Structural Chemistry

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http://pcss.xmu.edu.cn/old/users/xlu/group/courses/structurechem/

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参考书:

1. 《结构化学》

厦门大学化学系物构组编

2. Physical Chemistry

P.W. Atkins

3. 《化学键的本质》鲍林

上海科学技术出版社

4. 《结构化学基础》周公度编著，北京大学出版社

5.《结构化学习题解析》周公度 等，北京大学出版社

三点说明：

1. 作业(15%, - 2%/次) + 考勤(15%, - 2%/次) → 平时成绩
   - 符合理科作业规范， 每周三交
   - 若全缺席+无作业，则理论上可及最高分为**40**分！

2. 考试方式：
   - 随堂考试
   - 期中/期末（30%/40%）

   → 期平成绩 = 平时(30%) + 期中(30%) + 期末(40%)

3. 化学前沿 (课外)： 科技媒体如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

“钱学森之问”早有答案：

清华大学经管学院 钱颖一教授 讲述的小故事：

爱因斯坦在1921年获得诺贝尔物理学奖后首次到美国访问，有记者问他声音的速度是多少？爱因斯坦拒绝回答，并说我不回答你这个问题，因为你可以在任何一本物理书中查到答案。接下来爱因斯坦说了句后来特别有名的话，他说“大学教育的价值不在于记住很多事实，而是训练大脑会思考”。这是将近一百年前的一句话。在当时，很多事实是从书中可以查到的。在今天，更多的事实可以上网查到。在未来，又有更多的知识和事实机器会帮你查到。所以这句话在当前和未来更值得深思。

结论：如果你只专注于学习知识，你肯定会被机器取代！

- 知识是人类智慧的结晶, 但 知识 ≠ 智慧!
  智慧是运用知识解决各种问题的能力！

- 学习 知识 ≠ 学习 智慧，智慧蕴含于知识中！
- Learning knowledge is the bridge to approach wisdom!

- 道德修养 ＝ 习惯养成！
- 抄作业 ＝ 学术道德问题！
- 考试作弊 ＝ 学术道德问题！

Plagiarism(剽窃) ＝ Academic Crime!

To **plagiarize** is to give the impression that something you have written is your own when it was in fact taken from someone else’s work. Plagiarism may take the form of :

- repeating another’s sentences as your own.
- adopting a particularly good phrase as your own.
- paraphrasing someone else’s argument.
- presenting someone else’s form of organization as your own.

In the West, plagiarism is considered a serious academic crime and may lead to expulsion from the university!

Follow these guidelines and you’ll never be accused of plagiarism.

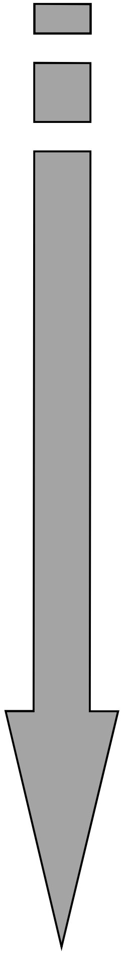
1. Use your own words and sentence structures.
2. When putting someone else’s idea in your own words avoid using any words from the original.
3. If you use any original words, use a quotation.
4. Acknowledge all ideas taken from other writers, except commonly held knowledge in the field.

It is plagiarism to use some original words or phrases from a sentence while changing others. It is also plagiarism to keep the sentence structure and change all the words to synonyms.

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

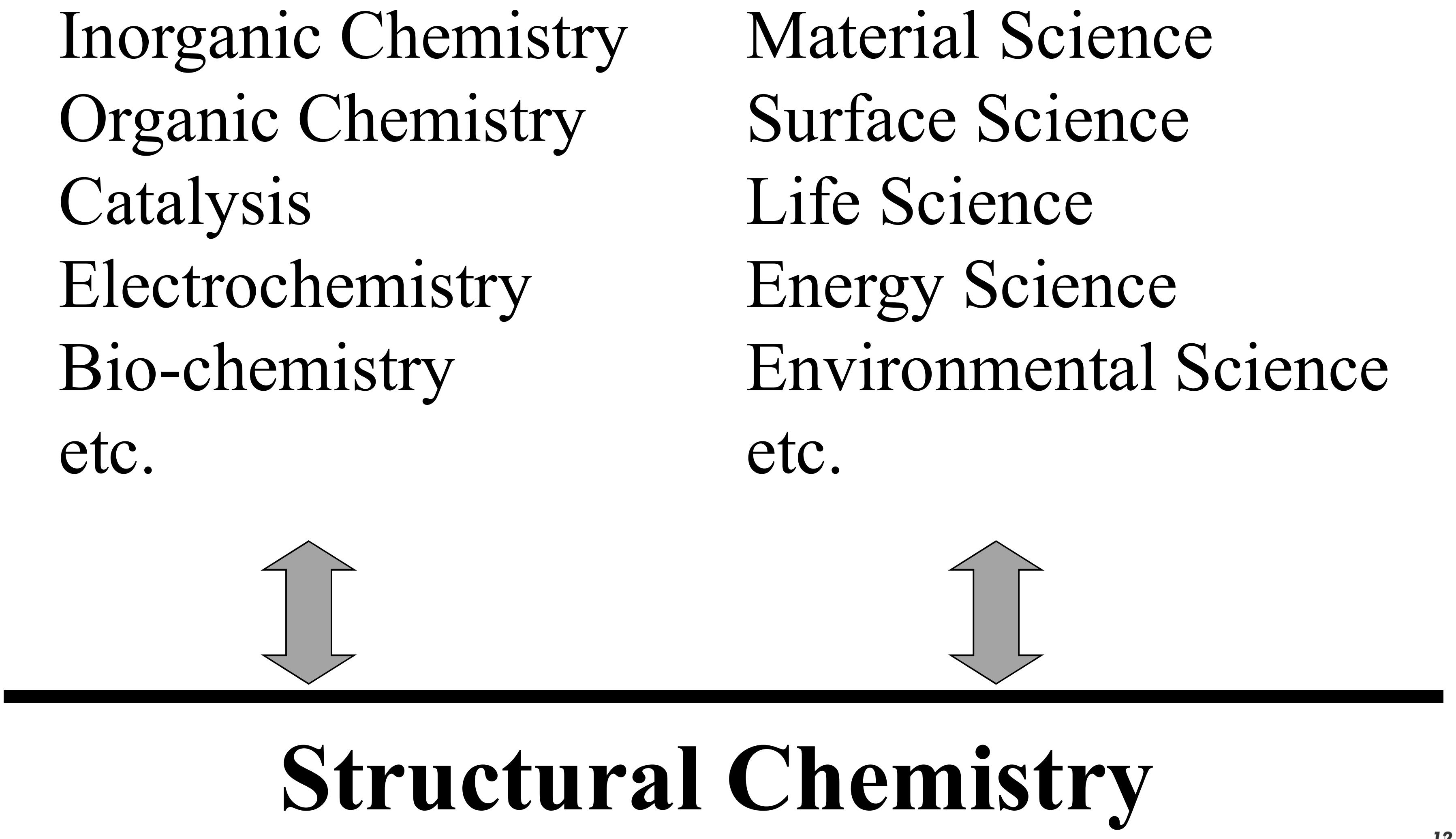
Geometric Structure

Size
makes the difference

Electronic Structure

Structure vs. Properties

Structure determines properties
Properties reflect structures



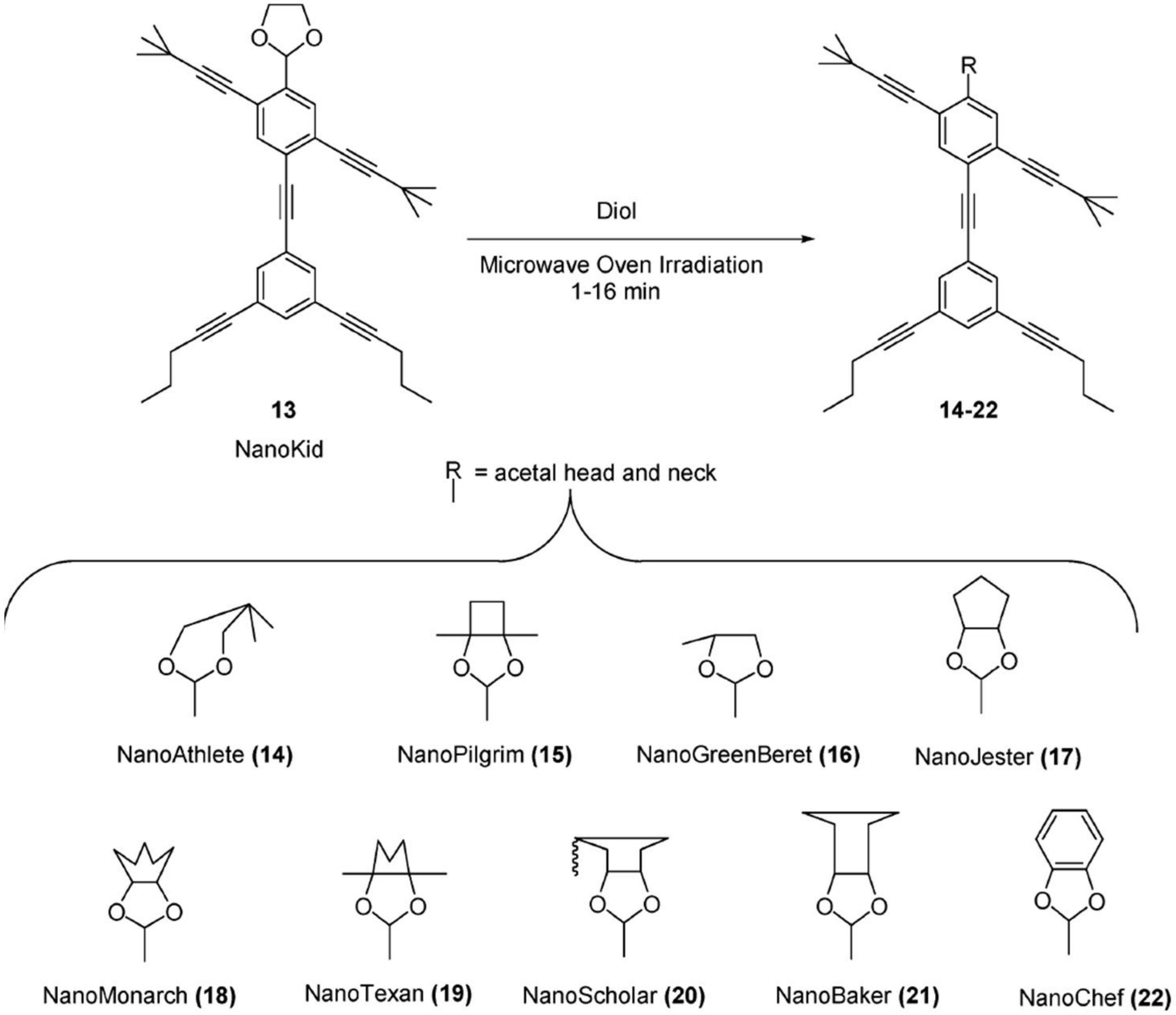
Inorganic Chemistry
Organic Chemistry
Catalysis
Electrochemistry
Bio-chemistry
etc.

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

Structural Chemistry

Funny things in Structural Chemistry

Nanoputians: Anthropomorphic Molecules



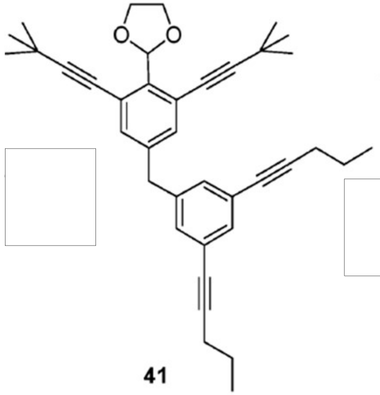
- "Nanoputian" is a portmanteau of <u>nano</u> and <u>lilliputian</u>.

- Lilliput is a fictional island nation that appears in the first part of the 1726 novel *Gulliver's Travels* by Jonathan Swift.

Tour, J.M. et al, *J. Org. Chem*. 2003, 68,8750; *J. Chem. Edu*. 2003, 80, 395.

Funny things in Chemistry

Nanoputians: Anthropomorphic Molecules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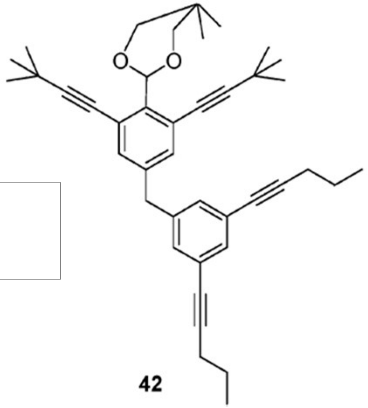
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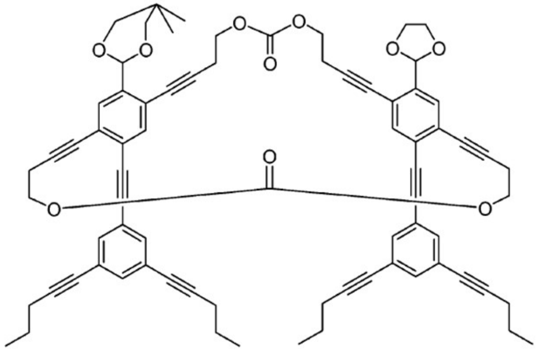
NanoBalletdancers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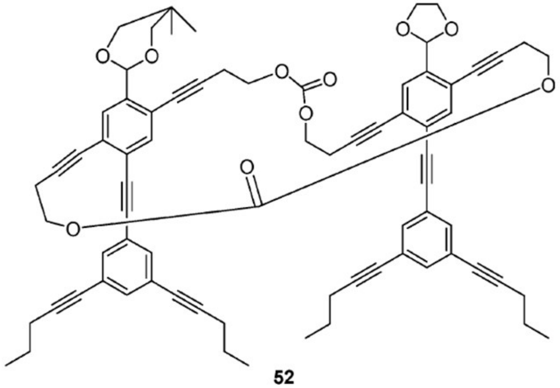
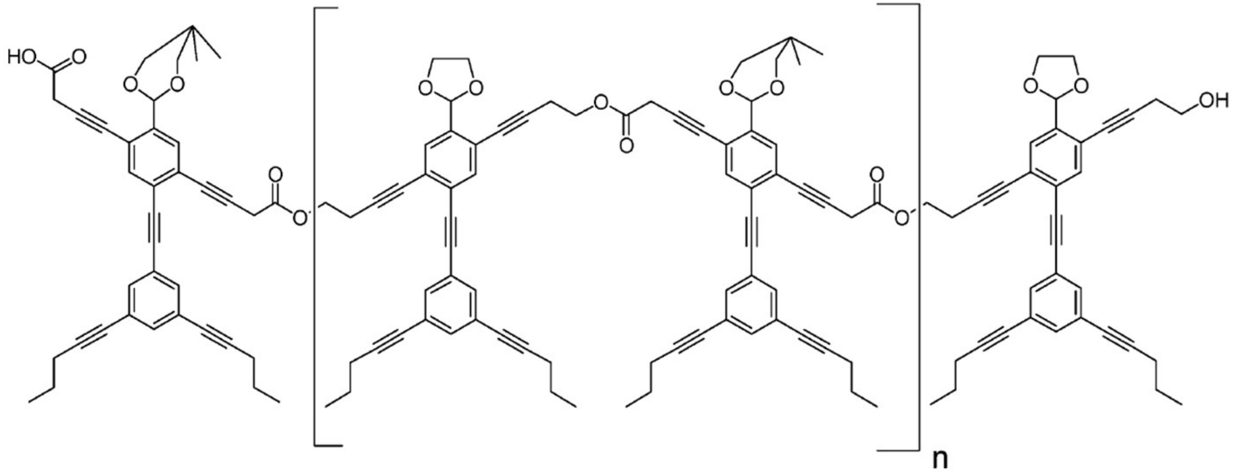
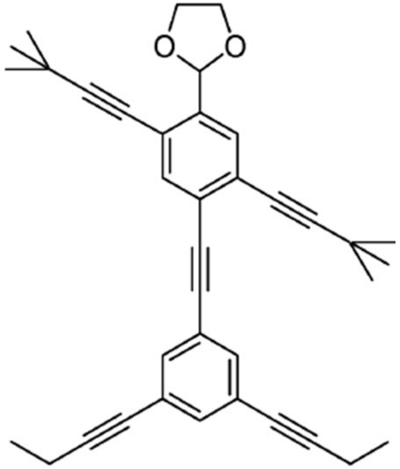

52

Pas de duex

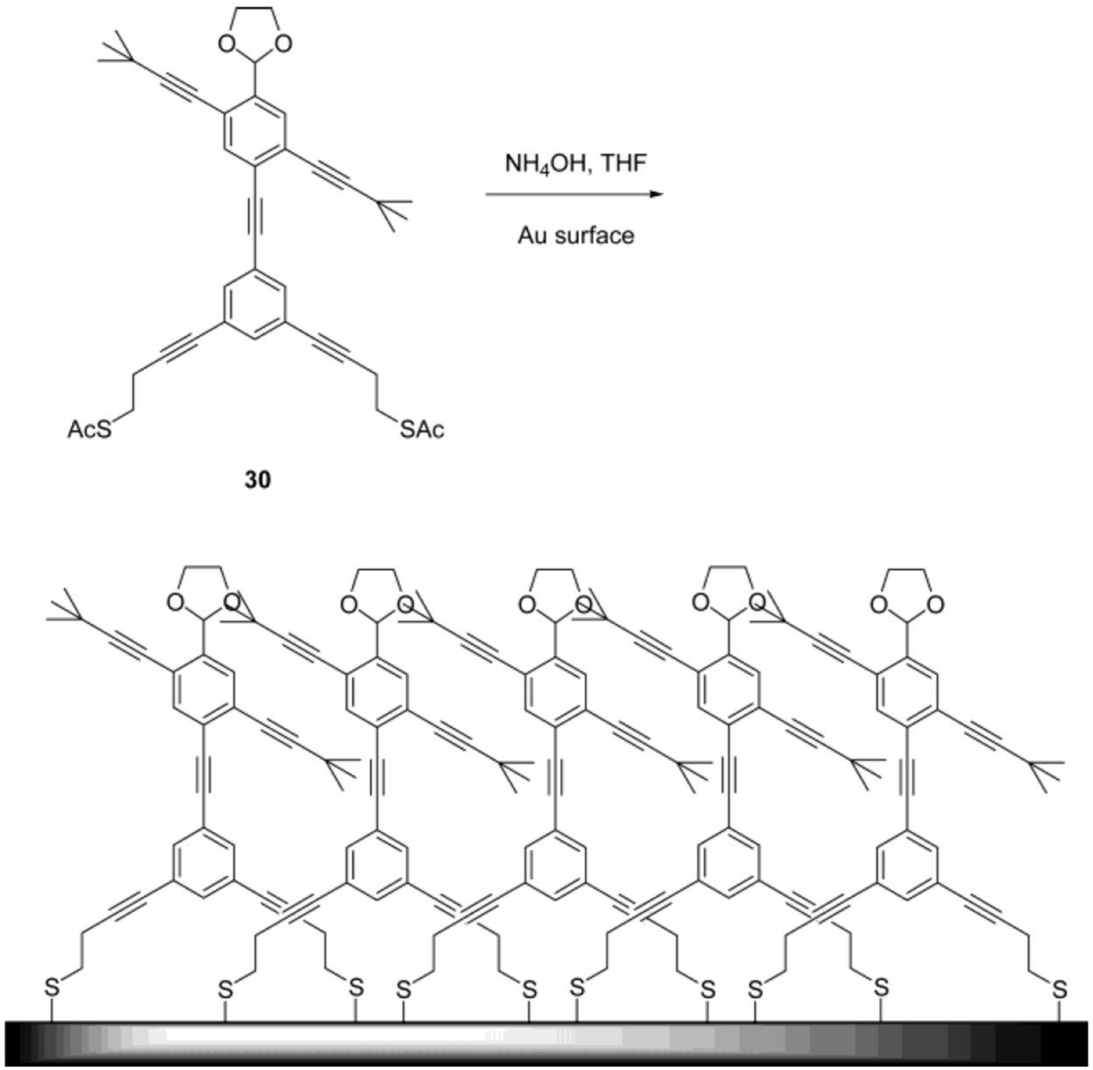

Chain of Nanoputians


NanoToddler

Tour, J.M. et al, *J. Org. Chem*. 2003, 68,8750; *J. Chem. Edu*. 2003, 80, 395.

Funny things in Structure Chemistry

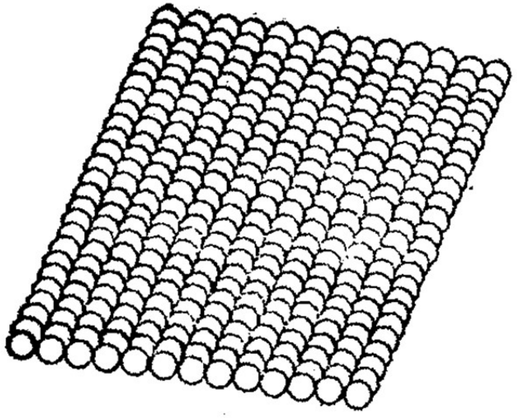
Self-assembly of Nanoputians on Gold Surface



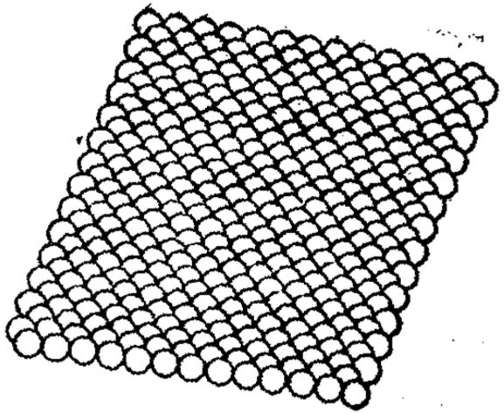
Tour, J.M. et al, *J. Org. Chem*. 2003, 68,8750; *J. Chem. Edu*. 2003, 80, 395.

Role of Structural Chemistry in Surface Science

NC - Coordination Number

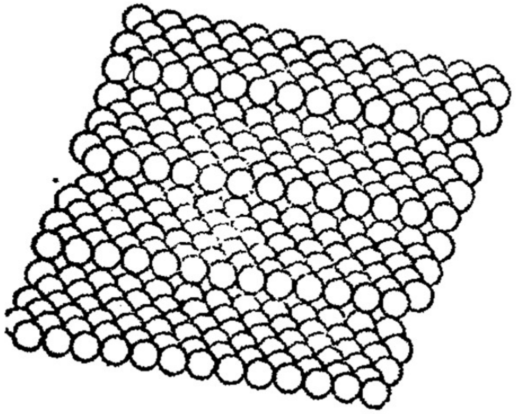


fcc(100)

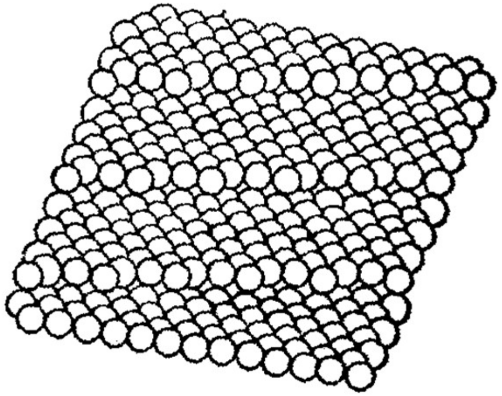


fcc(111)

Low-index surface:
$NC_S^{LIS} < NC_B$.



fcc(775)

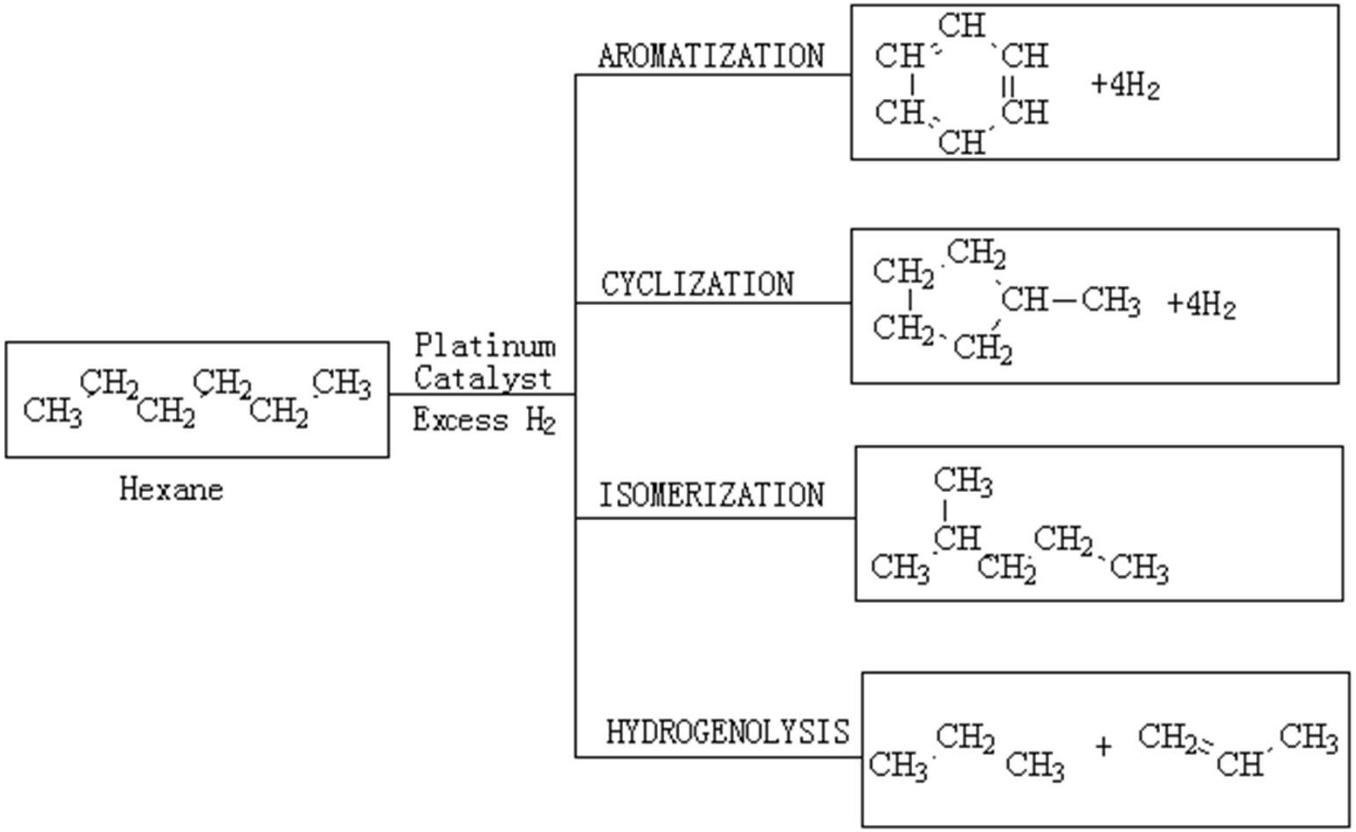


fcc(10 8 7)

High-index surface:

- Abundant edge sites.
- $NC_{es} < NC_S^{LIS} < NC_B$
- Lower NC ~ higher reactivity.

Surface structures of Pt single crystal



(111)

(775)

(100)

(10 8 7)

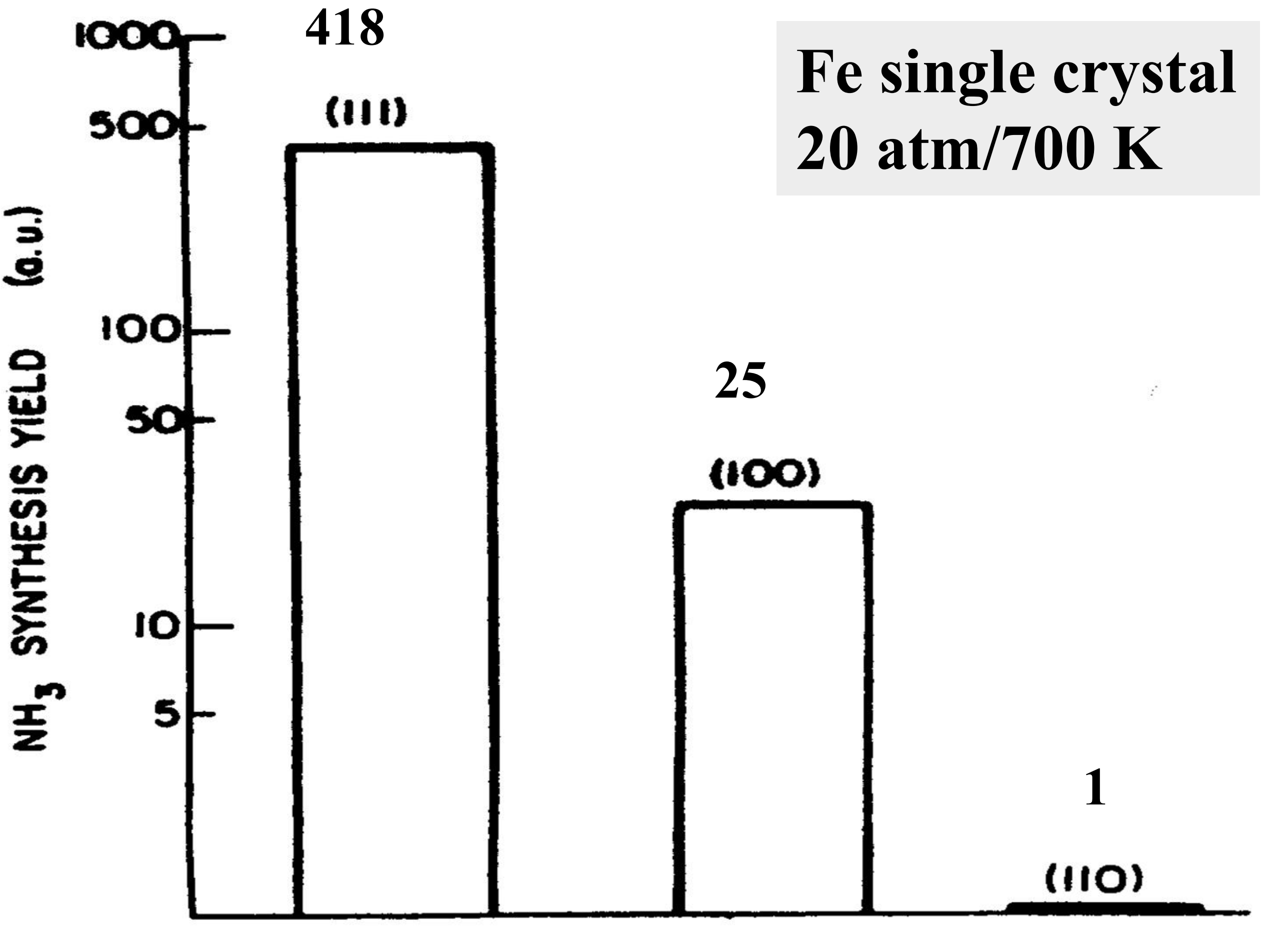
Different surfaces do different chemistry.

Structure-sensitive Catalysis!

Another example of Structure-sensitive Catalysis

Surface Structure vs. Catalytic Activity

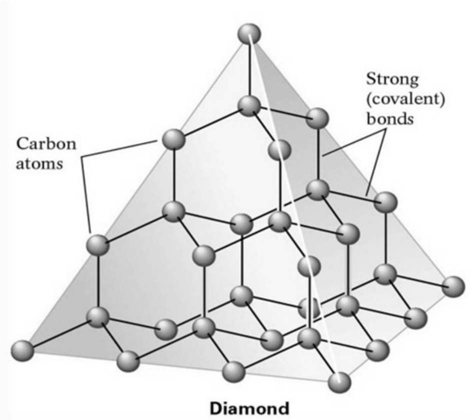
$$N_2 + 3H_2 \xrightarrow[Fe]{} 2NH_3$$

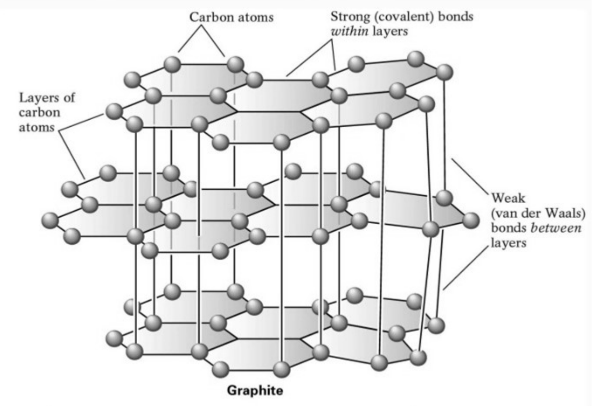


Fe single crystal
20 atm/700 K

Role of Structural Chemistry in Material Science

C Crystal Structures





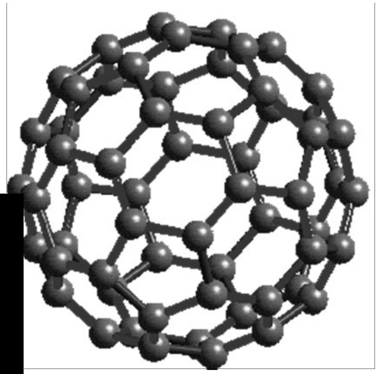
➲ Graphite & Diamond Structures

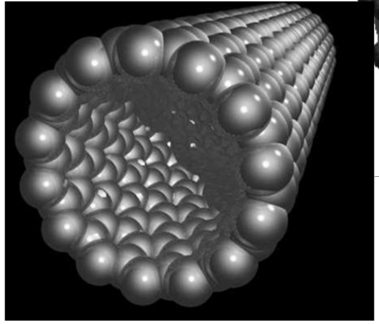
- **Diamond:** Insulator or wide bandgap semiconductor: →→→ →→→
- **Graphite:** Planar structure: →→→
  ***sp*^{2} bonding** ≈ 2d metal (in plane)

Same Element vs. Different Structures

Different structure → different properties!

➲ *Other* Carbon allotropes





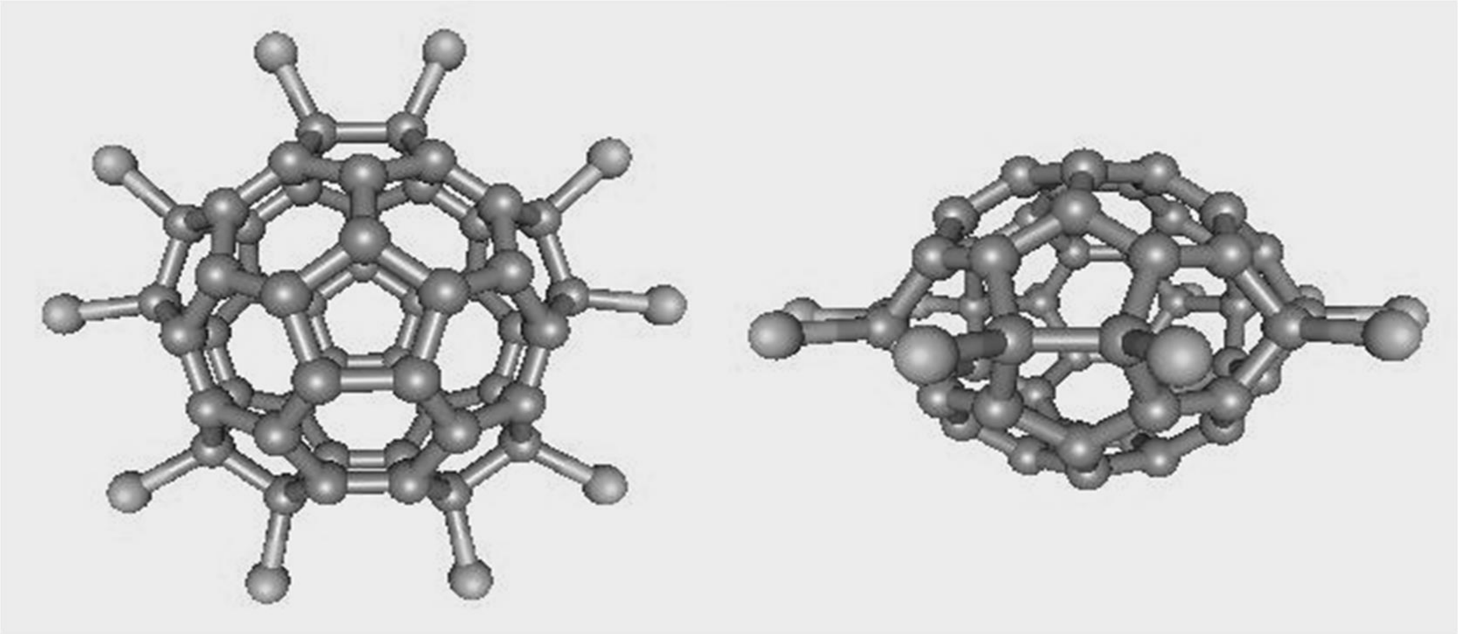
"**Buckyballs**" (C_{60}, C_{70} etc) →→→
"**Buckytubes**" (nanotubes),
other fullerenes →→→

Stable hollow fullerenes: IPR
IPR = isolated pentagon rule

Zheng LS (郑兰荪), et al.

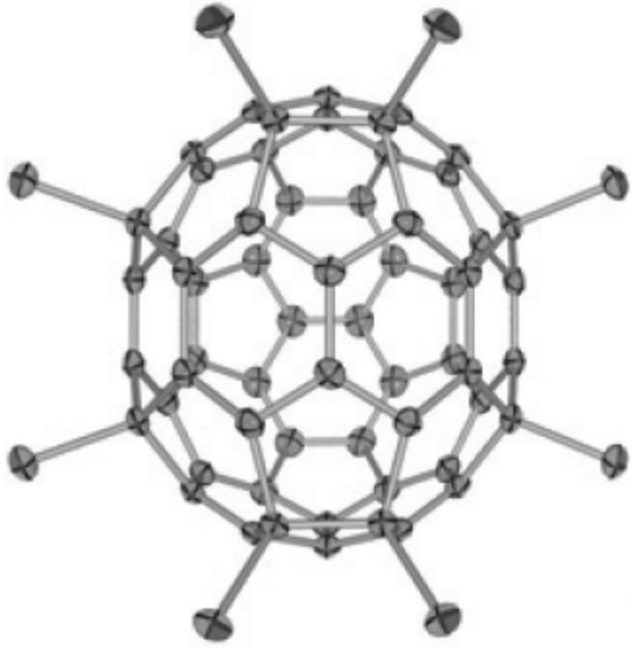
Capturing the labile fullerene[50] as $C_{50}Cl_{10}$

SCIENCE 304 (5671): 699-699 Apr 30, 2004.

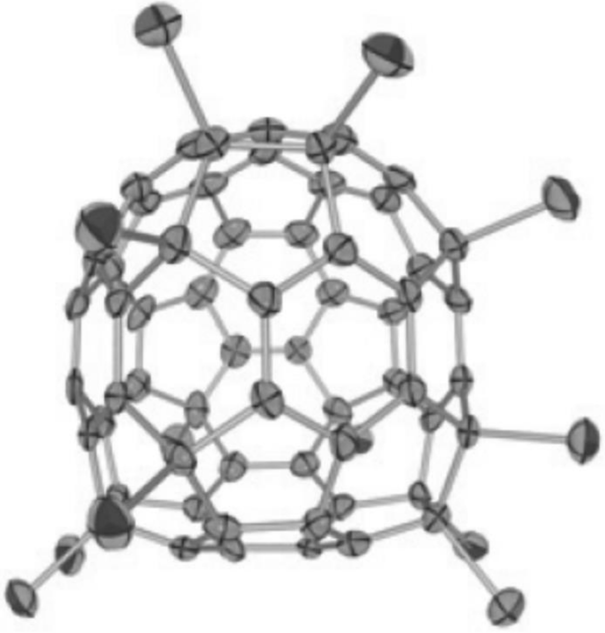


- The pentagon-pentagon fusions in pristine C_{50}-D_{5h} are sterically strained and highly reactive.
- Perchlorination of these active sites stabilizes the labile C_{50}-D_{5h}.

Two I_h-symmetry-breaking C_{60} isomers stabilized by chlorination



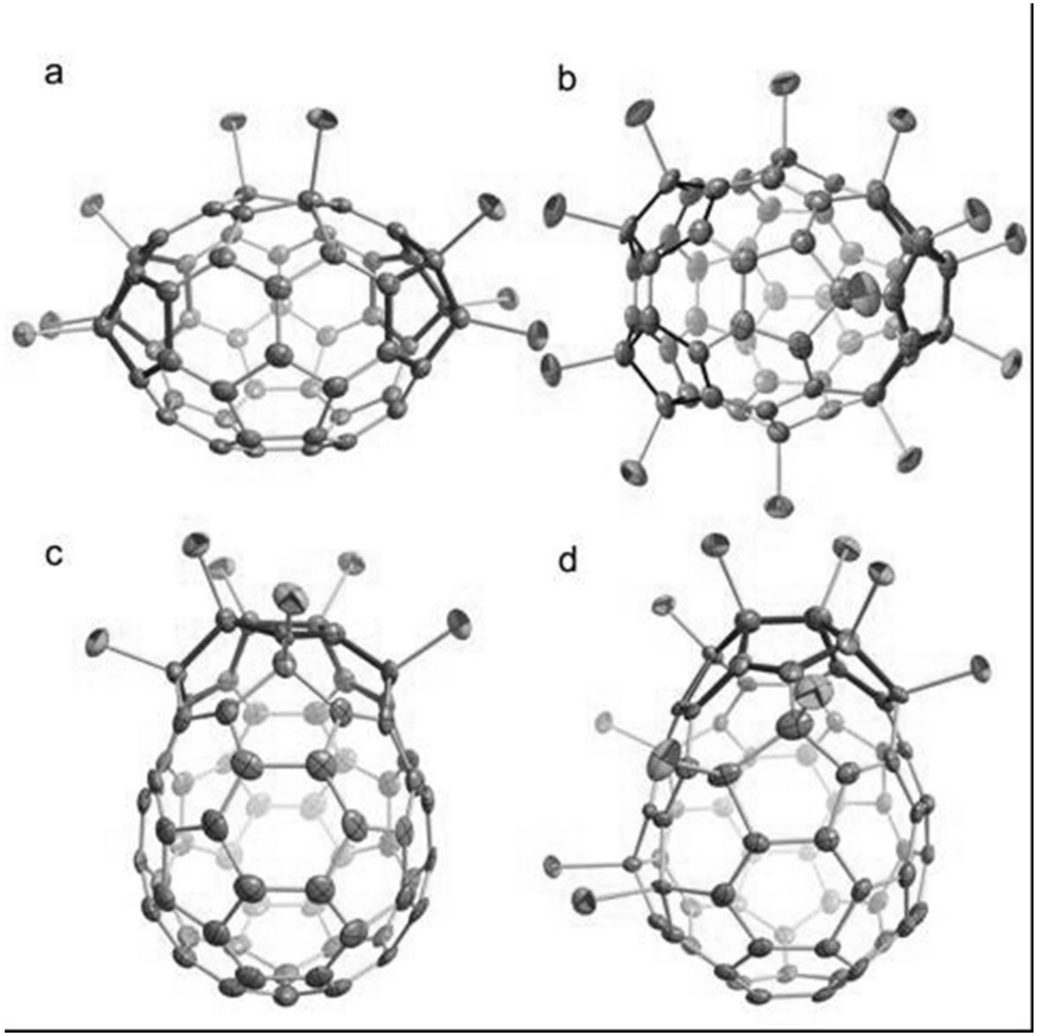
$^{\#1,809}C_{60}\,Cl_8$ **(1)**



$^{\#1,804}C_{60}\,Cl_{12}$ **(2)**

YUAN-ZHI TAN*, ZHAO-JIANG LIAO*, ZHUO-ZHEN QIAN, RUI-TING CHEN, XIN WU, HUA LIANG, XIAO HAN, FENG ZHU, SHENG-JUN ZHOU, ZHIPING ZHENG, XIN LU, SU-YUAN XIE†, RONG-BIN HUANG AND LAN-SUN ZHENG

Nature Materials, 2008, 7, 790.



$^{\#540}C_{54}Cl_8$ (a), $^{\#864}C_{56}Cl_{12}$ (b), $^{\#4,169}C_{66}Cl_6$ (c), $^{\#4,169}C_{66}Cl_{10}$ (d).

Chlorofullerenes featuring triple sequentially fused pentagons

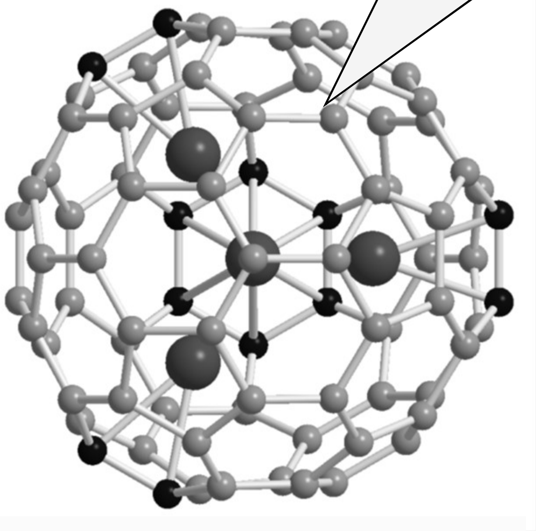
Xie S.Y., Lu X., Zheng, L.S. et al

Nature Chem. 2010, 2, 269.

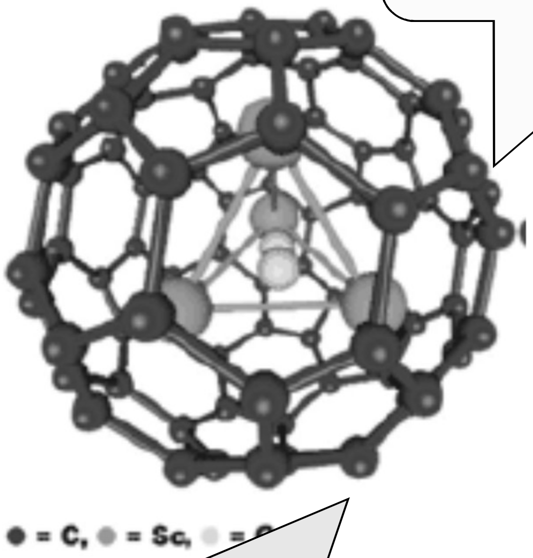
Endohedral Metallofullerene: $Sc_4@C_{82}$ (C_{3v}) vs. $Sc_4C_2@C_{80}$ (I_h)

Proposed

QM-predicted in 2006
X-ray diffract. in 2009



$Sc_4@C_{82}$
$\Delta E = 28.8$ kcal/mol



$\Delta E = 0.0$ kcal/mol
$C_2^{6-}@(Sc^{3+})_4@C_{80}^{6-}$-$I_h$
A Russian-Doll endofullerene

- $(Sc^{2+})_4@C_{82}^{8-}$

Shinohara, H. Rep. Prog. Phys. **2000**, 63, 843.

***X.Lu, J. Phys. Chem. B*. 2006, 110, 11098;**
***Lu & Wang, J. Am. Chem. Soc*. 2009, 131, 16646**
Highlighted by C&EN and Nat. Chem.

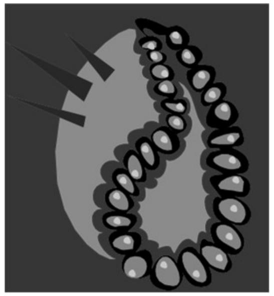
Role of Structural Chemistry in Life Science

What do proteins do ?

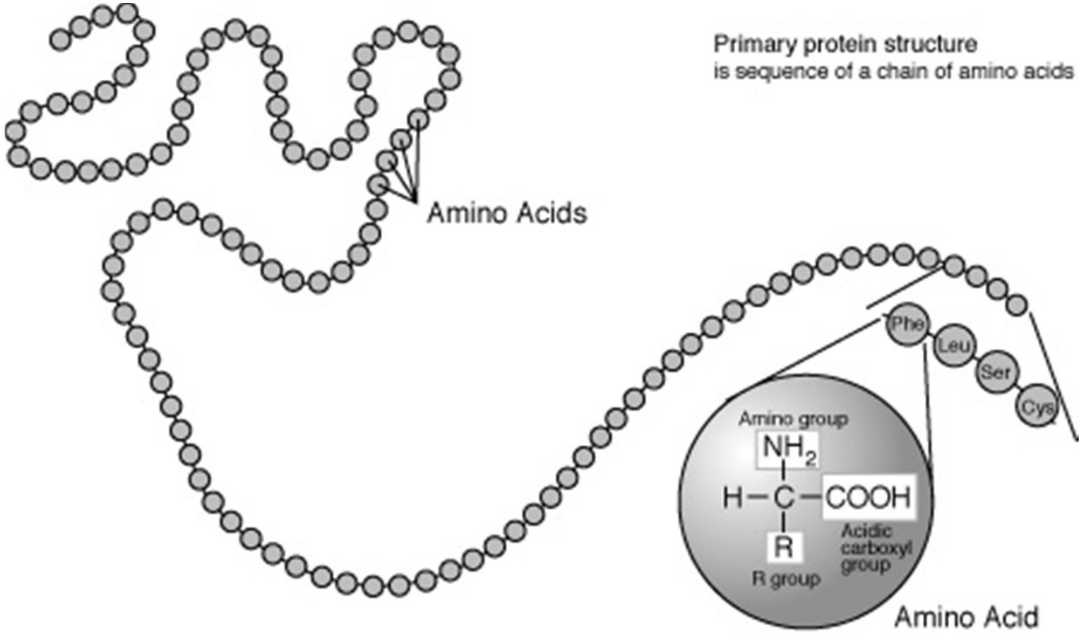
Proteins are the basis of how biology gets things done.

- 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.



Definition of 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 a known substance
2) Understanding the structure-property relationship

3) Predicting a substance with specific structure and property

Outline and Schedule

Chapter 1	basics of quantum mechanics	4
Chapter 2	Atomic structure	4
Chapter 3	Symmetry	4-5
Chapter 4	Diatomic molecules	3
	Midterm Exam !	
Chapter 5/6	Polyatomic structures	4
Chapter 7	Basics of Crystallography	3-4
Chapter 8	Metals and Alloys	1
Chapter 9	Ionic compounds	2

Chapter 1 The basic knowledge of quantum mechanics

1.1 The origin of quantum mechanics

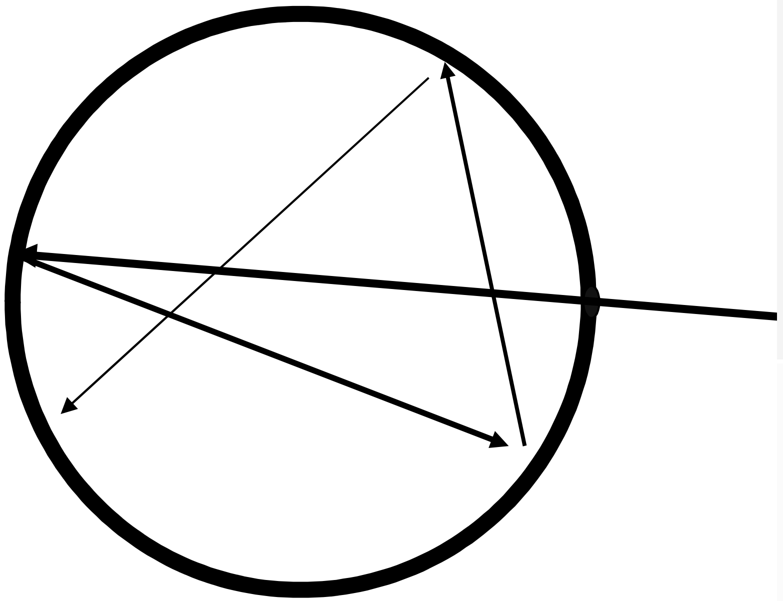
--- The failures of classical physics

Black-body radiation, Photoelectric effect, Atomic and molecular spectra

- Classical physics: (prior to 1900)
  - Newtonian classical mechanics
  - Maxwell’s theory of electromagnetic waves
  - Thermodynamics and statistical physics

1.1.1 Black-body radiation

- An object that absorbs all **radiation** falling on it, at all wavelengths, is called a **black body**.
- When a **black body** is at a uniform temperature, its **emission** has a characteristic frequency distribution that depends on the temperature. Its **emission** is called **black-body radiation**.

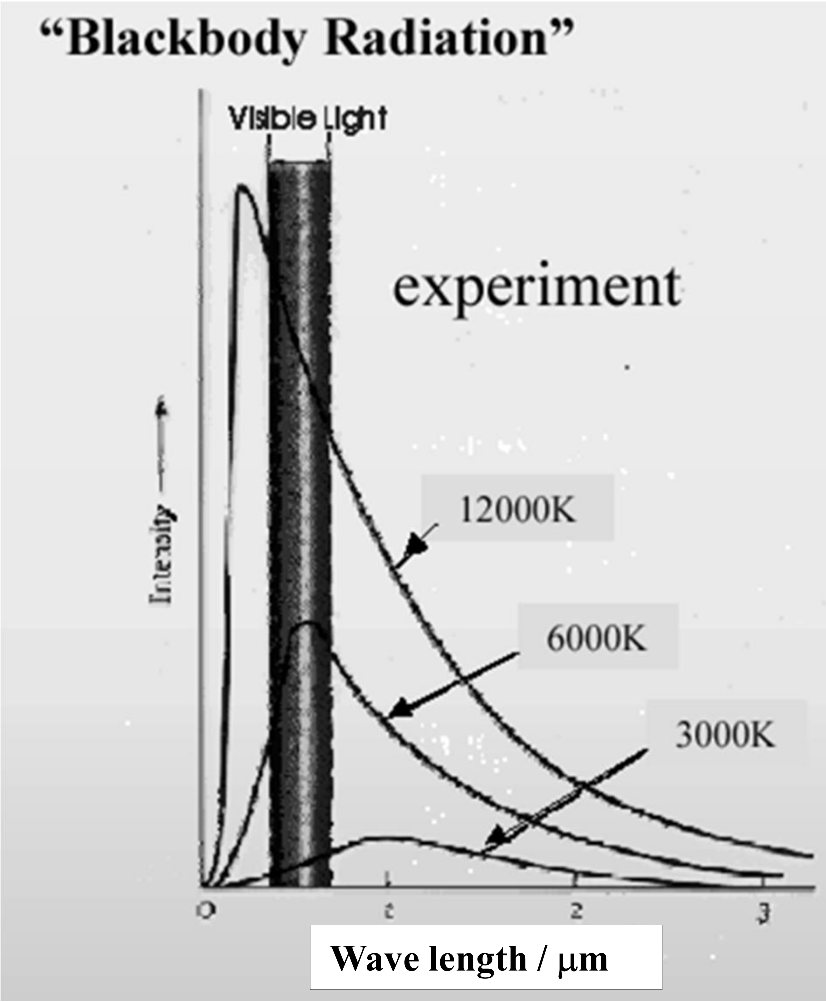


Device for experimenting black-body radiation.

The **radiation** represents a conversion of a body's thermal energy into electromagnetic energy, and is therefore called thermal radiation.

In classical physics, atomic oscillators were supposed to have continuously distributed vibrational energy and therefore radiate energy continuously.

Black-Body Radiation Experiments



A large number of experiments revealed the temperature-dependence of λ_{max} (or ν_{max}) of blackbody radiation and its independence on the substance made of the black-body device!

Prior explanations based on statistical mechanics & Maxwell's theory of electromagnetic waves are not satisfying at all, especially in the high-frequency portion!

Note that according to classical theory, atomic oscillators radiate energy continuously!

Classical solution I: Stefan-Boltzmann law and Wien’s law (high energy, low T)

（1）Stefan-Boltzmann Law

$$M(T) = \int_0^\infty M_\lambda(T)\mathrm{d}\lambda = \sigma T^4$$

Stefan—Boltzmann const.

$$\sigma = 5.670\times10^{-8}\,\mathrm{W\cdot m^{-2}\cdot K^{-4}}$$

（2）Wien’s approximation

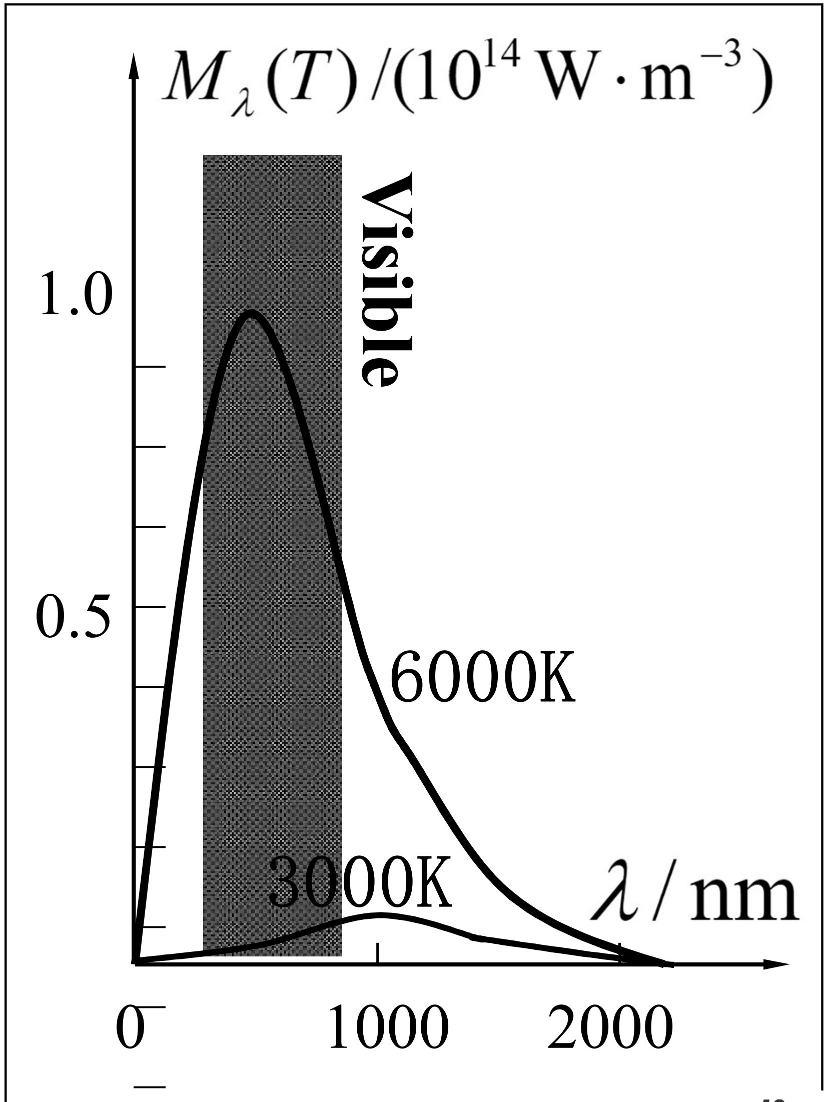
$$M_\nu(T) = \frac{2h\nu^3}{c^2}e^{-h\nu/kT}$$

Spectral energy density

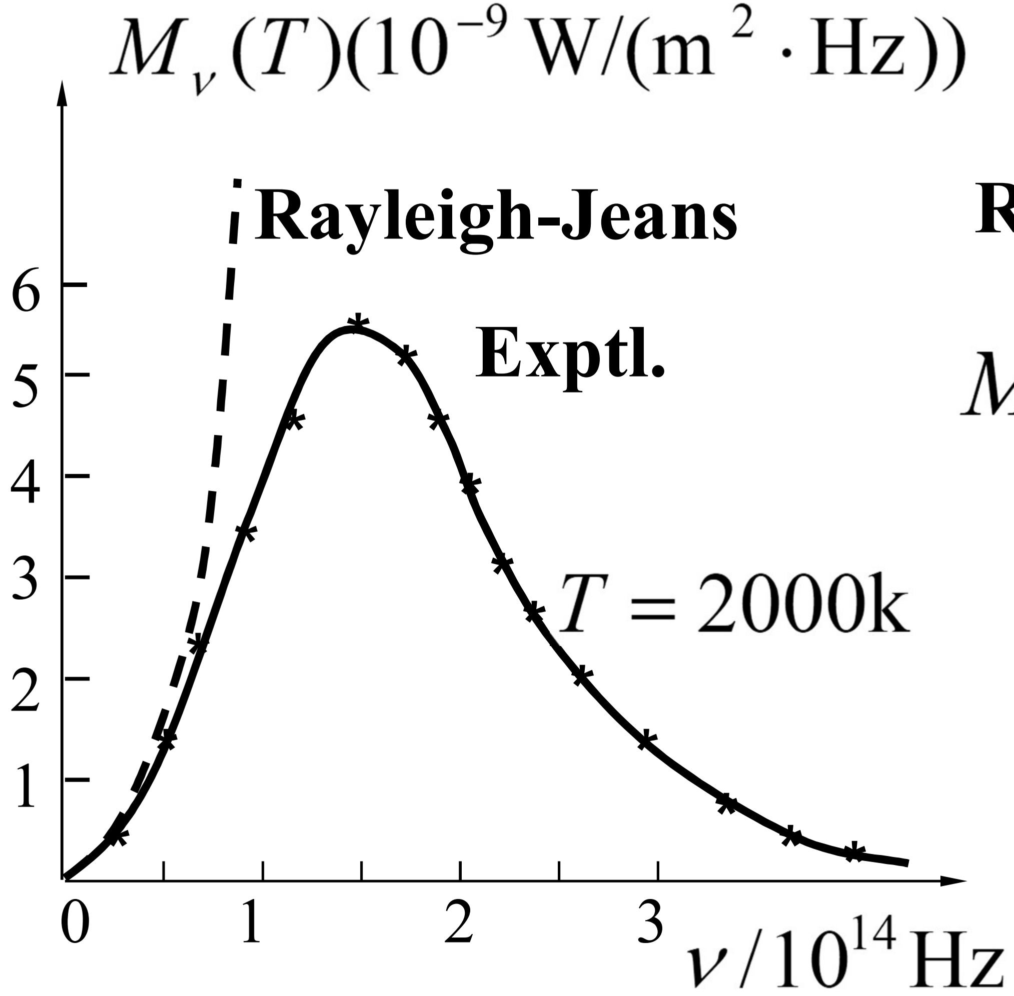
$$\lambda_m T = b$$

λ_{max}

$$b = 2.898\times10^{-3}\,\mathrm{m\cdot K}$$



Classical solution II: Rayleigh-Jeans Law
(low energy, high T)



Rayleigh-Jeans law

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

Ultraviolet Disaster

at low T!

Solution to Blackbody problem

(problem: theory diverges at low wavelength)

won 1918 Nobel Prize in Physics.

solution:

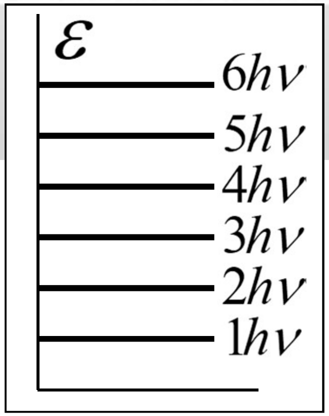
- 1900: Max Planck proposed a formula which fit the experimental data.
- required that the energy in the atomic vibrations of frequency ν was an integer n times a small, minimum, discrete energy,

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

- h is now known as Planck's constant,

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

- no known physical basis for the "fitting"



Quantized energy levels of atomic vibrations
-- The dawn of quantum mechanics!

Key point!

Black Body Radiation

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

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

To make this equation rationally approachable, the atomic oscillators could only gain or lose energy in chunks, $E_n = nh\nu$!

Hypothesis!

Many stellar sources can usefully be approximated to be black bodies

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

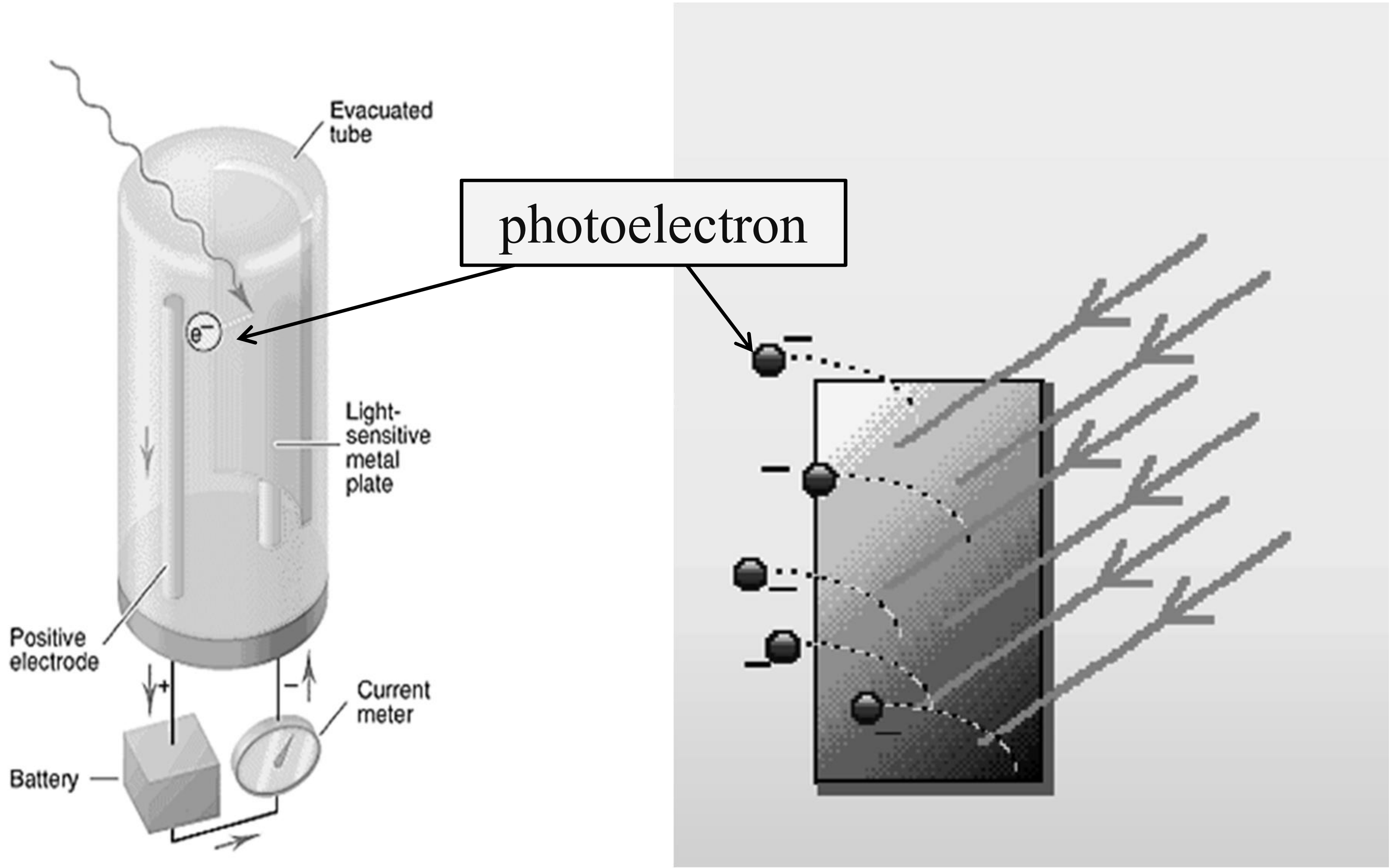
Wien's Approximation
(high energy, low T)

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

Rayleigh-Jeans Law
(long wavelength, high T)

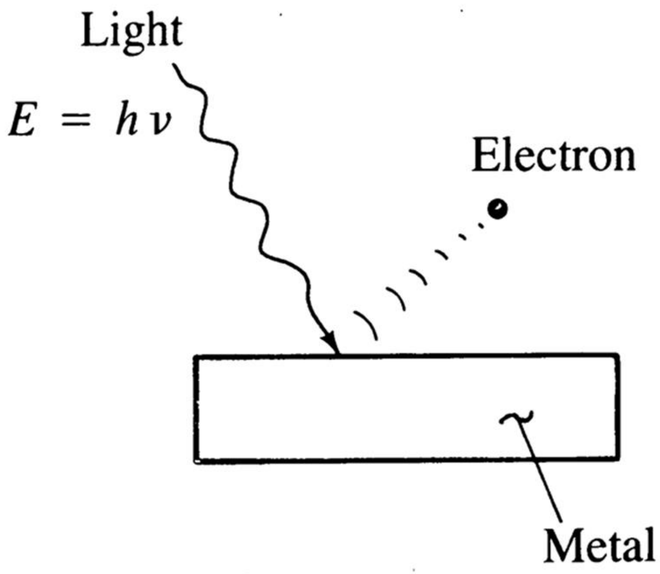
1.1.2 The photoelectric effect

The photoelectric effect

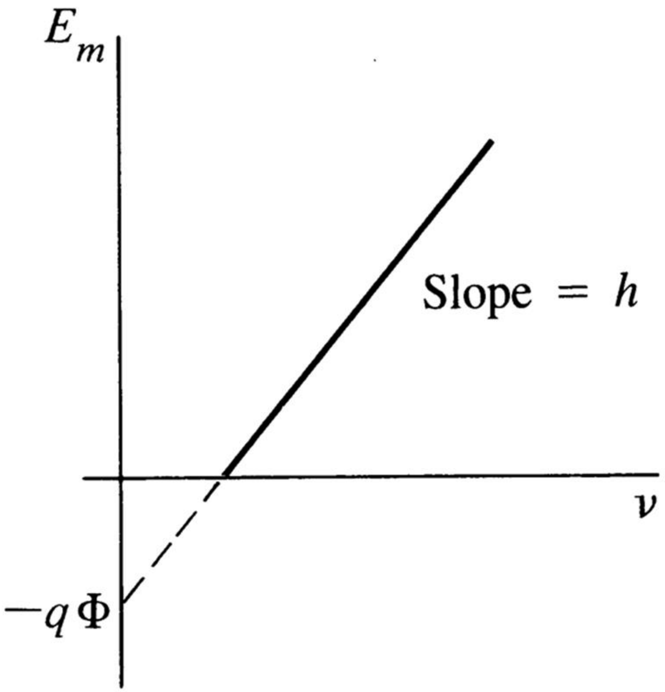


photoelectron

The Photoelectric Effect



(a)

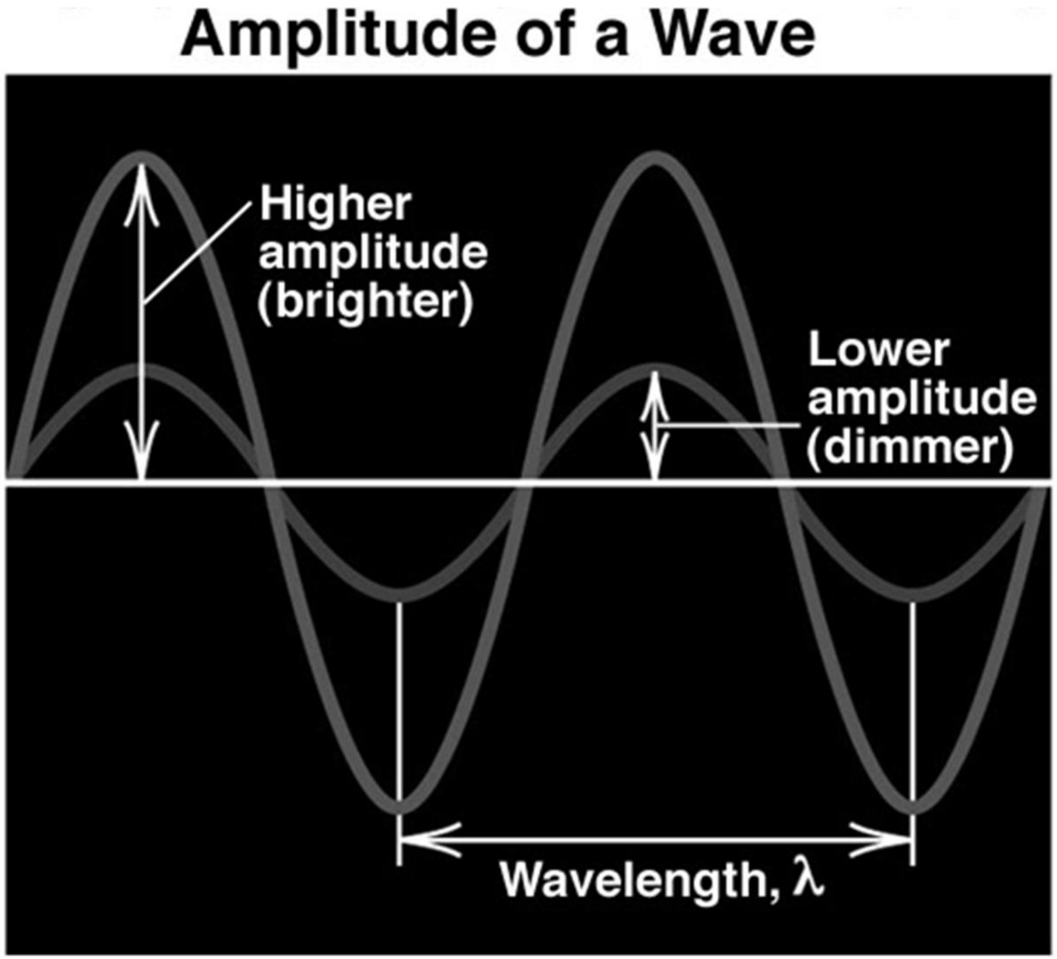


(b)

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

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

3. The increase of the light intensity results in the increase of the number of photoelectrons (current intensity).



Classical physics: The energy of light wave should be directly proportional to intensity, but not affected by frequency, which unfortunately is unable to account for the phenomena of photoelectric effects.

Explaining the Photoelectric Effect

- ***Albert Einstein***
  - Proposed a corpuscular theory of light in 1905.
  - won the Nobel prize in 1921

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

$$\varepsilon = h\nu \qquad (h \text{ -- Planck's constant})$$

2. A photon has energy as well as mass. Mass-energy relationship: $\varepsilon = mc^2$ → mass-frequency rel.: $m = h\nu/c^2$

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 the sum of the photoelectron's kinetic energy ($\boldsymbol{E_k}$) and the binding energy ($\boldsymbol{E_b}$) of the electron in metal.

$$\boldsymbol{E_{photon} = E_{binding} + E_{Kinetic\ energy}}$$

$$\boldsymbol{h\nu = W + E_k} \quad \text{(work function of metal: } \boldsymbol{W = E_{binding}}\text{)}$$

However， it should be mentioned that the particulate nature of light had long been proposed by I. Newton et al. in later 1600s, while C. Huyghens et al. noticed the wave nature of light!

Example I: Calculation Energy from Frequency

Problem: 1) What is the energy of a photon of electromagnetic radiation emitted by an FM radio station at 97.3 x 10^8 cycles/sec?
2) 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 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=hν to calculate the energy.*

Solution:

$$\lambda = 122 \text{ mm} = 1.22 \text{ x } 10^{-1}\text{m}$$

$$\boxed{\begin{aligned} &E_{photon} = h\nu = hc/\lambda \\ &= \frac{(6.626\times10^{-34}\,\text{Js})(3.0\times10^{8}\,\text{m/s})}{1.22\times10^{-1}\,m} = 1.63\times10^{-24}\,J \end{aligned}}$$

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 !

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

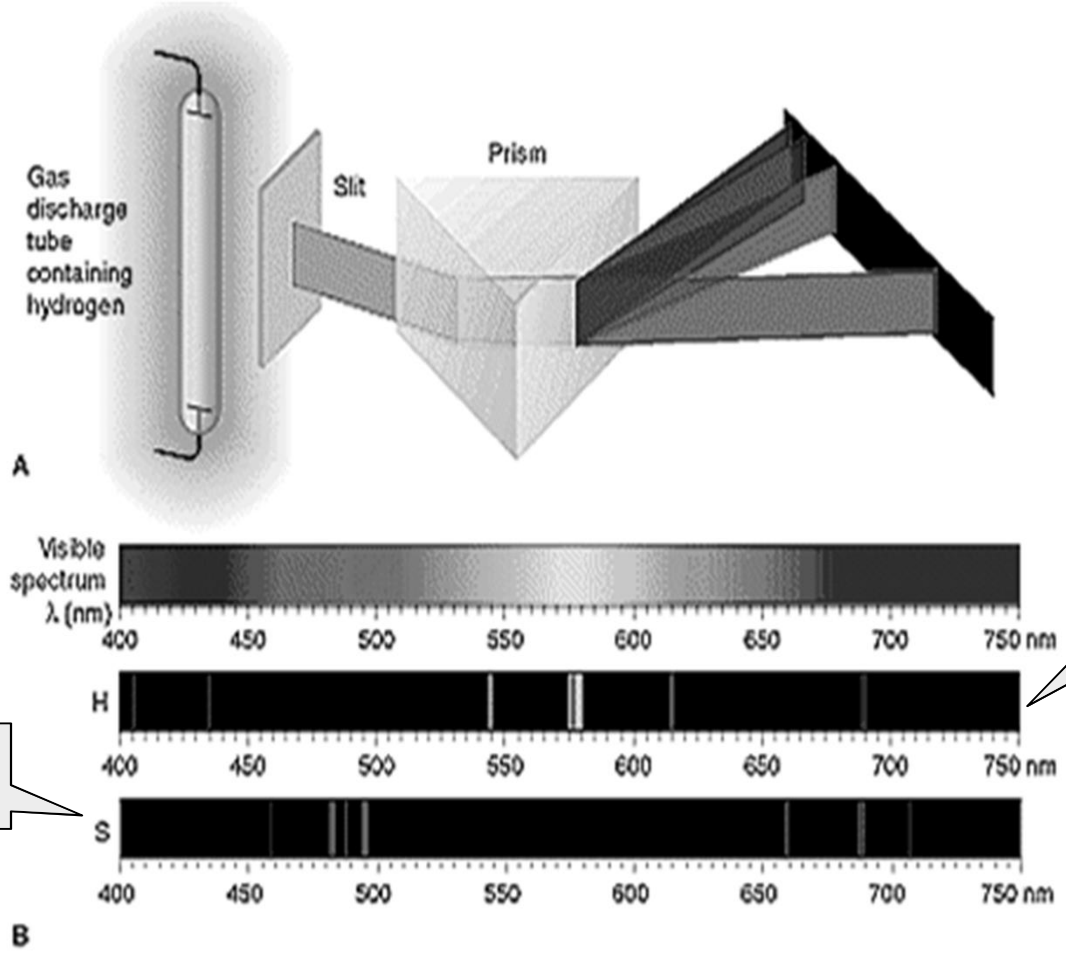
  $\mathbf{= 1.3 \times 10^{-19} Joules}$

思考题：

- 光电效应在化学研究中有哪些用途？

1.1.3 Atomic and molecular spectra

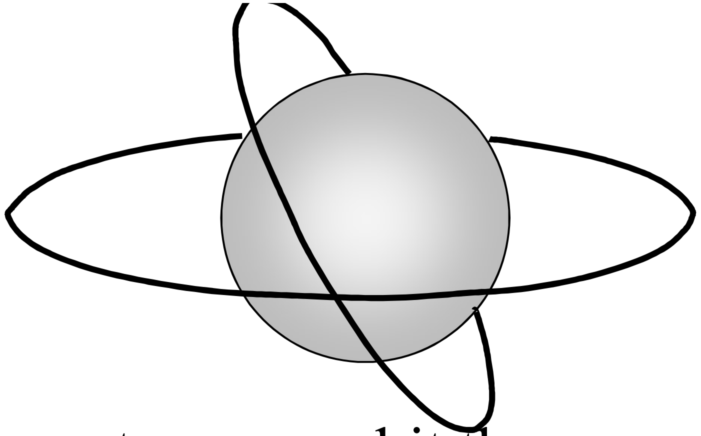
- An atom can emit lights of discrete & specific frequencies upon electric/photo-excitation.



spectrum of H

spectrum of S

Planetary model:



- First proposed by Rutherford in 1911.
- The electrons are like planets of the solar system --- orbit the nucleus (the Sun).
- Light of energy E given off when electrons change orbits of different energies.

Based on classical physics, the electrons would be attracted by the nucleus and eventually fall into the nucleus by continuously emitting energy/light!!

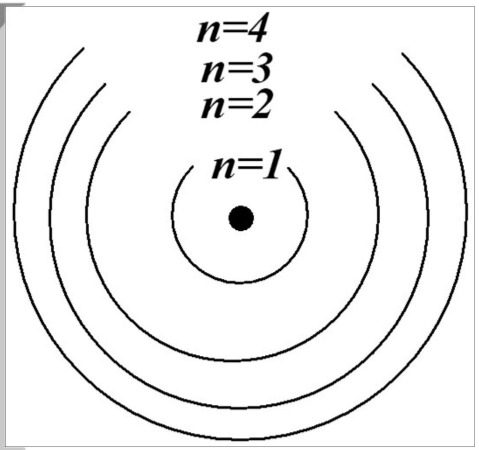
Why do the electrons not fall into the nucleus?

Why are they in discrete energies?

Bohr's atomic model

- Niels Bohr, a Danish physicist, combined the Plank's quanta idea, Einstein's photon theory and Rutherford's Planetary model, and first introduced the idea of electronic energy level into atomic model. (Proposed in 1913)

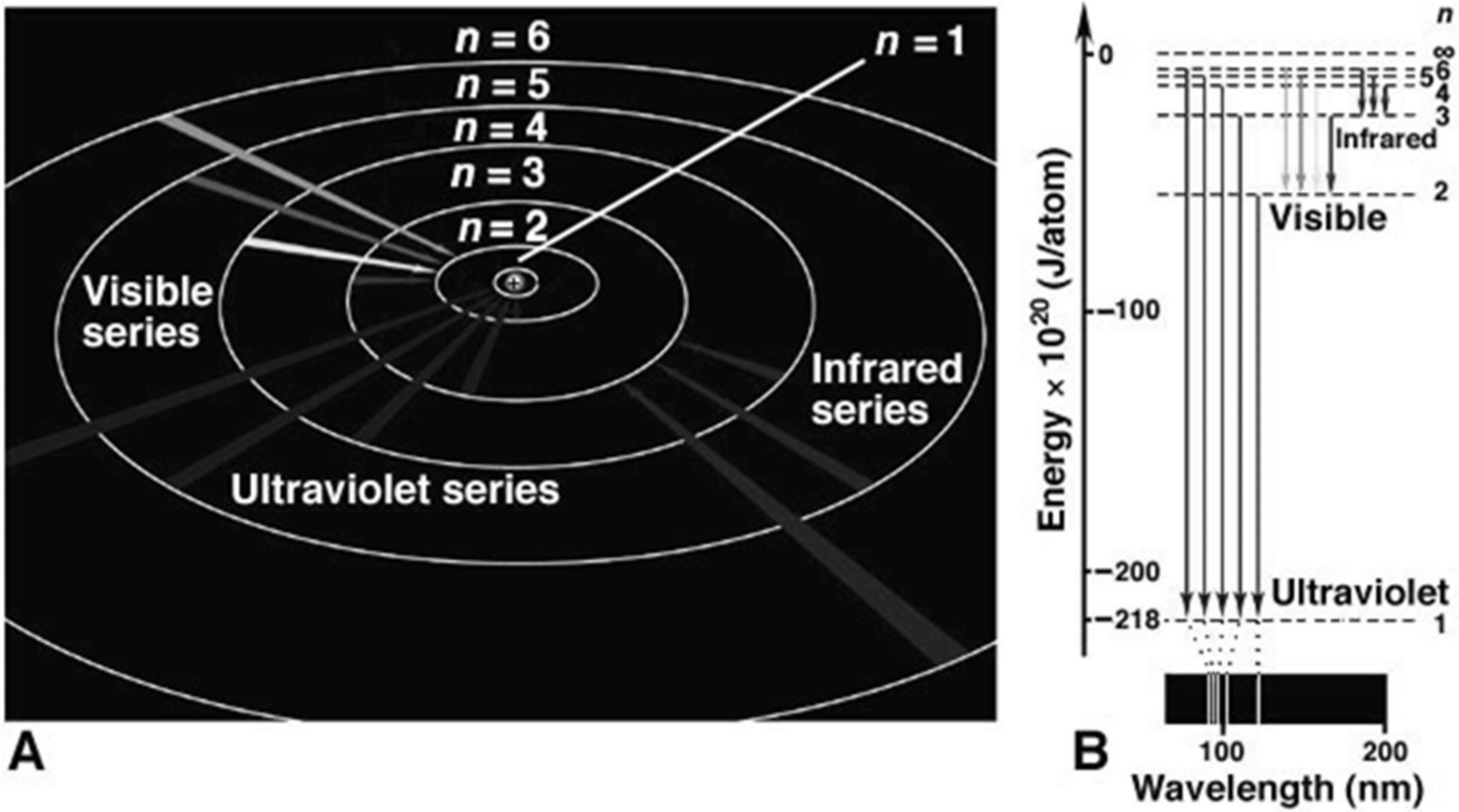
- ***Quantum Theory*** **of Energy.**
- **The *energy levels* in atoms can be pictured as orbits in which electrons travel at definite distances from the nucleus.**
- **These he called "*quantized energy levels*", also known as *principal energy levels*.**



n : principal quantum number

(Proposed in 1913, won 1922 Nobel Prize in Physics)

The Bohr Model Explanation of the Three Series of Spectral Lines



The electron in H atom can be promoted to higher energy levels by photons or electricity.

The Energy States of Hydrogen-like Atom/Ions

Bohr derived the energy for a system consisting of a nucleus plus a single electron (H and H-like ions),

e.g. H He^{+} Li^{2+}

and predicted a set of quantized energy levels given by :

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

Rydberg Equation

- *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:

$$\because E_n = -RZ^2 / n^2 \quad (\mathrm{R} = 2.18 \times 10^{-18} J)$$

$$\therefore \Delta E = E_{n1} - E_{n2} = -R(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$= -R(\frac{1}{4^2} - \frac{1}{2^2}) = 3R/16 = 4.09 \times 10^{-19} J$$

$$\lambda_{photon} = \frac{hc}{E_{photon}} = \frac{hc}{\Delta E} = 4.87 \times 10^{-7}\ \mathrm{m} = 487\ \mathrm{nm}$$

Summary of Class 1

1.1 The failures of classical physics

1.1.1 Black-Body Radiation

Planck’s quanta idea $E = nh\nu$ for atomic vibrations

1.1.2 The photoelectric effect

A corpuscular theory of light (photons)

$\varepsilon = h\nu = mc^2$ h = Planck’s constant

$p = h/\lambda$ (particle nature of light !)

Qualitative model

1.1.3 Atomic and molecular spectra

Planetary model: orbits of electrons around the nucleus

Bohr’s atomic model: quantized energy levels of orbits

Quantitative model

For H-like atom/ions $E_n = -\frac{RZ^2}{n^2}$

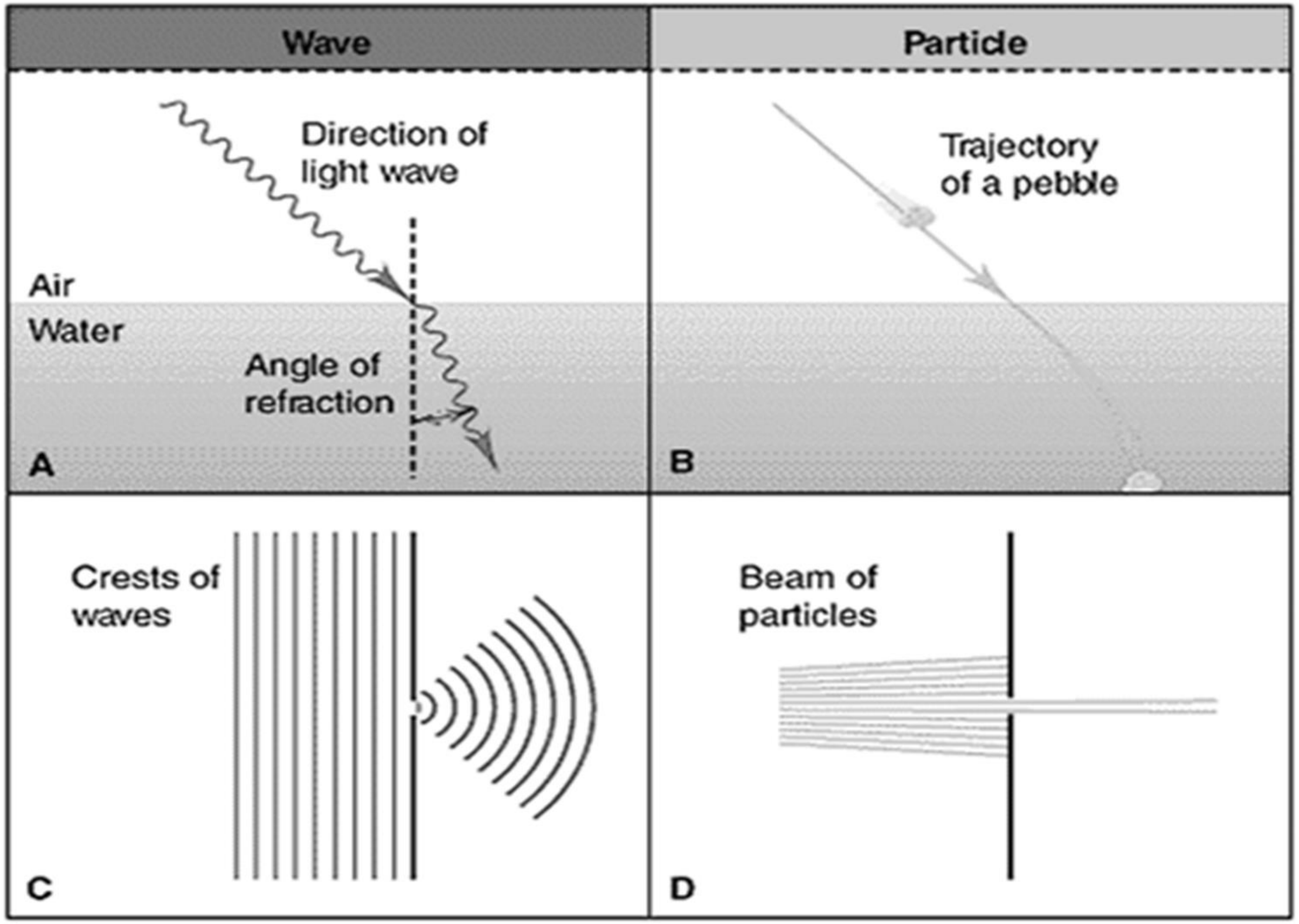
The aforementioned experiments implied, for the first time, distinctive quantum effects pertaining to the behaviors of such microscopic particles as atomic oscillator, photon, and electron (within atoms) .

1.2 The characteristic of the motion of microscopic particles

Wave-particle duality & The uncertainty principle

1.2.1 The wave-particle duality of microscopic particles

In classical physics, waves and particles behave differently and can be described by rather different theories.



Einstein's Corpuscular Theory of Lights for the first time introduced the wave-particle duality of photon:

$E = mc^2 = h\nu$ & $p = h/\lambda$ (Wave-particle relationship)

♦ In 1924, ***de Broglie*** suggested that **microscopic particles** such as electron and proton might also have **wave properties** in addition to their particle properties.

$$E = h\nu \quad (1)$$

$$p = h/\lambda \quad (2)$$

p **-particle momentum**

λ **-de Broglie wavelength**

1929 Nobel prize!

- The wavelength of a particle:

$\lambda = h/p = h/m\mathbf{v}$ ($\mathbf{v}$: velocity, m: mass)

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

The mass and speed of an electron are:

$$\mathbf{m_e = 9.11 \times 10^{-31}\ kg} \qquad \mathbf{v_e = 3.00 \times 10^{6}\ m/s}$$

Its momentum can be expressed as: $p = m\mathrm{v}$ & $p = h/\lambda$

Thus its wavelength can be expressed as,

$$\lambda = \frac{h}{m_e \mathrm{v_e}} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s}}{(\,9.11 \times 10^{-31}\mathrm{kg}\,)(\,1.00 \times 10^{6}\ \mathrm{m/s}\,)}$$

$$1\ \mathrm{J} = \frac{1\ \mathrm{kg \cdot m^2}}{\mathrm{s^2}} \quad \textbf{hence}$$

Wavelength of the electron: $\underline{\lambda = \mathbf{2.42 \times 10^{-10}\ m = 0.242\ nm}}$

Q： How to make use of the wave nature of electrons?

An moving electron accelerated by an electric field:

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

$$\boxed{E_k = m_e v_e^2 / 2 = eV \Rightarrow v_e = \sqrt{2eV/m_e}} \qquad (\text{If } \boldsymbol{v_{e,0}} = 0)$$

$$\boxed{1\ \boldsymbol{eV} = 1.602\text{x}10^{-19}\ \text{J}}$$

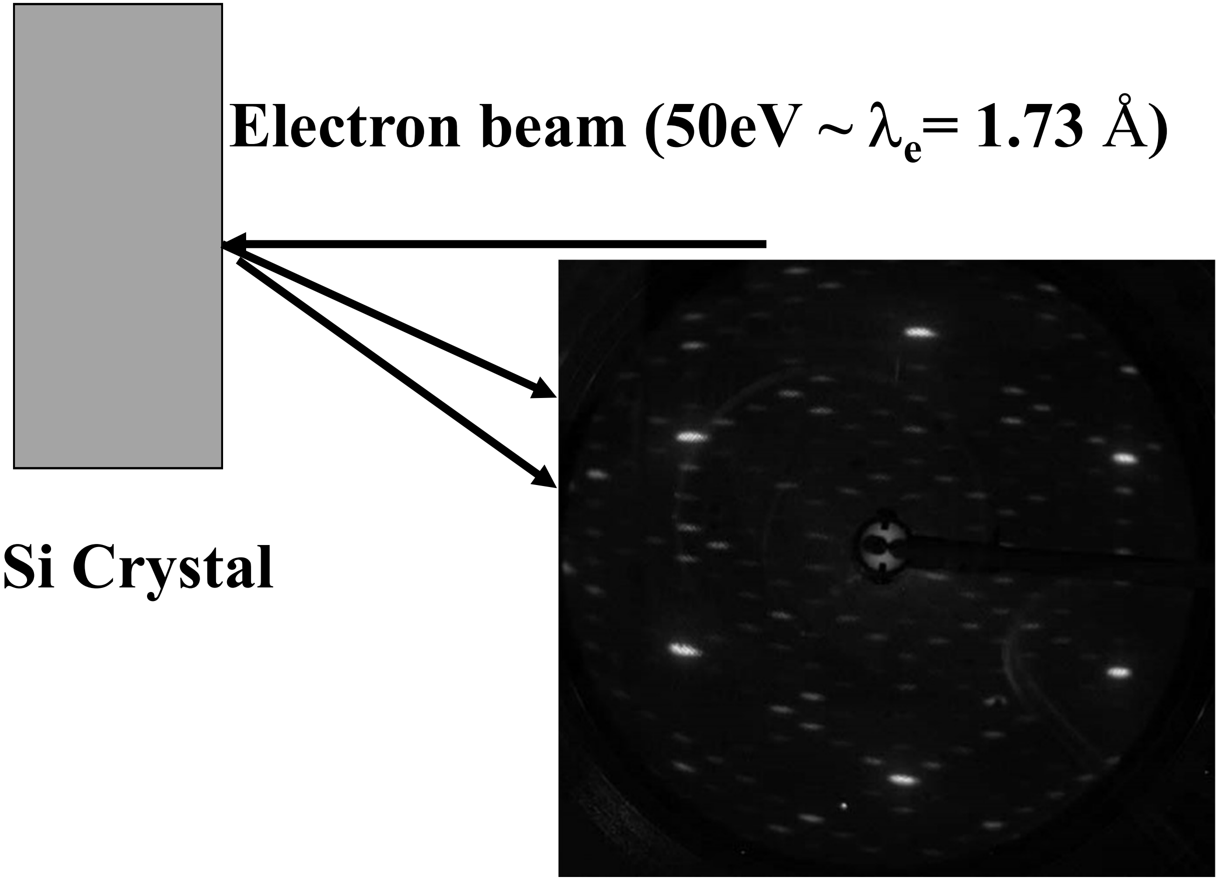
If the unit of ***V*** is volt, then the wavelength is:

$$\boxed{\begin{aligned} &\lambda = h/p = h/m_e v_e = h/\sqrt{2m_e eV} \\ &= \frac{6.626\times10^{-34}}{\sqrt{2\times9.110\times10^{-31}\times1.602\times10^{-19}}}\frac{1}{\sqrt{V}} \\ &= \frac{1.226\times10^{-9}}{\sqrt{V}}\ \ (m) = 1.226/\sqrt{V}\ \ (nm) \end{aligned}}$$

The de Broglie Wavelengths of Several particles

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

The diffraction of electrons --Evidence of wave-like behavior

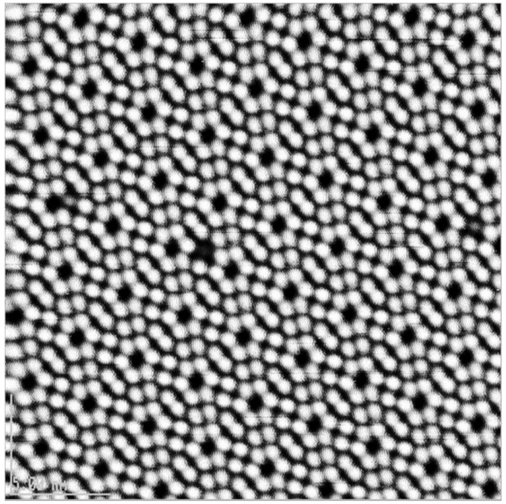


Electron beam (50eV ~ λ_e= 1.73 Å)

Si Crystal

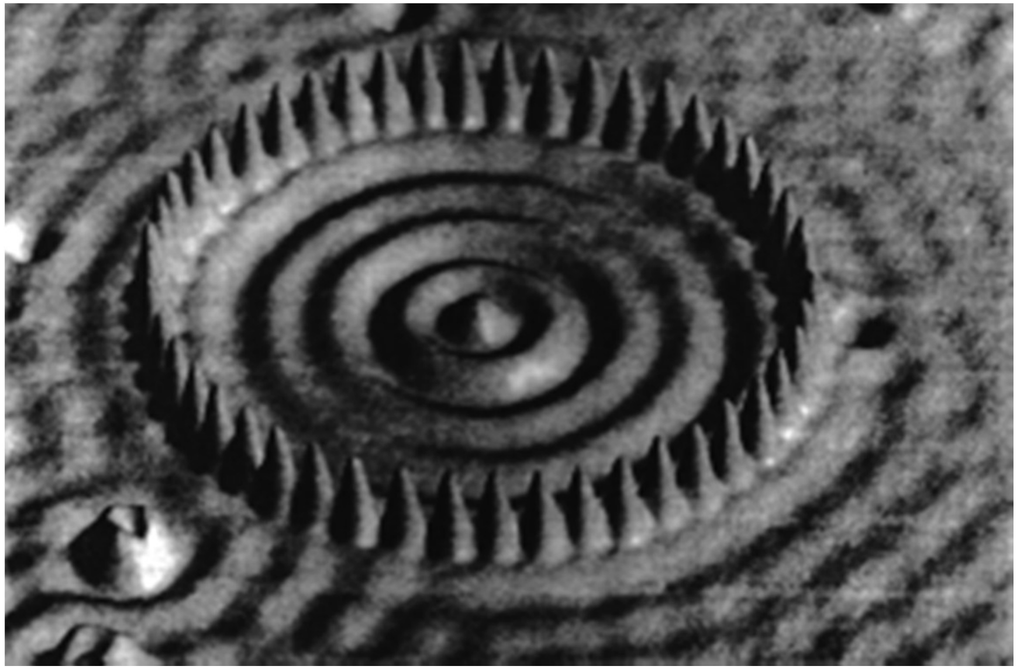
(Si-Si = 2.35 Å)

Pattern of
electron diffraction



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***

The wave-particle duality

- **Wave (e.g., light)**
  - can be wave-like (**diffraction**)
  - can be particle-like ($\boldsymbol{p = h/\lambda}$)
- **Particles (e.g., electron)**
  - can be wave-like ($\boldsymbol{\lambda = h/p}$)
  - can be particle-like (classical, $\boldsymbol{p = mv}$)

- A wave of microscopic particles is a ***probability wave***, neither like the macroscopic mechanical wave nor like the normal electromagnetic wave!

- It reflects the statistic probability of particle motion in space!

The differences between photon and microscopic particles

For photon:

$p = mc$ (*c* is a constant, variable *m*)

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

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

For microscopic particles:

$p = m\mathrm{v}$ (*given m! velocity* v)

$E = m\mathrm{v}^2/2 = p^2/(2m) = p\mathrm{v}/2$ $\boxed{\neq p\mathrm{v}}$

Wave-like

↓

$$\boxed{\begin{array}{l} E = h\nu \\ p = h/\lambda \end{array}}$$

↑

Particle-like

$\boxed{\lambda = u/\mathrm{v} \quad \text{… what is the meaning of } u\text{?}}$

For photon: $\mathrm{v} \equiv c$, $\lambda = h/p = h/(mc)$ ➔ $u = h/m$ (variable)

For particles: $\lambda = h/p = h/(m\mathrm{v})$ ➔ $u = h/m$ (given value!)

Ira N. Levine's words regarding "wave-particle duality"

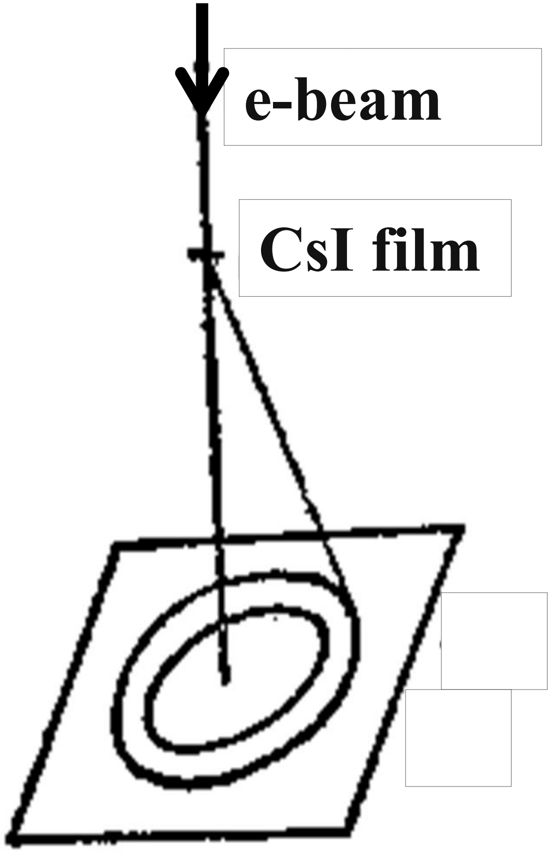
How can an electron be both a particle， which is a localized entity, and a wave, which is nonlocalized? The answer is that ***an electron is neither a wave nor a particle, but something else***. An accurate pictorial description of an electron's behavior is impossible using the wave or particle concept of classical physics. The concepts of classical physics have been developed from experience in the macroscopic world and do not properly describe the microscopic world. Evolution has shaped human brain to allow it to understand and deal effectively with macroscopic phenomena. ***The human nervous system was not developed to deal with phenomena at the atomic and molecular level***, so it is not surprising if we cannot fully understand such phenomena.

I. N. Levine, *Quantum Chemistry* (5th ed.)

1.2.2 The uncertainty principle

- In classical Physics, the position and momentum of a macroscopic particle (a body) can be certainly determined at a given time.
- This is not the case for a microscopic particle!
- In the diffraction experiments that imply the wave nature of electrons, the observed ***wave pattern*** is just a ***statistic distribution of electron motion***. The exact position and momentum of an electron at a given time remain uncertain.

In 1925, Heisenberg developed the matrix formulation of quantum mechanics and noticed the uncertainty in position of electrons in an atom.



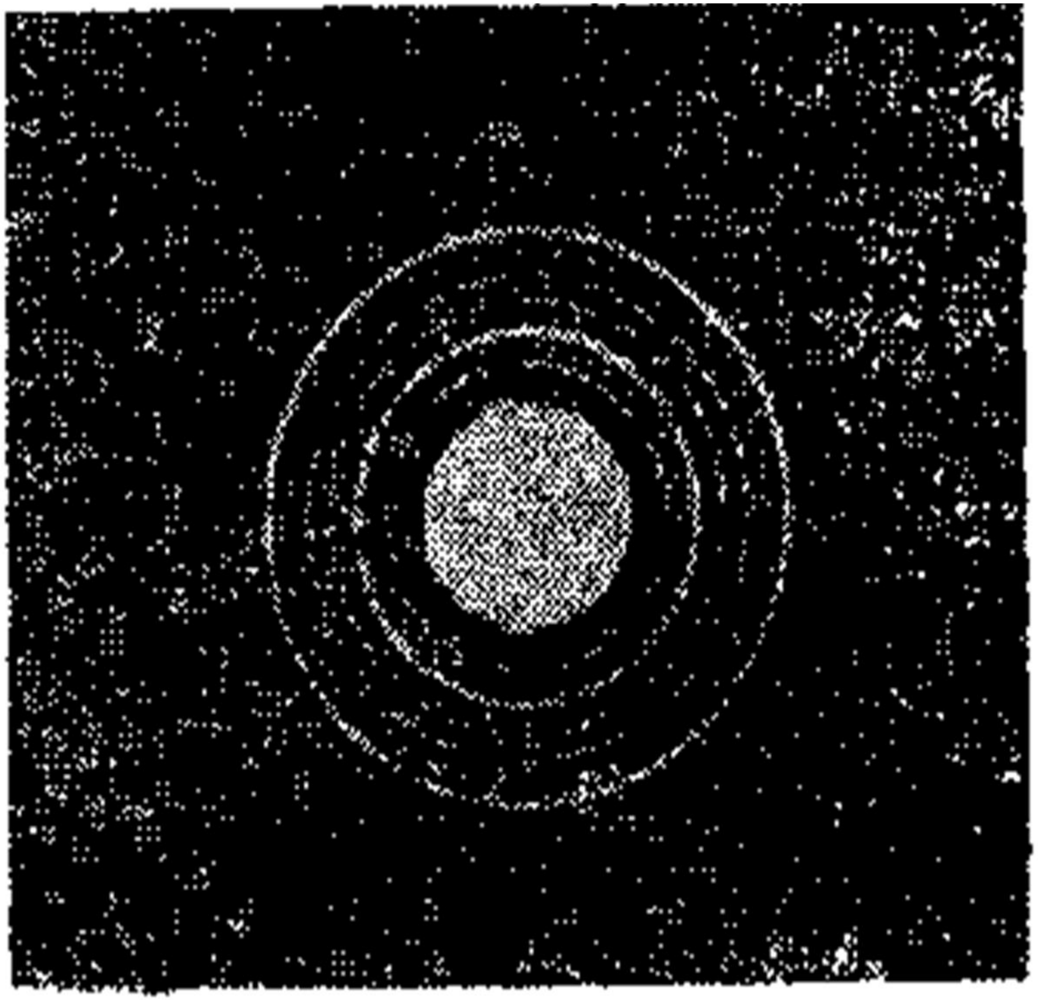
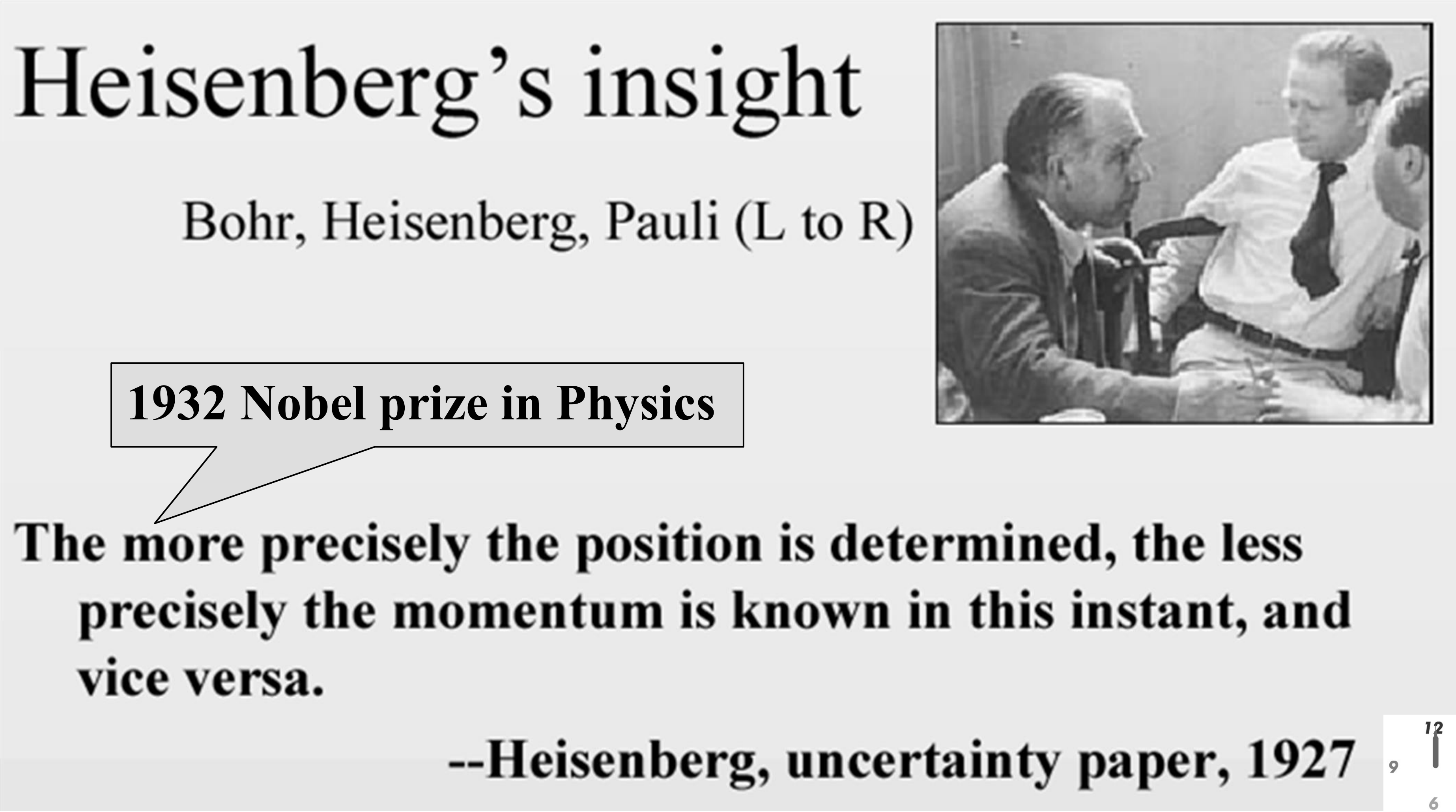


Image of electron diffraction of CsI

The CsI film works as a (atomic-level) slit!

- The experiments of electron diffraction revealed:
  The narrower the slit is, the larger is the central area of the diffraction pattern.
- **What is behind such phenomena?**



Heisenberg's insight

Bohr, Heisenberg, Pauli (L to R)

1932 Nobel prize in Physics

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

--Heisenberg, uncertainty paper, 1927

The experiments of electron beam diffraction revealed that the narrower the slit is, the larger is the central area of the diffraction pattern. **What is behind this phenomenon?**

- **The width of the slit**:

  position uncertainty of electrons passing through the slit.

- **The central area of the diffraction pattern**:

  The 1st–order diffraction area, which reflects the momentum uncertainty of electrons passing through the slit!

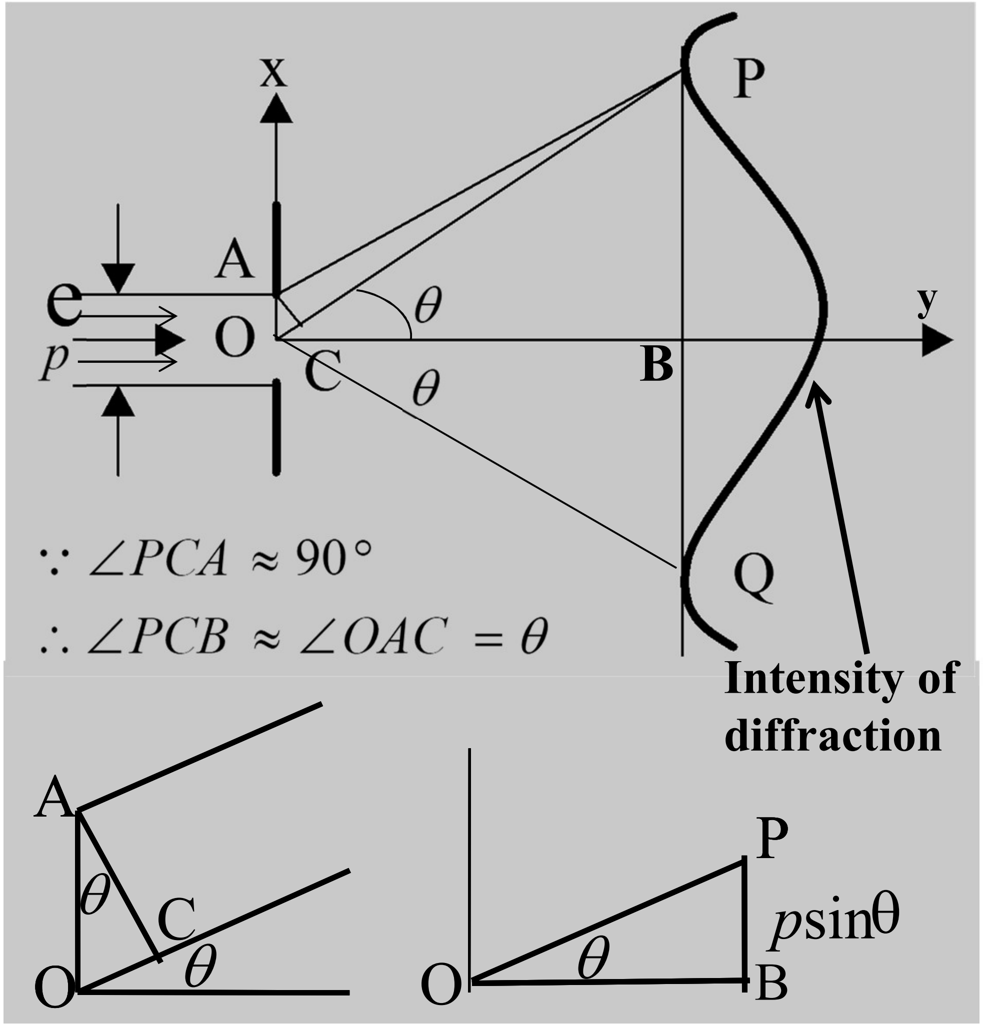
- **Thus, the phenomenon of electron diffraction** illustrates that “the more precisely the position of electron is determined, the less precisely momentum is known…”

How to prove the uncertainty principle?

Electron diffraction vs. Uncertainty principle

$$\Delta x = D = 2\overline{OA} \text{ (width of the slit)}$$

(position uncertainty!)



$\because \angle PCA \approx 90°$

$\therefore \angle PCB \approx \angle OAC = \theta$

The electron "waves" reaching the edge of the 1st-order diffraction area should be destructively interfered:

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

$$\Rightarrow \boldsymbol{sin}\theta = \overline{OC} / \overline{OA} = \lambda / D$$

Meanwhile, the electron deflected upward/downward by an angle θ has an ***x*** component of momentum:

$$p_x = \pm p\,\boldsymbol{sin}\theta \quad \Rightarrow \Delta p = p\,\boldsymbol{sin}\theta$$

$$\Rightarrow \Delta x \Delta p = Dp(\lambda/D) = h$$

Including higher-order diffractions,

$$\Delta p \geq p\,\boldsymbol{sin}\theta \quad \Rightarrow \quad \Delta x \Delta p \geq h$$

A quantitative version

$$\Delta x \Delta p \geq h / 4\pi \quad or \quad \hbar / 2$$

Example

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

Accuracy of speed: $\boldsymbol{\sigma} = \mathbf{0.001\%}$

The uncertainty in its momentum: $\boldsymbol{\Delta p = m_e}\mathbf{v}\boldsymbol{\sigma}$

The uncertainty in its position: $\boldsymbol{\Delta x = h/\Delta p = h/(m_e}\mathbf{v}\boldsymbol{\sigma)}$

$= (6.626 \text{ x } 10^{-34})/[\ (9.11 \text{ x } 10^{-31})(1 \text{ x } 10^{3})\text{x}0.001\%]$

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

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.

Accuracy of speed: $\sigma = \mathbf{0.001\%}$

The uncertainty in its momentum: $\Delta p = m\mathrm{v}\sigma$

The uncertainty in its position: $\Delta x = h/\Delta p = h/(m\mathrm{v}\sigma)$

$= 6.626 \times 10^{-34} /[(0.01\ \mathrm{kg})\ (1 \times 10^{3}\ \mathrm{m/s}) \times 0.001\%]$

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

Another form of the Uncertainty Principle!

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

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?

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

$$= 1.06 \text{ x } 10^{-26} \text{ J} = \frac{1.06\times10^{-26}}{1.6\times10^{-19}} \text{ eV}$$

$$= 0.66\times10^{-7} \text{ eV}$$

课后思考一：

经过电场加速后的电子在自由空间高速“直线”运动，看似未表现出波动特性，但通过原子级衍射光栅（晶体）后在检测器上产生了衍射图样，是否可以认为其波动特性是在通过光栅后才拥有？或可认为其在到达衍射光栅前就不具备波动性？

课后思考二：

原子中的电子受核的静电束缚，一般被限制在距离核<2Å的范围内运动，电子是否具有波动性？如果有，如何理解其波动性？以氢原子基态为例，已知1s轨道的平均半径为0.528Å,试由此估算1s电子的能量和de Broglie波长。

(静电力常数 $\boldsymbol{k} = -9\times10^{9}\ \mathrm{N\cdot m/C^{2}}$，电子电量 $\boldsymbol{e} = 1.6\times10^{-19}\ \mathrm{C}$，普朗克常数 $\boldsymbol{h} = 6.63\times10^{-34}\ \mathrm{J\cdot s}$，真空中光速$c=3.00\times10^{8}\ \mathrm{m/s}$)

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.

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. …

Description of the behavior of electron(s) in an atom requires a completely new theory-- “Quantum Theory”

Quantum mechanical description of Electron

- Quantum mechanics is basically ***statistical*** in nature.
- Quantum mechanics does not say that an electron is distributed over a large region of space as a wave is distributed.
- Rather it is the ***probability patterns*** used to describe the electron's motion that behave like waves!

1.3 The basic assumptions (postulates) of quantum mechanics

- ***Wavefunction $\Psi(r, t)$ of QM State***
- ***Operator of Mechanical Quantity***
- ***Time-dependent Schrödinger Equation***
- ***Superposition Principle***
- ***Pauli's Principle***

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

$$\Psi(r, t)$$

***CM (classical mechanics)*：**

The state of a system of *N* particles is specified totally by giving:

3N spatial coordinates (x_i, y_i, z_i)
&
3N velocity coordinates (v_{xi}, v_{yi}, v_{zi}).

Phase Space : $\{(x_i, y_i, z_i)\}, \{(p_{xi}, p_{yi}, p_{zi})\}$

QM(Quantum Mechanics):

The state of a system of *N* particles is described by

a wave function $\psi(r, t)$ that depends on the coordinates of the particles and on time.

Hilbert space

For example:

The wavefunction of plane monochromatic light:

$$\psi = A\,\boldsymbol{exp}[\ i2\pi(\,x/\lambda - \nu t\,)]$$

Now let us consider the wave function for a microscopic particle of a 1-D free motion.

- Its particle-wave duality gives,

$$\boldsymbol{E = h\nu \ \&\ p = h/\lambda \Rightarrow \nu = E/h \ \&\ 1/\lambda = p/h.}$$

- Thus, its wave function Ψ can be derived as:

$$\psi = A\,\boldsymbol{exp}[(\ i2\pi/h\,)(\,xp - Et\,)]$$

A wave function must satisfy 3 mathematical conditions:

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

a) The product of wave function ***$\Psi(r,t)$*** and its complex conjugate ***$\Psi(r,t)^*$*** represents ***the probability distribution function*** of the system. (Physical meaning of wave function!)

probability density: $|\Psi(r,t)|^2 = \Psi^*(r,t)\Psi(r,t)$

b) The wave function ***$\Psi(r,t)$*** must be ***continuous in space***. Otherwise its second derivative would not be attainable.

c) The wave function of a system must be ***quadratically integrable*** so as to evaluate the statistical average values of its physical properties.

The probability distribution function is $\psi^*(r,t)\psi(r,t)$

Thus the probability that the particle presents in the volume element ***dτ (=****dxdydz)* around *r* at time *t* is

$$\psi^*(r,t)\psi(r,t)dxdydz$$

To be generally **normalized**

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

- Wave functions of different states for a given system must be generally **orthogonal:**

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_i(r,t)\psi_j(r,t)dxdydz = 0$$

Postulate 2. Each observable mechanical quantity of a microscopic system is associated respectively with 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, and then replace each coordinate $\boldsymbol{x}$ by the operator $\boldsymbol{x}$, and each momentum component $\boldsymbol{p_x}$ by the operator $-i\hbar\partial/\partial \boldsymbol{x}$.

In quantum mechanics, the coordinates *p (momentum)* and *q(position)* of *phase space* normally become **hermitian operators** in a **Hilbert space**.

Definition of *operator*:

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

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

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

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

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

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

Operators obey the associative law of multiplication:

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

- **A linear operator means**

$$\boxed{\begin{aligned}&\hat{A}(\psi_1+\psi_2)=\hat{A}\psi_1+\hat{A}\psi_2\\&\hat{A}c\psi=c\hat{A}\psi\end{aligned}}$$

- **A Hermitian (自共轭 or 厄米) operator means**

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

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

- **A Hermitian operator ensures its eigenvalue being a real number!**

Eigenfunction and Eigenvalue

Suppose that the effect of an operation on a function ***f(x)*** by 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*.

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

$$\text{e.g.,}\ \ (d/dx)e^{2x} = 2e^{2x}$$

Hence, e^{2x} is an ***eigenfunction*** of the operator ***d/dx*** with an ***eigenvalue* 2**.

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	Mathematical Operator
Position	x	$\hat{x} = x$
Momentum (x)	p_x	$\hat{p}_x = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}$
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	$E = T + V$	$\hat{H} = -\frac{h^2}{8\pi^2 m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) + \hat{V}$

Hamiltonian

The average value of a physical observable

If a system is in a state described by a **normalized** wave function Ψ, then the average value of the observable ***A*** corresponding to operator $\hat{A}$ is given by –

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\tau$$

$$\text{with} \int \Psi^* \Psi d\tau = 1$$

(normalized function!)

General case: Whether Ψ is normalized or not, the average value of the observable ***A*** corresponding to operator $\hat{A}$ is given by

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

(Please always use this formula!)

If the wave function Ψ_n is an eigenfunction of $\hat{A}$, with eigenvalue a_n, then a measurement of the observable corresponding to $\hat{A}$ will give the value a_n with certainty.

$$\because \int \Psi_n{}^*\Psi_n d\tau = 1 \;\; \& \;\; \hat{A}\Psi_n = a_n\Psi_n$$ →

$$\begin{aligned}\langle a\rangle &= \int \Psi_n{}^*\hat{A}\Psi_n d\tau \\ &= \int \Psi_n{}^* a_n \Psi_n d\tau \\ &= a_n \int \Psi_n{}^*\Psi_n d\tau = a_n\end{aligned}$$

$$\begin{aligned}\langle a^2\rangle &= \int \Psi_n{}^*\hat{A}^2\Psi_n d\tau \\ &= \int \Psi_n{}^*\hat{A}\,(a_n\Psi_n) d\tau \\ &= a_n^2 \int \Psi_n{}^*\Psi_n d\tau = a_n^2\end{aligned}$$

Scattering difference

$$\sigma_a{}^2 = \langle a^2\rangle - \langle a\rangle^2 = a_n^2 - a_n^2 = 0$$

Thus the only value we measure for $\hat{A}$ is the value a_n.

Commuted operators (对易算符)

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

Poisson bracket

- When two operators are ***commutable***, their corresponding mechanical quantities can be measured simultaneously.

Example: What is the value of $[\hat{\mathrm{x}}, \hat{\mathrm{p}}_{\mathrm{x}}^2]$? Are the two operators commutable?

$$\hat{\boldsymbol{x}} = x \qquad \hat{\boldsymbol{p}}_{\mathrm{x}} = -i\hbar\frac{\partial}{\partial x}$$

$$\hat{\boldsymbol{p}}_{\mathrm{x}}^2 = \hat{\boldsymbol{p}}_{\mathrm{x}}\hat{\boldsymbol{p}}_{\mathrm{x}} = -\hbar^2\frac{\partial^2}{\partial x^2}$$

$$[\hat{\boldsymbol{x}}, \hat{\boldsymbol{p}}_{\mathrm{x}}^2]\psi = (\hat{\boldsymbol{x}}\hat{\boldsymbol{p}}_{\mathrm{x}}^2 - \hat{\boldsymbol{p}}_{\mathrm{x}}^2\hat{\boldsymbol{x}})\psi\,)$$

$$= [\,x(-\hbar^2\frac{\partial^2}{\partial x^2}\psi\,) + \hbar^2\frac{\partial^2}{\partial x^2}(x\psi\,)]$$

$$= -\hbar^2[\,x\frac{\partial^2}{\partial x^2}\psi - \frac{\partial}{\partial x}(\psi + x\frac{\partial}{\partial x}\psi\,)]$$

$$= -\hbar^2[\,x\frac{\partial^2}{\partial x^2}\psi - (\frac{\partial}{\partial x}\psi + \frac{\partial}{\partial x}\psi + x\frac{\partial^2}{\partial x^2}\psi\,)]$$

$$= 2\hbar^2\frac{\partial}{\partial x}\psi = 2i\hbar\,\hat{\boldsymbol{p}}_{\mathrm{x}}\,\psi \Rightarrow [\,x, \hat{\boldsymbol{p}}_{\mathrm{x}}^2] = 2i\hbar\,\hat{\boldsymbol{p}}_{\mathrm{x}} \neq 0 \;\; (\because\, \hat{\boldsymbol{p}}_{\mathrm{x}} = -i\hbar\frac{\partial}{\partial x})$$

The two operators are not commutable! How about $[\hat{\mathrm{x}}, \hat{\mathrm{p}}_{\mathrm{x}}]$?

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

$$\boxed{i\hbar\frac{\partial\Psi(r,t)}{\partial t}=\hat{H}\Psi(r,t),\quad \hat{H}=\hat{T}+\underline{V(r,t)}}$$

Potential-energy function

(This concept was first discovered in 1926 by the Austrian physicist Erwin **Schrödinger** (1887-1961), who won the 1933 Nobel Prize.)

Let’s consider a **free** particle of 1D-motion. Its wavefunction is

$$\boxed{\psi(x,t)=A\,\boldsymbol{exp}[-\frac{i}{\hbar}(Et-px)]}\Rightarrow\frac{\partial\psi}{\partial t}=-\frac{iE}{\hbar}\psi\quad\Rightarrow i\hbar\frac{\partial\psi}{\partial t}=E\psi$$

$$\&\ \frac{\partial^2\psi}{\partial x^2}=-\frac{p^2}{\hbar^2}\psi\Rightarrow-\frac{\hbar^2}{2\text{m}}\frac{\partial^2\psi}{\partial x^2}=\frac{p^2}{2m}\psi\ \because E=\frac{p^2}{2m}\quad(note:\text{V}=0)$$

$$\therefore i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2\text{m}}\frac{\partial^2\psi}{\partial x^2}$$

Time-dependent Schrödinger equation for a **free** particle of 1D-motion.

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

e.g., $\hat{H}=\hat{T}+V(r)$

In case the Hamiltonian ***H*** is ***t***ime-independent, the variables in this equation are separable, i.e.,

$$\Psi(r,t)=\psi(r)\cdot f(t)$$

$$\Rightarrow i\hbar\psi(\mathrm{r})\frac{df(t)}{dt}=f(t)\cdot\hat{H}\psi(r)$$

divided by ***ψ(r) •f(t)***

$$\Rightarrow\frac{i\hbar}{f(t)}\cdot\frac{df(t)}{dt}=\frac{\hat{H}\psi(\mathrm{r})}{\psi(\mathrm{r})}=E$$

$$f(t)=e^{-iEt/\hbar}$$

$$\hat{H}\psi(r)=E\psi(r)$$

Time-independent Schrödinger Equation!

$$\Rightarrow\psi(r,t)=\psi(r)\,e^{-iEt/\hbar}$$

-- wavefunction of stationary state

or simply using $\psi(r)$

$$\boxed{\psi(r,t) = \psi(r)\, e^{-iEt/\hbar} \quad (1)}$$ **wavefunction of stationary state**

Its probability density can be expressed as,

$$\boxed{|\psi(r,t)|^2 = \psi(r,t)^* \psi(r,t)}$$

$$= [e^{-iEt/\hbar}\psi(r)]^* e^{-iEt/\hbar}\psi(r)$$

$$= e^{iEt/\hbar}\psi(r)^* e^{-iEt/\hbar}\psi(r)$$

$$= \psi(r)^* \psi(r) = |\psi(r)|^2$$

Time-independent!

- For the states defined by equation (1), the probability density is solely given by $|\psi(r)|^2$, being **time-independent!**
- These so-called **stationary states have constant *E* and time-independent distribution of probability density**.

For a one-particle QM system, its wave function fulfills the

Time-independent Schrödinger's Equation

$$\boxed{\hat{H}\psi(x,y,z) = E\psi(x,y,z)}$$ *one-particle Eigenequation*

$$\hat{H} = \hat{T} + \hat{V} \qquad \hat{T} = \hat{P}^2 / 2m$$

$$\hat{P}^2 = \hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2 \quad \hat{P}_x = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x} \Rightarrow \hat{P}_x^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$$

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

Dirac constant

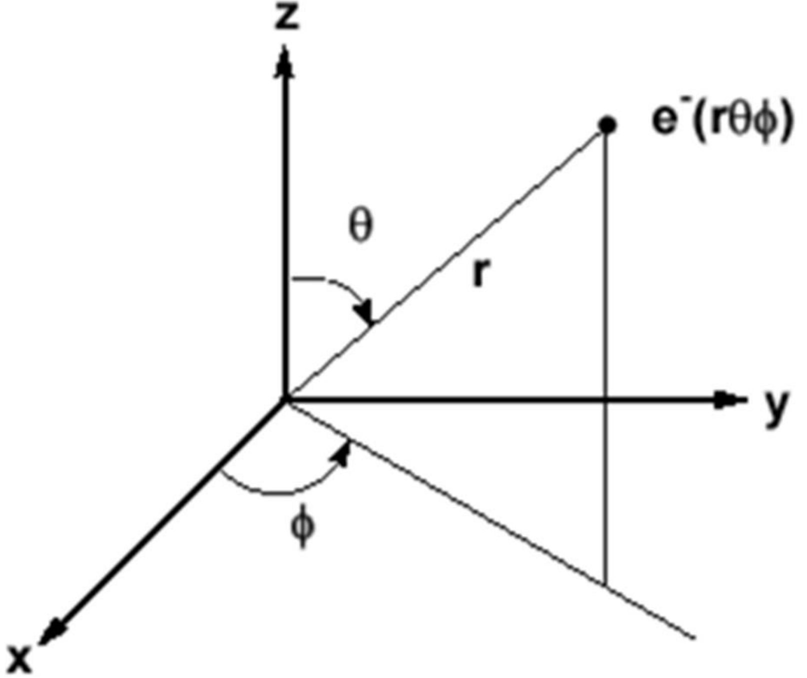
$$= -\frac{h^2}{8\pi^2 m}\nabla^2 + \hat{V} \qquad (Let\ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$$

Laplacian

For the electron in a H-like ion:

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + \hat{V}_{n-e} = -\frac{h^2}{8\pi^2 m_e}\nabla^2 + \hat{V}_{n-e}}$$

Spherical polar coordinates



$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

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

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Laplacian

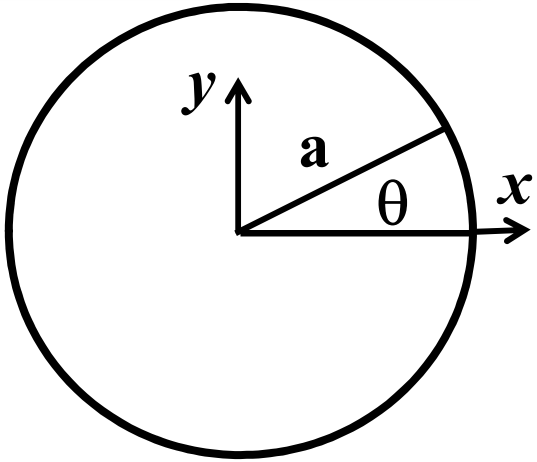
Example : For a particle moving around a circle of ***r = a*** with ***V = 0,*** please derive its Schrödinger equation and wavefunction(s).

(p.21, 1.28)

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

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\nabla^2$$

$$\psi(x, y)\ or\ \psi(\theta)$$



$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{a^2}\frac{\partial^2}{\partial \theta^2}$$

$$(\because x = a\cos\theta,\quad y = a\sin\theta)$$

$$\Rightarrow -\frac{\hbar^2}{2ma^2}\frac{\partial^2}{\partial\theta^2}\psi = E\psi \quad \& \ \psi(\theta) = \psi(\theta + 2\pi)$$

Boundary condition

$$\psi_n = (2\pi)^{-1/2} e^{in\theta}, E_n = \frac{h^2 n^2}{8\pi^2 m a^2}, \quad n = 0, \pm 1, \pm 2, \cdots$$

Their real form: $\psi_{n,1} = \pi^{-1/2}\sin(n\theta), \ \ \psi_{n,2} = \pi^{-1/2}\cos(n\theta)$

There exist two degenerate states for each energy level, except for n=0!

The **Schrödinger's Equation is an** eigenequation.

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

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the *eigenvalues* a, which satisfy the **eigenequation**.

- For a QM system, an eigenfunction of the Schrödinger equation describes a pure quantum state, namely eigenstate.
- A system in a linear combination of multiple different eigenstates (i.e., a mixed quantum state) *does* in general have quantum uncertainty for the given observable.

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

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

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

$$\because \int \psi(\hat{A} * \psi *)d\tau = \int \psi * \hat{A}\psi d\tau \qquad \therefore a = a^*$$

Quantum mechanical operators have to have real eigenvalues.

II. The eigenfunctions of Hermitian operators are orthogonal

$$\int \psi_i * \psi_j d\tau = \delta_{ij} = 0$$

II. The eigenfunctions of an Hermitian operator are orthogonal

Consider two eigenequations of a system

$$\hat{A}\psi_n = a_n\psi_n \qquad \hat{A}\psi_m = a_m\psi_m$$

which corresponds to two different states of the system concerned.

- Multiply the left of the 1st eqn. by $\boldsymbol{\psi_m}$* and integrate, then take the complex conjugate of eqn. 2, multiply by $\boldsymbol{\psi_n}$ and integrate

$$\int \psi_m^* \hat{A}\, \psi_n d\tau = \mathrm{a_n} \int \psi_m^* \psi_n d\tau$$

$$\int \psi_n \hat{A}^* \psi_m^* d\tau = \mathrm{a_m^*} \int \psi_n \psi_m^* d\tau$$

Substracting the two equations gives

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

As $\hat{A}$ is Hermitian, it gives

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

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

There are 2 cases, ***n* = *m***, or ***n* ≠ *m*.**

i) If ***n* = *m***, by normalization, the equation becomes

$$(\mathrm{a}_\mathrm{n} - \mathrm{a}_\mathrm{n}{}^*) = 0 \qquad \because \int \psi_\mathrm{n}{}^* \psi_n d\tau = 1 \ \ \text{(normalization!)}$$

$$\therefore \mathrm{a}_\mathrm{n} = \mathrm{a}_\mathrm{n}{}^*$$

The eigenvalue is a real number!

ii) If $\boldsymbol{n \neq m}$, and the two states of the system are **nondegenerate** (i.e. different eigenfunctions do not have the same eigenvalues, $\mathbf{a_n \neq a_m}$), then

$$(\mathrm{a_n} - \mathrm{a_m})\int \psi_m{}^* \psi_n d\tau = 0$$

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

The eigenfunctions of an Hermitian operator are orthogonal.

$$\int \psi_i{}^* \psi_j d\tau = \delta_{ij} = 0 \quad (\mathrm{i} \neq \mathrm{j})$$

Example: The 1s and 2s orbitals of H atom.

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

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

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

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

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

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

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

Postulate 4 : Superposition Principle (态叠加原理)

- 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.

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

1) The coefficient c_i reflects the contribution of ψ_i to Ψ.

2) If $\{\psi_i\}$ are eigenstates fulfilling the eigenequations $\{\hat{A}\psi_i = A_i\psi_i\}$, a system in such a *mixed quantum state* (Ψ) does in general have quantum uncertainty for the given observable A, the average value of which can be derived as,

$$\langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\sum_i c_i^2 A_i}{\sum_i c_i^2}$$

$$In\ case\ \int \Psi^* \Psi d\tau = \sum_i c_i^2 = 1$$

$$\langle A \rangle = \sum_i c_i^2 A_i$$

$$\because \Psi = \sum_i c_i\psi_i;\quad \hat{A}\psi_i = A_i\psi_i;\quad \int \psi_i{}^*\psi_i d\tau = 1;\quad \int \psi_i{}^*\psi_j d\tau = 0$$

$$\therefore \int \Psi^*\Psi d\tau = \int \Big(\sum_i c_i\psi_i\Big)^*\Big(\sum_i c_i\psi_i\Big)d\tau$$

$$= \sum_i c_i^2\int\psi_i^*\psi_i\, d\tau + \sum_{i\neq j} c_i^* c_j \int \psi_i^*\psi_j\, d\tau = \sum_i c_i^2$$

=1, Ψ is normalized!

≠1, Ψ is not normalized yet!

$$\int \Psi^*\hat{A}\Psi d\tau = \int \Big(\sum_i c_i\psi_i\Big)^*\hat{A}\Big(\sum_i c_i\psi_i\Big)d\tau$$

$$= \sum_i c_i^2\int\psi_i^*\hat{A}\psi_i\, d\tau + \sum_{i\neq j} c_i c_j\int\psi_i^*\hat{A}\psi_j\, d\tau = \sum_i c_i^2 A_i$$

normalizing

$$\therefore \langle A\rangle = \frac{\int\Psi^*\hat{A}\Psi d\tau}{\int\Psi^*\Psi d\tau} = \frac{\sum_i c_i^2 A_i}{\sum_i c_i^2}$$

$$If\ \int\Psi^*\Psi d\tau = \sum_i c_i^2 = 1$$

$$\langle A\rangle = \sum_i c_i^2 A_i$$

$$\Psi_N = \Psi\Big/\sqrt{\sum_i c_i^2}$$

$$\int \Psi_N^*\Psi_N d\tau = 1$$

c_i^2 is the probability of the particle (described by Ψ) presenting the eigenstate ψ_i.

Example:

When ***l*** = 1, atomic ***p*** orbitals in complex form have three components (p_0, p_{+1} and p_{-1}). The real forms of atomic *p* orbitals can be constructed as,

$$p_0 = p_z$$

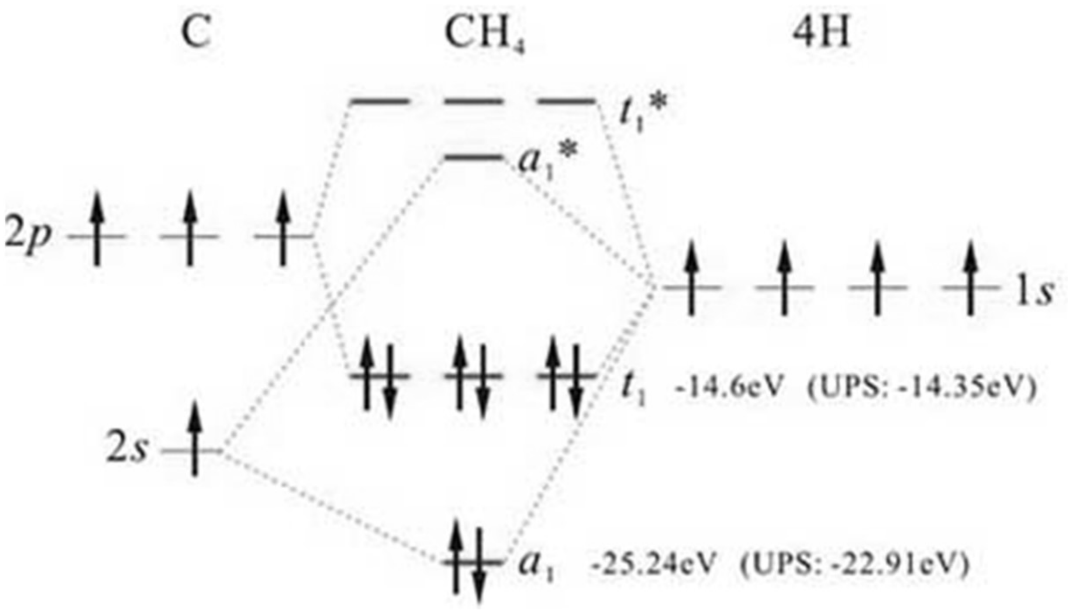
$$p_x = (p_{+1} + p_{-1})/\sqrt{2}$$

$$p_y = (p_{+1} - p_{-1})/\sqrt{2}i$$

The p_x (or p_y) is not an eigenfunction, having 50% p_{+1} and 50% p_{-1}.

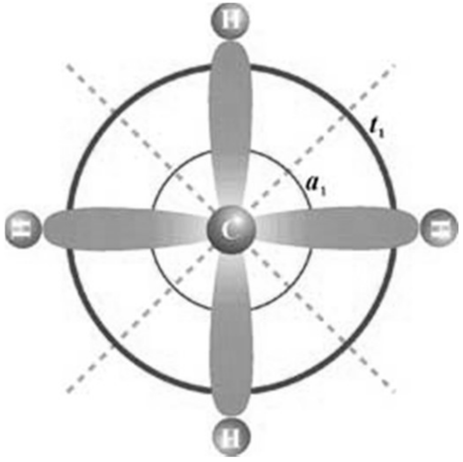
Example: CH_4 has four valence MO's (canonical MO's or delocalized MO's) Ψ_i of different energies, i.e., a lower-energy MO of a_1 symmetry, and three higher-energy MOs of t_1 symmetry. The four localized MO's of this molecule can be constructed as,

$$\Phi_i^{LMO} = \sum_{j=1}^{4} c_{ij} \Psi_j^{CMO}$$



On the contrary, if we know the localized MO's of this molecule, its canonical MO's can be derived as

$$\Psi_j^{CMO} = \sum_{i=1}^{4} c_{ij} \Phi_i^{LMO}$$

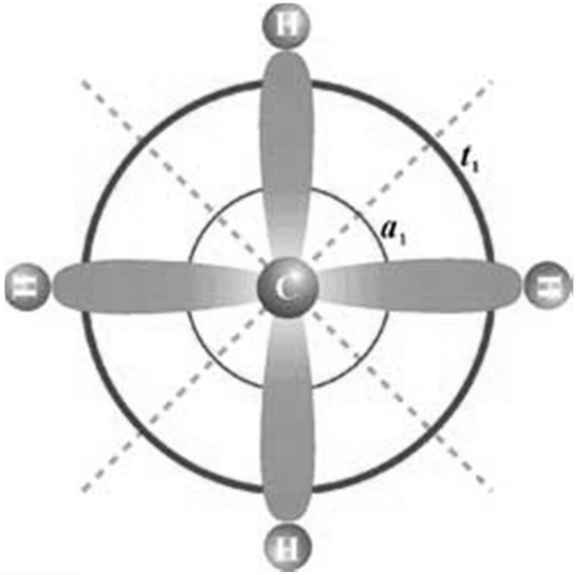


Generally, the CMO's of a molecule are expressed in the form of linear combination of all atomic orbitals (LCAOs) of its constituent atoms. Thus, CMOs are delocalized in nature.

$$\Psi_i^{CMO} = \sum_m c_{im}\varphi_m^{AO}$$

CMOs of CH_4

ε_i^{CMO}	CMO	AO_C	AOs of H atoms
ε_1	$a_1 : \Psi_s =$	s	$+(1s_a + 1s_b + 1s_c + 1s_d)/2$
ε_2	$t_1 : \Psi_x =$	p_x	$+(1s_a + 1s_b - 1s_c - 1s_d)/2$
ε_2	$t_1 : \Psi_y =$	p_y	$+(1s_a - 1s_b - 1s_c + 1s_d)/2$
ε_2	$t_1 : \Psi_z =$	p_z	$+(1s_a - 1s_b + 1s_c - 1s_d)/2$



LMOs of CH_4

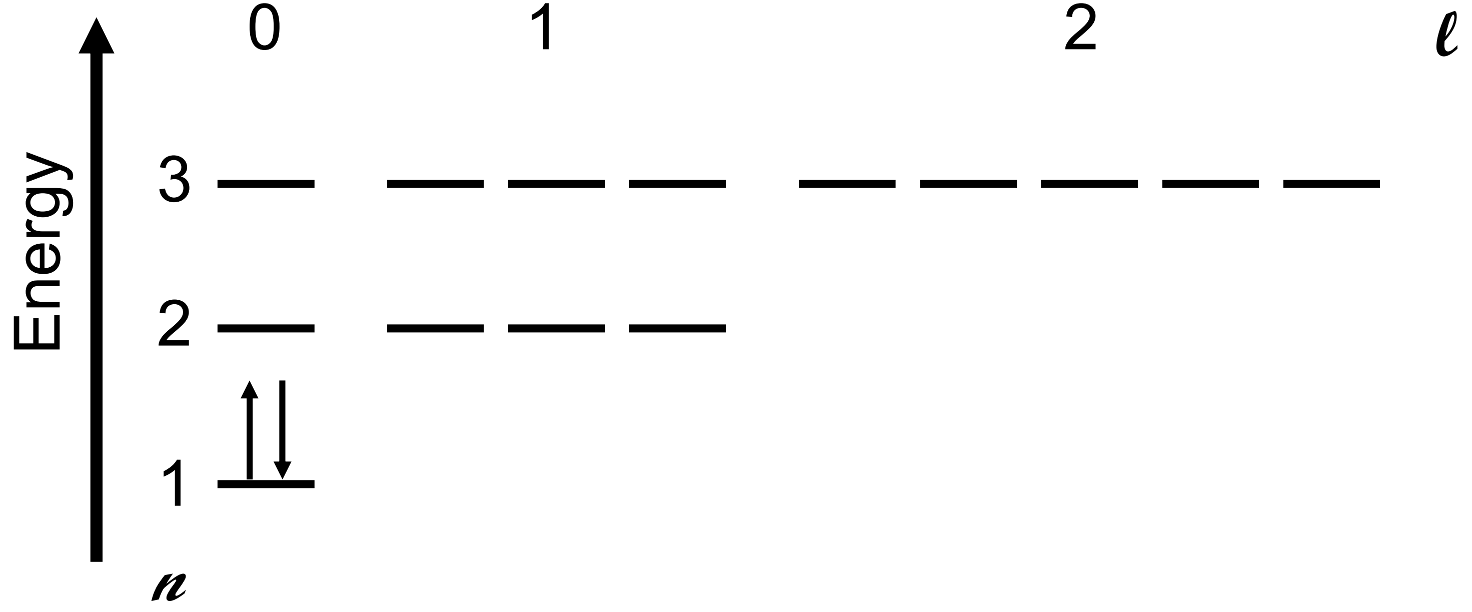
LMO	CMOs	HO of C,	H 1s
$\Phi_a =$	$\Psi_s + \Psi_x + \Psi_y + \Psi_z =$	$(s + p_x + p_y + p_z)/2 +$	$1s_a$
$\Phi_b =$	$\Psi_s + \Psi_x - \Psi_y - \Psi_z =$	$(s + p_x - p_y - p_z)/2 +$	$1s_b$
$\Phi_c =$	$\Psi_s - \Psi_x - \Psi_y + \Psi_z =$	$(s - p_x - p_y + p_z)/2 +$	$1s_c$
$\Phi_d =$	$\Psi_s - \Psi_x + \Psi_y - \Psi_z =$	$(s - p_x + p_y - p_z)/2 +$	$1s_d$

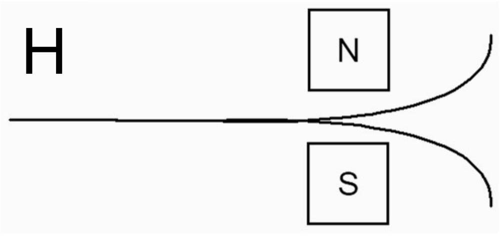
Are the four LMOs equal in energy? Pls prove!

Postulate 5 : Pauli’s principle(泡利不相容原理).

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

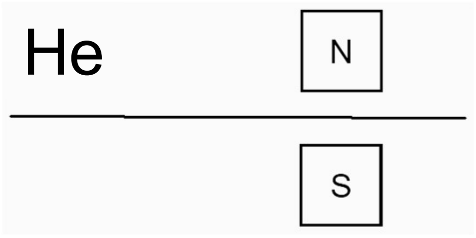
Energy level diagram for ***He***. Electron configuration: $\mathbf{1s^2}$





$1s^1$

paramagnetic – one (more) unpaired electrons



$1s^2$

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 quantum number* → electron spin

$m_s = \pm½$ $(-½ = \alpha)$ $(+½ = \beta)$

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 purely a quantum mechanical concept.**

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

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

$$\begin{aligned}&e.g., \textit{For a two-particle system}\\&\phi(q_{1,}q_2)\\&\left|\phi(q_{1,}q_2)\right|^2 = \left|\phi(q_{2,}q_1)\right|^2\\&\phi(q_{1,}q_2) = \pm\phi(q_{2,}q_1)\end{aligned}$$

$\begin{cases} + & \text{symmetry (Bosons)} \\ - & \text{Antisymmetry (Fermions)} \end{cases}$

- Fermions (e.g., electron) obey the Pauli Exclusion Principle.
- Bosons (e.g., photon) **do not** obey the Pauli Exclusion Principle

Note: Electrons within a many-electron molecule/atom are fermions! Thus, the wavefunction to describe any of the states of such a many-electron system should be antisymmetric!

Permutation operator $\hat{P}_{12}$

$$e.g., wavefunction\ \ for\ a\ two\text{-}particle\ system: \quad \phi(q_{1,}q_2)$$

$$\hat{P}_{12}\phi(q_{1,}q_2) = \phi(q_{2,}q_1) \Rightarrow \hat{P}_{12}\hat{P}_{12}\phi(q_{1,}q_2) = \hat{P}_{12}\phi(q_{2,}q_1) = \phi(q_{1,}q_2)$$

$$\text{Suppose } \ \hat{P}_{12}\phi(q_{1,}q_2) = c\phi(q_{1,}q_2) \quad (c: \text{ eigenvalue of } \hat{P}_{12})$$

$$\Rightarrow \hat{P}_{12}\hat{P}_{12}\phi(q_{1,}q_2) = \hat{P}_{12}[c\phi(q_{1,}q_2)] = c^2\phi(q_{1,}q_2)$$

$$\Rightarrow c^2 = 1,\ c = \pm 1 \quad (fermion: c = -1; \quad boson: c = 1)$$

e.g., the wavefunction of two electrons in the ground state of He ($1s^2$) should be antisymmetric upon permutation (i.e. fermionic)!

$$\phi(1,2) = [1s(1)1s(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

Orbital part
Symmetric

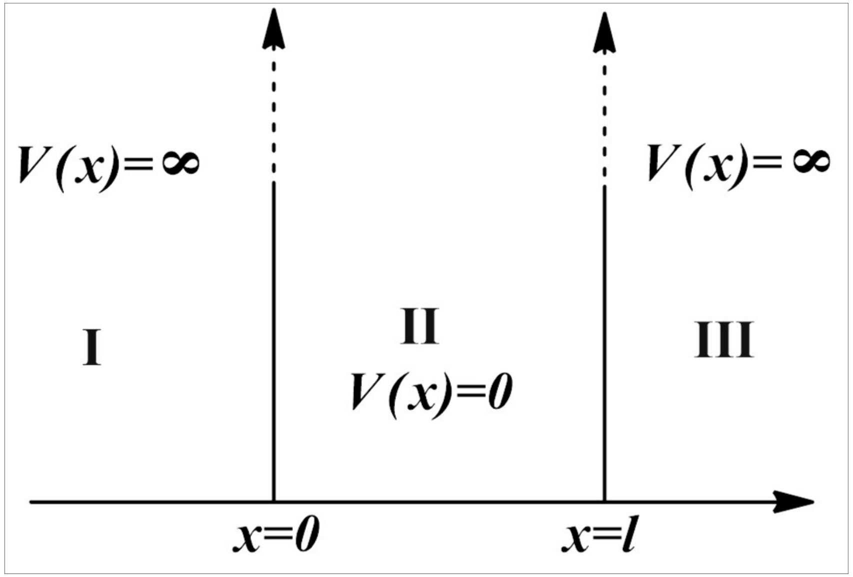
Spin part
anti-symmetric

which is a linear combination of the possible microstates of the very electronic configuration!

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

1.4.1 The free particle in a 1-dimensional box

1. The Schrödinger's Equation and its solution



(1D potential trap)

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

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

In I & III:

$$\because V = \infty \Rightarrow V - E = V$$

$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = V\psi(x) \Longrightarrow \psi(x) = \frac{h^2}{8\pi^2 mV}\cdot\frac{d^2\psi}{dx^2} = 0$$

$$(x \le 0 \quad \text{or} \quad x \ge l)$$

→ The probability of the particle presenting in either area ***I*** or ***III*** is ***0***. That is, the particle is completely **trapped** in area ***II***.

Area II: V=0 $\hat{\mathrm{H}}\psi = E\psi$ with $\hat{\mathrm{H}} = -\dfrac{h^2}{8\pi^2\mathrm{m}}\dfrac{d^2}{dx^2} + \hat{\mathrm{V}} = -\dfrac{h^2}{8\pi^2\mathrm{m}}\dfrac{d^2}{dx^2}$

⇨ $\dfrac{d^2\psi(x)}{dx^2} + \dfrac{8\pi^2 m}{h^2}E\psi(x) = 0$ Now set $8\pi^2 mE/h^2 = \alpha^2$

The equation becomes $\dfrac{d^2\psi(x)}{dx^2} + \alpha^2\psi(x) = 0$

with

$$\psi(x) = A' e^{i\alpha x} + B' e^{-i\alpha x} \text{ or}$$
$$\psi(x) = A\,\mathbf{cos}\,\alpha x + B\,\mathbf{sin}\,\alpha x$$

Considering the boundary conditions: $\psi(0)=0,\ \psi(l)=0$

We have $\psi(0) = A\cos 0 + B\sin 0 = A + 0 = 0 \rightarrow A = 0$

$\therefore\quad \psi(x) = B\sin\alpha x \quad (\mathrm{B}\neq 0)$

$\psi(l) = B\sin\alpha l = 0 \rightarrow \sin\alpha l = 0 \rightarrow \alpha l = n\pi,\quad \alpha = n\pi/l\ (n=1,2,\ldots)$

$$\therefore \frac{8\pi^2 mE}{h^2} = \alpha^2 = \frac{n^2\pi^2}{l^2} \qquad \Rightarrow E = \frac{n^2h^2}{8ml^2} \quad (n = 1,2,3\ldots)$$

$$\therefore \psi(x) = B\,\mathbf{sin}\,\alpha x = B\,\mathbf{sin}\left(\frac{n\pi}{l}x\right)$$

Now normalizing it, $\because \int_0^l \left|\psi(x)\right|^2 dx = 1$

$$\therefore \int_0^l B^2\left(\mathbf{sin}\frac{n\pi x}{l}\right)^2 dx = 1 \qquad \left(\because \int (\mathbf{sin}\,x)^2 dx = \left|\frac{1}{2}\left(x - \frac{1}{2}\mathbf{sin}\,2x\right)\right)\right.$$

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

$$\Rightarrow B = \sqrt{\frac{2}{l}} \qquad \therefore \psi(x) = B\,\mathbf{sin}\frac{n\pi}{l}x = \sqrt{\frac{2}{l}}\,\mathbf{sin}\frac{n\pi}{l}x$$

2. Properties of the solutions $E = \frac{n^2 h^2}{8ml^2}$ & $\psi = \sqrt{\frac{2}{l}}\, sin(\frac{n\pi x}{l})$ $(n = 1,2,3...)$

a. The particle can exist in many pure quantum states (eigenstates).

b. Quantization of energy.

c. The existence of zero-point energy (minimum energy).

($E_{min} = h^2/8ml^2$)

Ground-state energy

n=1 $E_1 = \frac{h^2}{8ml^2}$ $\psi_1 = \sqrt{\frac{2}{l}} \sin \frac{\pi x}{l}$

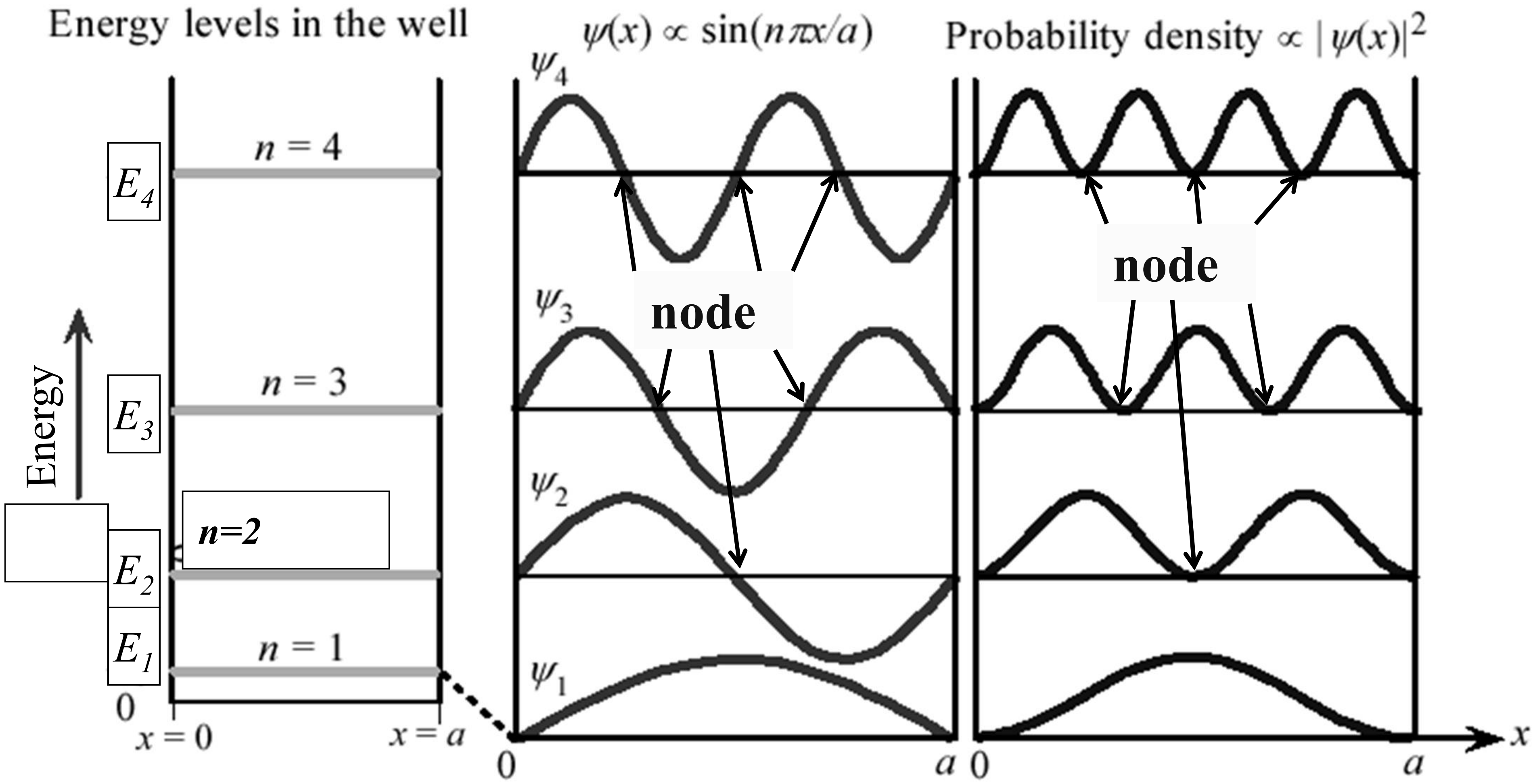
n=2 $E_2 = \frac{4h^2}{8ml^2}$ $\psi_2 = \sqrt{\frac{2}{l}} \sin \frac{2\pi x}{l}$

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

……

d. There is no trajectory but only probability distribution!

e. The presence of nodes.



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

Discussion:

i. Normalization and **orthogonality**

$$\int_0^l \psi_n(x)\psi_m(x)dx = \frac{2}{l}\int_0^l \sin\frac{n\pi x}{l}\sin\frac{m\pi x}{l}dx = \begin{cases} 1 & (\mathrm{n=m}) \\ 0 & (\mathrm{n \neq m}) \end{cases}$$

ii. Average value

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

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

$$< p \ >= \int_0^l \varphi_n^* \hat{p}\ \varphi_n dx = \int_0^l (\sin\frac{n\pi x}{l})[-i\hbar\frac{d}{dx}(\sin\frac{n\pi x}{l})]dx = 0$$

$$\because \hat{H} = \hat{T} = \hat{p}^2/2m \quad (\text{Thus } \hat{p}^2 \text{ and } \hat{H} \text{ are commutable!})$$

$$\Rightarrow \hat{p}^2\psi_\mathrm{n} = 2m\hat{H}\psi_n = 2mE_n\psi_n$$

$$\Rightarrow < p^2 >= |p|^2 = 2mE = \frac{n^2h^2}{4l^2} \Rightarrow |\,\mathrm{p}\,| = \frac{nh}{2l}$$

Differing from <p>!

iii. Uncertainty

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

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

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

$$When \;\; n = 1 \;\; \boldsymbol{(}ground \;\; state\boldsymbol{)}$$

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

iv. Wave-particle duality

$$\left|\vec{p}\right|^2 = 2mE \;\; = \frac{n^2 h^2}{4l^2} \Rightarrow \left|\vec{p}\right| = \frac{nh}{2l}$$

$$\left|\vec{p}\right| = h / \lambda \Rightarrow \lambda = \frac{h}{\left|\vec{p}\right|} = \frac{2l}{n}$$

i.e., de Broglie wavelength of the particle in the 1D potential box!

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 (e.g., boundary conditions)

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

Remarks on the 1-D system with an infinite potential well

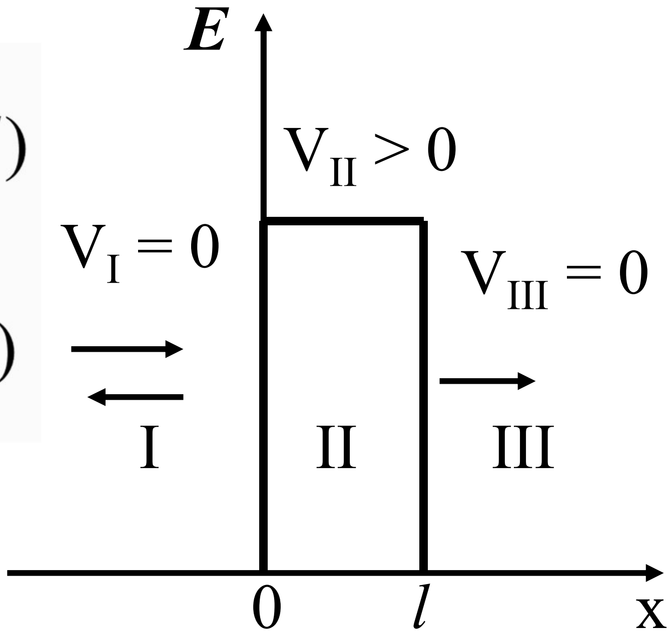
- The aforementioned 1-D (or even 3-D) system with an infinite potential well is just an ideal system that can never be found in reality.

- In reality, we always encounter such microscopic systems that have finite potential wells/barriers. The probability for a microscopic particle to present out of a ***finite potential well*** is not zero. It is difficult to imprison microscopic particles exclusively within a finite potential well.

→ ***Quantum leak/tunneling***!

3. Quantum leaks --- tunneling

- In classical mechanics, all particles with ***E* > *V*** can pass through the barrier of potential ***V***, whereas the particles with ***E*<*V*** can not pass through the potential barrier.
- This is not the case in quantum mechanics.



$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x} = E\psi \quad (I : x < 0; III : x > l)$$

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

When ***E*<*V***, $\psi_{II}(x) \neq 0 \quad (0 < x < l)$

$$\int_0^{-\infty} |\psi_I|^2 dx + \int_0^l |\psi_{II}|^2 dx + \int_0^{\infty} |\psi_{III}|^2 dx = 1$$

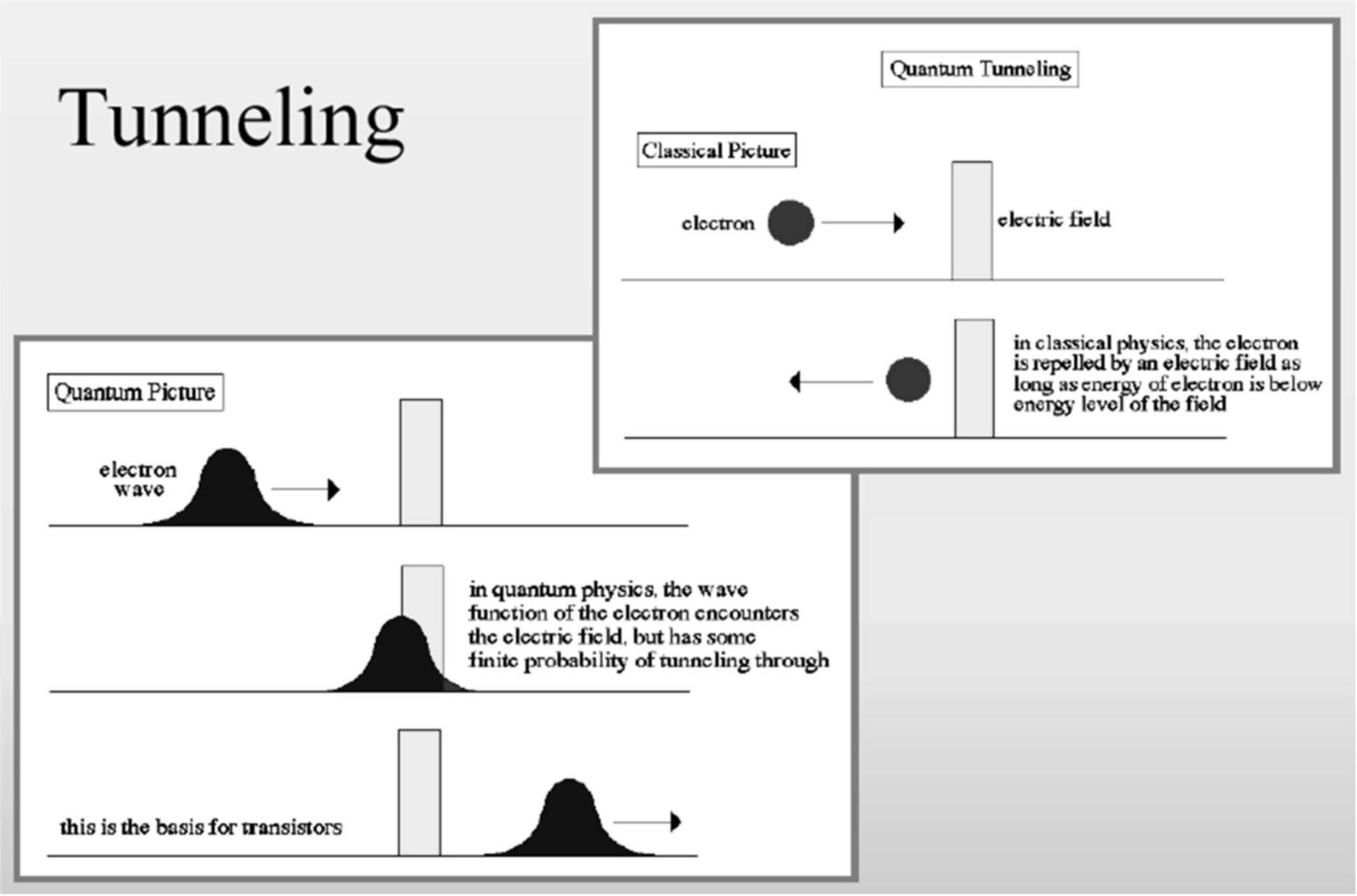
$$0 < \int_0^l |\psi_{II}|^2 dx << 1 \qquad \Rightarrow$$

The probability for particles to penetrate the barrier is not zero!!!!

- The probability of penetration is given by

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

P decreases exponentially with increasing ***V*** and its width ***l*** and ***m***!!



Tunneling

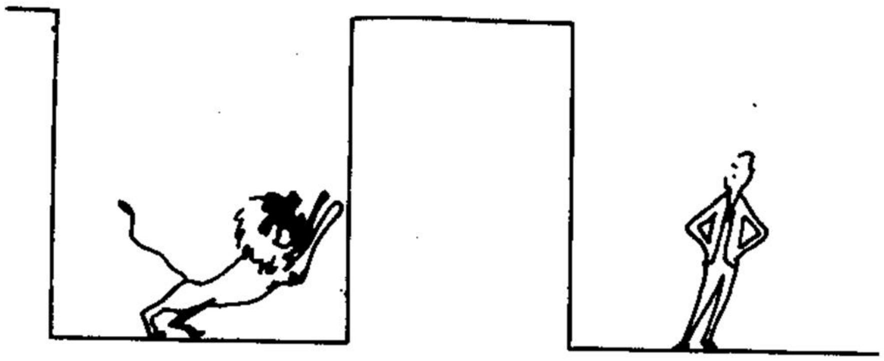
in classical physics, the electron is repelled by an electric field as long as energy of electron is below energy level of the field

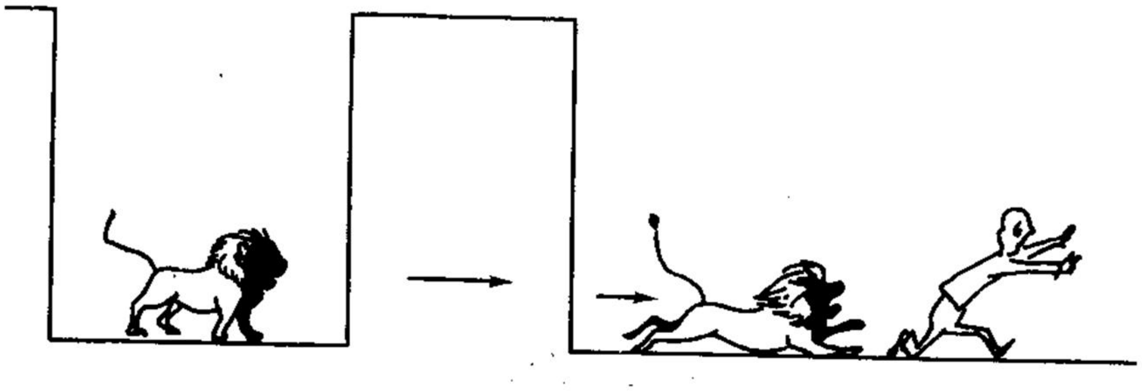
in quantum physics, the wave function of the electron encounters the electric field, but has some finite probability of tunneling through

this is the basis for transistors

Quantum Tunneling

CLASSICAL MECHANICS





QUANTUM MECHANICS

Tunneling in the “real world”

- Tunneling is widely exploited:

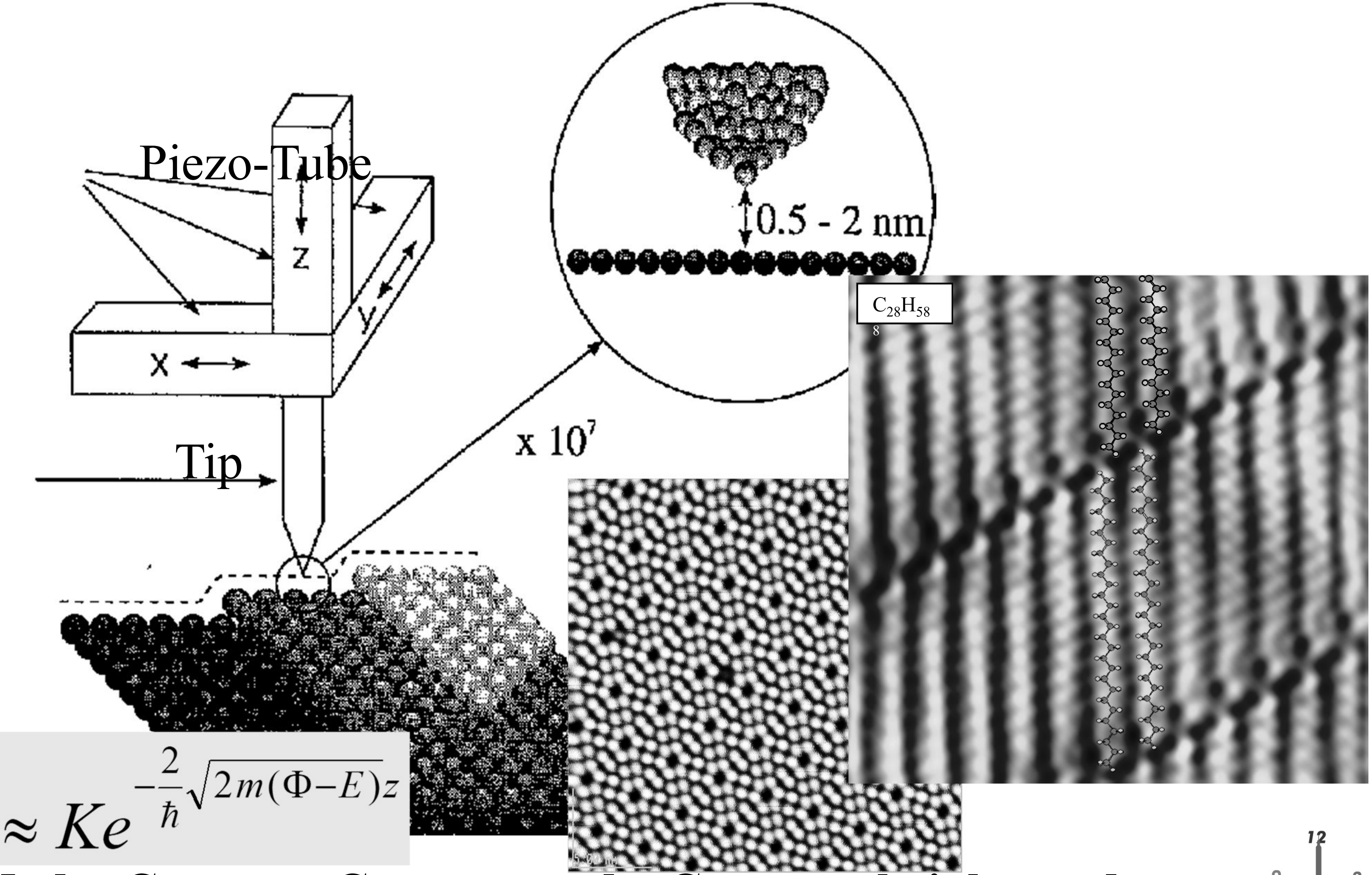
- for the operation of many microelectronic devices (tunneling diodes, flash memory, …)

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

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

STM System

Free electrons of metals can tunnel between the surfaces of two metals of atomic distances (~ 1 nm) driven by a suitable bias voltage.



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

Mode: Constant Current mode, Constant height mode

1.4.2 The free particle in a three-dimension box

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

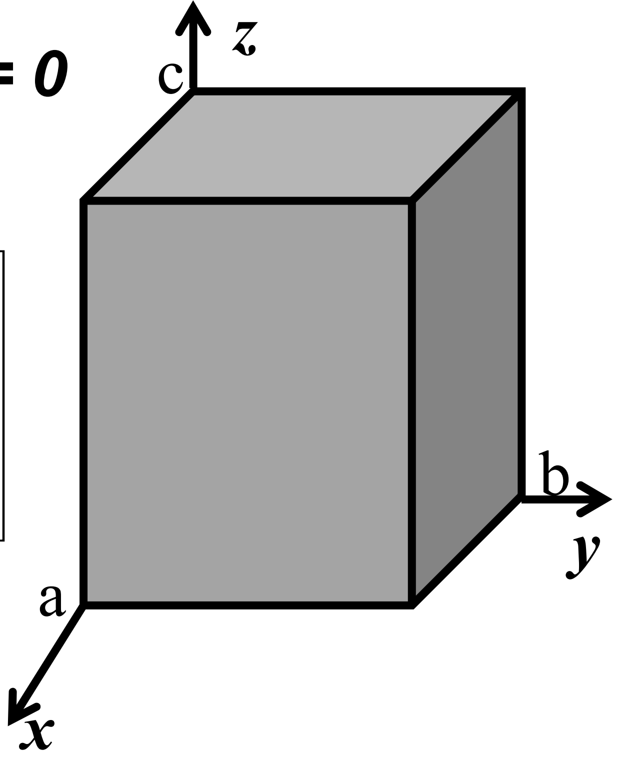
Out of the box, ***V(x, y, z) = ∞ → ψ(x,y,z) = 0***

In the box, ***V(x, y, z) = 0***

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

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

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



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

Separation → *of variables*

Let ***ψ(x, y, z)= X (x)·Y (y)·Z (z)***

and substitute into the Schrödinger equation.

(separation of variables)

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

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

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

Divided by XYZ

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

Let $E_x = E - (E_z+E_y)$

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

$$E=E_x+E_y+E_z$$

The three equations separately give:

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}$$ $$E_x = \frac{h^2}{8m} \frac{n_x^2}{a^2}$$ **(n_x= 1, 2, ……)**

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}$$ $$E_y = \frac{h^2}{8m} \frac{n_y^2}{b^2}$$ **(n_y= 1, 2, ……)**

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}$$ $$E_z = \frac{h^2}{8m} \frac{n_z^2}{c^2}$$ **(n_z= 1, 2, ……)**

Then

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

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

A pure quantum state (eigenstate) of the particle in a 3-D box is defined by a unique set of quantum numbers, (n_x,n_y,n_z)!

When the box is cubic, degenerate energy levels present.

(i.e., a = b = c)

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

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

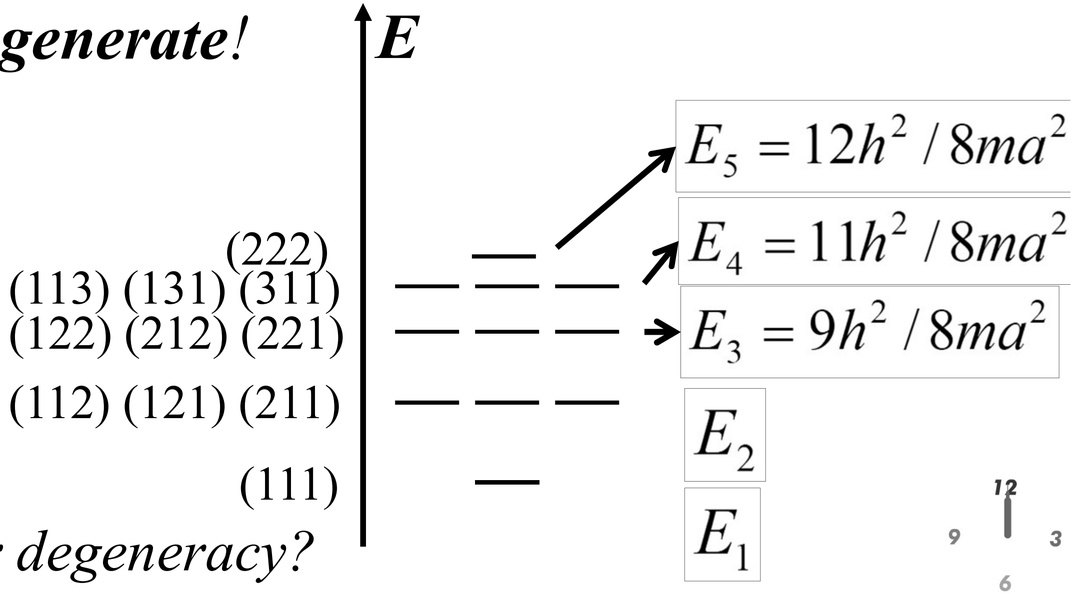
$$E_1 = 3h^2/8ma^2$$

ii. The first excited states: $n_i = n_j = 1,\ n_k = 2$

$$E_2 = 6h^2/8ma^2$$

- This energy level is ***triply degenerate***!
- Degeneracy = ***3***

$$\begin{array}{ccc} n_x & n_y & n_z \\ \hline 1 & 1 & 2 \\ 1 & 2 & 1 \\ 2 & 1 & 1 \end{array}$$



E

(222)

(113) (131) (311)

(122) (212) (221)

(112) (121) (211)

(111)

$E_5 = 12h^2/8ma^2$

$E_4 = 11h^2/8ma^2$

$E_3 = 9h^2/8ma^2$

E_2

E_1

Is there an energy level with higher degeneracy?

m-dimensional box (*m*=1-3)

- Wave functions

$$\psi = \prod_{i=1}^{m} \psi_i, \quad \psi_\mathrm{i} = \sqrt{\frac{2}{l_i}} \sin\frac{n_i \pi x_i}{l_i} \qquad (i = 1, \ldots m)$$

- Energy

$$E = \sum_{i=1}^{m} E_i = \frac{h^2}{8m} \sum_{i=1}^{m} \frac{n_i^{\;2}}{l_i^2}; \qquad E_i = \frac{n_i^{\;2} h^2}{8 m l_i^2} \qquad (i = 1, \ldots m)$$

Quantum number: $n_i = 1, 2, \ldots\ldots\ldots$

1.4.3 Simple applications of potential-box model

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

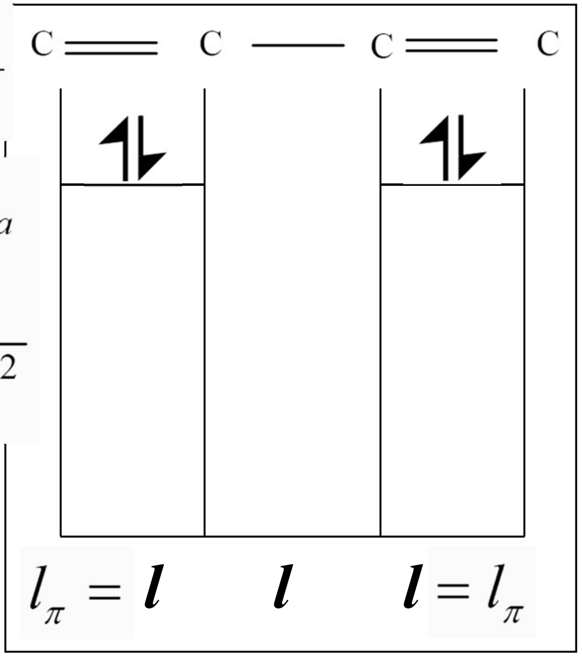
(Suppose ***l*** = C-C bond length)

Localized model I

Four π electrons form two localized π-bonds

Delocalized model II

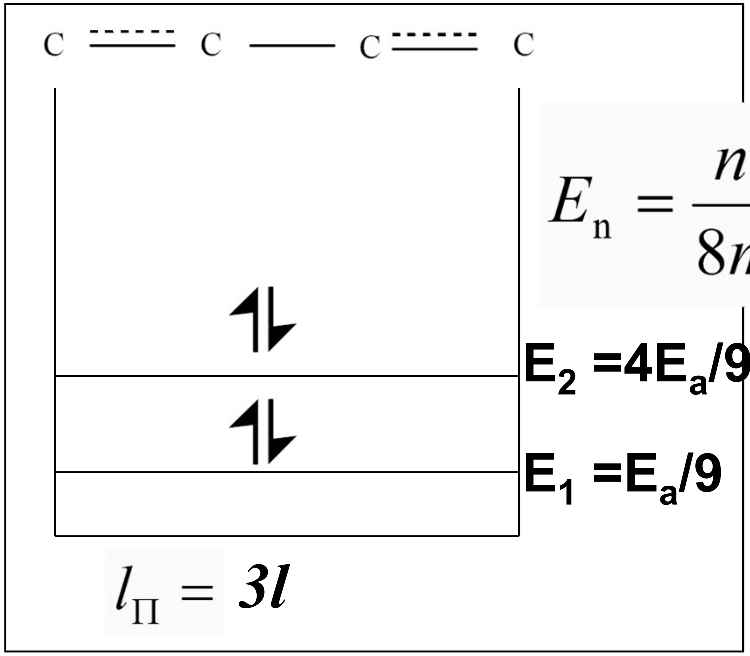
Four π electrons form a delocalized Π_4^4 bond.



$$E_n = \frac{n^2h^2}{8m_e l_\pi^2}$$

$$E_1 = E_a = \frac{h^2}{8m_e l^2}$$

$l_\pi = \boldsymbol{l}$ $\quad \boldsymbol{l} \quad$ $\boldsymbol{l} = l_\pi$



$$E_n = \frac{n^2h^2}{8m_e l_\Pi^2}$$

$E_2 = 4E_a/9$

$E_1 = E_a/9$

$l_\Pi = 3l$

$$E^I = 2 \times 2 \times E_1 = 4E_a \; > \; E^{II} = 2 \times E_1 + 2 \times E_2 = (10/9)E_a$$

$$E_{deloc} = E^{II} - E^I = (10/9)E_a - 4E_a = -(26/9)E_a$$

Example 2: The adsorption spectrum of cyanines

The general formula of cyanines:

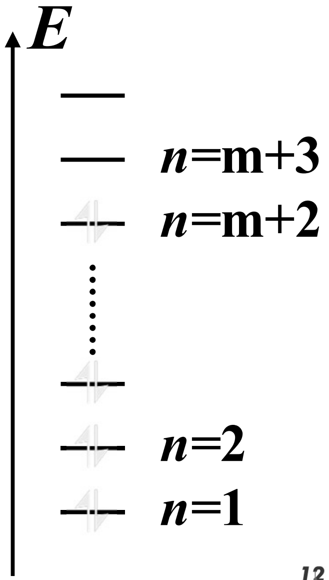
$$R_2\ddot{N}\text{-}(CH{=}CH\text{-})_m\text{-}CH{=}\overset{+}{N}R_2$$

- 1D-box model of their Π-bond:

  The ***n***th π-molecular orbital (MO)

$$E_{\rm n} = \frac{n^2h^2}{8m_el^2}$$

- The Π bond has a total of ***2m+4*** π-electrons.
- Ground state: the lowest ***m+2*** π-MO′s occupied
- The longest-wavelength absorption corresponds to photo-excitation of an electron from the highest occupied MO (HOMO, ***n=m+2***) to the lowest unoccupied MO (LUMO, ***n=m+3***).



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

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

$$\lambda = \frac{\mathrm{c}}{\nu} = \frac{8m_e l^2 c}{h(2m+5)} = \frac{3.3l^2}{2m+5} \quad (pm)$$

$$l \approx 248m + 565 \quad (pm)$$

Table 1. The absorption spectrum of the cyanine dye

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

m	λ_{max} (calc) / nm	λ_{max} (expt) /nm
1	311.6	309.0
2	412.8	409.0
3	514.6	511.0

More Examples

1. Are $e^{im\phi}$ and $\cos(m\phi)$ eigenfunctions of operator $id/d\phi$? If so, please determine the eigenvalue.

$$\text{a)}\quad i\frac{d}{d\phi}e^{im\phi} = ie^{im\phi} \bullet im = -me^{im\phi}$$

So $e^{im\phi}$ is an eigenfunction of operator $id/d\phi$ with an eigenvalue of $-m$.

$$\text{b)}\quad i\frac{d}{d\phi}\cos m\phi = i(-\sin m\phi)\bullet m = -im\sin m\phi \neq c\cos m\phi$$

So $\cos m\phi$ is not an eigenfunction of operator $id/d\phi$.

2. For the π-conjugate molecule $CH_2(CH)_6CH_2$, its UV-vis spectrum shows the first long-wavelength absorption at 460 nm. Please estimate the length of its carbon chain using the 1-D box model.

Ans: The energies of π-MOs given by 1-D box model are

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

In the ground state of this delocalized Π^8_8 bond, MOs 1-4 are doubly occupied. The energy of the first excitation is given by the energy difference between the 5th and 4th MOs.

$$\Delta E = E_5 - E_4 = \frac{h^2}{8ml^2}(5^2 - 4^2) = \frac{9h^2}{8ml^2} = \frac{hc}{\lambda}$$

$$\because \Delta E_{photon} = \frac{hc}{\lambda}$$

$$\therefore l = \sqrt{\frac{9h^2\lambda}{8mhc}} = \sqrt{\frac{9h\lambda}{8mc}} = 1120\,pm$$

l: the length of carbon chain.

3. Does the following function represent a state of a particle in a 1-dimensional box?

$$\varphi(x) = 2\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a} - 3\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

If yes, does it have a certain value of energy and what is the energy of this state? If not, determine the average energy.

Ans: The wavefunctions and energy levels of a particle in a 1-d box of length ***a*** are given by

$$\varphi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \quad \mathrm{E}_{\mathrm{n}} = \frac{n^2h^2}{8ma^2}$$

Thus, the first two lowest-energy eigenstates are,

$$\varphi_1(x) = \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}; \qquad \varphi_2(x) = \sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

$$\Rightarrow \varphi(x) = 2\varphi_1(x) - 3\varphi_2(x)$$

So ***φ(x)*** represents a possible state of a 1-D-box particle, according to the superposition principle. However,

$$\hat{H}\varphi(x) = 2E_1\varphi_1(x) - 3E_2\varphi_2(x) \neq c\varphi(x)$$

So ***φ(x)*** is not an eigenfunction of Hamiltonian and has not a certain energy.

To evaluate ***<E>***, ***φ(x)*** must be normalized.

Define $\boxed{\varphi'(x) = A\varphi(x)}$, then

$$\int_0^a |\varphi'(x)|^2 dx = \int_0^a |A\varphi(x)|^2 dx = A^2 \int_0^a \varphi^2(x) dx$$

$$= A^2 \int_0^a \left(2\sqrt{\frac{2}{a}} \sin\frac{\pi x}{a} - 3\sqrt{\frac{2}{a}} \sin\frac{2\pi x}{a} \right)^2 dx = 13A^2 = 1 \quad \Rightarrow A^2 = \frac{1}{13} \quad \Rightarrow A = 1/\sqrt{13}$$

$\Rightarrow \varphi'(x) = \varphi(x)/\sqrt{13}$ i.e., the normalized form of ***φ(x)*.**

$$\therefore <E> = \int_0^a \varphi'^*(x) \hat{H} \varphi'(x) dx, \qquad \hat{H} = -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2}$$

$$= A^2 \int_0^a (2\varphi_1 - 3\varphi_2) \hat{H} (2\varphi_1 - 3\varphi_2) dx$$

$$= A^2 (4E_1 + 9E_2) = A^2 \left(4 \times \frac{h^2}{8ma^2} + 9 \times \frac{4h^2}{8ma^2}\right) = \frac{5h^2}{13ma^2}$$

Note: φ_1 and φ_2 are eigenstates, being normalized and mutually orthogonal!

Complementary Concepts

Complex and its conjugate

Suppose there is a complex ***A* = *a* + *ib***, its conjugate should be in the form of ***A** = *a-ib***.

The absolute value of ***A***: $$\boxed{|\mathrm{A}| = \sqrt{a^2 + b^2}}$$

Relationship between ***A*** and its complex conjugate ***A****:

$$\boxed{A \cdot A^* = a^2 + b^2 = |A|^2}$$

or $$\boxed{A^* = |A|^2 / A}$$

Summary of Chapter 1

1.1 The failures of classical physics

1.1.1 Black-Body Radiation

Planck's quanta idea $E = nh\nu$ for atomic vibrations

1.1.2 The photoelectric effect

A corpuscular theory of light (photons)

$\varepsilon = h\nu = mc^2$ **h** = Planck's constant

$p=h/\lambda$ (particle nature of light !)

Qualitative model

1.1.3 Atomic and molecular spectra

Planetary model: orbits of electrons around the nucleus

Bohr's atomic model: quantized energy levels of orbits

Quantitative model

For H-like atom/ions $E_n = -\dfrac{RZ^2}{n^2}$

1.2 The characteristic of the motion of microscopic particles

1.2.1 wave-particle duality (e.g., electrons)

$\boldsymbol{E = h\nu,\ \ p = h/\lambda}$ (de Broglie wavelength of particle)

- A wave of microscopic particles is a ***probability wave***.
- The wave pattern is the statistic distribution of particle motion.

1.2.2 The uncertainty Principle

$$\Delta x \Delta p \geq h; \quad or \quad \Delta x \Delta p \geq \hbar / 2$$

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

1.3 Basic assumptions of quantum mechanics

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

Ψ(r,t): single-value, continuous, quadratically integrable.

$\psi^*(r,t)\psi(r,t)$ ***Probability density distribution function***.

For a given state,

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

Normalization!

For different states of a QM system,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_i^*(r,t)\psi_j(r,t)\,dxdydz = 0$$

Orthogonality!

Postulate 2: Each observable mechanical quantity of a microscopic system is associated respectively with 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, and then replace each coordinate ***x*** by the operator ***x***, and each momentum component $\boldsymbol{p_x}$ by the operator $-i\hbar\partial/\partial x$.

- A Hermitian operator means

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

Some Mechanical quantities and their Operators

Mechanical quantities		**Mathematical Operator**
Position	x	$\hat{x} = x$
Momentum (x)	p_x	$\hat{p}_x = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}$
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	$E = T + V$	$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}$

Hamiltonian

The average value of a physical observable

If a system is in a state described by a ***normalized*** wave function ψ, then the average value of the observable ***A*** corresponding to operator $\hat{A}$ is given by –

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

Commuted operators

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

- When two operators are ***commutable***, their corresponding mechanical quantities can be measured simultaneously.

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

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

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

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

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

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

$$\Rightarrow f(t) = e^{-iEt/\hbar}$$

$$(\because \hat{H}\psi(x,y,z) = E\,\psi(x,y,z) \qquad)$$

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

Time-independent Schrödinger's Equation

$$\boxed{\hat{H}\psi(x,y,z) = E\psi(x,y,z)}$$ *Eigenvalue equation*

$$\hat{H} = \hat{T} + \hat{V} \qquad \because T = mv^2/2 = p^2/2m \qquad \therefore \hat{T} = \hat{P}^2/2m$$

$$\hat{P}^2 = \hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2 \qquad \hat{P}_x = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x} \qquad \hat{P}_x^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$$

$$\hat{V} = \frac{Ze^2}{4\pi\varepsilon_0 r}$$ e.g. H atom or H-like ions

Laplace operator

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

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

Time-independent Schrödinger's Equation

$$\boxed{\hat{H}\psi(x,y,z) = E\psi(x,y,z)}$$

Eigenvalue equation

$$\hat{H} = \hat{T} + \hat{V} \qquad \because T = mv^2/2 = p^2/2m \qquad \therefore \hat{T} = \hat{P}^2/2m$$

$$\hat{P}^2 = \hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2 \qquad \hat{P}_x = -\frac{ih}{2\pi}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x} \qquad \hat{P}_x^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$$

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

e.g. H atom or H-like ions

Laplace operator

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

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

Postulate 4：Superposition Principle
(态叠加原理)

- 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.

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

1) The coefficient c_i reflects the contribution of wavefunction ψ_i to Ψ.

2) In case the system has $\int \Psi^*\Psi d\tau = 1$

$$\int \psi_i{}^*\psi_i d\tau = 1; \quad \int \psi_i{}^*\psi_j d\tau = 0 \quad \hat{A}\psi_i = A_i\psi_i$$

the average value of $\hat{A}$ of this state (Ψ) can be derived as,

$$\left\langle \hat{A} \right\rangle = \frac{\int \Psi^*\hat{A}\Psi d\tau}{\int \Psi^*\Psi d\tau} \Rightarrow \left\langle \hat{A} \right\rangle = \sum_i c_i^2 A_i$$

Postulate 5 : Pauli’s principle(泡利不相容原理).

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

m_s = *spin magnetic* → electron spin

$m_s = \pm½$ (-½ = α) (+½ = β)

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

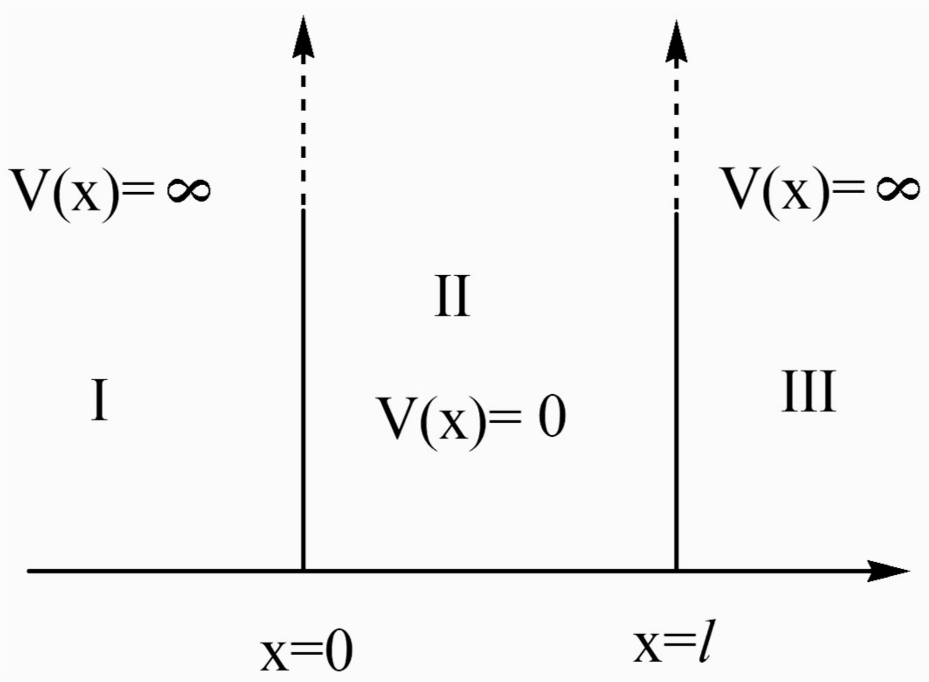
Pauli exclusion principle:

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.**

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

1.4.1 The free particle in a 1D box



1D box

1. The Schrödinger’s Equation and its solution

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

In area I, III:

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

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

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

(i.e., the probability of particle presenting in area I and III is 0).

Area II: V =0

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

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + \hat{V} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} \quad \boxed{\Rightarrow E_n = \frac{n^2h^2}{8ml^2}} \quad \boxed{\psi_n = \sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l}}$$

(n =1,2,3,…)

2. The properties of the solutions

a. The particle can exist in many states.

b. quantization of 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 $\quad E_1 = \frac{h^2}{8ml^2} \quad \psi_1 = \sqrt{\frac{2}{l}}\sin\frac{\pi x}{l}$

n=2 $\quad E_2 = \frac{4h^2}{8ml^2} \quad \psi_2 = \sqrt{\frac{2}{l}}\sin\frac{2\pi x}{l}$

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

1.4.2 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

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

$$\boxed{\begin{matrix} 0<x<a \\ 0<y<b \\ 0<z<\mathrm{c} \end{matrix}}$$

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

Let ψ **= ψ*(x, y, z)*= *X (x) Y (y) Z (z)*** *(separation of variables)*

Substituting into 3-D Schrödinger equation:

$$\boxed{E=E_x+E_y+E_z}$$

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

The solution is:

$$X(x)=\sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a} \qquad E_x=\frac{h^2}{8m}\frac{n_x^2}{a^2}$$ **(n_x= 1, 2, ……)**

$$Y(y)=\sqrt{\frac{2}{b}}\sin\frac{n_y\pi y}{b} \qquad E_y=\frac{h^2}{8m}\frac{n_y^2}{b^2}$$ **(n_y= 1, 2, ……)**

$$Z(z)=\sqrt{\frac{2}{c}}\sin\frac{n_z\pi z}{c} \qquad E_z=\frac{h^2}{8m}\frac{n_z^2}{c^2}$$ **(n_z= 1, 2, ……)**

Then

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

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

Each state of a 3-D box system is defined by a unique set of quantum numbers, (n_x,n_y,n_z)!

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: $n_x=n_y=n_z=1$

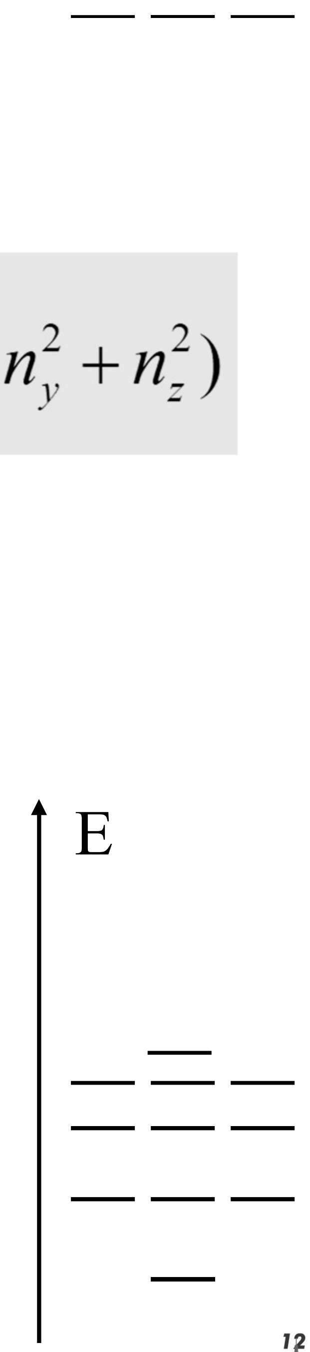
$$E = \frac{3h^2}{8ma^2}$$

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

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

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

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



Brief Summary of Chapter 1

微观粒子波动性--运动粒子在空间出现的几率分布呈现波的特征--几率波！

量子力学的统计学本质

量子力学体系的状态函数--波函数 $\Psi(r,t)$

简单体系：*i*维势箱

$$\psi=\prod_{i=1-3}\sqrt{\frac{2}{l_i}}\sin\frac{n_i\pi x_i}{l_i}\qquad E=\frac{h^2}{8m}\sum_{i=1-3}\frac{n_i^2}{l_i^2}\quad(n_i=1,2,3,\ldots)$$

A. 能量量子化

B. 测不准原理：$\Delta x\Delta p$ or $\Delta E\Delta t\geq\hbar$

1. 几率密度分布函数 $|\Psi|^2$
2. 正交归一性：$\int\Psi_i{}^*\Psi_j d\tau=\delta_{ij}$

   $(i=j,\ \delta_{ij}=1;\ i\neq j,\ \delta_{ij}=0)$
3. 本征函数/方程：$\hat{A}\Psi=a\Psi$
4. Schrödinger方程：$\hat{H}\Psi(r)=E\Psi(r)$
5. 态叠加原理：$\Psi=\Sigma c_i\psi_i$，$\hat{A}\psi_i=A_i\psi_i$

求平均值：$\langle A\rangle=\int\Psi^*\hat{A}\Psi d\tau/\int\Psi^*\Psi d\tau$

$$=\Sigma c_i^2A_i/\Sigma c_i^2$$

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).

第一章作业完成情况总结：

- 数理基础（微积分）需要复习
- 算符运算的理解欠佳
- 势箱模型： 1）量子态（能级）的理解欠佳；2）未掌握多电子体系电子排布的能量最低原则。