Origin of quantum mechanics

By 1900 classical physics — Newton's mechanics together with Maxwell's electromagnetism — had failed to explain three experiments on the interaction of radiation with matter. Their explanation needed a new idea, that energy is exchanged in discrete quanta, and this is where quantum mechanics began.

1. Blackbody radiation (Planck, 1900)

A blackbody absorbs all the radiation falling on it and, when hot, emits a continuous spectrum that depends only on its temperature. Classical theory (the Rayleigh–Jeans law, $u(\nu) \propto \nu^2 T$) predicts an energy density that keeps rising with frequency — the "ultraviolet catastrophe" — whereas the measured spectrum peaks and then falls. Planck obtained the correct spectrum by assuming that the oscillators in the walls of the cavity emit and absorb radiation only in discrete packets (quanta) of energy

$$E = h\nu, \qquad h = 6.626 \times 10^{-34}\ \text{J s}$$

which gives Planck's radiation law for the energy per unit volume in the frequency range ν to ν + dν:

$$u(\nu, T)d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1}d\nu$$

Wien's displacement law, $\lambda_{max}T = 2.898 \times 10^{-3}$ m K, and the Stefan–Boltzmann law (total radiated power $\propto T^4$) both follow from it.

2. Photoelectric effect (Einstein, 1905)

Light falling on a metal surface ejects electrons — but only if its frequency exceeds a threshold ν_0 characteristic of the metal, however intense the light; the maximum kinetic energy of the electrons depends on the frequency and not on the intensity, which fixes only their number; and the emission is instantaneous. None of this fits a wave picture, in which energy should accumulate gradually. Einstein explained it by treating light as a stream of photons of energy hν, each absorbed by a single electron:

$$K_{max} = h\nu - \varphi = h(\nu - \nu_0)$$

where $\varphi = h\nu_0$ is the work function of the metal. The maximum kinetic energy is measured by the stopping potential V_0, $eV_0 = K_{max}$; Millikan's measurements (1916) of V_0 against ν gave a straight line of slope h/e, confirming the equation and the value of Planck's constant.

3. Compton effect (1923)

X-rays scattered by the electrons of a target emerge with a longer wavelength, the shift depending only on the scattering angle θ — impossible for a classical wave, which would be re-radiated at its own frequency. Treating the X-ray as a photon of energy hν and momentum h/λ colliding elastically with a free electron at rest, conservation of energy and momentum give

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c}(1 - \cos\theta)$$

where $h/m_0 c = 2.43 \times 10^{-12}$ m is the Compton wavelength of the electron. This established that a photon carries momentum p = h/λ as well as energy hν.

Radiation, which shows wave behaviour in interference and diffraction, thus behaves as a stream of particles in these three experiments — wave–particle duality. In 1924 de Broglie proposed the converse: that matter, too, has wave properties.

de Broglie hypothesis

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

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

where $K = \frac{p^2}{2m}$ is the kinetic energy. For an electron accelerated from rest through a potential difference V (K = eV):

$$\lambda = \frac{h}{\sqrt{2meV}} = \frac{12.26}{\sqrt{V}} \text{ Å} \quad \text{(V in volts)}$$

Note that these are matter waves, not electromagnetic waves. The wave itself is not observable: it is a probability wave, whose squared magnitude gives the probability of finding the particle.

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

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

In terms of the wave number $k = 2\pi/\lambda$ and the angular frequency $\omega = 2\pi\nu$ these relations read $p = h/\lambda = \hbar k$ and $E = h\nu = \hbar\omega$, where $\hbar = h/2\pi$.

Wave function

The wave function associated with a free particle of definite momentum can be taken as a monochromatic plane wave $\psi(x,t) = Ae^{i(kx-\omega t)}$.

Physical meaning (Born): $|\psi(x,t)|^2 dx$ is the probability of finding the particle between x and x + dx at time t, so that $\int |\psi(x,t)|^2 dx = 1$ (normalization). The wave function itself can be complex; only $|\psi|^2$ is measurable.

Properties of a wave function

A wave function must be

finite everywhere
single valued
continuous, with a continuous first derivative
normalizable (square-integrable), so that $\int |\psi|^2 dx$ is finite

The expectation (average) value of any function f(x) of position is $\langle f(x) \rangle = \int_{-\infty}^{\infty} \psi^*(x) f(x) \psi(x) dx$, provided ψ is normalized.

Time dependent Schrödinger equation

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 both sides by $\psi(x,t)$:

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

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

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

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

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

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 the time-dependent Schrödinger equation. Comparing it with Eψ = (p²/2m)ψ + Vψ shows that the energy and momentum act on ψ as the operators

$$E \to i\hbar\frac{\partial}{\partial \mathrm{t}}, \qquad p \to -i\hbar\frac{\partial}{\partial \mathrm{x}}$$

In three dimensions it can be written as

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

The operator $\frac{-\hbar^2}{2m}\nabla^2 + V$ is called the Hamiltonian and is denoted by H. The equation can then be written compactly as

$$H\psi(\boldsymbol{r},t) = i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial \mathrm{t}}$$

For a state of definite energy E (a stationary state — see below) this reduces to the eigenvalue equation $H\psi = E\psi$.

Particle in box

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

It describes a particle free to move inside a region bounded by impenetrable walls.

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

Since $V(x)$ is independent of time, the wave function can be separated into a space part and a time part:

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

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

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

$\psi(x)$ must vanish at x = 0 and at x = L. A particle is unlikely to be found where the potential is high, so the probability density $|\psi(x)|^2$ must be small there and decrease as the potential rises; where the potential is infinite it must be zero, so $\psi(x)$ itself is zero outside the box. Continuity of the wave function then requires

$$\psi(0) = 0, \qquad \psi(L) = 0$$

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

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

Thus $B = 0$

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

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

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

with n = 1, 2, 3, … (n = 0 is excluded, since it would make ψ vanish everywhere). The lowest level, $E_1 = \frac{h^2}{8mL^2}$, is the zero-point energy — a confined particle can never be at rest — and $E_n = n^2E_1$, so the levels spread apart as n increases and crowd together as the box is made larger.

The above gives the energy eigenvalues (energy levels) of the system: the energy of the confined particle is quantized.

Thus the wave function becomes

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

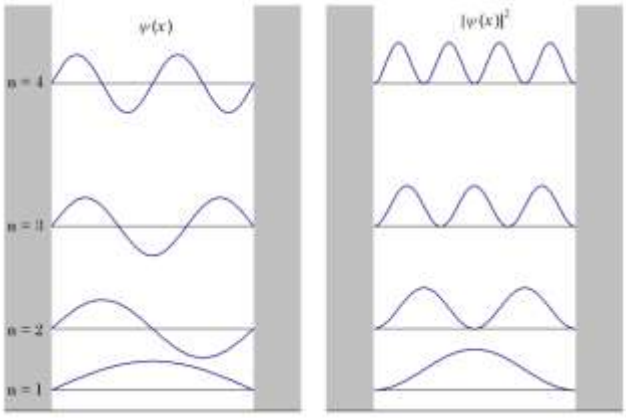
Normalizing the above

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

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

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

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

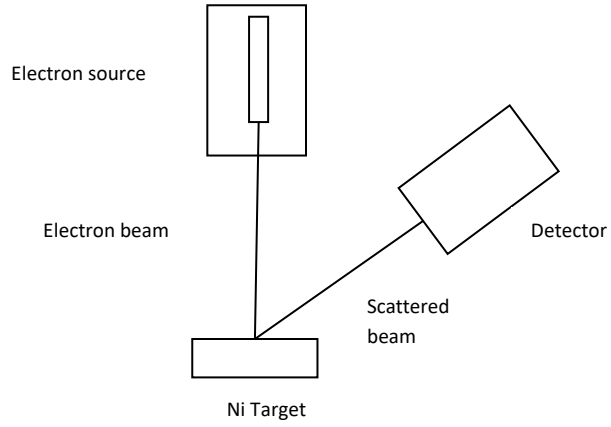


Classically the particle is equally likely to be found anywhere in the box. Quantum mechanically, in the ground state (n = 1) it is most likely to be found at the centre, while in the first excited state (n = 2) the probability of finding it at the centre is zero — a node. For large n the many narrow peaks of $|\psi|^2$ average out to the classical uniform distribution (the correspondence principle).

Davisson-Germer Experiment

A beam of monoenergetic electrons struck a nickel target, and a movable detector measured the current of scattered electrons as a function of

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

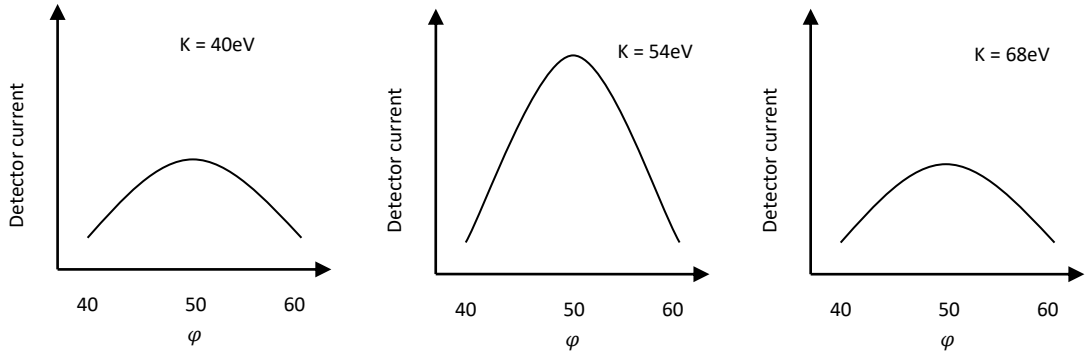


Classical theory predicts that the scattered electrons should emerge in all directions, their intensity varying smoothly with angle and depending only weakly on the energy of the primary electrons.

To avoid collisions of the electrons with gas molecules on their way to the surface, the experiment was conducted in a 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.

Treating the surface layer of nickel atoms as a plane reflection grating with the atoms spaced 2.15Å apart, constructive interference of the scattered waves occurs for

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

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

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

$$= 1.65 \times 10^{-10}\, m = 1.65\ \text{Å}$$

Calculate λ for electron with $K = 54eV$

$$\lambda = \frac{h}{\sqrt{2mK}} = 1.67\ \text{Å}$$

The agreement between the two values confirms the de Broglie hypothesis. (The surface-grating picture is a simplification: many combinations of λ and φ can give strong reflections, and the full treatment uses Bragg reflection from the crystal planes, which predicts the same maximum.)

Heisenberg Uncertainty principle

Single slit diffraction method

The position and the momentum of a particle cannot both be determined simultaneously with arbitrary precision: the product of their uncertainties is at least of the order of $\hbar$. The same holds for energy and time:

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

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

(The precise statement, with Δ denoting standard deviations, is $\Delta x \cdot \Delta p \geq \hbar/2$; the order-of-magnitude form above is what is used in estimates.)

Consider a beam of electrons of momentum p incident on a slit of width Δy. If Δy is comparable to the de Broglie wavelength of the electrons, they are diffracted as in single-slit diffraction, forming a central maximum M_0 bounded by the first-order minima P_1 and P_2. The condition for the first-order minimum is

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

Here Δy is the uncertainty in the y-position of an electron as it passes through the slit. Before the slit the electron has momentum p along x only; after diffraction it has acquired a y-component as well, which for electrons within the central maximum lies between

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

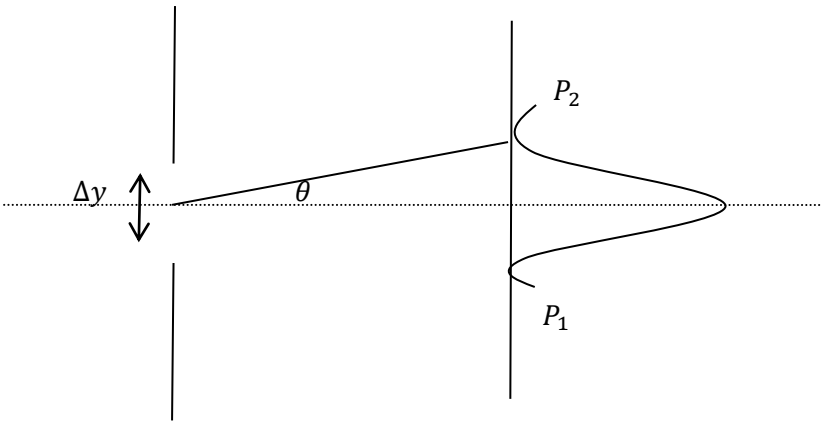
So the uncertainty in the momentum in y direction is

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

Thus

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

which is of the order of h, consistent with $\Delta y \cdot \Delta p_y \geq \hbar$: the narrower the slit (the better the position is known), the wider the diffraction pattern (the less certain the momentum). This is not a limitation of the instrument but a property of matter waves.



Tutorial questions

1. Using the uncertainty principle prove that an electron does not exist inside the nucleus. Hint: with $\Delta x \approx 10^{-14}$ m, $\Delta p \gtrsim \hbar/\Delta x \approx 10^{-20}$ kg m/s; since $pc \gg m_0c^2$ the electron would be relativistic with $E \approx pc \approx 20$ MeV, whereas electrons emitted by nuclei have energies of only a few MeV — so an electron cannot be confined in the nucleus.
2. What is the potential difference required to accelerate electrons to a given wavelength of 0.1 Angstroms? Ans: $V = (12.26/\lambda[\text{Å}])^2 \approx 1.5 \times 10^4$ V (15 kV).

Applications

- Electron microscopy and diffraction: electrons accelerated through 100 kV have $\lambda \approx 0.04$ Å, thousands of times shorter than visible light, which is why electron microscopes resolve atoms; electron and neutron diffraction (the Davisson–Germer idea made routine) are standard tools for determining crystal and surface structures.
- Particle in a box in practice: the energy levels $E \propto 1/L^2$ of an electron confined to a nanometre-sized region are the physics of quantum wells and quantum dots — the colour of a quantum-dot display is set simply by the size of the dots, and quantum-well lasers drive CD/DVD players and optical-fibre links; long conjugated dye molecules absorb at wavelengths fixed by their length in the same way.
- Photoelectric effect: photodiodes, solar cells, CCD and CMOS camera sensors, photomultiplier tubes and night-vision devices all convert photons to electrons one at a time.
- Blackbody radiation: pyrometers and thermal-imaging cameras read temperature from the spectrum; the efficiency of incandescent lamps versus LEDs is a Planck-law calculation; the 2.7 K cosmic microwave background is the most perfect blackbody spectrum ever measured.
- Compton scattering: it is the dominant interaction of gamma rays with matter at MeV energies, so it governs radiotherapy dose, gamma-ray detectors and the scatter that blurs X-ray and CT images.
- Uncertainty principle: it sets the zero-point energy, the size and stability of atoms (an electron confined to 0.1 nm must carry a few eV of kinetic energy), the natural width of spectral lines

through ΔE·Δt, and — as in tutorial question 1 — rules out electrons as constituents of the nucleus.

Explore further

- PhET: Blackbody Spectrum (HTML5, runs in the browser) — slide the temperature and watch the Planck curve, its peak (Wien) and its area (Stefan–Boltzmann) change.
- PhET: Photoelectric Effect — choose the metal, wavelength, intensity and voltage, and plot current against voltage and electron energy against frequency: Millikan's experiment on screen.
- PhET: Davisson–Germer: Electron Diffraction — fire electrons at a crystal and see the diffraction maxima move as the energy and the lattice spacing are varied.
- Falstad: 1-D Quantum Mechanics (JavaScript, runs in the browser) — the infinite well is the default: click on energy levels to see the wave functions and probability densities, and combine levels to watch a wave packet move.