Chapter 12

Statistical Thermodynamics

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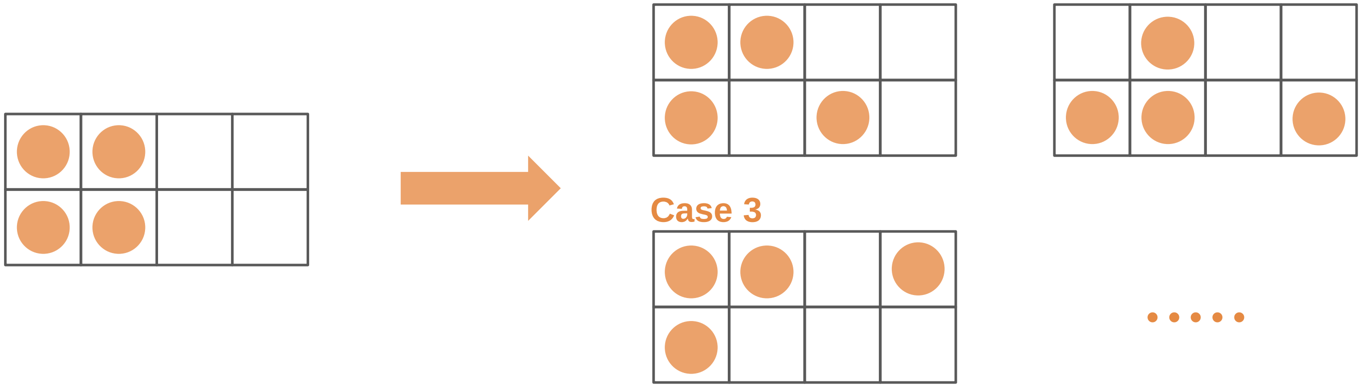
12.1 Introduction

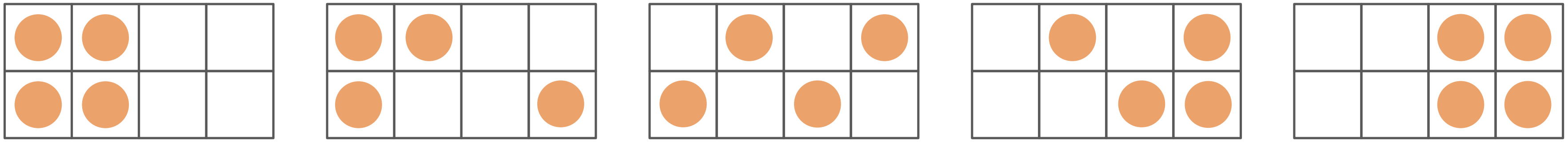
- Toy model: Configuration of molecules in a room
  - Initial state which 4 molecules exist at left side
  - How many rearrangement if one molecule moves to right side?



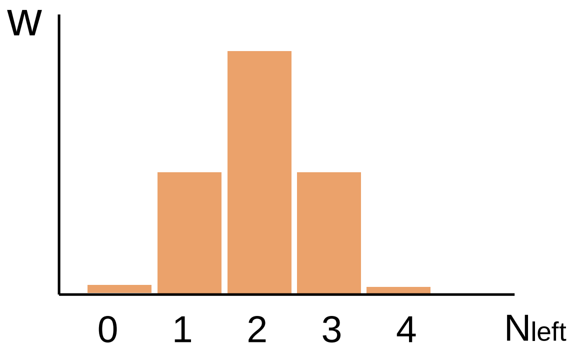
$w = {}_4C_3 \times {}_4C_1 = 16$: sixteen rearrangements!

12.1 Introduction

- Rearrangements for all states



N_{left}	4	3	2	1	0
N_{right}	0	1	2	3	4
w	1	16	32	16	1

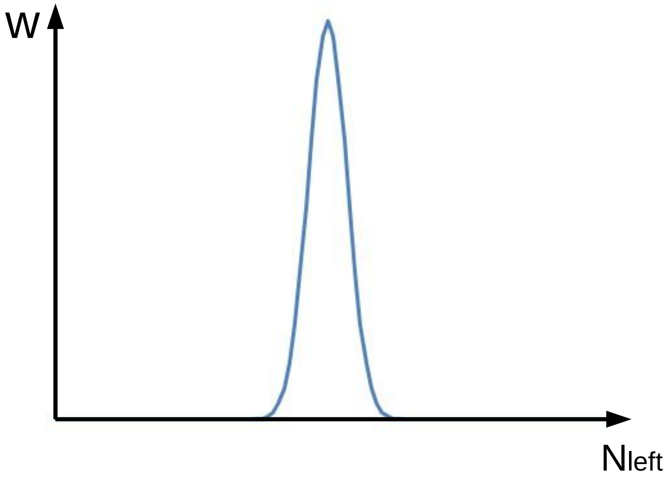


State with 2 molecules at left is most probable

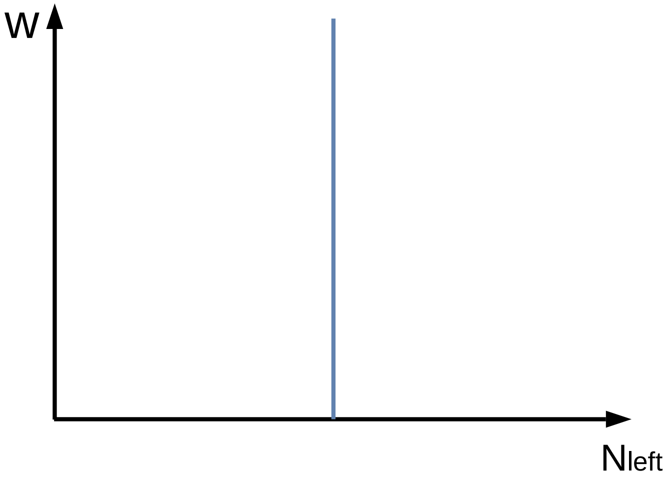
12.1 Introduction

- What if there are large number of molecules and spaces

100 molecules with 200 spaces



1000 molecules with 2000 spaces

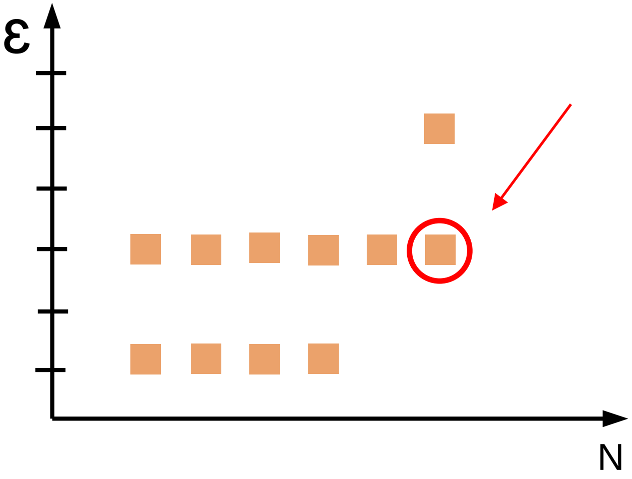


→ For a large system, only most probable state is possible.
Nature always converge to most probable state

12.1 Introduction

- Equilibrium of macroscopic system

Energy level



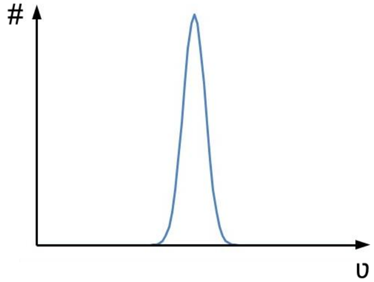
: energy state (quantum state)

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/

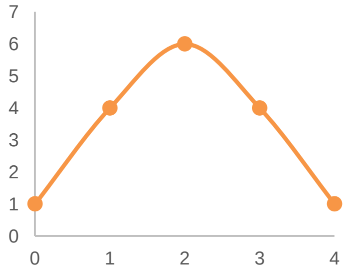
12.2 Coin-Tossing Experiment

Macro state level	Macro state specification		Micro state				Thermo dynamic 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

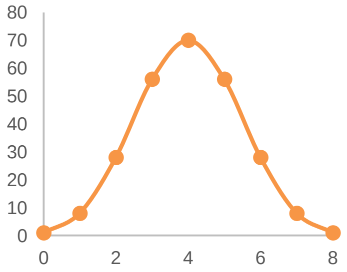
12.2 Coin-Tossing Experiment

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

$$w_{max} = {}_N C_{N/2} = \frac{N!}{(N/2)!\,(N/2)!}$$

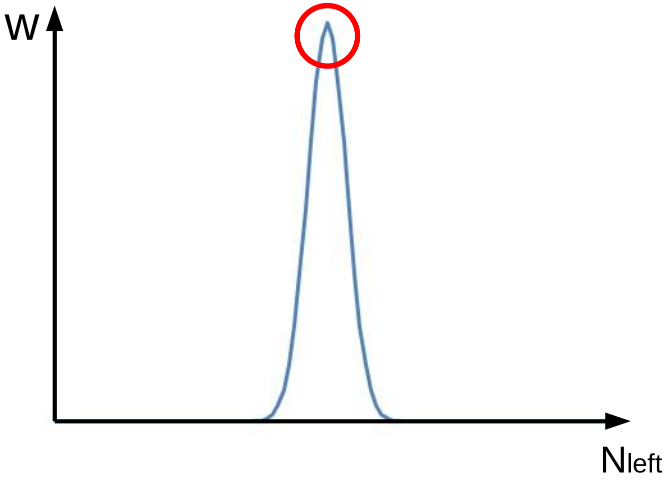


$N_{coin} = 4$
$w_{max} = 6$



$N_{coin} = 8$
$w_{max} = 70$

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

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

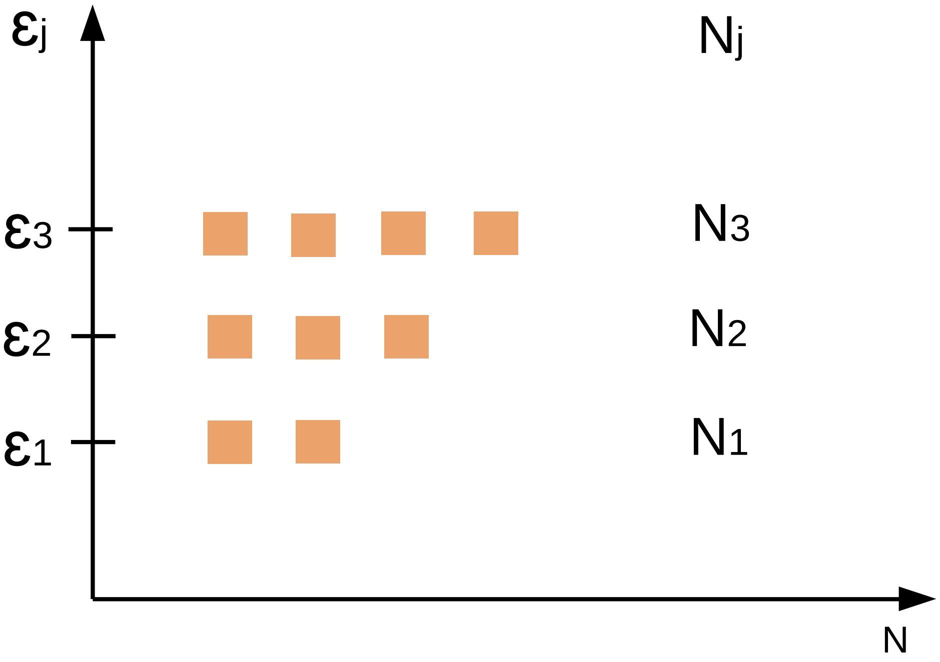
$$\log(w_{max}) = \log(e)\ln(w_{max}) = 0.4343 \cdot 693 \approx 300$$

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

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



$$\sum N_i = N$$

$$\sum N_i \varepsilon_j = U$$

12.3 Assembly of Distinguishable Particles

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

Macro state level	Macro state specification				Micro state			Thermo dynamic 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

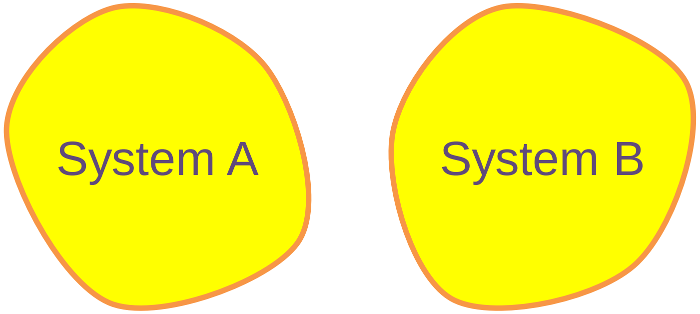
There are a few characteristics for the function of entropy.

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, $w_{A+B} = w_A w_B$

$$\Rightarrow \quad f(w_{A+B}) = f(w_A) + f(w_b)$$



$S_A = f(w_A)$

$S_B = f(w_B)$

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)

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

$|\Psi|^2$ · · · probability distribution function [probability density

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

h : Planck constant

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)

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

12.5 Quantum states and Energy levels

- Time dependent part

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

- Spatial part

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

$$\psi(x, y, z) = X(x)Y(y)Z(z), \qquad E = E_x + E_y + \overset{\frac{1}{2}mv_z{}^2}{\nearrow} E_z$$

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

12.5 Quantum states and Energy levels

- Boundary condition

B.C. $X(0) = 0$ → $X(L) = 0$

$$\left(\begin{array}{l} x = 0, X = 0 \\ x = L, X = 0 \end{array} \right)$$

from

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

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

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

12.5 Quantum states and Energy levels

For linear motion of a free particle

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

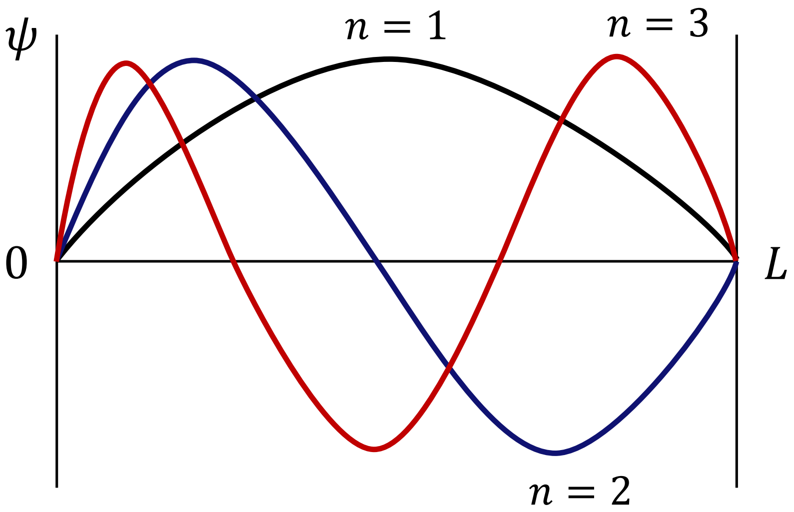
The last step is to normalize the wave function

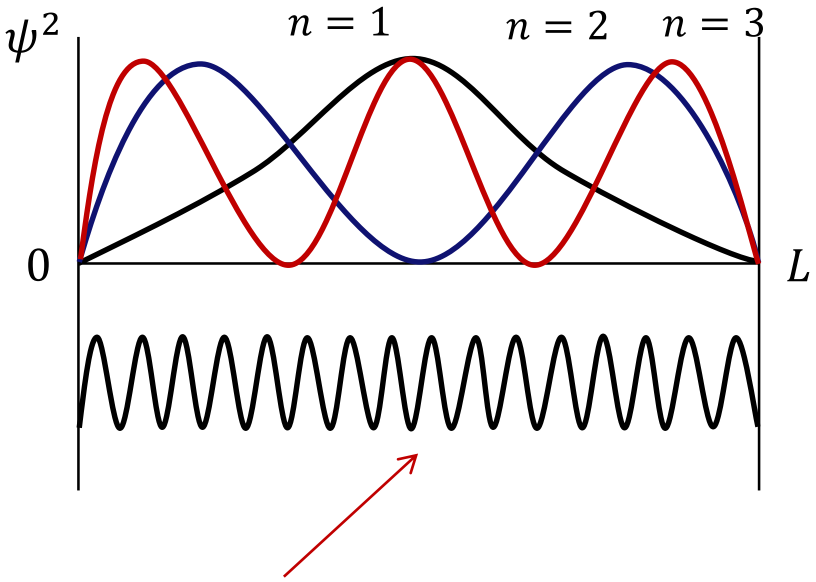
$$\int_0^L X^2 dx = 1 \rightarrow X_0 = \sqrt{\frac{2}{L}}$$

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

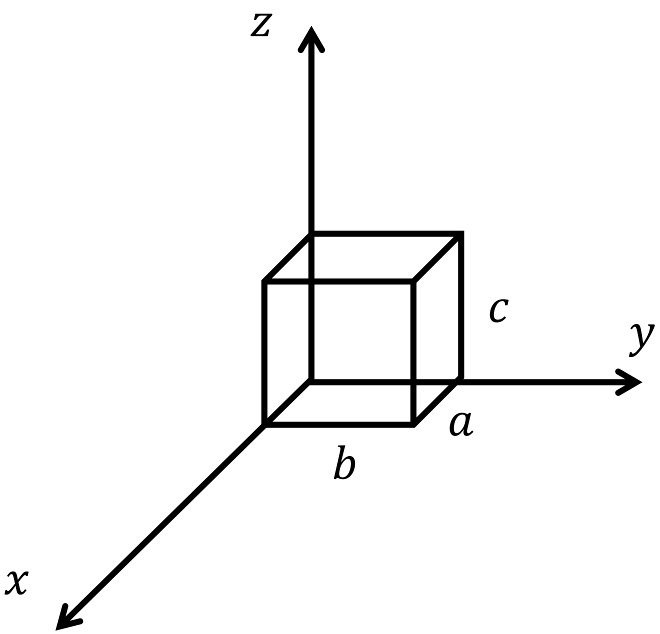
12.5 Quantum states and Energy levels

- 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 $\psi = 0 \quad (V \to \infty)$

→ continuous wave function

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

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

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

12.5 Quantum states and Energy levels

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

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

→ 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

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

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

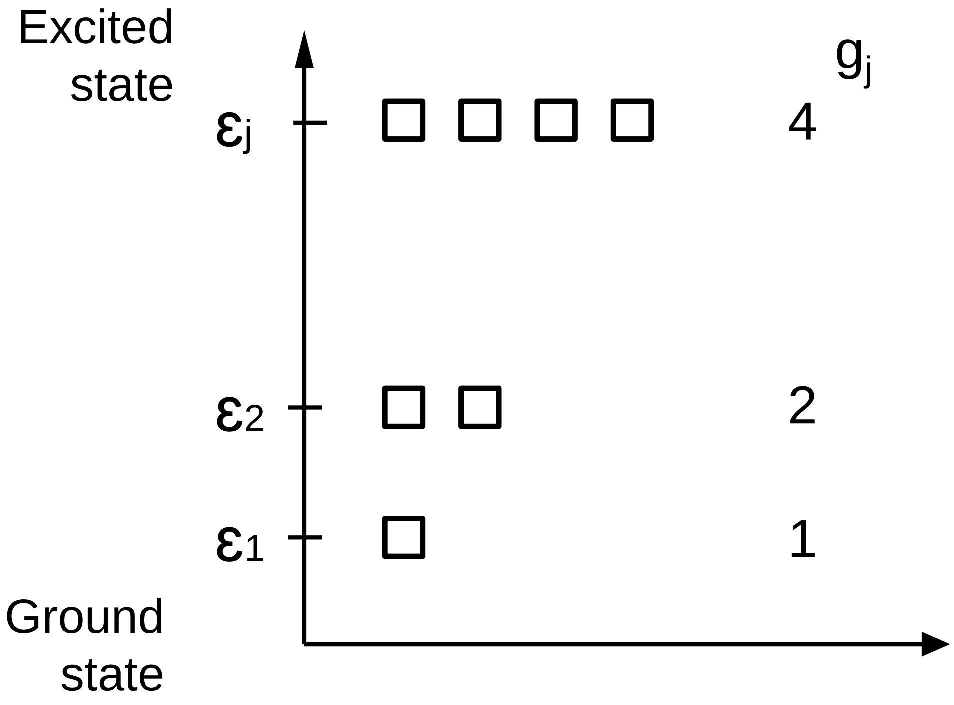
$$X_0{}^2 Y_0{}^2 Z_0{}^2 = \frac{8}{abc}$$

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

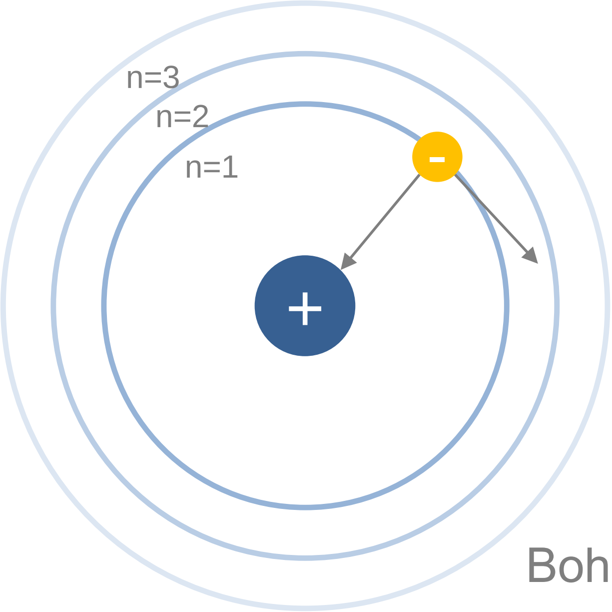
- Degeneracy (statistical weight of the energy level)



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



Coulomb's potential :

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

Schrödinger's equation :

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

Bohr's hydrogen model

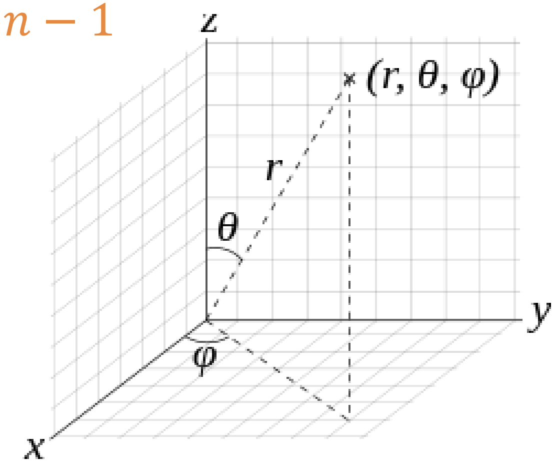
12.5 Quantum states and Energy levels

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

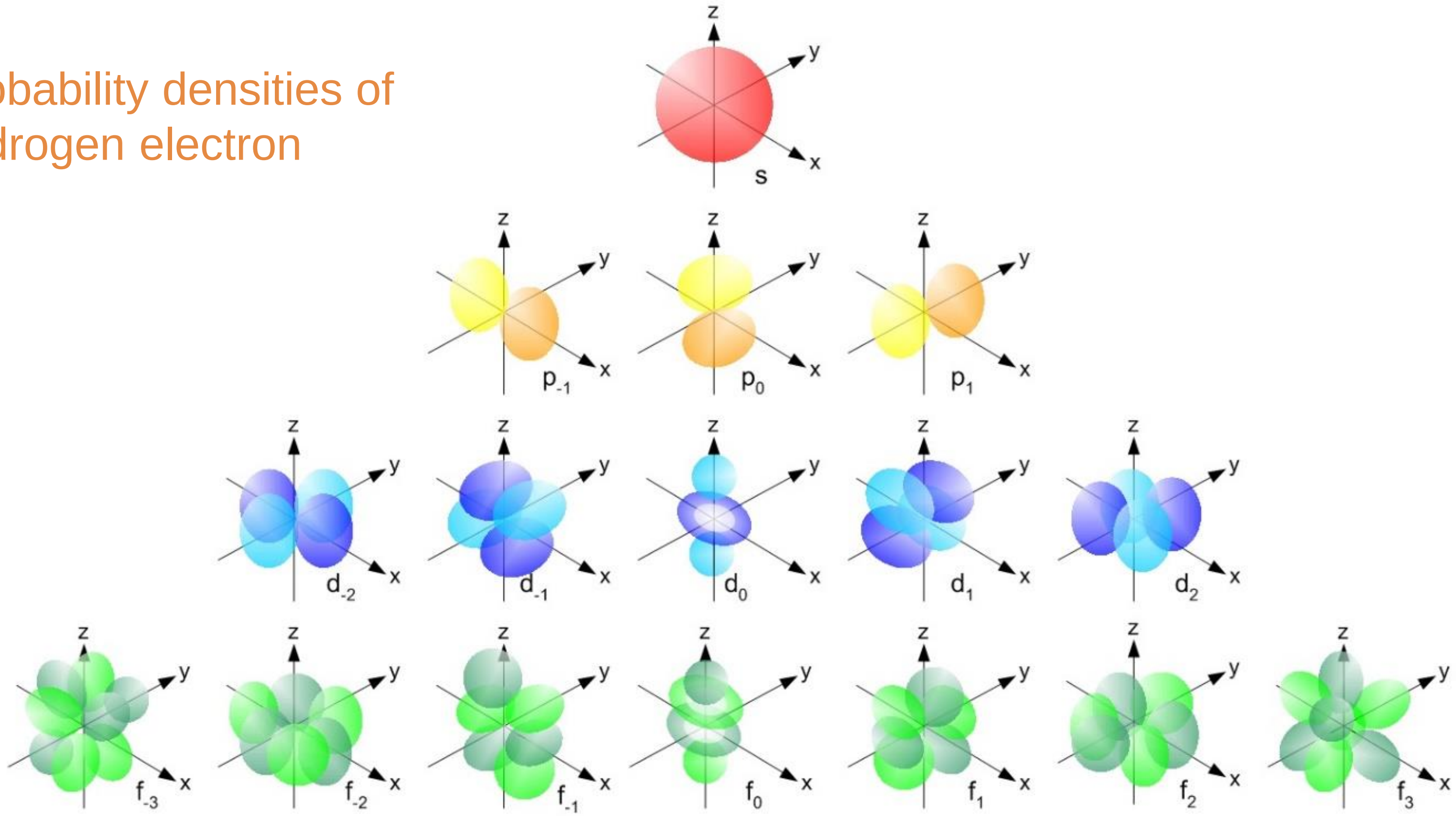
$r - \text{coordinate, n}$	$n = 1,2,3 \cdots \infty$
$\theta - \text{coordinate}, l$	$l = 1(s), 2(p), 3(d) \cdots n-1$
$\varphi - \text{coordinate}, m$	$m = 0, \pm1, \pm2 \cdots +l$



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

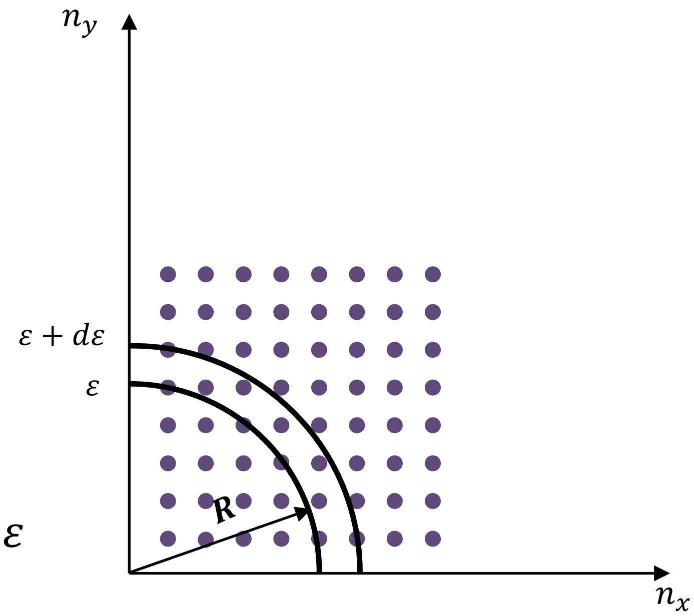
$$\epsilon_1 = \frac{h}{8mV^{2/3}}\left({n_x}^2 + {n_y}^2 + {n_z}^2\right) = \frac{3h}{4mV^{2/3}} = 2\epsilon_0$$

$$g(\epsilon_1) = 3$$

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 $\varepsilon < \quad < \varepsilon + d\varepsilon$

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

12.6 Density of Quantum states

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

Positive integer area

✡ Degeneracy

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

# of integer point