de Broglie hypothesis

The dual nature of light possessing both wave and particle properties is illustrated by combining Plank's relation for energy of a photon $E = h\nu$ with Einstein mass energy relation $E = mc^2$

$$h\nu = mc^2$$

$$mc = \frac{h\nu}{c}$$

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

The wavelength associated with a particle of mass m having momentum p can be written as

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}}$$

Note that these are matter waves and not electromagnetic waves. They cannot be observed. The are probability waves.

The momentum of a particle p and wavelength λ of the wave associated with it are connected by the de Broglie relation

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

The corresponding relations like $p = \frac{h}{\lambda} = \hbar \mathrm{k}$, $E = h\nu$ can be derived

Wave function

The wave function associated by a particle can be thought of a monochromatic wave $\psi(x,t) = Ae^{i(kx-\omega t)}$.

Properties of a wave function

A wave function must be

finite everywhere
single valued
continuous and have continuous derivatives

Expectation value of any function $f(x) = \langle f(x) \rangle = \int \psi(x)\, f(x) \psi^*(x) dx$If $\psi(x)$ is normalized.

Time dependent Schrödinger equation

Version 4.0

Consider a particle with total energy 'E' and momentum 'p' moving in x direction.

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

$$\psi(x,t) = Ae^{i\left(\frac{2\pi h}{\lambda h}x-\frac{2\pi \nu h}{h}t\right)}$$

$$\psi(x,t) = Ae^{\frac{i}{\hbar}(px-Et)}$$

Consider the equation

$$E = \frac{p^2}{2m} + V$$

Multiplying $\psi(x,t)$ from both the sides

$$E\psi(x,t) = \frac{p^2}{2m}\psi(x,t) + V(x,t)\psi(x,t)$$

Consider $\psi(x,t) = A\psi(x,t) = Ae^{\frac{i}{\hbar}(px-Et)}$

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

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

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

Thus

$E\psi(x,t) = \frac{p^2}{2m}\psi(x,t) + V\psi(x,t)$becomes

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

known as **time dependent Schrödinger equation**

In three dimensions it can be written as

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

The operator $\frac{-\hbar^2}{2m}\nabla^2 + V$ is called Himiltonian and is represented by H. Thus the above equation can be written as

$$H\psi(\boldsymbol{r},t) = E\psi(\boldsymbol{r},t)$$

Particle in box

(Also known as Infinite potential well or infinite square well)

It describes a free particle moving in a small space with impenetrable barriers.

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & elsewhere \end{cases}$$

Since $V(x)$is independent of time the Schrödinger equation can be written in the time independent form

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

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

Substituting in

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

$$\mathrm{i}\hbar\left(\frac{-\mathrm{iE}}{\hbar}\right)\psi(x) = \frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}\big(E - V(x)\big)\psi(x) = 0$$

Known as time independent Schrödinger equation

Substituting $V(x)$ from above

For$0 < x < L$

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

$$\psi(x) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

Boundary condition

$\psi(x)$ equal zero at x = 0 and x = L. The particle is unlikely to be found at a location with a high potential, thus the probability of finding the particle, $|\psi(x)|^2$, must be small in these regions and decreases with increasing potential. For the case of an infinite potential, $|\psi(x)|^2$must be infinitesimally small or 0, thus $\psi(x)$ must also be zero in this region. ψ 0 =0, L =0

$$\psi(0) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}0\right) + B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}0\right) = 0$$

$$\psi(0) = A.0 + B.1 = 0$$

Thus B=0

$$\psi(L) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) + 0\cos\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = 0$$

$$\sqrt{\frac{2mE}{\hbar^2}}L = n\pi$$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

The above gives the energy eigenvalues

(or energy levels) of the system. This shows that the energy of the particle is quantized.

Thus the wave function becomes

$$\psi(x) = A\sin\left(\frac{n\pi}{L}x\right)$$

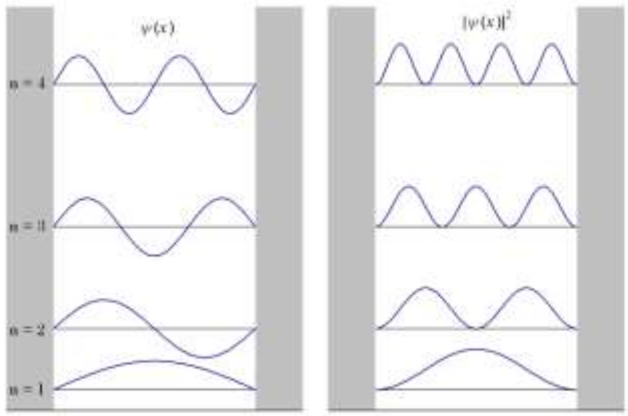
Normalizing the above

$$\int_0^L A\sin\left(\frac{n\pi}{L}x\right)A\sin\left(\frac{n\pi}{L}x\right)dx = 1$$

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

$$A = \sqrt{\frac{2}{L}}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

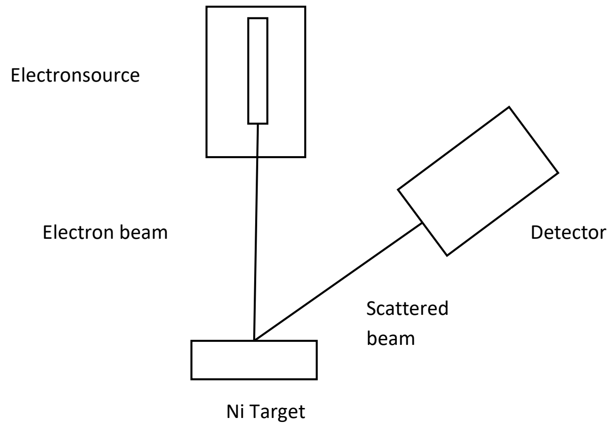


Classically, the probability of particle being found anywhere in the box is the same. However the above theory (known as Quantum theory) says that if the particle is in ground state it is more likely to be found in the middle of the box, but if it is in first excited state, this probability is zero.

Davisson-Germer Experiment

A beam of monoenergetic electron struck a nickel single crystal target. The detector studied the current of reflected electron as a function of

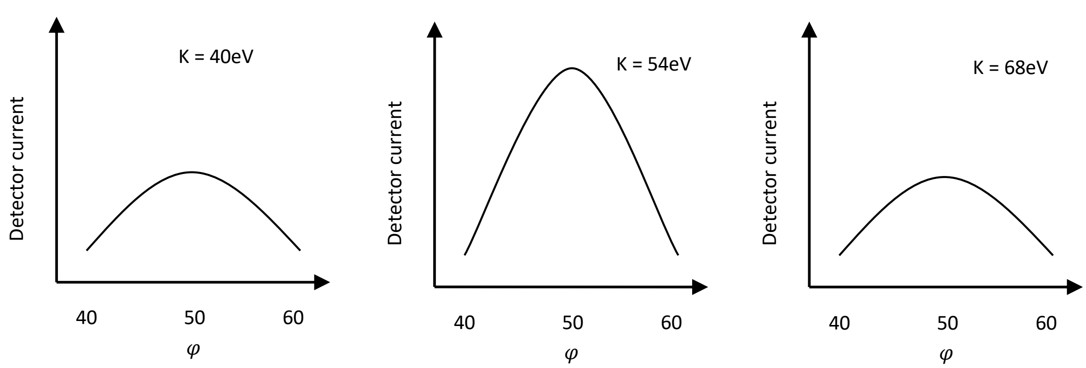
a. Incident energy
b. Emergent angle
c. Orientation of the crystal



Classical theory predicts that scattered electrons will emerge in all the directions with a continuous variation in scattered electron intensity with angle. The dependence being even less upon energy of primary electrons.

To avoid collusion of electrons with other molecules on their way towards the surface , the experiment was conducted in vacuum chamber. During the experiment an accident occurred and air entered the chamber, producing an oxide film on the nickel surface. To remove the oxide, Davisson and Germer heated the specimen in a high temperature oven, not knowing that this affected the formerly polycrystalline structure of the nickel to form large single crystal areas with crystal planes continuous over the width of the electron beam.

With the new target the results were quite different. At certain angles there was a peak in the intensity of the scattered electron beam. This peak indicated wave behaviour for the electrons, and could be interpreted by the Bragg law to give values for the lattice spacing in the nickel crystal.



This selective angle dependence of energy can be explained on the basis of wave theory.

Considering the Nickel behaving as a mirror diffraction grating with each atom placed at a spacing of 2.15Å the constructive interfere can occur for

$$n\lambda = d \sin \varphi$$

$$d = 2.15\text{Å} \quad \varphi = 50° \qquad n = 1\ (Let)$$

$$\lambda = 2.15\ \times 10^{-10} \sin 50°$$

$$1.65\text{Å}$$

Calculate λ for electron with $K = 54eV$

$$\lambda = \frac{h}{\sqrt{2mK}} = 1.66\text{Å}$$

The constructive maxima are explained from above. The deBroglie hypothesis is confirmed. Surface diffraction is not the complete picture as many combinations of λ and φ would produce strong reflections and successive maxima.

Heisenberg Uncertainty principle

Single slit diffraction method

The position and momentum of a particle cannot be determined simultaneously with highest accuracy.

$$\Delta x \cdot \Delta p \geq \hbar$$

$$\Delta t \cdot \Delta E \geq \hbar$$

Consider the electron beam with momentum p incident on the slit of widthΔy. If Δy is comparable to the wavelength of the electron beam , then the electrons will diffract according to single slit diffraction pattern and form a central maximum M_0 and two secondary minima P_1 and P_2. According to diffraction theory the first order diffraction minima condition is

$$\Delta y \sin \theta = \lambda$$

Where Δy is the position of the electron before being diffracted which is having momentum p only along x-axis. Before diffraction electron is having momentum p only along x-axis but after diffraction they are having momentum along y-axis also. The component of momentum along y-axis is

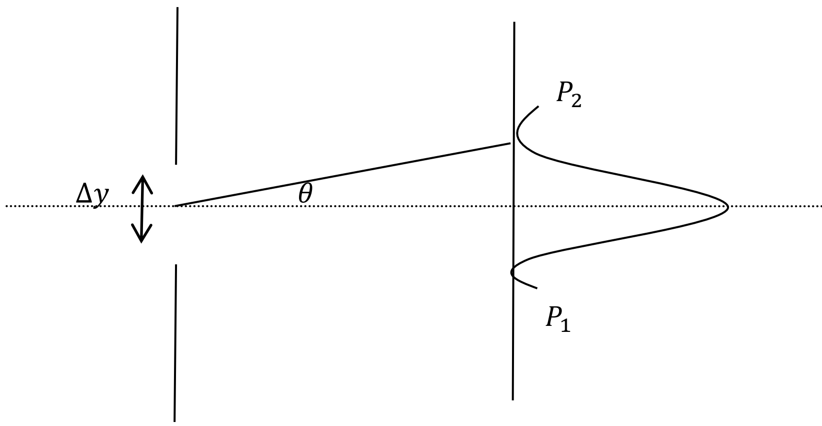
$$p \sin \theta \ \ and - p \sin \theta$$

So the uncertainty in the momentum in y direction is

$$\Delta p_y = p \sin \theta - (-p \sin \theta) = 2p \sin \theta = 2\frac{h}{\lambda} \sin \theta$$

Thus

$$\Delta y \Delta p_y = \frac{\lambda}{\sin\theta} 2\frac{h}{\lambda}\sin\theta = 2h \geq \hbar$$



Tutorial question

1. Using the uncertainty principle prove that an electron does not exist inside the nucleus.
2. What is the potential difference required to accelerate electrons to a given wavelength of 0.1 Angstroms?