m\omega}$ and find the normalising constant.

3.7 Use

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger) = \ell(\hat{a} + \hat{a}^\dagger)$$

to show for a harmonic oscillator that in the energy representation the operator $\hat{x}$ is

$$\hat{x}_{jk} = \ell \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots & & & \\ \sqrt{1} & 0 & \sqrt{2} & 0 & & & & \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots & & & \\ & & \sqrt{3} & \cdots & & & & \\ \cdots & & \cdots & & \cdots & & \cdots & \\ & & & \cdots & 0 & \sqrt{n-1} & \cdots & \\ & & & & \sqrt{n-1} & 0 & \sqrt{n} & \\ & & & & & \sqrt{n} & 0 & \sqrt{n+1} & \cdots \\ & & & & & & \sqrt{n+1} & 0 \\ \cdots & & \cdots & & \cdots & & \cdots & & \cdots \end{pmatrix}$$

Calculate the same entries for the matrix $\hat{p}_{jk}$.

3.8 At $t = 0$ the state of a harmonic oscillator of mass m and frequency ω is

$$|\psi\rangle = \frac{1}{2}|N-1\rangle + \frac{1}{\sqrt{2}}|N\rangle + \frac{1}{2}|N+1\rangle.$$

Calculate the expectation value of x as a function of time and interpret your result physically in as much detail as you can.

Homework 7: More problems on basic quantum mechanics

3.9 A three-state system has a complete orthonormal set of states $|1\rangle, |2\rangle, |3\rangle$. With respect to this basis the operators $\hat{H}$ and $\hat{B}$ have matrices

$$\hat{H} = \hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \hat{B} = b \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

where ω and b are real constants.
(a) Are $\hat{H}$ and $\hat{B}$ Hermitian?
(b) Write down the eigenvalues of $\hat{H}$ and find the eigenvalues of $\hat{B}$. Solve for the eigenvectors of both $\hat{H}$ and $\hat{B}$. Explain why neither matrix uniquely specifies its eigenvectors.
(c) Show that $\hat{H}$ and $\hat{B}$ commute. Give a basis of eigenvectors common to $\hat{H}$ and $\hat{B}$.

3.10 A system has a time-independent Hamiltonian that has spectrum $\{E_n\}$. Prove that the probability P_k that a measurement of energy will yield the value E_k is is time-independent. Hint: you can do this either from Ehrenfest's theorem, or by differentiating $\langle E_k, t|\psi\rangle$ w.r.t. t and using the TDSE.

3.11 Let $\psi(x)$ be a properly normalised wavefunction and $\hat{Q}$ an operator on wavefunctions. Let $\{q_r\}$ be the spectrum of $\hat{Q}$ and $\{u_r(x)\}$ be the corresponding correctly normalised eigenfunctions. Write down an expression for the probability that a measurement of Q will yield the value q_r. Show that $\sum_r P(q_r|\psi) = 1$. Show further that the expectation of Q is $\langle Q \rangle \equiv \int_{-\infty}^{\infty} \psi^* \hat{Q} \psi \, \mathrm{d}x$.

3.12 (a) Find the allowed energy values E_n and the associated normalized eigenfunctions $\phi_n(x)$ for a particle of mass m confined by infinitely high potential barriers to the region $0 \le x \le a$.
(b) For a particle with energy $E_n = \hbar^2 n^2 \pi^2 / 2ma^2$ calculate $\langle x \rangle$.
(c) Without working out any integrals, show that

$$\langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \frac{a^2}{4}.$$

Hence find $\langle (x - \langle x \rangle)^2 \rangle$ using the result that $\int_0^a x^2 \sin^2(n\pi x/a) \, \mathrm{d}x = a^3(1/6 - 1/4n^2\pi^2)$.
(d) A classical analogue of this problem is that of a particle bouncing back and forth between two perfectly elastic walls, with uniform velocity between bounces. Calculate the classical average values $\langle x \rangle_{\mathrm{c}}$ and $\langle (x - \langle x \rangle)^2 \rangle_{\mathrm{c}}$, and show that for high values of n the quantum and classical results tend to each other.

3.13 A **Fermi oscillator** has Hamiltonian $\hat{H} = \hat{f}^\dagger \hat{f}$, where $\hat{f}$ is an operator that satisfies

$$\hat{f}^2 = 0, \quad \hat{f}\hat{f}^\dagger + \hat{f}^\dagger \hat{f} = 1.$$

Show that $\hat{H}^2 = \hat{H}$, and thus find the eigenvalues of $\hat{H}$. If the ket $|0\rangle$ satisfies $\hat{H}|0\rangle = 0$ with $\langle 0|0\rangle = 1$, what are the kets (a) $|a\rangle \equiv \hat{f}|0\rangle$, and (b) $|b\rangle \equiv \hat{f}^\dagger|0\rangle$?
In quantum field theory the vacuum is pictured as an assembly of oscillators, one for each possible value of the momentum of each particle type. A boson is an excitation of a harmonic oscillator, while a fermion in an excitation of a Fermi oscillator. Explain the connection between the spectrum of

$\hat{f}^\dagger \hat{f}$ and the Pauli exclusion principle (which states that zero or one fermion may occupy a particular quantum state).

3.14* Numerical solutions of the Schrödinger equation By following the discussion given in the lecture notes construct numerical solutions for the first 10 eigenstates $|\phi_n\rangle$ of the Hamiltonian

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda\hat{x}^4.$$

for $\frac{\lambda\ell^4}{\hbar\omega} = 0.1$. You can download a Mathematica file for doing this from the course webpage. Now use the eigenvectors to obtain an expression for the ground state of the harmonic oscillator Hamiltonian ($\lambda = 0$) in terms of the eigenstates of H

$$|0\rangle \approx \sum_{n=0}^{N} \langle\phi_n|0\rangle \, |\phi_n\rangle.$$

Now assume that we initially prepare our system in the state $|\Phi(0)\rangle = |0\rangle$ and then consider time evolution under the Hamiltonian H. We have

$$|\Phi(t)\rangle \approx \sum_{n=0}^{N} \langle\phi_n|0\rangle \, e^{-\frac{i}{\hbar}E_n t}|\phi_n\rangle. \tag{303}$$

We now want to determine the probability density $|\langle x|\Phi(t)\rangle|^2$ to find the particle at position x at time t. To do this we express $|\Phi(t)\rangle$ in terms of harmonic oscillator wave functions $\psi_k(x)$

$$
\begin{aligned}
\langle x|\Phi(t)\rangle &\approx \sum_{n=0}^{N} \langle\phi_n|0\rangle \, e^{-\frac{i}{\hbar}E_n t}\langle x|\phi_n\rangle = \sum_{n=0}^{N} \langle\phi_n|0\rangle \, e^{-\frac{i}{\hbar}E_n t}\langle x|\sum_{k=0}^{\infty}|k\rangle\langle k|\phi_n\rangle \\
&\approx \sum_{k=0}^{N}\sum_{n=0}^{N} \langle\phi_n|0\rangle \, e^{-\frac{i}{\hbar}E_n t}\langle k|\phi_n\rangle \, \psi_k(x).
\end{aligned} \tag{304}
$$

In the last step we have cut off the sum over k in the resolution of the identity, which is justified because $\langle k|\phi_n\rangle\langle\phi_n|0\rangle$ are negligible for large k. We have explicit expression for the harmonic oscillator wave functions and know $\langle k|\phi_n\rangle$ and E_n from our numerics. We therefore can plot $P(x,t) = |\langle x|\Phi(t)\rangle|^2$ for any given time. In order to keep our discussion very general we note that we essentially have two dimensionful quantities in our problem

- A time scale $1/\omega$.

- A length scale ℓ.

We use these scales to introduce dimensionless variables parametrizing the time and position by $x = z\ell$, $t = \tau/\omega$. The probability to observe our particle in the interval $[x, x+dx]$ is $P(x,t)dx = p(z,\tau)dz$, where

$$p(z,\tau) = |\langle z\ell|\Phi(\tau/\omega)\rangle|^2\ell.$$

The nice thing is that $p(z,\tau)$ no longer contains any dimensionful quantities

$$p(z,\tau) \approx \left|\frac{e^{-z^2/4}}{(2\pi)^{\frac{1}{4}}}\sum_{k=0}^{N}\sum_{n=0}^{N}\langle\phi_n|0\rangle \, \langle k|\phi_n\rangle \, e^{-i(E_n/\hbar\omega)\tau}\frac{H_k(z/\sqrt{2})}{\sqrt{k!2^k}}\right|^2. \tag{305}$$

Plot $p(x,\tau)$ as a function of z for some values of τ.

Part III
TRANSFORMATIONS

> Hermann Weyl
> *"The goal of mathematics is the symbolic comprehension of the infinite with human, that is finite, means."*

7 TRANSFORMATIONS AND SYMMETRIES

A very important concept in QM is that of a *transformation*. Our QM system is described by a ket $|\psi\rangle$. We now want to ask the question how $|\psi\rangle$ changes if we move our quantum mechanical system by a distance $\mathbf{a}$, or rotate it by some angle around some axis. Of particular interest are transformations that leave our system unchanged – these correspond to *symmetries*, which have been one of the most important organizing principles of physics in the last century.

> **Aside 6:** ACTIVE VS PASSIVE TRANSFORMATIONS
>
> As our lectures follow the book by Binney and Skinner we will focus on transformations where we change our QM system by e.g. moving it. These are call *active transformations*. There is an equivalent viewpoint in which we leave our system unchanged, but transform our co-ordinate system. Such transformations are called *passive*. The two kinds of transformations are related in a simple way. For example, translating our system by a vector $\mathbf{a}$ is equivalent to moving our co-ordinate system by $-\mathbf{a}$.

7.1 TRANSLATIONS

If we move a quantum mechanical system in some state $|\psi\rangle$ by a distance $\mathbf{a}$ we expect that the ket describing it will change to some new ket $|\psi'\rangle$. It turns out that we can obtain $|\psi'\rangle$ by acting with the *translation operator* $U(\mathbf{a})$

$$|\psi'\rangle = U(\mathbf{a})|\psi\rangle . \tag{306}$$

To see this, let us consider a basis of position eigenstates $|\mathbf{x}\rangle$. On physical grounds these must transform under a translation as

$$|\mathbf{x}\rangle \longrightarrow |\mathbf{x} + \mathbf{a}\rangle. \tag{307}$$

The transformed ket can be written in terms of momentum eigenstates as

$$
\begin{aligned}
|\mathbf{x} + \mathbf{a}\rangle &= \int d^3\mathbf{p}\, \langle\mathbf{p}|\mathbf{x} + \mathbf{a}\rangle\, |\mathbf{p}\rangle = \int \frac{d^3\mathbf{p}}{(2\pi\hbar)^{3/2}}\, e^{-\frac{i}{\hbar}(\mathbf{x}+\mathbf{a})\cdot\mathbf{p}}\, |\mathbf{p}\rangle \\
&= \int d^3\mathbf{p}\, \langle\mathbf{p}|\mathbf{x}\rangle\, e^{-\frac{i}{\hbar}\mathbf{a}\cdot\mathbf{P}}|\mathbf{p}\rangle = \int d^3\mathbf{p}\, \langle\mathbf{p}|\mathbf{x}\rangle\, e^{-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}}|\mathbf{p}\rangle \\
&= e^{-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}} \int d^3\mathbf{p}\, \langle\mathbf{p}|\mathbf{x}\rangle\, |\mathbf{p}\rangle = e^{-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}}|\mathbf{x}\rangle.
\end{aligned}
\tag{308}
$$

This tells us that we have

$$|\mathbf{x} + \mathbf{a}\rangle = U(\mathbf{a})|\mathbf{x}\rangle , \quad U(\mathbf{a}) = e^{-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}}. \tag{309}$$

As the three momentum operators commute we have

$$U(\mathbf{a})U^{\dagger}(\mathbf{a}) = \mathbf{1}, \tag{310}$$

so $U(\mathbf{a})$ is a unitary operator. By the same reasoning we have

$$U(\mathbf{a})U(\mathbf{b}) = U(\mathbf{a} + \mathbf{b}) , \quad U^{\dagger}(\mathbf{a}) = U(-\mathbf{a}), \tag{311}$$

so translations form a *group*. Finally, because momentum eigenstates form a basis we can conclude that a general state $|\psi\rangle$ transforms under a translation as

$$|\psi'\rangle = U(\mathbf{a})|\psi\rangle. \tag{312}$$

Indeed, expanding $|\psi\rangle$ in position eigenstates, we have

$$|\psi\rangle = \int d^3\mathbf{x}\langle\mathbf{x}|\psi\rangle \, |\mathbf{x}\rangle \longrightarrow |\psi'\rangle = \int d^3\mathbf{x}\langle\mathbf{x}|\psi\rangle \, |\mathbf{x} + \mathbf{a}\rangle = U(\mathbf{a}) \int d^3\mathbf{x}\langle\mathbf{x}|\psi\rangle \, |\mathbf{x}\rangle = U(\mathbf{a})|\psi\rangle. \tag{313}$$

7.1.1 EXPECTATION VALUES

The expectation value of the three position operators in the translated state are

$$\begin{aligned}
\langle\psi'|\hat{\mathbf{x}}|\psi'\rangle &= \int d^3\mathbf{x}'\langle\psi'|\hat{\mathbf{x}}|\mathbf{x}'\rangle\langle\mathbf{x}'|\psi'\rangle = \int d^3\mathbf{x}' \, \mathbf{x}' \, |\psi'(\mathbf{x}')|^2 \\
&= \int d^3\mathbf{x}' \, \mathbf{x}' \, |\psi(\mathbf{x}' - \mathbf{a})|^2 = \int d^3\mathbf{x} \, (\mathbf{x} + \mathbf{a}) \, |\psi(\mathbf{x})|^2 \\
&= \langle\psi|\hat{\mathbf{x}} + \mathbf{a}|\psi\rangle = \langle\psi|\hat{\mathbf{x}}|\psi\rangle + \mathbf{a}.
\end{aligned} \tag{314}$$

This result is as expected: the average position has been shifted by $\mathbf{a}$ by our transformation. Using that $|\psi'\rangle = U(\mathbf{a})|\psi\rangle$ and that in the above $|\psi\rangle$ is arbitrary we conclude that

$$U^{\dagger}(\mathbf{a})\hat{\mathbf{x}}U(\mathbf{a}) = \hat{\mathbf{x}} + \mathbf{a}. \tag{315}$$

To arrive at this conclusion we have used the following

Theorem 3 *Let A and B be two operators. If for any state $|\psi\rangle$*

$$\langle\psi|A|\psi\rangle = \langle\psi|B|\psi\rangle, \tag{316}$$

then $A = B$.

Proof: Take $|\psi\rangle = |\chi_1\rangle + c|\chi_2\rangle$. Then by the assumption that the expectation values in $|\psi\rangle$ are equal we have

$$0 = \langle\chi_1|A - B|\chi_1\rangle + |c|^2\langle\chi_2|A - B|\chi_2\rangle + c\langle\chi_1|A - B|\chi_2\rangle + c^*\langle\chi_2|A - B|\chi_1\rangle. \tag{317}$$

Using that the expectation values of A and B in $|\chi_1\rangle$ and $|\chi_2\rangle$ are equal this simplifies to

$$0 = c\langle\chi_1|A - B|\chi_2\rangle + c^*\langle\chi_2|A - B|\chi_1\rangle. \tag{318}$$

Considering this equation for $c = 1$ and $c = i$ we conclude that we must have

$$\langle\chi_1|A - B|\chi_2\rangle = 0. \tag{319}$$

As $|\chi_{1,2}\rangle$ are arbitrary this implies that $A = B$.

As $U(\mathbf{a})$ only involves the momentum operators (which commute with one another) we conclude that $[U(\mathbf{a}), \mathbf{p}] = 0$ or equivalently

$$U^\dagger(\mathbf{a})\hat{\mathbf{p}}U(\mathbf{a}) = \hat{\mathbf{p}}. \tag{320}$$

Hence expectation values of the momentum operator do not change under translations

$$\langle\psi'|\hat{\mathbf{p}}|\psi'\rangle = \langle\psi|\hat{\mathbf{p}}|\psi\rangle. \tag{321}$$

7.1.2 Wave functions

We can now ask how wave functions change under translations. This gives us information not only about the average position but about the entire probability distribution. The original and translated wave functions are

$$\psi(\mathbf{x}) = \langle\mathbf{x}|\psi\rangle , \quad \psi'(\mathbf{x}) = \langle\mathbf{x}|\psi'\rangle. \tag{322}$$

They are related by

$$\psi'(\mathbf{x}) = \langle\mathbf{x}|U(\mathbf{a})|\psi\rangle = \langle\mathbf{x} - \mathbf{a}|\psi\rangle = \psi(\mathbf{x} - \mathbf{a}). \tag{323}$$

Here we have used that $U^\dagger(\mathbf{a}) = U(-\mathbf{a})$ and

$$\langle\mathbf{x}|U(\mathbf{a})|\psi\rangle = \langle\psi|U^\dagger(\mathbf{a})|\mathbf{x}\rangle^* = \langle\psi|\mathbf{x} - \mathbf{a}\rangle^* = \langle\mathbf{x} - \mathbf{a}|\psi\rangle. \tag{324}$$

An equivalent way of expressing the relation between wave functions is

$$\psi'(\mathbf{x} + \mathbf{a}) = \psi(\mathbf{x}). \tag{325}$$

This makes perfect sense: the value of the new wave function at the new position equals the value of the original wave function at the original position. The probability densities are related by

$$|\psi(\mathbf{x} - \mathbf{a})|^2 = |\psi'(\mathbf{x})|^2, \tag{326}$$

expressing the fact that the probability of finding the translated system at position $\mathbf{x}$ is the same as finding the original system at position $\mathbf{x} - \mathbf{a}$.

7.1.3 Translational Invariance and momentum as a "good quantum number"

As we have seen the Hamiltonian plays a special role in Quantum Mechanics because it determines the time evolution of quantum states. Because of this its behaviour under translations is particularly important. Let H be the Hamiltonian of our system. We call our system *translationally invariant* if there exists a basis of energy eigenstates $|E_n\rangle$ such that for any state $|\psi\rangle$

$$|\langle E_n|\psi\rangle|^2 = |\langle E_n|U(\mathbf{a})|\psi\rangle|^2. \tag{327}$$

This condition is equivalent to energy measurements being unaffected by translations. Eqn (327) implies that the states $|E_n\rangle$ are eigenstates of $U(\mathbf{a})$, which in turn implies that $U(\mathbf{a})$ and H commute

$$HU(\mathbf{a}) = U(\mathbf{a})H. \tag{328}$$

The condition of translational invariance can thus be cast in the form

$$U^\dagger(\mathbf{a})HU(\mathbf{a}) = H. \tag{329}$$

In the above discussion the vector $\mathbf{a}$ has been arbitrary – our transformation depends on a continuous parameter $\mathbf{a}$ and (329) expresses the fact that H possesses a *continuous symmetry*.

Taking it infinitesimally small we have

$$U(d\mathbf{x}) = 1 - \frac{i}{\hbar} d\mathbf{x} \cdot \mathbf{p} \tag{330}$$

This allows us to recast translational invariance as the requirement that the Hamiltonian commutes with the momentum operators

$$[H, \mathbf{p}] = 0. \tag{331}$$

This then implies that momentum and energy are compatible observables and there exists a simultaneous basis of eigenstates. This in turn means that we can use the momentum eigenvalues to label the energy eigenstates. We say that *momentum is a good quantum number.*

Let us look at a simple example of all this: a free particle in three spatial dimensions with Hamiltonian

$$H = \frac{\hat{\mathbf{p}}^2}{2m} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m}. \tag{332}$$

Clearly this is translationally invariant

$$[\hat{p}_a, H] = 0 , \quad a = x, y, z. \tag{333}$$

Momentum is therefore a good quantum number and there is a basis of simultaneous eigenstates of energy and momentum, namely that of momentum eigenstates

$$H|p_x, p_y, p_z\rangle = \underbrace{\frac{p_x^2 + p_y^2 + p_z^2}{2m}}_{E(p_x, p_y, p_z)} |p_x, p_y, p_z\rangle. \tag{334}$$

This principle generalizes: if we have a set of Hermitian operators $I^{(n)}$ ($n = 1, \ldots, N$) such that

$$[I^{(n)}, I^{(m)}] = 0 = [I^{(n)}, H] , \quad 1 \leq n, m \leq N, \tag{335}$$

there exists a basis of simultaneous eigenstates $|E, \boldsymbol{\lambda}\rangle = |E, \lambda^{(1)}, \ldots, \lambda^{(N)}\rangle$ of all these operators

$$\begin{aligned} I^{(n)}|E, \boldsymbol{\lambda}\rangle &= \lambda^{(n)}|E, \boldsymbol{\lambda}\rangle , \\ H|E, \boldsymbol{\lambda}\rangle &= E|E, \boldsymbol{\lambda}\rangle . \end{aligned} \tag{336}$$

We see that we can use the eigenvalues $\lambda^{(j)}$ to label these states! You may ask why labelling the states by just the energy is not enough. The answer is that

- the extra labels *always* tell us that we are dealing with an eigenstate not only of energy, but also of the other observables $I^{(n)}$. This is clearly useful information!

- the energy eigenvalues are in general *degenerate*, i.e. there are several eigenstates with the same eigenvalue. Just knowing the energy in such situations is insufficient for identifying energy eigenstates;

7.2 REFLECTIONS (PARITY)
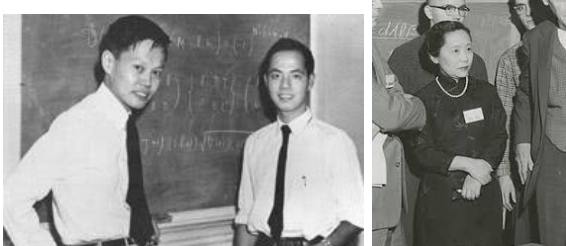
Parity plays a very important role in Quantum Field Theory and the Standard Model of Particle Physics.

C.N. Yang and T.D. Lee (Nobel Prize in Physics 1957)

C.S. Wu (Wolf Prize in Physics 1978)

A very important transformation is spatial reflection or *parity*. It acts on position eigenstates as

$$\hat{P}|\mathbf{x}\rangle = |-\mathbf{x}\rangle. \tag{337}$$

So if the system was originally at position $\mathbf{x}$ with certainty, it will be at position $-\mathbf{x}$ after the parity transformation. The parity operator is Hermitian $\hat{P} = \hat{P}^\dagger$ because

$$\langle \mathbf{x}'|\hat{P}|\mathbf{x}\rangle = \langle \mathbf{x}'|-\mathbf{x}\rangle = \delta^{(3)}(\mathbf{x}' + \mathbf{x}) = \langle \mathbf{x}|\hat{P}|\mathbf{x}'\rangle^*. \tag{338}$$

If we carry out the parity transformation twice we return to where we started. Therefore

$$\hat{P}^2 = \mathbf{1} \,, \tag{339}$$

which together with $\hat{P} = \hat{P}^\dagger$ implies that $\hat{P}$ is a unitary operator. Using (337) and

$$\hat{\mathbf{x}} = \int d^3\mathbf{x}\, \mathbf{x}\, |\mathbf{x}\rangle\langle \mathbf{x}|, \tag{340}$$

we can work out how the parity operator acts on the position operator

$$\boxed{\hat{P}\hat{\mathbf{x}}\hat{P} = -\hat{\mathbf{x}}.} \tag{341}$$

Similarly we find

$$\langle \mathbf{x}'|\hat{P}\hat{p}_a\hat{P}|\mathbf{x}\rangle = \langle -\mathbf{x}'|\hat{p}_a|-\mathbf{x}\rangle = i\hbar \frac{\partial}{\partial x_a}\delta^{(3)}(\mathbf{x} - \mathbf{x}') = -\langle \mathbf{x}'|\hat{p}_a|\mathbf{x}\rangle, \tag{342}$$

and hence

$$\boxed{\hat{P}\hat{\mathbf{p}}\hat{P} = -\hat{\mathbf{p}}.} \tag{343}$$

The wave function of a parity-transformed state is

$$\psi'(\mathbf{x}) = \langle \mathbf{x}|\psi'\rangle = \langle \mathbf{x}|\hat{P}|\psi\rangle = \langle -\mathbf{x}|\psi\rangle = \psi(-\mathbf{x}). \tag{344}$$

By following through the same considerations as for translations we term a quantum system *parity invariant* if

$$[H, \hat{P}] = 0. \tag{345}$$

Parity is an example of a *discrete* symmetry in QM – if we repeat the transformation twice we return to where we started. In parity invariant systems there exists a basis of simultaneous eigenstates of the Hamiltonian and the energy operator. As $\hat{P}^2 = \mathbf{1}$ the eigenvalues of $\hat{P}$ can only be ± 1. The corresponding eigenstates are called parity-even and parity-odd states. We have encountered parity-symmetric systems before, when we studied Hamiltonians of the form

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}}). \tag{346}$$

Parity invariance requires

$$H = \hat{P}H\hat{P} = \frac{\hat{\mathbf{p}}^2}{2m} + V(-\hat{\mathbf{x}}) \Rightarrow V(-\hat{\mathbf{x}}) = V(\hat{\mathbf{x}}). \tag{347}$$

This is the case for the harmonic oscillator and various of the potential step problems we have considered earlier. Let us now consider the implications of parity invariance for the infinite square well potential considered in section 5.2. The Hamiltonian is invariant under a parity transformation around the centre of the well $x = a/2$ and we therefore have a simultaneous basis of energy and parity eigenstates

$$H\psi_n(x) = E_n\psi_n(x) \,, \quad P_{a/2}\psi_n(x) = p_n\psi_n(x) \,. \tag{348}$$

Here we have denoted the position representation of the parity transformation operator by $P_{a/2}$. We know that the parity eigenvalues can only be ± 1, and hence

$$\hat{P}_{a/2}\psi_n(x) = \psi_n(a - x) = p_n\psi_n(x), \tag{349}$$

which tells us that the wave functions of energy eigenstates must be either symmetric or antisymmetric around $a/2$. This is indeed the case as we have seen before.
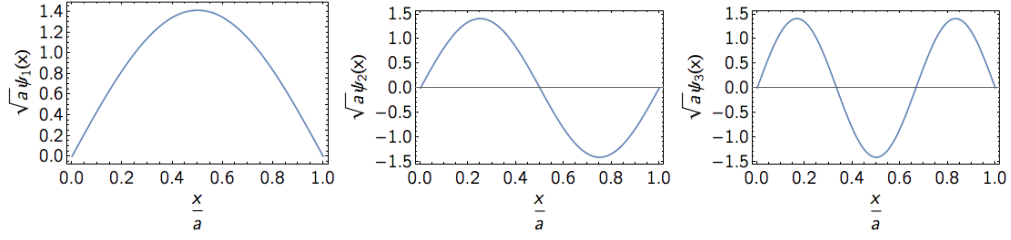
Figure 10: Wave functions for the 3 lowest energy states in the infinite square well potential.

7.3 ROTATIONS

We now turn to rotations. In QM there is a subtlety associated with rotations because of the existence of *spin*. This is an intrinsic property of most particles and we will discuss it later. For now we restrict our discussion to rotations for a *spinless* quantum mechanical particle.

Let's consider a rotation around the z-axis by an infinitesimal angle $d\alpha$

$$
\begin{aligned}
x' &= x - y\, d\alpha\ , \\
y' &= y + x\, d\alpha\ , \\
z' &= z.
\end{aligned}
\tag{350}
$$

NB 6

This is the infinitesimal version of

$$
\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.
\tag{351}
$$

Let us parametrize this rotation in terms of the vector $\mathbf{e_z}d\alpha$, where the direction of the vector denotes the rotation axis and its magnitude the angle of rotation. Position eigenstates should therefore transform as

$$
U(\mathbf{e_z}d\alpha)|\mathbf{x}\rangle = |\mathbf{x}'\rangle.
\tag{352}
$$

We can work out an explicit expression for $U(\mathbf{e_z}d\alpha)$ by using the results we obtained for translations

$$
|\mathbf{x} + \mathbf{dx}\rangle = \left[\mathbf{1} - \frac{i}{\hbar}\mathbf{dx}\cdot\hat{\mathbf{p}}\right]|\mathbf{x}\rangle.
\tag{353}
$$

To reproduce (350) we require $\mathbf{dx} = (-yd\alpha, xd\alpha, 0)$, which depends on x and y itself and we therefore should take

$$
U(\mathbf{e_z}d\alpha) = \mathbf{1} - \frac{i}{\hbar}\left(-\hat{y}\hat{p}_x + \hat{x}\hat{p}_y\right)d\alpha \equiv \mathbf{1} - \frac{i}{\hbar}\hat{L}_z\, d\alpha.
\tag{354}
$$

Here we have defined the operator for the z-component of orbital angular momentum

$$
\boxed{\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.}
\tag{355}
$$

In order to carry out a rotation by a finite angle we should consider

$$
U(\mathbf{e_z}\alpha) = \lim_{N\to\infty}\left[U(\mathbf{e_z}\frac{\alpha}{N})\right]^N = \lim_{N\to\infty}\left[\mathbf{1} - \frac{i}{\hbar}\hat{L}_z\frac{\alpha}{N}\right]^N = e^{-\frac{i}{\hbar}\alpha\hat{L}_z}.
\tag{356}
$$

The last step can be proved in essentially the same way as the identity for numbers

$$\lim_{N \to \infty} \left[1 + \frac{x}{N} \right]^N = e^x. \tag{357}$$

It is straightforward to repeat the above analysis for rotations around the x or y axis. These are induced by the x and y components of the orbital angular momentum

$$\begin{aligned} \hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y , \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z. \end{aligned} \tag{358}$$

A rotation by an angle α around a general direction $\mathbf{n}$ (where $\mathbf{n}$ is a vector of unit length) is generated by the operator

$$\boxed{U(\mathbf{n}\alpha) = e^{-\frac{i}{\hbar}\alpha\mathbf{n}\cdot\hat{\mathbf{L}}}.} \tag{359}$$

8 HEISENBERG PICTURE AND HEISENBERG EQUATION OF MOTION

Recall that the TDSE can be written as

$$i\hbar \frac{d|\psi(t)\rangle}{dt} = H|\psi(t)\rangle. \tag{360}$$

You can check by taking the derivative with respect to time that the formal solution of this equation is (for time-independent Hamiltonians)

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}Ht}|\psi(0)\rangle. \tag{361}$$

The operator

$$\boxed{U(t) = e^{-\frac{i}{\hbar}Ht}} \tag{362}$$

is called *time-evolution operator*. As H is Hermitian $U(t)$ is unitary

$$U(t)U^\dagger(t) = \mathbf{1}. \tag{363}$$

This shows that quantum mechanical time evolution can be viewed as a unitary transformation of states. So far our discussion has been based on time-independent operators and time evolving states. This is known as the *Schrödinger picture* of QM. In daily quantum mechanical practice the objects of interest are not states but rather matrix elements of operators

$$\langle\psi(t)|\mathcal{O}|\phi(t)\rangle. \tag{364}$$

In the Schrödinger picture we work out the states at time t and then use them to obtain the desired matrix element. Using the time evolution operator we can write our matrix element as

$$\langle\psi(t)|\mathcal{O}|\phi(t)\rangle = \langle\psi(0)|U^\dagger(t)\mathcal{O}U(t)|\phi(0)\rangle. \tag{365}$$

Defining a time-dependent operator

$$\mathcal{O}_H(t) = U^\dagger(t)\mathcal{O}U(t), \tag{366}$$

we can write matrix elements as

$$\langle\psi(0)|\mathcal{O}_H(t)|\phi(0)\rangle. \tag{367}$$

This is known as the *Heisenberg picture*: here we fix a basis of quantum states once and for all, but operators evolve in time. This turn out to be often a more convenient approach! The time evolution of operators is governed by the *Heisenberg equation of motion*

$$\boxed{\frac{d}{dt}\mathcal{O}_H(t) = \frac{i}{\hbar}[H, \mathcal{O}_H(t)] .} \tag{368}$$

To see this we simply use that $HU(t) = U(t)H$ (which holds as the Hamiltonian commutes with itself) and

$$\frac{d}{dt}U^\dagger(t) = \frac{i}{\hbar}HU^\dagger(t) \ , \quad \frac{d}{dt}U(t) = -\frac{i}{\hbar}U(t)H \ . \tag{369}$$

Homework 8: TRANSFORMATIONS AND HEISENBERG EQUATIONS OF MOTION

4.1 *Reflection symmetry around a point* $\mathbf{x_0}$
Let $P_{\mathbf{x_0}}$ be the operator that induces reflections around a point $\mathbf{x_0}$. Argue that

$$\begin{aligned}
\hat{P}_{\mathbf{x_0}}|\mathbf{x_0} + \mathbf{x}\rangle &= |\mathbf{x_0} - \mathbf{x}\rangle \ , \\
\hat{P}_{\mathbf{x_0}}\hat{\mathbf{x}}\hat{P}_{\mathbf{x_0}} &= 2\mathbf{x_0}\mathbf{1} - \hat{\mathbf{x}} \ , \\
\hat{P}_{\mathbf{x_0}}\hat{\mathbf{p}}\hat{P}_{\mathbf{x_0}} &= -\hat{\mathbf{p}},
\end{aligned} \tag{370}$$

and that the transformed wave function fulfils

$$\psi'(\mathbf{x}) = \psi(2\mathbf{x_0} - \mathbf{x}). \tag{371}$$

4.2 For which potentials V is the Hamiltonian $H = \frac{\hat{p}^2}{2m} + V(\hat{\mathbf{x}})$ translationally invariant?

4.3 Show that the orbital angular momentum operators $\hat{L}_a$ $(a = x, y, z)$ are Hermitian.

4.4 A spinless QM system is called *rotationally invariant* if its Hamiltonian commutes with the orbital angular momentum operators $[H, \hat{L}_a] = 0$, $a = x, y, z$. Rotational invariance expresses the fact the energy measurements remain unchanged under rotations of the system. If the Hamiltonian commutes only with $\hat{L}_z$ it is called invariant under rotations around the z-axis. Consider Hamiltonians of the form

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}}). \tag{372}$$

Show that potentials that depend only on the distance $\|\mathbf{x}\|$ lead to rotationally symmetric Hamiltonians, while potentials that depend on x and y only through the combination $x^2 + y^2$ leads to Hamiltonians that invariant under rotations around the z-axis.

4.5 Show that

$$\lim_{N\to\infty}\left[1 + \frac{x}{N}\right]^N = e^x. \tag{373}$$

Give arguments that an analogous formula holds for operators.

4.6 *Heisenberg equations of motion for the SHO*
Derive the Heisenberg equations of motion for the creation and annihilation operators in the simple harmonic oscillator and show that their solution is

$$a(t) = a(0)e^{-i\omega t} \ , \quad a^\dagger(t) = a^\dagger(0)e^{i\omega t} \ . \tag{374}$$

From these, obtain equations of motion for the position and momentum operators. Comment on the relation of your results to Ehrenfest's theorem.

Part IV
ANGULAR MOMENTUM

We have seen above that angular momentum generates rotations in QM. For spinless particles rotations are induced by the orbital angular momentum operators, which can be written compactly as

$$\hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k. \tag{375}$$

> **NB 7**
>
> In order to arrive at this compact set of notations we have made the identifications
>
> $$\hat{x} = \hat{x}_1 , \ \hat{y} = \hat{x}_2 , \ \hat{z} = \hat{x}_3 , \quad \hat{p}_x = \hat{p}_1 , \ \hat{p}_y = \hat{p}_2 , \ \hat{p}_z = \hat{p}_3 . \tag{376}$$

Using the commutation relations for position and momentum operators $[\hat{x}_j, \hat{p}_k] = i\hbar\delta_{j,k}$ we can derive commutation relations between the components of angular momentum

$$\boxed{[\hat{L}_j, \hat{L}_k] = i\hbar\epsilon_{jkl}\hat{L}_l .} \tag{377}$$

Let's see how this works for one example:

$$
\begin{aligned}
[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\
&= \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}] + \hat{p}_y\hat{x}[\hat{z}, \hat{p}_z] = -i\hbar\hat{y}\hat{p}_x + i\hbar\hat{p}_y\hat{x} = i\hbar\hat{L}_z.
\end{aligned} \tag{378}
$$

Here we have used in the first line that

$$[A + B, C + D] = [A, C] + [A, D] + [B, C] + [B, D] \tag{379}$$

and

$$[\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] = 0 = [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x]. \tag{380}$$

In the second line we have used e.g. that

$$\hat{y}\hat{p}_z\hat{z}\hat{p}_x = \hat{y}\hat{p}_x\hat{p}_z\hat{z} , \tag{381}$$

which follows from the fact that $\hat{p}_x$ commutes with $\hat{z}$ and $\hat{p}_z$.

> **Aside 7: Angular momentum and $SU(2)$**
>
> he commutation relations (377) give rise to a mathematical structure known as a *Lie algebra*. In the case of angular momentum this algebra is called $SU(2)$.

9   ROTATIONAL INVARIANCE AND ANGULAR MOMENTUM AS A GOOD QUANTUM NUMBER

We have seen above that the angular momentum operators $\hat{L}_i$ induce rotations. A QM system with Hamiltonian H is called *rotationally symmetric* if the results of energy measurements are insensitive to rotations. This is equivalent to the requirement

$$U(\mathbf{n}\alpha)H = HU(\mathbf{n}\alpha) , \tag{382}$$

where the rotation axis $\mathbf{n}$ and angle α are arbitrary. By virtue of (359) this is equivalent to the requirement that H commutes with the angular momentum operators

$$[H, \hat{L}_a] = 0 , \quad a = x, y, z. \tag{383}$$

In analogy with translations we would like to use angular momentum as a good quantum number to label energy eigenstates. In contrast to the momentum operators relevant for translational invariance angular momentum operators do not commute, *cf.* (377). It is therefore impossible to find a basis of simultaneous eigenstates of different angular momentum operators. However, given that $[H, \hat{L}_a] = 0$ any function of the angular momentum operators will also commute with H! In particular we have

$$[H, \hat{\mathbf{L}}^2] = 0 , \quad \hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \tag{384}$$

Moreover we have

$$[\hat{\mathbf{L}}^2, \hat{L}_j] = 0. \tag{385}$$

For example we have

$$
\begin{aligned}
[\hat{\mathbf{L}}^2, \hat{L}_z] &= [\hat{L}_x^2 + \hat{L}_y^2, \hat{L}_z] = \hat{L}_x[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_x + \hat{L}_y[\hat{L}_y, \hat{L}_z] + [\hat{L}_y, \hat{L}_z]\hat{L}_y \\
&= -i\hbar\hat{L}_x\hat{L}_y - i\hbar\hat{L}_y\hat{L}_x + i\hbar\hat{L}_y\hat{L}_x + i\hbar\hat{L}_x\hat{L}_y = 0.
\end{aligned}
\tag{386}
$$

The maximal set of operators involving angular momentum that commute with one another and with the Hamiltonian is $\mathbf{L}^2$ and any one component $\hat{L}_j$. It is customary to choose this to be $\hat{L}_z$. Note that this is not a restriction for a rotationally invariant system as we can always choose our co-ordinate system such that the z-axis is along any direction we want.

To summarize, for a rotationally invariant system we have

$$\boxed{[H, \hat{\mathbf{L}}^2] = 0 = [H, \hat{L}_z] = [\hat{\mathbf{L}}^2, \hat{L}_z].} \tag{387}$$

This means that the eigenvalues of $\hat{L}_z$ and $\hat{\mathbf{L}}^2$ are good quantum numbers and can be used to label energy eigenstates. This will be very useful and in order to exploit this fact we construct a basis of simultaneous eigenstates of $\hat{L}_z$ and $\hat{\mathbf{L}}^2$ next.

10   Eigenstates of $\mathbf{L}^2$ and $\hat{L}_z$

As $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ commute there exists a basis of simultaneous eigenstates

$$
\begin{aligned}
\hat{\mathbf{L}}^2|\beta, m\rangle &= \beta\hbar^2|\beta, m\rangle , \\
\hat{L}_z|\beta, m\rangle &= m\hbar|\beta, m\rangle .
\end{aligned}
\tag{388}
$$

We will assume that these can be normalized

$$\langle\beta, m|\beta', m'\rangle = \delta_{\beta,\beta'}\delta_{m,m'}. \tag{389}$$

Importantly m must be integers, because a rotation by 2π around the z-axis must be equal to the identity

$$U(2\pi\mathbf{e_z}) = e^{-\frac{2\pi i}{\hbar}\hat{L}_z} = \mathbf{1}. \tag{390}$$

Acting with this on an $\hat{L}_z$ eigenstate shows that $e^{2\pi i m} = 1$, i.e. m are integers. In order to learn more about the structure of these states we now employ a procedure that is somewhat similar to the use of creation and annihilation operators for the harmonic oscillator. We start by defining so-called *ladder operators*

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y , \quad \hat{L}_\pm^\dagger = \hat{L}_x \mp i\hat{L}_y . \tag{391}$$

Using the commutation relations (377) we find

$$[\hat{L}_\pm, \hat{\mathbf{L}}^2] = 0 , \quad [\hat{L}_\pm, \hat{L}_z] = \mp\hbar\hat{L}_\pm . \tag{392}$$

Acting with ladder operators on eigenstates gives other eigenstates:

$$\hat{\mathbf{L}}^2 \hat{L}_\pm |\beta, m\rangle = \beta \hbar^2 \hat{L}_\pm |\beta, m\rangle \ ,$$
$$\hat{L}_z \hat{L}_\pm |\beta, m\rangle = \left([\hat{L}_z, \hat{L}_\pm] + \hat{L}_\pm \hat{L}_z\right)|\beta, m\rangle = \left(\pm\hbar\hat{L}_\pm + \hat{L}_\pm \hat{L}_z\right)|\beta, m\rangle = (m \pm 1)\hbar\hat{L}_\pm|\beta, m\rangle \ . \quad (393)$$

These tell us that $\hat{L}_\pm\rangle|\beta, m\rangle$ is a simultaneous eigenstate of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ with eigenvalues $\hbar^2\beta$ and $\hbar(m \pm 1)$ respectively. Writing

$$\hat{L}_\pm|\beta, m\rangle = \alpha_\pm|\beta, m \pm 1\rangle \ , \quad (394)$$

we can work out $\alpha_\pm$ as follows. On the one hand we have

$$\langle\beta, m|\hat{L}_\mp \hat{L}_\pm|\beta, m\rangle = \langle\beta, m \pm 1|\alpha_\pm^* \alpha_\pm|\beta, m \pm 1\rangle = |\alpha_\pm|^2 \ , \quad (395)$$

while on the other hand

$$\langle\beta, m|\hat{L}_\mp \hat{L}_\pm|\beta, m\rangle = \langle\beta, m|\hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x, \hat{L}_y]|\beta, m\rangle = \langle\beta, m|\hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z|\beta, m\rangle$$
$$= \beta\hbar^2 - \hbar^2 m^2 \mp \hbar^2 m = \beta\hbar^2 - \hbar^2 m(m \pm 1). \quad (396)$$

Combining (395) and (396) and using that the overall phase of the eigenstates can be chosen freely we conclude that

$$\hat{L}_\pm|\beta, m\rangle = \hbar\sqrt{\beta - m(m \pm 1)}|\beta, m \pm 1\rangle. \quad (397)$$

What we mean by this is that without loss of generality we may *define* the eigenstate $|\beta, m \pm 1\rangle$ through this relation. A constraint on the allowed range of the eigenvalues $\hbar m$ can be obtained by noting that as $\hat{L}_i^\dagger = \hat{L}_i$ we have $\langle\psi|\hat{L}_i^2|\psi\rangle = \langle\phi|\phi\rangle \geq 0$, where $|\phi\rangle = \hat{L}_i|\psi\rangle$. As a consequence we have

$$\beta\hbar^2 = \langle\beta, m|\hat{\mathbf{L}}^2|\beta, m\rangle = \langle\beta, m|\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2|\beta, m\rangle \geq \langle\beta, m|\hat{L}_z^2|\beta, m\rangle = \hbar^2 m^2. \quad (398)$$

This implies that we cannot act indefinitely with ladder operators in order to produce new angular momentum eigenstates, but that eventually we must obtain zero once we have reached maximal/minimal values of m defined by

$$\beta - m_{\max}(m_{\max} + 1) = 0 \ , \qquad \beta - m_{\min}(m_{\min} - 1) = 0 \ . \quad (399)$$

The only solution to these requirements with $m_{\min} \leq m_{\max}$ is

$$m_{\min} = -m_{\max}. \quad (400)$$

At this point it is customary to introduce notations $\ell = m_{\max}$ and use the integer quantum number $\ell = 0, 1, 2, \dots$ rather than β to label the states:

$$\boxed{\begin{aligned}
\hat{\mathbf{L}}^2|\ell, m\rangle &= \hbar^2 \ell(\ell + 1)|\ell, m\rangle \ , \\
\hat{L}_z|\ell, m\rangle &= \hbar m|\ell, m\rangle \ , \\
\hat{L}_\pm|\ell, m\rangle &= \hbar\sqrt{\ell(\ell + 1) - m(m \pm 1)}|\ell, m \pm 1\rangle.
\end{aligned}} \quad (401)$$

The structure of eigenstates is shown in Fig. There are $2\ell + 1$ eigenstates with the same $\hat{\mathbf{L}}^2$ quantum number ℓ, but different $\hat{L}_z$ quantum numbers m, which range in integer steps between $-\ell$ and ℓ.

10.1 Matrix representations

As we have seen before, given a basis of states we can obtain matrix representations of operators. Let us see how this works for angular momentum operators. A basis of states is given by $\{|\ell, m\rangle\}$ with $m = -\ell, -\ell + 1, \dots, \ell - 1, \ell$ and

$$\langle\ell, m|\ell', m'\rangle = \delta_{\ell,\ell'}\delta_{m,m'}. \quad (402)$$
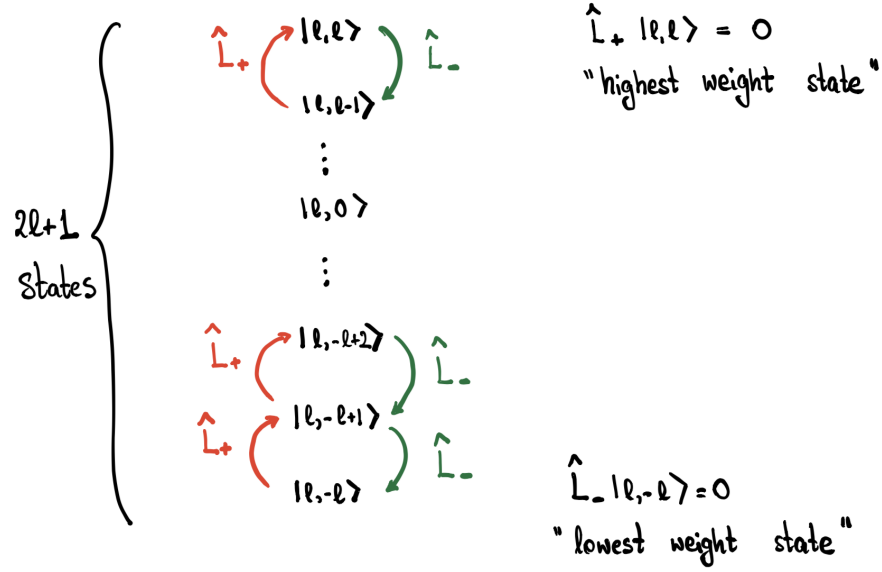
Figure 11: Angular momentum eigenstates of a "spin-ℓ" representation of angular momentum.

To obtain a matrix representation we wish to work out the matrix elements

$$\langle \ell, m | \hat{L}_j | \ell', m' \rangle . \tag{403}$$

Importantly it follows from (401) that $\langle \ell, m | \hat{L}_j | \ell', m' \rangle \propto \delta_{\ell,\ell'}$. This implies that if we order our basis states as $\{|0,0\rangle, |1,1\rangle, |1,0\rangle, |1,-1\rangle, |2,2\rangle, |2,1\rangle, |2,0\rangle, |2,-1\rangle, |2,-2\rangle, \dots \}$ the angular momentum operators will be of "block-diagonal" form, *cf.* Fig. 12. The blocks can be labelled by the $\hat{\mathbf{L}}^2$ quantum number ℓ and have
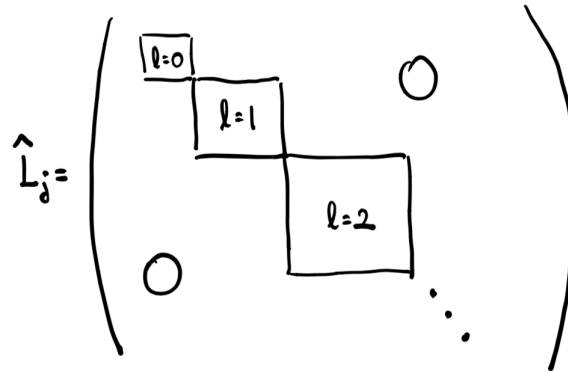
Figure 12: Angular momentum eigenstates of a "spin-ℓ" representation of angular momentum.

dimension $2\ell + 1$. The blocks are known as *spin-ℓ representations* of angular momentum.

10.1.1   SPIN-1 REPRESENTATION

It is instructive (and required by the syllabus) to work out the simplest block, which corresponds to $\ell = 1$. To ease notations we will assume that we know that for our QM system we have $\ell = 1$, so that this is in fact

the only block. Given that the basis states are eigenstates of $\hat{L}_z$ with known eigenvalues we can immediately write down the corresponding matrix

$$\boxed{\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.}$$

(404)

In order to obtain the representations of $\hat{L}_x$ and $\hat{L}_y$ it is convenient to consider $\hat{L}_\pm$. It follows from (401) that

$$\langle 1, m' | \hat{L}_\pm | 1, m \rangle = \hbar \sqrt{2 - m(m \pm 1)} \delta_{m',m \pm 1}.$$

(405)

This results in the following matrix representations

$$\hat{L}_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} , \quad \hat{L}_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}.$$

(406)

Using that $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$ we conclude that

$$\boxed{\hat{L}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} , \quad \hat{L}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}.}$$

(407)

You can check by explicitly carrying out the matrix multiplications that these matrices fulfil the angular momentum commutation relations (377). We say that the matrices furnish a *spin-1 representation* of the angular momentum algebra.

10.2 MEASUREMENTS

Now that we have worked out eigenstates and eigenvalues of angular momentum we can address questions regarding angular momentum measurements. Apart from its physical relevance this topic has a habit of cropping up in exam question, so it is perhaps worthwhile to spend a few lines on it. The basic principles of QM of course still apply. If we know that our system in a state $|\psi\rangle$ we should express it as a linear superposition of angular momentum eigenstates, i.e.

$$|\psi\rangle = \sum_{\ell,m} \langle \ell, m | \psi \rangle \, |\ell, m\rangle.$$

(408)

Let us assume that we now measure the z-component of angular momentum and obtain the result m_0. Recalling that $|m| \leq \ell$ this tells us that after our measurement the system can be in any of the states $|\ell, m_0\rangle$ with $\ell \geq |m_0|$, i.e. after the measurement the normalized ket describing our system is

$$|\psi_{\text{after}}\rangle = \frac{1}{\mathcal{N}} \sum_{\ell \geq |m_0|} \langle \ell, m_0 | \psi \rangle \, |\ell, m_0\rangle \, , \quad \mathcal{N}^2 = \sum_{\ell \geq |m_0|} |\langle \ell, m_0 | \psi \rangle|^2.$$

(409)

The interesting aspect here is that the measurement does not select a single angular momentum eigenstate! The probability of obtaining the outcome m_0 when measuring $\hat{L}_z$ is given by

$$P(m_0) = \sum_{\ell \geq m_0} |\langle \ell, m_0 | \psi \rangle|^2 \, .$$

(410)

To see this imagine you are measuring $\hat{\mathbf{L}}^2$ simultaneously. Then the probability of the measurement outcome (ℓ_0, m_0) is $|\langle \ell_0, m_0 | \psi \rangle|^2$, but as we have no information about ℓ_0 we need to sum these probabilities of all possible values ℓ_0.

Another way to understand this is as follows: Previously we talked about measurements of observables with non-degenerate eigenvalues in a state $|\psi\rangle$. We worked out the probability for a particular measurement outcome λ by writing $|\psi\rangle$ as a linear combination of a normalized ket $|\psi_\lambda\rangle$ in which the measurement outcome was certain to be λ and an orthogonal "rest" $|\psi'\rangle$

$$|\psi\rangle = A|\psi_\lambda\rangle + |\psi'\rangle . \tag{411}$$

The probability of measuring λ was then $|A|^2 = |\langle\psi_\lambda|\psi\rangle|^2$ and the system was in the normalized state $|\psi_\lambda\rangle$ after the measurement. *In the degenerate case we do exactly the same:* We decompose $|\psi\rangle$ as

$$|\psi\rangle = \mathcal{N}\underbrace{\frac{1}{\mathcal{N}}\sum_{\ell\geq|m_0|}\langle\ell,m_0|\psi\rangle\,|\ell,m_0\rangle}_{|\psi_{m_0}\rangle} + \sum_{\ell,m\neq m_0}\langle\ell,m|\psi\rangle\,|\ell,m\rangle, \tag{412}$$

The probability of obtaining m_0 is

$$|\langle\psi|\psi_{m_0}\rangle|^2 = \mathcal{N}^2 \tag{413}$$

and after the measurement the system is in the normalized state $|\psi_{m_0}\rangle$.

11 POSITION REPRESENTATION AND ANGULAR MOMENTUM

As we have seen before, the position representation can be very useful for analyzing Hamiltonians of the form

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}}). \tag{414}$$

In particular we saw that the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle \tag{415}$$

can be re-cast as a partial differential equation for the wave function:

$$i\hbar\frac{\partial}{\partial t}\langle\mathbf{x}|\psi(t)\rangle = \langle\mathbf{x}|H|\psi(t)\rangle \Leftrightarrow i\hbar\frac{\partial\psi(\mathbf{x},t)}{\partial t} = \mathrm{H}\psi(\mathbf{x},t) , \tag{416}$$

where $\psi(\mathbf{x},t) = \langle\mathbf{x}|\psi(t)\rangle$ and

$$\mathrm{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}) . \tag{417}$$

An analogous construction holds for the angular momentum operators as we will now show. Let us consider the position representation of the state $\hat{L}_j|\psi\rangle$

$$\langle\mathbf{x}|\hat{L}_j|\psi\rangle = \epsilon_{jkl}\langle\mathbf{x}|\hat{x}_k\hat{p}_l|\psi\rangle . \tag{418}$$

Using that $\hat{x}_k|\mathbf{x}\rangle = x_k|\mathbf{x}\rangle$ and

$$\langle\mathbf{x}|\hat{p}_l|\psi\rangle = -i\hbar\frac{\partial\psi(\mathbf{x})}{\partial x_l}, \tag{419}$$

we find

$$\langle\mathbf{x}|\hat{L}_j|\psi\rangle = -i\hbar\epsilon_{jkl}x_k\frac{\partial\psi(\mathbf{x})}{\partial x_l} \equiv \hat{\mathrm{L}}_j\psi(\mathbf{x}). \tag{420}$$

Here $\hat{\mathrm{L}}_j$ are differential operators

$$\boxed{\hat{\mathrm{L}}_j = -i\hbar\epsilon_{jkl}x_k\frac{\partial}{\partial x_l}.} \tag{421}$$

So when working with wave functions the angular momentum operators are given by (421).

11.1 Spherical polar co-ordinates

Rather than using Cartesian co-ordinates we can express the position eigenvalues in spherical polar co-ordinates

$$
\begin{aligned}
x &= r\sin\theta\cos\phi \,, \\
y &= r\sin\theta\sin\phi \,, \\
z &= r\cos\theta.
\end{aligned} \tag{422}
$$

We denote the corresponding position eigenstates as $|r,\theta,\phi\rangle$ and the wave-function associated with a state $|\psi\rangle$ would be

$$
\psi(r,\theta,\phi) = \langle r,\theta,\phi|\psi\rangle. \tag{423}
$$

NB 8

In the way we have introduced the states they amount to a mere change of labelling for the usual position eigenstates $|\mathbf{x}\rangle$. This however has important ramifications for their normalization: let (r,θ,ϕ) and (r',θ',ϕ') be parametrizations of $\mathbf{x}$ and $\mathbf{x}'$ respectively. Then

$$
\langle\mathbf{x}|\mathbf{x}'\rangle = \langle r,\theta,\phi|r',\theta',\phi'\rangle = \delta^{(3)}(\mathbf{x}-\mathbf{x}') = \frac{\delta(r-r')\delta(\theta-\theta')\delta(\phi-\phi')}{r^2\sin\theta}. \tag{424}
$$

An easy way to see that the extra factor in the denominator must be there is by integrating the last equation over $\mathbf{x}$

$$
1 = \int dx\,dy\,dz\ \delta^{(3)}(\mathbf{x}-\mathbf{x}') \tag{425}
$$

and note that $dx\,dy\,dz = r^2\sin\theta\,dr\,d\theta\,d\phi$. Similarly the normalization condition for wave functions (of bound states) becomes

$$
1 = \int d^3\mathbf{x}|\psi(\mathbf{x})|^2 = \int d^3\mathbf{x}|\langle\mathbf{x}|\psi\rangle|^2 = \int dr\,d\theta\,d\phi\ r^2\sin\theta|\underbrace{\langle r,\theta,\phi|\psi\rangle}_{\psi(r,\theta,\phi)}|^2 \tag{426}
$$

So remember the volume element in spherical polar co-ordinates!

The differential operators $\hat{L}_j$ can be readily transformed to spherical polar co-ordinates using the chain rule, e.g.

$$
\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi} \,. \tag{427}
$$

The required partial derivatives can be worked out using e.g.

$$
r = \sqrt{x^2+y^2+z^2}\,, \quad \tan\phi = \frac{y}{x}\,, \quad \sin\theta = \frac{\sqrt{x^2+y^2}}{r} \,. \tag{428}
$$

This gives

$$
\begin{aligned}
\frac{\partial}{\partial x} &= \cos\phi\sin\theta\frac{\partial}{\partial r} + \frac{\cos\phi\cos\theta}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \,, \\
\frac{\partial}{\partial y} &= \sin\phi\sin\theta\frac{\partial}{\partial r} + \frac{\sin\phi\cos\theta}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \,, \\
\frac{\partial}{\partial z} &= \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta} \,.
\end{aligned} \tag{429}
$$

Combining (422) and (429) we can express the differential operators $\hat{L}_j$ in spherical polar co-ordinates

$$
\begin{aligned}
\hat{L}_x &= -i\hbar \left[-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right] , \\
\hat{L}_y &= -i\hbar \left[\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right] , \\
\hat{L}_z &= -i\hbar \frac{\partial}{\partial\phi} .
\end{aligned}
\tag{430}
$$

These allow us to work out how the total angular momentum operator acts on wave functions

$$
\begin{aligned}
\langle r, \theta, \phi | \hat{\mathbf{L}}^2 | \psi \rangle &= \hat{\mathbf{L}}^2 \psi(r, \theta, \phi) , \\
\hat{\mathbf{L}}^2 &= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] .
\end{aligned}
\tag{431}
$$

11.2 SPHERICAL HARMONICS

The differential operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ only involve the angular variables by virtue of (401) their eigenvalue equations reads

$$
\begin{aligned}
\hat{\mathbf{L}}^2 Y_{\ell,m}(\theta, \phi) &= \hbar^2 \ell(\ell+1) Y_{\ell,m}(\theta, \phi) , \\
\hat{L}_z Y_{\ell,m}(\theta, \phi) &= \hbar m Y_{\ell,m}(\theta, \phi) .
\end{aligned}
\tag{432}
$$

The eigenfunctions $Y_{\ell,m}$ are called *spherical harmonics*. We can work out their explicit expressions by solving the differential equations (432). The lowest spherical harmonic fulfils the equations

$$
\hat{\mathbf{L}}^2 Y_{0,0}(\theta, \phi) = 0 = \hat{L}_z Y_{0,0}(\theta, \phi) .
\tag{433}
$$

These are solved by $Y_{0,0}(\theta, \phi) = \text{const}$. The constant is fixed by the normalization condition

$$
\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, |Y_{\ell,m}(\theta, \phi)|^2 = 1 ,
\tag{434}
$$

where the $\sin\theta$ arises because the volume element in spherical polar co-ordinates is $dV = r^2 \sin\theta dr \, d\theta \, d\phi$. This then leads to

$$
Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} .
\tag{435}
$$

The $\ell = 1$ spherical harmonics fulfil the differential equations

$$
\begin{aligned}
- \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y_{1,m}(\theta, \phi) &= 2 Y_{1,m}(\theta, \phi) , \\
\frac{\partial}{\partial\phi} Y_{1,m}(\theta, \phi) &= im Y_{1,m}(\theta, \phi) .
\end{aligned}
\tag{436}
$$

The second equation tells us that the ϕ-dependence is

$$
Y_{1,m}(\theta, \phi) \propto e^{im\phi} .
\tag{437}
$$

Substituting this into the first equation we can rewrite it as

$$
[\sin\theta \partial_\theta (\sin\theta \partial_\theta) - m^2 + 2\sin^2\theta] Y_{1,m}(\theta, \phi) = 0 .
\tag{438}
$$

This allows us to infer the θ-dependencies and conclude that

$$
Y_{1,\pm 1}(\theta, \phi) = A \sin\theta \, e^{\pm i\phi} , \qquad Y_{1,0}(\theta, \phi) = B \cos\theta .
\tag{439}
$$

Finally we fix A and B through the normalization[2] to obtain

$$Y_{1,0}(\theta, \phi) = \sqrt{\frac{6}{8\pi}} \cos\theta \ , \quad Y_{1,\pm 1}(\theta, \phi) = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \ e^{\pm i\phi} \ .$$

(440)

Homework 9: ORBITAL ANGULAR MOMENTUM

4.7

(a) Show by explicit calculation using $\hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k$ that $[\hat{L}_i, \hat{x}_j] = i\hbar\epsilon_{ijk}\hat{x}_k$ and $[\hat{L}_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k$.

(b) Evaluate $[\hat{L}_x, \hat{L}_y]$ by writing $\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$ and using the results from part (a) of this question.

(c) Show that in the position representation we have

$$\langle\mathbf{x}|\hat{L}_i|\psi\rangle = \hat{\mathrm{L}}_i\psi(\mathbf{x}) \ ,$$

(441)

and obtain explicit expressions for the differential operators $\hat{\mathrm{L}}_i$. Show that for any differentiable function f

$$(\hat{\mathrm{L}}_x\hat{\mathrm{L}}_y - \hat{\mathrm{L}}_y\hat{\mathrm{L}}_x)f(x, y, z) = i\hbar\hat{\mathrm{L}}_z f(x, y, z).$$

Since this holds for any f it can be written as an operator equation $[\hat{\mathrm{L}}_x, \hat{\mathrm{L}}_y] = \hat{\mathrm{L}}_x\hat{\mathrm{L}}_y - \hat{\mathrm{L}}_y\hat{\mathrm{L}}_x = i\hbar\hat{\mathrm{L}}_z$, as you will have found in part (b). Deduce similar expressions for $[\hat{\mathrm{L}}_y, \hat{\mathrm{L}}_z]$ and $[\hat{\mathrm{L}}_z, \hat{\mathrm{L}}_x]$.

(d) Defining $\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$, show that (Hint: remember $[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}$)

$$[\hat{L}_x, \hat{\boldsymbol{L}}^2] = [\hat{L}_y, \hat{\boldsymbol{L}}^2] = [\hat{L}_z, \hat{\boldsymbol{L}}^2] = 0.$$

(e) Show that in spherical polar co-ordinates the differential operators $\hat{\mathrm{L}}_i$ take the form

$$\hat{\mathrm{L}}_x \ = \ i\sin\phi\frac{\partial}{\partial\theta} + i\cot\theta\cos\phi\frac{\partial}{\partial\phi} \ , \quad \hat{\mathrm{L}}_y = -i\cos\phi\frac{\partial}{\partial\theta} + i\cot\theta\sin\phi\frac{\partial}{\partial\phi} \ , \quad \hat{\mathrm{L}}_z = -i\frac{\partial}{\partial\phi} \ . \quad (442)$$

4.8 (a) Verify that the three functions $\cos\theta$, $\sin\theta\,e^{i\phi}$ and $\sin\theta\,e^{-i\phi}$ are all eigenfunctions of $\hat{\boldsymbol{L}}^2$ and $\hat{\mathrm{L}}_z$.

(b) Find normalization constants N for each of the above functions so that

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \ \sin\theta \ N^2 \ |\psi(\theta, \phi)|^2 = 1.$$

(c) Once normalized, these functions are called spherical harmonics and given the symbol $Y_\ell^m(\theta, \phi)$. Hence deduce that your results are consistent with the functions:

$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta; \qquad Y_1^1(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin\theta\,e^{i\phi}; \qquad Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta\,e^{-i\phi}.$$

(Note, you can't use this method to get the signs of Y_1^0, Y_1^1 and Y_1^{-1}. The minus sign in Y_1^1 can be deduced by using a raising operator $\hat{L}_+$ on Y_1^0. This is not required.)

(d) Rewrite these functions in terms of Cartesian variables [$x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $z = r\cos\theta$]. Sketch $|Y_1^0|^2$, $|Y_1^1|^2$ and $|Y_1^{-1}|^2$. (They are angular functions, so keep r fixed and look only at the angle dependence. A cross section in the x–z plane will do. Why?)

4.9 The angular part of a system's wavefunction is

$$\langle\theta, \phi|\psi\rangle \propto (\sqrt{2}\cos\theta + \sin\theta\,e^{-i\phi} - \sin\theta\,e^{i\phi}).$$

---

[2]As usual this does not allows us to determine the overall phase of the wave function, but as this is not observable we can fix it as we like. The phases in (440) are chosen in order to reproduce the definition of the spherical harmonics from the mathematical literature.

What are the possible results of measurement of (a) $\hat{\boldsymbol{L}}^2$, and (b) $\hat{L}_z$, and their probabilities? What is the expectation value of $\hat{L}_z$?

4.10 A system's wavefunction is proportional to $\sin^2\theta\,\mathrm{e}^{2\mathrm{i}\phi}$. What are the possible results of measurements of (a) $\hat{L}_z$ and (b) $\hat{\boldsymbol{L}}^2$?

4.11 A system's wavefunction is proportional to $\sin^2\theta$. What are the possible results of measurements of (a) $\hat{L}_z$ and (b) $\hat{\boldsymbol{L}}^2$? Give the probabilities of each possible outcome.

4.12 A particle of mass m is described the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} - e\mathcal{E}\hat{x}.$$

(a) What is the physical origin of the last term in $\hat{H}$?

(b) Which of the observables represented by the operators $\hat{\boldsymbol{L}}^2$, $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ are constants of the motion assuming (i) $\mathcal{E}=0$; (ii) $\mathcal{E}\neq 0$ (Hint: Use the results for $[\hat{L}_i,\hat{x}]$ from **4.7**.)

4.13 Show that $\hat{L}_i$ commutes with $\hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{p}}$.

11.3 Spherically symmetric potentials

An important class of problems involves potentials with spherical symmetry, i.e. potentials depend only on the distance r

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{r}) , \quad \hat{r}^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2. \tag{443}$$

This Hamiltonian is rotationally invariant, which means that we can use the angular momentum quantum numbers ℓ and m to label energy eigenstates. Let's denote the corresponding simultaneous eigenstates by $|n,\ell,m\rangle$, where we introduced a label n to allow for the possibility that there will be energy eigenstates with the same values of ℓ and m but different energies

$$H|n,\ell,m\rangle = E_{n,\ell,m}|n,\ell,m\rangle. \tag{444}$$

The TISE then takes the following form in the position representation in spherical polar co-ordinates

$$\langle r,\theta,\phi|H|n,\ell,m\rangle = E_{n,\ell,m}\langle r,\theta,\phi|n,\ell,m\rangle \quad \Leftrightarrow \quad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi_{n,\ell,m}(r,\theta,\phi) = E_{n,\ell,m}\psi_{n,\ell,m}(r,\theta,\phi) , \tag{445}$$

where $\psi_{n,\ell,m}(r,\theta,\phi) = \langle r,\theta,\phi|n,\ell,m\rangle$ and

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\left[-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{446}$$

Comparing (446) with (431) we observe that

$$\boxed{\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\frac{\hat{\mathrm{L}}^2}{\hbar^2}.} \tag{447}$$

This implies that for spherically symmetric potentials we can solve the TISE for the wave function by *separation of variables*

$$\boxed{\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r)Y_{\ell,m}(\theta,\phi).} \tag{448}$$

Substituting (448) into the TDSE we obtain an equation for the *radial wave function* $R_{n,\ell}(r)$ only

$$\left[\frac{\hat{p}_r^2}{2m} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} + V(r) \right] R_{n,\ell}(r) = E_{n,\ell,m} R_{n,\ell}(r), \tag{449}$$

where we have defined the radial momentum operator

$$\hat{p}_r = -i\hbar \left[\frac{\partial}{\partial r} + \frac{1}{r} \right]. \tag{450}$$

Eqn (449) is sometimes called *radial Schrödinger equation*. It has a nice physical interpretation: the term $\hat{p}_r^2/2m$ is the kinetic energy due to radial motion, while $\hbar^2 \ell(\ell+1)/2mr^2$ is the kinetic energy associated with tangential motion. One immediate implication of (449) is that the energy eigenvalues are in fact independent of the quantum number m. This means that in rotationally invariant problems we always have *degenerate energy eigenvalues*.

Now you see why angular momentum eigenstates and eigenvalues are so important in QM: they solve the angular part of the Schrödinger equation for *any* rotationally invariant problem!

12 ANGULAR MOMENTUM AND MAGNETIC MOMENTS

Let us consider a charged particle moving in a constant magnetic field $\mathbf{B}$. The corresponding vector potential is

$$\mathbf{A}(\mathbf{x}) = \frac{1}{2} \mathbf{B} \times \mathbf{x}. \tag{451}$$

The Hamiltonian for this problem is given by

$$H = \frac{\left(\hat{\mathbf{p}} - e\mathbf{A}(\hat{\mathbf{x}}) \right)^2}{2m} = \frac{\hat{\mathbf{p}}^2}{2m} - e \left[\mathbf{A}(\hat{\mathbf{x}}) \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{x}}) \right] + e^2 \mathbf{A}^2(\hat{\mathbf{x}}). \tag{452}$$

Let's assume that we can neglect the $\mathbf{A}^2$ term (which is justified in the context of atoms we are interested in here). Then the Hamiltonian can be written as

$$H = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{e}{2m} \mathbf{B} \cdot \hat{\mathbf{L}}, \tag{453}$$

where $\hat{\mathbf{L}}$ is a vector made from the three angular momentum operators. This is just what we would have if the charged particle induced a magnetic moment proportional to its angular momentum

$$\boxed{ \boldsymbol{\mu} = \frac{e}{2m} \hat{\mathbf{L}}. } \tag{454}$$

Let us now put our magnetic field along the z-direction

$$H = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{eB}{2m} \hat{L}_z. \tag{455}$$

We have

$$[H, \hat{\mathbf{p}}^2] = 0 = [H, \hat{L}_z] = [\hat{\mathbf{p}}^2, \hat{L}_z], \tag{456}$$

and therefore can use the kinetic energy eigenvalue E_K and the $\hat{L}_z$ quantum number m to label energy eigenstates. Let us now consider two eigenstates with the same kinetic energy but opposite $\hat{L}_z$ eigenvalues $\pm n$ ($n \geq 0$). We have

$$H |E_K, \pm n\rangle = \left[E_k \mp \frac{eBn}{2m} \right] |E_K, \pm n\rangle. \tag{457}$$
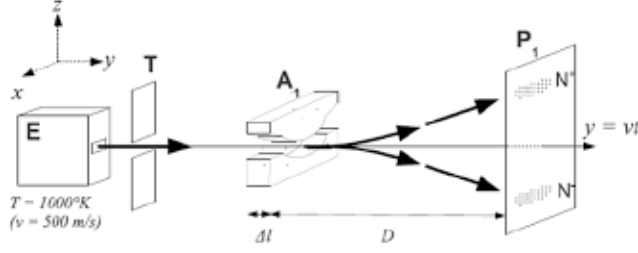
Figure 13: Setup for the Stern-Gerlach experiment.

This tells us that the energy of $|E_K, n\rangle$ *decreases* if we increase B, while the energy $|E_K, -n\rangle$ increases. Classically the force on a particle is minus the gradient of its potential energy. This suggests that if our magnetic field was slightly varying in space, the particle in the $|E_K, n\rangle$ state would move towards regions of larger magnetic field, while in the state $|E_K, -n\rangle$ the particle would move into the regions of lower magnetic field. This observation is the basis of the celebrated *Stern-Gerlach experiment*.

The idea is to have a magnetic field gradient along the z-axis, which according to the arguments we just presented should result in

- Particles with positive $\hat{L}_z$ quantum number m will be deflected upwards;

- Particles with negative $\hat{L}_z$ quantum number m will be deflected downwards;

- Particles with $\hat{L}_z$ quantum number $m = 0$ will pass through the apparatus with being deflected.

The original beam of particles is such that each emitted particle will have equal probability to have any m value. According to our theory for orbital angular momentum, the experiments should show

- A single beam for particles with $\ell = 0$ quantum number;

- Three symmetrically split beams for particles with $\ell = 1$ quantum number, corresponding to $m = 0$ and $m = \pm 1$ respectively;

- Five symmetrically split beams for particles with $\ell = 2$ quantum number, corresponding to $m = 0$, $m = \pm 1$ and $m = \pm 2$ respectively.

In particular, there always should be particles that do not get deflected. This is not what was observed in the experiments. In particular, electrons are always split into an even number of beams! This suggests that for some reason the angular momentum eigenvalues are not integers, but half-odd integers.

13 Spin and total angular momentum

Wolfgang Pauli (Nobel Prize in Physics 1945)

"I do not mind if you think slowly, but I do object when you publish more quickly than you think."

"This is not only not correct, it is not even wrong."

Apart from his ground breaking contributions to Physics Pauli is known for the *Pauli-effect*, which refers to numerous instances in which demonstrations involving equipment suffered technical problems only when he was present. For fear of the Pauli effect, the experimental physicist Otto Stern banned Pauli from his laboratory in spite of their friendship. One incident occurred in the physics laboratory at the University of Göttingen. An expensive measuring device, for no apparent reason, suddenly stopped working, although Pauli was in fact absent. James Franck, the director of the institute, reported the incident with the humorous remark that at least this time Pauli was innocent. However, it turned out that Pauli had been on a railway journey to Copenhagen and had switched trains at the Göttingen rail station at about the time of the failure.

The resolution of the puzzle posed by the Stern-Gerlach experiments is that position alone is insufficient to specify the quantum states of electrons, and additional quantum numbers are required. These are called *spin* quantum numbers. Let us denote the position eigenstates for the time being by

$$|\mathbf{x}, s\rangle , \tag{458}$$

where the index s specifies the spin state of the particle. To figure out how to think of these states let's work backwards from the observation that the Stern-Gerlach experiment would be compatible with our theory if the $\hat{L}_z$ eigenvalues were half integer numbers. Going all the way back to rotations, we now have

$$|\mathbf{x}', s'\rangle = U(\mathbf{n}\alpha)|\mathbf{x}, s\rangle . \tag{459}$$

The important point is that spin quantum numbers can and do transform under rotations as well. As we have seen above, the orbital angular momentum operators generate rotations of the position. The idea is then to write the operator that describes the rotation as the product of rotations of the position and spin respectively

$$U(\mathbf{n}\alpha) = e^{-\frac{i}{\hbar}\alpha\mathbf{n}\cdot\mathbf{L}}e^{-\frac{i}{\hbar}\alpha\mathbf{n}\cdot\mathbf{S}}. \tag{460}$$

Here we have introduced *spin angular momentum operators* $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ that fulfil the angular momentum algebra

$$[\hat{S}_j, \hat{S}_k] = i\hbar\epsilon_{jkl}\hat{S}_l , \tag{461}$$

and commute with the orbital angular momentum operators

$$[\hat{L}_j, \hat{S}_k] = 0. \tag{462}$$

The *total angular momentum* operators are defined as the sums of orbital and spin angular momentum operators

$$\hat{J}_j = \hat{L}_j + \hat{S}_j . \tag{463}$$

By construction they also fulfil the angular momentum algebra

$$\boxed{[\hat{J}_j, \hat{J}_k] = i\hbar\epsilon_{jkl}\hat{J}_l .} \tag{464}$$

Following the spinless case we can now construct simultaneous eigenstates of $\hat{J}_z$ and $\mathbf{J}^2$. We can in fact repeat the construction of angular momentum eigenstates we have carried out for the spinless case step by step with only on crucial difference: in the spinless case we had required

$$U(2\pi\mathbf{e_z}) = \mathbf{1} , \qquad \text{spinless case,} \tag{465}$$

which forced the $\hat{L}_z$ eigenvalues to be integers. In order to accommodate the Stern-Gerlach experiment we want the eigenvalues of $\hat{J}_z$ to be half-integer numbers and therefore require

$$U(4\pi\mathbf{e_z}) = \mathbf{1} . \tag{466}$$

In particular we do not require that the spin state of the system is unchanged under a rotation by 2π. The simultaneous eigenstates of $\hat{J}_z$ and $\hat{\mathbf{J}}^2$ fulfil

$$\begin{aligned}
\hat{\mathbf{J}}^2|j,j_z\rangle &= \hbar^2 j(j+1)|j,j_z\rangle , \\
\hat{J}_z|j,j_z\rangle &= \hbar j_z|j,j_z\rangle , \\
\hat{J}_\pm|j,j_z\rangle &= \hbar\sqrt{j(j+1) - j_z(j_z \pm 1)}|j,j_z \pm 1\rangle ,
\end{aligned} \tag{467}$$

where

$$-j \leq j_z \leq j , \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \tag{468}$$

The crucial difference to orbital angular momentum is that the total angular momentum quantum number now takes half-integer values.

> **Aside 8:** SPIN AND THE STERN-GERLACH EXPERIMENT
>
> The existence of spin fixes our problem with Stern-Gerlach experiments as follows. The Hamiltonian describing the motion of an electron in a magnetic field follows from the *Dirac equation* and turns out to be given by
>
> $$H = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{eB}{2m}(\hat{L}_z + g_s\hat{S}_z) , \tag{469}$$
>
> where $g_s = 2$ is the so-called gyromagnetic ratio. Repeating our previous arguments we see that electrons without orbital angular momentum are split into *two beams*.

13.1 SPIN-1/2 REPRESENTATION AND PAULI MATRICES

The simplest representation of total angular momentum has $\hat{\mathbf{J}}^2$ quantum number $j = 1/2$. There are two states with $\hat{J}_z$ quantum numbers $\pm 1/2$

$$\left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle . \tag{470}$$

These states are sometimes called $|\uparrow\rangle$ and $|\downarrow\rangle$ respectively and as they span a linear vector space of dimension two they can be represented as

$$|\uparrow\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} , \qquad |\downarrow\rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} . \tag{471}$$

The total angular momentum operators in this representation can be expressed in terms of 2×2 matrices called *Pauli matrices*

$$\begin{pmatrix} \langle\uparrow|\hat{J}_j|\uparrow\rangle & \langle\uparrow|\hat{J}_j|\downarrow\rangle \\ \langle\downarrow|\hat{J}_j|\uparrow\rangle & \langle\downarrow|\hat{J}_j|\downarrow\rangle \end{pmatrix} = \frac{\hbar}{2}\sigma_j , \quad j = x, y, z , \tag{472}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{473}$$

13.2 Spin angular momentum

The spin angular momentum is described by the Hermitian operators $\hat{S}_j$ that fulfil the angular momentum algebra. By the same arguments as for orbital and total angular momenta we can therefore construct simultaneous eigenstates of $\hat{S}_z$ and $\hat{\mathbf{S}}^2$

$$
\begin{aligned}
\hat{\mathbf{S}}^2|s, s_z\rangle &= \hbar^2 s(s+1)|s, s_z\rangle \ , \\
\hat{S}_z|s, s_z\rangle &= \hbar s_z|s, s_z\rangle \ , \\
\hat{S}_\pm|s, s_z\rangle &= \hbar\sqrt{s(s+1) - s_z(s_z \pm 1)}|s, s_z \pm 1\rangle \ ,
\end{aligned}
\tag{474}
$$

The s_z quantum numbers are *half-integers* because rotations by 4π must be equivalent to the identity. The total spin quantum number s is an intrinsic property of quantum mechanical particles. In particular, electrons, neutrinos, quarks, neutrons and protons are all spin-1/2 objects.

13.3 Stern-Gerlach filters

As we have seen, the Stern-Gerlach experiment separates particles according to their angular momentum. This can be viewed as providing a measurement of the component of angular momentum in the direction of the applied magnetic field. Combining Stern-Gerlach filters with different orientations provides a very nice playground for understanding the mechanics of measurements in QM. Let's consider the example of a beam of particles incident on a SG filter aligned along the z-direction. Let's assume that the particles have $\hat{J}_z$ quantum numbers $\pm\hbar/2$ with equal probabilities and the total angular momentum quantum number is $j = 1/2$. So there are two relevant states

$$
|\frac{1}{2}, \frac{1}{2}\rangle = |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \ , \qquad |\frac{1}{2}, -\frac{1}{2}\rangle = |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} .
\tag{475}
$$

The angular momentum operators can be represented as

$$
\hat{J}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \quad \hat{J}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \ , \quad \hat{J}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ .
\tag{476}
$$

The SG filter splits the beam into two, and the particles deflected upwards will have quantum numbers $j_z = 1/2$. We can think of this as a measurement of $\hat{J}_z$. After this "measurement" the particles will be in the quantum state $|\uparrow\rangle$. Let us then pass this beam of particles through a second SG filter, but with a magnetic field pointing along a direction $\mathbf{n} = (0, \sin(\theta), \cos(\theta))$. The angular momentum along $\mathbf{n}$ is

$$
\mathbf{J} \cdot \mathbf{n} = \cos(\theta)\hat{J}_z + \sin(\theta)\hat{J}_y = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & -i\sin\theta \\ i\sin\theta & -\cos\theta \end{pmatrix} \ .
\tag{477}
$$

In order to work out the outcomes of measuring $\mathbf{J} \cdot \mathbf{n}$ we require its eigenvalues and eigenvectors. The eigenvalues are $\pm\hbar/2$ and the corresponding eigenvectors are

$$
|\theta, \downarrow\rangle = \begin{pmatrix} i\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix} \ , \qquad |\theta, \uparrow\rangle = \begin{pmatrix} \cos(\theta/2) \\ i\sin(\theta/2) \end{pmatrix} \ .
\tag{478}
$$

We now write the state of the system after the first SG filter as a linear combination of these two eigenstates

$$
|\uparrow\rangle = \cos(\theta/2)|\theta, \uparrow\rangle - i\sin(\theta/2)|\theta, \downarrow\rangle \ .
\tag{479}
$$

This tells us that after the second SG filter we will have two beams corresponding to particles with angular momentum $\pm\hbar/2$ along the $\mathbf{n}$ direction but with different intensities, because

$$
\begin{aligned}
P(\hbar/2) &= |\langle\uparrow|\theta, \uparrow\rangle|^2 = \cos^2(\theta/2) \ , \\
P(-\hbar/2) &= |\langle\uparrow|\theta, \downarrow\rangle|^2 = \sin^2(\theta/2) \ .
\end{aligned}
\tag{480}
$$

Aside 9: Vector operators

In classical physics a vector is a quantity that transforms under rotations as

$$V_i' = \sum_{j=1}^{3} R_{ij} V_j \ , \tag{481}$$

where R is a rotation matrix. It is natural to ask whether quantum mechanical *vector operators* like $(\hat{x}, \hat{y}, \hat{z})$ have analogous transformation properties. We know that position eigenstates transform under rotations as

$$|\mathbf{x}'\rangle = |R(\mathbf{n}\alpha)\mathbf{x}\rangle = U(\mathbf{n}\alpha)|\mathbf{x}\rangle \ , \tag{482}$$

where $R(\mathbf{n}\alpha)$ is a rotation matrix describing rotations by an angle α around the axis $\mathbf{n}$ and $U(\mathbf{n}\alpha)$ is the associated quantum mechanical rotation operator. Matrix elements of the position operators transform as

$$\langle \mathbf{x}'|\hat{x}_i|\mathbf{y}'\rangle = x_i'\langle \mathbf{x}'|\mathbf{y}'\rangle = x_i'\langle \mathbf{x}|U^\dagger(\mathbf{n}\alpha)U(\mathbf{n}\alpha)|\mathbf{y}\rangle = x_i'\langle \mathbf{x}|\mathbf{y}\rangle = \big(R(\mathbf{n}\alpha)\big)_{ij}x_j\langle \mathbf{x}|\mathbf{y}\rangle = \langle \mathbf{x}|\big(R(\mathbf{n}\alpha)\big)_{ij}\hat{x}_j|\mathbf{y}\rangle. \tag{483}$$

Combining this with

$$\langle \mathbf{x}'|\hat{x}_i|\mathbf{y}'\rangle = \langle \mathbf{x}|U^\dagger(\mathbf{n}\alpha)\hat{x}_i U(\mathbf{n}\alpha)|\mathbf{y}\rangle \tag{484}$$

we conclude that

$$U^\dagger(\mathbf{n}\alpha)\hat{x}_i U(\mathbf{n}\alpha) = \big(R(\mathbf{n}\alpha)\big)_{ij}\hat{x}_j. \tag{485}$$

In our shorthand vector notation these become

$$U^\dagger(\mathbf{n}\alpha)\hat{\mathbf{x}}U(\mathbf{n}\alpha) = R(\mathbf{n}\alpha)\hat{\mathbf{x}}. \tag{486}$$

Vectors of operators $\hat{\mathbf{V}}$ that fulfil

$$\boxed{U^\dagger(\mathbf{n}\alpha)\hat{\mathbf{V}}U(\mathbf{n}\alpha) = R(\mathbf{n}\alpha)\hat{\mathbf{V}}.} \tag{487}$$

are called *vector operators*. An equivalent definition can be arrived at by considering infinitesimal rotations

$$U(\mathbf{n}d\alpha) = 1 - \frac{id\alpha}{\hbar}\mathbf{n}\cdot\hat{\mathbf{J}} \ . \tag{488}$$

Substituting this into (487) gives

$$\hat{V}_j + \frac{d\alpha}{i\hbar}[\hat{V}_j, \mathbf{n}\cdot\hat{\mathbf{J}}] = \sum_k \big(R(\mathbf{n}d\alpha)\big)_{jk}\hat{V}_k \ . \tag{489}$$

These in turn are equivalent to

$$\boxed{[\hat{V}_j, \hat{J}_k] = i\hbar\epsilon_{jkl}\hat{V}_l \ .} \tag{490}$$

Operators that fulfil these commutation relations are vector operators. Examples are position, momentum and angular momentum.

5.1 Write down the expression for the commutator $[\sigma_i, \sigma_j]$ of two Pauli matrices. Show that the anticommutator of two Pauli matrices is

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}.$$

5.2 Let $\boldsymbol{n}$ be any unit vector and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ be the vector whose components are the Pauli matrices. Why is it physically necessary that $\boldsymbol{n} \cdot \boldsymbol{\sigma}$ satisfy $(\boldsymbol{n} \cdot \boldsymbol{\sigma})^2 = I$, where I is the 2×2 identity matrix? Let $\boldsymbol{m}$ be a unit vector such that $\boldsymbol{m} \cdot \boldsymbol{n} = 0$. Why do we require that the commutator $[\boldsymbol{m} \cdot \boldsymbol{\sigma}, \boldsymbol{n} \cdot \boldsymbol{\sigma}] = 2\mathrm{i}(\boldsymbol{m} \times \boldsymbol{n}) \cdot \boldsymbol{\sigma}$? Prove that these relations follow from the algebraic properties of the Pauli matrices. You should be able to show that $[\boldsymbol{m} \cdot \boldsymbol{\sigma}, \boldsymbol{n} \cdot \boldsymbol{\sigma}] = 2\mathrm{i}(\boldsymbol{m} \times \boldsymbol{n}) \cdot \boldsymbol{\sigma}$ for any two vectors $\boldsymbol{n}$ and $\boldsymbol{m}$.

5.3 Let $\boldsymbol{n}$ be the unit vector in the direction with polar coordinates (θ, ϕ). Write down the matrix $\boldsymbol{n} \cdot \boldsymbol{\sigma}$ and find its eigenvectors. Hence show that the state of a spin-half particle in which a measurement of the component of spin along $\boldsymbol{n}$ is certain to yield $\frac{1}{2}\hbar$ is

$$|+, \boldsymbol{n}\rangle = \sin(\theta/2)\, \mathrm{e}^{\mathrm{i}\phi/2}|-\rangle + \cos(\theta/2)\, \mathrm{e}^{-\mathrm{i}\phi/2}|+\rangle,$$

where $|\pm\rangle$ are the states in which $\pm\frac{1}{2}$ is obtained when s_z is measured. Obtain the corresponding expression for $|-, \boldsymbol{n}\rangle$. Explain physically why the amplitudes in the previous equation have modulus $2^{-1/2}$ when $\theta = \pi/2$ and why one of the amplitudes vanishes when $\theta = \pi$.

5.4 For a spin-half particle at rest, the operator $\boldsymbol{J}$ is equal to the spin operator $\boldsymbol{S}$. Use the properties of the Pauli spin matrices to show that in this case the rotation operator $U(\boldsymbol{\alpha}) \equiv \exp(-\mathrm{i}\boldsymbol{\alpha} \cdot \boldsymbol{J}/\hbar)$ is

$$U(\boldsymbol{\alpha}) = I \cos\left(\frac{\alpha}{2}\right) - \mathrm{i}\hat{\boldsymbol{\alpha}} \cdot \boldsymbol{\sigma} \sin\left(\frac{\alpha}{2}\right),$$

where $\hat{\boldsymbol{\alpha}}$ is the unit vector parallel to $\boldsymbol{\alpha}$. Comment on the value this gives for $U(\boldsymbol{\alpha})$ when $\alpha = 2\pi$.

5.5 Explain why a spin-$\frac{1}{2}$ particle in a magnetic field $\boldsymbol{B}$ has a Hamiltonian given by

$$H = -\gamma \boldsymbol{S} \cdot \boldsymbol{B},$$

where γ is the gyromagnetic ratio which you should define.
In a coordinate system such that $\boldsymbol{B}$ lies along the z-axis, a proton is found to be in a eigenstate $|+, x\rangle$ of $\hat{S}_x$ at $t = 0$. Find $\langle \hat{S}_x \rangle$ and $\langle \hat{S}_y \rangle$ for $t > 0$.

5.6 Write down the 3×3 matrix that represents S_x for a spin-one system in the basis in which S_z is diagonal (i.e., the basis states are $|0\rangle$ and $|\pm\rangle$ with $S_z|+\rangle = |+\rangle$, etc.)
A beam of spin-one particles emerges from an oven and enters a Stern–Gerlach filter that passes only particles with $J_z = \hbar$. On exiting this filter, the beam enters a second filter that passes only particles with $J_x = \hbar$, and then finally it encounters a filter that passes only particles with $J_z = -\hbar$. What fraction of the particles stagger right through?

5.7 A system that has spin angular momentum $\sqrt{6}\hbar$ is rotated through an angle ϕ around the z-axis. Write down the 5×5 matrix that describes a rotation by an angle ϕ around the z-axis.

SOME OPTIONAL (!) HARD PROBLEMS ON OFF SYLLABUS TOPICS

5.8* *Vector operators*

(a) Show that expectation values of the position operators in a state $|\psi\rangle$ transform like a classical vector under a rotation around an axis $\mathbf{n}$ by an angle α.

(b) Show that the commutation relations

$$[\hat{V}_j, \hat{J}_k] = i\hbar\epsilon_{jkl}\hat{V}_l \ , \tag{491}$$

are equivalent to

$$\hat{V}_j + \frac{d\alpha}{i\hbar}[\hat{V}_j, \mathbf{n} \cdot \hat{\mathbf{J}}] = \sum_k \left(R(\mathbf{n}d\alpha)\right)_{jk}\hat{V}_k \ , \tag{492}$$

where $\mathbf{n}$ is a unit vector and $R(\mathbf{n}d\alpha)$ is the rotation matrix around the axis $\mathbf{n}$ by an angle $d\alpha$.

(c) Let $\mathbf{e}_{1,2,3}$ be three orthonormal vectors. Show that the operators $\mathbf{e}_j(\hat{x}, \hat{y}, \hat{z})$ defined through their actions on position eigenstates

$$\mathbf{e}_j(\hat{x}, \hat{y}, \hat{z})|\mathbf{x}\rangle = \begin{pmatrix} x\ \mathbf{e}_j \cdot \mathbf{e}_x \\ y\ \mathbf{e}_j \cdot \mathbf{e}_y \\ z\ \mathbf{e}_j \cdot \mathbf{e}_z \end{pmatrix} |\mathbf{x}\rangle \tag{493}$$

are vector operators.

Part V
COMPOSITE SYSTEMS

So far we have focussed on the QM of a single particle. Most QM systems involve several particles that interact with one another, e.g. the electron and nucleus in a hydrogen atom. In order to understand them we have to develop a description of quantum mechanical systems that are composed of several parts. In order to do so we first consider QM systems composed of two parts, e.g. two particles.

14 QM SYSTEMS COMPOSED OF TWO PARTS

Let A and B be two quantum mechanical systems and $\{|A; j\rangle\}$, $\{|B; k\rangle\}$ two corresponding bases of quantum states. A basis of states of the composite system is then obtained by taking[3]

$$|AB; j, k\rangle = |A; j\rangle|B; k\rangle \ . \tag{494}$$

In these states A and B are in quantum states $|A; j\rangle$ and $|B; k\rangle$ respectively. For example, if we have two independent (distinguishable) particles a basis of position eigenstates is given by

$$|AB; x_1, x_2\rangle = |A; x_1\rangle|B; x_2\rangle \ , \tag{495}$$

in which the first particle is at position x_1 with certainty, while the second particle is at position x_2 with certainty. The bra states corresponding to (494) are denoted by

$$\langle AB; j, k| = \langle A; j|\langle B; k|, \tag{496}$$

and scalar products fulfil

$$\langle AB; j, k|AB; m, n\rangle = \langle A; j|A; m\rangle\ \langle B; k|B; n\rangle. \tag{497}$$

---

[3]The mathematical structure we are describing here is a tensor product of two linear vector spaces.

A general state of the composite system can then be written as a linear combination of basis states (as usual)

$$|AB; \psi\rangle = \sum_{j,k} \langle AB; j, k | AB; \psi \rangle \, |AB; j, k\rangle. \tag{498}$$

> **Example 4: Two spins** $1/2$
>
> Let us consider a system composed of two spins $1/2$. For each spin there are two basis states $|\uparrow\rangle$ and $|\downarrow\rangle$ and a basis of the composite system is then given by
>
> $$|\uparrow\uparrow\rangle = |\uparrow\rangle|\uparrow\rangle \,, \quad |\uparrow\downarrow\rangle = |\uparrow\rangle|\downarrow\rangle \,, \quad |\downarrow\uparrow\rangle = |\downarrow\rangle|\uparrow\rangle \,, \quad |\downarrow\downarrow\rangle = |\downarrow\rangle|\downarrow\rangle. \tag{499}$$
>
> An arbitrary state can be written as a linear combination of these four basis states
>
> $$|\psi\rangle = \langle\uparrow\uparrow\,|\psi\rangle|\,\uparrow\uparrow\rangle + \langle\uparrow\downarrow\,|\psi\rangle|\,\uparrow\downarrow\rangle + \langle\downarrow\uparrow\,|\psi\rangle|\,\downarrow\uparrow\rangle + \langle\downarrow\downarrow\,|\psi\rangle|\,\downarrow\downarrow\rangle. \tag{500}$$

14.1 OPERATORS

Let $\mathcal{O}_A$ and $\mathcal{O}_B$ be operators acting only on parts A and B of our composite system. We can define their actions on states $|\psi\rangle$ of the composite system as follows:

- Write $|\psi\rangle$ as a linear combination of the basis states $|AB; j, k\rangle$ defined above

$$|\psi\rangle = \sum_{j,k} \langle AB; j, k | \psi \rangle \, |AB; j, k\rangle = \sum_{j,k} \langle AB; j, k | \psi \rangle \, |A; j\rangle |B; k\rangle \tag{501}$$

- Now define the actions of $\mathcal{O}_A$ and $\mathcal{O}_B$ on $|\psi\rangle$ by

$$
\begin{aligned}
\mathcal{O}_A |\psi\rangle &= \sum_{j,k} \langle AB; j, k | \psi \rangle \left(\mathcal{O}_A |A; j\rangle \right) |B; k\rangle \,, \\
\mathcal{O}_B |\psi\rangle &= \sum_{j,k} \langle AB; j, k | \psi \rangle \, |A; j\rangle \left(\mathcal{O}_B |B; k\rangle \right).
\end{aligned}
\tag{502}
$$

A general operator acting on the composite system will have the form

$$\boxed{\sum_{j,k} c_{j,k} \mathcal{O}_{A,j} \mathcal{O}_{B,k}} \tag{503}$$

where $\mathcal{O}_{A,j}$ and $\mathcal{O}_{B,k}$ are operators acting only on systems A and B respectively and $c_{j,k}$ are complex numbers.

> **Example 5: Two spins** $1/2$
>
> Denote the spin operators of the first and second particles by $\hat{S}_j^{(1)}$ and $\hat{S}_j^{(2)}$ respectively. Then
>
> $$\hat{S}_j^{(1)} |\uparrow\uparrow\rangle = \left(\hat{S}_j^{(1)} |\uparrow\rangle \right) |\uparrow\rangle \,, \quad \hat{S}_j^{(2)} |\uparrow\uparrow\rangle = |\uparrow\rangle \left(\hat{S}_j^{(2)} |\uparrow\rangle \right) \,, \dots \tag{504}$$
>
> More general operators act e.g. as
>
> $$S_x^{(1)} S_z^{(2)} |\uparrow\uparrow\rangle = \left(S_x^{(1)} |\uparrow\rangle \right) \left(S_z^{(2)} |\uparrow\rangle \right) = \left(\frac{\hbar}{2} |\downarrow\rangle \right) \left(\frac{\hbar}{2} |\uparrow\rangle \right) = \frac{\hbar^2}{4} |\downarrow\uparrow\rangle. \tag{505}$$

14.2 Position representation

A very important case of a composite system are several particles that have kinetic energy and interact with one another by e.g. the Coulomb interaction. A basis of position eigenstates of a system with two particles is provided by the states

$$|\mathbf{x}_1, \mathbf{x}_2\rangle . \tag{506}$$

The resolution of the identity reads

$$\mathbf{1} = \int d^3\mathbf{x}_1 \int d^3\mathbf{x}_2 \; |\mathbf{x}_1, \mathbf{x}_2\rangle\langle\mathbf{x}_1, \mathbf{x}_2|. \tag{507}$$

The Hamiltonian would contain terms describing the kinetic energies of the two particles as well as potential energy terms that include the interactions between the two particles. This leads to a Hamiltonian of the form

$$H = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V_1(\hat{\mathbf{x}}_1) + V_2(\hat{\mathbf{x}}_2) + V_{\text{int}}(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2). \tag{508}$$

Importantly, in case we have independent particles ($V_{\text{int}} = 0$) the Hamiltonian is the *sum* of the Hamiltonians of the individual particles. The position representation is now constructed by following the single-particle case. Let's take the TDSE as our starting point

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle . \tag{509}$$

Projecting onto a position eigenbra gives

$$i\hbar \frac{d}{dt} \underbrace{\langle\mathbf{x}_1, \mathbf{x}_2|\psi(t)\rangle}_{\psi(\mathbf{x}_1, \mathbf{x}_2, t)} = \langle\mathbf{x}_1, \mathbf{x}_2|H|\psi(t)\rangle . \tag{510}$$

The right-hand side is worked out by inserting a resolution of the identity

$$\langle\mathbf{x}_1, \mathbf{x}_2|H|\psi(t)\rangle = \int d^3\mathbf{x}_1' \int d^3\mathbf{x}_2' \; \langle\mathbf{x}_1, \mathbf{x}_2|H|\mathbf{x}_1', \mathbf{x}_2'\rangle \; \langle\mathbf{x}_1', \mathbf{x}_2'|\psi(t)\rangle. \tag{511}$$

The action of the various terms on position eigenstates follows from (502), e.g.

$$\begin{aligned}
\langle\mathbf{x}_1, \mathbf{x}_2|V_1(\hat{\mathbf{x}}_1)|\mathbf{x}_1', \mathbf{x}_2'\rangle &= \langle\mathbf{x}_1|V_1(\hat{\mathbf{x}}_1')|\mathbf{x}_1'\rangle\langle\mathbf{x}_2|\mathbf{x}_2'\rangle = V_1(\mathbf{x}_1') \, \delta^{(3)}(\mathbf{x}_1 - \mathbf{x}_1')\delta^{(3)}(\mathbf{x}_2 - \mathbf{x}_2') \, , \\
\langle\mathbf{x}_1, \mathbf{x}_2|\hat{p}_{1,\alpha}|\mathbf{x}_1', \mathbf{x}_2'\rangle &= \langle\mathbf{x}_1|\hat{p}_{1,\alpha}|\mathbf{x}_1'\rangle\langle\mathbf{x}_2|\mathbf{x}_2'\rangle \\
&= \left(-i\hbar\frac{\partial}{\partial x_{1,\alpha}} \, \delta^{(3)}(\mathbf{x}_1 - \mathbf{x}_1')\right)\delta^{(3)}(\mathbf{x}_2 - \mathbf{x}_2') \, , \quad \alpha = x, y, z.
\end{aligned} \tag{512}$$

When working out matrix elements of the interaction potential we use that

$$\hat{\mathbf{x}}_j|\mathbf{x}_1', \mathbf{x}_2'\rangle = \mathbf{x}_j'|\mathbf{x}_1', \mathbf{x}_2'\rangle \, , \quad j = 1, 2, \tag{513}$$

and hence

$$V_{\text{int}}(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2)|\mathbf{x}_1', \mathbf{x}_2'\rangle = V_{\text{int}}(\mathbf{x}_1', \mathbf{x}_2')|\mathbf{x}_1', \mathbf{x}_2'\rangle. \tag{514}$$

Carrying out the integrals over the delta-functions we arrive at

$$\langle\mathbf{x}_1, \mathbf{x}_2|H|\psi(t)\rangle = \left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + V_1(\mathbf{x}_1) + V_2(\mathbf{x}_2) + V_{\text{int}}(\mathbf{x}_1, \mathbf{x}_2)\right]\psi(\mathbf{x}_1, \mathbf{x}_2, t) \tag{515}$$

Altogether the TDSE in the position representation becomes

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{x}_1, \mathbf{x}_2, t) = \left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + V_1(\mathbf{x}_1) + V_2(\mathbf{x}_2) + V_{\text{int}}(\mathbf{x}_1, \mathbf{x}_2)\right]\psi(\mathbf{x}_1, \mathbf{x}_2, t). \tag{516}$$

14.2.1 INDEPENDENT PARTICLES

It is instructive to consider the case of independent particles, e.g.

$$H = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V_1(\hat{\mathbf{x}}_1) + V_2(\hat{\mathbf{x}}_2) = H_1 + H_2 \ . \tag{517}$$

Here the Hamiltonians H_1 and H_2 only act on the first and second particles respectively. Let us denote the energy eigenstates of $H_{1,2}$ by $|E_n, 1\rangle$ and $|E'_n, 2\rangle$ respectively

$$H_1|E_n, 1\rangle = E_n|E_n, 1\rangle \ , \quad H_2|E'_n, 2\rangle = E'_n|E'_n, 2\rangle \ , \tag{518}$$

we can immediately construct the eigenstates of H as (tensor) *products*

$$\boxed{\begin{aligned} H|E_n, 1\rangle \, |E'_m, 2\rangle &= \Big(H_1|E_n, 1\rangle\Big)|E'_m, 2\rangle + |E_n, 1\rangle \, \Big(H_2|E'_m, 2\rangle\Big) \\ &= (E_n + E'_m)|E_n, 1\rangle \, |E'_m, 2\rangle \ . \end{aligned}} \tag{519}$$

This structure carries over to the position representation: *the wave functions of energy eigenstates are products of the wave functions of the energy eigenstates of H_1 and H_2.* Denoting

$$\langle \mathbf{x}_1|E_n, 1\rangle = \psi_n(\mathbf{x}_1) \ , \quad \langle \mathbf{x}_2|E'_n, 2\rangle = \phi_n(\mathbf{x}_2) \ , \tag{520}$$

and then using the position representation of the TISE, *cf.* (516), we have

$$\left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + V_1(\mathbf{x}_1) + V_2(\mathbf{x}_2) \right] \psi_n(\mathbf{x}_1)\phi_m(\mathbf{x}_2) = (E_n + E'_m)\psi_n(\mathbf{x}_1)\phi_m(\mathbf{x}_2) \ . \tag{521}$$

The wave function of a general state $|\chi\rangle$ can be expressed as a linear combination of these energy eigenstates

$$\chi(\mathbf{x}_1, \mathbf{x}_2) = \sum_{n,m} c_{n,m}\psi_n(\mathbf{x}_1)\phi_m(\mathbf{x}_2) \ . \tag{522}$$

Exercise 1

Show that the coefficients $c_{n,m}$ are given by

$$c_{n,m} = \big(\langle E_n, 1|\langle E'_m, 2|\big)\, |\chi\rangle \ . \tag{523}$$

14.3 MEASUREMENTS

Let us now imagine that we measure a physical property of only one of the parts of our system. As a simple example let's consider measuring the position of the first particle when the composite system is in a quantum state $|\psi\rangle$ and obtain the result $\mathbf{x}_1$. To understand this process we express $|\psi\rangle$ as a superposition of position eigenstates

$$|\psi\rangle = \int d^3\mathbf{x}'_1 \int d^3\mathbf{x}'_2 \, \langle \mathbf{x}'_1, \mathbf{x}'_2|\psi\rangle \, |\mathbf{x}'_1, \mathbf{x}'_2\rangle = \int d^3\mathbf{x}'_1 \int d^3\mathbf{x}'_2 \, \psi(\mathbf{x}'_1, \mathbf{x}'_2) \, |\mathbf{x}'_1\rangle|\mathbf{x}'_2\rangle \ . \tag{524}$$

Recalling that $|\psi(\mathbf{x}_1, \mathbf{x}'_2)|^2$ is the probability density for the first and second particles to be at positions $\mathbf{x}_1$ and $\mathbf{x}'_2$ respectively, we conclude that the probability of obtaining the result $\mathbf{x}_1$ when measuring the position of the first particle is

$$P(\mathbf{x}_1) = \int d^3\mathbf{x}'_2 \, |\psi(\mathbf{x}_1, \mathbf{x}'_2)|^2. \tag{525}$$

After the measurement the system will be in the normalized state

$$|\psi\rangle_{\text{after}} = \frac{1}{N} \int d^3\mathbf{x}_2' \; \psi(\mathbf{x}_1, \mathbf{x}_2') \; |\mathbf{x}_1\rangle|\mathbf{x}_2'\rangle \; , \tag{526}$$

where

$$N = \left[\int d^3\mathbf{x}_2' \; |\psi(\mathbf{x}_1, \mathbf{x}_2')|^2 \right]^{1/2} . \tag{527}$$

As a second example let us consider measuring $S_z^{(1)}$ in the normalized state

$$|\psi\rangle = \frac{1}{2}|\uparrow\uparrow\rangle + \sqrt{\frac{3}{4}}|\downarrow\uparrow\rangle. \tag{528}$$

The possible outcomes are $\pm\hbar/2$. To work out the probability for obtaining $\hbar/2$ we decompose $|\psi\rangle$ into a linear combination of states which lead to the observed outcome and an orthogonal component

$$|\psi\rangle = \frac{1}{2}\underbrace{|\uparrow\uparrow\rangle}_{|\psi_+\rangle} + \sqrt{\frac{3}{4}}\underbrace{|\downarrow\uparrow\rangle}_{|\psi_-\rangle} \tag{529}$$

According to our general rule we then have

$$P\left(\frac{\hbar}{2}\right) = |\langle\psi_+|\psi\rangle|^2 = \frac{1}{4}. \tag{530}$$

After the measurement the system is in the normalized state

$$|\psi\rangle_{\text{after},+} = |\uparrow\uparrow\rangle \; . \tag{531}$$

The probability for obtaining the result $-\hbar/2$ is

$$P\left(-\frac{\hbar}{2}\right) = |\langle\psi_-|\psi\rangle|^2 = \frac{3}{4} \; , \tag{532}$$

and the measurement leaves the system in the state

$$|\psi\rangle_{\text{after},-} = |\downarrow\uparrow\rangle \; . \tag{533}$$

15 PRODUCT STATES VS ENTANGLED STATES

In composite systems there is a particular class of states called *product states*. Their defining characteristic is that they can be written as products of states of the constituent parts. For two subsystems A and B such states take the form

$$|AB;\psi\rangle = |A;\psi_A\rangle|B;\psi_B\rangle \; . \tag{534}$$

For a system made from two spin-1/2 product states can be written in the form

$$\left(\alpha_1|\uparrow\rangle + \beta_1|\downarrow\rangle\right)\left(\alpha_2|\uparrow\rangle + \beta_2|\downarrow\rangle\right) \; . \tag{535}$$

A particular example is the state in (528) as it can be written as

$$|\psi\rangle = \left(\frac{1}{2}|\uparrow\rangle + \sqrt{\frac{3}{4}}|\downarrow\rangle\right)|\uparrow\rangle. \tag{536}$$

Product states have the particular property that *measuring only one part of the system does not affect the other part.* So see what we mean by this let's return to the example of measuring $S_z^{(1)}$ in the state (528): the

outcomes of measuring $S_j^{(2)}$ are independent of the outcomes of measuring $S_z^{(1)}$. Indeed, depending on what result we obtained in the $S_z^{(1)}$ measurement the system will be either in state $|\psi\rangle_{\text{after},+}$ or in state $|\psi\rangle_{\text{after},-}$. However, in both cases the second spin is in state $|\uparrow\rangle$ with certainty and measuring $S_z^{(2)}$ will therefore give identical results. Product states are rather special and typically measuring one part of a composite system *will* affect subsequent measurements on the other part. This property is called *entanglement*. Let us consider our two spin-1/2 system in the state

$$|\phi\rangle = \frac{1}{\sqrt{2}}\big[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big] \ , \tag{537}$$

which you'll hear a lot more about later on in the course. Let us measure first $S_z^{(1)}$ and then $S_z^{(2)}$. The first measurement yields the results $\pm\hbar/2$ with equal probabilities $1/2$, but leaves the system in different states

$$|\phi\rangle_{\text{after},+} = |\uparrow\downarrow\rangle \ , \qquad |\phi\rangle_{\text{after},-} = |\downarrow\uparrow\rangle \ . \tag{538}$$

This tells us that if the outcome of the first measurement was $\hbar/2$, the second measurement with give $-\hbar/2$ with probability 1. On the other hand, if the outcome of the first measurement was $-\hbar/2$, the second measurement with give $\hbar/2$ with probability 1. Entanglement expresses the fact that in general the quantum state of each spin cannot be described independently of the state of the other. As a result measurements of position, momentum, spin etc performed on entangled particles are *correlated*.

15.1 Entanglement Growth

Under time evolution quantum mechanical systems consisting of many particles become more entangled. This ultimately explains how statistical mechanics can arise from QM. To see how entanglement can be induced by time evolving a quantum mechanical system let's return to our system made from two spins-1/2. Let's assume that initially the system is in the state $|\psi(0)\rangle = |\uparrow\uparrow\rangle$, and that the Hamiltonian of the system is

$$H = \frac{4J}{\hbar} S_x^{(1)} S_x^{(2)} \ . \tag{539}$$

The time evolved state is given by

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}Ht}|\psi(0)\rangle \ . \tag{540}$$

Using that

$$H|\uparrow\uparrow\rangle = J\hbar|\downarrow\downarrow\rangle \ , \quad H|\downarrow\downarrow\rangle = J\hbar|\uparrow\uparrow\rangle \ , \tag{541}$$

and expanding the exponential in a power series in H we find that

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}Ht}|\uparrow\uparrow\rangle = \cos(Jt)|\uparrow\uparrow\rangle - i\sin(Jt)|\downarrow\downarrow\rangle. \tag{542}$$

This shows that while $|\psi(0)\rangle$ is a product state and thus unentangled, $|\psi(t>0)\rangle$ is entangled as the outcome of a measurement of the first spin affects the possible outcomes of subsequent measurements of the second spin. *Time evolution has generated entanglement.* For small systems as the one discussed here the time evolution of entanglement is not monotonic. We can see this because at time $t = \pi/2J$ our state becomes again unentangled. This changes when we have *many* particles in the sense that entanglement keeps on growing on "experimentally relevant" time scales.

16 Addition of angular momenta

Let us consider a composite system of two angular momenta with Hamiltonian

$$H = \lambda \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 \ . \tag{543}$$

The angular momenta of the individual parts are not good quantum numbers because

$$[\hat{J}_{1,j}, H] = i\lambda\epsilon_{jkl}\hat{J}_{1,l}\hat{J}_{2,k} \neq 0. \tag{544}$$

However, total angular momentum $\hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ does provide good quantum numbers because

$$[\hat{J}_{1,j} + \hat{J}_{2,j}, H] = i\lambda\epsilon_{jkl}\left(\hat{J}_{1,l}\hat{J}_{2,k} + \hat{J}_{1,k}\hat{J}_{2,l}\right) = 0. \tag{545}$$

This provides a typical example of the following problem: *given a composite system with two angular momenta $\hat{\mathbf{J}}_1$, $\hat{\mathbf{J}}_2$, how do we construct eigenstates of the total angular momentum $\hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$?*

Example 6: Two particles interacting by a central potential

Another example is provided by a rotationally invariant system composed of two spinless particles interacting by a central potential

$$H = \frac{\hat{\mathbf{p}}_1^2}{2m} + \frac{\hat{\mathbf{p}}_2^2}{2m} + V\left((\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2)^2\right). \tag{546}$$

The angular momenta of the first/second particle are not good quantum numbers in this case because

$$[\hat{L}_{1,j}, H] \neq 0 , \qquad [\hat{L}_{2,j}, H] \neq 0 . \tag{547}$$

To see this we first note that as we have established before the kinetic energy terms do commute with the angular momenta, but

$$\begin{aligned}
[\hat{L}_{1,j}, (\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2)^2 &= \epsilon_{jkl}\hat{x}_{1,k}[\hat{p}_{1,l}, (\hat{x}_1 - \hat{x}_2)^2 + (\hat{y}_1 - \hat{y}_2)^2 + (\hat{z}_1 - \hat{z}_2)^2] \\
&= -2i\hbar\epsilon_{jkl}\hat{x}_{1,k}(\hat{x}_{1,l} - \hat{x}_{2,l}) = 2i\hbar\epsilon_{jkl}\hat{x}_{1,k}\hat{x}_{2,l}.
\end{aligned} \tag{548}$$

On the other hand we see that

$$[\hat{L}_{1,j} + \hat{L}_{2,j}, (\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2)^2] = 0 , \tag{549}$$

which tells us that *total* orbital angular momentum is conserved.

Our starting point are the bases of angular momentum eigenstates of the the two parts

$$\begin{aligned}
\hat{\mathbf{J}}_1^2|j_1, j_{1,z}\rangle &= \hbar^2 j_1(j_1 + 1)|j_1, j_{1,z}\rangle , \\
\hat{J}_{1,z}|j_1, j_{1,z}\rangle &= \hbar j_{1,z}|j_1, j_{1,z}\rangle , \\
\hat{\mathbf{J}}_2^2|j_2, j_{2,z}\rangle &= \hbar^2 j_2(j_2 + 1)|j_2, j_{2,z}\rangle , \\
\hat{J}_{2,z}|j_2, j_{2,z}\rangle &= \hbar j_{2,z}|j_2, j_{2,z}\rangle .
\end{aligned} \tag{550}$$

We know that a basis of states of the composite system is given by the products

$$|j_1, j_{1,z}\rangle|j_2, j_{2,z}\rangle . \tag{551}$$

We wish to know how these states are related to the eigenstates of total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. We know that these eigenstates can be labelled by the $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ quantum numbers, but because

$$[\hat{\mathbf{J}}_1^2, \hat{J}_j] = 0 = [\hat{\mathbf{J}}_2^2, \hat{J}_j] , \quad j = x, y, z , \tag{552}$$

there are altogether *four* good quantum numbers

$$\begin{aligned}
\hat{\mathbf{J}}^2|j_1, j_2, j, j_z\rangle &= \hbar^2 j(j + 1)|j_1, j_2, j, j_z\rangle , \\
\hat{J}_z|j_1, j_2, j, j_z\rangle &= \hbar j_z|j_1, j_2, j, j_z\rangle , \\
\hat{\mathbf{J}}_\alpha^2|j_1, j_2, j, j_z\rangle &= \hbar^2 j_\alpha(j_\alpha + 1)|j_1, j_2, j, j_z\rangle , \quad \alpha = 1, 2.
\end{aligned} \tag{553}$$

The question is now how the states $|j_1, j_{1,z}\rangle|j_2, j_{2,z}\rangle$ and $|j_1, j_2, j, j_z\rangle$ are related. Let us first give the answer and then explain how to derive it. For fixed j_1 and j_2 we have

$$\boxed{|j_1, j_{1,z}\rangle|j_2, j_{2,z}\rangle = \sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{j_z=-j}^{j} C(j, j_z; j_1, j_{1,z}, j_2, j_{2,z}) \, |j_1, j_2, j, j_z\rangle \,,}$$

(554)

where the amplitudes $C(j, j_z; j_1, j_{1,z}, j_2, j_{2,z})$ are called *Clebsch-Gordan* coefficients. As the Clebsch-Gordan coefficients are tabulated we will not get into the details of how they are calculated in the general case. We note that the Clebsch-Gordan coefficients can be written as probability amplitudes

$$C(j, j_z; j_1, j_{1,z}, j_2, j_{2,z}) = \langle j_1, j_2, j, j_z | \Big(|j_1, j_{1,z}\rangle|j_2, j_{2,z}\rangle \Big).$$

(555)

So if we have a system of two "gyros" in a state of well-defined angular momentum, the Clebsch-Gordan coefficients provide the probability amplitudes for finding the first and second gyros in angular momentum eigenstates with quantum numbers $j_{1,z}$ and $j_{2,z}$ respectively.

16.1   ADDING TWO SPINS $1/2$

Let us investigate how these relations come about by considering the simplest case of $j_1 = j_2 = 1/2$. A basis of states is given by the products

$$|\uparrow\uparrow\rangle \,, \quad |\uparrow\downarrow\rangle \,, \quad |\downarrow\uparrow\rangle \,, \quad |\downarrow\downarrow\rangle \,.$$

(556)

The eigenvalues of $\hat{J}_z = \hat{J}_{1,z} + \hat{J}_{2,z}$ are easily worked out

$$\hat{J}_z|\uparrow\uparrow\rangle = \hbar|\uparrow\uparrow\rangle \,, \quad \hat{J}_z|\uparrow\downarrow\rangle = 0 = \hat{J}_z|\downarrow\uparrow\rangle \,, \quad \hat{J}_z|\downarrow\downarrow\rangle = -\hbar|\downarrow\downarrow\rangle \,.$$

(557)

This tells us that $|\uparrow\uparrow\rangle$ is an eigenstate of $\hat{J}_z$ and as the corresponding eigenvalue is non-degenerate it must also be an eigenstate of $\hat{\mathbf{J}}^2$.

Exercise 2

Show that the total angular momentum operator can be written as

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + \hat{J}_{1,+}\hat{J}_{2,-} + \hat{J}_{1,-}\hat{J}_{2,+} + 2\hat{J}_{1,z}\hat{J}_{2,z} \,,$$

(558)

where $J_{1,\pm} = J_{1,x} \pm iJ_{1,y}$ are ladder operators. Use this to show that

$$\hat{\mathbf{J}}^2|\uparrow\uparrow\rangle = 2\hbar^2|\uparrow\uparrow\rangle.$$

(559)

The ladder operators for total angular momentum are defined as

$$\hat{J}_\pm = \hat{J}_{1,\pm} + \hat{J}_{2,\pm} \,, \qquad J_{\alpha,\pm} = J_{\alpha,x} \pm iJ_{\alpha,y} \,, \quad \alpha = 1, 2.$$

(560)

As $[\hat{J}_-, \hat{\mathbf{J}}^2] = 0$ we can use these to construct eigenstates with the same $\hat{\mathbf{J}}^2$ quantum number from $|\uparrow\uparrow\rangle$. Recalling that $\hat{J}_{1,-}|\uparrow\rangle = \hbar|\downarrow\rangle$ we find that

$$\hat{J}_-|\uparrow\uparrow\rangle = \hbar\big(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\big) \,, \quad \hat{J}_-^2|\uparrow\uparrow\rangle = 2\hbar^2|\downarrow\downarrow\rangle \,.$$

(561)

Correctly normalizing the eigenstates we obtain a $j = 1$ representation of angular momentum

$$\boxed{|\uparrow\uparrow\rangle \,, \quad \frac{1}{\sqrt{2}}\big(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\big) \,, \quad |\downarrow\downarrow\rangle \,.}$$

(562)

The $\hat{J}_z$ quantum numbers of the three states are $1, 0, -1$ respectively. The states (562) are called *triplet states*. In terms of our general notations introduced earlier the three states are denoted by

$$|\frac{1}{2}, \frac{1}{2}, 1, 1\rangle , \quad |\frac{1}{2}, \frac{1}{2}, 1, 0\rangle , \quad |\frac{1}{2}, \frac{1}{2}, 1, -1\rangle. \tag{563}$$

We are left with one eigenstate with $j_z = 0$. As this has to be orthogonal to the $j_z = 0$ triplet state we conclude that it must be given by

$$\boxed{\frac{1}{\sqrt{2}} \left(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle \right) .}$$

$$\tag{564}$$

This state is called *singlet* and has $\hat{\mathbf{J}}^2$ quantum numbers zero. In our general notations it is denoted by

$$|\frac{1}{2}, \frac{1}{2}, 0, 0\rangle . \tag{565}$$

The Clebsch-Gordan coefficients can now be read off:

$$C(1, 1; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = 1 ,$$
$$C(1, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) = \frac{1}{\sqrt{2}} , \quad C(1, 0; \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = \frac{1}{\sqrt{2}} ,$$
$$C(1, -1; \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) = 1 ,$$
$$C(0, 0; \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = \frac{1}{\sqrt{2}} , \quad C(0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) = -\frac{1}{\sqrt{2}} . \tag{566}$$

Summary 2: Adding two spins 1/2

1. The eigenvalues of $\hat{J}_z$ on product states $|\sigma\tau\rangle$ is easy to calculate;

2. Note that maximal value of j_z, and hence j, is one. The $j_z = 1$ state is $|\uparrow\uparrow\rangle$;

3. Use the ladder operator $\hat{J}_-$ to obtain all other $j = 1$ states; This gives the *triplet*.

4. There remains one $j_z = 0$ state, which must be orthogonal to the $j = 1$, $j_z = 0$ state. This gives the *singlet*.

16.2 ADDING TWO SPINS 1

The idea behind adding two spins 1 is the same. We first note that the action of $\hat{J}_z$ on product states is simple

$$\hat{J}_z|1, j_{1,z}\rangle|1, j_{2,z}\rangle = \hbar(j_{1,z} + j_{2,z})|1, j_{1,z}\rangle|1, j_{2,z}\rangle . \tag{567}$$

This immediately tells us that the maximal value of j_z, and hence j, is 2 and

$$|1, 1, 2, 2\rangle = |1, 1\rangle|1, 1\rangle . \tag{568}$$

Using that the ladder operators act as

$$\hat{J}_{1,-}|1, j_z\rangle \propto |1, j_z - 1\rangle , \tag{569}$$

we can construct the other states in the $j = 2$ representation

$$\hat{J}_-|1, 1, 2, 2\rangle \propto |1, 0\rangle|1, 1\rangle + |1, 1\rangle|1, 0\rangle ,$$
$$\hat{J}_-^2|1, 1, 2, 2\rangle \propto |1, -1\rangle|1, 1\rangle + 2|1, 0\rangle|1, 0\rangle + |1, 1\rangle|1, -1\rangle ,$$
$$\hat{J}_-^3|1, 1, 2, 2\rangle \propto |1, -1\rangle|1, 0\rangle + |1, 0\rangle|1, -1\rangle ,$$
$$\hat{J}_-^4|1, 1, 2, 2\rangle \propto |1, -1\rangle|1, -1\rangle . \tag{570}$$

Normalizing the states we have

$$
\begin{aligned}
|1,1,2,2\rangle &= |1,1\rangle|1,1\rangle \,, \\
|1,1,2,1\rangle &= \frac{1}{\sqrt{2}}\Big(|1,0\rangle|1,1\rangle + |1,1\rangle|1,0\rangle\Big) \,, \\
|1,1,2,0\rangle &= \frac{1}{\sqrt{6}}\Big(|1,-1\rangle|1,1\rangle + 2|1,0\rangle|1,0\rangle + |1,1\rangle|1,-1\rangle\Big), \\
|1,1,2,-1\rangle &= \frac{1}{\sqrt{2}}\Big(|1,0\rangle|1,-1\rangle + |1,-1\rangle|1,0\rangle\Big) \,, \\
|1,1,2,-2\rangle &= |1,-1\rangle|1,-1\rangle \,.
\end{aligned}
\tag{571}
$$

According to our general rule the next representation we need to consider has $j = 1$. The $j_z = 1$ state must be orthogonal to $|1,1,2,1\rangle$, which tells us that

$$
|1,1,1,1\rangle = \frac{1}{\sqrt{2}}\Big(|1,0\rangle|1,1\rangle - |1,1\rangle|1,0\rangle\Big) \,.
\tag{572}
$$

Acting again with the ladder operator and normalizing the resulting states gives

$$
\begin{aligned}
|1,1,1,0\rangle &= \frac{1}{\sqrt{2}}\Big(|1,-1\rangle|1,1\rangle - |1,1\rangle|1,-1\rangle\Big) \,, \\
|1,1,1,-1\rangle &= \frac{1}{\sqrt{2}}\Big(|1,-1\rangle|1,0\rangle - |1,0\rangle|1,-1\rangle\Big) \,.
\end{aligned}
\tag{573}
$$

This leaves us with one missing state, which has $j = j_z = 0$. It must be orthogonal to both $|1,1,2,0\rangle$ and $|1,1,1,0\rangle$, which fixes it to be

$$
|1,1,0,0\rangle = \frac{1}{\sqrt{3}}\Big(|1,-1\rangle|1,1\rangle - |1,0\rangle|1,0\rangle + |1,1\rangle|1,-1\rangle\Big).
\tag{574}
$$

Bingo!

17 EPR EXPERIMENT AND BELL INEQUALITIES

Entanglement has very strange and counterintuitive consequences. A nice example is provided by the Gedankenexperiment put forward by Einstein, Podolsky and Rosen in 1935. They considered the consequences of the quantum mechanical prediction for such kinds of experiments to be so disturbing that they advocated the idea that QM cannot be the whole story. A simplified version of their Gedankenexperiment is shown in Fig. 14. A source creates electron/positron pairs through the decay of nuclei from between two
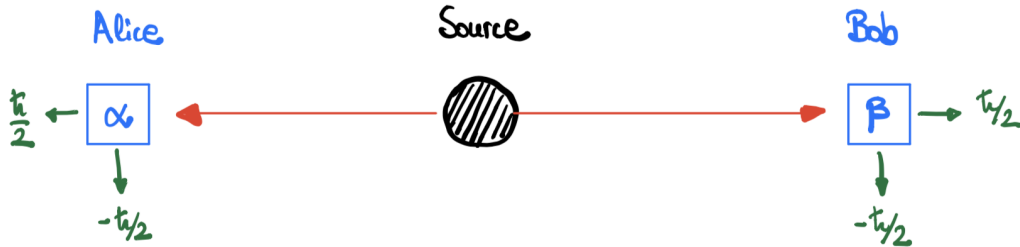

Figure 14: Setup for an EPR-like experiment.

states with both zero momentum and zero angular momentum. As electrons and positions are spin-1/2 particles the angular momentum part of the corresponding quantum state is therefore

$$
|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big).
\tag{575}
$$

Electron and positrons move away from the source with equal but opposite momenta and eventually reach two detectors (SG filters) operated by two physicists called Bob and Alice. The detectors measure the angular momentum along directions $\mathbf{n}_\alpha = (0, \sin(\alpha), \cos(\alpha))$ and $\mathbf{n}_\beta = (0, \sin(\beta), \cos(\beta))$ respectively. As we have seen before in our discussion of SG filters, Bob and Alice will always measure $\pm\hbar/2$, but with probabilities that depend on α and β. In order to describe the measurement outcomes we require the relation between the eigenstates $|\theta, \uparrow\rangle$ of the angular momentum operator in $\mathbf{n}_\theta$ direction and the eigenstates $|\uparrow\rangle$ $|\downarrow\rangle$ of $\hat{J}_z$

$$
\begin{aligned}
|\uparrow\rangle &= \cos(\alpha/2)|\alpha, \uparrow\rangle - i\sin(\alpha/2)|\alpha, \downarrow\rangle \ , \\
|\downarrow\rangle &= -i\sin(\alpha/2)|\alpha, \uparrow\rangle + \cos(\alpha/2)|\alpha, \downarrow\rangle \ .
\end{aligned}
\tag{576}
$$

Expressing $|\Psi\rangle$ in terms of these states gives

$$
\begin{aligned}
|\Psi\rangle &= \frac{i}{\sqrt{2}} \sin\left(\frac{\alpha-\beta}{2}\right)\left[|\uparrow, \alpha\rangle|\uparrow, \beta\rangle - |\downarrow, \alpha\rangle|\downarrow, \beta\rangle\right] \\
&+ \frac{1}{\sqrt{2}} \cos\left(\frac{\alpha-\beta}{2}\right)\left[|\uparrow, \alpha\rangle|\downarrow, \beta\rangle - |\downarrow, \alpha\rangle|\uparrow, \beta\rangle\right].
\end{aligned}
\tag{577}
$$

Let us first consider repeated separate measurements by Alice and Bob. Both of them will obtain results $\pm\hbar/2$ with equal probabilities $1/2$. So far so good. Things start to look strange once we consider combined measurements by Alice and Bob. Denoting the probability of Alice obtaining the result $\sigma\hbar/2$ and Bob the result $\sigma'\hbar/2$ by $P(\alpha, \sigma|\beta, \sigma')$ where $\sigma = \pm$, $\sigma' = \pm$, we have

$$
\begin{aligned}
P(\alpha, +|\beta, +) &= \left|\left(\langle\alpha, \uparrow|\langle\beta, \uparrow|\right)|\psi\rangle\right|^2 = \frac{1}{2}\sin^2\left(\frac{\alpha-\beta}{2}\right) \ , \\
P(\alpha, +|\beta, -) &= \left|\left(\langle\alpha, \uparrow|\langle\beta, \downarrow|\right)|\psi\rangle\right|^2 = \frac{1}{2}\cos^2\left(\frac{\alpha-\beta}{2}\right) \ , \\
P(\alpha, -|\beta, +) &= \left|\left(\langle\alpha, \downarrow|\langle\beta, \uparrow|\right)|\psi\rangle\right|^2 = \frac{1}{2}\cos^2\left(\frac{\alpha-\beta}{2}\right) \ , \\
P(\alpha, -|\beta, -) &= \left|\left(\langle\alpha, \downarrow|\langle\beta, \downarrow|\right)|\psi\rangle\right|^2 = \frac{1}{2}\sin^2\left(\frac{\alpha-\beta}{2}\right) \ .
\end{aligned}
\tag{578}
$$

A useful quantity to consider is the correlation coefficient defined as the probability of equal outcomes minus the probability of different outcomes

$$
C(\alpha, \beta) = \sum_{\sigma=\pm} P(\alpha, \sigma|\beta, \sigma) - P(\alpha, \sigma|\beta, -\sigma) = -\cos(\alpha - \beta).
\tag{579}
$$

To see that (578) is quite strange consider the case $\alpha = \beta$. Let say Alice measures first and obtains the result $\hbar/2$ $(-\hbar/2)$. Then Bob will obtain the result $-\hbar/2$ $(\hbar/2)$ *with certainty.* It is as if the particle Bob measures somehow knew the outcome of Alice's result! We can arrange things in such a way that the time elapsed between Bob's and Alice's measurements is too short to enable information to travel between them, which makes the perfect correlation between the measurements look absurd. One way of avoiding is to introduce *hidden variables.* Let's postulate that the probabilistic nature of QM is merely a result of our lack of knowledge of certain deterministic properties of the two particles. We could for example assume that the particles carry common information which determines measurement outcomes. The first and second particles could be characterized by some functions $\sigma_A(\alpha, \lambda) = \pm 1/2$ and $\sigma_B(\beta, \lambda) = \pm 1/2$ that deterministically determine the outcome of angular momentum measurements along angles α and β respectively. Importantly, as the two particles were created together, the two functions could be *correlated.* For example we could have $\sigma_B(\alpha, \lambda) = -\sigma_A(\alpha, \lambda)$ and this could explain the perfect anticorrelation of the measurements in this case. The parameter λ is unknown, and measurements correspond to averages over λ with some probability density $\rho(\lambda)$. Equipped with this model we can now make predictions for measurements, e.g.

$$
\begin{aligned}
P(\alpha, +) &= \int d\lambda \, \rho(\lambda) \left(\frac{1}{2} + \sigma_A(\alpha, \lambda)\right) \ , \\
P(\alpha, -) &= \int d\lambda \, \rho(\lambda) \left(\frac{1}{2} - \sigma_A(\alpha, \lambda)\right).
\end{aligned}
\tag{580}
$$

To agree with the quantum mechanical predictions we want these to equal 1/2. Joint probabilities can be calculated analogously

$$P(\alpha, \tau | \beta, \tau') = \int d\lambda \, \rho(\lambda) \left(\frac{1}{2} + \tau \sigma_A(\alpha, \lambda) \right) \left(\frac{1}{2} + \tau' \sigma_B(\beta, \lambda) \right). \tag{581}$$

Using these results we find that the correlation coefficient can be written as

$$C(\alpha, \beta) = 4 \int d\lambda \, \rho(\lambda) \, \sigma_A(\alpha, \lambda) \, \sigma_B(\beta, \lambda). \tag{582}$$

Let us now consider a situation where Alice (Bob) chooses among two measurement directions parametrized by angles α and α' (β and β'). Then the quantity

$$s(\lambda, \alpha, \alpha', \beta, \beta') = \sigma_A(\alpha, \lambda) \big[\sigma_B(\beta, \lambda) - \sigma_B(\beta', \lambda) \big] + \sigma_A(\alpha', \lambda) \big[\sigma_B(\beta, \lambda) + \sigma_B(\beta', \lambda) \big] \tag{583}$$

can only take the values $\pm\frac{1}{2}$. Hence

$$-\frac{1}{2} \leq \int d\lambda \rho(\lambda) \, s(\lambda, \alpha, \alpha', \beta, \beta') \leq \frac{1}{2}. \tag{584}$$

Expressing the integral in terms of correlation coefficients gives *Bell's inequality*

$$\boxed{|C(\alpha, \beta) - C(\alpha, \beta') + C(\alpha', \beta) + C(\alpha', \beta')| \leq 2.} \tag{585}$$

Importantly the quantum mechanical result (579) violates this inequality, i.e. there are choices for $\alpha, \alpha', \beta, \beta'$ such that the left hand side exceeds 2. To see this recall that the QM result for the correlation coefficient is $C(\alpha, \beta) = -\cos(\alpha - \beta)$. Choosing

$$\alpha = 0 \,, \alpha' = \frac{\pi}{2} \,, \beta = \frac{\pi}{4}, \, \beta' = \frac{3\pi}{4} \tag{586}$$

gives

$$|C(\alpha, \beta) - C(\alpha, \beta') + C(\alpha', \beta) + C(\alpha', \beta')| = 2\sqrt{2} > 2. \tag{587}$$

As measurements are found to be in agreement with QM predictions, this means that they are incompatible with hidden variable theories of the class discussed here!

Homework 11: Composite Systems

5.10 A system AB consists of two non-interacting parts A and B. The dynamical state of A is described by $|a\rangle$, and that of B by $|b\rangle$, so $|a\rangle$ satisfies the TDSE for A and similarly for $|b\rangle$. What is the ket describing the dynamical state of AB? In terms of the Hamiltonians H_A and H_B of the subsystems, write down the TDSE for the evolution of this ket and show that it is automatically satisfied. Do H_A and H_B commute? How is the TDSE changed when the subsystems are coupled by a small dynamical interaction H_{int}? If A and B are harmonic oscillators, write down H_A, H_B. The oscillating particles are connected by a weak spring. Write down the appropriate form of the interaction Hamiltonian H_{int}. Does H_A commute with H_{int}? Explain the physical significance of your answer.

5.11 Explain what is implied by the statement that "the physical state of system A is correlated with the state of system B." Illustrate your answer by considering the momenta of cars on (i) London's circular motorway (the M25) at rush-hour, and (ii) the road over the Nullarbor Plain in southern Australia in the dead of night.

5.12 Consider a system of two particles of mass m that each move in one dimension along a given rod. Let $|1; x\rangle$ be the state of the first particle when it's at x and $|2; y\rangle$ be the state of the second particle when it's at y. A complete set of states of the pair of particles is $\{|xy\rangle\} = \{|1; x\rangle |2; y\rangle\}$. Write down the Hamiltonian of this system given that the particles attract one another with a force that's equal to C times their separation.

Suppose that the particles experience an additional potential $V(x, y) = \frac{1}{2}C(x + y)^2$. Show that the dynamics of the two particles is now identical with that of a single particle that moves in two dimensions in a particular potential $\Phi(x, y)$, and give the form of Φ.

5.13 In the lectures we considered measurements by Alice and Bob on an entangled pair of spins prepared in a singlet state. Bob measures the component of spin along an axis that is inclined by angle θ to that used by Alice. Given the expression

$$|-, \boldsymbol{b}\rangle = \cos(\theta/2)\, \mathrm{e}^{\mathrm{i}\phi/2}|-\rangle - \sin(\theta/2)\, \mathrm{e}^{-\mathrm{i}\phi/2}|+\rangle,$$

for the state of a spin-half particle in which it has spin $-\frac{1}{2}$ along the direction $\boldsymbol{b}$ with polar angles (θ, ϕ), with $|\pm\rangle$ the states in which there is spin $\pm\frac{1}{2}$ along the z-axis, calculate the amplitude that Bob finds the positron's spin to be $-\frac{1}{2}$ given that Alice has found $+\frac{1}{2}$ for the electron's spin. Hence show that the corresponding probability is $\cos^2(\theta/2)$.

Part VI
THE HYDROGEN ATOM

One of the great early triumphs of QM was to provide an explanation for emission spectra of atoms. We now have all pieces in place to work out the quantum theory of the *gross structure* of the simplest atom, hydrogen. For later convenience we will consider the case of *hydrogen-like ions*, where a single electron is bound to a nucleus of charge Ze. In order to arrive at an exactly solvable problem we will make the following simplifying assumptions:

1. We will ignore the fact that both the electron and the nucleus have spin;

2. We neglect relativistic effects and take the interaction between the electron and the nucleus to be described by the Coulomb interaction;

These assumptions lead to the following Hamiltonian

$$H = \frac{\mathbf{p}_n^2}{2m_n} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0|\hat{\mathbf{x}}_e - \hat{\mathbf{x}}_n|} \ . \tag{588}$$

This Hamiltonian has the attractive feature that its energy eigenvalues and eigenfunctions can be calculated exactly. You will see later how to take the spin degrees of freedom and relativistic effects into account. It turns out that these only lead to small corrections (which however can be measured).

18 POSITION REPRESENTATION

We have seen before that the position representation of the TISE takes the form

$$\left[-\frac{\hbar^2}{2m_n}\boldsymbol{\nabla}_n^2 - \frac{\hbar^2}{2m_e}\boldsymbol{\nabla}_e^2 - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{x}_e - \mathbf{x}_n|} \right] \psi(\mathbf{x}_e, \mathbf{x}_n) = E\psi(\mathbf{x}_e, \mathbf{x}_n) \ . \tag{589}$$

We first rewrite this equation in terms of centre-of-mass co-ordinates

$$\mathbf{X} = \frac{m_e \mathbf{x}_e + m_n \mathbf{x}_n}{m_e + m_n} \ , \qquad \mathbf{r} = \mathbf{x}_e - \mathbf{x}_n \ . \tag{590}$$

After some calculations we find that

$$-\frac{\hbar^2}{2m_n} \boldsymbol{\nabla}_n^2 - \frac{\hbar^2}{2m_e} \boldsymbol{\nabla}_e^2 = -\frac{\hbar^2}{2} \left[\frac{1}{m_e + m_n} \boldsymbol{\nabla}_{\mathbf{X}}^2 + \frac{1}{\mu} \boldsymbol{\nabla}_{\mathbf{r}}^2 \right] , \tag{591}$$

where the *reduced mass* μ is given by

$$\boxed{\mu = \frac{m_e m_n}{m_e + m_n}} \ . \tag{592}$$

In the case of hydrogen we have $m_n = 1836 m_e$ and hence $\mu = 0.99945 m_e$, so the reduced mass is extremely close to the electron mass. Substituting (589) back into (587) we arrive at

$$\boxed{\left[-\frac{\hbar^2}{2(m_e + m_n)} \boldsymbol{\nabla}_{\mathbf{X}}^2 - \frac{\hbar^2}{2\mu} \boldsymbol{\nabla}_{\mathbf{r}}^2 - \frac{Ze^2}{4\pi\epsilon_0 |\mathbf{r}|} \right] \psi(\mathbf{X}, \mathbf{r}) = E\psi(\mathbf{X}, \mathbf{r})} \ . \tag{593}$$

This PDE can be solved by separation of variables. Substituting

$$\psi(\mathbf{X}, \mathbf{r}) = \phi(\mathbf{X}) \chi(\mathbf{r}) \tag{594}$$

back into (591) and dividing by $\psi(\mathbf{X}, \mathbf{r})$ we obtain

$$\frac{1}{\phi(\mathbf{X})} \left[-\frac{\hbar^2}{2(m_e + m_n)} \boldsymbol{\nabla}_{\mathbf{X}}^2 \phi(\mathbf{X}) \right] + \frac{1}{\chi(\mathbf{r})} \left[-\frac{\hbar^2}{2\mu} \boldsymbol{\nabla}_{\mathbf{r}}^2 - \frac{Ze^2}{4\pi\epsilon_0 |\mathbf{r}|} \right] \chi(\mathbf{r}) = E. \tag{595}$$

As the first term only depends on $\mathbf{X}$ and the second depends only on $\mathbf{r}$ they can sum up to a constant only if they both are constant. This breaks the TISE into two pieces

$$\boxed{\begin{aligned} -\frac{\hbar^2}{2(m_e + m_n)} \boldsymbol{\nabla}_{\mathbf{X}}^2 \phi(\mathbf{X}) &= E_{\mathrm{CM}} \phi(\mathbf{X}) \ , \\ \left[-\frac{\hbar^2}{2\mu} \boldsymbol{\nabla}_{\mathbf{r}}^2 - \frac{Ze^2}{4\pi\epsilon_0 |\mathbf{r}|} \right] \chi(\mathbf{r}) &= E_r \chi(\mathbf{r}) \ , \end{aligned}} \tag{596}$$

where the energy eigenvalue equals the sum of the energies of the centre of mass motion and the relative motion

$$E = E_{\mathrm{CM}} + E_r. \tag{597}$$

We see that the problem splits into two parts

- The centre of mass has only kinetic energy and the corresponding wave functions are plane waves

$$\phi(\mathbf{X}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{K} \cdot \mathbf{X}} \ , \quad E_{\mathrm{CM}} = \frac{\hbar^2 \mathbf{K}^2}{2(m_n + m_e)} \ . \tag{598}$$

- The TISE describing the relative motion looks like the TISE for a particle with mass μ in a Coulomb potential centred at zero. Our task in to solve this differential equation.

19   Rotational invariance and radial Schrödinger equation

We may now use our previous result on Schrödinger equations for particles in rotationally symmetric potentials. Recalling that in spherical polar co-ordinates we have

$$\nabla_{\mathbf{r}}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\frac{\hat{L}^2}{\hbar^2}, \tag{599}$$

we can solve our PDE for the wave function by separation of variables

$$\chi(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) . \tag{600}$$

Substituting (598) into the TISE we have

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\frac{\hat{L}^2}{\hbar^2} \right) - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{r}|} - E_{n\ell} \right] R_{n\ell}(r)Y_{\ell m}(\theta, \phi) = 0. \tag{601}$$

Using that $\hat{L}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell+1)Y_{\ell m}(\theta, \phi)$ and dividing the resulting equation by $Y_{\ell m}(\theta, \phi)$ we arrive at the radial Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} \right] + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) R_{n\ell}(r) = E_{n\ell}R_{n\ell}(r) . \tag{602}$$

It is useful to rewrite this differential equation in terms of the dimensionless variable

$$\rho = \frac{r}{a_Z} , \quad a_Z = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2 Z}. \tag{603}$$

Replacing μ by m_e and setting $Z = 1$ the length scale a_Z reduces to the *Bohr radius*

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.2917721067(12) \times 10^{-11}m . \tag{604}$$

After the change of variables the radial Schrödinger equation reads

$$-R_{n\ell}''(\rho) - \frac{2}{\rho}R_{n\ell}'(\rho) + \left(\frac{\ell(\ell+1)}{\rho^2} - \frac{2}{\rho} \right) R_{n\ell}(\rho) = \epsilon_{n\ell}R_{n\ell}(\rho) , \tag{605}$$

where

$$\epsilon_{n\ell} = \frac{2\mu a_Z^2}{\hbar^2}E_{n\ell}. \tag{606}$$

19.1   Small-ρ behaviour

For $\rho \to 0$ we have a highly divergent term proportional to $\ell(\ell+1)/\rho^2$, which for $\ell \geq 1$ is much larger than the terms proportional to $Ze^2/(4\pi\epsilon_0\rho)$ and $\epsilon_{n\ell}$. The leading behaviour for $\rho \to 0$ is therefore determined by the simpler ODE

$$-R_{n\ell}''(\rho) - \frac{2}{\rho}R_{n\ell}'(\rho) + \frac{\ell(\ell+1)}{\rho^2}R_{n\ell}(\rho) = 0 , \quad \rho \to 0. \tag{607}$$

Making the Ansatz $R_{n\ell} \propto \rho^s$ and substituting it back into (605) we obtain two solutions

$$s_+ = \ell , \quad s_- = -(\ell+1) . \tag{608}$$

The second solution is not allowed as the wave function would be non-normalizable due to the singularity at the origin. Hence we have

$$R_{n\ell}(\rho) \propto \rho^\ell , \quad \text{for } \rho \to 0. \tag{609}$$

We have shown this for $\ell \geq 1$ but it turns out that it is correct for $\ell = 0$ as well (see below).

19.2   Large-ρ behaviour

For large values of ρ we can neglect the terms proportional to $\ell(\ell+1)/\rho^2$ and $Ze^2/(4\pi\epsilon_0\rho)$ compared to the term proportional to $\epsilon_{n\ell}$. The radial Schrödinger equation can then be rewritten as

$$\frac{R''_{n\ell}(\rho)}{R_{n\ell}(\rho)} + \frac{2}{\rho}\frac{R'_{n\ell}(\rho)}{R_{n\ell}(\rho)} = -\epsilon_{n\ell} , \quad \rho \to \infty. \tag{610}$$

Now we use that we are interested in *bound state* solutions to the TISE, that is radial wave functions that vanish at infinity. This tells us that the behaviour at large ρ is exponential

$$R_{n\ell}(\rho) \propto \rho^\alpha e^{-\lambda_{n\ell}\rho} , \quad \lambda_{n\ell}^2 = -\epsilon_{n\ell} > 0. \tag{611}$$

This tells us that bound state solutions correspond to negative energy

$$E_{n\ell} < 0 . \tag{612}$$

We note that the power-law factor ρ^α is not fixed by the simple $\rho \to \infty$ argument.

19.3   Full solution

We now make the following Ansatz for the radial wave functions

$$R_{n\ell}(\rho) = \rho^\ell e^{-\lambda_{n\ell}\rho} F_{n\ell}(\rho) . \tag{613}$$

Substituting this into (603) we obtain an ODE for the unknown functions $F_{n\ell}(\rho)$

$$-\rho F''_{n\ell}(\rho) - 2(\ell+1-\lambda_{n\ell}\rho)F'_{n\ell}(\rho) + 2(\lambda_{n\ell}(\ell+1)-1)F_{n\ell}(\rho) = 0. \tag{614}$$

Finally we change variables to

$$y = 2\rho\lambda_{n\ell} . \tag{615}$$

Defining $F_{n\ell}(\rho) = f_{n\ell}(y)$ we arrive at the following ODE for $f_{n\ell}(y)$

$$\boxed{yf''_{n\ell}(y) + f'_{n\ell}(y)\big(2\ell+2-y\big) + \big(\frac{1}{\lambda_{n\ell}}-\ell-1\big)f_{n\ell}(y) = 0.} \tag{616}$$

We can recognize this as a *generalized Laguerre equation*. The standard form of the latter is

$$yg''(y) + g'(y)\big(\alpha+1-y\big) + kg(y) = 0. \tag{617}$$

We seek solutions to this equation that grow sufficiently slowly when $y \to \infty$ so that the associated radial part of the wave function $R_{n\ell}(\rho)$ still vanishes when $\rho \to \infty$ (as we are looking for bound state solutions). This is the case only when k are non-negative integers, and the corresponding solutions to (615) are the *Laguerre polynomials*

$$g(y) = L_k^{(\alpha)}(y) , \qquad k = 0, 1, 2, \ldots \tag{618}$$

We can map our problem onto this by taking

$$\alpha = 2\ell+1 , \qquad k = \frac{1}{\lambda_{n\ell}}-\ell-1 . \tag{619}$$

The requirement that the solutions to our differential equation vanish when $\rho \to \infty$ quantizes the allowed values of $\lambda_{n\ell}$ and hence the energy! As k is a non-negative integer $1/\lambda_{n\ell}$ must be a positive integer such that

$$\boxed{\lambda_{n\ell} = \frac{1}{n} , \quad n \geq 1 , \ \ell < n.} \tag{620}$$

Putting everything together we arrive at the following result for the solutions of the radial Schrödinger equation

$$\boxed{R_{n\ell}(r) = N_{n\ell} \, r^\ell \, L_{n-\ell-1}^{(2\ell+1)}(2r/na_Z) \, e^{-(r/na_Z)} \, ,}$$

(621)

where $N_{n\ell}$ are normalizations fixed by the requirement that the wave function is normalized

$$1 = \int_0^\infty dr r^2 \int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\phi |R_{n\ell}(r) Y_{\ell m}(\theta, \phi)|^2 = \int_0^\infty dr r^2 |R_{n\ell}(r)|^2.$$

(622)

20 ENERGY EIGENVALUES AND EMISSION SPECTRA OF HYDROGEN

We have succeeded in constructing solutions to the TISE of the form

$$\boxed{\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \, ,}$$

(623)

labelled by three good quantum numbers

- The positive integer n is called *principal quantum number*;

- The non-negative integer ℓ is the quantum number associated with total orbital angular momentum and has a range

$$\boxed{0 \le \ell \le n - 1 \, ;}$$

(624)

- The integer m is the quantum number associated with the z-component of orbital angular momentum and has a range

$$\boxed{-\ell \le m \le \ell.}$$

(625)

The energy eigenvalues associated with $\psi_{n\ell m}(r, \theta, \phi)$ are

$$\boxed{E_n = -\frac{E_R}{n^2} \frac{\mu Z^2}{m_e} \, , \quad E_R = \frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = 13.605693\text{eV}}.$$

(626)

Here E_R is called *Rydberg energy. Importantly the energies only depend on the principal quantum number n.* This means that the energy eigenstates are degenerate with degeneracies

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2.$$

(627)

20.1 EMISSION SPECTRA

The emission spectra of hydrogen are obtained by considering transitions between different energy eigenstates. You will see why this is in the Further QM course. The basic idea is that the atom is initially in an eigenstate with energy E_m and then undergoes a transition to another energy eigenstate E_n by emitting a photon (hence we must have $m > n$). The photon energy is

$$h\nu = E_m - E_n = \frac{\mu}{m_e} E_R \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \, .$$

(628)

The photon energies can be grouped in so-called *series*. The first few of these are
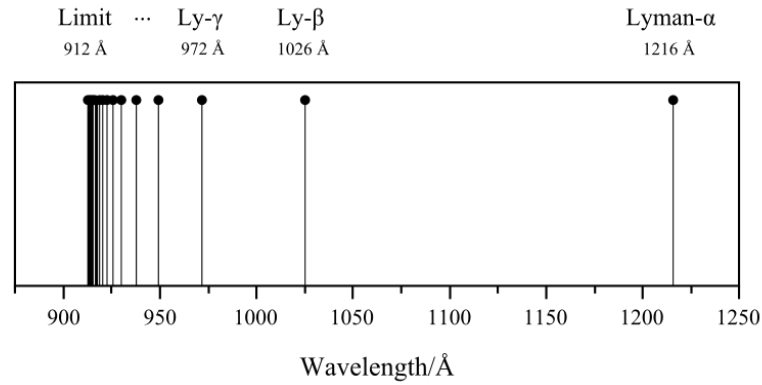
Figure 15: Lyman series for hydrogen atom spectral lines.

1. Lyman series: $n = 1$, $m = 2, 3, 4 \ldots$

   This was discovered by Theodore Lyman between 1906 and 1914. All the wavelengths in the Lyman series are in the ultraviolet.

2. Balmer series: $n = 2$, $m = 3, 4, 5 \ldots$

   This is named after Johann Balmer, who discovered the Balmer formula, an empirical equation to predict the Balmer series, in 1885.

Figure 16: The four visible hydrogen emission spectrum lines in the Balmer series.

3. Paschen series: $n = 3$, $m = 4, 5, 6 \ldots$

   Named after the German physicist Friedrich Paschen who first observed them in 1908. The Paschen lines all lie in the infrared.

A good question is how well our "gross structure" calculation accounts for these spectral lines. Our results for the Lyman series are $\lambda_j = 121.569$, 102.574, 97.2556, 94.9762, 93.7822, while the measured values are are $\lambda_j = 121.57$, 102.57, 97.254, 94.974, 93.780. We see that that our simple theory already gives an excellent account of experimental observations! Spin and relativistic effects account for the differences.

Homework 12: THE HYDROGEN ATOM

6.1 Some things about hydrogen's gross structure that it's important to know (ignore spin throughout, and you may set the reduced mass to be equal to the electron mass):

(a) What quantum numbers characterise stationary states of hydrogen?

(b) What combinations of values of these numbers are permitted?

(c) Give the formula for the energy of a stationary state in terms of the Rydberg $\mathcal{R}$. What is the value of $\mathcal{R}$ in eV?

(d) How many stationary states are there in the first excited level and in the second excited level?

(e) What is the wavefunction of the ground state?

(f) Write down an expression for the mass of the reduced particle.

(g) We can apply hydrogenic formulae to any two charged particles that are electrostatically bound. How does the ground-state energy then scale with (i) the mass of the reduced particle, and (ii) the charge Ze on the nucleus? (iii) How does the radial scale of the system scale with Z?

6.2 An electron is in the ground state of a hydrogen-like atom with nuclear charge $+Ze$. For simplicity neglect the difference between the reduced mass and the electron mass.

(a) What is its average distance from the nucleus?

(b) At what distance from the nucleus is it most likely to be found?

(c) Show that the expectation value of the potential energy of the electron is the same as that given by the Bohr model, namely $-Ze^2/4\pi\epsilon_0 r_0$ where $r_0 = a_0/Z$.

(d) Show that the expectation value of the kinetic energy is equal to the value given by the Bohr model, namely $Ze^2/8\pi\epsilon_0 r_0$.

(e) Hence verify that the expectation value of the total energy agrees with the Bohr model.

6.3 Show that the speed of a classical electron in the lowest Bohr orbit is $v = \alpha c$, where $\alpha = e^2/4\pi\epsilon_0\hbar c$ is the fine-structure constant. What is the corresponding speed for a hydrogen-like Fe ion (atomic number $Z = 26$)? Given these results, what fractional errors must we expect in the energies of states that we derive from non-relativistic quantum mechanics.

6.4 Show that the electric field experienced by an electron in the ground state of hydrogen is of order $5 \times 10^{11}\,\mathrm{V\,m^{-1}}$. Why is it impossible to generate comparable macroscopic fields using charged electrodes. Lasers are available that can generate beam fluxes as big as $10^{22}\,\mathrm{W\,m^{-2}}$. Show that the electric field in such a beam is of comparable magnitude.

6.5 Positronium consists of an electron e^- and a positron e^+ (both spin-half and of equal mass) in orbit around one another. What are its energy levels? By what factor is a positronium atom bigger than a hydrogen atom?

6.6 Muonium consists of an electron e^- and a positive muon μ^+ (both spin-half particles but $m_\mu = 206.7 m_\mathrm{e}$) in orbit around one another. What are its energy levels? By what factor is muonium atom bigger than a hydrogen atom?

6.7 The emission spectrum of the He$^+$ ion contains the Pickering series of spectral lines that is analogous to the Lyman, Balmer and Paschen series in the spectrum of hydrogen

Balmer $i = 1, 2, \ldots$	0.456806	0.616682	0.690685	0.730884
Pickering $i = 2, 4, \ldots$	0.456987	0.616933	0.690967	0.731183

The table gives the frequencies (in $10^{15}\,\mathrm{Hz}$) of the first four lines of the Balmer series and the first four even-numbered lines of the Pickering series. The frequencies of these lines in the Pickering series

are almost coincident with the frequencies of lines of the Balmer series. Explain this finding. Provide a quantitative explanation of the small offset between these nearly coincident lines in terms of the reduced mass of the electron in the two systems. (In 1896 E.C. Pickering identified the odd-numbered lines in his series in the spectrum of the star ζ Puppis. Helium had yet to be discovered and he believed that the lines were being produced by hydrogen. Naturally he confused the even-numbered lines of his series with ordinary Balmer lines.)

21 EXPLICIT FORM OF THE WAVE FUNCTIONS

21.1 GROUND STATE

The ground state has quantum numbers $n = 1$, $\ell = m = 0$. Its normalized wave function is

$$\chi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_Z^3}} e^{-r/a_Z} . \tag{629}$$

21.2 $n = 2$ STATES

For principal quantum number $n = 2$ there are two allowed values of ℓ. The so-called $2s$ state has $\ell = m = 0$ and its wave function is

$$\chi_{200}(r, \theta, \phi) = \frac{1}{\sqrt{8\pi a_Z^3}} \left[1 - \frac{r}{2a_Z} \right] e^{-r/2a_Z} . \tag{630}$$

The other allowed value is $\ell = 1$. There are altogether three such states with $\hat{L}_z$ quantum numbers $m = 0, \pm 1$. The wave-functions of these so-called $2p$ states are

$$\begin{aligned}
\chi_{211}(r, \theta, \phi) &= -\frac{1}{8\sqrt{\pi a_Z^3}} \frac{r}{a_Z} e^{-r/2a_Z} \sin(\theta) e^{i\phi} , \\
\chi_{210}(r, \theta, \phi) &= -\frac{1}{4\sqrt{2\pi a_Z^3}} \frac{r}{a_Z} e^{-r/2a_Z} \cos(\theta) , \\
\chi_{21-1}(r, \theta, \phi) &= \frac{1}{8\sqrt{\pi a_Z^3}} \frac{r}{a_Z} e^{-r/2a_Z} \sin(\theta) e^{-i\phi} .
\end{aligned} \tag{631}$$

21.3 RADIAL PROBABILITY DENSITY

Given that the reduced mass μ is very close to the electron mass we can think of $|\chi_{n\ell m}(r, \theta, \phi)|^2$ as the probability density to find the electron at co-ordinates (r, θ, ϕ). The probability of finding the electron between (r, θ, ϕ) and $(r + dr, \theta + d\theta, \phi + d\phi)$ is obtained by multiplying with the volume element in spherical polar co-ordinates, i.e.

$$P(r, \theta, \phi) = |\chi_{n\ell m}(r, \theta, \phi)|^2 \, r^2 \sin(\theta) dr \, d\theta \, d\phi \tag{632}$$

The radial part of this expression

$$P(r) \, dr = |R_{n\ell}(r)|^2 r^2 \, dr \tag{633}$$

is shown in Fig. 17. We see that in its ground state the electron is most likely to be found at a distance of one Bohr radius from the nucleus.
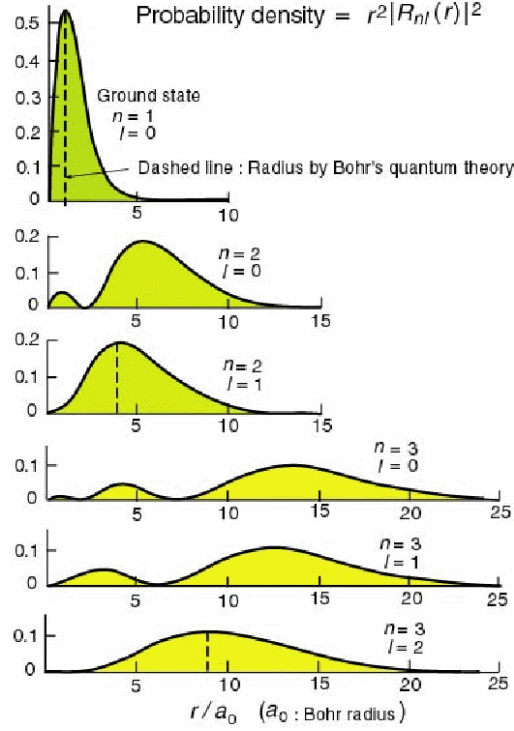
Figure 17: $r^2|R_{n\ell}(r)|^2$ for the first few energy eigenstates in hydrogen.

21.4 VISUALISING THE ANGULAR DEPENDENCE

The angular dependence is described by $|Y_{\ell m}(\theta, \phi)|^2$ and a useful way of visualising the angular dependence is to use that $|Y_{\ell m}(\theta, \phi)|^2$ is in fact independent of ϕ, i.e. rotationally symmetric around the z-axis. Plotting for each value of θ a point at distance $r = |Y_{\ell m}(\theta, \phi)|^2$ from the origin then produces a contour $r(\theta)$, and rotating it around the z-axis gives an account of the angular probability distribution.
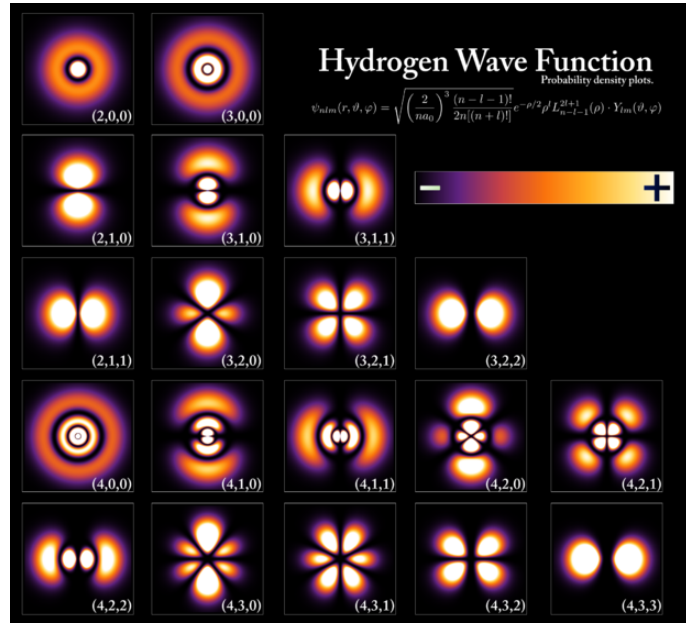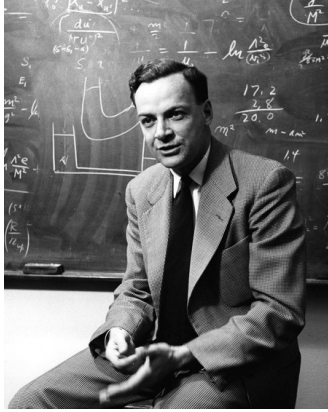
Figure 18: $r^2|R_{n\ell}(r)|^2$ for the first few energy eigenstates in hydrogen.

Richard Feynman (Nobel Prize in Physics 1965).

We started with Feynman, and we will finish with him as well: *If you think you understand Quantum Mechanics, you don't understand Quantum Mechanics.*