A3: Quantum Mechanics

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November 15, 2016

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1. *Introduction*

This chapter will serve as an introduction to the fundamental concepts that form the basis of Quantum Mechanics, including:

- Quantum States
- Operators and Observables
- The Position Representation
- The Momentum Representation

This material will assume familiarity with Dirac notation and the mathematics of operators found in Chapter 1 of the Mathematical Methods notes. It will form the mathematical and conceptual groundwork from which one can work to understand more interesting concepts.Many texts will make use of the hat symbol to denote an operator. That shall not be done here, as it turns out to be more trouble than it is worth; most things you will write will be operators!

"Quantum Mechanics is a unique and special subject to study as an undergraduate as it is the great intellectual accomplishment of the last century. It is the piece of Physics the least understood...It is fundamentally mysterious, and is extraordinarily specific to Physics, and yet it underpins everything." - Professor James Binney

1.1 Quantum States

Many readers may already be familiar with the general concept of a quantum state; the words like to get thrown around a lot in popular physics as a loose term used to refer to some configuration of a system. Here, we shall define it more rigorously.

The state of a quantum-mechanical system can be specified by giving the quantum amplitudes (a_i, which may be complex) to possible outcomes of measurements, and we can completely specify the state of a system by giving a complete set of quantum amplitudes. We will see what exactly a quantum amplitude represents shortly. For example, consider the spin of a spin-1/2 particle, such as an electron, in the z-direction. This can take on two values; $\pm 1/2\hbar$. We can then assign the amplitudes as

$$\begin{aligned} a_+ &: \quad \text{amplitude to measure} \quad +\frac{1}{2}\hbar \\ a_- &: \quad \text{amplitude to measure} \quad -\frac{1}{2}\hbar \end{aligned}$$

This means that the set $\{a_+, a_-\}$ forms a complete set of amplitudes for the state of the system.

The knowledge of any quantum-mechanical system can be encoded in some quantum state that is written as $|\psi\rangle$. Evidently, the system may be in a linear combination of some possible basis states $|i\rangle$, and so it can be written as

$$\boxed{|\psi\rangle = \sum_i a_i |i\rangle} \tag{1.1}$$

where a_i are the quantum amplitudes of each state. We can now begin to answer the question of what exactly a quantum amplitude is. Consider $\langle\psi|\psi\rangle$.

$$\begin{aligned} \langle\psi|\psi\rangle &= \left(\sum_i a_i^* \langle i|\right)\left(\sum_j a_j |j\rangle\right) \\ &= \sum_{ij} a_i^* a_j \langle i|j\rangle \\ &= \sum_{ij} a_i^* a_j \delta_{ij} \\ &= \sum_i |a_i|^2 = 1 \end{aligned}$$

Let us assume that $|\psi\rangle$ is normalised such that this last sum is equal to one. Then we have the sum of the moduli of the quantum amplitudes are equal to one. The system must, by definition, be in some linear combination of the states $|i\rangle$; in other words, it has unit probability to be in said linear combination. Thus, we can think of *the modulus-square of the quantum amplitudes a_i as being the probability of finding the system in the state $|i\rangle$.*

Suppose that we wanted to know the probability of the system being in some state $|k\rangle$ for $|k\rangle \in \{|i\rangle\}$. We can then find a_k by

$$\begin{aligned}\langle k|\psi\rangle &= \langle k| \left(\sum_i a_i |i\rangle\right) \\ &= \sum_i a_i \langle k|i\rangle \\ &= \sum_i a_i \delta_{ik} \\ &= a_k\end{aligned}$$

In a very similar way to writing a vector as a linear combination of some basis, we can find the quantum-amplitudes as

$$\boxed{a_k = \langle k|\psi\rangle} \tag{1.2}$$

Let us consider an example. *A particle can 'tunnel' between potential wells that form a chain, and so it's state can be written as*

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

where

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

Find the probability of the particle being in the centre well, or anywhere to the 'right' (towards positive n) of it.

Let us begin by finding the probability of being in the n^{th} well. Evidently, this is just square of the real part of a_n. Thus,

$$P_n = \frac{1}{2} \cdot \frac{1}{3^n}$$

Hence, the probability of being in the centre well or anywhere to the right of it is given by an infinite sum.

$$\begin{aligned}P_{\geq 0} &= |a_o|^2 + |a_1|^2 + |a_2|^2 + \dots \\ &= \frac{1}{2} + \frac{1}{2} \cdot \frac{1}{3} + \frac{1}{2} \cdot \frac{1}{3^2} + \dots \\ &= \frac{1}{2} \sum_{n=0}^{\infty} \frac{1}{3^n} \\ &= \frac{1}{2} \cdot \frac{1}{1 - 1/3} \\ \rightarrow P_{\geq 0} &= \frac{3}{4}\end{aligned}$$

We could have also performed this calculation very quickly by recognising the symmetry of the problem; the probability of it being on both sides of the centre must be the same. Thus, as $P_o = 1/2$, we can automatically conclude that $P_{\geq 0} = 3/4$.

1.1.1 Energy Representation

Suppose that our system is has a set (which may be infinite) of allowable energy states E_i, each with quantum amplitudes a_i. As usual, we can write

$$|\psi\rangle = \sum_i a_i |i\rangle$$

What is the physical meaning of $|k\rangle$, for some k? Suppose that $|\psi\rangle = |k\rangle$. We clearly then have that $a_i = 0$ for $i \neq k$ and $a_k = 1$. It follows that $|k\rangle$ corresponds to the state of the system in which we are certain to measure the energy E_k. The state $|k\rangle = |E_k\rangle$ is called a *state of well defined energy*. We can then write the state of the system as

$$|\psi\rangle = \sum_i a_i |E_i\rangle$$

It is always important to remember that $|E_i\rangle$ represents the state of the system in which we are **certain** to measure the energy of the system as E_i, as otherwise these basis states would not be mutually orthogonal. This is a logical necessity of the way in which we want to interpret the mathematics in Quantum Mechanics.

1.1.2 Measurement

Suppose that our system is in the state

$$|\psi\rangle = \sum_i a_i |E_i\rangle$$

with many of the a_i being non-zero. We then measure the energy and find that $|\psi\rangle$ is in the energy state E_k. Then by definition

$$|\psi\rangle = |E_k\rangle$$

Thus, the state of the system has completely changed from the initial state. This is what is known as the 'collapse of the wave-function' that is probably the most common thing that popular science points to when talking about the weird nature of Quantum Mechanics. The reason for this will be explained later in these notes, but in the meantime it should just be taken as a consequence of the mathematical apparatus that we use to describe quantum systems.

1.2 Operators and Observables

Operators are used extensively in Quantum Mechanics; nearly everything is defined in terms of some operator. In general, these operators correspond to some observable, such as momentum, position or spin. Much of the mathematics and properties of linear operators are covered in Chapter 1 of the Mathematical Methods notes, so we shall only recap some of the material briefly. Instead, we shall focus on examining some of the consequences of these properties of operators for the 'physics' of the situation.

Recall that an operator Q is defined as

$$Q = \sum_i q_i \left|q_i\right\rangle \left\langle q_i\right|$$

Consider this acting on some state $\left|q\right\rangle_k$.

$$\begin{aligned}
Q\left|q_k\right\rangle &= \left(\sum_i q_i \left|q_i\right\rangle \left\langle q_i\right|\right)\left|q_k\right\rangle \\
&= \sum_i q_i \left|q_i\right\rangle \left\langle q_i|q_k\right\rangle \\
&= \sum_i q_i \left|q_i\right\rangle \ \delta_{ik} \\
\rightarrow Q\left|q_k\right\rangle &= q_k \left|q_k\right\rangle
\end{aligned}$$

This reduces to an eigenvalue problem. The eigenvalues q_k are known as the *spectrum* of the observable that corresponds to the operator Q, and the eigenstates $\left|q_k\right\rangle$ are the states of observing the state of the system as q_k. By definition, the product

$$\left\langle q_i|q_j\right\rangle = a_{ij} = \delta_{ij}$$

gives the amplitude to find the system in state q_i given that it is already in q_j. For the eigenstates of the operator to be well defined, we require that this product is orthogonal; that if the system is in q_j, it cannot be in q_i. This means that most, but not all, operators of observables turn out to be hermitian as a result of this logical necessity.

Seeing as operators correspond to observables, we want to be able to find the expectation value of an operator, as this should give us some interpretable complex number for the system. Let us postulate that the expectation value $\langle Q\rangle$ for a hermitian operator Q for a system in a state $\left|\psi\right\rangle$ is given by $\left\langle\psi|Q|\psi\right\rangle$.

$$\begin{aligned}
\left\langle\psi|Q|\psi\right\rangle &= \left(\sum_j a_j^* \left\langle q_j\right|\right)\left(\sum_k q_k \left|q_k\right\rangle \left\langle q_k\right|\right)\left(\sum_i a_i \left|q_i\right\rangle\right) \\
&= \left(\sum_j a_j^* \left\langle q_j\right|\right)\left(\sum_{ik} q_k a_i \left|q_k\right\rangle \left\langle q_k|q_i\right\rangle\right) \\
&= \sum_{ij} a_j^* a_i q_i \left\langle q_i|q_j\right\rangle \\
&= \sum_i \left|a_i\right|^2 q_i \\
&= \sum_i P_i \, q_i
\end{aligned}$$

Thus, we indeed find that the expectation value of the operator Q is given by'

$$\boxed{\langle Q\rangle = \langle\psi|Q|\psi\rangle = \sum_i P_i\, q_i} \tag{1.3}$$

In general, the quantum analogue to the determination of an observable in classical physics is finding the expectation value of the operator that corresponds to that observable.

1.2.1 The Hamiltonian Operator

The most important operator in Quantum Mechanics is the Hamiltonian operator (we will see why it is so important later). It is defined as

$$\boxed{H = \sum_i E_i \,|E_i\rangle\,\langle E_i|} \tag{1.4}$$

It is a simple calculation to show that $\langle H\rangle$ will give the expectation value of the energy of a system.

1.2.2 Shared Eigenstates

Suppose that we have two operators A and B. Consider their commutator

$$\begin{aligned}
[A, B] &= AB - BA \\
&= \left(\sum_i a_i\,|a_i\rangle\,\langle a_i|\right)\left(\sum_j b_j\,|b_j\rangle\,\langle b_j|\right) - \left(\sum_i b_i\,|b_i\rangle\,\langle b_i|\right)\left(\sum_j a_j\,|a_j\rangle\,\langle a_j|\right) \\
&= \sum_i a_ib_j\,|a_i\rangle\,\langle a_i|\,|b_j\rangle\,\langle b_j| - \sum_i a_ib_j\,|b_i\rangle\,\langle b_i|\,|a_j\rangle\,\langle a_j| \\
&= \sum_i a_ib_i\,(|a_i\rangle\,\langle b_i| - |b_i\rangle\,\langle a_i|)
\end{aligned}$$

In order for this to be zero, we require that $|a_i\rangle = |b_i\rangle$. Thus, we obtain the condition that *if* $[A, B] = 0$*, then the operators* A *and* B *share a complete set of mutual eigenstates.* The fact that it is complete means that we can write any state as a linear combination of these states. This is a very powerful statement.

Most texts, at this point, will state that if two operators share a set of mutual eigenstates, then they can be simultaneously determined. This is in fact too weak of a condition. This can be illustrated by considering a particle that moves in a potential $V(\underline{x})$ and is known to have energy E_k. Can it have well defined momentum for a particular $V(\underline{x})$? If we consider the energy to be the sum of the kinetic ($p^2/2m$) and potential ($V(\underline{x})$) energies, then energy is only well defined given that the kinetic energy (and thus momentum) is well defined. However, this is only valid provided that $V(\underline{x}) = \text{constant}$. This means that under certain conditions, the particle can have well-defined momentum. If we had blindly worked out the commutator, we would have concluded that it could not have well defined momentum.

Another trap that students can fall into is assuming that if $[A, B] = 0$, and the system is in an eigenstate of A, then it is also in an eigenstate of B. This is not the case, mainly as a result of degeneracy. Essentially, just because there is a complete set of eigenstates which spans both operators, this does not mean that both operators contain all of said eigenstates. For example, if we have $A\,|u\rangle = a\,|u\rangle$ and $A\,|v\rangle = a\,|v\rangle$, then $|\theta\rangle = \cos\theta\,|u\rangle + \sin\theta\,|v\rangle$ also satisfies $A\,|\theta\rangle = a\,|\theta\rangle$. But we might also have $B\,|u\rangle = b_1\,|u\rangle$ and $B\,|v\rangle = b_2\,|v\rangle$. So we can use $|u\rangle$ and $|v\rangle$ as a complete set of mutual eigenstates, but $|\pi/4\rangle$ and $|-\pi/4\rangle$ are orthogonal states of A that are not eigenstates of B.

1.2.3 The Uncertainty Principle

Consider two hermitian operators A and B. Let us define

$$F = A - \langle A \rangle$$
$$G = B - \langle B \rangle$$

It is easy to check that both F and G are also hermitian, and that $[F, G] = [A, B]$. For some real number s, and properly normalised state $|\psi\rangle$:

$$\begin{aligned}|\phi\rangle &= (F + isG)\,|\psi\rangle \\ \langle\phi|\phi\rangle &= \langle\phi|\,|(F^* - isG^*)(F + isG)|\,|\phi\rangle \\ &= \left\langle F^2 \right\rangle + s^2 \left\langle G^2 \right\rangle + is\,\langle [F, G] \rangle\end{aligned}$$

By the definition of the product $\langle\phi|\phi\rangle$, this must be real and positive. This means that it must be of the form

$$\begin{aligned}as^2 + bs + c &\geq 0 \\ 4ac &\geq b^2\end{aligned}$$

Defining $\sigma_a^2 = \left\langle F^2 \right\rangle$ and $\sigma_b^2 = \left\langle G^2 \right\rangle$, we arrive at the result that

$$\boxed{\sigma_a\,\sigma_b \geq= \frac{1}{2}|\,\langle [A, B] \rangle\,|} \tag{1.5}$$

As we shall see later, this gives rise to some of the more commonly known uncertainty relations.

1.3 The Position Representation

The position operator unsurprisingly takes the form x. As we define everything that we deal with as being over all real space, it has spectrum $[-\infty, \infty]$. This means that instead of working in a discrete basis, we instead have to work over a continuous interval. In this space, we write

$$\boxed{|\psi\rangle = \int_{-\infty}^{\infty} dx\; \psi(x)\, |x\rangle} \tag{1.6}$$

By analogy to (1.1), we can see that the function $\langle x|\psi\rangle = \psi(x)$ is the amplitude to be at a particular position x. This is what is known as the *wave-function* in Quantum Mechanics, as is essentially the extension of the discrete probability amplitudes a_i that we saw before to continuous space; a probability density function. In the position representation, the identity operator is defined by

$$I = \int_{-\infty}^{\infty} dx\; |x\rangle \langle x| \tag{1.7}$$

Let us check that this works:

$$\begin{aligned} I\,|\psi\rangle &= \left(\int_{-\infty}^{\infty} dx\; |x\rangle \langle x|\right)\left(\int_{-\infty}^{\infty} dx\; \psi(x)\, |x\rangle\right) \\ &= \int_{-\infty}^{\infty} dx\; \psi(x)\, |x\rangle \langle x|x\rangle \\ &= \int_{-\infty}^{\infty} dx\; \psi(x)\, |x\rangle \\ &= |\psi\rangle \end{aligned}$$

The condition for a wave-function to be properly normalised is then give by

$$\begin{aligned} \langle\psi|\psi\rangle &= \langle\psi\,|I|\,\psi\rangle \\ &= \int_{-\infty}^{\infty} dx\; \langle\psi|x\rangle \langle x|\psi\rangle \\ 1 &\overset{!}{=} \int_{-\infty}^{\infty} dx\; |\psi(x)|^2 \end{aligned}$$

This is why the function space L_w^2 is so important; it is the space in which wave-functions, amongst other important functions, exist. Normalisation is very important in Quantum Mechanics, as without it, we would not be able to interesting the results of calculations; we require all wave-functions to be square-normalised in order to think of them as the amplitude of a particle being at a particular point. Another thing we might want to consider is the expectation value:

$$\begin{aligned} \langle Q\rangle &= \langle\psi|Q|\psi\rangle \\ &= \langle\psi|I|Q|I|\psi\rangle \\ &= \int_{-\infty}^{\infty} dx\; \langle\psi|x\rangle \langle x|Q|x\rangle \langle x|\psi\rangle \end{aligned}$$

Thus, the expectation value of an operator in position space is given by

$$\boxed{\langle Q\rangle = \int_{-\infty}^{\infty} dx\; \langle\psi|x\rangle\, Q_x\, \langle x|\psi\rangle} \tag{1.8}$$

where $Q_x = \langle x|Q|x\rangle$ is the representation of the operator in x-space. For the position operator, we find simply that $\langle x\rangle = x \cdot \psi(x)$. This means that it acts simply by ordinary multiplication.

1.4 The Momentum Representation

Readers will (hopefully) remember from Special Relativity that

$$p = \frac{h}{\lambda} = \hbar k$$

for wavelength λ and wave-number k. Suppose that we have some wave-function $\psi(x)$ in x-space, and perform a Fourier Transform to k-space.

$$\widetilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-ikx}\, \psi(x)$$

This is the momentum representation of the same wave-function. Next, let us calculate the expectation value of momentum:

$$\begin{aligned}
\langle p \rangle &= \int_{-\infty}^{\infty} dk\, \widetilde{\psi}^*(x)\, (\hbar k)\, \widetilde{\psi}(x) \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx\, \psi^*(x)\, e^{ikx} \int_{-\infty}^{\infty} dx'\, (\hbar k)\, \psi(x')\, e^{-ikx} \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dk\, e^{ik(x-x')}\, \psi^*(x') \left(-i\hbar \frac{\partial}{\partial x'} \right) \psi(x') \\
&= \int_{-\infty}^{\infty} dx\, \delta(x-x')\, \psi^*(x') \left(-i\hbar \frac{\partial}{\partial x'} \right) \psi(x') \\
&= \int_{-\infty}^{\infty} dx\, \psi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x)
\end{aligned}$$

Thus, the momentum operator is given by

$$\boxed{p = -i\hbar \nabla = -i\hbar \frac{\partial}{\partial x}} \tag{1.9}$$

in the position representation. That last phrase is important, as the momentum operator is not always a slave to the x-operator.

$$\begin{aligned}
\langle \phi | p | \psi \rangle &= \int_{-\infty}^{\infty} dx\, \langle \phi | x \rangle \langle x | p | \psi \rangle \\
&= \int_{-\infty}^{\infty} dx\, \phi^*(x) \left(-i\hbar \frac{\partial \psi}{\partial x} \right) \\
&= -i\hbar \left[\phi^*(x) \psi(x) \right]_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} dx\, \psi(x) \frac{\partial \phi^*}{\partial x} \\
&= i\hbar \int_{-\infty}^{\infty} dx\, \psi(x) \frac{\partial \phi^*}{\partial x} \\
&= \left(-i\hbar \int_{-\infty}^{\infty} dx\, \psi^*(x) \frac{\partial \phi}{\partial x} \right)^* \\
&= \langle \psi | p | \phi \rangle^*
\end{aligned}$$

This means that *p is a hermitian operator*.

2. *The Schrödinger Equations*

With the ground-work out of the way, we can examine the principal equations that define all of Quantum Mechanics, and some of their consequences, namely:

- The Time-Independent Schrödinger Equation
- The Time-Dependent Schrödinger Equation
- Probability Current
- Ehrenfest's Theorem

Students may be surprised, upon reading this chapter, by the simplicity of the material covered, despite being so fundamental to this discipline, but no simplification has been made; these are the most general forms of the Schrödinger equations. All of Quantum Mechanics results from the manipulation of these two equations, which is quite a fascinating thing to come to grips with.

2.1 The Time-Independent Schrödinger Equation

Suppose that a system is in a state of well defined energy, such that $|\psi\rangle$ can be written as a linear combination of energy states E_n. Then by definition

$$\boxed{H\,|E_n\rangle = E_n\,|E_n\rangle} \tag{2.1}$$

This is known as the The Time-Independent Schrödinger Equation (TISE). It is a simple statement of the fact that states of well defined energy are eigenstates of the Hamiltonian operator H. Not all wave-functions will satisfy the TISE, as this requires that they are in a state of well defined energy. The full importance of this equation shall be seen in Section (2.2.1).

The form of the Hamiltonian is entirely dependent on the system being examined. That being said, a useful general form of H is simply writing it as the sum of the kinetic and potential energies:

$$\boxed{H = \frac{p^2}{2m} + V(\underline{x})} \tag{2.2}$$

Evidently, $V(\underline{x})$ may take multiple forms. For a free particle, we say that $V(\underline{x}) = 0$.

2.1.1 The Nodal Theorem

A small disclaimer to begin with: to our knowledge, there is no actual theorem with this name. It has simply been used as a snappy title.

We want to prove that *An n^{th} order wave-function that satisfies the TISE has n-nodes for any time independent Hamiltonian.* Note that in this case, we consider the ground state wave-function to be the 0^{th} order wave-function. The proof makes use of the results of (3.6), and is as follows.

Consider a particle of energy $E(x)$ that obeys the TISE under some one-dimensional potential $V(x)$ over all space. Let us construct a new set of potentials $V_\varepsilon(x)$ such that

$$V_\varepsilon(x) = \begin{cases} V(x) & \text{for } |x| \le \varepsilon \\ \infty & \text{for } |x| > \varepsilon \end{cases}$$

For a sufficiently well-defined potential, we can approximate $V(x)$ to be a square well with infinite sides, as any variation in the potential along the bottom of the well will be negligible in comparison to it's depth. For such a particle in an infinite well, we know the solutions to be

$$\psi(x)_{\text{odd}} \propto \sin\left(\frac{(n+1)\pi x}{\varepsilon}\right)$$
$$\psi(x)_{\text{even}} \propto \cos\left(\frac{(2n+1)\pi x}{2\varepsilon}\right)$$

for $n = 0, 1, 2, 3, \dots$. Suppose that we make the transformation from $V_\varepsilon(x)$ to $V_{\varepsilon+d\varepsilon}(x)$ i.e to increase the sides of the well by $d\varepsilon$, where $d\varepsilon$ is small. Let us assume that ε and $d\varepsilon$ are both finite. We assume that the solutions are well-behaved, meaning that they must be zero outside the well.

Let us now postulate that ψ develops another node in the transformation $V_\varepsilon(x) \to V_{\varepsilon+d\varepsilon}(x)$. This can occur in one of two ways:

1. The sign of ψ changes, meaning that it crosses the zero-axis within the well. However, in this case, ψ will be discontinuous at the boundary in this case as $\psi \neq 0$. This means that it cannot develop another node in this way.

2. The derivatives at $\pm(\varepsilon + d\varepsilon)$ do not change, but the wave-function develops an extra zero between these boundaries. There must be a value for x at which it touches the zero-axis, becoming tangent at this point, which we will call x_o. Thus,

$$\psi(x_o) = 0$$
$$\psi^{(1)}(x_o) = 0$$

However, ψ is a solution to

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

Taking successive derivatives according to Leibnitz' Theorem:

$$-\frac{\hbar^2}{2m}\psi^{(k+2)} + \left(V^{(k)}\psi + \cdots + \binom{k}{k}V\psi^{(k)}\right) = \left(E^{(k)}\psi + \cdots + \binom{k}{k}E\psi^{(k)}\right)$$

Suppose that $\psi^{(k+2)}$ is zero. Then:

$$V^{(k)}\psi + \cdots + \binom{k}{k}V\psi^{(k)} = E^{(k)}\psi + \cdots + \binom{k}{k}E\psi^{(k)}$$

This implies that all derivatives from $j = 0$ to $j = k$ will be zero, as $V(x) \neq E(x)$ by the definition of H. For $\psi^{(k+3)}$:

$$\begin{aligned}
\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\psi^{(k+2)} + \left(V^{(k)}\psi + \cdots + \binom{k}{k}V\psi^{(k)}\right)\right) &= \frac{\partial}{\partial x}\left(E^{(k)}\psi + \cdots + \binom{k}{k}E\psi^{(k)}\right)\\
-\frac{\hbar^2}{2m}\psi^{(k+3)} + \frac{\partial}{\partial x}\left(V^{(k)}\psi + \cdots + \binom{k}{k}V\psi^{(k)}\right) &= \frac{\partial}{\partial x}\left(E^{(k)}\psi + \cdots + \binom{k}{k}E\psi^{(k)}\right)\\
-\frac{\hbar^2}{2m}\psi^{(k+3)} + \frac{\partial}{\partial x}(0) &= \frac{\partial}{\partial x}(0)\\
\rightarrow \psi^{(k+3)} &= 0
\end{aligned}$$

Thus, we have shown that all successive derivatives vanish as $\psi = \psi^{(1)} = 0$ at x_o. This means that the wave-function must vanish if it is to become tangent at x_o. But as we have assumed that there is a non-trivial solution to the TISE, it cannot develop a node in this way.

Continually deforming ε in small changes $d\varepsilon$ such that $\varepsilon \to \infty$ means that it cannot develop a node over all space. Hence we have proven the theorem.

2.2 The Time-Dependent Schrödinger Equation

The Time-Dependant Schrödinger Equation (TDSE) states that

$$\boxed{i\hbar \frac{\partial \left|\psi\right\rangle}{\partial t} = H\left|\psi\right\rangle} \tag{2.3}$$

This governs the time evolution of the state of the system $\left|\psi\right\rangle$. All wave-functions must satisfy this equation, unlike with the TISE. As the equation is first order, the initial information required to solve for $t > 0$ is the initial state $\left|\psi, 0\right\rangle$ that consists of a complete set of amplitudes. If the equation was second order, then the boundary data would have to also include $\partial\left|\psi, 0\right\rangle/\partial t$. However, this would mean that $\left|\psi, 0\right\rangle$ was in fact not a complete set of amplitudes, which would break the 'predicting power' of Physics.

2.2.1 Time Evolution

Suppose that at $t = 0$ the system is in some set of states of well-defined energy E_n that satisfied the TISE. Then according to the TDSE, the time-evolution of this state is given by

$$i\hbar \frac{\partial \left|E_n\right\rangle}{\partial t} = H\left|E_n\right\rangle = E_n\left|E_n\right\rangle$$

which implies that

$$\left|E_n, t\right\rangle = \left|E_n, 0\right\rangle e^{-iE_n t/\hbar}$$

We can use this to find the time evolution of some arbitrary state $\left|\psi\right\rangle$. The energy representation of this state is

$$\left|\psi, t\right\rangle = \sum_n a_n(t)\left|E_n, t\right\rangle$$

Substituting this into the TDSE:

$$i\hbar \frac{\partial \left|\psi\right\rangle}{\partial t} = i\hbar \sum_n \left(\dot{a}_n \left|E_n, t\right\rangle + a_n \frac{\partial \left|E_n\right\rangle}{\partial t}\right) = \sum_n a_n\, H\left|E_n\right\rangle$$

The right-hand term will cancel with the middle term, meaning that we obtain $\dot{a}_n = 0$. This means that the time evolution of $\left|\psi\right\rangle$ is simply given by

$$\boxed{\left|\psi, t\right\rangle = \sum_n a_n e^{-iE_n t/\hbar}\left|E_n, 0\right\rangle} \tag{2.4}$$

Thus, evolution in time for a quantum state corresponds simply to change in complex phase that is dependent on the given state E_n. This means that the probability that the system will be in any energy state E_n is time-independent as $P_n = |a_n|^2$ and $\dot{a}_n = 0$. This is also the reason why the TISE is so important; if we can find the stationary states of a system, we can then find the time-evolution of the system in any state that is a linear combination of these states of well-defined energy.

2.3 Probability Current

In Section (1.3), we saw the idea that $\psi(\underline{x},t)$ is the probability density function for a particle to be at a particular point in space. Now we can ask the question of how this evolves with time as the particle moves through space. Let us define $\rho(\underline{x},t) = |\psi(\underline{x},t)|^2$. Multiply the TDSE by ψ^* and subtract this from the result of multiplying the complex-conjugate of the TDSE by ψ. Then we are left with

$$\begin{aligned} i\hbar\left(\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right) &= -\frac{\hbar^2}{2m}\left(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi\right) \\ \frac{\partial\rho}{\partial t} &= -\frac{i\hbar}{2m}\left(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi\right) \end{aligned}$$

We can now define the *probability current* as

$$\boxed{\underline{J} = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right)} \tag{2.5}$$

This means that we actually obtain a conservation equation

$$\begin{aligned} \frac{\partial\rho}{\partial t} &= -\nabla\cdot\underline{J} \\ \frac{\partial}{\partial t}\int_V dV\ \rho &= -\int_V dV\ \nabla\cdot\underline{J} \\ &= -\oint_{\partial V} \underline{J}\cdot d\underline{S} \end{aligned}$$

Thus, the rate of change of probability in a region is equal to the 'amount' of probability that flows out of a region. This demonstrates the conversation of probability.

Any wave-function can be written in the form

$$\psi(x,t) = |\psi|e^{i\theta(x,t)}$$

Substitute this into (2.5)

$$\begin{aligned} \nabla\psi &= \left(\nabla|\psi| + i|\psi|\nabla\theta\right)e^{i\theta} \\ \underline{J} &= \frac{i\hbar}{2m}\left[|\psi|\left(\nabla|\psi| - i|\psi|\nabla\theta\right) - |\psi|\left(\nabla|\psi| + i|\psi|\nabla\theta\right)\right] \\ &= \frac{i\hbar}{2m}(-2i\nabla\theta)|\psi|^2 \end{aligned}$$

Hence we obtain the useful expression of

$$\boxed{\underline{J} = |\psi|^2\frac{\hbar}{m}\nabla\theta} \tag{2.6}$$

This means that the probability $|\psi|^2$ is carried along at the velocity $\underline{v} = \frac{\hbar}{m}\nabla\theta$. An interesting case to be considered is that of a decaying or evanescent wave of the form

$$\psi(\underline{x}) = |\psi|e^{-q\underline{x}}$$

If this is substituted into (2.6), we find that $\underline{J} = 0$. This means that a decaying wave does not actually carry any probability with it; we can actually have decaying waves in classically forbidden regions without breaking probability conservation.

2.4 Ehrenfest's Theorem

Given the results of Section (2.2), we are equipped with the ability to calculate the rate of change of the expectation value of some observable (operator) Q.

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\langle\psi|Q|\psi\rangle &= i\hbar\left(\frac{\partial\langle\psi|}{\partial t}Q|\psi\rangle + \langle\psi|\frac{\partial Q}{\partial t}|\psi\rangle + \langle\psi|Q\frac{\partial|\psi\rangle}{\partial t}\right)\\
&= \left(i\hbar\frac{\partial\langle\psi|}{\partial t}\right)Q|\psi\rangle + \langle\psi|Q\left(i\hbar\frac{\partial|\psi\rangle}{\partial t}\right) + i\hbar\langle\psi|\frac{\partial Q}{\partial t}|\psi\rangle\\
&= -\langle\psi|HQ|\psi\rangle + \langle\psi|QH|\psi\rangle + i\hbar\langle\psi|\frac{\partial Q}{\partial t}|\psi\rangle\\
i\hbar\frac{\partial}{\partial t}\langle\psi|Q|\psi\rangle &= \langle\psi|[Q,H]|\psi\rangle + i\hbar\langle\psi|\frac{\partial Q}{\partial t}|\psi\rangle
\end{aligned}$$

This expression is known as *Ehrenfrest's Theorem.* Generally, the rate of change of an operator is zero, and so this reduces to the much more compact expression

$$\boxed{i\hbar\frac{\partial}{\partial t}\langle Q\rangle = \langle[Q,H]\rangle} \tag{2.7}$$

If Q commutes with H, then $\langle Q\rangle$ is a constant of motion. In this case, we say that the spectrum of Q are 'good quantum numbers'. Suppose that at $t = 0$, $|\psi\rangle = q_i$.

$$\begin{aligned}
\langle Q\rangle &= q_i\\
\langle Q^2\rangle &= q_i^2\\
\rightarrow \sigma_Q &= \langle Q^2\rangle - \langle Q\rangle^2 = 0
\end{aligned}$$

Thus, the variance of Q vanishes for all time; this is because the system remains in the state of well defined energy that it was in at $t = 0$.

Let us look at some specific, and interesting, cases of Ehrenfest's Theorem:

- The Hamiltonian (H) - Evidently, $[H,H] = 0$, and so for a time-independent Hamiltonian, it is a constant of motion, meaning that *energy is conserved.* A time-dependent Hamiltonian thus indicates that work is being done on the particle. This makes sense, as it takes energy to modify the kinetic and potential energies.

- The Position Operator (x) - For this calculation, we will have to assume that H is of the form given by (2.2). Let us first calculate the commutator of x and p as this will come in handy later.

$$\begin{aligned}
\langle x|[x,p]|\psi\rangle &= \langle x|xp|\psi\rangle - \langle x|px|\psi\rangle\\
&= -i\hbar x\frac{\partial\psi}{\partial x} + i\hbar\left(x\frac{\partial\psi}{\partial x} + \psi\right)\\
&= i\hbar\psi\\
&= i\hbar\langle x|\psi\rangle
\end{aligned}$$

Hence,

$$\boxed{[x,p] = i\hbar} \tag{2.8}$$

This is known as a *canonical commutation relation.*

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\langle\psi|\,x\,|\psi\rangle &= \langle\psi|\,[x,H]\,|\psi\rangle \\
&= \langle\psi|\left[x,\left(\frac{p^2}{2m}+V(x)\right)\right]|\psi\rangle \\
&= \frac{1}{2m}\langle\psi|\,[x,p^2]\,|\psi\rangle \\
&= \frac{1}{2m}\langle\psi|\,([x,p]p+p[x,p])\,|\psi\rangle \\
&= \frac{i\hbar}{m}\langle\psi|\,p\,|\psi\rangle
\end{aligned}$$

We thus obtain

$$\boxed{\frac{\partial}{\partial t}\langle\psi|\,x\,|\psi\rangle = \langle\psi|\,\frac{p}{m}\,|\psi\rangle} \tag{2.9}$$

We have recovered the classical relationship between the rate of change of position (speed) and momentum.

- The Momentum Operator (p) - As the rate of change of momentum (in Classical physics) is equal to the applied force, we expect to find the quantum analogue of Newton's Second Law.

$$\begin{aligned}
-\hbar\frac{\partial}{\partial t}\langle\psi|\,p\,|\psi\rangle &= \langle\psi|\,[p,H]\,|\psi\rangle \\
&= \langle\psi|\left[p,\left(\frac{p^2}{2m}+V(x)\right)\right]|\psi\rangle \\
&= \langle\psi|\,[p,V]\,|\psi\rangle \\
&= -i\hbar\,\langle\psi|\,\frac{\partial V}{\partial x}\,|\psi\rangle
\end{aligned}$$

We thus obtain

$$\boxed{\frac{\partial}{\partial t}\langle\psi|\,p\,|\psi\rangle = -\left\langle\frac{\partial V}{\partial x}\right\rangle} \tag{2.10}$$

This is indeed the analogue of NII, with the force of the form $F=-\nabla V$.

- An Interesting Product (xp) - All stationary states satisfy the relation that

$$\frac{\partial}{\partial t}\langle E|\,Q\,|E\rangle = 0$$

Suppose that we let $Q = xp$.

$$\begin{aligned}
0 &= \frac{\partial}{\partial t}\langle E|\,xp\,|E\rangle \\
&= \langle E|\left[\underline{x}\underline{p},\left(\frac{p^2}{2m}+V(\underline{x})\right)\right]|E\rangle
\end{aligned}$$

Calculating the commutators:

$$\begin{aligned}
[\underline{x}\underline{p},p^2] &= [\underline{x},p^2]\underline{p}+\underline{x}[\underline{p},p^2] \\
&= 2i\hbar p^2 \\
[\underline{x}\underline{p},V] &= [\underline{x},V]\underline{p}+\underline{x}[\underline{p},V] \\
&= -i\hbar\,\underline{x}\cdot\nabla V
\end{aligned}$$

Then,

$$0 = 2i\hbar \langle E| \frac{p^2}{2m} |E\rangle - i\hbar \langle E| \underline{x} \cdot \nabla V |E\rangle$$

Re-arranging, this becomes

$$2 \langle T\rangle = \langle E| \underline{x} \cdot \nabla V |E\rangle$$

Suppose that the potential is of the form

$$V(\underline{x}) = A|\underline{x}|^\alpha$$

This could be, for example, a Coulomb potential with $a = -1$. Then:

$$\begin{aligned} \underline{x} \cdot \nabla V &= A|\underline{x}|^{\alpha-1}\ \underline{x} \cdot \nabla|\underline{x}|\alpha \\ &= \alpha A\,|\underline{x}|^{\alpha-1}\ \underline{x} \cdot \frac{\underline{x}}{|\underline{x}|} \\ &= \alpha V \end{aligned}$$

Substituting this back in, we obtain the expression

$$\boxed{2\langle T\rangle = \alpha \langle V\rangle} \tag{2.11}$$

This is known as the *Virial Theorem*. As it has been derived in a Quantum Mechanical setting, it must also be true on a Classical level; this means we can apply it to a lot of other scenarios. Astute students will have noticed this relationship cropping up a lot when dealing with gravitational forces and orbits.

Only the last of these is a particularly interesting result, but it confirms our expectation that Quantum Mechanics in some way agrees with Classical Mechanics.

3. *Quantum Mechanics and Waves*

This chapter shall deal with the wave-mechanics that results from considering the TISE in one-dimenion, including:

- A General Framework
- The Potential Step
- The Square Well
- A Pair of Square Wells

This may seem like a little bit of a step-back from the more advanced Quantum Mechanics that we have been dealing with; after all, solving a single variable, first-order differential equation is not particularly difficult. However, it can lead to some interesting results that illustrate some of the weird behaviours that can result from the consideration of systems quantum-mechanically.

3.1 A General Framework

This entire chapter focusses on finding solutions to the equation

$$-\frac{h^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi$$

for some wave-function ψ in the position representation. This is a specific, one-dimensional case of the TISE with a Hamiltonian of the form (2.2) for a particle with some initial energy E.

The general framework of the solution, as with most wave questions, is to first consider the waves that are present in each section of the problem, generally in regions where the potential $V(x)$ is constant. We then impose the continuity conditions of ψ and $\partial\psi/\partial x$ at the boundary, and solve the resulting equations for some sort of interpretable solution. However, in Quantum Mechanics, we have a couple of tricks up our sleeve, which we will demonstrate in the next section.

3.1.1 Parity and Phase

The idea of 'parity' can be used to help significantly in this context, as well as many others. Note that this is not a full treatment of the concept of parity; that shall come later. For now, we shall simply state that the Parity Operator P acts in the following way:

$$P\,Q(x)=Q(-x)$$

It can be shown that if

$$[P,H]=0$$

the solutions outside of the finite, symmetric potential $V(x)$ form a complete set of stationary states of H. Now why is this useful? For that, let us turn to an example.

Consider a particle travelling along the x-axis towards positive x that reaches a large square potential step of the form

$$V=\begin{cases}V_o & \text{for } |x|<a\\ 0 & \text{otherwise}\end{cases}$$

Graphically, we can represent this as

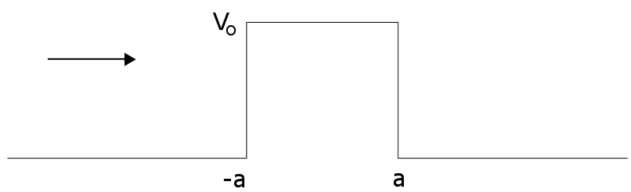

Figure 3.1: A square-potential barrier

At $|x|>a$, the relevant solutions are

$$\left.\begin{array}{ll}\sin(kx+\phi) & \text{at } x>a\\ \pm\sin(-kx+\phi) & \text{at } x<-a\end{array}\right\}\ \text{for } k=\sqrt{\frac{2mE}{\hbar^2}}$$

For $|x| < a$, we are going to consider the simpler case where $E > V_o$ such that the solutions are sinusoidal, and of the form

$$e^{\pm iKx} \quad \text{or} \quad \begin{Bmatrix} \cos Kx \\ \sin Kx \end{Bmatrix} \qquad \text{for } K = \sqrt{\frac{2m(E-V_o)}{\hbar^2}}$$

In this case, we are looking for even parity solutions of the form

$$\psi_e(x) = \begin{cases} B\sin(k|x|+\phi) & \text{for } \ |x| > a \\ cosKx & \text{otherwise} \end{cases}$$

or odd parity solutions of the form

$$\psi_o(x) = \begin{cases} B'\sin(kx+\phi') & \text{for } \ x > a \\ A\sin kx & \text{for } \ |x| \leq a \\ -B'\sin(k|x|+\phi') & \text{otherwise} \end{cases}$$

We shall assume that there are no particles approaching from the right. This imposes the condition that

$$B' = -Be^{i(\phi'-\phi)}$$

Taking a linear combination of the odd and even parity solutions for $x > a$,

$$\begin{aligned} \psi(x) &= \psi_e(x) + \psi_o(x) \\ &= B\sin(kx+\phi) + B'\sin kx + \phi' \\ &= \frac{e^{ikx}}{2i}\left(Be^{i\phi} + B'e^{i\phi'}\right) - \frac{e^{-ikx}}{2i}\left(Be^{-i\phi} + B'e^{-i\phi'}\right) \\ &= \frac{e^{ikx}}{2i}Be^{i\phi}\left(1 - 2e^{i(\phi'-\phi)}\right) \end{aligned}$$

Similarly for $x < -a$,

$$\begin{aligned} \psi(x) &= \psi_e(x) + \psi_o(x) \\ &= B\sin(-kx+\phi) - B'\sin\bigl(-kx+\phi'\bigr) \\ &= e^{ikx}iBe^{-i\phi} + \frac{e^{-ikx}}{2i}Be^{i\phi}\left(1 + 2e^{2i(\phi'-\phi)}\right) \end{aligned}$$

Thus, we can conclude that the amplitudes for the incoming, reflected and transmitted waves are

$$\begin{aligned} A_i &= iBe^{-i\phi} \\ A_r &= \frac{B}{2i}e^{i\phi}\left(1 + e^{2i\Delta\phi}\right) \\ A_t &= \frac{B}{2i}e^{i\phi}\left(1 - e^{2i\Delta\phi}\right) \end{aligned}$$

where $\Delta\phi = \phi' - \phi$ is the phase difference between the odd and even parity solutions. Taking the ratio's and moduli-squared of these solutions, we find that

$$\boxed{\begin{aligned} P_{\text{reflect}} &= \cos^2(\Delta\phi) \\ P_{\text{trans}} &= \sin^2(\Delta\phi) \end{aligned}} \qquad \begin{aligned} (3.1) \\ (3.2) \end{aligned}$$

This means that *the phase difference between the odd and even parity solutions determines reflection and transmission.* Notice that these formulae for the transmission and reflection probabilities have been obtained without reference to the form of the wave-function within the barrier; this means that they hold for any potential $V(x)$ that has odd and even parity, and vanishes outside some finite region. We will make use of this property extensively.

3.2 The Potential Step

The potential step takes the form:

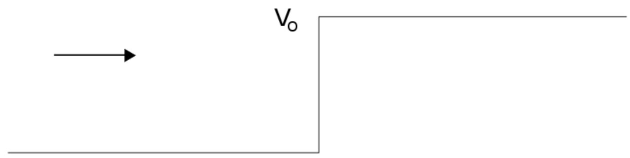

Figure 3.2: A potential step

Let us assume that $E > V_o$ (the other case is left as an exercise to the reader). Let us also place the origin of our coordinate system at the potential step. The solutions for $x < 0$ will be of the form

$$\psi(x) = A_{i/r}e^{\pm ikx} \quad \text{for} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

where A_i and A_r are the amplitudes for the incident and reflected waves respectively. For $x > 0$

$$\psi(x) = A_t e^{iKx} \quad \text{for} \quad K = \sqrt{\frac{2m(E - V_o)}{\hbar^2}}$$

where A_t is the amplitude for the transmitted wave. Imposing continuity at the boundary:

$$A_i + A_r = A_t$$
$$ikA_i - ikA_r = iKA_t$$

It follows quickly that

$$\frac{A_r}{A_i} = \frac{k-K}{k+K} \longrightarrow P_r = \left(\frac{k-K}{k+K}\right)^2$$
$$\frac{A_t}{A_i} = \frac{2k}{k+K} \longrightarrow P_t = \frac{4kK}{(k+K)^2}$$

Unlike in normal wave mechanics, transmission and reflection coefficients give the probability of transmission. This means that it is actually defined as the ratio of the probability currents for the two wave-functions being considered, as we have to take account of how 'quickly' the probability is being transported away from the boundary in either direction. Recalling (2.6), we can define a probability ratio $P_{i\to j}$ moving from region i to region j as

$$\boxed{P_{i\to j} = \frac{|A_j|^2}{|A_i|^2}\frac{k_j}{k_i}} \tag{3.3}$$

This gives rise to the probabilities shown above. It is very easy to check that P_r and P_t sum to unity, meaning that the flux of particles moving away from the origin is equal to the incident particle flux.

We can re-obtain a 'classical' result by looking at the limiting case for initial energies $E \gg V_o$, $k \backsim K$, meaning that $t = 1$ as we would expect. However, if we take $V_o \ll 0$ and $V_o \gg 1$, we find that $r = -1$; oddly, a particle is totally reflected by a very large-cliff, in complete contradiction of what we would expect classically.

3.3 Square Well

In this case, the potential takes the form

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

Graphically, we can represent this as

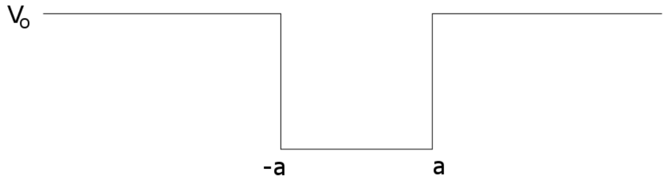

Figure 3.3: A square potential well

Consider the bounded solutions for $E < V_o$. The fact they are bounded means that there will be exponentially decaying solutions on either side of the well. Outside the well:

$$\psi(x) = Ae^{\pm kx} \quad \text{for} \quad k = \sqrt{\frac{2m(V_o - E)}{\hbar^2}}$$

The odd parity solutions inside the well are of the form

$$\psi(x) = B \sin Kx \quad \text{for} \quad K = \sqrt{\frac{2mE}{\hbar^2}}$$

We need continuity at $|x| = a$ in order for the solutions to be stable, and so the conditions we obtain are

$$B \sin Ka = Ae^{-ka}$$
$$KB \cos Ka = -kAe^{-ka}$$

Dividing the second equation by the first

$$\begin{aligned} K\frac{\cos Ka}{\sin Ka} &= -\frac{ke^{-ka}}{e^{-ka}} \\ K \cot Ka &= -k \\ &= -\sqrt{\frac{2mV_o}{\hbar^2} - \frac{2mE}{\hbar^2}} \\ &= -\sqrt{\frac{2mV_o}{\hbar} - K^2} \\ \cot Ka &= -\sqrt{\frac{W^2}{(Ka)^2} - 1} \end{aligned}$$

for $W = \sqrt{(2mV_oa^2)/\hbar^2}$. The figure below is a plot of both sides of this equation.

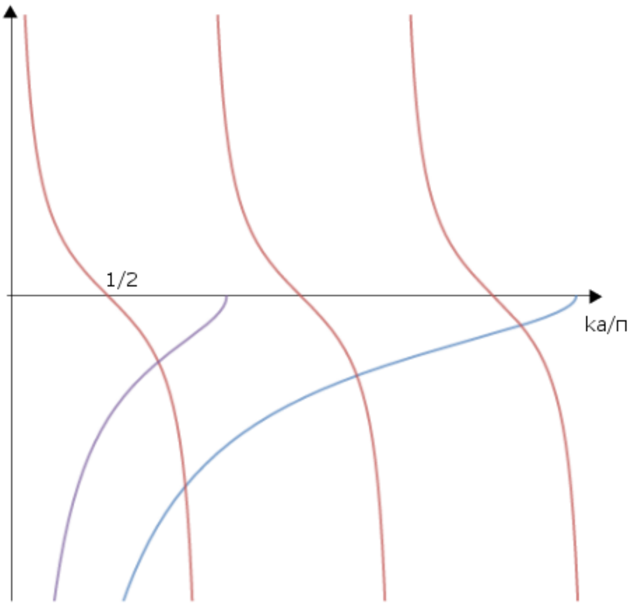

Figure 3.4: The odd-parity solutions

The left-hand side is graphed in red, while the remaining two lines are the right-hand side with larger (blue) and smaller (purple) values of W. Evidently, for an odd parity solution to exist, the minimum value that Ka/π can take is 1/2.

$$\begin{aligned}\frac{W^2}{(Ka)^2}-1 &\geq 0\\ W &\geq Ka\\ \rightarrow W &\geq \frac{\pi}{2}\end{aligned}$$

This is the minimum value of W for odd parity solutions to exist.

We can repeat the same calculation for the even parity solution, and we obtain the relationship that

$$\tan Ka = \sqrt{\frac{W^2}{(Ka)^2}-1}$$

This always has a solution, regardless of the values of W and a. This leads to the idea that *if a shallower and narrower potential well has a bound state, then the larger potential well must also have a bound state.* Essentially, if we are able to 'fit' a square well within the larger potential, then the larger potential must also have a bound state.

3.3.1 Transmission and Reflection

Let us now find the reflection and transmission coefficients for a particle $E > V_o$ incident on this potential well. Considering the solutions to the TISE in each of the regions, we have the following wave-functions

- $x < -a$: $\psi_1(x) = e^{ikx} + Re^{-ikx}$
- $|x| < a$: $\psi_2(x) = Ae^{iKx} + B^{-iKx}$
- $x > a$: $\psi_3(x) = Te^{ikx}$

where k and K have the same values are before. We now impose the continuity condition at $x = a$.

$$\begin{aligned} Te^{ika} &= Ae^{iKa} + Be^{-iKa} \\ ikTe^{ika} &= iKAe^{iKa} - iKBe^{-iKa} \end{aligned}$$

Eliminating A and B, as we are not interested in the solutions inside the well.

$$Ae^{iKa} = \frac{1}{2}Te^{ika}\left(1 + \frac{k}{K}\right) \tag{3.4}$$

$$Be^{-iKa} = \frac{1}{2}Te^{ika}\left(1 - \frac{k}{K}\right) \tag{3.5}$$

Imposing continuity at the $x = -a$ boundary:

$$\begin{aligned} e^{-ika} + Re^{ika} &= Ae^{-iKa} + Be^{iKa} \\ ike^{-ika} - ikRe^{ika} &= iKAe^{-iKa} - iKBe^{iKa} \end{aligned}$$

Substitute (3.4) and (3.5) into these results.

$$\begin{aligned} e^{-ika} + Re^{ika} &= \frac{1}{2}Te^{ika}\left[\left(1 + \frac{k}{K}\right)e^{-2iKa} + \left(1 - \frac{k}{K}\right)e^{2iKa}\right] \\ e^{-ika} - Re^{ika} &= \frac{1}{2}Te^{ika}\left[\left(\frac{K}{k} + 1\right)e^{-2iKa} - \left(\frac{K}{k} - 1\right)e^{2iKa}\right] \end{aligned}$$

Adding these two equations to eliminate R.

$$\begin{aligned} 2e^{-ika} &= \frac{1}{2}Te^{ika}\left[\left(2 + \frac{K}{k} + \frac{k}{K}\right)e^{-2iKa} + \left(2 - \frac{K}{k} - \frac{k}{K}\right)e^{2iKa}\right] \\ 4e^{-2ika} &= T\left[4\cos(2Ka) - 2i\left(\frac{k}{K} + \frac{K}{k}\right)\sin(2Ka)\right] \\ T &= \frac{2kKe^{-2ika}}{2kK\cos(2Ka) - i(k^2 + K^2)\sin(2Ka)} \end{aligned}$$

We have thus obtained the transmission and reflection probabilities as

$$\begin{aligned} P_t &= \frac{1}{1 + (k^2 - K^2)\sin^2(2Ka)/(4k^2K^2)} \\ P_r &= \frac{(k^2 - K^2)\sin^2(2Ka)/(4k^2K^2)}{1 + (k^2 - K^2)\sin^2(2Ka)/(4k^2K^2)} \end{aligned}$$

Evidently, there will be no reflection for all the values of K that satisfy

$$\begin{aligned} \sin^2(2Ka) &= 0 \\ 2Ka &= n\pi \\ \rightarrow Ka &= \frac{n\pi}{2} \end{aligned}$$

This condition can be interpreted in terms of the interference between the forward travelling waves and reflected travelling waves in the well, as there is a phase change of π at only one of the boundaries, meaning the waves are in perfect anti-phase. Interestingly, this also gives us the reflection and transmission probabilities for a square potential step as in Section (3.1.1) for the case where $E < V_o$ by making the substitution that

$$K = i\sqrt{\frac{2m(V_o - E)}{2m}} = i\kappa$$

This will give a transmission coefficient of

$$T = \frac{2k\kappa e^{-2ika}}{2k\kappa\cosh(2\kappa a) - i(k^2-\kappa^2)\sinh(2\kappa a)}$$

and so a transmission probability of

$$P_t = \frac{1}{\cosh^2(2\kappa a) + (k^2-\kappa^2)^2\sinh^2(2\kappa a)/(4k^2\kappa^2)}$$

Consider the limiting case of a very think potential barrier such that $\kappa a \gg 1$. Then:

$$\cosh(2\kappa a) \backsim \frac{1}{2}e^{2\kappa a}$$
$$\sinh(2\kappa a) \backsim \frac{1}{2}e^{2\kappa a}$$

This means that the transmission probability becomes

$$\begin{aligned} P_t &\backsim \frac{1}{\frac{1}{4}e^{4\kappa a}\left(\frac{4k^2\kappa^2+k^4+\kappa^4-2k^2\kappa^2}{4k^2\kappa^2}\right)} \\ &= \frac{1}{\frac{1}{4}e^{4\kappa a}\left(\frac{k^2+\kappa^2}{2k\kappa}\right)^2} \\ &\propto e^{-4\kappa a} \end{aligned}$$

This expression is thus very sensitive to the value of a, with a very small amount of electrons tunnelling through the barrier. This is actually the principle for the tunnelling electron microscope. Electrons in the surface of the material tunnel across the classically forbidden vacuum to the electrically sensitive tip of the microscope. The distance between the tip and the surface is varied, and due to the sensitive dependence of the expression on a, we can obtain a very detailed picture of the surface of the substance.

Evidently, this was quite an algebraically heavy method to find these results. Instead, let us find the same results by considering parity. Inside the well, the solutions are either of odd or even parity. As $[P,H]=0$, we know that the waves outside the well must be stationary states. Thus, we can write

	inside	outside
even	$\cos Kx$	$A\sin(kx+\phi)$
odd	$\sin Kx$	$B\sin(kx+\phi')$

Applying continuity at the $x=a$ boundary for the even parity solutions:

$$\begin{aligned} \cos(Ka) &= A\sin(ka+\phi) \\ -K\sin(Ka) &= KA\cos(ka+\phi) \\ -\frac{k}{K}\cot(Ka) &= \tan(ka+\phi) \end{aligned}$$

Doing the same of the odd parity solutions:

$$\frac{k}{K}\tan(Ka) = \tan\big(ka+\phi'\big)$$

Solving for ϕ and ϕ', with $Ka=\pi/2$.

$$\tan(ka+\phi)=0 \quad\longrightarrow\quad ka+\phi = n\pi$$
$$\tan\big(ka+\phi'\big)=\infty \quad\longrightarrow\quad ka+\phi' = (2n+1)\frac{\pi}{2}$$

Thus,

$$\begin{aligned}\Delta\phi &= \phi' - \phi = \frac{r\pi}{2} \\ P_r &= \cos^2\left(\frac{r\pi}{2}\right) \\ &= 0\end{aligned}$$

Thus, we were able to obtain the same result through much simpler algebra, though we do not have explicit forms for the reflection and transmission coefficients.

3.3.2 The Infinite Well

This is a limiting case of the square well. As $V_o \to \infty$ with a fixed, $W \to \infty$, meaning that the values of k that solve the defining equations for the odd and even solutions tend to $k = n\pi/2a$ and $k = (2n+1)\pi/2a$ respectively. This means we obtain the wave-function

$$\psi(x) = \begin{cases} \frac{1}{\sqrt{a}}\cos\left(\frac{(2n+1)\pi x}{2a}\right) & \text{for even parity} \\ \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right) & \text{for odd parity} \end{cases} \tag{3.6}$$

for $n = 0, 1, 2, 3, \ldots$, and the pre-factor has come from simply normalising the wave-function. We can infer from this that wave-functions vanish at the edges of a region with infinite potential energy.

$$\begin{aligned}k &= \sqrt{\frac{2mE}{\hbar^2}} \\ E &= \frac{\hbar^2}{2m}k^2\end{aligned}$$

The solutions are of the form $\cos(kx)$ and $\sin(kx)$, and so we obtain an expression for the energy of each stationary state as

$$\boxed{E_n = \frac{\hbar^2\pi^2}{2ma^2}n^2} \tag{3.7}$$

for $n = 1, 2, 3, \ldots$. Know that we know these values, it is simple to find the time evolution of the system using (2.4).

The infinite well is one of these problems for which there is a clear classical analogue of a ball bouncing completely elastically between two walls at $x = \pm a$. The Correspondence Principle dictates that for high energies, and thus high n, that the quantum and classical results must agree. In this case, let us shift the well to the right such that the zero point is located at the left-hand edge of the well; otherwise, we would get trivial results for the expectation values, making it uninteresting. For this, the odd parity solutions will remain the same.

$$\begin{aligned}\langle x\rangle &= \int_0^{2a} dx\, x\left(\frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right)\right)^2 \\ &= a\end{aligned}$$

Interestingly, this is independent of the energy of the state; the expectation value is being in the centre of the box in both cases.

$$\begin{aligned}\langle x^2 \rangle &= \int_0^{2a} dx\, x^2 \left(\frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)\right)^2 \\ &= \frac{1}{a} \cdot \frac{a^3}{24\pi^3 n^3} \left(32\pi^3 n^3 - 12\pi n\right) \\ &= a^2 \left(\frac{4}{3} - \frac{1}{2(\pi n)^2}\right)\end{aligned}$$

Thus

$$\begin{aligned}\sigma^2 &= a^2 \left(\frac{4}{3} - \frac{1}{2(\pi n)^2}\right) - a^2 \\ &= a^2 \left(\frac{1}{3} - \frac{1}{2(\pi n)^2}\right)\end{aligned}$$

Classically, the probability density function must also be normalised, and equal to a constant.

$$\begin{aligned}\int_0^{2a} dx\, |\psi_c|^2 &\overset{!}{=} 1 \\ 2a\, \psi_c^2 &= 1 \\ \psi_c &= \frac{1}{\sqrt{2a}}\end{aligned}$$

From this, we can calculate the expectation values.

$$\begin{aligned}\langle x \rangle_c &= \int_0^{2a} dx\, x \left(\frac{1}{\sqrt{2a}}\right)^2 \\ &= a \\ \langle x^2 \rangle_c &= \int_0^{2a} dx\, x^2 \left(\frac{1}{\sqrt{2a}}\right)^2 \\ &= \frac{1}{2a}\left[\frac{x^3}{3}\right]_0^{2a} \\ &= \frac{4}{3}a^3 \\ \sigma_c^2 &= \frac{1}{3}a^2\end{aligned}$$

Thus, it is clear that in the limit as $n \to \infty$ that $\sigma^2 = \sigma_c^2$, confirming our expectations.

3.4 The Dirac-Delta Well

Consider a very narrow well with a potential of the form $V(x) = -V_\delta \, \delta(x)$. From the TISE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_\delta \, \delta(x)\psi = E\psi$$

Let us integrate this equation in the region of $x = 0$, namely in the range $[-\varepsilon, \varepsilon]$ for $\varepsilon \to 0$.

$$\begin{aligned}
-\int_{-\varepsilon}^{\varepsilon} dx \, \frac{d^2\psi}{dx^2} &= \frac{2m}{\hbar^2}\left(V_\delta \, \psi(0) + E\int_{-\varepsilon}^{\varepsilon} dx \, \psi\right) \\
-\left[\frac{d\psi}{dx}\right]_{-\varepsilon}^{\varepsilon} &= \frac{2m}{\hbar^2}\left(V_\delta \, \psi(0) + E\int_{-\varepsilon}^{\varepsilon} dx \, \psi\right)
\end{aligned}$$

The last integral will vanish as $\varepsilon \to 0$, and so we obtain the condition

$$\boxed{\left[\frac{d\psi}{dx}\right]_{-\varepsilon}^{\varepsilon} = -\frac{2mV_\delta}{\hbar^2}\,\psi(0)} \tag{3.8}$$

This means that the first derivative is discontinuous across a delta-function well. Again, as $[P, H] = 0$, we can consider stationary states outside the well.

	$x < 0$	$x > 0$
even	$\sin(k\lvert x\rvert + \phi)$	$\sin(k\lvert x\rvert + \phi)$
odd	$-\sin(k\lvert x\rvert + \phi')$	$\sin(k\lvert x\rvert + \phi')$

for $k = \sqrt{2mE/\hbar^2}$. Imposing the boundary conditions at $x = 0$ for the even parity solutions.

$$\begin{aligned}
\sin\phi &= \sin\phi \qquad \text{very useful....} \\
2k\cos\phi &= -\frac{2mV_\delta}{\hbar^2}\sin\phi \\
\tan\phi &= \frac{\hbar^2 k}{mV_\delta}
\end{aligned}$$

Doing the same for the odd parity solutions.

$$\begin{aligned}
-\sin\phi' &= \sin\phi' \\
\phi' &= 0
\end{aligned}$$

This means that no odd parity solutions exist. It follows that

$$\Delta\phi = \phi' - \phi = -\tan^{-1}\left(\frac{\hbar^2 k}{mV_\delta}\right)$$

Thus, it follows that the transmission probability is given by

$$\begin{aligned}
P_t &= \cos^2(\phi' - \phi) \\
&= \left(\frac{mV_\delta}{\sqrt{\hbar^4 k^2 + m^2 V_\delta^2}}\right)^2 \\
\to P_t &= \left(1 + \frac{m^2 V_\delta^2}{\hbar^4 k^2}\right)^{-1}
\end{aligned}$$

Inside the well, we expect solutions to exponentially decay, and so they will be of the form

$$\psi_\delta(x) = Ae^{\mp Kx}$$

where the negative sign applies for $x = 0^+$. Substituting this result into (3.8):

$$\begin{aligned} -KA - KA &= -\frac{2mV_\delta}{\hbar^2}A \\ -2K &= -\frac{2mV_\delta}{\hbar^2} \\ K &= \frac{mV_\delta}{\hbar^2} \end{aligned}$$

Letting $\psi_\delta(x) = Ae^{-Kx}$ into the TISE for $x > 0$ and re-arranging, we find that

$$E_\delta = -\frac{mV_\delta^2}{2\hbar^2}$$

Thus, the energy of the particle is dependent on the depth of the well.

A particle of mass m moves in one dimension along the x-axis, and is subject to the potential $V = V_\delta\left[\delta(x-a) + \delta(x+a)\right]$, where V_δ is a negative constant. Using symmetry arguments, find the implicit equations for the energy eigenvalues in the odd and even cases.

As $[P, H] = 0$, we can consider odd and even solutions. This means that we will have solutions of the form

	$x < -a$	$-a < x < a$	$x > a$
even	Ae^{Kx}	$B\cosh(x)$	Ae^{-Kx}
odd	Ae^{Kx}	$C\sinh(x)$	Ae^{-Kx}

where $K = \sqrt{2m|E|/\hbar^2}$. Note the signs of the exponentials; the solutions need to be decaying outside the wells. As in (3.4), we will have a discontinuity at $x = \pm a$. For the even case, let us impose the boundary conditions at $x = a$:

$$\begin{aligned} \text{Continuity in } \psi\text{:} \quad & B\cosh(Ka) = A^{-Ka} \\ \text{Discontinuity in } \psi'\text{:} \quad & kB\sinh(Ka) + KAe^{-Ka} = \frac{2mV_\delta}{\hbar^2}B\cosh(Ka) \end{aligned}$$

Solving these equations, and their odd counterparts, simultaneously will yield:

$$\tanh(Ka) = \left(\frac{W}{ka} - 1\right)^{\pm 1}$$

where the positive sign corresponds to the even solutions, and $W = \sqrt{2m|E|/\hbar^2}$. Sketching these solutions makes it clear that there will always be a single even parity solution, but for $W \geq ka$, there will be both an odd and an even parity solution.

4. *The Quantum Harmonic Oscillator*

This chapter aims to cover the basics of the Quantum Harmonic Oscillator, including:

- The Hamiltonian and Operators
- Stationary States
- Wave-functions of Stationary States
- Dynamics of Oscillators

Arguably, the Harmonic Oscillator is the most important entity in all of Physics as the Harmonic Oscillator potential can be used to approximate many physical phenomena. Almost any system near equilibrium is at least approximately harmonic as one can expand the potential energy as a Taylor series around this equilibrium point, and the linear term is zero by construction. It is thus imperative that students become quickly familiar with the concepts covered in this chapter, as they will come up again and again.

4.1 The Hamiltonian and Operators

As previously stated, any system near equilibrium is approximately harmonic. Let us suppose that a system moves under a well-defined potential $V(x)$ through a point of stable equilibrium x_o. Consider the Taylor expansion of $V(x)$ about this point.

$$V(x) \backsim V(x_o) + V^{(1)}(x_o)(x - x_o) + \frac{1}{2!}V^{(2)}(x_o)(x - x_o)^2 + \dots$$

However, by definition, x_o is the point of stable equilibrium, and so must be a minimum. $V^{(1)}(x_o)$ must vanish, meaning that the potential can be approximated by

$$V(x) \backsim \frac{1}{2}V^{(2)}(x_o)(x - x_o)^2$$

In this case, let us assume that $V(x)$ is a quadratic potential, and that is equal to zero at the equilibrium point $x_o = 0$. Then, we can write it as

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$$

Writing our Hamiltonian in the form (2.2), it becomes

$$\boxed{H = \frac{p^2 + (m\omega x)^2}{2m}} \tag{4.1}$$

We want to find the stationary states of the system; rather, the energy eigenstates that satisfy the TISE. This will allow us to find the time evolution of the system assuming that the system was initially in a linear combination of these energy eigenstates.

4.1.1 Creation and Annihilation Operators

In order to do this, let us introduce the dimensionless operators

$$A = \frac{m\omega x + ip}{\sqrt{2m\hbar\omega}} \qquad \text{annihilation} \tag{4.2}$$

$$A^\dagger = \frac{m\omega x - ip}{\sqrt{2m\hbar\omega}} \qquad \text{creation} \tag{4.3}$$

It will become clear why they have these names later on in the chapter. Consider the operator product $A^\dagger A$.

$$\begin{aligned} A^\dagger A &= \frac{(m\omega x - ip)(m\omega x + ip)}{2m\hbar\omega} \\ &= \frac{p^2 + (m\omega x)^2}{2m\hbar\omega} + \frac{im\omega[x,p]}{2m\hbar\omega} \\ &= \frac{H}{\hbar\omega} + \frac{i}{2\hbar}[x,p] \\ &= \frac{H}{\hbar\omega} + \frac{i(i\hbar)}{2\hbar} \end{aligned}$$

This means we have almost factorised the Hamiltonian with these operators, writing it as

$$\boxed{A^\dagger A = \frac{H}{\hbar\omega} - \frac{1}{2}} \tag{4.4}$$

Evidently, reversing the order of the operator product will just change the sign.

What about the commutator of these two operators?

$$
\begin{aligned}
[A^\dagger, A] &= \frac{1}{2m\hbar\omega}[m\omega x - ip, m\omega x + ip] \\
&= \frac{1}{2m\hbar\omega}\left(im\omega[x,p] - im\omega[p,x]\right) \\
&= \frac{i}{\hbar}[x,p] \\
&= -1
\end{aligned}
$$

Thus,

$$\boxed{[A^\dagger, A] = -1} \tag{4.5}$$

This is all just groundwork for the derivations in the next sections, so do not worry if it feels a little disjointed.

4.2 Stationary States

Suppose that we have a stationary state $|E\rangle$ such that

$$H|E\rangle = E|E\rangle$$

Apply (4.3) to both sides of this equation

$$\begin{aligned}
EA^\dagger|E\rangle &= A^\dagger H|E\rangle \\
&= (HA^\dagger + [A^\dagger, H])|E\rangle \\
&= \left(HA^\dagger + \left[A^\dagger, A^\dagger A + \frac{1}{2}\right]\hbar\omega\right)|E\rangle \\
&= \left(HA^\dagger + A^\dagger[A^\dagger, A]\hbar\omega\right)|E\rangle \\
&= HA^\dagger|E\rangle - \hbar\omega A^\dagger|E\rangle \\
H(A^\dagger|E\rangle) &= (E+\hbar\omega)(A^\dagger|E\rangle)
\end{aligned}$$

Hence, we have shown that $A^\dagger|E\rangle$ is also a stationary state, with eigenvalue $E+\hbar\omega$. The application of the creation operator thus raises the energy of the system (excitation) by $\hbar\omega$; hence it's name. Through entirely analogous algebra, we can show that

$$H(A|E\rangle) = (E-\hbar\omega)(A|E\rangle)$$

The annihilation operator lowers the energy of the system by $\hbar\omega$. However, this seems to imply that we can continue lowering the energy of the system arbitrarily. Consider the expectation value of the energy.

$$\begin{aligned}
\langle E\rangle &= \langle E|H|E\rangle \\
&= \frac{1}{2m}\langle E|p^\dagger p|E\rangle + \frac{m^2\omega^2}{2m}\langle E|x^\dagger x|E\rangle \\
&= \frac{|p|E\rangle|^2 + m^2\omega^2|x|E\rangle|^2}{2m} \\
&\geq 0
\end{aligned}$$

This means that the annihilation operator A can only act assuming that $A|E\rangle \neq 0$. Suppose that for some energy E_o,

$$\begin{aligned}
A|E_o\rangle &= 0 \\
0 &= |A|E_o\rangle|^2 \\
&= \langle E_o|A^\dagger A|E_o\rangle \\
&= \langle E_o|\left(\frac{H}{\hbar\omega} - \frac{1}{2}\right)|E_o\rangle \\
\rightarrow E_o &= \frac{1}{2}\hbar\omega
\end{aligned}$$

$|E_o\rangle$ thus represents the minimum energy state, known as the ground-state. This means that the energy eigenvalues are given by

$$\boxed{E_n = \left(n+\frac{1}{2}\right)\hbar\omega} \tag{4.6}$$

Thus, there is an infinite 'ladder' of possible energy eigenvalues. This is why $A^\dagger$ and A are often called 'ladder operators'.

4.2.1 Normalisation

As we have established that the energy eigenvalues are quantised, we shall now write the energy eigenstates as $|0\rangle, |1\rangle, |2\rangle, \ldots$. We saw that when the creation operator is applied, the states satisfy

$$A^\dagger |n\rangle = \alpha |n+1\rangle$$

for some constant α.

$$\begin{aligned}
\alpha^2 &= \langle n| A^\dagger A |n\rangle \\
&= \langle n| A^\dagger A + [A, A^\dagger] |n\rangle \\
&= \langle n| \left(\frac{H}{\hbar\omega} - \frac{1}{2} + 1\right) |n\rangle \\
&= \langle n| \frac{H}{\hbar\omega} |n\rangle + \frac{1}{2} \\
&= \left(n + \frac{1}{2}\right) + \frac{1}{2} \\
&= n + 1 \\
\rightarrow \alpha &= \sqrt{n+1}
\end{aligned}$$

Repeating the same process for

$$A |n\rangle = \beta |n-1\rangle$$

we find that $\beta = \sqrt{n}$. Thus, we obtain the very useful relations that

$$\boxed{\begin{aligned}
|n+1\rangle &= \frac{1}{\sqrt{n+1}} A^\dagger |n\rangle \qquad (4.7) \\
|n-1\rangle &= \frac{1}{\sqrt{n}} A |n\rangle \qquad (4.8)
\end{aligned}}$$

These equations can be remembered quite easily as dividing through by the square root of the highest ladder number involved in the operation.

4.2.2 The Number Operator

Let us now introduce the operator

$$\boxed{N = A^\dagger A} \tag{4.9}$$

This is known as the number operator. Apply it to some general state $|n\rangle$.

$$\begin{aligned}
N(H|n\rangle) &= N(E_n |n\rangle) \\
(A^\dagger A) H |n\rangle &= E_n (A^\dagger A) |n\rangle \\
A^\dagger (A(H|n\rangle)) &= E_n\, A^\dagger (A|n\rangle) \\
A^\dagger (H|n-1\rangle) &= E_n \sqrt{n} A^\dagger |n\rangle \\
(H|n\rangle) &= n(E_n |n\rangle)
\end{aligned}$$

Thus, the number operator does not modify the state of the system; it simply returns the number of the energy eigenstate that the system is currently occupying.

4.2.3 Matrix Representations

With these results established, we can actually find matrix representations for the x and p operators by writing them in terms of the ladder operators.

$$\begin{aligned} A + A^\dagger &= \frac{2m\omega x}{\sqrt{2m\hbar\omega}} \\ x &= \sqrt{\frac{\hbar}{2m\omega}}(A + A^\dagger) \\ &= \ell(A + A^\dagger) \end{aligned}$$

where we have defined $\ell = \sqrt{\hbar/(2m\omega)}$. In the energy representation, the matrix of x is given by

$$\begin{aligned} x_{jk} &= \langle n_j| \, x \, |n_k\rangle \\ &= \ell\left(\langle n_j| \, A \, |n_k\rangle + \langle n_j| \, A^\dagger \, |n_k\rangle\right) \\ &= \ell\left(\sqrt{n_k}\,\langle n_j|n_{k-1}\rangle + \sqrt{n_{k+1}}\,\langle n_j|n_{k+1}\rangle\right) \end{aligned}$$

As the eigenstates are orthogonal,

$$x_{jk} = \ell\left(\sqrt{n_k}\,\delta_{j,k-1} + \sqrt{n_{k+1}}\,\delta_{j,k+1}\right)$$

There will only be non-zero terms for $j = k+1$ and $j = k-1$. The first term will contribute entries on the upper diagonal, and the second will contribute entries to the lower diagonal. Thus, we obtain the matrix

$$x_{jk} = \ell\begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & \dots \\ 0 & 0 & 0 & \sqrt{4} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Similarly, using the fact that

$$p = \frac{i\hbar}{2\ell}(A^\dagger - A)$$

we arrive at the expression

$$P_{jk} = \frac{i\hbar}{2\ell}\left(\sqrt{n_{k+1}}\delta_{j,k+1} - \sqrt{n_k}\delta_{j,k-1}\right)$$

This gives us the matrix

$$p_{jk} = \frac{i\hbar}{2\ell}\begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & -\sqrt{4} & \dots \\ 0 & 0 & 0 & \sqrt{4} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

4.3 Wave-functions of Stationary States

We want the find the position representation of these energy eigenstates. Using the definition of the ground-state:

$$\begin{aligned}
0 &= A\left|0\right\rangle \\
&= \left\langle x\right| A\left|0\right\rangle \\
&= \left\langle x\right| (m\omega x + ip)\left|0\right\rangle \\
&= m\omega\left\langle x\right| x\left|0\right\rangle + i\left\langle x\right| p\left|0\right\rangle \\
&= \left(\frac{m\omega}{\hbar}x + \frac{\partial}{\partial x}\right)\langle x|0\rangle
\end{aligned}$$

Using the integrating factor method,

$$\begin{aligned}
\frac{\partial}{\partial x}\left(\langle x|0\rangle\, e^{x^2/4\ell^2}\right) &= 0 \\
\langle x|0\rangle &= A\cdot e^{-x^2/4\ell^2}
\end{aligned}$$

for some constant A. Now, remark that $\langle x|0\rangle$ is of the form of a Gaussian. We require it's modulus-square to be properly normalised to one:

$$\begin{aligned}
P_0(x) &= |\,\langle x|0\rangle\,|^2 \\
&= A^2 e^{-x^2/2\ell^2}
\end{aligned}$$

Comparing this to the normal form of the Gaussian, it follows that the ground-state wave-function is

$$\langle x|0\rangle = \frac{1}{(2\pi\ell^2)^{1/4}}\, e^{-x^2/4\ell^2}$$

It follows quite quickly that we can obtain successive wave-functions by repeatedly applying the creation operator $A^\dagger$ to this. That is;

$$\langle x|n\rangle = (A^\dagger)^n\,\langle x|0\rangle$$

In order to do this, it is helpful to write $A^\dagger$ in a more useful form.

$$\begin{aligned}
A^\dagger &= \frac{m\omega x - ip}{\sqrt{2m\hbar\omega}} \\
&= \frac{\ell m\omega}{\hbar}x - \frac{i\ell}{\hbar}p \\
&= \frac{2\ell}{4\ell^2}x - \frac{i\ell}{\hbar}\left(-i\hbar\frac{\partial}{\partial x}\right)
\end{aligned}$$

Simplifying, this becomes

$$\boxed{A^\dagger = \frac{x}{2\ell} - \ell\frac{\partial}{\partial x}} \tag{4.10}$$

As an example, let us apply this to the ground-state to obtain the wave-function of the first excited state.

$$\begin{aligned}
\langle x|1\rangle &= A^\dagger\,\langle x|0\rangle \\
&= \left(\frac{x}{2\ell} - \ell\frac{\partial}{\partial x}\right)\frac{1}{(2\pi\ell^2)^{1/4}}\, e^{-x^2/4\ell^2} \\
&= \frac{1}{(2\pi\ell^2)^{1/4}}\,\frac{x}{\ell}\, e^{-x^2/4\ell^2}
\end{aligned}$$

It turns out that the n^{th} wave-function is of the form

$$\boxed{\langle x|n\rangle = \frac{H_n(x)}{(2\pi\ell^2)^{1/4}}\, e^{-x^2/4\ell^2}} \tag{4.11}$$

where $H_n(x)$ are Hermite polynomials, as we saw in the Mathematical Methods notes.

4.3.1 Back to Classical Physics

Let us try and connect these results back to Classical Physics. Looking back at the results of Section (4.2.3), we have already shown that both $\langle x\rangle = \langle p\rangle = 0$ as the diagonal elements of the matrix are equal to zero. This is what we would expect for a classical harmonic oscillator centred at the origin; it's average position is also at the origin, and it has no net motion in a particular direction.

Let us also examine the second moments of position and momentum.

$$\begin{aligned}
\langle n|\, x^2\, |n\rangle &= \ell^2 \langle n| \left(A + A^\dagger\right)^2 |n\rangle \\
&= \ell^2 \langle n| \left(A^2 + (A^\dagger)^2 + AA^\dagger + A^\dagger A\right) |n\rangle \\
&= \ell^2 \langle n| \left(AA^\dagger + A^\dagger A\right) |n\rangle \\
&= \ell^2 \left(\sqrt{n+1}\,\langle n|\, A\, |n+1\rangle + \sqrt{n}\,\langle n|\, A^\dagger\, |n-1\rangle\right) \\
&= \ell^2 (2n+1) \\
&= \frac{\hbar^2}{2m\omega}\,\frac{2E_n}{\hbar\omega} \\
\langle n|\, x^2\, |n\rangle &= \frac{E_n}{m\omega^2}
\end{aligned}$$

Similarly for momentum

$$\begin{aligned}
\langle n|\, p^2\, |n\rangle &= -\frac{\hbar^2}{4\ell^2}\langle n| \left(A^2 + (A^\dagger)^2 - AA^\dagger - A^\dagger A\right) |n\rangle \\
&= \frac{\hbar^2}{4\ell^2}\langle n| \left(AA^\dagger + A^\dagger A\right) |n\rangle \\
&= \frac{\hbar^2}{4\ell^2}\,(2n+1) \\
&= \frac{m\hbar\omega}{4}\left(\frac{2E_n}{\hbar\omega}\right) \\
\langle n|\, p^2\, |n\rangle &= mE_n
\end{aligned}$$

We already know from the Virial Theorem that the kinetic and potential energies are equal in accordance with the classical result, but let us confirm this using these moments.

$$\begin{aligned}
\langle V\rangle &= \frac{1}{2}m\omega^2 \left\langle x^2\right\rangle & \langle T\rangle &= \frac{1}{2m}\left\langle p^2\right\rangle \\
&= \frac{1}{2}m\omega^2\,\frac{E_n}{m\omega^2} & &= \frac{1}{2m}\,mE_n \\
&= \frac{1}{2}E_n & &= \frac{1}{2}E_n
\end{aligned}$$

We re-obtain the classical result as expected.

4.4 Dynamics of Oscillators

If a system is dynamic (that is, it is moving in a classical sense) then it cannot be in a state of well-defined energy by definition. However, it can be the time evolution of some initial linear combination of these states. Suppose that the system is initially in some state

$$|\psi, 0\rangle = \sum_n a_n \; |n\rangle$$

Then the time-evolution of the system is given simply by

$$|\psi, t\rangle = \sum_n a_n \, e^{-i\left(n+\frac{1}{2}\right)\omega t} \, |n\rangle$$

Let us now find the expectation value of position.

$$\begin{aligned}
\langle x\rangle &= \langle\psi|\, x \,|\psi\rangle \\
&= \sum_{nm} a_n^* \, e^{i\left(n+\frac{1}{2}\right)\omega t} \, \langle n|\, x \,|m\rangle \, a_m \, e^{-i\left(m+\frac{1}{2}\right)\omega t} \\
&= \sum_{nm} a_n^* a_m e^{i(n-m)\omega t} \, \langle n|\, x \,|m\rangle \\
&= \ell \sum_{nm} \left(a_n^* a_m e^{i(n-m)\omega t}\right) \left(\sqrt{m}\, \delta_{n,m-1} + \sqrt{m+1}\, \delta_{n,m+1}\right) \\
&= \ell \sum_n a_n^* a_{n+1} \, \sqrt{n+1}\, e^{-i\omega t} + \ell \sum_n a_n^* a_{n-1} \, \sqrt{n}\, e^{i\omega t}
\end{aligned}$$

In the first sum, let $n = n' - 1$.

$$\langle x\rangle = \ell \sum_{n'} a_{n'-1}^* a_{n'} \, \sqrt{n'}\, e^{-i\omega t} + \ell \sum_n a_n^* a_{n-1} \, \sqrt{n}\, e^{i\omega t}$$

Doing another arbitrary relabelling, we arrive at

$$\boxed{\langle x\rangle = \ell \sum_n \sqrt{n}\left(a_n^* a_{n-1}\, e^{i\omega t} + a_{n-1}^* a_n \, e^{-i\omega t}\right)} \tag{4.12}$$

This is not a particularly enlightening result in this form. If we let $2\sqrt{n}\, a_n^* a_{n-1} = X_n e^{i\phi_n}$ where both X_n and ϕ_n are real, then it follows that

$$\langle x\rangle = \ell \sum_n X_n \; \cos(\omega t + \phi_n)$$

Thus, we have obtained sinusoidal oscillations, with each of the initial stationary states oscillating at the same frequency ω regardless of their amplitudes a_n. Thus we have recovered the classical result that the frequency at which the harmonic oscillator oscillates is independent of amplitude and equal to $\sqrt{k/m}$, where k is the 'spring-constant' for the system.

By analogy, the expectation value of momentum in the same general state is given by

$$\boxed{\langle p\rangle = \frac{i\hbar}{2\ell} \sum_n \sqrt{n}\left(a_n^* a_{n-1}\, e^{i\omega t} - a_{n-1}^* a_n \, e^{-i\omega t}\right)} \tag{4.13}$$

As an example, let the initial state of the system be

$$|\psi, 0\rangle = \frac{1}{2}\,|N-1\rangle + \frac{1}{\sqrt{2}}\,|N\rangle + \frac{1}{2}\,|N+1\rangle$$

for large N. Using (4.12), we find that

$$\begin{aligned}
\langle x\rangle &= \ell\left[\sqrt{N}\left(\frac{1}{2\sqrt{2}}e^{-i\omega t}+\frac{1}{2\sqrt{2}}e^{i\omega t}\right)+\sqrt{N+1}\left(\frac{1}{2\sqrt{2}}e^{-i\omega t}+\frac{1}{2\sqrt{2}}e^{i\omega t}\right)\right]\\
&= \frac{\ell}{\sqrt{2}}\left[\frac{1}{2}\sqrt{N}\left(e^{i\omega t}+e^{-i\omega t}\right)+\frac{1}{2}\sqrt{N+1}\left(e^{i\omega t}+e^{-i\omega t}\right)\right]\\
&= \frac{\ell}{\sqrt{2}}\left[\sqrt{N}+\sqrt{N+1}\right]\cos(\omega t)\\
&\backsim \ell\,\frac{2\sqrt{N}}{\sqrt{2}}\cos(\omega t)\\
&= \sqrt{2}\,\ell\sqrt{N}\cos(\omega t)
\end{aligned}$$

Compare this with the classical oscillator with energy $E = N\hbar\omega$. Let X be the maximum displacement of the oscillator.

$$\begin{aligned}
E &= \frac{1}{2}m\omega^2X^2\\
&= N\hbar\omega\\
X^2 &= 2\frac{\hbar N}{m\omega}\\
X &= 2\ell\sqrt{N}
\end{aligned}$$

Interestingly, we find that we do not actually recover Classical Physics, as

$$X_{\text{classical}} = \sqrt{2}\cdot X_{\text{ quantum}}$$

This is because we require a large number of initial states clustered around some large N in order to have enough uncertainty in the oscillation for the correspondence principle to hold. In this case, let us assume that the initial state of the system is

$$|\psi,0\rangle = \frac{1}{\sqrt{K}}\sum_{k=N}^{N+K-1}|k\rangle$$

for $N \gg K \gg 1$. Using (4.12):

$$\begin{aligned}
\langle x\rangle &= \ell\sum_{k=N}^{N+K-1}\sqrt{k}\left(a_{k-1}^*a_k\,e^{-i\omega t}+a_k^*a_{k-1}\,e^{i\omega t}\right)\\
&= \frac{\ell}{K}\sum_{k=N}^{N+K-1}\sqrt{k}\left(e^{i\omega t}+e^{-i\omega t}\right)\\
&= \frac{2\ell}{K}\sum_{k=N}^{N+K-1}\sqrt{k}\,\cos(\omega t)
\end{aligned}$$

We can use the fact that $K \ll N$ to say that all K of the $\sqrt{k}$ terms are $\sqrt{N}$ as they are all close enough to this large number N. Then

$$\langle x\rangle \backsim \frac{2\ell}{K}K\sqrt{N}\,\cos(\omega t) = 2\ell\sqrt{N}\cos(\omega t)$$

We thus re-obtain Classical Physics. If the correspondence principle does not appear to initially hold, it is usually because the problems being considered are in fact not equivalent, rather than a fault in Quantum Theory!

4.4.1 Heisenberg's Uncertainty Principle

Another thing to be considered with an oscillator is it's uncertainty relation, as this gives us constraints on x and p for a dynamical system. Using the results of Section (4.3.1),

$$\begin{aligned}
\sigma_x^2 &= \frac{E}{m\omega^2} \\
\sigma_p^2 &= mE \\
\sigma_x\sigma_p &= \frac{E}{\omega} \\
&= \left(n + \frac{1}{2}\right)\hbar
\end{aligned}$$

Thus, as we have an infinite spectrum of energy values, we can simply write

$$\boxed{\sigma_x\sigma_p \geq \frac{\hbar}{2}} \tag{4.14}$$

This is what most people will commonly recognise as *Heisenberg's Uncertainty Principle.*

5. *Angular Momentum*

This chapter aims to cover the basics of Angular Momentum in Quantum Mechanics, including:

- Symmetries and Conservation Laws
- Orbital Angular Momentum
- Spin Angular Momentum
- Composite Systems
- The Hydrogen Atom

Hopefully, the previous chapters will have built in the reader a solid understanding of the basic concepts and manipulations that are involved in Quantum Mechanics. This chapter will extend this understanding to a slightly more involved concept, namely that of Angular Momentum. This is a particularly important area, as it will allow us to better understand the behaviour of particles, as well as more complex systems such as the Hydrogen atom. It is important that readers are familiar with the manipulations associated with eigenfunctions and eigenvectors, as well as commutators, as these will be used extensively throughout this chapter.

5.1 Symmetries and Conservation Laws

In physics, a *symmetry* of a physical system is a physical or mathematical feature of the system (meaning that it is either observed or intrinsic) that is preserved or remains unchanged under some transformation, such as rotation, reflection and translation. Let C be some operator that performs such an invariant transformation. C can either be *discrete* (such as parity, which we will discuss next) or *continuous* (such as a translation).

If a system in invariant under C, we say that the system posses the symmetry corresponding to C. In this case, we would expect probabilities, and thus the inner product, to be preserved. This means that for the two states $|\psi'\rangle = C|\psi\rangle$ and$|\phi'\rangle = C|\phi\rangle$, we require that

$$\left|\langle\psi'|\phi'\rangle\right|^2 = |\langle\psi|\phi\rangle|^2 \longrightarrow \begin{cases} \langle\psi'|\phi'\rangle = \langle\psi|\phi\rangle \\ \langle\psi'|\phi'\rangle = \langle\phi|\psi\rangle \end{cases}$$

This means that C is either unitary or anti-unitary. However, continuous operations need to contain the identity as their limiting, 'zero-transformation' case, meaning that C must be unitary.

Now let us consider the action of C on the TISE. Consider the same state $|\psi\rangle$ as before. Applying the operator to both sides of (2.1):

$$C\, i\hbar\frac{\partial}{\partial t}|\psi\rangle = CH|\psi\rangle \longrightarrow i\hbar\frac{\partial}{\partial t}\left|\psi'\right\rangle = (HC + [C,H])|\psi\rangle = H\left|\psi'\right\rangle + [C,H]|\psi\rangle$$

This means that we require that $[C,H] = 0$ for the system to have the symmetry associated with the operator C.

5.1.1 Parity

The *parity* operator P is defined by the equation

$$\boxed{P\langle x|\psi\rangle = \langle -x|\psi\rangle} \tag{5.1}$$

We can think of this as changing the sign of all vectors. Finding it's eigenvalues:

$$\begin{aligned} P|\psi\rangle &= \lambda|\psi\rangle \\ P^2|\psi\rangle &= \underbrace{P}_{\text{Unitary}}|\psi\rangle = \lambda^2|\psi\rangle \end{aligned}$$

This means that it's eigenvalues are $\lambda = \pm 1$. If a state satisfies $\lambda = 1$, we say that it is a state of *even* parity, and $\lambda = -1$ is *odd* parity. We met this concept in Section (3.1) when talking about the behaviour of particles in one-dimensional potentials. A property that results from this is that concerning vector operators. Let $|\psi\rangle$ be a state of well-defined parity, and $\underline{v}$ some vector operator.

$$\langle\psi|\,\underline{v}\,|\psi\rangle = -\langle\psi|\,P\underline{v}P\,|\psi\rangle = -(\pm 1)\langle\psi|\,\underline{v}P\,|\psi\rangle = -(\pm 1)^2\langle\psi|\,\underline{v}\,|\psi\rangle$$

This means that *the expectation value of any vector quantity in a state of well-defined parity is zero.* This is quite an intuitive result. For example, consider a particle trapped in an infinite square well, and it's classical analogue of a ball bouncing back and forth between two walls. In the latter case, we would expect the average value of the position of the ball to be mid-way between to two walls, which is what we observe quantum-mechanically for an appropriately centred well.

5.1.2 Continuous Symmetries

Suppose that our transformation operator C now depends on some parameter θ. We require that $C(\theta) = I$ in the limit that $\theta \to 0$, as this corresponds to no transformation at all. If $\delta\theta$ is small, we can expand our operator as

$$C(\delta\theta) = I - i\delta\theta\tau + \mathcal{O}(\delta\theta^2)$$

We require that T is hermitian, and so

$$I = C^\dagger(\delta\theta)C(\delta\theta) = I + i\delta\theta(\tau^\dagger - \tau) + \mathcal{O}(\delta\theta^2)$$

This means that we require our complex coefficient τ to be Hermitian, and so it might correspond to an observable. We can think of building up some total transformation θ out of infinitesimal transformations $\delta\theta$. Suppose that $\theta = N\delta\theta$. Then:

$$\left|\psi'\right\rangle = C(\theta)\left|\psi\right\rangle = \lim_{N\to\infty}\left[C(\delta\theta)\right]^N\left|\psi\right\rangle = \lim_{N\to\infty}\left[I - i\frac{\delta\theta\tau}{N}\right]^N\left|\psi\right\rangle$$

Recalling this limiting definition of the exponential function, we find that

$$\boxed{\left|\psi'\right\rangle = e^{-i\theta\tau}\left|\psi\right\rangle} \tag{5.2}$$

Differentiating both sides of this equation with respect to the parameter θ:

$$i\frac{\partial}{\partial\theta}\left|\psi'\right\rangle = \tau\left|\psi'\right\rangle$$

Thus, τ gives the rate of change of the original state of the system as we vary our transformation parameter θ. The operator τ is thus known as the *generator* of the transformation; the momentum operator is the generator of translational symmetry (the uniformity of space), and we will soon encounter the generator for rotational symmetry (the isotropy of space). With this in mind, consider again the commutator of our transformation C with the Hamiltonian.

$$[C(\tau), H] = [\tau, H]\frac{\partial C}{\partial\tau}$$

This means that if τ commutes with the Hamiltonian, then the system has the symmetry described by C; eigenstates of the system with said symmetry must thus be eigenstates of the generator. This means that we usually do not work with the transformation itself, but rather the associated generator.

5.1.3 Spatial Symmetries

Suppose that we have some state $|\psi\rangle$ that we can describe in the position representation by $\langle \underline{x}|\psi\rangle = \psi(\underline{x})$. How does the state change when we make the shift $\underline{x} \to \underline{x} - \underline{a}$?

$$\langle \underline{x} - \underline{a}|\psi\rangle = \langle \underline{x}|\psi\rangle - \underline{a}\cdot\frac{\partial\psi}{\partial\underline{x}} + \frac{1}{2}a^2\frac{\partial^2\psi}{\partial\underline{x}^2} + \cdots = \exp\left(-\underline{a}\cdot\frac{\partial}{\partial\underline{x}}\right)\langle \underline{x}|\psi\rangle = \underbrace{\exp\left(-\frac{i}{\hbar}\underline{a}\cdot\underline{p}\right)}_{T(\underline{a})}\langle \underline{x}|\psi\rangle$$

Our transformation operator for our parameter $\underline{a}$ is thus $T(\underline{a})$ as shown, with the generator of the transformation being the momentum operator $\underline{p}$. How have the expectation values changed under this transformation? Let $|\psi'\rangle = T|\psi\rangle$.

$$\left\langle\psi'\right|\underline{p}\left|\psi'\right\rangle = \langle\psi|T^\dagger\underline{p}T|\psi\rangle = \langle\psi|\underline{p}|\psi\rangle$$

as the generator must commute with the operation by definition. This means that the expectation value of momentum is unchanged under the translation.

$$\langle\psi'|\,\underline{x}\,|\psi'\rangle = \langle\psi|\,T^\dagger \underline{x} T\,|\psi\rangle = \langle\psi|\,T^\dagger T \underline{x} + T^\dagger [T, \underline{x}]\,|\psi\rangle = \langle\psi|\,\underline{x} - \underline{a}\,|\psi\rangle$$

As one could have guessed, the expected value of position is changed simply by the original translation that was made.

5.1.4 Rotational Symmetries

Suppose that we want to rotate our system by some angle $\underline{\alpha}$. Then, by direct analogy, the transformation operator will be given by

$$\boxed{U(\underline{\alpha}) = \exp\left(-\frac{i}{\hbar}\underline{\alpha}\cdot\underline{J}\right)} \tag{5.3}$$

where $\underline{J}$ is the generator of the rotations. This can be thought of as an operator associated with angular momentum, though we can only substantiate this claim by saying that in Classical Mechanics, dynamical symmetry about some axis implies that the component of angular momentum about that axis is conserved. However, we can already derive some useful commutation relations concerning these operators. Consider the state $|\psi'\rangle = U\,|\psi\rangle$, and the expectation value in this state of:

- Some scalar operator a. Being a scalar, a will be unaffected by rotations:

  $$\langle\psi'|\,a\,|\psi'\rangle = \langle\psi|\,U^\dagger a U\,|\psi\rangle = \langle\psi|\,a\,|\psi\rangle$$

  As this must hold for all states $|\psi\rangle$, we have that

  $$U^\dagger a U = a \;\longrightarrow\; [a, U] = 0$$

  As U can be expanded as a power series in $\underline{J}$, this means that $\underline{J}$ must also commute with a

- Some vector operator $\underline{v}$. Then, we can describe the action of U on the expectation value of $\underline{v}$ by a single rotational operator R:

  $$\langle\psi'|\,\underline{v}\,|\psi'\rangle = R(\underline{\alpha})\,\langle\psi|\,\underline{v}\,|\psi\rangle \;\longrightarrow\; U^\dagger \underline{v} U = R\underline{v}$$

  where the second expression follows from the fact that this must hold for any state $|\psi\rangle$. Consider a small rotation $\delta\underline{\alpha}$ that adds $\delta\underline{\alpha}\times\underline{v}$ to $\underline{v}$. Then, using a small angle expansion of U to first order:

  $$\begin{aligned}\left(I + \frac{i}{\hbar}\delta\underline{\alpha}\cdot\underline{J}\right)\underline{v}\left(I - \frac{i}{\hbar}\delta\underline{\alpha}\cdot\underline{J}\right) &= \underline{v} + \delta\underline{\alpha}\times\underline{v}\\ \frac{i}{\hbar}[\delta\underline{\alpha}\cdot\underline{J}, \underline{v}] + \mathcal{O}(\delta\underline{\alpha}^2) &= \delta\underline{\alpha}\times\underline{v}\\ [v_i, J_j] &= i\hbar\epsilon_{ijk}v_k\end{aligned}$$

  as this must hold for arbitrary $\delta\underline{\alpha}$. The product $\delta\underline{\alpha}\cdot\underline{J}$ must be invariant under coordinate rotations because the operator U depends on the direction $\delta\underline{\alpha}$ and not on the numbers used to quantify that direction. Since $\delta\underline{\alpha}$ is an arbitrary vector, the invariance of $\delta\underline{\alpha}\cdot\underline{J}$ under rotations implies that under rotations the components of $\underline{J}$ transform like those of a vector, meaning that we can simply substitute $v_i = J_i$ into the last relationship.

Together, these commutation relations imply that we can find a complete set of eigenstates for $J^2 = \underline{J} \cdot \underline{J}$ and one component of $\underline{J}$ (but only one). A summary of these results is shown in the box below.

$$\boxed{\begin{aligned} &[a, J_j] = 0 \quad \text{for a scalar operator } a \\ &[v_i, J_j] = i\hbar\epsilon_{ijk}v_k \text{ for a vector operator } \underline{v} \end{aligned}} \qquad \begin{aligned} (5.4) \\ (5.5) \end{aligned}$$

Eigenvalues of J_z and J^2

We cannot find a complete set of simultaneous eigenkets for two components of $\underline{J}$, but we are within our rights to find this information for one component and J^2. We can use the above commutation relations to find the associated eigenvalues, though we will need more specific information about the form of $\underline{J}$ to be able to find the eigenfunctions.

Without loss of generality, let our known direction be J_z. We are going to choose $|j, m\rangle$ to be our ket that is simultaneously an eigenket of J_z and J^2, such that

$$J_z |j, m\rangle = m\hbar |j, m\rangle \quad \text{and} \quad J^2 |j, m\rangle = \beta\hbar^2 |j, m\rangle$$

Note that our labelling of the eigenvalue of J^2 is arbitrary; we have simply chosen to call it β. We now define the *raising and lowering operators*

$$J_\pm = J_x \pm iJ_y \tag{5.6}$$

These evidently commute with J^2, meaning that they have no effect on the total angular momentum. Their commutators with J_z satisfy

$$[J_z, L_\pm] = [J_z, J_x] \pm i[J_z, J_y] = i\hbar J_y \pm i(-i\hbar J_x) = \pm\hbar(J_x \pm iJ_y) = \pm\hbar J_\pm \tag{5.7}$$

The kets $J_\pm |j, m\rangle$ are eigenkets of J^2 with eigenvalue $j(j + 1)$. Operating on one of these kets with J_z:

$$J_z J_\pm |j, m\rangle = (J_\pm J_z + [J_z, J_\pm]) |j, m\rangle = (m \pm 1)\hbar J_\pm |j, m\rangle$$

Thus, $J_\pm |j, m\rangle$ are members of the complete set of eigenstates of J^2 and J_z, but their eigenvalues with respect to J_z differ by one from the original. We then write

$$J_\pm |j, m\rangle = \alpha_\pm |j, m \pm 1\rangle$$

where $\alpha_\pm$ are some (possibly complex) coefficients. In a similar way to finding the raising and lowering coefficient for the Harmonic Oscillator (Section (4.2.1)), we can now evaluate these coefficients:

$$\begin{aligned} |\alpha_\pm|^2 &= \langle j, m| J_\pm^\dagger J_\pm |j, m\rangle = \langle j, m| (J_x \mp iJ_y)(J_x \pm iJ_y) |j, m\rangle \\ &= \langle j, m| (J^2 - J_z^2 \mp \hbar J_z) |j, m\rangle = \beta\hbar^2 - m(m \pm 1)\hbar^2 \end{aligned}$$

This means that we can write

$$\alpha_\pm = \sqrt{\beta - m(m \pm 1)}\hbar$$

It cannot be possible to create states with ever larger eigenvalues of J_z by repeated application of J_+. All that can stop us doing this is the vanishing of α_+ when we reach some maximum eigenvalue m_{max}, and similarly for J_- and α_-. We thus expect, for some maximum $m_{\text{max}} = j$:

$$J_\pm |\beta, j\rangle = 0 \longrightarrow \langle \beta, j| J_\pm^\dagger J_\pm |\beta, j\rangle = \langle \beta, j| J^2 - J_z^2 - \hbar J_z |\beta, j\rangle = \beta - j(j + 1)\hbar^2 = 0$$

This means that $\beta = j(j+1)$ for some value of j. This also means that $-j < m < j$; there is thus a $2j + 1$ degeneracy in m for each value of j.

A summary of these important results is shown in the box below.

$$\boxed{\begin{aligned} &J_z\,|j,m\rangle = m\hbar\,|j,m\rangle && (5.8)\\ &J^2\,|j,m\rangle = j(j+1)\hbar^2\,|j,m\rangle && (5.9)\\ &J_\pm\,|j,m\rangle = \sqrt{j(j+1)-m(m\pm1)}\hbar\,|j,m\pm1\rangle && (5.10)\end{aligned}}$$

Rotational Spectra for Diatomic Molecules

We can now use our knowledge of the eigenvalues of the angular momentum operator $\underline{J}$ to look at the rotational spectra for diatomic molecules. Suppose that we can model a diatomic molecule as two hard spheres connected by a light spring that is aligned along the z-axis.

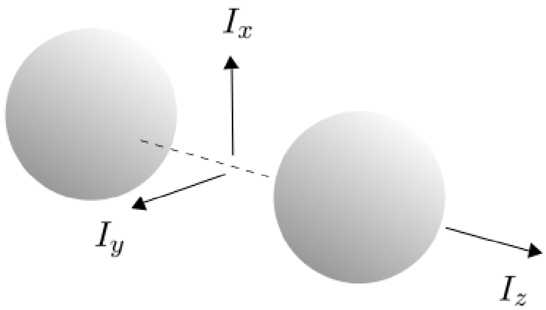

Figure 5.1: A diatomic molecule with it's axis aligned with the z-axis

We can then write the Hamiltonian in the form

$$H = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} = \frac{J^2}{2I_x} + J_z\left(\frac{1}{2I_z} - \frac{1}{2I_x}\right)$$

as $I_x = I_y$. From our knowledge of momentums of inertia, $I_z \ll I_x$.

$$H\,|j,m\rangle = \left[\frac{j(j+1)\hbar^2}{2I_x} + \frac{m^2\hbar^2}{2}\left(\frac{1}{I_z} - \frac{1}{I_y}\right)\right]|j,m\rangle$$

This means that it is very hard to create rotation around the axis of the molecule (aligned with the z-axis), and so we can effectively set $m = 0$. Then, the energy of such a rotating molecule is given by

$$\boxed{E_j = \frac{\hbar^2}{2I_x}j(j+1)} \tag{5.11}$$

It is quite easy to show using the centre of mass that $I_x = \mu s^2$, where μ is the reduced mass of the molecule, and s is the typical separation of the two molecules.

If the molecule undergoes a change in rotational energy, the only way that it can do this is by emitting a photon of energy $\hbar\omega$. It's energy is then given by

$$\hbar\omega = E_j - E_{j-1} = \frac{\hbar^2}{I_x}j$$

If we are given two different frequencies of photons that are emitted, and their corresponding transitions, we can approximate the spring constant for the molecule by finding the change in the force $F = \mu s\omega^2$ and the change in the distance s, as $k = \Delta F/\Delta s$.

The Uncertainty Principle

As we did with the Harmonic Oscillator, we are now going to consider the uncertainty relation that is associated with the angular momentum $\underline{J}$. We know from (1.5) that

$$\sigma_{J_x}\sigma_{J_y} \geq \frac{\hbar}{2}\left|\langle J_z\rangle\right| = \frac{m\hbar^2}{2}$$

The states $|j,m\rangle$ are symmetric with respect to x and y as z is the only direction that we know about, meaning that $\sigma_{J_x}\sigma_{J_y} = (\sigma_{J_x})^2$. As $\langle J_x\rangle = 0$, $\sigma_{J_x}^2 = \left\langle J_x^2\right\rangle$. By symmetry,

$$\left\langle J_x^2\right\rangle = \frac{1}{2}\left\langle J^2 - J_z^2\right\rangle = \frac{1}{2}(j(j+1) - m^2)\hbar^2$$

Substituting these results into the uncertainty relation above, we find that

$$j(j+1) \geq m(m+1)$$

which we know to be true as $m \leq j$. This means that angular momentum does in fact satisfy the uncertainty relation.

Decomposing $\underline{J}$

Suppose that we can decompose our angular momentum operator $\underline{J}$ into two components, namely

$$\underbrace{\underline{J}}_{\text{Total}} = \underbrace{\underline{L}}_{\text{Orbital}} + \underbrace{\underline{S}}_{\text{spin}}$$

It is completely within our rights to do this, as we are simply writing $\underline{J}$ as the sum of two other operators. As we shall see in following sections, $\underline{L}$ corresponds to orbital angular momentum (that is analogous to the classical angular momentum that we are used to), while $\underline{S}$ corresponds to the intrinsically quantum-mechanical effect that is spin angular momentum.

What effect does this have on our rotational transform U?

$$U(\underline{J}) = \exp\left(-\frac{i}{\hbar}\underline{\alpha}\cdot\underline{J}\right) = \exp\left(-\frac{i}{\hbar}\underline{\alpha}\cdot(\underline{L}+\underline{S})\right) = \exp\left(-\frac{i}{\hbar}\underline{\alpha}\cdot\underline{L}\right)\exp\left(-\frac{i}{\hbar}\underline{\alpha}\cdot\underline{S}\right)$$

This means that we can simply write that

$$\boxed{U(\underline{J}) = U(\underline{L})\,U(\underline{S})} \tag{5.12}$$

This means that our rotation can be decomposed into a rotation associated with the orbital angular momentum, and a rotation associated with the spin angular momentum. The order is unimportant.

The last important thing to note about this decomposition is that due to linearity, *both $\underline{L}$ and $\underline{S}$ obey the same commutation relations, and thus eigenvalue equations as $\underline{J}$.* This means that the results derived in Section (5.1.4) hold for both $\underline{L}$ and $\underline{S}$. We will make the changes $j \to \ell$ and $j \to s$ respectively.

5.2 Orbital Angular Momentum

We are first going to take a look orbital angular momentum, as it has an already quite familiar classical analogue. We define the orbital angular momentum operator as

$$\boxed{\underline{L} = \underline{r} \times \underline{p} = -i\hbar\, \underline{r} \times \nabla} \tag{5.13}$$

The forms of each of the components of $\underline{L}$ are thus very easy to work out in Cartesian coordinates by evaluating the above cross product. However, we are must more interested in their forms in polar coordinates, particularly those of our special direction z and the total angular momentum. It can be shown that the polar coordinate representations of these operators are

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \tag{5.14}$$

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \tag{5.15}$$

Note that the former of these can be proven by observing that

$$\frac{\partial}{\partial \phi} = \frac{\partial x}{\partial \phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi}\frac{\partial}{\partial \phi} + \frac{\partial z}{\partial \phi}\frac{\partial}{\partial z}$$

and using the polar coordinate representations of x, y, z in comparison to the Cartesian definition of L_z.

5.2.1 Eigenfunctions of L_z and L^2

Looking at the first of these expressions, it is clear that the eigenvalues of L_z are the functions $e^{im\phi}$. However, this has to be a single valued function, due to rotational symmetry, meaning that m (and thus ℓ) *must be an integer*. Readers may have implicitly assumed this was the case, but now we have demonstrated it exactly.

We now want to find the eigenfunctions of the operator L^2. We know from Section (5.1.4) that the maximum value that m can take is ℓ. We are going to consider the eigenfunctions of the state $|\ell, \ell\rangle$, and work backwards from here. Suppose that

$$Y_\ell^\ell(\theta, \phi) = \langle \theta, \phi | \ell, \ell \rangle$$

Apply the raising operator L_+ to this state in polar representation:

$$\langle \theta, \phi | \, L_+ \, |\ell, \ell\rangle = e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot\theta \frac{\partial}{\partial \phi} \right) Y_\ell^\ell = 0$$

Suppose that Y_ℓ^ℓ is an eigenstate of L_z such that $L_z Y_\ell^\ell = \ell\hbar\, Y_\ell^\ell$. This implies that $Y_\ell^\ell = f(\theta)\, e^{i\ell\phi}$. Then:

$$\frac{\partial f}{\partial \theta} - \ell \cot\theta f(\theta) = 0 \longrightarrow \frac{\partial}{\partial \theta}\left(f(\theta) \sin^{-\ell}\theta \right) = 0$$

From this, we find the important result of

$$\boxed{Y_\ell^\ell(\theta, \phi) \propto \sin^\ell\theta\, e^{i\ell\phi}} \tag{5.16}$$

Successive applications of the lowering operator L_- to this expression should yield all other eigenfunctions. A rule worth remembering that when this occurs, the powers of the θ dependant cosine functions *always remains equal to ℓ.* It can be shown that the eigenfunctions of L^2 are given by the *spherical harmonics*

$$\boxed{\langle\theta,\phi|\ell,m\rangle = Y_\ell^m(\theta,\phi) \propto P_\ell^m(\cos(\theta))\, e^{im\phi}} \tag{5.17}$$

where $P_\ell^m(\cos\theta)$ are the associated Legendre polynomials. By the definition of m, we have $2\ell+1$ possible eigenfunctions for a given value of ℓ, and so we have to specify both ℓ and m when denoting a particular eigenfunction. Some of the results for lower values of ℓ are worth remembering, and are as follows:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\theta}$$

The normalisation constants come from integrating these eigenfunctions over both θ and ϕ; this is obvious, but not worth forgetting. However, we often find that normalisation is irrelevant, as we are more interested in determining the values of ℓ and m based on the form of the eigenfunctions.

A system's wavefunction is proportional to $\sin^2\theta$. What are the possible measurements of L_z and L^2? Give the probabilities of each outcome.

We need to write the angular dependence as the sum of the spherical harmonics, because then it becomes very easy to to read off the possibilities. This can be done by observing that

$$\sin^2\theta = 1 - \cos^2\theta = -\frac{1}{3}(3\cos^2\theta - 1) + \frac{2}{3}$$

This means that

$$\langle\theta,\phi|\psi\rangle \propto -\frac{1}{3}\sqrt{\frac{16\pi}{5}}\,Y_2^0 + \frac{2}{3}\sqrt{4\pi}\,Y_0^0 \propto -Y_2^0 + \sqrt{5}\,Y_0^0$$

Thus, clearly a measurement of L_z will always yield zero, though we could have read this off immediately from the fact that the angular part of the wavefunction is independent of ϕ. L^2 has possibilities 0 and 6 ($\ell = 2$) with probabilities $\frac{5}{6}$ and $\frac{1}{6}$ respectively.

We are now going to consider the parity of the spherical harmonics, as this can often become very useful in order to simplify integrals, and in other such calculations. In polar coordinates, an application of the parity operator P gives rise to the transformation $[\theta,\phi] \mapsto [\pi-\theta,\phi+\pi]$. Recalling Equation (5.16):

$$P\,\langle\theta,\phi|\ell,\ell\rangle \propto P\sin^\ell\theta e^{i\ell\phi} = \sin^\ell(\pi-\theta)e^{i\ell(\phi+\pi)} = (-1)^\ell\sin^\ell\theta e^{i\ell\phi} = (-1)^\ell\,\langle\theta,\phi|\ell,\ell\rangle$$

As the lowering and raising operators $L_\pm$ are parity symmetric, applying them to the above state will not change it's parity. This means that the parity of a general state is given by

$$\boxed{P\,|\ell,m\rangle = (-1)^\ell\,|\ell,m\rangle} \tag{5.18}$$

5.2.2 Angular Momentum and Orbits

In a similar way to our treatment of orbits in Classical Mechanics, we want to decompose the momentum into a radial and angular part, such that we can reduce it to a one-dimensional problem. Our first instinct would be to define the radial momentum operator as $\underline{p} \cdot \underline{r}$; however, this clearly does not work as this would make p_r manifestly not Hermitian. We thus use the alternative definition

$$p_r = \frac{1}{2}\left(\widehat{\underline{r}} \cdot \underline{p} + \underline{p} \cdot \widehat{\underline{r}}\right) = \frac{i\hbar}{2}\left(\frac{1}{r}\underline{r} \cdot \nabla + \nabla \cdot (r/\underline{r})\right) = -\frac{i\hbar}{2}\left(\frac{\partial}{\partial r} + \frac{3}{r} - \frac{r}{r^2} + \frac{\partial}{\partial r}\right)$$

Simplifying, we obtain the surprisingly simple expression of

$$\boxed{p_r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)} \tag{5.19}$$

Squaring up this expression:

$$p_r^2 = -\hbar^2\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2} + \frac{1}{r^2}\right) = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

We note how this is the radial part of the Laplacian in spherical polar coordinates. This means that we can decompose the momentum as

$$\frac{p^2}{2m} = \underbrace{\frac{p_r^2}{2m}}_{\text{Radial}} + \underbrace{\frac{L^2}{2mr^2}}_{\text{Angular}} \tag{5.20}$$

This means that we re-obtain the classical result, but instead dealing with Hermitian operators.

5.3 Spin Angular Momentum

Spin is an intrinsic form of angular momentum carried by elementary particles who's existence was inferred from experiments, such as the Stern-Gerlach experiment (discussed below), in which particles are observed to possess angular momentum that cannot be accounted for by orbital angular momentum alone. We could also anticipate this from our arguments about generators; seeing as we know that $\underline{J}$ and $\underline{L}$ cause particular transformations, we can define $\underline{S}$ to simply be causing the difference between the two transformations. As previously stated, $\underline{S}$ shares all the commutation and eigenvalue relations with $\underline{J}$.

5.3.1 Spin Operators

In a similar way to with orbital angular momentum, we want to find an explicit expression for the various components of our spin angular momentum $\underline{S} = (S_x, S_y, S_z)$. One particularly common way of doing this is by finding their matrix representation. We shall do this in a basis that is diagonalised with respect to S_z. Recall that for some state $|s,m\rangle$, m can take values $-s < m < s$. This means that we can automatically write down the matrix for S_z as the diagonal matrix of it's eigenvalues:

$$S_z = \hbar \begin{pmatrix} s & 0 & 0 & 0 & \dots \\ 0 & s-1 & 0 & 0 & \dots \\ 0 & 0 & s-2 & 0 & \dots \\ 0 & 0 & 0 & s-3 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

This matrix will always have an odd number of diagonal entries $(2s+1)$, where the 'middle' entry will always be zero. For the other two components, we will use the definitions of the raising and lowering operators:

$$S_\pm = S_x \pm i S_y \longrightarrow \begin{cases} S_x = \frac{1}{2}(S_+ + S_-) \\ S_y = \frac{1}{2i}(S_+ - S_-) \end{cases}$$

This means that we can write in matrix representation that

$$\begin{aligned} \langle s,m'|\, S_x \,|s,m\rangle &= \langle s,m'|\, \frac{1}{2}(S_+ + S_-) \,|s,m\rangle \\ &= \frac{\hbar}{2}\left(\sqrt{s(s+1) - m(m+1)}\delta_{m',m+1} + \sqrt{s(s+1) - m(m-1)}\delta_{m',m-1}\right) \\ \langle s,m'|\, S_i \,|s,m\rangle &= \langle s,m'|\, \frac{1}{2i}(S_+ + S_-) \,|s,m\rangle \\ &= \frac{\hbar}{2i}\left(\sqrt{s(s+1) - m(m+1)}\delta_{m',m+1} - \sqrt{s(s+1) - m(m-1)}\delta_{m',m-1}\right) \end{aligned}$$

We are not going to include the explicit matrix forms for these two operators here as they become too complicated in the general case. However, we will quote the results for the $s = 1$ matrices here for reference:

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad S_y = \frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \qquad S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Pauli Spin Matrices

In this section, we will consider the case of the above results for $s = \frac{1}{2}$; as most of matter is made up of spin-$\frac{1}{2}$ particles, we will often be working in this regime. We can define a vector of matrices $\underline{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ such that

$$\underline{S} = \frac{\hbar}{2}\underline{\sigma}$$

The component matrices that make up $\underline{\sigma}$ are known as the *Pauli Spin Matrices* and have the form

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

It is easy to show that these satisfy the commutation relations

$$\boxed{\begin{aligned} [\sigma_i, \sigma_j] &= 2i\epsilon_{ijk}\sigma_k \qquad (5.21) \\ \{\sigma_i, \sigma_j\} &= 2\delta_{ij} \qquad (5.22) \end{aligned}}$$

The corresponding spin matrices have eigenvalues $\pm\frac{\hbar}{2}$, as is appropriate for spin-half particles. Suppose that the eigenstates of S_z are $|+\rangle$ and $|-\rangle$, often referred to as *spin-up* and *spin-down* states. This means that we can write the general state of a spin-half particles as

$$|\psi\rangle = a\,|+\rangle + b\,|-\rangle$$

where a and b are complex constants such that $|a|^2 + |b|^2 = 1$. This state vector is known as a *spinor*.

Now, let $\underline{n}$ be the unit vector in the direction denoted by the polar coordinates (θ, ϕ); that is, $\underline{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$. Then:

$$\underline{n} \cdot \underline{\sigma} = \begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}$$

This has eigenvectors corresponding to eigenvalues ± 1 of

$$\underline{v}^+ = \begin{pmatrix} \cos\theta/2\, e^{-i\phi/2} \\ \sin\theta/2\, e^{i\phi/2} \end{pmatrix} \quad \text{and} \quad \underline{v}^- = \begin{pmatrix} -\sin\theta/2\, e^{-i\phi/2} \\ \cos\theta/2\, e^{i\phi/2} \end{pmatrix}$$

Then, in the basis $(|+\rangle, |-\rangle)$, we can write the states of a spin-half particle in which the measurement of a component of spin along $\underline{n}$ is certain to yield $\pm\frac{1}{2}\hbar$ as

$$\begin{aligned} |+, \underline{n}\rangle &= \sin\theta/2\, e^{i\phi/2}\,|-\rangle + \cos\theta/2\, e^{-i\phi/2}\,|+\rangle \\ |-, \underline{n}\rangle &= \cos\theta/2\, e^{i\phi/2}\,|-\rangle - \sin\theta/2\, e^{-i\phi/2}\,|+\rangle \end{aligned}$$

Let us look at some cases of these results. For $\theta = \pi/2$, we find that both $|+, \underline{n}\rangle$ and $|-, \underline{n}\rangle$ have equal probabilities due to symmetry; it is equally likely for the particle to be in a spin-up and a spin-down state. For $\theta = \pi$, there is complete certainty to measure the spin in the negative z direction, as $\underline{n}(\pi) = -\widehat{\underline{z}}$. Note the useful cases of:

$$\boxed{|\pm, x\rangle = \frac{1}{\sqrt{2}}(|+\rangle \pm |-\rangle) \quad \text{and} \quad |\pm, y\rangle = \frac{1}{\sqrt{2}}(|+\rangle \pm i\,|-\rangle)} \qquad (5.23)$$

5.3.2 Spin and Magnetic Fields

As we have seen in the A2 course, magnetic dipoles are influenced by magnetic fields. Spin causes particles to have an intrinsic dipole moment of

$$\underline{\mu} = \gamma \underline{S}$$

where the constant of proportionality $\gamma = e/(2m)$ is known as the *gyromagnetic ratio*. When this is placed in an external magnetic field $\underline{B}$, it experiences a torque $\underline{\mu} \times \underline{B}$. The energy, and consequently the Hamiltonian, that is associated with this torque is

$$\boxed{H = -\underline{\mu} \cdot \underline{B} = -\gamma \underline{S} \cdot \underline{B}} \tag{5.24}$$

The Hamiltonian lacks any kinetic energy term, as if the particle is initially at rest (we can move to a frame in which it is), there is no change in kinetic energy as the external magnetic field does no work on the particle.

A spin-half particle is placed in a magnetic field of magnitude B_0, orientated along the z-axis. It is found that at $t = 0$, the particle is in an eigenstate of $|+, \underline{x}\rangle$ of S_x. At later times, find $\langle S_x \rangle$, $\langle S_y \rangle$ and the probability to be in $|-, x\rangle$.

The first step is to evaluate our expression for the Hamiltonian.

$$H = -\frac{\gamma\hbar}{2}\underline{\sigma} \cdot \underline{B} = -\frac{\gamma\hbar}{2}\sigma_z B_0 = -\underbrace{\frac{1}{2}\gamma\hbar B_0}_{E_0}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

This means that the eigenstates of the Hamiltonian are eigenstates of S_z with eigenvalues $\pm E_0$. The initial state of the system in the basis $(|+\rangle, |-\rangle)$ is

$$|\psi, 0\rangle = |+, \underline{x}\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$$

As $\dot{H} = 0$, the time evolution of the system is given by (2.4):

$$|\psi, t\rangle = \frac{1}{\sqrt{2}}e^{iE_0 t/\hbar}|+\rangle + \frac{1}{\sqrt{2}}e^{-iE_0 t/\hbar}|-\rangle$$

We can then go about calculating the desired quantities using this expression.

$$\langle S_x \rangle = \frac{\hbar}{2}\langle \psi, t|\sigma_x|\psi, t\rangle = \frac{\hbar}{2}\langle \psi, t|\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}|\psi, t\rangle = \frac{\hbar}{4}\left(e^{2iE_0 t/\hbar} + e^{-2iE_0 t/\hbar}\right) = \frac{\hbar}{2}\cos(\gamma B_0 t)$$
$$\langle S_y \rangle = \frac{\hbar}{2}\langle \psi, t|\sigma_y|\psi, t\rangle = \frac{\hbar}{2}\langle \psi, t|\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}|\psi, t\rangle = \frac{i\hbar}{4}\left(e^{2iE_0 t/\hbar} - e^{-2iE_0 t/\hbar}\right) = -\frac{\hbar}{2}\sin(\gamma B_0 t)$$

From the eigenvectors of S_x, it is clear that in the basis $(|+\rangle, |-\rangle)$ that

$$|-, x\rangle = \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle)$$

Thus, the probability of being along $-x$ is

$$P_{-x} = |\langle -, x|\psi, t\rangle|^2 = \sin^2\left(\frac{1}{2}\gamma B_0 t\right)$$

All of these results describe the procession of the spin of the particle in the magnetic field.

5.3.3 Stern-Gerlach Experiment

The Stern-Gerlach Experiment was first conducted by the German physicists Otto Stern and Walther Gerlach, in 1922. It involved the use of an inhomogeneous magnetic field (in the z direction) that results in a force being exerted on anything with a magnetic dipole moment, given by

$$F = \mu_z \frac{\partial B_z}{\partial z}$$

If we had a continuous spectrum of values for the magnetic dipole moment, we would expect to observe a continuous spread of beams coming out of the apparatus. However, when performed with electrons (spin-half particles), only two beams were observed, as we have come to expect through our treatment of spin. This was the first experimental demonstration of the effect of spin.

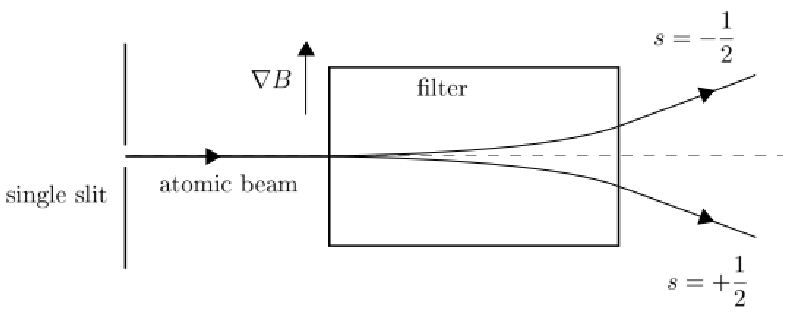

Figure 5.2: A schematic diagram of the Stern-Gerlach apparatus

The Stern-Gerlach experiment can be best understood by realizing that it effectively counts as a measurement, and so the wavefunction is collapsed into whatever eigenstate we measure it to be in. For initially unpolarised atoms/electrons, the equal-probabilities assumption from Statistical Mechanics tells us that there will be equal probabilities to find the atoms with their spin up or down along some axis when passed through a filter. We can find the transmission amplitudes for subsequent filters with inner products - for example, say we pass a beam of spin-up particles through a filter aligned along $\underline{n}$ that transmits plus along the positive $\underline{n}$ direction. Using the results of Section (5.3.1), we know that the probability of transmission is

$$P_t = |\langle +, z | +, \underline{n} \rangle|^2 = \cos^2 \theta/2$$

A consequence of these collapses is that if we line up a filter along $+z$, then $+x$, then z, we still get some transmission even though classically we'd expect all of the z to be filtered out - the only relevant thing is the most recent filter, as that determines the eigenstate that the particles are collapsed into, rather than what has come before.

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 that passes only $J_x = \hbar$ and finally a third that passes only $J_z = -\hbar$. What is the probability that a particle makes it through all three filters?

Before the filter, all three spins are equally likely, and so the probability of transmission for a given particle through the first filter is $P_1 = \frac{1}{3}$. We now need to calculate the eigenvector corresponding to $|+,x\rangle$.

$$S_x\,|+,x\rangle = \hbar\,|+,x\rangle \;\longrightarrow\; |+,x\rangle = \frac{1}{2}\begin{pmatrix}1\\ \sqrt{2}\\ 1\end{pmatrix}$$

Then, the probability of transmission through the second filter is

$$P_2 = |\langle +,x|+\rangle|^2 = \left|\frac{1}{2}\begin{pmatrix}1\\ \sqrt{2}\\ 1\end{pmatrix}\begin{pmatrix}1\\ 0\\ 0\end{pmatrix}\right|^2 = \frac{1}{4}$$

Similarly, for the third filter

$$P_3 = |\langle +,x|-\rangle|^2 = \left|\frac{1}{2}\begin{pmatrix}1\\ \sqrt{2}\\ 1\end{pmatrix}\begin{pmatrix}0\\ 0\\ 1\end{pmatrix}\right|^2 = \frac{1}{4}$$

Thus, the probability that any one particle passes through the whole system is given by

$$P_t = P_1P_2P_3 = \frac{1}{48}$$

5.4 Composite Systems

Suppose that we have two systems A and B that we can describe by the kets

$$|A\rangle = \sum_i a_i |a_i\rangle \quad \text{and} \quad |B\rangle = \sum_j b_j |b_j\rangle$$

Then, quite generally, we can write the state of the composite system as

$$|\psi\rangle = \sum_{ij} c_{ij} |a_i, b_j\rangle$$

We will consider two different cases for composite systems in the following sections.

5.4.1 Product States

In some cases, we can write the state of the composite system as a product of the two separate systems

$$\boxed{|\psi\rangle = |A\rangle \otimes |B\rangle} \tag{5.25}$$

This is called a *product state* as the the probabilities for the state of the composite system are the product of the probabilities for the respective states of the systems.

$$P_{a_i b_j} = |\langle a_i b_j|\psi\rangle|^2 = |\langle a_i|A\rangle|^2 |\langle b_j|B\rangle|^2 = P_{a_i} P_{b_j}$$

In such states, each system behaves independently of the other. For example, consider a composite system of two independent electrons. We can write their separate states as

$$|A\rangle = a_1 |+\rangle_A + a_2 |-\rangle_A$$
$$|B\rangle = b_1 |+\rangle_B + b_2 |-\rangle_B$$

The product state is then given by

$$|\psi\rangle = a_1 b_1 |+,+\rangle + a_1 b_2 |+,-\rangle + a_2 b_1 |-,+\rangle + a_2 b_2 |-,-\rangle$$

Suppose that we wanted to find the probability that A is in $|+\rangle$ given that B is in $|-\rangle$.

$$P(A \text{ in } |+\rangle \, |B \text{ in } |-\rangle) = \frac{P(|+,-\rangle)}{P(B \text{ in } |-\rangle)} = \frac{|a_1 b_2|^2}{|a_1 b_2|^2 + |a_2 b_2|^2} = |a_1|^2$$

This means that the condition on B makes zero difference to the state of A. This is why product states are said to be *uncorrelated* or *separable* states.

Suppose that our states A and B are now described by Hamiltonians H_A and H_B. Let $|a,b\rangle = |a\rangle |b\rangle$ describe the state of the combined system. Substitute this into the TDSE:

$$i\hbar \frac{\partial |a,b\rangle}{\partial t} = i\hbar \left(\frac{\partial |a\rangle}{\partial t} |b\rangle + |a\rangle \frac{\partial |b\rangle}{\partial t} \right) = H_A |a\rangle |b\rangle + H_B |a\rangle |b\rangle = \underbrace{(H_a + H_b)}_{H_{AB}} |a,b\rangle$$

Thus, the composite system satisfies the TDSE with $H_{AB} = H_A + H_B$. For two independent systems, we must have that $[H_A, H_B] = 0$ as they cannot modify one another's equations of motion, and thus their energy.

5.4.2 Correlated States

If you cannot write the state of the composite system as a product state, then it is known as a *correlated* or *entangled state.* In this case, the systems must be interacting. This means that for a state of the system

$$|a,b\rangle = \sum_{a,b} c_{ab} |a\rangle |b\rangle$$

we write that the Hamiltonian is

$$H_{AB} = H_A + H_B + H_{\text{int.}}$$

where the last term is the *interaction Hamiltonian* that describes how the two sub-systems influence one-another. We shall once again substitute our state vector into the TDSE:

$$i\hbar\frac{\partial |a,b\rangle}{\partial t} = i\hbar\frac{\partial}{\partial t}\left(\sum_{a,b} c_{ab}|a\rangle|b\rangle\right) = i\hbar\sum_{a,b}\left(\frac{\partial c_{ab}}{\partial t} + c_{ab}\frac{\partial}{\partial t}(|a\rangle|b\rangle)\right)$$

Cancelling terms with the RHS of the TDSE, we find that

$$\boxed{i\hbar\sum_{a,b}\frac{\partial c_{ab}}{\partial t}|a,b\rangle = H_{\text{int.}}|a,b\rangle} \tag{5.26}$$

The time evolution of the expansion coefficients is thus governed by the interaction coupling $H_{\text{int.}}$, and so governs how the motion of each particle is modified in time. Evidently, this means that $[H_{\text{int.}}, H_A] \neq 0$; neither are constants of motion, as energy is continuously transferred between systems A and B.

Let us now consider the important example of two interacting spin-half particles. Their interaction Hamiltonian is given by

$$H_{\text{int.}} = \frac{A}{4\hbar^2}\underline{S}_1\cdot\underline{S}_2 = \frac{A}{4}\underline{\sigma}_1\cdot\underline{\sigma}_2$$

We need to use the basis $|+,+\rangle, |+,-\rangle, |-,+\rangle, |-,-\rangle$ to describe the state of the combined system. Calculating the matrix elements with respect to this basis, we find that

$$\underline{S}_1\cdot\underline{S}_2 = \frac{\hbar^2}{4}\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 2 & 0\\ 0 & 2 & -1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix}$$

This allows us to find the eigenvalues and eigenvectors of the interaction Hamiltonian as

State	Energy Eigenvalue	Total z component of spin
$\|+,+\rangle$	$A/4$	$\hbar$
$\frac{1}{\sqrt{2}}(\|+,-\rangle + \|-,+\rangle)$	$A/4$	0
$\|-,-\rangle$	$A/4$	$-\hbar$
$\frac{1}{\sqrt{2}}(\|+,-\rangle - \|-,+\rangle)$	$-3A/4$	0

Thus, the energy eigenstates consist of a triplet of levels at $E = A/4$ and a singlet level at $E = -3A/4$.

5.4.3 Combining Angular Momentum

As we are now working with composite systems, we want to examine how to combine angular momenta. Suppose that we have two angular momenta denoted by quantum numbers j_1 and j_2 that lead to a combined angular momenta denoted by the quantum number J with z-component M. J_1^2 and J_2^2 will commute with all components of $\underline{J}$, but components of $\underline{J}_1$ and $\underline{J}_2$ do not individually commute with J^2. This means that we can know

- j_1, m_1, j_2, m_2 and M but not J **OR**
- j_1, j_2, M and J but not m_1 or m_2

We know that $M = m_1 + m_2 \leq j_1 + j_2$. When $M = j_1 + j_2$, we have one state of the system, $M = j_1 + j_2 - 1$, we have two states....the number of states will increase until we reach $M = |j_1 - j_2|$. This means that J can take values

$$\boxed{J = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2} \tag{5.27}$$

We have already seen that the multiplicity of the individual angular momenta are

$$g(j_1) = 2j_1 + 1$$
$$g(j_2) = 2j_2 + 1$$

Using (5.27), we multiplicity of the combined angular momentum is then given by

$$g(J) = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} M = \sum_{J=|j_1-j_2|}^{j_1+j_2} 2J + 1 = \sum_{n=0}^{2j_2} 2(j_1 - j_2 + n) + 1$$
$$= (2j_2 + 1)(2j_1 - 2j_2 + 1) + 2\sum_{n=0}^{2j_2} n = (2j_1 + 1)(2j_2 + 1)$$

We hence find that

$$\boxed{g(J) = g(j_1 + j_2) = g(j_1)g(j_2)} \tag{5.28}$$

This is equal to the number of states of the two angular momenta as the system is a product state of the two original states, giving rise to this degeneracy.

Clebsh-Gordan Coefficients

We can write the total state of the system as

$$|J, M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C_{JM} |j_1, m_1, j_2, m_2\rangle$$

where $C_{JM} = \langle j_1, m_1, j_2, m_2 | J, M\rangle$ are known as the *Clebsch-Gordan coefficients.* The evaluation of these is quite a lengthy, and annoying process, so they are generally looked up in a set of reference tables, such as those overleaf.

A box containing two spin-1 objects A and B is found to have angular momentum quantum numbers $J = 2$ and $M = 1$. Determine the the probabilities for the various eigenvalues when J_z is measured for A.

$j_1 = \frac{1}{2}$ and $j_2 = \frac{1}{2}$

m_1	m_2	M	$J=1$, $M=1$	$J=1$, $M=0$	$J=0$, $M=0$	$J=1$, $M=-1$
$\frac{1}{2}$	$\frac{1}{2}$	1	1			
$\frac{1}{2}$	$-\frac{1}{2}$	0		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	
$-\frac{1}{2}$	$\frac{1}{2}$	0		$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	
$-\frac{1}{2}$	$-\frac{1}{2}$	-1				1

$j_1 = 1$ and $j_2 = \frac{1}{2}$

m_1	m_2	M	$J=\frac{3}{2}$, $M=\frac{3}{2}$	$J=\frac{3}{2}$, $M=\frac{1}{2}$	$J=\frac{1}{2}$, $M=\frac{1}{2}$	$J=\frac{3}{2}$, $M=-\frac{1}{2}$	$J=\frac{1}{2}$, $M=-\frac{1}{2}$	$J=\frac{3}{2}$, $M=-\frac{3}{2}$
1	$\frac{1}{2}$	1	1					
1	$-\frac{1}{2}$	0		$\sqrt{\frac{1}{3}}$	$\sqrt{\frac{2}{3}}$			
0	$\frac{1}{2}$	0		$\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{1}{3}}$			
0	$-\frac{1}{2}$	-1				$\sqrt{\frac{2}{3}}$	$\sqrt{\frac{1}{3}}$	
-1	$\frac{1}{2}$	0				$\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{2}{3}}$	
-1	$-\frac{1}{2}$	-1						1

Figure 5.3: Tables of Clebsch-Gordan coefficients for two sets of j_1 and j_2

We know that the system must be in the state $|J, J-1\rangle$ as $J = 2$ and $M = 1$. We can find this state by using

$$J_- = J_{1_-} + J_{2_-} = (J_{x_1} - iJ_{y_1})(J_{x_2} - iJ_{y_2})$$

on the state $|J, J\rangle$. We know that

$$J_- |J, J\rangle = \sqrt{2J}\, |J, J-1\rangle$$

from (5.10). Then:

$$J_- |J, J\rangle = (J_{1_-} + J_{2_-}) |j_1, j_2\rangle |j_2, j_2\rangle = \sqrt{2j_1}\, |j_1, j_1 - 1\rangle |j_2, j_2\rangle + \sqrt{2j_2}\, |j_1, j_1\rangle |j_2, j_2 - 1\rangle$$

Hence, we arrive at the general result of

$$|J, J-1\rangle = \sqrt{\frac{j_1}{J}}\, |j_1, j_1 - 1\rangle |j_2, j_2\rangle + \sqrt{\frac{j_2}{J}}\, |j_1, j_1\rangle |j_2, j_2 - 1\rangle$$

In this case, we have that $J = 2$, $j_1 = j_2 = 1$. Then:

$$|2, 1\rangle = \frac{1}{\sqrt{2}}(|1, 0\rangle |1, 1\rangle + |1, 1\rangle |1, 0\rangle)$$

This means that the probabilities that we require are

$$P(m = -\hbar) = 0$$
$$P(m = \hbar) = 1/2$$
$$P(m = 0) = 1/2$$

where we have simply read off the coefficients from the state vector above.

5.5 The Hydrogen Atom

We have spent the vast majority of this chapter building up our mathematical and physical apparatus concerning angular momentum in Quantum Mechanics; it is now to time to put this into practise by looking at the hydrogen atom. In fact, we will look at *hydrogenic atoms*; those with any nucleus (of nucleic charge Ze) but only a single orbiting electron. We are going to ignore the effects of relativity, spin and magnetism.

5.5.1 The Bohr Model

Many students will already be familiar with the Bohr model, but it has been included here to give comparison to the quantum mechanical treatment that will come later. This classical model is of course wrong, but gives a lot of correct answer to some simple questions.

Let m_n be the mass of the nucleus, m_e the mass of the orbiting electron, and μ be the *reduced mass* of the system.

$$\mu = \frac{m_e m_n}{m_e + m_n}$$

In most circumstances, we can write that $\mu \backsim m_e$ as $m_n \gg m_e$ even for just a single proton. We are going to consider our equivalent particle (which is effectively the electron) to be in a fixed orbit of radius r around the centre of mass of the system (essentially the centre of mass of the nucleus in most scenarios). Classically, we can write the energy of this system as

$$E = \frac{L^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

If we minimise this energy curve, with the assumption that $L = n\hbar$, we find that the most probable radius is

$$r = a_\mu \frac{n^2}{Z} \tag{5.29}$$

Note that $a_\mu = \frac{m_e}{\mu} a_0$, where a_0 is defined as

$$\boxed{a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \backsim 5 \times 10^{-11} \text{ m}} \tag{5.30}$$

This is known as the *Bohr radius*, and is the standard unit for length in atomic physics. At this stage, it is also useful to define the *fine structure constant*

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \backsim \frac{1}{137} \tag{5.31}$$

Putting these results together, we find that that the energy levels of the system are given by

$$\boxed{E_n = -\frac{1}{2}\mu(\alpha c)^2 \frac{Z^2}{n^2}} \tag{5.32}$$

For the hydrogen atom, the coefficient of the fraction is known as a *Rydberg* of energy that has value $\mathcal{R} = 13.6$ eV. The bound states in the system will thus all have energy $E_n < 0$. Interestingly, as we shall see, this turns out to be the correct answer when you treat the same problem quantum mechanically.

5.5.2 With Quantum Mechanics

Let M and P be the mass and momenta of the centre of mass of the system respectively, and $\underline{r} = \underline{r}_e - \underline{r}_n$. Then, we can write the Hamiltonian of the system as

$$H = \frac{p_e^2}{2m_e} + \frac{p_n^2}{2m_n} + V(r_e - r_n) = \underbrace{\frac{P^2}{2M}}_{\text{centre of mass motion}} + \underbrace{\frac{p^2}{2\mu} + V(\underline{r})}_{\text{relative mass motion}}$$

We can arbitrarily move to a coordinate system in which there is no motion of the centre of mass. As we saw in Section (5.2.2), we can decompose the momentum into a radial and angular components:

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} = H_r + \frac{L^2}{2\mu r^2}$$

It follows that L^2 commutes with H as L^2 is spherically symmetric, and the remainder of the terms in H depend only on radius. Therefore, there exists a complete set of mutual eigenkets of H, L^2 and L_z, which we use to denote the states of hydrogenic atoms. We write this as $|n,\ell,m\rangle$, which can be thought of as a product state of $|n,\ell\rangle$ and $|\ell,m\rangle$. This means that we can automatically write that

$$\langle r,\theta,\phi|n,\ell,m\rangle = \underbrace{\langle r|n,\ell\rangle}_{\text{radial}}\underbrace{\langle\theta,\phi|\ell,m\rangle}_{\text{angular}} = R_\ell(r)\,Y_\ell^m(\theta,\phi)$$

Substituting this trial solution into the TISE:

$$\begin{aligned} H\,\langle r,\theta,\phi|\psi\rangle &= E\,\langle r,\theta,\phi|\psi\rangle \\ \left(H_r + \frac{L^2}{2\mu r^2}\right) RY &= ERY \\ \underbrace{\frac{1}{Y}L^2\,Y}_{\text{function of }\theta,\phi\text{ only}} &= \underbrace{2\mu r^2\left(E - \frac{1}{R}HR\right)}_{\text{function of }r\text{ only}} \end{aligned}$$

Evidently, as we know that the angular eigenfunctions are the spherical harmonics, we have an easy choice of separation constant. This means that the radial equation becomes

$$-\frac{\hbar^2}{2\mu}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \left[\frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\right]R(r) = ER(r)$$

Let our trial solution be of the form $R(r) = \rho^\ell e^{-\lambda\rho}L(2\lambda\rho)$ for $\rho = Zr/a_\mu$, some constant λ, and an arbitrary function L. Letting $y = 2\lambda\rho$, we arrive at

$$yL''(y) + L'(y)\left[2(\ell+1) - y\right] - \left[\ell + 1 - \frac{1}{\lambda}\right]L(y) = 0$$

This differential equation can be solved by the methods covered in the Mathematical Methods course, but the solutions turn out to be associated Laguerre polynomials

$$L_k^{2\ell+1}(y) \quad \text{for} \quad \lambda = \frac{1}{k+\ell+1}$$

where k sums over integers. This means that we have the restrictions that $k \geq 0$ and $\ell \leq n-1$. We call n the principle quantum number. If we look at the multiplicity of each of the states denoted by the n, we find that

$$g(n) = \underbrace{2}_{\text{spin states}}\sum_{\ell=0}^{n-1}(2\ell+1) = 2n^2$$

Putting all of these results together, we finally find that the eigenfunctions for the states of a hydrogenic atom are given by

$$\langle r,\theta,\phi|n,\ell,m\rangle \propto r^{\ell}e^{-\frac{Zr}{na_\mu}}L_{n-\ell-1}^{2\ell+1}\left(\frac{2Zr}{na_\mu}\right)Y_\ell^m(\theta,\phi)$$

These eigenfunctions give the same value for energy as predicted by the Bohr model if we calculate the expectation values of the kinetic and potential energy. When normalising these functions, remember to integrate over r,θ and ϕ. It is often easier to separately normalise the radial and the angular parts separately.

Let us quickly consider an interesting property of the spherical harmonics in the context of an 'orbiting' electron. What is the probability of finding an electron at (r,θ,ϕ) given that it is in a state of well defined angular momentum? Suppose that we do not know anything else about the angular dependence of the wave-functions. This means that the only fair assumption we can make is that the electron as an equal probability of being in any of the states for a given ℓ,θ and ϕ. It in fact turns out that

$$P(\text{electron at }\theta,\phi) = \frac{1}{2\ell+1}\sum_{m=-\ell}^{\ell}|Y_\ell^m|^2 = \frac{1}{4\pi}$$

Note how the last term is essentially the inverse of the solid angle for a sphere, essentially telling us that there is equal probability at being at each (θ,ϕ) in the absence of further information.

Radial Wavefunctions

Evidently, one does not have to be able to recall all of the radial wave-functions, but the one worth remembering is that of the ground-state, given by

$$\boxed{\langle r|1,0,0\rangle = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2}e^{-Zr/a_\mu}} \tag{5.33}$$

where again $a_\mu = \frac{m_e}{\mu}a_0$. Note that this had been normalised over all space. A notable point about the groundstate (as well as all other $\ell = 0$ states) is that it has a non-vanishing probability of being near $r = 0$, as the Coulomb potential is unbounded near the origin, only held in check by the Strong Force. Some graphs of the lower order radial wavefunctions are shown in the figure overleaf.

The plots in the left-hand column simply show the wavefunction, while those in the right-hand column show the probability of finding the electron in the range $[r, r+dr]$. There are $n-1$ nodes for each value of n, and so as you increase n, you will obtain more frequent, and sharper peaks. This means that for higher n, the electrons tend to be found in more and more discrete bands further away from the origin.

Size of Orbit

Let us finish by calculating the expectation value of $\langle r\rangle$ to give us an idea of the typical size of a 'circular' orbit. To get this, we take $\ell = \ell_{\max} = n-1$. This means that $L_0^{2\ell+1} = 1$, and we have a much simpler radial wavefunction of the form

$$R(r) \propto r^{n-1}e^{-Zr/(na_\mu)}$$

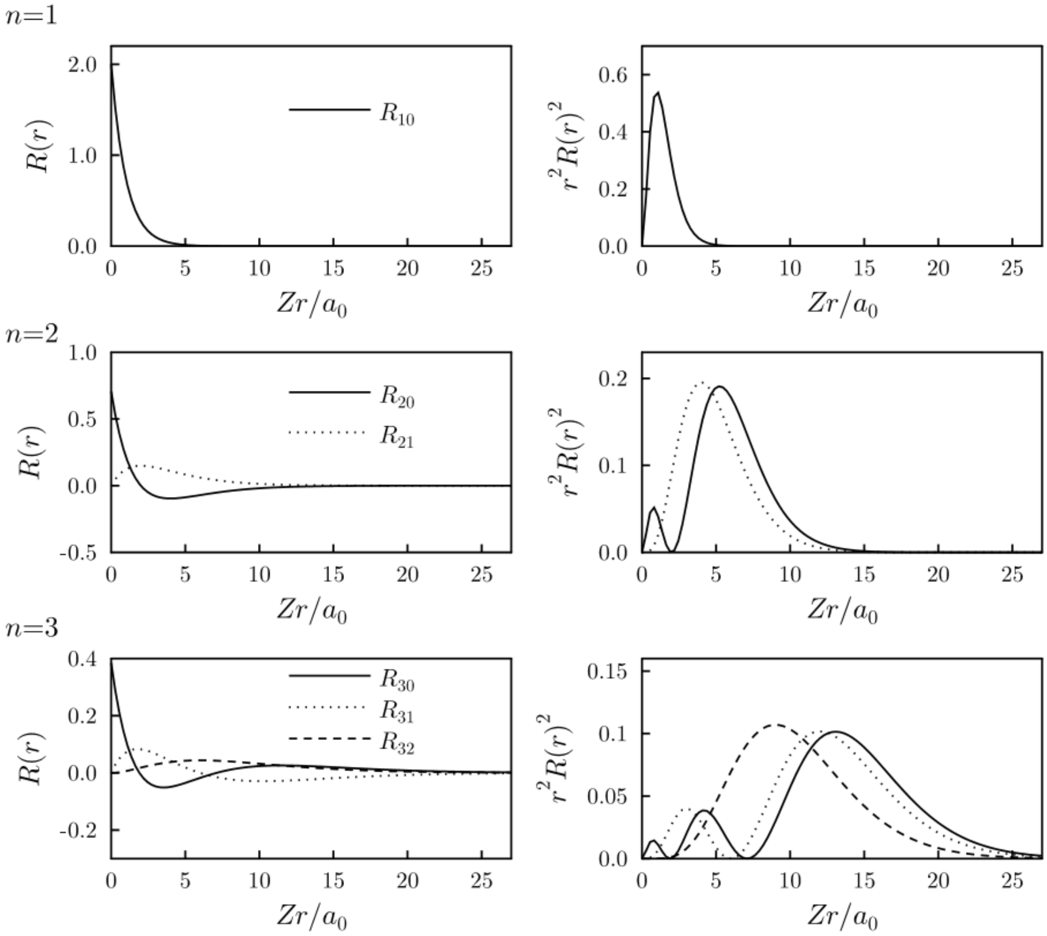

Figure 5.4: Graphs of some wavefunctions (left) and probability densities (right) for low values of n

Then, the expectation value is calculated as

$$\langle r \rangle = \frac{\int_0^\infty dr\, r^2\, |\psi|^2 r}{\int_0^\infty dr\, r^2 |\psi|^2} = \frac{\int_0^\infty dr\, r^{2n+1} e^{-2Zr/(na_\mu)}}{\int_0^\infty dr\, r^{2n} e^{-2Zr/(na_\mu)}} = \frac{na_\mu}{2}\frac{(2n+1)!}{(2n)!}$$

This means that our expression for our orbital size is

$$\boxed{\langle r \rangle = n\left(n+\frac{1}{2}\right)a_\mu} \tag{5.34}$$

Similarly, it can be shown that

$$\langle r^2 \rangle = n^2 (n+1)\left(n+\frac{1}{2}\right)a_\mu^2$$

This means that for large n, $\langle r \rangle \propto n^2$ while $\sigma_r \propto n^{3/2}$. This means that the variance around the average does not scale with the average, allowing the latter to tend towards a very sharp peak. In this limit, we recover the Bohr model.

A summary of the important results in this section is shown in the box below.

$$|n,\ell,m\rangle \quad \text{for} \quad \begin{cases} 1 \leq n \\ 0 \leq \ell \leq n-1 \\ -\ell \leq m \leq \ell \end{cases} \tag{5.35}$$

$$E_n = -\frac{1}{2}\mu(\alpha c)^2 \frac{Z^2}{n^2} \tag{5.36}$$

$$\langle r|1,0,0\rangle = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu} \tag{5.37}$$

$$\langle r\rangle = n\left(n+\frac{1}{2}\right)a_\mu \tag{5.38}$$

It is, to varying degrees of accuracy, often a good approximation to use hydrogenic formulae for different atoms - however relativistic effects start to become important for helium and anything more complex. What sort of fractional error would we expect when neglecting relativistic effects for hydrogen? We have that

$$E_{\text{clas.}} = \frac{1}{2}\mu(\alpha c)^2 \frac{Z^2}{n^2}$$
$$E_{\text{rel.}} = \gamma mc^2$$

where γ is defined as normal in Special Relativity. The fractional error is given by

$$\frac{\delta E}{E_{\text{rel.}}} = \frac{E_{\text{rel.}} - E_{\text{clas.}}}{E_{\text{rel.}}} \backsim \frac{1}{2}\left(\frac{v}{c}\right)^2 \backsim \alpha^2 \backsim 10^{-4}$$

So the fractional error isn't particularly large when neglecting relativistic effects in the hydrogen atom.

6. *Perturbation Theory*

This chapter aims to extend the knowledge gained in the preceding chapters by introducing the various aspects of Perturbation Theory, including:

- Time-Independent Perturbation Theory
- The Variational Principle
- Time-Dependent Perturbation Theory
- Selection Rules and Transitions
- Atoms in a Weak Magnetic Field

Perturbation Theory is used to calculate the changes that a system experiences when the Hamiltonian is modified in some way. The perturbation is generally applied to a system for which we have well-understood solutions, such as the Quantum Harmonic Oscillator, or the particle in the infinite square well. These systems are relatively 'boring'; perturbation theory is where the interesting Quantum Mechanics actually lies.

Some useful integrals:

$$\begin{aligned}
\int_{-\infty}^{\infty} dx\, e^{-(b^2x^2+ax)} &= \frac{\sqrt{\pi}}{b} e^{a^2/4b^2} \\
\int_{0}^{\infty} dx\, x^n e^{-ax} &= \frac{n!}{a^{n+1}} \\
\int_{0}^{\infty} dx\, x^{2n+1} e^{-ax^2} &= \frac{1}{2}\frac{n!}{a^{n+1}}
\end{aligned}$$

6.1 Time-Independent Perturbation Theory

Let us begin by considering time-independent changes to our Hamiltonian, for which we will have to consider solutions to Equation (2.1). Suppose that we can write our Hamiltonian in the form

$$H = \underbrace{H_0}_{\text{original Hamiltonian}} + \underbrace{\delta H}_{\text{small perturbation}}$$

This will give rise to some changes in energy that we will denote by

$$E = \underbrace{E_n}_{\text{original eigenvalue}} + \underbrace{\delta E_n}_{\text{first order correction}} + \dots$$

and some change in the original wave-function that we will denote by

$$|\psi\rangle = \underbrace{|E_n\rangle}_{\text{original eigenfunction}} + \underbrace{|\delta E_n\rangle}_{\text{perturbed eigenfunction}} + \dots$$

In order for these approximations to be valid, they must be a solution to the TISE. Thus, substituting the above terms:

$$(H_0 + \delta H)(|E_n\rangle + |\delta E_n\rangle + \dots) = (E_n + \delta E_n + \delta^2 E_n + \dots)(|E_n\rangle + |\delta E_n\rangle + \dots)$$

We now equate the various orders of terms that appear in this equation, as we know that each order must satisfy separate equalities as we can arbitrarily get rid of certain orders by scaling the size of the perturbation term.

$$H_0 |E_n\rangle = E_n |E_n\rangle \tag{6.1}$$

$$H_0 |\delta E_n\rangle + \delta H |E_n\rangle = E_n |\delta E_n\rangle + \delta E_n |E_n\rangle \tag{6.2}$$

Evidently, the first of these equations simply tells us that the original system satisfies the TISE, as we would expect. Let us find the first order correction in the energy. Bra through by $\langle E_n|$ in Equation (6.2):

$$H_0 \langle E_n|\delta E_n\rangle + \langle E_n| \delta H |E_n\rangle = E_n \langle E_n|\delta E_n\rangle + \delta E_n \langle E_n|E_n\rangle$$

This gives the first order change in the energy as the matrix element

$$\boxed{\delta E_n = \langle E_n| \delta H |E_n\rangle} \tag{6.3}$$

In the case of the change in the wave-function, we bra through by $\langle E_m|$ for $m \neq n$:

$$\begin{aligned} \langle E_m| H_0 |E_n\rangle + \langle E_m| \delta H |E_n\rangle &= E_n \langle E_m|\delta E_n\rangle + \delta E_n \langle E_m|E_n\rangle \\ \langle E_m| \delta H |E_n\rangle &= E_n \langle E_m|\delta E_n\rangle - E_m \langle E_m|\delta E_n\rangle \\ \langle E_m|\delta E_n\rangle &= \frac{\langle E_m| \delta H |E_n\rangle}{E_n - E_m} \end{aligned}$$

Thus, the first order change in the wave-function is given by

$$\boxed{|\delta E_n\rangle = \sum_{n\neq m} \frac{\langle E_m| \delta H |E_n\rangle}{E_n - E_m} |E_m\rangle} \tag{6.4}$$

The second order change in the energy is then given by the expectation value of the perturbation given the first order change in energy:

$$\delta^2 E_n = \langle E_n | \delta H | \delta E_n \rangle = \sum_{n \neq m} \frac{\langle E_n | \delta H | E_m \rangle \langle E_m | \delta H | E_n \rangle}{E_n - E_m}$$

This gives the simple expression of

$$\boxed{\delta^2 E_n = \sum_{n \neq m} \frac{| \langle E_n | \delta H | E_m \rangle |^2}{E_n - E_m}} \tag{6.5}$$

Note that the above expressions are all power-order approximations to the changes that occur upon the application of the perturbation δH. In some cases, one can actually find the exact change in the energy or the eigenfunctions; these can then be Taylor expanded to show agreement with the predictions of Perturbation Theory.

6.1.1 Some Examples

We are now going to consider a couple of illustrative examples of perturbations that will allow us to apply the results above.

- *When treating the hydrogen atom, we have so far assumed that the nucleus is point-like, when it fact it has finite size. Treating the nucleus as a uniformly charged sphere of radius $a_p \backsim 10^{-15}$ m, find the first order change in the ground-state energy of hydrogen.*

  We need to find our perturbing Hamiltonian in order to calculate these energy changes. For the normal hydrogen atom, the potential due to the nucleus outside it's radius must be given by

  $$V(r > a_p) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

  The potential inside the sphere is found using techniques from classical electromagnetism:

  $$V(r < a_p) = -\int_\infty^{a_p} dr\, \frac{eQ}{4\pi\epsilon_0} \frac{1}{r^2} - \int_{a_p}^{r} dr\, \frac{eQ}{4\pi\epsilon_0} \frac{r}{a_p^3} = -\frac{Ze^2}{8\pi\epsilon_0 a_p}\left(3 - \frac{r^2}{a_p^2}\right)$$

  This means that the perturbation acts only for $0 < r < a_p$, and is given by

  $$\delta H = V(r < a_p) - V(r > a_p) = \frac{Ze^2}{8\pi\epsilon_0 a_p}\left(\frac{r^2}{a_p^2} - 3 + \frac{2a_p}{r}\right)$$

  Using Equation (6.3) with $n = 1$ for the ground-state:

  $$\delta E = \langle E_1 | \delta H | E_1 \rangle = \frac{Ze^2}{2\pi\epsilon_0 a_p}\left(\frac{Z}{a_0}\right)^3 \int_0^{a_p} dr\, r^2 \left(\frac{r^2}{a_p^2} - 3 + \frac{2a_p}{r}\right) e^{-2Zr/a_0}$$

  We know that $a_p/a_0 \backsim 10^4 \ll 1$. This means that over the range of our integral , we can approximate that $e^{-2Zr/a_0} \backsim 1$.

  $$\delta E \backsim \frac{Ze^2}{2\pi\epsilon_0 a_p}\left(\frac{Z}{a_0}\right)^3 \int_0^{a_p} dr\, r^2 \left(\frac{r^2}{a_p^2} - 3 + \frac{2a_p}{r}\right) \backsim \frac{ze^2}{2\pi\epsilon_0 a_p} \frac{Z^3}{5} \left(\frac{a_p}{a_0}\right)^2$$

The ground-state energy for hydrogen is given by

$$|E_1| = \frac{Z^2 e^2}{8\pi\epsilon_0 a_0}$$

This means that we can write our value for the first order change in the energy as

$$\delta E = \frac{4}{5}|E_1|\left(\frac{Za_p}{a_0}\right)^2$$

Evidently, as $a_p/a_0 \backsim 10^{-4}$, this correction in the energy is vanishingly small. Note that the charge of the nucleus has a quadratic effect on the change in the energy.

- *Suppose that a Quantum Harmonic Oscillator is subject to a perturbing potential $\delta H = \lambda x^3$. Find the correction in the energies of the eigenstates.*

  We can consider x^3 to be a vector operator. As the states $|E_n\rangle$ are states of well-defined parity (the normal oscillator has a symmetric, quadratic potential), we can immediately say that

  $$\delta E_n = \langle n|\,\delta H\,|n\rangle = 0$$

  This can also be seen by writing $x = \ell(A^\dagger + A)$ as in Section (4.2); the terms in the expansion of x^3 all have un-even powers of $A^\dagger$ and A, meaning that the resultant states are orthogonal to $|E_n\rangle$. This means that we have to find the second order correction to the energy. As $A\,|0\rangle = 0$, the only terms that remain in the expansion of x^3 are those with ${A^\dagger}^2$ or higher.

  $$\begin{aligned}\langle n|\,\lambda x^3\,|n\rangle &= \lambda\ell^3\,\langle n|\,(A^\dagger + A)^3\,|0\rangle = \lambda\ell^3\,\langle n|\,{A^\dagger}^3 + A^\dagger A A^\dagger + AA^\dagger A^\dagger\,|0\rangle \\ &= \lambda\ell^3\,\langle n|\,(\sqrt{6}\,|3\rangle + 3\,|1\rangle) = \lambda\ell^3(\sqrt{6}\,\delta_{n,3} + 3\,\delta_{n,1})\end{aligned}$$

  Using Equation (6.5), we find the second order correction to the energy as

  $$\delta^2 E_n = \lambda^2\ell^6\left(\frac{6}{(E_0 - E_3)^2} + \frac{9}{(E_0 - E_1)^2}\right) = 11\frac{\lambda^2\ell^6}{\hbar\omega}$$

  As expected, the correction to the energy scales with both the constant λ, as well as the typical scale of the system ℓ.

6.1.2 Degenerate Perturbation Theory

The formalism above fails in the degenerate case where more than one state has the same energy. We can see that the sums in Equation (6.4) and (6.5) have a denominator that will clearly diverge for $m = n$. A way to understand this is that - if there is an eigenspace where the system has equal energy - the small perturbation can move us anywhere in this large, degenerate space. This means that small perturbations can give large changes in the state, and we have to abandon the assumption that the change in the wave-function is small in comparison to the original wave-function; that is, our Taylor expansion is no longer valid. The key to perturbation theory is that we can only talk about different states as those that have different energies, and the perturbation Hamiltonian δH is what determines states with different energies.

In order to be able to use the techniques of perturbation theory on degenerate states, we need to move to a basis in which the perturbed state is diagonal, as this means that we will not have to worry about degeneracy. We use the following steps:

1. Express the perturbation Hamiltonian δH in the basis of all new degenerate vectors.
2. Evaluate all the matrix elements to give a Hermitian matrix.
3. Diagonalise this matrix to find the eigenvalues and eigenvectors.

The eigenvalues will give the first order changes in the energy, and the eigenvectors are the new energy levels created as a result of the splitting of the degenerate levels.

The Quadratic Stark Effect

This is a very common example of a problem involving degenerate perturbation theory. Imagine that we place a hydrogen atom in the first excited state in a uniform electric field aligned along the z-axis. The perturbation to the system will then be

$$\boxed{\delta H = e\mathcal{E}\hat{\underline{z}} = e\mathcal{E}r\cos\theta} \tag{6.6}$$

Evidently, the $n = 2$ state is degenerate in both ℓ and m, as $0 \leq \ell \leq n-1$ and $-\ell \leq m \leq \ell$. The perturbing matrix is thus

$$\delta H_{ij} = \begin{pmatrix} \langle 2,0,0|\,\delta H\,|2,0,0\rangle & \langle 2,0,0|\,\delta H\,|2,1,0\rangle & \langle 2,0,0|\,\delta H\,|2,1,1\rangle & \langle 2,0,0|\,\delta H\,|2,1,-1\rangle \\ \langle 2,1,0|\,\delta H\,|2,0,0\rangle & \langle 2,1,0|\,\delta H\,|2,1,0\rangle & \langle 2,1,0|\,\delta H\,|2,1,1\rangle & \langle 2,1,0|\,\delta H\,|2,1,-1\rangle \\ \langle 2,1,1|\,\delta H\,|2,0,0\rangle & \langle 2,1,1|\,\delta H\,|2,1,0\rangle & \langle 2,1,1|\,\delta H\,|2,1,1\rangle & \langle 2,1,1|\,\delta H\,|2,1,-1\rangle \\ \langle 2,1,-1|\,\delta H\,|2,0,0\rangle & \langle 2,1,-1|\,\delta H\,|2,1,0\rangle & \langle 2,1,-1|\,\delta H\,|2,1,1\rangle & \langle 2,1,-1|\,\delta H\,|2,1,-1\rangle \end{pmatrix}$$

This looks like a horrible matrix to evaluate, but in fact we have some tricks up our sleeve. We know that for any state of even parity, the matrix element will be zero. Recalling Equation (5.18), we know that only terms where ℓ is odd will have odd parity and can contribute to the matrix. Also, remarking that $[L_z, z] = 0$:

$$L_z z\,|n,\ell,m\rangle = zL_z\,|n,\ell,m\rangle = m\hbar z\,|n,\ell,m\rangle$$

This means that $z\,|n,\ell,m\rangle$ is an eigenket of L_z, meaning that only terms where $m = 0$ are able to contribute. This means that we obtain a massively simplified matrix of

$$\delta H_{ij} = \begin{pmatrix} 0 & v & 0 & 0 \\ v & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

where $v = e\mathcal{E}\,\langle 2,0,0|\,z\,|2,1,0\rangle = -3e\mathcal{E}a_0$. It is easy to show that the new eigenvalues are $\mp 3e\mathcal{E}a_0$, 0, 0, with corresponding eigenstates

$$\frac{1}{\sqrt{2}}(|2,0,0\rangle \pm |2,1,0\rangle),\ \ |2,1,1\rangle\,,\ \ |2,1,-1\rangle$$

Note how two of the eigenstates have remained the same; these are unaffected by the perturbing Hamiltonian, and so we only observe the 'mixing' of the two states effected.

6.2 The Variational Principle

This is alternative method to perturbation theory that allows us to obtain some upper bound estimate for the ground-state energy given that we do not have explicit solutions for the form of the wave-functions for the new system.

Consider some general wave-function in the energy representation

$$|\psi\rangle = \sum_n a_n |E_n\rangle$$

Let us calculate the expectation value of the Hamiltonian in this state:

$$\begin{aligned}\langle\psi| H |\psi\rangle &= \sum_{n,m} a_m^* a_n \langle E_m| H |E_n\rangle \\ &= \sum_n |a_n|^2 E_n \\ &= \sum_n |a_n|^2 E_0 + \sum_n |a_n|^2 (E_n - E_0) \\ &= E_0 + \underbrace{\sum_n |a_n|^2 (E_n - E_0)}_{\geq 0}\end{aligned}$$

This means that we obtain the useful expression

$$\boxed{E_0 \leq \langle\psi| H |\psi\rangle} \tag{6.7}$$

We can use this in conjunction with *Rayleigh's Theorem*:

> *The stationary points of the expectation value of an Hermitian operator occur at the eigenstates of the operator. Moreover, all eigenstates provide stationary points of the operator*

Given that all eigenstate are stationary points, it is clear that the ground-state will be a minimum. Thus, if we take $|\psi\rangle$ to be a reasonable guess of the wave-function with some adjustable parameter, we can then minimise $\langle\psi| H |\psi\rangle$ (assuming that $|\psi\rangle$ is normalised) in order to obtain an upper bound on the ground-state energy of the system.

Show that for the un-normalised spherically symmetric wave-function $\psi(r)$ the expectation value of the gross structure Hamiltonian of hydrogen is

$$\langle H\rangle = \left(\frac{\hbar^2}{2m}\int dr\, r^2 \left|\frac{\partial\psi}{\partial r}\right|^2 - \frac{e^2}{4\pi\epsilon_0}\int dr\, r|\psi|^2\right) \Big/ \int dr\, r^2|\psi|^2$$

Using the trial wave-function $\psi = e^{-br}$, use the Variational Principle to find the definitions of a_0 and $\mathcal{R}$.

As this is a spherically symmetric wave-function, the angular components will cancel in the normalisation. The second term in $\langle H\rangle$ is clearly the expectation value with the scalar potential energy. We now need to consider the kinetic energy term. Using Equation (5.19):

$$|p_r|\psi\rangle|^2 = \hbar^2 \int dr\, r^2 \left|\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\psi\right|^2 = \hbar^2 \int dr\, r^2 \left|\frac{\partial\psi}{\partial r}\right|^2 + \frac{\partial}{\partial r}\left(r|\psi|^2\right) = \hbar^2 \int dr\, r^2 \left|\frac{\partial\psi}{\partial r}\right|^2$$

where the last equality follows from evaluating the second term in the integrand, assuming that the wave-function is well defined in space. This means that, with normalisation, we obtain the required result.

Now for $\psi = e^{-br}$. As an exercise for the reader, it is trivial integration to show that $\langle H \rangle$ becomes:

$$\langle H \rangle = \frac{\hbar^2 b^2}{2m} - \frac{e^2 b}{4\pi\epsilon_0}$$

This is a function of the free parameter b. By Rayleigh's Theorem, we want to minimise this expression:

$$\frac{\partial \langle H \rangle}{\partial b} : \quad \frac{\hbar^2}{m} b - \frac{e^2}{4\pi\epsilon_0} = 0 \longrightarrow b = \frac{me^2}{4\pi\hbar^2\epsilon_0} = a_0^{-1}$$

We thus re-obtain the un-normalised form of the ground-state wave-function with the Bohr radius. Substituting this value for b back into $\langle H \rangle$, we obtain:

$$\langle H \rangle = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{1}{2} m(\alpha c)^2 = -\mathcal{R}$$

We thus also obtain the expression for the Rydberg constant, assuming that we know that the energy takes the form given in Equation (5.32).

Equation (6.7) can also be used to prove the useful result that *any potential well has at least one bound state.* Suppose that a potential well is described by V_w, and consequently the Hamiltonian H_w. Let $V_{sq} > V_w$ be the potential describing a square well that 'fits' inside the potential V_w. For some state $|\psi\rangle$:

$$0 > \langle\psi| H_{sq} |\psi\rangle = \langle\psi| H_w - (V - V_{sq}) |\psi\rangle = \langle\psi| H |\psi\rangle - \langle\psi| \underbrace{V - V_{sq}}_{<0} |\psi\rangle$$

It follows that

$$\langle\psi| H |\psi\rangle < \langle\psi| H_{sq} |\psi\rangle < 0$$

As we know that the square well as at least one bound state, this means that our potential V_w must also have a bound state by the variational principle.

6.3 Time-Dependent Perturbation Theory

The result for time evolution in Equation (2.4) only holds for the case where the Hamiltonian in time-independent, meaning that we need another method to find the time evolution of states if $H = H(t)$. In essence, we need to solve

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

The method we use depends on how 'quickly' the Hamiltonian changes, measured with respect to the time-scale

$$\tau_H = \frac{\hbar}{E_n - E_m} \tag{6.8}$$

where E_n and E_m are the energy eigenvalues of two energy levels n and m respectively. τ_H corresponds to the evolution of a state under a time-independent Hamiltonian. We shall detail the main methods used in the following sections.

6.3.1 The Sudden Approximation

In this case, we assume that the change occurs over a time $t \ll \tau_H$ such that the system does not have enough time to modify it's wave-function to 'adjust' to the change. Suppose that the system is initially in a state that satisfies some time-independent Hamiltonian H_i, which is suddenly (almost instantaneously) changed to another time-independent Hamiltonian H_f. In this case, we write the Hamiltonian as

$$H(t) = \begin{cases} H_i & t < 0 \\ H_f & t > 0 \end{cases}$$

We know that the state for $t > 0$ must satisfy the TDSE. Suppose that the eigenstates of H_f are labelled by $\left|E_n\right\rangle$ with corresponding eigenvalues E_n. Then, it is clear that for $t > 0$:

$$\left|\psi, t\right\rangle = \sum_n a_n e^{-iE_nt/\hbar}\left|n\right\rangle$$

The only question that remains is what are the coefficients a_n? Are the TDSE is first order in time, it is pretty evident that these should be given by

$$\boxed{a_n = \left\langle n\middle|\psi(t=0^-)\right\rangle} \tag{6.9}$$

This means that calculations using the sudden approximation are typically very easy, as they simply involve calculating matrix elements.

A tritium atom, ^3H is in its ground state when the nucleus undergoes a beta decay and becomes ^3He. Assuming that the decay occurs over a short time interval, calculate the probability that this helium ion is in the $1s$ state.

The only difference between the initial and final states in the nucleic charge:

$$\begin{aligned} \text{Initial State}: &\ \left|1,0,0,Z=1\right\rangle \\ \text{Final State}: &\ \left|1,0,0,Z=2\right\rangle \end{aligned}$$

In both cases, $a_\mu \backsim a_0$ as $m_n \gg m_e$. Let a_t be the amplitude for the transition.

$$\begin{aligned} a_t &= \langle 1,0,0,Z=2|1,0,0,Z=1\rangle \\ &= \int_0^\infty dr\, r^2 R_{1,0,Z=2}\, R_{1,0,Z=1} \\ &= \frac{4(2^{3/2})}{a_0^3}\int_0^\infty dr\, r^2 e^{-3r/a_0} \\ &= \frac{8(2)^{3/2}}{3^3} \end{aligned}$$

Thus, the probability that the atom is left in the ground-state is given by

$$P_t = |a_t|^2 \backsim 0.702$$

As we will see later, the probability of the atom remaining in the same state is much greater than the probability that it undergoes a transition to any other state over a short time interval.

6.3.2 The Adiabatic Approximation

The adiabatic principle states that *if a system is already in an eigenstate of the Hamiltonian, if will remain in said eigenstate under slow time evolution of the Hamiltonian.* In this case, the change in the system occurs on a time-scale $t \gg \tau_H$.

To prove this, consider the instantaneous eigenstates $|n,t\rangle$ of the system that satisfy the

$$H(t)\,|n,t\rangle = E_n(t)\,|n,t\rangle$$

Then we can write

$$|\psi,t\rangle = \sum_n a_n(t)e^{-\frac{i}{\hbar}\int dt\, E_n(t)}\,|n,t\rangle = \sum_n a_n(t)e^{-\frac{i}{\hbar}I(t)}\,|n,t\rangle$$

Substitute this into the TDSE:

$$\sum_n e^{-\frac{i}{\hbar}I(t)}\left[\left(i\hbar\frac{\partial a_n}{\partial t} + \cancel{a_n E_n}\right)|n,t\rangle + i\hbar a_n\frac{\partial\,|n,t\rangle}{\partial t}\right] = \cancel{\sum_n e^{-\frac{i}{\hbar}I(t)}a_n \underbrace{H(t)\,|n,t\rangle}_{E_n(t)}}$$

Multiply both sides by $\langle m,t|$ and $\frac{1}{i\hbar}e^{i/\hbar\, I(t)}$:

$$\frac{\partial a_m}{\partial t} = -\sum_n a_n e^{\frac{i}{\hbar}\int dt\,(E_m - E_n)}\,\langle m,t|\,\frac{\partial\,|n,t\rangle}{\partial t}$$

Now let us bring some time-independent perturbation theory to bear on this problem. Consider an interval $[t, t+\delta t]$ for small δt.

$$\begin{aligned} H(t+\delta t) &\backsim H(t) + \delta t\frac{\partial H}{\partial t} \\ |n,t+\delta t\rangle &\backsim |n,t\rangle + \delta t\frac{\partial\,|n,t\rangle}{\partial t} \end{aligned}$$

The term $\partial\,|n,t\rangle/\partial t$ is simply our first order correction to the wave-function. By analogy to Equation (6.4)

$$\frac{\partial\,|n,t\rangle}{\partial t} = \sum_{m\neq n}\frac{\langle m|\,\frac{\partial H}{\partial t}\,|n\rangle}{E_n(t) - E_m(t)}\,|m(t)\rangle$$

Now suppose that $H(t)$ changes on a time-scale $\tau \gg \tau_H$. Make the substitution that $s = t/\tau$ so that $s = 0$ initially, and $s = 1$ finally. Putting all of this together, we arrive at the expression of

$$\frac{\partial a_m(s)}{\partial t} = -\sum_n a_n(s) e^{-\frac{i\tau}{\hbar}\int ds\,(E_m - E_n)} \frac{\langle m, s|\,\frac{\partial H}{\partial s}\,|n, s\rangle}{E_n(s) - E_m(s)}$$

As τ is very large in comparison to the other terms, there will be rapid oscillations in the integral that will average to zero upon integration to find a_m, meaning that the integral is zero for large times. This means that a_m is constant, and hence that the system remains in the eigenstate that it was in initially.

Consider a harmonic oscillator whose frequency is ω_0 for $t \leq 0$, and which is in an energy eigenstate $E = 3\hbar\omega_0/2$. For $t > 0$, the frequency slowly increases until a time t_1 where it has reached a value $2\omega_0$. Find the energy of the oscillator at $t = t_1$.

Recalling Equation (4.6), it is clear that the oscillator is in the $n = 1$ state at $t = 0$. According to the adiabatic principle, the oscillator is still in the $n = 1$ state, except the frequency is now $2\omega_0$. This means that the new energy is $E' = 3\hbar\omega_0$.

6.3.3 A Time-Dependent Perturbation

In this case, we assume that the original time-independent Hamiltonian H_0 is modified by some small time-dependent variation $\delta H(t)$. In this case, let us suppose that the solutions to the TDSE are of the form:

$$|\psi, t\rangle = \sum_n a_n(t) e^{-iE_n t/\hbar} |n\rangle$$

We are assuming that the energy eigenvalues and eigenfunctions are fixed by H_0, and only the coefficients that determine the superposition of states changes with time. Substitute this into the TDSE:

$$\begin{aligned}\sum_n e^{-iE_n t/\hbar} (i\hbar \dot{a}_n + \cancel{E_n a_n}) |n\rangle &= \sum_n e^{-iE_n t/\hbar} a_n (\cancel{H_0 |n\rangle} + \delta H |n\rangle) \\ i\hbar \sum_n \dot{a}_n e^{-iE_n t/\hbar} |n\rangle &= \sum_n e^{-iE_n t/\hbar} a_n \delta H |n\rangle\end{aligned}$$

Bra through by $\langle m|$ and $\frac{1}{i\hbar} e^{iE_m t/\hbar}$:

$$\dot{a}_m = -\frac{i}{\hbar} \sum_n e^{i(E_m - E_n)t/\hbar} \langle m|\,\delta H\,|n\rangle\, a_n$$

Suppose that the system is initially in the state n. Then, $a_n = \delta_{nm}$. This means that the amplitude of the transition to some state m is given by

$$\boxed{\dot{a}_m \backsim -\frac{i}{\hbar} e^{i(E_m - E_n)t/\hbar} \langle m|\,\delta H\,|n\rangle} \tag{6.10}$$

For short times, we would expect that $a_m \backsim 1$, meaning $\dot{a}_m$ is very small, and can often be neglected. At long times, however, all bets are off. Under this approximation, we are working to first order in δH as we have neglected all but the first order terms in the sum.

With an explicit expression for δH, one can then find expressions for the probability of a transition $n \mapsto m$, which we shall denote by P_{nm}. However, in some cases, it is actually possible to solve for the evolution of the system exactly, assuming that the perturbation is introduced 'suddenly' to the system. In this case, we use the following steps.

1. Find the matrix corresponding to the perturbed Hamiltonian.
2. Diagonalise this matrix to find the eigenvectors and eigenvalues. The eigenvalues are the new energies, while the eigenvectors correspond to the new energy levels of the system.
3. Express the eigenvectors in terms of the original basis.
4. Express the initial state of the system in terms of the new eigenvectors.
5. Bra through appropriately to find amplitudes.

A spin-half particle of magnetic moment μ is travelling at a speed v under the influence of a magnetic field of magnitude B that is orientated along z. Over small distance ℓ, another magnetic field of magnitude $b \ll B$ is applied along x. Given that the Hamiltonian satisfies

$$H(t) = \begin{cases} -\mu(B\sigma_z + b\sigma_x) & \text{for } 0 < t < \ell/v \\ -\mu B & \text{otherwise} \end{cases}$$

and that the initial spin-state of the particle was $|+\rangle$, find the probability that it transitions to $|-\rangle$.

Let us begin by solving this system exactly, and confirm our result using the results of this section. Consider the perturbed Hamiltonian:

$$H = -\mu B \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \mu b \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -\mu \begin{pmatrix} B & b \\ b & -B \end{pmatrix}$$

As above, let us diagonalise this to find the eigenvalues and eigenstates:

$$\begin{vmatrix} B-\lambda & b \\ b & -B-\lambda \end{vmatrix} \stackrel{!}{=} 0 \longrightarrow \lambda = \pm\mu\sqrt{b^2+B^2}$$

By the definition of some eigenvector (α, β):

$$\begin{pmatrix} B - \sqrt{b^2+B^2} & b \\ b & -B-\sqrt{b^2+B^2} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

This means that

$$r = \frac{\alpha}{\beta} = \frac{B}{b} \pm \sqrt{1 + \left(\frac{B}{b}\right)^2} \backsim \frac{2B}{b}$$

where we have used the fact that $b << B$. We can thus form our new eigenstates of the system as

$$|\tilde{+}\rangle = |+\rangle + \frac{b}{2B}|-\rangle$$
$$|\tilde{-}\rangle = |-\rangle - \frac{2b}{B}|+\rangle$$

They have been labelled as such as the first is an 'approximately up' state, while the other is an 'approximately down' state, both of which reduce to the original basis assuming that the perturbation tends to zero.

$$|+\rangle = c_1|\tilde{+}\rangle + c_2|\tilde{-}\rangle = \left(c_1 - \frac{2b}{B}c_2\right)|+\rangle + \left(c_2 + \frac{b}{2B}c_1\right)|-\rangle$$

This means that

$$|\psi, 0\rangle = |\widetilde{+}\rangle - \frac{b}{2B}|\widetilde{-}\rangle$$

Note that this state is already properly normalised as we can neglect the contribution from the second term. Let $E = \mu\sqrt{b^2 + B^2}$, and $\tau = \ell/v$.

$$\langle -|\psi, 0\rangle = \frac{b}{2B}\left(e^{-iE\tau/\hbar} - e^{iE\tau/\hbar}\right) = \frac{b}{B}\sin\left(\frac{\mu\sqrt{b^2+B^2}\tau}{\hbar}\right) \backsim \frac{b}{B}\sin\left(\frac{\mu B}{\hbar}\tau\right)$$

Thus, the required probability for the transition is

$$P_t = \left(\frac{b}{B}\right)^2 \sin^2\left((\frac{\mu B}{\hbar}\tau\right)$$

Let us now turn to perturbation theory. We can model the perturbation as

$$\delta H(t) = \begin{cases} \Lambda & \text{for } 0 < t < \tau \\ 0 & \text{otherwise} \end{cases}$$

such that the matrix elements of δH are denoted by Λ_{nm}. For $\omega_{nm} = (E_m - E_n)/\hbar$, we can write Equation (6.10) as

$$a_m = -\frac{i}{\hbar}\int dt\, e^{i\omega_{nm}t}\langle m|\,\delta H\,|n\rangle = \frac{2i\Lambda_{nm}}{\hbar\omega_{nm}}\sin\left(\frac{\omega_{nm}\tau}{2}\right)$$

giving associated probability

$$\boxed{P_{mn} = 4|\Lambda_{nm}|^2 \frac{\sin^2(\omega_{nm}\tau/2)}{(\hbar\omega_{nm})^2}} \tag{6.11}$$

In this case, it is clear that $\Lambda_{nm} = \mu B$, and that $\hbar\omega_{nm} = 2\mu B$. Plugging these into the expression above re-obtains the exact result. Notice how using perturbation theory is significantly faster; approximation is (nearly) always faster than not!

6.4 Transitions and Selection Rules

We are now going to consider the case of a sinusoidal perturbation on the system, as we know from Fourier analysis that we can represent a large number of functions to a high degree of accuracy as a sum of sinusoidal components. Let

$$\delta H(t) = V_0 e^{-i\omega t}$$

Let $\omega_{nm} = (E_m - E_n)/\hbar$, meaning that our amplitude for the transition can be written as

$$a_m = -\frac{i}{\hbar}\int dt\, e^{i\omega_{nm}t} \langle m|\,\delta H\,|n\rangle = -\frac{1}{\hbar}\langle m|\,V_0\,|n\rangle \frac{e^{i(\omega_{nm}-\omega)t}-1}{\omega_{nm}-\omega}$$

with associated probability

$$P_{nm} = \frac{|\langle m|\,V_0\,|n\rangle|^2}{\hbar^2} \underbrace{\frac{\sin^2\left(\frac{\omega_{nm}-\omega}{2}t\right)}{\left(\frac{\omega_{nm}-\omega}{2}\right)^2}}_{\text{transition cross section } \sigma(t)}$$

For a given t, $\sigma(t)$ is dominated by a bump around the origin that is of height t^2 and width $2\pi/t$. Hence, the area under the bump is proportional to t, and in the limit of large t we can write

$$\sigma(t) \propto t\,\delta(\omega_{nm} - \omega)$$

The constant of proportionality turns out to be 2π, which can be found by integrating the area under $\sigma(t)$. Thus, the rate at which the transition $n \mapsto m$ occurs is given by

$$\boxed{\nu_{mn} = \frac{2\pi}{\hbar^2}|\langle m|\,V_0\,|n\rangle|^2\,\delta(\omega_{nm}-\omega)} \tag{6.12}$$

This expression gives rise to what is known as *Fermi's Golden rule* of perturbation theory:

> *A perturbation $V_0 e^{-i\omega t}$ causes a system to transition to a new state higher in energy by $\hbar\omega$ at a rate proportional to the mod-square of the matrix element of V_0 between the initial and final states.*

It is very easy to see that for $\delta H = V_0 e^{i\omega t}$, there will be a transition to a new state that is lower in energy by $\hbar\omega$. To find the 'total' transition rate, we must integrate over all possible rates of transitioning from a given state n to all other possible states m. There are two possible cases:

1. We can have discrete E_n and E_m that are being considered, meaning that ω_{nm} remains fixed. However, there may be a range of ω in the incoming energy, with associated density of states $g(\omega)$.

$$\sum \nu_{nm} = \int d\omega\, g(\omega)\nu_{nm} = \frac{2\pi}{\hbar^2}|\langle m|\,V_0\,|n\rangle|^2 g(\omega_{nm})$$

2. The energies may vary continuously (meaning a continuous range in E_m), but ω of the incoming energy remains constant. Let the number of final states in $[E_m, E_m + dE_m]$ be $g(E_m)dE_m$.

$$\sum \nu_{nm} = \int dE_m\, g(E_m)\nu_{nm} = \frac{2\pi}{\hbar}|\langle m|\,V_0\,|n\rangle|^2 g(E_m + \hbar\omega)$$

Note that in this last expression, a factor of $\hbar$ has disappeared when integrating over energy.

6.4.1 Radiative Transitions

Radiative transitions occur between atomic energy levels in atoms, and are usually induced by some incoming electromagnetic wave. As $\lambda \ll a_0$ for most incident radiation, we can consider the strength of the electric and magnetic fields to be roughly constant over the transition cross-section. Furthermore, as the force due to the magnetic field is significantly less than that due to the electric field, we can neglect it's contribution. This is known as the *electric dipole approximation.*

In principle, we should describe the light wave using scalar and vector potentials V and $\underline{A}$, but a uniform oscillating electric field can be represented with a simple scalar potential. Suppose that the system is orientated such that the direction of the electric field is along the z-axis. Then we can describe the interaction by the perturbation

$$\delta H(t) = e\mathcal{E}z\, e^{\pm i\omega t}$$

By (6.12), the corresponding transition rates are given by:

$$\sum \nu_{nm} = \frac{2\pi}{\hbar^2} e^2\mathcal{E}^2 |\langle m|\, z\, |n\rangle|^2 g(\omega_{nm})$$

The relative magnitude of these expressions essentially translates to how strong an absorption or emission line is in a particular spectrum. The question now arises as to whether or not a transition actually occurs, which brings us to the topic of the next section.

6.4.2 Selection Rules

As we had already seen in the case of the transitions considered in Section (6.1.2), not all transitions are possible due to parity and symmetry arguments. Let us go about finding some *selection rules* that allow us to quickly determine whether a transition is possible or not, for which we will consider matrix elements of the form $\langle n', \ell', m'|\, v\, |n, \ell, m\rangle$ for a vector operator $\underline{v}$. Note that we will be working in the regime of the electric dipole approximation.

Recall from Equation (5.18) that the eigenstates of hydrogen are of well-defined parity satisfying

$$P\,|\ell, m\rangle = (-1)^\ell\, |\ell, m\rangle$$

We also know that the expectation value of any vector operator is zero in a state of well-defined parity. This means that if both ℓ and ℓ' are odd or even, then both states are of the same parity, and the matrix element must vanish. This automatically forces us to conclude that

$$|\ell - \ell'| = 1$$

in order for the state to be one of mixed parity. We shall now consider the case where $\underline{v} = z$. In a similar argument used before, as $[L_z, z] = 0$, we can write

$$L_z(z\,|n, \ell, m\rangle) = zL_z\,|n, \ell, m\rangle = m\hbar(z\,|n, \ell, m\rangle)$$

This means that $z\,|n, \ell, m\rangle$ is an eigenket of L_z, and is therefore orthogonal to all other eigenkets of L_z. This leads us to conclude that

$$|m - m'| = 0 \quad \text{for } z$$

Now, define the operators $x_\pm = x \pm iy$. It follows quickly from the commutation relations of angular momentum with vector operators that $[L_z, x_\pm] = \pm\hbar x_\pm$. Then:

$$L_z(x_\pm |n, \ell, m\rangle) = x_\pm(L_z \pm 1) |n, \ell, m\rangle = (m + 1)(x_\pm |n, \ell, m\rangle)$$

So $x_\pm |n, \ell, m\rangle$ is an eigenket of L_z with eigenvalue $m \pm 1$. Given that x and y can both be written in terms of $x_\pm$, we conclude that the matrix elements for x and y are zero unless

$$|m - m'| = 1$$

for orthogonality reasons. Note that $x_\pm$ do not commute with L^2; this means that we cannot use them in the place of $L_\pm$ to derive the eigenvalue relations as in Section (5.1.4). In any case, as summary of the important results is shown in the box below. We are assuming that the electric field is orientated along z.

$$\boxed{\begin{aligned} &\Delta\ell = \pm 1 &(6.13)\\ &\Delta m = 0 \quad \text{for } z &(6.14)\\ &\Delta m = \pm 1 \quad \text{for } x, y &(6.15)\end{aligned}}$$

How can we interpret these selection rules physically? This can be thought about in terms of the polarisation of the photon that is emitted as a result of these radiative transitions. Suppose that the photon is emitted in the same direction as the imposed electric field. If we observe the system along z, then the electric field vector of the radiation will be in the x-y plane, giving rise to circular polarisation. In fact, $\Delta m = 1$ corresponds to left-hand circularly polarised light, while $\Delta m = -1$ corresponds to right-hand circular. When the direction of observation is perpendicular to the imposed field, the electric vector of the radiation can be either perpendicular to the field, in which case $\Delta m = \pm 1$, or parallel to the field, and then $\Delta m = 0$. This means that linear polarisation can only be observed in the x-y plane, as linear polarisation requires no angular momentum.

On these grounds, one may argue that the emitted radiation may be circularly polarised even in the absence of the electric field. This argument is bogus. The introduction of the electric field splits the energy levels, meaning that the frequencies of the radiation observed along z depends on the polarisation state (eg. left-handed has higher energy). Without the field, the circular polarisations will have the same energy, meaning that one cannot distinguish between them; the superposition thus creates linearly polarised light.

6.5 Atoms in a Weak Magnetic Field

The entirety of the last section was done under the electric dipole approximation; that is, without any consideration of the effects of magnetic fields on particles. We will now bring this back into consideration.

Our knowledge of magnetic fields from Electromagnetism gives us the fact that the magnetic component of the Lorentz force does not do any work on the particle. This leads to a problem, as it means that we cannot simply write it as a potential that we can then include in our Hamiltonian. A way of solving this is taking the classical Hamiltonian that comes from Lagrangian mechanics, and then making operator substitutions.

$$\boxed{H = \frac{1}{2m}(\underline{p} - q\underline{A})^2 + q\phi} \tag{6.16}$$

where $\underline{B} = \nabla \times \underline{A}$ and $\underline{E} = -\nabla\phi - \dot{\underline{A}}$. Note that as we have change the momentum term in the Hamiltonian, our expression for probability current must be modified. However, this is simple to do, as we can remark that $\underline{J}$ can be written in the form

$$\underline{J} = \frac{1}{2m}(\psi^*\underline{p}\psi - \psi\underline{p}\psi^*)$$

and then make the transformation $\underline{p} \mapsto \underline{p} - q\underline{A}$, being careful of the order of the operators. Using the same simplification as in Section (2.3), we find that

$$\boxed{\underline{J} = |\psi|^2\left(\frac{\hbar}{m}\nabla\theta - \frac{q}{m}\underline{A}\right)} \tag{6.17}$$

A particle moves in the x-y plane with a uniform magnetic field in the z-direction, represented by

$$\underline{A} = \frac{B}{2}(-y, x, 0)$$

Show that the function

$$\phi(x,y) = \exp\left(-[x^2+y^2]/4\ell_B^2\right)$$

is an eigenfunction for a suitably chosen value for ℓ_B, which you should find. Evaluate $\underline{J}$ for this state, and discuss the physical significance of this result.

This problem has to be treated component-wise. Let $\gamma = qB/2$. Then:

$$\underline{p} - q\underline{A} = \begin{pmatrix} p_x - \gamma y \\ p_y + \gamma x \\ p_z \end{pmatrix}$$

Evidently, $\phi(x,y)$ is an eigenfunction of p_z with eigenvalue zero. This means that we can now only deal with the x and y components.

$$H = \frac{1}{2m}(\underline{p} - q\underline{A})^2 = \frac{1}{2m}(p_x^2 + p_y^2 + \gamma^2(x^2+y^2) - \gamma p_x y - \gamma y p_x + \gamma p_y x + \gamma x p_y)$$

Then, consider derivatives of our wave-function $\phi(x,y)$.

$$\frac{\partial\phi}{\partial x} = -\frac{2x}{4\ell_B^2}\phi = -\frac{x}{2\ell_B^2}\phi$$
$$\frac{\partial^2\phi}{\partial x^2} = \left(-\frac{1}{2\ell_B^2} + \frac{x^2}{4\ell_B^4}\right)\phi$$

We require that this is a solution to the TISE:

$$\begin{aligned} H\phi &= -\frac{\hbar^2}{2m}\left(-\frac{1}{2\ell_B^2}+\frac{x^2}{4\ell_B^4}\right)\phi - \frac{\hbar^2}{2m}\left(-\frac{1}{2\ell_B^2}+\frac{y^2}{4\ell_B^4}\right)\phi + \frac{\gamma^2(x^2+y^2)}{2m}\phi + \frac{1}{2m}\left(\cancel{\frac{2\gamma xy}{2\ell_B^2}}\phi - \cancel{\frac{2\gamma xy}{2\ell_B^2}}\phi\right) \\ &= \frac{1}{2m}\left[x^2\left(\gamma^2 - \frac{\hbar^2}{4\ell_B^4}\right) + y^2\left(\gamma^2 - \frac{\hbar^2}{4\ell_B^4}\right) + \frac{\hbar^2}{\ell_B^2}\right]\phi \end{aligned}$$

For ϕ to be an eigenfunction of the Hamiltonian, we require that

$$\gamma^2 = \frac{\hbar^2}{4\ell_B^4} \longrightarrow \ell_B = \sqrt{\frac{\hbar}{qB}}$$

We can now evaluate the probability current using Equation (6.17). Observing that $\phi = 0$ as the function is real, we find that

$$\underline{J} = -\frac{q}{m}\underline{A}e^{-r^2/2\ell_B^2}$$

where $r^2 = x^2 + y^2$. This has a maximum around $r = \ell_B$, and goes to zero for $r \to \infty$. Physically, this describes how the particle is localised around a classical orbit of radius $r = \ell_B$.

6.5.1 Gauge Transformations

We have a choice of the potentials ϕ and $\underline{A}$ that we can use to represent $\underline{E}$ and $\underline{B}$ but introducing some scalar *gauge* $f(t)$. This means that we make the transformation

$$\begin{aligned} \underline{A} &\mapsto \underline{A}' = \underline{A} + \nabla f \\ \phi &\mapsto \phi' = \phi - \frac{\partial f}{\partial t} \end{aligned}$$

However, what happens to both the Hamiltonian H and the state $|\psi\rangle$ when a gauge is applied? We need these two quantities to satisfy the TISE independently of the choice of gauge, or else they do not contain complete information about the system. Consider the gauge transformation:

$$\begin{aligned} H &\mapsto H' = \frac{1}{2m}(\underline{p} - q\underline{A}')^2 + q\phi' \\ |\psi\rangle &\mapsto |\psi'\rangle = e^{ifq/\hbar}|\psi\rangle \end{aligned}$$

We can now substitute these into the TDSE. The left-hand side gives

$$i\hbar\frac{\partial}{\partial t}\left(e^{ifq/\hbar}|\psi\rangle\right) = e^{ifq/\hbar}\left(-q\dot{f}|\psi\rangle + i\hbar\frac{\partial|\psi\rangle}{\partial t}\right)$$

The right-hand side gives

$$\begin{aligned} \frac{1}{2m}(\underline{p} - q\underline{A}')^2|\psi'\rangle + \phi'|\psi'\rangle &= \frac{1}{2m}(\underline{p} - q\underline{A} - q\nabla f)^2 e^{ifq/\hbar}|\psi\rangle - q\dot{f}e^{ifq/\hbar}|\psi\rangle \\ &= \frac{1}{2m}e^{ifq/\hbar}(\underline{p} - q\underline{A} - q\nabla f + q\nabla f)^2|\psi\rangle - q\dot{f}e^{ifq/\hbar}|\psi\rangle \\ &= e^{ifq/\hbar}\left(-q\dot{f}|\psi\rangle + H|\psi\rangle\right) \end{aligned}$$

This means that the TDSE is *gauge invariant*, and so we will not run into any problems when choosing a particular gauge in our work with vector and scalar potentials.

6.5.2 The Classical Limit

Let us examine whether our form of the Hamiltonian given by Equation (6.16) is a sensible one by looking at the classical limit; that is, by taking expectation values. By Ehrenfest's Theorem, for some operator Q:

$$\frac{\partial^2 \langle Q \rangle}{\partial t^2} = \frac{1}{(i\hbar)^2} \langle [H, [H, Q]] \rangle$$

If we take $Q = x_k$, where x_k is a particular component of the position of the particle, we can find some sort of analogue of Newton's Second Law. Calculating the first commutator:

$$\begin{aligned} [H, x_k] &= \frac{1}{2m}[(\underline{p} - q\underline{A})^2, x_k] = \frac{1}{2m}\big((\underline{p} - q\underline{A})[(\underline{p} - q\underline{A}), x_k] + [(\underline{p} - q\underline{A}), x_k](\underline{p} - q\underline{A})\big) \\ &= -\frac{i\hbar}{m}(p_k - qA_k) \end{aligned}$$

where we have used the fact that $p_i x_k = \delta_{ik}$. Now for the second commutator:

$$\begin{aligned} [H, [H, x_k]] &= -\frac{i\hbar}{m}\left(\frac{1}{2m}\left[(p_j - qA_j)^2, p_k - qA_k\right] + [q\phi, p_k - qA_k]\right) \\ &= \frac{(-i\hbar)^2}{m}\left(\frac{q}{m}(p_j - qA_j)\left(\frac{\partial A_j}{\partial x_k} - \frac{\partial A_k}{\partial x_j}\right) - q\frac{\partial \phi}{\partial x_k}\right) \end{aligned}$$

Putting this all together:

$$m\frac{\partial^2 \langle x_k \rangle}{\partial t^2} = q\epsilon_{ij\ell}(v_j \times (\nabla \times \underline{A})_\ell) - q\frac{\partial \phi}{\partial x_k} = (q(\underline{v} \times \underline{B}) - q\underline{E}) \cdot \widehat{\underline{k}}$$

We have thus re-produced the familiar Lorentz Force result for the k component of position, meaning that we should have at least a little confidence that our Hamiltonian is along the right lines.

6.5.3 The Zeeman Effect

Consider an electron with orbital angular momentum $\underline{L}$ and spin angular momentum $\underline{S}$. We define the *Bohr magneton* as

$$\boxed{\mu_B = \frac{e\hbar}{2m}} \tag{6.18}$$

Consider an atom in a magnetic field. This will have Hamiltonian

$$H = \frac{1}{2m}(\underline{p} - q\underline{A})^2 + V(r) = \underbrace{\frac{p^2}{2m} + V(r)}_{\text{Original Hamiltonian} H_0} - \frac{1}{2m}(2q\underline{p} \cdot \underline{A} - q^2\underline{A} \cdot \underline{A})$$

Now assume that the magnetic field is weak. This means that $q^2|\underline{A}|^2/2m \ll H_0$, and so we can neglect terms of $\mathcal{O}(A^2)$ and above.

$$H \backsim H_0 - \frac{q}{m}\underline{p} \cdot \underline{A}$$

We shall consider the magnetic field to be uniform, as it is very difficult to create a field that has significant variation in space over the size of an atom. This means that a convenient choice of $\underline{A}$ is

$$\underline{A} = \frac{1}{2}\underline{B} \times \underline{r}$$

This means that the extra term in the Hamiltonian becomes

$$-\frac{q}{2m}\underline{p}\cdot(\underline{B}\times\underline{r}) = -\frac{q}{2m}\underline{B}\cdot(\underline{r}\times\underline{p}) = -\frac{\mu_B}{\hbar}\underline{L}\cdot\underline{B}$$

This means that the electron has an orbital angular momentum magnetic moment of

$$\underline{\mu}_L = -\frac{\mu_B}{\hbar}\underline{L}$$

Similarly, the intrinsic electron spin also gives rise to a magnetic dipole moment:

$$\underline{\mu}_S = -\frac{\mu_B}{\hbar}g_s\underline{S} \backsim -2\frac{\mu_B}{\hbar}\underline{S}$$

as $g_S \backsim 2$ for an electron. This means that the total dipole moment for an electron in an external magnetic field is given by

$$\boxed{\underline{\mu} = -\frac{\mu_B}{\hbar}(\underline{L}+2\underline{S})} \tag{6.19}$$

The perturbing Hamiltonian of the system is thus

$$\delta H_B = -\underline{\mu}\cdot\underline{B} = \frac{\mu_B}{\hbar}(\underline{L}+2\underline{S})\cdot\underline{B}$$

Suppose that the magnetic field is orientated along the z-axis. We will also assume that the effect of this magnetic field is small in comparison to the spin-orbit interaction (see Section (6.5.4)). Then, it is clear that J^2, J_z, L^2, and S^2 all commute with the perturbation, meaning that we can characterise the states as $|j,m_j,\ell,s\rangle$. Consequently, when we use perturbation theory to calculate the smaller effect of an imposed magnetic field, the degenerate eigenspace in which we have to work is that spanned by the states that have given values of j, ℓ and s but differ in their eigenvalues m_j of J_z. Fortunately, δH_B is already diagonal within this space because $[J_z,S_z]=0$. The first order change in the energy is thus given by

$$\delta E = \frac{\mu_B}{\hbar}B\langle j,m_j,\ell,s|(L_z+2S_z)|j,m_j,\ell,s\rangle = \frac{\mu_B}{\hbar}B\left(m_j\hbar + \langle j,m_j,\ell,s|S_z|j,m_j,\ell,s\rangle\right)$$

where we have used the fact that $J_z = L_z+S_z$. Let us express $\underline{S}$ in terms of other quantities that we know:

$$\underline{J}\times(\underline{S}\times\underline{J}) = J^2\underline{S} - (\underline{S}\cdot\underline{J})\underline{J} \longrightarrow J^2\underline{S} = (\underline{S}\cdot\underline{J})\underline{J} + \underline{J}\times(\underline{S}\times\underline{L})$$

It can be shown, though the proof is not detailed here, that the expectation value of the second term with these states is zero. This means that be obtain:

$$\langle j,m_j,\ell,s|S_z|j,m_j,\ell,s\rangle = \frac{\langle\underline{J}\cdot\underline{S}\rangle m_j}{j(j+1)}$$

We can then write that

$$\boxed{\underline{J}\cdot\underline{S} = \frac{1}{2}\left(J^2-L^2+S^2\right)} \tag{6.20}$$

so we find that the total energy shift due to the application of this weak magnetic field is

$$\boxed{\delta E = m_j\mu_B B\left[1+\frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}\right]} \tag{6.21}$$

It is clear from this equation that the Zeeman effect splits the degenerate energy levels corresponding to a given j into $2j+1$ levels, proportionally to the applied magnetic field.

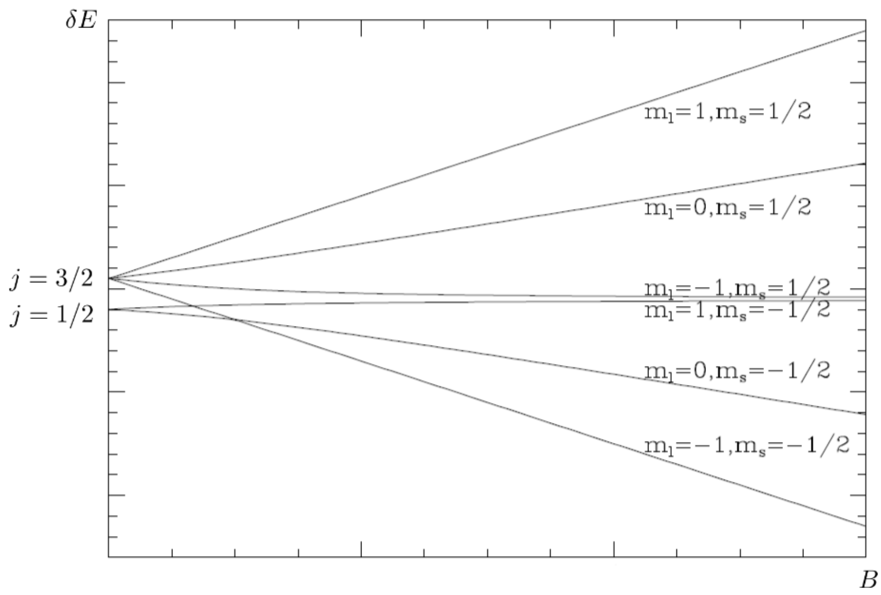

Figure 6.1: Zeeman splitting for $\ell = 1$ and $s = 1/2$.

This allows us to actually determine j for an atom, and subsequently other quantum numbers. This also gives rise to pairs of lines in emission spectra; they are split by the weak magnetic field of the Earth.

In the ground-state of hydrogen, we have that $\ell = 0$ and $s = 1/2$, meaning that $j = 1/2$ and $m_j = \pm 1/2$. Thus, we obtain the familiar energy shift of $\delta E = \pm \mu_B B$.

All of these calculations have been on the assumption that the effect of the magnetic field is small in comparison to the spin-orbit interaction. However, suppose that we neglect the spin-orbit interaction; this means that we can no longer treat it as being small, and so cannot ignore the torque that it applies to the system. Suppose again that the magnetic field is oriented along the z-axis. This means that J^2 is no longer a constant of the motion, and so we characterise our states by L^2, L_z, S^2 and S_z. The energy splitting is given by

$$\delta E = \frac{\mu_B}{\hbar} B \langle n, \ell, m_\ell, s, m_s | (L_z + 2S_z) | n, \ell, m_\ell, s, m_s \rangle = \mu_B B (m_\ell + 2m_s)$$

Hence, each energy level of the Hamiltonian is split by the magnetic field into as many sub-levels as $m_\ell + 2m_s$ can take. In general, this will be the case that we are dealing with, as the spin-orbit interaction is not on syllabus.

6.5.4 The Spin-Orbit Interaction

The spin-orbit interaction a relativistic correction to the fact that the electron is moving through an attractive Coulomb potential provided by the nucleus. Suppose that the potential is of the form $\phi(r)$. Then we know from relativistic electrodynamics that for an electron moving at some speed v:

$$\underline{B} = -\frac{1}{c^2}(\underline{v} \times \underline{E})) = -\frac{1}{c^2}(\underline{v} \times (-\nabla\phi))$$

The spin of the electron will then interact with this magnetic field to produce another perturbation term in the Hamiltonian (note that we are ignoring the factor of g_s).

$$\delta H_{SO} = -\underline{\mu} \cdot \underline{B} = -\frac{\mu_B}{\hbar c^2} \underline{S} \cdot (\underline{v} \times \nabla\phi) = -\frac{e}{2m^2c^2}\, \underline{S} \cdot \left(\underline{p} \times \frac{\hat{\underline{r}}}{r} \frac{\partial \phi}{\partial r} \right) = -\frac{e}{2m^2c^2} \underline{S} \cdot \underline{L} \frac{1}{r} \frac{\partial \phi}{\partial r}$$

where we have observed that $\underline{L} = \underline{r} \times \underline{p}$. In hydrogenic atoms, we can assume that the potential is the Coulomb potential, namely

$$\phi(r) = \frac{Ze}{4\pi\epsilon_0 r}$$

This means that we arrive at the final expression for the perturbation Hamiltonian of

$$\delta H_{SO} = \frac{Ze^2}{8\pi\epsilon_0 m^2 c^2}\, \underline{S} \cdot \underline{L}\, \frac{1}{r^3}$$

Evidently, both J^2 and J_z are constants of the motion, meaning that they must commute both with the unperturbed Hamiltonian, and δH_{SO}, as are J^2 and S^2. This means that we can use the basis labelled by the kets $|j, m_j, \ell, s\rangle$. We need to consider the expectation values of $1/r^3$ and $\underline{S} \cdot \underline{L}$. For a hydrogenic atom with nucleic charge Z, the first of these is:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2}{\ell(\ell+1)(2\ell+1)} \frac{Z^3}{(na_0)^3}$$

The second can be calculated by recognising that

$$\boxed{\underline{S} \cdot \underline{L} = \frac{1}{2}(J^2 - L^2 - S^2)} \tag{6.22}$$

Then

$$\langle \underline{S} \cdot \underline{L} \rangle = \frac{1}{2} \langle j, m_j, \ell, s|\, J^2 - L^2 - S^2\, |j, m_j, \ell, s\rangle = \frac{1}{2} \left[j(j+1) - \ell(\ell+1) - s(s+1) \right] \hbar^2$$

Putting all of this together, and re-writing the numerical pre-factor in δH_{SO}, the first order changes in the energy are given by

$$\boxed{\delta E = \frac{1}{4} mc^2 (\alpha Z)^4 \left[\frac{j(j+1) - \ell(\ell+1) - 3/4}{n^3 \ell(\ell+1/2)(\ell+1)} \right]} \tag{6.23}$$

In a similar way to the Zeeman effects, the spin orbit interaction splits the energy levels labelled by j into the $2j+1$ energy levels. This leads to the splitting of energy levels shown to the left of Figure (6.1). For a general level in hydrogen, we have that $j_\pm = \ell \pm 1/2$. The 'spin-up' states are shifted by an amount

$$\delta E_+ \propto j_+(j_+ + 1) - \ell(\ell+1) - \frac{3}{4} \propto \left(\ell + \frac{1}{2}\right)\left(\ell + \frac{3}{2}\right) - \ell(\ell+1) - \frac{3}{4} \propto \ell$$

Likewise, the 'spin-down' states are shifted by an amount

$$\delta E_- \propto j_-(j_- + 1) - \ell(\ell+1) - \frac{3}{4} \propto \left(\ell - \frac{1}{2}\right)\left(\ell + \frac{1}{2}\right) - \ell(\ell+1) - \frac{3}{4} \propto -(\ell+1)$$

For each value of j, the spin-orbit interaction creates another $2j+1$ energy levels (due to degeneracy), and so the mean energy shift for the system is proportional to

$$\delta \bar{E} \propto (2j_+ + 1)\delta E_+ + (2j_- + 1)\delta E_- \propto 0$$

Thus, the mean energy shift for a system under the spin-orbit interaction is zero. This makes sense in the context of energy conservation; as the spin-orbit interaction is created by motion within the system, it cannot raise the mean energy of the system.

7. *Multiple Particle Systems*

This chapter aims to put all of the apparatus that we have learnt up until this point into practise, particular with reference to:

- Exchange Symmetry
- The Helium Atom
- The Periodic Table

We have already touched on multiple particle systems in Section (5.4), but here will extend this fully to systems involving multiple particles, where we take account of all aspects of the wave-function. In doing so, we will discover some fundamental principles that under-pin the behaviour of multiple particle systems, as well as gain some insight into the organisational form of the Periodic Table of Elements.

7.1 Exchange Symmetry

Let $|a, b\rangle$ be the ket representing the state of two particles; the first particle on the left (in state 1) and the second particle on the right (in state 2). Let us now 'swap' the two particles. Assuming that they are indistinguishable, this should not change the modulus of the state vector; this is analogous to not changing the value of any physical observables.

$$\begin{aligned} \left| |a, b\rangle \right|^2 &= \left| |b, a\rangle \right|^2 \\ |b, a\rangle &= e^{i\phi} |a, b\rangle \end{aligned}$$

If we now swap the particles in the second ket, we obtain

$$|b, a\rangle = \underbrace{e^{2i\phi}}_{e^{i\phi}=\pm 1} |b, a\rangle$$

This means that there are two possible *exchange symmetries*:

1. $|a, b\rangle = |b, a\rangle$ for bosons that have integer spin
2. $|a, b\rangle = -|b, a\rangle$ for fermions that have half odd-integer spin

Suppose now that that the states "a" and "b" are in fact the same state. This means that for fermions $|a, a\rangle = -|a, a\rangle = 0$; that is, *no two fermions can occupy the same quantum state*. This is known, quite famously, as the *Pauli Exclusion Principle.*

7.1.1 Wave-Functions and Exchange Symmetry

These exchange symmetries restrict the behaviour of particles in a multiple particle system, and thus restrict the way that we form our wave-functions as we have to preserve said symmetries. In general, for a system of N identical particles, the Hamiltonian will be of the form

$$H = \underbrace{\sum_i^N H_i}_{\text{individual particle Hamiltonians}} + \underbrace{H_{\text{int.}}}_{\text{interaction Hamiltonian}}$$

If $H_{\text{int.}} = 0$ (the particles are non-interacting), then the TISE can simply be solved via separation of variables, as the states are uncorrelated. However, this does not apply in the general case. When solving a partial differential equation like the above, the general solution is usually a superposition of factored solutions. Let us consider a system of two identical bosons or fermions, with wave-functions ϕ_i. Then we can write the spatial wave-function as

$$\boxed{\psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_1(\underline{r}_1)\phi_2(\underline{r}_2) \pm \phi_1(\underline{r}_2)\phi_2(\underline{r}_1)\right]} \tag{7.1}$$

where the positive sign corresponds to bosons, and the negative sign to fermions. Notice how the wave-function disappears in the case where $\phi_1 = \phi_2$; this is the Pauli Exclusion Principle in action.

Suppose that we have p indistinguishable particles, and n single-particle states available to the system. How many distinct states of the system are possible? The best way to answer this equation is combinatorially. Following the lead of Statistical Mechanics, let Ω_p denote the number of distinct states that the system may occupy. Then for fermions, we have to find the number of ways of putting p particles into n states, where as for bosons we instead need to find a way to divide up p particles into n states using $n-1$ 'divisions'. This yields

$$\Omega_p^f = \frac{n!}{(n-p)!}\frac{1}{p!} \quad \text{and} \quad \Omega_p^b = \frac{(p+n-1)!}{(n-1)!}\frac{1}{p!}$$

Let us now extend these symmetry arguments to a system of N particles. In the case of bosons, we need to create a wave-function that is completely symmetric under the exchange of particles. This means that we essentially have to incorporate every single permutation of ϕ_i and $\underline{r}_i$ into our wave-function, which can become quite a pain for large N. For fermions, however, there is a much more systematic way of computing the wave-function, given orbitals $\phi_1, \ldots, \phi_N$:

$$\psi(\underline{r}_1, \ldots \underline{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\underline{r}_1) & \phi_2(\underline{r}_1) & \ldots & \phi_N(\underline{r}_1) \\ \phi_1(\underline{r}_2) & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \phi_1(\underline{r}_N) & \ldots & \ldots & \phi_N(\underline{r}_N) \end{vmatrix} \tag{7.2}$$

This is known as the *Slater Determinant.* We know from linear algebra that a determinant is antisymmetric under row swapping, and this is analogous to the swapping of particle coordinates, so the correct symmetry is preserved. It is trivial to check that this gives the fermionic result from Equation (7.1) for the $N = 2$ case.

Fermionic Systems

Thus far, we have just considered the spatial wave-function of our multi-particle systems. Let us now bring our attention to the issue of spin. Suppose that we can write our wave-function in the form

$$|\psi\rangle = |\text{spatial}\rangle \otimes |\text{spin}\rangle$$

For bosons, both of these have to be either symmetric or antisymmetric under particle exchange, while for fermions, we can make *either* symmetric, with the other being anti-symmetric.

Consider two spin-half particles of angular momentum quantum numbers j_1 and j_2. The single particle basis states are the eigenstates of S_z given by $|+\rangle$ and $|-\rangle$. Let us denote the total angular momentum by J with z-component M, and the total spin by S. Let us denote the states of the system by $|m_1, m_2\rangle$.

$$\text{Symmetric:} \quad |\psi\rangle = \begin{cases} |+,+\rangle & M = 1, S = 1 \\ |-,-\rangle & M = -1, S = 1 \\ \frac{1}{\sqrt{2}}\left(|+,-\rangle + |-,+\rangle\right) & M = 0, S = 1 \end{cases}$$

$$\text{Antisymmetric:} \quad |\psi\rangle = \frac{1}{\sqrt{2}}\left(|+,-\rangle - |-,+\rangle\right) \qquad M = 0, S = 0$$

These are known as the *triplet* and *singlet* states respectively, which we have already encountered in Section (5.4.2). From the addition of angular momenta

$$|j_1 - j_2| \leq J \leq j_1 + j_2 \longrightarrow 0 \leq J \leq 1$$

Then

$$-J \leq M \leq J \longrightarrow 0 \leq S \leq 1$$

This means that $S = 0, 1$. Looking at the values of S for each of the states listed above, we can conclude that $S = 1$ implies a *symmetric spin wave-function*, and an *anti-symmetric spatial wave-function*, while $S = 0$ implies an *antisymmetric spin wave-function*, and a *symmetric spatial wave-function.*

7.1.2 Exchange Interaction

The forces experienced between the two particles will depend on their coordinates, which is effected by the symmetry of the spatial wave-function. This itself is determined by the symmetry of the spin wave-function. This means that there is an energy difference between the $S = 0$ and $S = 1$ cases. We can calculate this using first order perturbation theory. Suppose that the interaction term is a function of the separation of the two particles.

$$\delta H = V\left(|\underline{r}_1 - \underline{r}_2|\right)$$

Equation (6.3) tells us that

$$\delta E = \langle\psi|\,\delta H\,|\psi\rangle = \int d^3\underline{r}_1 d^3\underline{r}_2\ |\psi(\underline{r}_1, \underline{r}_2)|^2\ V(|\underline{r}_1 - \underline{r}_2|)$$

The wave-function will be of the form given by Equation (7.1). This means that the energy shift becomes

$$\delta E = \delta E_{\text{direct}} \pm \delta E_{\text{exchange}}$$

where

$$\delta E_{\text{direct}} = \int d^3\underline{r}_1 d^3\underline{r}_2\ |\phi_1(\underline{r}_1)\phi_2(\underline{r}_2)|^2\ V(|\underline{r}_1 - \underline{r}_2|) \tag{7.3}$$

$$\delta E_{\text{exchange}} = \int d^3\underline{r}_1 d^3\underline{r}_2\ \phi_1^*(\underline{r}_1)\phi_2^*(\underline{r}_2)\phi_2(\underline{r}_1)\phi_1(\underline{r}_2)\ V(|\underline{r}_1 - \underline{r}_2|) \tag{7.4}$$

There is thus an energy difference $2\delta E_{\text{exchange}}$ between the $S = 1$ and $S = 0$ states. Assuming that $V\left(|\underline{r}_1 - \underline{r}_2|\right)$ is large and positive for a small separation (such as a Coulomb potential), then $\delta E_{\text{exchange}}$ is positive. This means that the $S = 1$ state is *lower* in energy than the $S = 0$ states.

7.1.3 Systems of Fermions and Bosons

Suppose that we have two identical macroscopic particles that are each made up of N_F fermions and N_B bosons. Are they fermions or bosons? If we exchange the positions of the constituents, we will obtain an overall phase of $(-1)^{N_F}$, meaning that bosons correspond to N_F being even, and fermions to N_F being odd.

Let the spins of the particles be labelled by quantum numbers s_1 and s_2, while the total spin of the system be S. Then

$$|s_1 - s_2| \le S \le s_1 + s_2$$

in integer steps. This means that depending on whether s_1 and s_2 are integers or half-integers, the spin of the composite system with either be an integer or half integer, as shown in the table below.

s_1	s_2	S	Particle Type
Half integer	Half integer	Integer	Boson
Half integer	Integer	Half Integer	Fermion
Integer	Half Integer	Half Integer	Fermion
Integer	Integer	Integer	Boson

7.2 The Helium Atom

The Helium atom is the simplest multi-particle system, consisting of two electrons and a nucleus that provides a fixed Coulomb potential. For the purposes of this section, we shall assume that the nucleus is fixed, which is a pretty good assumption given it's size.

$$H = \underbrace{-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)}_{\text{kinetic energy term}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{\text{coulomb interaction with nucleus}} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\underline{r}_1 - \underline{r}_2|}}_{\text{repulsive electron interaction}} \tag{7.5}$$

We cannot solve the TDSE exactly using this Hamiltonian, and so we need to make some approximations. This is usually to ignore the interaction term between the two electrons, as the equation then simply becomes separable in r_1 and r_2. This means that we can characterise our states via the normal quantum numbers used for hydrogen. In this case, Equation (5.32) with $Z = 2$ gives the energy levels.

$$\boxed{E_n^{He} = -\frac{1}{2}\mu(\alpha c)^2 Z^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)} \tag{7.6}$$

Consider the ground-state. In this case, we have that:

$$\begin{aligned} n_1 &= n_2 = 1 \\ \ell_1 &= \ell_2 = 0 \\ m_1 &= m_2 = 0 \\ s_1 &= \frac{1}{2},\ s_2 = -\frac{1}{2} \end{aligned}$$

The spatial wave-function is thus symmetric, as all of the quantum numbers are the same apart from the spin part. This means that both S and L are zero, meaning that $J = 0$. Conventionally, this state is notated as $1s^2\,{}^1S_0$. This sort of notation is known as *spectroscopic notation* that are used to label the various states of elements. The significance of each of the terms used is detailed in the figure below.

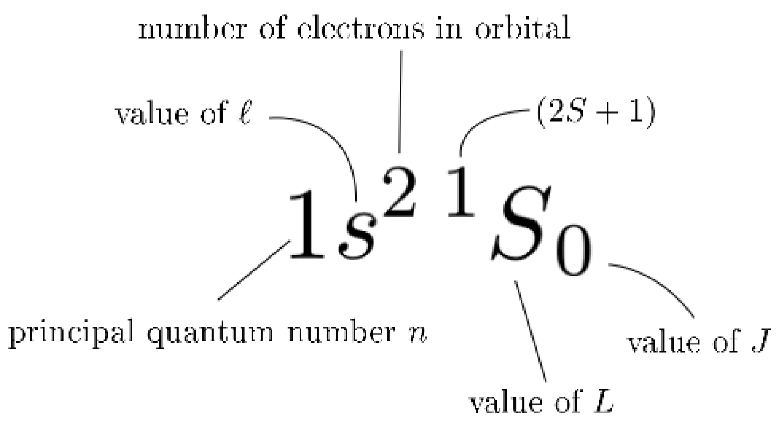

Figure 7.1: An explanation of spectroscopic notation

For $L = 0$, we use S, and then P, D and F for the successive values of L. We will make extensive use of this notation in following sections, so it is important that readers take the time to become familiar with it before progressing.

7.2.1 The Electron Interaction

We will now estimate the effect of the electron-electron interaction term in Equation (7.5). We shall assume that the atom is in the ground state, meaning that each electron has a wave-function given by Equation (5.33). From first order perturbation theory:

$$\delta E_1 = \int d^3\underline{r}_1 d^3\underline{r}_2 \, |\psi(\underline{r}_1, \underline{r}_2)|^2 \, \frac{e^2}{4\pi\epsilon_0 |\underline{r}_1 - \underline{r}_2|} = \frac{e^2 Z^6}{4\pi^3 \epsilon_0 a_0^6} \int d^3\underline{r}_1 d^3\underline{r}_2 \, \frac{e^{-2Z(r_1+r_2)/a_0}}{|\underline{r}_1 - \underline{r}_2|}$$

We can evaluate this integral using the result that

$$\int d^3\underline{r}_1 d^3\underline{r}_2 \, \frac{e^{-(r_1+r_2)}}{|\underline{r}_1 - \underline{r}_2|} = 20\pi^2$$

Then:

$$\delta E_1 = \frac{e^2 Z^6}{4\pi^3 \epsilon_0 a_0^6} \frac{a_0^5}{32 Z^5} \int d^3\underline{r}_1 d^3\underline{r}_2 \, \frac{e^{-(r_1+r_2)}}{|\underline{r}_1 - \underline{r}_2|} = \frac{5}{8} Z\mu(\alpha c)^2$$

This means that the energy shift (from perturbation theory) due to the Coulomb interaction between the two electrons in the ground-state is

$$\boxed{\delta E_1 = \frac{5}{8} Z\mu(\alpha c)^2 \backsim \frac{5}{4}\mathcal{R}Z} \tag{7.7}$$

Putting this together, this means that the energy of the ground state is given by

$$E_{\text{ground}} = E_1 + \delta E_1 = -4\mu(\alpha c)^2 + \frac{5}{4}\mu(\alpha c)^2 = -8\mathcal{R} + \frac{5}{2}\mathcal{R} \backsim -74.8 \text{ eV}$$

The actual value is $\backsim -79$ eV, meaning that our first-order estimate is not too inaccurate. Note that in this case, the singlet state is $\backsim 1.2$ eV (from calculation) higher in energy than the triplet state due to the exchange energy difference.

Let us now use the Variational Principle to calculate an upper bound for the ground-state energy. Let the individual particle Hamiltonians be $H_1(\widetilde{Z})$ and $H_2(\widetilde{Z})$, with the variational parameter in our wave-function being $\widetilde{Z}$. The Hamiltonian for the system can then be written as

$$H = H_1(\widetilde{Z}) + H_2(\widetilde{Z}) + \delta H(\widetilde{Z}) + H_c(\widetilde{Z})$$

where

$$H_c(\widetilde{Z}) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{\widetilde{Z} - 2}{r_1} + \frac{\widetilde{Z} - 2}{r_2} \right)$$

This term accounts for the fact that the actual charge of the nucleus is $Z = 2$, rather than our new variational parameter $\widetilde{Z}$. The expectation value of the first two terms is simply given by Equation (5.32), and the third given by Equation (7.7) above. Then we need the result that

$$\langle\psi| \, r_i^{-1} \, |\psi\rangle = \frac{\widetilde{Z}^6}{\pi^2 a_0^6} \int d^3\underline{r}_1 d^3\underline{r}_2 \, r_i^{-1} e^{-2\widetilde{Z}(r_1+r_2)/a_0} = \frac{\widetilde{Z}}{2a_0} \left(\int_0^\infty dx \, x e^{-x} \right) \left(\int_0^\infty dy \, y^2 e^{-y} \right) = \frac{\widetilde{Z}}{a_0}$$

Putting all of these results together, including the electron-interaction term, we arrive at the result of

$$\langle\psi| \, H \, |\psi\rangle = 2\mathcal{R} \left(\widetilde{Z}^2 - \frac{27}{8}\widetilde{Z} \right)$$

Minimising this expression, one finds that $\widetilde{Z}_{\text{min}} = 27/16$, and that $E_{\widetilde{Z}_{\text{min}}} \backsim -77.5$ eV, which is a more accurate result that that obtained previously. The physical significance of $\widetilde{Z}_{\text{min}} < 2$ reflects the fact that part of the nucleic charge seen by an electron is partially screened by the presence of the other electron, reducing the charge that it sees.

7.2.2 Higher Excited States

For a single particle in a Coulomb potential, the energy only depends on the principle quantum number. However, as we have seen, for an atom with many electrons, the presence of electrons can partially screen the nucleic charge from others, which acts to reduce the magnitude of the charge seen. Let us consider the potential seen by an electron for different values of r. Close to the nucleus ($r \backsim a_p$), the potential is dominated by that of the nucleus. At large radius ($r \backsim a_0$), the potential is dominated by the interaction between electrons, as the other screen the nucleic charge and thus reduce the strength of the potential. In general, electrons with a larger value for ℓ stay further away from the nucleus (for a given n). This is due to the conversation of angular momentum; small radii imply large momenta, which prevents the electron from getting close to the nucleus if ℓ is large: $\underline{L} = \underline{r} \times \underline{p} \propto r \backsim \ell$. This means that the energy of the orbitals will depend on ℓ as well as n in the helium atom, as well as for larger elements.

Consider the first excited state of helium. In this case, $n_1 = 1$ and $n_2 = 2$ (and other degenerate combinations), with $\ell_1 = \ell_2 = 0$. This means that the *configuration state* of the system is $1s^1 2s^1$. There are then two possibilities for the symmetry; a symmetric, triplet state with $S = 1$, or an antisymmetric singlet state with $S = 0$. This means that we can write the two possible states as

$$\begin{aligned} \text{symmetric}: &\quad 1s^1 2s^1\,{}^3S_1 \\ \text{antisymmetric}: &\quad 1s^1 2s^1\,{}^1S_0 \end{aligned}$$

However, we can also consider cases of non-zero angular momentum. Suppose that $\ell_1 = 0$ and $\ell_2 = 1$. This state, notated as $1s^1 2p^1$, is higher in energy than $1s^1 2s^1$. We have that $L = 1$ and $S = 0$ (singlet) or $S = 1$ (triplet), meaning that

$$J = 0, 1, 2 \quad \text{as} \quad |S - L| \leq J \leq S + L$$

This means that we have the following possibilities:

$$\underbrace{{}^1P_1}_{\text{singlet}}, \underbrace{{}^3P_0,\ {}^3P_1,\ {}^3P_2}_{\text{triplet}}$$

This sort of process can be repeated for higher excited states of Helium.

7.3 The Periodic Table

We are now in a position to provide some reasoning as to the structure of the Periodic Table of Elements. Initially, it will be assumed that the electrons only experience a Coulomb interaction with the nucleus; we are neglecting the electron-electron interaction. We shall use the quantum numbers n, ℓ, m and m_s (z-component of spin) to label the states. Let us consider the number of states associated with each value of n.

- $n = 1: \ \left\{\ell = 0,\ m = 0,\ m_s = \pm\frac{1}{2}\right.$

  This gives rise to two total states, accounting for H and He.

- $n = 2: \ \begin{cases} \ell = 0,\ m = 0,\ m_s = \pm\frac{1}{2} \\ \ell = 1,\ m = -1, 0, 1,\ m_s = \pm\frac{1}{2} \end{cases}$

  This gives rise to 8 states, accounting for Li to Ne.

- $n = 3: \ \begin{cases} \ell = 0,\ m = 0,\ m_s = \pm\frac{1}{2} \\ \ell = 1,\ m = -1, 0, 1,\ m_s = \pm\frac{1}{2} \\ \ell = 2,\ m = -2, -1, 0, 1, 2,\ m_s = \pm\frac{1}{2} \end{cases}$

  This gives rise to 18 states. We would thus expect 18 elements across the third row.

However, our Coulomb approximation begins to break down for $n = 3$ due to electron screening; the single particle picture is not enough to describe the situation. For example, it turned out that $n = 4$, $\ell = 0$ is lower in energy than $n = 3$, $\ell = 1$ because the electrons are on average found closer to the nucleus, and are more effected by nucleic screening.

7.3.1 Electronic States of the First Two Rows

In this section, we will simply list the electronic structure of most of the first two rows of the periodic table. In general, we want to take the highest spin state allowed by the Pauli Exclusion Principle as this minimises the exchange energy, and then take the highest L consistent with this.

- H: $1s^1\,{}^2S_{1/2}$
- He: $1_s^2\,{}^1S_0$
- Li: $1s^2 2s^1\,{}^2S_{1/2}$
- Be: $1s^2 2s^2\,{}^1S_0$
- B: $1s^2 2s^2 2p^1\,{}^2P_J$ for $J = \frac{1}{2},\ \frac{3}{2}$
- C: $1s^2 2s^2 2p^2$
- N: $1s^2 2s^2 2p^3\,{}^4S_{3/2}$
- O: $1s^2 2s^2 2p^4$
- F: $1s^2 2s^2 2p^5\,{}^2P_J$ for $J = \frac{1}{2},\ \frac{3}{2}$
- Ne: $1s^2 2s^2 2p^6\,{}^1S_0$

For example, with nitrogen, we have 3 electrons in the $2p$ state ie. $\ell = 1$, $m = -1, 0, 1$, $m_s = \pm 1/2$. Suppose that all the spins for $m = -1, 0, 1$ are up. This means that we have a symmetric spin state, and an antisymmetric spatial state, giving the lowest Coulomb energy: $M = 0$, $L = 0$, $J = 3/2$.