Doc Dave

MPhys Notes

Introduction to Quantum Mechanics

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Chapter 1

Principles of Quantum Mechanics

God does not play dice with the universe.
— Albert Einstein, *The Born-Einstein Letters 1916-55*

1.1 Postulates of Quantum Mechanics

Explaining the processes underlying quantum mechanics is a hotly debated topic which has so far spanned 100 years and spawned dozens of interpretations. At the time of writing this document, the most commonly accepted interpretation of quantum mechanics is the Copenhagen interpretation, which models particles as "waves" of probability. The principle of the Copenhagen interpretation is to set out a number of **postulates** upon which all further understanding can be built.

Definition 1.1: Postulate

A postulate is an assumed truth used as a basis for reasoning. Other examples of postulates in physics include Newton's third law and Einstein's postulates of special relativity.

1. The state of a quantum mechanical system is completely described by a wavefunction, $\Psi(t, x)$, which is dependent upon the particle's spatio-temporal coordinates. For a single particle system, the probability of finding the particle somewhere must be equal to 1:

$$\int_{-\infty}^{+\infty} \Psi^*(t, x)\Psi(t, x)\,\mathrm{d}x = 1.$$

2. Every physical observable has an associated operator, $\hat{Q}$, which must be Hermitian for observable quantities, i.e.

$$\hat{Q} = \hat{Q}^\dagger.$$

3. When an operator acts upon a wavefunction it yields an observable quantity, q, which satisfies the eigenvalue equation:

$$\hat{Q}\Psi(t, x) = q\Psi(t, x).$$

4. The average value of a quantity, q, for a system that can be described using a wavefunction is equal to the expectation integral of its associated operator, $\hat{Q}$, i.e.

$$\langle q \rangle \equiv \int_{-\infty}^{\infty} \Psi^*(t, x)\hat{Q}\Psi(t, x)\,\mathrm{d}x.$$

5. A wavefunction or state of a system evolves in time according to the time-dependent Schrödinger equation, i.e.

$$i\hbar \frac{\partial}{\partial t}\,\Psi(t, x) = \left(-\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2} + V\right)\Psi(t, x).$$

6. The total wavefunction corresponding to the coordinate interchange of fermions is antisymmetric, i.e. for a wavefunction describing a two-fermion system whose particles can exist at positions $\mathbf{r}_1$ or $\mathbf{r}_2$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1).$$

   The Pauli exclusion principle (covered later) is a direct result of this antisymmetry principle.

These postulates will be clarified and used extensively, so it would be wise to commit them to memory, even if not yet completely understood.

1.2 Born Constraints on the Wavefunction

In order to represent a real, physically observable system, the wavefunction must satsify a number of constraints which were set about by Max Born.

1. The wavefunction must be single-valued. This means that, for any position in space and time $\Psi(t, x)$ must have a unique value, thus guaranteeing that the wavefunction has a single value for the probability of the system being in a given state. Furthermore, it must be a solution of the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(t, x) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right) \Psi(t, x).$$

2. The wavefunction must be normalisable, also known as square-integrable - this ensures that the integral of the square modulus, $|\Psi|^2$, over all space is finite. This implies that it tends to zero as position approaches infinite distances, i.e.

$$\lim_{x \to \pm\infty} \Psi \to 0.$$

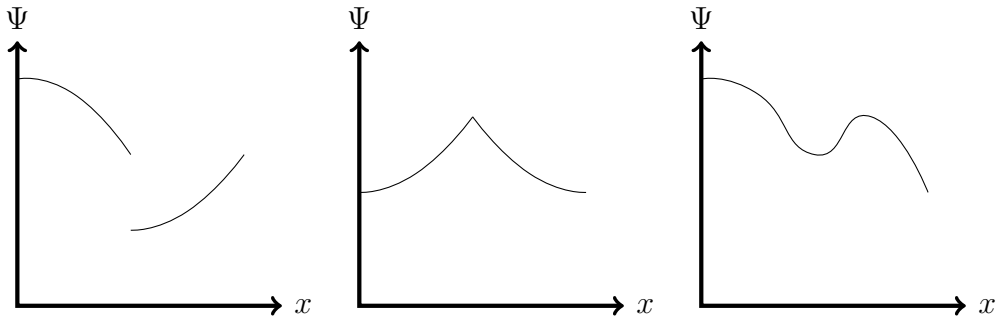
3. The wavefunction must be **continuous** everywhere. That is to say, there are no sudden jumps in the probability density when moving through space. Should a wavefunction has a discontinuity, i.e. a "jump" that takes no duration, then the first derivative of the wavefunction at that point is infinite, which is unphysical.

4. All first-order derivatives of the wavefunction, e.g. $\frac{\partial \Psi}{\partial x}$, must be continuous everywhere. A discontinuous first derivative would imply an infinite second derivative and, since the energy of the system is found by second derivative (covered later), a discontinuous first derivative would imply infinite energy being possible, which is not physically realistic.

As was the case for the postulates of quantum mechanics, these constraints will be used extensively and should be memorised for the moment.

Definition 1.2: Continuous Functions

Mathematically speaking, a function is described as **continuous** if it can be graphed in the Cartesian plane as a single unbroken curve, otherwise the function is described as **discontinuous**. Examples of continuous and discontinuous functions are illustrated by Figure **??**.



(a) Discontinuous Ψ, discontinuous $\frac{\partial \Psi}{\partial x}$.

(b) Continuous Ψ, discontinuous $\frac{\partial \Psi}{\partial x}$.

(c) Continuous Ψ, continuous $\frac{\partial \Psi}{\partial x}$.

Figure 1.1: Examples of (dis)continuous functions and derivatives.

1.3 Operators

As earlier mentioned, observable phenomena are associated with operators acting upon wavefunctions. These quantum mechanical observables are analogous to those in classical mechanics, e.g. momentum and position, but with minor differences to be expected. Table **??** provides a brief overview of some operators as well as the manners in which they act upon the wavefunction.

Table 1.1: A selection of quantum mechanical operators.

Name	Operator	Application
Translation	$\hat{\mathcal{T}}_a$	$\hat{\mathcal{T}}_a\Psi(t,x) = \Psi(t,x+a)$
Position	$\hat{x}$	$\hat{x}\Psi = x\Psi$
Momentum	$\hat{p}$	$\hat{p}\Psi = -i\hbar\frac{\partial}{\partial x}\Psi$
Wavevector	$\hat{k}$	$\hat{k}\Psi = -i\frac{\partial}{\partial x}\Psi$
Angular Frequency	$\hat{\omega}$	$\hat{\omega}\Psi = -i\frac{\partial}{\partial t}\Psi$
Kinetic Energy	$\hat{T}$	$\hat{T}\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi$
Total Energy	$\hat{E}$	$\hat{E}\Psi = i\hbar\frac{\partial}{\partial t}\Psi$
Hamiltonian	$\hat{H}$	$\hat{H}\Psi = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\Psi$

Proof 1.1: Position Operator

According to the first postulate of quantum mechanics, the squared modulus of the wavefunction, $|\Psi|^2 = \Psi^*\Psi$, represents the probability density of finding the particle at a position x. The expected value of a measurement of the position of the particle in one dimension is then

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\Psi|^2\,\mathrm{d}x = \int_{-\infty}^{\infty} \Psi^* x\Psi\,\mathrm{d}x.$$

The measured value of an observable is its expected value, thus the position operator is

$$\hat{x}\Psi(x) = x\Psi(x).$$

Proof 1.2: Momentum Operator

Newtonian momentum is given as $p = mv$, where m and v are respectively the mass and speed of the object. Quantum particles do not have specified positions, and so "speed" is instead given by the rate of change of its *expected* position, i.e. $\langle v\rangle = \frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t}$, which can be calculated using Proof **??**, i.e. since the wavefunctions are time-dependent but

the position (not the expected position) is time-independent;

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{-\infty}^{\infty} \Psi^* x \Psi \,\mathrm{d}x\right) = \int_{-\infty}^{\infty} x\left(\frac{\partial \Psi^*}{\partial t}\,\Psi + \Psi^*\,\frac{\partial \Psi}{\partial t}\right)\,\mathrm{d}x.$$

Postulate 5 provides the time-dependent Schrödinger equation which can be used to replace temporal derivatives with spatial derivatives;

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{i\hbar}{2m}\int_{-\infty}^{\infty} x\left(-\frac{\partial^2 \Psi^*}{\partial x^2}\Psi + \Psi^*\frac{\partial^2 \Psi}{\partial x^2}\right)\,\mathrm{d}x.$$

Noting that $\frac{\partial}{\partial x}\left(-\frac{\partial \Psi^*}{\partial x}\Psi + \Psi^*\frac{\partial \Psi}{\partial x}\right) = -\frac{\partial^2 \Psi^*}{\partial x^2}\Psi + \Psi^*\frac{\partial^2 \Psi}{\partial x^2}$, integration by parts then gives the equation for speed as

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{i\hbar}{2m}\left[x\left(-\frac{\partial \Psi^*}{\partial x}\,\Psi + \Psi^*\,\frac{\partial \Psi}{\partial x}\right)\Bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\left(-\frac{\partial \Psi^*}{\partial x}\,\Psi + \Psi^*\,\frac{\partial \Psi}{\partial x}\right)\,\mathrm{d}x\right].$$

By the second Born constraint the boundary terms tend to zero, hence by a second integration by parts:

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = -\frac{i\hbar}{m}\int_{-\infty}^{\infty} \Psi^*\,\frac{\partial \Psi}{\partial x}\,\mathrm{d}x.$$

Rearranging this, one manages to demonstrate by the classical momentum relation that the momentum operator is then given by $\hat{p} = -i\hbar\,\dfrac{\partial}{\partial x}$:

$$m\langle v\rangle = \langle p\rangle = \int_{-\infty}^{\infty} \Psi^* \underbrace{\left(-i\hbar\,\frac{\partial}{\partial x}\right)}_{\equiv \hat{p}} \Psi\,\mathrm{d}x.$$

Proof 1.3: Kinetic Energy Operator

Classically, kinetic energy, T, is defined using momentum as

$$T = \frac{p^2}{2m}.$$

The kinetic energy operator is then given by

$$\begin{aligned}\hat{T} &= \frac{\hat{p}^2}{2m} \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}.\end{aligned}$$

Proof 1.4: Hamiltonian Operator

The Hamiltonian of a system is the sum of the kinetic and potential energies, i.e.

$$H = T + V.$$

There is no operator for potential energy, however there is a kinetic energy operator, given by Proof **??**. The Hamiltonian operator is therefore

$$\begin{aligned}\hat{H} &= \hat{T} + V \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V.\end{aligned}$$

The expected value of an operator when the wavefunction is normalised ($\int|\Psi|^2 = 1$) is given by

$$\langle\hat{Q}\rangle = \int_{-\infty}^{+\infty} \Psi^*\hat{Q}\Psi \,\mathrm{d}x.$$

When the wavefunction is not normalised, dividing by the magnitude of the wavefunction over all space automatically normalises the integral:

$$\langle\hat{Q}\rangle = \frac{\int_{-\infty}^{+\infty} \Psi^*\hat{Q}\Psi \,\mathrm{d}x}{\int_{-\infty}^{+\infty}|\Psi|^2 \,\mathrm{d}x}.$$

One can compare this with the average value of a function, $Q(x)$, with a probability distribution, $P(x)$;

$$\langle Q(x) \rangle = \overline{Q}(x) = \int_{-\infty}^{+\infty} Q(x) P(x) \, \mathrm{d}x.$$

The uncertainty of an operator $\hat{Q}$ is given by

$$\sigma_{\hat{Q}} = \langle \hat{Q}^2 \rangle - \langle \hat{Q} \rangle^2.$$

Proof 1.5: Uncertainty

The deviation of an operator, $\Delta\hat{Q}$, is defined by the difference between its actual value and its expected value, i.e.

$$\Delta\hat{Q} = \hat{Q} - \langle \hat{Q} \rangle,$$

and thus the variance (uncertainty) is

$$\begin{aligned} \sigma_{\hat{Q}} \equiv \left\langle \left(\Delta\hat{Q} \right)^2 \right\rangle &= \langle \hat{Q}^2 - 2\hat{Q}\langle \hat{Q} \rangle + \langle \hat{Q} \rangle^2 \rangle \\ &= \langle \hat{Q}^2 \rangle - \langle 2\hat{Q}\langle \hat{Q} \rangle \rangle + \langle \hat{Q} \rangle^2 \\ &= \langle \hat{Q}^2 \rangle - 2\langle \hat{Q} \rangle^2 + \langle \hat{Q} \rangle^2 \\ &= \langle \hat{Q}^2 \rangle - \langle \hat{Q} \rangle^2. \end{aligned}$$

Chapter 2

The Schrödinger Equation

Thus it seems Einstein was doubly wrong when he said, God does not play dice. Not only does God definitely play dice, but He sometimes confuses us by throwing them where they can't be seen.

— Stephen Hawking, *Does God play Dice?*

2.1 The Time-Dependent Schrödinger Equation (TDSE)

The **Schrödinger equation** is a statement of energy conservation and is mathematically formulated as

$$\hat{H}\Psi = \hat{E}\Psi,$$

where $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$ and for a time-dependent system $\hat{E} = i\hbar\frac{\partial}{\partial t}$ whereas for time-independent systems $\hat{E} = E$.

There are a number of different ways to arrive at the time-dependent Schrödinger equation. The method presented will utilise the wave equation and Einstein's special theory of relativity.

Proof 2.1: Time-Dependent Schrödinger Equation

Consider the magnetic field wave equation for free space:

$$\frac{\partial^2 B}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 B}{\partial t^2} = 0.$$

A solution to this equation can be found to be a plane wave, i.e.

$$B = B_0 e^{i(kx-\omega t)},$$

where $k = \frac{2\pi}{\lambda}$, and $\omega = 2\pi\nu$ are respectively the spatial and temporal frequencies, and ν is the frequency of the wave. Recalling that the momentum of a photon is $p = \frac{h}{\lambda} = \hbar k$ and the energy of a photon, E, is given by $E = h\nu = \hbar\omega$ then Equation (**??**) can be written

$$B = B_0 e^{\frac{i}{\hbar}(px-Et)}.$$

Substituting this into the wave equation gives

$$-\frac{1}{\hbar^2}\left(p^2 - \frac{E^2}{c^2}\right) B_0 e^{\frac{i}{\hbar}(px-Et)} = 0,$$

or

$$E^2 = p^2c^2,$$

which is just the relativistic energy for a massless particle. It will be assumed that the relations between frequency and energy, and wavelength and momentum are the same for classical particles as for photons.

Since it is no longer a magnetic field that is being dealt with but instead a quantum particle, denote the state with a new function of the wave, $\phi(t, x)$. In so doing, the homogeneity (ability to separate spatial and temporal components) of the wave equation can be exploited and hence the units of the wavefunction are arbitrary. By applying the plane wave solutions to Equation (**??**) and using the fact that the relativistic energy is given by $\mathcal{E}^2 = p^2c^2 + m^2c^4$ one obtains a modified wave equation of the form

$$-\frac{1}{\hbar^2}\left(p^2 - \frac{\mathcal{E}^2}{c^2} + m^2c^2\right) \phi e^{\frac{i}{\hbar}(px-\mathcal{E}t)} = 0.$$

Using the operator relations given in Table **??** to substitute for p and $\mathcal{E}$ one gets

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right)\phi e^{\frac{i}{\hbar}(px-\mathcal{E}t)} = 0.$$

The square of the electric field, $|E|^2 = E_0^2$, is proportional to the number of photons and hence, by analogy, the wavefunction is described by

$$\phi(t,x) = \phi_0 e^{\frac{i}{\hbar}(px-\mathcal{E}t)},$$

which must be normalisable to unit probability. Therefore the probability of finding the particle somewhere in space is given by

$$\int_{-\infty}^{+\infty} \phi^*\phi \,\mathrm{d}x = 1.$$

One considers the non-relativistic case by approximating the particle energy:

$$\begin{aligned}
\mathcal{E} &= \sqrt{p^2c^2 + m^2c^4} \\
&= mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} \\
&\approx mc^2\left(1 + \frac{1}{2}\frac{p^2}{m^2c^2}\right) \\
&= mc^2 + T,
\end{aligned}$$

where it has been assumed that $p^2 \ll m^2c^2$, implying $mv \ll mc$, and T is the classic kinetic energy given by $T = \frac{p^2}{2m}$. The particle wavefunction may therefore be written as

$$\begin{aligned}
\phi(t,x) &= \phi_0 e^{\frac{i}{\hbar}(px-mc^2t-Tt)} \\
&= e^{-\frac{i}{\hbar}mc^2}\phi_0 e^{\frac{i}{\hbar}(px-Tt)}.
\end{aligned}$$

As $p^2 \ll m^2c^2$, the leading mass exponential will oscillate much faster than the latter kinetic energy term, the kinetic term can be absorbed with the initial wavefunction into a second wavefunction, Ψ, such that

$$\Psi = \phi_0 e^{\frac{i}{\hbar}(px-Tt)}.$$

The derivatives with respect to time are then

$$\frac{\partial \phi}{\partial t} = -\frac{i}{\hbar} mc^2 e^{-\frac{i}{\hbar}mc^2 t}\Psi + e^{-\frac{i}{\hbar}mc^2 t}\frac{\partial \Psi}{\partial t}$$
$$\frac{\partial^2 \phi}{\partial t^2} = \left(-\frac{m^2c^4}{\hbar^2}e^{-\frac{i}{\hbar}mc^2 t}\Psi - \frac{2i}{\hbar}mc^2 e^{-\frac{i}{\hbar}mc^2 t}\frac{\partial \Psi}{\partial t}\right) + e^{-\frac{i}{\hbar}mc^2 t}\frac{\partial^2 \Psi}{\partial t^2}\,.$$

Extending Equation (**??**) to three spatial dimensions and rearranging, one obtains the so-called **Klein-Gordon equation**, i.e.

$$\nabla^2 \phi - \frac{m^2c^2}{\hbar^2}\phi = \frac{1}{c^2}\frac{\partial^2 \phi}{\partial t^2}\,.$$

The bracketed terms in the second time-derivative are large compared to the second derivative of a slowly oscillating wavefunction, hence the last term can be ignored. Using this approximation in the Klein-Gordon equation, one gets

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2im}{\hbar}\frac{\partial \Psi}{\partial t} = 0.$$

Again, extending this to three spatial dimensions and rearranging, one arrives at the time-dependent Schrödinger for a free particle (zero potential):

$$-\frac{\hbar^2}{2m}\nabla^2 \Psi = i\hbar\frac{\partial \Psi}{\partial t}\,.$$

One can see that this is equivalent to the time-independent Schrödinger equation with the Hamiltonian and total energy operators being implemented, i.e.

$$\hat{H}\Psi = \hat{E}\Psi$$
$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2 \Psi = i\hbar\frac{\partial \Psi}{\partial t}\,.$$

As earlier demonstrated, this is modified if there is a potential present, hence the generalised time-dependent Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\nabla^2 \Psi + V\Psi = i\hbar\frac{\partial \Psi}{\partial t}\,.$$

2.2 Stationary and Non-Stationary States

Max Born suggested that the probability of measuring an observable of a wavefunction between values q and $q + \mathrm{d}q$, $P(t, x)\,\mathrm{d}q$, is given by

$$P(t, x)\,\mathrm{d}q = \left|\Psi(t, x)\right|^2\,\mathrm{d}q.$$

The probability of measuring an observable of the particle between values a and b ($b > a$) is then given by

$$P_{ab} = \int_a^b \left|\Psi(t, x)\right|^2\,\mathrm{d}q.$$

If the state is **stationary** then there are no physically observable phenomena associated with time, hence

$$\Psi^*(t, x)\Psi(t, x) \to \Psi^*(x)\Psi(x).$$

Definition 2.1: (Non-)Stationary States

A stationary state is a quantum state that does not vary with time, i.e. it has no time evolution, thus can be described by the TISE, $\hat{H}\Psi = E\Psi$. However, if the system does vary with time then it is known as a non-stationary state and is described by the TDSE, $-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$.

Statationary states can be written as a different spatial wavefunction and an exponentially-varying time component, i.e. of the form $\Psi(t, x) = \Phi(x)e^{\frac{i}{\hbar}Et}$. This results in wavefunctions being independent of time.

Proof 2.2: $\Psi(t, x) = \Phi(x)e^{\frac{i}{\hbar}Et}$ wavefunctions are stationary

Let $\Psi(t, x) = \Phi(x)e^{\frac{i}{\hbar}Et}$, then the magnitude of the wavefunction is

$$\begin{aligned}
|\Psi(t, x)|^2 &= \Psi^*(t, x)\Psi(t, x) \\
&= \Phi(x)^* e^{-\frac{i}{\hbar}Et}\Phi(x)e^{\frac{i}{\hbar}Et} \\
&= \Phi(x)^*\Phi(x) \\
&= |\Psi(x)|^2,
\end{aligned}$$

and hence is independent of time.

2.3 Boundary Conditions of the Wavefunction

Wavefunctions must satisfy certain boundary conditions in order to be solutions to the TISE, often being restricted to a **discrete set** of solutions.

Definition 2.2: Discrete Sets: Eigenfunctions and Eigenvalues

The third postulate of quantum mechanics states that an operator $\hat{Q}$ acting upon a wavefunction Ψ produces the same wavefunction scaled by an observable q, i.e. $\hat{Q}\Psi = q\Psi$ - this is known as the **eigenvalue equation**. For a given operator not all wavefunctions automatically satisfy this equation, nor do they necessarily produce the same observable value. Instead, there is a **discrete set** of wavefunctions, known as **eigenvectors** or **eigenfunctions**, denoted Ψ_n, that satisfy the eigenvalue equation. Each eigenfunction has an associated set of possible observable values, known as **eigenvalues**, q_n. As such, the generalised eigenvalue equation has the form

$$\hat{Q}\Psi_n = q_n\Psi_n.$$

Example 2.1: The Schrödinger Equation

The TISE, $\hat{H}\Psi = E\Psi$, is an example of the eigenvalue equation in which the Hamiltonian operator $\hat{H}$ acts upon a wavefunction Ψ to produce an energy value E. This is not satisfied by all wavefunctions, hence the eigenfunctions of $\hat{H}$, Ψ_n, instead produce an eigenvalue E_n;

$$\hat{H}\Psi_n = E_n\Psi_n.$$

Solutions of the form $\Psi_n(t,x) = \Phi_n(x)e^{\frac{i}{\hbar}E_n t}$ are states of definite energy, E_n, however, whilst the solutions $\Psi(t,x)$ are not time-independent, the probability density $\left|\Psi(t,x)\right|^2$ is - for this reason these are called **stationary states**.

Definition 2.3: Superposition

The **principle of superposition** states that the quantum state of a system with solutions Ψ_1 and Ψ_2 also has solutions that are linear combinations of these, i.e.

$$\Psi(t,x) = c_1\Psi_1(t,x) + c_2\Psi_2(t,x),$$

where c_1 and c_2 are arbitrary, possibly complex, constants.

For a time-dependent system with two solutions, the total wavefunction is given by their superposition, i.e.

$$\Psi(t,x) = c_1\Psi_1(x)e^{\frac{i}{\hbar}E_1 t} + c_2\Psi_2(x)e^{\frac{i}{\hbar}E_2 t}.$$

The state of the system is therefore normalised if

$$\|c_1\|^2 + \|c_2\|^2 = 1.$$

One should note that the total system is not a stationary state as it has no definite energy value due to being a superposition of different energies.

An experiment that measures the energy of a system with two solutions will yield either E_1 or E_2 probabilities of $\|c_1\|^2$ and $\|c_2\|^2$ respectively. As such, a series of these experiments will not necessarily repeatedly measure the same value. However, immediately after measurement the system will exist in either of the stationary states, $\Psi_1(t,x)$ or $\Psi_2(t,x)$, corresponding to the energy measured, E_1 or E_2. The system then remains in this state until a time-dependent force or potential disturbs it. The position probability density in the case of real c_1 and c_2 is given by

$$\begin{aligned}\left|\Psi(t,x)\right|^2 = c_1^2|\Psi_1(x)|^2 + c_2^2|\Psi_2(x)|^2 \\ + c_1c_2\left(\Psi_1^*(x)\Psi_2(x) + \Psi_2^*(x)\Psi_1(x)\right)\cos\left(\frac{i}{\hbar}(E_2 - E_1)t\right),\end{aligned}$$

and hence the probability density oscillates with an angular frequency

$$\omega = \frac{E_2 - E_1}{\hbar}.$$

This means that the probability of finding a particle at a given position will vary with time.

2.4 Commutation Relations

Definition 2.4: Commutation

The act of **commutation** between two operators indicates to what level of precision their respective observables can be known simultaneously, known as **compatibility**. If their commutation is zero then they are said to 'commute' and can both be exactly known simultaneously.

The **commutation** between two operators $\hat{A}$ and $\hat{B}$ is denoted $\left[\hat{A}, \hat{B}\right]$, pronounced "A commute with B", and is given by

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

If $\left[\hat{A}, \hat{B}\right] = 0$, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$, then the operators are said to commute and are **compatible**, in which case they can share eigenfunctions Ψ_n.

Commutations, like operators, have no intrinsic meaning without acting upon a state $|f\rangle$, i.e. $[\hat{A}, \hat{B}]\,|f\rangle = \hat{A}\hat{B}\,|f\rangle - \hat{B}\hat{A}\,|f\rangle$. Multiple operators acting upon a ket work from the closest operator outward, i.e. $\hat{A}\hat{B}\hat{C}\,|f\rangle$ can more explicitly be written with parentheses as $\hat{A}\left(\hat{B}\left(\hat{C}\,|f\rangle\right)\right)$

2.5 Particles in a Central Potential

In quantum physics, one often considers a free particle moving in a space surrounded by impenetrable barriers, called the **particle in a box model**. There are two schemes of this model; infinite-walled and finite-walled, between which many quantum mechanical phenomena can be illustrated.

2.5.1 Infinite-Walled Box

The barriers surrounding the "box" can be modelled as regions of infinite potential, forming a so-called "infinite square well".

Figure **??** demonstrates the one-dimensional case of a particle in a box of length L, which is mathematically described by

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

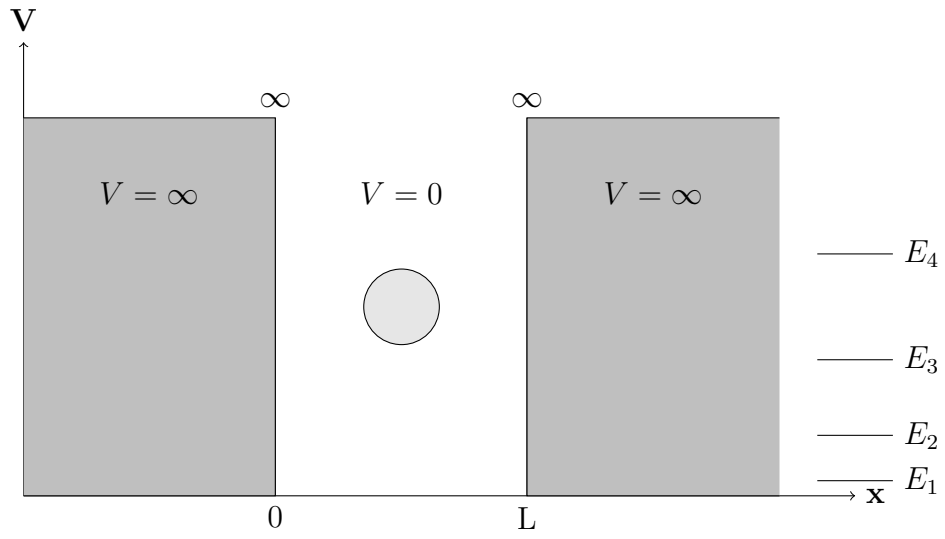


Figure 2.1: One-dimensional particle in an infinite square well. The particle is confined to the region between 0 and L as the infinite potential regions prevent the particle from traversing outside.

The time-dependent wavefunction solution to this is given by

$$\Psi(t, x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{i}{\hbar}E_n t},$$

where n is an integer energy level of the particle. The time-independent solution drops the temporal exponential.

Proof 2.3: 1D Infinite Square Well

For a free particle, i.e. $V = 0$, inside a box the wavefunction solution can be put in the form of a plane wave:

$$\Psi(t, x) = \Psi(x) e^{-\frac{i}{\hbar}E_n t}.$$

The time-independent Schrödinger equation is

$$\hat{H}\Psi = E_n\Psi,$$

where E_n are the energy eigenvalues of the system. Substituting the plane wave solution into the TISE yields

$$\begin{aligned}\frac{\hbar^2 k_n^2}{2m}\Psi &= E_n\Psi \\ \Rightarrow E_n &= \frac{\hbar^2 k_n^2}{2m}.\end{aligned}$$

Using this with the original TISE gives

$$\frac{\partial^2}{\partial x^2}\,\Psi = -k_n^2\Psi,$$

which has a general solution of

$$\Psi(x) = M\cos(k_n x) + N\sin(k_n x).$$

The boundary conditions at either wall can be used to further specify the solution. The condition at the left-side $\Psi(0) = 0$, thus the coefficient of the cosine term must be equal to zero, hence

$$\Psi(x) = N\sin(k_n x).$$

Furthermore, $\Psi(L) = 0$ and so the argument of sine becomes $k_n L = n\pi$, giving the wavevector as

$$k_n = \frac{n\pi}{L}.$$

Using this with Equation (**??**) then gives the energy eigenvalues as

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

and the eigenfunctions as

$$\Psi(t, x) = N\sin\left(\frac{n\pi x}{L}\right)e^{-\frac{i}{\hbar}E_n t}.$$

However, the wavefunction must be normalised, i.e. $\int_{-\infty}^{\infty}|\Psi|^2 = 1$, thus

$$\int_{-\infty}^{\infty}|\Psi|^2\,\mathrm{d}x = N^2\int_{-\infty}^{\infty}\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x \stackrel{!}{=} 1.$$

The probability of finding the particle outside of the box is zero, hence the integrals over the ranges $-\infty \to 0$ and $L \to \infty$ are zero, giving

$$N^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = 1.$$

The integral is equal to $\frac{L}{2}$, hence the coefficient, N, is given by

$$N = \sqrt{\frac{2}{L}}.$$

The wavefunction solution to the particle in a box model is therefore

$$\Psi(t,x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)e^{-\frac{i}{\hbar}E_n t}.$$

These solutions manifest themselves as sine functions of increasing energy and frequency, as shown in Figure **??**.

The energy levels are quantised, corresponding to different values of n, which is the first **quantum number** to be introduced. The energy is independent of position, however the probability of finding the electron at one position the box varies with position. The positions of zero probability, i.e. $|\Psi|^2 = 0$, are called 'nodes'.

The state where $n = 1$ is know as the **ground state** and is the first eigenfunction that has a non-zero energy, $E_1 = \frac{h^2}{8mL^2}$. States with higher quantum number n have higher energies (**excited states**), with the $n = 2$ state known as the 'first excited state'. If $V(x)$ is symmetric about some point, the eigenfunctions are either odd (antisymmetric) or even (symmetric) about that

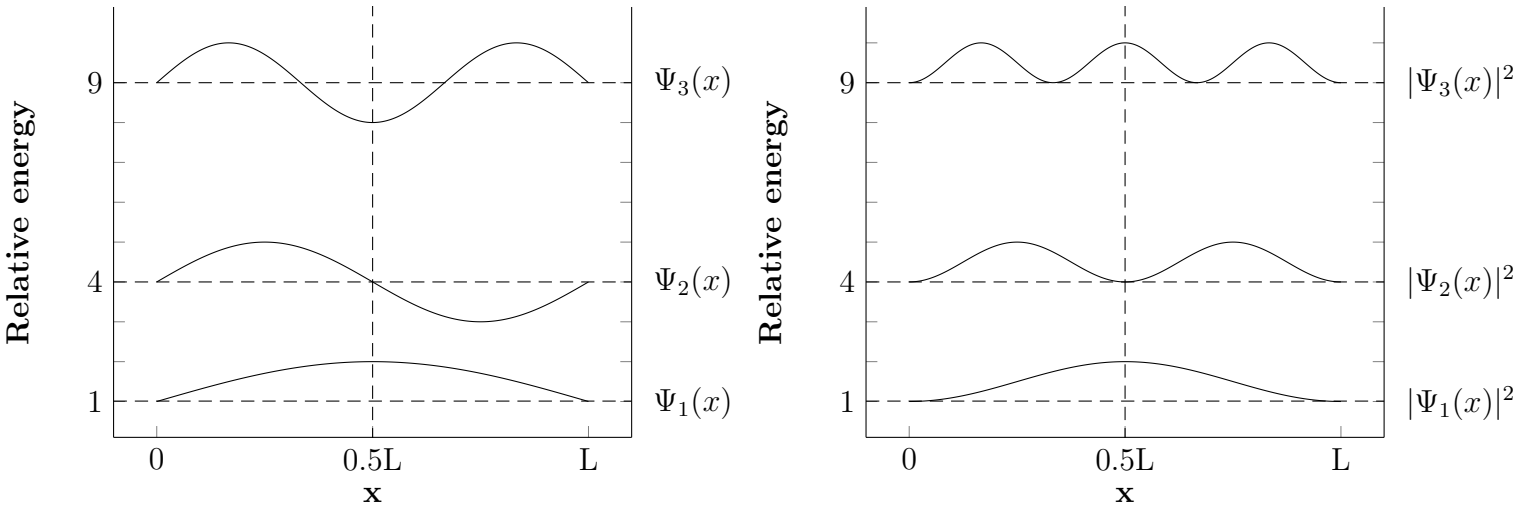


Figure 2.2: Harmonics of the particle in a box model.
Left: States of the system. Right: Probability functions.

point. The product of two wavefunctions is

$$\begin{aligned}\int_{-\infty}^{\infty} \Psi_n^*(x)\Psi_m(x)\,\mathrm{d}x &= \int_0^L \Psi_n^*(x)\Psi_m(x)\,\mathrm{d}x \\ &= \frac{2}{L}e^{-\frac{i}{\hbar}(E_n-E_m)t}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)\,\mathrm{d}x \\ &= \begin{cases}1 & n=m \\ 0 & n\neq m,\end{cases}\end{aligned}$$

demonstrating **orthogonality** of quantum states.

Definition 2.5: Orthogonality

In quantum mechanics states are **orthogonal** if they have no overlap with one another, resulting in the system being discretised into unique states. As such, if a particle described by wavefunction Ψ_1 is measured then it will have zero probability of being found with wavefunction Ψ_2.

2.5.2 Finite-Walled Box

Instead of infinite potential barriers around the box, one can consider finite-valued potential walls of width A and value V_B, such that

$$V(x) = \begin{cases} V_B & 0 \leq x \leq A \\ 0 & \text{otherwise.} \end{cases}$$

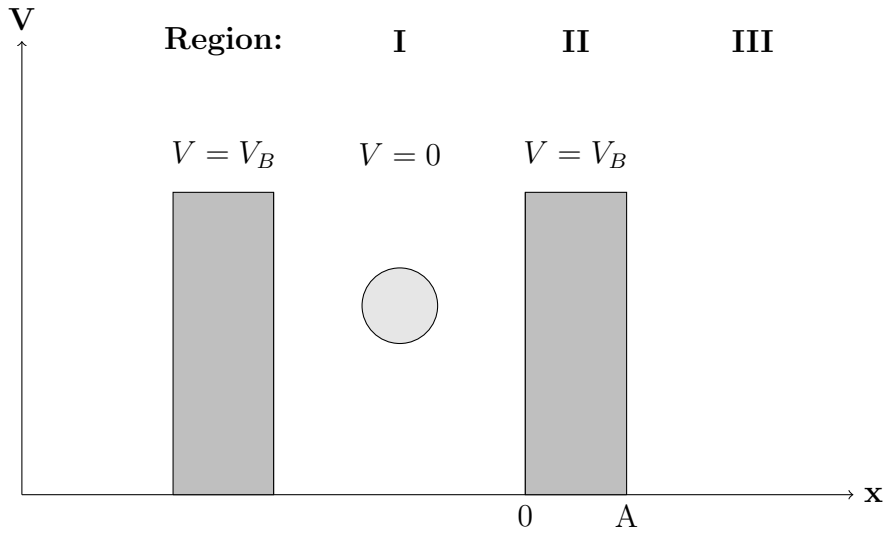


Figure 2.3: One-dimensional particle in a finite square well.

Classically, if the particle energy is less than the potential barrier, i.e. $E < V_B$, then the particle remains confined within the well. However, in quantum mechanics there is a probability of finding the particle outside the well, a phenomenon known as **quantum tunnelling**.

The probability of tunnelling (transmission) through the potential wall, T, is given by

$$T = \frac{16E(V_B - E)}{V_B^2} e^{-2\beta A},$$

where $\beta^2 = \frac{2m(V_B - E)}{\hbar^2}$ and $k^2 = \frac{2mE}{\hbar^2}$.

Proof 2.4: Transmission Probability

The time-independent Schrödinger equation can be rearranged as

$$\frac{\partial^2}{\partial x^2}\Psi(x) = -k^2\Psi(x),$$

where $k^2 = \frac{2m(E-V_B)}{\hbar^2}$, which is used to describe the system across the regions.

1. In region I ($x < 0$) the potential V is zero, thus

$$k^2 = \frac{2mE}{\hbar^2}.$$

Using this in the TISE gives

$$\frac{\partial^2}{\partial x^2}\Psi(x) = -\frac{2mE}{\hbar^2}\Psi(x),$$

which has solutions

$$\Psi(x) = e^{\pm ikx},$$

where the positive solution represents a forward-travelling wave (*incident*) and the negative solution represents a backward-travelling wave (*reflected*). By the principle of superposition, a linear combination of these two solutions must also be a solution. Coefficients are affixed to these solutions to demonstrate the amplitude of the wavefunction incident upon and reflected by the wall, i.e.

$$\Psi(x) = \underbrace{A_I e^{ikx}}_{\text{Incident}} + \underbrace{A_R e^{-ikx}}_{\text{Reflection}}.$$

2. In region II ($0 \leq x \leq A$) the potential is equal to V_B. Since, if the energy is greater than the potential, the particle can simply move out of the well, and so is trivial. Instead, the case in which the energy is less than the potential, i.e. $E < V_B$, will be considered. This then gives

$$k^2 = \frac{2m(E-V_B)}{\hbar^2} < 0,$$

thus k is imaginary. The modulus of k, denoted β, can be written $|k| = \sqrt{k^2} = i\beta$, such that

$$\beta^2 = \frac{2m(V_B - E)}{\hbar^2}.$$

The TISE is then written as

$$\frac{\partial^2}{\partial x^2}\Psi(x) = \beta^2\Psi(x),$$

hence the solutions are

$$\Psi(x) = e^{\pm\beta x}.$$

Again, by superposition these solutions can be written as a linear combination with arbitrary complex coefficients B and B':

$$\Psi(x) = \underbrace{Be^{\beta x}}_{\substack{\text{Forward-}\\\text{travelling}}} + \underbrace{B'e^{-\beta x'}}_{\substack{\text{Backward-}\\\text{travelling}}}.$$

3. Finally, in region III ($x > A$) the potential V is again equal to zero, hence the TISE is again given by

$$\frac{\partial^2}{\partial x^2}\Psi(x) = -\frac{2mE}{\hbar^2}\Psi(x).$$

There is no way in which the wavefunction can be reflected back and so the coefficient of reflection outside the well is zero, hence the only solution is prefaced by a coefficient denoting the transmission amplitude:

$$\Psi(x) = \underbrace{A_T e^{ikx}}_{\text{transmission}}.$$

In summary:

$$\Psi(x) = \begin{cases} A_I e^{ikx} + A_R e^{-ikx} & x < 0 \\ Be^{\beta x} + B'e^{-\beta x'} & 0 \leq x \leq A \\ A_T e^{ikx} & x > A. \end{cases}$$

The Born constraints (Section **??**) on the wavefunction and conditions at boundaries can be used to find the coefficients A_I, A_R, A_T, B, B'. For example, the wavefunction and its first spatial derivative must be **continuous** across boundaries.
At the boundary between regions I and II, i.e. at $x = 0$, the wavefunction Ψ and its first spatial derivative Ψ' are given by

$$\Psi(0) = A_I + A_R = B + B'$$
$$\Psi'(0) = ik(A_I - A_R) = \beta(B - B').$$

By taking the sum $ik\Psi(0) + \Psi'(0)$ one gets

$$2ikA_I = (ik + \beta)B + (ik - \beta)B'.$$

Since $k = i\beta$ the B coefficient is zero, hence the incident coefficient is given by

$$A_I = \frac{ik - \beta}{2ik} B'.$$

Between regions II and III, i.e. at $x = A$, the boundary conditions are

$$\Psi(A) = Be^{\beta A} + B'e^{-\beta A} = A_T e^{ikA}$$
$$\Psi'(A) = \beta\left(Be^{\beta A} - B'e^{-\beta A}\right) = ikA_T e^{ikA}.$$

One should note that the transmission terms in Equations (**??**) and (**??**) are equivalent by a factor of ik, hence the left-hand-sides of both equations must also be related as $ik\Psi(A) = \Psi'(A)$. Therefore

$$ik(Be^{\beta A} + B'e^{-\beta A}) = \beta\left(Be^{\beta A} - B'e^{-\beta A}\right)$$
$$\Rightarrow B = \left(\frac{\beta + ik}{\beta - ik}\right) B'e^{-2\beta A}.$$

Substituting this back into Equation (**??**) yields

$$\begin{aligned} A_T e^{ikA} &= \left(\frac{\beta + ik}{\beta - ik}\right) B'e^{-2\beta A}e^{\beta A} + B'e^{-\beta A} \\ &= \left(\frac{\beta + ik}{\beta - ik} + 1\right) B'e^{-\beta A} \\ &= \left(\frac{2\beta}{\beta - ik}\right) B'e^{-\beta A}, \end{aligned}$$

hence the transmission coefficient is

$$A_T = \left(\frac{2\beta}{\beta - ik}\right) B' e^{-(\beta+ik)A}.$$

The probability of transmission, T, is given by the ratio of the modulo-squared amplitudes, i.e. probabilities, of the transmitted and incident wavefunctions, i.e.

$$\begin{aligned} T &\equiv \left|\frac{A_T}{A_I}\right|^2 \left(= \frac{A_T^* A_T}{A_I^* A_I}\right) \\ &= \frac{16k^2\beta^2}{(\beta^2 + k^2)^2} e^{-2\beta A}, \end{aligned}$$

where $\beta^2 = \frac{2m(V_B - E)}{\hbar^2}$ and $k^2 = \frac{2mE}{\hbar^2}$. Therefore

$$T = \frac{16E(V_B - E)}{V_B^2} e^{-2\beta A}.$$

The intensity (probability) of the incident wavefunction must be equal to the sum of the reflection and transmission intensities, i.e.

$$|A_I|^2 = |A_R|^2 + |A_T|^2.$$

Therefore, by dividing all terms by $|A_I|^2$, one gets

$$R = 1 - T,$$

where R is the probability of reflection, given by

$$R = \left|\frac{A_R}{A_I}\right|^2.$$

One can check these probabilities are consistent with an infinite well by letting V_B tend to infinity, i.e. since $T \propto \frac{1}{V_B}$ then

$$\lim_{V_B \to \infty} T = 0,$$

and since $R = 1 - T$

$$\lim_{V_B \to \infty} R = 1,$$

thus within this limit the wave is totally internally reflected and none is transmitted, as expected.

2.6 Simple Harmonic Oscillators

Quantum systems often experience restoring forces which are proportional to displacement, akin to a simple harmonic oscillator (SHO). As such these systems are extremely important, with more advanced quantum mechanics being increasingly general SHO models.

Classically, Hooke's force law for a mass-spring system is given by

$$F = -kx,$$

where F is the restoring force, k is the spring constant and x is the displacement. Newton's second law is given by the equation

$$F = m\ddot{x},$$

hence the equation of motion for a mass-spring system is

$$\begin{aligned} m\ddot{x} &= -kx \\ \Rightarrow \ddot{x} &= -\omega^2 x, \end{aligned}$$

where the angular frequency of simple harmonic motion, ω, has been defined by $\omega \equiv \sqrt{\frac{k}{m}}$.

Furthermore, the potential of this system, $V(x)$, is given by the integral over the restoration of the spring:

$$\begin{aligned} V(x) &= \int_x^0 F \,\mathrm{d}x \\ &= \int_x^0 -kx \,\mathrm{d}x \\ &= \frac{1}{2}kx^2. \end{aligned}$$

The total energy, U, of the simple harmonic oscillator is the sum of the kinetic and potential energies, i.e.

$$\begin{aligned} U &= T + V \\ &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2. \end{aligned}$$

2.6.1 1D SHO

The potential of a quantum mechanical system is again given by

$$V = \frac{1}{2}m\omega^2 x^2.$$

The TISE is given by

$$\hat{H}\Psi(x) = E\Psi(x),$$

where the Hamiltonian operator is now given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2.$$

The earlier wavefunction constraints required that the wavefunction is bounded, that is to say that at the extremities of space the wavefunction falls off sufficiently fast, i.e. $\lim_{x\to\pm\infty}\Psi(x) \to 0$. The system may therefore be assumed to be described by a general Gaussian wavefunction, i.e.

$$\Psi(x) = Ae^{-\frac{x^2}{2a}},$$

where A and a are constants to be determined. The final wavefunction is

$$\Psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}}.$$

Proof 2.5: Determination of Gaussian variables A and a

The first and second derivatives of the Gaussian wavefunction are

$$\frac{\mathrm{d}\Psi}{\mathrm{d}x} = -\frac{x}{a}\Psi(x);$$

$$\begin{aligned}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} &= \frac{\mathrm{d}}{\mathrm{d}x}\left(-\frac{x}{a}\Psi(x)\right)\\ &= -\frac{1}{a}\Psi(x) - \frac{x}{a}\frac{\mathrm{d}}{\mathrm{d}x}\Psi(x)\\ &= \left(\frac{x^2}{a^2} - \frac{1}{a}\right)\Psi(x).\end{aligned}$$

Substituting this into the TISE gives

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

Separating this by orders of x one can find a, i.e. the terms of order x^0 give

$$\frac{\hbar^2}{2m}=E$$
$$\Rightarrow a=\frac{\hbar^2}{2mE},$$

while the terms of order x^2 give

$$-\frac{\hbar^2}{2ma^2}+\frac{1}{2}m\omega^2=0$$
$$\Rightarrow a=\frac{\hbar}{m\omega}.$$

Comparison of the values for a given by Equations (**??**) and (**??**) one finds the energy eigenvalue of the system E as

$$E=\frac{1}{2}\hbar\omega.$$

A more generalised result is

$$E=\left(n+\frac{1}{2}\right)\hbar\omega,$$

where $n=0,1,2\ \ldots$ are the excitation level, i.e. $n=0$ is the ground state, $n=1$ is the first excited state etc. Using Equation (**??**) the wavefunction is hence given by

$$\Psi(x)=Ae^{-\frac{m\omega x^2}{2\hbar}}.$$

The coefficient A is the normalisation constant, which can be calculated by

$$1=\int_{-\infty}^{\infty}\left|\Psi(x)\right|^2\,\mathrm{d}x$$
$$=A^2\int_{-\infty}^{\infty}e^{-\frac{m\omega x^2}{\hbar}}\,\mathrm{d}x.$$

At this point an identity can be used to finally solve the equation:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}},$$

hence the normalisation constant A is given by

$$A^2\sqrt{\frac{\pi\hbar}{m\omega}} = 1$$
$$\Rightarrow A = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}.$$

To a good approximation, the force between atoms in a diatomic molecule (H_2, O_2 etc.) is well-described by a simple harmonic oscillator for small displacements from the equilibrium separation, i.e. the potential $V(r)$ is quadratic near the minimum. The total energy of a system with two particles of masses m_1 and m_2 within a well of potential V_0 is then

$$\begin{aligned} E &= \frac{1}{2}kx^2 + \frac{p^2}{2m_1} + \frac{p^2}{2m_2} - V_0 \\ &= \frac{1}{2}kx^2 + \frac{p^2}{2\mu} - V_0, \end{aligned}$$

where $\mu \equiv \frac{m_1 m_2}{m_1+m_2}$ is the reduced mass of the system. The $-V_0$ term represents a downward shift of total energy, hence creating the potential well. This term is usually ignored, resulting in the energies being measured relative to the bottom of the well;

$$E = \frac{1}{2}kx^2 + \frac{p^2}{2\mu}.$$

This is equivalent to a single particle of mass μ undergoing SHO in a one-dimensional well with $V = \frac{1}{2}kx^2$. One therefore expects the SHO solutions to also apply to diatomic molecules, hence

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega;$$
$$\omega = \sqrt{\frac{k}{\mu}}.$$

2.6.2 2D SHO

In two dimensions, the simple harmonic oscillator has a potential that is dependent upon two spatial variables, i.e.

$$V(x,y) = \frac{1}{2}m\omega^2(x^2+y^2) = \frac{1}{2}m\omega^2 r^2.$$

The Hamiltonian of a 2D quantum mechanical SHO is given by

$$\begin{aligned} H &= T + V \\ &= \left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m}\right) + \left(\frac{1}{2}m\omega^2\left(x^2+y^2\right)\right). \end{aligned}$$

This can be written as the sum of two separate Hamiltonians, i.e.

$$H = H_x + H_y,$$

where

$$\begin{aligned} H_x &= \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2; \\ H_y &= \frac{p_y^2}{2m} + \frac{1}{2}m\omega^2 y^2. \end{aligned}$$

Consider two independent operators $\hat{A}$ and $\hat{B}$ with eigenfunctions and eigenvalues given by the eigenvalue equations

$$\begin{aligned} \hat{A}\Psi_A &= a\Psi_A; \\ \hat{B}\Psi_B &= b\Psi_B. \end{aligned}$$

A linear combination of these operators, $\hat{C} = \hat{A} + \hat{B}$, has eigenfunction of the form

$$\hat{C}\Psi_C = (a+b)\,\Psi_A\Psi_B.$$

Applying this to the 2D SHO yields

$$\begin{aligned} \hat{H} &= \hat{H}_x + \hat{H}_y \\ \hat{H}_x\Psi_{n_x}(x) &= \left(n_x + \frac{1}{2}\right)\hbar\omega\Psi_{n_x}(x) \\ \hat{H}_y\Psi_{n_y}(y) &= \left(n_y + \frac{1}{2}\right)\hbar\omega\Psi_{n_y}(y), \end{aligned}$$

where $n_{x,y} = 0, 1, 2 \ \ldots$ The eigenfunctions for a 2D SHO Hamiltonian are labelled by two quantum numbers, n_x and n_y, i.e.

$$\Psi_{n_x n_y}(x, y) = \Psi_{n_x}(x)\Psi_{n_y}(y),$$

which has energy eigenvalues

$$E_{n_x n_y} = (n_x + n_y + 1)\hbar\omega.$$

This behaviour results in so-called **degeneracy** of energy levels, in which there are different combinations of n_x and n_y that result in the same energy value. A brief summary of this is shown in Table **??**.

Definition 2.6: Degeneracy

In quantum mechanics an energy level is said to be **degenerate** if it corresponds to two or more different measurable states of a system. Conversely, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement.

Table 2.1: Demonstration of how degeneracy of a 2D quantum SHO varies with Hamiltonian eigenfunctions and eigenvalues.

Eigenfunctions (n_x, n_y)	**Eigenvalue**	**Degeneracy**
(0, 0)	$\hbar\omega$	1
(1, 0)	$2\hbar\omega$	2
(0, 1)		
(2, 0)	$3\hbar\omega$	3
(1, 1)		
(0, 2)		
$\vdots$	$\vdots$	$\vdots$

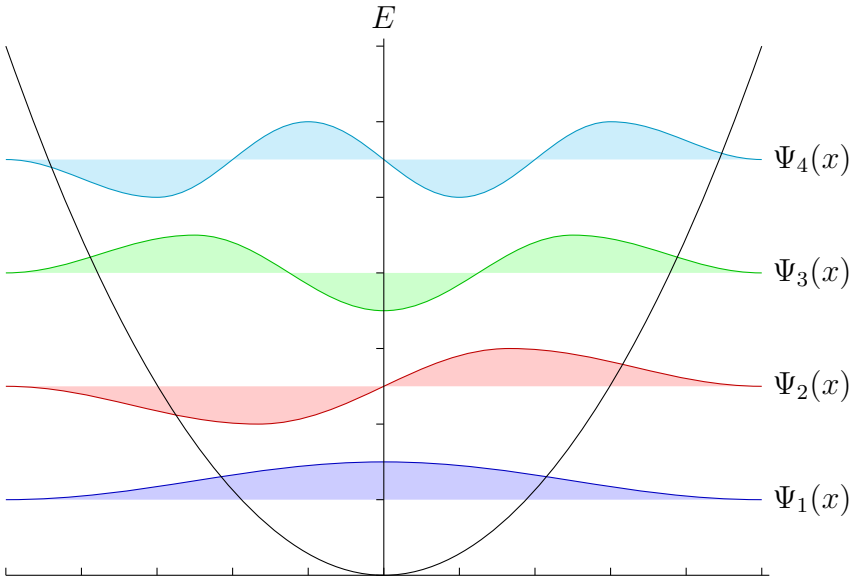


Figure 2.4: States of a quantum harmonic oscillator.

Example 2.2

Consider the first excited energy level, such that the eigenfunctions are $\Psi(1,0)$ and $\Psi(0,1)$. The state, Ψ, is a linear combination of the two solutions, i.e.

$$\Psi = \alpha\Psi_{10}(x,y) + \beta\Psi_{01}(x,y),$$

where α and β are arbitrary complex coefficients. Each eigenfunction can be split such that

$$\begin{aligned}\Psi_{10}(x,y) &= \Psi_1(x)\Psi_0(y)\\ \Psi_{01}(x,y) &= \Psi_0(x)\Psi_1(y).\end{aligned}$$

The Hamiltonian of this system is

$$\begin{aligned}\hat{H}\Psi &= \alpha\hat{H}\Psi_{10}(x,y) + \beta\hat{H}\Psi_{01}(x,y)\\ &= 2\hbar\omega\left(\alpha\Psi_{10}(x,y) + \beta\Psi_{01}(x,y)\right)\\ &= 2\hbar\omega\Psi.\end{aligned}$$

Therefore the state is an eigenfunction of the Hamiltonian with eigenvalue $2\hbar\omega$.

Chapter 3

Rotational Motion of Quantum Systems

Stop telling God what to do with his dice.

— Niels Bohr

3.1 Angular Momentum

In classical mechanics, angular momentum, L, is a vector given by the cross-product of position, r, and momentum p, i.e.

$$\begin{aligned}\mathbf{L} &= \mathbf{r} \times \mathbf{p} \\ &= \begin{vmatrix} \hat{\mathbf{e}}_\mathbf{x} & \hat{\mathbf{e}}_\mathbf{y} & \hat{\mathbf{e}}_\mathbf{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix},\end{aligned}$$

where $\hat{\mathbf{e}}_{\mathbf{x},\mathbf{y},\mathbf{z}}$ are unit vectors in directions corresponding to the x-, y- and z-axes, respectively.

The components of angular momentum are then

$$\begin{aligned} L_x &= yp_z - zp_y; \\ L_y &= zp_x - xp_z; \\ L_z &= xp_y - yp_x. \end{aligned}$$

In quantum mechanics these are written in terms of the position and momentum operators, i.e.

$$\begin{aligned} \hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \end{aligned}$$

As force is the temporal derivative of momentum, the rate of change of angular momentum is given by

$$\frac{\mathrm{d}\mathbf{L}}{\mathrm{d}t} = \mathbf{r} \times \mathbf{F}.$$

For a particle moving in a central potential, i.e. with no component perpendicular to the radial vector, $V(r, \theta, \phi) = V(r) = \alpha \cdot \hat{\mathbf{r}}$, where α is chosen to satisfy the potential, the angular momentum of the system is conserved.

Theorem 3.1: Angular Momentum in a Central Potential is Conserved

$$\begin{aligned} \frac{\mathrm{d}\mathbf{L}}{\mathrm{d}t} &= \mathbf{r} \times V(r) \\ &= r\hat{\mathbf{r}} \times \alpha \cdot \hat{\mathbf{r}} \\ &= r\alpha \cdot (\hat{\mathbf{r}} \times \hat{\mathbf{r}}) \\ &= 0. \end{aligned}$$

In plane polar coordinates, the z-component of angular momentum is

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

Proof 3.1: $\hat{L}_z = -i\hbar \dfrac{\partial}{\partial \phi}$

Transforming from Cartesian to plane polar coordinates gives:

$$\begin{aligned} x &= r\cos(\phi); \\ y &= r\sin(\phi); \\ r^2 &= x^2 + y^2; \\ \tan(\phi) &= \frac{y}{x}. \end{aligned}$$

The Cartesian chain rule gives

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \\ &= \frac{x}{\sqrt{x^2+y^2}}\frac{\partial}{\partial r} - \frac{y}{x^2+y^2}\frac{\partial}{\partial \phi}; \\ \frac{\partial}{\partial y} &= \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi} \\ &= \frac{y}{\sqrt{x^2+y^2}}\frac{\partial}{\partial r} + \frac{x}{x^2+y^2}\frac{\partial}{\partial \phi}. \end{aligned}$$

Furthermore, by extension of the chain rule to plane polar coordinates:

$$\begin{aligned} \frac{\partial}{\partial r} &= \frac{\partial x}{\partial r}\frac{\partial}{\partial x} + \frac{\partial y}{\partial r}\frac{\partial}{\partial y} \\ &= \frac{r}{\sqrt{r^2-y^2}}\frac{\partial}{\partial x} + \frac{r}{\sqrt{r^2-x^2}}\frac{\partial}{\partial y} \\ \frac{\partial}{\partial \phi} &= \frac{\partial x}{\partial \phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi}\frac{\partial}{\partial y} \\ &= -r\sin(\phi)\frac{\partial}{\partial x} + r\cos(\phi)\frac{\partial}{\partial y} \\ &= -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}. \end{aligned}$$

The z-component of angular momentum is hence

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial \phi}.$$

The eigenvalue equation for the $\hat{L}_z$ operator has eigenfunctions $\Psi(\phi)$ and eigenvalues L_z, i.e.

$$\hat{L}_z\Psi(\phi) = L_z\Psi(\phi).$$

This is then

$$-i\hbar\frac{\partial}{\partial\phi}\Psi(\phi) = L_z\Psi(\phi),$$

which has solution

$$\Psi(\phi) = \frac{1}{\sqrt{2\pi}}e^{\frac{iL_z\phi}{\hbar}}.$$

This is subject to the boundary condition that the wavefunction must be singularly valued over rotation, i.e. if the angle is rotated by 2π then the wavefunction is unchanged;

$$\Psi(\phi + 2\pi) = \Psi(\phi).$$

This therefore means that

$$\begin{aligned}\frac{1}{\sqrt{2\pi}}e^{\frac{iL_z(\phi+2\pi)}{\hbar}} &= \frac{1}{\sqrt{2\pi}}e^{\frac{iL_z\phi}{\hbar}}\\ \Rightarrow e^{\frac{iL_z2\pi}{\hbar}} &= 1,\end{aligned}$$

hence $\frac{L_z}{\hbar}$ must be equal to an integer. This integer is denoted m, where $m = 0, \pm1, \pm2\ldots$, hence the z-component of angular momentum is quantised in units of $\hbar$ as

$$L_z = m\hbar.$$

Henceforth both radial and angular components of a wavefunction must be considered separately, i.e.

$$\Psi(r,\phi) = R(r)e^{im\phi}.$$

The Hamiltonian operator of a two-dimensional simple harmonic oscillator can be written as

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right) + \frac{1}{2}m\omega^2r^2.$$

Proof 3.2: 2D SHO Hamiltonian

It has already been shown that

$$\begin{aligned}\hat{H} &= \hat{H}_x + \hat{H}_y \\ &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 r^2.\end{aligned}$$

The 2D momentum operator is given by

$$\begin{aligned}\hat{p}^2 &= \hat{p}_x^2 + \hat{p}_y^2 \\ \Rightarrow &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right),\end{aligned}$$

and hence

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right) + \frac{1}{2}m\omega^2 r^2.$$

Consider the ground state of a 2-dimensional Guassian simple harmonic oscillator, Ψ_{00}, of length a in both directions;

$$\begin{aligned}\Psi_{00} &= Ae^{-\frac{x^2}{2a^2}-\frac{y^2}{2a^2}} \\ &= Ae^{-\frac{r^2}{2a^2}}.\end{aligned}$$

As there is no explicit angular dependence on the ground state wavefunction, its angular momentum eigenvalue equation becomes

$$\hat{L}_z\Psi_{00} = -i\hbar\frac{\partial}{\partial\phi}\Psi_{00} = 0,$$

thus Ψ_{00} is an eigenfunction of $\hat{L}_z$ with eigenvalue 0. If, instead, the first excited states (either $x = 1, y = 0$ or $x = 0, y = 1$) are considered, which are

$$\begin{aligned}\Psi_{10} &= Bxe^{-\frac{r^2}{2a^2}}; \\ \Psi_{01} &= Bye^{-\frac{r^2}{2a^2}},\end{aligned}$$

where B is a new normalisation coefficient, the eigenvalue equation then becomes

$$\begin{aligned}\hat{L}_z\Psi_{10} &= -i\hbar\frac{\partial}{\partial\phi}\left(Br\cos(\phi)e^{-\frac{r^2}{2a^2}}\right)\\ &= i\hbar\left(Br\sin(\phi)e^{-\frac{r^2}{2a^2}}\right)\\ &= i\hbar\Psi_{01}.\end{aligned}$$

Ψ_{10} and Ψ_{01} are therefore not eigenfunctions of $\hat{L}_z$. However, by the principle of linear superposition, a combination of the two should be.

Proof 3.3: Angular momentum eigenvalue for first excitation

Initially defining a normalised linear combination of the two wavefunctions gives a total wavefunction, $\Psi_\pm$, of

$$\begin{aligned}\Psi_\pm &= \frac{1}{\sqrt{2}}\left(\Psi_{01} \pm i\Psi_{10}\right)\\ &= \frac{1}{\sqrt{2}}\left(Br\right)\left(\cos(\phi) \pm i\sin(\phi)\right)e^{-\frac{r^2}{2a^2}}\\ &= \frac{1}{\sqrt{2}}Bre^{\pm i\phi}e^{-\frac{r^2}{2a^2}}.\end{aligned}$$

The eigenvalue equation of this with the z-component of angular momentum is

$$\begin{aligned}\hat{L}_z\Psi_\pm &= -i\hbar\frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2}}Bre^{\pm i\phi}e^{-\frac{r^2}{2a^2}}\right)\\ &= \pm\hbar\frac{1}{\sqrt{2}}Bre^{\pm i\phi}e^{-\frac{r^2}{2a^2}}\\ &= \pm\hbar\Psi_\pm.\end{aligned}$$

The combined wavefunctions $\Psi_\pm$ are therefore eigenfunctions of $\hat{L}_z$ with eigenvalues $\pm\hbar$. These two states have the same total energy of $2\hbar\omega$.

This can be extended to show that the z-component of angular momentum and the Hamiltonian commute, i.e. $\left[\hat{H},\hat{L}_z\right] = 0$, and hence the energy and

angular momentum values of the system have definite values for a given state. However, this is not true for the original states, $\Psi_{n_x,n_y}(x,y)$, as only appropriate linear combinations of degenerate states are eigenfunctins of $\hat{L}_z$.

The coordinate system can be extended to 3D to reflect the three-dimensional spatial universe:

$$\begin{aligned} x &= r\sin(\theta)\cos(\phi) \\ y &= r\sin(\theta)\sin(\phi) \\ z &= r\cos(\theta), \end{aligned}$$

which leaves the angular momentum operator unchanged since, extending Proof **??**, one gets a further term of $\frac{\partial z}{\partial \phi}$, which is equal to zero.

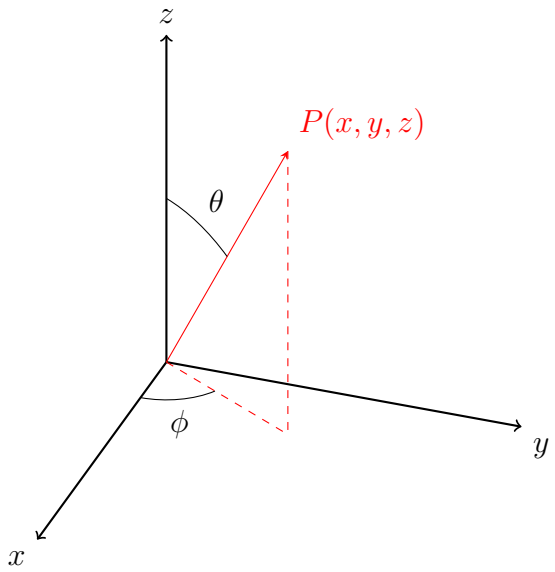


Figure 3.1: Illustration of 3D cartesian and spherical coordinates.

One can extend this to x- and y-components of angular momentum to give

$$\begin{aligned} \hat{L}_x &= -i\hbar\left(-\sin(\phi)\frac{\partial}{\partial\theta} - \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\right); \\ \hat{L}_y &= -i\hbar\left(\cos(\phi)\frac{\partial}{\partial\theta} - \cot(\theta)\sin(\phi)\frac{\partial}{\partial\phi}\right); \\ \hat{L}_z &= -i\hbar\frac{\partial}{\partial\phi}. \end{aligned}$$

Summing the squares of these gives the overall magnitude as

$$\begin{aligned}\hat{L}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \cot(\theta)\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\,\frac{\partial^2}{\partial\phi^2} \right),\end{aligned}$$

which is independent of of radius, r. One can now write the time-independent Schrödinger equation in terms of 3D spherical coordinates as

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r}\right]\Psi + \frac{\hat{L}^2}{2mr^2}\Psi + V(r)\Psi = E\Psi.$$

Proof 3.4: Spherical TISE

The time-independent Schrödinger equation is

$$\hat{H}\Psi = E\Psi,$$

where $\hat{H}$ is the sum of the kinetic and potential energy operators. The kinetic energy operator is

$$\begin{aligned}\hat{T} &= \frac{\hat{p}^2}{2m} \\ &= -\frac{\hbar^2}{2m}\nabla^2 \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2} + \cot(\theta)\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\,\frac{\partial^2}{\partial\phi^2}\right]\right).\end{aligned}$$

One can see that this contains the terms for $\hat{L}^2$, hence

$$\hat{T} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2}.$$

The potential energy operator for a central potential is simply $\hat{V} = V(r)$, hence the Schrödinger equation becomes

$$\underbrace{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r}\right)}_{\text{Radial}}\Psi + \underbrace{\frac{\hat{L}^2}{2mr^2}}_{\text{Angular}}\Psi + \underbrace{V(r)}_{\text{Potential}}\Psi = E\Psi.$$

The first term contains the radial dependence of the kinetic energy operator, whereas the second term contains the dependence on the angles, θ and ϕ. The wavefunction can therefore be separated into the product of a radial and a rotational part:

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi).$$

3.2 Rotational and Vibrational States of Diatomic Molecules

A diatomic molecule is comprised of two atoms, henceforth denoted 1 and 2, each of which having its own mass and location in space. The rotations of diatomic molecules about a central axis may be modelled as a rigid rotor with masses concentrated at either end, often called a dumbbell model.

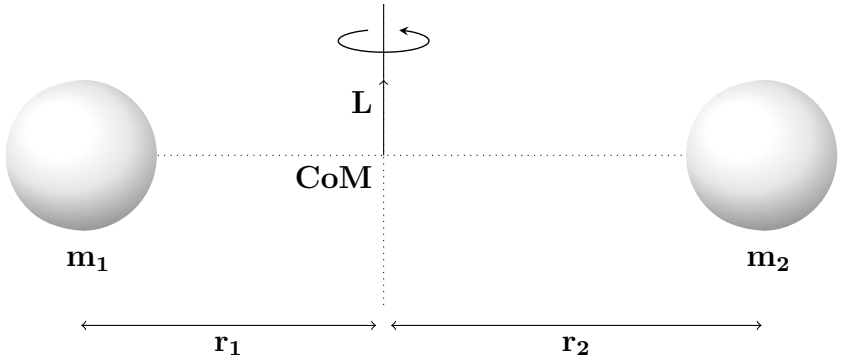


Figure 3.2: Illustration of the dumbbel model.

The centre of mass of the diatomic molecule is a distance r_1 from atom 1 and r_2 from atom 2, giving a total molecular length of $r = r_1 + r_2$. The moment of inertia, I, can be written in terms of the effective reduced mass, μ_{eff}, as

$$I = \mu_{\text{eff}}\, r^2.$$

Proof 3.5: Moment of Inertia

The centre of mass is the point at which the moments of the individual masses are equal, i.e. $m_1 r_1 = m_2 r_2$. Using this, one can calculate the atomic-CoM distances in terms of the total molecular length and masses:

$$\begin{aligned} m_1 r_1 &= m_2 r_2 \\ m_1 r_1 (+ m_2 r_1) &= m_2 r_2 (+ m_2 r_1) \\ \Rightarrow r_1 &= \frac{m_2 r}{m_1 + m_2}. \end{aligned}$$

By the same reasoning

$$r_2 = \frac{m_1 r}{m_1 + m_2}.$$

The moment of inertia of a multibody system is given by

$$I = \sum_i m_i r_i^2,$$

hence for a diatomic molecule this becomes

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= \frac{m_1 m_2^2}{(m_1 + m_2)^2} r^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} r^2 \\ &= \frac{m_1 m_2}{m_1 + m_2} r^2 \\ &\equiv \mu_{\text{eff}}\, r^2, \end{aligned}$$

where the effective reduced mass has been introduced, defined by

$$\mu_{\text{eff}} = \frac{m_1 m_2}{m_1 + m_2}.$$

A diatomic molecule with angular velocity ω has rotational kinetic energy

$$E_{\text{rot}} = \frac{1}{2} I \omega^2.$$

Given that the angular momentum about the axis is given by

$$L = I\omega,$$

the rotational kinetic energy is hence given by

$$E_{\text{rot}} = \frac{L^2}{2I}.$$

One may wish to draw parallels between the forms of this and the translational kinetic energy, E_{trans}, given by

$$E_{\text{trans}} = \frac{p^2}{2m}.$$

In quantum mechanics angular momentum is an operator, hence $L^2 \to \hat{L}^2$, with eigenvalues $l(l+1)\hbar$, i.e. $\hat{L}^2\Psi = l(l+1)\hbar\Psi$. One thus expects the rotational kinetic energies to be quantised, with allowed values of

$$E_{\text{rot}} = \frac{l(l+1)\hbar}{2I} = \frac{l(l+1)\hbar}{2\mu_{\text{eff}}\, r^2}.$$

As the reduced mass and length are both quantities inherent to the molecule, a **rotational constant** of each molecule, $B \equiv \frac{\hbar^2}{2I}$, is introduced in order to simplify the equation:

$$E_{\text{rot}} = l(l+1)B.$$

The spacing in energy between adjacent rotation levels is thus

$$\begin{aligned}\Delta E_{\text{rot}} &= E_l - E_{l-1} \\ &= l(l+1)B - (l-1)lB \\ &= 2lB.\end{aligned}$$

This rotational constant is experimentally verifiable via rotational spectroscopy.

3.2.1 Hydrogen Molecule

The simplest example of a diatomic molecule is a hydrogen molecule, H_2. For hydrogen; $r \approx 1$ Å, $\mu \approx 10^{-27}$ kg, hence $B \approx 10^{-22}$ J $= 10^{-3}$ eV. At room temperature $k_bT \approx 10^{-21}$ J $= 10^{-2}$ eV, hence the rotational energy levels of

a typical molecule is well populated with a distribution over a wide range of excited states.

The TISE, $\hat{H}\Psi = E\Psi$, expands to

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\Psi + V_{\text{eff}}(r)\Psi = E\Psi,$$

where V_{eff} is the effective potential. This incorporates a radially-dependent potential and a centrifugal potential as a result of the orbital angular momentum:

$$V_{\text{eff}} = V(r) + \frac{\hat{L}^2}{2mr^2}.$$

As the radial and angular parts are distinct, one can look for a separable solution of the form

$$\Psi(r, \theta, \phi) = R_{nlm}(r)Y_{lm}(\theta, \phi),$$

thus the radial components of the TISE becomes

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)R_{nlm}(r) + V_{\text{eff}}(r)R_{nlm}(r) = E_{nlm}R_{nlm}(r),$$

where n, l, and m are respectively the energy, orbital angular momentum and z-component angular momentum quantum numbers.

3.2.2 Spin

Definition 3.1: Spin

Spin is an intrinsic form of angular momentum carried by all particles. Classically, angular momentum is a vector with direction and magnitude which describes the inertia of the angular motion. However, spin has no classical manifestation; it is a fundamental property of a quantum particle that bears little resemblance to classical rotating objects. The direction of spin is said to be either "up", denoted $\uparrow$, or "down", denoted $\downarrow$, with the direction depending on how it relates to other angular momentum components. The spin wavefunction is often denoted χ_σ, where σ is the direction of spin.

3.2.3 Stern-Gerlach Experiment

The Stern-Gerlach experiment was a fundamental keystone of early quantum mechanics. Conducted by its namesake's Otto Stern and Walther Gerlach in 1922, the Stern-Gerlach experiment cemented the idea of spin quantisation, as it demonstrated that electrons have quantised intrinsic spins. A furnace was used to heat metal in order to delocalise electrons, which were passed through a small hole in the furnace and collimated using slits, producing an electron beam. This beam was then directed through an inhomogeneous magnet and their deflections were observed on a sheet behind.

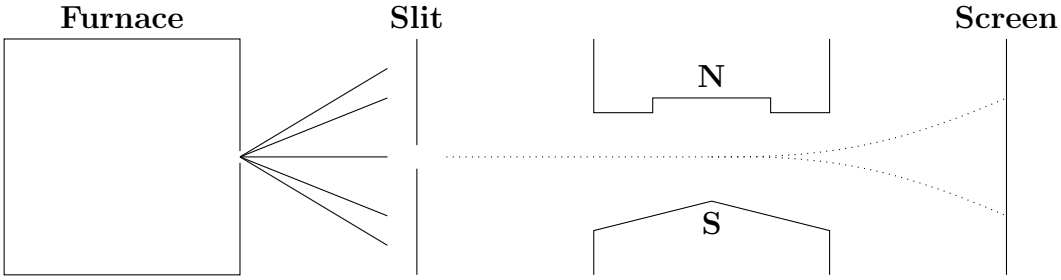


Figure 3.3: Schematic of Stern-Gerlach experiment.

A charged particle with angular momentum possesses a magnetic moment, hence experiences a deflecting force when passing through an inhomogeneous magnetic field, due to the differences in magnetic field strength between the two poles. The particle thus has its direction altered, which is dependent on the particle's charge and its movement relative to the magnetic field orientation. The force exerted upon the particle, $\mathbf{F}$, is given by

$$\mathbf{F} = \mu_z \frac{\partial \mathbf{B}}{\partial z} ,$$

where μ is the magnetic moment and B is the external magnetic field. If the particle spins could take any values then they would form a continuous spectrum on the screen, hence a solid line would have been observed. However, Stern and Gerlach observed only two bright spots, and thus they concluded that spin is a quantised property.

The **orbital angular momentum** quantum number, l, bounds the **secondary orbital angular momentum** quantum number, denoted m_l, allowing it to take integer-separated values within the range $-l \rightarrow l$, i.e.

$m = -l, -l+1, \ldots, l-1, l$. This therefore has a degeneracy of $2l+1$ since there are $2l+1$ values for which the angular momentum may take. As with angular momentum, the spin quantum number, s, bounds the secondary spin quantum number, m_s, i.e. $m_s = -s, -s+1, \ldots, s-1, s$. However, there are only two orientations, thus the degeneracy g is equal to 2. The degeneracy is again given by $g = 2s+1$, hence $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$, where the $\pm$ are "up" and "down" spins, respectively. The eigenvalues of spins are therefore

$$S^2 = s(s+1)\hbar^2 = \frac{3\hbar^2}{4}$$
$$S_z = m_s\hbar = \pm\frac{1}{2}\hbar.$$

Whilst this treatment is suitable for non-relativistic quantum mechanics, Paul Dirac introduced a correction in 1928, which demonstrates that instead of two quantum numbers, there are in fact four. Thus to completely specify the quantum state of an electron in an atom, one requires four quantum numbers:

$$n, l, m_l, m_s.$$

3.3 Multi-Body Systems

In a two-body system, the wavefunction for the combined state can be written as a product of the individual wavefunction, i.e.

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, t) = \Psi_A(\mathbf{r_1})\Psi_B(\mathbf{r_2})e^{-\frac{iEt}{\hbar}},$$

where particle 1 is at $\mathbf{r_1}$ and in state A and particle 2 is at $\mathbf{r_2}$ and in state B. The total energy of the system, E is given by $E = E_A + E_B$, where E_A and E_B are the energy eigenvalues corresponding to eigenfunctions Ψ_A and Ψ_B, respectively.

3.3.1 Distinguishability and Symmetry

An important concept of particle and quantum physics' is the so-called **distinguishability** of particles.

Definition 3.2: Distinguishability

In a general sense, **indistinguishability** (or **identicality**) of particles indicates that under an exchange of the particles, there would be no observable changes to the system. More specifically, they have the same quantum numbers (mass, angular momentum, spin etc).

In order to investigate indistinguishability the exchange operator, $\hat{P}$, must be introduced. This operator acts upon a combined wavefunction to exchange the particle positions, i.e.

$$\hat{P}\Psi(\mathbf{r_1}, \mathbf{r_2}) = \Psi(\mathbf{r_2}, \mathbf{r_1}).$$

Applying the exchange operator twice returns the initial state, i.e.

$$\begin{aligned}\hat{P}^2\Psi(\mathbf{r_1}, \mathbf{r_2}) &= \hat{P}\left(\hat{P}\Psi(\mathbf{r_1}, \mathbf{r_2})\right) \\ &= \hat{P}\Psi(\mathbf{r_2}, \mathbf{r_1}) \\ &= \Psi(\mathbf{r_1}, \mathbf{r_2}).\end{aligned}$$

The eigenvalue of $\hat{P}^2$ is then equal to 1, thus the eigenvalues of the exchange operator are ± 1. This means that the combined wavefunctions are either equal (*symmetric*) or negative-equal (*anti-symmetric*), i.e.

$$\begin{aligned}\Psi(\mathbf{r_1}, \mathbf{r_2}) &= \Psi(\mathbf{r_2}, \mathbf{r_1}); \\ \Psi(\mathbf{r_1}, \mathbf{r_2}) &= -\Psi(\mathbf{r_2}, \mathbf{r_1}).\end{aligned}$$

This symmetry (or lack thereof) introduces a differentiation between particles; the symmetric particles are called "bosons" and the anti-symmetric particle are called "fermions". By the principle of superposition the two combinations of the separate wavefunctions results in these behaviours:

$$\begin{aligned}\Psi_s &= \frac{1}{\sqrt{2}}\left[\Psi_A(\mathbf{r_1})\Psi_B(\mathbf{r_2}) + \Psi_B(\mathbf{r_1})\Psi_A(\mathbf{r_2})\right]; \\ \Psi_a &= \frac{1}{\sqrt{2}}\left[\Psi_A(\mathbf{r_1})\Psi_B(\mathbf{r_2}) - \Psi_B(\mathbf{r_1})\Psi_A(\mathbf{r_2})\right].\end{aligned}$$

One should note that symmetric wavefunctions constructively interfere when the two particle co-habit in space, whereas anti-symmetric wavefunctions

destructively interfere, destroying them both. Therefore fermions cannot exist in the same region of space simultaneously - a phenomenon known as the **Pauli exclusion principle**. Generally, these effects are collectively known as the **exchange energy**.

Definition 3.3: Exchange energy and the exclusion principle

The **exchange energy** (or an **exchange interaction**) occurs when two particles approach one another and can result in the particles being pulled together or pushed apart. The mechanism of this interaction should not be thought of as a force as there are no fundamental force carriers involved, but rather the proximity of the particles alter the expectation values of the overlapping wavefunctions such that it can appear that the particles are being repelled or attracted. For fermions, which are "repelled" from one another, this is better known as the **Pauli exclusion principle**, whereas bosons, which "attract" one another, form a new state of matter, called Bose-Einstein condensate.

3.3.2 Multi-Electron Atoms

Simple two-electron systems have two sets of stationary states and energy levels; one described by symmetric wavefunctions and the other by anti-symmetric wavefunctions. If $\Psi_A = \Psi_B$ the anti-symmetric wavefunctions equal annihilate and hence only symmetric orbitals remain.

Unfortunately it is impossible to find an exact solution to the Schrödinger equation for any system containing more than one particle. This is because the potential is now influenced not only by the Coulombic attraction between the electrons and the nucleus/nuclei, but also by the repulsion between the electrons, producing a coupling between the electrons themselves and the nucleus which cannot be calculated exactly - known as the **three-body problem**. To overcome this super computers are used to numerically simulate the atoms/molecules and calculate the energy levels and orbitals. This works by implementing the **Born-Oppenheimer approximation**, which approximates the total wavefunction of the system as the product of the nuclear and electronic components, i.e.

$$\Psi_{\text{total}} = \Psi_{\text{electronic}} \times \Psi_{\text{nuclear}}.$$

3.3.3 Multi-Body Spin

The time-independent wavefunction for a single electron Ψ may be split into spatial, ϕ, and spin, χ, components, such that

$$\Psi(x, \sigma) = \phi(x)\chi_\sigma.$$

For a system with two electrons a good approximation is to split the overall state into spatial and spin wavefunctions with two arguments, i.e.

$$\Phi(x_1, x_2, \sigma_1, \sigma_2) = \phi(x_1, x_2)\chi_{\sigma_1,\sigma_2}.$$

Within the ground state, the spatial wavefunction is simply the product of the two ground states:

$$\phi(x_1, x_2) = \phi_0(x_1)\phi_0(x_2).$$

The spin of the system is given by the normalised superposition of the possible pairings of values:

$$\chi_{\sigma_1,\sigma_2} = \frac{1}{\sqrt{2}}\left(\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2)\right).$$

An example of a two-body system is a helium atom, for which the spin angular momentum has quantum numbers s and m_s. The eigenfunctions of these are written χ_{s,m_s} and hence the eigenvalue equation is written

$$\begin{aligned}\hat{S}_z\chi_{s,m_s} &= m_s\hbar\chi_{s,m_s};\\ \hat{S}^2\chi_{s,m_s} &= s(s+1)\hbar^2\chi_{s,m_s},\end{aligned}$$

where $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$. These spins denote two types of particle: bosons (integer) and fermions (half-integer).