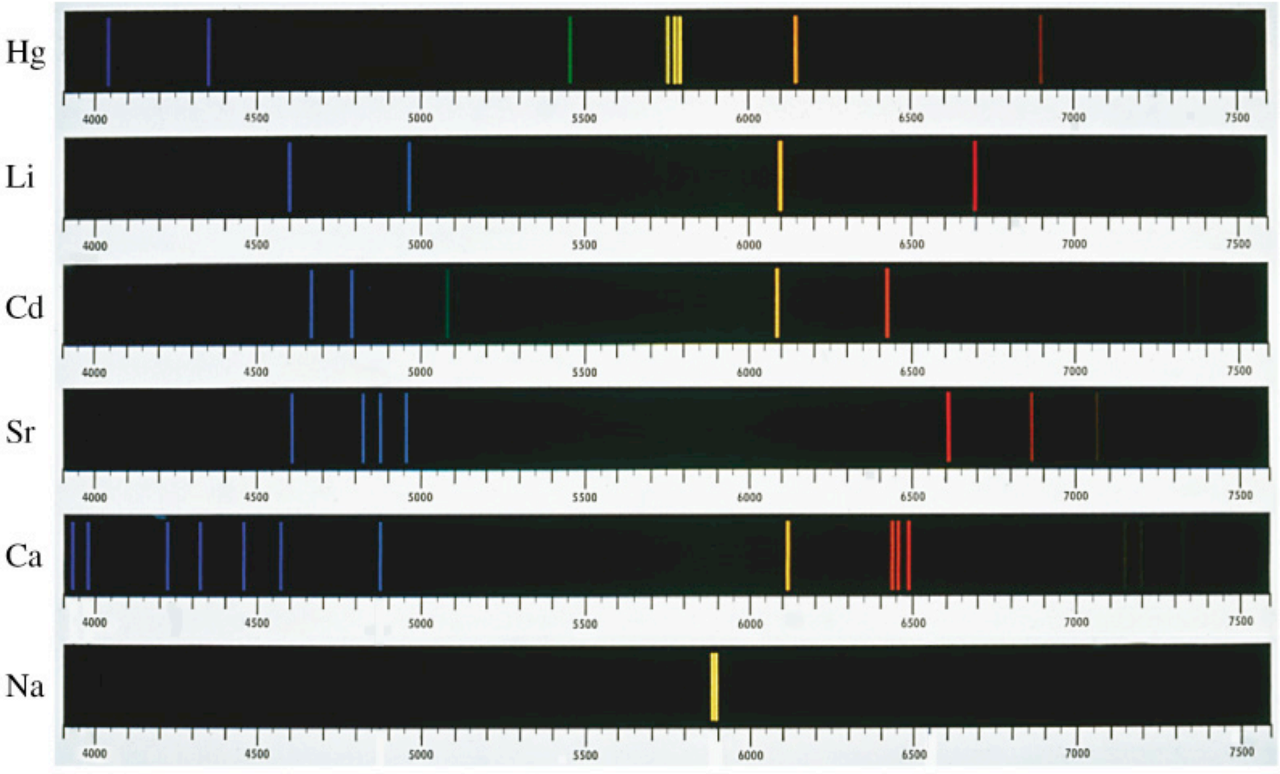
Reminder: http://www.star.le.ac.uk/nrt3/QM/

# Lecture 2: simple QM problems

*Quantum mechanics describes physical particles as waves of probability. We shall see how this works in some simple applications, and meet (a special case of) the fundamental differential equation which describes the evolution of these probability waves, the Schrodinger Equation.*



# Wave-functions

The mathematical basis of quantum mechanics is the description of physical entities as **wave-functions**. Thus individual matter particles have wave-functions (or perhaps “are wave-functions”). Systems of particles can also be described by their combined wave-function.

Wave-functions seemingly encode all the information that can be known about a particle. In practical terms, we use the wave-function of a particle to tell us the **probability** that it will be found in a particular place (or have some other property such as a particular momentum) at a particular time, *if* a measurement is made. Notice that there is a deep distinction here between a probability of a certain outcome when a measurement is made, and whether we can say anything about the “real” properties of the particle in the absence of a measurement. In quantum mechanics it seems that the probabilities don’t simply reflect a lack in our knowledge of the world, but instead reflect an inherent indefiniteness in nature until the point that a property is “magnified” to the **classical level**.

The evolution of the wave-function is *not* uncertain - it is fixed by an equation found by Schrodinger in 1926. But when a measurement is made, for example of position, the wave-function **collapses** to some particular allowed value of position (while the momentum becomes uncertain), before the well-defined time evolution starts again.

Many people regard the collapse of the wave-function as the most fundamental quantum mechanical mystery!

# Calculating probabilities

To make use of quantum mechanics we must have a way to calculate probabilities using the wave-function. It turns out the **square** of the wave-function amplitude corresponds to the **probability density**. (This makes sense since energy is proportional to the square of the *amplitude* of a classical oscillation)

Thus the probability that a particle is in some region of space, between $x_1$ and $x_2$, we must evaluate:

$$\Pr(x_1 \rightarrow x_2) = \int_{x_1}^{x_2} \psi^2(x)\,dx$$

And, since the probability of a particle existing somewhere must be unity, a wave-function should be **normalised** such that:

$$\int_{-\infty}^{\infty} \psi^2(x)\,dx = 1$$

This (usually) allows us to fix the constant coefficient in the wavefunction if it is not already known.

# Expectation values

From the wave-function for a particle we can calculate the **expected** (mean) values for physical properties that we could measure with an experiment, for example, position and velocity.  The quantum mechanical way of doing this is to form an integral of the wave-function and an **operator** which is specific to the quantity we want to measure.

Most simply, if we ask what the mean (average) position of a particle we must evaluate:

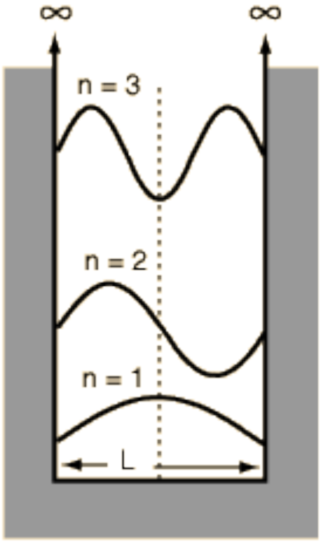
$$\int_{-\infty}^{\infty} x\psi^2(x)dx$$

This is essentially the same procedure one would use in classical physics where the probability corresponds to the time spent by the particle at a particular location.

# A particle in a box - infinite potential well

A very simple quantum mechanical situation is the analysis of a **particle in a box** (which is assumed to have perfectly reflecting walls). To make it even simpler we can consider just a one dimensional situation.

Physically, the crucial point here is that the waves must be **continuous**, and hence **standing waves**. As we shall see, it is this fact (due to the **boundary conditions**) which leads to **quantization** of energies.



x = 0 at left wall of box.

Each standing wave configuration is called an allowed **quantum state.**

$$\psi_n(x) = A_n \sin(n\pi x / L)$$

This situation is frequently referred to as a particle in an **infinite potential well**, since the walls of the box form a barrier that the particle cannot penetrate.

# Time-independent Schrodinger equation

This is the equation which the wave-function must obey, and allows us to evaluate the energy associated with it.  In the special case of a non-evolving system (where the potentia,l *V,* does not depend on time) the equation is known as the **time-independent Schrodinger equation**:

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

Where $E$ is the the energy of the state, $V(x)$ is the external potential.

As with problems in classical physics, we can usually only solve quantum mechanical problems in special or simplified cases. It can be hard, though, to produce even approximate solutions to complicated situations.

The simplest systems we can analyse are those involving single particles evolving in a simple potential (the electron orbiting in the Hydrogen atom is an obvious example).

# Applying Schrodinger to a particle in a box

Going back to the particle in a box, we can see that within the well the potential $V(x)$ is zero, so

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

Hence the wave-function must be of a form such that when double differentiated it returns to *minus* the same form. This is true of sine and cosine functions, and applying the boundary conditions we conclude (as before):

$$\psi_n(x) = A_n \sin(n\pi x/L)$$

Normalising gives:

$$\int_0^L A_n^2 \sin^2(n\pi x/L)dx = \int_0^L \frac{A_n^2}{2}(1-\cos(2n\pi x/L))dx$$

$$= \left[\frac{A_n^2}{2}\left(x - \frac{\sin(2n\pi x/L)}{2n\pi/L}\right)\right]_0^L = \frac{A_n^2 L}{2} \quad \Rightarrow \quad A_n = \sqrt{\frac{2}{L}}$$

# Applying Schrodinger to a particle in a box

Thus we find the general solution is:

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

Plugging this back into the Schrodiinger equation we find:

$$\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2\sqrt{\frac{2}{L}}\sin(n\pi x/L) = E_n\sqrt{\frac{2}{L}}\sin(n\pi x/L)$$

$$\Rightarrow \quad E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \frac{h^2n^2}{8mL^2}$$

This shows that the allowed states for a particle in a box have energy levels which are **quantized** with values proportional to $n^2$. Note that even the lowest “**ground state”** $(n=1)$ does not have zero energy!

As you will see later, application of quantum rules to electrons in atoms leads to the prediction of discrete energy levels which explains the **atomic line spectra** - the first great experimental verification of quantum mechanics.

# Applying Schrodinger to a particle in a box

Recalling de Broglie’s expression relating momentum to wavelength, and noting that the wavelength in this case is $2L/n$, we find that the energy of the allowed states is given by:

$$\begin{aligned} E_n &= \frac{h^2 n^2}{8mL^2} \\ &= \frac{h^2}{2m\lambda^2} = \frac{p^2}{2m} \end{aligned}$$

In other words, the energy is simply the Newtonian expression for kinetic energy of a particle of mass $m$ and momentum $p$ .

# Applying Schrodinger to a particle in a box

Considering the expected position of such a particle:

$$\bar{x} = \frac{2}{L}\int_0^L x\sin^2(n\pi x/L)dx$$

Integrating by parts gives:

$$\bar{x} = \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8n^2\pi^2/L^2}\right]_0^L$$

$$= \frac{2}{L}\left[\frac{L^2}{4}\right] = \frac{L}{2}$$

In other words, the expected position is (as we would expect by symmetry) the midpoint of the box.

# 3D Infinite well

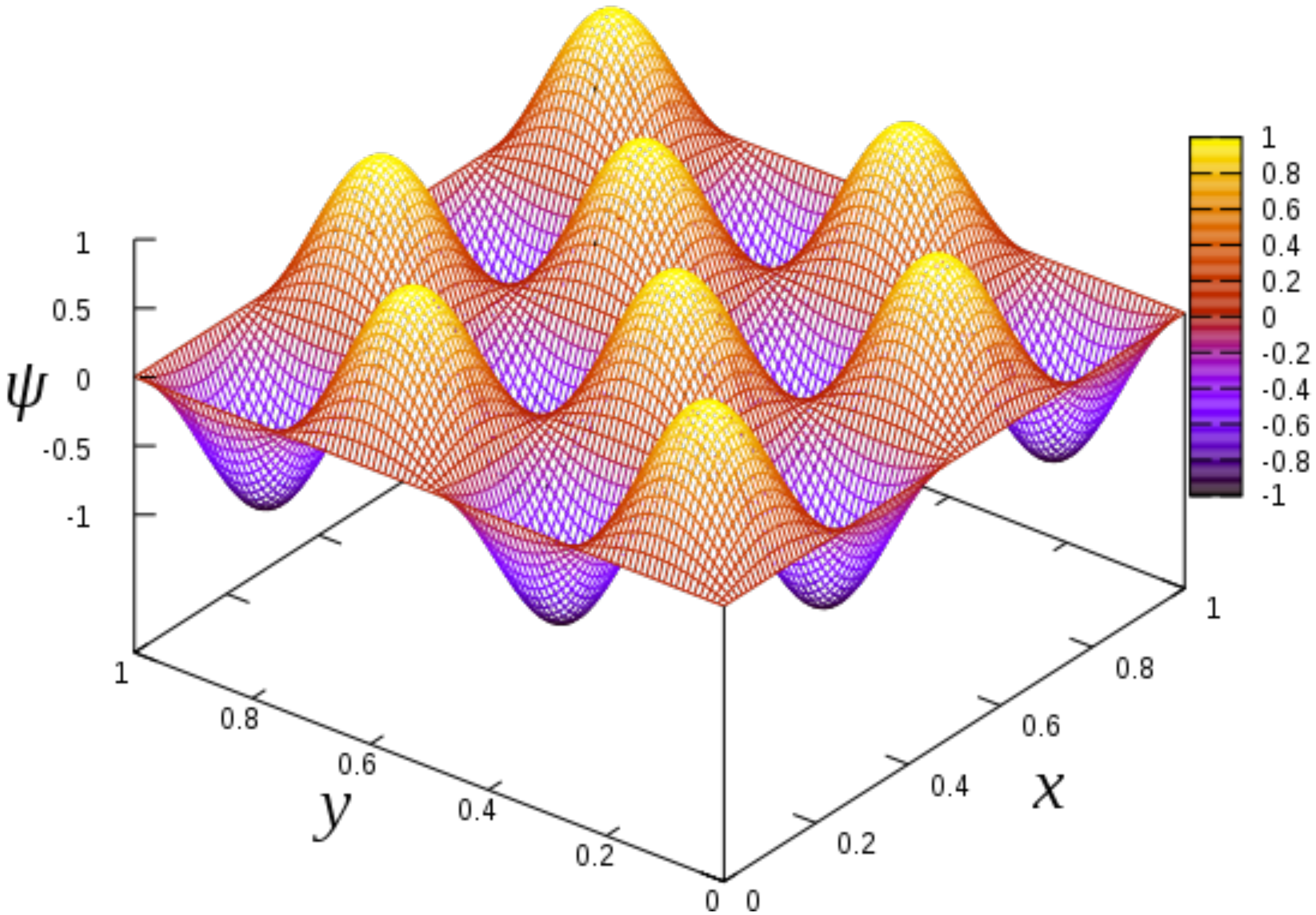
The solution to the 3D particle-in-a-box problem requires 3 **quantum numbers**:

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin(n_x \pi x / L) \sin(n_y \pi y / L) \sin(n_z \pi z / L)$$

$$E_{n_x n_x n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Notice that this means different sets of quantum numbers can have the same energy. Such states are called **degenerate**, and as you will learn later the existence of degenerate states has important implications for the properties of matter.

# Higher dimensions



2D example