

QUANTUM MECHANICS

by

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In the beginning of 20th century, classical physics seriously challenged on two major fronts:

validity of classical physics ceases at

1. **at very high speeds ($v \sim c$): Relativistic domain:** Einstein's 1905 theory of relativity showed that the validity of Newtonian mechanics ceases
2. **microscopic level: Microscopic domain:** newly discovered phenomena - atomic and subatomic structures – classical physics fails.

the and that *new concepts had to be invoked to describe, for instance, the structure of atoms and molecules and how light interacts with them.*

Classical physics fails to explain microscopic phenomena like -

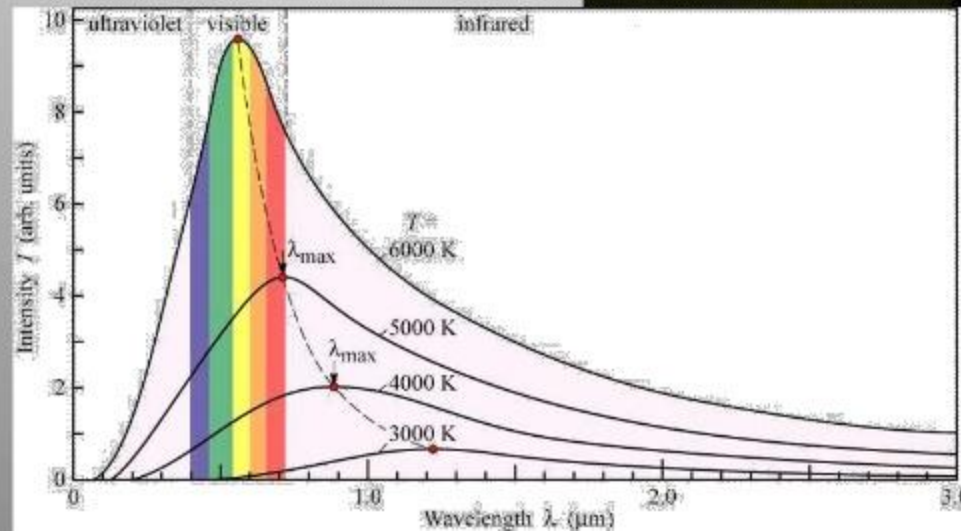
- Blackbody radiation
- photoelectric effect
- Compton scattering
- atomic stability
- atomic spectroscopy

Blackbody Radiation

Light emitted by hot object

Depends only on temperature

Characteristic spectrum of light



Blackbody Radiation

Max Planck, 1900

→ Developed mathematical formula for spectrum

$$I_{\lambda,b}(\lambda, T) = \frac{2hc_o^2}{\lambda^5 [\exp (hc_o/\lambda kT) - 1]}$$

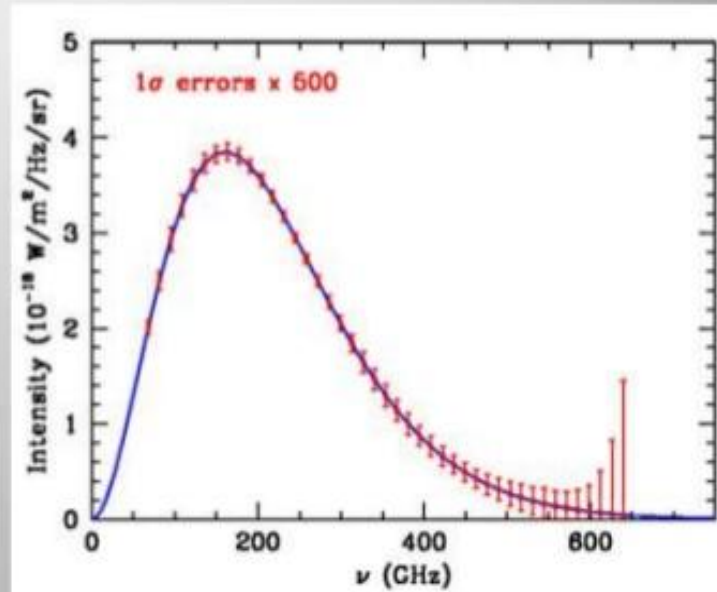
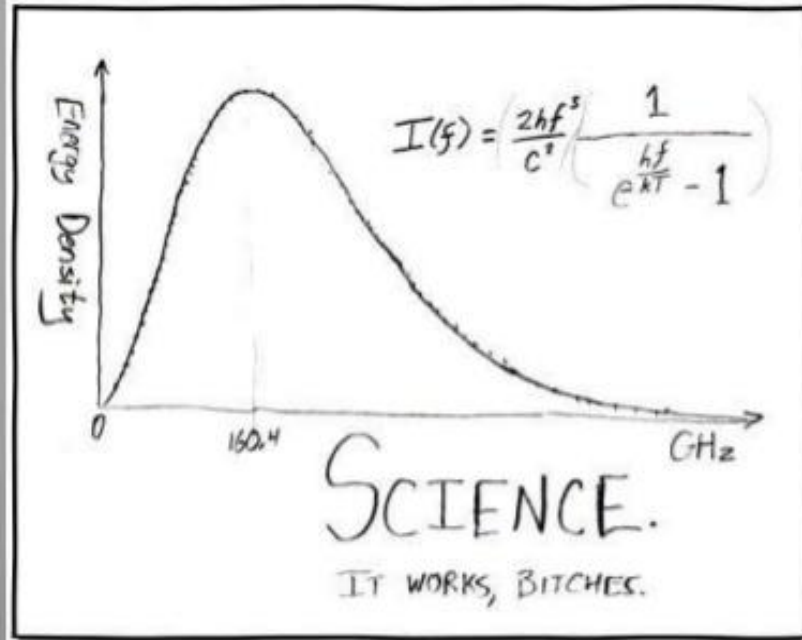


Problem: Derivation of formula required a mathematical trick

Introduced idea of “quantum” of energy

Completely overturned classical physics

Blackbody Spectrum



Photoelectric Effect

Shine light on some object,
electrons come out

Discovered by Heinrich Hertz, 1887

Simple model: Shaking electrons



- Predict:
- 1) Number of ejected electrons depends on intensity
 - 2) Energy of ejected electrons depends on intensity
 - 3) No obvious dependence on frequency

Photoelectric Effect: Experiment

Observations:



1) Number of electrons depends on intensity



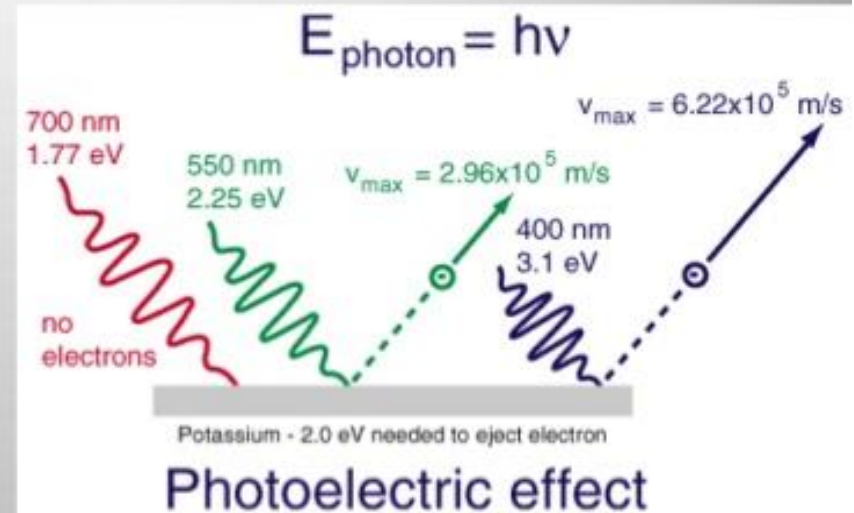
2) Energy of electrons DOES NOT depend on intensity



3) Cut-off frequency: minimum frequency to get any emission



4) Above cut-off, energy increases linearly with frequency



Photoelectric Effect: Einstein

Einstein, 1905: “Heuristic Model” of PE Effect

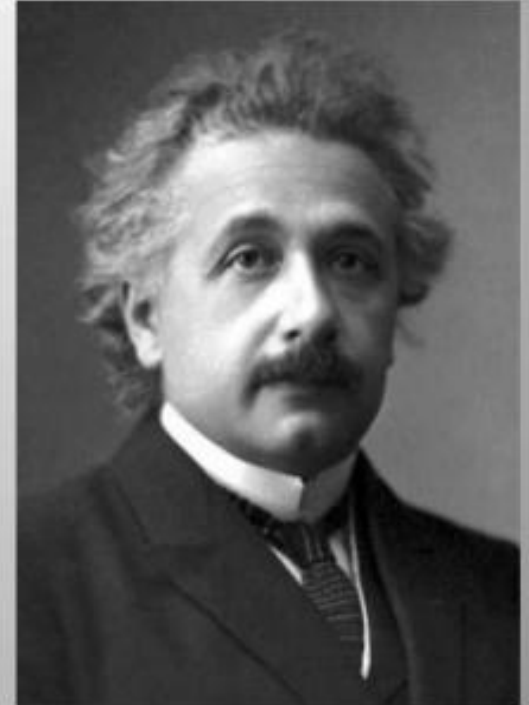
Particle model: “Light quanta” with energy

$$E = hf = h \frac{c}{\lambda}$$

Some minimum energy to remove electron:
“Work Function”

Energy of emitted electron:

$$KE = hf - \phi$$



Take's Planck's “trick” seriously, runs with the idea

Photoelectric Effect: Einstein

Observations:



1) Number of electrons depends on intensity

Higher intensity → More quanta



2) Energy of electrons DOES NOT depend on intensity

Only one photon to eject

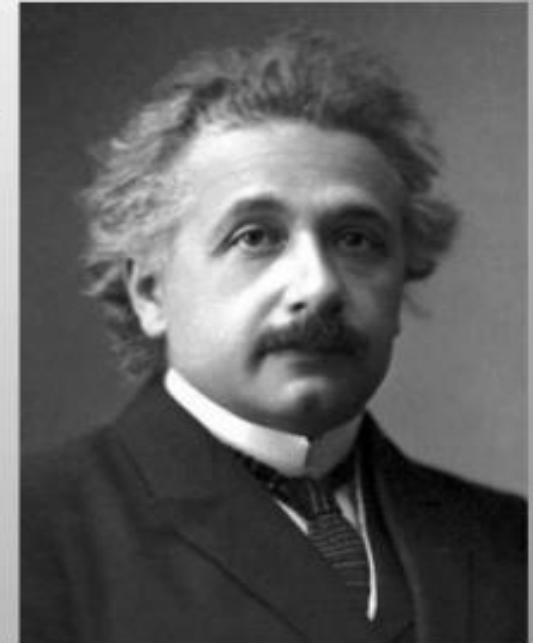


3) Cut-off frequency: minimum frequency to get any emission

$$KE = hf - \phi$$



4) Above cut-off, energy increases linearly with frequency

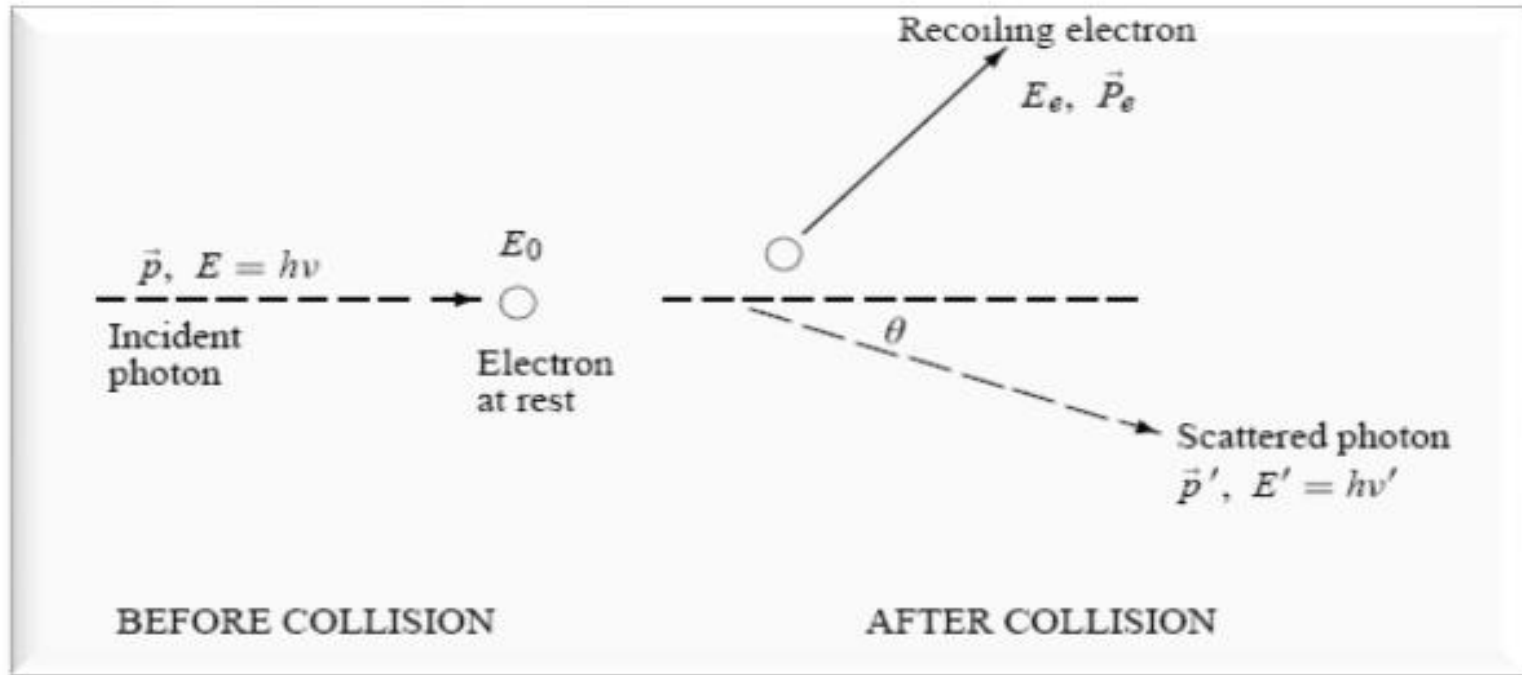


Einstein in 1921
Nobel Prize portrait
Cited for PE Effect

Compton Effect

Scattering of radiation as particles

- classical physics - the incident and scattered radiation should have the same wavelength
- scattering of X-rays by free electrons –
 - Wavelength of the scattered radiation is larger than the wavelength of the incident radiation.
 - This can be explained only by assuming that the X-ray photons behave like particles.
- Incident radiation as a stream of particles—photons—colliding *elastically with individual electrons*
- *Elastic collision – conservation of energy and momentum*



$$\text{wavelength shift, } \Delta\lambda = \lambda' - \lambda = \frac{h}{m \cdot c} (1 - \cos\theta) = 2\lambda_c \sin^2\left(\frac{\theta}{2}\right)$$

$$\text{compton wavelength, } \lambda_c = \frac{h}{m \cdot c} = 2.426 \times 10^{-12} \text{ m}$$

So the above examples show that some times waves behave like particles.

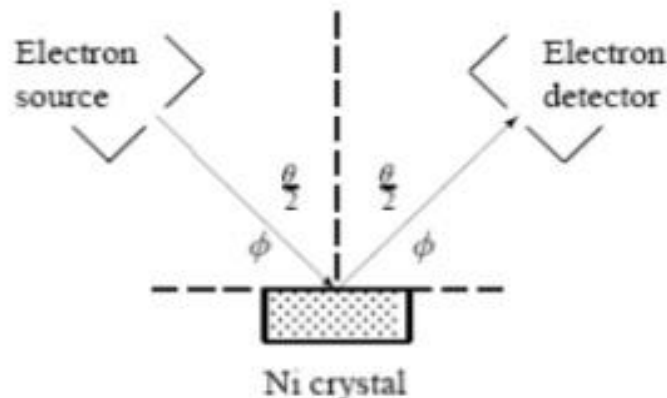
But the story is not complete. There are experiments where microscopic particles behave like waves e.g. interference and diffraction:

1. Davisson-Germer experiment of electron diffraction.
2. G. P. Thomson experiment of electron diffraction

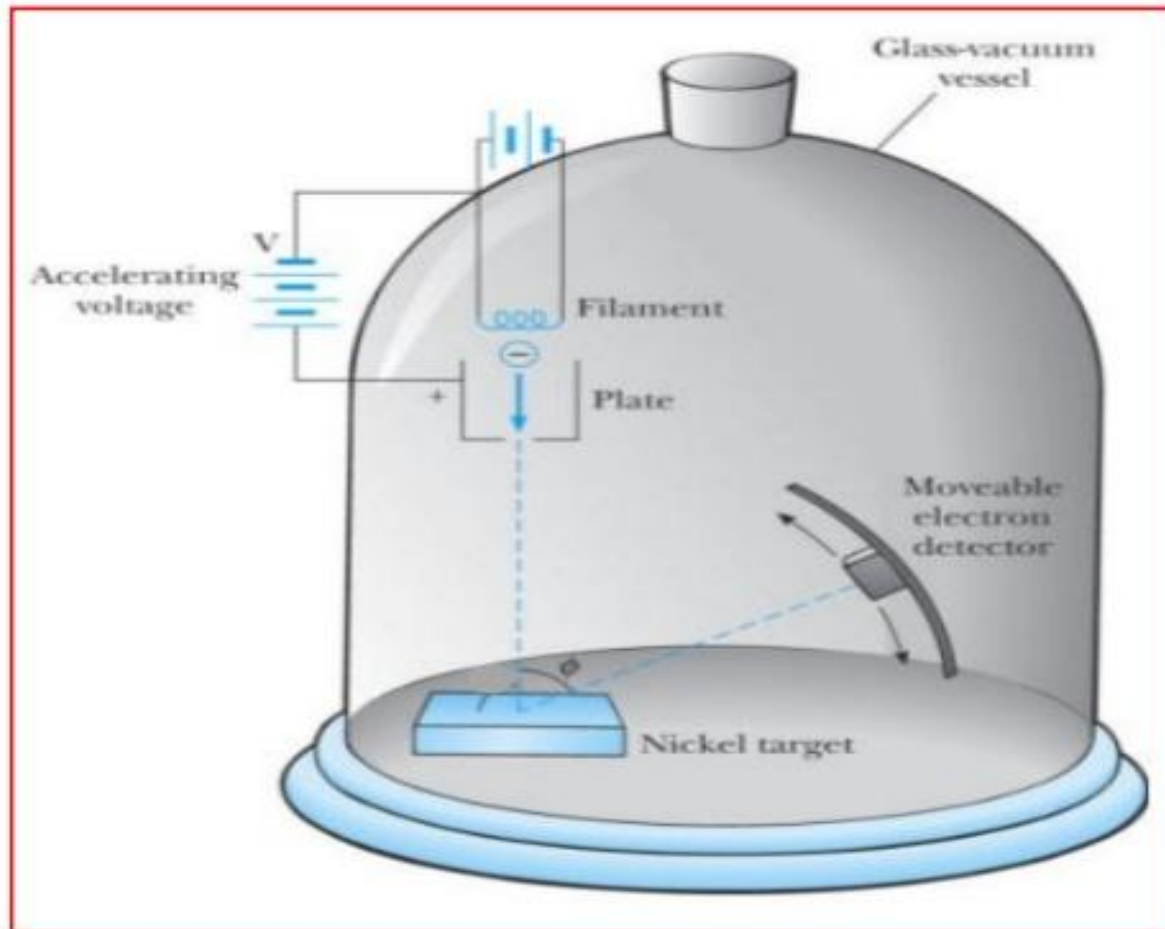
Davisson–Germer Experiment

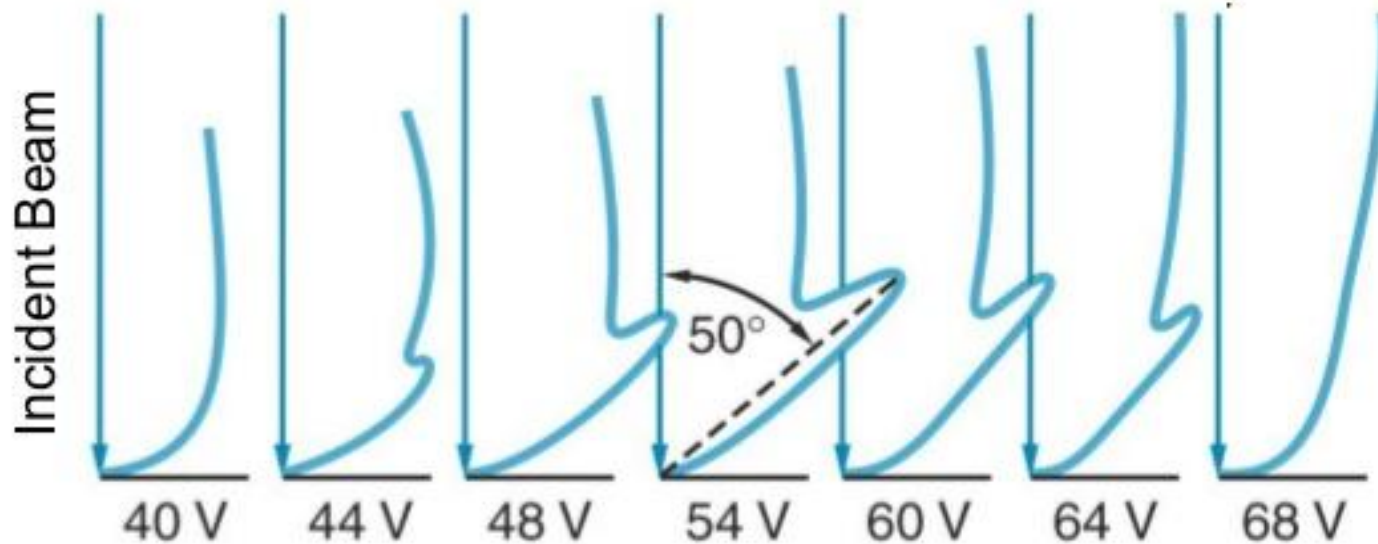
Experimental Confirmation of de Broglie's Hypothesis

- Mono-energetic (54eV) beam of electrons scattered at Nickel surface.
- Maximum intensity at $\theta = 50^\circ$.
- instead of the diffuse distribution pattern - material particles, the reflected electrons formed diffraction patterns - identical with Bragg's X-ray diffraction by a *grating*



Davisson and Germer Experiment

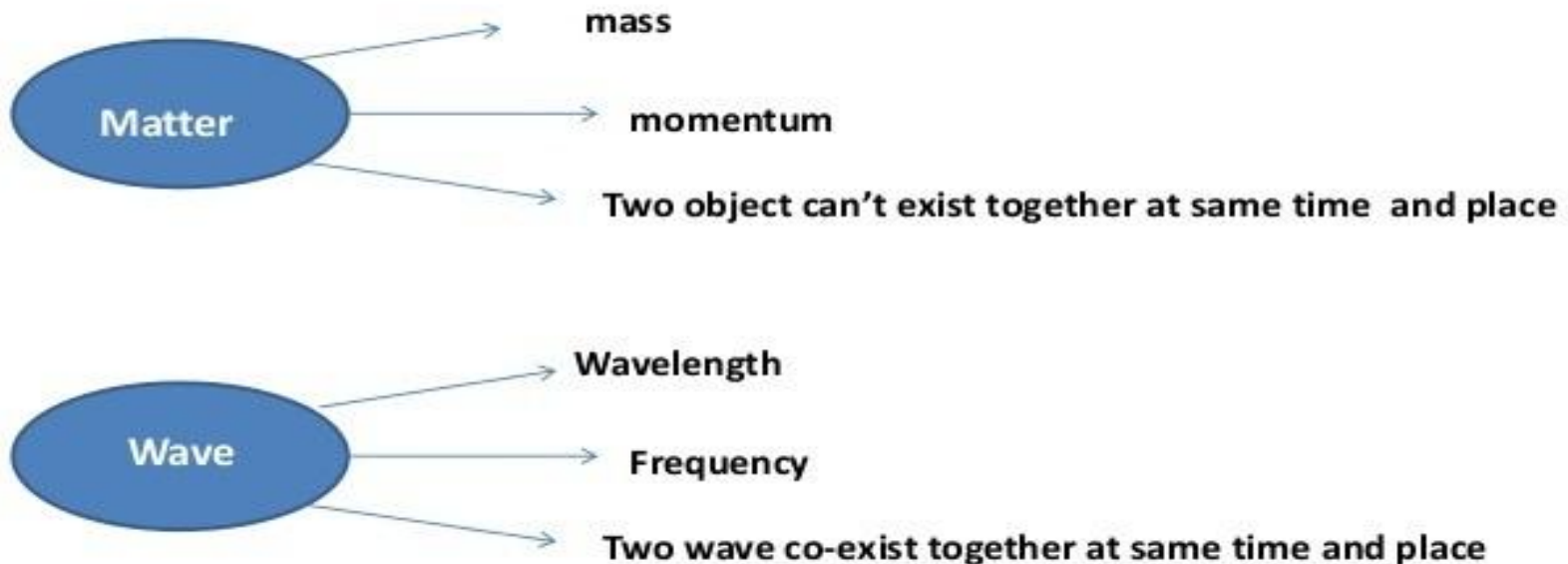




Current vs accelerating voltage has a maximum (a bump or kink noticed in the graph), i.e. the highest number of electrons is scattered in a specific direction.

The bump becomes most prominent for 54 V at $\varphi \sim 50^\circ$

Dual nature of wave and particles



Wave Aspect of Particles

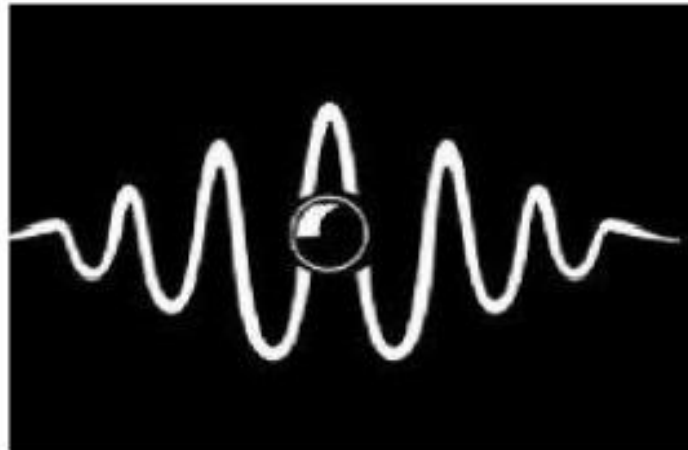
de Broglie's Hypothesis: Matter Waves

- In 1923 de Broglie - wave–particle duality is not restricted to radiation, but must be universal:
- *all material particles possess a dual wave–particle behavior*
- *each material particle of momentum p behaves as a group of waves (matter waves) whose wavelength λ and wave vector k are governed by the speed and mass of the particle*

$$\text{de Broglie relation, } \lambda = \frac{h}{p} \quad \text{or} \quad \vec{k} = \frac{\vec{p}}{\hbar}$$

Matter Wave

- A wave associated with the motion of a particle of atomic or subatomic size that describes effects such as the diffraction of beams of particles by crystals.



Heisenberg's Uncertainty Principle



The uncertainty principle also called the Heisenberg Uncertainty Principle, or Indeterminacy Principle, articulated (1927) by the German physicist Werner Heisenberg, that the position and the velocity of an object cannot both be measured exactly, at the same time.

Heisenberg Uncertainty Principle

It states that only one of the “position” or “momentum” can be measured accurately at a single moment within the instrumental limit.

or

It is impossible to measure both the position and momentum simultaneously with unlimited accuracy.

$\Delta x \rightarrow$ uncertainty in position

$\Delta p_x \rightarrow$ uncertainty in momentum

then

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

$$\therefore \hbar = \frac{h}{2\pi}$$

The product of Δx & Δp_x of an object is greater than or equal to $\frac{\hbar}{2}$

If Δx is measured accurately i.e. $\Delta x \rightarrow 0 \Rightarrow \Delta p_x \rightarrow \infty$

The principle applies to all canonically conjugate pairs of quantities in which measurement of one quantity affects the capacity to measure the other.

Like, energy E and time t.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

and angular momentum L and angular position θ

$$\Delta L \Delta \theta \geq \frac{\hbar}{2}$$

Wave Function

- It is variable quantity that mathematically describes the wave characteristics of a particle.
- The value of the wave function of a particle at a given point of space and time is related to the likelihood of the particle's being there at the time.
- By analogy with waves such as those of sound, a wave function, designated by the Greek letter psi, Ψ , may be thought of as an expression for the amplitude of the particle wave (or de Broglie wave), although for such waves amplitude has no physical significance.

Physical interpretation of wave function

- The wave function, at a particular time, contains all the information that anybody at that time can have about the particle.
- But the wave function itself has no physical interpretation.
- It is not measurable. However, the square of the absolute value of the wave function has a physical interpretation. We interpret $|\psi(x,t)|^2$ as a probability density, a probability per unit length of finding the particle at a time t at position x .
- The probability of finding the particle at time t in an interval Δx about the position x is proportional to $|\psi(x,t)|^2 \Delta x$.

Wave function

The quantity with which Quantum Mechanics is concerned is the wave function of a body.

Wave function, ψ is a quantity associated with a moving particle. It is a complex quantity.

$|\Psi|^2$ is proportional to the probability of finding a particle at a particular point at a particular time. It is the probability density.

$$|\psi|^2 = \psi^* \psi$$

ψ is the probability amplitude.

$$\text{Thus if } \psi = A + iB \text{ then } \psi^* = A - iB$$

$$\Rightarrow |\psi|^2 = \psi^* \psi = A^2 - i^2 B^2 = A^2 + B^2$$

Normalization

$|\Psi|^2$ is the probability density.

The probability of finding the particle within an element of volume $d\tau$

$$|\psi|^2 d\tau$$

Since the particle is definitely be somewhere, so

$$\int_{-\infty}^{\infty} |\psi|^2 d\tau = 1 \quad \therefore \text{Normalization}$$

A wave function that obeys this equation is said to be normalized.

Properties of wave function

1. It must be finite everywhere.

If ψ is infinite for a particular point, it mean an infinite large probability of finding the particles at that point. This would violates the uncertainty principle.

2. It must be single valued.

If ψ has more than one value at any point, it mean more than one value of probability of finding the particle at that point which is obviously ridiculous.

3. It must be continuous and have a continuous first derivative everywhere.

$$\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z} \quad \text{must be continuous}$$

4. It must be normalizable.

Schrödinger Equation

- Schrödinger equation is a linear, second order partial differential equation.
- It is a wave equation in terms of the wave function which predicts analytically the probability of the properties the system or events or outcome with precision.
- The Schrödinger equation is a more general and fundamental postulate of quantum physics.
- It plays the same role in quantum physics which Newton's laws and the conservation of energy play in classical physics i.e., it predicts the time evolution i.e. future behavior of a quantum dynamical system.

- An important feature of the Schrödinger equation is that it is *linear*. Hence it allows for the superposition of its solutions i.e. wave functions.
$$\psi = a\psi_1 + b\psi_2$$

- The Schrodinger equation has *two forms*, one in which time explicitly appears, and so describes how the wave function of a particle will evolve in time. In general, the wave function behaves like a wave, and so the equation is, often referred to as time dependent Schrodinger wave equation.
- The other is the equation in which the time dependence has been removed and hence is known as the time independent Schrodinger equation and is found to describe, amongst other things, what the allowed energies are of the particle.

The Schrödinger Wave Equation

- The Schrödinger wave equation in its time-dependent form for a particle of energy E moving in a potential V in one dimension is

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

m = mass of electron

- The extension into three dimensions is

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

where $i = \sqrt{-1}$ is an imaginary number.

The statement is in both cases that operators act on the wave function, $V = V(x,t)$ in the first equation for 1D, $V = V(x,y,z,t)$ in the second equation for 3D

Time-Independent Schrödinger Wave Equation

- The potential in many cases will not depend explicitly on time.
- The dependence on time and position can then be separated in the Schrödinger wave equation. Let $\Psi(x,t) = \psi(x)f(t)$,

$$\text{which yields: } i\hbar \psi(x) \frac{\partial f(t)}{\partial t} = -\frac{\hbar^2 f(t)}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x)f(t)$$

$$\text{Now divide by the wave function: } i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x)$$

- The left side depends only on time, and the right side depends only on spatial coordinates. Hence each side must be equal to a constant. The time dependent side is

$$i\hbar \frac{1}{f} \frac{df}{dt} = B$$

What might this B possibly be? given the fact that the Schrödinger equation is a statement on the conservation of total energy, which is constant in a stationary state

Time-Independent Schrödinger Wave Equation Continued

- We integrate both sides and find: $i\hbar \int \frac{df}{f} = \int B dt \quad i\hbar \ln f = Bt + C$

where C is an integration constant that we may choose to be 0. Therefore

$$\ln f = \frac{Bt}{i\hbar}$$

This determines f to be $f(t) = e^{Bt/i\hbar} = e^{-iEt/\hbar}$

In order to do this, $f(t)$ needs to be eigen function $i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E$

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

- This is known as the **time-independent Schrödinger wave equation**, and it is a fundamental equation in quantum mechanics.

What else could B possibly be? given the fact that the Schrödinger equation is a statement on the conservation of total energy

Stationary State

Remember when you see
E think ω and vice versa

- The wave function can be written as: $\Psi(x,t) = \psi(x)e^{-i\omega t}$
- Whenever the potential energy function is not time dependent
- The probability density becomes: $\Psi^* \Psi = \psi^2(x)(e^{i\omega t} e^{-i\omega t})$
$$\Psi^* \Psi = \psi^2(x)$$
- The probability distributions are constant in time. This is a standing wave phenomena that is called the stationary state.

$$E = \hbar \cdot \omega$$

So whenever you see circular frequency omega, you can also think total energy divided by h-bar

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

So whenever you see the wave number, you can also think linear momentum divided by h-bar

Operators

- *There is a linear hermitian mathematical operator in one-to-one correspondence with every mechanical variable.*
- This postulate states that for each operator there is one and only one variable, and
- for each variable there is one and only one mathematical operator.
- A mathematical operator is a symbol that stands for performing one or more mathematical operations.
- When the symbol for an operator is written to the left of the symbol for a function, the operation is to be applied to that function.

- The result of operating on a function with an operator is another function. If A is an operator and f is a function,

$$\hat{A} f(q) = g(q)$$

- Where g is another function. The symbol q is an abbreviation for whatever independent variables f and g depend on. shows an example of a function, $f(x)=\ln(x)$,
- and the function $g(x)=1/x$ that results when the operator d/dx is applied to $\ln(x)$.

Expectation Values, what one will measure on average is derived from correct wave function for a problem

- The **expectation value** is the expected result of the average of many measurements of a given quantity. The expectation value of x is denoted by $\langle x \rangle$
- Any measurable quantity for which we can calculate the expectation value is called a **physical observable**. The expectation values of physical observables (for example, position, linear momentum, angular momentum, and energy) must be real, because the experimental results of measurements are real.
- The average value of x is

$$\bar{x} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + N_4x_4 + \dots}{N_1 + N_2 + N_3 + N_4 + \dots} = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

Continuous Expectation Values

- We can change from discrete to continuous variables by using the probability $P(x,t)$ of observing the particle at a particular x and t .

$$\bar{x} = \frac{\int_{-\infty}^{\infty} xP(x) dx}{\int_{-\infty}^{\infty} P(x) dx}$$

- Using the wave function, the expectation value is:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)x\Psi(x,t) dx$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x\Psi^*(x,t)\Psi(x,t) dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t) dx}$$

- The expectation value of any function $g(x)$ for a normalized wave function:

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)g(x)\Psi(x,t) dx$$

x and $g(x)$ are operators !!!, x could also have been in the middle of conjugate complex wave function times wave function as it the rule for all operators

Some quantum-mechanical operators

Symbol	Physical quantity	Operator
$f(x)$	Any function of x —e.g., the position x , the potential energy $V(x)$, etc.	$f(x)$
p_x	x component of momentum	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
p_y	y component of momentum	$\frac{\hbar}{i} \frac{\partial}{\partial y}$
p_z	z component of momentum	$\frac{\hbar}{i} \frac{\partial}{\partial z}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$
E	Hamiltonian (time dependent)	$i \hbar \frac{\partial}{\partial t}$
E_k	kinetic energy	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i \hbar \frac{\partial}{\partial \phi}$

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

Eigenstates and eigenvalues

If measurement of any physical quantity by a corresponding operators on a wave function is such that

$$\hat{A} \psi = a \psi$$

then ψ is called an **eigenstate (or eigenfunction)** of operator \hat{A} with **eigenvalue** a . These are called determinate states of that operator or physical quantity. Since every physical measurement that is made upon this state by that operator would yield the same value or accurate value of associated physical quantity.

APPLICATIONS OF SCHRÖDINGER EQUATION

Particle in a Box

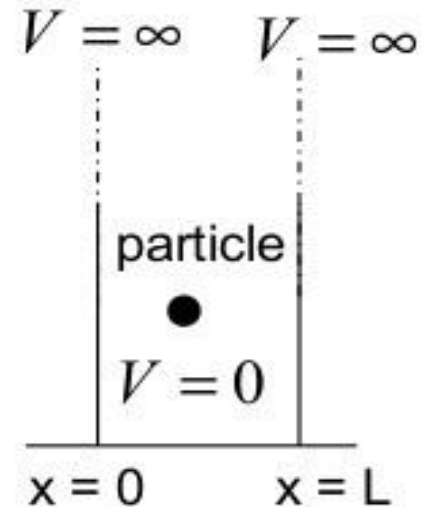
Consider a particle of rest mass m enclosed in a one-dimensional box (infinite potential well).

Boundary conditions for Potential

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{for } x < 0 \text{ or } x > L \end{cases}$$

Boundary conditions for ψ

$$\psi = \begin{cases} 0 & \text{for } x = 0 \\ 0 & \text{for } x = L \end{cases}$$



Thus for a particle inside the box Schrodinger equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad (i) \quad \therefore V = 0 \text{ inside}$$

$$\lambda = \frac{h}{p} = \frac{2\pi}{k} \quad (\text{k is the propagation constant})$$

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

$$\Rightarrow k^2 = \frac{2m E}{\hbar^2} \quad (\text{ii})$$

Equation (i) becomes

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad (\text{iii})$$

General solution of equation (iii) is

$$\psi(x) = A \sin kx + B \cos kx \quad (\text{iv})$$

Boundary condition says $\psi = 0$ when $x = 0$

$$\psi(0) = A \sin k.0 + B \cos k.0$$

$$0 = 0 + B.1 \quad \Rightarrow B = 0$$

Equation (iv) reduces to

$$\psi(x) = A \sin kx \quad (v)$$

Boundary condition says $\psi = 0$ when $x = L$

$$\psi(L) = A \sin k.L$$

$$0 = A \sin k.L$$

$$A \neq 0 \Rightarrow \sin k.L = 0$$

$$\Rightarrow \sin k.L = \sin n\pi$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \quad (\text{vi})$$

Put this in Equation (v)

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

When $n \neq 0$ i.e. $n = 1, 2, 3, \dots$, this gives $\psi = 0$ everywhere.

Put value of k from (vi) in (ii)

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

$$\left(\frac{n\pi}{L} \right)^2 = \frac{2m E}{\hbar^2}$$

$$\Rightarrow E = \frac{\hbar^2 k^2}{2m} = \frac{n^2 h^2}{8m L^2} \quad (\text{vii})$$

Where $n = 1, 2, 3, \dots$

Equation (vii) concludes

1. Energy of the particle inside the box can't be equal to zero.
The minimum energy of the particle is obtained for $n = 1$

$$E_1 = \frac{h^2}{8m L^2} \quad \textbf{(Zero Point Energy)}$$

If $E_1 \rightarrow 0$ momentum $\rightarrow 0$ i.e. $\Delta p \rightarrow 0$

$$\Rightarrow \Delta x \rightarrow \infty$$

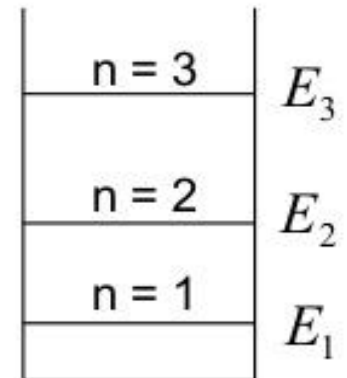
But $\Delta x_{\max} = L$ since the particle is confined in the box of dimension L .

Thus zero value of zero point energy violates the Heisenberg's uncertainty principle and hence zero value is not acceptable.

2. All the energy values are not possible for a particle in potential well.

Energy is Quantized

3. E_n are the eigen values and 'n' is the quantum number.
4. Energy levels (E_n) are not equally spaced.



Physical boundary condition

- Boundary conditions of the potential dictate that the wave function must be zero at $x = 0$ and $x = L$. This yields valid solutions for integer values of n such that $kL = n\pi$.

- The wave function is now $\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$

- We normalize the wave function

$$\int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx = 1 \quad A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

- The normalized wave function becomes

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

- These functions are identical to those obtained for a vibrating string with fixed ends.

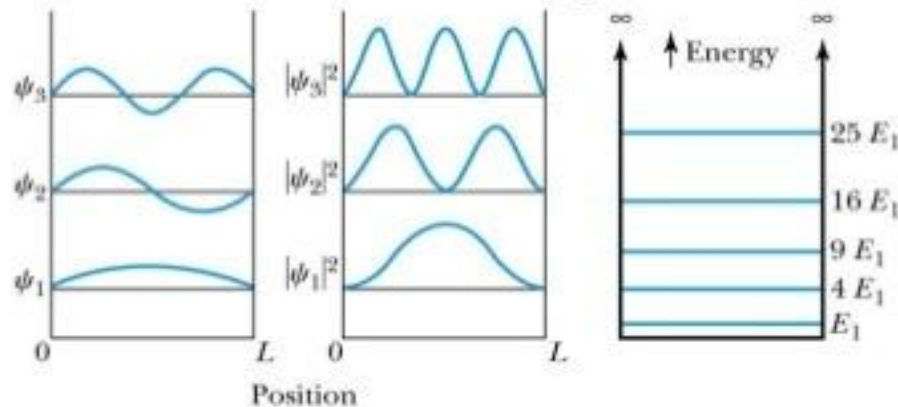
Quantized Energy

- The quantized wave number now becomes $k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$
- Solving for the energy yields

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \dots)$$

- Note that the energy depends on the integer values of n . Hence the energy is quantized and nonzero.

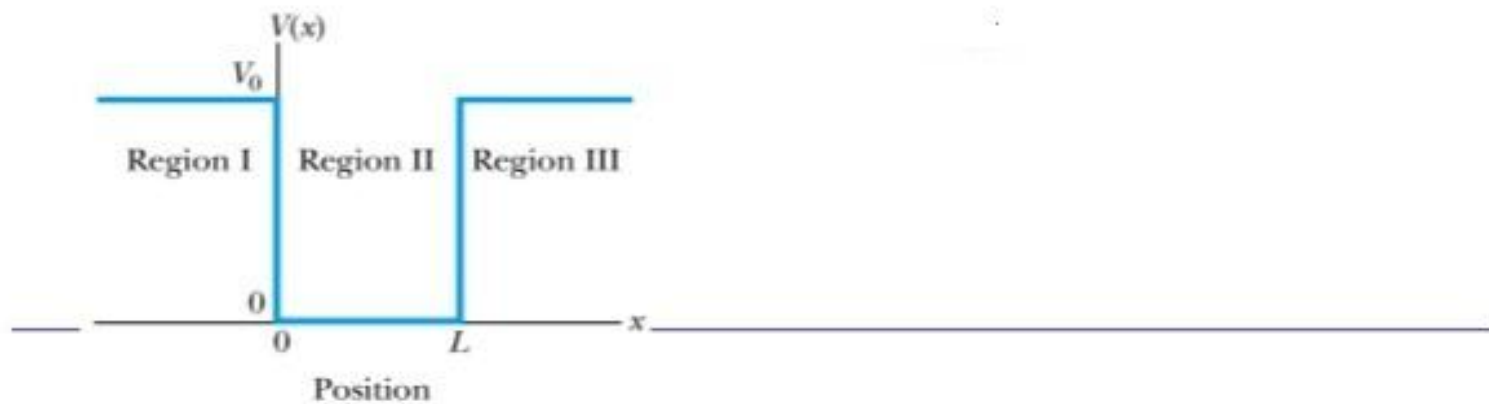
- The special case of $n = 1$ is called the ground state energy. $E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$



Ground state energy, zero point energy, there is no $n = 0$

Finite Square-Well Potential

- The finite square-well potential is
$$V(x) = \begin{cases} V_0 & x \leq 0 & \text{region I} \\ 0 & 0 < x < L & \text{region II} \\ V_0 & x \geq L & \text{region III} \end{cases}$$



Finite Square Well

- In regions I and III

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_I}{dx^2} + V\psi_I = E\psi_I$$

$$\frac{d^2\psi_I}{dx^2} - k_I^2\psi_I = 0 \text{ where } k_I = k_{III} = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

- In region II

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_{II}}{dx^2} = E\psi_{II}$$

$$\frac{d^2\psi_{II}}{dx^2} + k_{II}^2\psi_{II} = 0 \text{ where } k_{II} = k = \frac{\sqrt{2mE}}{\hbar}$$

Finite Square Well

- Solutions in region I and III

$$Ae^{k_I x} + Be^{-k_I x} \rightarrow Ae^{k_I x}$$

$$Ee^{k_{III} x} + Fe^{-k_{III} x} \rightarrow Fe^{-k_{III} x}$$

- Solutions in region II

$$Ce^{ikx} + De^{-ikx} \text{ or}$$

$$C \sin kx + D \cos kx$$

Finite Square Well

- The next step is to match boundary conditions inside and out for both ψ and $d\psi/dx$

– At $x=0$

$$A = D$$

$$k_I A = kC$$

– At $x=L$

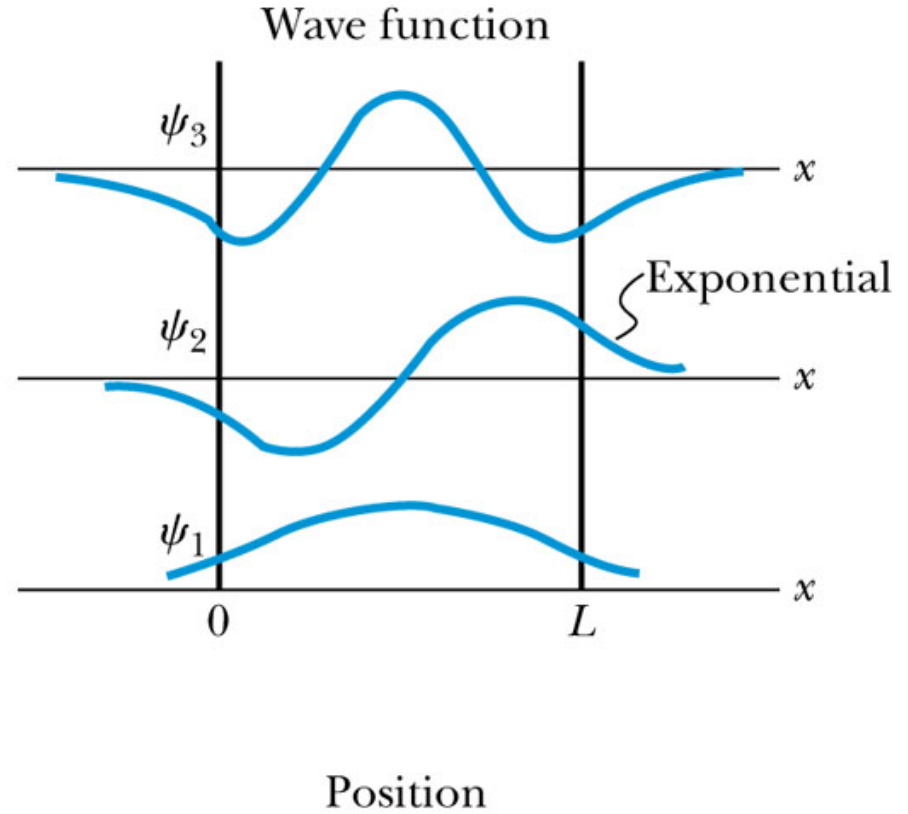
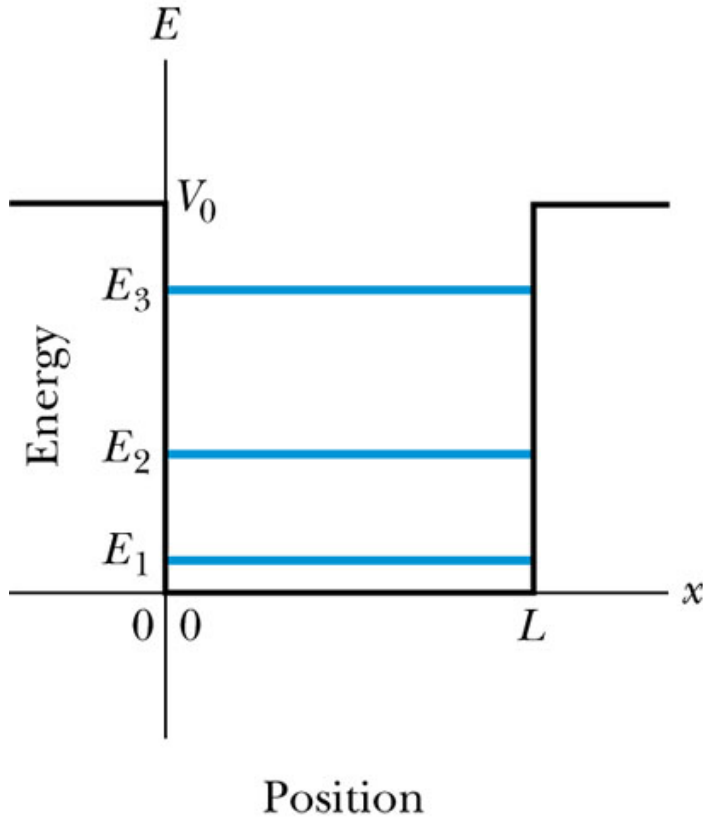
$$Fe^{-k_I L} = C \sin kL + D \cos kL$$

$$-k_I Fe^{-k_I L} = Ck \cos kL - Dk \sin kL$$

Finite Square Well

- As with the infinite well, application of the boundary conditions leads to energy quantization
- Although there are 4 equations for 4 unknowns the energy levels must be found numerically or graphically
- As with the infinite well, the n 'th eigenfunction will have $n-1$ nodes

Finite Square Well



Penetration Depth

- The penetration depth is the distance outside the potential well where the probability significantly decreases. It is given by

$$\delta \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

- It should not be surprising to find that the penetration distance that violates classical physics is proportional to Planck's constant.

Harmonic Oscillator

- The (simple) harmonic oscillator is one of the most important physical systems in physics
 - Any physical system in the neighborhood of a stable equilibrium position can be approximated by a harmonic oscillator (in the limit of small oscillations)
 - Vibrations of atoms in a molecule, oscillations of atoms in a crystal, ...

The Classical Linear Harmonic Oscillator

Classical mechanical problems are very often solved by introducing the so-called Hamiltonian, which is defined as:

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

The classical linear harmonic oscillator has the following Hamiltonian:

$$H(x, p) = \frac{p^2}{2m} + \frac{\kappa x^2}{2}$$

Where the frequency of the oscillator is:

$$\omega = 2\pi\nu = \sqrt{\frac{\kappa}{m}}$$

The Classical Linear Harmonic Oscillator

The trajectory $x(t)$, $p(t)$ of the oscillator is obtained by solving Hamilton's equations of motion:

$$\frac{\partial H(x, p)}{\partial x} = -\frac{dp(t)}{dt} \quad \frac{\partial H(x, p)}{\partial p} = \frac{dx(t)}{dt}$$

The solution is (homework) (A is the amplitude of the motion)

$$x(t) = A \cos \omega t \quad p(t) = -\omega m A \sin \omega t$$

We can introduce a quantum mechanical Hamiltonian as:

$$H = -\frac{h^2}{8m\pi^2} \frac{d^2}{dx^2} + V(x)$$

The Time-Independent Schroedinger Equation can be written:

$$H\psi(x) = E\psi(x)$$

Quantum Mechanical Linear Harmonic Oscillator

The quantum mechanical treatment of the linear harmonic oscillator (LHO) is one of the most important applications of quantum mechanics

The LHO is used as a simple approximation to molecular bond vibrations and rotations, for example, and forms the basis of much spectroscopy.

The time-independent Schroedinger equation for the LHO is:

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

This equation may be rewritten as:

$$\alpha = \frac{2\pi\nu m}{h} \qquad q = x\sqrt{\alpha} \qquad \varepsilon = \frac{4\pi E}{\omega h}$$

$$\frac{\partial^2 \psi(q)}{\partial q^2} - q^2 \psi(q) = \varepsilon \psi(x)$$

Quantum Mechanical Linear Harmonic Oscillator

$$\frac{\partial^2 \psi(q)}{\partial q^2} - q^2 \psi(q) = \epsilon \psi(q)$$

Although there are no solid boundary conditions as there was with the particle in the box, the wave function is localized in the sense that it must approach zero as x increases toward infinity. This just means that the probability of finding the particle must decrease as we move toward very large extensions.

The solution to Schroedinger's equation for the LHO is

$$\psi_n(q) = A_n e^{-q^2/2} H_n(q) \quad H_n(q) = (-1)^n e^{q^2} \frac{\partial^n}{\partial q^n} (e^{-q^2})$$

A_n is a constant and $H_n(q)$ is called a Hermite polynomial of the n^{th} order

Quantum Mechanical Linear Harmonic Oscillator

$$\frac{\partial^2 \psi(q)}{\partial q^2} - q^2 \psi(q) = \epsilon \psi(q) \quad \psi_n(q) = A_n e^{-q^2/2} H_n(q) \quad H_n(q) = (-1)^n e^{q^2} \frac{\partial^n}{\partial q^n} (e^{-q^2})$$

$$H_0(q) = 1 \quad H_1(q) = 2q \quad H_2(q) = 4q^2 - 2 \quad q = x\sqrt{\alpha}$$

As with the Particle-in-a-Box, the probability of finding a particle at $q = x\sqrt{\alpha}$

$$P = |\psi(q)|^2$$

By requiring that:

$$\int_{-\infty}^{+\infty} |\psi_n(q)|^2 dq = 1$$

We find:

$$A_n = \left(\frac{1}{2^n n! \sqrt{\pi}} \right)^{1/2}$$

Finally:

$$\psi_n(x) = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{-\alpha x^2/2} H_n(x\sqrt{\alpha})$$

Quantum Mechanical Linear Harmonic Oscillator

$$\frac{\partial^2 \psi(q)}{\partial q^2} - q^2 \psi(q) = \varepsilon \psi(x)$$

$$\psi_n(x) = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{-\alpha x^2 / 2} H_n(x \sqrt{\alpha})$$

The energy has the form:

$$\varepsilon = \frac{4\pi E}{h\omega} = 2n + 1$$

$$E_n = h\nu \left(n + \frac{1}{2} \right)$$

Note this is shifted by $h\nu/2$ from Planck's energy. This is called the zero point energy, the existence of which is required by the Heisenberg Uncertainty Principle.

Quantum Mechanical Linear Harmonic Oscillator

$$\psi_n(x) = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{-\alpha x^2/2} H_n(x\sqrt{\alpha})$$

It is interesting to calculate probabilities $P_n(x)$ for finding a harmonically oscillating particle with energy E_n at x ; it is easier to work with the coordinate q ; for $n=0$ we have:

$$\psi_0(q) = A_0 \left(\frac{1}{\sqrt{\pi}} \right)^{1/2} e^{-q^2/2} \Rightarrow P_0(q) = |\psi_0(q)|^2 \propto \frac{1}{\sqrt{\pi}} e^{-q^2}$$

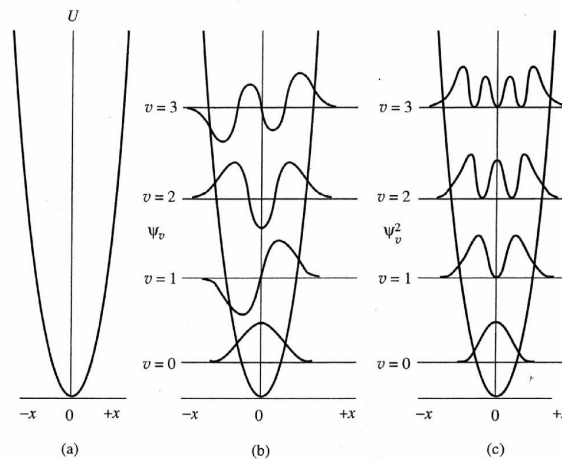
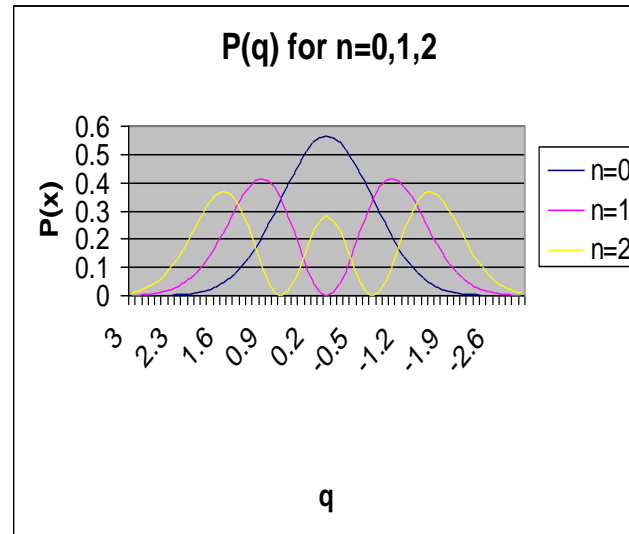
$$\psi_1(q) = A_1 \left(\frac{2}{\sqrt{\pi}} \right)^{1/2} q e^{-q^2/2} \Rightarrow P_1(q) = |\psi_1(q)|^2 \propto \frac{2q^2}{\sqrt{\pi}} e^{-q^2}$$

$$\psi_2(q) = A_2 \left(\frac{1}{2\sqrt{\pi}} \right)^{1/2} (2q^2 - 1) e^{-q^2/2} \Rightarrow P_2(q) = |\psi_2(q)|^2 \propto \frac{(2q^2 - 1)^2}{2\sqrt{\pi}} e^{-q^2}$$

$$\psi_3(q) = A_3 \left(\frac{1}{3\sqrt{\pi}} \right)^{1/2} (2q^3 - 3q) e^{-q^2/2} \Rightarrow P_3(q) = |\psi_3(q)|^2 \propto \frac{(2q^3 - 3q)^2}{3\sqrt{\pi}} e^{-q^2}$$

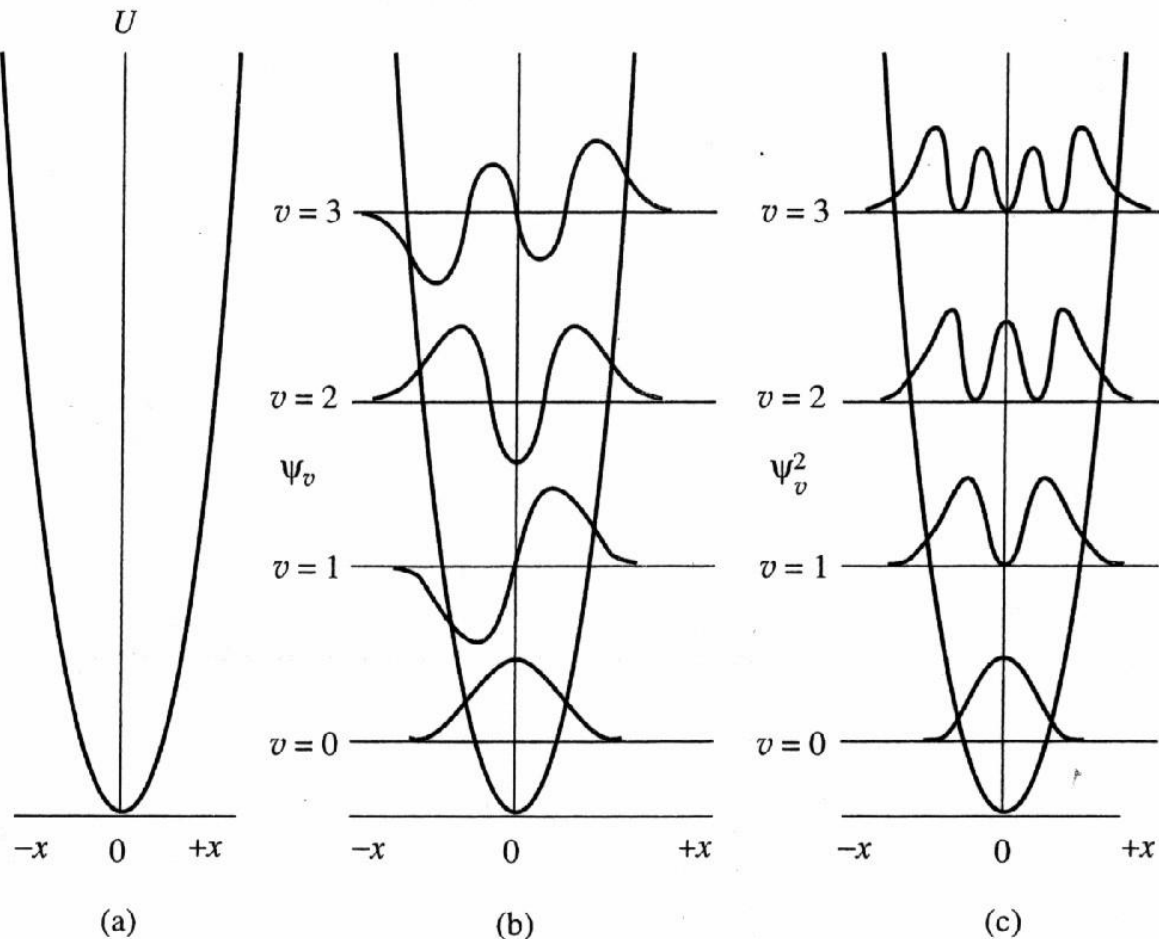
Quantum Mechanical Linear Harmonic Oscillator

Probabilities:



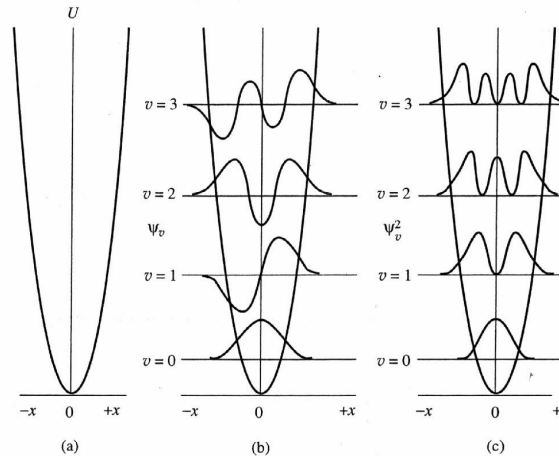
Quantum Mechanical Linear Harmonic Oscillator

Potential well, wave functions and probabilities:



Quantum Mechanical Linear Harmonic Oscillator

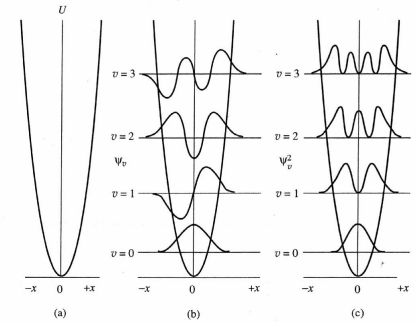
Potential well, wave functions and probabilities:



As the quantum number gets larger, the probability increases towards larger displacement values. This corresponds to a classical phenomenon, as the energy of an oscillator increases, motion becomes more extended away from the status of lowest energy. The fundamental frequency of the oscillator is also the same both classically and in quantum mechanics:

Quantum Mechanical Linear Harmonic Oscillator

Potential well, wave functions and probabilities:



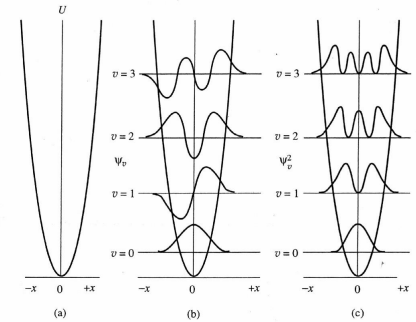
The fundamental frequency of the oscillator is also the same both classically and in quantum mechanics:

$$\omega_0 = \sqrt{\frac{\kappa}{\mu}}$$

There are however several differences between classical and quantum mechanics

Quantum Mechanical Linear Harmonic Oscillator

Potential well, wave functions and probabilities:



the first is that there is motion even in the lowest energy state (see the shape of the probability for $n=0$); the second is that the wave function extend beyond the classical limits for the motion in a region of space where the potential is very large and that are not expected to be observed classically. The term $1/2h\nu$ is called *zero point energy*. This states that an oscillator cannot be at complete rest; if it was at rest, we would know the momentum ($p=0$) and position precisely; the zero point energy allows Heisenberg's principle not to be violated. What that means is that molecules or solids vibrate even at 0 degree K.

THANK YOU