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Thermodynamics

Formula Essential

- Relationships between constants:

$$R = k_B N_A.$$

- Constants for specific ideal gases:

Table 1: Symbols That Are Unfamiliar

	Symbol	Viewpoint* (Macro micro)	Dimension† (in units)	Explanation
Statics	ν	M	mol	
	N	m	1	Number of molecules
	n	$C (m)$	m^{-3}	
	$m_0 (\mu)$	m	kg	Mass of a molecule
	M	$C (M)$	kg/mol	
Kinematics	$\bar{\varepsilon}$	m	J	Average molecular kinetic energy; $\bar{\varepsilon} = \frac{1}{2} \mu \overline{v^2}$
	$f(v)$	C	$m^{-1}s$	Percentage of molecules near v , i.e. $f(v) dv = \frac{dN}{N}$
	i	(m)	1	Degree of freedom (DOF). $i = 3 + \{0, 2, 3\}$
Dynamics	$C_{p,m}$	$C (M)$	$J mol^{-1} K^{-1}$	$C_x = \left(\frac{\Delta Q}{\Delta T} \right)_x$
	$C_{V,m}$			
	c_x		$J kg^{-1} K^{-1}$	
	γ		1	$\gamma = C_{p,m}/C_{V,m}$
Constants	$k (k_B)$		J/K	Boltzmann constant. $k \approx 1.381 \cdot 10^{-23} J/K$ (k_B)
	R		$J mol^{-1} K^{-1}$	Ideal gas constant. $R \approx 8.314 J mol^{-1} K^{-1}$ (IdealGas)
	N_A		mol^{-1}	$N_A = 6.022 140 76 \cdot 10^{23} mol^{-1}$
	V_m	(M)	m^3/mol	Molar volume of ideal gas at 273.15 K, 101.325 kPa. $V_m \approx 22.4 m^3/mol$ (V_m101)

* The column “Viewpoint” refers to the scale of measurement on molecules. “C” (Constant) means this is independent on our viewpoint. “m” usually means this quantity focuses on the behavior of a single molecule, and when we use macro/micro view to measure a quantity that is actually micro/macro, we will usually get a overly large/small value (in the same unit system).

† In following contents, dimensions are usually expressed in units (SI) for convenience.

$$C_{V,m} = \frac{i}{2}R,$$

$$C_{p,m} = \left(1 + \frac{i}{2}\right)R,$$

$$C_{p,m} = C_{V,m} + R \text{ (Mayer formula),}$$

$$\gamma = 1 + \frac{2}{i};$$

Related quantities:

$$E_{\text{per-DOF}} = \frac{1}{2}kT, \text{ (For a single molecule)}$$

$$\Rightarrow U = \frac{i}{2}\nu RT,$$

where $i = t + r + 2s$, because each s leads to 2 shares of both kinetic energy and potential energy.

- On p and T :

$$pV = \nu RT,$$

$$p = nkT,$$

$$\frac{p}{\rho} = \frac{RT}{M}.$$

- On other p :

$$\begin{aligned} p &= \frac{1}{3}\rho\overline{v^2} \\ &= \frac{2}{3}n\bar{\varepsilon}. \end{aligned}$$

Maxwell's law of speed distribution

$$\begin{aligned} f(v) &= 4\pi \left(\frac{\mu}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{\mu v^2}{2kT}} \\ &= \frac{4}{\sqrt{\pi}} \cdot \frac{1}{v} \left(\frac{1}{k} \cdot \frac{\varepsilon}{T} \right)^{\frac{3}{2}} \exp\left(-\frac{1}{k} \cdot \frac{\varepsilon}{T}\right) \end{aligned}$$

(This won't be tested in exams. 😊)

- 3 “ v ”:

$$v_p = \sqrt{\frac{2RT}{M}} \text{ (Most probable } v),$$

$$\sqrt{v^2} = \sqrt{\frac{3RT}{M}},$$

$$\bar{v} = \sqrt{\frac{8}{\pi} \frac{RT}{M}}.$$

- About distributions...

$$\frac{n}{n_0} = \frac{p}{p_0} = e^{-\frac{\varepsilon_p}{kT}},$$

where $\varepsilon_p = m_0gh$ is the potential energy of a molecule. **Note:** This also applies to conditions where ε is discrete! 😊

- Molecular kinetics:

Mean-free-path length

$$\bar{\lambda} = \frac{1}{\sqrt{2}\pi d^2 n},$$

where d is the effective diameter;

Mean collision frequency

$$\bar{Z} = \frac{\bar{v}}{\bar{\lambda}} = \sqrt{2}\pi d^2 n \bar{v}.$$

Macro view begins...

- First law of thermodynamics:

$$Q = \Delta E + W,$$

where Q is the heat from the external to the gas; E is the internal energy of the gas; W is the work made by the gas to the external.

Some derivation around it...

$$C_{V,m} = \frac{dE}{dT},$$

$$\left(\frac{dE}{dT}\right)_p = \left(\frac{dE}{dT}\right)_V = \frac{dE}{dT},$$

$$\begin{aligned} \Rightarrow C_{p,m} &= \frac{dE}{dT} + p \left(\frac{dV}{dT}\right)_p \\ &= C_{V,m} + R. \end{aligned}$$

About Adiabatic process...

$$d(pV) = \nu R dT,$$

~~Breaking it down to 2 aspects~~ We can cancel out dT using

$$p dV = dW = -dU = -\nu C_{V,m} dT,$$

and get

$$(C_{V,m} + R)p dV + C_{V,m} V dp = 0.$$

That is,

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0,$$

or

$$pV^\gamma = C.$$

We can also use $pVT^{-1} = \nu R$ to get relationships between p , V and T , i.e.:

$$\begin{aligned} V^{\gamma-1}T &= C', \\ p^{1-\gamma}T^\gamma &= C'' \\ (\text{or } p^{\gamma-1}T^{-\gamma} &= C'''). \end{aligned}$$

The exponents of p , V , T follow

$$\begin{aligned} ([p], [V], [T]) &= \alpha(1, \gamma, 0) + \beta(1, 1, -1) \\ &= (\alpha + \beta, \alpha\gamma + \beta, -\beta) \quad (\alpha, \beta \in \mathbb{R}) \\ &= \beta \left(1 + \frac{\alpha}{\beta}, 1 + \gamma \frac{\alpha}{\beta}, -1 \right). \end{aligned}$$

Based on the basic knowledge above, we can talk about more high-level things...

In adiabatic process, work made by the gas

$$\begin{aligned} W &= \int_{V_1}^{V_2} p dV \quad (\text{Area under } p-V \text{ curve}) \\ &= \int_{V_1}^{V_2} \frac{p_1 V_1^\gamma}{V^\gamma} dV \quad (\text{Using initial condition}) \\ &= \frac{-\Delta(pV)}{\gamma - 1} = -\frac{\nu R}{\gamma - 1} \Delta T \\ &= -\nu C_{V,m} \Delta T \quad (\text{Comply with previous}) \end{aligned}$$

• About η ...

$$\eta = \frac{W}{Q_{\text{Absorb}}} = 1 - \frac{Q_{\text{Emit}}}{Q_{\text{Absorb}}},$$

where Q_{Absorb} is usually denoted by Q_1 , and Q_{Emit} is by Q_2 .

Refrigeration coefficient

$$w = \frac{Q_2}{W},$$

where Q_2 is the heat absorbed from the desig-nated cold source by the working medium.

► Carnot heat engine (Clockwise)

1. Constant T

$$T = T_H, V_1 \nearrow V_2$$

$$Q_H = \nu R T_H \Delta \ln(V) \quad (\text{External} \rightarrow \text{gas})$$

2. Adiabatic

$$\begin{aligned} V^{\gamma-1}T &= V_2^{\gamma-1}T_H, T_H \searrow T_L, \\ V_2 \nearrow V_3, \Delta U &\searrow = \frac{i}{2} \nu R \Delta T \end{aligned}$$

3. Constant T

$$T = T_L. \text{ Similarly, we can get } Q_L.$$

4. Adiabatic

Similar.

From the adiabatic processes, we can get $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ or $\frac{V_1}{V_4} = \frac{V_2}{V_3}$.

Finally, we can get the efficiency

$$\begin{aligned} \eta &= 1 - \frac{Q_L}{Q_H} \\ &= 1 - \frac{\nu R T_L \ln \frac{V_3}{V_4}}{\nu R T_H \ln \frac{V_2}{V_1}} \\ &= 1 - \frac{T_L}{T_H} \end{aligned}$$

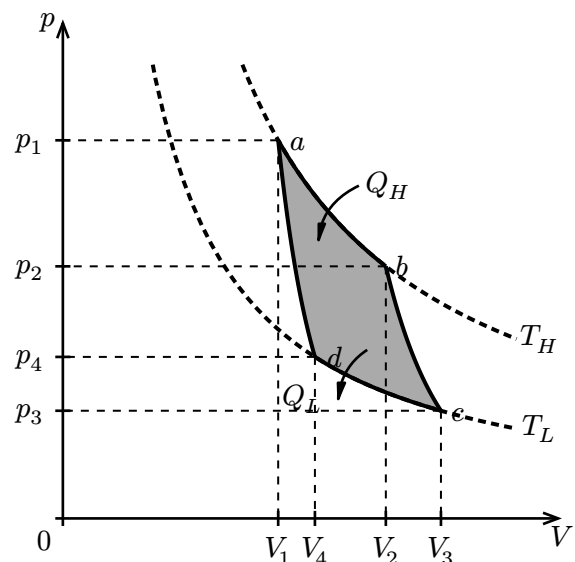


Figure 1: Carnot heat engine principle

Things to Recite (Maybe)...

1st Law of Thermodynamics

$$dQ = dE + dW$$

系统从外界吸收的热量，一部分使其内能增加，另一部分则用以对外界做功。

2nd Law of Thermodynamics

开尔文表述 (Kelvin Statement) 不可能从单一热源吸收热量，使之完全转化为功而不引起其他变化。

克劳修斯表述 (Clausius Statement) 不可能使热量从低温物体传向高温物体而不引起其他变化。

Carnot's theorem

卡诺定理的内容有两条：

- (1) 在温度分别为 T_1 与 T_2 的两个给定热源之间工作的一切可逆热机，其效率相同，都等于理想气体可逆卡诺热机的效率，即 $\eta = 1 - T_2/T_1$ 。
- (2) 在相同的高、低温热源之间工作的一切不可逆热机，其效率都不可能大于可逆热机的效率。

The Entropy World

Some conditions for the definition of S :

Quote 1 **Single-valued** : Similar to U , S should be a function of the (micro) state of the system.

Quote 2 **Additive** : S of a system should be the *sum* of S of each part of the system. (However, Ω of a system is the *product* of each part of it.)

$$S = k \ln \Omega,$$

(Boltzmann's principle)

$$dS \geq 0.$$

(Principle of entropy increase)

All processes of an isolated system are processes of increasing S , and S reaches its maximum when the system are at an equilibrium state.

In a free expansion from V_1 to V_2 ,

$$\frac{\Omega_2}{\Omega_1} = \left(\frac{V_2}{V_1} \right)^N,$$

where N is the molecule number of the gas. Thus,

$$\Delta S = kN \ln \frac{V_2}{V_1} = \nu R \Delta \ln V.$$

So, in this kind of process, $dS \leq 0 \Rightarrow \frac{V_2}{V_1} \geq 1$.

Below are some knowledge points in “*”:

- For an infinitely small reversible isothermal process, $dS = \frac{dQ}{T}$.

Quantum Mechanics

Planck constant

$$h = 6.626\,070\,15 \cdot 10^{-34} \text{ kg m}^2 \text{ s}^{-1} \text{ or J s}$$

Intro: 4 phenomena...

Thermal Radiation

When radiation and absorption reach equilibrium, T of the object no longer changes and the object enters the state of thermal equilibrium.

Monochromatic radiant exitance

$$M_\lambda(T) = \frac{dM_\lambda}{d\lambda},$$

where dM_λ W/m³ Dimension is the radiant power in $[\lambda, \lambda + d\lambda]$.

Radiant exitance

$$M(T) \text{ W/m² Dimension } = \int_0^\infty M_\lambda(T) d\lambda.$$

能够全部吸收各种波长辐射能而完全不发生反射和透射的物体称为**绝对黑体**或**黑体**.

Stefan-Boltzmann's Law

$$M_B(T) = \sigma T^4,$$

where B denote blackbody, and $\sigma \approx 5.670 \cdot 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.

Wien's displacement law

$$\lambda_m = \frac{b}{T},$$

where λ_m is the λ with the max magnitude, and $b = 2.898 \cdot 10^{-3} \text{ m K}$.

Planck's formula

$$M_{B\lambda}(T) = \frac{2\pi hc^2 \lambda^{-5}}{e^{\frac{hc}{\lambda kT}} - 1},$$

where $h = 6.626 \cdot 10^{-34} \text{ J s}$ (Planck's constant).

Photoemission

Phenomena:

1. Saturation current
2. Cut-off frequency
3. stopping voltage
4. Photoelectrons are emitted in real time, with a lag time of no more than $1 \cdot 10^{-9} \text{ s}$.

Compton Effect

When photons interact with particles, the effects depends on the energy of photons. From low to high is: 1. photoemission ($h\nu < 0.5 \text{ MeV}$); 2. Compton effect; 3. generating electron-positron pairs (γ photons, $h\nu > 1.02 \text{ MeV}$).

(In contrast, *Rayleigh scattering* is the scattering with a constant wavelength.)

In Compton effect, there are some hypotheses:

Quote 3 **Electrons are free** : X-ray photons mainly interact with the electrons that are weakly bound to the nuclei in the scattering material. So these electrons are deemed as free electrons.

Quote 4 **Electrons are static** : Because the energy of X-photons are much higher than thermal motion energy of these electrons, so the latter are approximately zero.

Quote 5 **About the process...** :

- *Relativistic effects* cannot be ignored.
- The collision is *completely elastic*.

Based on these, we have

$$\frac{h\nu}{c} \begin{pmatrix} \cos \theta \\ \sin \theta \end{pmatrix} + mv \begin{pmatrix} \cos(-\varphi) \\ \sin(-\varphi) \end{pmatrix} = \frac{h\nu_0}{c} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (\text{Momentum})$$

$$h\nu_0 + m_0 c^2 = h\nu + mc^2, \quad (\text{Energy})$$

together with

$$m = \frac{m_0}{\sqrt{1 - (\frac{v}{c})^2}}, \lambda = \frac{c}{\nu}.$$

Solving them, we have

$$\Delta\lambda = \frac{c}{\nu \parallel - \nu_0} = \lambda_C (1 - \cos \theta)$$

$$= 2\lambda_C \sin^2 \frac{\theta}{2},$$

where $\lambda_C = \frac{h}{m_0 c}$ is the Compton wavelength of electron.

The spectrum of Hydrogen

Assumptions of Bohr's theory:



Quote 6 **Stationary state** : Atoms can only exist in a series of stable states, with discontinuous energy.

Quote 7 **Photons...** :

$$\nu_{k \rightarrow n} = \frac{|E_k - E_n|}{h}.$$

Quote 8 **Orbital angular momentum $L = mvr$ is Quantized** :

$$L = n\hbar, n \in \mathbb{N}_+,$$

where $\hbar = \frac{h}{2\pi}$, and n is called *quantum number*.

Bohr has another ingenious idea 🍎 that the centripetal force is equal to the Coulomb force. Thus, solving the equation, we have

$$r_n = n^2 \frac{\epsilon_0 \hbar^2}{\pi m e^2},$$

$$E_n = -\frac{1}{8\pi\epsilon_0} \frac{e^2}{r_n}.$$

(Around this chapter, we collected a new symbol σ $\boxed{\text{m}^{-1}}$ Dimension denoting *wavenumber*.)

The correct results of quantum mechanics:

$$E_n = -\frac{1}{n^2} \frac{m e^4}{8 \epsilon_0^2 \hbar^2}, n \in \mathbb{N}_+,$$

$$L = \sqrt{l(l+1)}\hbar, \quad l \in \mathbb{N} \cap [0, n),$$

$$L_z = m_l \hbar, \quad m_l \in \mathbb{Z} \cap [-l, l],$$

$$\text{Plus... } S_z = m_s \hbar, \quad m_s \in \left\{ \pm \frac{1}{2} \right\}.$$

Of the equations above, n, l, m_l, m_s are respectively 1) principal, 2) secondary, 3) magnetic, and 4) spin quantum number.

The m_l has a close relationship with l . l denotes the quantum number for the *magnitude* of angular momentum and m_l denotes the *z-component* of it. (The direction of z here is the direction of the external magnetic field B .) They form an L together.

Plus, surrounding L_z we can use some ~~forgotten~~ knowledge in electromagnetism to get extras:

0. First, the conclusion is, for the electron “orbiting” around the nucleus, we have

$$\mu = \frac{-e}{2m} L,$$

where μ is the magnetic moment \mathbb{G} 🖱️, and L is the angular momentum 🌀.

1. The hypotheses are:

- The orbit of the electron is a circle, with a radius r .
- The electron orbits at a constant period T .

2. Then we can deduce:

$$\begin{aligned} \mu &= IS = \frac{(\Delta Q)_T}{T} \cdot \pi r_x \times r_y = \frac{-e}{\frac{2\pi}{\omega}} \cdot \pi r^2 e_z \\ &= \frac{-e}{2} r^2 \omega = \frac{-e}{2} r \times v \\ &= \frac{-e}{2m} L. \quad \text{😊} \end{aligned}$$

3. Thus,

$$\begin{aligned} \mu_z &= \frac{-e}{2m} L_z \\ &= \frac{-e}{2m} (m_l \hbar) = -m_l \mu_B, \\ m_l &\in \mathbb{Z} \cap [-l, l], \end{aligned}$$

where μ_B $\boxed{\text{J/T}}$ Dimension is called Bohr magneton.

4. Finally, *sturdy grass withstands high winds; true gold stands the test of fire*. (Not aimed at you. 🤖) In the external magnetic field B , each different orientation of the magnetic moment μ can result in a different additional energy as this shows:

$$\begin{aligned} \Delta E &= -\mu \cdot B \\ &= -\mu_z B = m_l \mu_B B, \\ m_l &\in \mathbb{Z} \cap [-l, l], \end{aligned}$$

where z is the direction of B .

Zeeman effect From the above, we can derive the Zeeman effect: The bigger m_l , the bigger ΔE . Therefore, an energy level originally determined by a pair of n, l will split into $(2l+1)$ sub energy levels in a magnetic field.



We had to say a little more about the spin of electrons. It is quite similar to their orbiting: We can make a **bold** assumption that

$$S = \sqrt{s(s+1)}\hbar,$$

$$S_z = m_s\hbar,$$

where S is the magnitude of spin angular momentum, s is the spin quantum number, and m_s is the spin magnetic quantum number. So, recalling that in orbital motion, when l is determined, m_l can have $(2l+1)$ different values, for spin, since m_s has only 2 different values (at any time), we can assert that $s = \frac{1}{2}$. (Note: It is not that #(possible values) of s determines #(possible values) of m_s , but the value of s itself determines #(possible values) of m_s .) So our conclusion is

$$s = \frac{1}{2}, \quad m_s = \pm \frac{1}{2}.$$

Further, we have

$$S = \frac{\sqrt{3}}{2}\hbar, \quad (\text{Unlike } L, \text{ this is a constant!})$$

$$S_z = \pm \frac{1}{2}\hbar. \quad (\text{Unlike } L_z, \text{ \#(possible } S_z) \text{ is an even number.)}$$

If we are looking for magnetic moment, we can still use $\mu_z = \frac{-e}{2m}L_z$.

Wave, start!

For a single particle...

$$p = \frac{h}{\lambda},$$

$$E = h\nu,$$

where ν, λ are determined by current m, v (Note: instead of rest mass m_0).

$$\Delta p_x \Delta x \geq \frac{h}{4\pi},$$

$$\Delta E \Delta t \geq \frac{h}{4\pi}.$$

An application for the second:

Def. In an atom, the average time for electrons to stay on an energy level (hereinafter abbreviated as E_n) is referred to as the *average lifetime* of that energy level. So, *thread 1.* according to the energy-time uncertainty relation, the higher the average lifetime (that is, Δt), the lower ΔE (that is, the width of E_n); *thread 2.* according to common knowledge, the longer electrons stay on E_n , the more stable E_n is. From the 2 threads we have a conclusion: The more stable E_n , the smaller ΔE , \Leftrightarrow the more definite E_n .

As for specific applications, the ground state E_1 is the most definite, and due to $E_n \downarrow \Rightarrow \Delta t \uparrow \Rightarrow \Delta E \downarrow \Rightarrow \Delta \lambda_{\text{Emitted}}$, so it helps in selecting light emitting materials.

For mathematicians...

$$\left(\begin{array}{c} \text{Wave-mechanics} \\ \text{Matrix-mechanics} \end{array} \right) = \left(\begin{array}{c} \text{Schrödinger} \\ \text{Heisenberg, Born, Pauli, etc.} \end{array} \right)$$

The book regards us as Schrödinger and we are going to build some **basic** wave mechanics.

Actually, we only need one prerequisite knowledge point: for waves, a traditional *monochromatic plane wave* can be expressed as

$$y(x, t) = Ae^{-i \cdot 2\pi(\nu t - \frac{x}{\lambda})}.$$

Similarly, for a free particle, its wave function is

$$\Psi(x, t) = \Psi_0 e^{-i \cdot \dots} = \Psi_0 e^{-\frac{i}{\hbar}(Et - px)},$$

where (recap ☺) $E = h\nu$, $p = \frac{h}{\lambda}$. **Note:** Ψ_0 here is still to be determined (using the normalization method mentioned later).

The probability of a particle appearing in the volume element near \mathbf{r} at time t is

$$dW = |\Psi(\mathbf{r}, t)|^2 dV,$$

where we can substitute $|\Psi|^2$ as $\Psi\Psi^*$.

Wave functions must be 1) single-valued, 2) finite, 3) continuous, and 4) normalized ($\iiint dW(\mathbf{r}, t) = 1$).

Time-independent Schrödinger equation (Stationary Schrödinger equation)

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(\mathbf{r}) + \frac{2m(E - V)}{\hbar^2} \Psi(\mathbf{r}) = 0,$$

where $\Psi(\mathbf{r})$ is simplified from $\Psi(\mathbf{r}, t)$; E is the energy of the particle, and $V(\mathbf{r})$ is the potential energy (for example, in hydrogen atom, $V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0 r}$; in one-dimensional harmonic oscillator, $V(\mathbf{r}) = \frac{1}{2}m\omega^2 x^2$).

Example – One-dimensional infinite well:

$\Psi(x)$ satisfies

$$\begin{cases} \frac{d^2\Psi(x)}{dx^2} + k^2\Psi(x) = 0, & \left(\begin{array}{l} \text{Within the potential} \\ \text{well's range } (0, a), \end{array} \right) \\ \Psi(x) = 0, & x \in (-\infty, 0] \cup [a, +\infty), \end{cases}$$

where $k = \frac{\sqrt{2mE}}{\hbar}$.

The first equation has the general solution $\Psi(x) = A \sin kx + B \cos kx$. Using the 2 boundary conditions, we get

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

and $k = \frac{n\pi}{a} = \frac{\sqrt{2mE}}{\hbar}$. Further substitution yields

$$\Psi_n(x) = \pm \sqrt{\frac{2}{a}} \sin\left(n\pi \frac{x}{a}\right), n \in \mathbb{N}_+.$$

So, we can also know the wave length and energy of the particle at some energy level $n \in \mathbb{N}_+$:

$$\lambda_n = \frac{2a}{n},$$

$$E_n = n^2 \frac{h^2}{8ma^2}.$$

There are several types of $V(x)$, including C , infinite/finite well, step potential, potential barrier, and (harmonic) oscillator. It is surprising that particles have a certain probability to enter the regions where $E < V$; for harmonic oscillators, the zero-point energy is $\frac{1}{2}h\nu$ ($E_n = \left(n + \frac{1}{2}\right)h\nu$), instead of 0 (cases are free particle, step potential, and potential barrier, but their energies are all continuous 😊, i.e. they are in an unbound state).

Let's build an atom!

First, deal with the electrons in the shell structure

In an atom, (n, k, m_l, m_s) determines a unique electron. n -th shell layer contains at most $Z_n = \sum_{l=0}^{n-1} (2l+1) \times 2 = 2n^2$ electrons; a sub-layer with some l can contain at most $(2l+1) \times 2$ electrons.

(The end, because we've already learned how to build an atom's shell in high school chemistry, e.g. Pauli exclusion principle and the principle of minimum energy. ...)

Solid State Physics

Bands

Energy band A group of an split energy level.

Full band All energy levels within it are filled with e 's.

Valence band Formed by split valence levels. (Usually has the highest energy.)

Empty band Levels corresponding to excited states of an atom. Is empty if the atom is at the unexcited state.

Conduction band Not filled with e 's.

Band gap (Forbidden band) Is NOT an energy band! As its name reveals, it is the gap between two adjacent band.

Three-body (?)

(Here we focus on crystals only.)

Insulators Their highest valence band is filled with valence e 's, and thus becomes a *full band*. And it is far from the nearest empty band above it, with a distance of $\Delta E_g = 3 \sim 6 \text{ eV}$.

Conductors There are 3 types of band structures:

a) Valence band is not fully filled.

Example: Li.

b) Valence band is connected, or partially overlaps with an empty band.

Example: Mg, Be, Zn. Taking Mg, its e 's fill up to 3s, and its 3s overlaps with 3p. Hence, e 's on 3s can jump to 3p's energy levels. So the 3s+3p are filled 2/8 (sounds like hybrid orbitals?), and thus Mg is a good conductor.

c) Adding a) and b) together. Some metals' valence bands are not fully filled and overlap with empty bands.

Example: Na, K, Al, Cu, Ag.

Semiconductors Their band structures are similar to insulators', but the ΔE_g -s are much smaller, at around $0.1 \sim 1.5 \text{ eV}$. The "hole"s left by the excited e 's (which are usually from the top of the full band and to the empty band) are familiar to us. 😊