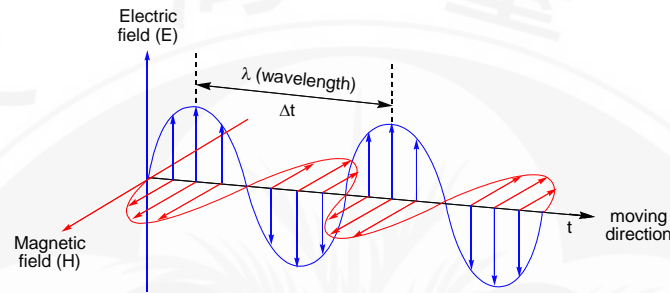※ Electromagnetic radiation (Maxwell, 1864)
  (nature of light)

Composed of perpendicular electric field and magnetic field

Electric field (E)

λ (wavelength)

Δt

moving direction

t

Magnetic field (H)

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)

intensity

Rayleigh-Jeans law

5000 K

observed spectrum

4000 K

3000 K

UV   Visible   Infra-red

wavelength (λ)

ULTRAVIOLET CATASTROPHE

Ex. A glowing iron when heated

T increases
red → white light
λ decreases
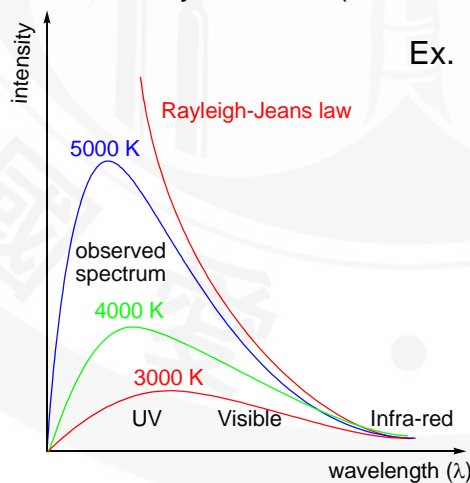
Classical physics predicts continuous profile with no maxima

1901　Max Planck postulate
　　　The energies are discrete and are integers of $h\nu$
　　　　$h = 6.626 \times 10^{-34}$ Js

　　　　└── Planck constant

　　　Energies are gained or lost in $nh\nu$
　　　　　　$\Delta E = nh\nu$

⇨ 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)

1887　Hertz
　　　Light strikes on metal　　　⇨　　　e^- emitted
　　　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
  ✓   Electromagnetic radiation is quantized
$$E_{photon} = h\nu = hc/\lambda$$
      Predicted:
$$h\nu - h\nu_o = KE_{e^-} = \tfrac{1}{2}mv^2$$

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
Particle also has wave nature

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

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

Ex. $m_e = 9.11 \times 10^{-31}$ kg
If traveling at a speed of 1.0×10^7 m/s

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

$$= 7.3 \times 10^{-11}\ m$$

In the range of X-ray

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   ⟷   Photons
More particulate-like   More wave-like

4

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※ 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
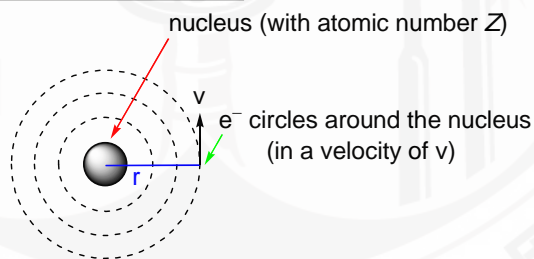　　　　　　　　　　　　　　　　　⇨　　　emits light

410 nm　434 nm　486 nm　　　　　656 nm

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

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※ The Bohr model

1913　Bohr

nucleus (with atomic number Z)

v

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

r

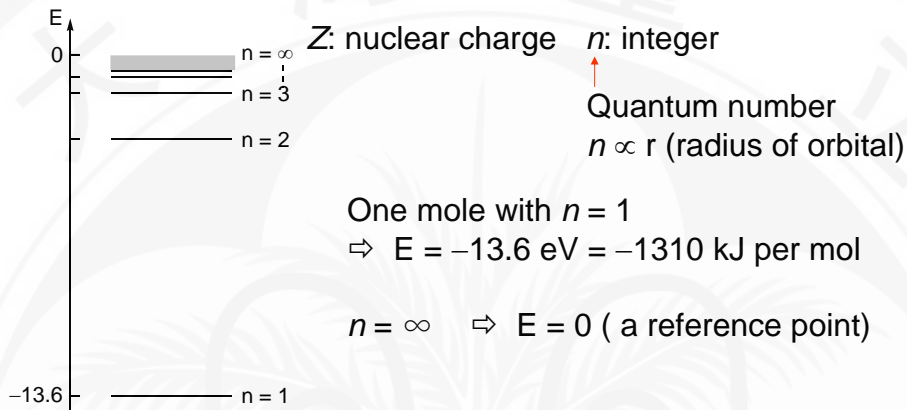Problems of classical physics:
　　accelerating charged particle　⇨　radiate energy
　　　　　　　　　　　　　　　　　⇨　lose E
　　　　　　　　　　　　　　　　　⇨　drops into nucleus

Bohr's model was based on experimental results
    Proposed the angular momentum of the electron
    could occur only in certain increment

$$mvr = n\hbar \qquad\qquad \hbar = h/2\pi$$
$$n = 1, 2, 3....$$
$$\Rightarrow E = -2.178 \times 10^{-18} (Z^2/n^2) \text{ J}$$

Z: nuclear charge n: integer

Quantum number
$n \propto r$ (radius of orbital)

One mole with $n = 1$
$\Rightarrow E = -13.6 \text{ eV} = -1310 \text{ kJ per mol}$

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

E axis: 0, -13.6
Levels: $n = \infty$, $n = 3$, $n = 2$, $n = 1$

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

Overall: $\Delta E = E_{final} - E_{initial} = -2.178 \times 10^{-18} \text{ J} \left(\dfrac{1}{n^2_f} - \dfrac{1}{n^2_i} \right)$

$n = 1 \quad \Rightarrow$ ground state
From $n = 1 \rightarrow n = \infty \quad \Rightarrow$ remove e^- from the ground state

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

The idea of quantization is influential

※ The quantum mechanical model
of the atom

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

◎ A simple model: standing wave of a confined string

Length = l

$\frac{1}{2}\lambda$ λ: wave length

A node (節點): zero amplitude

$\lambda \; (= {}^2/_2\,\lambda)$

With one node:
λ is smaller ⇨ energy is higher
$$E = h\nu = hc/\lambda$$

${}^3/_2\,\lambda$

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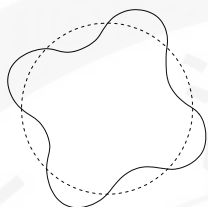
Limitations: $2\pi r = n\lambda$ $n = 1, 2, 3 \ldots\ldots$

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

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

Energy of the atom: PE + KE of e^-

Wave function: describe e^- position in space

An operator called Hamiltonian

$\Rightarrow$ Found many solutions

Ψ_1 E_1
Ψ_2 E_2
Ψ_3 E_3

orbital   corresponding E

cf. for 1s

$$\Psi = 2(\frac{Z}{a_o})^{3/2} e^{-\rho/2}$$

$$a_o = \frac{4\pi\varepsilon_o\hbar^2}{m_e e^2} \quad \rho = \frac{2Zr}{a_o}$$

※ 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

momentum
Δ(mv): uncertainty of particle momentum

※ 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

◎ Born interpretation:

$$\frac{\Psi_1^2}{\Psi_2^2} = \frac{N_1}{N_2}$$ Probability of finding e⁻ at position 1

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 $|\Psi(r)|^2 d\tau$
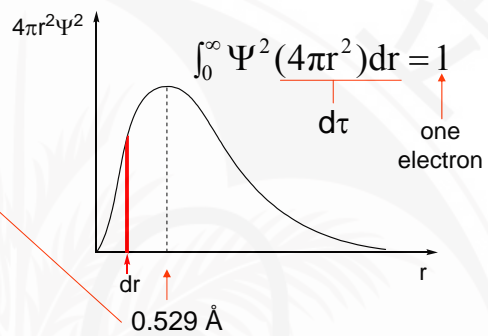
Ex.   1s orbital for H atom

Ψ^2

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

Distance from the nucleus   r
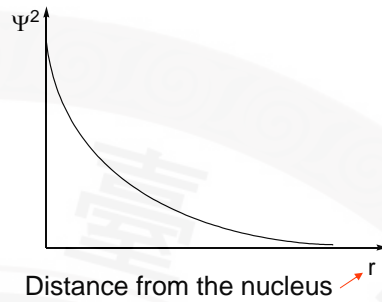
The real probability
distribution:
    $\Psi^2 \cdot (4\pi r^2)$

The most probable
distance to find e⁻

⇨ Same as based on
    Bohr model (n = 1)
⇨ Called Bohr radius

$4\pi r^2 \Psi^2$

$$\int_0^\infty \Psi^2 (4\pi r^2) dr = 1$$

$d\tau$

one
electron

r

dr

0.529 Å

◎ Summary

Bohr model: a fixed path

Quantum mechanics: a probability

Normally the pictorial boundary shows 90% probability
inside the boundary

※ Quantum numbers

✓ The principal quantum number: *n* (integer)

n = 1, 2, 3……

Related to the size and E

n ↑   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

$n = 1$	$l = 0$	⇨	1s
$n = 2$	$l = 0$	⇨	2s
$n = 2$	$l = 1$	⇨	2p

✓ The magnetic quantum number: m_l (integer)
$m_l = l \ldots\ldots -l$ (including 0)
Related to the orientation in space

$l = 1 \quad \Rightarrow \quad m_l = 1, 0, -1 \qquad \Rightarrow \quad p_x, p_y, p_z$

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

◎ Summary

n determines the total E: $\quad E_n = -\dfrac{1}{n^2}\left(\dfrac{Z^2 e^2}{2a_0}\right)$

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
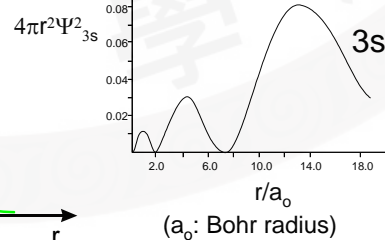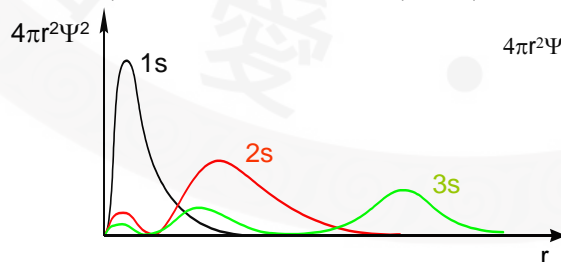
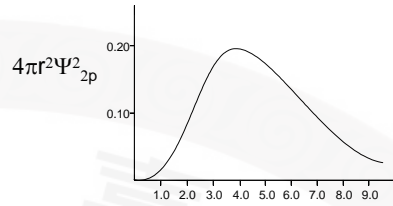✓ Probability distribution
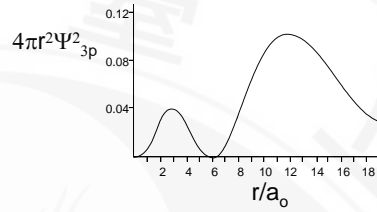of s orbitals   ⇨
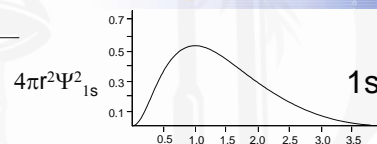
Spherical shape
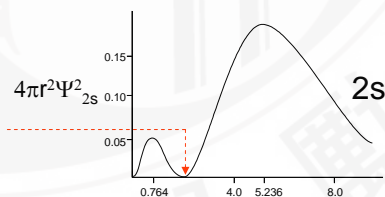
Nodal surface or node

$n \uparrow$ number of nodes $\uparrow$ E $\uparrow$

$4\pi r^2 \Psi^2_{1s}$ 1s

$4\pi r^2 \Psi^2_{2s}$ 2s

$4\pi r^2 \Psi^2_{3s}$ 3s

r/a_0
(a_0: Bohr radius)

$4\pi r^2 \Psi^2$ 1s   2s   3s   r

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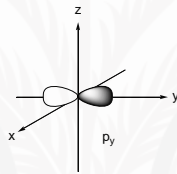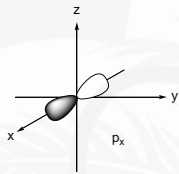✓ Probability distribution
  of p orbitals $\implies$

$4\pi r^2 \Psi^2_{2p}$

Contain two lobes

Three subshells

p_x p_y p_z

$4\pi r^2 \Psi^2_{3p}$

r/a_o
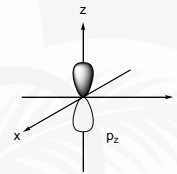
✓ d subshells: 5 orbitals

$m_l = 0$ ± 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}
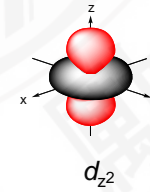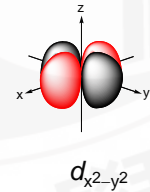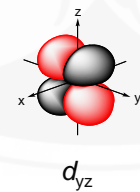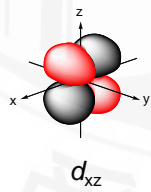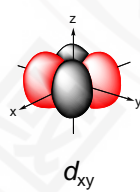
✓ The energy level

For H atom: E is determined by n
same n ⇨ same E
⇨ these orbitals are degenerate
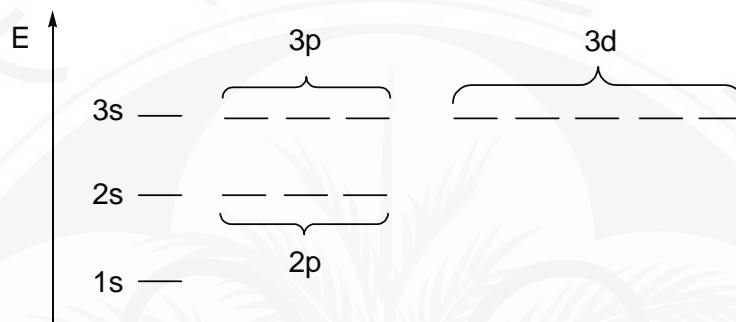
※ Electron spin and Pauli principle

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

$$m_s = +1/2 \text{ or } -1/2$$

Electron has its own angular momentum
⇨ Imagine the electron as spinning on its own axis like earth
⇨ Behaves like a tiny magnet

✓ Pauli 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

Ex.　　He　　　e^-
　　　　　$(+2)$　e^-

　　　　　↓ $-e^-$　　2372 kJ

He$^+$　　$(+2)$　e^-　　⎫ Large difference
　　　　　　　　　　　　　　due to e^--e^-
　　　　　↓ $-e^-$　　5248 kJ　　repulsion

He^{2+}　$(+2)$
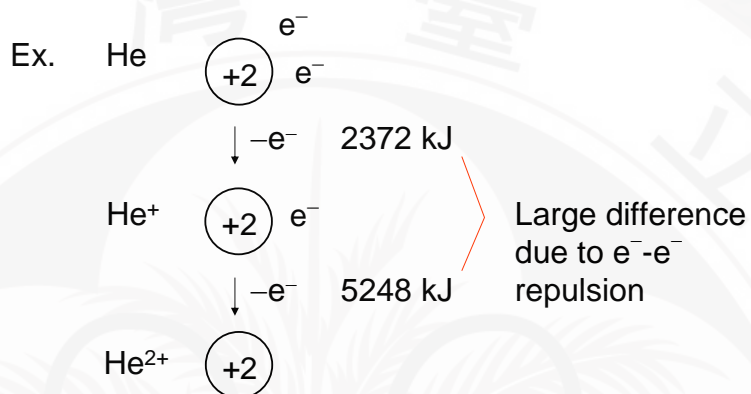
◎ The effective charge approximation
　　　　(A very rough model)

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

　　　　　(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

✓ In polyatomic atoms

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

2s is more penetrating
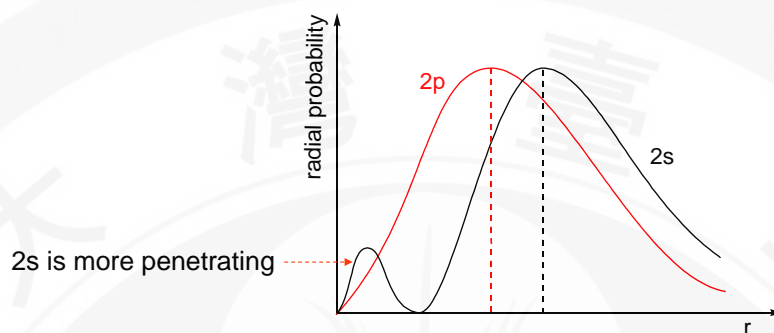
Most probable distance is smaller for 2p
But $E_{2s} < E_{2p}$ because of the penetrating effect of 2s
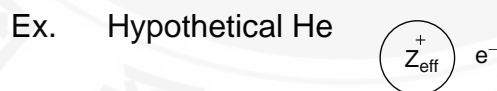
Similarly, $E_{4s} < E_{3d}$

More penetrating

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

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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 ↓↑

    ᴸ $n = 1$ 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

    ᴸ $n = 1$
      $n = 2$ } 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

1A   8A

H	2A		d block							3A	4A	5A	6A	7A	He
Li	Be		Transition metals							B	C	N	O	F	Ne
										Al	Si	P	S	Cl	
											Ge	As	Se	Br	
												Sb	Te	I	
	La												Po		
	Ac														

lanthanides: | Ce | | | | | | | | | | | | |

actinides: | Th | | | | | | | | | | | | |
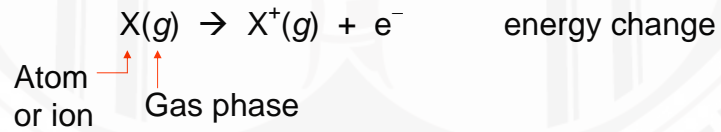
f block

4. Group labels: 1A, 2A….......8A

⎿ The total number of valance e⁻

5. 1A–8A : the main group elements

※ Periodic trends in atomic properties
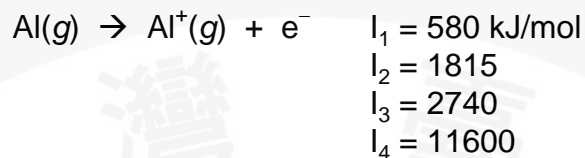
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◎ Ionization energy

$$X(g) \rightarrow X^+(g) + e^- \qquad \text{energy change}$$

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: $[Ne]3s^2 3p^1$

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

$I_1 = 580$ 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^-

	$[Ne]3s^1$	$3s^2$	$3s^2 3p^1$	$3s^2 3p^2$	$3s^2 3p^3$	$3s^2 3p^4$	$3s^2 3p^5$	$3s^2 3p^6$
	Na	Mg	Al	Si	P	S	Cl	Ar
I_1 (kJ/mol)	495	735	580	780	1060	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
Rb	409
Cs	382

decreasing ↓   increasing ↓

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   --   −141.4 (kJ/mol)

not available

$1s^2 2s^2 2p^2$ $1s^2 2s^2 2p^3$ $1s^2 2s^2 2p^4$

↓   ↓   ↓

$1s^2 2s^2 2p^3$ $1s^2 2s^2 2p^4$ $1s^2 2s^2 2p^5$

Z^+_{eff} ———————→ increase

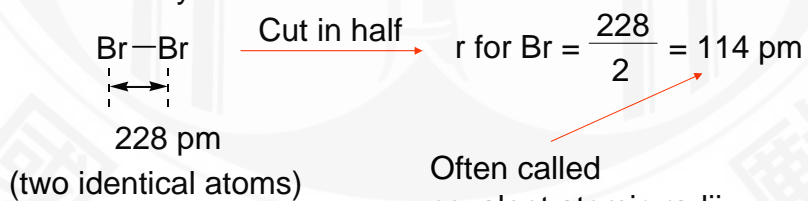N^-: unstable due to e^--e^- repulsion

Down a group

	kJ/mol
F	−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   Cut in half   r for Br = $\dfrac{228}{2}$ = 114 pm

228 pm
(two identical atoms)

Often called
covalent atomic radii
⇨ Smaller than orbital size

overlap