

# *Appendix Lecture 2*

## **Quantum Mechanics**

# Particle-Wave Duality

To explain the photo-electric effect, Einstein proposed that the photon acts as a particle with its energy  $E$  related to its wave frequency  $f$  as

$$E = hf = \frac{hc}{\lambda} \quad (B.1)$$

$$h = 6.626 \times 10^{-34} \text{ joule.seconds} \quad (B.2)$$

In the above equation  $h$  is the **Planck constant**

From special relativity  $E^2 = (pc)^2 + (mc^2)^2$ . The photon has mass zero and, for the photon  $E = pc$

$$E = \frac{hc}{\lambda} = pc \quad \Rightarrow \quad \lambda = \frac{h}{p} \quad (B.3)$$

If a light-wave can also act like a particle, why shouldn't matter-particles also act like waves? The answer of this question came as a result of several experiments in the turn of the 19<sup>th</sup>/20<sup>th</sup> century. Now we know that a particle with momentum  $p$  also behaves as a wave with wavelength  $\lambda$  so that

$$\lambda = \frac{h}{p} \quad (B.4)$$

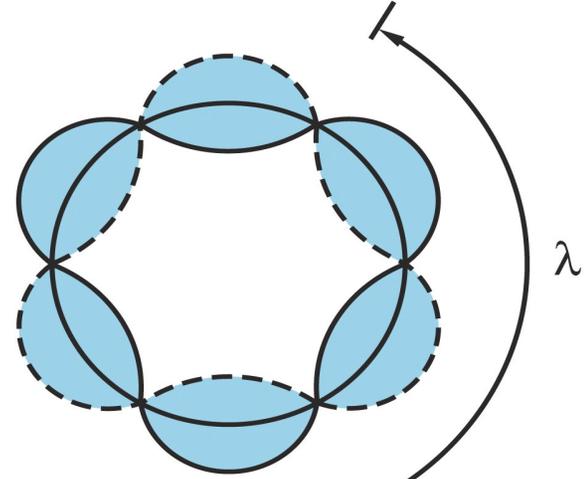
$\lambda$  is called the **de Broglie wavelength** of matter waves.

# Matter Waves

**Bohr's hydrogen atom** model assumed that the angular momentum of the electron is an integral multiple of  $h/2\pi$ .

The electron is a standing wave in an orbit around the proton. This standing wave will have nodes and be an integral number of wavelengths.

(B.5)



$2\pi r = n\lambda = \text{circumference of orbit, for } n = \text{integer}$

The angular momentum of the electron is thus quantized:

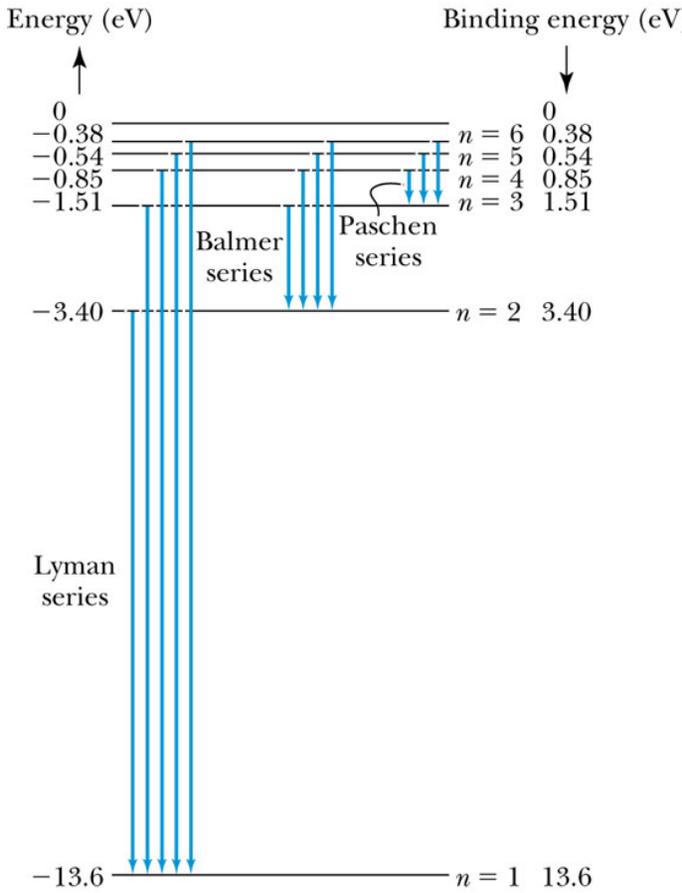
$$L = pr = mvr = \frac{nh}{2\pi} = n\hbar,$$
 where  $n$  is an integer and  $\hbar = \frac{h}{2\pi}$

(B.6)

Bohr's model worked for the hydrogen atom.

**Lyman series:** The atom will remain in the excited state for a short time before emitting a photon and returning to a lower stationary state.  $n_i \rightarrow n_f = 1$ . (invisible light)

**Balmer series:** When sunlight passes through the atmosphere, hydrogen atoms in water vapor absorb energy and later might decay from  $n_i > 2$  to  $n_f = 2$  (visible).



# The Schrödinger Equation

De Broglie matter waves should be described in the same manner as light waves. The matter wave should be a solution to a wave equation like the one for electromagnetic waves. Something like

$$\frac{\partial^2 \Psi}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} = 0 \quad (B.7)$$

Bohr's model failed for more complex systems. Schrödinger postulated a proper wave equation to get the correct answer. In its time-dependent form for a particle of energy  $E$  moving in a potential  $V$  in one dimension it is a bit different than (B.7). And it works! One gets results with impressive agreement with experiments and applications.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m^2} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (B.8)$$

Here  $\Psi(x,t)$  and  $V(x,t)$  are functions of space  $x$  and time  $t$  and the partial derivatives mean derivatives with respect to one variable, keeping the other variable constant.

In this equation  $i = \sqrt{-1}$  the **imaginary number**. Even if the potential  $V$  acting on the particle is real, the solution of the equation (B.8) is of the form  $\psi = a + ib$ , where  $a$  and  $b$  are real functions of space and time.

$\psi(x,t)$  is said to be a **complex function** of space and time. It is called a **wave function**. Schrödinger had to find a way to relate the wave function  $\psi$  to particle's properties and its dynamics.

# Wavefunction and probabilities

The probability  $P(x) dx$  of a particle being between  $x$  and  $x + dx$  is given in the equation

$$P(x)dx = \Psi^*(x,t)\Psi(x,t)dx \quad (B.9)$$

The probability of the particle being between  $x_1$  and  $x_2$  is given by

$$P = \int_{x_1}^{x_2} \Psi^*(x,t)\Psi(x,t) dx = \int_{x_1}^{x_2} |\Psi(x,t)|^2 dx \quad (B.10)$$

And the probability of the particle anywhere (this is called **normalization**)

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t) dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \quad (B.11)$$

For the free particle,  $V = 0$ , and the solution of Eq. (B.8) is

$$\Psi(x,t) = A \left[ \cos(kx - \omega t) + i \sin(kx - \omega t) \right] \quad (B.12)$$

which also describes a wave moving in the  $+x$  direction. In general the amplitude  $A$  is complex. The wavenumber  $k$  and angular frequency  $\omega$  is related to the particle wavelength  $\lambda$  and the wave period  $T$  by means of

$$k = \frac{2\pi}{\lambda} \quad (B.13)$$

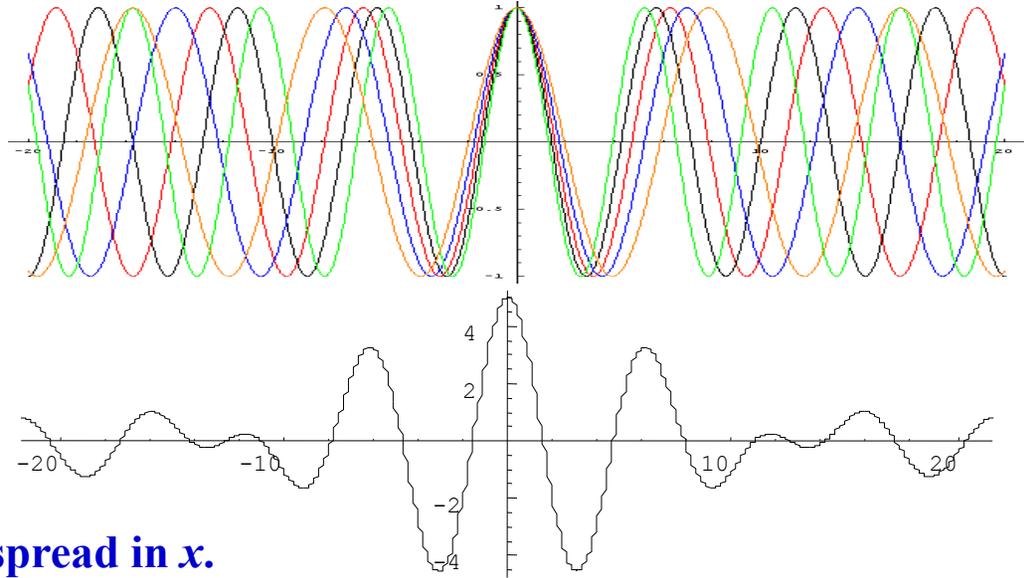
$$\omega = 2\pi f = \frac{2\pi}{T} \quad (B.14)$$

# The Heisenberg Uncertainty Principle

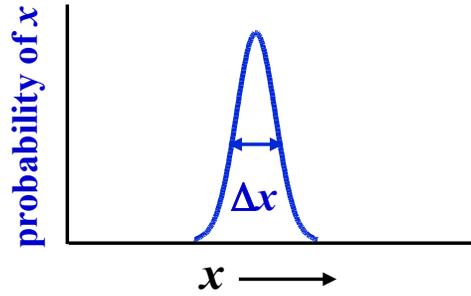
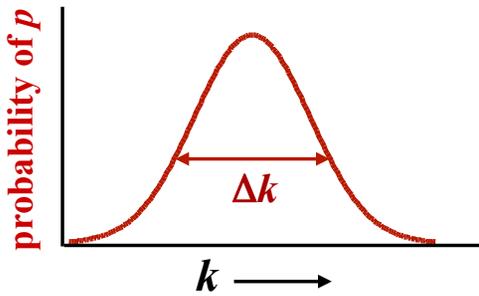
A wave can be a nice sine or cosine wave, with a fixed wavelength. But it can also be a mixture of waves in which case the waves of different wavelengths can be added. Add 5 waves.

$$\lambda = 1.2, 1.1, 1.0, 0.9, 0.8$$

Superimposing 5 waves concentrates probability in a region of space, but now there are 5 values of the momentum.

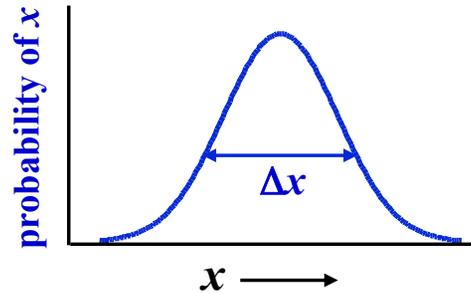
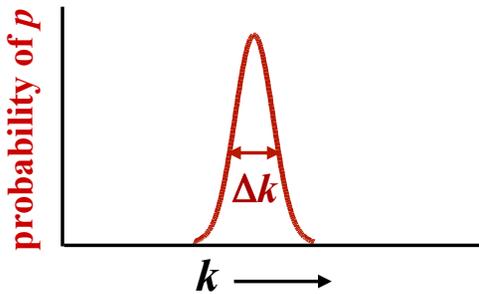


large spread in  $p$   $\longleftrightarrow$  small spread in  $x$ .



A general superposition of waves leads to the situation in the figure on the left.

small spread in  $p$   $\longleftrightarrow$  large spread in  $x$ .



We can know the wavenumber  $k$  and position more or less. The more well defined one is the less well defined the other is.

In general one finds for waves

$$\Delta k \Delta x \geq \frac{1}{2} \quad (B.15)$$

# The Heisenberg Uncertainty Principle

Using the de Broglie relation in the form  $k = p/\hbar = 2\pi/\lambda$ , we get from the previous equation

$$\Delta p \Delta x \geq \frac{\hbar}{2} \quad (B.16)$$

For a wave one also finds that the frequency spread  $\Delta\omega$  and the time spread of a wave packet are related by

$$\Delta\omega \Delta t \geq \frac{1}{2} \quad (B.17)$$

Using Einstein's relation in the form  $E = hf = \hbar\omega$ , we get from the previous equation

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad (B.18)$$

The equations (B.16) and (B.18) are known as **Heisenberg uncertainty relations**.

A position and momentum of a quantum particle (incl. photons) cannot be simultaneously well-defined: their uncertainties  $\Delta x$  and  $\Delta p$  are inter-related. Heisenberg went beyond the simple analogy to state that an experiment cannot simultaneously determine a component of the momentum of a particle,  $p$ , and the exact value of the corresponding coordinate,  $x$ .

# Particle in a box using Heisenberg relations

Since we're always uncertain as to the exact position,  $\Delta x = L$ , of a particle, for example, an electron somewhere inside an atom, the particle can't have zero kinetic energy:

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{\hbar}{2L} \quad (B.19)$$

The average of a positive quantity must always equal or exceed its uncertainty:

$$p_{ave} \geq \Delta p \geq \frac{\hbar}{2\Delta x} = \frac{\hbar}{2L} \quad (B.20)$$

so that the average kinetic energy is

$$K_{ave} = \frac{p_{ave}^2}{2m} \geq \frac{(\Delta p)^2}{2m} \geq \frac{\hbar^2}{8mL^2} \quad (B.21)$$

An exact solution of this problem can be obtained using the Schroedinger equation (SE). But (B.21) already yields a good estimate.

Even without solving the SE we can get exact solutions by treating particles as waves, as we will see next.

# Particle in a box (quantization)

The figure shows a particle (wave) of mass  $m$  is in a one-dimensional box of width  $L$ .

The box puts boundary conditions on the wave. The wavefunction must be zero at the walls of the box and on the outside.

In order for the probability to vanish at the walls, we must have an integral number of half wavelengths in the box:

$$\frac{n\lambda}{2} = L, \quad \text{or} \quad \lambda_n = \frac{2L}{n} \quad (n = 1, 2, 3, \dots) \quad (B.22)$$

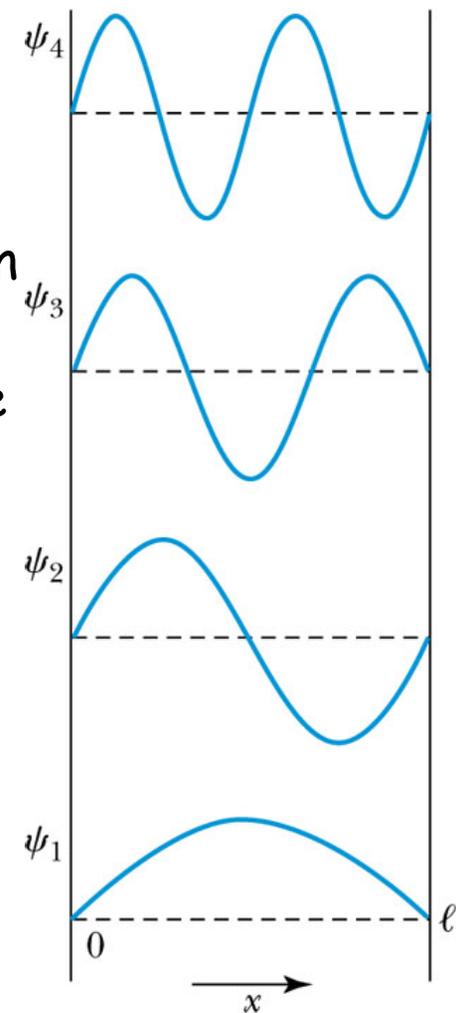
The energy is only kinetic as we can set the bottom of the well at zero height

$$E = K.E. = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \quad (B.23)$$

The possible wavelengths are quantized and hence so are the energies (note that we get  $h$  instead of  $\hbar$  in this more exact approach (still in accordance with the Heisenberg principle):

$$E_n = \frac{h^2}{2m} \left( \frac{n}{2L} \right)^2 = n^2 \frac{h^2}{8mL^2} \quad (n = 1, 2, 3, \dots) \quad (B.24)$$

That is, the possible energies of the particle are discrete, or **quantized**.



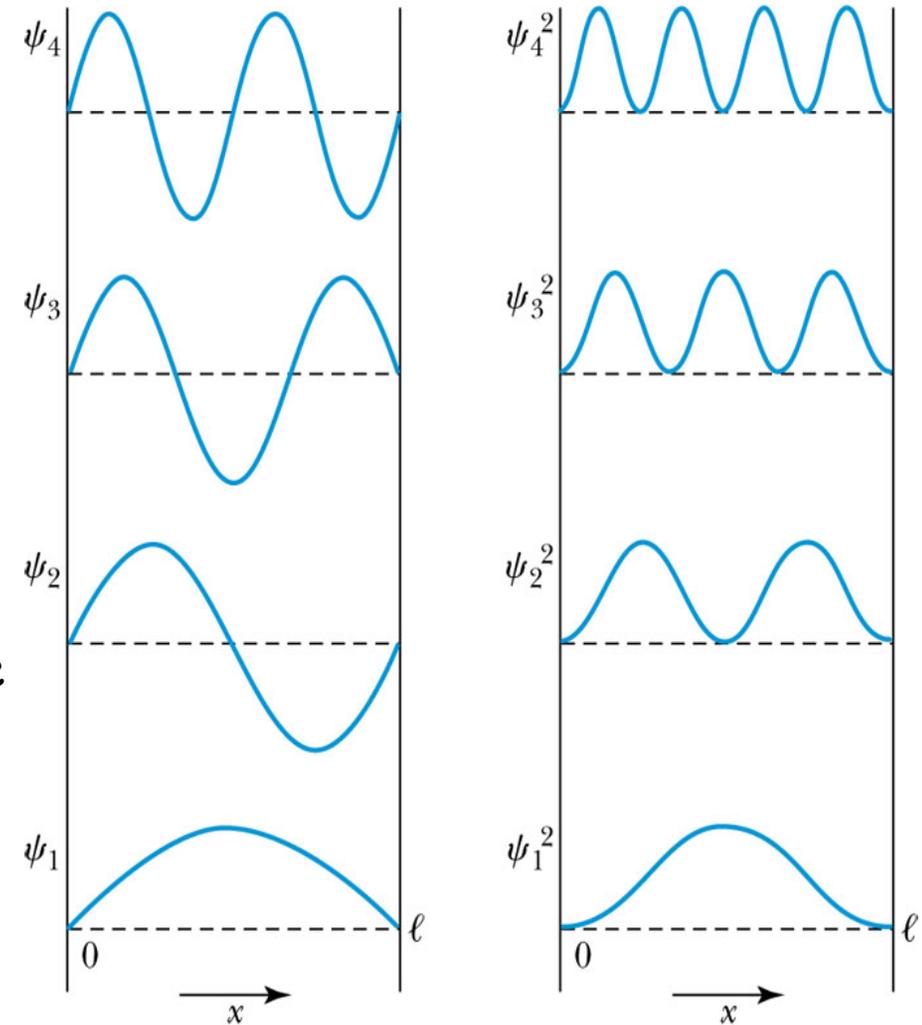
# Particle in a box - conclusions

$E_0 = 0$  is **not** a possible energy level.

According to Eq. (B.9) the probability of observing the particle around a location  $x$  is proportional to  $\psi^* \psi = |\psi|^2$  which is shown in the figure on the right.

## Conditions on the wave function

1. In order to avoid infinite probabilities, the wave function must be finite everywhere.
2. The wave function must be single valued.
3. The wave function must be twice differentiable. This means that it and its derivative must be continuous. (An exception to this rule occurs when  $V$  is infinite.)
4. In order to normalize a wave function, it must approach zero as  $x$  approaches infinity.



# Time-Independent Schrödinger Wave Equation

The potential  $V$  in many cases will not depend explicitly on time.

In this case we assume

$$\Psi(x, t) = \psi(x) f(t) \quad (B.25)$$

which yields

$$i\hbar\psi(x)\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}f(t)\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)f(t) \quad (B.26)$$

Now divide by the wave function  $\psi(x) f(t)$ , and

$$i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + V(x) \quad (B.27)$$

The left side depends only on  $t$ , and the right side depends only on  $x$ . So each side must be equal to a constant. The time dependent side is:

$$i\hbar\frac{1}{f}\frac{\partial f}{\partial t} = B \quad (B.28)$$

or

$$\frac{\partial f}{\partial t} = \frac{Bf}{i\hbar} \quad (B.29)$$

# Time-Independent Schrödinger Wave Equation

Ignoring the proportionality constant, which will come from the normalization condition, the solution of the previous equation is given by

$$f(t) = e^{Bt/i\hbar} = e^{-iBt/\hbar} \quad (B.30)$$

The temporal part of a wave propagating to the right is  $f(t) = \exp(-i\omega t)$ . Thus, by analogy with our solution  $\omega = B/\hbar$  or  $B = \hbar\omega$ , which means that  $B = E$ . So,

$$f(t) = e^{-iEt/\hbar} \quad (B.31)$$

Multiplying by  $\psi(x)$ , the spatial Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) = E\psi(x) \quad (B.32)$$

This equation is known as the **time-independent Schrödinger wave equation**.

The total wave function can be written as

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \quad (B.33)$$

The probability becomes (time independent)

$$\Psi^* \Psi = \psi^*(x) e^{i\omega t} \psi(x) e^{-i\omega t} = |\psi(x)|^2 \quad (B.34)$$

# Expectation values

In quantum mechanics, we'll compute expectation values. The **expectation value**,  $\langle x \rangle$ , is the weighted average of a given quantity. In general, the expected value of  $x$  is weighted with the probabilities  $P_n$  of obtaining  $x_n$ :

$$\langle x \rangle = P_1 x_1 + P_2 x_2 + \cdots + P_N x_N = \sum_i P_i x_i \quad (B.35)$$

If there are an infinite number of possibilities, and  $x$  is continuous:

$$\langle x \rangle = \int P(x) x dx \quad (B.36)$$

Quantum-mechanically

$$\langle x \rangle = \int \Psi(x) \Psi^*(x) x dx = \int \Psi^*(x) x \Psi(x) dx \quad (B.37)$$

And the expectation of some function of  $x$ ,  $g(x)$ :

$$\langle g(x) \rangle = \int \Psi^*(x) g(x) \Psi(x) dx \quad (B.38)$$

This expression is so important that physicists have a special notation for it.

$$\langle g(x) \rangle = \int \Psi^*(x) g(x) \Psi(x) dx \equiv \langle \Psi | g | \Psi \rangle \quad (B.39)$$

The entire expression (B.39) is thought to be a “bracket.” And  $\langle \Psi |$  is called the **bra** with  $|\Psi\rangle$  the **ket**.

In this notation, the normalization condition is

$$\langle \Psi | \Psi \rangle = 1 \quad (B.40)$$

# Real and complex solutions

Consider this differential equation  $\frac{d^2\psi}{dx^2} = k^2\psi$  with  $k$  real

Because the constant  $k^2$  is positive, the solution is

$$\psi(x) = Ae^{kx} \quad (B.42)$$

Now suppose the differential equation is

$$\frac{d^2\psi}{dx^2} = -k^2\psi \quad (B.43)$$

Because the constant  $-k^2$  is negative, the solution is

$$\psi(x) = Ae^{ikx} \quad \text{or} \quad A\sin(kx) + B\cos(kx) \quad (B.44)$$

Above we can express the solution either in terms of a sum of sine and cosine functions or in terms of the complex exponential

$$e^{ikx} = \cos(kx) + i\sin(kx) \quad (B.45)$$

This relation is known as the "**pearl of mathematics**". With it, we can work with complex exponentials which are simpler to deal with than trigonometric functions.

# Step potential

Consider a particle of energy  $E$  approaching a potential barrier of height  $V_0$ , and the potential everywhere else is zero.

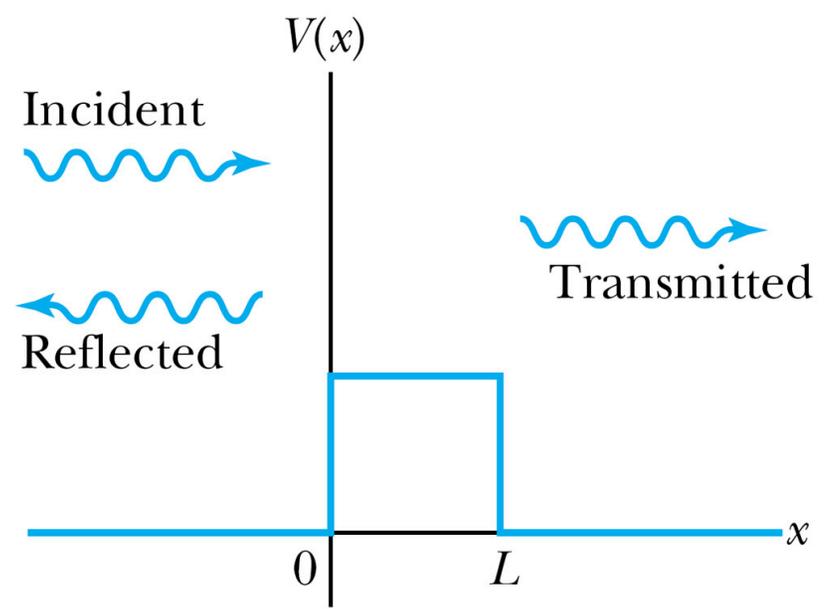
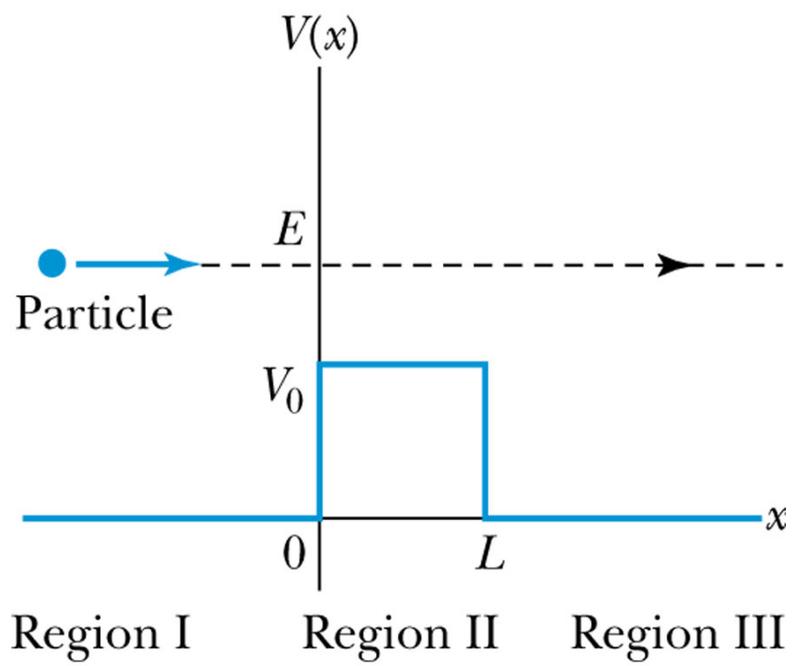
First consider the case of the energy greater than the potential barrier.

In regions I and III, the wave numbers are

$$k_I = k_{III} = \frac{\sqrt{2mE}}{\hbar} \quad (B.46)$$

And in the barrier region  $k_{II} = \frac{\sqrt{2m(E - V_0)}}{\hbar}$

$$(B.47)$$



# Step potential

The wave function will consist of an incident wave, a reflected wave, and a transmitted wave (see previous slide).

The potentials and the Schrödinger wave equation for the three regions are

$$\begin{array}{lll} \text{Region I } (x < 0) & V = 0 & \frac{d^2\psi_{\text{I}}}{dx^2} + \frac{2m}{\hbar^2} E\psi_{\text{I}} = 0 \\ \text{Region II } (0 < x < L) & V = V_0 & \frac{d^2\psi_{\text{II}}}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi_{\text{II}} = 0 \\ \text{Region III } (x > L) & V = 0 & \frac{d^2\psi_{\text{III}}}{dx^2} + \frac{2m}{\hbar^2} E\psi_{\text{III}} = 0 \end{array} \quad \left. \vphantom{\begin{array}{l} \text{Region I} \\ \text{Region II} \\ \text{Region III} \end{array}} \right\} \begin{array}{l} \text{All three constants} \\ \text{are negative.} \\ \\ (B.48) \end{array}$$

The corresponding solutions are

$$\begin{array}{lll} \text{Region I } (x < 0) & \psi_{\text{I}} = Ae^{ik_{\text{I}}x} + Be^{-ik_{\text{I}}x} \\ \text{Region II } (0 < x < L) & \psi_{\text{II}} = Ce^{ik_{\text{II}}x} + De^{-ik_{\text{II}}x} \\ \text{Region III } (x > L) & \psi_{\text{III}} = Fe^{ik_{\text{I}}x} + Ge^{-ik_{\text{I}}x} \end{array} \quad \left. \vphantom{\begin{array}{l} \text{Region I} \\ \text{Region II} \\ \text{Region III} \end{array}} \right\} \begin{array}{l} \text{Sines and cosines in all three} \\ \text{regions} \\ \\ (B.49) \end{array}$$

Since the wave moves from left to right, we can reject some solutions:

$$\begin{array}{ll} \text{Incident wave} & \psi_{\text{I}}(\text{incident}) = Ae^{ik_{\text{I}}x} \\ \text{Reflected wave} & \psi_{\text{I}}(\text{reflected}) = Be^{-ik_{\text{I}}x} \\ \text{Transmitted wave} & \psi_{\text{III}}(\text{transmitted}) = Fe^{ik_{\text{I}}x} \end{array} \quad (B.50)$$

# Barrier transmission

The probability of the particle being reflected  $R$  or transmitted  $T$  is

$$R = \frac{|\psi_I(\text{reflected})|^2}{|\psi_I(\text{incident})|^2} = \frac{B^* B}{A^* A} \quad (B.51)$$

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

Because the particle must be either reflected or transmitted,

$$R + T = 1 \quad (B.52)$$

By applying the boundary conditions  $x \rightarrow \pm \infty$ ,  $x = 0$ , and  $x = L$ , we arrive at the transmission probability

$$T = \left[ 1 + \frac{V_0^2 \sin^2(k_{II} L)}{4E(E - V_0)} \right]^{-1} \quad (B.53)$$

Note that the transmission probability can be 1.

# Barrier transmission: tunneling

Now we consider the situation where classically the particle doesn't have enough energy to surmount the potential barrier,  $E < V_0$ .

The wave function in region II becomes

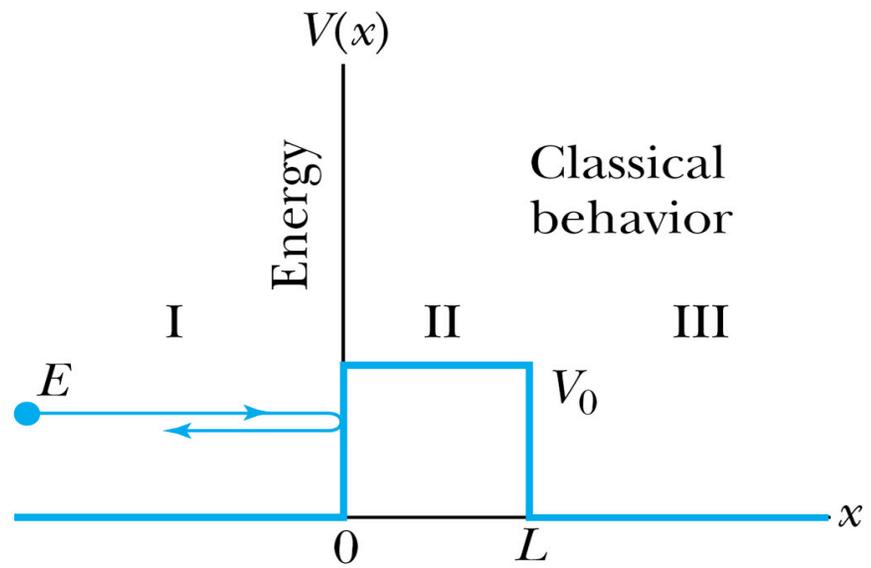
$$\psi_{II} = Ce^{\kappa x} + De^{-\kappa x} \quad \text{where} \quad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

The transmission probability for **tunneling** is

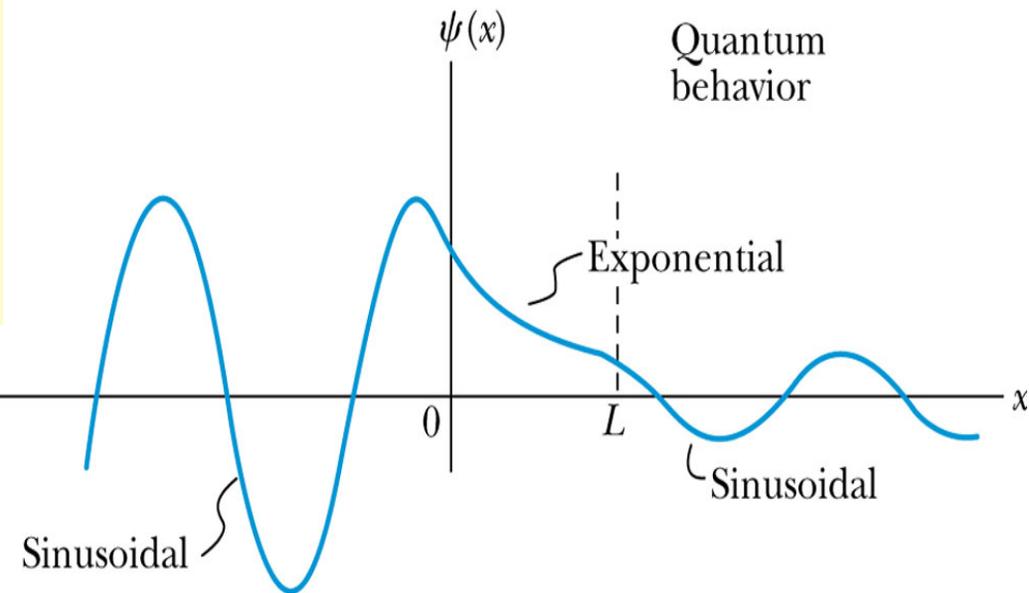
$$T = \left[ 1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)} \right]^{-1} \quad (B.55)$$

The quantum mechanical result is one of the most remarkable features of modern physics. There is a finite probability that the particle penetrates the barrier and even emerges on the other side.

This violation of classical physics is allowed by the uncertainty principle. The particle can violate classical physics by  $\Delta E$  for a short time,  $\Delta t \sim \hbar / \Delta E$  while inside the barrier.



(B.54)



# Alpha-particle decay

The phenomenon of tunneling explains alpha-particle decay of heavy, radioactive nuclei.

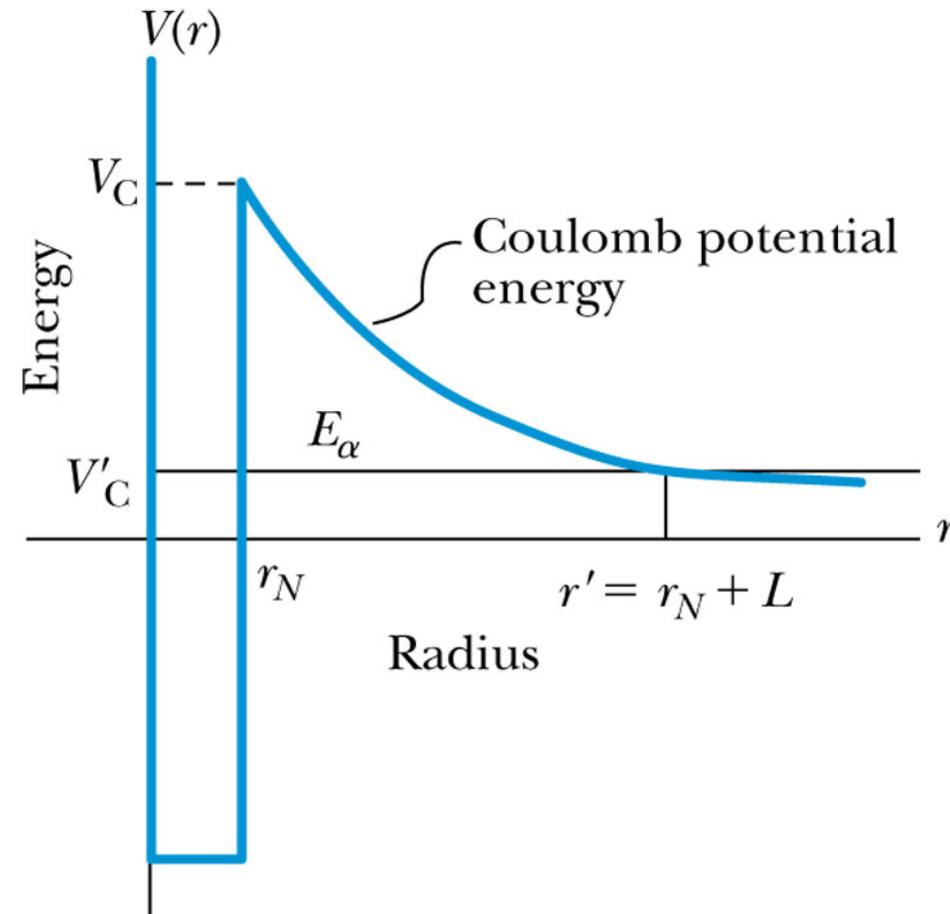
Inside the nucleus, an alpha particle feels the strong, short-range attractive nuclear force as well as the repulsive Coulomb force.

The nuclear force dominates inside the nuclear radius where the potential is approximately a square well.

The Coulomb force dominates outside the nuclear radius.

The potential barrier at the nuclear radius is several times greater than the energy of an alpha particle.

In quantum mechanics, however, the alpha particle can **tunnel** through the barrier. This is observed as radioactive decay.

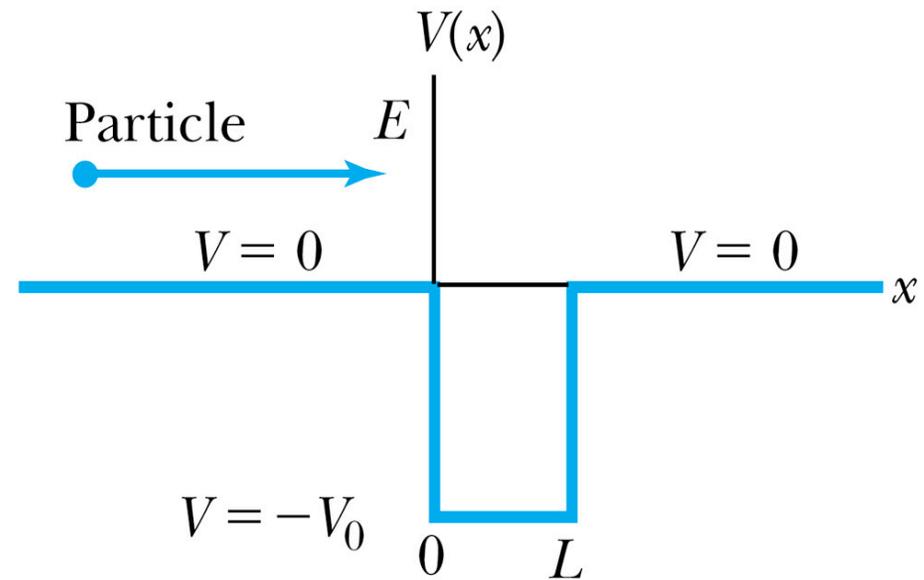


# Potential Well

Consider a particle passing through a potential well, rather than a barrier.

Classically, the particle would speed up in the well region because

$$K = \frac{mv^2}{2} = E + V_0 \quad (B.56)$$



Quantum mechanically, reflection and transmission may occur, but the wavelength decreases inside the well.

When the width of the potential well is precisely equal to half-integral or integral units of the wavelength, the reflected waves may be out of phase or in phase with the original wave, and cancellations or resonances may occur.

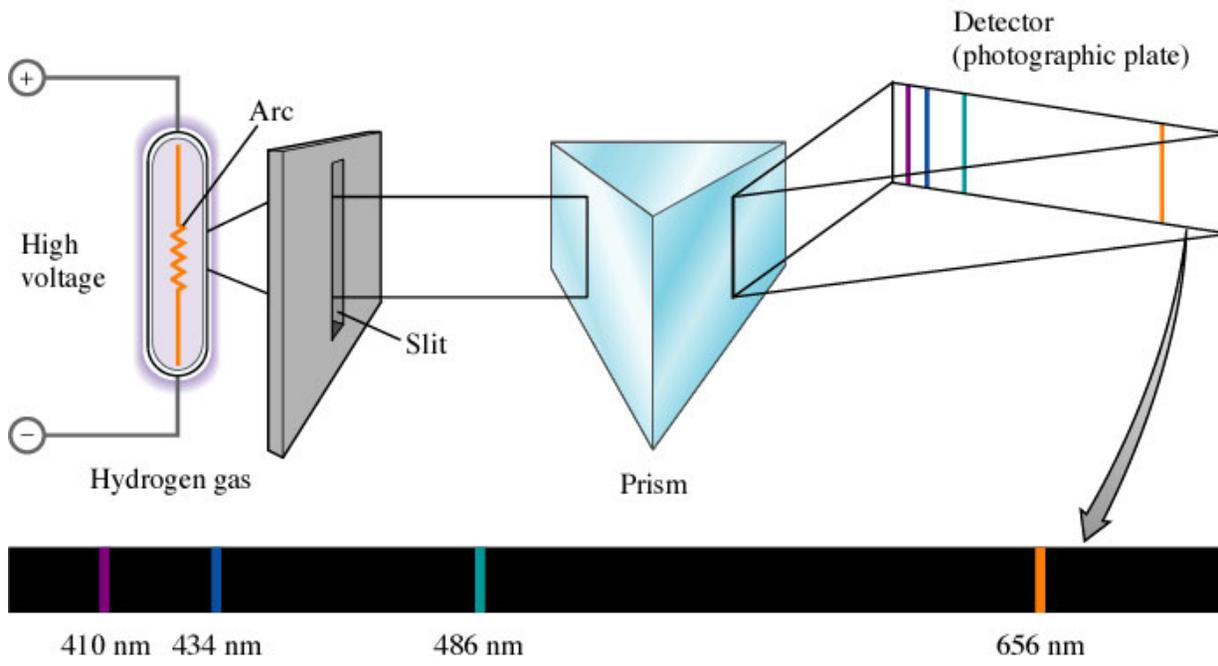
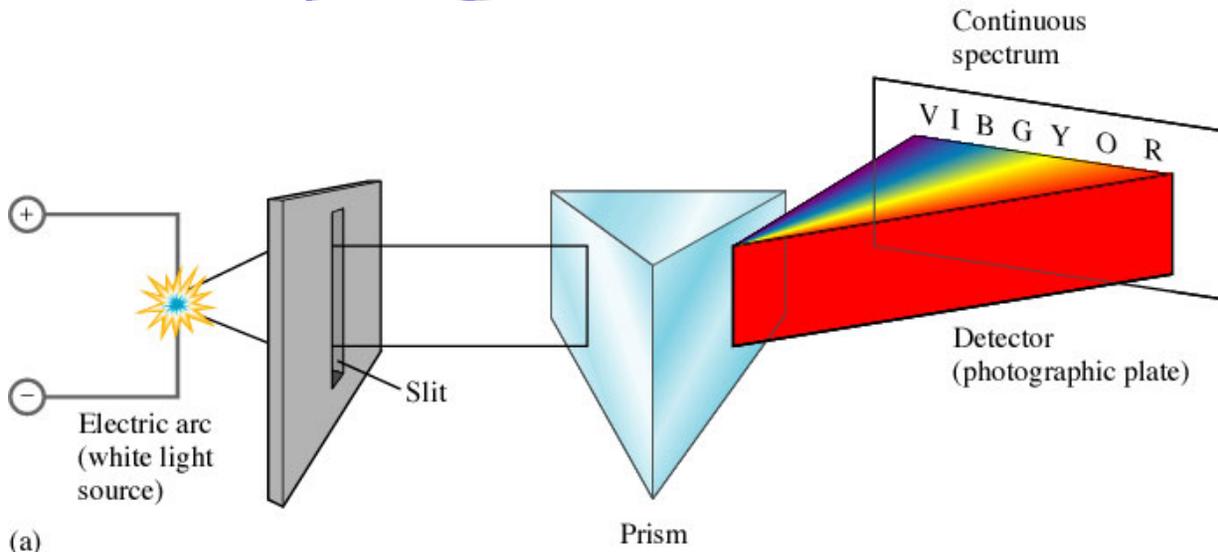
The reflection/cancellation effects can lead to almost pure transmission or pure reflection for certain wavelengths. For example, at the second boundary ( $x = L$ ) for a wave passing to the right, the wave may reflect and be out of phase with the incident wave.

The effect would be a cancellation inside the well.

# A three dimensional problem: Hydrogen Atom

When hydrogen atoms absorb energy, it is released by emitting light of various wavelengths to produce the emission spectrum of hydrogen atom.

- **(a) Continuous spectrum:** Contains all the wavelengths of light.
- **(b) Line (discrete) spectrum:** Contains only some of the wavelengths of light. Only certain energies are allowed, i.e., the energy of the electron in the hydrogen atom is quantized.



# Hydrogen Atom

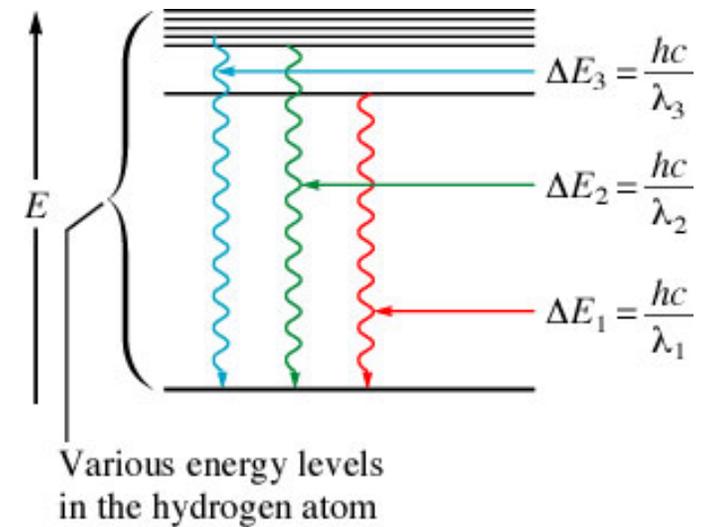
The energy is released due to a change between two discrete (“quantized”) energy levels.

As we mentioned before (see Eq. (B.6)), the Bohr model assumes that the electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits. The energy levels available to the hydrogen atom can be calculated in this way, yielding

$$E_n = (-2.178 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2}$$

Where  $E$  = energy of the levels in the H-atom,  $Z$  = nuclear charge (for H,  $Z = 1$ ) and  $n$  = an integer, the larger the value, the larger is the orbital radius.

Bohr was able to calculate hydrogen atom energy levels that exactly matched the experimental value. The negative sign in the above equation means that the energy of the electron bound to the nucleus is lower than it would be if the electron were at an infinite distance.



# Hydrogen Atom

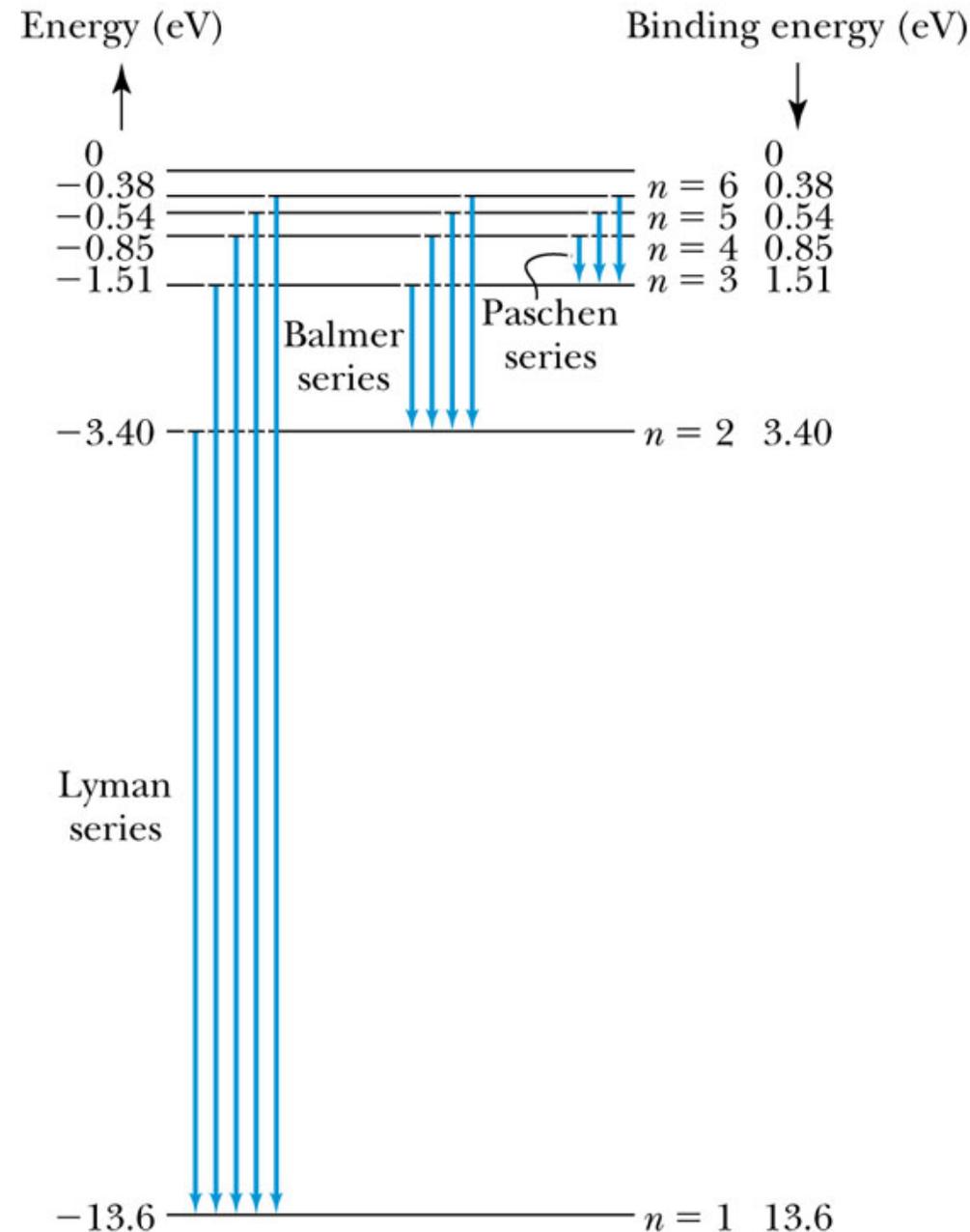
According to Bohr's model, a photon is emitted when the electron changes from a state, or orbital, with quantum number  $n_2$  to quantum number  $n_1$ . The resulting energy of the emitted photon is

$$\Delta E = (2.178 \times 10^{-18} \text{ J}) Z^2 \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

This prediction agrees remarkably well with the experimentally obtained radiation energy emitted by excited hydrogen atoms. Such atoms can be excited (i.e., electrons change to higher orbits) by atomic collisions, such as those occurring in hot plasmas in stars.

For

- Lyman transitions:  $n_1 = 1$
- Balmer:  $n_1 = 2$
- Paschen:  $n_1 = 3$



# Quantum Numbers

The solution of the Schrodinger equation (in three-dimensions) for the hydrogen atom yields many wave functions (orbitals). Each of these orbitals is characterized by a series of numbers called quantum numbers, which describe various properties of the orbital.

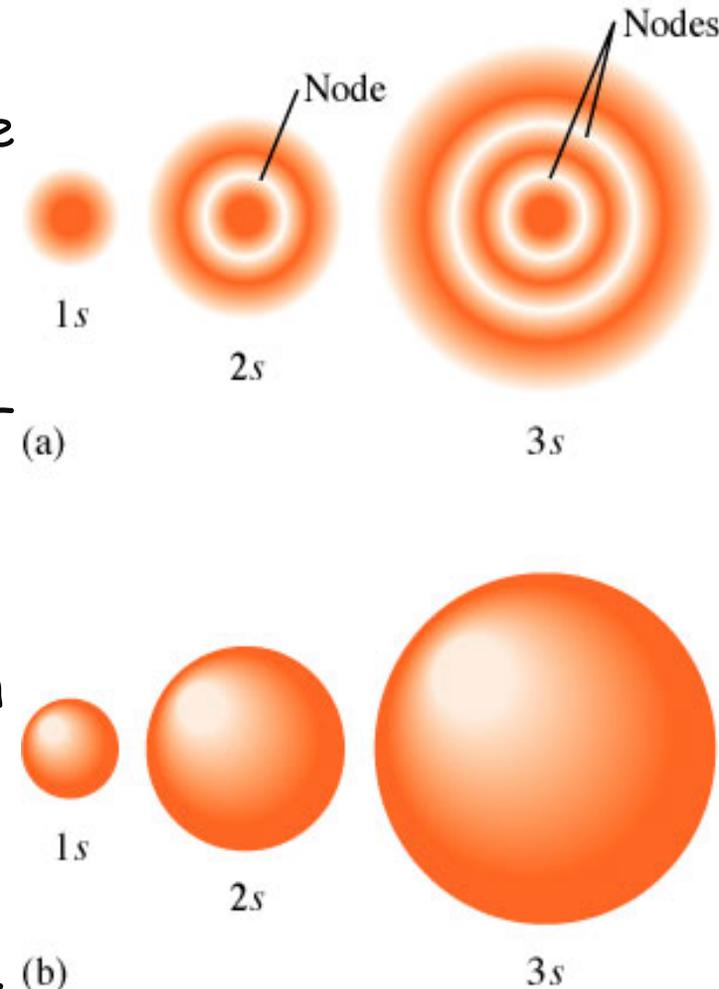
1. **Principal quantum number** ( $n = 1, 2, 3, \dots$ ) - related to size and energy of the orbital.

2. **Angular Momentum** ( $l = 0$  to  $n - 1$ ) - relates to shape of the orbital.  $l = 0$  is called *s*;  $l = 1$  is called *p*;  $l = 2$  is called *d*;  $l = 3$  is called *f*, and so on.

3. **Magnetic quantum number** ( $m_l = l$  to  $-l$  including 0) - relates to orientation of the orbital in space relative to other orbitals.

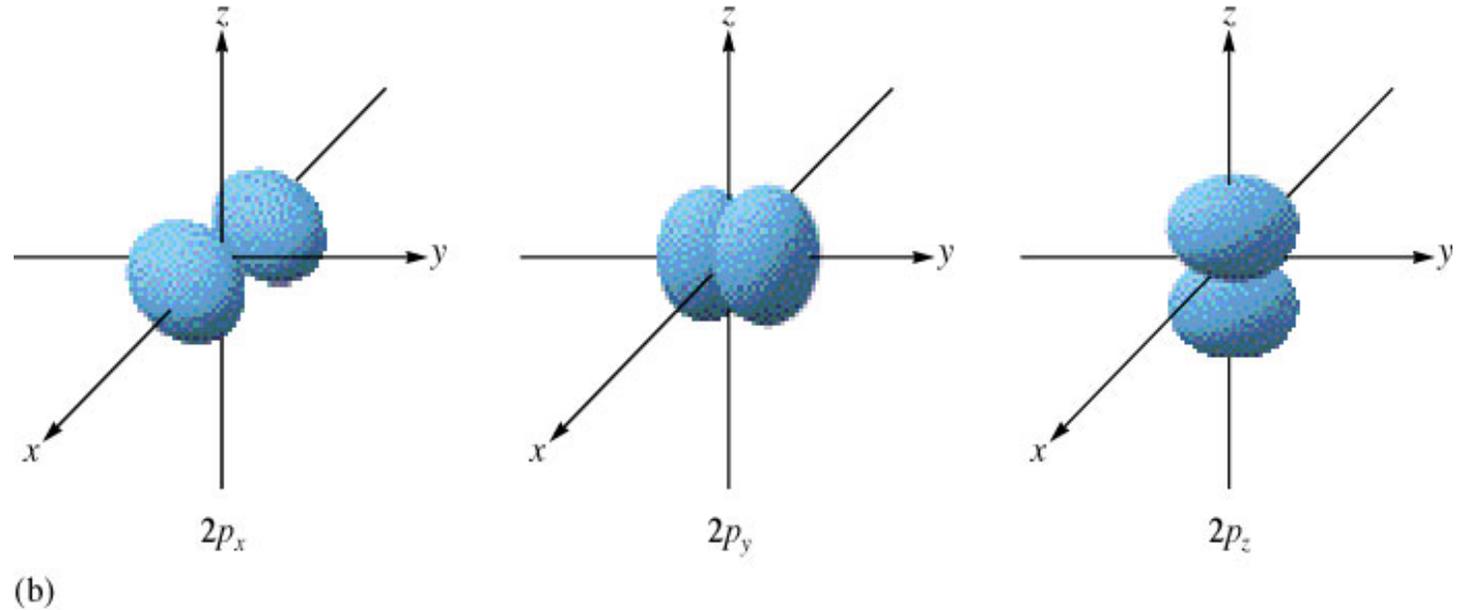
4. **Electron Spin** ( $m_s = +1/2, -1/2$ ) - relates to the spin states of the electrons.

Two types of representations for the *1s*, *2s* and *3s* orbitals are shown. The *s* orbitals are spherical shaped. (b)

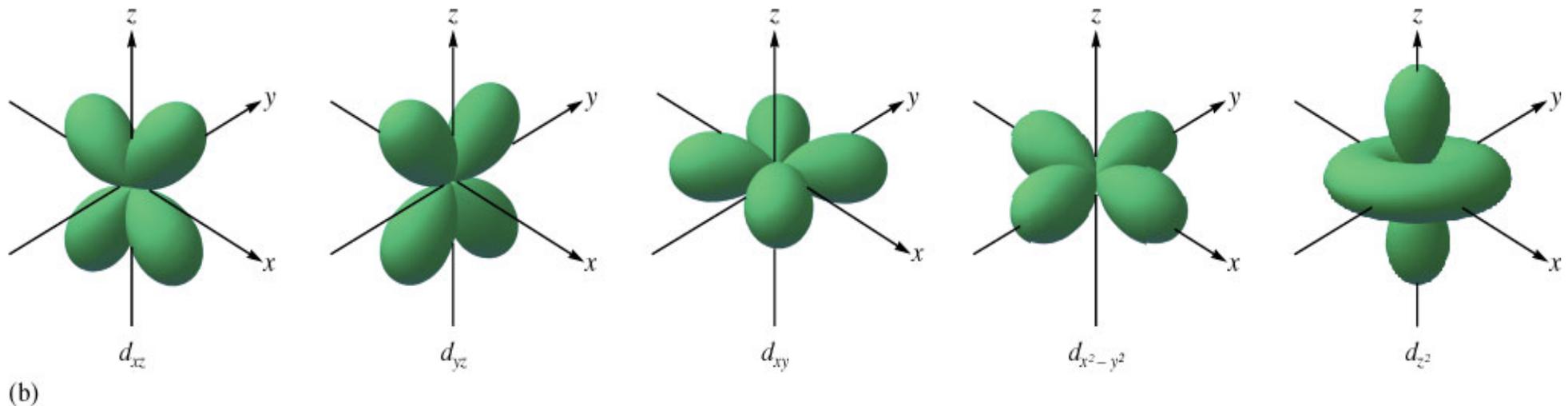


# Quantum Numbers

The  $p$  orbitals are not spherical like  $s$  orbital but have two lobes separated by a node at the nucleus. The  $p$  orbitals are labeled according the axis of the  $xyz$  coordinate system.



The five  $d$  orbital shapes are shown below. The  $d$  orbitals have two different fundamental shapes.



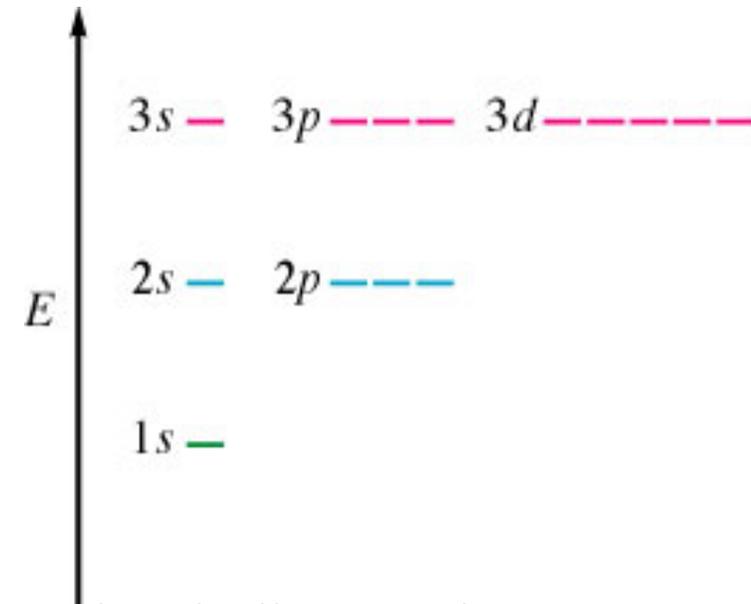
# Energy Diagram for Hydrogen Atom

The energy of a particular orbital is determined by its value of  $n$ . All orbitals with the same value of  $n$  have the same energy and are said to be **degenerate**.

Hydrogen single electron occupy the lowest energy state, the **ground state**. If energy is put into the system, the electron can be transferred to higher energy orbital called **excited state**.

## Pauli exclusion principle

- In a given atom, no two electrons can have the same set of four quantum numbers ( $n, l, m_l, m_s$ ).
- Therefore, an orbital can hold only two electrons, and they must have opposite spins.



For multi-electron atoms in a given principal quantum level all orbitals are not in same energy (degenerate). For a given principal quantum level the orbitals vary in energy as follows:

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

In other words, when electrons are placed in a particular quantum level, they prefer the orbital in the order  $s, p, d$  and then  $f$ .