Quantum –

Section 1. Wave Mechanics

Waves

A "perfect" or monochromatic wave in 1d has the form $u(x,t) = \sin 2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)$

or cos . . . . .

where λ = wavelength

T = period : related to the frequency ν ("nu") by $\nu = 1/T$

This wave travels to the right with a speed $v = \lambda/T = \lambda\nu$

Why? write as $\sin \frac{2\pi}{\lambda}\left(x - \frac{\lambda}{T} t\right)$ and compare with $F(x-vt)$ for an arbitrary function $F(x)$ translating to the right with speed v.

It is convenient to define

$k = 2\pi/\lambda$ called the "wavenumber"

$\omega = 2\pi/T = 2\pi\nu$ called the "angular frequency"

This lets us write $\sin(kx-\omega t)$ or $\cos(kx-\omega t)$

Complex waves have the form

$$u(x,t) = e^{\pm i(kx-\omega t)}$$
$$= \cos(kx-\omega t) \pm i\sin(kx-\omega t)$$

from Euler's Identity $e^{\pm i\theta} = \cos\theta \pm i\sin\theta$

It is easy to verify that all of these wave forms satisfy a partial differential equation (PDE) called the "wave equation"

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}$$ where $v = \omega/k$ is the speed of wave propagation in the medium

This is a linear PDE ⇒ sum of solutions are solutions

given any two solutions $u_1(x,t)$, $u_2(x,t)$,

$u_\Sigma = u_1 + u_2$ is also a solution

Hence a completely general wave, ie not perfect, not monochromatic has the form

$$\sum_{n=0}^{\infty} a_n \sin(k_n x - \omega_n t) + b_n \cos(k_n x - \omega_n t)$$

or

$$\sum_{n=-\infty}^{\infty} C_n e^{i(k_n x - \omega_n t)}$$

a_n, b_n are real constants

C_n complex constants

where for each term, the wavenumber and angular frequency are related by $v = \omega_n / k_n$

Called a Fourier series. a_n, b_n, c_n are Fourier coefficients.

Extension to 3d

Monochromatic waves in 3d look like

$\sin(\underline{k} \cdot \underline{r} - \omega t)$, $\cos(\underline{k} \cdot \underline{r} - \omega t)$, $e^{i(\underline{k} \cdot \underline{r} - \omega t)}$

where $\underline{k} = (k_x, k_y, k_z)$ = wavevector

$\underline{r} = (x, y, z)$ = position vector

the wavevector $\underline{k}$ points in the direction of propagation and has length $|\underline{k}| = 2\pi/\lambda$

with ω defined as before, $\omega = 2\pi/T = 2\pi\nu$

The 3d wave equation is

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

or, in more concise notation, $\nabla^2 u = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}$

where ∇^2 is the Laplacian operator $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Particles characterized by position $\underline{r}$, momentum $\underline{p}$, and kinetic energy T.

$$\underline{p} = m\underline{v} \quad , \quad T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad \text{where } p^2 \equiv |\underline{p}|^2 = p_x^2 + p_y^2 + p_z^2$$

$\underline{p}$ and T are related to the application of a force $\underline{F}$ over time & space, respectively:

① $d\underline{p} = \underline{F}\,dt$ — This is Newton's 2nd Law

$$\underline{F} = m\underline{a} = m\frac{d\underline{v}}{dt} = \frac{d}{dt}(m\underline{v}) = \frac{d\underline{p}}{dt}$$

② $dT = \underline{F} \cdot d\underline{r}$

$$dT = d\left(\frac{p^2}{2m}\right) = \frac{1}{2m}2\underline{p}\cdot d\underline{p} = \underline{v}\cdot\underline{F}\,dt$$

Now, $\underline{v} = \frac{d\underline{r}}{dt} \Rightarrow \underline{v}\,dt = d\underline{r}$

If $\underline{F} = -\underline{\nabla}V$ where $V(x,y,z)$ is called the potential energy function, then

$$dT = -\underline{\nabla}V \cdot d\underline{r} = -dV$$

Hence $dT + dV = 0 \Rightarrow d(T+V) = 0 \Rightarrow dE = 0$

conservation of energy in a conservative field

Not all forces are conservative.
Not all forces can be associated with a potential energy function

eg friction $\longrightarrow$ depends on velocity
magnetic forces $\longrightarrow$ depends on velocity

Photons

Planck 1900 "blackbody" radiation
Einstein 1905 photoelectric effect

Light (and EM radiation) behaves like a field of particles called "photons", each with energy $E = h\nu$

From EM theory, the momentum should be $p = E/c$ as verified by Compton (1922) in the scattering of x-rays from electrons

Using $c = \lambda\nu$ we can write $p = h/\lambda$.

Wave - Particle Duality

de Broglie (1923): if light (a "wave" phenomenon) can behave like particles, then particles should behave like waves. Wave properties (λ, ν) and particle properties (p, E) are connected by

$p = h/\lambda$, $E = h\nu$ or, in terms of k, ω

$p = \hbar k$, $E = \hbar\omega$ where $\hbar = h/2\pi$

Schroedinger Equation

"Matter waves" in 1d could have the form

$\sin(kx-\omega t)$, $\cos(kx-\omega t)$, $e^{i(kx-\omega t)}$ where k and ω are related by $E = p^2/2m \Rightarrow \hbar\omega = \dfrac{\hbar^2 k^2}{2m}$

For "ordinary" waves, we had $\omega = kv$ and therefore matter waves cannot satisfy the "ordinary" wave equation.

After considering the effect of $\partial/\partial x$ and $\partial/\partial t$ on the three waves above, we deduce that:

1. a linear wave equation consistent with $\hbar\omega = \frac{\hbar^2 k^2}{2m}$ cannot be found for $\sin(kx-\omega t)$ or $\cos(kx-\omega t)$

2. for $\psi = e^{i(kx-\omega t)}$ the equation

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

works!

Notice that both the wave equation and its solutions $\psi(x,t)$ are complex. The general solution is a Fourier Series like before $\psi = \sum_{n=-\infty}^{\infty} C_n e^{i(k_n x - \omega_n t)}$ where $\hbar\omega_n = \frac{\hbar^2 k_n^2}{2m}$

called the Schroedinger Wave Equation (1926)

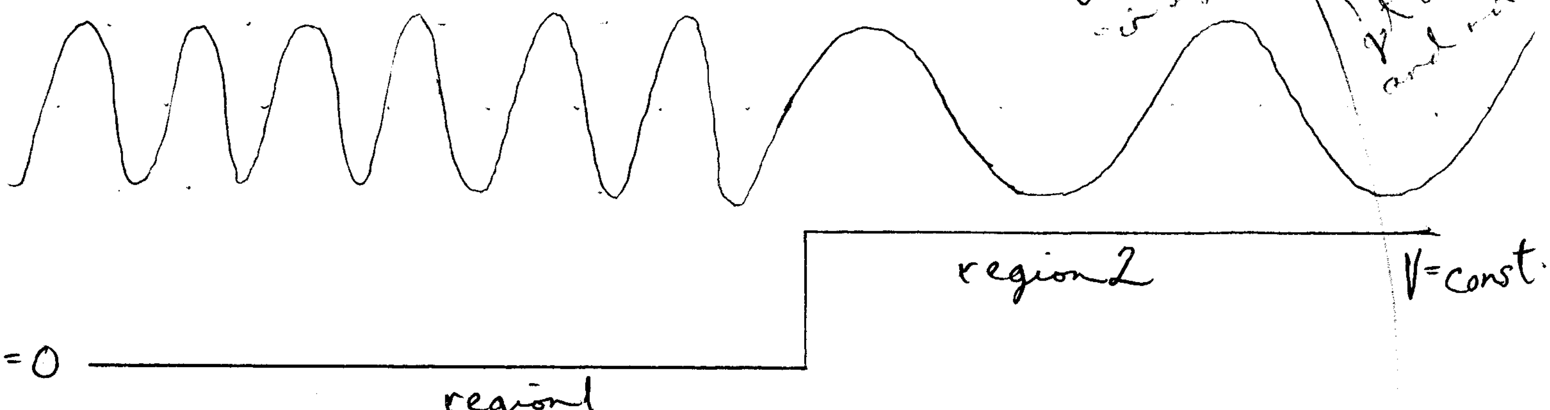
in 3d, has the form $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi$

and is valid for particles in free space only.

Schroedinger Equation in a Potential

Why? Just to stay "in synch", otherwise the two parts would get out of phase and not join

Consider the simple situation below:



Constant potential in both regions (ie zero force) hence we have a wave of form $e^{i(kx-\omega t)}$ on both sides of the boundary

For continuity at the boundary, ω (ie the frequency) must be the same on both sides. This suggests that ω is related to the total energy E and not the kinetic energy T because only the total energy E is conserved over the barrier.

$$\text{Therefore } E\,(\text{total}) = \hbar\omega \qquad (\text{both sides})$$

However, k changes.

In region 1 $\quad E = \frac{p_1^2}{2m} \Rightarrow \hbar\omega = \frac{\hbar^2 k_1^2}{2m}$

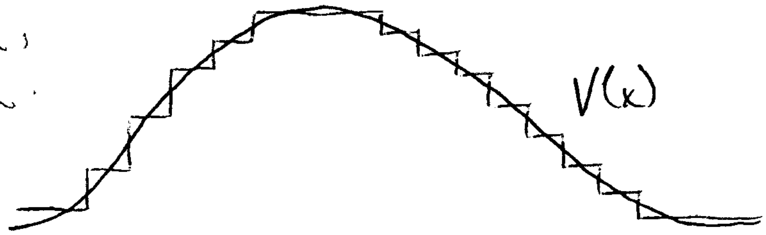
In region 2, $\quad E = \frac{p_2^2}{2m} + V_{const} \Rightarrow \hbar\omega = \frac{\hbar^2 k_2^2}{2m} + V_{const}$

A wave equation that works in both regions is

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

For a general potential $V(x)$, think about the model:

Approx. by step-like potential, then take limit.



and imagine the limit of infinitely small steps. We get

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

In 3d, becomes $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\underline{r})\Psi$

called Schroedinger's time-dependent equation

solutions $\Psi(x, y, z, t)$ are called wavefunctions

Interpretation of Ψ

What is the physical interpretation of Ψ ?

$|\Psi|^2 = \Psi^* \cdot \Psi = \bar{\Psi}\cdot\Psi$ where $*$ denotes the complex conjugate

$z^* = \bar{z}$, $z = x+iy \Rightarrow \bar{z} = x - iy$

$|\Psi|^2$ is a probability density. ie the probability of finding the particle in the volume element $dx\,dy\,dz$ at time t is

$$|\Psi|^2\, dx\, dy\, dz$$

This can be motivated by analogy with EM theory in which the energy density is related to the square of the field strength.

Since the total probability of finding the particle somewhere in all space must be one, we have the constraint / condition

$$\iiint_{\text{all space}} |\Psi|^2 \, dx\, dy\, dz = 1$$

Wavefunctions satisfying this condition are called normalized (though this is not always possible)
eg waves in free space

General Solution for $\Psi(x, y, z, t)$

space only
time only

Try separation of variables : $\Psi(x,y,z,t) = \psi_n(x,y,z)\,\theta_n(t)$

ie a simple product of a space part and a time part (the subscript n will be explained shortly)

Obviously $\dfrac{\partial \Psi}{\partial t} = \psi_n \dfrac{d\theta_n}{dt}$ and $\nabla^2 \Psi = (\nabla^2 \psi_n)\,\theta_n$

Plugging into the Schroedinger time-dependent equation gives

$$i\hbar \psi_n \frac{d\theta_n}{dt} = -\frac{\hbar^2}{2m}(\nabla^2 \psi_n)\theta_n + V\psi_n\theta_n$$

$$= \left(-\frac{\hbar^2}{2m}\nabla^2 \psi_n + V\psi_n\right)\theta_n$$

Now divide both sides by $\psi_n \theta_n$:

$$i\hbar \frac{1}{\theta_n}\frac{d\theta_n}{dt} = \frac{1}{\psi_n}\left(-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n\right)$$ Separated

The LHS is a function of time only, and the RHS is a function of space only.

Can only be true if both sides are equal to a constant.

Since the dimensions of the constant are energy, call it E_n.

Then

① LHS becomes $i\hbar \frac{1}{\theta_n} \frac{d\theta_n}{dt} = E_n$

$$\Rightarrow \frac{d\theta_n}{dt} = \frac{E_n}{i\hbar} \theta_n = -\frac{iE_n}{\hbar} \theta_n$$

This ODE has the simple solution $\theta_n = e^{-iE_n t/\hbar}$ (take care of constant later)

② RHS $-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V\psi_n = E_n \psi_n$ with solutions depending on the potential energy V.

This equation has many solutions for many different E_n values (hence the n subscript, to label the different solutions). Called the Schrodinger time-independent equation.

Return now to the general solution for $\Psi(x,y,z,t)$.
Using linearity, we write

$$\Psi(x,y,z,t) = \sum_n c_n \psi_n(x,y,z)\, \theta_n(t)$$

$$= \sum_n c_n \psi_n(x,y,z) e^{-iE_n t/\hbar} \quad , c_n \text{ complex}$$

Analogous to the Fourier series for free particles (expansion in plane waves).