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WAVE MECHANICS.

QUANTUM THEORY OF WAVES AND PARTICLES

We found that the particles behave as waves. It turns out that we can use the wave picture to completely describe the behavior of the particle. This approach, called quantum mechanics or wave mechanics is the key for understanding the behavior of matter on molecular, atomic and nuclear scales.

① Wave function and one dimensional Schrödinger equation

We described the mechanical waves (e.g. transverse wave in a string or longitudinal sound wave) using a WAVE FUNCTION $\psi(x,t)$ that represents the displacement from equilibrium, at time t , of a point at a distance x from the origin. Once known the wave function, we know everything about the motion.

The wave function $\psi(x,t)$ satisfy the wave equation

$$\boxed{\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi(x,t)}{\partial t^2}}$$

; v = speed of wave

If $\psi(x,t) = A \cos(kx - \omega t)$ or $\psi(x,t) = A e^{i(kx - \omega t)}$

we get $\omega = vk$

$k = \frac{2\pi}{\lambda}$

$\Rightarrow \frac{\omega}{v} = \frac{2\pi}{\lambda} f$

We need a quantum-mechanical version of the wave equation valid for particle-waves.

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

$\Rightarrow \frac{d\psi}{dx} = ik A e^{i(kx - \omega t)} = ik \psi$

$$\frac{d^2\psi}{dx^2} = (ck)^2 A e^{i(kx - \omega t)} = (ck)^2 \psi = -k^2 \psi \quad -2-$$

but $K = \frac{2\pi}{\lambda} = \frac{2\pi}{h} p = \frac{p}{\hbar}$

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

$$\Rightarrow \frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2} \psi \quad \Rightarrow \quad \boxed{-\hbar^2 \frac{d^2\psi}{dx^2} = p^2 \psi} \quad (1)$$

We can write now the total mechanical energy of the particle-wave $E = K + U$

$$E = \frac{1}{2} m v^2 + U = \frac{p^2}{2m} + U \quad \Rightarrow$$

$$E\psi = \frac{p^2}{2m} \psi + U\psi \quad (2)$$

From (1) and (2) \Rightarrow

$$E\psi = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U\psi \quad \Rightarrow$$

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

TIME INDEPENDENT
SCHRÖDINGER
EQUATION

Time dependent Schrödinger equation

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

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

but $E = hf = \hbar\omega$

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

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

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If we put this in the time independent Schrödinger equation \Rightarrow

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U\psi = i\hbar \frac{\partial\psi}{\partial t}$$

TIME DEPENDENT
 (A) Schrödinger equation

Interpreting the wave function

$\psi(x,t)$ describes the distribution of the particle in space just as wave functions for electromagnetic fields describe the space distributions of \vec{E} and \vec{B} .

\rightarrow For a wave, the intensity in a point is proportional to the square of the amplitude (e.g. E^2 for the electromagnetic field). When analyzing an interference pattern, the intensity at each point is proportional to the number of photons striking around that point, or alternatively, to the probability that an individual photon will strike around that point. Thus, the square of the electric field magnitude at each point is proportional to the probability that an individual photon strike around that point.

\rightarrow Similarly, the square of the wave function of a particle at each point tells us about the probability of finding the particle around that point. More precisely, we shall say the square of the absolute value of the wave function, because ψ is a complex quantity with real and imaginary parts.

For a particle that can move around the x axis, the quantity

$|\psi(x,t)|^2 dx$ represents the probability to find the particle at time t at a coordinate in the range $[x, x+dx]$.

The particle is most likely to be found in regions where $|\psi(x,t)|^2$ is large. This interpretation, first made by Max Born, requires that the wave functions to be normalized

$$\Rightarrow \int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1 \quad (\text{probability} = 1 \Leftrightarrow \text{particle is always somewhere})$$

Obs: $|\psi|^2$ is the probability distribution function for a particle that is described by the wave function ψ

\Leftrightarrow probability density

$$\psi \rightarrow \text{complex quantity} \Rightarrow \boxed{|\psi|^2 = \psi^* \psi}$$

$$\text{MATH} \left[\begin{array}{l} c = a + ib \\ c^* = a - ib \\ |c|^2 = cc^* = a^2 + b^2 \quad (i^2 = -1) \end{array} \right]$$

Uncertainty

$$\psi = A e^{i(kx - \omega t)} ; \psi^* = A^* e^{-i(kx - \omega t)}$$

$$\Rightarrow |\psi|^2 = \psi \psi^* = AA^* = |A|^2 \quad \text{does not depend on position}$$

\Rightarrow the particle is equally likely to be found everywhere along the x axis.

② Wave packets

The wave function described before is not localized. The probability distribution function extends from $-\infty$ to $+\infty$.

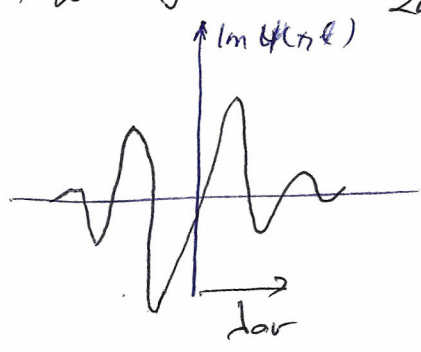
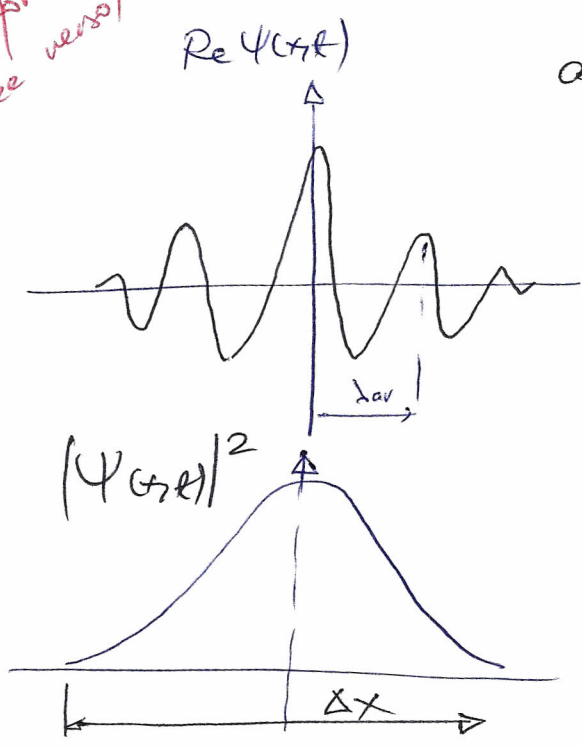
Superposing a large number of sinusoidal waves with different wave numbers k and appropriate amplitudes can produce a wave pulse that has a wavelength $\lambda_{av} = \frac{2\pi}{k_{av}}$ and is localized within a region of space Δx . This localized pulse has aspects of both particle and wave.

$$\Psi(x,t) = \int_{-\infty}^{+\infty} A(k) e^{i(kx - \omega t)} dk$$

wave packet

Fourier transform
(* see verso)

↳ superposition of very large number of waves each with different k and frequency $\omega = \hbar \frac{k^2}{2m}$ and $A(k)$



Obs: There is an important relationship between $\Psi(x,t)$ and $A(k)$

Harmonical analysis

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k) e^{i(kx - \omega t)} dk$$

the wave function represents the Fourier transform of the amplitude function $A(k)$

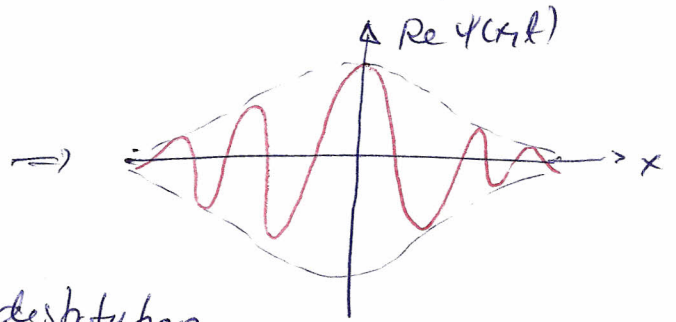
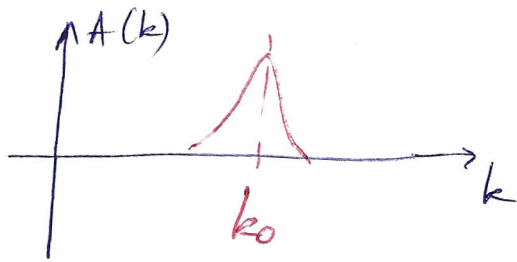
$\Rightarrow A(k)$ is the inverse Fourier transform of the wave function $\psi(x, t)$

$$A(k) = \int_{-\infty}^{+\infty} \psi(x, t) e^{-i(kx - \omega t)} dx$$

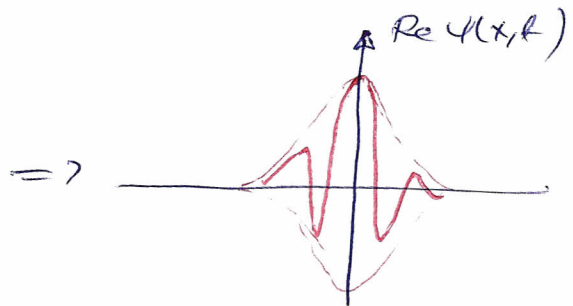
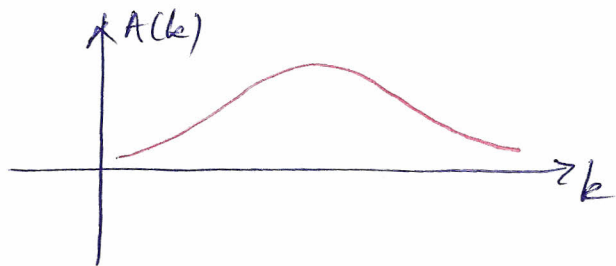
$$\int_{-\infty}^{+\infty} |\psi(x, t)|^2 dx = 1 \quad \Rightarrow \quad \int_{-\infty}^{+\infty} |A(k)|^2 dk = 1$$

$\Rightarrow |A(k)|^2 =$ the probability to have a wave vector k .

A narrow $A(k)$ gives a $\psi(x,t)$ with a broad spatial extent -6-



and vice versa: wide $A(k)$ distribution
 \Rightarrow narrow $\psi(x,t)$ extent



\Downarrow

Principle of UNCERTAINTY

narrow $A(k) \Leftrightarrow$ "fixing" $k \Leftrightarrow$ fixing p_x
 \Rightarrow uncertainty in position x

$$\Rightarrow \Delta p_x \Delta x \geq \frac{\hbar}{2} \quad \text{HEISENBERG PRINCIPLE}$$

3) Stationary states of Schrödinger equation

\Updownarrow
 time-independent

$$\psi(x,t) = A e^{ikx} e^{-i\omega t} = \phi(x) \eta(t)$$

Each sinusoidal wave corresponds to a state of definite energy:

$$E = \hbar\omega = \frac{\hbar^2 k^2}{2m} + U \quad \text{and a definite}$$

angular frequency $\omega = \frac{E}{\hbar} \Rightarrow$

$$\Rightarrow \psi(x,t) = A e^{ikx} e^{-\frac{iEt}{\hbar}}$$

$$\psi(x,t) = \psi(x) e^{-\frac{iEt}{\hbar}}$$

time independent
wave function
 $\psi(x)$

$$e^{-\frac{iEt}{\hbar}}$$

for a free particle $\psi(x) = e^{ikx}$

STATE OF
DEFINITE ENERGY
 $E =$ stationary
state.

$$|\psi(x,t)|^2 = \psi^*(x,t) \psi(x,t) =$$

$$= \psi^*(x) e^{+\frac{iEt}{\hbar}} \psi e^{-\frac{iEt}{\hbar}} = \psi^* \psi = |\psi(x)|^2$$

which does not depend
on time.

4) Hamilton approach

In the analytical mechanics the quantity equal to the sum between the kinetic and potential energy of a system is called HAMILTONIAN OF THE SYSTEM H .

From:

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

$$\left(\frac{\hbar^2 k^2}{2m} + U(x) \right) \psi = E\psi$$

we can create an operator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x)$$

so that;

= Hamilton operator

The Schrödinger equation to be written as:

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$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

where the Hamilton operator \hat{H} acts on the wave function ψ .

Obs : $\frac{\hbar^2 k^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ represents the kinetic energy operator

but $K = \frac{p^2}{2m} \Rightarrow \hat{p} = \frac{\hbar}{i} \frac{d}{dx} \Rightarrow$ momentum operator

Schrödinger equation in 3D

$$K = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \Rightarrow$$

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U = -\frac{\hbar^2}{2m} \Delta + U$$

$$\Rightarrow \hat{H}\psi = -\left(\frac{\hbar^2}{2m} \Delta + U(x,y,z) \right) \psi = i\hbar \frac{\partial \psi}{\partial t}$$

In case when the Hamilton operator is time-independent the Schrödinger eq. solution will be always:

$$\psi(\vec{r}, t) = \phi(\vec{r}) e^{-\frac{iEt}{\hbar}} = \phi(\vec{r}) \cdot \eta(t)$$

where $\phi(\vec{r})$ simply verifies the time-independent Schrödinger equation

$$\hat{H}\phi(\vec{r}) = E\phi(\vec{r})$$

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Solving this time-independent eq. one gets directly the stationary states of the system \Rightarrow possible energy levels and corresponding wave functions for the system.

The stationary states are extremely important in QM (quantum mechanics) because they describe a system which does not evolve in time: for example an atom in the fundamental (lower energy) state

⑤ Average values

We saw that the wave mechanics shows a probabilistic character. We shall define, therefore, physical quantities not in a deterministic way, likewise classical mechanics, but statistically.

From statistics, we know that the average value is given by:

$$\langle A \rangle = \int_{\text{space}} P(\vec{r}) A(\vec{r}) d^3r$$

where $P(\vec{r})$ is the statistical probability (probability density)

In wave quantum mechanics, we replace:

$$P(\vec{r}) = |\Psi(\vec{r}, t)|^2$$

$$\Rightarrow \langle A \rangle = \int_{\text{space}} \Psi^*(\vec{r}, t) A(\vec{r}) \Psi(\vec{r}, t) d^3r$$

(6) Flux of particles. Equation of continuity

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A particle cannot be described by a discontinuous wave function that would lead to a discontinuous density of presence probability. Therefore, the wave function has to be continuous in the space. If the space is separated in two regions (e.g. if the potential seen by the particle is different) when the particle passes from one region to the other, its wave function has to be continuous.

However, not only the wave function has to be continuous but also its derivative. $\frac{d\psi}{dr}$

In classical mechanics a current density of particles is written as:

$$\vec{j}(\vec{r}, t) = \rho(\vec{r}, t) \vec{v}(\vec{r}, t)$$

v = velocity
 ρ = density of particles

with a continuity equation:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0$$

$$\vec{\nabla} = \frac{\partial}{\partial x} \vec{i} + \frac{\partial}{\partial y} \vec{j} + \frac{\partial}{\partial z} \vec{k}$$

We can ~~prove~~ that a similar equation of continuity exist in quantum mechanics for the "fluid of probability":

\Rightarrow we define $\rho(\vec{r}, t) = |\psi(\vec{r}, t)|^2$ density of probability

$$\Rightarrow \frac{\partial \rho}{\partial t} = \frac{\partial |\psi|^2}{\partial t} = \frac{\partial (\psi^* \psi)}{\partial t} = \frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t}$$

from Schrödinger: $\hat{H} \psi = i\hbar \frac{\partial \psi}{\partial t} \Rightarrow \frac{\partial \psi}{\partial t} = \frac{\hat{H} \psi}{i\hbar}$

conjugated complex: $\hat{H} \psi^* = -i\hbar \frac{\partial \psi^*}{\partial t} \Rightarrow \frac{\partial \psi^*}{\partial t} = -\frac{\hat{H} \psi^*}{i\hbar}$

$$\Rightarrow \frac{\partial \rho}{\partial t} = \frac{\partial |\psi|^2}{\partial t} = \left(-\frac{\hat{H}\psi^*}{i\hbar} \right) \psi + \psi^* \left(\frac{\hat{H}\psi}{i\hbar} \right)$$

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$$\hat{H}\psi = -\frac{\hbar^2}{2m} \Delta\psi$$

$$\hat{H}\psi^* = -\frac{\hbar^2}{2m} \Delta\psi^*$$

$$\frac{\partial |\psi|^2}{\partial t} = \frac{\hbar^2}{i\hbar 2m} \Delta\psi^* \psi - \psi^* \frac{\hbar^2}{2m i\hbar} \Delta\psi =$$

$$\boxed{\frac{1}{i} = -i}$$

$$= -\frac{i\hbar}{2m} \psi \Delta\psi^* + \frac{i\hbar}{2m} \psi^* \Delta\psi$$

$$= -\frac{i\hbar}{2m} (\psi \Delta\psi^* - \psi^* \Delta\psi)$$

$$\psi \Delta\psi^* - \psi^* \Delta\psi = \nabla \cdot (\psi \nabla\psi^* - \psi^* \nabla\psi)$$

$$\text{in 1D: } \psi \frac{d^2\psi^*}{dx^2} - \psi^* \frac{d^2\psi}{dx^2} = \frac{d}{dx} \left(\psi \frac{d\psi^*}{dx} - \psi^* \frac{d\psi}{dx} \right)$$

$$\Rightarrow \frac{\partial |\psi|^2}{\partial t} + \nabla \cdot \left[\frac{i\hbar}{2m} (\psi \nabla\psi^* - \psi^* \nabla\psi) \right] = 0$$

one can identify:

$$\vec{j}(\vec{r}, t)$$

$$\boxed{\vec{j}(\vec{r}, t) = \frac{i\hbar}{2m} (\psi \nabla\psi^* - \psi^* \nabla\psi)}$$

current
probability
density

which leads to continuity equation:

$$\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0}$$

analogous to
classical mechanics

In one dimension:

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$$j(x,t) = \frac{i\hbar}{2m} \left(\psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right)$$
$$= \text{Re} \left(\frac{i\hbar}{m} \psi \frac{\partial \psi^*}{\partial x} \right)$$

density of probability current.

The continuity of the density of current probability implies that the derivative of the wave function has to be continuous.

=> At the boundary between two regions (with $U_1 \neq U_2$ - different potential seen by particle -)

ψ and $\frac{\partial \psi}{\partial x}$ has to be continuous.

⑦ Direct applications of wave mechanics

Strategy to solve a QM problem

In all QM problems one has to determine the particle wave functions and the corresponding energies by solving the time-independent Schrödinger equation, $\hat{H}\psi = E\psi$.

=> one has to solve a second order differential equation with non-constant coefficient (the potential energy U)

$$(1D): \hat{H}\psi = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U\psi = E\psi$$

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

The limit conditions will be essential to determine the constants of integration for the differential equations. These conditions complete the continuity conditions for the function and its derivatives at boundary between two regions with different potential energy U .

Strategy:

- (1) solve mathematically the Schrödinger equation
- (2) Write the continuity of the wave function and its derivative
- (3) Write the normalization condition so that the integral over all the space of the wave-function has to be equal to one.

Using this strategy we will solve some interesting QM systems (some during the seminary).

- Particle in a box (infinite quantum well)
- Potential barrier and tunneling through a rectangular barrier
- The harmonic oscillator, (quantum harmonic oscillator)
- * Particles in a 3D box.
- The Hydrogen atom
- The diatomic molecule
- Electrons in periodic potential:
energy bands. Basis of solid state electronics
Metals, insulators, semiconductors.