Structural Chemistry

参考书:

<<结构化学>>厦门大学化学系物构组编

<<Physical Chemistry>> P.W. Atkins

<<结构化学基础>> 周公度编著, 北京大学出版社

What is Chemistry

The branch of natural science that deals with composition, structure, properties of substances and the changes they undergo.

Types of substances

Atoms
Molecules

Clusters
Congeries

Nano materials

Bulk materials

Geometric Structure

Size
makes the difference

Electronic Structure

Structure vs. Properties

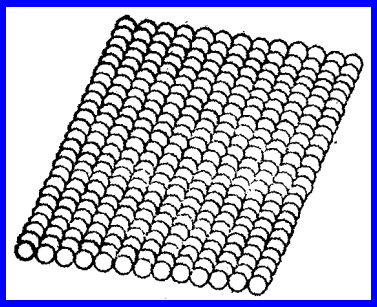
Structure determines properties
Properties reflects structures

Inorganic Chemistry
Organic Chemistry
Catalysis
Electrochemistry
Bio-chemistry
etc.

Material Science
Surface Science
Life Science
Energy Science
Environmental Science
etc.

Structural Chemistry

Role of Structural Chemistry in Surface Science



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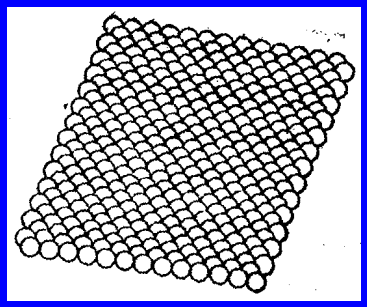

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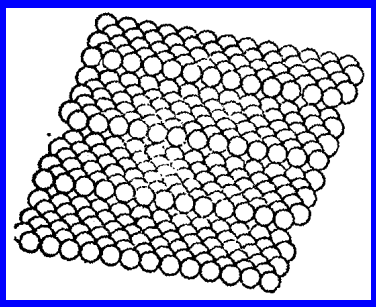

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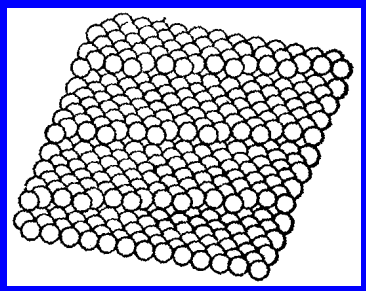

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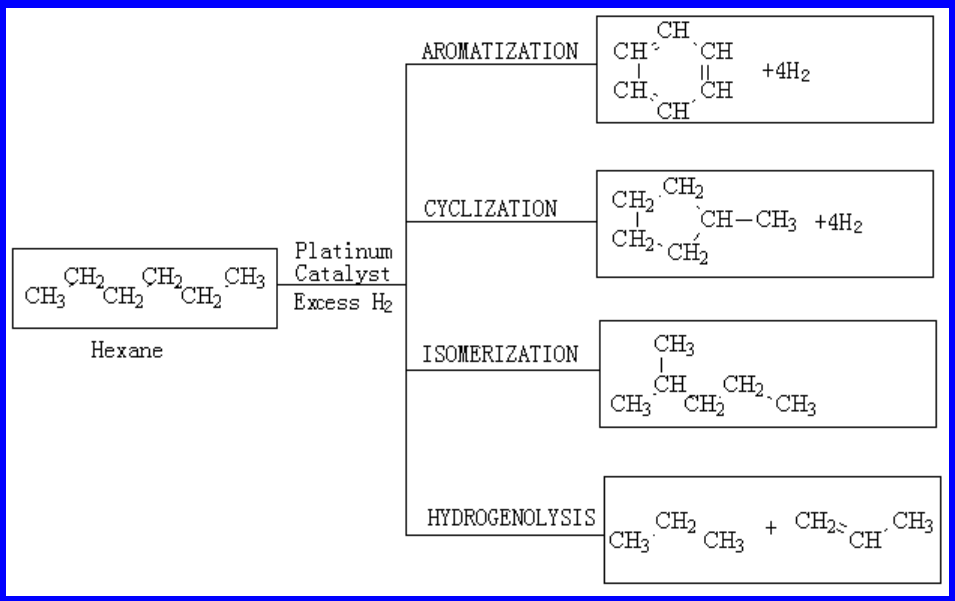
Surface structures of Pt single crystal



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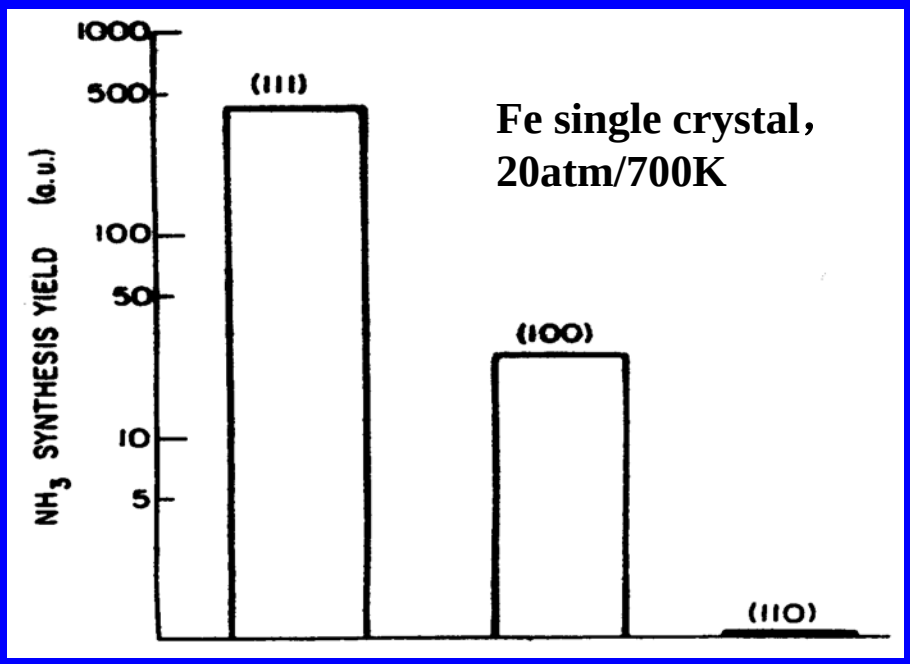
Different surfaces do different chemistry

Surface Structure vs. Catalytic Activity

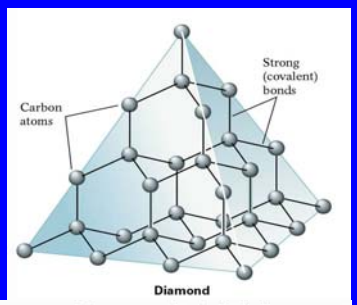
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

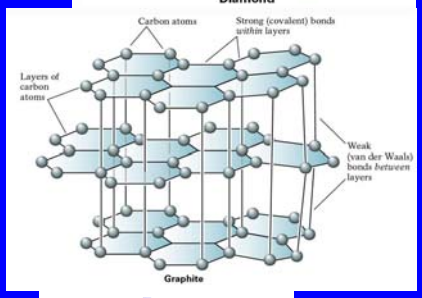


Role of Structural Chemistry in Material Science

C Crystal Structures

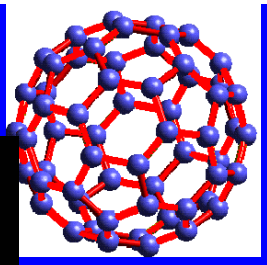
- Graphite & Diamond Structures
  - Diamond: Insulator or wide bandgap semiconductor: →→→ →→→
  - Graphite: Planar structure: →→→
    sp^2 bonding ≈ 2d metal (in plane)

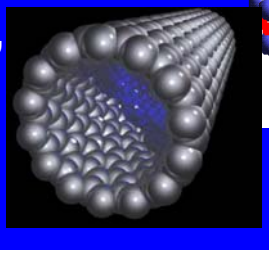


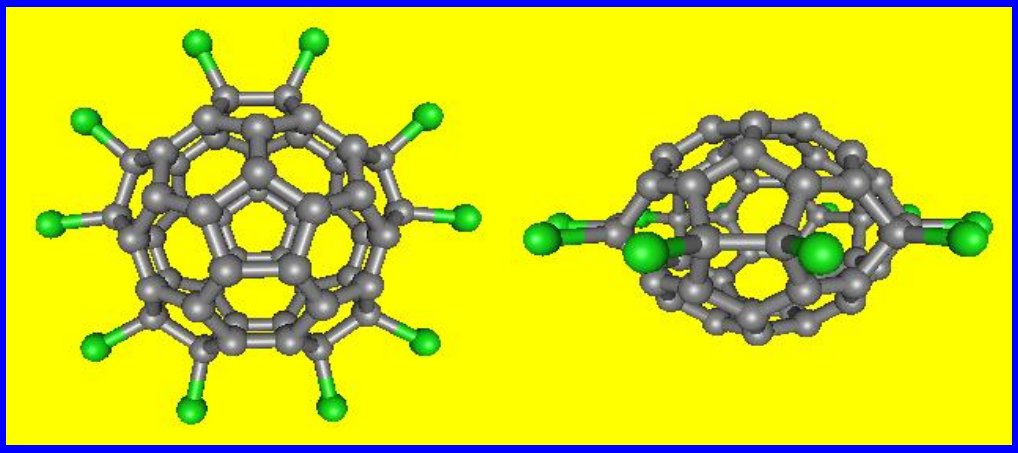


Structure makes the difference

- *Other* Carbon Crystal Structures
  "Buckyballs" (C_{60}) →→→→→→
  "Buckytubes" (nanotubes), other fullerenes →→→







Zheng LS (郑兰荪), et al.

Capturing the labile fullerene[50] as C50Cl10

SCIENCE 304 (5671): 699-699 APR 30 2004

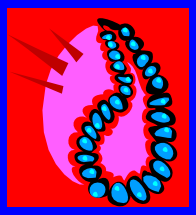
Role of Structural Chemistry in Life Science

What do proteins do ?

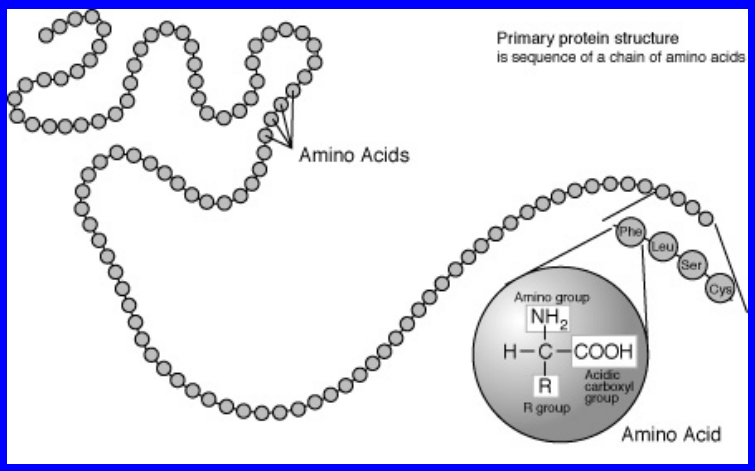
Proteins are the basis of how biology gets things done.

- As enzymes, they are the driving force behind all of the biochemical reactions which makes biology work.
- As structural elements, they are the main constituents of our bones, muscles, hair, skin and blood vessels.
- As antibodies, they recognize invading elements and allow the immune system to get rid of the unwanted invaders.

What are proteins made of ?



- Proteins are necklaces of amino acids, i.e. long chain molecules.



Objective of Structural Chemistry

1) **Determining the structure of a known substance**
2) **Understanding the structure-property relationship**

3) **Predicting a substance with specific structure and property**

Outline

Chapter 1 The basic knowledge of quantum mechanics
Chapter 2 Atomic structure
Chapter 3 Symmetry
Chapter 4 Diatomic molecules
Chapter 5/6 Polyatomic structures
Chapter 7 Basics of Crystallography
Chapter 8 Metals and Alloys
Chapter 9 Ionic compounds

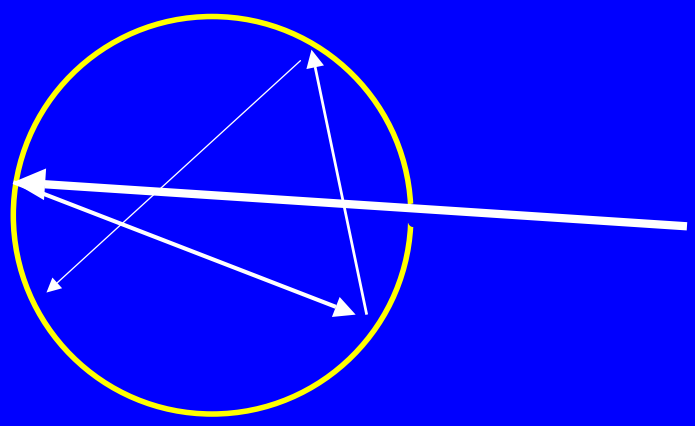
Chapter 1 The basic knowledge of quantum mechanics

1.1 The failures of classical physics

- Classical physics: (prior to 1900)

  Newtonian classical mechanics
  Maxell's theory of electromagnetic waves
  Thermodynamics and statistical physics

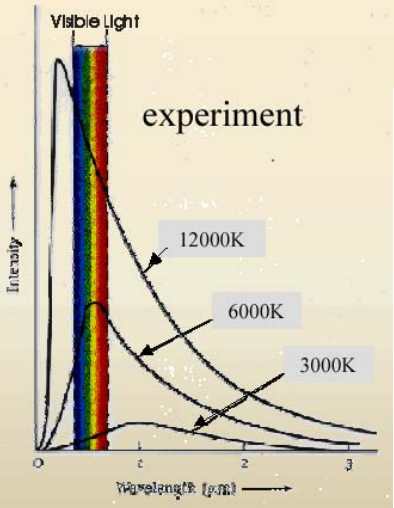
1.1.1 Black-body radiation



Black-Body Radiation

Nagging problem 1

"Blackbody Radiation"



Infrared (10μm) "thermal" image

Classical solution:

Rayleigh-Jeans Law

(high energy, Low T)

Wien Approximation

(long wave length)

It can not be explained by classical thermodynamics and statistical mechanics.

Solution to Blackbody problem

(problem: theory diverges at low wavelength)

solution:

- 1900: Max Planck proposed a formula which fit the experimental data.
- required that the energy in the atomic vibrations of frequency ν was an integer n times a small, minimum, discrete energy,

$$E = n\,h\nu \qquad (n = 0,1,2,...)$$

- h is now known as Planck's constant,

$$= 6.62 \times 10^{-34}\ \mathrm{J\ s}$$

- no known physical basis for the "fitting"

Black Body Radiation

Planck showed using quantum mechanics that a black body would emit radiation of the form

$$B_\nu(T) = \frac{2h\nu^3 / c^2}{e^{h\nu/kT} - 1}$$

Many stellar sources can usefully be approximated to be black bodies

$$\frac{h\nu}{kT} >> 1 \qquad B_\nu(T) = \frac{2h\nu^3}{c^2} e^{-h\nu/kT}$$

Wien's Approximation
(high energy, low T)

$$\frac{h\nu}{kT} << 1 \qquad B_\nu(T) = \frac{2\nu^2}{c^2} kT$$

Rayleigh-Jeans Law
(long wavelength, high T)

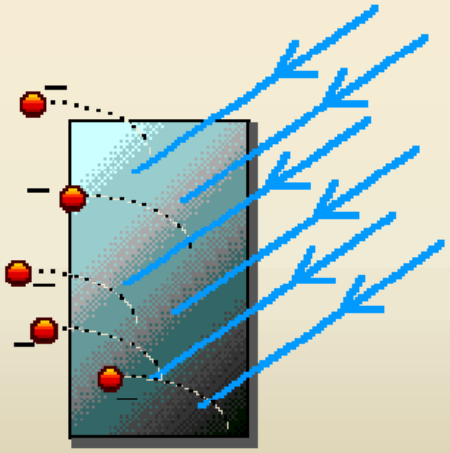
1.1.2 The photoelectric effect

Nagging problem 2

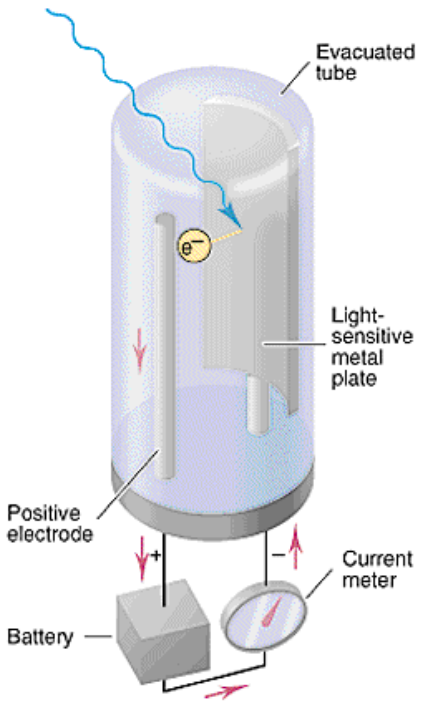
"Photoelectron effect"

Observed by Hertz in 1887

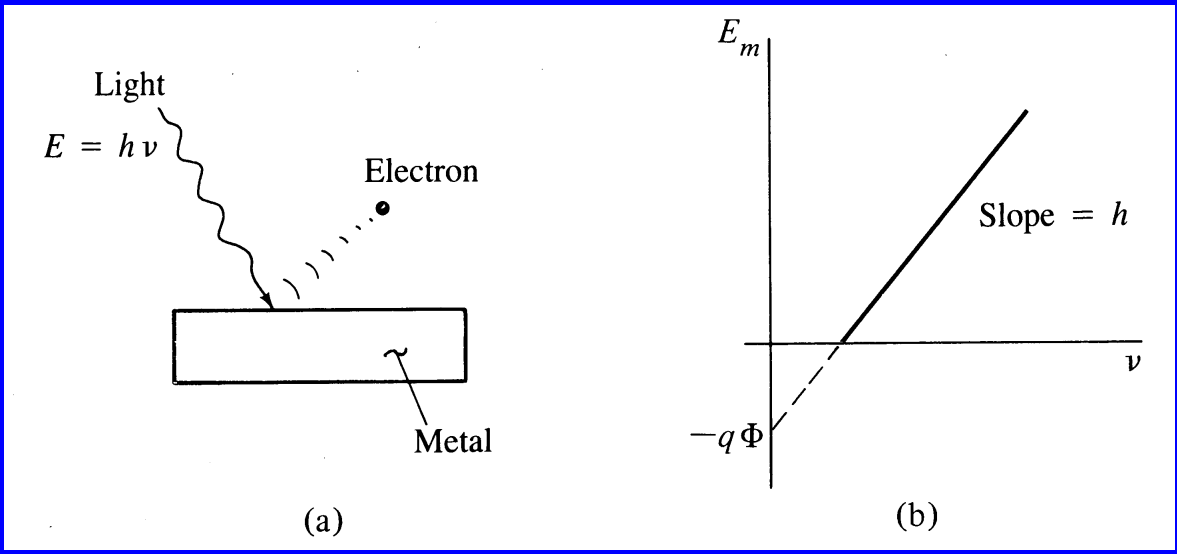
Light causes electrons to come out of a metal, but only above a threshold frequency ν (i.e., a threshold energy hν)



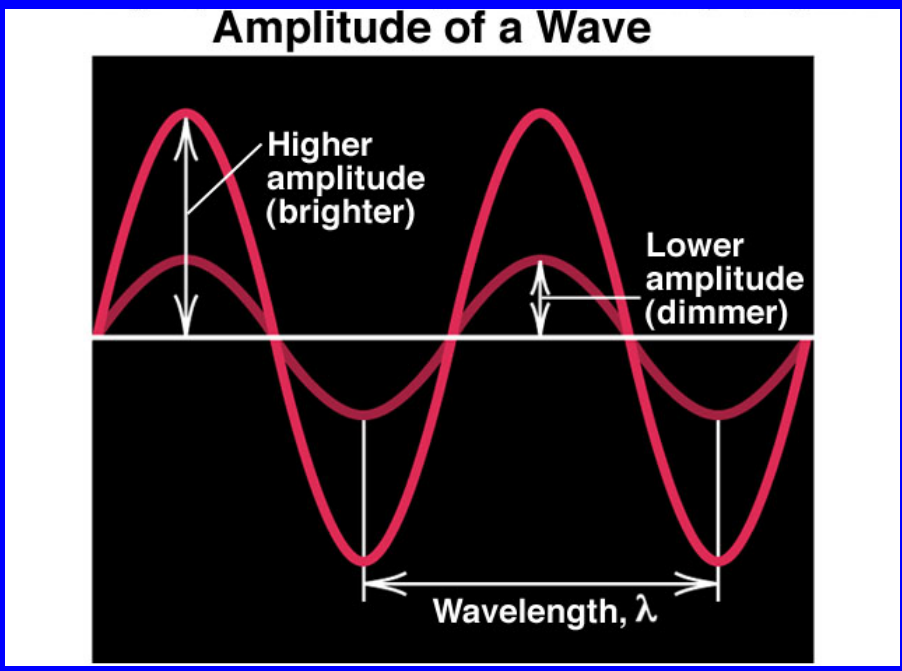
The photoelectric effect



The Photoelectric Effect



1. The kinetic energy of the ejected electrons depends linearly on the frequency of the light.
2. There is a particular threshold frequency for each metal.
3. The increase of the intensity of the light results in the increase of the number of photoelectrons.



Classical physics: The energy of light wave should be directly proportional to intensity and not be affected by frequency.

Explaining the Photoelectric Effect

- **Albert Einstein**
  - Proposed a corpuscular theory of light (photons).
  - won the Nobel prize in 1921

1. Light consists of a stream of photons. The energy of a photon is proportional to its frequency.

   $\varepsilon = h\nu$ h = Planck's constant

2. A photon has energy as well as mass. $m = h\nu / c^2$
3. A photon has a definite momentum. $p = mc = h\nu / c = h/\lambda$
4. The intensity of light depends on the photon density

Explaining the Photoelectric Effect

Therefore, the photon's energy is equaled to the electron's kinetic energy added to the electron's binding energy

- $E_{photon} = E_{binding} + E_{Kinetic\ energy}$
- $h\nu = W + E_k$

Example I: Calculation Energy from Frequency

Problem: What is the energy of a photon of electromagnetic radiation emitted by an FM radio station at 97.3×10^8 cycles/sec?
What is the energy of a gamma ray emitted by Cs^{137} if it has a frequency of 1.60×10^{20}/s?

Plan: *Use the relationship between energy and frequency to obtain the energy of the electromagnetic radiation ($E = h\nu$).*

Solution:

$$E_{photon} = h\nu = (6.626 \times 10^{-34} Js)(9.73 \times 10^9/s) = 6.447098 \times 10^{-24} J$$

$$E_{photon} = \mathbf{6.45 \times 10^{-24}\ J}$$

$$E_{gamma\ ray} = h\nu = (6.626 \times 10^{-34} Js)(1.60 \times 10^{20}/s) = 1.06 \times 10^{-13} J$$

$$E_{gamma\ ray} = \mathbf{1.06 \times 10^{-13} J}$$

Example II: Calculation of Energy from Wavelength

Problem: What is the photon energy of of electromagnetic radiation that is used in microwave ovens for cooking, if the wavelength of the radiation is 122 mm ?

Plan: *Convert the wavelength into meters, then the frequency can be calculated using the relationship;wavelength x frequency = c (where c is the speed of light), then using $E=h\nu$ to calculate the energy.*

Solution:

$$\text{wavelength} = 122\ \text{mm} = 1.22 \times 10^{-1} m$$

$$\text{frequency} = \frac{c}{\text{wavelength}} = \frac{3.00 \times 10^8\ m/s}{1.22 \times 10^{-1} m} = 2.46 \times 10^{10}/s$$

$$\text{Energy} = E = h\nu = (6.626 \times 10^{-34} Js)(2.46 \times 10^{10}/s) = \mathbf{1.63 \times 10^{-23}\ J}$$

Example III: Photoelectric Effect

- The energy to remove an electron from potassium metal is 3.7×10^{-19}J. Will photons of frequencies of 4.3×10^{14}/s (red light) and 7.5×10^{14} /s (blue light) trigger the photoelectric effect?

- $E_{red} = h\nu = (6.626 \times 10^{-34} Js)(4.3 \times 10^{14} /s)$
  $E_{red} = 2.8 \times 10^{-19}$ J

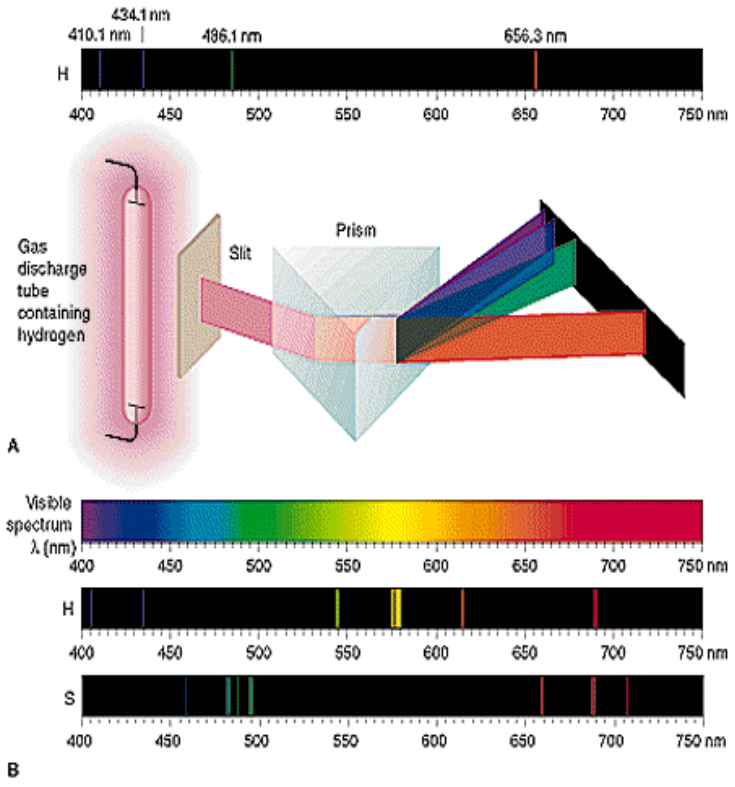
- $E_{blue} = h\nu = (6.626 \times 10^{-34} Js)(7.5 \times 10^{14} /s)$
  $E_{blue} = 5.0 \times 10^{-19}$ J

- The binding energy of potassium is $= 3.7 \times 10^{-19}$ J
- The red light will not have enough energy to knock an electron out of the potassium, but the blue light will eject an electron !

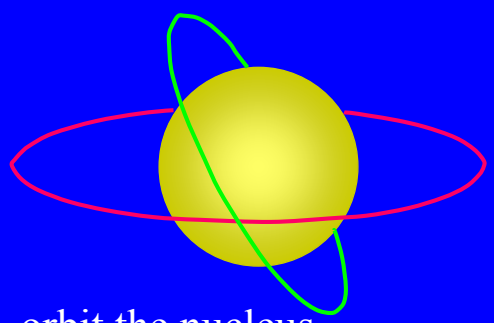
- $E_{Total} = E_{Binding\ Energy} + E_{Kinetic\ Energy\ of\ Electron}$
- $E_{Electron} = E_{Total} - E_{Binding\ Energy}$
- $E_{Electron} = 5.0 \times 10^{-19}$J $- 3.7 \times 10^{-19}$ J
  $= 1.3 \times 10^{-19}$Joules

1.1.3 Atomic and molecular spetra

The Line Spectra of Several Elements



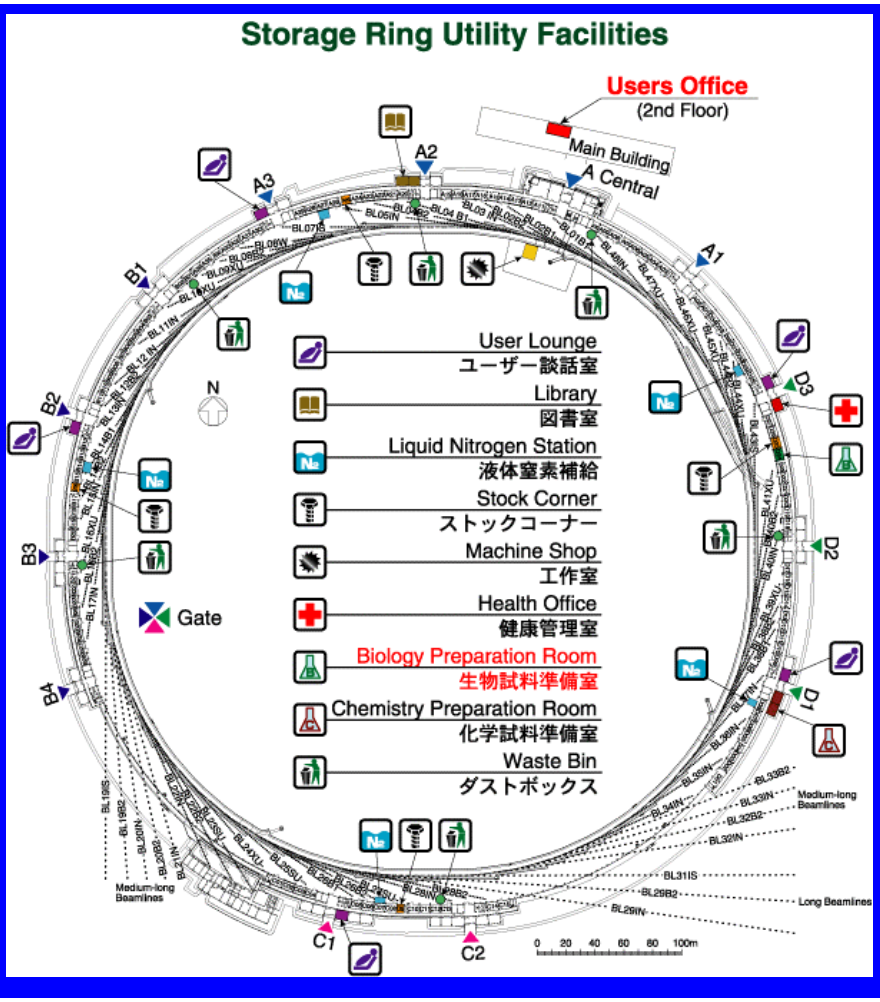
Planetary model:



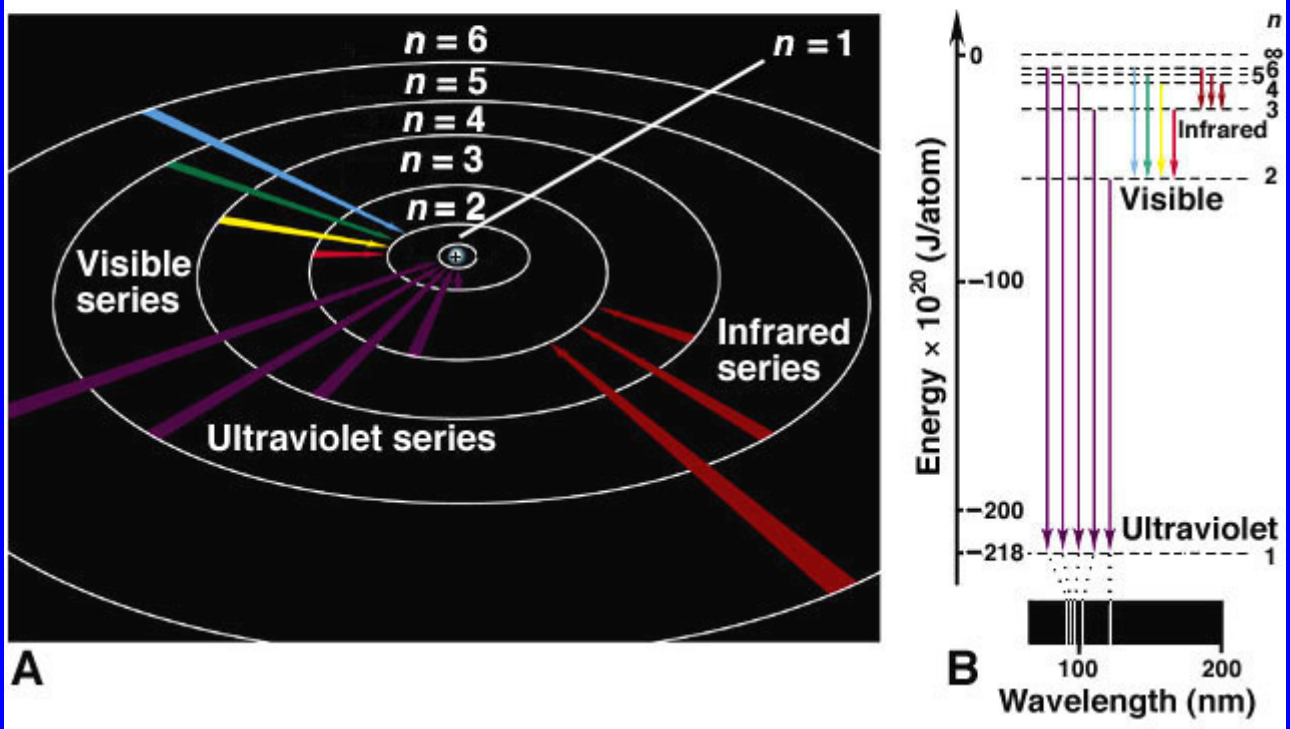
- The electron are like planets --- orbit the nucleus
- Light of energy E given off when electrons change orbits (i.e., different energies)

Why do the electrons not fall into the nucleus?

Why only discrete energies?



The Bohr Model Explanation of the Three Series of Spectral Lines



The Energy States of the Hydrogen Atom

Bohr derived the energy for a system consisting of a nucleus plus a single electron

eg. H He^{+} Li^{2+}

He predicted a set of quantized energy levels given by :

$$E_n = -\frac{RZ^2}{n^2} \qquad n = 1, 2, 3\ldots$$

- *R is called the Rydberg constant (2.18 x 10^{-18} J)*
- *n is a quantum number*
- *Z is the nuclear charge*

Problem: Find the energy change when an electron changes from the n=4 level to the n=2 level in the hydrogen atom? What is the wavelength of this photon?

Plan: Use the Rydberg equation to calculate the energy change, then calculate the wavelength using the relationship of the speed of light.

Solution:

$$E_{photon} = -2.18 \times 10^{-18} J \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) =$$

$$E_{photon} = -2.18 \times 10^{-18} J \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = \mathbf{-4.09 \times 10^{-19} J}$$

$$\lambda = \frac{h \times c}{E} = \frac{(6.626 \times 10^{-34} Js)(3.00 \times 10^{8} m/s)}{4.09 \times 10^{-19} J}$$

$$\mathbf{= 4.87 \times 10^{-7} m = 487 nm}$$

Lesson 1 Summary

1.1 The failures of classical physics

Black-Body Radiation

The photoelectric effect

A corpuscular theory of light (photons)

$\varepsilon = h\nu$ h = Planck's constant

$p = h/\lambda$

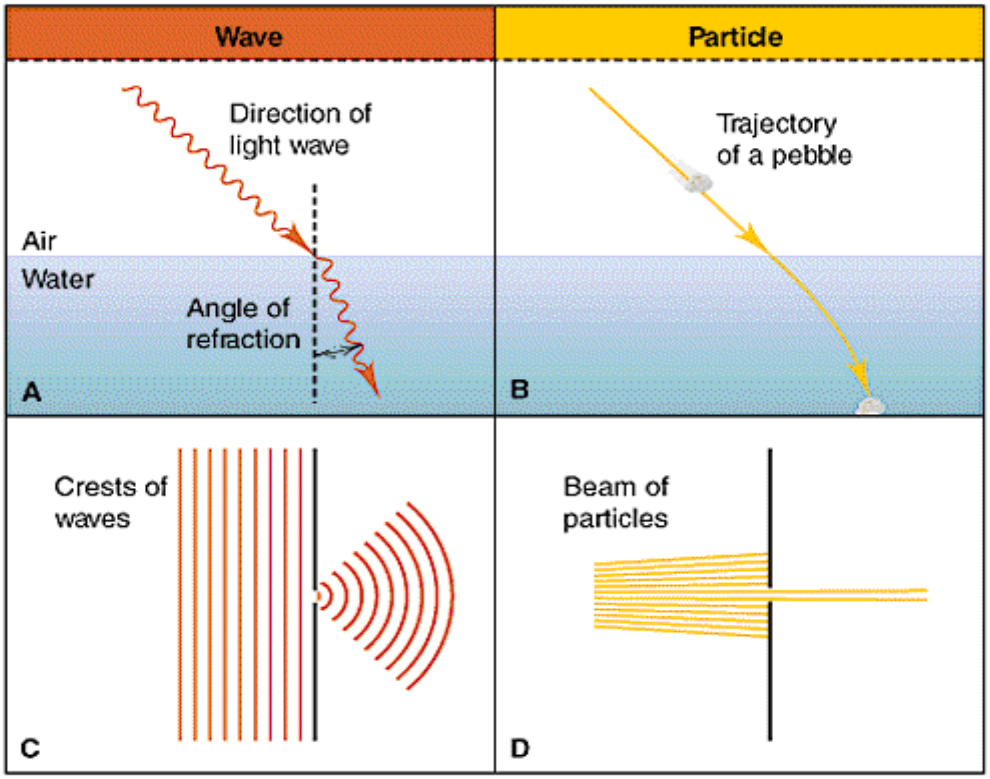
Atomic and molecular spetra

1.2 The characteristic of the motion of microscopic particles

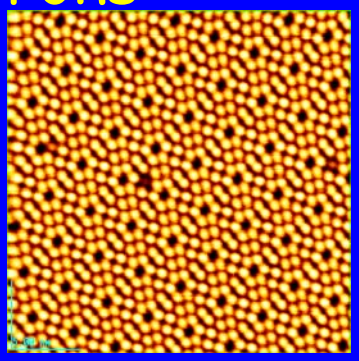
1.2.1 The wave-particle duality of microscopic particles

In 1924 de Beoglie suggested that microscopic particles might have wave properties.

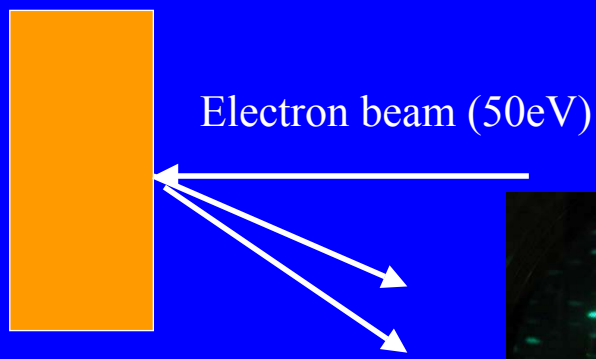
Different Behaviors of Waves and Particles

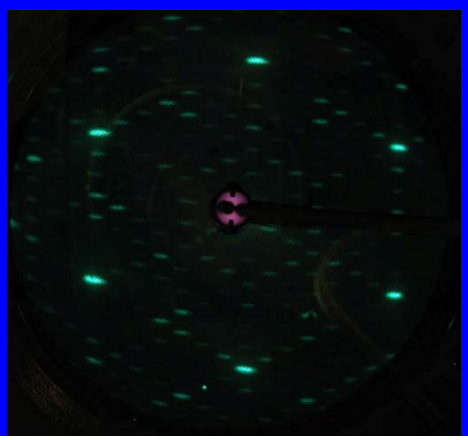


The diffraction of electrons

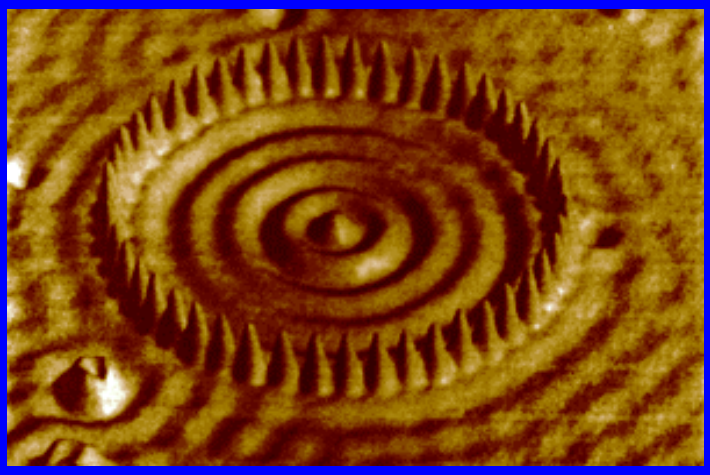


STM image of Si(111) 7x7 surface





Electron as waves



Spatial image of the confined electron states of a quantum corral. The corral was built by arranging 48 Fe atoms on the Cu(111) surface by means of the STM tip. ***Rep. Prog. Phys. 59(1996) 1737***

De Broglie considered that the wave-particle relationship in light is also applicable to particles of matter, i.e.

$$E = h\nu$$

$$p = h/\lambda$$

h = Planck's constant,

p = particle momentum,

λ = de Broglie wavelength

The wavelength of a particle could be determined by

$$\lambda = h/p = h/m\text{v}$$

de Broglie Wavelength

Example: Calculate the de Broglie wavelength of an electron with speed 3.00×10^6 m/s.

electron mass = 9.11×10^{-31} kg

velocity = 3.00×10^6 m/s

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\text{Js}}{(9.11 \times 10^{-31}\,\text{kg})(1.00 \times 10^6\,\text{m/s})}$$

$$\text{J} = \frac{\text{kg m}^2}{\text{s}^2}$$ hence

Wavelength λ = **2.42×10^{-10} m = 0.242 nm**

The moving speed of an electron is determined by the potential difference of the electric field (V)

$$\frac{1}{2}mv^2 = eV$$

1eV=1.602×10^{-19} J

If the unit of V is volt, then the wavelength is:

$$\lambda = h/mv = \frac{h}{\sqrt{2me}\sqrt{V}}$$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.110 \times 10^{-31} \times 1.602 \times 10^{-19}}} \frac{1}{\sqrt{V}}$$

$$= \frac{1.226 \times 10^{-9}}{\sqrt{V}} \quad (m)$$

The de Broglie Wavelengths of Several particles

Particles	Mass (g)	Speed (m/s)	λ (m)
Slow electron	9×10^{-28}	1.0	7×10^{-4}
Fast electron	9×10^{-28}	5.9×10^{6}	1×10^{-10}
Alpha particle	6.6×10^{-24}	1.5×10^{7}	7×10^{-15}
One-gram mass	1.0	0.01	7×10^{-29}
Baseball	142	25.0	2×10^{-34}
Earth	6.0×10^{27}	3.0×10^{4}	4×10^{-63}

The wave-particle duality

- Wave (i.e., light)
  - can be wave-like (diffraction)
  - can be particle-like ($p=h/\lambda$)
- Particles
  - can be wave-like ($\lambda = h/p$)
  - can be particle-like (classical)

Discussions:

For photon:

$p=mc$,

$E=h\nu=h\,(c/\lambda) = pc = mc^2$

$\neq\ p^2/2m = (1/2)\,mv^2$

For particles:

$p=mv$,

$E=(1/2)\,mv^2 = p^2/2m = pv/2$

$\neq\ pv$

$E=h\,\nu$

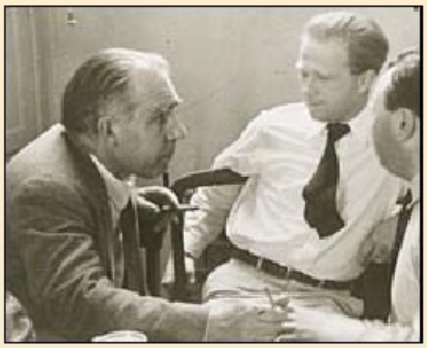
$p = h/\lambda$

$\lambda = u / \nu$ … u is not the moving speed of particles.

1.2.2 The uncertainty principle

Heisenberg's insight

Bohr, Heisenberg, Pauli (L to R)



The more precisely the position is determined, the less precisely the momentum is known in this instant, and vice versa.

--Heisenberg, uncertainty paper, 1927

$$\overline{OP} - \overline{AP} = \frac{1}{2}\lambda$$

$$\sin\theta = \overline{OC}/\overline{OA} = \frac{1}{2}\lambda / \frac{1}{2}D = \lambda / D$$

$$p_x = p\sin\theta$$

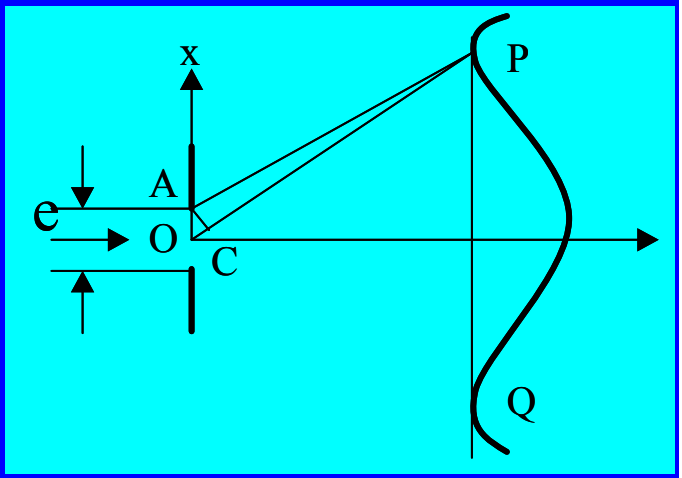
$$\Delta p = p\sin\theta \qquad (p_{xo} = 0)$$

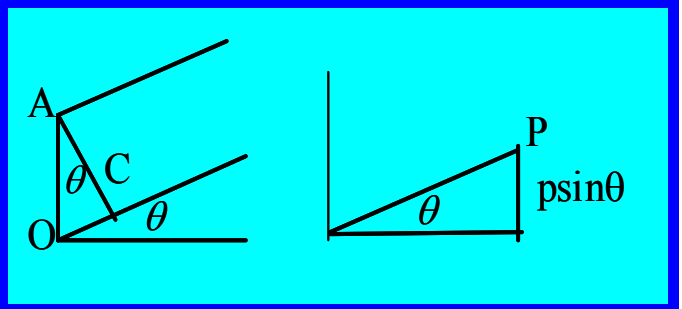
$$= p\lambda / D = \frac{h}{\lambda}\lambda / D = \frac{h}{D}$$

$$\Delta x \Delta p = h$$

Include higher order,

$$\Delta x \Delta p \geq h$$





A quantitative version

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad or \quad \frac{1}{2}\hbar$$

Measurement

- **Classical:** the error in the measurement depends on the precision of the apparatus, could be arbitrarily small.

- **Quantum:** it is physically impossible to measure simultaneously the exact position and the exact velocity of a particle.

Example

The speed of an electron is measured to be 1000 m/s to an accuracy of 0.001%. Find the uncertainty in the position of this electron.

The momentum is

$p = mv = (9.11 \times 10^{-31}\ \text{kg})\ (1 \times 10^{3}\ \text{m/s})$

$= 9.11 \times 10^{-28}\ \text{kg.m/s}$

$\Delta p = p \times 0.001\% = 9.11 \times 10^{-33}\ \text{kg m/s}$

$\Delta x = h / \Delta p = 6.626 \times 10^{-34} / (9.11 \times 10^{-33})$

$= 7.27 \times 10^{-2}\ (\text{m})$

Example

The speed of a bullet of mass of 0.01 kg is measured to be 1000 m/s to an accuracy of 0.001%. Find the uncertainty in the position of this bullet.

The momentum is

$p = mv = (0.01\ \text{kg})\ (1 \times 10^{3}\ \text{m/s}) = 10\ \text{kg.m/s}$

$\Delta p = p \times 0.001\% = 1 \times 10^{-4}\ \text{kg m/s}$

$\Delta x = h / \Delta p = 6.626 \times 10^{-34} / (1 \times 10^{-4})$

$= 6.626 \times 10^{-30}\ (\text{m})$

Example

The average time that an electron exists in an excited state is 10^{-8} s. What is the minimum uncertainty in energy of that state?

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

$$\Delta E_{\min} = \hbar / \Delta t = 1.06 \times 10^{-34}\ \text{Js}/\ 10^{-8}\ \text{s}$$

$$= 1.06 \times 10^{-26}\ \text{J} = \frac{1.06 \times 10^{-26}}{1.6 \times 10^{-19}}\ \text{eV}$$

$$= 0.66 \times 10^{-7}\ \text{eV}$$

CLASSICAL vs QUANTUM MECHANICS

Macroscopic matter - Matter is particulate, energy varies continuously. The motion of a group of particles can be predicted knowing their positions, their velocities and the forces acting between them.

Microscopic particles - microscopic particles such as electrons exhibit a wave-particle "duality", showing both particle-like and wave-like characteristics. The energy level is discrete. …

The description of the behavior of electrons in atoms requires a completely new "quantum theory".

What is Quantum Mechanics?

QM is the theory of the behavior of very small objects (e.g. molecules, atoms, nuclei, elementary particles, quantum fields, etc.)

One of the essential differences between classical and quantum mechanics is that physical variables that can take on continuous values in classical mechanics (e.g. energy, angular momentum) can only take on discrete (or quantized) values in quantum mechanics (e.g. the energy levels of electrons in atoms, or the spins of elementary particles, etc).

Lesson 2 Summary

The wave-particle duality

- Wave (i.e., light)
  - can be wave-like (diffraction)
  - can be particle-like ($p=h/\lambda$)
- Particles
  - can be wave-like ($\lambda = h/p$)
  - can be particle-like (classical)

The uncertainty principle

1.3 The basic assumptions (postulates) of quantum mechanics

Postulate 1. The state of a system is described by a wave function of the coordinates and the time.

In CM (classical mechanics), the state of a system of N particles is specified totally by giving 3N spatial coordinates (Xi, Yi, Zi) and 3N velocity coordinates (Vxi, Vyi, Vzi).

In QM, the wave function takes the form ψ(r, t) that depends on the coordinates of the particle and on the time.

For example:

The wavefunction of plane monochromatic light:

$$\psi = A\exp[i2\pi(x/\lambda - vt)$$

The wavefunction Ψ for a single particle of 1-D motion is:

$$\psi = A\exp[(i2\pi/h)(xp_x - Et)$$

A wave function must satisfy 3 mathematical conditions:

1. Single-value
2. Continuous
3. Quadratically integrable.

The probability

$\psi^*(r,t)\psi(r,t)dxdydz$	The probability that the particle lies in the volume element dxdydz, located at r, at time t.

To be generally **normalized**

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(r,t)\psi(r,t)dxdydz = 1$$

Postulate 2. For every observable mechanical quantity of a microscopic system, there is a corresponding linear Hermitian operator associated with it.

To find this operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates and corresponding linear-momentum, and then replace each corrdinate x by the operator, and each momentum component p_x by the operator $-i\hbar\partial/\partial x$.

An **operator** is a rule that transforms a given function into another function. E.g. d/dx, sin, log

$$\hat{D} = d/dx \qquad f(x) = x^3 - 5$$

$$\hat{D}f(x) = (x^3 - 5)' = 3x^2$$

$$(\hat{A} + \hat{B})f(x) \equiv \hat{A}f(x) + \hat{B}f(x)$$

$$(\hat{A} - \hat{B})f(x) \equiv \hat{A}f(x) - \hat{B}f(x)$$

$$\hat{A}\hat{B}f(x) \equiv \hat{A}[\hat{B}f(x)]$$

Operators obey the associative law of multiplication:

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

- A linear operator means

$$\hat{A}(\psi_1 + \psi_2) = \hat{A}\psi_1 + \hat{A}\psi_2$$

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

- A Hermitian operator means

$$\int \psi_1^* \hat{A}\psi_1 = \int \psi_1 (\hat{A}\psi_1)^* \qquad \int \psi_1^* \hat{A}\psi_2 = \int \psi_2 (\hat{A}\psi_1)^*$$

* A Hermitian operator ensures that the eigenvalue of the operator is a real number

Eigenfunctions and Eigenvalues

Suppose that the effect of operating on some function *f(x)* with the operator Â is simply to multiply *f(x)* by a certain constant *k*. We then say that *f(x)* is an *eigenfunction* of Â with *eigenvalue k.*

Eigen is a German word meaning *characteristic*.

$$\hat{A}f(x) \equiv kf(x)$$

$$(d/dx)e^{2x} = 2e^{2x}$$

Examples

$\hat{x}, \hat{p}_x$ *Hermiton operators*

$\frac{\partial}{\partial x}, \frac{d}{dx}$ *Not Hermiton operators*

Examples for calculation

$$\int_{-\infty}^{\infty} \psi_1^* \hat{x} \psi_2 d\tau = \int_{-\infty}^{\infty} \psi_1^* \hat{x} \psi_2 d\tau = \int_{-\infty}^{\infty} x \psi_1^* \psi_2 d\tau =$$

$$\int_{-\infty}^{\infty} \psi_2 x \psi_1^* d\tau = \int_{-\infty}^{\infty} \psi_2 (x\psi)_1^* d\tau = \int_{-\infty}^{\infty} \psi_2 \hat{x} \psi_1^* d\tau$$

$$\int_{-\infty}^{\infty} \psi_1^* \hat{p}_x \psi_2 d\tau = \int_{-\infty}^{\infty} \psi_1^* (-i\hbar \frac{\partial}{\partial x}) \psi_2 d\tau = -i\hbar \int_{-\infty}^{\infty} \psi_1^* \frac{\partial}{\partial x} \psi_2 d\tau =$$

$$-i\hbar[\psi_1^* \psi_2 |_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi_2 \frac{\partial}{\partial x} \psi^*{}_1 d\tau] = i\hbar \int_{-\infty}^{\infty} \psi_2 \frac{\partial}{\partial x} \psi^*{}_1 d\tau = \int_{-\infty}^{\infty} \psi \hat{p}_x{}^* \psi_1{}^*$$

Mechanical quantities and their Operators

To every physical observable there corresponds a linear Hermitian operator. To find this operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates and corresponding linear-momentum components, and then replace each coordinate x by the operator x. and each momentum component p_x by the operator $-i\hbar\partial/\partial x$.

Some Mechanical quantities and their Operators

Mechanical quantities		Methematical Operator
Position	x	$\hat{x} = x$
Momentum (x)	p_x	$\hat{p} = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}$
Angular Momentum (z)	$M_z = xp_y - yp_x$	$\hat{M}_z = -\frac{ih}{2\pi}(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$
Kinetic Energy	$T = p^2/2m$	$\hat{T} = -\frac{h^2}{8\pi^2 m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) = -\frac{h^2}{8\pi^2 m}\nabla^2$
Potential Energy	V	$\hat{V} = V$
Total Energy	E =T+V	$\hat{H} = -\frac{h^2}{8\pi^2 m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) + \hat{V}$

The average value of the physical observable

If a system is in a state described by a normalized wave function ψ, then the average value of the observable corresponding to A is given by –

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi \, d\tau$$

Exercise :

Suppose a particle in a box is in a state -

$$\Psi(x) = \left(\frac{30}{a^5}\right)^{\frac{1}{2}} x(a-x) \qquad 0 \le x \le a$$

$$= 0 \quad \text{otherwise}$$

Note that the wave function ψ(x) is not an eigenfunction for a particle in a box. Sketch ψ(x) vs. x and show that y(x) is normalized. Calculate the average energy associated with this state. (Assume V = 0).

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

$$\langle E \rangle = \int_0^a \Psi^* \hat{H} \Psi \, dx \qquad \frac{5h^2}{4\pi^2 m a^2}$$

If the wave function is an ***eigenfunction*** *of A, with* ***eigenvalue*** a_n, *then the a measurement of the observable corresponding to A will give the value* a_n *with* ***certainty***.

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi_n^* A \Psi_n d\tau$$

$$= \int_{-\infty}^{\infty} \Psi_n^* a_n \Psi_n d\tau$$

$$= a_n \int_{-\infty}^{\infty} \Psi_n^* \Psi_n d\tau$$

$$= a_n$$

$$\langle a^2 \rangle = \int_{-\infty}^{\infty} \Psi_n^* A^2 \Psi_n d\tau$$

$$= a^2{}_n$$

$$\sigma_a{}^2 = \langle a^2 \rangle - \langle a \rangle^2$$

$$= a^2{}_n - a^2{}_n$$

$$= 0$$

Thus the only value we measure is the value a_n.

Commuted operators

$$\left[\hat{F},\ \hat{G}\right] = \hat{F}\hat{G} - \hat{G}\hat{F} = 0$$

- When the two operators **commute**, their corresponded mechanical quantities can be measured simultaneously.

Postulate 3: The wave-function of a system evolves in time according to the time-dependent Schrödinger equation

Assumption 3: The wave-function of a system evolves in time according to the time-dependent Schrödinger equation -

$$\hat{H}\Psi(x,y,z,t) = i\hbar\frac{\partial\Psi}{\partial t}$$

In general the Hamiltonian H is not a function of t, so we can apply the method of separation of variables.

$$\Psi(x,y,z,t) = \psi(x,\ y,\ z)\ f(t)$$

$$\hat{H}\psi(\mathrm{x,y,z})\cdot f(t) = i\hbar\,\psi(\mathrm{x,y,z})\frac{df(t)}{dt}$$

$$\frac{\hat{H}\psi(\mathrm{x,y,z})}{\psi(\mathrm{x,y,z})} = i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = E$$

$$\boxed{\begin{aligned}&\hat{H}\psi(\mathrm{x,y,z}) = E\psi(\mathrm{x,y,z})\\ &i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = E\end{aligned}}$$

$$\psi(x,y,z,t) = \psi(x,y,z)\,e^{\frac{-iEt}{\hbar}}$$

Time-independent Schrödinger's Equation

$$\hat{H}\psi = E\psi$$

Eigenvalue equation

$$\hat{H} = \hat{T} + \hat{V}$$

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$\hat{p} = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}$$

$$\hat{V} = \frac{Ze^2}{4\pi\varepsilon_0 r}$$

e.g. H atom

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}$$

The **Schrödinger's Equation is** eigenvalue equation.

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

In any measurement of the observable associated with the operator A, the only values that will ever be observed are the *eigenvalues* ***a***, which satisfy the eigenvalue equation.

I. The eigenvalue of a Hermitian operator is a real number.

Proof:

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

$$\int \psi^*\hat{A}\psi = a\int \psi^*\psi$$

$$\int \psi(\hat{A}^*\psi^*) = a^*\int \psi\psi^*$$

$$\Rightarrow \quad a = a^*$$

Quantum mechanical operators have to have real eigenvalues

II. The eigenfunctions of Hermitian operators are orthogonal

$$\int \psi_i^* \psi_j dx = \delta_{ij}$$

II. The eigenfunctions of Hermitian operators are orthogonal

Consider these two eigen equations

$$\hat{A}\psi_n = a_n \psi_n$$

$$\hat{A}\psi_m = a_m \psi_m$$

Multiply the left of the 1st eqn by ψ_m^* and integrate, then take the complex conjugate of eqn 2, multiply by ψ_n and integrate

$$\int \psi_m^* \hat{A} \psi_n dx = \mathrm{a}_\mathrm{n} \int \psi_m^* \psi_n dx$$

$$//$$

$$\int \psi_n \hat{A}^* \psi_m^* dx = \mathrm{a}_\mathrm{m}^* \int \psi_n \psi_m^* dx$$

Subtracting these two equations gives -

$$\int \psi_m^* \hat{A} \psi_n dx - \int \psi_n \hat{A}^* \psi_m^* dx$$
$$= (a_n - a_m^*) \int \psi_m^* \psi_n dx = 0$$

$$(a_n - a_m^*) \int \psi_m^* \psi_n^{\neq} dx = 0$$

There are 2 cases, n = m, or n ≠ m

If n = m, the integral = 1, by normalization, so $a_n = a_n^*$

If n ≠ m, and the system is **nondegenerate** (i.e.different eigenfunctions have the same eigenvalues, $a_n \neq a_m$), then

$$(a_n - a_m) \int \psi_m^* \psi_n dx = 0$$

$$\int \psi_m^* \psi_n dx = 0$$

The eigenfunctions of Hermitian operators are orthogonal

$$\int \psi_i^* \psi_j dx = \delta_{ij}$$

Example:

$$\varphi_{1s}(H)=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_o} \qquad \varphi_{2s}=\frac{1}{\sqrt{32\pi a_0^3}}e^{-r/2a_0}(2-\frac{r}{a_0})$$

$$\int_{-\infty}^{+\infty}\varphi_{1s}\varphi_{2s}d\tau=\frac{1}{4\sqrt{2}\pi a_0^3}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}e^{-r/a_0}e^{-r/2a_0}(2-\frac{r}{a_0})r^2\sin\theta drd\theta d\phi$$

$$=\frac{4\pi}{4\sqrt{2}\pi a_0^3}\int_0^{\infty}e^{-\frac{3r}{2a_0}}r^2(2-\frac{r}{a_0})dr$$

$$=\frac{1}{\sqrt{2}a_0^3}[\int_0^{\infty}e^{-\frac{3r}{2a_0}}r^2dr-\int_0^{\infty}e^{-\frac{3r}{2a_0}}\frac{r^3}{a_0}dr$$

$$\boxed{\frac{3r}{2a_0}=y}$$

$$=\frac{1}{\sqrt{2}}[\frac{16}{27}\int_0^{\infty}e^{-y}y^2dy-\frac{16}{81}\int_0^{\infty}e^{-y}y^3dy]$$

$$=\frac{1}{\sqrt{2}}[\frac{16}{27}\cdot\Gamma(3)-\frac{16}{81}\Gamma(4)]=\frac{1}{\sqrt{2}}[\frac{16}{27}\cdot 2!-\frac{16}{81}\cdot 3!]=0$$

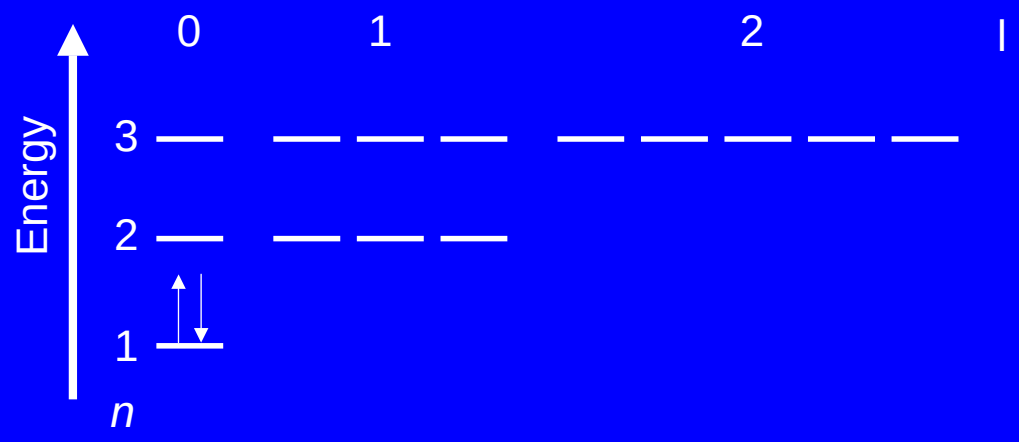
Postulate 4 : If ψ_1, ψ_2,... ψ_n are the possible states of a microscopic system (a complete set), then the linear combination of these states is also a possible state of the system.

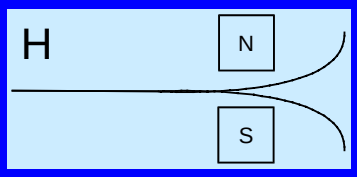
Assumption 4 : If $\psi_1, \psi_2, \ldots \psi_n$ are the possible states of a microscopic system (a complete set), then the linear combination of these states is also a possible state of the system.

$$\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 \cdots + c_n\psi_n = \sum_i c_i\psi_i$$

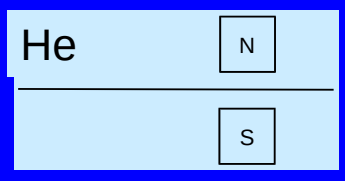
Postulate 5 : Pauli's principle. Every atomic or molecular orbital can only contain a maximum of two electrons with opposite spins.

Energy level diagram for He. Electron configuration: $1s^2$



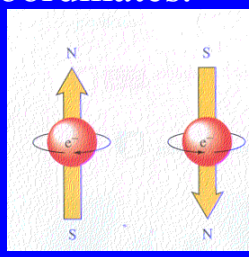


paramagnetic – one (more) unpaired electrons



diamagnetic – all paired electrons

The complete wavefunction for the description of electronic motion should include a spin parameter in addition to its spatial coordinates.



m_s = *spin magnetic* → electron spin

$m_s = \pm ½$ (-½ = α) (+½ = β)

Pauli exclusion principle:

Each electron must have a unique set of quantum numbers.

- *Two electrons in the same orbital must have opposite spins.*

- Electron spin is a purely quantum mechanical concept.

The complete wavefunction for the description of electronic motion should include a spin parameter in addition to its spatial coordinates.

$$\Phi = \Psi(n, l, m_l) \cdot \chi(s, m_s)$$

$$for \quad two-electron \quad atom(He)$$

$$\phi(q_{1,} q_2)$$

$$\left|\phi(q_{1,} q_2)\right|^2 = \left|\phi(q_{2,} q_1)\right|^2$$

$$\phi(q_{1,} q_2) = \pm\phi(q_{2,} q_1)$$

+ symmetry(Bosons)

- antisymmetry(Fermions)

Fermions

- Particles that **<u>do</u>** obey the Pauli Exclusion Principle.

Bosons

- Particles that **<u>do not</u>** obey the Pauli Exclusion Principle

Lesson 3 Summary

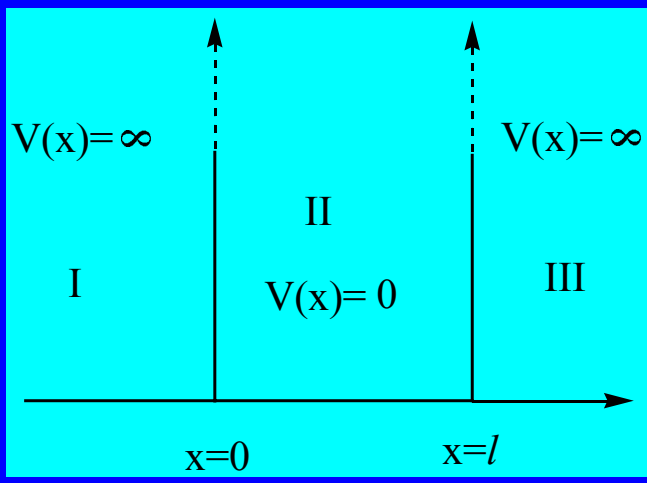
The basic assumptions (postulates) of quantum mechanics

1.4 Solution of free particle in a box – a simple application of Quantum Mechanics

1.4.1 The free particle in a one dimensional box

1. The Schrödinger's Equation and its solution

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



I, III:

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x} + V\psi = E\psi$$

$$\frac{\partial^2\psi}{\partial^2 x} - \frac{8\pi^2 m}{h^2}V\psi = 0 \qquad \because (V=\infty) \therefore V - E = V$$

$$\psi = \frac{\partial^2\psi}{\partial^2 x}\cdot\frac{h^2}{8\pi^2 mV} = 0$$

II: V=0

$$\frac{\partial^2\psi}{\partial^2 x}+\frac{8\pi^2 m}{h^2}E\psi=0$$

$$\Psi_1=e^{i\alpha x} \qquad \frac{d\Psi_1}{dx}=i\alpha e^{i\alpha x} \qquad \frac{d^2\Psi_1}{dx^2}=-\alpha^2 e^{i\alpha x}$$

$$\Psi_2=e^{-i\alpha x} \qquad \frac{d\Psi_2}{dx}=-i\alpha e^{-i\alpha x} \qquad \frac{d^2\Psi_2}{dx^2}=-\alpha^2 e^{-i\alpha x}$$

$$set \qquad \frac{8\pi^2 mE}{h^2}=\alpha^2$$

$$\frac{\partial^2\psi}{\partial^2 x}+\alpha^2\psi=0$$

$$e^{i\alpha x}=\cos\alpha x+i\sin\alpha x$$

$$e^{-i\alpha x}=\cos\alpha x-i\sin\alpha x$$

$$\psi=A'e^{i\alpha x}+B'e^{-i\alpha x}$$

$$\psi=A\cos\alpha x+B\sin\alpha x$$

Boundary condition and continuous condition: $\psi(0)=0$, $\psi(l)=0$

Hence, $\psi(0)=A\cos 0+B\sin 0$

$A=0$, $B\neq 0$ $\quad \psi=B\sin\alpha x$

$\psi(l)=B\sin\alpha x=B\sin\alpha l=0$, $\quad$ Thus, $\alpha l=n\pi$,

$$\frac{8\pi^2 mE}{h^2}=\alpha^2=\frac{n^2\pi^2}{l^2}$$

$$E=\frac{n^2h^2}{8ml^2} \qquad (n=1,2,3\ldots)$$

$$\psi=B\sin\frac{n\pi}{l}x$$

Normalization of wave-function:

$$\int_0^l|\psi|^2dx=1$$

$$\int_0^l B^2\sin^2\frac{n\pi}{l}xdx=1$$

$$\int\sin^2 xdx=\frac{1}{2}x-\frac{1}{4}\sin 2x$$

$$B^2\cdot\frac{1}{2}\frac{n\pi}{l}\left(\frac{l}{n\pi}x\right)_0^l=B^2\cdot\frac{1}{2}\frac{n\pi}{l}\cdot\frac{l}{n\pi}\cdot l=1$$

$$B=\sqrt{\frac{2}{l}}$$

$$\psi=\sqrt{\frac{2}{l}}\sin\frac{n\pi}{l}x$$

2. The properties of the solutions

a. The particle can exist in many states

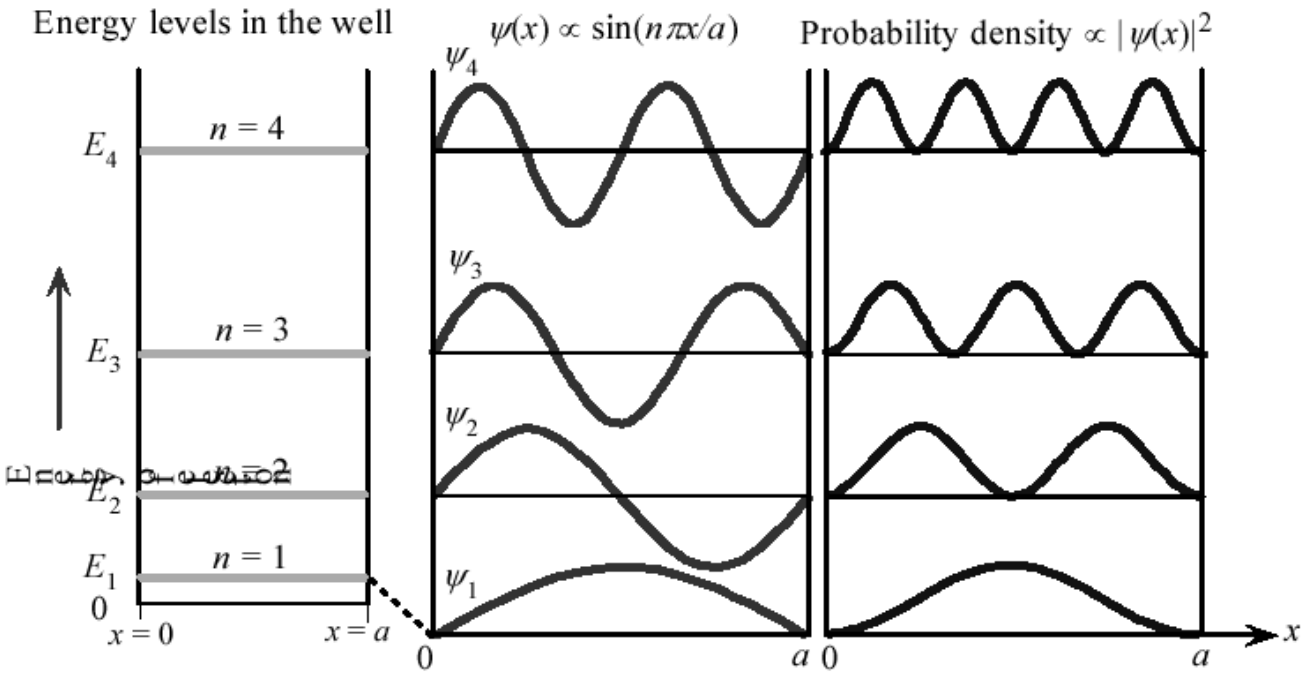
b. quantization energy

c. The existence of zero-point energy. minimum energy ($h^2/8ml^2$)

d. There is no trajectory but only probability distribution

e. The presence of nodes

n=1	$E_1 = \frac{h^2}{8ml^2}$	$\psi_1 = \sqrt{\frac{2}{l}} \sin \frac{\pi x}{l}$
n=2	$E_2 = \frac{4h^2}{8ml^2}$	$\psi_2 = \sqrt{\frac{2}{l}} \sin \frac{2\pi x}{l}$
n=3	$E_3 = \frac{9h^2}{8ml^2}$	$\psi_3 = \sqrt{\frac{2}{l}} \sin \frac{3\pi x}{l} \cdots\cdots$



Discussion:

i. Normalization and orthogonality

$$\int_0^l \psi_n(x)\psi_m(x)dx = \frac{2}{l}\int_0^l \sin\frac{n\pi x}{l}\sin\frac{m\pi x}{l}dx = 0$$

ii. Average value

$$< x >= \frac{2}{l}\int_0^l \sin\frac{n\pi x}{l}\, x \sin\frac{n\pi x}{l}dx = \frac{l}{2}$$

$$< x^2 >= \frac{2}{l}\int_0^l \sin\frac{n\pi x}{l}\, x^2 \sin\frac{n\pi x}{l}dx = \frac{l^2}{3}$$

$$< p >= 0$$

$$< p^2 >= \frac{n^2h^2}{4l^2}$$

If the wave function is an ***eigenfunction*** *of* $\hat{A}$

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A}\Psi d\tau = \int_{-\infty}^{\infty} \Psi^* a\Psi d\tau$$

$$= a\int_{-\infty}^{\infty} \Psi^*\Psi d\tau = a$$

iii. Uncertainty

$$\Delta x = \sqrt{< x^2 > - < x >^2} = \frac{l}{2\sqrt{3}}$$

$$\Delta p = \sqrt{< p^2 > - < p >^2} = \frac{nh}{2l}$$

$$\Delta x \Delta p = \frac{l}{2\sqrt{3}}\frac{nh}{2l} = \frac{nh}{4\sqrt{3}}$$

$$when \quad n = 1 \qquad (ground \quad state)$$

$$\Delta x \Delta p \approx \frac{h}{2\pi}$$

The general steps in the quantum mechanical treatment:

a. Obtain the potential energy functions followed by deriving the Hamiltonian operator and Schrödinger equation.

b. Solve the Schrödinger equation. (obtain ψ_n and E_n)

c. Study the characteristics of the distributions of ψ_n.

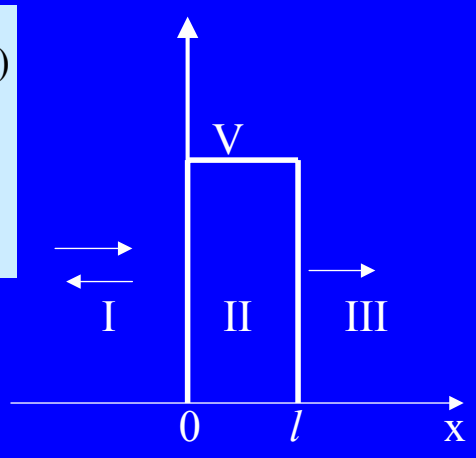
d. Deduce the values of the various physical quantities of each corresponding state.

3. Quantum leaks --- tunneling

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x}+V\psi=E\psi \qquad (0<x<l)$$

and

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x}=E\psi \qquad (x<0, x>l)$$

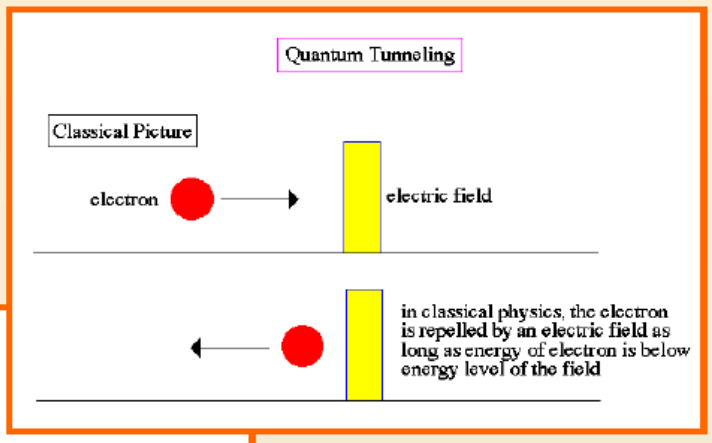


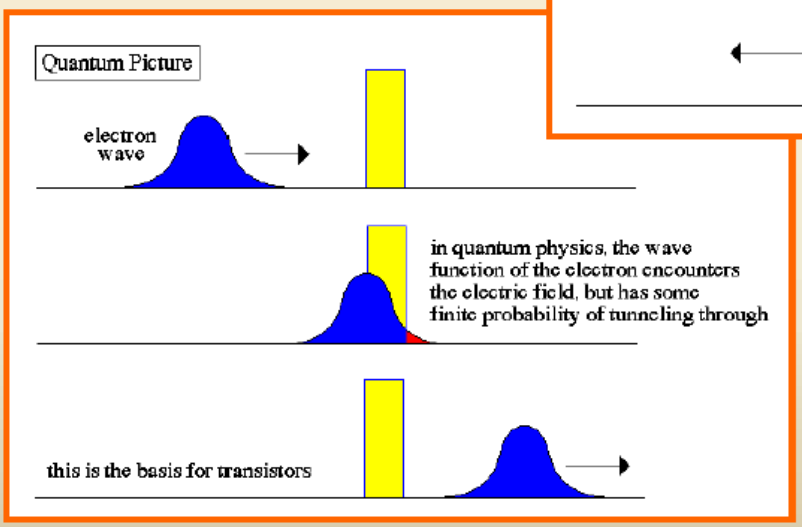
The probability of penertration is given by

$$P \approx 4(E/V)[1-(E/V)]e^{-\frac{2}{\hbar}\sqrt{2m(V-E)}l}$$

When E<V

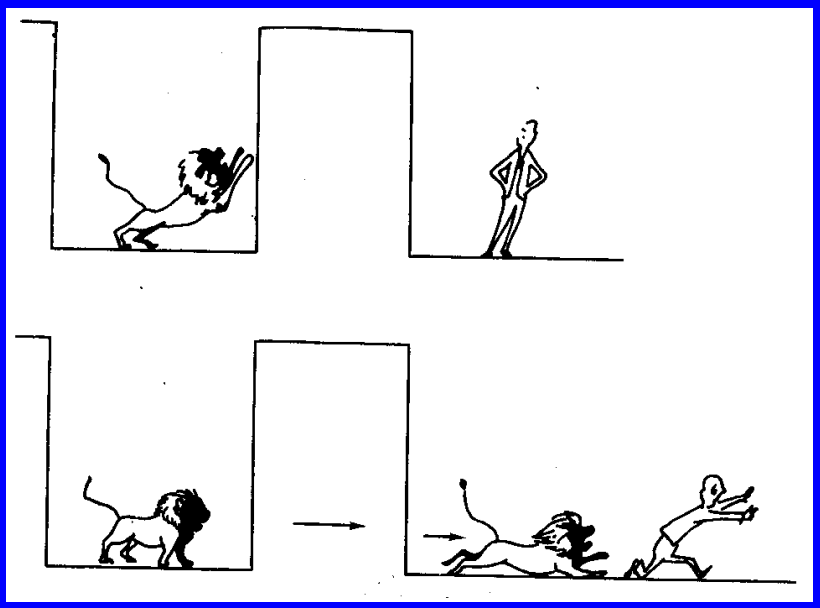
Tunneling





Tunneling

CLASSICAL MECHANICS



QUANTUM MECHANICS

Tunneling in the "real world"

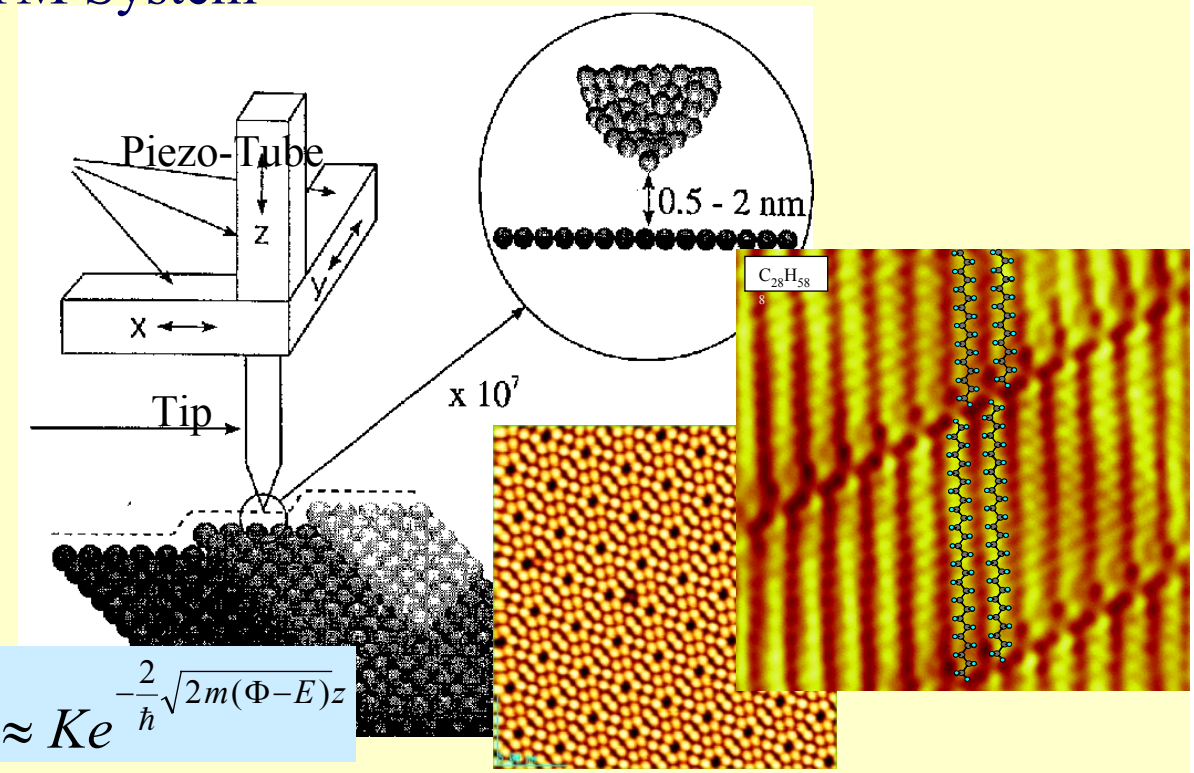
- Tunneling is used:

- for the operation of many microelectronic devices (tunneling diodes, flash memory, …)

- for advanced analytical techniques (scanning tunneling microscope, STM)

- Responsible for radioactivity (e.g. alpha particles)

STM System



$$P \approx K e^{-\frac{2}{\hbar}\sqrt{2m(\Phi - E)}z}$$

Mode: Constant Current mode, Constant high mode

1.4.2 The free particle in a three dimensional box

Particle in a 3-D box of dimensions a, b, c

Out of the box, V(x, y, z) = ∞
In the box, V(x, y, z) =0

$$-\frac{h^2}{8\pi^2 m}\nabla^2\psi = E\psi$$

$$0 < x < a$$
$$0 < y < b$$
$$0 < z < z$$

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)\psi = E\psi$$

Let $\psi = \psi(x, y, z) = X(x)\,Y(y)\,Z(z)$ *(separation of variables)*
Substituting into 3-D Schroedinger equation

(separation of variables)

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)\psi = E\psi$$

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)XYZ = EXYZ_x$$

$$-\frac{h^2}{8\pi^2 m}\left(\frac{YZ\partial^2 X}{\partial^2 x}+\frac{XZ\partial^2 Y}{\partial^2 y}+\frac{XY\partial^2 Z}{\partial^2 z}\right) = EXYZ$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 X}{X\partial^2 x} = E + \frac{h^2}{8\pi^2 m}\left(\frac{\partial^2 Y}{Y\partial^2 y}+\frac{\partial^2 Z}{Z\partial^2 z}\right) = E_x$$

Let $E_z = E - E_x + E_y$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 x}X = E_x X \qquad -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 y}Y = E_y Y \qquad -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 z}Z = E_z Z$$

$E = E_x + E_y + E_z$

The solution is:

$$X(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x \pi x}{a}$$

$$Y(y) = \sqrt{\frac{2}{b}}\sin\frac{n_y \pi y}{b}$$

$$Z(z) = \sqrt{\frac{2}{c}}\sin\frac{n_z \pi z}{c}$$

$$\psi = XYZ = \sqrt{\frac{8}{abc}}\sin\frac{n_x \pi x}{a}\sin\frac{n_y \pi y}{b}\sin\frac{n_z \pi z}{c}$$

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$$

Multiply degenerate energy level when the box is cubic

(a = b = c)

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

The ground state: $n_x = n_y = n_z = 1$

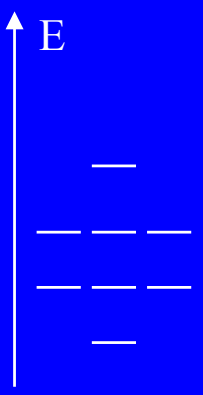
$$E = \frac{3h^2}{8ma^2}$$

The first excited state: $n_i = n_j = 1$, $n_k = 2$

The wave-functions are called *degenerate (triply degenerate)*

$$E = \frac{6h^2}{8ma^2}$$

$$\begin{cases} 1 & 1 & 2 \\ 1 & 2 & 1 \\ 2 & 1 & 1 \end{cases}$$



1.4.3 Simple applications of a one-dimensional potential box model

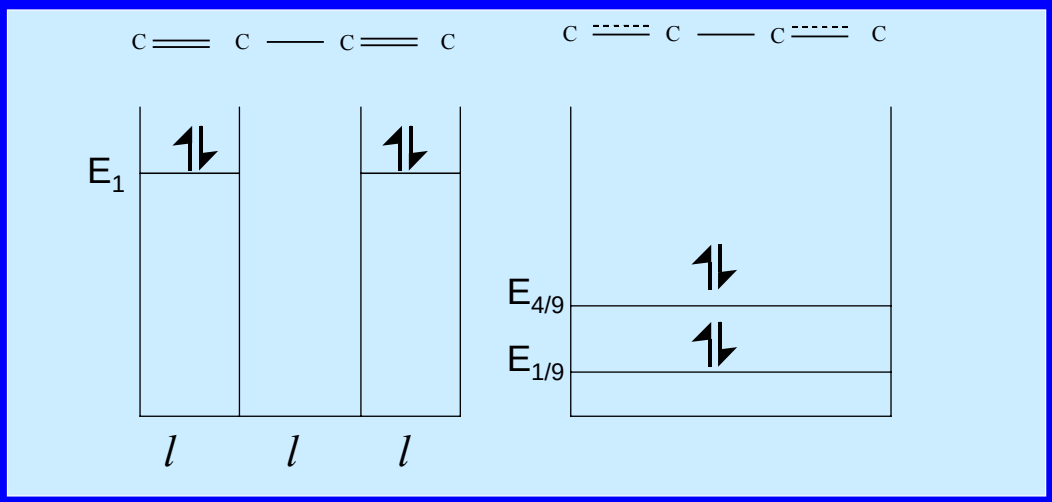
Example 1: The delocalization effect of 1,3-butadiene

Four π electron form two π localized bonds

$E=2\times 2\times h^2/8ml^2=4E_1$ >

Four π electron form a π_4^4 delocalized bonds

$E=2\times h^2/8m(3l)^2+2\times 2^2\times h^2/8m(3l)^2=(10/9)E_1$



Example 2: The adsorption spectrum of cyanines

The general formula of the cyanine dye:

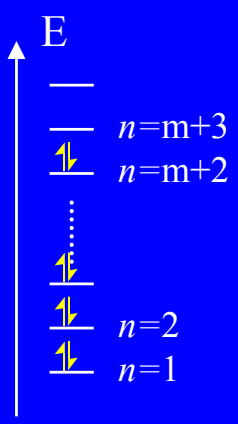
$R_2\ddot{N}\text{-}(CH{=}CH\text{-})_mCH{=}\overset{+}{N}R_2$

Total π electrons: 2m+4

In the ground state, these electrons occupy m+2 molecular orbitals

The adsorption spectrum correspond to excitation of electrons from the highest occupied (m+2) orbital to the lowest unoccupied (m+3) orbital.

$$\Delta E=\frac{h^2}{8m_el^2}[(m+3)^2-(m+2)^2]=\frac{h^2}{8m_el^2}(2m+5)$$



$$\nu = \frac{\Delta E}{h} = \frac{h}{8m_e l^2}[(m+3)^2 - (m+2)^2] = \frac{h}{8m_e l^2}(2m+5)$$

$$\lambda = \frac{8m_e l^2 c}{h(2m+5)} = \frac{3.30 l^2}{2m+5} \quad (pm)$$

$$l = 248m + 565(pm)$$

Table 1. The absorption spectrum of the cyanine dye

$R_2\ddot{N}\text{-}(CH{=}CH\text{-})_mCH{=}\overset{+}{N}R_2$

m	λmax (calc) / nm	λmax (expt) /nm
1	311.6	309.0
2	412.8	409.0
3	514.6	511.0