PH105
Q. Mech

Autumn Semester 2023

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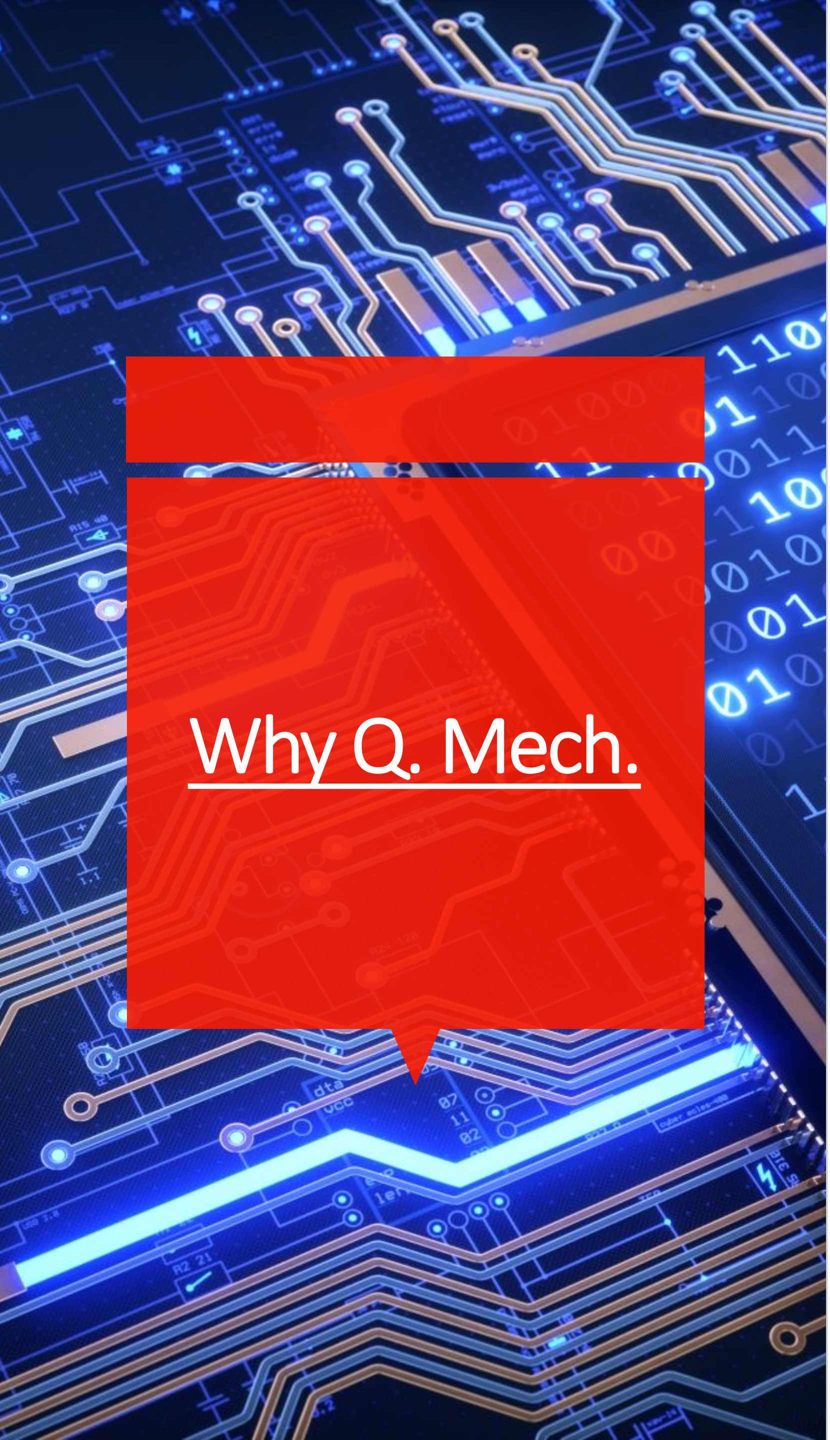
Concepts of Modern Physics, by Beiser

Why Q. Mech ???



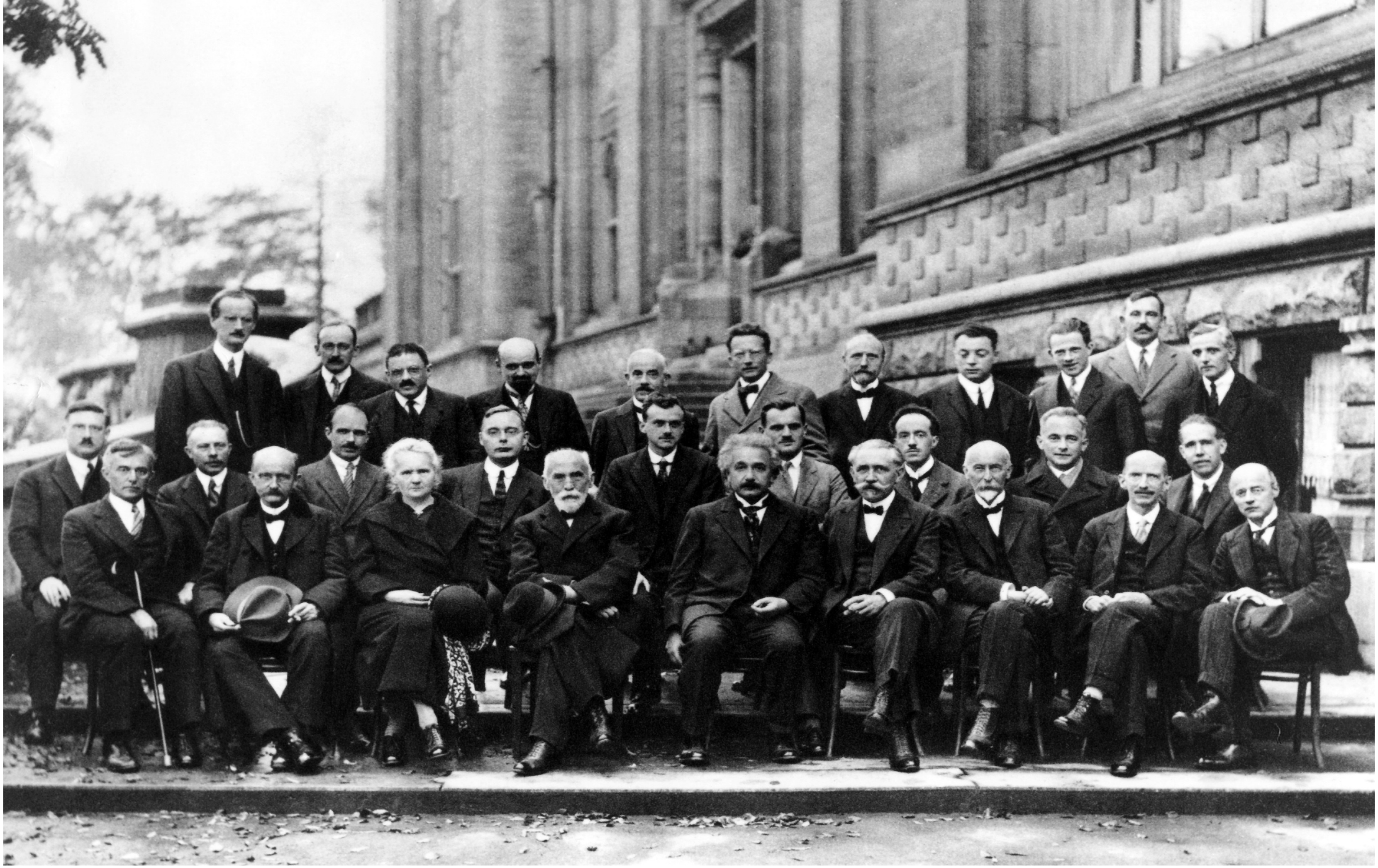
Why Q. Mech.

- ✓ First computer based on vacuum-tube weighed 30 tons. Vacuum tubes can be replaced by transistors which rely on the unique properties of semiconductors
- ✓Atomic clocks
- ✓Quantum Cryptography
- ✓**Lasers**
- ✓**Quantum computers**
- ✓**Instantaneous communication : quantum entanglement**

Classical physics explains matter and energy at the macroscopic level : *scale familiar to human experience*

End of the 19th Century observers discovered phenomena in large (macro) and the small (micro) worlds that ***classical physics could not explain***

- **Development of Q. Mech: A major revolution in physics**



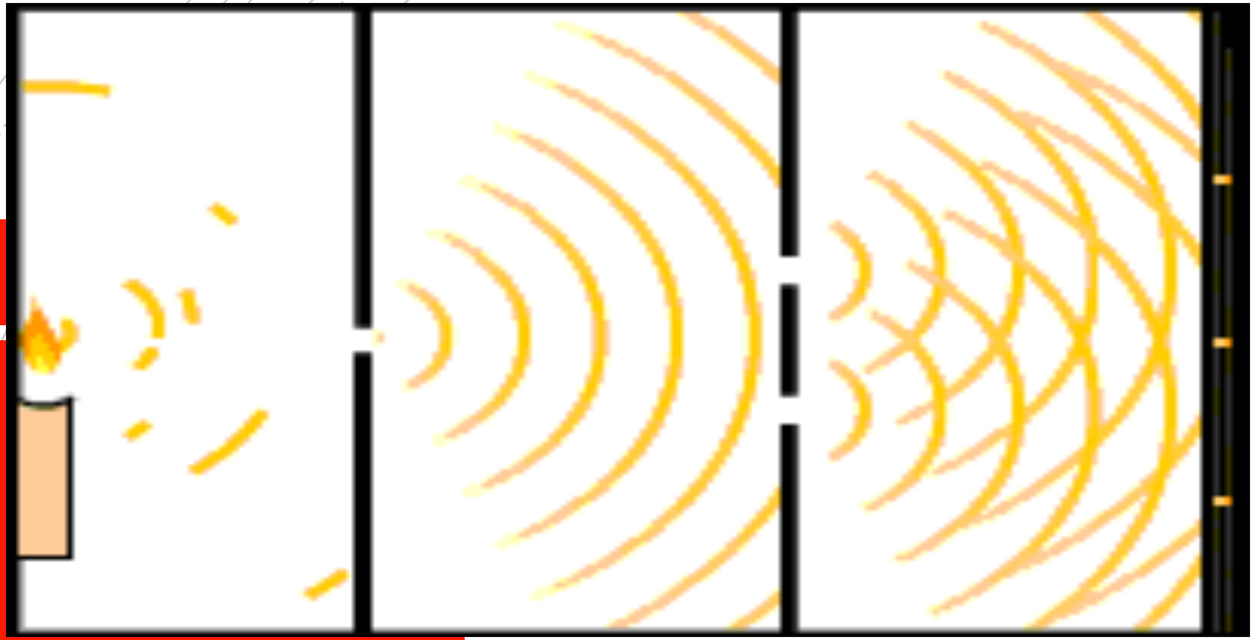
A. Piccard, E. Henriot, P. Ehrenfest, E. Herzen, Th. De Donder, E. Schrödinger, J.E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin; P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr; I. Langmuir, M. Planck, M. Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch. E. Guye, C.T.R. Wilson, O.W. Richardson
Fifth conference participants, 1927. Institut International de Physique Solvay in Leopold Park.

Turbulence Control

- Soon, quantum physics may have eliminated that bumpy ride that causes you to spill your drink on an airplane. By creating quantum turbulence in an ultra-cold atom gas in the laboratory, scientists may have come across a method of studying the turbulence that interferes with airplanes and boats. For centuries, turbulence has stumped scientists because of the difficulty in re-creating the conditions that cause it to form
- Electronics

Photons behave in some respects like particles and in other respects like waves

Radiators of photons have emission spectra that are discontinuous



Even if the source intensity is turned down so that only one particle is passing through the apparatus at a time, the same interference pattern develops over time. ***The quantum particle acts as a wave when passing through the double slits, but as a particle when it is detected.***

Wave-particle duality

- In 1924, Louis de Broglie proposed that just as light, **matter also has wave-like properties**.
- The wavelength associated with a particle is related to its momentum:

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

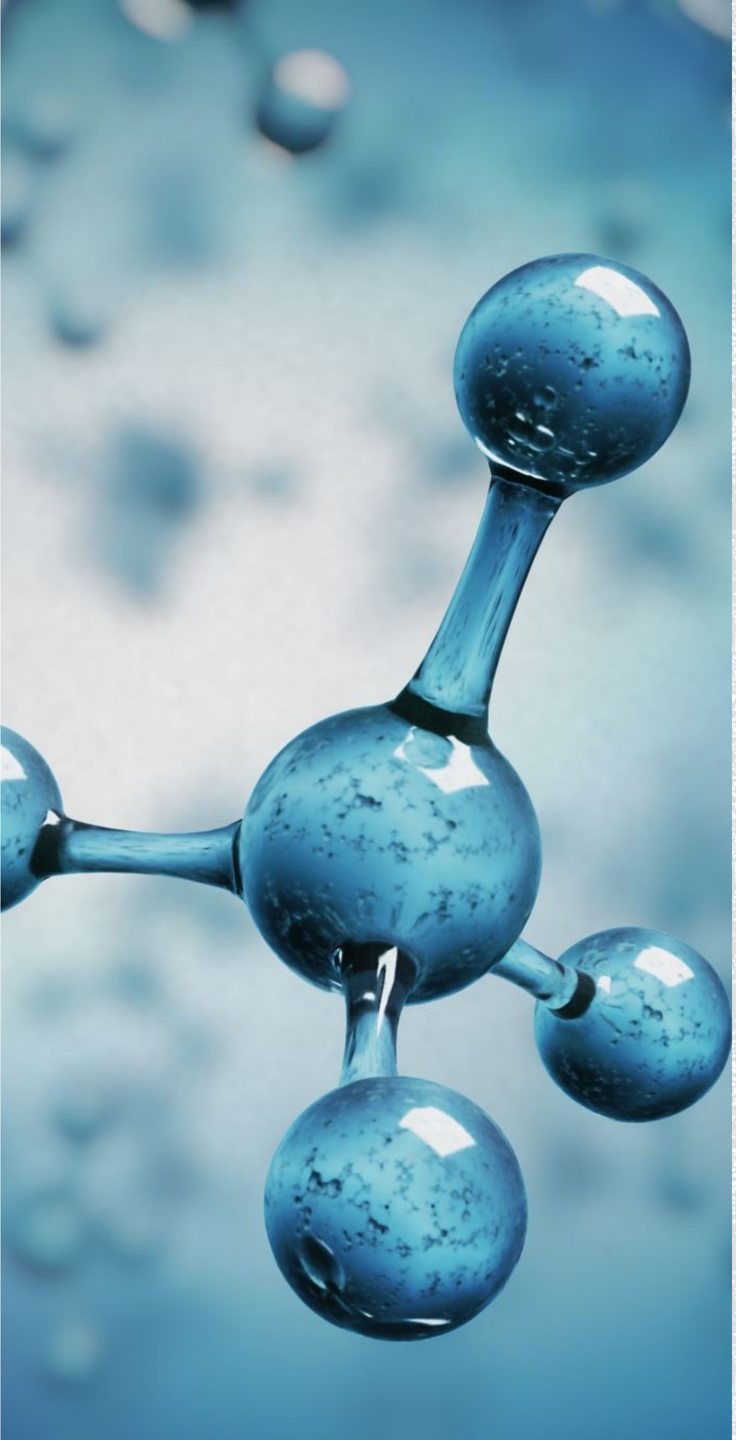
HAI

Find the Broglie wave length for the following

a 70 kg man travelling at 6 km/h.

a 1 g stone travelling at 10 m/s.

A 10^(-6) g stone travelling at 1 m/s.



BOHR THEORY

- Quantized electron orbits.

electrons could inhabit only certain orbits around the atomic nucleus.

- It explained many aspects of atomic phenomena, but has severe limitations
  - It applies only to hydrogen and one electron ion such as ….
  - Certain spectral lines are more intense than others
  - Many spectral lines consist of several separate lines whose wavelength differ slightly

BOHR THEORY (1913 BY NIELS BOHR) + DEBROGLI

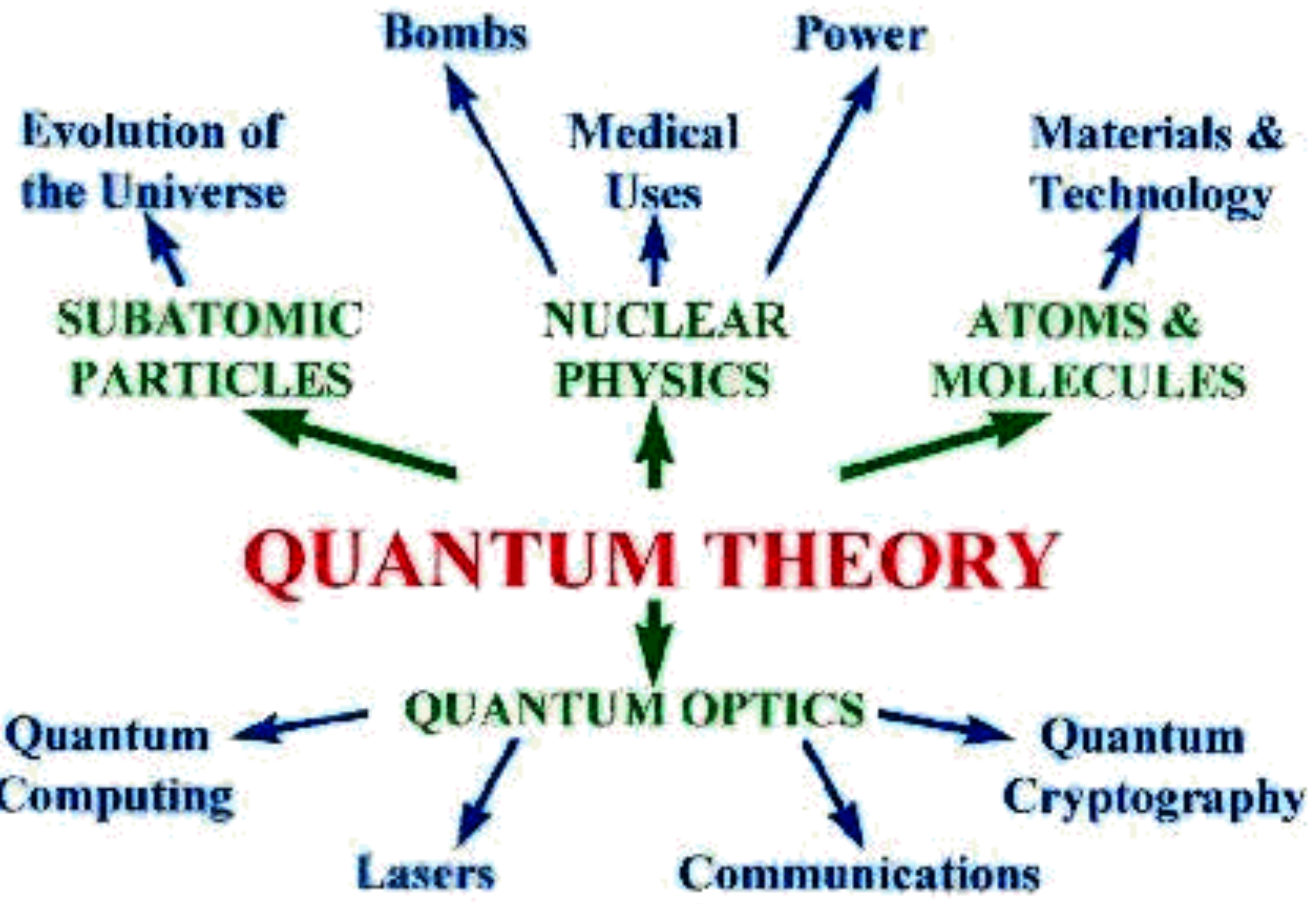
Electron wave in the atom :

an electron will be observed only in situations that permit a standing wave around a nucleus

De Broglie suggested that the allowed electron orbits were those for which the circumference of the orbit would be an integer number of wavelengths

- Example: wave behavior of an electron in orbit around a hydrogen atom
  - De Broglie wavelength of the electron

Quantum Psychic


Bombs
Power
Evolution of the Universe
Medical Uses
Materials & Technology
SUBATOMIC PARTICLES
NUCLEAR PHYSICS
ATOMS & MOLECULES
QUANTUM THEORY
QUANTUM OPTICS
Quantum Computing
Quantum Cryptography
Lasers
Communications

Foundation of Q.Mech

➢ ***Basic fact of Q. Physics : " discretization of energy level "***
(Max Planck 1900)

$\Delta E = h\nu$ *(quantum of action)*
Jump "ΔE" between discrete energy levels

- Einstein : ***photo-electric effect -1905***
- De Broglie : ***wave particle duality -1924*** (universal characteristic of nature)

World of Quantum mechanics

- Schrödinger, Heisenberg, Max Born, Paul Dirac and *many* others: 1925-1926

"it was like a miracle"

By 1930's Application of Quantum mechanics to problems involving nuclei, atoms, molecules , and matter in solid state

<u>describe</u>

"a large part of physics and the whole chemistry"

<u>Q.Mech has survived every experimental test thus far</u>

Quantum vs. classical

- characteristic length

$$\lambda/x = h/xp << 1$$

wave aspect of matter will be hidden

In classical world $xp >> h$

Exercise: calculate wave length for an atom with KE corresponding to T=10^(-6) K.

C Mech is *limiting form* of Q Mech

Quantum Mechanics

- **Fundamental difference**:

  ➢C.Mech: Future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it

  ➢Q.Mech: Nature of an observable quantity is different in the atomic realm

Cause and effect are related, but “certainty” is “impossible”

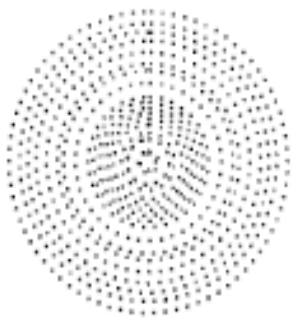
probabilistic concept

➢For example:

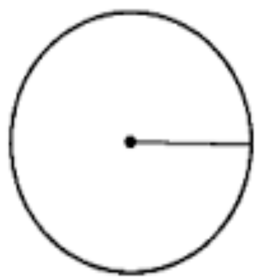
In Bohr theory: radius of the electron's orbit in ground state hydrogen atom is always exactly 5.3*10^(-11) m

Q.Mech states that ***"this is the most probable radius"***

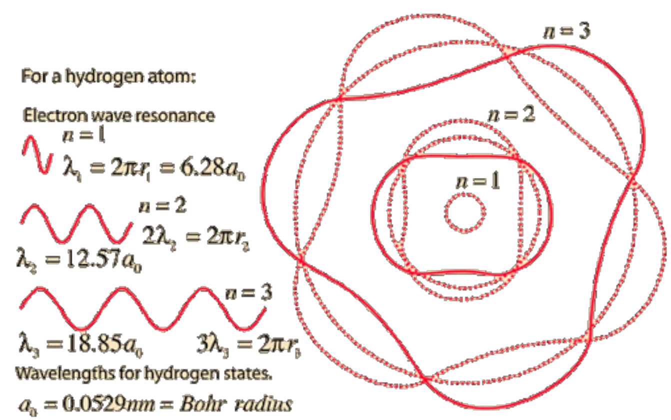
⇒In suitable experiments most trial will yield a diff value, either larger or smaller, but value ***most likely*** will be 5.3 * 10^(-11) m



(i) Radius of maximum probability (0.529 Å)



(ii) Bohr radius (0.529 Å)



$\Rightarrow$C. Mech is an approximate of Q.Mech:

"certainties are illusory"

Ordinary object consist of large atoms and we observe average behavior

UNCERTAINLY PRINCIPLE

$\Delta x \, \Delta p \approx \hbar$ (1927)

``Un-bestimmtheit'' (indeterminacy) (Un-sicherheit)

<u>Its impossible to know both the exact position and exact momentum of an object at same time</u>

Real essence: particle described by wave group

Critical reaction by Einstein

- Einstein, disenchanted with Heisenberg’s "Uncertainty Principle," remarked

"God does not play dice."

  - Bohr replied,

    "Einstein, stop telling God what to do.”

Why electron can not exist in the nucleus of an atom?

By Heisenberg's uncertainty principle

$$\Delta x.\,\Delta p \geq \frac{h}{4\pi}$$

$$\text{momentum}\left(p\right) = \text{mass}\left(m\right) \text{ x } \text{velocity}\left(v\right)$$

$$v \geq \frac{h}{4\pi \Delta x.m}$$

$$= \frac{6.626 \text{ x } 10^{-34}}{4 \text{ x } 3.14 \text{ x } 10^{-15} \text{ x } 9.1 \text{ x } 10^{-31}}$$

$$= 5.79 \text{ x } 10^{10} m/s$$

As a result, the velocity uncertainty will be $5.79 \text{ x } 10^{10} m/s$ which is far more than the speed of light, which is not possible.

Exercise

In one dimension, consider yourself (60 kg) confined to the width of a room, which may be 10 m across. What is the uncertainty of your momentum? What is the uncertainty of your velocity? Compare this uncertainty with a typical walking speed of 10 km/h. Is this uncertainty significant on this macroscopic scale?

Exercise

In one dimension, consider an electron confined to a length interval of 1 °A, which is of the order of the diameter of an atom. What is the uncertainty in its momentum? What is the indeterminacy of its velocity? What is the uncertainty of its kinetic energy? Compare this energy with the ionisation energy of hydrogen, which is 13.6 eV. Is the calculate energy uncertainty significant on an atomic scale?

- Quantum mechanics differs significantly from classical mechanics in its predictions when the scale of observations becomes comparable to the atomic level : **quantum realm**

- However, many **macroscopic properties** can only be fully understood and explained with the use of quantum mechanics.

Superconductivity, the properties of material such as semiconductors and nuclear and chemical reaction mechanisms

Wave equation

<u>The main task is to write down the wave function for the particle, and then solve it</u>

Schrodinger equation: *fundamental equation of Q.Mech (like second law of motion in Newtonian mechanics)*

<u>Background:</u>

Wave equation:

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

a) governs a wave whose variable quantity is u that propagates in x direction with speed v:

Example: a string located in x-y plane: the displacement u takes place in *y*-direction

b) can have many possible solutions

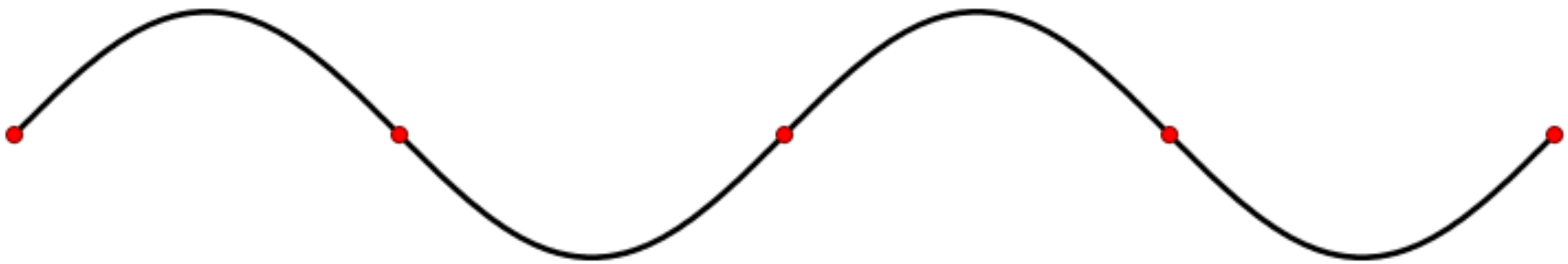
Partial Derivatives: first order, second order

Wave equation

Background:

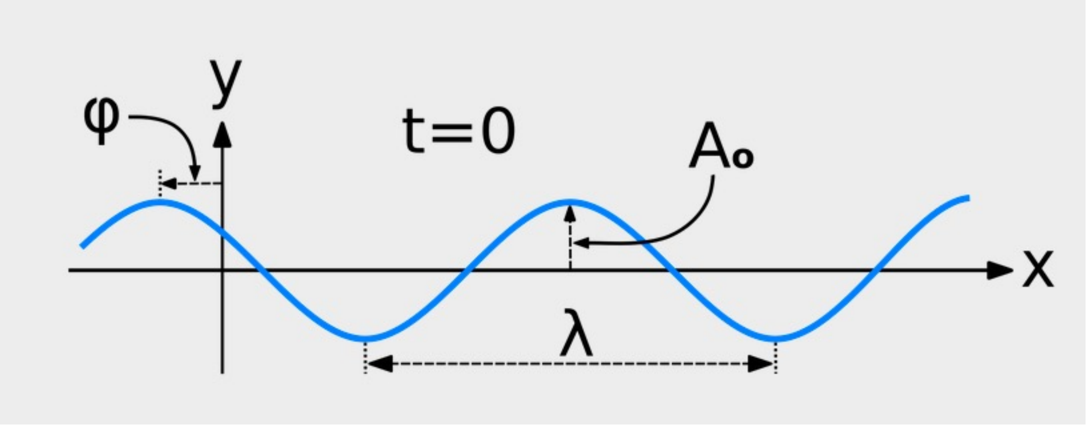
$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2}$$

- Can have many possible solutions
- Those satisfying the boundary conditions



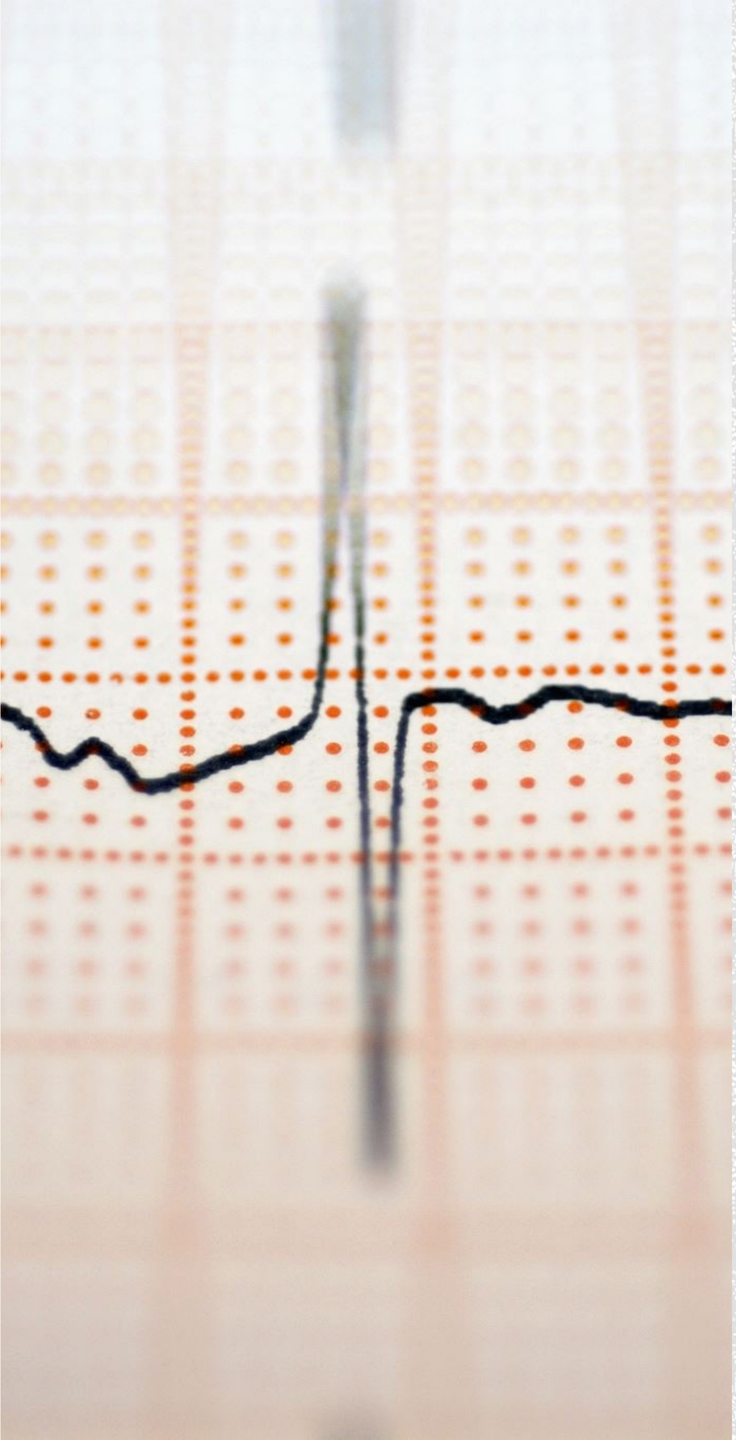
- Solution:

$$u(x, t) = A\sin(kx - \omega t + \phi)$$



Verify that above is solution of the wave equation

- Example 5.1



WAVE FUNCTION

$\Psi = A + i B$

A and B are real function

$\Psi^* = A - i B$ (complex conjugate)

- I $\Psi|^2$ is always a positive quantity
- It is proportional to the probability density (P) of finding the body described by Ψ
- Normalization

WELL BEHAVED WAVE FUNCTION:

(1) Ψ must be continuous and single valued everywhere

(2) Derivatives of Ψ must be continuous and single valued (momentum consideration requirement)

(3) Ψ must be normalizable

SCHRÖDINGER EQUATION

➢ By Erwin Schrödinger (1926): it describes how the quantum state of a physical system changes in time

* ψ corresponds to the wave variable y

BUT

it is not a measurable quantity itself, and may be complex

$$\psi = A\, e^{-i\omega\left(t-\frac{x}{v}\right)}$$

$$\psi = Ae^{-\frac{i}{h}(Et-px)}$$

$$\psi = Ae^{-\frac{i}{h}(Et-px)}$$

Describes the wave of an "unrestricted particle" of total energy E and momentum p moving in the +x direction :

freely moving particle

When particle is subject to various restrictions ???

For example: an electron bound to an atom

Force: electric field of its nucleus

SCHRODINGER EQUATION: STEADY STATE FORM

U varies with the position of the particle only

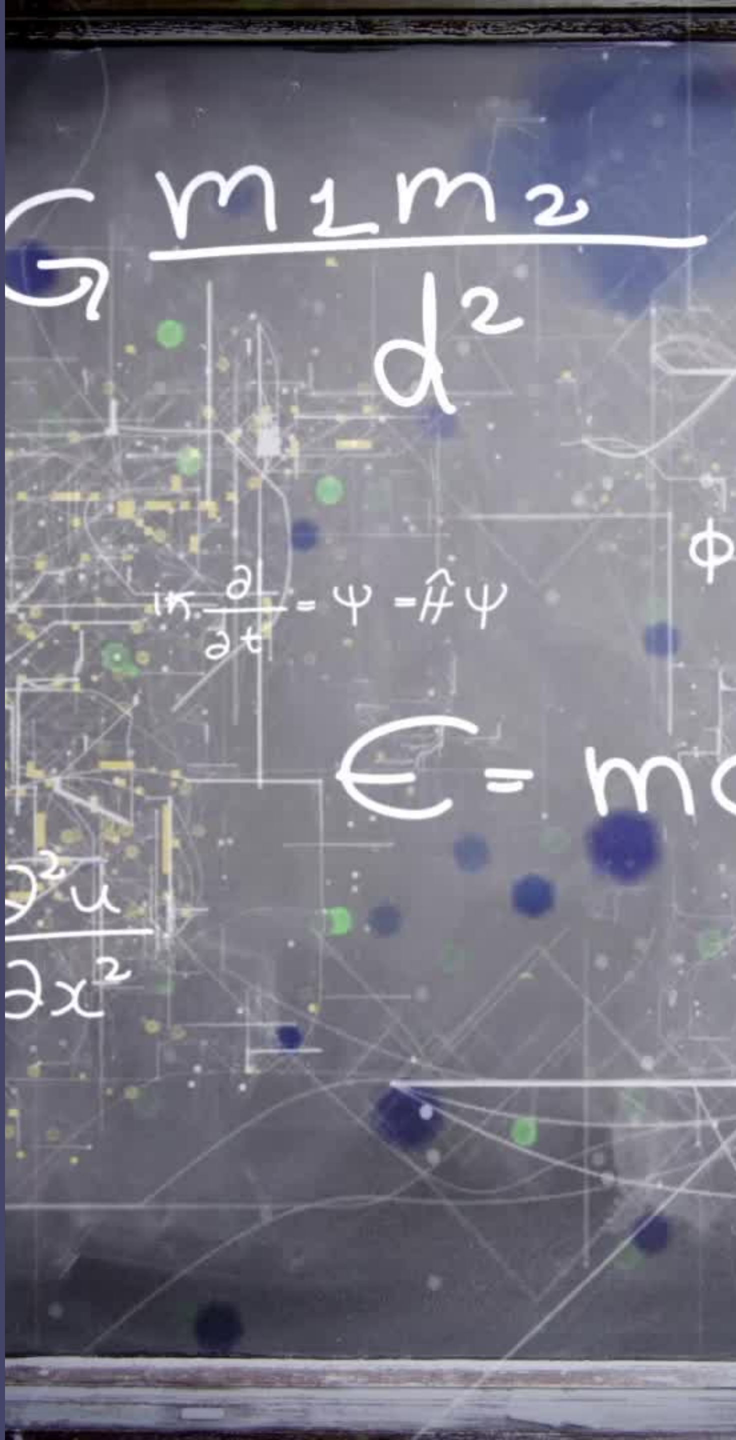
SE in three dimension

$$\Delta^2 \psi + \frac{2m}{\hbar^2} (E - U)\psi = 0$$

ABOUT SE

It can not be derived from other basic principles of physics, it is a basic principle in itself.

SE has turned out be *remarkably accurate* in predicting the results of experiments.



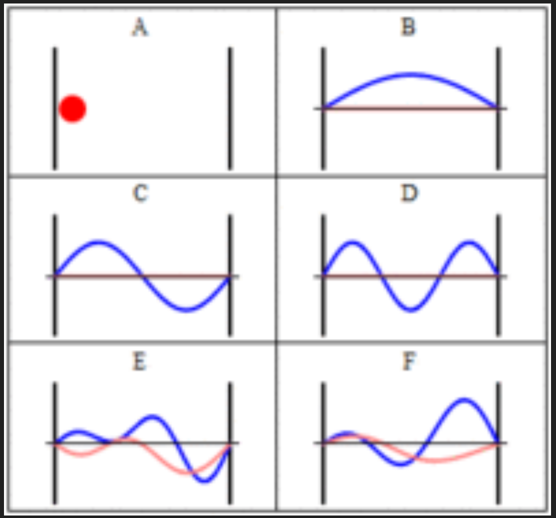
Schrodinger Equation:

Total energy of the particle E = KE + potential energy

- $E = \frac{p^2}{2m} + U(x,t)$
- $E\psi = \frac{p^2\psi}{2m} + U\psi$
- $\psi = Ae^{-i\omega\left(t-\frac{x}{v}\right)}$

Particle in a box: Alternate way

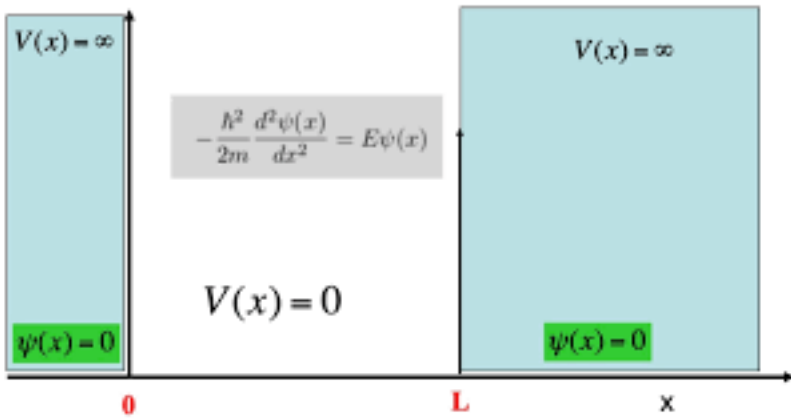
Wave function: dependence of boundary conditions and normalization

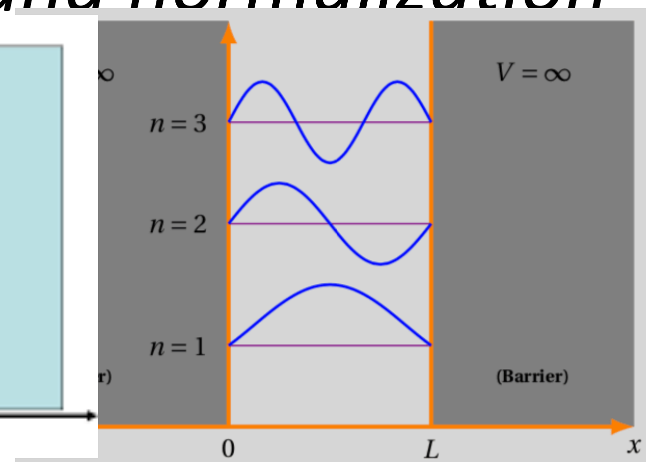


- Particle is restricted to certain region
- It bounces back and forth between the walls
- Assumption: walls are infinitely hard

Particle in a box: Alternate way

Wave function: dependence of boundary conditions and normalization





<u>*Crude treatment:*</u>

- *wave variable must be 0 at wall*
- *Longest wavelength $\lambda = 2L$, then $\lambda = L$, $\lambda = 2L/3$*

λ = 2L/n n=1,2,3 …….

- Kinetic energy:

$$KE = \frac{h^2}{2m\lambda^2}$$

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

- Permitted energy levels: E_n = ??

n: quantum number

$$\boxed{E_n = \frac{n^2 h^2}{8\, m\, L^2}}$$

Well behaved wave function:

(1) Ψ must be continuous and single valued everywhere

(2) Derivatives of Ψ must be continuous and single valued (momentum consideration requirement)

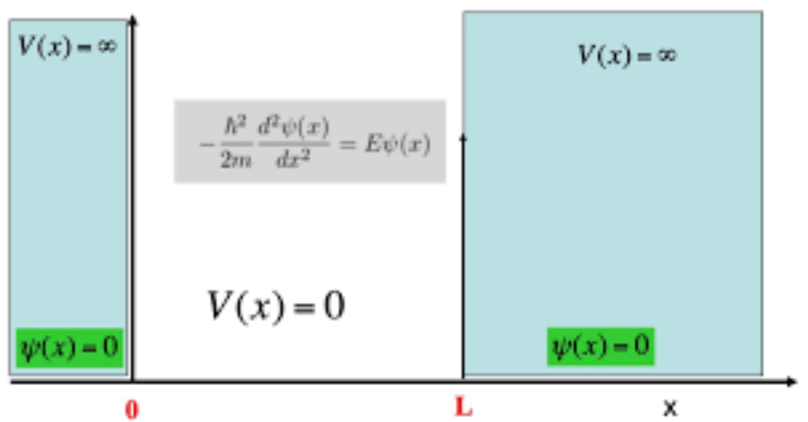
(3) Ψ must be normalizable

$$\Psi \rightarrow 0 \text{ as } x \rightarrow \text{infinity}$$

Particle in a box

Wave function: dependence of boundary conditions and normalization

- Particle is restricted to certain region
- It bounces back and forth between the walls
- Assumption: walls are infinitely hard



Wave function of Particle in a box

- SE within the box:

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

(assume U=const=0)

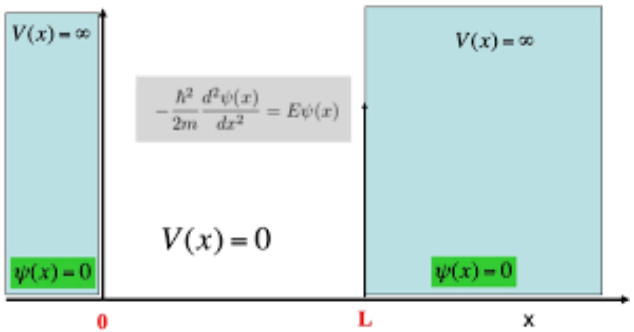
- Solution:

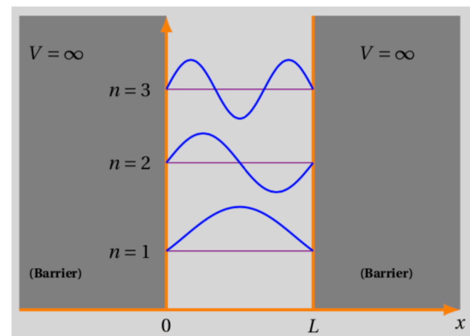
$$\psi = A \sin\left(\frac{\sqrt{2mE}}{\hbar}\right)x + B \cos\left(\frac{\sqrt{2mE}}{\hbar}\right)x$$

Find out A and B with given B.C.

Particle in a box

Wave function: dependence of boundary conditions and normalization





$\Psi = A \sin (\sqrt{2mE}/\hbar)\, x + B \cos(\sqrt{2mE}/\hbar)\, x$

B.C. wave variable must be 0 at wall

$$\psi(x=0)=0 \rightarrow \quad B=0$$

$$\psi(x=L)=0 \;\Rightarrow\; A\sin\left(\frac{\sqrt{2mE}}{\hbar}\right)L=0 \;\Rightarrow\; \frac{\sqrt{2mE}}{\hbar}=n\pi$$

- $$\frac{\sqrt{2\,m\,E}}{\hbar}\,L = n\,\pi$$ n=1,2,3…

$$E_n = \frac{n^2 h^2}{8\,m\,L^2}$$

- **Wave functions corresponding to Eigenvalue** E_n

$$\psi_n = A \sin\left(\frac{\sqrt{2mE_n}}{\hbar}\,x\right)$$

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

Calculate A : Exercise

Wave function

$$\Psi = A + i\,B$$

A and B are real function

- I Ψ | ^2 is always a positive quantity
- It is proportional to the probability density (P) of finding the body described by Ψ
- Normalization

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 \, dx$$

- $$\psi_n = A \sin\left(\frac{\sqrt{2mE_n}}{\hbar}\, x\right)$$ n=1,2,3, ……

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

- Exercise:

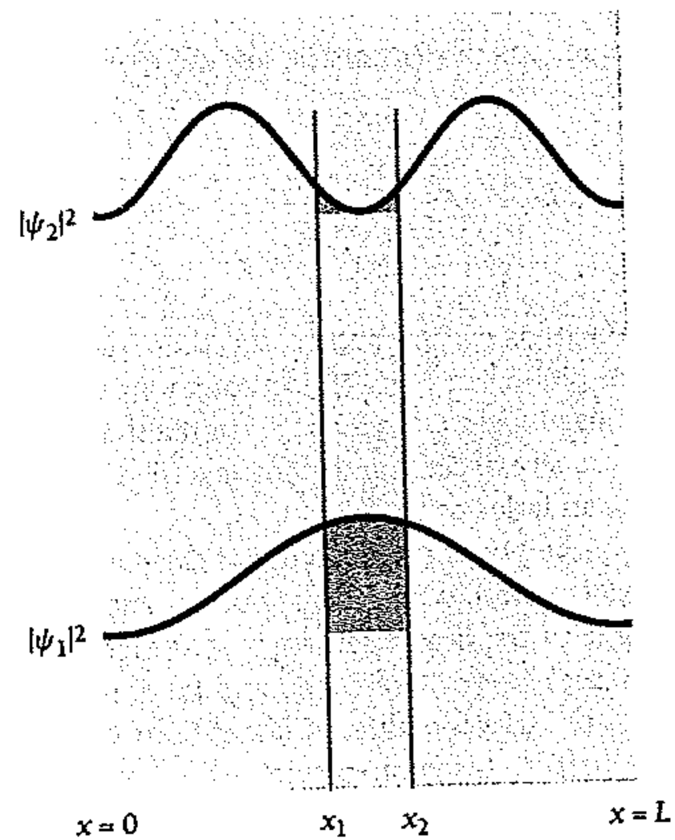
Find the probability that a particle trapped in a box L wide can be found between 0.45 L and 0.55 L for the ground and first excited states.

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\psi_n|^2\, dx$$

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\psi_n|^2\,dx = \frac{2}{L}\int_{x_1}^{x_2} \sin^2\frac{n\pi x}{L}\,dx$$

For n=1, probability of finding the particle =0.198

For n= 2, its 0.0065



trapped particle

$$E_n = \frac{n^2\hbar^2}{8m\ L^2}$$

- Trapped particle *can not* have an arbitrary energy (as a free particle)

Energy depends on mass, and details how it is trapped

It can not have zero energy, since $\lambda = h/mv$
In classical physics all E are allowed including `-' and 0

Planck constant is small, quantization we observe only when m and L are small

Example

- An electron is in a box 0.10 nm across, which is the order of magnitude of atomic dimensions. Find its permitted energies
- Given:
  - » $m = 9.1 \times 10^{-31}$ kg
  - » $H = 6.63 \times 10^{-34}$ J.s
  - » $E_n = 6.0 \times 10^{-10} n^2$ J
  - » $= 38 n^2$ eV

Energy quantization is prominent in the case of atomic electron

Example2

- A 10g marble is in a box 10 cm across. Find its permitted energies

- Given: m, L, h

E = 5.5 X 10^(-64) n^2 J

K E corresponding to n=1 is **3.3 X 10^(-31) m/s**

Permissible energy levels are so close to each

in everyday experience Q effects are imperceptible
Success of Newtonian mechanics

Extracting information from ψ

- Once SE is solved, we have $\psi\ (x,y,z,t)$

  now how to get observable quantities ??

Expectation value $\underline{\langle x\rangle = \int x\, \psi^*\, \psi\, dx}$

- What is the average position x of a number of identical particles distributed along x axis

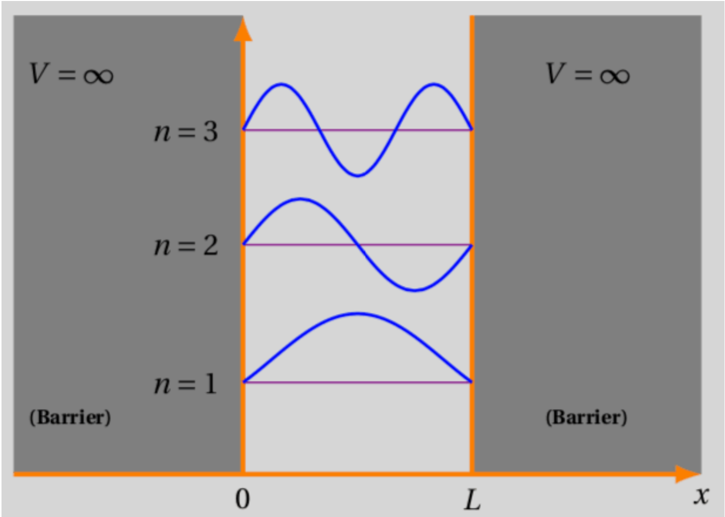
Exercise

- Find the expectation value <x> of the position of a particle trapped in a box L wide

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x|\Psi|^2\, dx}{\int_{-\infty}^{\infty} |\Psi|^2\, dx}$$

$$\psi_n = A \sin \frac{n\pi x}{L}$$

- <x> = L/2



- Average position of the particle is the middle of the box in all quantum states
- Note that probability density is 0 at middle for n=2,4,6…..but not <x>
- |ψ|^2 reflects the symmetry about the middle of the box

- What would be <p> … ?

- Given:

$$\psi_n = A \sin\left(\frac{\sqrt{2mE_n}}{\hbar}\, x\right)$$

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

Eigenvalues and Eigenfunctions

- The value of energy E_n for which Schrodinger steady state equation can be solved are called **eigenvalues**

- Corresponding wave function ψ_n : Eigenfunction

- Certain dynamical variable G is quantized

$$\boldsymbol{G}\,\psi_n = G_n\psi_n$$

G is an operator, and G_n real numbers

- Energy levels: quantized
- A dynamical variable G may not be quantized, measurement of G on **identical systems** will **not give unique result,** instead
  - Spread of values
  - Average: $\langle G \rangle = \int G\ |\psi|^* \underline{\psi}\ dx$

Example: Hydrogen atom
- Electron position is not quantized => it may be anywhere inside the atom with a certain probability
- Experiment gives average value

- Wave function is akin to wave variable y of wave motion (in general):

  For a particle moving freely in +x direction:

$$\Psi = Ae^{-i\omega(t-x/v)}$$

$\omega = 2\,\pi\nu,$ $v = \lambda\nu$ $\psi = A\,e^{2\,\pi i\left(\nu t-\frac{x}{\lambda}\right)}$

We know frequency and wavelength in terms of total energy ($E = h\,\nu = 2\pi\,\hbar\,\nu$) and momentum ($\lambda = \frac{h}{p} = \frac{2\nu\hbar}{p}$):

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

Operators associated with various Observable:

Quantity	**Operator**
Position, x	***x***
Linear momentum, p	***Ћ/i ∂/∂x***
Potential energy, U(x)	***U(x)***
Kinetic energy, KE = p^2/2m	***-Ћ^2/2m ∂^2/∂ x^2***
Total energy, E	***iЋ ∂/∂t***
Total energy(Hamiltonian form)H	***-Ћ^2/2m ∂^2/∂ x^2 + U(x)***

Momentum eigenfunction

$\underline{p}\ \psi\_n = p\_n\ \psi\_n$

Exercise: Show that

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

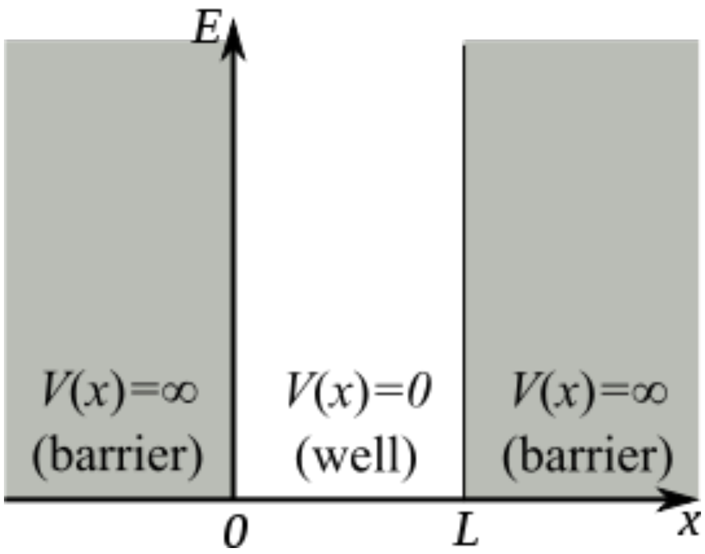
is **not** a momentum eigenfunction.

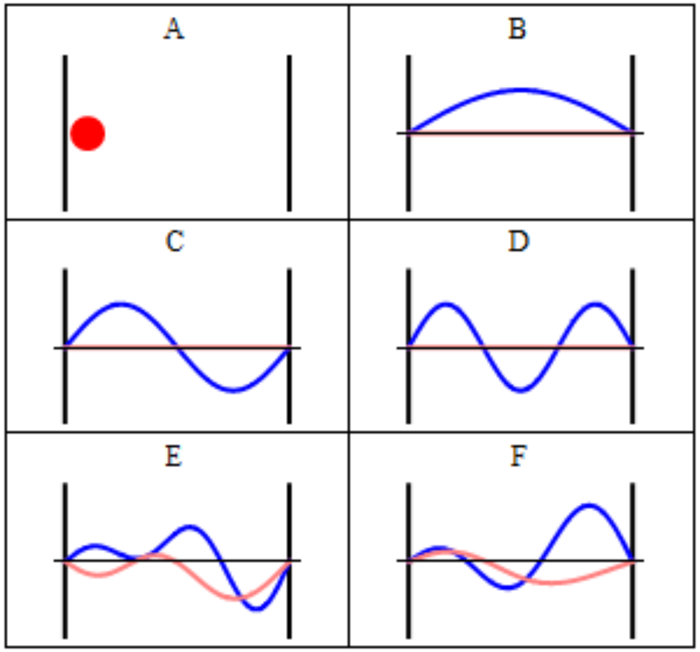
What would be correct momentum eigenfunction ??

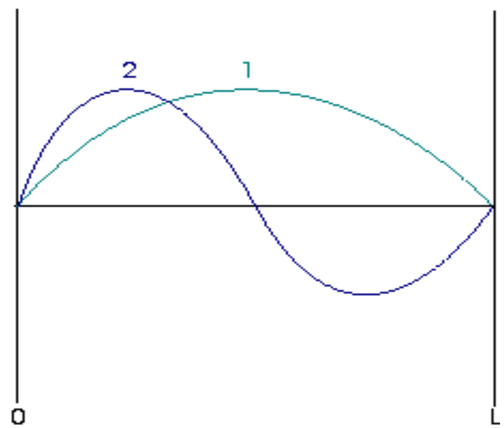
- What would be <p> … ?
- Given:

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

Particle trapped in a well

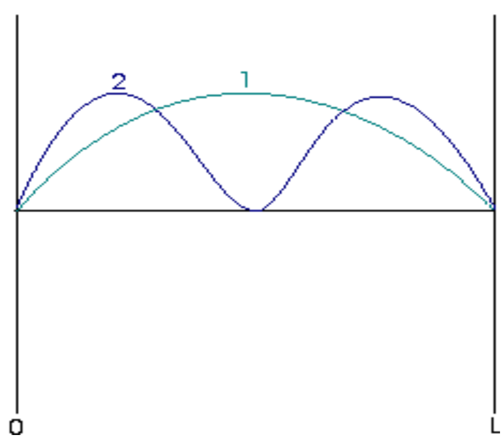






The probability distribution is non-uniform at low quantum number (low n)

As n increases, it becomes more uniform



At high n, it is consistent with the classical result: particle moving between the two walls, on average' should spend equal amounts of time at all position

- Suppose the energy measurement results in the value

$$E_n = \frac{4\,\hbar^2\pi^2}{2\,m\,L^2}$$

What will the expected (average) value of the position 'immediately after' this measurement.

☑ It means that the wave function collapses ψ_2

☑ Subsequent measurement of the position will give the value x with probability $\left|\sqrt{\frac{2}{L}}\,\sin\frac{(n\pi x)}{L}\right|^2$

☑ The expected value will be L/2

- Let wave function is linear combination of two wave functions:
- Momentum wave function:

$$\psi_n^+ = \left(\frac{1}{2i}\right)\sqrt{\frac{2}{L}}\exp\left(\frac{in\pi x}{L}\right)$$

$$P_n^+ = \frac{n\pi\hbar}{L}$$

Exercise

- <p> = 0

- How ???
=======

- Particle is moving back and forth, and so its average momentum for any value of n is 0

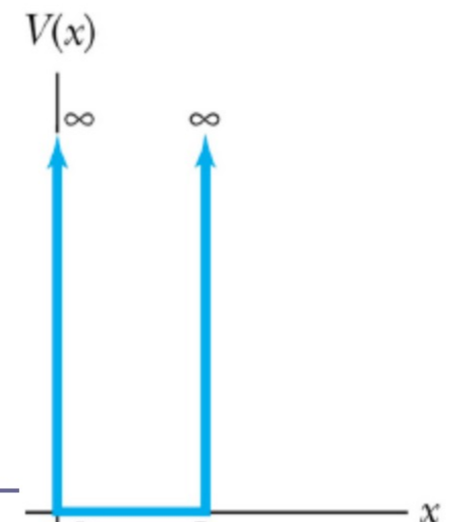
- We think that $E= p^2/2m$ => $p = +,- \sqrt{(2mE_n)} = +,- (n \Pi \hbar/L)$

Infinite potential well

- Where the potential is zero inside the box, the Schrödinger wave equation becomes $\dfrac{d^2\psi}{dx^2} = -\dfrac{2mE}{\hbar^2}\psi = -k^2\psi$ where $k = \sqrt{2mE/\hbar^2}$

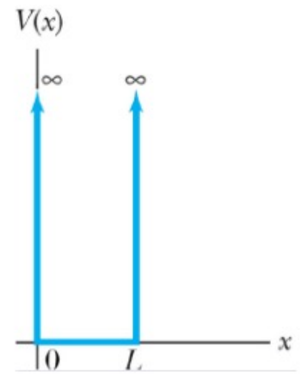
- The general solution is $\psi(x) = A\sin kx + B\cos kx$

- **Boundary conditions** dictate that the wave function must be zero at *x* = 0 and *x* = *L*.
  - to ensure *ψ=0* at *x = 0* ➔ ***B = 0***.
  - to ensure *ψ=0* at *x = L* ➔ ***k = nπ/L*** *(where n= 1,2,3,...).*



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

Quantization



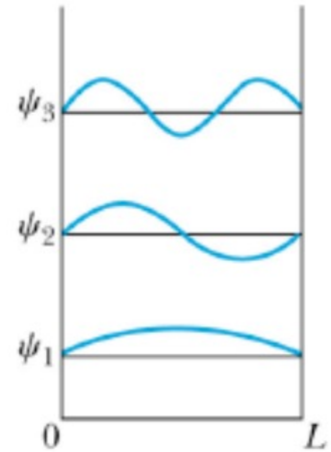
$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$$

- We normalize the wave function:

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

- The normalized wave function becomes

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



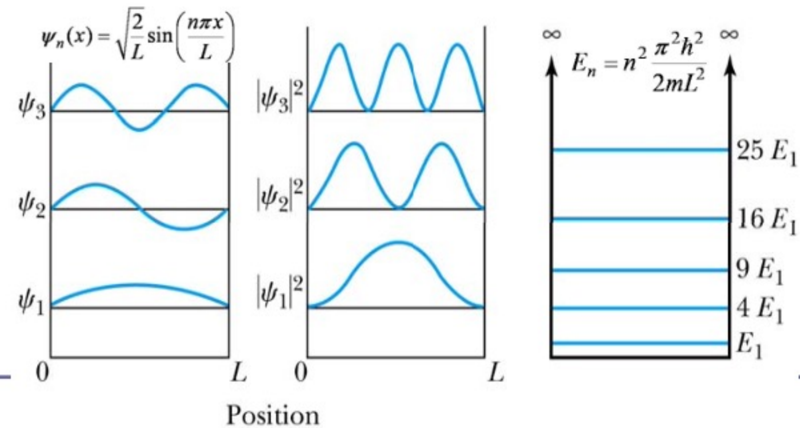
- These functions are identical to those obtained in classical physics for a vibrating string with fixed ends.

Quantized Energy

- The quantized wave number now becomes $k_n = \frac{n\pi}{L} \overset{\downarrow}{=} \sqrt{\frac{2mE_n}{\hbar^2}}$ $k = \sqrt{2mE/\hbar^2}$

- Solving for the energy yields $\boxed{E_n = n^2 \frac{\pi^2\hbar^2}{2mL^2} \qquad (n = 1, 2, 3, \ldots)}$

- 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** ➔ $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$
  - Classically probability is uniform *P(x) = 1/L*
  - For large n classical and quantum results should agree.



- Determine expectation value for p and p^2 of a particle in an infinite square well in the first excited state

The first excited state corresponds to n=2:

$$\psi_2(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$$

$$\langle p\rangle_{n=2}=(-i\hbar)\frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left[\frac{d}{dx}\sin\left(\frac{2\pi x}{L}\right)\right]dx=\frac{4\pi i\hbar}{L^2}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\cos\left(\frac{2\pi x}{L}\right)dx=\frac{2i\hbar}{L}\int_{\sin 0}^{\sin 2\pi} u\,du=0$$

For $< p^2 >$:

$$\langle p^2\rangle_{n=2}=(-i\hbar)^2\frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left[\frac{d^2}{dx^2}\sin\left(\frac{2\pi x}{L}\right)\right]dx$$

$$=\hbar^2\frac{8\pi^2}{L^3}\int_0^L \sin^2\left(\frac{2\pi x}{L}\right)dx=\hbar^2\frac{8\pi^2}{L^3}\left(\frac{L}{2}\right)=\frac{4\pi^2\hbar^2}{L^2}$$

The first excited state corresponds to n=2:

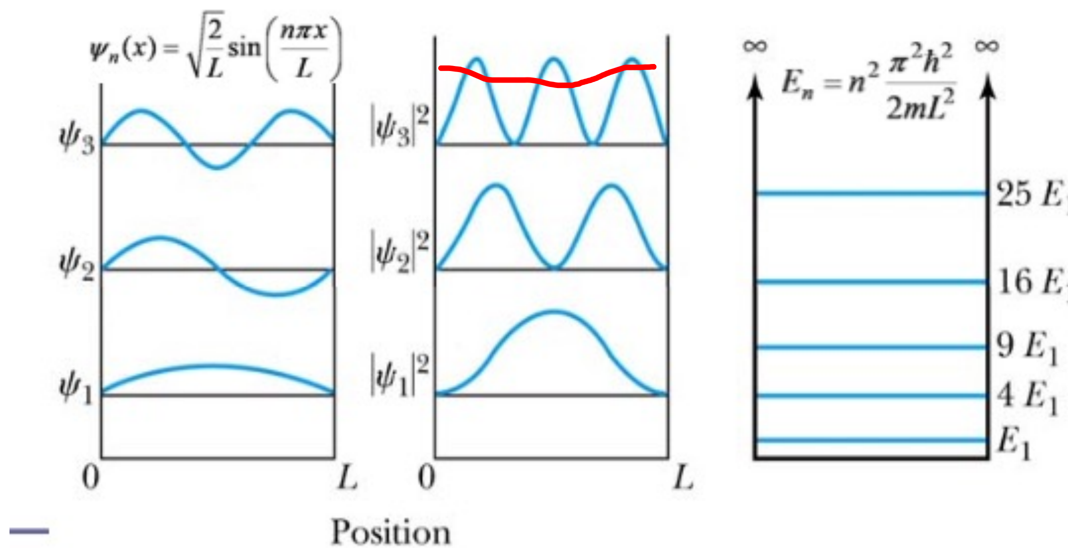
For <p²>:

$$\langle p^2\rangle_{n=2} = (-i\hbar)^2 \frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left[\frac{d^2}{dx^2}\sin\left(\frac{2\pi x}{L}\right)\right]dx$$

$$= \hbar^2 \frac{8\pi^2}{L^3}\int_0^L \sin^2\left(\frac{2\pi x}{L}\right)dx = \hbar^2 \frac{8\pi^2}{L^3}\left(\frac{L}{2}\right) = \frac{4\pi^2\hbar^2}{L^2}$$

→ Comparing with E_2:

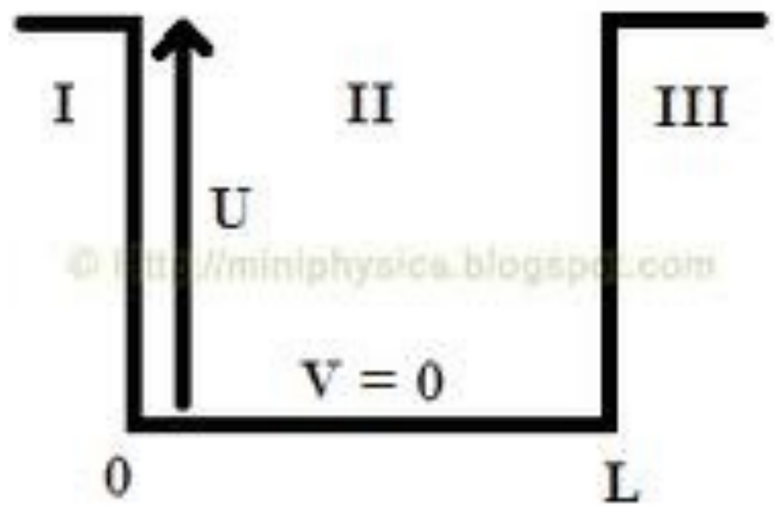
$$E_2 = \frac{4\pi^2\hbar^2}{2mL^2} = \frac{\langle p^2\rangle_{n=2}}{2m}$$



Finite potential well

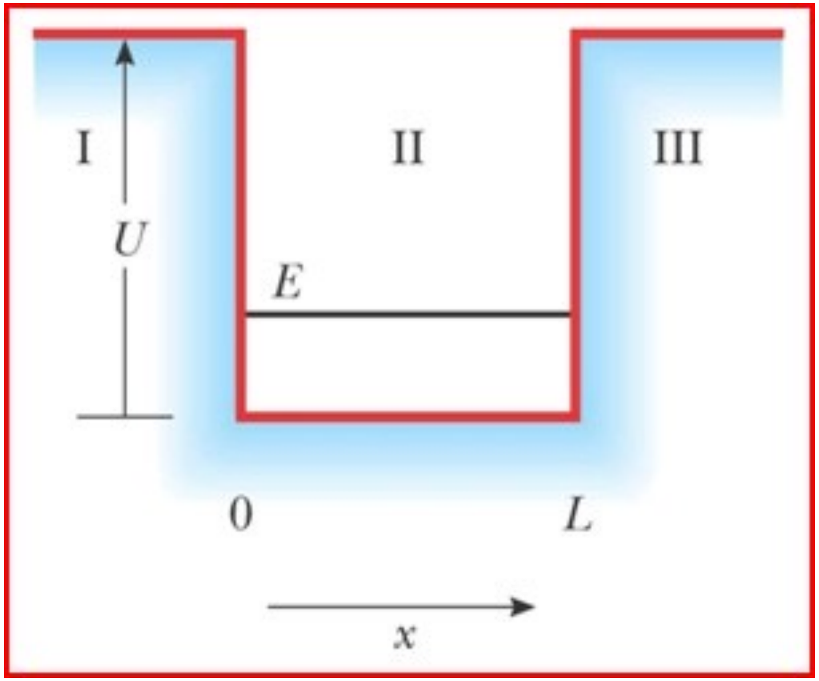
- *More realistic situation:*
  - Potential barrier has finite height (U)

- Let particle's energy E < U
- **C.Mech: Particle bounces back and forth within the well**
- **Q.Mech: Certain probability to enter into I and III**



- SE in region II:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar} E\psi = 0$$

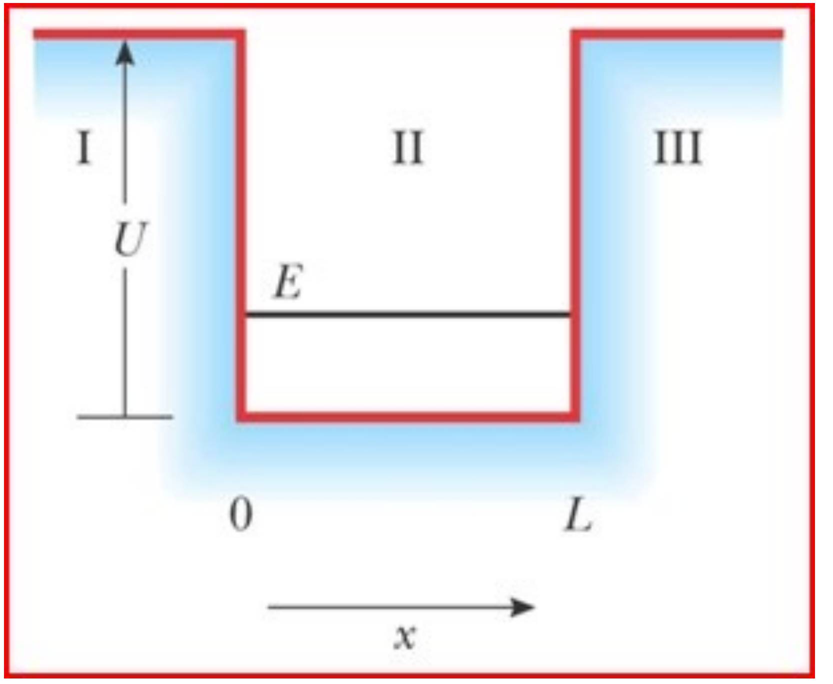


- SE in regions I and III

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar} (E - U)\psi = 0$$

SE in the regions I and III:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$



Which we can write as:

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \qquad \begin{matrix} x < 0 \\ x > L \end{matrix}$$

Where,

$$a = \frac{\sqrt{2m(U - E)}}{\hbar}$$

Solution to this second order differential equation:

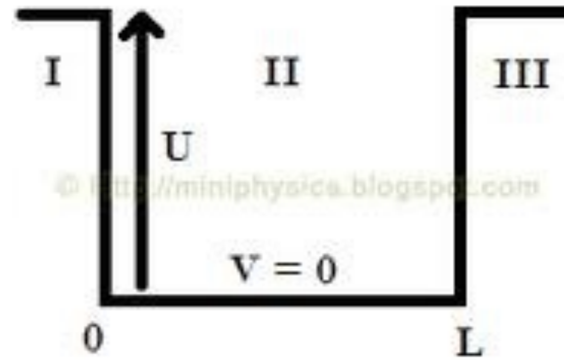
$$\psi_{\mathrm{I}} = Ce^{ax} + De^{-ax}$$

$$\psi_{\mathrm{III}} = Fe^{ax} + Ge^{-ax}$$

SE for particle in a finite potential box

$$\psi_{\mathrm{I}} = Ce^{ax} + De^{-ax}$$

$$\psi_{\mathrm{III}} = Fe^{ax} + Ge^{-ax}$$



Both ψ_I and ψ_{III} must be finite everywhere

$$e^{-ax} \rightarrow \infty \; as \; x \rightarrow -\infty, and \; e^{ax} \rightarrow \infty \; as \; x \rightarrow \infty$$

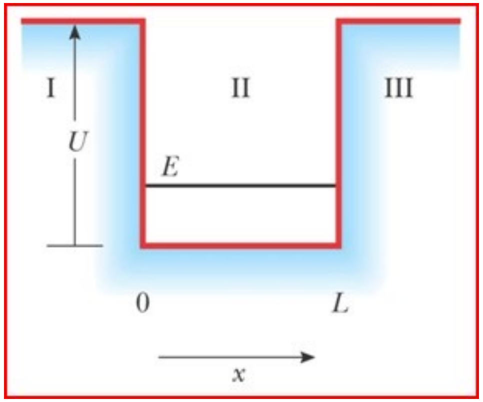
D and F must be zero

$$\psi_{\mathrm{I}} = Ce^{ax}$$

$$\psi_{\mathrm{III}} = Ge^{-ax}$$

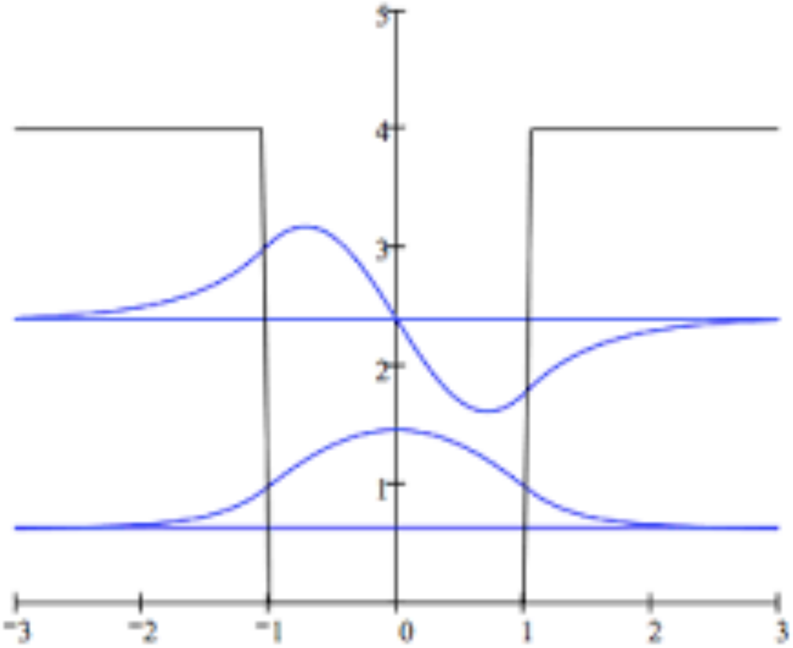
- SE in region II:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar} E\psi = 0$$

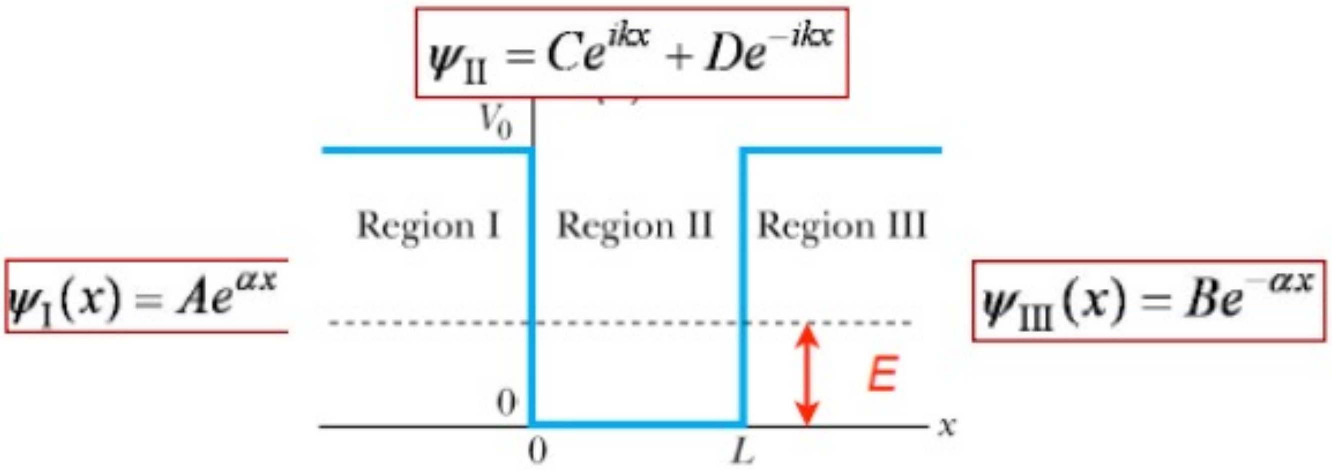


- $\psi_{II} = C\,\frac{sin\sqrt{2mE}}{\hbar}x + D\,\frac{cos\sqrt{2mE}}{\hbar}x$

- $\psi_I = A\,e^{ax}$
- $\psi_{III} = B\,e^{ax}$



Particle in Finite Square-Well:

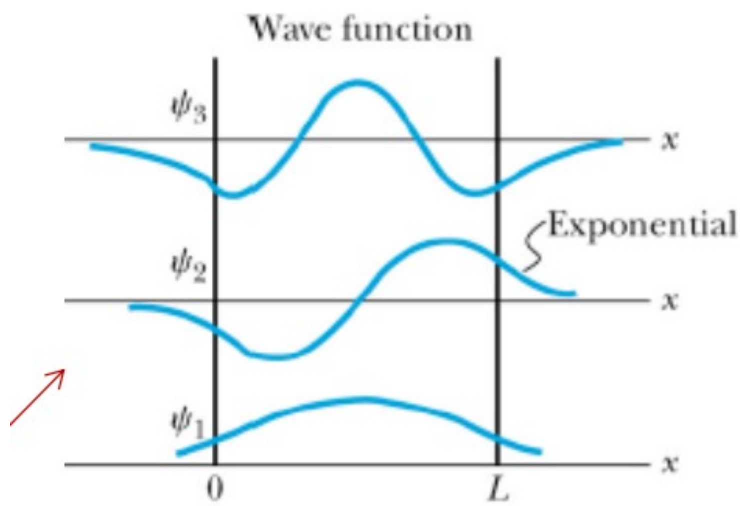


- now apply boundary conditions:

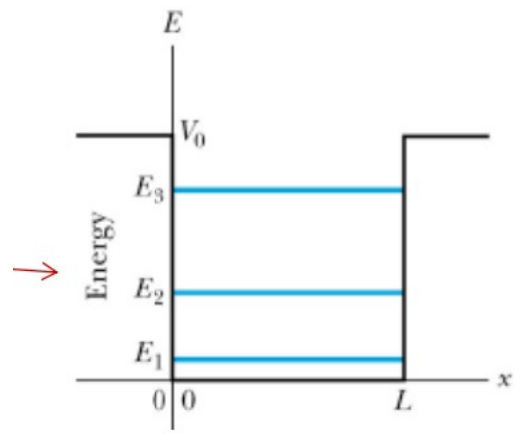
$$\left.\begin{aligned}\psi_I &= \psi_{II}\\ \frac{\partial\psi_I}{\partial x} &= \frac{\partial\psi_{II}}{\partial x}\end{aligned}\right\}\text{at } x=0 \qquad \left.\begin{aligned}\psi_{II} &= \psi_{III}\\ \frac{\partial\psi_{II}}{\partial x} &= \frac{\partial\psi_{III}}{\partial x}\end{aligned}\right\}\text{at } x=L$$

Finite Potential Well Problem:

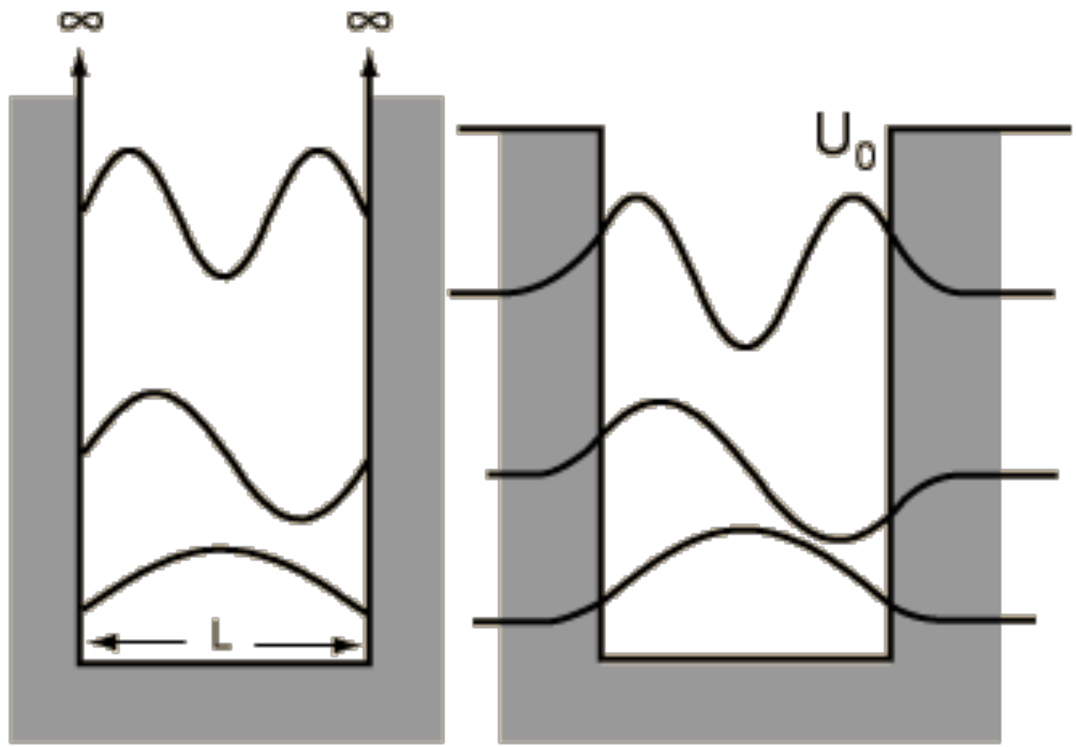
- Applying BC and finding all the unknown coefficients are not straight forward, hence results are shown here graphically
- Similar to the infinite well problem, here also one gets quantized energy levels



Infinite case: the wave
function is
non-zero
outside of the box



Particle in a finite potential well



Comparison with infinite potential well

- Wavelength that fits into well are longer than for infinite potential well (of the same width)
- Corresponding particle momenta are lower ($\lambda = h/p$)
- Energy levels E_n are lower for each n

Exercise 1

- Consider the one-dimensional potential step defined by
- $V(x)=0$, $x<0$,
- $V(x)=V_{0},\ x>0$.
- Suppose a wave incident from the left has energy $E = 4V_0$. What is the probability that the wave will be reflected?

Suppose a proton is confined in a box of width L=1.00x 10^(-14) m (which is atypical nuclear radius). What are the energies of the ground and the first excited states ? If the proton makes a transition from the first excited state to the ground state, what are the energy and the frequency of the emitted photon

- Let is model this problem as particle in a box problem. Mass of the proton is $m = 1.76\ 10^{-27}\ kg$.
- The emitted photon carries away the energy difference $E = E_2 - E_1$
- We can use the relation $E_f = hf$ to find its frequency f
- The ground state energy:

$E_1 = \pi^2 \frac{\hbar^2}{2m\, L^2} = \frac{\pi^2 \left(1.05\ 10^{-34}\ \mathrm{Js}\right)^2}{2(1.67\ 10^{-27}\mathrm{kg})(1.00\ 10^{-14}\mathrm{m})^2}$= 3.28 10^(-13) J = 2.05 MeV

- The first excited state: $E_2 = 2^2\ E_1 = 4(2.05\ MeV) = 8.20\ MeV$
- The energy of the emitted photon:

$$E_f = E = E_2 - E_1 = 8.20\ MeV - 2.05\ MeV = 6.15\ MeV$$

- The frequency of the emitted photon is

$$f = \frac{E_f}{h} = \frac{6.15\ MeV}{4.14\ 10^{-21}\ MeVs} = 1.49\ 10^{21} Hz$$

A Classical Particle in a Box: A small 0.40-kg cart is moving back and forth along an air track between two bumpers located 2.0 m apart. We assume no friction; collisions with the bumpers are perfectly elastic so that between the bumpers, the car maintains a constant speed of 0.50 m/s. Treating the cart as a quantum particle, estimate the value of the principal quantum number that corresponds to its classical energy.

- Let us find the kinetic energy of the cart and its ground state energy E_1 s though it's a quantum particle. The energy of the cart is completely kinetic: $K = n^2 E_1 \rightarrow n = \left(\frac{K}{E_1}\right)^{1/2}$
- The kinetic energy of the cart is: $K = \frac{1}{2} m\, u^2 = \frac{1}{2}\,(0.40\; kg)\left(0.50\,\frac{m}{s}\right)^2 = 0.050\; J.$

Therefore, $n = \left(\frac{K}{E_1}\right)^{\frac{1}{2}} = \left(\frac{0.050}{1.7000\; 10^{-68}}\right)^{\frac{1}{2}} = 1.2\; 10^{33}$

Significance:

- energy of a classical system is characterized by a very large quantum number. Bohr's corr espondence principle concerns this kind of situation.
- We can apply the formalism of quantum mechanics to any kind of system, quantum or cla ssical, and the results are correct in each case.
- In the limit of high quantum numbers, there is no advantage in using quantum formalism because we can obtain the same results with the less complicated formalism of classical mechanics. However, we cannot apply classical formalism to a quantum system in a low-n umber energy state.

- Using the quantum particle in a box model, describe how the possible energies of the particle are related to the size of the box.

- Is it possible that when we measure the energy of a quantum particle in a box, the measurement may return a smaller value than the ground state energy?

- What is the highest value of the energy that we can measure for this particle?

- For an infinite square well, the spacing between energy levels increases with the quantum number *n*. The *smallest* energy measured corresponds to the transition from *n* = 2 to 1, which is three times the ground state energy.

The largest *energy* measured corresponds to a transition from $n = \infty$ to 1, which is infinity. (Note: Even particles with extremely large energies remain bound to an infinite square well—they can never “escape”)

- For a quantum particle in a box, the first excited state has zero value at the midpoint position in the box, so that the probability density of finding a particle at this point is exactly zero.

- Explain what is wrong with the following reasoning:

“If the probability of finding a quantum particle at the midpoint is zero, the particle is never at this point, right? How does it come then that the particle can cross this point on its way from the left side to the right side of the box?

HA2

- Electrons of kinetic energy 10 eV travel a distance of 2 km. If the size of the initial wave packet is 10^{-9} m, estimate the size at the and of their travel.

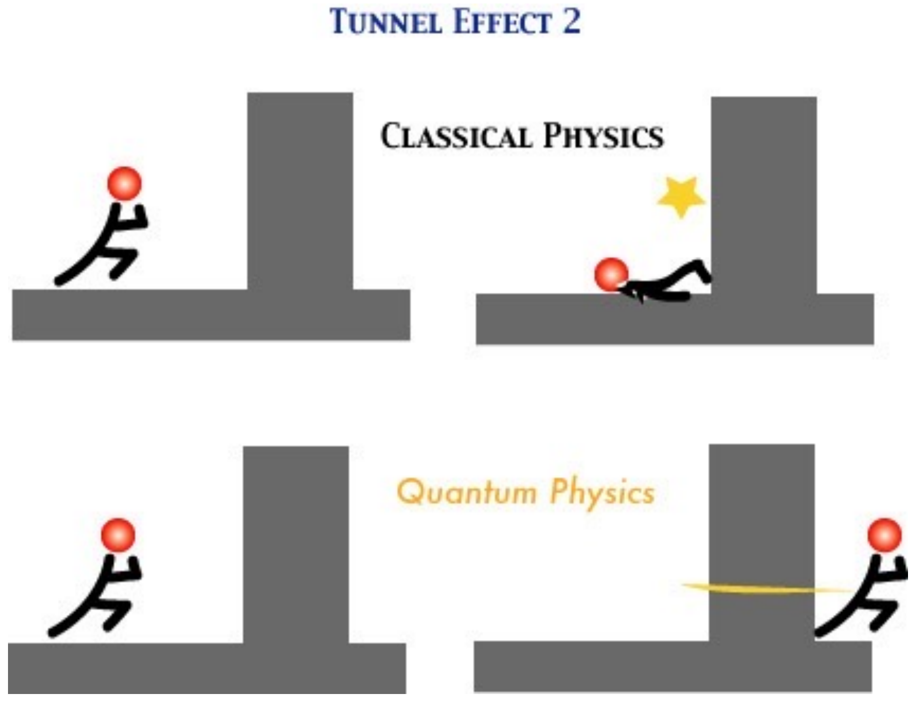
Home Assignment

- Use the uncertainty relation to find an estimate of the ground state energy of the harmonic oscillator. The energy of the harmonic oscillator is :

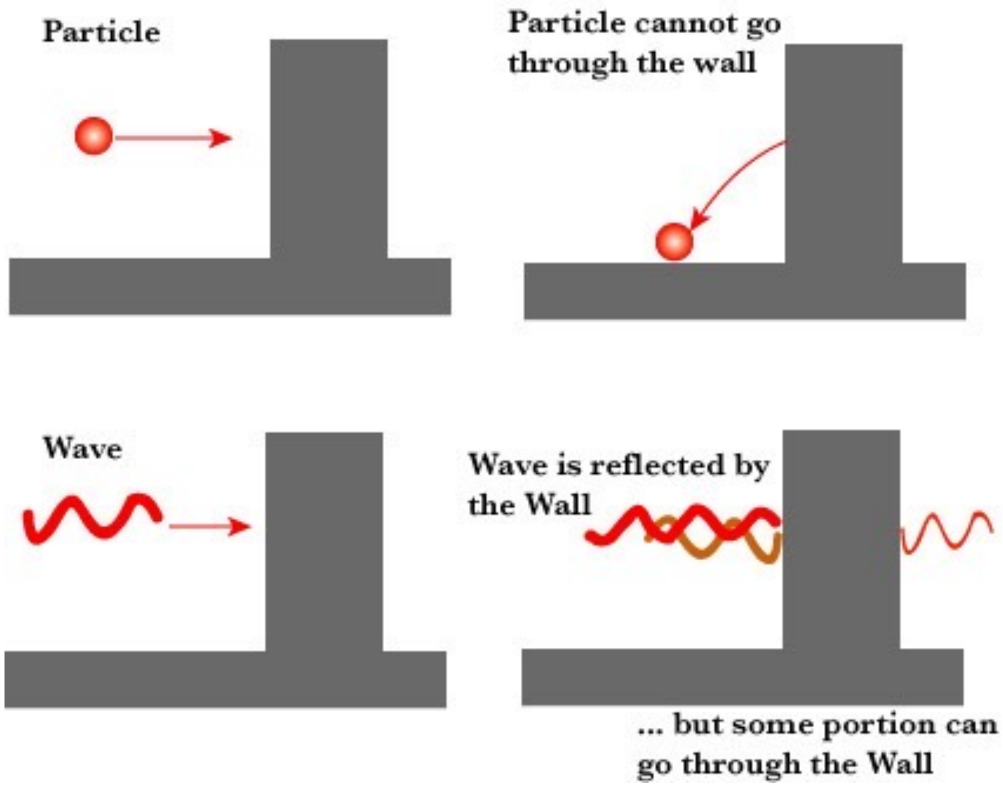
$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

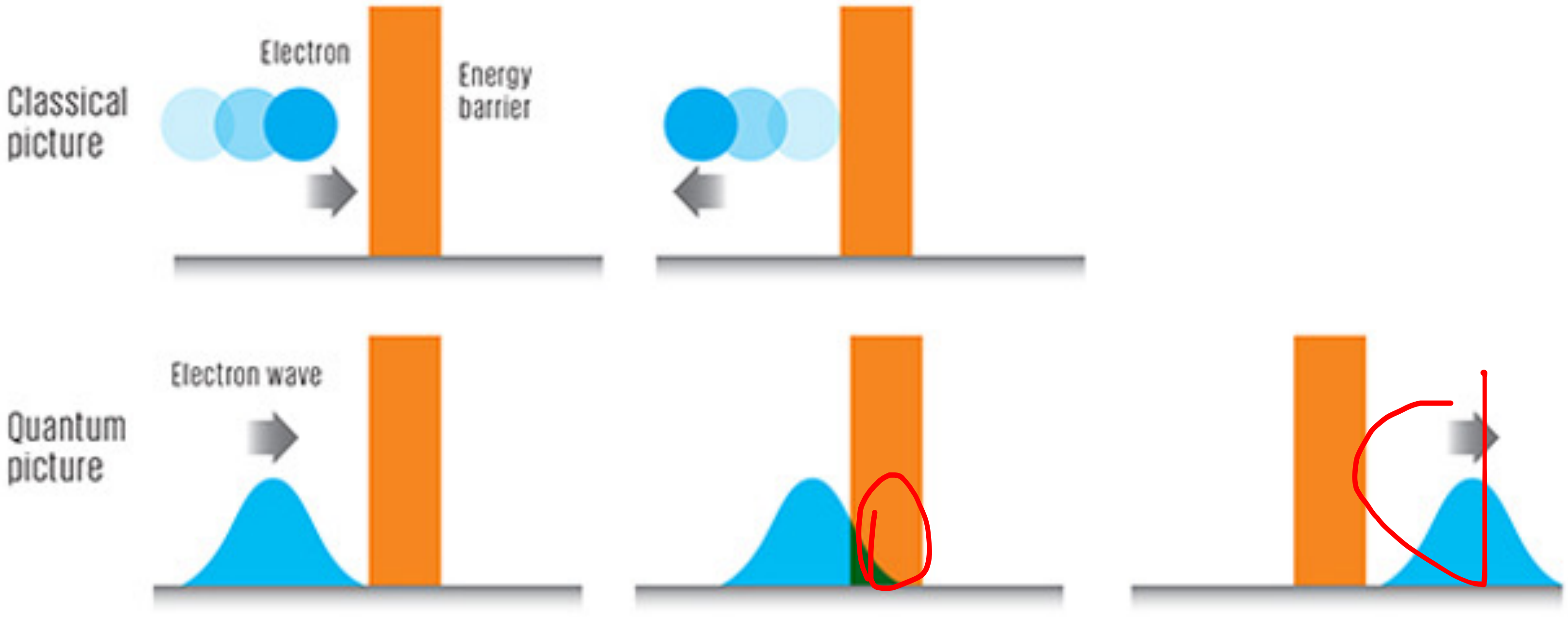
Tunnel Effect

- ***<u>A particle without the energy to pass over a potential barrier may still tunnel through it</u>***



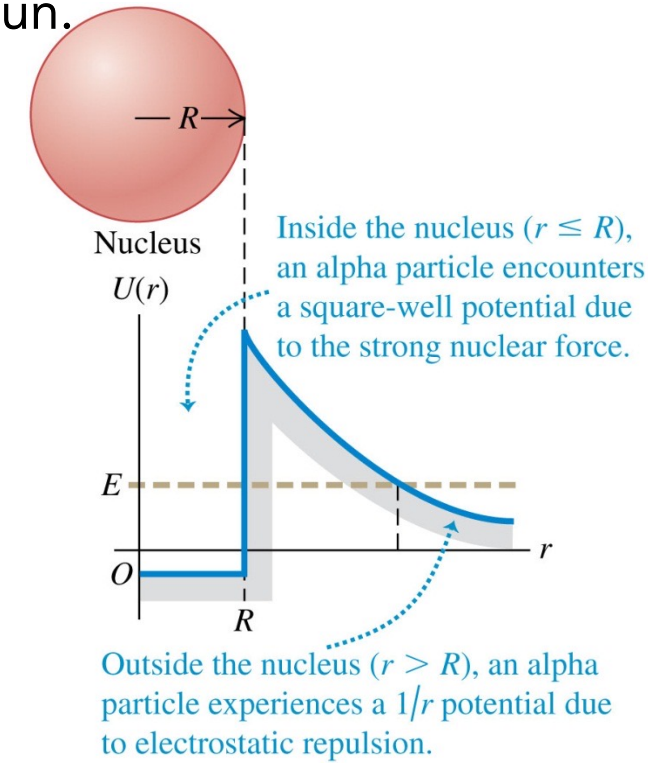
Tunnel Effect



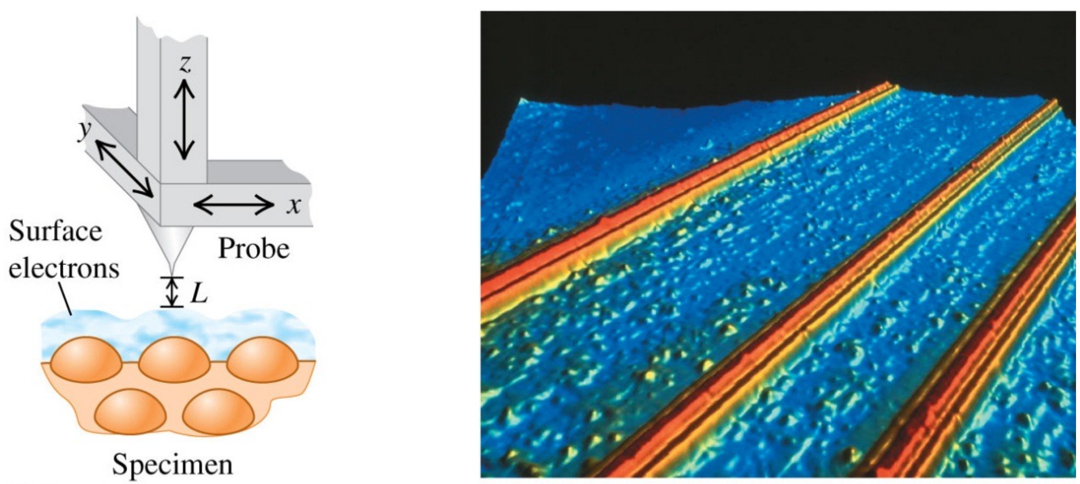

Classical picture
Electron
Energy barrier
Quantum picture
Electron wave

Applications of tunneling

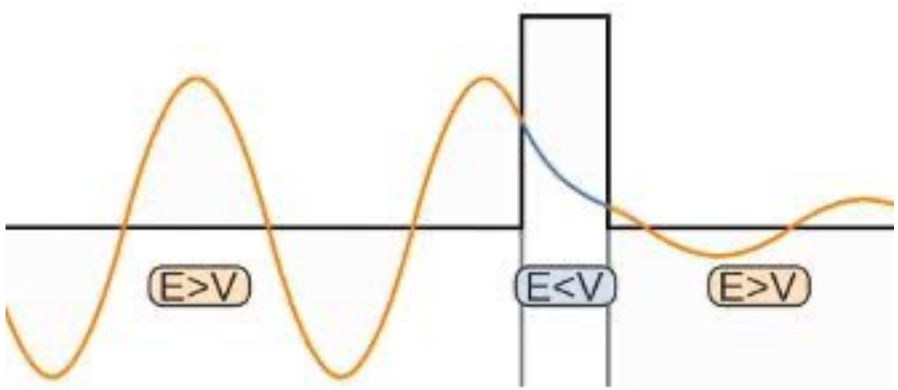
- A scanning tunneling microscope measures the atomic topography of a surface. It does this by measuring the current of electrons tunneling between the surface and a probe with a sharp tip. As the tip nears an atom, the barrier gets thinner, so the current indicates how close the atom is to the tip (the height of the surface)
- An alpha particle inside an unstable nucleus can only escape via tunneling. The reverse happens in fusion, such as what goes on in the Sun.



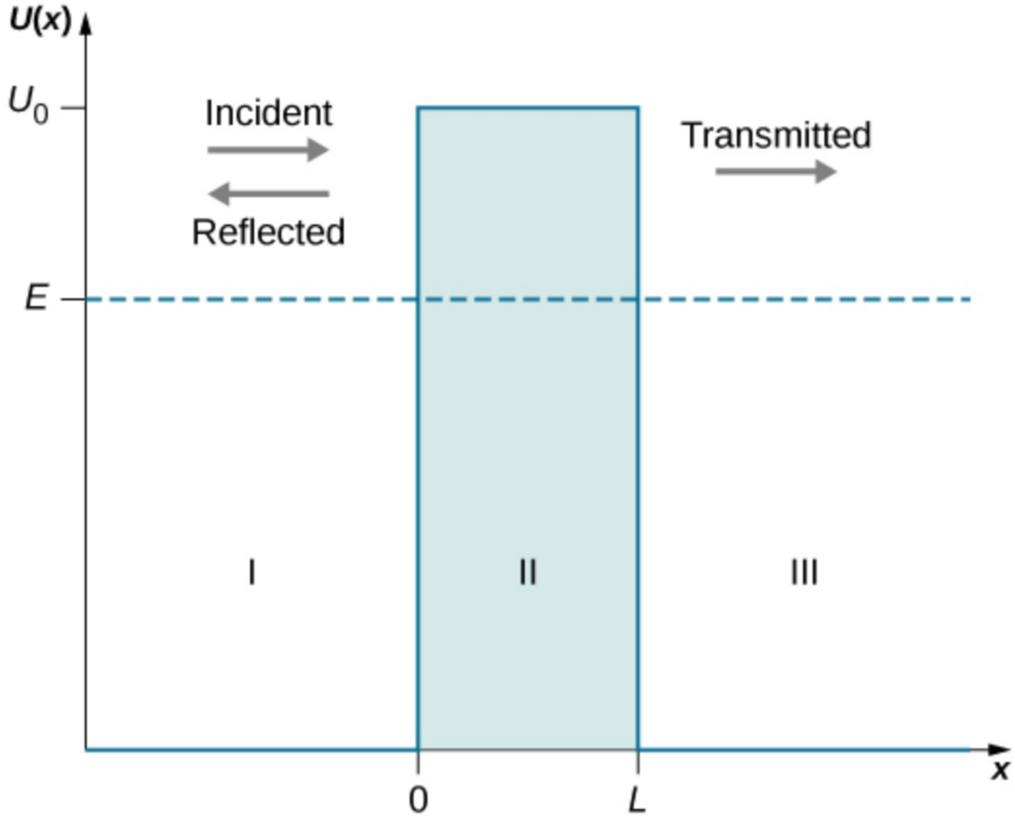
(a) (b)



- Examples:
  - alpha particles emitted by certain radioactive nuclei (radioactivity 1896)
  - Shining stars
- Tunnel diode :
  - type of semiconductor diode capable of very fast operation, well into microwave frequency region (led noble prize to Leo Esaki in 1973)
- Scanning tunneling microscope
  - To study surfaces on an atomic scale of size
  - Noble prize in 1986



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



file:///Users/SARIKA%201/Sarika/IITI/Teaching/7.7%20Quantum%20Tunneling%20of%20Particles%20through%20Potential%20Barriers%20-%20Physics%20LibreTexts.html

Probability of Reflection and Transmission

- The probability of the particles being reflected *R* or transmitted *T* is:

$$R = \frac{|\psi_{\mathrm{I}}(\text{reflected})|^2}{|\psi_{\mathrm{I}}(\text{incident})|^2} = \frac{B^* B}{A^* A}$$

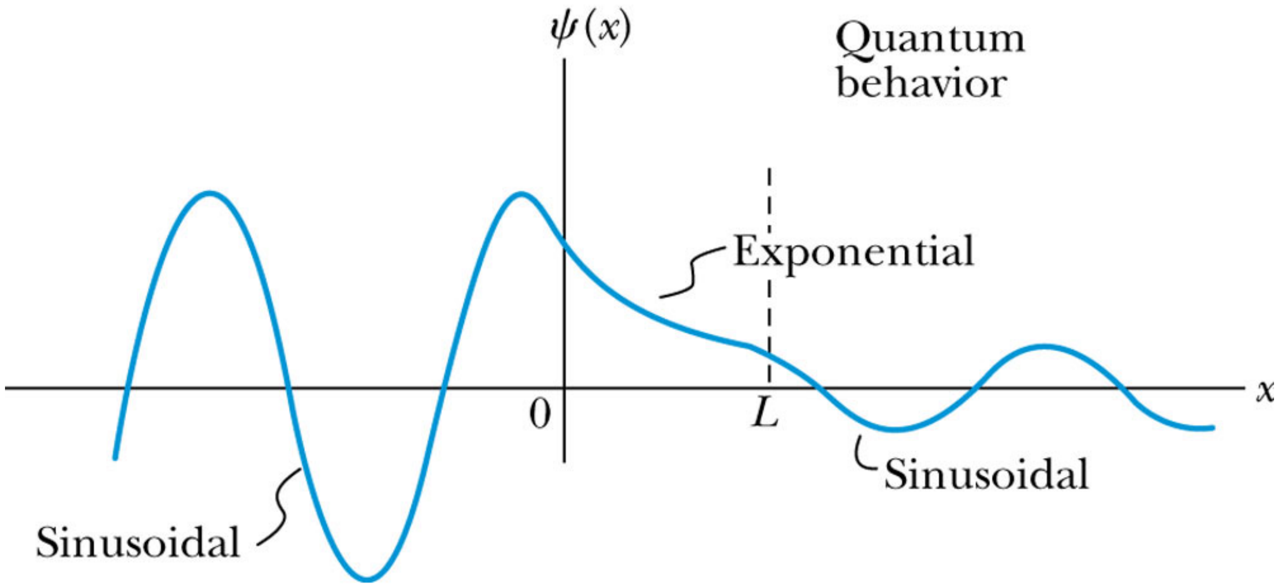
$$T = \frac{|\psi_{\mathrm{III}}(\text{transmitted})|^2}{|\psi_{\mathrm{I}}(\text{incident})|^2} = \frac{F^* F}{A^* A}$$

- The maximum kinetic energy of the photoelectrons depends on the value of the light frequency *f* and not on the intensity.
- Because the particles must be either reflected or transmitted we have: $R + T = 1$.
- By applying the boundary conditions $x \to \pm\infty$, $x = 0$, and $x = L$, we arrive at the transmission probability:

$$T = \left[1 + \frac{V_0^{\,2} \sin^2(k_{\mathrm{II}} L)}{4E(E - V_0)}\right]^{-1}$$

HA. Show that there is a situation in which the transmission probability is 1.

Uncertainty Explanation



- Region I: incidence and transmitted
- Region III: transmitted
- Region II: Ψ does not oscillate

- Approximate transmission probability:

$$T = \exp\left(-2k_2 L\right)$$

Where,

$$k_2 = \frac{\sqrt{2m(U-E)}}{\hbar}$$

L is width of the barrier

The Schrodinger recipe

- Begin by writing SE with appropriate U(x) (note U(x) may be discontinuous but not $\psi(x)$)
- Find generalized mathematical function which is solution to the above equation
- Applying BC's
- Continuity condition for $\psi(x)$ and $\partial\Psi/\partial x$

Validity of SE equation

- Schrodinger equation we solved for the wave function of free particle (U= constant)

- ***How it would apply to any general case (U=U(x,y,z,t)) ???***

HA

- Two copper nanowires are insulated by a copper oxide nano-layer that provides a 10.0-eV potential barrier. Estimate the tunnelling probability between the nanowires by 7.00-eV electrons through a 5.00-nm thick oxide layer. What if the thickness of the layer were reduced to just 1.00 nm? What if the energy of electrons were increased to 9.00 eV?

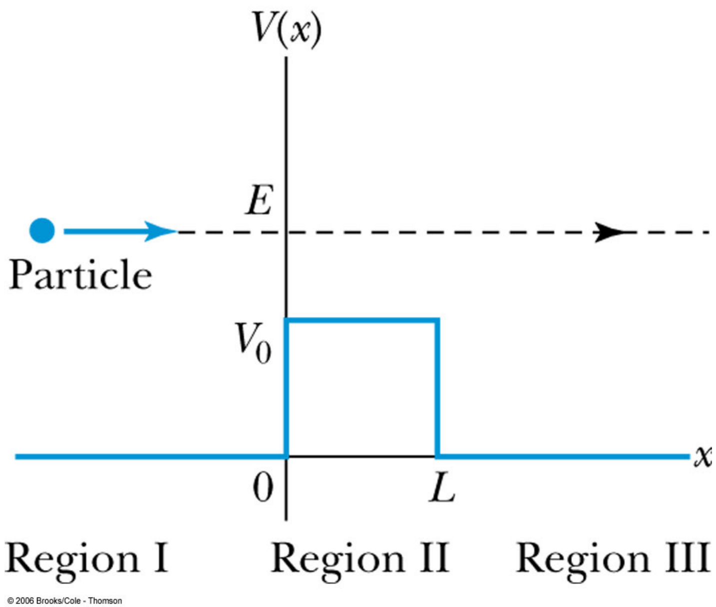
Step Potential Problem

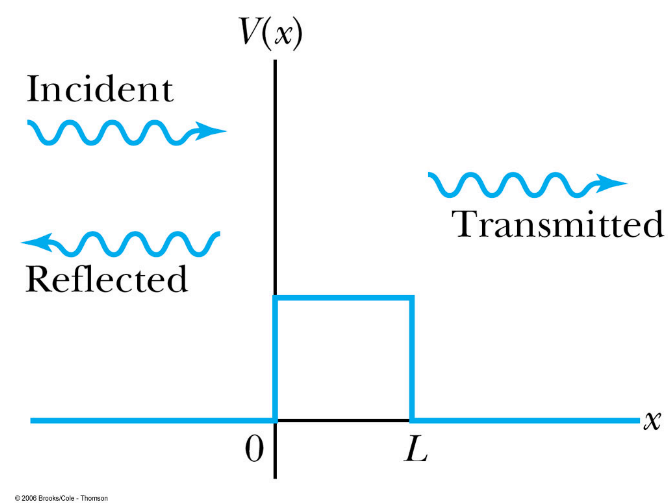
- Consider a particle of energy E approaching a potential barrier of height V_0 and the potential everywhere else is zero.
- We will first consider the case when the energy is greater than the potential barrier.
- In regions I and III the wave numbers are:

$$k_{\mathrm{I}} = k_{\mathrm{III}} = \frac{\sqrt{2mE}}{\hbar}$$

- In the barrier region we have

$$k_{\mathrm{II}} = \frac{\sqrt{2m(E - V_0)}}{\hbar} \qquad \text{where } V = V_0$$





Reflection and Transmission

- The wave function will consist of an incident wave, a reflected wave, and a transmitted wave
- The potentials and the Schrödinger wave equation for the three regions are as follows:

Region I $(x<0)$	$V=0$	$\dfrac{d^2\psi_1}{dx^2}+\dfrac{2m}{\hbar^2}E\psi_1=0$
Region II $(0<x<L)$	$V=V_0$	$\dfrac{d^2\psi_{\mathrm{II}}}{dx^2}+\dfrac{2m}{\hbar^2}(E-V_0)\psi_{\mathrm{II}}=0$
Region III $(x>L)$	$V=0$	$\dfrac{d^2\psi_{\mathrm{III}}}{dx^2}+\dfrac{2m}{\hbar^2}E\psi_{\mathrm{III}}=0$

- The corresponding solutions are:

Region I $(x<0)$	$\psi_{\mathrm{I}}=Ae^{ik_{\mathrm{I}}x}+Be^{-ik_{\mathrm{I}}x}$
Region II $(0<x<L)$	$\psi_{\mathrm{II}}=Ce^{ik_{\mathrm{II}}x}+De^{-ik_{\mathrm{II}}x}$
Region III $(x>L)$	$\psi_{\mathrm{III}}=Fe^{ik_{\mathrm{I}}x}+Ge^{-ik_{\mathrm{I}}x}$

- As the wave moves from left to right, we can simplify the wave functions to:

Incident wave	$\psi_{\mathrm{I}}(\text{incident})=Ae^{ik_{\mathrm{I}}x}$
Reflected wave	$\psi_{\mathrm{I}}(\text{reflected})=Be^{-ik_{\mathrm{I}}x}$
Transmitted wave	$\psi_{\mathrm{III}}(\text{transmitted})=Fe^{ik_{\mathrm{I}}x}$

HA1 : particle in potential well

A particle of mass m is inside a one-dimensional infinite well with walls a distance L apart. One of the walls is suddenly moved by a distance L so that the wall separation becomes $2L$. The wall moves so suddenly that the particle wave function has no time to change during the motion. Suppose that the particle is originally in the ground state.

(a) What is its energy E_0 and wave function y_0 before the width is doubled?

(b) What are the energy eigenvalues **after** the width is doubled?

(c) If we measure the energy **after** the width is doubled, what is the probability that it will not change?

(d) If we measure the energy **after** the width is doubled, what is the probability that the particle have lost some energy?

(e) What is the expectation value of the energy before and after the doubling of the width?

hint

- For a particle in an infinite well we have :

$$\psi_n = A \sin\left(\frac{\sqrt{2mE_n}}{\hbar}\, x\right)$$

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

$$E_n = \frac{n^2 h^2}{8\, m\, L^2}$$

Home assignment 2

- You are given a one dimensional potential barrier of height V which extends from $x=0$ to $x=a$. A particle of mass m and energy $E<V$ is incident from the left.
- (a) Derive expressions for the coefficients of transmission T and reflection R for the barrier.
- (b) Show that $T+R=1$.

- Consider an electron in the ground state of a one-dimensional box.
- It is exposed to electromagnetic radiation.
- Under the influence of this "perturbation" the electron moves into a state that is a time-dependent linear superposition of the ground state and the manifold of excited states

$$\psi = c_1.\psi_1 \exp(-i\, E_i\, t) + \sum_{n=2}^{\infty} c_n.\psi_n .\ \exp\,(-i\, E_n t)$$

Linearity and superposition

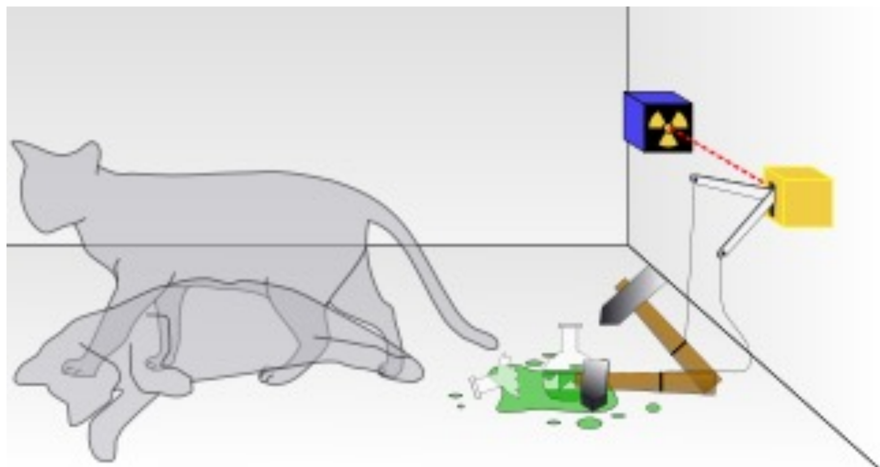
- SE is linear =>

$$\underline{\psi = a1\ \psi1 + a2\ \psi2}$$

is also a solution => *interference effects can occur for wave functions as they can for light, sound, water, EM*

$$P1=\psi1^{*}\psi1$$

$$P2=\psi2^{*}\psi2$$



Schrodinger’s cat

Ref: Qunatum mechanics by Merschbekar

Double slit experiment (1800)

(voted most beautiful experiment till date)

- Young's experiment vanquishing the theory of light proposed by Isaac Newton (17th and 18th centuries).

- discovery of the photoelectric effect demonstrated that under different circumstances, light can behave as if it's composed of discrete particles

<u>goes beyond classical physics and takes quantum nature into account</u>

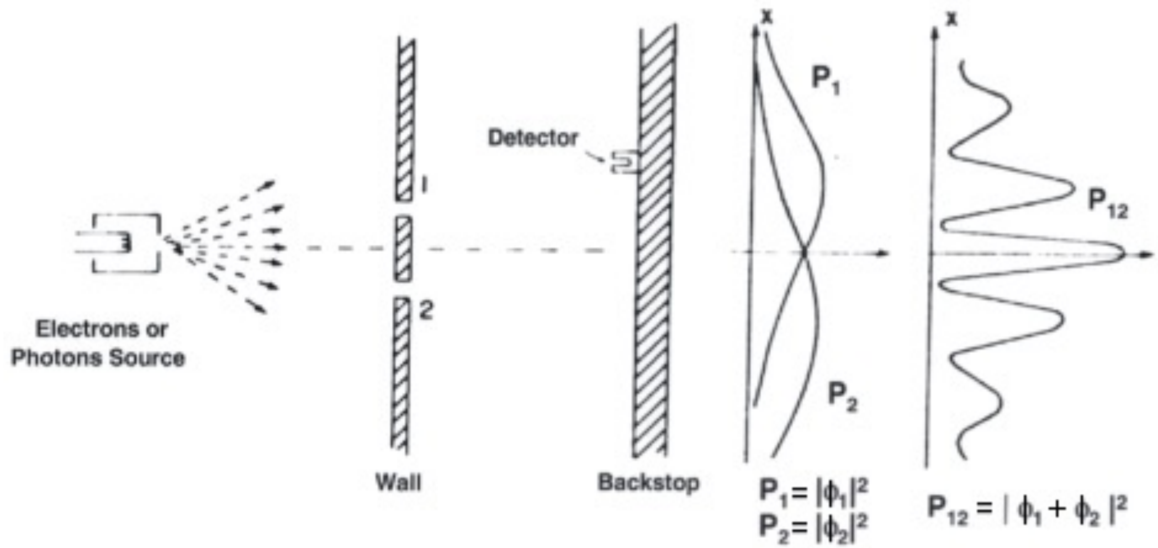


Figure 2. The double-slit experiment.

- **Measurement in Quantum theory**

Fact:

- In Quantum mechanics, variables can take set of values **=> a state in quantum theory is superposition of different states**
- Let $\psi 1$: has position x1

$\Psi 2$: has position x2

The superposed state: $c1\ \psi 1 + c2\ \psi 2$

- When experiment gives value x1 => system collapses into $\psi 1$ after the measurement

EPR paradox

- Let two spin particles A and B (physically far away from each other).
- Now let us consider the state with combined A+B with total zero spin
  - $\Psi 1$ = A(up) B(down)
  - $\Psi 2$ = A(down)B(up)
- Now let us have one state:

$$\Psi = \psi 1 + \psi 2$$

If measurement (on say A) is done and found that its in up => Ψ collapses into $\Psi 1$

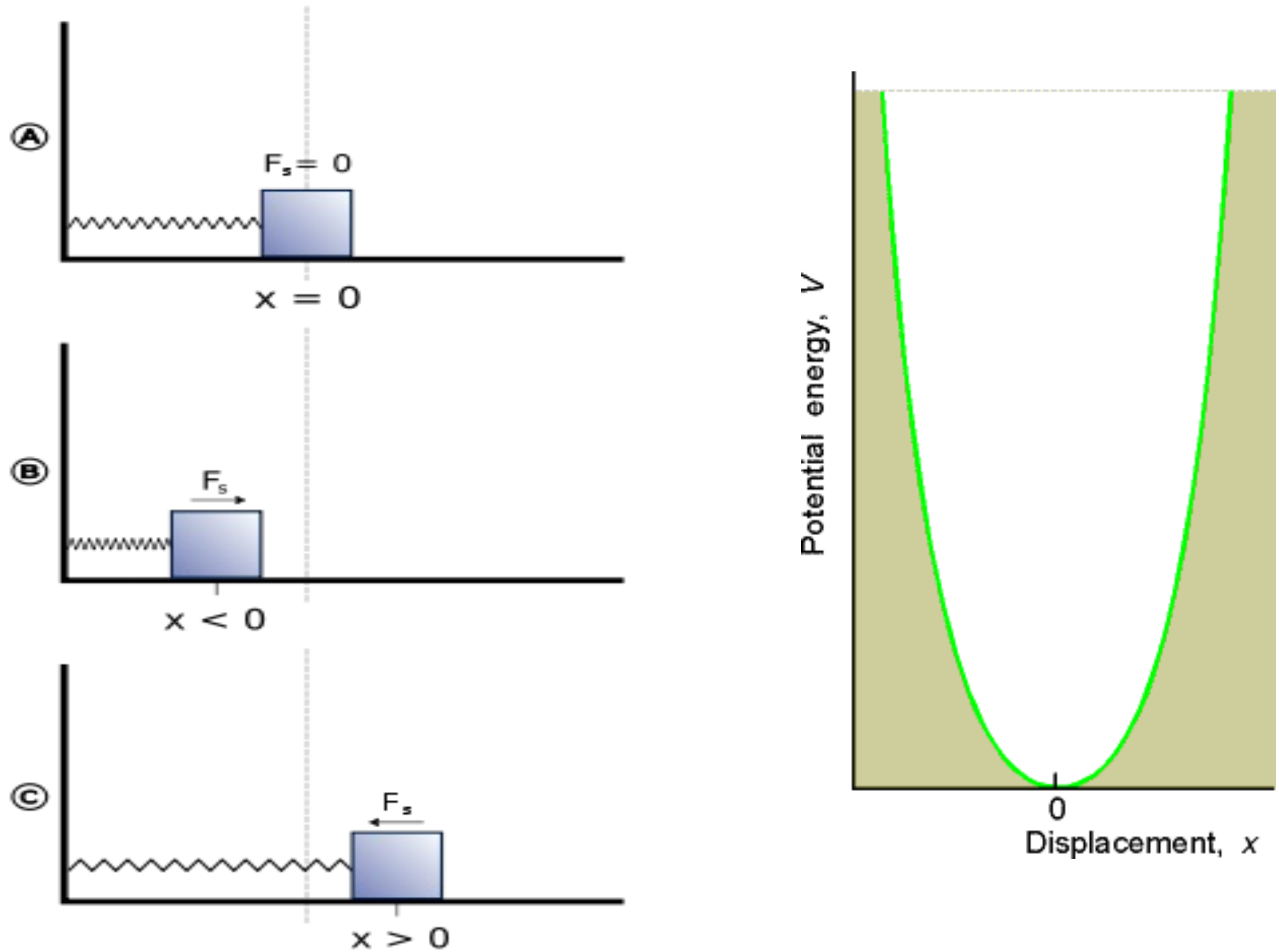
Harmonic Oscillator

The Classical Harmonic Oscillator

- A vibrating body subject to a restoring force, which increases in proportion to the displacement from equilibrium, will undergo harmonic motion at constant frequency and is called a harmonic oscillator.

- When the system is at equilibrium, the mass will be at rest, and at this point the displacement, *x, from equilibrium has the value zero. As the mass is pulled to the right, there will be a restoring* force, *f, which is proportional to the displacement. For a spring obeying Hooke's law,*

$$\underline{f = -kx = m\ d\hat{\ }2x/dt\hat{\ }2}$$



A
F_s = 0
x = 0
B
F_s
x < 0
C
F_s
x > 0
Potential energy, V
0
Displacement, x

- The equation of motion is a second order ordinary differential equation,

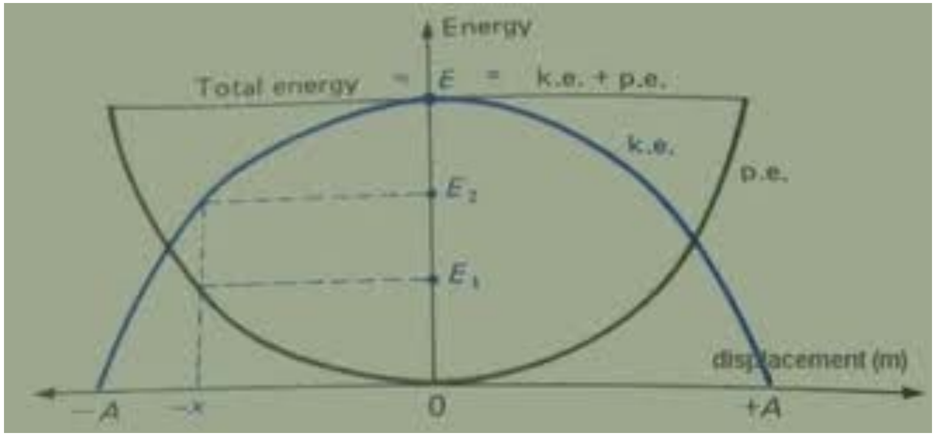
$$F = ma = m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -kx.$$

<u>General solution:</u>

X(t) = A sin ωt + B cos ωt,

Where $\omega = \sqrt{k/m}$

BC: B=0

- Total energy (E + U) would be constant
- 

- The probability of finding the mass at any given value of x is inversely proportional to the velocity : ***the faster the mass is moving, the less likely it is to observe the mass*.**
- the probability of observing the mass is minimum at x = 0, where velocity is at maximum and maxima when x = ±A.

Quantum Oscillator

(quantum-mechanical analog of the classical harmonic oscillator)

- Example: vibrations of the atoms in a diatomic molecule about their equilibrium position and the **oscillations** of atoms or ions of a crystalline lattice. Also the energy of electromagnetic waves in a cavity can be looked upon as the energy of a large set of **harmonic oscillators**

The Schrodinger equation for a harmonic oscillator:

$$\frac{-\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2}+\frac{1}{2}m\omega^2x^2\Psi(x)=E\Psi(x)$$

Where $\omega=\sqrt{k/m}$

Since the derivative of the wavefunction must give back the square of x plus a constant times the original function, the following form is suggested:

$$\Psi(x)=Ce^{-\alpha x^2/2}$$

- Exercise: Normalize ψ

For serious readers

- We can solve the differential equation in the coordinate basis, using a spectral method. It turns out that there is a family of solutions.

- Spectral methods: are a class of techniques used in applied mathematics and scientific computing to numerically solve Dynamical Systems, involving the use of the FFT

- Substituting this function into the Schrodinger equation by evaluating the second derivative gives:

$$\frac{d\Psi}{dx} = -C\frac{\alpha}{2}e^{-\alpha x^2/2}2x$$

$$\frac{d^2\Psi}{dx^2} = -C\alpha e^{-\alpha x^2/2} + C\alpha^2 x^2 e^{-\alpha x^2/2}$$

$$\frac{-\hbar^2}{2m}\left[-\alpha + \alpha^2 x^2\right]\Psi + \frac{1}{2}m\omega^2 x^2 \Psi = E\Psi$$

For this to be a solution to the Schrodinger equation for all values of x, the coefficients of each power of x must be equal.

- Setting the coefficients of the square of x equal to each other:

$$\frac{-\hbar^2\alpha^2}{2m}+\frac{1}{2}m\omega^2=0 \qquad\qquad \alpha=\frac{m\omega}{\hbar}$$

Setting the constant terms equal gives:

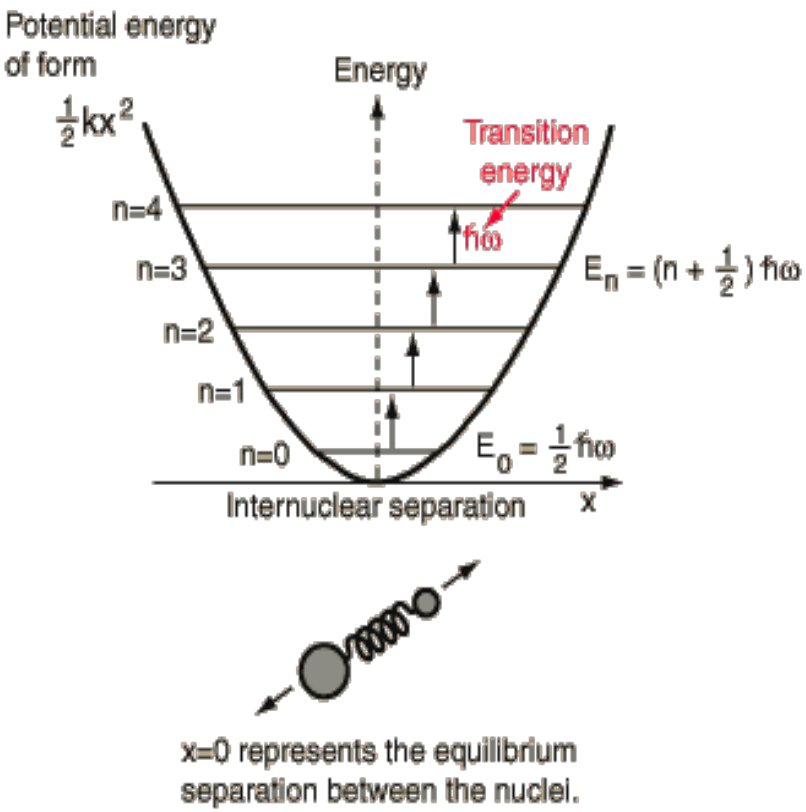
$$\frac{-\hbar^2}{2m}\frac{m\omega}{\hbar}=E_0=\frac{\hbar\omega}{2}$$

<u>Smallest energy allowed by the uncertainty principle</u>

zero point energy
$E=1/2\ h\ \nu$

- This is a very significant physical result:
  - *It tells that the energy of system described by a harmonic oscillator potential can not have zero energy.*
  - Physical systems (such as atoms in a solid lattice or polyatomic molecules in a gas) can not have zero energy *"even at absolute zero temperature"*

- The energy levels of the Quantum harmonic oscillator are:



$$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad n = 0,1,2,3 \ldots$$

$$\omega = 2\pi(\text{frequency})$$

$$\hbar = \text{Planck's constant}/2\pi$$

<u>All energy levels are evenly spaced</u>

Quantization of energy levels

- The discrete values for the allowed energies of the oscillator would go "***unnoticed"*** if spacing is too small "*to be detected*"

- Macroscopic level: m=0.01 kg (say) on a spring with k=0.1N/m
- Atomic level: Hydrogen molecule k=510.5 N/m, reduced mass=8.37 X 10^(-28) kg

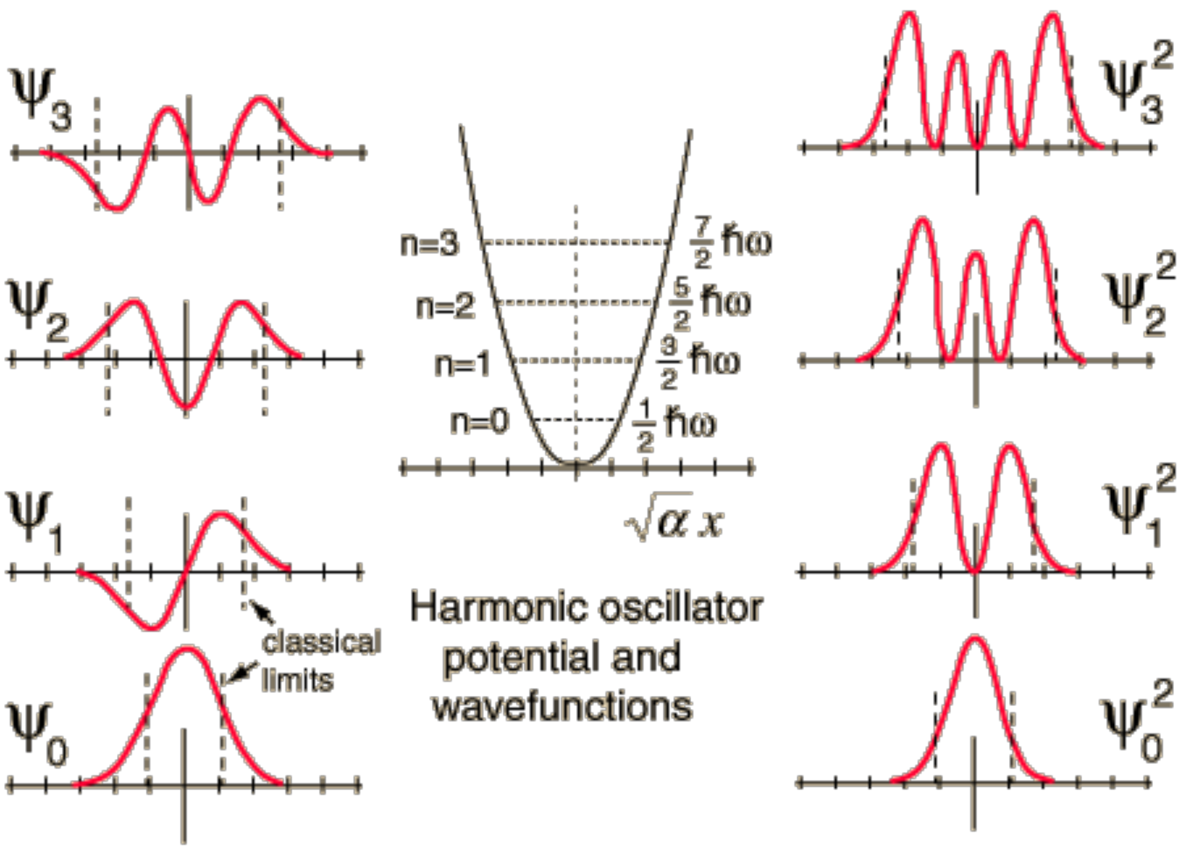
- For macroscopic region: $\omega = 3.16$ rad/s

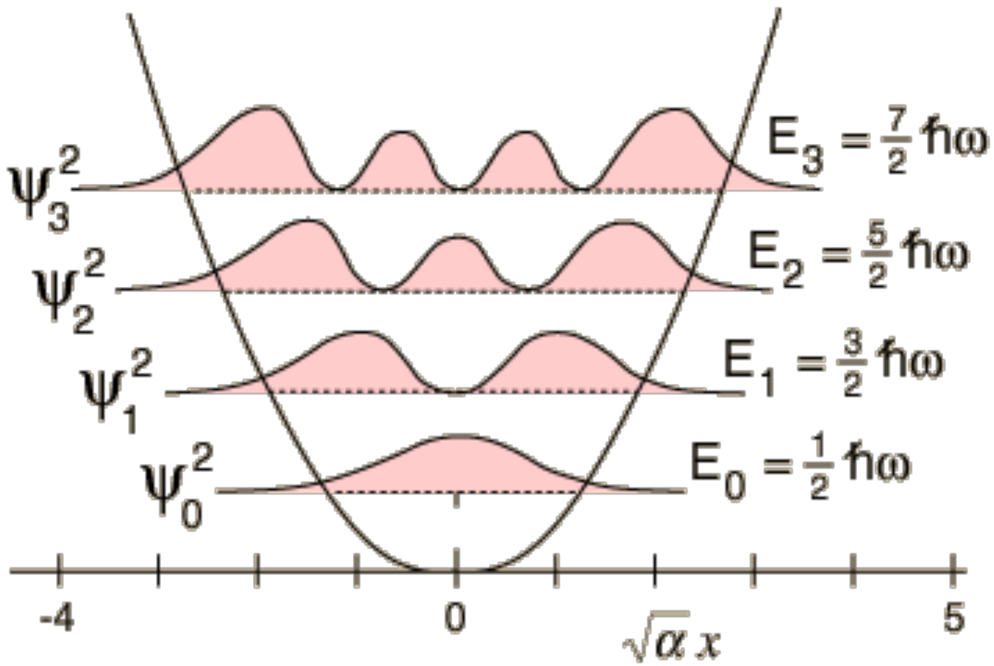
  $\Delta E = \hbar\omega = 2.08 \times 10^{-15}$ eV

For Hydrogen atom: $\omega = 7.81 \times 10^{14}$ rad/s

$\Delta E = 0.531$ eV

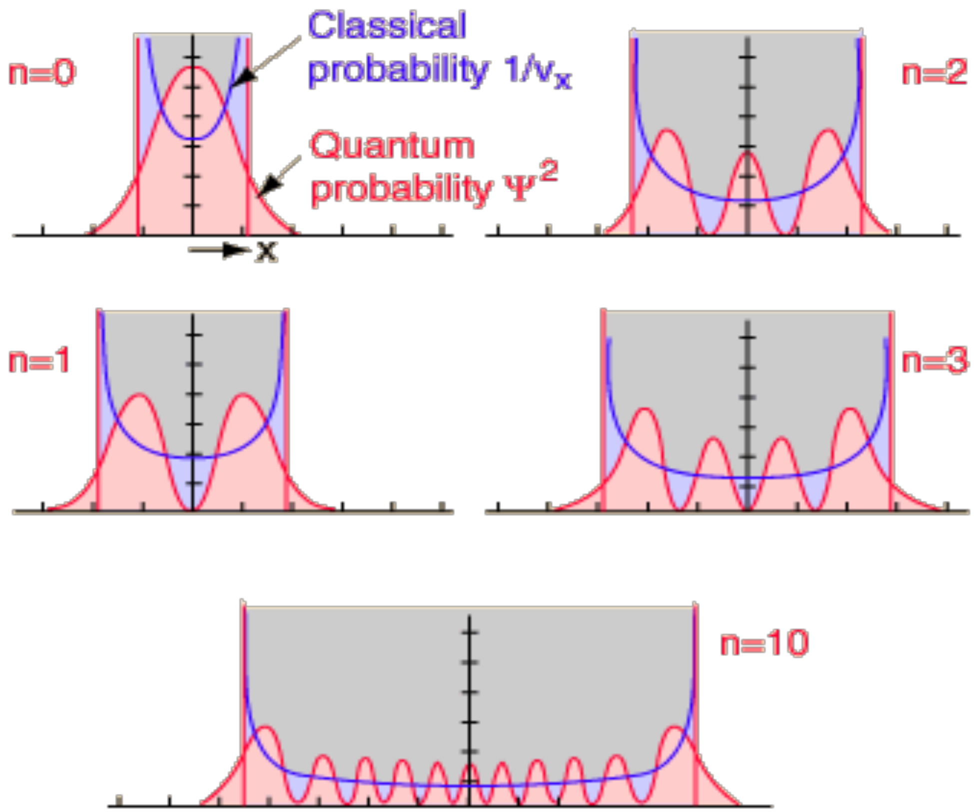
Wave function and probability





There would be finite probability that the oscillator would be found outside the “potential well”

Comparison between classical and Quantum



Exercise:

- Find the expectation value <x> for the first two states of the harmonic oscillator

- Calculate the probability that a quantum oscillator in its ground state will be found outside the range permitted for a classical oscillator with the same energy

Vibrational Energies of the Hydrogen Chloride Molecule

The HCl diatomic molecule consists of one chlorine atom and one hydrogen atom. Because the chlorine atom is 35 times more massive than the hydrogen atom, the vibrations of the HCl molecule can be quite well approximated by assuming that the Cl atom is motionless and the H atom performs harmonic oscillations due to an elastic molecular force modeled by Hooke's law. The infrared vibrational spectrum measured for hydrogen chloride has the lowest-frequency line centered at $f = 8.88 \ 10^{13}\,\text{Hz}.$.

What is the spacing between the vibrational energies of this molecule?
What is the force constant *k* of the atomic bond in the HCl molecule?

Strategy The lowest-frequency line corresponds to the emission of lowest-frequency photons. These photons are emitted when the molecule makes a transition between two adjacent vibrational energy levels. Assuming that energy levels are equally spaced, we use (Figure) to estimate the spacing. The molecule is well approximated by treating the Cl atom as being infinitely heavy and the H atom as the mass *m* that performs the oscillations. Treating this molecular system as a classical oscillator, the force constant is found from the classical relation $k = m\omega^2.$.

1. A particle of mass m moves in a one-dimensional box of length L, with boundaries at x = 0 and x = L. Thus, $V(x) = 0$ for $0 \le x \le L$, and $V(x) = \infty$ elsewhere. The normalized eigenfunctions of the Hamiltonian for this system are given by $\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \mathrm{Sin}\frac{n\pi x}{L}$, with $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$, where the quantum number n can take on the values n=1,2,3,....

a. Assuming that the particle is in an eigenstate, $\Psi_n(x)$, calculate the probability that the particle is found somewhere in the region $0 \le x \le \frac{L}{4}$. Show how this probability depends on n.

b. For what value of n is there the largest probability of finding the particle in $0 \le x \le \frac{L}{4}$?

c. Now assume that Ψ is a superposition of two eigenstates, $\Psi = a\Psi_n + b\Psi_m$, at time t = 0. What is Ψ at time t? What energy expectation value does Ψ have at time t and how does this relate to its value at t = 0?

d. For an experimental measurement which is capable of distinguishing systems in state Ψ_n from those in Ψ_m, what fraction of a large number of systems each described by Ψ will be observed to be in Ψ_n? What energies will these experimental measurements find and with what probabilities?

e. For those systems originally in $\Psi = a\Psi_n + b\Psi_m$ which were observed to be in Ψ_n at time t, what state (Ψ_n, Ψ_m, or whatever) will they be found in if a second experimental measurement is made at a time t' later than t?

f. Suppose by some method (which need not concern us at this time) the system has been prepared in a nonstationary state (that is, it is not an eigenfunction of **H**). At the time of a measurement of the particle's energy, this state is specified by the normalized wavefunction $\Psi = \left(\frac{30}{L^5}\right)^{1/2} x(L-x)$ for $0 \le x \le L$, and $\Psi = 0$ elsewhere. What is the probability that a measurement of the energy of the particle will give the value $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$ for any given value of n?

Quantum Theory of Hydrogen atom

- Electron with charge (-e), bound by the force of electrostatic attraction to the nucleus with charge (+Ze)
- Z: atomic number (for hydrogen atom Z=1)
- Attractive force which binds electron is Coulomb force, and its associated potential energy

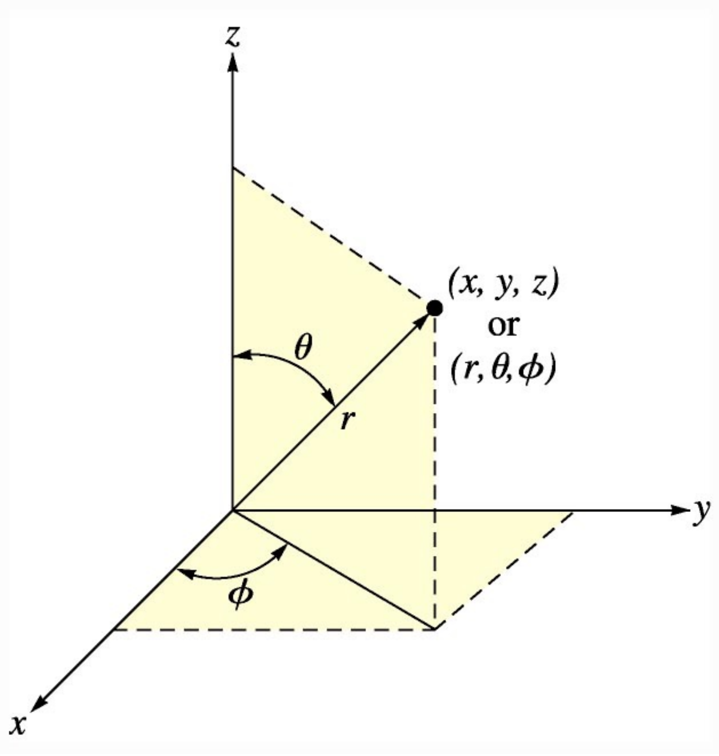
$$\mathbf{U(r) = k\,(+Ze)\,(-e)/r}$$

- k: coulomb constant

- (1) SE for the hydrogen atom in 3-d
-
- Hydrogen atom potential energy is given by:

$$U(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

The radial dependence of the potential suggests that we should switch from Cartesian coordinates to spherical polar coordinates



r = interparticle distance

θ = angle between radius vector and +z axis

Φ = measures rotation in "xy plane" : azimuth angle

SE in 3-d

$$\frac{-\hbar^2}{2m}\nabla^2\Psi + U(r,\theta,\phi)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

SE in spherical coordinates

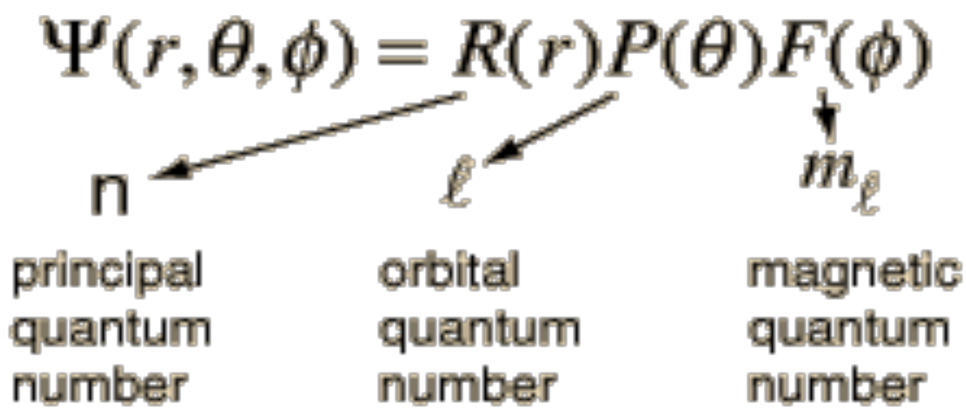
$$\frac{-\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right]$$

$$+U(r)\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

- Can be solved using separation of variable

The hydrogen atom

- The solution is managed by separating the variables so that the wavefunction is represented by the product:



The separation leads to three equations for the three spatial variables, and their solutions give rise to **three quantum numbers** associated with the hydrogen energy levels.

Quantum numbers

- The solution to the **radial equation** can exist only when a constant which arises in the solution is restricted to integer values. This gives the **principal quantum number**:
- $$R(r) \xrightarrow{\text{Solution exists if and only if ...}} n = 1,2,3 \ldots$$

Similarly, a constant arises in the equation for θ which gives the **orbital quantum number**:

$$P(\theta) \xrightarrow{\text{Solution exists if and only if ...}} \ell = 0,1,2,3,\ldots n-1$$

- Finally, constraints on the azimuthal equation give what is called the **magnetic quantum number**:

$$F(\phi) \xrightarrow[\text{if and only if ...}]{\text{Solution exists}} m_\ell = -\ell, -\ell + 1, \ldots + \ell$$

m lying between +l and –l guarantees that z component of angular momentum never exceeds the magnitude of the vector

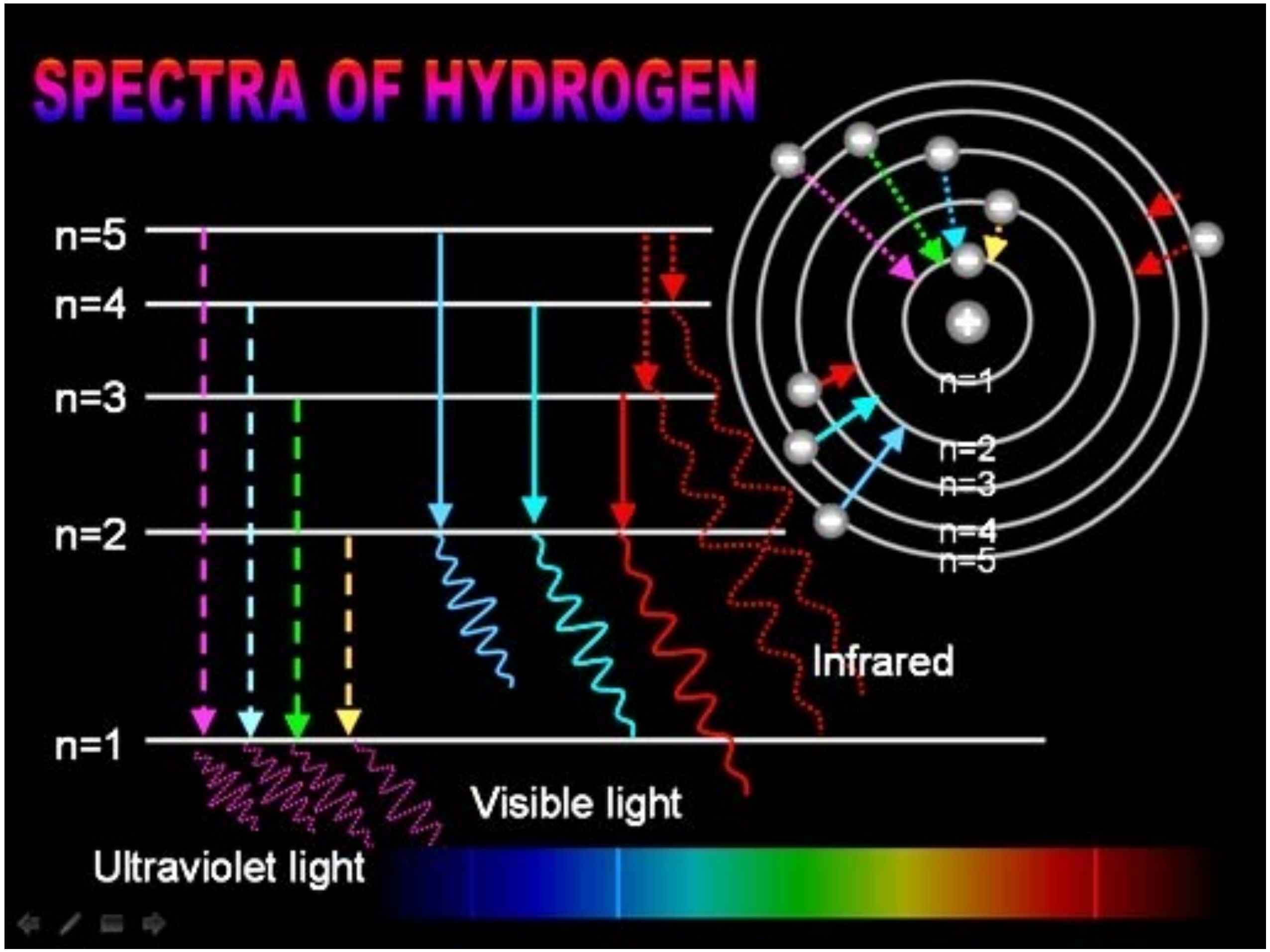
- **We can characterize the wavefunctions based on the quantum numbers (n,l,m)**

Energy levels and Q numbers

- Energy arises from the solution of the radial part of SE:

$$E_n = \frac{-me^4}{8\varepsilon_0^2 h^2}\,\frac{1}{n^2} = \frac{-13.6eV}{n^2} \qquad n = 1,2,3,\ldots$$

For hydrogen and other nuclei stripped to one electron, the energy depends only upon the principal quantum number n.


SPECTRA OF HYDROGEN
n=5
n=4
n=3
n=2
n=1
n=1
n=2
n=3
n=4
n=5
Infrared
Visible light
Ultraviolet light

Exercise:

- Enumerate all states of the hydrogen atom corresponding to the principle quantum number n=4, giving spectroscopic designation to each.

- Calculate the energies of each states.

Relevance of Q.Numbers

- In the solution to the SE for the hydrogen atom, 3 quantum numbers arise from the space geometry of the solution and a fourth arises from electron spin.

- **Pauli exclusion principle**: *No two electrons can have an identical set of Q numbers, so the Q numbers set limits on the number of electrons which can occupy a given state and therefore give insight into the building up of the periodic table of the elements.*

Orbital shapes

Naming orbitals is done as follows

– n is simply referred to by the quantum number

– l (0 to n-1) is given a letter value as follows:

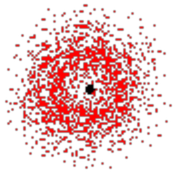
$$0 = s,\ 1 = p,\ 2 = d,\ 3 = f$$

- Lowest energy orbital: "1s orbital" (n=1,l=0,m=0)

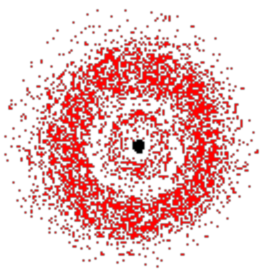
  $\Psi = 1/\sqrt{\Pi}\ (Z/a0)^{3/2}\ \exp(-Z/a0)r$
- a0: Bohr radius
- Probability $= \Psi^*\ \Psi$

Orbital Shapes

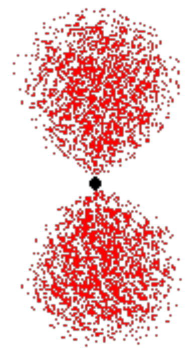
- s (l = 0) orbitals (r dependence only)



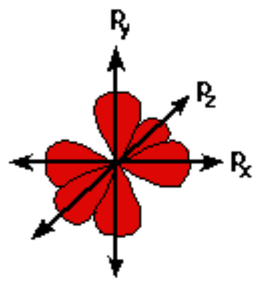
a 1s orbital

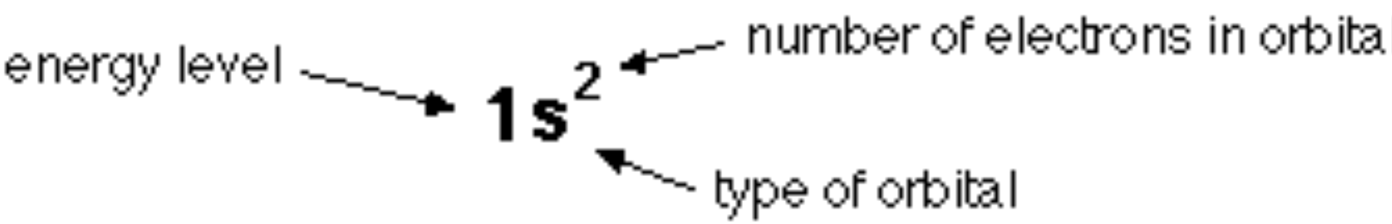


a 2s orbital



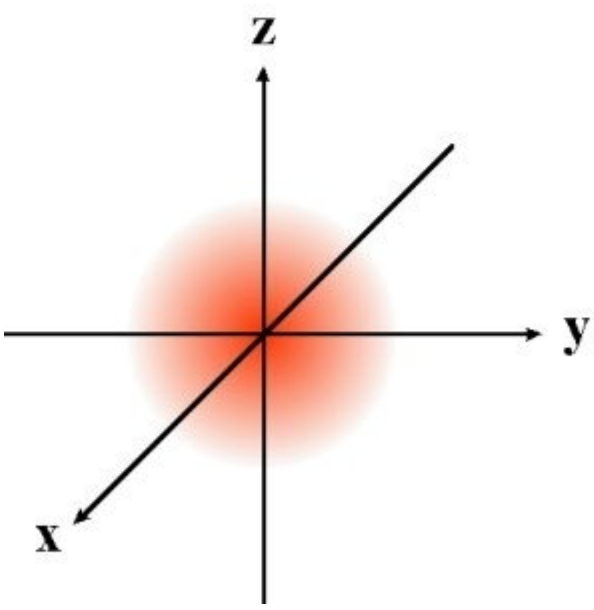
a p orbital





Departure from the Bohr model

- In the Bohr model, the electron is in a ***defined orbit***, in the Schrödinger model we can speak only of probability distributions
- Example: an electron in the ground state in a Hydrogen atom would have a probability distribution

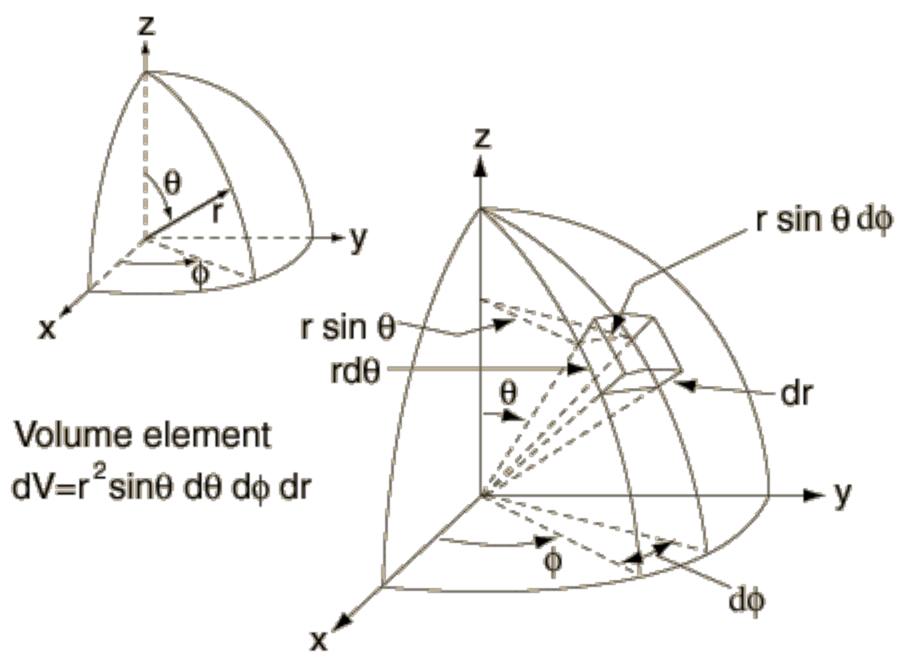


Exercise

- Calculate the probability that the electron in the ground state of hydrogen will be found outside the first Bohr radius

Exercise

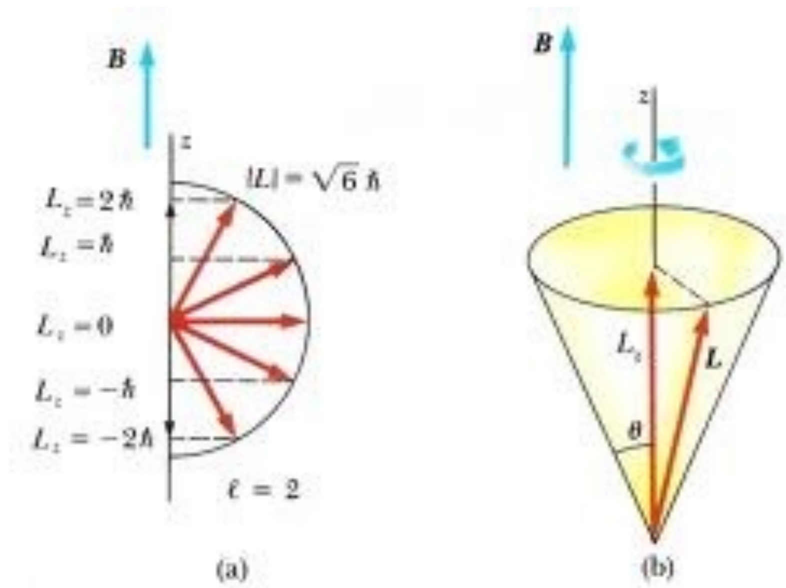
- Verify that average value of 1/r for a 1s electron in the hydrogen atom is 1/a0
  - $dV = (dr)\ (r\ d\ \theta)\ (r \sin\theta\ d\phi)$



- ***Principle quantum number 'n'***
- Has integral values of 1, 2, 3, etc, are denoted by **K, L, M, …**
- As n increases the electron density is further away from the nucleus
- As n increases the electron has a higher energy and is less tightly bound to the nucleus

- ***Orbital (second) quantum number 'l'*** Has integral values from 0 to (n-1) for each value of n
- Instead of being listed as a numerical value, typically 'l' is referred to by a letter (***'s'=0, 'p'=1, 'd'=2, 'f'=3***)
- Defines the ***shape*** of the orbital:
- total angular momentum= $\sqrt{l(l+1)}\hbar$

- ***Magnetic (third) quantum number 'm_l'*** Has integral values between 'l' and -'l', including 0
- Describes **the orientation** of the orbital in space
- l_z = m_l ħ

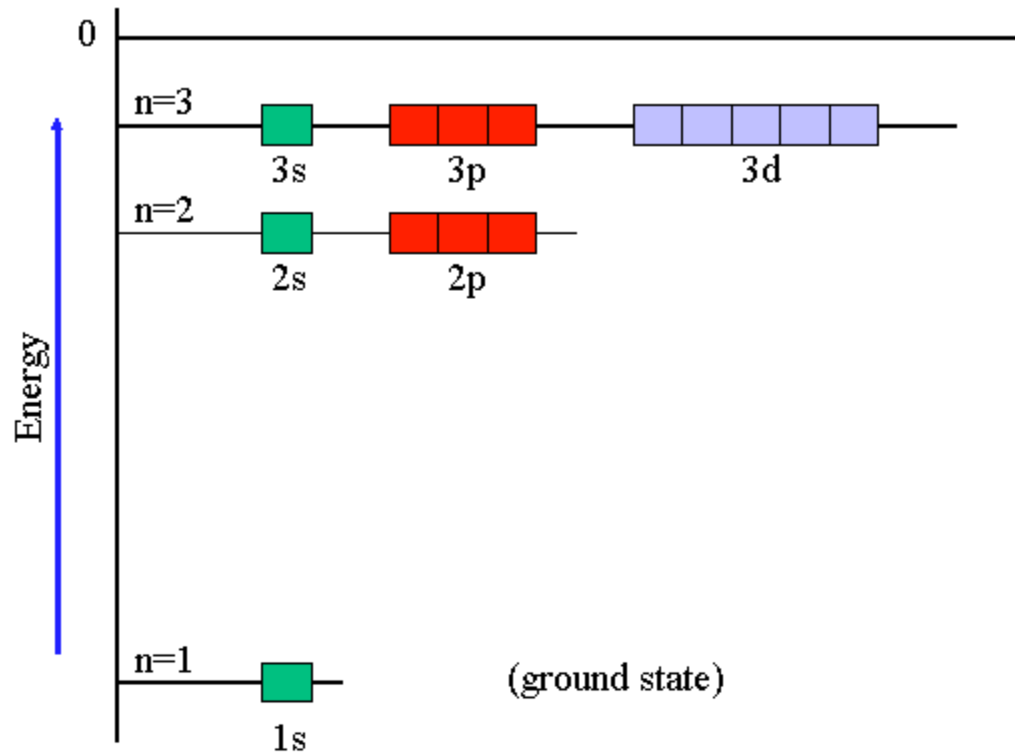


Allowed projections of the orbital angular momentum for the case l=2. Orbital angular momentum L lies on the surface of a cone. L_x and L_y change continually while L_z maintains the fixed value m_l ℏ

Exercise on space quantization

- Consider an atomic electron in the $l=3$ state. Calculate the magnitude of the total angular momentum, and the allowed value of z-component of angular momentum

The number and relative energies of all hydrogen electron orbitals



Home exercise

- A particle of mass m moves in one dimension in the potential . $V(x) = \frac{m\omega^2}{2}x^2$
- Write down the Hamiltonian.
- Write down the time-independent Schrödinger equation.
- Show that by appropriate choice of a dimension less coordinate z the Schrödinger equation can be written as

$$\frac{\hbar\omega}{2}\left(-\frac{d^2}{dz^2} + z^2\right)\psi = E\psi$$

- Verify that normalized solutions to this equation are

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{1}{2}z^2} \quad \text{and} \quad \psi_1 = \left(\frac{4m\omega}{\pi\hbar}\right)^{\frac{1}{4}} z e^{-\frac{1}{2}z^2}$$

and find the corresponding eigenvalues E_0 and E_1 .

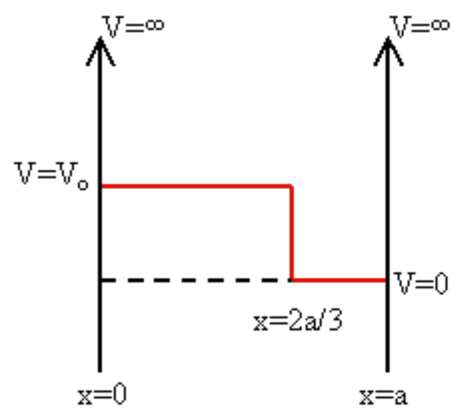
- Suppose that at $t=0$ the system was prepared in such a way that its wavefunction was .

$$\psi = \left(\frac{2m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-z^2}$$

- What is the probability that a measurement of the energy at $t=0$ would yield the value of E_0 ?

HA2: particle in potential well

- For the infinite well shown, the wave function for a particle of mass *m*, at $t=0$, is
- (a) Calculate $<x>$, $<p_x>$, and $<H>$ at $t=0$.



Recall SE

- General solution:

$$\psi_n(x) = \sqrt{\frac{1}{2^n\, n!}} \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \cdot e^{-\frac{m\omega x^2}{2\hbar}} \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right), \qquad n = 0,1,2,\ldots.$$

* H_n(y) is a Hermite polynomial of order n
* First few Hermite polynomials are:

H_0(y) = 1, H_1(y) = 2y

* General recursion relation:

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x).$$