# The Schrödinger Wave Equation

## Wavepackets: group & phase velocities of particles

A wave travelling in the positive $x$ direction may be represented by the expression:
$A_o \cos(\omega t - \beta x)$

where $A_o$ is the amplitude of the wave, $\omega$ is the angular frequency and $\beta$ is the phase constant, which is related to the wavelength by, $\beta = 2\pi/\lambda$.

Mathematically, it is more convenient to represent the wave by an exponential function:

$$A_o \operatorname{Re} \exp[j(\omega t - \beta x)] \qquad (1)$$

Most books omit the 'Re' part, but only the real part of any subsequent operation is valid.

The propagation of a wave is characterised by two velocities – the phase velocity, $v_{ph}$ and group velocity, $v_g$. Phase velocity is defined as the velocity of planes of constant phase along the propagation direction of the waves.

Let us examine the motion of a point of constant phase, which is given by the condition:

$$\omega t - \beta x = constant \qquad (2)$$

Phase velocity is obtained by differentiating this equation with respect to time:

$$\omega\text{-}\beta\delta x/dt = 0 \qquad or \qquad v_{ph} = \omega/\beta \tag{3}$$

(this is the velocity with which the phase moves – nothing material propagates with this velocity – indeed $v_{ph}$ can be greater than the speed of light without violating any physical laws.)

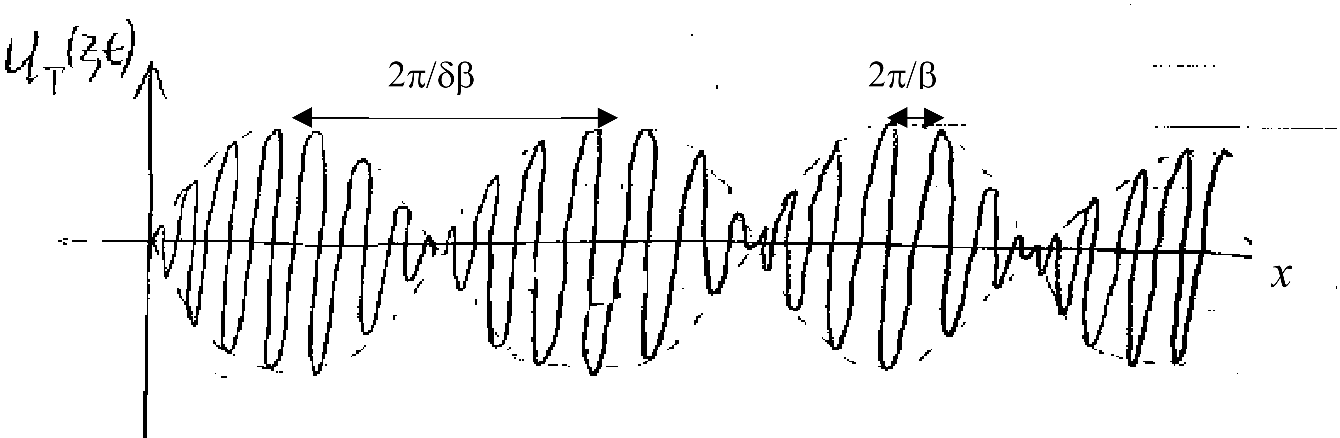
If we consider two waves with the same amplitude but small differences of $\delta\omega$ and $\delta\beta$ in wavelength propagating simultaneously in the x direction. The resultant wave can be represented by the sum:

$$A_o \cos(\omega t\text{-}\beta x) + A_o \cos[\cos(\omega+\delta\omega)t\text{-}(\beta+\delta\beta)x]$$

$$= 2\, A_o \{½[\cos(2\omega+\delta\omega)t\text{-}(2\beta+\delta\beta)x\} \cos[½(\delta\omega t\text{-}\delta\beta x)]$$

$$\approx 2\, A_o \cos[½(\delta\omega t\text{-}\delta\beta x)] \cos(\omega t\text{-}\beta x) \tag{4}$$

(since $\delta\omega << 2\omega....)$




Interaction of two waves with different frequencies

Thus the resultant total wave consists of a high frequency wave varying as $\cos(\omega t - \beta x)$ , whose amplitude varies at a slower rate given by $\cos[\frac{1}{2}(\delta\omega t - \delta\beta x)]$. The wave is modulated by constructive and destructive interference effects.

From (3), the high frequency wave has a phase velocity $v_{ph} = \omega/\beta$.

The envelope of the wavegroup varies sinusoidally with time and distance with a relatively long wavelength, $2\pi/\delta\beta$.

Group velocity is defined as the velocity of propagation of a plane of constant phase on the envelope. It corresponds to the velocity of the packet of waves along the direction of propagation. A plane of constant phase on the envelope is given as in (2) by:

$$\delta\omega t - \delta\beta x = constant \tag{5}$$

Doing the same thing as before, we see that the group velocity is given by:

$$v_g = \delta\omega/\delta\beta \tag{5a}$$

This velocity is the velocity with which energy is transmitted in the direction of propagation. (Think of AM of radio waves or modulation of light in an optical fibre).

We know that the momentum and kinetic energy (T) of a particle are given by:

$p = mv = h/\lambda$

$T = \frac{1}{2}mv^2 = hf$ (6)

We know from (1) that an infinite plane wave travelling in x direction has the form:

$A_o \exp[-j(\omega t-\beta x)]$

For the particle wave, using expression (6) above:

$\beta = 2\pi/\lambda = 2\pi p/h = p/\hbar$ (7)

$\omega = 2\pi T/h = T/\hbar$ (8)

This suggests that it might be possible to represent a particle by a function $\psi$ called a wavefunction, where

$\psi = A_o \exp[-j(\mathrm{T}t-px)/ \hbar]$ (9)

Using (7) & (8),

$v_{ph} = \omega/\beta = T/p = \frac{1}{2}mv^2/mv = v/2$

*(for photons travelling in a vacuum, $v_{ph} = c$)*

This result is not valid for a single particle since this must be represented by a wavepacket and the concept of phase velocity is only applicable to infinite wavetrains.

From (6),
$\frac{1}{2}mv^2 = hf$, *or*
$\omega = \frac{1}{2}mv^2/\hbar$
$\delta\omega = (mv/\hbar)\delta v$

From (7),
$\beta = p/\hbar = mv/\hbar$
$\delta\beta = (m/\hbar)\delta v$

From (5a), and above,
$$v_g = \delta\omega/\delta\beta \qquad (10)$$

Therefore a single electron can be represented by a wavepacket travelling at the same velocity as the electron. This is physically plausible as group velocity is defined as the rate at which energy (or information) is being transported by the wave.

(If the difference between $v_p$ and $v_g$ is still confusing, let us take something familiar. Think about how a caterpillar moves! Its ‘group velocity’ is much slower than its ‘phase velocity’.)

## **The Schrödinger wave equation**

Erwin Schrödinger (1887-1961), placed Planck's quantum theory on a firm mathematical basis in 1926. (Nobel prize (with Dirac) in 1933).

The Schrödinger equation predicts $\psi$ the wavefunction of a particle. There is no formal proof for the Schrödinger wave equation - same for Newton's laws. Agreement with experiment has been found to be valid in all circumstances, especially with microscopic particles, where relativistic effects can be significant. In the large size limit, it agrees with Newton.

Equation (9) gave an expression for $\psi$ including the K.E., T, of a particle. In general, the particle can also have P.E. due to the particle moving in a field in the crystal lattice.

$$E = \hbar\omega = K.E. + P.E. = T + V$$

$$\psi = A_o \exp[-j(Et-px)/\hbar] \qquad (11)$$

What equation does this generalised wavefunction satisfy?

Let us look at the magnetic field of a plane wave propagating in a medium with permittivity ε and permeability μ.

The solution for

$$\delta^2 H/\delta x^2 = \varepsilon\mu\, \delta^2 H/\delta t^2 \qquad (12)$$

is

$H = H_o \exp[-j(\omega t - \beta x)]$

Let us try and find a wavequation similar to (12) for which the solution for $\psi$ is given by (11).

If we differentiate (11) w.r.t. $t$

$$\frac{\partial \psi}{\partial t} = -\frac{j}{\hbar} E \psi = -\frac{j}{\hbar}\left(V + \tfrac{1}{2} m v^2\right)\psi \tag{13}$$

Let us also differentiate $\psi$ w.r.t. $x$, twice

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi = -\frac{m^2 v^2}{\hbar^2}\psi \tag{14}$$

Rearrange (13) to give:

$$-\tfrac{1}{2} m v^2 \psi = -j\hbar \frac{\partial \psi}{\partial t} + V\psi \tag{15}$$

Rearrange (14) to give:

$$-\tfrac{1}{2} m v^2 \psi = \frac{1}{2m}\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \tag{16}$$

Equate (15) to (16) and rearrange to give:

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{2m}{\hbar^2} V\psi + j\frac{2m}{\hbar}\frac{\partial \psi}{\partial t} = 0 \qquad (17)$$

If motion is allowed in 3-dimensions:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \frac{2m}{\hbar^2} V\psi + j\frac{2m}{\hbar}\frac{\partial \psi}{\partial t} = 0$$

This is the 3-dimensional time dependent Schrödinger equation. It can be used for electrons or *any* particle, provided the appropriate mass and P.E. are used.

If the total particle energy is constant ( as is normally the case), the Schrödinger equation can be simplified by separating out time and position dependent parts. Let us look at a 1-D problem for simplicity, and assume a solution of the form:

$$\psi = \Psi(x)\Gamma(t) \qquad (18)$$

where $\Psi$ and $\Gamma$ are respectively functions of position and time only.

By differentiating (18) w.r.t. $x$ twice and w.r.t. $t$, and substituting into (17), you get:

$$\frac{\hbar^2}{2m\Psi}\frac{d^2\Psi}{dx^2} - V = -j\frac{\hbar}{\Gamma}\frac{d\Gamma}{dt} \tag{19}$$

Provided $V$ is time independent, the L.H.S. is a function of position only and the R.H.S. is a function of time only. Thus each side must independently equal to some constant, say $C$.

$$C = -j\frac{\hbar}{\Gamma}\frac{d\Gamma}{dt}$$

or $\Gamma(t) = \exp(jCt/\hbar)$

If we compare this with (11), then the time dependent constant $C$ must be $-E$, *i.e.*
$\Gamma(t) = \exp(-jEt/\hbar)$

Substitute this into (18) gives,
$\psi = \Psi(x)\exp(-jEt/\hbar)$

The L.H.S. of (19) is equal to $-E$, so substitution and rearranging gives,

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0$$

This is the one dimensional time independent Schrödinger equation. It can be used to find the space-dependent part of the wavefunction, e.g. for bound particles.

**What is the wavefunction $\psi$?**

What property of the particle is behaving like a wave?
For radio waves it is the oscillation of the electric and magnetic field vectors.
For sound waves it is varying pressure.

$\psi(x,y,z,t)$ is a function of position and time so we may expect that it represents the position of a particle at some time $t$. However we know from Heisenberg that it is impossible to locate a particle without there being some uncertainty in position and momentum.

We can only consider the probability of the particle being at a particular point in space at a time $t$.
Another complication is that since $\psi$ is a solution to Schrödinger's equation, it is usually a complex quantity.

Max Born overcame this problem in 1928 by showing that $|\psi|^2$, the square of the absolute magnitude, is proportional to the probability of a particle being in a unit volume of space, centred at the point where $\psi$ is evaluated, at time $t$.

Although the *exact* position of the particle cannot be predicted, it is possible to find its most *probable* location. $|\psi|^2\Delta V$ is therefore *proportional* to the *probability* that a particle will be found in a volume element $\Delta V$. (V is volume here – not voltage)

$|\psi(x.y.z,t)|^2 \, dx \, dy \, dz = \psi\psi^* \, dx \, dy \, dz$
where $\psi^*$ is the complex conjugate of the wavefunction.

If we solve Schrödinger's equation and obtain a wavefunction $\psi$, the probability density, $|\psi|^2$, can be used to predict accurately what the spatial distribution of particles will be at some time, $t$.

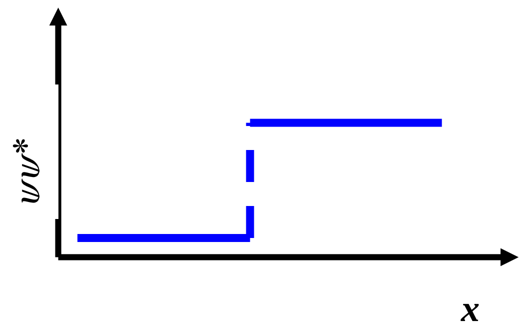
If a particle exists, it is located somewhere in space. We use this to choose the constant of proportionality such that the integral of the probability density over all space equals unity, or

$$\iiint_{-\infty}^{+\infty} \psi\psi^* \, dxdydz = 1$$

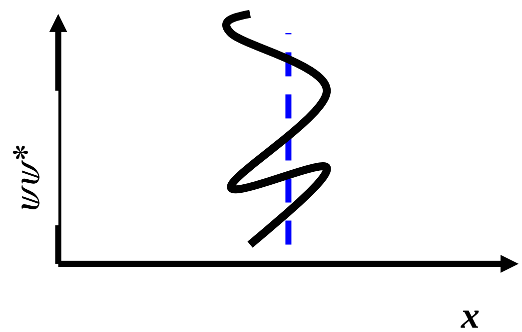
Such a wavefunction is said to be normalised. When this happens, $|\psi|^2\Delta V$ is now *equal* to the *probability* that a particle will be found in a volume element $\Delta V$.

**Boundary conditions:**
Before solving Schrödinger's equation, we need to know the boundary conditions to set on $\psi$. First, $\psi$ must be continuous and a single-valued function of position. If not, $\psi\psi^*$ would also be discontinuous. By similar reasoning the deratives of $\psi$, $\partial\psi/\partial x$, $\partial\psi/\partial y$ *and* $\partial\psi/\partial z$ must be continuous and single-valued across any boundary.

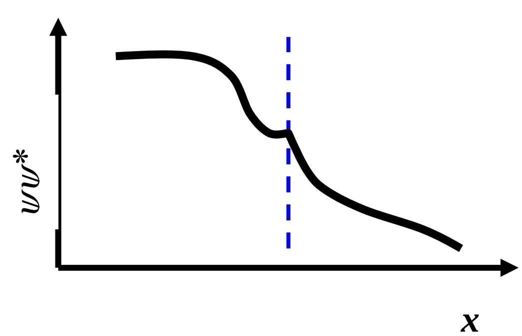
Some examples:




The probability, $\psi\psi^*$, is different, depending on whether we approach from the left or right – not physical to have a discontinuity in probability.




The probability, $\psi\psi^*$, is multi-valued at a particular position – again not physical.




The gradient of the probability, $\psi\psi^*$, cannot be discontinuous – not physical.