Structural Chemistry

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辅导：赵媛　张向飞

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
- <<**结构化学**>> 江元生编著, 高等教育出版社
- <<**结构化学习题解析**>>周公度 等，北京大学出版社

http://ctc.xmu.edu.cn/zxcao/

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课程说明

- **作业要求：** 按时、规范、独立完成
- **考勤与考试：** 期中/期末/随堂考试，期平成绩等
- **课外阅读：**

  科技媒体：科学网-新闻；**C&EN**；**…**

  文献搜索引擎：**Web of Science, SciFinder, Google**

  文献阅读：各大杂志社在线网站，图书馆

Structural Chemistry

结构化学是研究原子、分子和晶体的微观结构，研究原子和分子运动规律，研究物质的结和性能关系的科学

主要研究从原子、分子片、分子、超分子，到分子和原子的各种不同尺度和不同复杂程度的聚集态和组装态的合成和反应，分离和分析，结构和形态，物理性能和生物活性及其规律和应用的自然科学　　－－－ 徐光宪

1998年诺贝尔化学奖获得者Kohn和Pople认为：

“量子化学已经发展成为广大化学家所使用的工具，将化学带入一个新时代，在这个新时代里实验和理论能够共同协力探讨分子体系的性质。化学不再是纯粹的实验科学了”

The Nobel Prize in Chemistry 2013
Martin Karplus, Michael Levitt, Arieh Warshel

Nobel Prize in Chemistry 1981
Fukui & Hoffmann

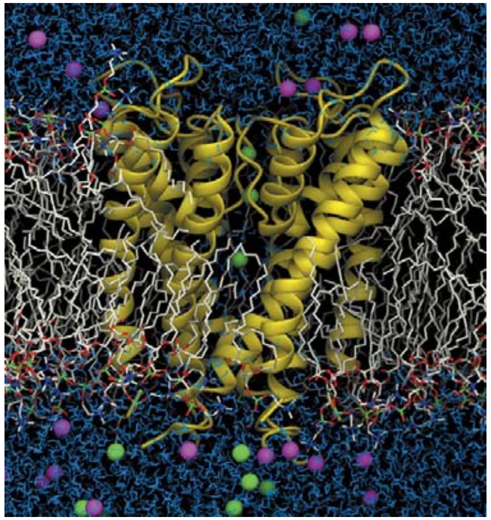
The Nobel Prize in Chemistry 2013

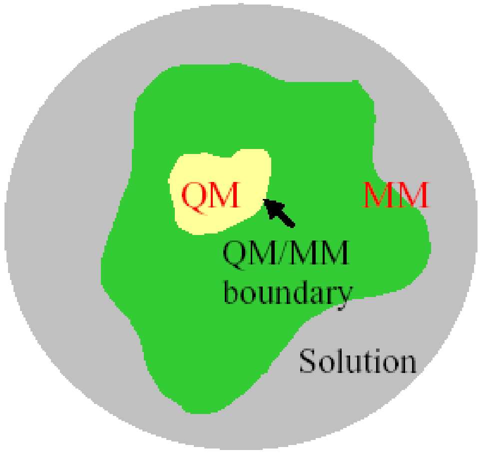

© Nobel Media AB
Martin Karplus


Photo: Keilana via Wikimedia Commons
Michael Levitt


Photo: Wikimedia Commons
Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems".*





2013年诺贝尔化学奖获奖理由：复杂体系多尺度模型

Know-How about Structural Chemistry

- **3+2+1原则**

3种理论：量子理论，化学键理论，点阵理论
3种结构：原子结构，分子结构，晶体结构
3个基础：量子化学基础，对称性原理基础，结晶化学基础
2个因素：电子因素，空间因素
1条主线：结构决定性能，性能反映结构

- 理解为主，记忆为辅（预习--- 复习--- 总结)

- 发展的观点

分子→超分子，微观→介观（纳米）→宏观，相对论？
光速不变？…

What is Chemistry

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

Chemistry = Chem + is + try ?

Structure vs. Properties

The structure determines properties

Properties reflect the structure

Types of substances

Atoms
Molecules

Clusters
Congeries

Nano materials

Bulk materials

Geometric Structure

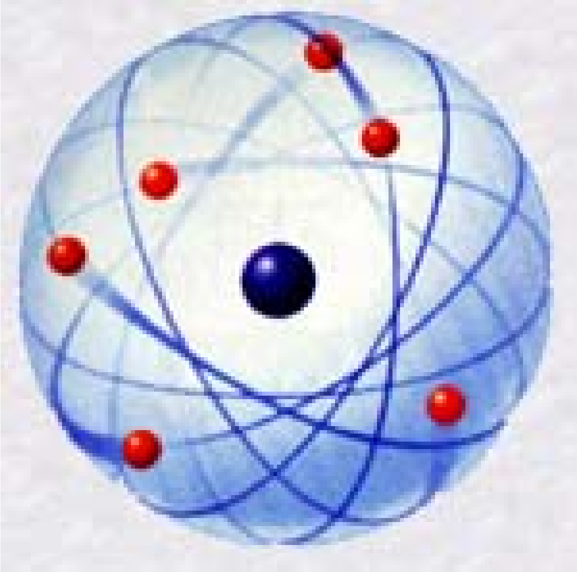
Size
makes the difference

Electronic Structure

Basic Units

Atom

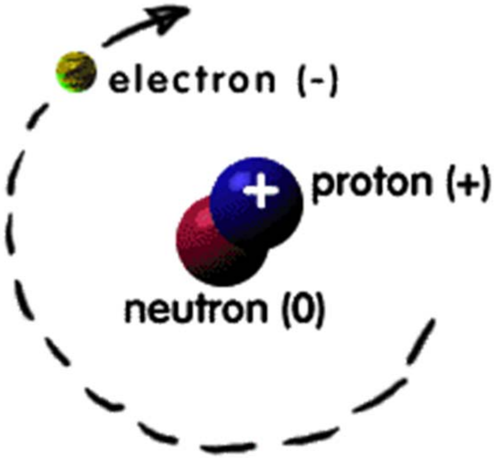
The basic building block of all matter. The smallest particle of an element that has the same properties as the element.



Composed of an electron cloud and a central nucleus.

Atomic Structure

All the matter around you is made of atoms, and all atoms are made of only three types of subatomic particle, protons, electrons, and neutrons.

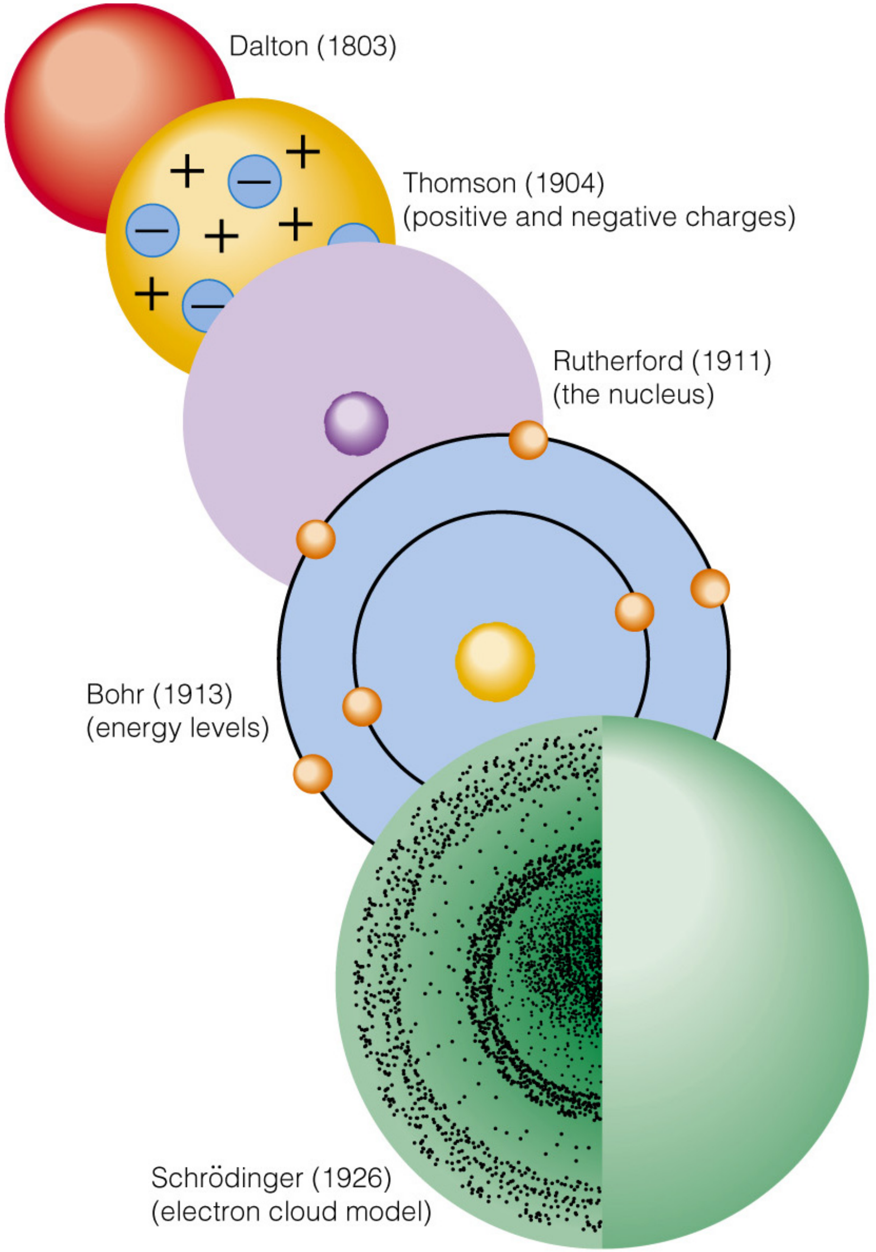


All protons are exactly the same, all neutrons are exactly the same, and all electrons are exactly the same.

There are many elements in the PERIODIC TABLE. Over 100! The thing that makes those elements different is the number of electrons, protons, and neutrons.

History of Atomic Models

Understanding atomic structure is a first step to understand structure of the matter

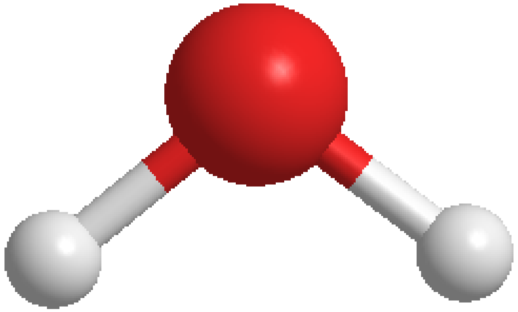


Basic Units

Molecule

The simplest structural unit of a substance that retains the properties of the substance.

Composed of one or more atoms.



Understanding Molecular Structure

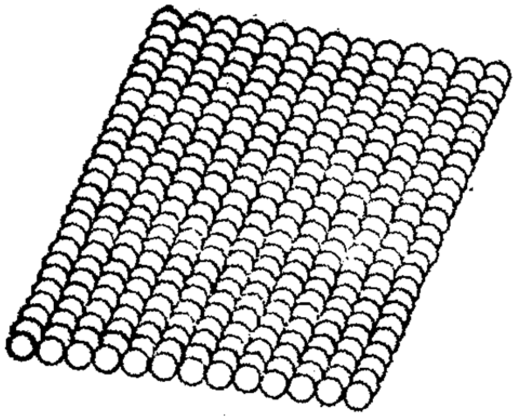
Inorganic molecules	**O_2; H_2O, Si, Pt, TiO_2, etc.**
Organic molecules	**CH_4; C_2H_4, C_6H_6, CH_3OH, etc.**
Bio-molecules	**DNA, RNA, Protein, Enzyme, etc.**

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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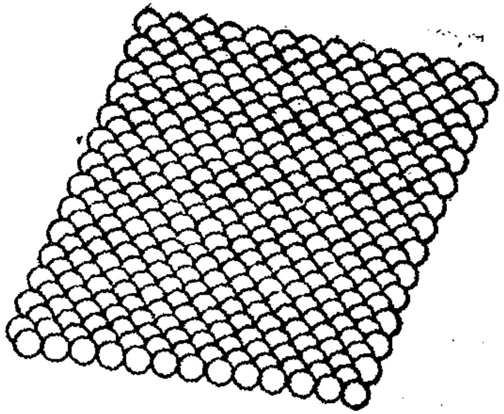

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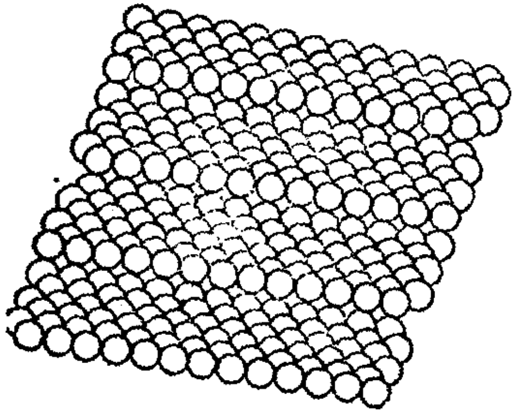

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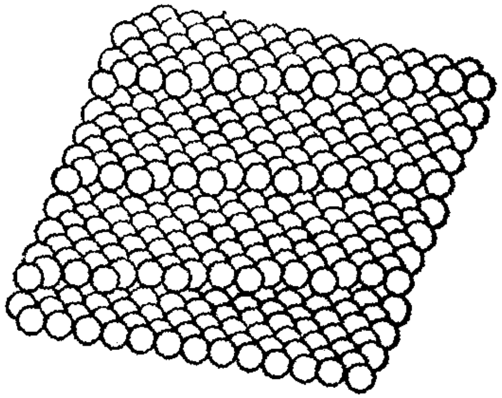

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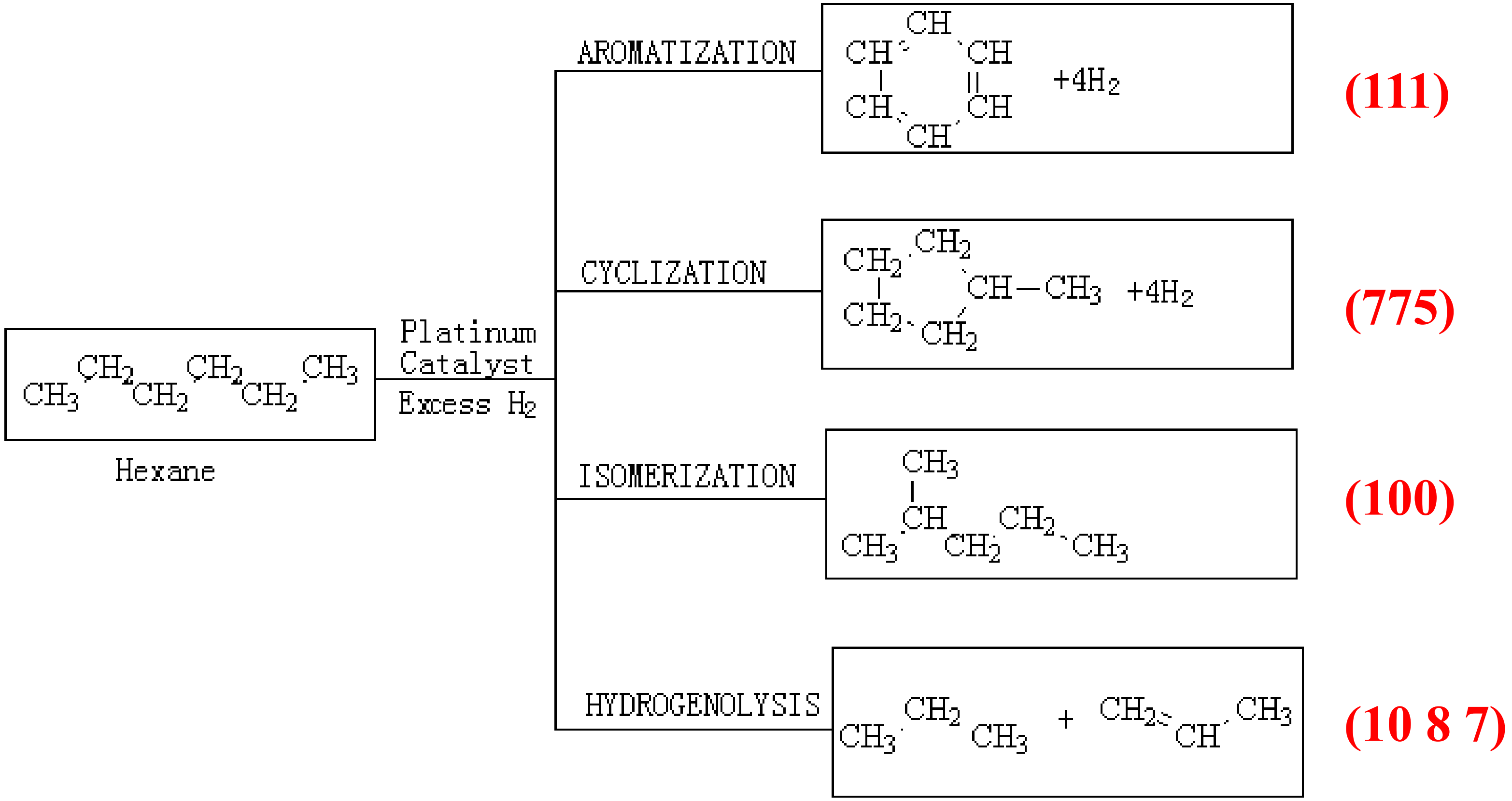
Surface structures of Pt single crystal

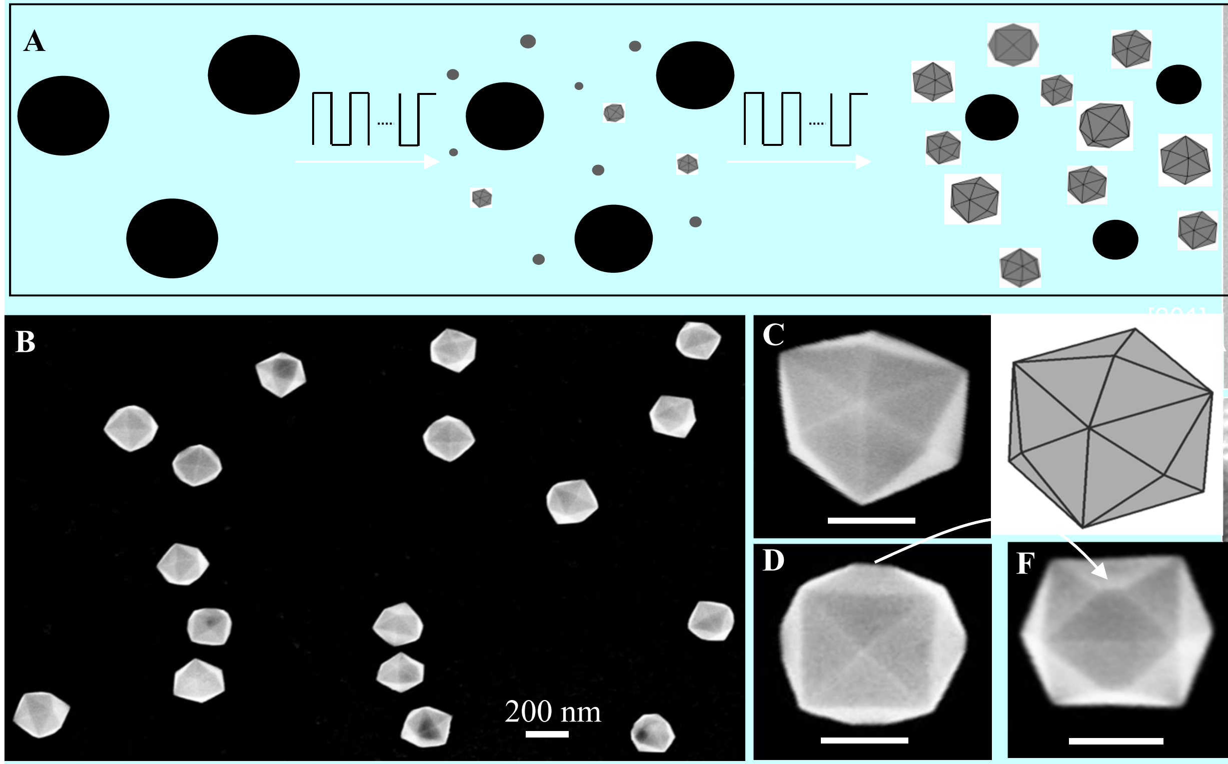


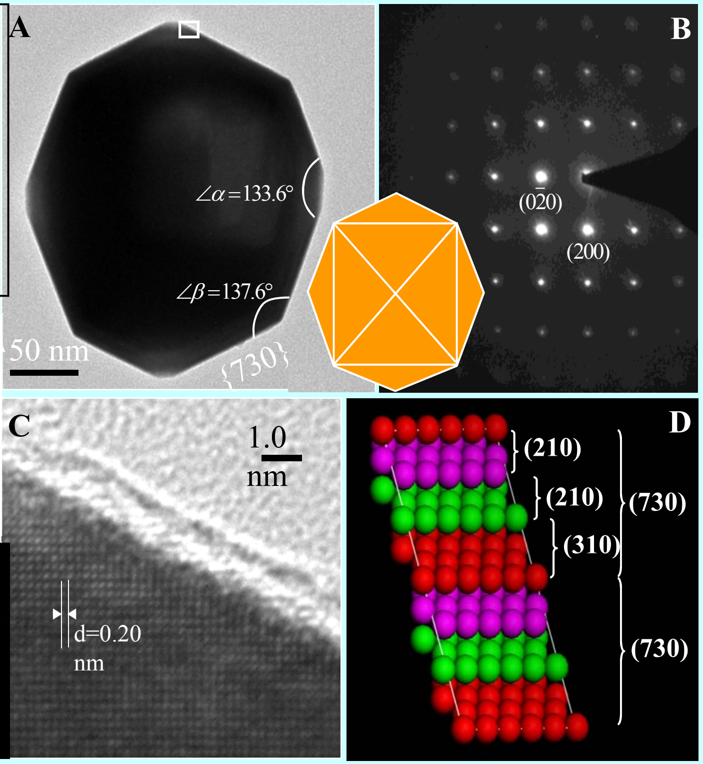
Different surfaces do different chemistry

Synthesis of Tetrahexahedral Pt Nanocrystals with High Index Faces and High Electro-Oxidation Activity

Na Tian, Zhi-You Zhou, Shi-Gang Sun*, Yong Ding and Zhong Lin Wang*

Science, May 4, 2007

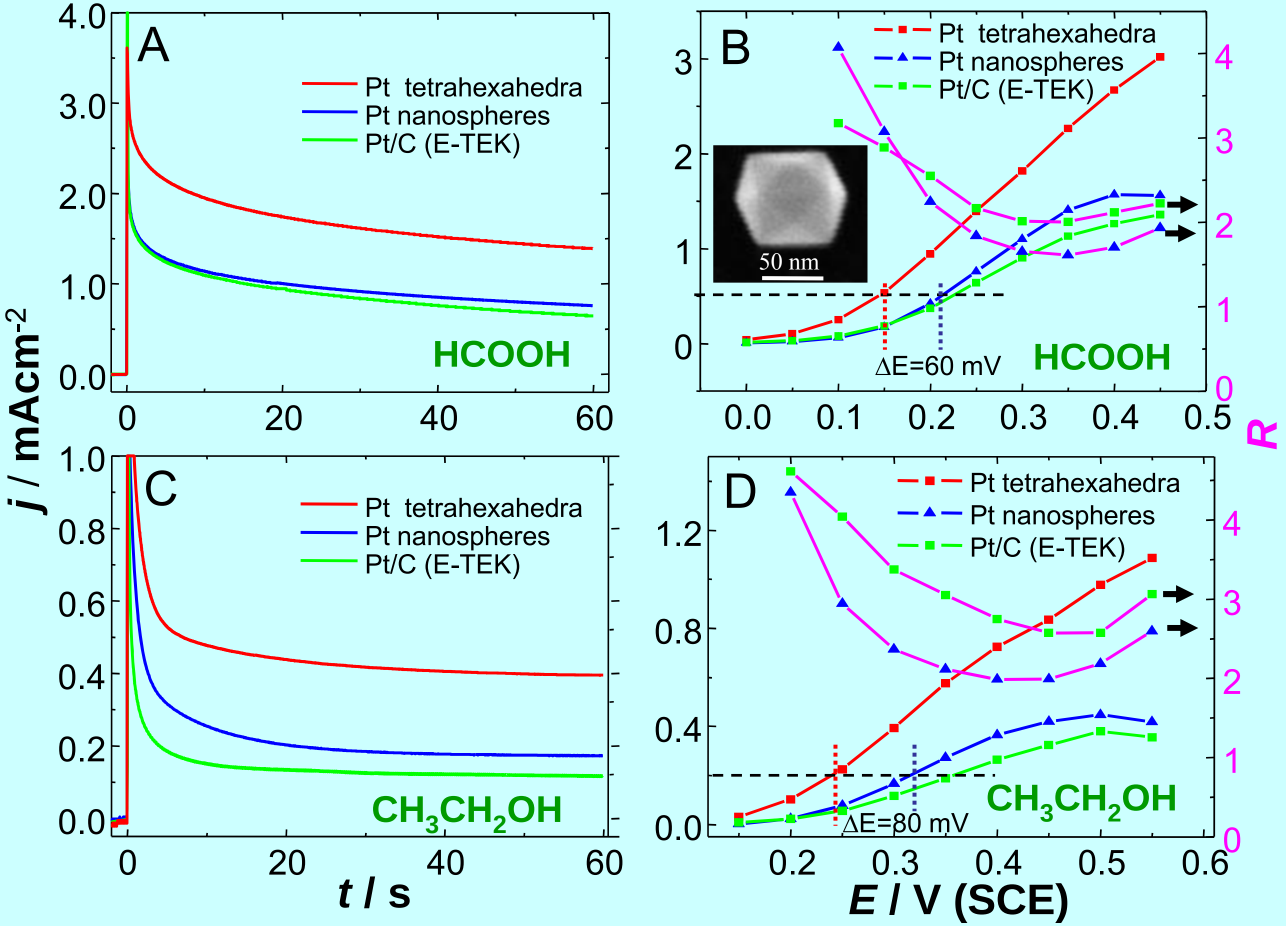




Platinum NCs of very unusual tetrahexahedral (THH) shape were prepared at high yield by an electrochemical treatment of Pt nanospheres

Synthesis of Tetrahexahedral Pt Nanocrystals with High Index Faces and High Electro-Oxidation Activity

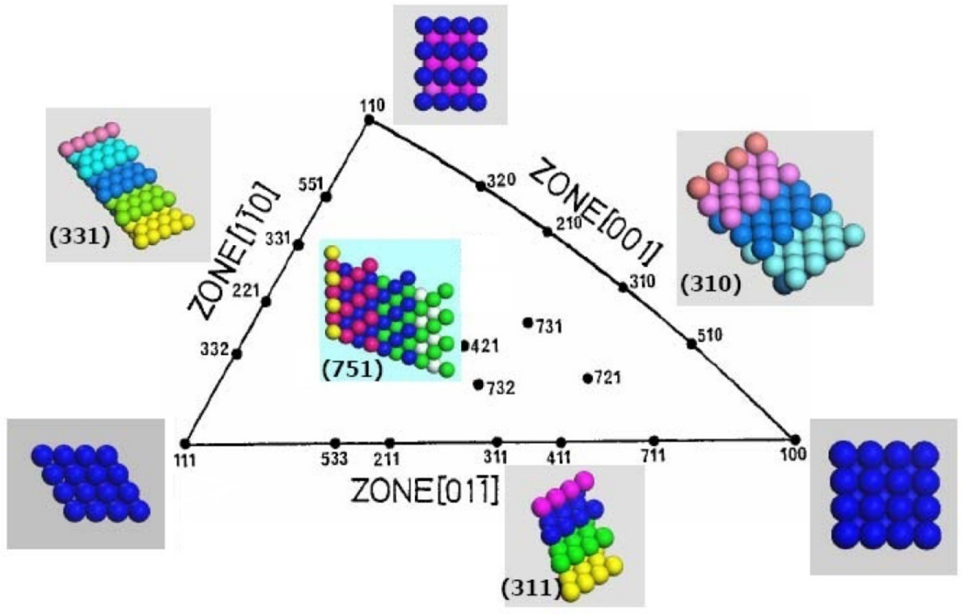
Science, May 4, 2007

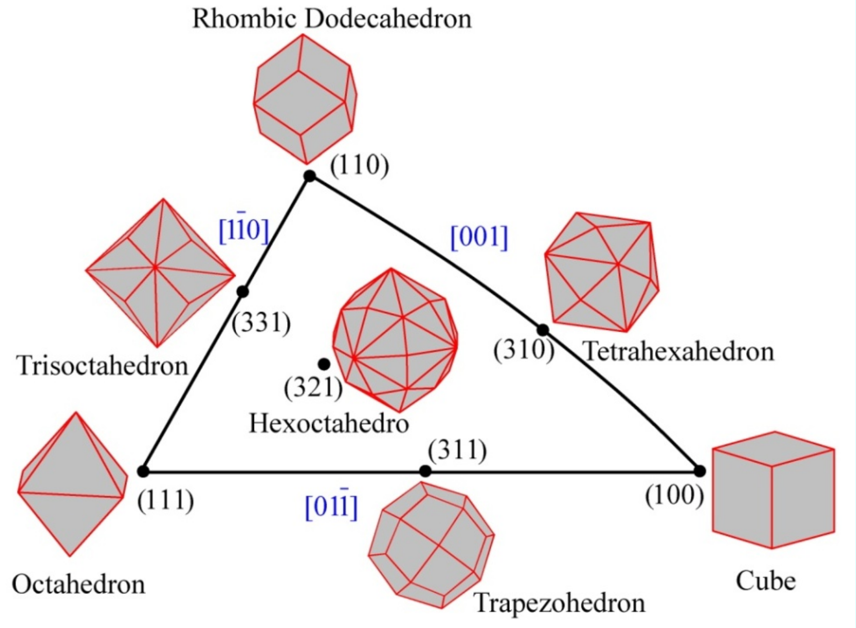


These high-energy surfaces are surprisingly thermal (to 800 ºC) and chemical stable and exhibit much enhanced (up to 400%) catalytic activity for equivalent Pt surface areas for electro-oxidation of small organic fuels such as formic acid and ethanol.

Model and practical catalysts

The single crystal planes vs nanparticles' surface structure





Unit stereographic triangle of fcc single-crystal and models of surface atomic arrangement

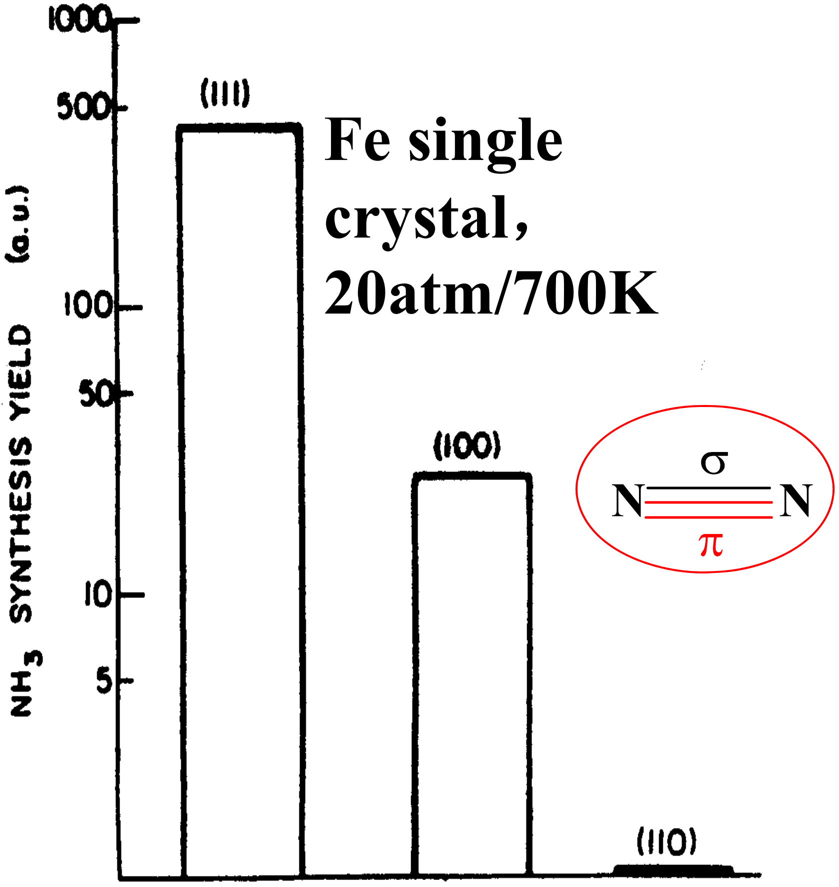
Unit stereographic triangle of polyhedral nanocrystals bounded by different crystal planes

Zhou, Tian, Sun, Faraday Discuss., 2008,140:81–92

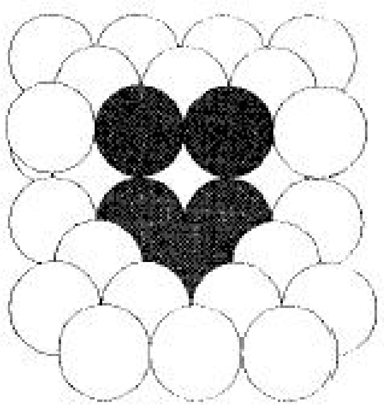
Surface Structure vs. Catalytic Activity

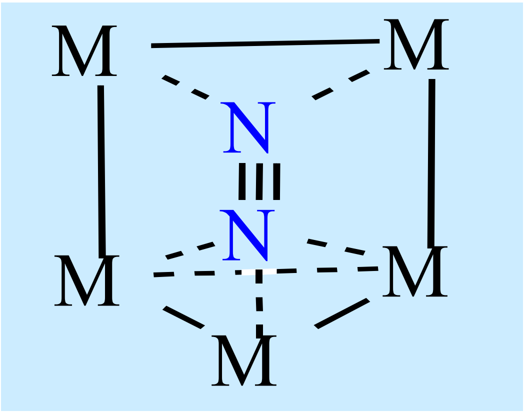
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

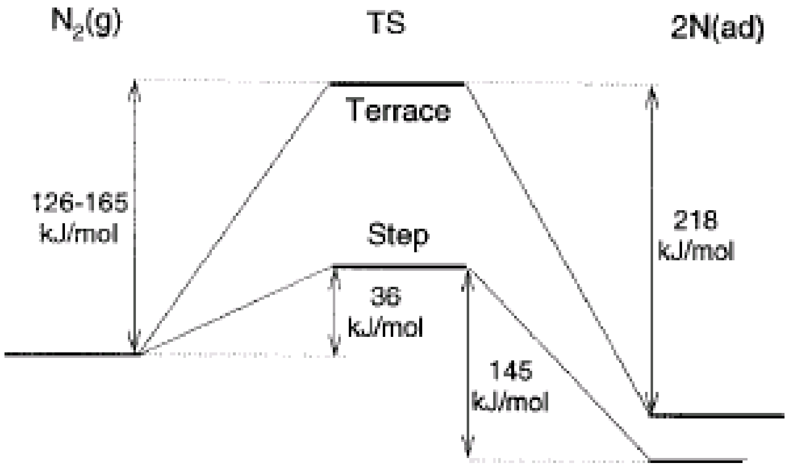
B5 中心



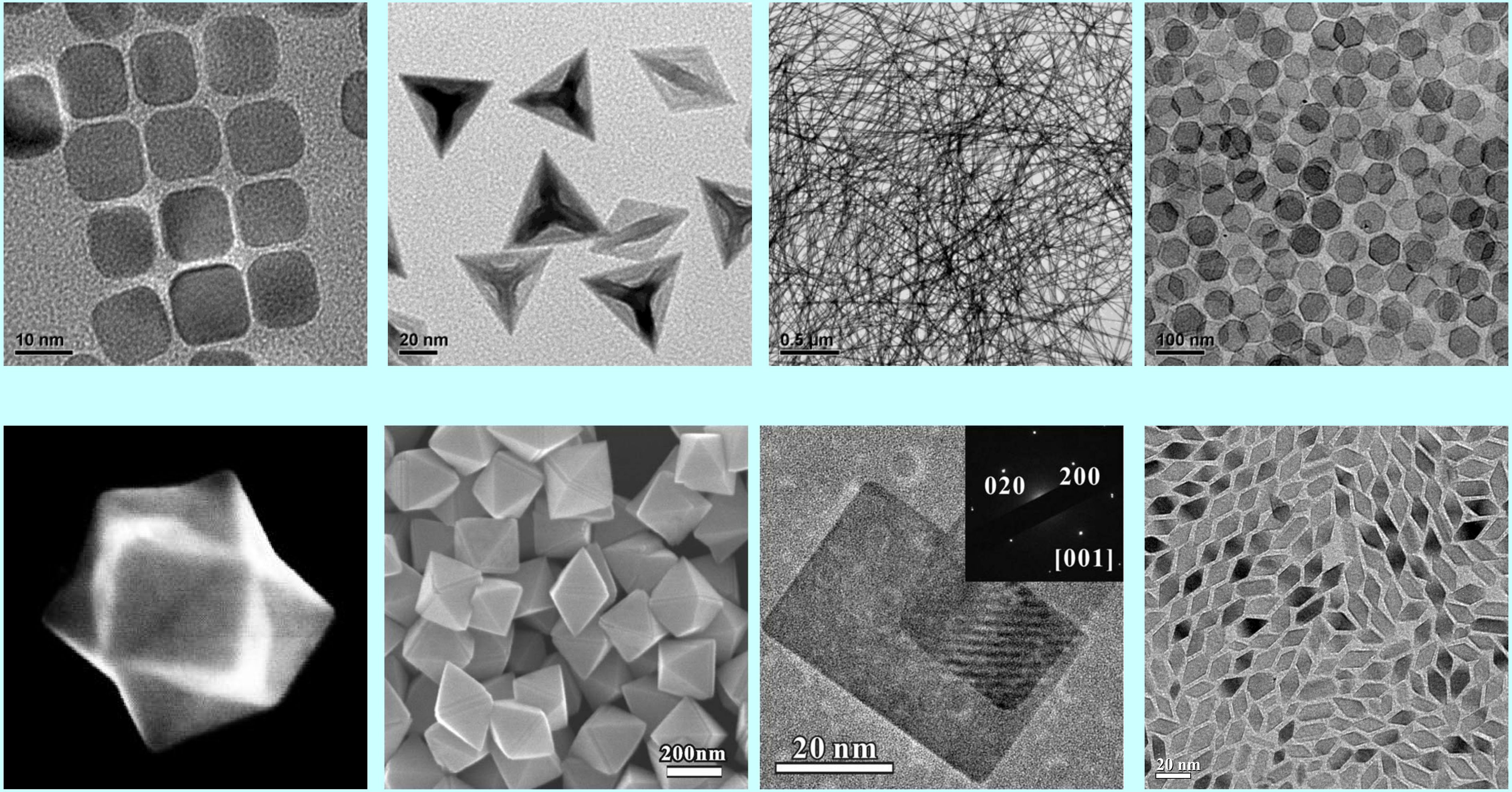
Fe single crystal, 20atm/700K







Small Molecules Control Surface Structures

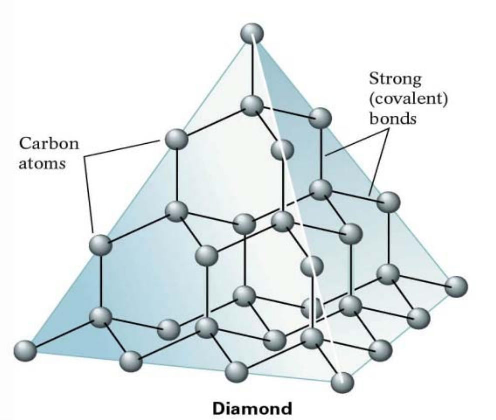


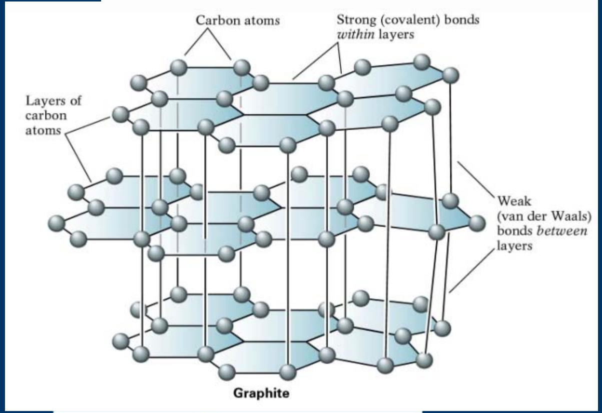
Angew. Chem. Int. Ed. 2008, *47*, 8901
Angew. Chem. Int. Ed. 2009, *48*, 4808
Angew. Chem. Int. Ed. 2009, 48, 9344

J. Am. Chem. Soc. 2008, *130*, 17563
J. Am. Chem. Soc. 2009, *131*, 3152
J. Am. Chem. Soc. 2009, *131*, 4602
J. Am. Chem. Soc. 2009, *131*, 13916

Role of Structural Chemistry in Materials Science

C Crystal Structures





➲ Graphite & Diamond Structures

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

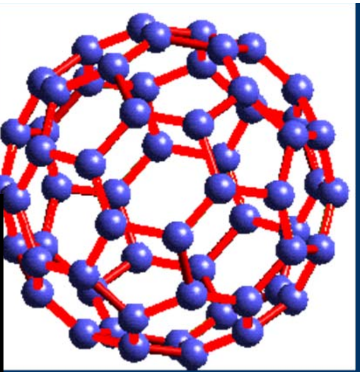
Structure makes the difference

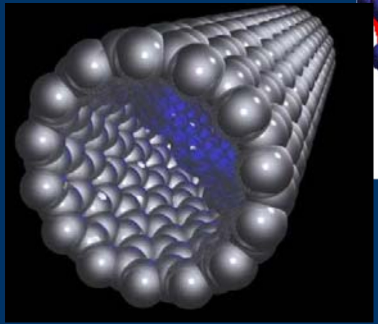
➲ *Other* Carbon Crystal Structures

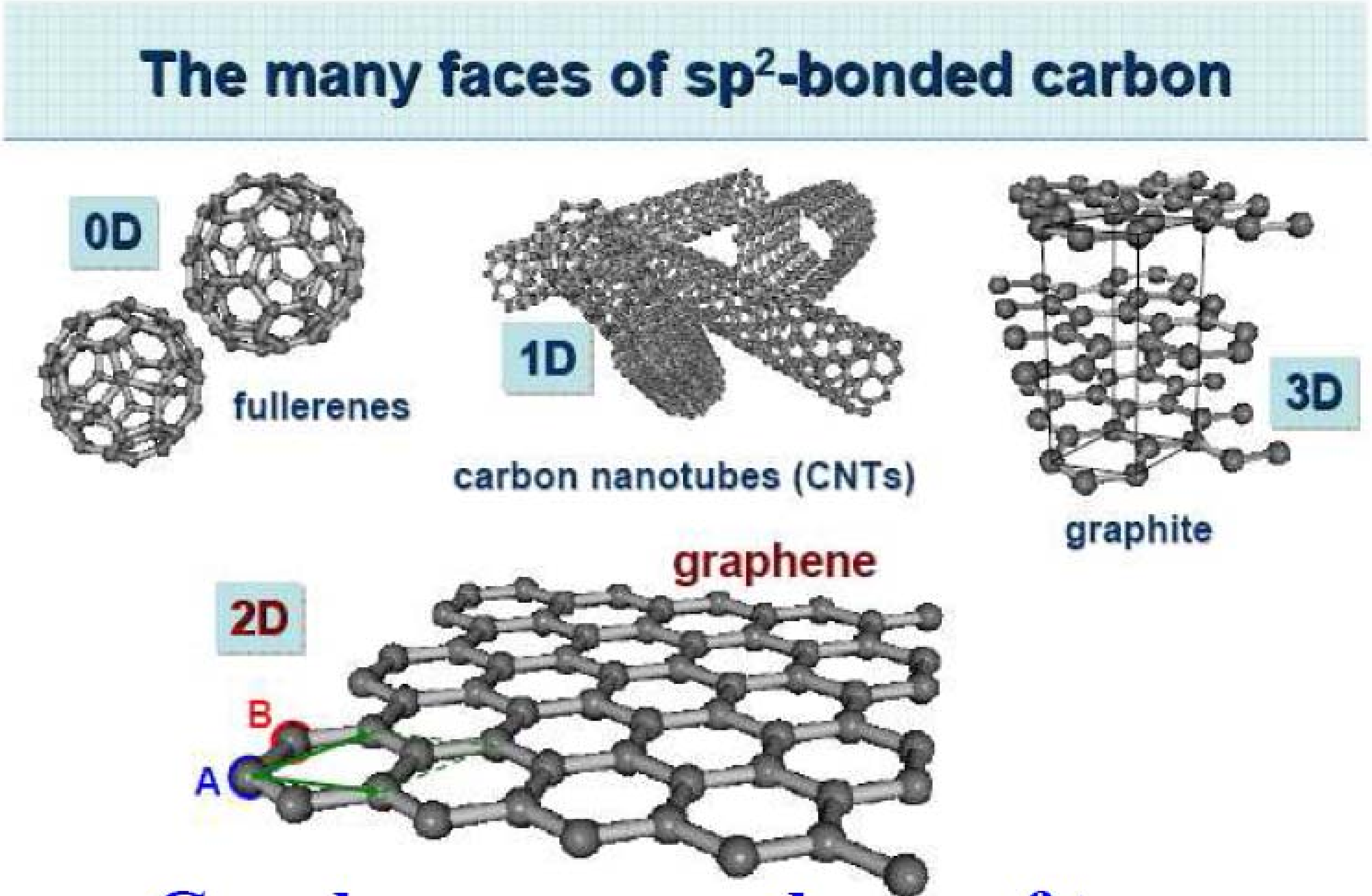
"Buckyballs" (C_{60}) →→→→→→

"Buckytubes" (nanotubes),

other fullerenes →→→

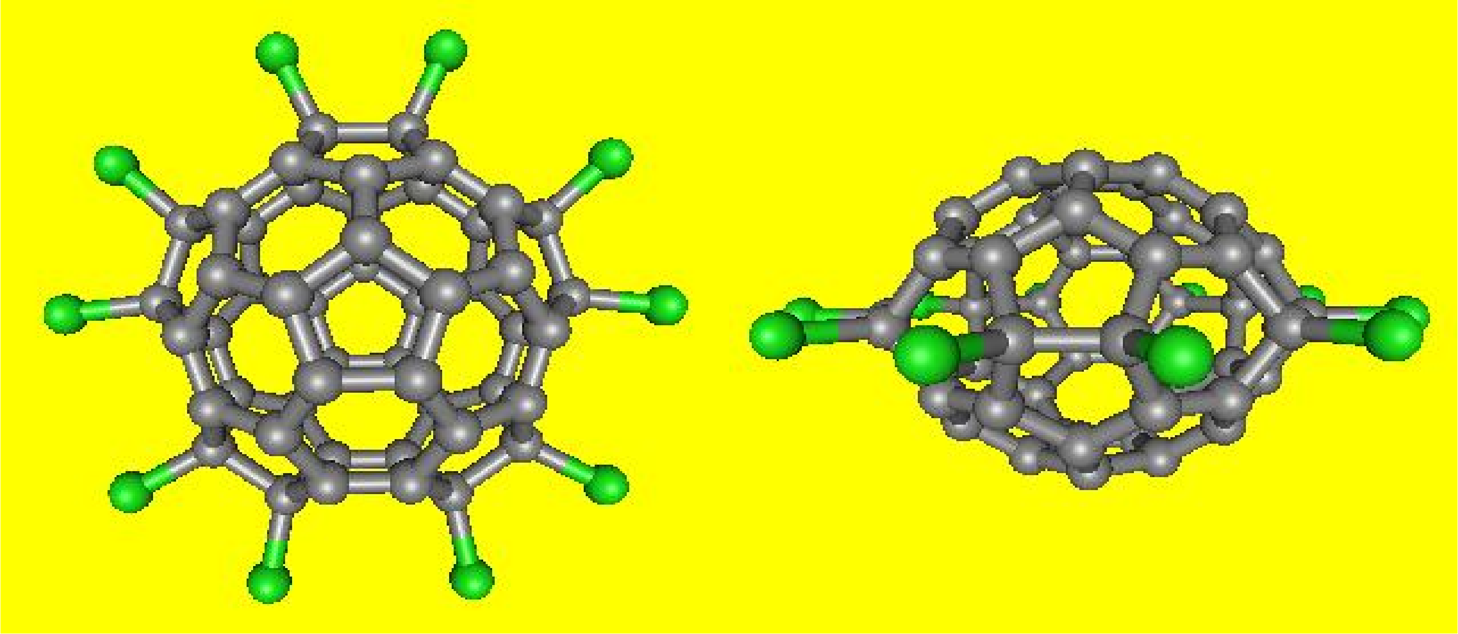






The many faces of sp^2-bonded carbon

Graphene: a monolayer of two-dimensional carbon atoms



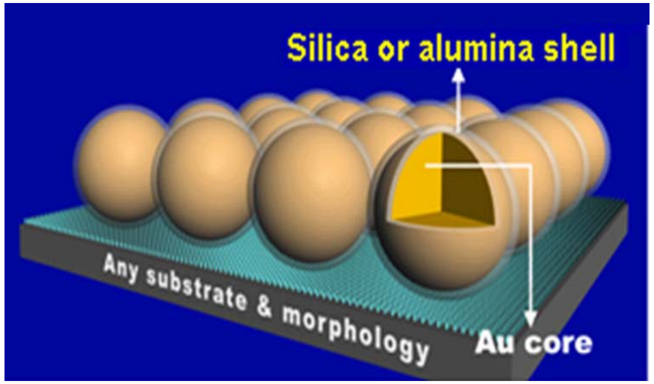
Zheng LS (郑兰荪), et al.

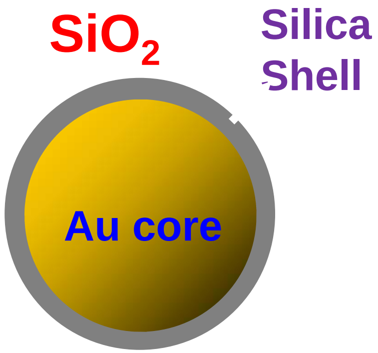
Capturing the labile fullerene[50] as C50Cl10

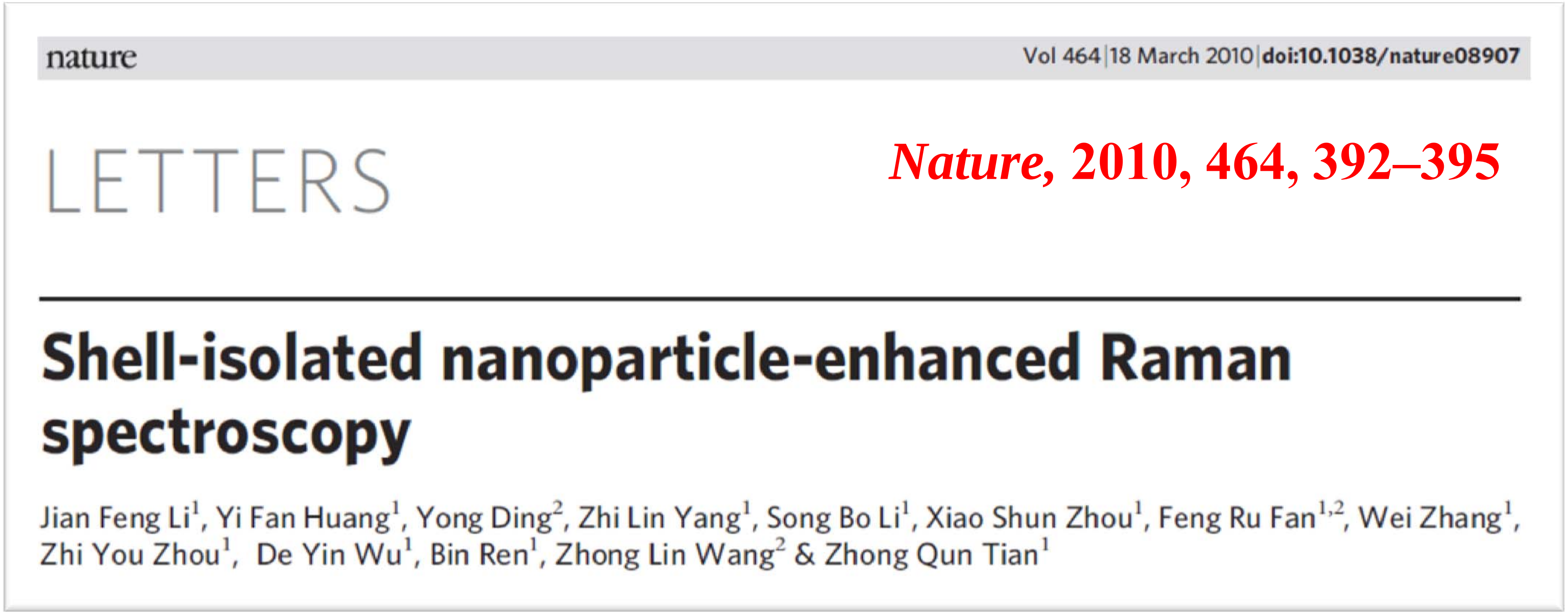
SCIENCE 304 (5671): 699-699 APR 30 2004

壳层隔绝纳米粒子增强拉曼光谱（SHINERS）

可以适用于任何的基底材料和任何形状的电极（单晶）表面和体系，极大拓宽了拉曼光谱的通用性







nature Vol 464 | 18 March 2010 | doi:10.1038/nature08907

LETTERS

Nature, 2010, 464, 392–395

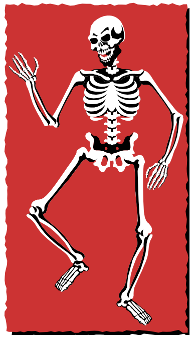
Shell-isolated nanoparticle-enhanced Raman spectroscopy

Jian Feng Li[1], Yi Fan Huang[1], Yong Ding[2], Zhi Lin Yang[1], Song Bo Li[1], Xiao Shun Zhou[1], Feng Ru Fan[1,2], Wei Zhang[1], Zhi You Zhou[1], De Yin Wu[1], Bin Ren[1], Zhong Lin Wang[2] & Zhong Qun Tian[1]

Role of Structural Chemistry in Life Science

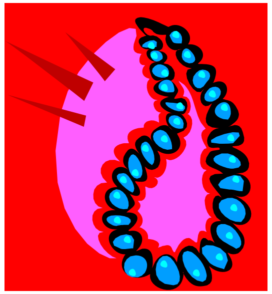
What do proteins do ?

Proteins are the basis of how biology gets things done.

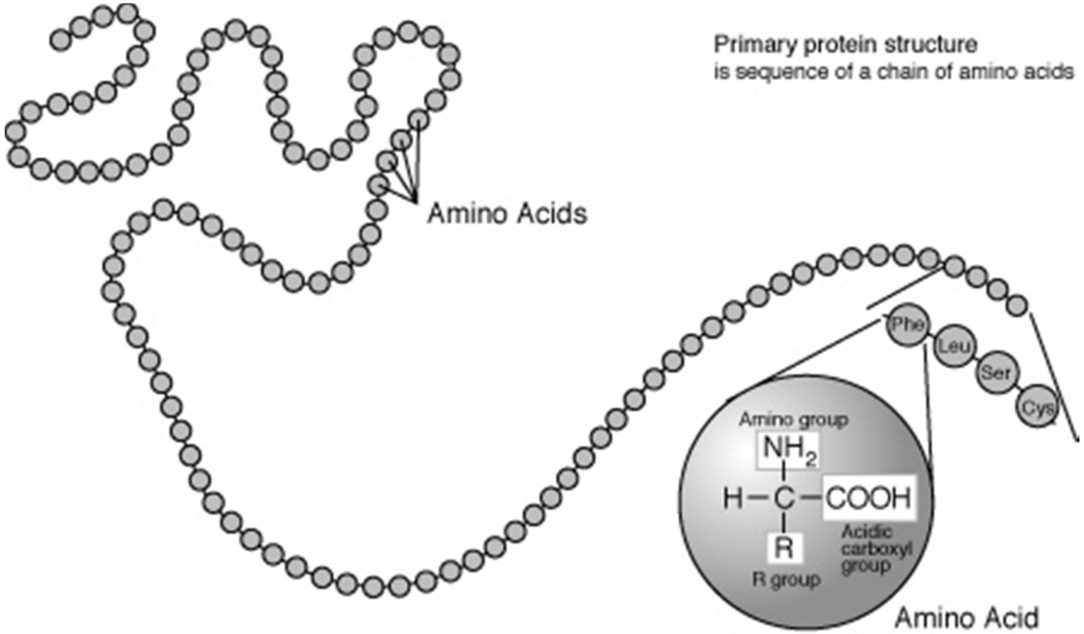


- As enzymes, they are the driving force behind all of the biochemical reactions which makes biology work.
- As structural elements, they are the main constituents of our bones, muscles, hair, skin and blood vessels.
- As antibodies, they recognize invading elements and allow the immune system to get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

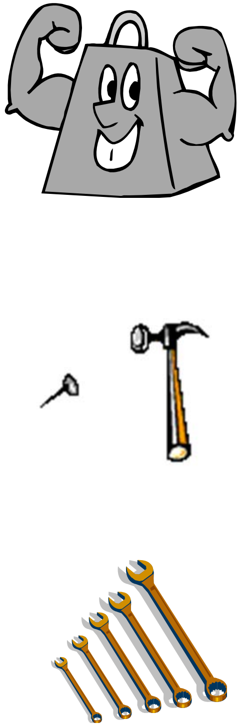
What are proteins made of ?



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



Form determines function



- Suppose you have some molten iron. You may turn it into nails, hammers, wrenches, etc. What makes these tools different from each other is their form (i.e. their shape and structure)
- Similarly proteins, though basically being built as similar chains of amino acids, very rapidly fold onto their own “correct” form, so as to be able to carry out the function that is assigned to them

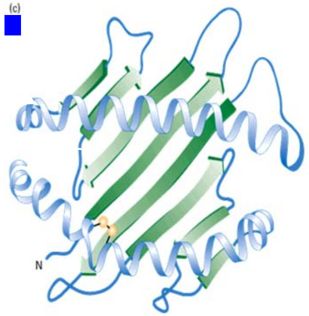
How do prions (朊蛋白) fold ?

Evidence indicates that the infectious agent in **transmissible spongiform encephalopathy** is a protein. Stanley Prusiner pioneered the study of these proteins and received the **Nobel Prize in medicine (1997).** He has named them prion proteins (referred to as PrP) or simply prions.

Proteins have primary structures, which is their sequence of amino acids, and secondary structures, which is the three dimensional shape that one or more stretches of amino acids take. The most common shapes are the alpha helix and the beta conformation.

The normal protein is called PrPC (for cellular). Its secondary structure is dominated by alpha helices. The abnormal, disease producing protein called PrPSc (for scrapie), has the same primary structure as the normal protein, but its secondary structure is dominated by beta conformations.

Examples of alpha helices
and beta sheets



The “kiss of death”

A person ingests an abnormally-shaped prion from contaminated food or other contaminated sources.

The abnormally-shaped prion gets absorbed into the bloodstream and crosses into the nervous system.

The abnormal prion touches a normal prion and changes the normal prion's shape into an abnormal one, thereby destroying the normal prion's original function.

Both abnormal prions then contact and change the shapes of other normal prions in the nerve cell.

The nerve cell tries to get rid of the abnormal prions by clumping them together in small sacs. Because the nerve cells cannot digest the abnormal prions, they accumulate in the sacs

that grow and engorge the nerve cell, which eventually dies.

When the cell dies, the abnormal prions are released to infect other cells.

Large, sponge-like holes are left where many cells die.

Structural Chemistry

- **It is a subject to study the microscopic structures of matters at the atomic/molecular level using *Chemical Bond Theory*.**

- **Chemical bonds→structures→properties.**

Objective of Structural Chemistry

1) Determining the structure of known substance

2) Understanding the structure-property relationship

3) Predicting the substance with specific structure and property

Outline & Schedule

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

Chapter 1

The basic knowledge of quantum mechanics

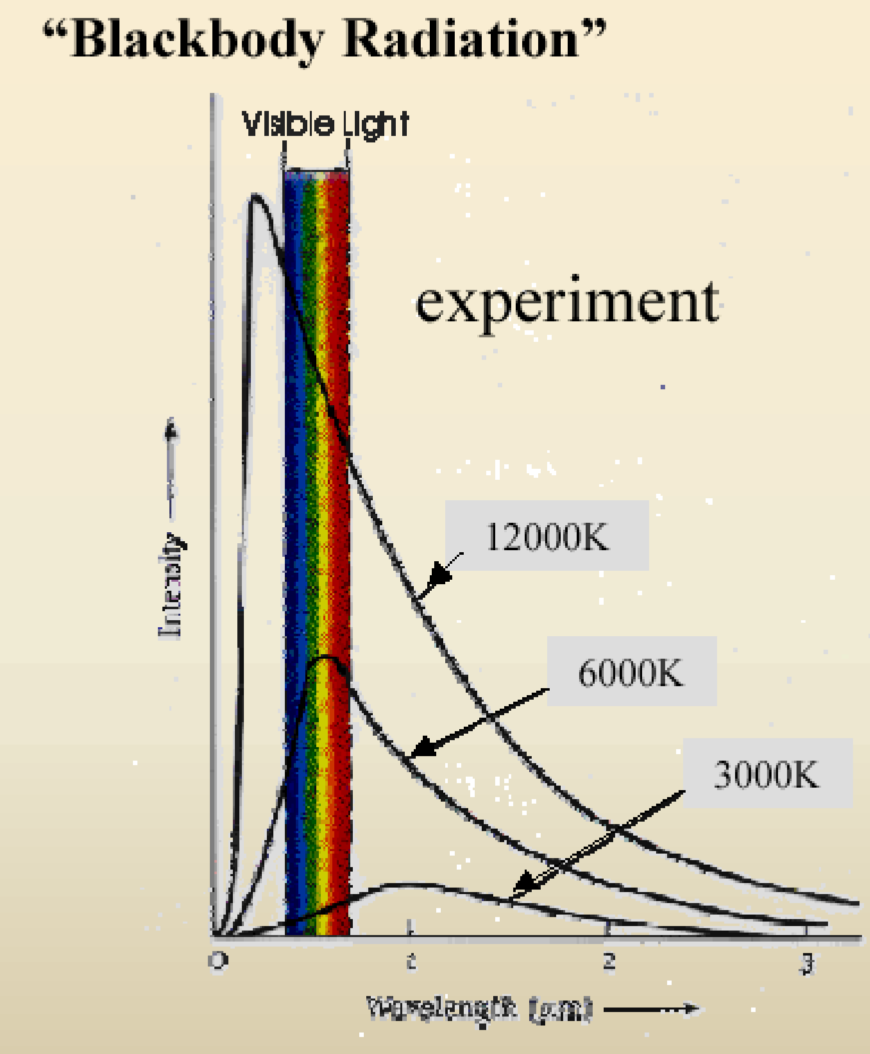
1.1 The failures of classical physics

- **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



A large number of experiments revealed the temperature-dependence of λ_{max} and independence on the substance made of the black-body device.

Classical solution:

Rayleigh-Jeans Law

$$B_\nu(T) = \frac{2\nu^2}{c^2} kT$$

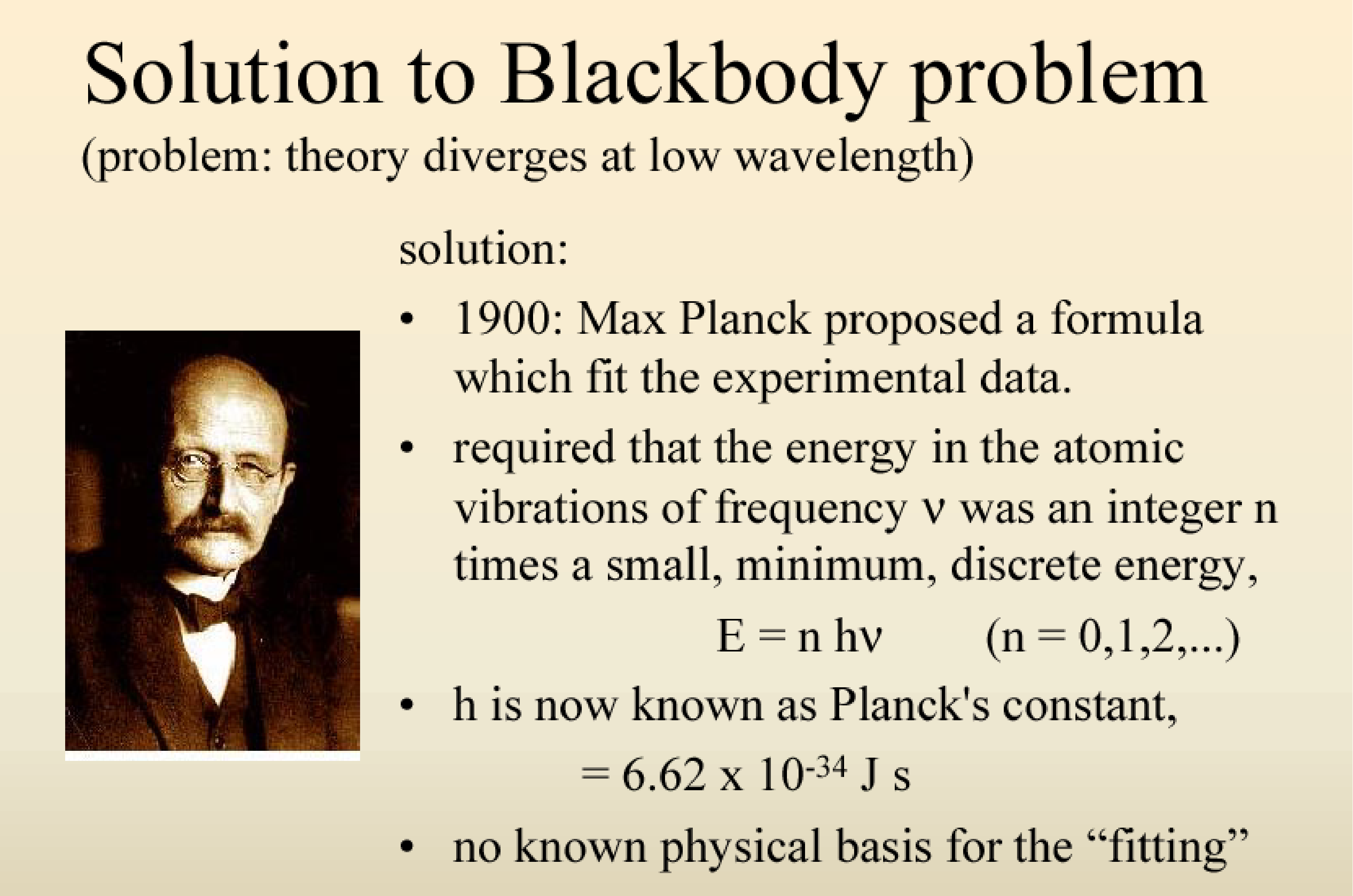
(long wave length, high T)

Wien Approximation

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

(high energy, Low T)

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,

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

- h is now known as Planck's constant,

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

- no known physical basis for the "fitting"

Max Karl Ernst Ludwig Planck (April 23, 1858 – October 4, 1947) was a German physicist who is regarded as the founder of the quantum theory, for which he received the Nobel Prize in Physics in 1918)

Black Body Radiation

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

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

Many stellar sources can usefully be approximated to be black bodies

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

(high energy, low T)

Wien's Approximation

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

(long wavelength, high T)

Rayleigh-Jeans Law

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots, \qquad -\infty < x < \infty$$

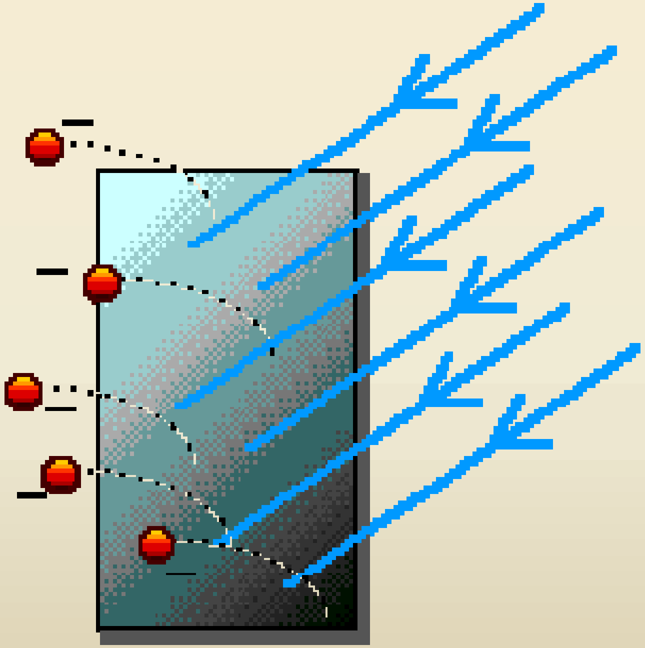
1.1.2 The photoelectric effect

Nagging problem 2

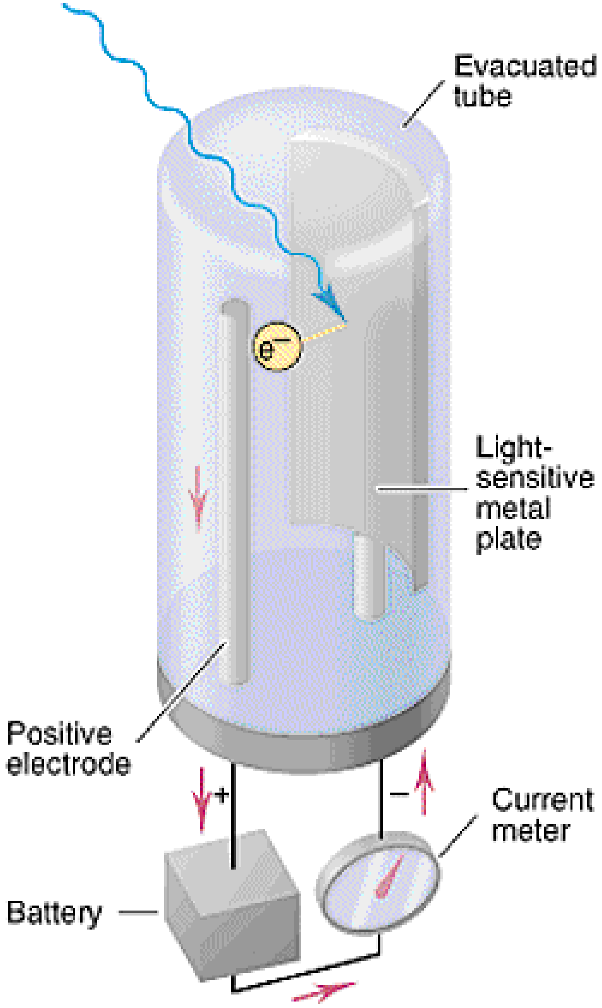
“Photoelectron effect”

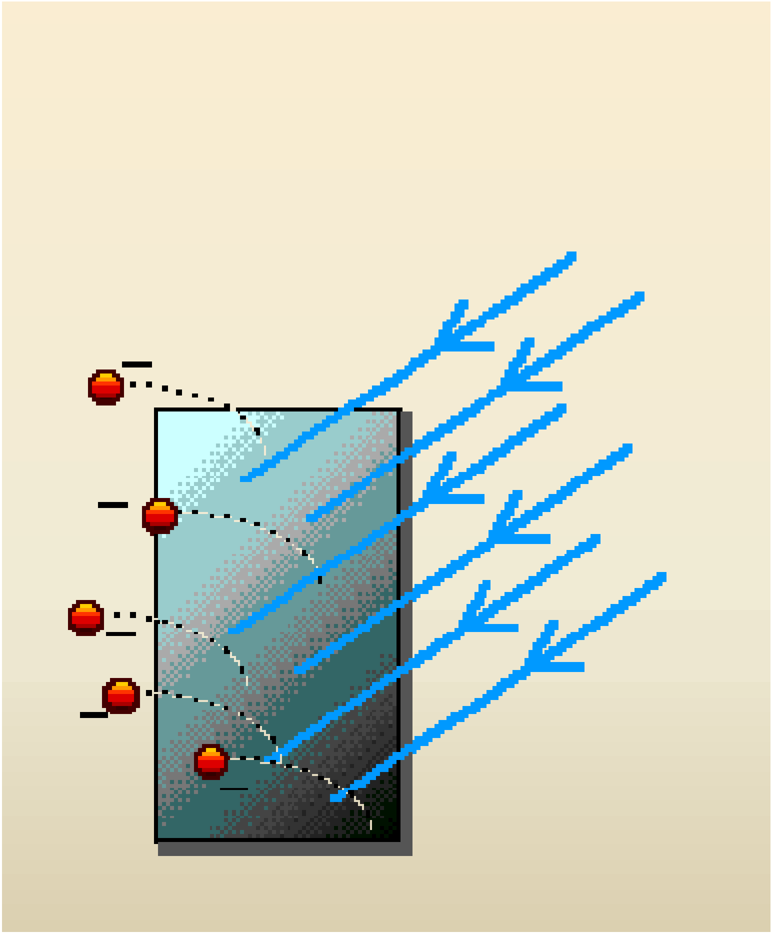
Observed by Hertz in 1887

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

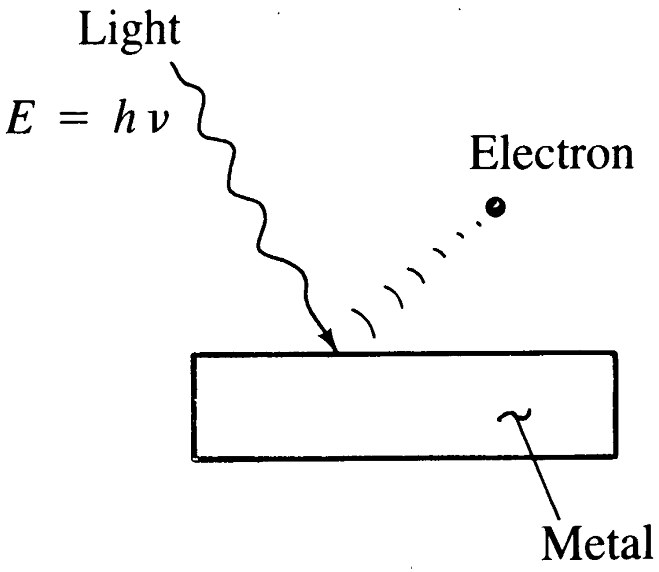


The photoelectric effect

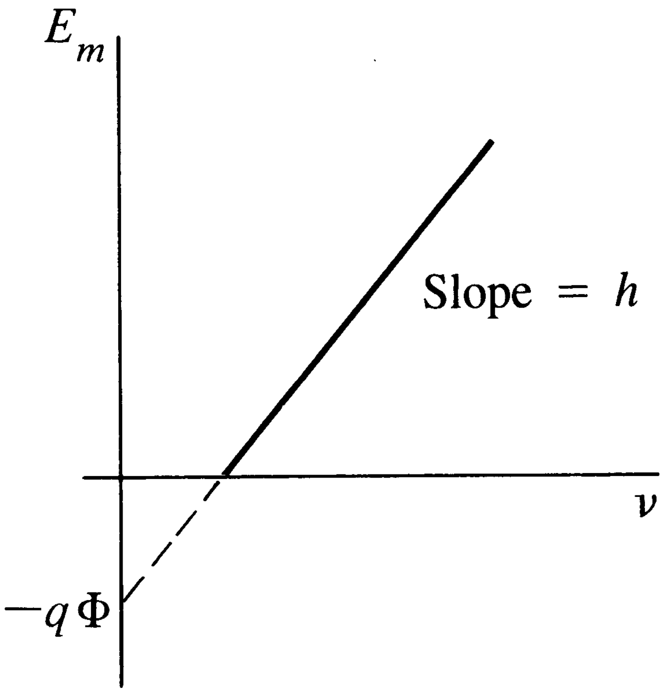




The Photoelectric Effect



(a)

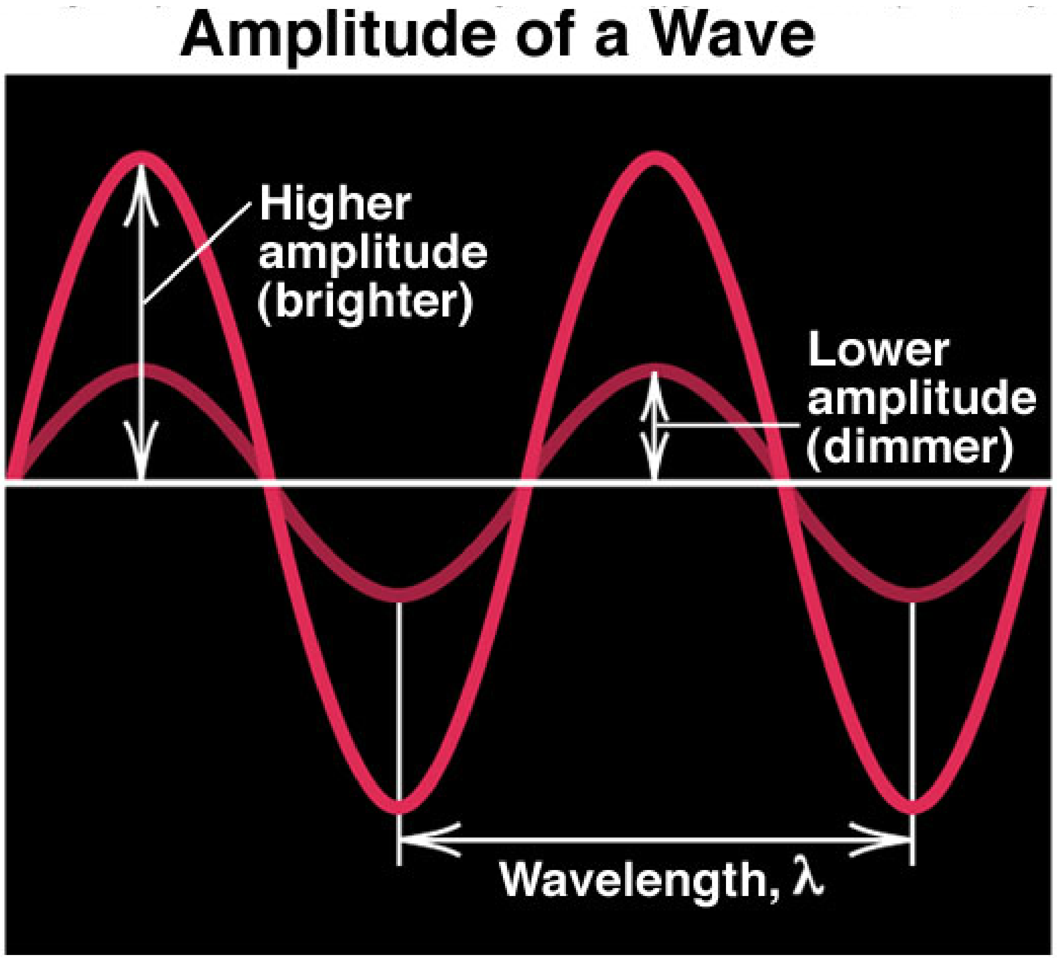


(b)

1. The kinetic energy of the ejected electrons depends linearly on the frequency of the light.

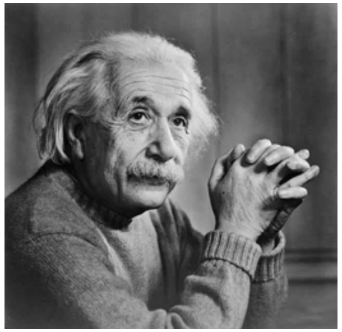
2. There is a particular threshold frequency for each metal.

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** (**1879-1955, 1921 Nobel Prize in Physics**)
  - – 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.

$$\varepsilon = h\nu \qquad \mathbf{h} = \text{Planck's constant}$$

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 equal 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 of Energy from Frequency

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

Solution:

wavelength = 122 mm = 1.22 x 10 $^{-1}$m

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

Energy = E = hν = (6.626 x 10 $^{-34}$Js)(2.46 x 10^{10}/s) = **1.63 x 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

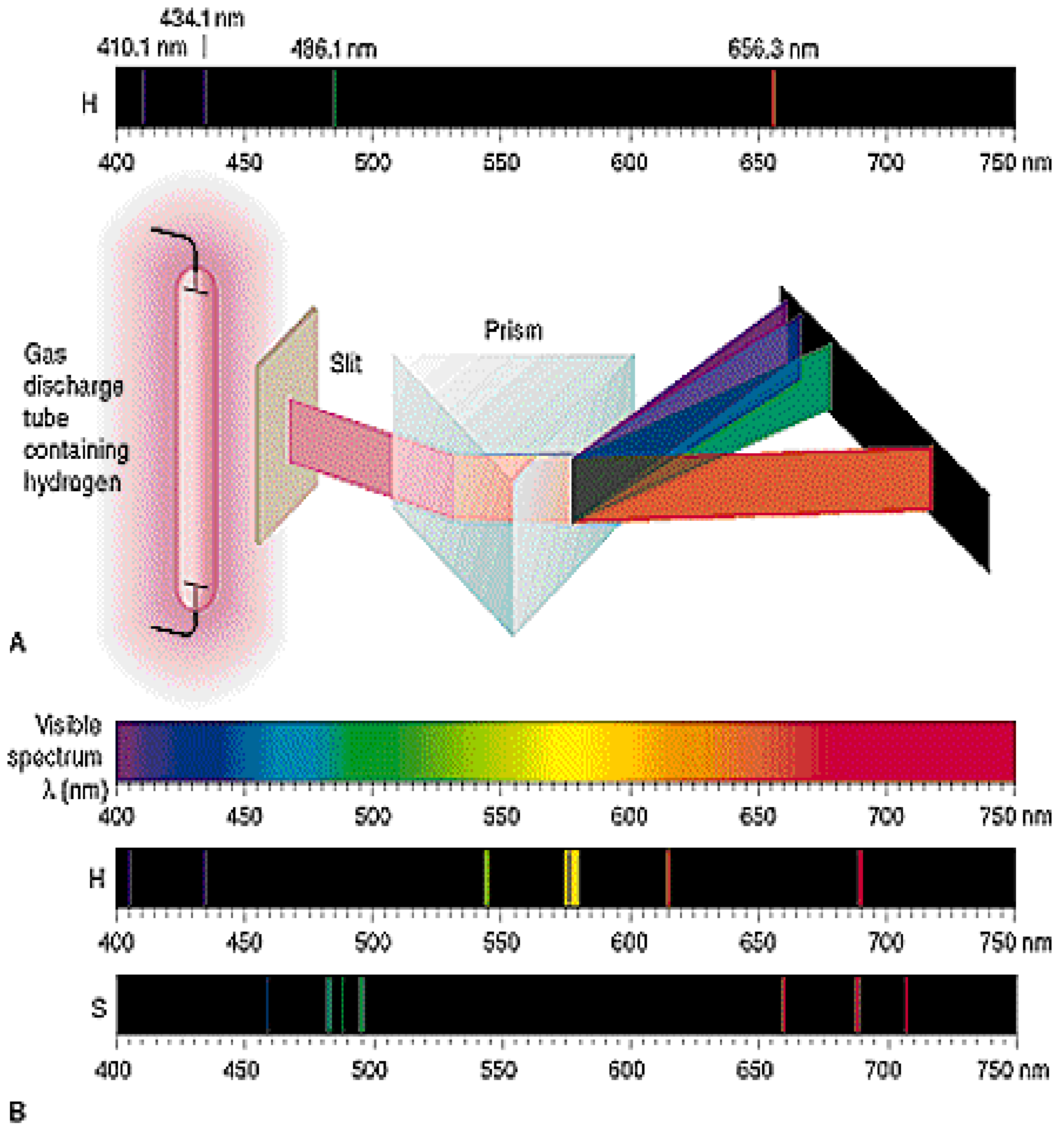
- The binding energy of potassium is = 3.7×10^{-19} J
- The red light will not have enough energy to knock an electron out of the potassium, but the blue light will eject an electron !

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

  $= 1.3 \times 10^{-19}$Joules

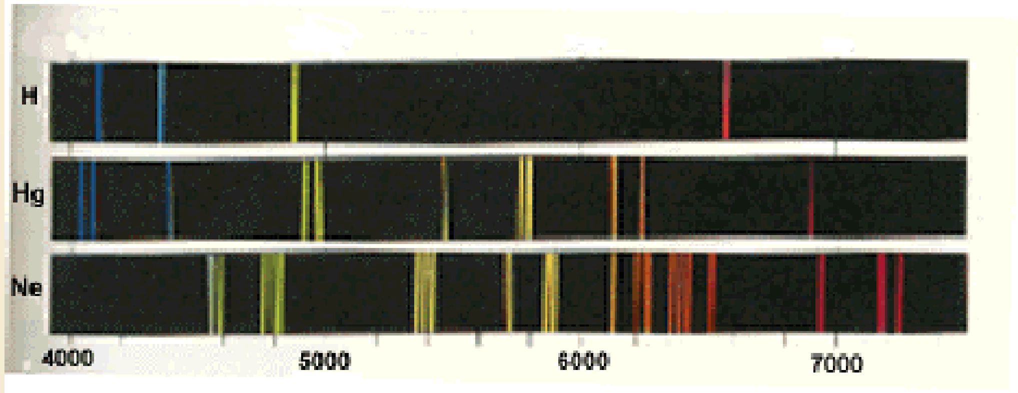
1.1.3 Atomic and molecular spectra

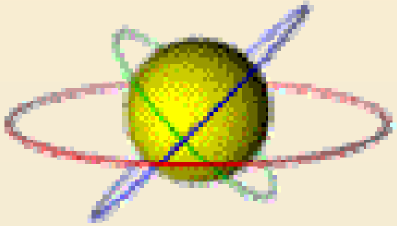
The Line Spectra of Several Elements



Nagging problem 3

Spectral lines in gases

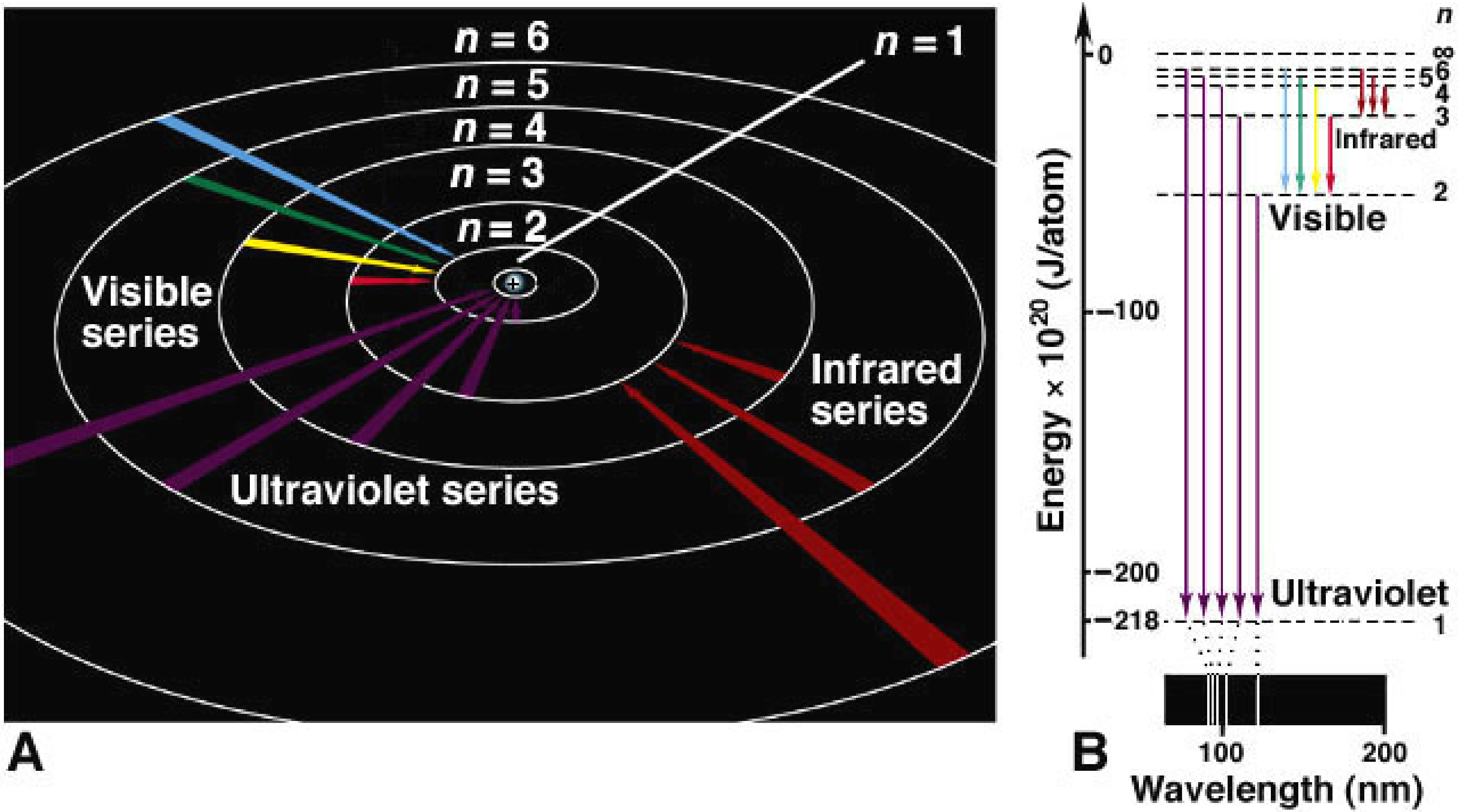




<u>planetary model:</u>

- the electrons are like planets - orbit the nucleus
- light of energy E given off when electrons change orbits (i.e., different energies) - instead of gravitational force (for planets), use electrostatic force - same analogous effect
- spectral lines are inconsistent with planetary model of the atom - why only discrete energies?

The Bohr Model Explanation of the Three Series of Spectral Lines



The Energy States of Hydrogen Atom

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

eg. $H \qquad He^{+} \qquad Li^{2+}$

He predicted a set of quantized energy levels given by :

$$E_n = -\frac{RZ^2}{n^2} \qquad n = 1,2,3\ldots$$ **R = 13.6 eV**

- R is called the Rydberg constant (2.18 x 10^{-18} J)

- n is a quantum number; - Z is the nuclear charge

$$\Delta E = E_{n1} - E_{n2} = -RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$|\Delta E| = h\nu = h\frac{c}{\lambda}$$

Photon energy in absorption and emission along electron transition.

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:

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

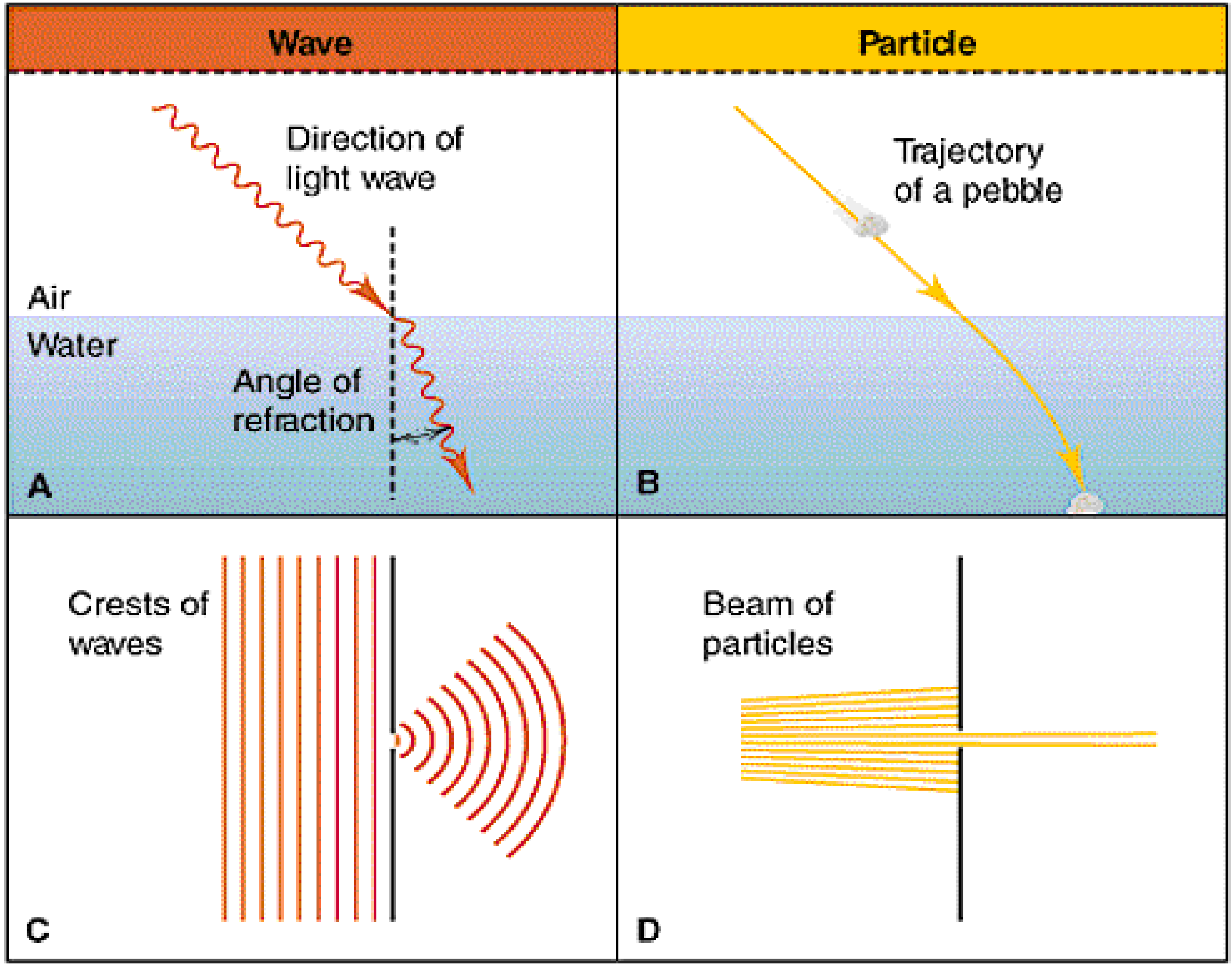
$$= 2.18 \times 10^{-18} J\left(\frac{1}{4_1^2} - \frac{1}{2_2^2}\right) = -4.09 \times 10^{-19} J$$

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

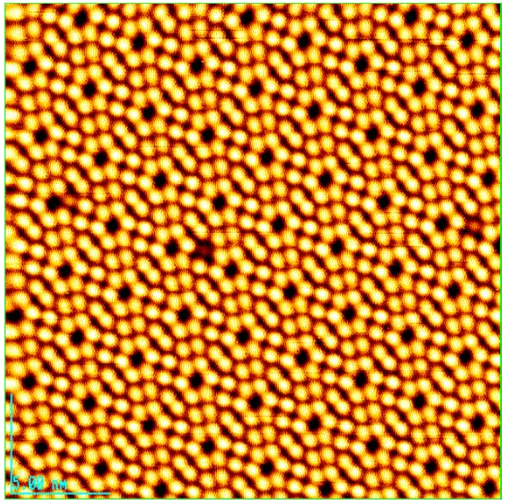
$$= \mathbf{4.87 \times 10^{-7}\ m = 487\ nm}$$

1.1.4 The diffraction of electrons

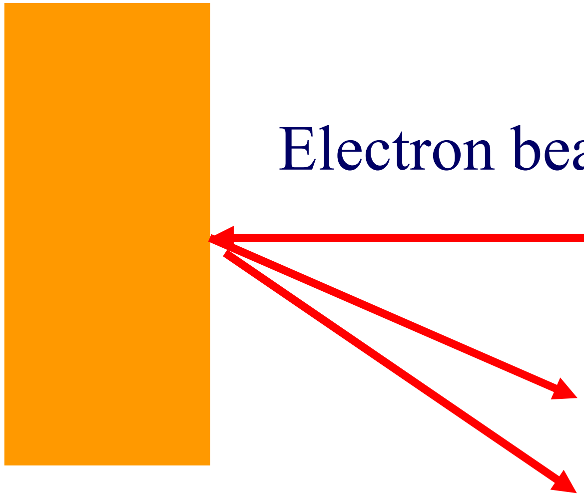
Different Behaviors of Waves and Particles



The diffraction of electrons



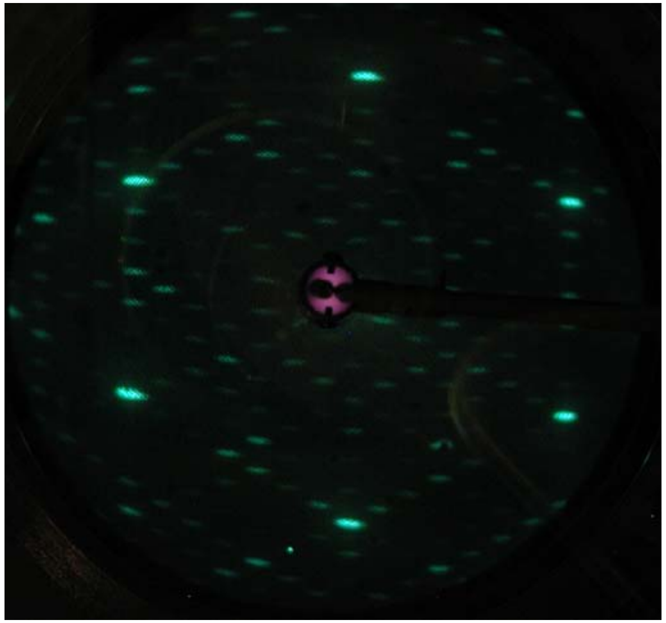
STM image of Si(111) 7x7 surface



Electron beam (50eV)

Si Crystal

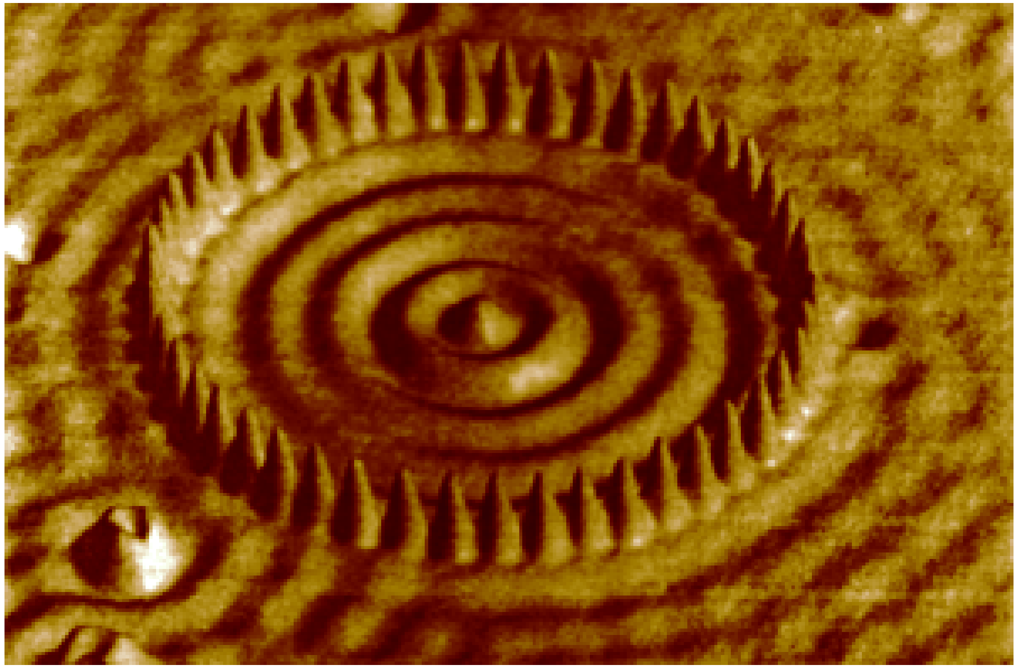
235 pm (2.35Å)



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.



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

$$E = h\nu$$

$$p = h/\lambda$$

$$\boxed{p = mc = \frac{mc^2}{c} = \frac{E}{c} = \frac{h\nu}{\nu\lambda} = \frac{h}{\lambda}}$$

The wavelength of a particle could be determined by

$$\lambda = h/p = h/mv$$

h = Planck's constant,

p = particle momentum,

λ = de Broglie wavelength

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

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

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

hence

Wavelength $\lambda = \mathbf{2.42 \times 10^{-10}\ m = 0.242\ nm}$

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

$$\frac{1}{2}m\mathrm{v}^2 = eV$$

1eV=1.602x10^{-19} J

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

$$\lambda = h/m\mathrm{v} = \frac{h}{\sqrt{2me}\sqrt{\mathrm{V}}}$$

$$= \frac{6.626\times10^{-34}}{\sqrt{2\times9.110\times10^{-31}\times1.602\times10^{-19}}}\frac{1}{\sqrt{V}}$$

$$= \frac{1.226\times10^{-9}}{\sqrt{V}} \quad (m)$$

$$m^2\mathrm{v}^2 = 2meV$$

$$m\mathrm{v} = \sqrt{2meV}$$

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)

Discussion:

For photon:

$p = mc,$

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

For particles:

$p = mv,$

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

$E = h\,\nu$

$p = h/\lambda$

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

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

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

$$p_x=p\sin\theta$$

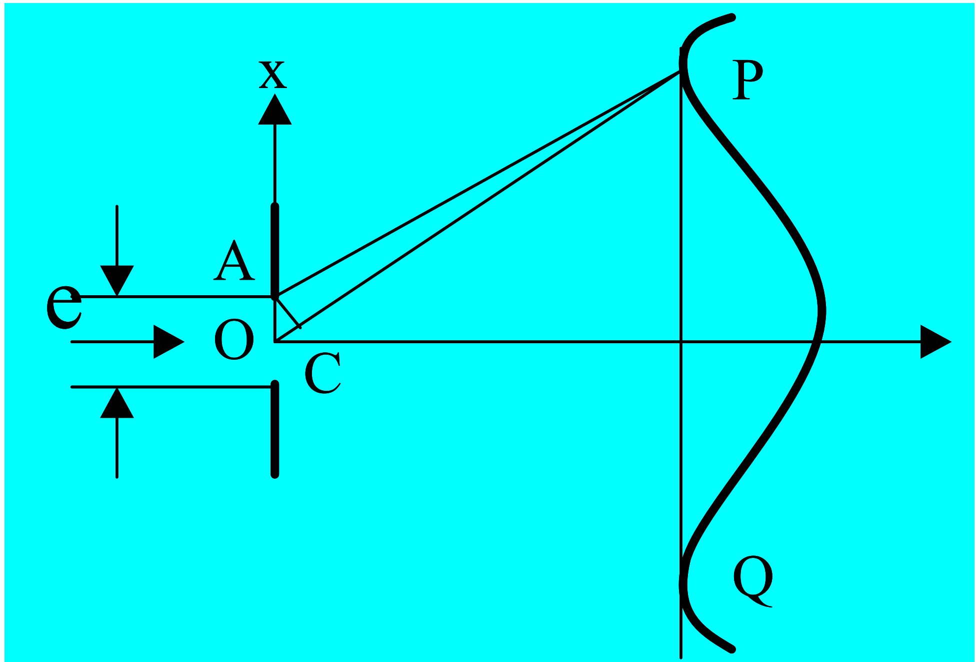
$$\Delta p=p\sin\theta \qquad (p_{xo}=0)$$

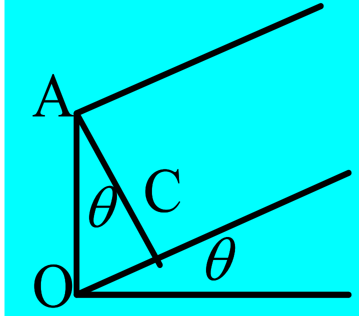
$$=p\lambda/D=\frac{h}{\lambda}\lambda/D=\frac{h}{D}$$

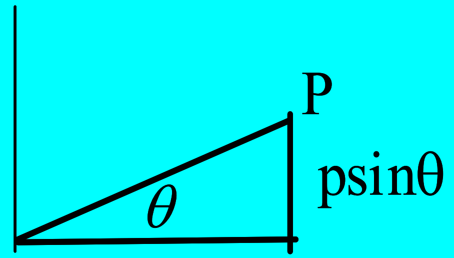
$$\Delta x\Delta p=h$$

Include higher order,

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







A quantitative version

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

$$\Delta t\Delta E\geq\frac{h}{4\pi}$$

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?

$\Delta E\,\Delta t \geqq \hbar \qquad \Delta E \geqq \hbar / \Delta t$

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

$= 1.06 \times 10^{-26}\ \mathrm{J} = \dfrac{1.06 \times 10^{-26}}{1.6 \times 10^{-19}}\ \mathrm{eV} =$

$$\boxed{\Delta E_{min} = 0.66 \times 10^{-7}\ \mathrm{eV}}$$

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 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).

1.3 The basic assumptions (postulates) of quantum mechanics

Postulate 1.

The state of 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 the time.

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

$$\boxed{\psi = A\exp[(i2\pi/h)(xp_x - Et)] = Ae^{[(i2\pi/h)(xp_x - Et)]}}$$

deduced from the wavefunction of plane monochromatic light:

$$\boxed{\psi = A\exp[i2\pi(x/\lambda - vt)] = Ae^{[i2\pi(\frac{x}{\lambda} - \upsilon t)]}}$$

A wave function must satisfy 3 mathematical conditions:

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

To be generally **normalized**

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

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.

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 coordinate **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

$$\hat{D} = d/dx$$

$$f(x) = x^3 - 5$$

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

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

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

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

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**

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

*** 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.*

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

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

***Eigen* is a German word meaning *characteristic*.**

Examples

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

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

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

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

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

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

Every physical observable corresponds to 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 **-iħ∂/∂x.**

$$f(x, x^2, \cdots, p, p^2, \cdots) \Rightarrow \hat{F} = f(\hat{x}, \hat{x}^2, \cdots, \hat{p}, \hat{p}^2, \cdots)$$

Some Mechanical quantities and their Operators

Mechanical quantities		**Mathematical 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)	$M_z = xp_y - yp_x$	$\hat{M}_z = -\frac{ih}{2\pi}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$
Kinetic Energy	$T = p^2/2m$	$\hat{T} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{h^2}{8\pi^2 m}\nabla^2$
Potential Energy	V	$\hat{V} = V$
Total Energy	$E = T + V$	$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}$

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

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

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.

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

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

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

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

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

Time-independent Schrödinger's Equation

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

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

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

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

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

e.g. H atom

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

Schrödinger’s Equation is an 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:

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

$$\left.\begin{array}{l} \int \psi^{*}\hat{A}\psi d\tau = a\int \psi^{*}\psi d\tau \\ \int \psi(\hat{A}^{*}\psi^{*})d\tau = a^{*}\int \psi\psi^{*}d\tau \end{array}\right\} \Rightarrow a = a^{*}$$

Quantum mechanical operators have to have real eigenvalues

II. The eigenfunctions of Hermitian operators are orthogonal

$$\int \psi_i{}^* \psi_j \, d\tau = \delta_{ij}$$

II. The eigenfunctions of Hermitian operators are orthogonal

Consider these two eigen equations

$$\hat{A}\psi_n = a_n\psi_n \qquad (1)$$

$$\hat{A}\psi_m = a_m\psi_m \qquad (2)$$

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

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

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

Subtracting these two equations gives -

$$\int \psi_m * \hat{A}\psi_n d\tau - \int \psi_n \hat{A} * \psi_m * d\tau$$
$$= (\mathrm{a}_n - \mathrm{a}_m *)\int \psi_m * \psi_n d\tau$$

$$(\mathrm{a}_n - \mathrm{a}_m *)\int \psi_m * \psi_n d\tau = 0$$

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 different eigenvalues, $a_n \neq a_m$), then

$$(\mathrm{a}_\mathrm{n} - \mathrm{a}_\mathrm{m})\int \psi_m{}^*\psi_n d\tau = 0$$

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

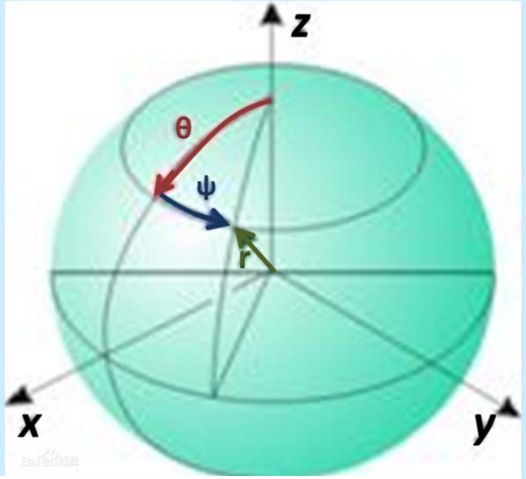
The eigenfunctions of Hermitian operators are orthogonal

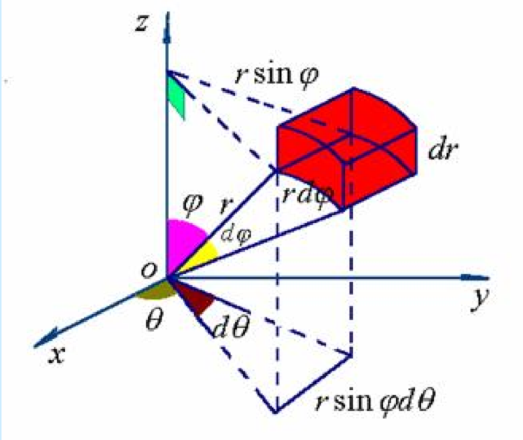
$$\int \psi_m{}^*\psi_n d\tau = 0$$

Example:

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

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





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

$$\boxed{\Gamma(n)=\int_0^{+\infty}x^{n-1}e^{-x}dx}$$

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

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

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

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

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.

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

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 –

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

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

Exercise :

Suppose a particle in a box is in a state -

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

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

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 ψ(x) is normalized. Calculate the average energy associated with this state. (Assume V = 0).

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

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

* The average value of a mechanical quantity with eigenstate.

Suppose the wave function happens to be an eigenfunction of A, i.e. $\mathbf{A\psi_n = \boldsymbol{a}_n\psi_n}$ so

$$\begin{aligned}\langle a\rangle &= \int_{-\infty}^{\infty} \Psi_n * A\Psi_n d\tau \\ &= \int_{-\infty}^{\infty} \Psi_n * a_n \Psi_n d\tau \\ &= a_n \int_{-\infty}^{\infty} \Psi_n * \Psi_n d\tau \\ &= a_n\end{aligned}$$

$$< a >= \int \Psi^* \hat{A} \Psi d\tau = \int (\sum_j c_j^* \psi_j^*) \hat{A} (\sum_i c_i \psi_i) d\tau$$

$$= \sum_i (c_i)^2 a_i \int \psi_i^* \psi_i d\tau = \sum_i (c_i)^2 a_i$$

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**.

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

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

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

$$= a_n$$

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

$$= a^2{}_n$$

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

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

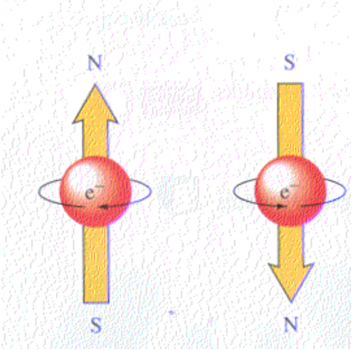
$$= 0$$

Thus the only value we measure is the value a_n.

Postulate 5 :

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

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

$m_s = \pm ½$ $(-½ = \alpha)$ $(+½ = \beta)$

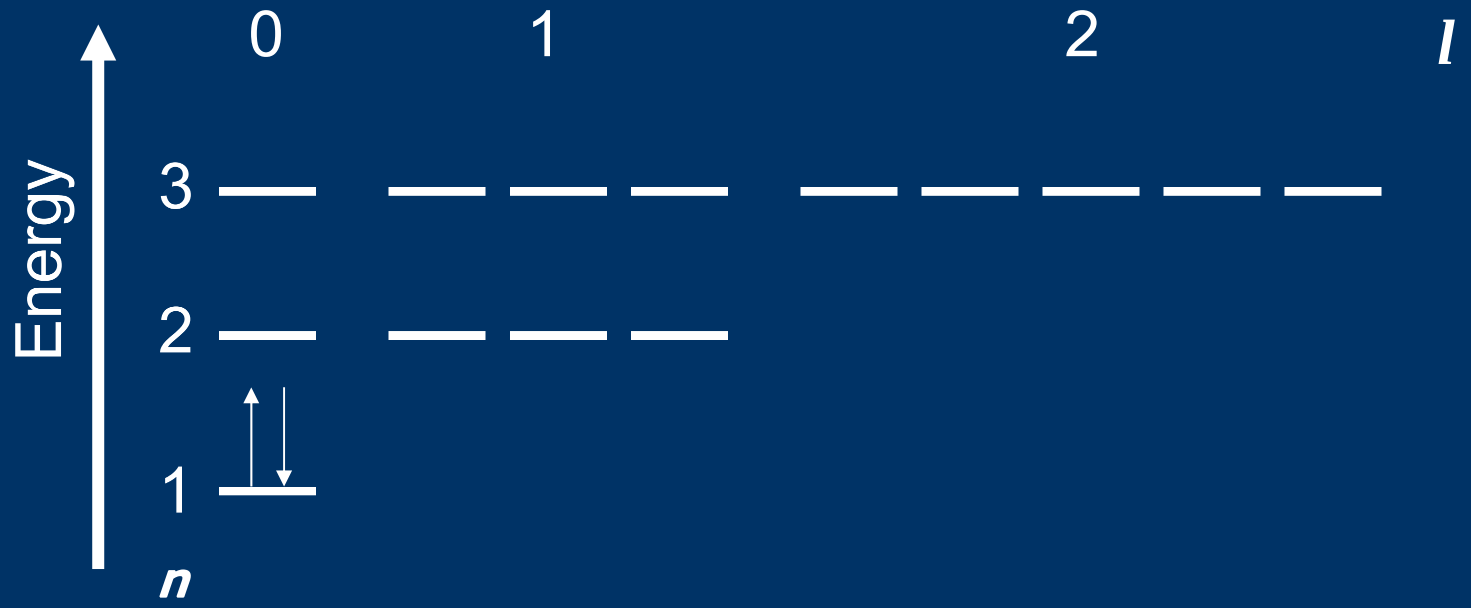
Pauli exclusion principle:

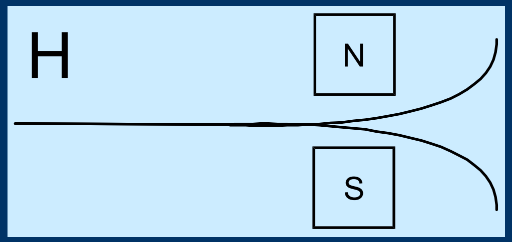
Each electron must have a unique set of quantum numbers.

Two electrons in the same orbital must have opposite spins.

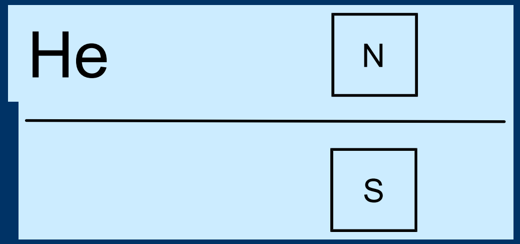
Electron spin is a purely quantum mechanical concept.

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.

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

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

$$\phi(q_1,q_2)$$

$$\left|\phi(q_1,q_2)\right|^2 = \left|\phi(q_2,q_1)\right|^2$$

$$\phi(q_1,q_2) = \pm\phi(q_2,q_1)$$

\+ symmetry (Bosons)

\- Antisymmetry (Fermions)

Fermions

- Particles that **do** obey the Pauli Exclusion Principle.

Bosons

- Particles that **do not** obey the Pauli Exclusion Principle

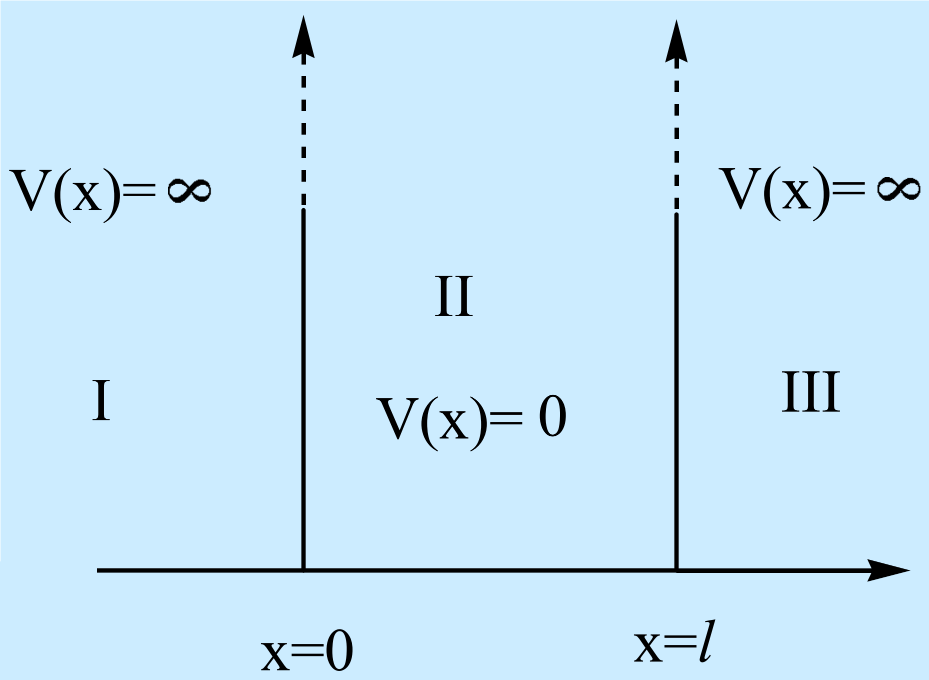
1.4 Solution of free particle in a box

— 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

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



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

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

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

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

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

$$\frac{\partial^2\psi}{\partial^2 x}+\alpha^2\psi=0 \qquad \Psi_1=e^{i\alpha x} \qquad \frac{d\Psi_1}{dx}=i\alpha e^{i\alpha x} \qquad \frac{d^2\Psi_1}{dx^2}=-\alpha^2 e^{i\alpha x}$$

$$\psi=A'e^{i\alpha x}+B'e^{-i\alpha x} \qquad \Psi_2=e^{-i\alpha x} \qquad \frac{d\Psi_2}{dx}=-i\alpha e^{i\alpha x} \qquad \frac{d^2\Psi_2}{dx^2}=-\alpha^2 e^{i\alpha x}$$

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

Boundary condition and continuous condition:

$\psi(0)=0$, $\psi(l)=0$

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

A=0, B≠0 **$\psi=B\sin\alpha x$**

$\psi(l)=B\sin\alpha x=B\sin\alpha l=0$, 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:

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

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

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

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

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

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

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 ($h^2/8ml^2$)

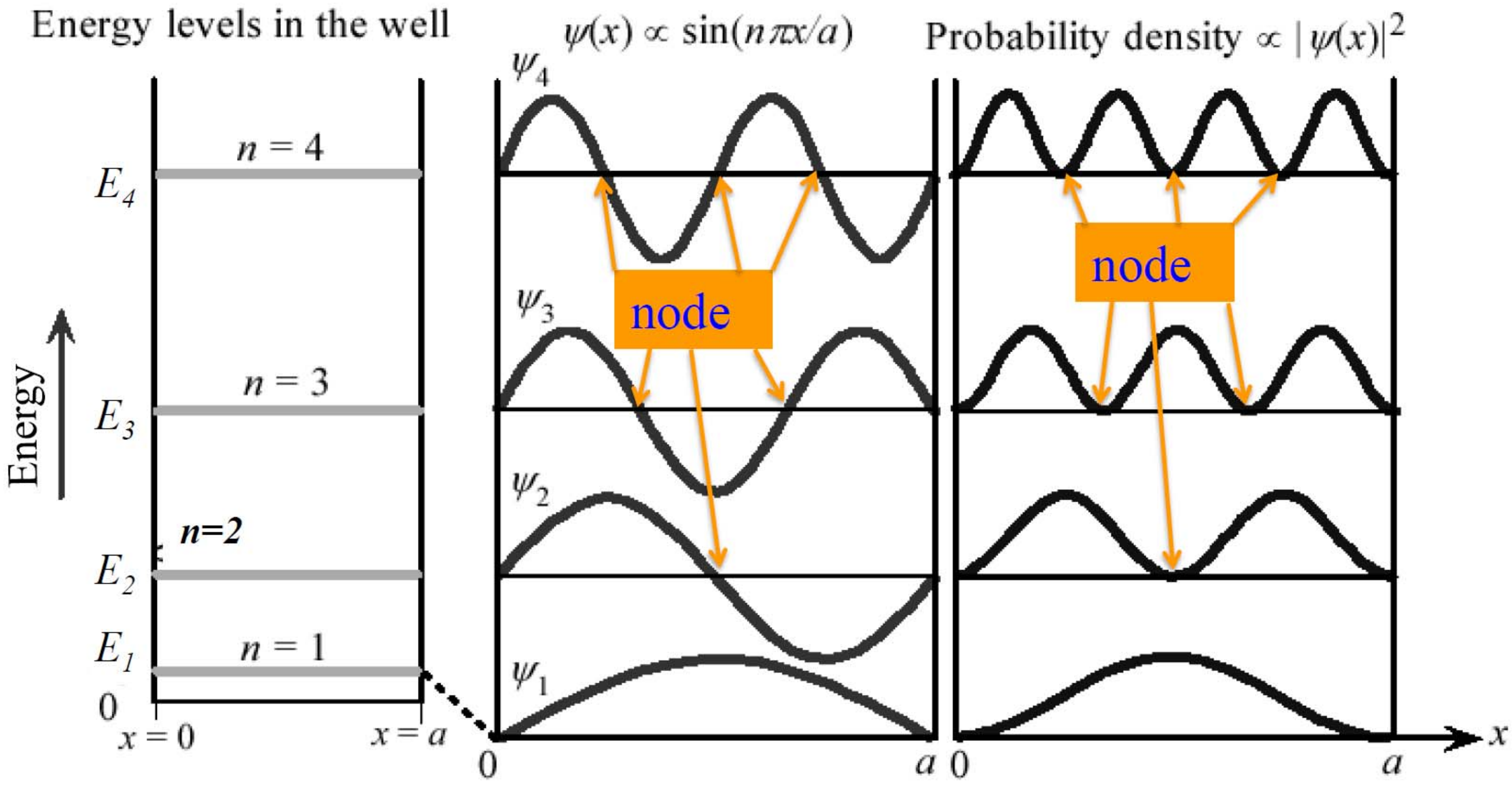
d. There is no trajectory but only probability distribution

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 $E_3 = \frac{9h^2}{8ml^2}$ $\psi_3 = \sqrt{\frac{2}{l}}\sin\frac{3\pi x}{l}$……



- **In the ground state (n=1), the highest probability of the particle occurs at the location *l/2*.**
- **In the first excited state (n=2), the highest probability of the particle occurs at the locations *l/4* and *3l/4*, the lowest probability at the location *l/2*.**

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* $\hat{A}$

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

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

$$\cos(\alpha \pm \beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$

$$\cos\alpha + \cos\beta = 2\cos\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$\cos\alpha - \cos\beta = -2\sin\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}$$

$$\sin\alpha + \sin\beta = 2\sin\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$\sin\alpha - \sin\beta = 2\cos\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}$$

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.

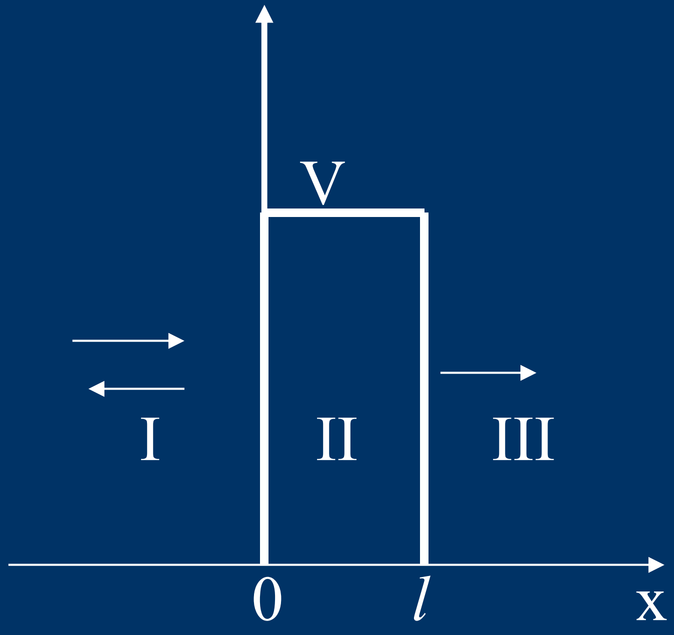
d. Deduce the values of the various physical quantities of each corresponding state.

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

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

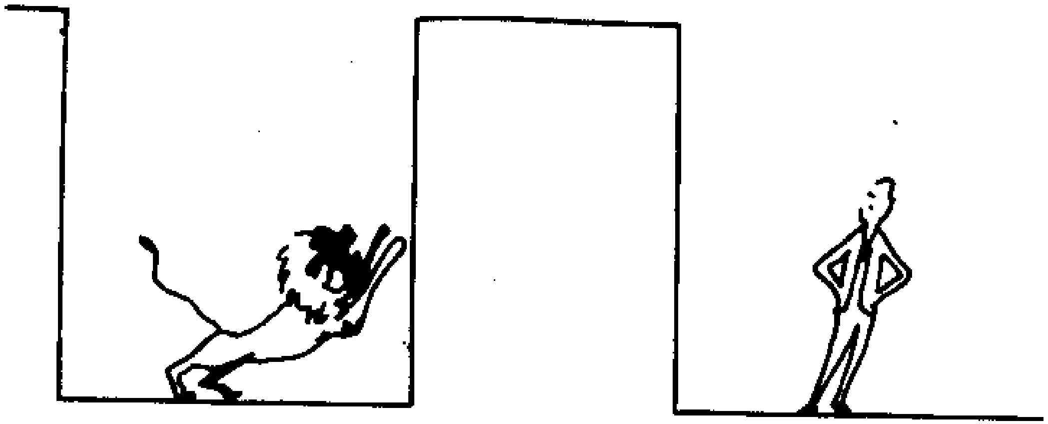


The probability of penetration is given by

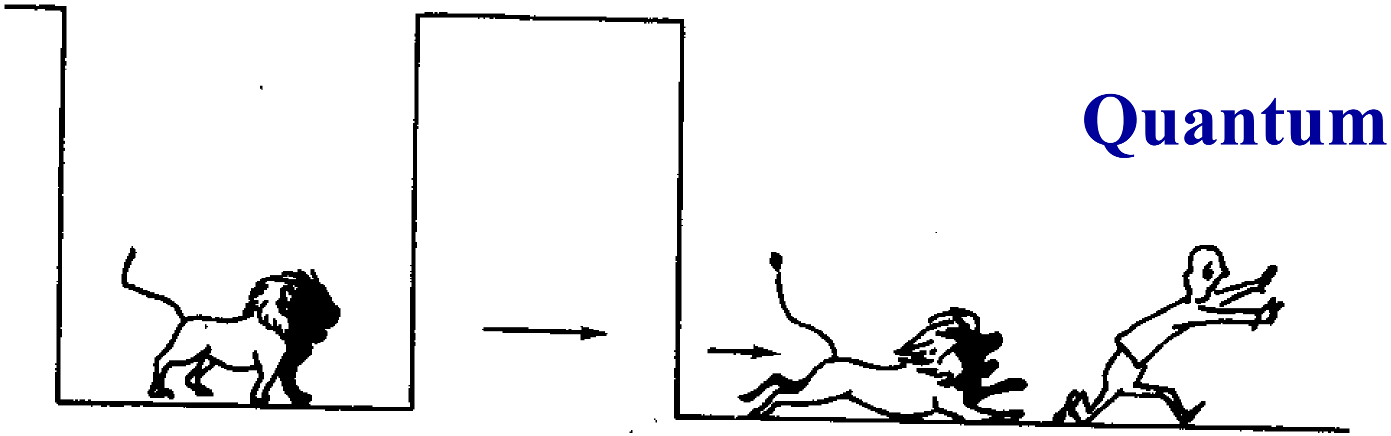
$$P \approx 4(E/V)[1-(E/V)]e^{-\frac{2}{\hbar}\sqrt{2m(V-E)}l}$$

When E<V

Tunneling

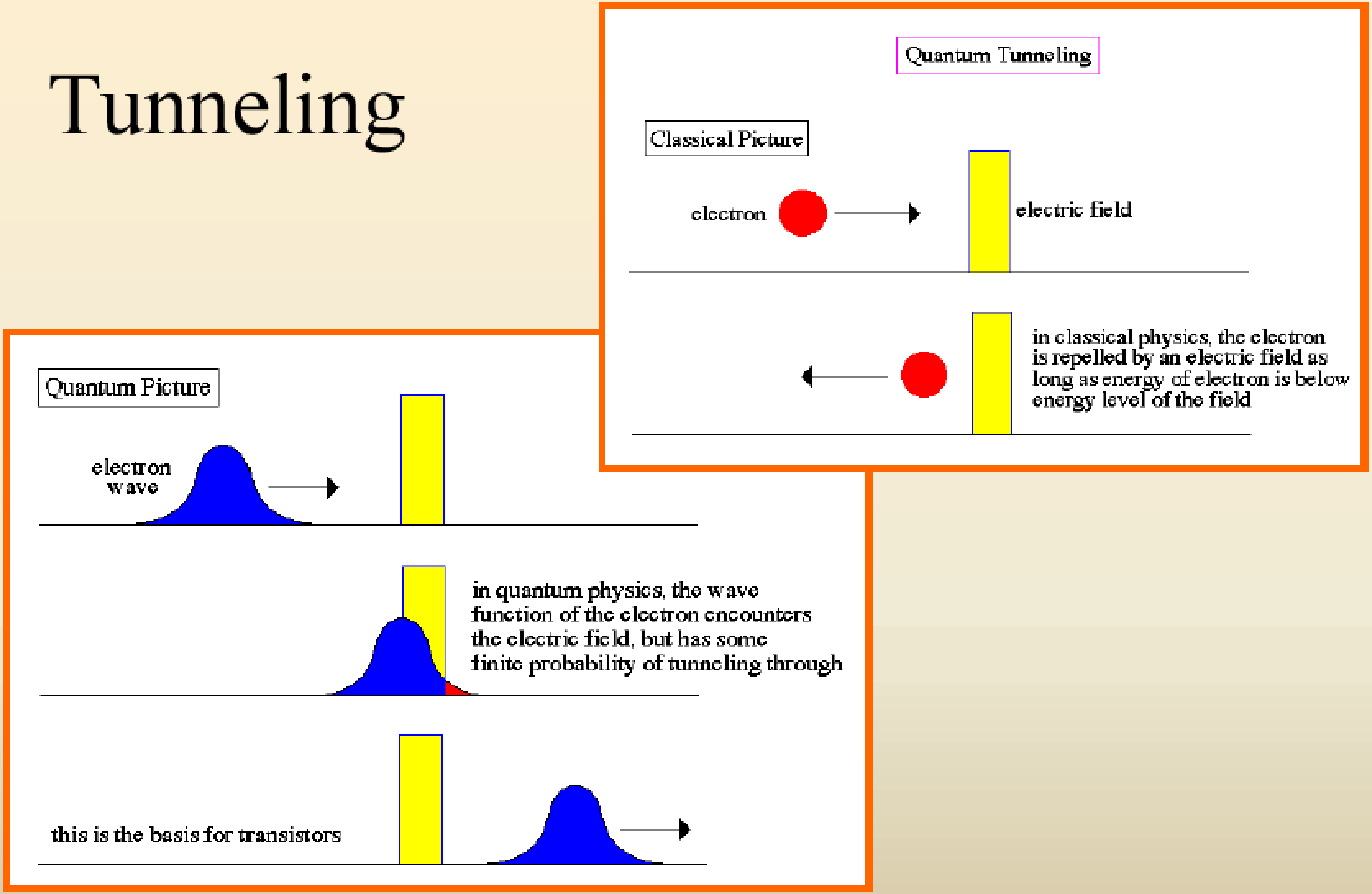


Classical Mechanics



Quantum Mechanics

Tunneling



in classical physics, the electron is repelled by an electric field as long as energy of electron is below energy level of the field

in quantum physics, the wave function of the electron encounters the electric field, but has some finite probability of tunneling through

this is the basis for transistors

Tunneling in the "real world"

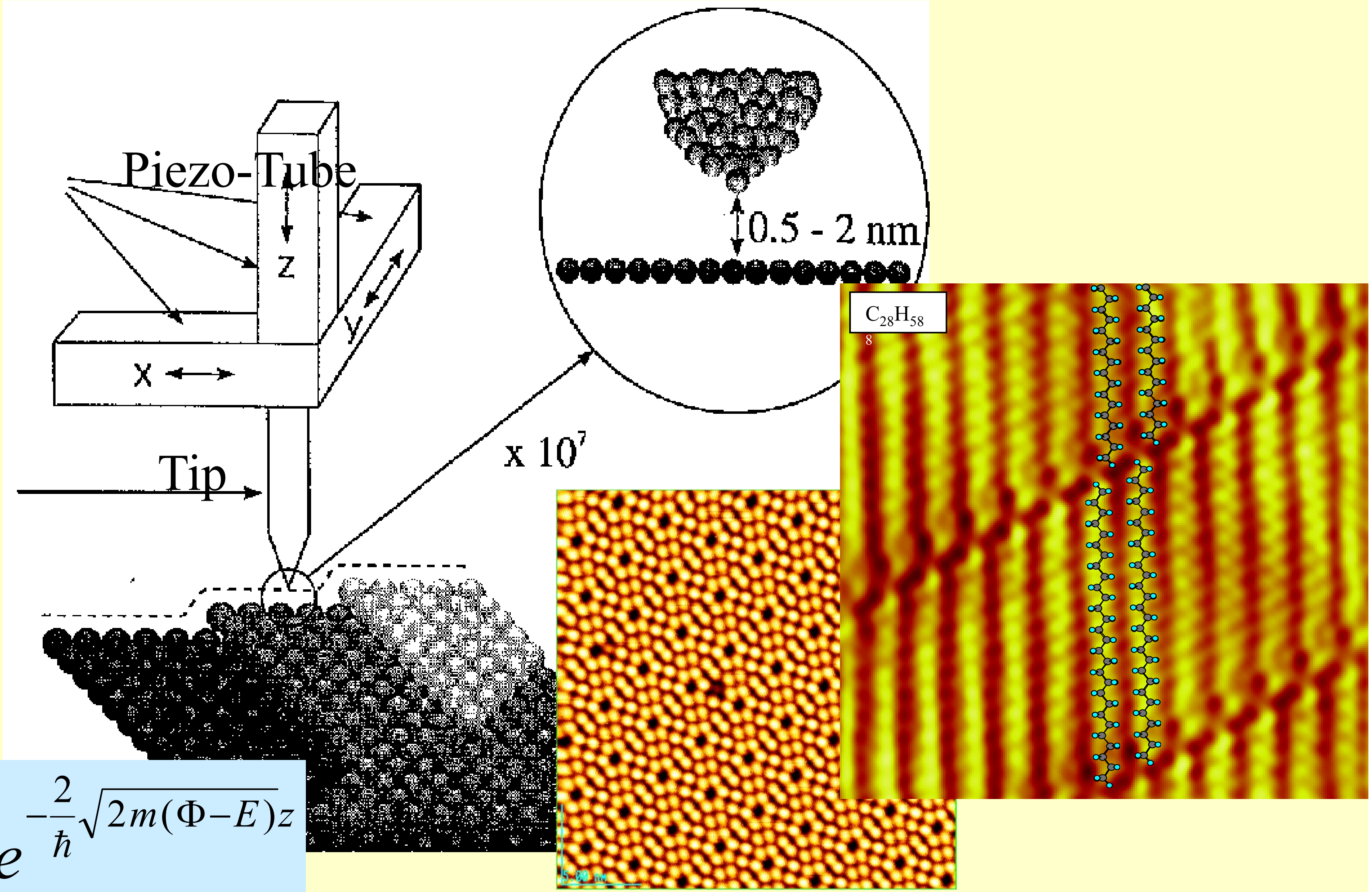
Tunneling is used:

- 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)

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

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

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

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

Let $E_z = E - E_x - E_y$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 x}X = E_x X$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 y}Y = E_y Y$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 z}Z = E_z Z$$

$E=E_x+E_y+E_z$

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: $n_x=n_y=n_z=1$

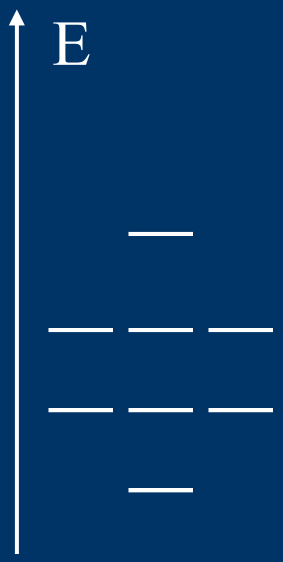
$$E = \frac{3h^2}{8ma^2}$$

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

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

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

$$\left\{\begin{matrix} 1 & 1 & 2 \\ 1 & 2 & 1 \\ 2 & 1 & 1 \end{matrix}\right.$$



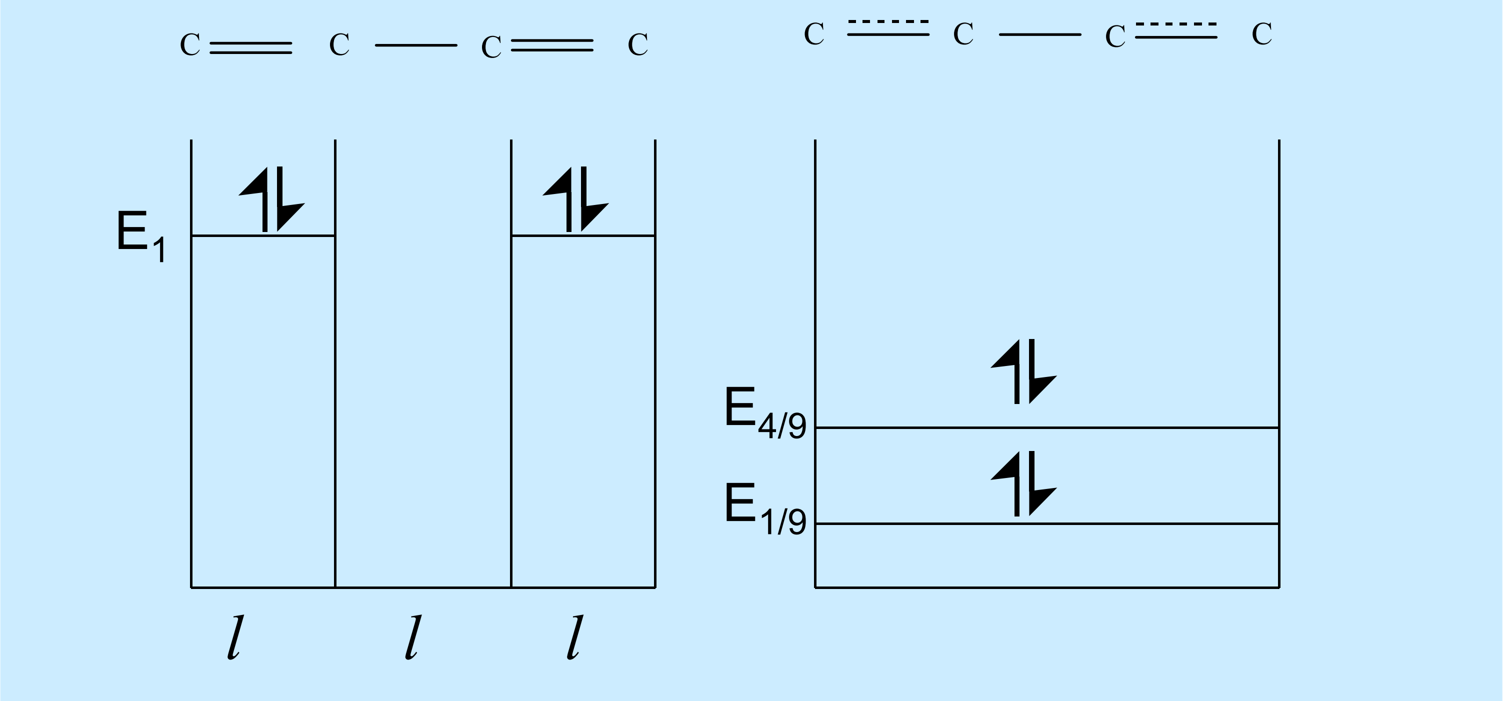
1.4.3 Simple applications of a one-dimensional potential box model

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

Four π electrons form two π localized bonds

Four π electron forms a π_4^4 delocalized bond

$E=2\times 2\times h^2/8ml^2=4E_1$ > $E=2\times h^2/8m(3l)^2+2\times 2^2\times h^2/8m(3l)^2=(10/9)E_1$



Example 2: The adsorption spectrum of cyanines

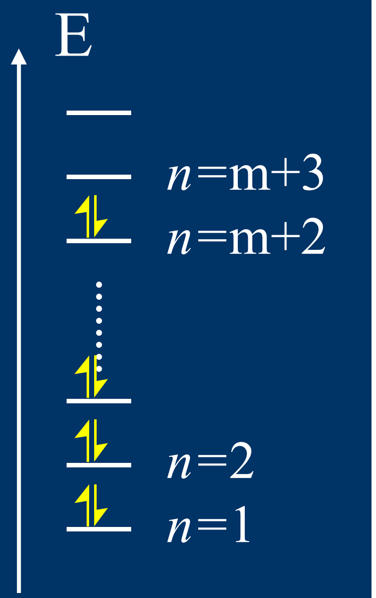
The general formula of the cyanine dye:

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

Total π electrons: 2m+4

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

The adsorption spectra correspond to electron excitations from the highest occupied (m+2) orbital to the lowest unoccupied (m+3) orbital.



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

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

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

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

Table 1. The absorption spectrum of the cyanine dye

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

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