Erwin Schrödinger published the **Schrödinger Equation** in January 1926. This is one of the most important relationships in **Quantum Theory** as it enables one to calculate the *probability* of a particle being at a particular location in space and time if the mathematical form of possible energies is known. Its development was influenced by the work of Louis de Broglie, who proposed that all particles have an associated wave expression, whose wavelength is related to the momentum of the particle.

Erwin Schrödinger
1887 – 1961
Nobel Prize 1933

de Broglie relationship

wavelength associated with particle → $\lambda = \frac{h}{p}$ ← Planck's constant 6.63 x 10^{-34} m^2kgs^{-1}; p ← momentum of particle

$\hbar = \frac{h}{2\pi}$, 'hbar' $\quad k = \frac{2\pi}{\lambda}$ wavenumber $\Rightarrow p = \hbar k$ **de Broglie relationship**

We can 'derive' the Schrödinger Equation by combining (1) the wave equation (2) the de Broglie relation and (3) the law of conservation of energy. We will assume it applies to particles moving much less than the speed of light i.e. a relativistic treatment is not need. (For a full relativistic treatment, the *Klein-Gordon* or *Dirac Equation* are needed, the latter for 'spin-half' particles such as the electron).

The *wave equation* describes the amplitude of a wave moving at speed c

$$\frac{\partial^2\psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}$$

$$c = f\lambda, \quad \omega = 2\pi f, \quad \omega = ck$$

Frequency f

For *plane waves of amplitude* ψ

$$\psi(x,t) = \psi_0 e^{i(kx-\omega t)} \quad \therefore \frac{\partial^2\psi}{\partial x^2} = -k^2\psi$$

Classical expression of energy:
(Total energy E. potential energy V)

$$E = \tfrac{1}{2}mv^2 + V$$

Momentum $p = mv \Rightarrow v = \frac{p}{m} \quad \therefore E = \frac{p^2}{2m} + V \quad \Rightarrow p^2 = 2m(E-V)$

Max Born
1882 – 1970
Nobel Prize 1954

Combining energy and the de Broglie relation

$$p = \hbar k$$

$$\therefore \hbar^2 k^2 = 2m(E-V)$$

$$\therefore k^2 = \frac{2m}{\hbar^2}(E-V)$$

Substituting back into the wave equation:

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

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

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

This is the **time independent Schrödinger Equation** i.e. you will be able to make analytical progress if solutions are of the form

$\psi(x,t) = X(x)T(t)$ i.e. 'separable'

A more general **time dependent** equation can be 'derived' by noting the energy of a *photon*, and by analogy, a 'wave-like particle' (!) is:

$$E = hf = \hbar\omega$$

For a plane wave:

$$\psi(x,t) = \psi_0 e^{i(kx-\omega t)}$$

$$\therefore \frac{\partial\psi}{\partial t} = -i\omega\psi$$

$$\therefore \frac{1}{-i}\frac{\partial\psi}{\partial t} = \omega\psi$$

$$\therefore i\hbar\frac{\partial\psi}{\partial t} = \hbar\omega\psi$$

$$\therefore i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

Hence:

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

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

Time dependent Schrödinger Equation

$\psi(x,t)$ is known as the **wavefunction**

So what does the *wavefunction* mean? In 1926 Max Born proposed that it relates to the **probability** of finding a particle. So although the Schrödinger Equation is *deterministic*, the exact location of a particle is *probabilistic*. Only the 'odds' can be inferred with definite precision.

Born interpretation

$|\psi(x,t)|^2\,dx$ is the *probability* of a particle being at location between x and $x + dx$

For a two or three dimensional problem (like the position of an electron in Hydrogen atom) we will need to consider x,y and z Schrödinger Equations, or the equivalent expressions using a more appropriate coordinate system which reflects the symmetry of the system such as spherical polars in the case of the Hydrogen atom.

Solution to the Schrödinger Equation example #1: Particle in a box

The potential energy associated with our box is given by:

$$V(x)=\begin{cases}\infty & x\le 0,\ x\ge a\\ 0 & 0<x<a\end{cases}$$

Let us assume the wavefunction of the particle is separable and the total energy E is constant

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

Time independent Schrödinger Equation

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

$$\therefore -\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}T=EXT$$

$$\therefore \frac{d^2X}{dx^2}+\frac{2mE}{\hbar^2}X=0$$

Now it is clear that the wavefunction *must vanish* at the boundaries of the box to satisfy the Schrödinger Equation**.** A sine function will have such a property, and is also the basic mathematical form of a wave of a fixed wavelength.

$$X(x)=A\sin kx,\quad ka=n\pi$$

← In order to make $\psi(0)=\psi(a)=0$

n is an integer

$$\therefore \frac{d^2X}{dx^2}+\frac{2mE}{\hbar^2}X=0$$

$$-k^2A\sin kx+\frac{2mE}{\hbar^2}A\sin kx=0$$

$$\therefore E=\frac{\hbar^2}{2m}k^2$$

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

So the *boundary condition* resulting from 'sine waves fitting into the box' means the particle energies are *quantized.* i.e. only integer values of *n* are allowed, and therefore the *particle energies are discrete values rather than a continuum.*

What about the time dependency?

$$E\psi=i\hbar\frac{\partial\psi}{\partial t}$$

$$\psi=XT$$

$$\therefore EXT=i\hbar X\frac{dT}{dt}$$

$$ET=i\hbar\frac{dT}{dt}$$

$$\frac{E}{i\hbar}dt=\frac{dT}{T}$$

$$-i\frac{E}{\hbar}t=\int\frac{dT}{T}=\ln T+\text{const}$$

$$\therefore T\propto e^{-\frac{iEt}{\hbar}}$$

Let us therefore write the (n^{th}) wave equation solution as:

$$\psi(x,t)=A_ne^{-\frac{iEt}{\hbar}}\sin\left(\frac{n\pi x}{a}\right)$$

To find the constant, let us apply the **Born interpretation**, and note that the probability of the particle being *somewhere* within the box must be *unity*

$$\int_0^a\left|\psi(x,t)\right|^2dx=1$$

$$\int_0^a\psi\psi^*dx=1$$

$$\int_0^aA_ne^{-\frac{iEt}{\hbar}}\sin\left(\frac{n\pi x}{a}\right)\times A_ne^{\frac{iEt}{\hbar}}\sin\left(\frac{n\pi x}{a}\right)dx=1$$

If we assume the wavefunction spatial amplitude A *to be real*

$$A_n^2\int_0^a\sin^2\left(\frac{n\pi x}{a}\right)dx=1$$

$$A_n^2\tfrac{1}{2}\int_0^a\left(1-\cos\left(\frac{2n\pi x}{a}\right)\right)dx=1$$

$$A_n^2\tfrac{1}{2}\left[x-\frac{a}{2n\pi}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^a=1$$

$$A_n^2\tfrac{1}{2}(a)=1$$

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

In summary:

$$\psi_n(x,t)=\sqrt{\frac{2}{a}}e^{-\frac{iEt}{\hbar}}\sin\left(\frac{n\pi x}{a}\right)$$

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

*which could be a simple model of some form of 'atomic trap'

Particle in a box and the Uncertainty Principle

Define the *uncertainties* in position and momentum as

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

i.e. these quantities are *the standard deviations* (or square roots of the *variance*) of variables *x* and *p*

$$E = \frac{p^2}{2m} + V$$ from the conservation of energy

Therefore since within the box $V = 0$

$$p^2 = 2mE$$

$$p^2 = 2m\frac{\hbar^2\pi^2 n^2}{2ma^2}$$

$$p^2 = \frac{\hbar^2\pi^2 n^2}{a^2}$$

$$\therefore \langle p^2 \rangle = \frac{\hbar^2\pi^2 n^2}{a^2}$$

Now to find the *expectation* of *p* we will need to find the **momentum wavefunction**, which is *not* $\psi(x,t)$

From the de Broglie relation $p = \hbar k$

So the momentum wavefunction must relate to wavenumber, *not* position. To interrelate these quantities we need a ***Fourier Transform***. We can therefore define the momentum wavefunction as:

$$\phi(p,t) = \phi(\hbar k) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x,t)e^{-ipx/\hbar}dx$$

One can use this result to show that $\langle p \rangle = 0$

$$\therefore \Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \frac{\hbar\pi n}{a}$$

Now we *can* use the position wavefunctions to find the *positional uncertainty*

$$\psi_n(x,t) = \sqrt{\frac{2}{a}}e^{-\frac{iEt}{\hbar}}\sin\left(\frac{n\pi x}{a}\right)$$

$$\langle x \rangle = \int_0^a x|\psi|^2 dx$$

$$\langle x \rangle = \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$\langle x \rangle = \frac{2}{a}\int_0^a x\sin^2(\alpha x)dx, \quad \alpha = \frac{n\pi}{a}$$

$$\langle x \rangle = \frac{2}{a}\left[\tfrac{1}{4}x^2 - \frac{x\sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2}\right]_0^a$$

$$\langle x \rangle = \frac{2}{a}\left[\left(\tfrac{1}{4}a^2 - \frac{a^2\sin 2n\pi}{4n\pi} - \frac{a^2\cos 2n\pi}{8n^2\pi^2}\right) - \left(-\frac{a^2}{8n^2\pi^2}\right)\right]$$

$$\langle x \rangle = \frac{2}{a}\left[\left(\tfrac{1}{4}a^2 - \frac{a^2}{8n^2\pi^2}\right) - \left(-\frac{a^2}{8n^2\pi^2}\right)\right]$$

$$\langle x \rangle = \tfrac{1}{2}a$$

$$\langle x^2 \rangle = \int_0^a x|\psi|^2 dx$$

$$\langle x^2 \rangle = \frac{2}{a}\int_0^a x^2\sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$\langle x^2 \rangle = \frac{2}{a}\int_0^a x^2\sin^2(\alpha x)dx, \quad \alpha = \frac{n\pi}{a}$$

$$\langle x^2 \rangle = \frac{2}{a}\left[\tfrac{1}{6}x^3 - \frac{x\cos 2\alpha x}{4\alpha^2} - \frac{(2\alpha^2x^2 - 1)\sin 2\alpha x}{8\alpha^3}\right]_0^a$$

$$\langle x^2 \rangle = \frac{2}{a}\left[\tfrac{1}{6}a^3 - \frac{a^3\cos 2\pi n}{4n^2\pi^2} - \frac{a^3(2n^2\pi^2 - 1)\sin 2\pi n}{8n^3\pi^3}\right]$$

$$\langle x^2 \rangle = \frac{2}{a}\left(\tfrac{1}{6}a^3 - \frac{a^3}{4n^2\pi^2}\right)$$

$$\langle x^2 \rangle = \tfrac{1}{3}a^2\left(1 - \frac{3}{2n^2\pi^2}\right)$$

Putting the above results together:

$$\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \tfrac{1}{3}a^2\left(1 - \frac{3}{2n^2\pi^2}\right) - \tfrac{1}{4}a^2 = \tfrac{1}{12}a^2\left(4 - \frac{12}{2n^2\pi^2} - 3\right)$$

$$\Delta x^2 = \tfrac{1}{12}a^2\left(1 - \frac{6}{n^2\pi^2}\right)$$

$$\Delta x\Delta p = a\tfrac{1}{\sqrt{12}}\sqrt{1 - \frac{6}{n^2\pi^2}} \times \frac{\hbar\pi n}{a}$$

$$\Delta x\Delta p = \tfrac{1}{2}\hbar\sqrt{\frac{\pi^2 n^2}{3} - \frac{6\pi^2 n^2}{3n^2\pi^2}}$$

$$\therefore \Delta x\Delta p = \tfrac{1}{2}\hbar\sqrt{\frac{\pi^2 n^2}{3} - 2}$$

Quote standard integrals for the above calculation:

$$\int x\sin^2\alpha x\,dx = \tfrac{1}{4}x^2 - \frac{x\sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2} + c$$

$$\int x^2\sin^2\alpha x\,dx = \tfrac{1}{6}x^3 - \frac{x\cos 2\alpha x}{4\alpha^2} - \frac{(2\alpha^2x^2 - 1)\sin 2\alpha x}{8\alpha^3} + c$$

This is an example of the **Heisenberg Uncertainty Principle**, which states

$$\Delta x\Delta p \geq \tfrac{1}{2}\hbar$$

In other words, we have a *limit* upon how precisely we can measure position and momentum of a particle

$\langle x \rangle \equiv E[x] \qquad \langle x^2 \rangle - \langle x \rangle^2 \equiv V[x]$