

Fourier transform to the wave equation

$$\psi(x, t) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{\psi}(k, \omega) e^{i(kx + \omega t)} dk d\omega$$

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} -k^2 \tilde{\psi}(k, \omega) e^{i(kx + \omega t)} dk d\omega$$

$$\frac{\partial^2 \psi}{\partial t^2} = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} -\omega^2 \tilde{\psi}(k, \omega) e^{i(kx + \omega t)} dk d\omega$$

Substituting these relations into the wave equation:

Fourier transform to the wave equation

$$\psi(x, t) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{\psi}(k, \omega) e^{i(kx + \omega t)} dk d\omega$$

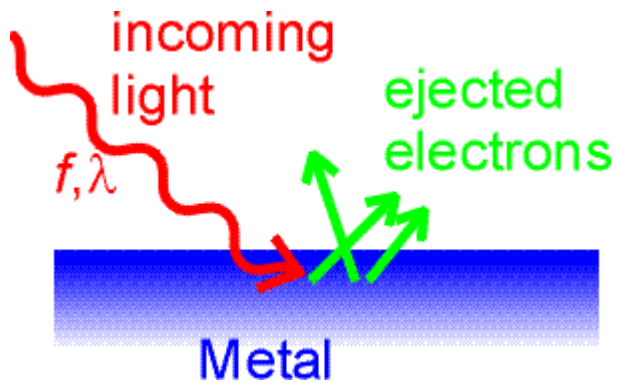
$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{\psi}(k, \omega) e^{i(kx + \omega t)} (-k^2 + \omega^2/c^2) dk d\omega = 0$$

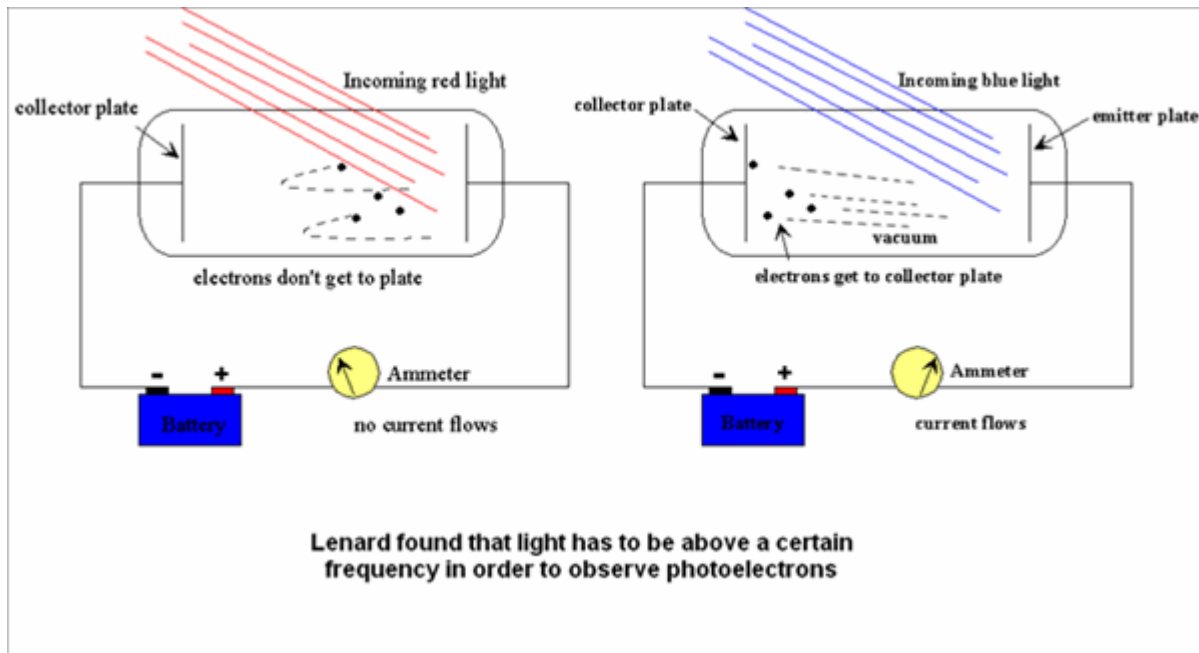
Due to the orthogonality of the different waves, the only way to satisfy the equation is $(-k^2 + \omega^2/c^2) = 0$

$\omega^2 = c^2 k^2$ is the dispersion relation we found before

The photoelectric effect



Hertz, late 19th century



The photoelectric effect

- ▶ Planck suggested that EM waves carry energy in packages (while investigating black body radiation)
- ▶ Einstein advanced the idea and suggested that light energy is quantized (photons).
- ▶ Millikan confirmed experimentally the ideas of Einstein.

$$h\nu = \hbar\omega = \Phi + K$$

h – Planck's constant

$$\hbar = h/2\pi \approx 1.05 \times 10^{-34} \text{Js}$$

$\nu = \omega/2\pi$ – frequency of the light

$\Phi > 0$ – binding energy of the electron

$K > 0$ – kinetic energy of the emitted electron

Emission only if $\nu \geq \Phi/h$

Is there a wave-particle duality?

- de Broglie postulated that every particle has an associated wave of wavelength:

$$\lambda = h/p$$

($h = 6.63 \times 10^{-34}$ J·s is Planck's constant. $hc \approx 12,400$ Å·eV)

- What was his reasoning?

For photons which are massless particles, the relation between momentum (p) and energy (E) is:

$$E = \hbar\omega = h\nu = \frac{hc}{\lambda} = pc \text{ which yields } \lambda = h/p$$

de Broglie suggested that this relationship is correct for particles having mass because it satisfies the requirements of the theory of relativity.

Is there a wave-particle duality?

- The wave nature of matter is confirmed by electron diffraction studies.
- If matter has wave-like properties, then there must be a mathematical function that is the solution to a differential equation that describes electrons, atoms and molecules.
- The differential equation is called the *Schrödinger equation* and its solution is called the *wavefunction, ψ* .

Relativistic de Broglie particles

► For relativistic particles the energy is given by

$E^2 = m^2 c^4 + p^2 c^2$ which for massless particles reduces to

$$E = |p|c$$

Using this relation and de Broglie's postulate, one finds

$$E = \hbar\omega = \sqrt{m^2 c^4 + p^2 c^2} = \sqrt{m^2 c^4 + \hbar^2 k^2 c^2}$$

Note that it implies that the phase velocity for particles with

nonzero mass (such that $v = \frac{p}{m} = \frac{\hbar k}{m}$), $v_p = \frac{\omega}{k} = \frac{\hbar\omega}{p} = \frac{\hbar\omega}{mv}$

$= \frac{\sqrt{m^2 c^4 + m^2 v^2 c^2}}{mv} = \frac{c^2}{v} \sqrt{1 + v^2/c^2}$ which for velocities smaller

than the speed of light approaches $v_p = c^2/v$.

Relativistic de Broglie particles

- ▶ Note that this speed, $v_p = c^2/v$, is always greater than the speed of light but this is not a problem because the phase does not carry information from one place to another.
- ▶ The group velocity is defined as

$$v_g \equiv \frac{d\omega}{dk}$$

$$\begin{aligned} v_g &= \frac{1}{\hbar} \frac{d\sqrt{m^2c^4 + \hbar^2k^2c^2}}{dk} = \frac{2\hbar^2c^2k}{2\hbar\sqrt{m^2c^4 + \hbar^2k^2c^2}} \\ &= \frac{v}{\sqrt{1 + v^2/c^2}} \end{aligned}$$

Which is consistent with the theory of relativity.

In the limit of $v \ll c$ the group velocity is simply the velocity of the particle, v .

Group velocity for non-relativistic de Broglie particle

- For non-relativistic particles the energy is given by

$$E = \hbar\omega = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \Rightarrow \omega = \frac{\hbar k^2}{2m}$$

Using the definition of the group velocity one finds

$$v_g = \frac{d\omega}{dk} = \frac{d\left(\frac{\hbar k^2}{2m}\right)}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v$$

This coincides with the limit of $v \ll c$ of the relativistic group velocity.

The group velocity is the actual velocity in which the information carried by the wave/particle propagates.

Phase velocity for non-relativistic de Broglie particle

- ▶ For non-relativistic particles the energy is given by $E = \frac{p^2}{2m}$.

Using this relation and de Broglie postulate one finds

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

Therefore, the phase velocity is given by, $v_p = \frac{\omega}{k} = \frac{\hbar k}{2m} = \frac{p}{2m} = \frac{v}{2}$

Note that this speed is different from the phase speed obtained from the relativistic expression in the limit of $v \ll c$. The reason for the difference is the fact that the energy is only defined up to a constant and this constant is not the same in our definitions of the energy. For rest, non-relativistic, particle it is zero while for rest relativistic particle it is mc^2 .

The classical wave equation

We have seen previously that the wave equation in 1D is:

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

Where c is the speed of the wave. Can this be used for **matter** waves in free space?

Try a solution, e.g., $\psi(x, t) = Ae^{i(kx - \omega t)}$

Which yields $c = \omega/k$. However, $E = \hbar\omega$ and $p = \hbar k$

$$\Rightarrow E = \hbar\omega = \hbar kc = pc$$

where $\hbar = h/2\pi$, $k = 2\pi/\lambda$. So, the equation would require $c = E/p$ or $E=pc$

Not correct!

For a free, non-relativistic particle we know that $E=p^2/2m$. So the classical wave equation **cannot** describe the wavefunction of a particle with mass.

The Schrödinger Equation in One Dimension

Schrödinger developed a wave equation shortly after the de Broglie hypothesis appeared.

His equation is not only consistent with that hypothesis, but it also correctly describes important phenomena that was not previously suspected.

Construct the Schrödinger equation:

1) Consider a particle of definite momentum $p = h/\lambda = \hbar k$

where $\hbar = h/2\pi$, and $k = 2\pi/\lambda$ is the wavenumber.

2) The total energy of the particle (kinetic energy plus potential energy) is equal to Planck's constant times the frequency of the wave:

$$E = \hbar\omega = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V = \frac{\hbar^2 k^2}{2m} + V$$

Which yields $k^2 = 2m(E - V)/\hbar^2$

3) Consider an arbitrary wavefunction having the form

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

The first spatial derivative yields:

$$\frac{\partial \psi(x, t)}{\partial x} = ik\psi(x, t)$$

And the second spatial derivative yields:

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = -k^2\psi(x, t)$$

From step (2) on the previous slide,

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

Therefore,

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

After rearranging the equation:

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

which is the time-independent Schrödinger equation (TISE).

To construct the time-dependent Schrödinger equation, we need to consider the time derivative of the wavefunction

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

Then

$$\frac{\partial \psi}{\partial t} = -i\omega Ae^{i(kx - \omega t)} = -i\omega \psi(x, t) = -\frac{iE}{\hbar} \psi(x, t)$$

In the last step we used de Broglie postulate, $E = \hbar\omega$

Combining the steps above we obtain

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = E\psi(x, t)$$

From the time-independent Schrödinger equation (TISE) we found:

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

Combining the spatial and temporal derivatives one obtains

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

which is the time-dependent Schrödinger equation (TDSE).

The time-dependent Schrödinger equation

For a particle in a potential $V(x, t)$, $E = \frac{p^2}{2m} + V(x, t)$ and we have Kinetic Energy+Potential Energy=Total energy.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x, t)\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{TDSE}$$

Points of note:

1. The TDSE is one of the postulates of quantum mechanics. Though the SE cannot be derived, it has been shown to be consistent with all experiments.
2. SE is first order with respect to *time*

(cf. classical wave equation $\frac{\partial^2 \psi(x, t)}{\partial t^2} = c^2 \frac{\partial^2 \psi(x, t)}{\partial x^2}$).

The time-dependent Schrödinger equation

Points of note:

3. SE involves the complex number i and so its *solutions are essentially complex*. This is different from classical waves where complex numbers are used simply for convenience – see later.

The Hamiltonian operator

LHS of TDSE can be written as:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x, t) \psi = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \psi \equiv \hat{H} \psi$$

where \hat{H} is called the ***Hamiltonian operator*** which is the differential operator that represents the ***total energy*** of the particle.

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) = \frac{\hat{p}_x^2}{2m} + V(x, t)$$

where the ***momentum operator*** is

$$\hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x}$$

Thus, shorthand for TDSE is:

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

Solving the TDSE – Challenging in general!

Suppose the potential is independent of time i.e., $V(x, t) = V(x)$ then the TDSE is:

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

The LHS involves variation of ψ with t while the RHS involves variation of ψ with x . Hence we look for a separated solution of the form:

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

The TDSE becomes

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

Solving the TDSE – Time independent potential

Dividing both sides by ψT we find

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

The LHS depends only upon x , the RHS only on t .

True for all x and t so both sides must equal a constant, E (E = separation constant).

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

$$i\hbar \frac{\partial T(t)}{\partial t} = ET(t)$$

Time-independent Schrödinger equation

Solving the time equation:

$$\frac{i\hbar}{T} \frac{\partial T(t)}{\partial t} = E \Rightarrow \frac{dT}{T} = -\frac{iE}{\hbar} dt \Rightarrow T(t) = T_0 e^{-\frac{iEt}{\hbar}} = T_0 e^{-i\omega t}$$

An oscillatory solution with frequency given by $\omega = E/\hbar$.

The frequency depends on the energy, E .

To find out what the energy actually is, we must solve the spatial part of the problem...

The spatial equation is:

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

This is the **time independent Schrödinger equation (TISE)**.

The TISE can often be very difficult to solve – it depends upon $V(x)$!

Eigenvalue equations

The *Schrödinger Equation* has the form of an *Eigenvalue Equation*:

$$\hat{H}\psi = E\psi$$

where \hat{H} is the **Hamiltonian operator**,

$$\hat{H} = \hat{K} + \hat{V} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

ψ is the spatial part of the wavefunction and is an *eigenfunction* of \hat{H} ;

E is the total energy ($T + V$) and an *eigenvalue* of \hat{H} . E is just a constant!

Later in the course we will see that the eigenvalues of an operator give the possible results that can be obtained when the corresponding physical quantity is measured.

TISE for a free-particle

For a free particle $V(x) = 0$ and the TISE is:

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

The solutions are of the form:

$$\psi(x) = Ae^{ikx}$$

With energy given by

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

Thus the full solution to the full TDSE is:

$$\Psi(x, t) = (Ae^{ikx})e^{-i\omega t}$$

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

TISE for a free-particle

Note that for a negative k , the sign of the energy (and therefore, the frequency), is the same as the sign for a positive k (the energy of a free particle is always non-negative).

$$\Psi(x, t) = (Ae^{-ikx})e^{-i\omega t}$$

The solutions correspond to waves traveling in either $\pm x$ direction with:

1. An angular frequency, $\omega = E/\hbar$ (or $E = \hbar\omega$)
2. A wavevector $k = \pm \frac{\sqrt{2mE}}{\hbar} = p/\hbar$ (or $|p| = \frac{h}{\lambda}$ where $\lambda = \frac{2\pi}{|k|} = h/\sqrt{2mE}$)

WAVE-PARTICLE DUALITY!

Interpretation of $\Psi(x,t)$ and how to use it

As mentioned previously, the TDSE has solutions that are inherently complex $\Rightarrow \Psi(x,t)$ *cannot* be a physical wave (e.g. electromagnetic waves). Therefore, how can $\Psi(x,t)$ relate to real physical measurements on a system?

The Born Interpretation

The Probability of finding a particle in the interval dx at position x and time t is equal to

$$\Psi^*(x,t)\Psi(x,t)dx = |\Psi(x,t)|^2dx = p(x,t)dx$$

$|\Psi(x,t)|^2$ is real as required for a probability distribution and is the probability *per unit length* (per unit area in 2D or per unit volume in 3D), namely it is a probability density.

The Born interpretation

- $\Psi(x, t)$ the *probability amplitude*
- $|\Psi(x, t)|^2 = p(x, t)$ the *probability density*
- $|\Psi(x, t)|^2 dx$ the *probability*.

Normalization

If a particle exists, the total probability of finding it anywhere must be 1:

$$\int_{-\infty}^{\infty} p(x, t) dx = \int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = 1$$

This requirement is known as the ***Normalization condition***. (This condition arises because the SE is linear in Ψ , and therefore, if Ψ is a solution of the TDSE so is $c\Psi$ where c is a constant.)

Hence, if original, unnormalized, wavefunction is $\Psi_{unnorm}(x, t)$, then the normalization integral is:

$$N^2 = \int_{-\infty}^{\infty} |\Psi_{unnorm}(x, t)|^2 dx$$

And the normalized (re-scaled) wavefunction is $\Psi(x, t) = \frac{1}{N} \Psi_{unnorm}(x, t)$

Example 1:

What value of N normalizes the function $f(x)$ given below?

$$f(x) = \begin{cases} Nx(x - L) & 0 \leq x \leq L \\ 0 & \text{else} \end{cases}$$

$$|f(x)|^2 = N^2 x^2 (x - L)^2 = N^2 (x^4 - 2x^3 L + x^2 L^2)$$

The normalization condition reads:

$$\int_{-\infty}^{\infty} |f(x)|^2 dx = \int_0^L |f(x)|^2 dx = N^2 \int_0^L (x^4 - 2x^3 L + x^2 L^2) dx$$

$$= N^2 \left(\frac{L^5}{5} - \frac{L^5}{2} + \frac{L^5}{3} \right) = \frac{N^2 L^5}{30} = 1 \Rightarrow N = \sqrt{\frac{30}{L^5}}$$

Example 2: Find the probability that a particle described by the wavefunction $g(x)$, given below, is found anywhere in the interval $0 \leq x \leq 0.25$.

$$g(x) = \begin{cases} \sqrt{2}\sin(\pi x) & 0 \leq x \leq 1 \\ 0 & \textit{else} \end{cases}$$

$$|g(x)|^2 = 2 \sin^2(\pi x) = 2 \frac{1 - \cos(2\pi x)}{2} = 1 - \cos(2\pi x)$$

First we verify the normalization

$$\begin{aligned} \int_{-\infty}^{\infty} |g(x)|^2 dx &= \int_0^1 |g(x)|^2 dx = \int_0^1 (1 - \cos(2\pi x)) dx \\ &= \left(x - \frac{1}{2\pi} \sin(2\pi x) \right) \Big|_0^1 = 1 \end{aligned}$$

Example 2: Find the probability that a particle described by the wavefunction $g(x)$, given below, is found anywhere in the interval $0 \leq x \leq 0.25$.

$$P(0 \leq x \leq 0.25) = \int_0^{0.25} |g(x)|^2 dx = \left(x - \frac{1}{2\pi} \sin(2\pi x) \right) \Big|_0^{0.25}$$
$$= 0.25 - \frac{1}{2\pi} \sin\left(\frac{\pi}{2}\right) = 0.25 - \frac{1}{2\pi} \approx 0.0908$$

Boundary conditions for Ψ

In order for Ψ to be a solution of the Schrödinger equation representing a physically observable system, Ψ must satisfy certain constraints:

- Must be a single-valued function of x and t ;
- Must be normalizable; this implies that $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$;
- $\psi(x)$ must be a continuous function of x ;
- The *slope* of ψ must be continuous, specifically $\partial\psi(x)/\partial x$ must be continuous (except at points where the potential diverges).

