Chapter 12

Statistical Thermodynamics

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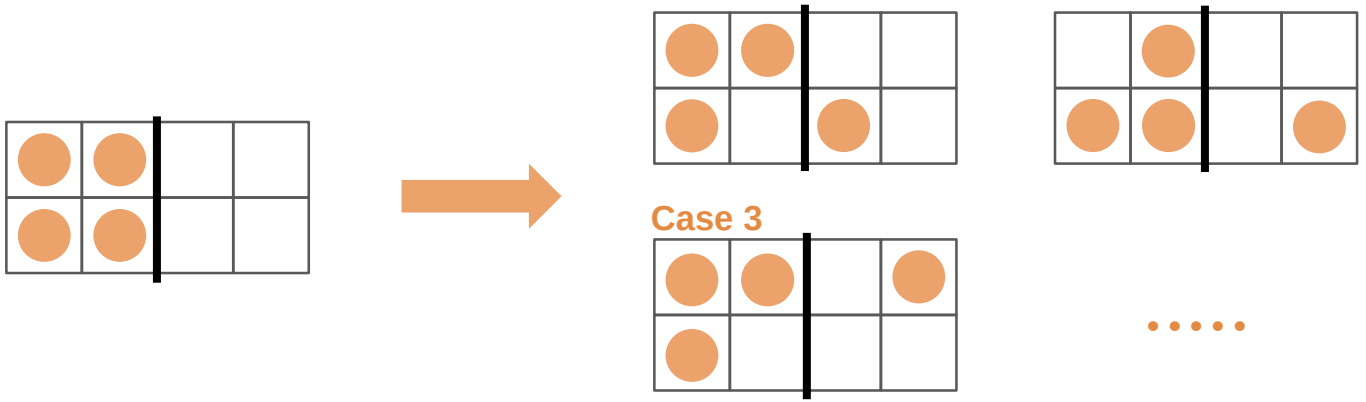
12.1 Introduction

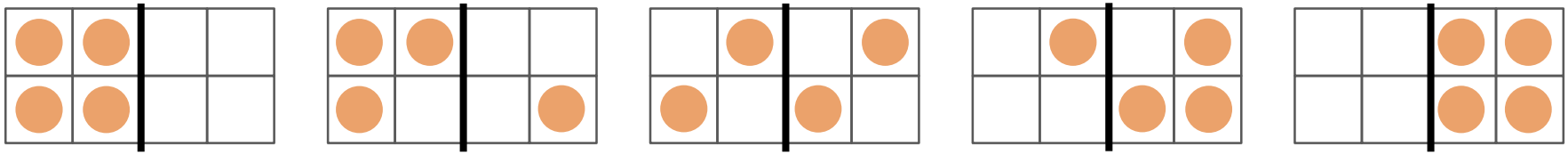
- Toy model: Configuration of molecules in a room
  - Initial state which 4 molecules exist at left side
  - How many rearrangement if one molecule moves to right side?



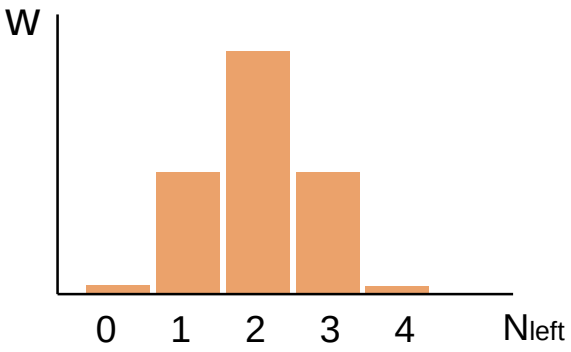
$w = {}_4C_3 \times {}_4C_1 = 16$: sixteen rearrangements!

12.1 Introduction

- Rearrangements for all states



N_{left}	4	N_{left}	3	N_{left}	2	N_{left}	1	N_{left}	0
N_{right}	0	N_{right}	1	N_{right}	2	N_{right}	3	N_{right}	4
w	1	w	16	w	36	w	16	w	1

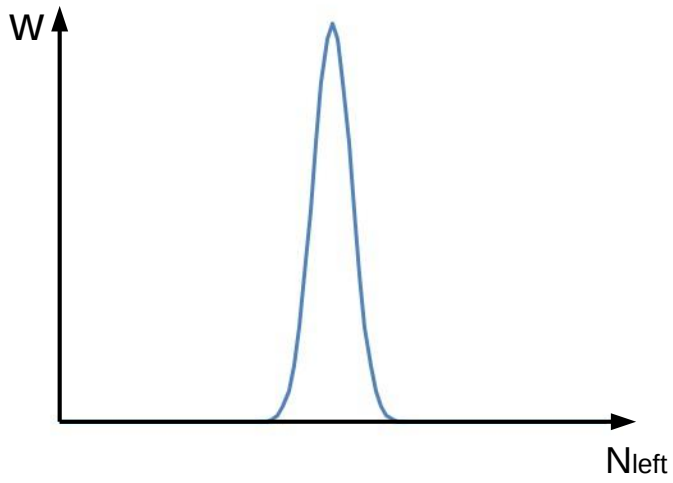


State with 2 molecules at left is most probable

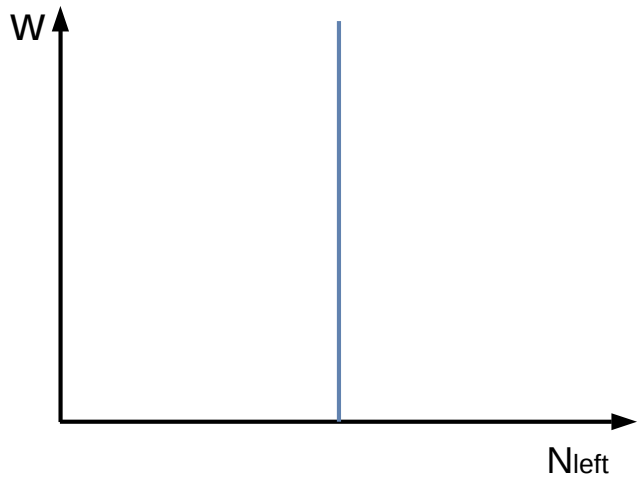
12.1 Introduction

- What if there are large number of molecules and spaces

100 molecules with 200 spaces



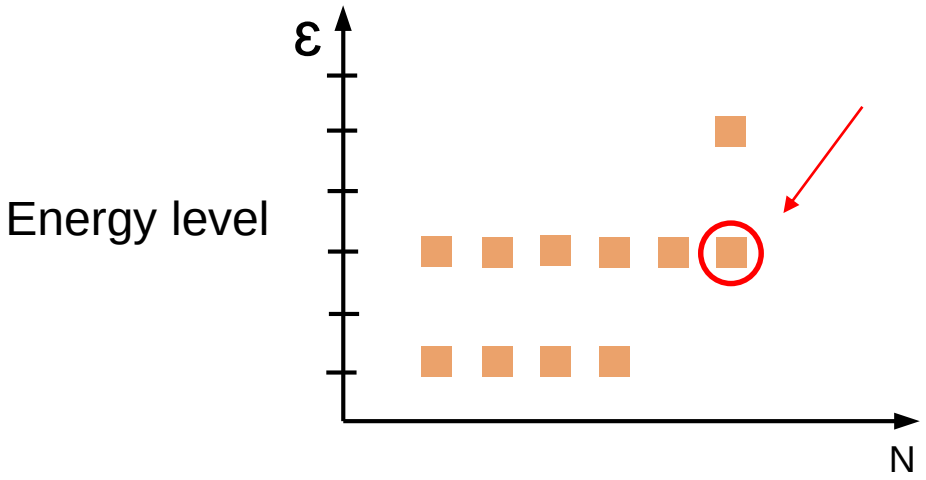
1000 molecules with 2000 spaces



For a large system, only most probable state is possible.
Nature always converge to most probable state

12.1 Introduction

- Equilibrium of macroscopic system



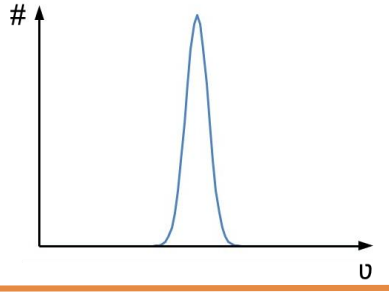
: energy state (quantum state)

Microstate
(# of molecules in each energy state)

: degeneracy

Macro State (# of molecules in each energy level)

Thermodynamic probability : # of microstates which leads a given microstate
(# of ways)



12.2 Coin-Tossing Experiment

- Coin tossing experiment: A simplified model of thermodynamic system

  How many coins of heads when tossing 4 coins on the floor?

  macro state : number distribution of coins of head and tails

  micro state : rearrangements of coins of head and tails

http://splatter.com/

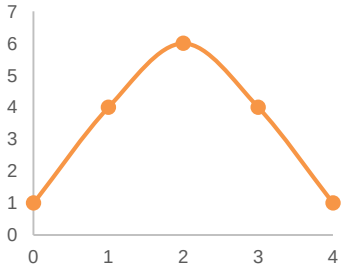
12.2 Coin-Tossing Experiment

Macro state level	Macro state specification		Micro state				Thermodynamic probability	True probability
k	N_1	N_2	coin 1	coin 2	coin 3	coin 4	w_k	p_k
1	4	0	H	H	H	H	1	1/16
2	3	1	H	H	H	T	4	4/16
			H	H	T	H		
			H	T	H	H		
			T	H	H	H		
3	2	2	H	H	T	T	6	6/16
			T	T	H	H		
			H	T	H	T		
			T	H	T	T		
			H	T	T	T		
			T	H	H	T		
4	1	3	H	T	T	T	4	4/16
			T	H	T	T		
			T	T	H	H		
			T	T	T	H		
5	0	4	T	T	T	T	1	1/16

12.2 Coin-Tossing Experiment

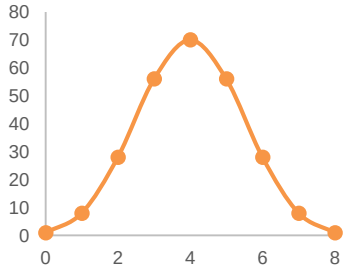
A macro state with $N_1 = N/2$ has largest number of μ-state.

The maximum value of thermodynamic probability: $w_{max} = {}_N C_{N/2} = \frac{N!}{(N/2)!\,(N/2)!}$



$N_{coin} = 4$

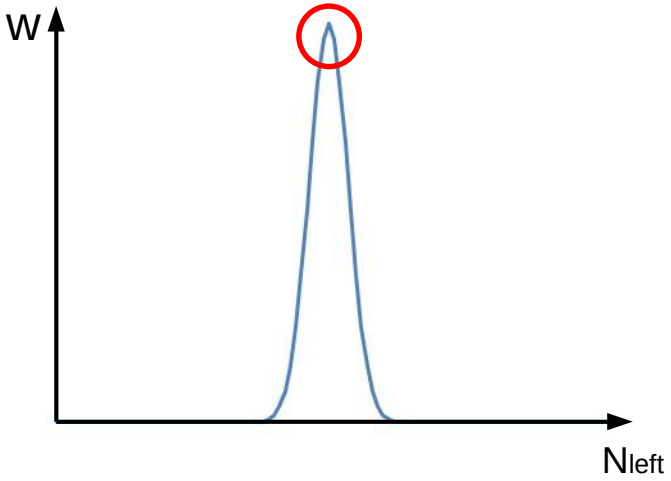
$w_{max} = 6$



$N_{coin} = 8$

$w_{max} = 70$

most probable micro state (equilibrium)



Repeating numerous times

12.2 Coin-Tossing Experiment

When repeat tossing 1000 times, $w_{max} = \frac{1000!}{(500)!(500)!}$

For such a large numbers, Stirring's approximation can be used

$$\ln(n!) = nln(n) - n$$

Then

$$\ln(w_{max}) = \ln(1000!) - 2\ln(500!) = 693$$

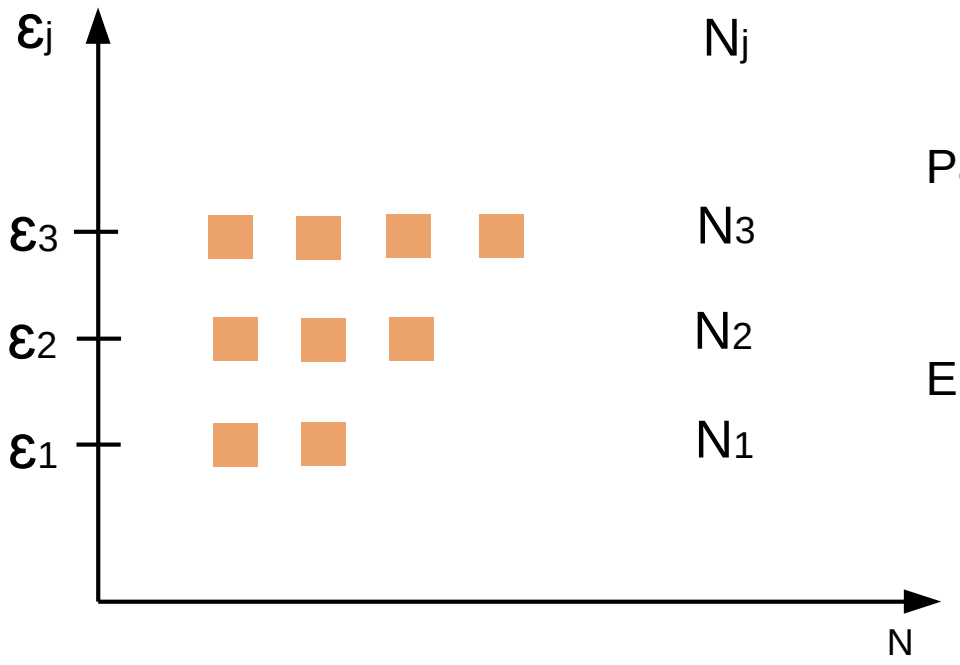
$$\log(w_{max}) = \log(\mathrm{e})\ln(w_{max}) = 0.4343 \cdot 693 \approx 300$$

$$\therefore\ w_{max} = 10^{300}$$

For a large system, the total number of microstates is very nearly equal to the maximum number; $\Omega = \sum w_k \approx w_{max}$

12.3 Assembly of Distinguishable Particles

- Distribution among energy levels for equilibrium state



Particle conservation $\sum N_i = N$

Energy conservation $\sum N_i \varepsilon_i = U$

12.3 Assembly of Distinguishable Particles

- Ex) N= 3 , U= 3ε with ε_j = 0, ε, 2ε, 3ε

Macro state level	Macro state specification				Micro state specification			Thermodynamic probability	True probability
k	N_0	N_1	N_2	N_3	A	B	C	w_k	p_k
1	2	0	0	1	0	0	3ε	3	0.3
					0	3ε	0		
					3ε	0	0		
2	1	1	1	0	0	ε	2ε	6	0.6
					0	2ε	ε		
					ε	0	2ε		
					ε	2ε	0		
					2ε	0	ε		
					2ε	ε	0		
3	0	3	0	0	ε	ε	ε	1	0.1

Most Probable → Equilibrium

12.4 Thermodynamic Probability and entropy

- Statistical concept of entropy

Ludwig Boltzmann constructed the connection between the classical concept of entropy and the thermodynamic probability.

He interpreted entropy as a degree of organization of microscopic energy.

$$S = f(w)$$

12.4 Thermodynamic Probability and entropy

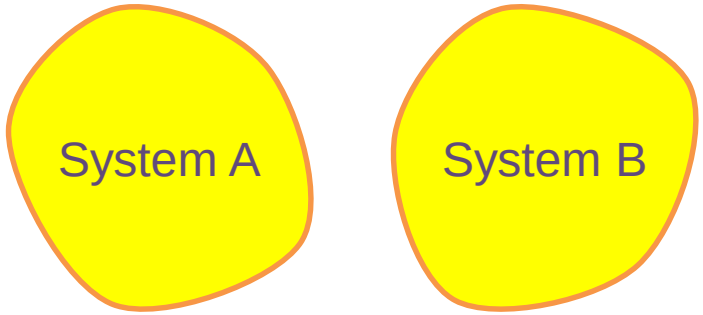
There are a few characteristics for the function of entropy.

① $f(w)$ must be a single valued, monotonically increasing function.

② Entropy is an extensive property. That is, $S_{A+B} = S_A + S_B$

③ Configuration of the system satisfies, $w_{A+B} = w_A w_B$

→ $f(w_{A+B}) = f(w_A) + f(w_b)$



$S_A = f(w_A)$ $S_B = f(w_B)$

12.4 Thermodynamic Probability and entropy

The only function for which this statement is true is the logarithm. Thus, Ludwig Boltzmann postulated the function of entropy as below.

$$S = k \ln w$$

k : Boltzmann constant (= 1.38 x 10^{-23} J/k)

w : Number of rearrangements

12.5 Quantum states and Energy levels

- Schrödinger's Equation (Postulate)

$$\Psi(x,y,z,t) = \psi(x,y,z)\phi(t) \quad \cdots$$ time dependent wave function

$$|\Psi|^2 \quad \cdots$$ probability distribution function [probability density

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

h : Planck constant

$V\Psi$: potential energy

Postulated by Schrödinger based on physical phenomena of matter wave

Also, Max born suggested statistical meaning of wave function.

12.5 Quantum states and Energy levels

- Schrödinger's Equation

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

- Separation of variables

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

Energy of the particle (constant)

$$\underbrace{\frac{1}{\psi}\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi\right]}_{f(x,y,z)\ \text{(space)}}=\underbrace{-\frac{h}{2\pi i}\frac{1}{\phi}\frac{d\phi}{dt}}_{f(t)\ \text{(time)}}=E$$

12.5 Quantum states and Energy levels

- Time dependent part

$$\frac{d\phi}{dt} = -\frac{2\pi iE}{h}\phi \longrightarrow \phi = -ce^{-\frac{2\pi iE}{h}t} \qquad [e^{i\theta} = \cos\theta + \sin\theta]$$

- Spatial part

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

$\frac{1}{2}mv_z{}^2$

$$\psi(x,y,z) = X(x)Y(y)Z(z), \qquad E = E_x + E_y + E_z$$

$$\longrightarrow \frac{\partial^2 X}{\partial x^2} + \frac{8\pi^2 m E_X}{h^2}X = 0 \longrightarrow X = A\cos px + B\sin px$$

p^2

12.5 Quantum states and Energy levels

- Boundary condition

B.C. $X(0) = 0 \longrightarrow X(L) = 0$

$$\begin{pmatrix} x = 0, X = 0 \\ x = L, X = 0 \end{pmatrix}$$

from

$$X = A\cos px + B\sin px$$

$$PL = n\pi \quad (n = 0,1,2,\dots)$$

$$P = \frac{2\pi\sqrt{2mE_X}}{h}$$

For linear motion of a free particle

$$X = X_0 \sin\frac{n\pi}{L}x = X_0 \sin\frac{2\pi\sqrt{2mE_X}}{h}x$$

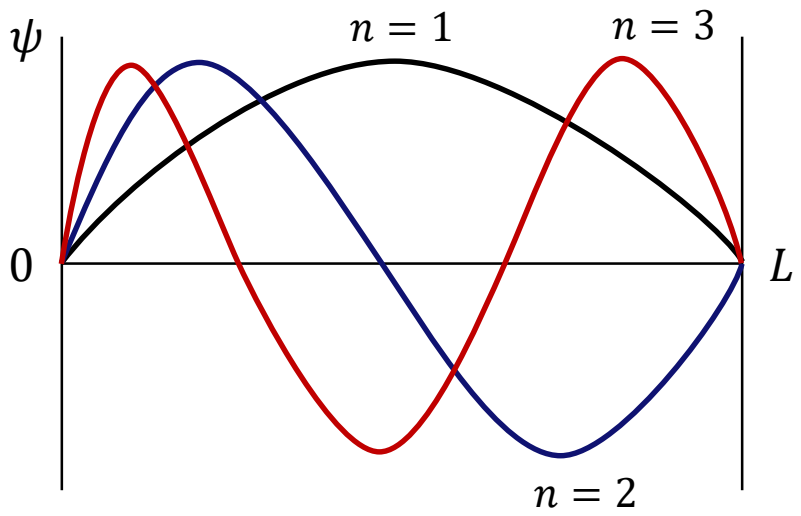
The last step is to normalize the wave function

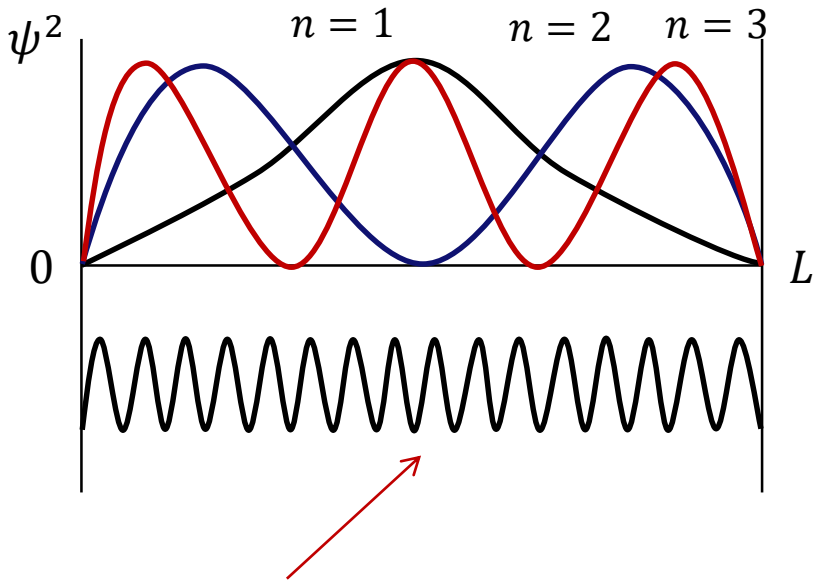
$$\int_0^L X^2 dx = 1 \rightarrow X_0 = \sqrt{\frac{2}{L}}$$

Thus, the wave function is given as below

$$X = \sqrt{\frac{2}{L}}\sin\frac{2\pi\sqrt{2mE_X}}{h}x$$

12.5 Quantum states and Energy levels





at high E level,

almost equally distributed

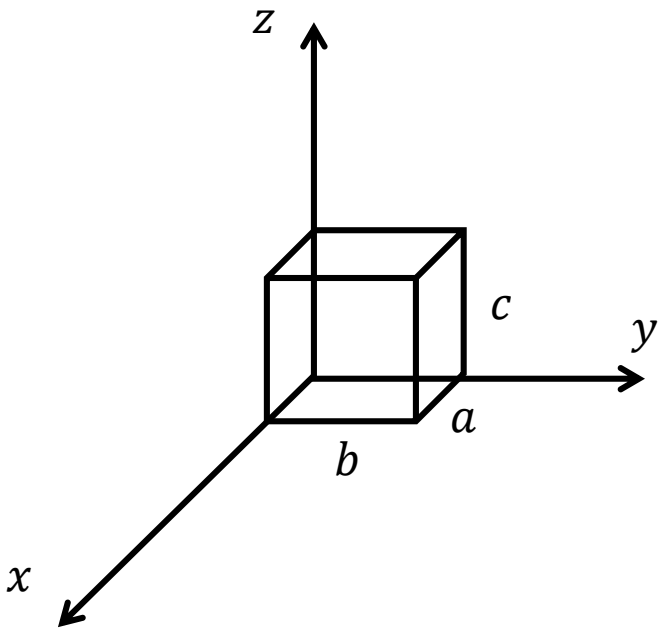
12.5 Quantum states and Energy levels

- Energy of a particle in 3-D space

For a particle in a box,

− constrained to stay in a box

= no external force



$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 mE}{h^2}\psi=0$$

12.5 Quantum states and Energy levels

- Out side the box $\psi = 0 \quad (V \to \infty)$

$\to$ continuous wave function

$\to \psi = 0$ at $\left.\begin{matrix} x = 0, a \\ y = 0, b \\ z = 0, c \end{matrix}\right\}$ B.C.

$$X = A \sin\left[\left(\frac{8\pi^2 m E_X}{h^2}\right)^{1/2} x\right] + B \cos\left[\left(\frac{8\pi^2 m E_X}{h^2}\right)^{1/2} x\right]$$

$\psi = 0$ at $\mathrm{x} = 0 \to \mathrm{B} = 0$

12.5 Quantum states and Energy levels

$$\psi = 0 \quad \text{at} \quad x = a \;\rightarrow 0 = A \sin \left(\frac{8\pi^2 m E_X}{h^2}\right)^{1/2} a$$

$$n_x \pi \; (n_x : integer)$$

→ Energy of a particle is quantized!

$$E_X = \frac{h^2 {n_x}^2}{8ma^2}$$

$$\therefore \quad E = E_X + E_Y + E_Z = \frac{h^2}{8m}\left(\frac{{n_x}^2}{a^2} + \frac{{n_y}^2}{b^2} + \frac{{n_z}^2}{c^2}\right)$$

12.5 Quantum states and Energy levels

- Wave function

$$\psi = X_0 Y_0 Z_0 \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}$$

$$\iiint \psi\psi^* dV = 1$$

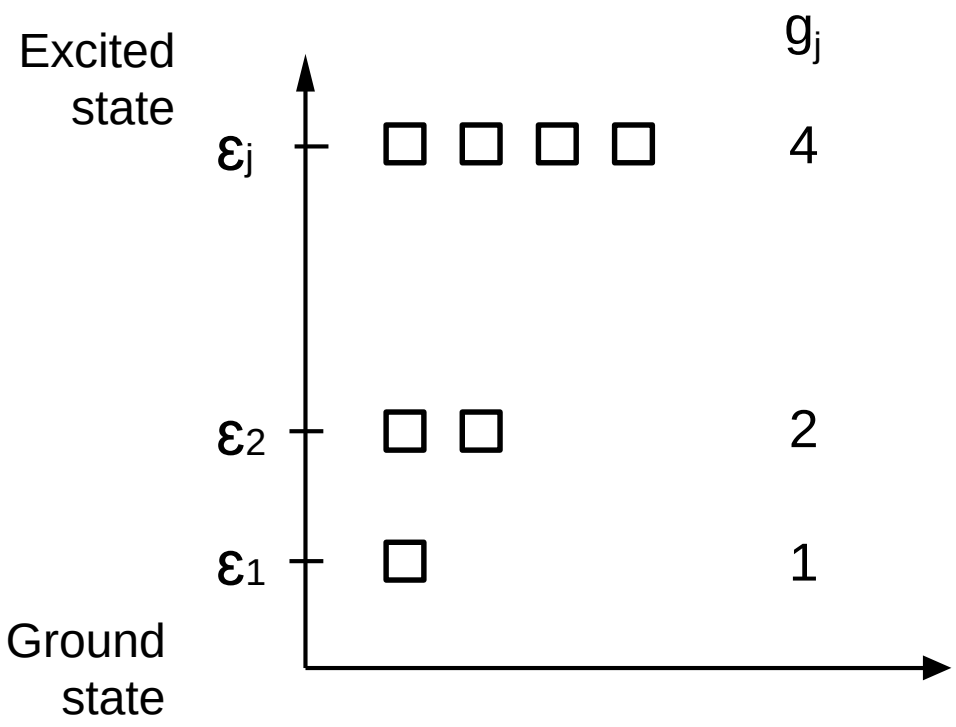
$$X_0{}^2 Y_0{}^2 Z_0{}^2 = \frac{8}{abc}$$

If a=b=c, (cube)

$$E = \frac{h^2}{8m}\frac{1}{a^2}\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right)$$

12.5 Quantum states and Energy levels

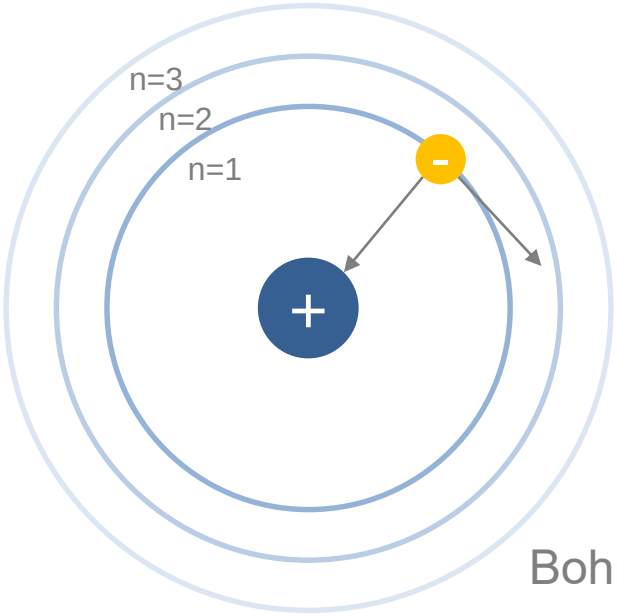
- Degeneracy (statistical weight of the energy level)



12.5 Quantum states and Energy levels

- Hydrogen atom in quantum mechanics

  Because their exist only one proton and one electron, hydrogen atom is an easiest model to examine quantum state of an electron



Bohr's hydrogen model

Coulomb's potential :

$$V_{elec} = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

Schrödinger's equation :

$$\nabla^2\psi_{elec} + \left(\frac{8\pi^2 m_e}{h^2}\right) + (\epsilon_{elec} - V_{elec})\psi_{elec} = 0$$

12.5 Quantum states and Energy levels

Wave function of an electron in spherical coordinate :

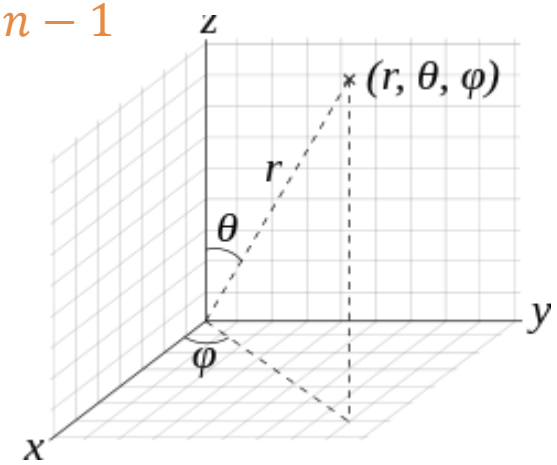
$$\psi_{nlm}(r,\theta,\varphi) = \sqrt{\left(\frac{\rho}{r}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^m(\theta,\varphi)$$

The wave state is discretized with 3 quantum numbers, n, l, and m

$r-\text{coordinate, n}$ $\quad n = 1,2,3 \cdots \infty$

$\theta-\text{coordinate, } l$ $\quad l = 1(s), 2(p), 3(d) \cdots n-1$

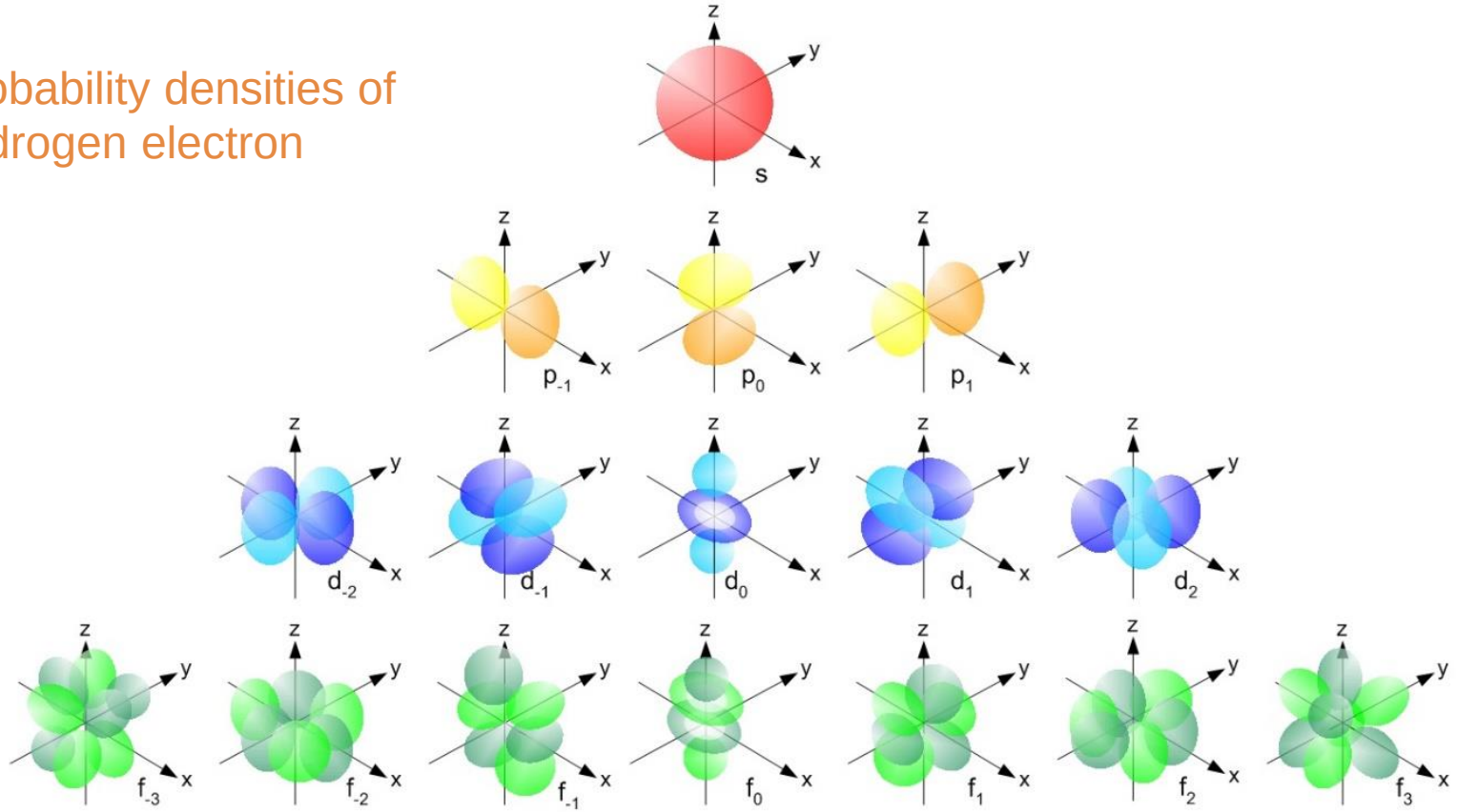
$\varphi-\text{coordinate, } m$ $\quad m = 0, \pm 1, \pm 2 \cdots + l$



12.5 Quantum states and Energy levels

- Hydrogen electron orbitals

Probability densities of hydrogen electron



http://chemwiki.ucdavis.edu/ogen orbitals

12.6 Density of Quantum states

- Degeneracy of energy state
  - For an energy level of a particle, there exist several states that meet the energy condition.
  - This number of state for an energy level is defined as degeneracy, g(ϵ)
  - For example, degeneracy of first excited energy level is as below

	n-combinations		
	n_x	n_y	n_z
State 1	2	1	1
State 2	1	2	1
State 3	1	1	2

$$\epsilon_1 = \frac{h}{8mV^{2/3}}\left({n_x}^2 + {n_y}^2 + {n_z}^2\right) = \frac{3h}{4mV^{2/3}} = 2\epsilon_0$$

$$g(\epsilon_1) = 3$$

12.6 Density of Quantum states

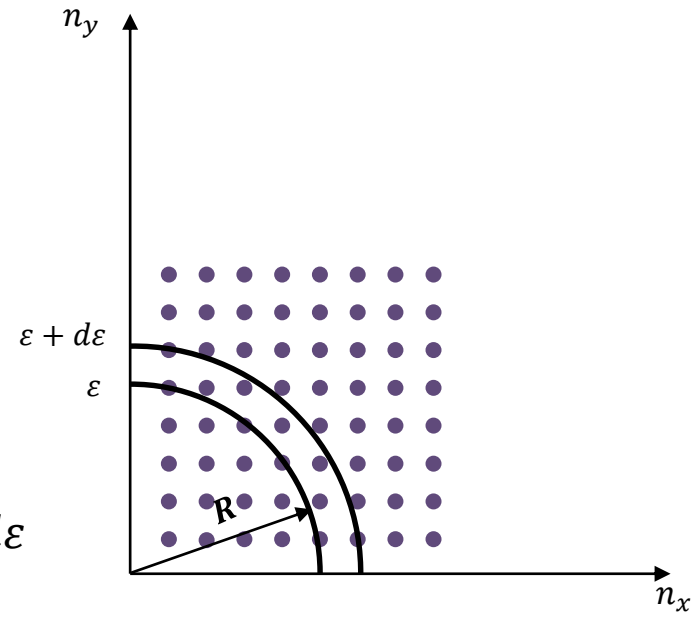
$$\frac{8ma^2\varepsilon}{h^2} = {n_x}^2 + {n_y}^2 + {n_z}^2$$

$$\frac{8mV^{\frac{2}{3}}\varepsilon}{h^2} = n^2 = R^2$$

$g(\varepsilon)d\varepsilon$

: number of quantum state $\varepsilon <$ $< \varepsilon + d\varepsilon$

$$g(\varepsilon)d\varepsilon = \mathrm{n}(\varepsilon + d\varepsilon) - n(\varepsilon) = \frac{dn(\varepsilon)}{d\varepsilon}d\varepsilon$$



12.6 Density of Quantum states

$$n(\varepsilon) = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) = \frac{1}{8}\frac{4}{3}\pi\left(\frac{4mV^{2/3}\varepsilon}{h^2}\right)^{3/2} = \frac{\pi}{6}V\left(\frac{8m}{h^2}\right)^{3/2}\varepsilon^{3/2}$$

Positive integer area

- Degeneracy

$$g(\varepsilon)d\varepsilon = \frac{\pi}{6}V\left(\frac{2^{9/2}m^{2/3}}{h^3}\right)\frac{3}{2}\varepsilon^{\frac{1}{2}}d\varepsilon = \boxed{\frac{4\sqrt{2}\pi V}{h^3}m^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}d\varepsilon}$$

# of integer point