

# Introduction To Quantum Mechanics

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# Chapter 1

## Wavefunctions and the Schroedinger Equation

### 1.1 Wavefunctions

By adding waves with lots of different momenta prevents us from knowing the position and momentum at the same time. By decreasing the uncertainty in position we increase it in momentum. This gives us a weak idea of Heisenberg Uncertainty!

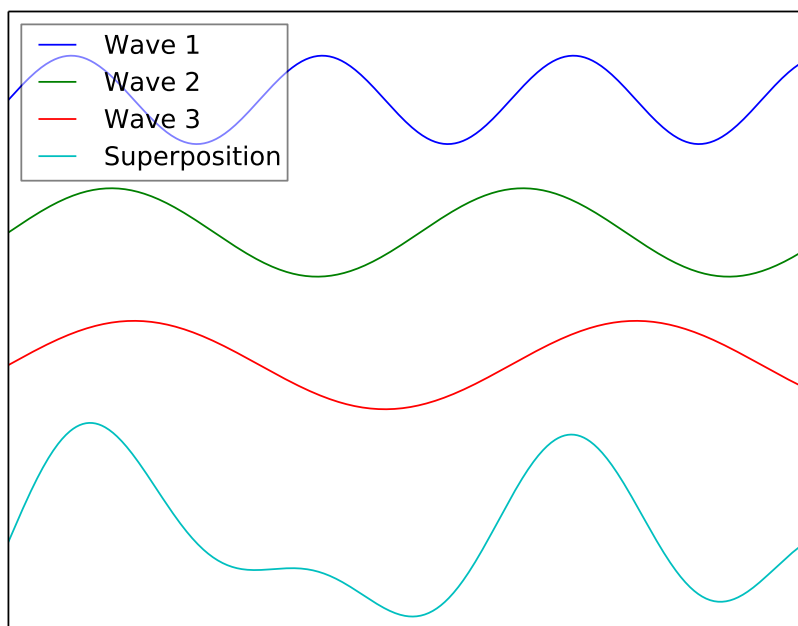


Figure 1.1: Adding waves together “localises” them more in space.

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

### 1.1.1 Classical Waves

We expect classical waves to move in a certain way, in accordance with the wave equation:

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}$$

and have the following properties:

- $v = \omega/k$
- $\omega = 2\pi f$
- $f = 2\pi/\lambda$

For example:

$$y(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

Which satisfies the above wave equation.

However, here, momentum ( $mv$ ) is not dependent on wavelength. This must be different in the quantum world, because of De Broglie's relation:

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

### 1.1.2 Quantum Waves

Let's just begin by studying a random wave:

$$\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

From the quantum world, we can use that:

- $p = h/\lambda = \hbar k$
- $E = hf = \hbar \omega$

And from the classical world:

- $E = p^2/2m = \hbar^2 k^2/2m$

Let's begin by getting a  $k^2$  out by differentiating the wavefunction with respect to  $x$  twice:

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

Plugging into the above formulae:

$$\Psi E = \Psi \hbar^2 k^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Now we need to get  $\omega$ . Let's try differentiating with respect to time.

$$\frac{\partial \Psi}{\partial t} = \omega [A \sin(kx - \omega t) - B \cos(kx - \omega t)]$$

However, this isn't really that useful. We want it to equal a multiple of our original wavefunction, or the maths is really hard to do.

$$\omega [A \sin(kx - \omega t) - B \cos(kx - \omega t)] = C\Psi = C [A \cos(kx - \omega t) + B \sin(kx - \omega t)]$$

We can now equate coefficients and find that (sub  $\sin(kx - \omega t) = s$ ):

$$\omega [As - Bc] = C[Ac + Bs] \rightarrow C = \frac{\omega A}{B}$$

And as such

$$B^2 = -A^2 \rightarrow B = \pm iA$$

From this we find that:

$$\Psi(x, t) = A [\cos(kx - \omega t) + i \sin(kx - \omega t)] = Ae^{i(kx - \omega t)}$$

And now we can put it all together to find the *Schroedinger Equation for a free particle*:

$$i\hbar = \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

This can be easily generalised to find *The Schroedinger Equation!*:

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

We can notice that the Schroedinger Equation is *linear* and *homogeneous*! This means that the linear sum of any two solutions is also a solution.

For the classical wave equation we needed two boundary conditions to solve, however here we only need one.

## 1.2 Interpretation of $\Psi$

This equation leads us to believe that there is an underlying statistical nature to The Universe.

Classically, we know that  $I \propto A^2$ . Quantum mechanically we think of this square of the wavefunction as the probability of finding the particle at that point.

$$P(\text{particle}) = |\Psi(x, t)|^2 = \Psi^* \Psi$$

We choose this because it will *always* be real - like probabilities must be.

## 1.3 Normalisation

Suppose we want to normalise some function  $f(x, t)$ . We need to find the total area under the function and then divide through by a constant to make sure this is unity:

$$|N|^2 \int_{-\infty}^{\infty} f^*(x, t) f(x, t) \cdot dx = 1$$

And so we can find the normalisation constant,  $N$ :

$$N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} f^*(x, t) f(x, t) \cdot dx}}$$

We simply need to do this for the wavefunction to normalise it.

### 1.3.1 Normalization condition

For the unbound particle, it is trivial to work out the normalization condition.

$$\int_{-\infty}^{\infty} \Psi^* \Psi \cdot dx = 1$$
$$A^2 \int_{-\infty}^{\infty} \exp(-i[kx - \omega t]) \exp(i[kx - \omega t]) \cdot dx = 1$$
$$A^2 \cdot \infty = 1$$

Oh dear! This is when we assume that the particle is not confined at all, when it is really confined to the length of our lab,  $L$ , giving:

$$A = \frac{1}{\sqrt{L}}$$

### 1.3.2 Gaussian wavefunction

What happens when we try to find the normalisation condition for a gaussian? The equation

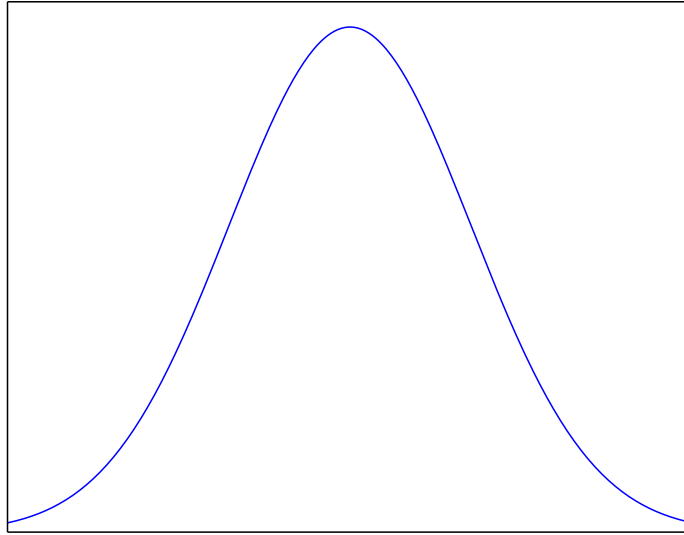


Figure 1.2: A Gaussian function

for a gaussian:

$$\Psi = N \exp\left(-\frac{ax^2}{2}\right)$$

To find the normalisation:

$$\int \Psi^* \Psi \cdot dx = 1 = \int_{-\infty}^{\infty} N^2 \exp(-ax^2) \cdot dx$$

Using WolframAlpha:

$$N^2 \frac{\sqrt{\pi}}{\sqrt{a}} = 1 \rightarrow N = \left(\frac{a}{\pi}\right)^{\frac{1}{4}}$$

Now, let's work out what the probability of finding the particle in the range of  $0 \rightarrow a$ !

$$\int_0^a P(x) \cdot dx = \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_0^a \exp(-ax^2) \cdot dx = \frac{\text{Erf}\left(a^{\frac{3}{2}}\right)}{2}$$

### 1.3.3 Normalization is time-independent

It is possible to show that:

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} \Psi^* \Psi \cdot dx = 0$$

This means you only need to normalize once!

## 1.4 Position

What's the average position of the particle with our Gaussian wavefunction? Let's denote it  $\langle x \rangle$ :

$$\langle x \rangle = \int P(x)x \cdot dx = \int \Psi^* x \Psi \cdot dx$$

Substituting in the Gaussian:

$$\langle x \rangle = \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x \exp(-ax^2) \cdot dx$$

Which we can solve to find:

$$\langle x \rangle = 0!$$

Which is exactly what you would expect, as the Gaussian is symmetric about 0.

### 1.4.1 Momentum

Similarly to how we worked out the average position, we must be able to work out the average momentum. Let's start with:

$$E\Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

From the definition of kinetic energy:

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

We can put these together to show:

$$\Psi p^2 = \Psi p \cdot p = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}$$

And extract:

$$p\Psi = -i\hbar \frac{\partial \Psi}{\partial x}$$

From this, we can try to find what the average momentum in the Gaussian is!

$$\langle p \rangle = \int p(x)P(x) \cdot dx$$

Now we substitute in for  $p\Psi$ :

$$-i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} \cdot dx$$

We already have the wavefunction, meaning we can substitute in to give:

$$\langle p \rangle = \left(\frac{a}{\pi}\right)^2 (-i\hbar) \int_{-\infty}^{\infty} -ax \exp(-ax^2) \cdot dx = 0$$

We can see that this is going to be 0 because of the fact that it is an odd function multiplied by an even function.

The reason that we would expect this result is because this is clearly a bound wavefunction. This means that there will be standing waves set up inside the two potential barriers leading to standing waves which, clearly, aren't going anywhere and as such have a mean momentum of zero.

### 1.4.2 Ehrenfest's Theorem

This theorem describes that these small quantum effects must add up to create the same overall behaviour as classical mechanics for a large system.

We can show that:

$$\langle p \rangle = m \frac{d \langle x \rangle}{dt}$$

and that:

$$\frac{d \langle p \rangle}{dt} = \langle F \rangle = - \left\langle \frac{\partial V}{\partial x} \right\rangle$$

### 1.4.3 General operators

This subsection deals with us generalising the discussion on momentum above. If we have a dynamical variable  $A(x, p, t, \dots)$  we can calculate an expectation of that quantity just by generalising to:

$$\langle A(x, p, t, \dots) \rangle = \int_{-\infty}^{\infty} \Psi^* A(x, p, t, \dots) \Psi \cdot dx$$

This is best demonstrated with an example:

#### Example: Kinetic Energy

$$E\Psi = \frac{p \cdot p}{2m} \Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

Now we will start from the original expression:

$$\langle E \rangle = \int E(x) P(x) dx = \int_{-\infty}^{\infty} \Psi^* E \Psi \cdot dx$$

Substituting in:

$$\langle E \rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \cdot dx$$

From here we can substitute any wavefunction in, for example with the Gaussian above we get an answer of

$$\langle E \rangle = \langle T \rangle = \frac{\hbar^2 a}{2m}$$

We use  $T$  as the operator for kinetic energy in general.

## 1.5 The Hamiltonian

If we take the bound particle:

$$E\Psi = T\Psi + V\Psi$$

And substitute in the operators:

$$i\hbar \frac{\partial}{\partial t} \Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = H\Psi$$

We call this function the Hamiltonian!

## 1.6 Relativistic systems

If we take the relativistic energy equation:

$$E^2 = p^2 c^2 + m^2 c^4$$

and plug in the operators:

$$-\hbar^2 \frac{\partial^2 \Psi}{\partial t^2} = -\hbar^2 c^2 \frac{\partial^2 \Psi}{\partial x^2} + m^2 c^4 \Psi$$

For a free particle. Now, what happens when the particle is massless..?

$$\frac{\partial^2 \Psi}{\partial t^2} = c^2 \frac{\partial^2 \Psi}{\partial x^2}$$

And the wave equation pops out! This is really exciting - it shows that we with our rather crappy ‘derivation’ of the Schroedinger Equation have satisfied the laws of physics!

## 1.7 Reality check

We have a lot of *is* floating about, so we need to check that our equations return real answers for things like kinetic energy. Let’s start with the normalisation condition:

$$\int_{-\infty}^{\infty} \Psi^* \Psi \cdot dx = 1$$

What happens when we take the time derivative of this?

$$\frac{d}{dt} \int_{-\infty}^{\infty} \Psi^* \Psi dx = 0$$



We can put our time differential inside the integral:

$$\int_{-\infty}^{\infty} \frac{\partial}{\partial t} (\Psi^* \Psi) \cdot dx = \int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial t} \Psi \cdot dx + \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial t} \cdot dx = 0$$

Using Hamiltonian notation to simplify:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

Which gives:

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= -\frac{i}{\hbar} H\Psi \\ \frac{\partial \Psi}{\partial t} &= \frac{i}{\hbar} H\Psi^* \end{aligned}$$

Put this into the original equation to get:

$$\int_{-\infty}^{\infty} (H\Psi)^* \Psi \cdot dx = \int_{-\infty}^{\infty} \Psi^* (H\Psi) \cdot dx$$

Which proves that:

$$\langle H \rangle = \langle H \rangle^* \rightarrow \langle H \rangle \in \mathbb{R}$$

This means that energy is always real! We can do a similar proof that shows that  $\langle p \rangle \in \mathbb{R}$ . These are both Hermitian operators and as such expected values are always real.

## 1.8 Non-Hermitian operators

What if we try an operator like  $\langle xp \rangle$ ? We shouldn't be able to measure these two together to an arbitrary precision!

$$\langle xp \rangle = \int_{-\infty}^{\infty} \Psi x (-i\hbar) \frac{\partial \Psi}{\partial x} dx$$

After a bit of trivial mathematics:

$$\langle xp \rangle = i\hbar \int_{-\infty}^{\infty} \Psi \frac{\partial}{\partial x} (x\Psi^*) \cdot dx = \langle px \rangle^*$$

Huh? What's going on? Surely this is all fine, because algebra is commutative? No chance. This is quantum mechanics. You don't get away with that sort of stuff here. In fact, we have that:

$$px\Psi = xp\Psi - i\hbar\Psi$$

Meaning that:

$$(px - xp)\Psi = -i\hbar\Psi$$

The order of operations matters. We define this as a commutator, with the notation:

$$[x, p] = xp - px = i\hbar$$

and this one is called the fundamental commutator. We say that if:

$$[A, B] = AB - BA \neq 0$$

the commutator is non-hermitian and as such not real.

**Example** with the Gaussian! We find that:

$$\langle xp \rangle = \frac{1}{2}i\hbar, \quad \langle px \rangle = -\frac{1}{2}i\hbar$$

which satisfies

$$[x, p] = xp - px = i\hbar$$

Even though these are non-reals, we can take the mean to find some sort of a value (as we know  $\langle x \rangle = 0$ ,  $\langle p \rangle = 0$  and as such expect  $\langle px \rangle = 0$ ):

$$\frac{1}{2}(xp + px) = 0$$

## 1.9 Commutators

If you have a commutator  $[A, B] \neq 0$ , then we say that it *doesn't commute*. In physical terms this means that you've hit the uncertainty principle and are trying to measure  $p$  and  $x$  simultaneously.

### 1.9.1 Commutators and the uncertainty principle

We can have a formal treatment of this, and it is reasonably short:

$$\sigma_A^2 \sigma_B^2 \geq \left( \frac{1}{2} \langle [A, B] \rangle \right)^2$$

Let's try with our  $[x, p]$  commutator:

$$\sigma_x^2 \sigma_p^2 \geq \left( \frac{i\hbar}{2i} \right)^2 = \left( \frac{\hbar}{2} \right)^2$$

Meaning:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

We chose the Gaussian function because it is the wavefunction that minimises the uncertainty, and for the Gaussian:

$$\sigma_x \sigma_p = \frac{\hbar}{2}$$

## Chapter 2

# The Time-Independent Schroedinger Equation

### 2.1 Finding the time independent Schroedinger Equation

We have the original, time-dependent Schroedinger Equation:

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

Everything here is a function of space and time. What if  $V$  is time independent?

$$V(x, t) = V(x)$$

Then the wavefunction is seprable:

$$\Psi(x, t) = \psi(x)T(t)$$

This gives us:

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x) = i\hbar \frac{1}{T(t)} \frac{dT(t)}{dt}$$

We know, because the left-hand side is a function of only  $x$ , and the right hand side is only a function of  $t$ , that this is equal to a constant. We'll call that constant energy,  $E$ .

#### 2.1.1 RHS

$$E = i\hbar \frac{1}{T(t)} \frac{dT(t)}{dt}$$

Gives

$$T(t) = A \exp\left(-\frac{iEt}{\hbar}\right)$$

### 2.1.2 LHS

$$E = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x)$$

Gives:

$$\hbar^2 2m \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

This is the *time independent schrodinger equation*. It also happens to be an eigenvalue equation:

$$Af(x) = af(x)$$

Where  $A$  is an operator, and  $a$  is the eigenvalue. This is because we have the Hermitian operator that operates on  $\psi(x)$ , giving a constant ( $E$ ) which is multiplied to the eigenfunction ( $\psi(x)$ ). So we have the time- independent schrodinger equation:

$$H\psi(x) = E\psi(x)$$

Normally we get multiple energy eigenvalues, so what about general solutions? We have that:

$$\Psi_n(x, t) = \psi_n(x)e^{-\frac{iE_nt}{\hbar}}$$

Leads to the general solution:

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-\frac{iE_nt}{\hbar}}$$

Where each  $c_n$  is chosen such that:

$$\int_0^L \Psi^*(x, t) \Psi(x, t) \cdot dx = 1$$

## 2.2 Bound particles

Let's put a particle wave in a potential. Let's have that:

$$\Psi(x, t) = Ae^{i(kx-\omega t)} - Ae^{-i(kx-\omega t)}$$

Where the left-hand side is the wave travelling to the right, and the right-hand side is the reflected wave that comes back. This reduces to:

$$\Psi(x, t) = 2Ae^{i\omega t} \sin kx$$

Let's take this at  $t = 0$ . We have that  $\sin(k0) = 0$  (no surprise) and that  $\sin(kL) = 0$  because the particle is trapped in an infinite square well. This gives us our first condition:

$$k = \frac{n\pi}{L}$$

Our potential has taken a travelling wave and turned it into a standing wave(s)! We can calculate the energy of each:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

Which gives us the result:

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

And using the above condition:

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

We now need to normalise the wavefunction, getting:

$$A_n = \sqrt{\frac{2}{L}}$$

And our energy eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

Finally:

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-\frac{iE_n t}{\hbar}}$$

Where:

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

We will probably now want to know how the probability changes as a function of time. However, due to the  $i$  in the time-dependent part - there is no time dependence! The complex conjugate cancels out the temporal section! We can now write down the full solution:

$$\Psi(x, t) = \sum_n \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-\frac{iE_n t}{\hbar}}$$

Where:

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