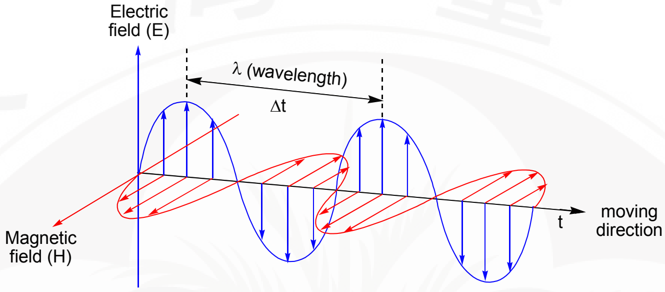
12 Quantum Mechanics and Atomic Theory

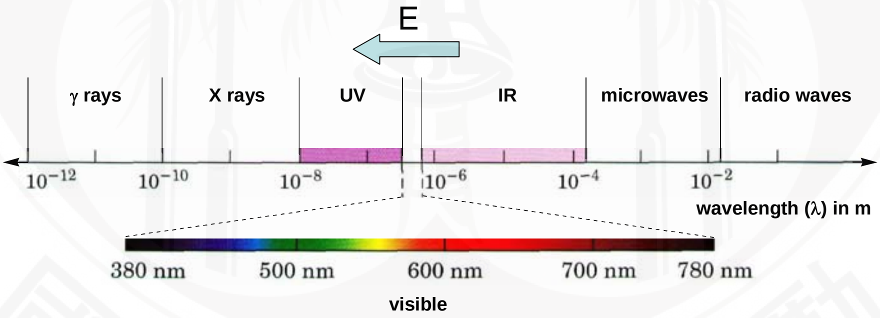
※ Electromagnetic radiation (Maxwell, 1864) (nature of light)

Composed of oscillating perpendicular electric field and magnetic field



If Δt = 1 sec ⇨ 1 cycle per second = 1 Hz = $1\ s^{-1}$

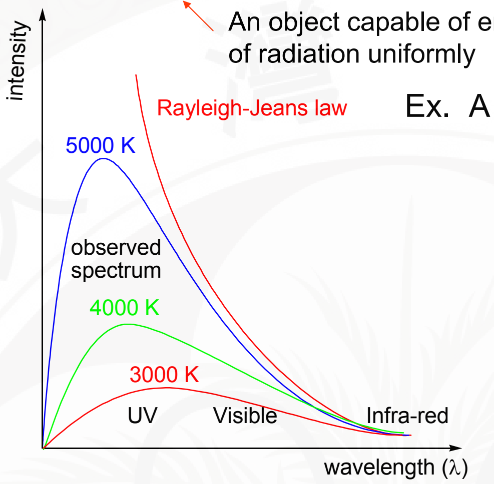
$\lambda\nu = c$ $c = 3.0 \times 10^{8}$ m/s



※ The nature of matter

◎ Black body radiation (or box with a pinhole)

An object capable of emitting and absorbing all freq. of radiation uniformly



Ex. A glowing iron when heated

T increases

red → white light

λ decreases

Classical physics predicts continuous profile with no maxima

ULTRAVIOLET CATASTROPHE

1901 Max Planck

Postulate: the energies are discrete and are integers of $h\nu$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

Planck constant

energy	0	E	$2E$	$3E$	$4E$ ……
# of particles	n_o	n_1	n_2	n_3	n_4 ……

$$E = h\nu$$

Energies are gained or lost in $nh\nu$

$\Delta E = nh\nu$ n is an integer

ν: freq. of radiation absorbed or emitted

⇨ Now the black body radiation profile can be derived

⇨ Meaning:

The energy of light is quantized

Energy exchanged in whole "quanta" (quantum是複數)

◎ Photoelectric phenomenon

1887 Hertz

Light strikes on metal ⇨ e^- emitted

Lenard

A minimum E required (ν_o)

$\nu < \nu_o$ no e^-

$\nu > \nu_o$ yes

Light intensity increases the number of e^- but not the E of e^-

---

1905 Einstein (1879 – 1955)

✓ Electromagnetic radiation is quantized

$$E_{photon} = h\nu = hc/\lambda$$

Predicted:

$$h\nu - h\nu_o = KE_{e^-} = ½mv^2$$

Unrelated to light intensity

Work function (P): The amount of work that the e^- must produce on leaving the body

Confirmed by Hughes, Richardson and Compton (1912) and Millikan (1916)

✓ Photon has mass (not a rest mass)

$$m = \frac{E}{c^2} = \frac{h}{\lambda c} \qquad \text{or } E = mc^2$$

1922 Compton: Confirmed by collision of X-rays and e^-

⇨ Light has dual nature: wave and particle

1924 de Broglie (1892 – 1987)

Particle also has wave nature

$$m = \frac{h}{\lambda v} \qquad (\text{cf: } m = \frac{h}{\lambda c})$$

de Broglie equation: $\lambda = \frac{h}{mv}$

Ex. $m_e = 9.11 \times 10^{-31}$ kg

If traveling at a speed of 1.0×10^7 m/s

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kgm}^2/\text{s}}{(9.11 \times 10^{-31}\ \text{kg})(1.0 \times 10^7\ \text{m/s})}$$

$$= 7.3 \text{ x } 10^{-11}\ \text{m}$$

In the range of X-ray

Same as the spacing between atoms in a crystal

1927 Davison and Germer (Bell lab)
A beam of e^- hitting a nickel crystal
⇨ diffraction occurs
Verified the wave properties of e^-

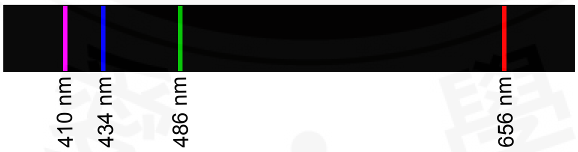
Conclusion
All matter exhibits both particulate and wave properties

Larger particle
More particulate-like
↔
Photons
More wave-like

※ The atomic spectrum of hydrogen

Atomic structure
Thomson: electron Rutherford: nucleus

Atomic spectrum of H
H_2 in a high voltage spark ⇨ excited H atom
⇨ emits light



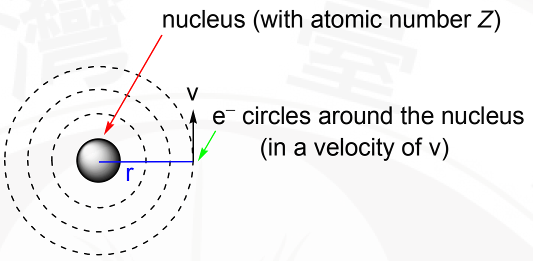
Line spectrum of H
⇨ The energy of e^- in H atom is quantized

$\Delta E = h\nu = hc/\lambda$

From one energy state to another

※ The Bohr model

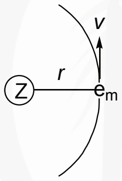
1913 Bohr (1885 – 1962)



e⁻ circles around the nucleus
(in a velocity of v)

Problems of classical physics:

accelerating charged particle ⇨ radiate energy
⇨ lose E
⇨ drops into nucleus



$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad ⇨ \quad \frac{1}{2}mv^2 = \frac{Ze^2}{2r} \quad \& \quad r = \frac{Ze^2}{mv^2}$$

centripetal force

coulombic attraction

$$E = KE + PE = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{1}{2}\frac{Ze^2}{r}$$

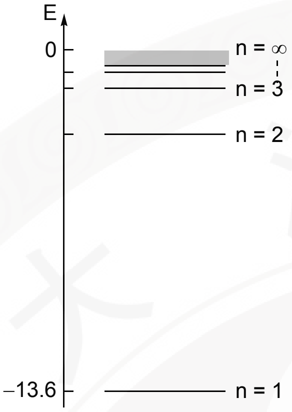
Bohr's model was based on experimental results

Proposed the angular momentum of the electron could occur only in certain increment

$mvr = n\hbar \qquad (\hbar = h/2\pi \qquad n = 1, 2, 3....)$

$$⇨ \quad v^2 = \frac{n^2\hbar^2}{m^2r^2} \quad ⇨ \quad r = \frac{Ze^2}{mv^2} = \frac{Ze^2}{m} \bullet \frac{m^2r^2}{n^2\hbar^2} = \frac{Ze^2mr^2}{n^2\hbar^2}$$

$$⇨ \quad E = -\frac{Ze^2}{2}\frac{1}{r} = -\frac{Ze^2}{2}\frac{Ze^2m}{n^2\hbar^2} \quad ⇨ \quad E = -2.178 \times 10^{-18} (Z^2/n^2)\ \text{J}$$



$E = -2.178 \times 10^{-18}$ (Z^2/n^2) J

Z: nuclear charge n: integer

Quantum number

$n\uparrow \;\Rightarrow\; r\uparrow$ (radius of orbital)

One mole with $n = 1$

⇨ $E = -13.6$ eV = –1310 kJ per mol

$n = \infty \;\Rightarrow\; E = 0$ (a reference point)

$n\downarrow \quad E\downarrow$

Has to be (–)

From $n = 6 \rightarrow n = 1$

$E_{n=6} = -2.178 \times 10^{-18}(1/6^2)$ $E_{n=1} = -2.178 \times 10^{-18}(1/1^2)$

$\Delta E = E_{n=1} - E_{n=6} = -2.178 \times 10^{-18}[(1/1^2) - (1/6^2)]$

$= -2.118 \times 10^{-18}$ J

$$\Delta E = h\frac{c}{\lambda} \quad \Rightarrow \quad \lambda = \frac{hc}{\Delta E}$$

$$\lambda = \frac{(6.626\times10^{-34})(2.9979\times10^{8})}{2.118\times10^{-18}} = 9.379\times10^{-8}\ \text{m}$$

Ex. $n = 1 \rightarrow n = 2$

$\Delta E = -2.178 \times 10^{-18}(^1/_{2^2} - 1)$

$= 1.634 \times 10^{-18}$ J

$\lambda = 1.216 \times 10^{-7}$ m $= 121.6 \times 10^{-9}$ m = 121.6 nm

For H: $n = 5 \rightarrow n = 2$ blue
$n = 4 \rightarrow n = 2$ green
$n = 3 \rightarrow n = 2$ red

Overall: $\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.178 \times 10^{-18}\ \text{J} \left(\frac{1}{n^2_{\text{f}}} - \frac{1}{n^2_{\text{i}}} \right)$

$n = 1$ ⇨ ground state
From $n = 1 \rightarrow n = \infty$ ⇨ remove e^- from the ground state
$\Delta E = -2.178 \times 10^{-18}(^1/_{\infty^2} - 1) = 2.178 \times 10^{-18}$ J

◎ Problems with Bohr's model
Only works for H atom
⇨ can not be correct

The idea of quantization is influential

※ The quantum mechanical description of the atom

臺灣大學化學系 NTU Chemistry

1925–1926
Heisenberg, de Broglie, Schrödinger
⇨ Wave mechanics
or quantum mechanics

The Nobel Prize in Physics

1911 Wilhelm **Wien** "for his discoveries regarding the laws governing the radiation of heat"

1918 Max Karl Ernst Ludwig **Planck** "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta"

1921 Albert **Einstein** "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect"

1922 Niels Henrik David **Bohr** "for his services in the investigation of the structure of atoms and of the radiation emanating from them"

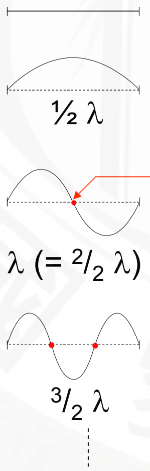
1929 Prince Louis-Victor Pierre Raymond **de Broglie** "for his discovery of the wave nature of electrons"

1932 Werner Karl **Heisenberg** "for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen"

1933 Erwin **Schrödinger and** Paul Adrien Maurice **Dirac** "for the discovery of new productive forms of atomic theory“

1945 Wolfgang **Pauli** "for the discovery of the Exclusion Principle, also called the Pauli Principle"

◎ A simple model: standing wave of a confined string



Length = l

λ: wave length

A node (節點): zero amplitude

With one node:

λ is smaller ⇨ energy is higher

$E = h\nu = hc/\lambda$

With two nodes:

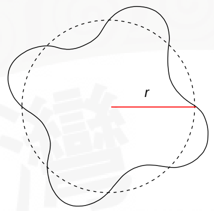
λ is even smaller ⇨ E is even higher

There are limitations: $l = n(\frac{1}{2}\lambda)$ or $\lambda = 2l/n$

$n = 1, \lambda = 2l$

$n = 2, \lambda = l$

If in a circle



Limitations: $2\pi r = n\lambda$ $n = 1, 2, 3\ldots\ldots$

Apply de Broglie equation:

$$\lambda = \frac{h}{mv} \quad \Rightarrow \quad 2\pi r = n\lambda = \frac{nh}{mv}$$

$$\Rightarrow \quad mvr = \frac{nh}{2\pi} = n\hbar$$

※ Schrödinger equation

A general form

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

- E: Energy of the atom: PE + KE of e^-
- Ψ: Wave function: describes e^- position in space
- $\hat{H}$: An operator called Hamiltonian

⇨ Found many solutions

Ψ_1	E_1
Ψ_2	E_2
Ψ_3	E_3
⋮	⋮
orbital	corresponding E

※ Heisenberg's uncertainty principle

In fact, the exact path of e⁻ can not be determined

$$\Delta x \cdot \Delta p \geqq \frac{h}{4\pi}$$

Uncertainty of particle position ← Δx

momentum ← Δp

$\Delta(mv)$: uncertainty of particle momentum

Ex. Hydrogen atom: $r \sim 0.05$ nm

Assume positional accuracy of e^-: 1% of r

Q: Δv ?

Soln: $\Delta x = (0.05 \text{ nm})(0.01) = 5 \times 10^{-4} \text{ nm} = 5 \times 10^{-13}$ m

$m_e = 9.11 \times 10^{-31}$ kg

$h = 6.626 \times 10^{-34}$ kg•m²/s

$$\Delta x \bullet \Delta p = \frac{h}{4\pi} \quad ⇨ \quad \Delta x \bullet m\Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi m \Delta x} = 1.15 \times 10^{8} \text{ m/s}$$ ← highly inaccurate

However, for a ball with $r = 0.05$ m, $m = 0.2$ kg

$\Delta x = (0.05 \text{ m})(0.01) = 5 \times 10^{-4}$ m

$\Delta v = 5 \times 10^{-31}$ m/s ← very accurate

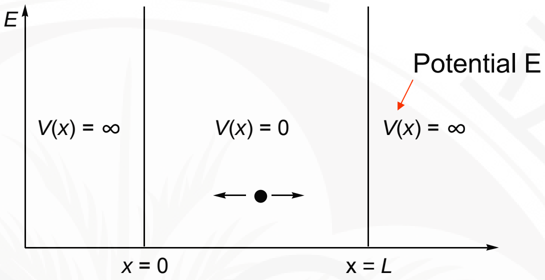
⇨ Macroscopically, no problem

※ The particle in a box

A hypothetical situation

1. Illustrate the math
2. Show some characteristics of wave function
3. Show how E quantization occurs

The model



Particle mass: *m*

One dimensional movement (on x-axis)

The only possible energy is KE

In Schrödinger equation

The operator for KE: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

A function of x

$$\hat{H}\Psi = E\Psi \quad ⇨ \quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

The connection with classical physics

The classical wave equation for standing wave:

$$y(x,t) = 2A\sin(\frac{2\pi}{\lambda}x)\cos(2\pi\nu t)$$

$$⇨ \quad \frac{d^2y(x)}{dx^2} = -(\frac{2\pi}{\lambda})^2 y(x)$$

Use de Broglie eq. $\frac{1}{\lambda} = \frac{p}{h}$ ⇨ $\frac{d^2y(x)}{dx^2} = -\frac{p^2}{\hbar^2}y(x)$

$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$ ⇨ $p^2 = 2mE$ ⇨ $\frac{d^2y(x)}{dx^2} = -\frac{2mE}{\hbar^2}y(x)$

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

⇨ $$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

2nd derivative of a function = the same function

⇨ Points to a sine function

Ex. $$\frac{d^2}{dx^2}(A\sin kx) = A\frac{d}{dx}\left(\frac{d\sin kx}{dx}\right) = A\frac{d}{dx}(k\cos kx)$$

$$= Ak\frac{d\cos kx}{dx} = Ak(-k\sin kx)$$

$$= -k^2 A\sin kx$$

Compare

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \qquad \text{and} \qquad \frac{d^2}{dx^2}(A\sin kx) = -k^2 A\sin kx$$

If $\boxed{A\sin kx = \Psi}$ ⇨ $\frac{d^2\psi}{dx^2} = -k^2\psi$

⇨ $k^2 = \frac{2mE}{\hbar^2}$ ⇨ $E = \frac{\hbar^2 k^2}{2m}$

A, *k* ?

Apply boundary conditions (to make sense):

1. Must be confined in the box
2. The total probability of finding the particle = 1
3. The wave function must be continuous

$\Psi = A\sin(kx)$

1. At $x = 0$ $\Psi = 0$
   At $x = L$ $\Psi = 0$

   for $\sin\theta = 0$ ⇨ $\theta = 0^{\circ}, 180^{\circ}, 360^{\circ}, \ldots.$

   At $x = 0$ $\Psi = A\sin(kx) = A\sin(0) = 0$
   At $x = L$ $\Psi = A\sin(kL) = 0$
   ⇨ $kL = n\pi$ ⇨ $\boxed{k = \frac{n\pi}{L} \quad n = 1, 2, 3, ..}$

2. Important: The physical meaning of Ψ is that Ψ^2 is the probability

Thus: Total probability of finding the particle in the box $= \int_0^L \psi^2(x)dx = 1$

$\Psi(x) = A\sin(kx)$

⇨ $\Psi^2(x) = A^2\sin^2(kx) = A^2\sin^2(\frac{n\pi}{L}x)$

⇨ $\int_0^L A^2\sin^2(\frac{n\pi}{L}x)dx = 1$

⇨ $$\underbrace{\int_0^L \sin^2(\frac{n\pi}{L}x)dx}_{\parallel} = \frac{1}{A^2}$$

Ref:

$$\int \sin^2(ax)dx = \frac{1}{2}x - \frac{1}{4a}\sin(2ax)$$

⇨ $\frac{L}{2} = \frac{1}{A^2}$ ⇨ $\boxed{A = \sqrt{\frac{2}{L}}}$

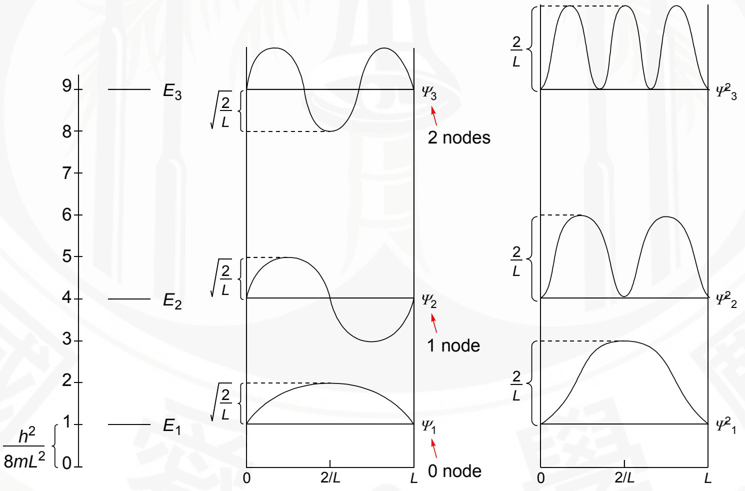
$\Psi = A\sin(kx)$ $\quad A = \sqrt{\frac{2}{L}}$ $\quad k = \frac{n\pi}{L}$ $\quad n = 1, 2, 3, \ldots.$

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

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (n\pi/L)^2}{2m} = \frac{n^2 h^2}{8mL^2}$$

$n = 1$ $\quad \psi_1 = \sqrt{\frac{2}{L}}\sin(\frac{\pi}{L}x)$ $\quad E_1 = \frac{h^2}{8mL^2}$

$n = 2$ $\quad \psi_2 = \sqrt{\frac{2}{L}}\sin(\frac{2\pi}{L}x)$ $\quad E_2 = \frac{4h^2}{8mL^2} = \frac{h^2}{2mL^2}$



Boundary cond. ⇨ quantized E level, n: quantum #

$n = 0$ ⇨ $\Psi(x) = 0$, $\Psi^2(x) = 0$ ⇨ can't be true

⇨ $n \neq 0$, lowest $E \neq 0$

⇨ $n = 1$ having the lowest E (zero-point energy)

※ The wave equation for the hydrogen atom

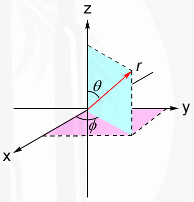
✓ The electron movement in three dimension is considered

✓ Potential E due to charge-charge attraction is included

⇨ Apply boundary conditions
⇨ Solve the differential equation
⇨ Obtain a set of solutions:
the wave functions for an electron

The quantum numbers appear:
n – the principal quantum number
l – the angular momentum quantum number
m_l – the magnetic quantum number

Using spherical polar coordinate



$$\psi_{n,l,m}(r,\theta,\phi)=R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_{m}(\phi)$$

$n = 1$, $l = 0$, $m_l = 0$ 1s orbital

$$\psi_{1s}=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2}e^{-\sigma}$$

$Z = 1$ for hydrogen $\sigma=\frac{Zr}{a_o}$

$$a_o=\frac{\varepsilon_o h^2}{\pi m e^2}=5.29\times10^{-11}\text{ m}$$

($\varepsilon_o = 8.85 \times 10^{-12}$ $C^2J^{-1}m^{-1}$)

↑ Vacuum permittivity (真空介電係數）

$n = 2$, $l = 1$, $m_l = +1$ $2p_x$ orbital

$$\psi_{2p_x}=\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2}\sigma e^{-\sigma/2}\sin\theta\cos\phi$$

✓ Energies of hydrogen's electron

$$\underset{\substack{\uparrow \\ n\,=\,1,\,2,\,3,\,..}}{E_n} = -\frac{Z^2}{n^2}\left(\frac{me^4}{8\varepsilon_o^2 h^2}\right) = -2.178\times10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$$

E depends only on *n*
(true for one electron system)
Same as derived from Bohr's model

Cf. Bohr's model

$$E = -\frac{2\pi^2 me^4}{h^2}\left(\frac{Z^2}{n^2}\right) = -2.178\times10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$$

(expressed in cgs unit)

※ Physical meaning of a wave function

Wave function Ψ:
Describes the state of a system
Contains information about all the properties of the system that are open to experimental determination
By uncertainty principle, it is difficult to know the exact position and direction of movement

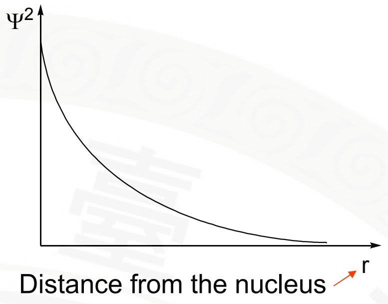
◎ Born interpretation:

$$\frac{\Psi_1^2}{\Psi_2^2} = \frac{\overset{\nwarrow \text{Probability of finding } e^- \text{ at position 1}}{N_1}}{N_2}$$

Ψ^2: a function about probability distribution

Postulate:
The probability that a particle will be found in the volume element $d\tau$ at the point r is proportional to $|\Psi(\text{r})|^2\, d\tau$

Ex. 1s orbital for H atom



Real interest:
Finding total probability of e^- at a particular distance

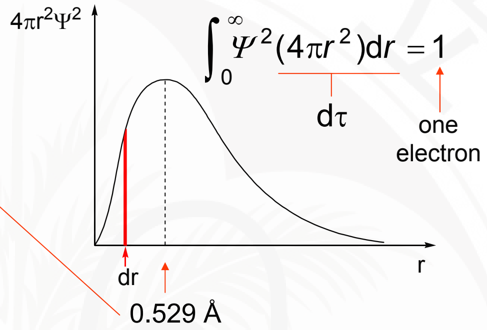
The real probability distribution:

$$\Psi^2 \cdot (4\pi r^2)$$

The most probable distance to find e^-

⇨ Same as based on Bohr model (n = 1)

⇨ Called Bohr radius



$$\int_0^\infty \underbrace{\Psi^2(4\pi r^2)dr}_{d\tau} = \underset{\text{one electron}}{1}$$

◎ Summary

Bohr model: a fixed path

Quantum mechanics: a probability

Normally the pictorial boundary shows 90% probability inside the boundary
(for 1s of H, r = 1.4 Å)

Note:
Simple pictorial models
always oversimplify the phenomenon

※ The characteristics of hydrogen orbitals

◎ Quantum numbers

✓ The principal quantum number: n (integer)

$n = 1, 2, 3, \ldots\ldots$

Related to the size and E

$n\uparrow$ r↑ E↑

↑

Average distance

✓ The angular quantum number: l (integer)

For each n, $l = 0 — n-1$

Related to the angular momentum of an e^-

Determines the shape

$l = 0$	s orbital
$l = 1$	p orbital
$l = 2$	d orbital
$l = 3$	f orbital

$n = 1 \quad l = 0 \quad ⇨ \quad 1s$

$n = 2 \quad l = 0 \quad ⇨ \quad 2s$

$n = 2 \quad l = 1 \quad ⇨ \quad 2p$

⋮ ⋮ ⋮

✓ The magnetic quantum number: m_l (integer)

$m_l = l$…….$-l$ (including 0)

Related to the orientation in space

$l = 1$ ⇨ $m_l = 1, 0, -1$ ⇨ p_x, p_y, p_z

$l = 2$ ⇨ $m_l = 2, 1, 0, -1, -2$ ⇨ $d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx}$

◎ Summary

n determines the total E: $E_n = -\frac{1}{n^2}(\frac{Z^2e^2}{2a_o})$

l determines the square of the total angular momentum:

$$M^2 = l(l+1)\hbar^2$$

m_l determines the z component of the angular momentum:

$$M_z = m\hbar$$

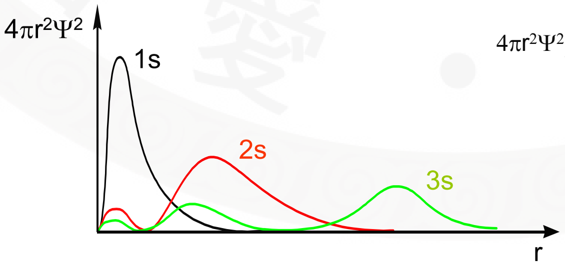
※ Orbital shapes and energies

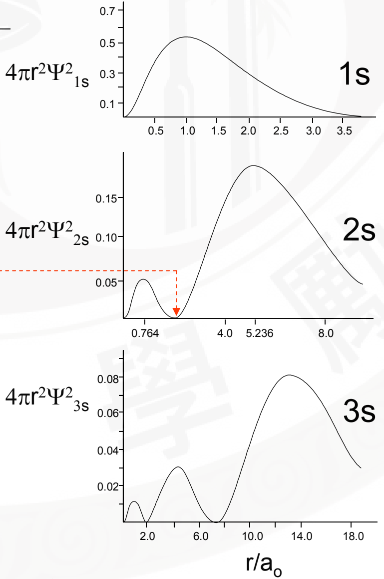
✓ Probability distribution of s orbitals ⇨

Spherical shape

Nodal surface or node

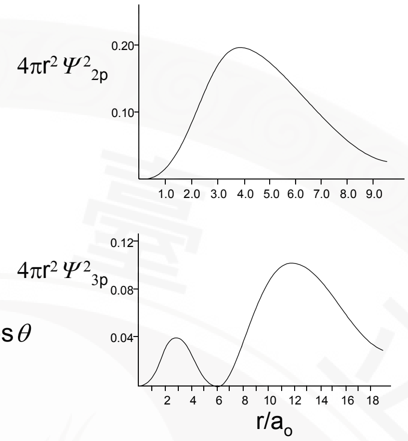
n ↑ number of nodes ↑ E ↑





(a_o: Bohr radius)

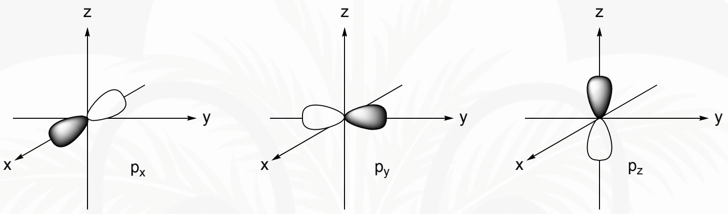
✓ Probability distribution of p orbitals



Contain two lobes

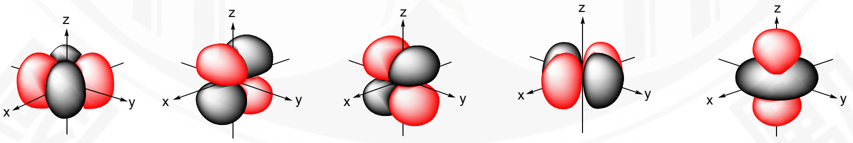
$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} \sigma\, e^{-\sigma/2} \cos\theta$$

Three subshells



✓ d subshells: 5 orbitals

m_l = 0	±1	±2
d_{z^2}	d_{xz}	d_{xy}
	d_{yz}	$d_{x^2-y^2}$



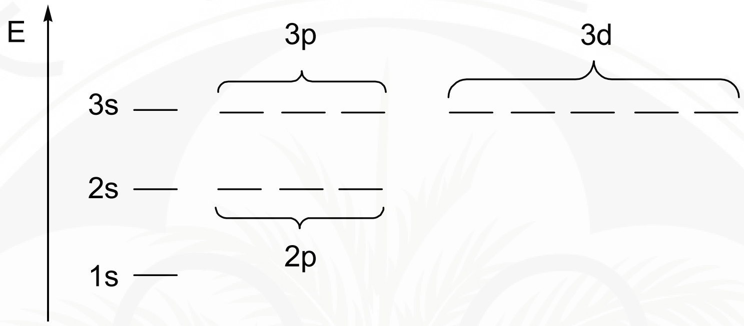
d_{xy} d_{xz} d_{yz} $d_{x^2-y^2}$ d_{z^2}

✓ The energy level

For H atom: E is determined by n

same n ⇨ same E

⇨ these orbitals are degenerate



※ Electron spin and Pauli principle

✓ In fact, a spin quantum number (m_s) exists

m_s = +1/2 or –1/2

Electron has its own angular momentum

⇨ Imagine the electron as spinning on its own axis like earth

⇨ Behaves like a tiny magnet

✓ Pauli (1900 – 1958) principle

In a given atom, two electrons can not have the same n, l, m_l and m_s

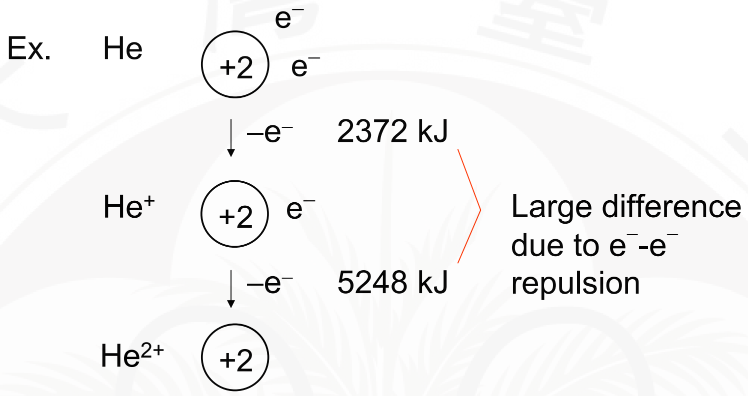
⇨ In the same orbital, n, l, and m_l must be the same

⇨ m_s must be different

※ Polyelectronic atoms

Very complicate

Problem: Electrons influence each other



Large difference due to e^--e^- repulsion

◎ The effective charge approximation

(A very rough model)

Considering e^--e^- repulsion as reducing the nuclear charge

In other words:

The electron is shielded (screened) from the nuclear charge by the other electrons

Ex. Hypothetical He $\overset{+}{Z_{eff}}$ e^-

Becomes a one e^- system

⇨ Leads to hydrogen like orbitals

⇨ But the sizes and energies are different from that of H atom

Gives only a qualitative picture
(similar to the hydrogen model)
Quantitatively not accurate

※ More about polyelectronic model

In hydrogen

Schrödinger equation can be solved exactly

In polyelectronic atoms

Schrödinger equation can not be solved exactly

Approximations are required

The self-consistent field (SCF) method can be used

✓ The self-consistent field (SCF) method

Considering the electron as residing in a field
Composed of the nucleus
and other electrons (in their various orbitals)

The differential equation contains four parts

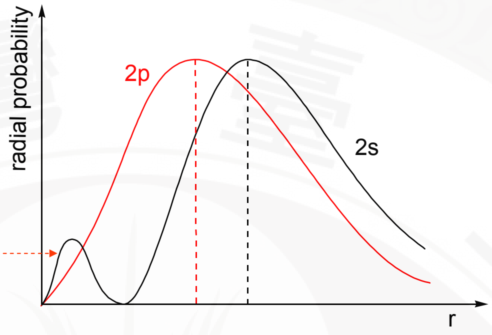
1. The usual KE contribution
2. $V_{\text{electron-nucleus}}$ (attraction)
3. The PE due to the charge density of the e^{-}s in the other occupied orbitals
4. The spin correlation effect

⇨ A set of one electron equations can be obtained and solved using successive approximation

✓ In polyatomic atoms

E of orbitals depend on *n* and *l*

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



2s is more penetrating

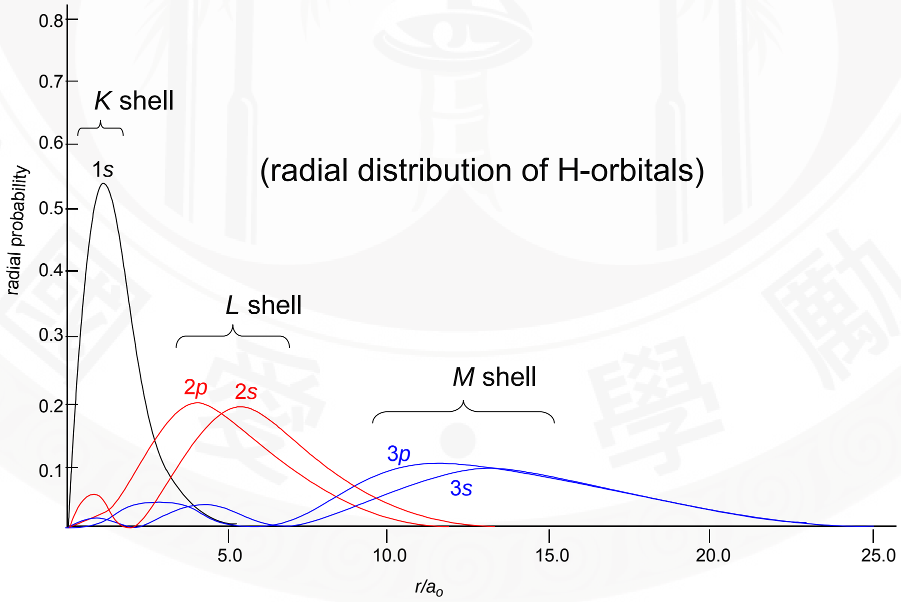
Most probable distance is smaller for 2p

But $E_{2s} < E_{2p}$ because of the penetrating effect of 2s

Similarly, $E_{4s} < E_{3d}$

More penetrating

✓ There is a sharp separation of the individual electron shells



(radial distribution of H-orbitals)

※ The aufbau principle (遞建原理) and the periodic table

1869 Mendeleev

The first periodic table

A correlation of chemical properties and AW of elements

◎ The periodicity based on quantum mechanics

The aufbau principle:
As the atomic number increased the electrons are added in order

---

atom electron configuration

1s 2s 2p

H $1s^1$ [↑]

He $1s^2$ [↓↑] ← Pauli exclusion principle

└ $n = 1$ completely filled

C $1s^2 2s^2 2p^2$ [↓↑] [↓↑] [↑][↑][ ]

Hund's rule: the lowest-energy config. Is the one having maximum number of unpaired e⁻s in a set of degenerate orbitals

O $1s^2 2s^2 2p^4$ [↓↑] [↓↑] [↓↑][↑][↑]

Ne $1s^2 2s^2 2p^6$

└ $n = 1$, $n = 2$ } completely filled

Core electrons ↓

Na $1s^2 2s^2 2p^6 3s^1$ or $[Ne]3s^1$

Valence electron (involved in bonding)

Elements with the same valence electronic configuration

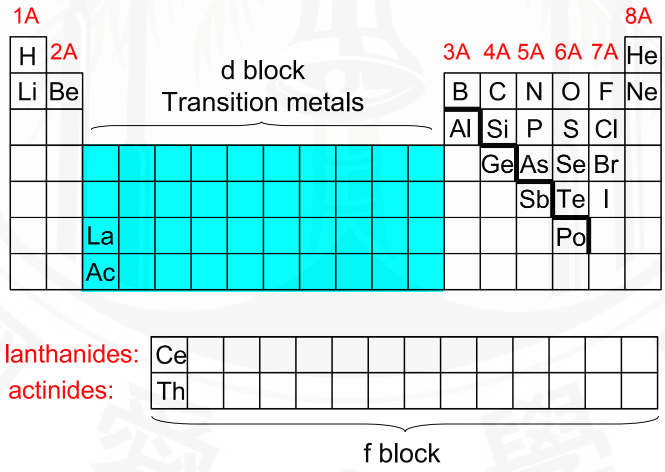
⇨ Show similar chemical behavior

⇨ Grouped in the vertical column

Li	[He] $2s^1$
Na	[Ne] $3s^1$
K	[Ar] $4s^1$

Some notes

1. $(n+1)$s before nd
2. After lanthanide (La: [Xe]$6s^2 5d^1$)
   - ⇨ starts to fill in 4f
     Ce: [Xe]$6s^2 4f^1 5d^1$
   - ⇨ the lanthanide series
3. After actinide (Ac: [Rn]$7s^2 6d^1$)
   - ⇨ fill in 5f
   - ⇨ actinide series



4. Group labels: 1A, 2A..........8A

   The total number of valance e^-

5. 1A–8A : the main group elements

※ Periodic trends in atomic properties

◎ Ionization energy

$X(g) \rightarrow X^+(g) + e^-$ energy change

Atom
or ion

Gas phase

Sometimes expressed as ionization potential

unit: eV = 1.602×10^{-19} J

~23 kcal/mol

~96 kJ/mol

Ex. Al: $[Ne]3s^23p^1$

$Al(g) \rightarrow Al^+(g) + e^-$

I_1 = 580 kJ/mol
I_2 = 1815
I_3 = 2740
I_4 = 11600

I_1: The first ionization E
- ⇨ Removes the highest-E e^-
- ⇨ Reflect the E of the orbital

I_2: The second ionization E
- ⇨ The charge effect comes to play

I_4: very large (Al^{3+}: [Ne])
- ⇨ Starts to remove core e^-

[Ne]	$3s^1$	$3s^2$	$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^4$	$3s^23p^5$	$3s^23p^6$
	Na	Mg	Al	Si	P	S	Cl	Ar
I_1 (kJ/mol)	495	735	$\boxed{580}$	780	1060	$\boxed{1005}$	1255	1527

General trend ⟶ increasing

Shielding effect of core e^- ⇨ similar
Increasing of Z^+_{eff} ⇨ more important

Special case
Al: the lower value is due to the shielding effect of $3s^2$

S: the lower value is due to pairing energy
(e^--e^- repulsion)

Down a group

	I_1 (kJ/mol)		size
Li	520	↓	↓
Na	495		
K	419	decreasing	increasing
Rb	409		
Cs	382		

Z^+_{eff} similar ⇨ Size is more important

◎ Electron affinity

$X(g) + e^- \rightarrow X^-(g)$ energy change
ΔH (–): exothermic

In a period: atomic number ↑
energy change: more negative

Ex.	C	N	O
	–122.5	not available	–141.4 (kJ/mol)
	$1s^22s^22p^2$	$1s^22s^22p^3$	$1s^22s^22p^4$
	↓	↓	↓
	$1s^22s^22p^3$	$1s^22s^22p^4$	$1s^22s^22p^5$

Z^+_{eff} ⟶ increase

N^-: unstable due to e^--e^- repulsion

Down a group

	kJ/mol
F	$\boxed{-327.8}$
Cl	–348.7
Br	–324.5
I	–295.2

← F is too small:
e^--e^- repulsion is important

↓ Less negative

Z^+_{eff} similar ⇨ Size is more important
(the difference is not large)

◎ Atomic radius

difficult to determine just like orbitals

Usual way

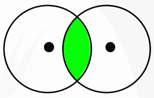
Br—Br $\xrightarrow{\text{Cut in half}}$ r for Br = $\frac{228}{2}$ = 114 pm

228 pm

(two identical atoms)

Often called covalent atomic radii

⇨ Smaller than orbital size



For metals: treat similarly

General trend

Across the period – size ↓

Z^{+}_{eff} is more important

Down a group – size ↑

due to the increase of *n*

※ The properties of a group: The alkali metals

◎ Information contained in the periodic table

✓ The config. of valence e^- determined the chemistry

✓ Fundamental classification of elements

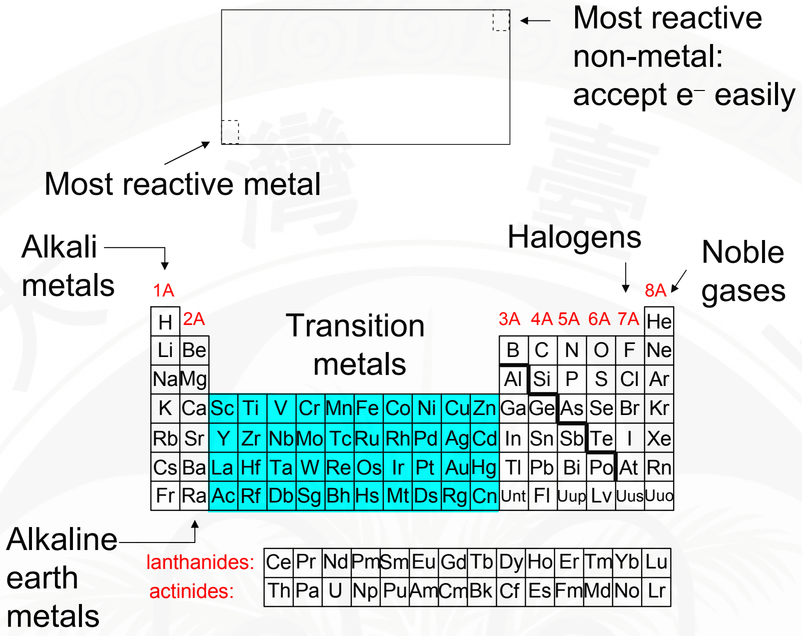
metals and nonmetals

metals: give up e^- easily

low IP

IP $\xrightarrow[\text{a period}]{}$ increasing

Elements at left-hand side have lower IP



1A																	8A
H	2A											3A	4A	5A	6A	7A	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Unt	Fl	Uup	Lv	Uus	Uuo

lanthanides:	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
actinides:	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

◎ The alkali metals

Li, Na, K, Rb, Cs, Fr

Most reactive but rare in nature

d →

mp ←

bp ←

IP ←

r →

Good reducing agents

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

$$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$

In general:

reducing ability

Li < Na < K < Rb < Cs

In aqueous solution

Li > K > Na

Ex. $2M(s) + 2H_2O(l) \rightarrow H_2(g) + 2M^+(aq) + 2OH^-(aq)$ + energy

Reason: Li^+ has high hydrating energy

Li^+	–500 kJ/mol	←	Small size
Na^+	–400		high charge density
K^+	–300		stronger interaction with H_2O