



Some Basic Aspects of Organic Semiconductors: from Material-Handling to Electronic Structure

有機半導体の電子構造：基礎編

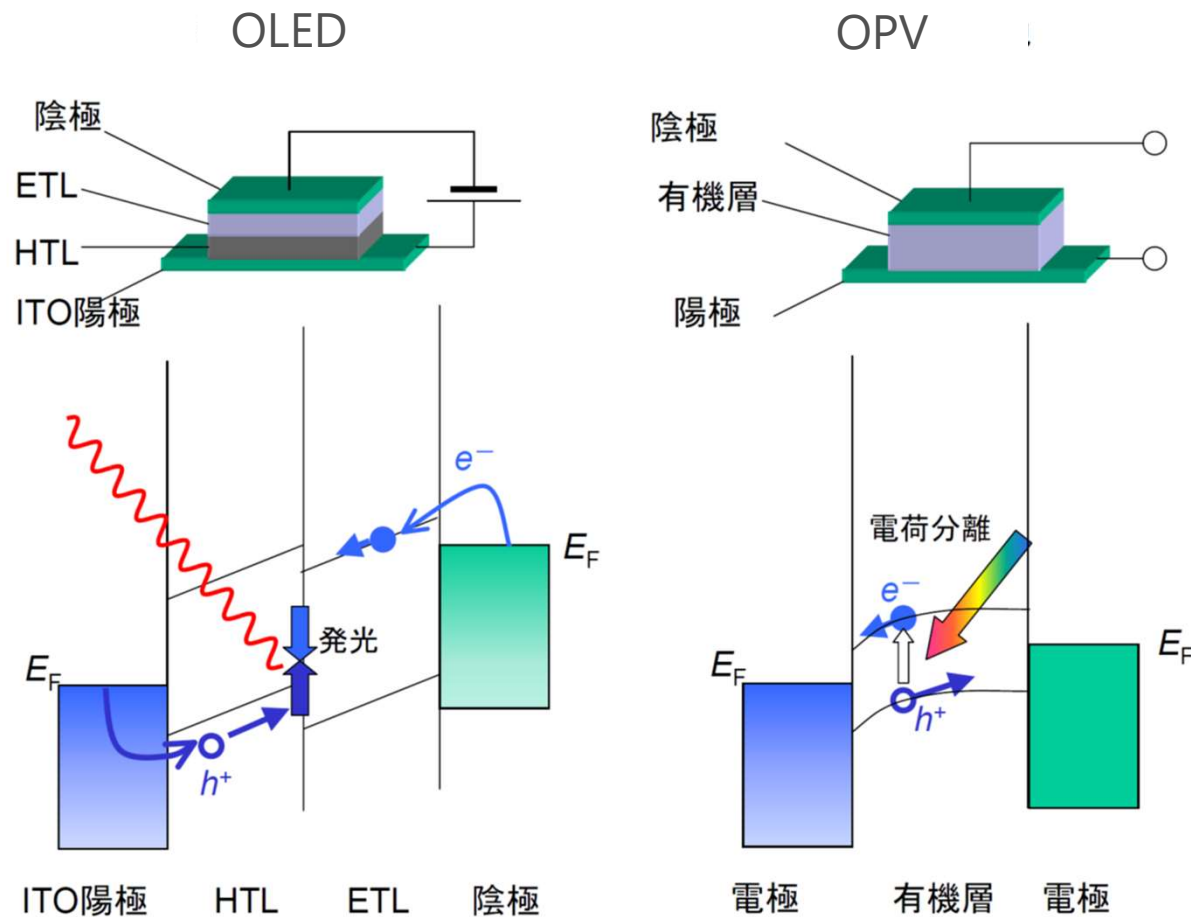
Electronic Structure of Organic Semiconductor: Basics

How the electronic structure of organic solid build up.
Ionization Energy, Electron Affinity,
Fermi Level, Work function etc...

Hisao ISHII

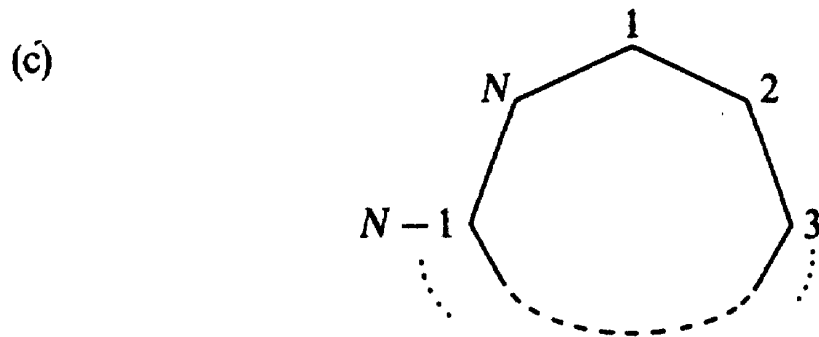
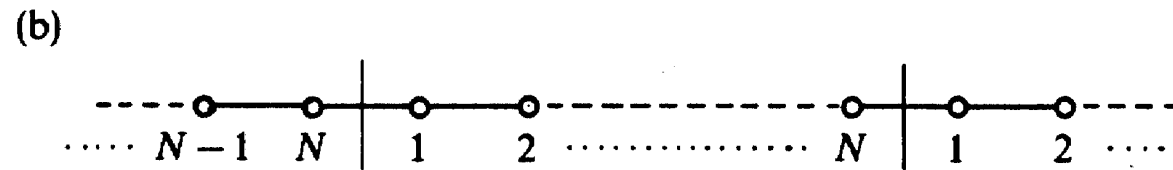
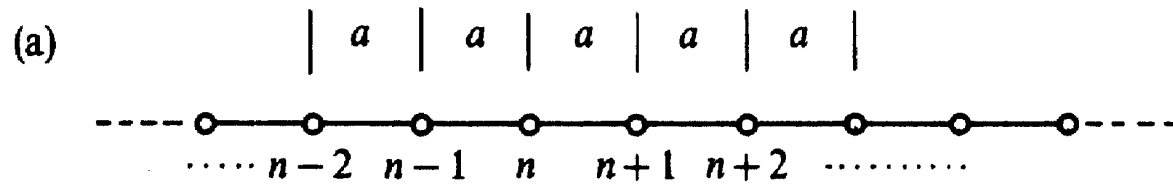
Chiba University

Energy Diagram of Organic Devices



To understand the device operation, we use an energy diagram.
Let us go around the basics of electronic structure.

In the case of crystal: Periodic Boundary Condition



Bloch's theorem

$$\Psi(x + Na) = \Psi(x)$$

$$\rho(x) = \Psi^*(x)\Psi(x)$$

$$\rho(x) = \rho(x + a) \text{ より}$$

$$\Psi(x + a) = \mu\Psi(x), \mu^* \mu = |\mu|^2 = 1$$

$$\Psi(x + Na) = \mu^N \Psi(x) = \Psi(x)$$

$$\text{よって } \mu^N = 1, \mu = \exp(2\pi ip/N) = \cos(2\pi p/N) + i \sin(2\pi p/N)$$

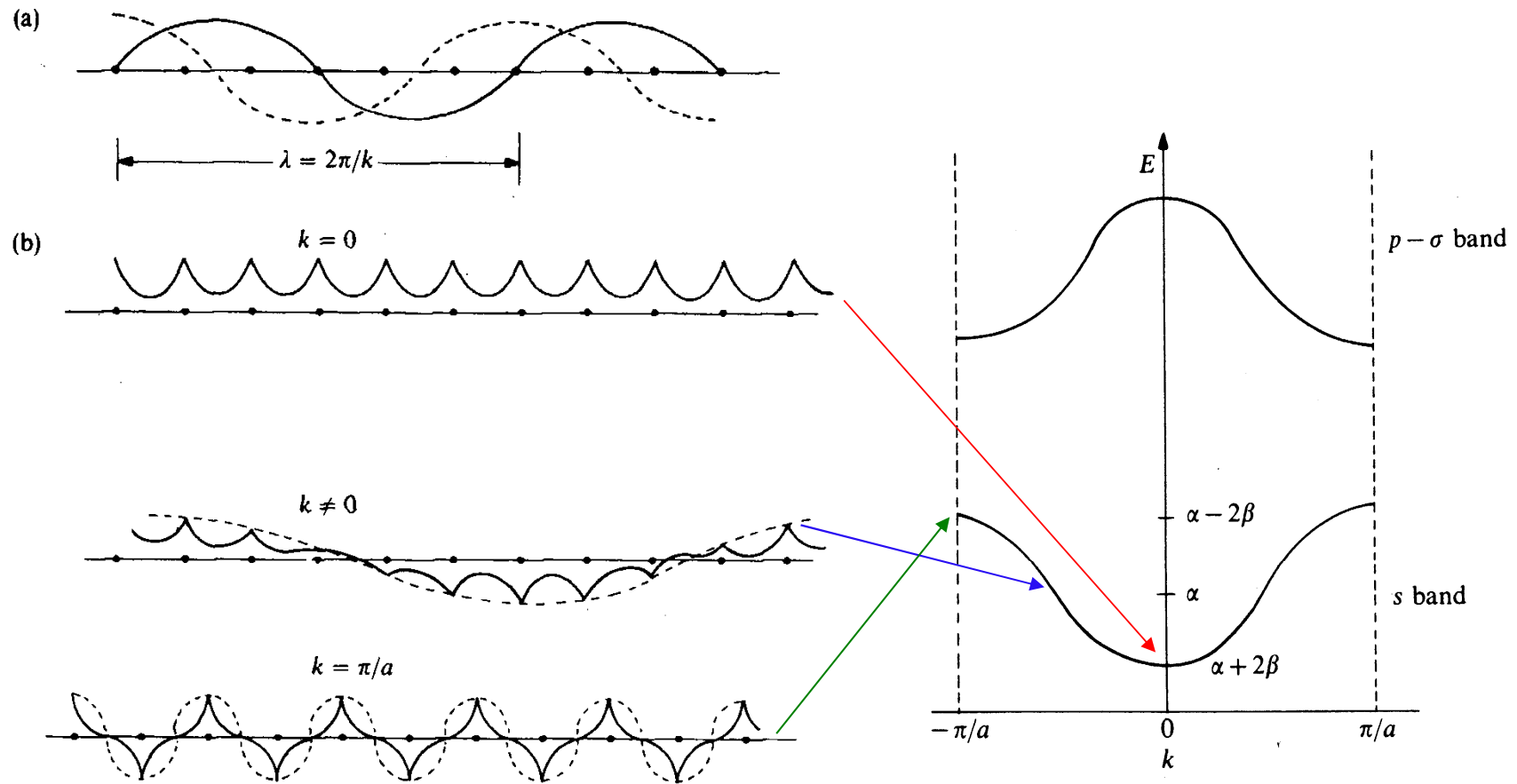
$$k = \frac{2\pi p}{Na} \text{ とすると}$$

$$\Psi(x + a) = \exp(ika)\Psi(x)$$

$$\Psi(x) = \exp(ikx)u(x), u(x + a) = u(x)$$

Bloch Wave

Complex value of wave function >> running wave



kとエネルギーの関係→エネルギーバンド分散

Good Quantum Number

Classical Theory 1

Free Space: Translational symmetry >>

Conservation of momentum law

Classical Theory 2

Planetary Systems

Rotational symmetry >> Conservation of angular momentum (Kepler's law, constant angular velocity)

Quantum theory for atoms:

Rotational symmetry >> Conservation of angular momentum

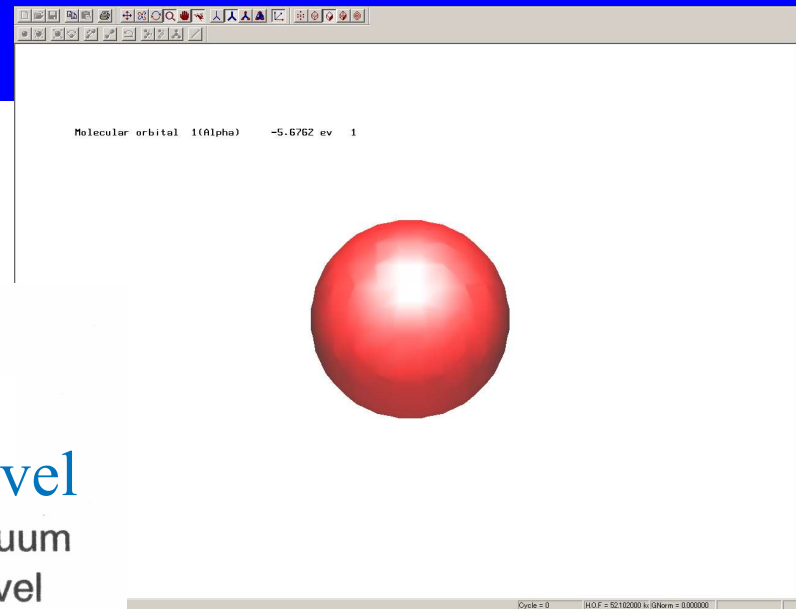
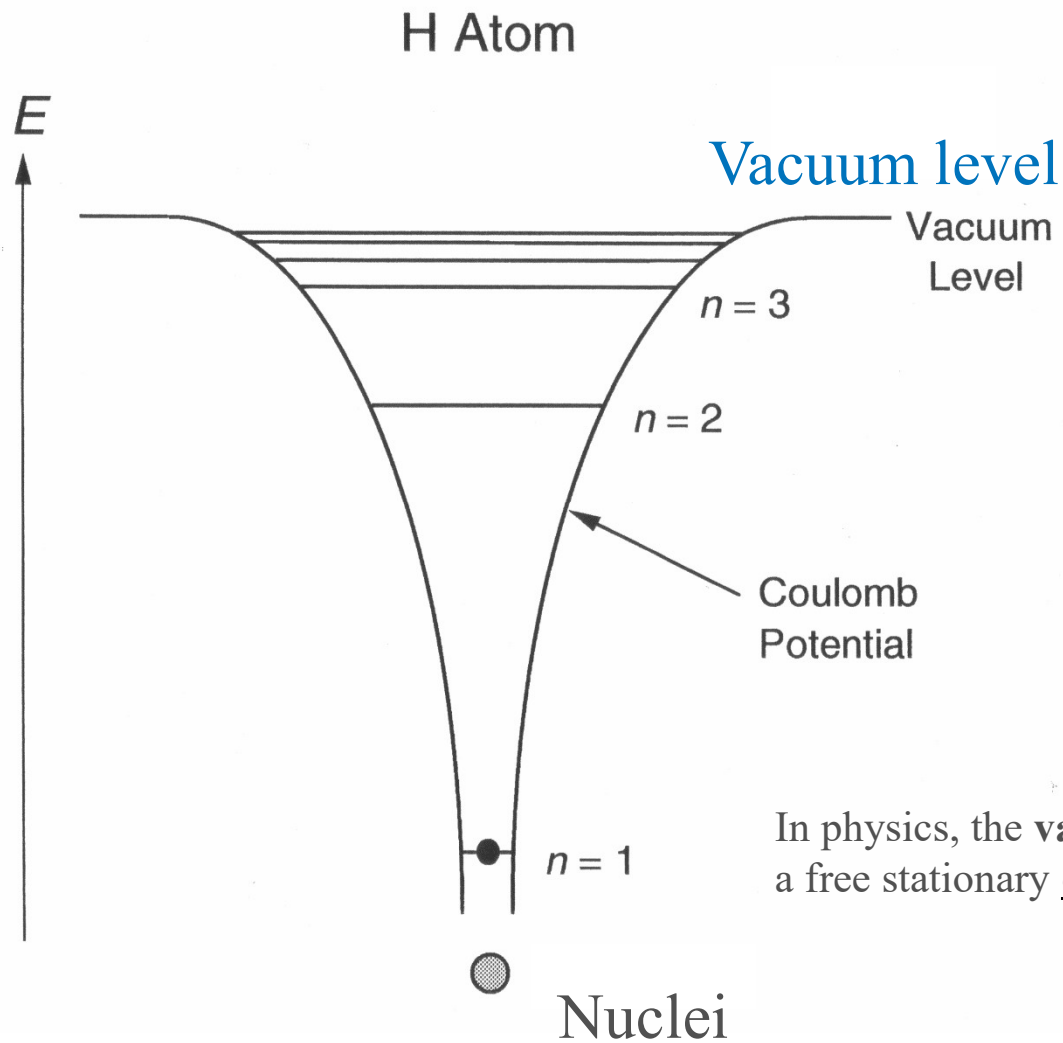
Angular momentum is a good quantum number in the system >> 1s 2s 2p.....

Crystal lattice: Translational symmetry with respect to lattice >>

Conservation of crystal momentum >> Crystal momentum, or wavenumber, is a good quantum number of the system >> band dispersion

Crystal momentum $\hbar k$

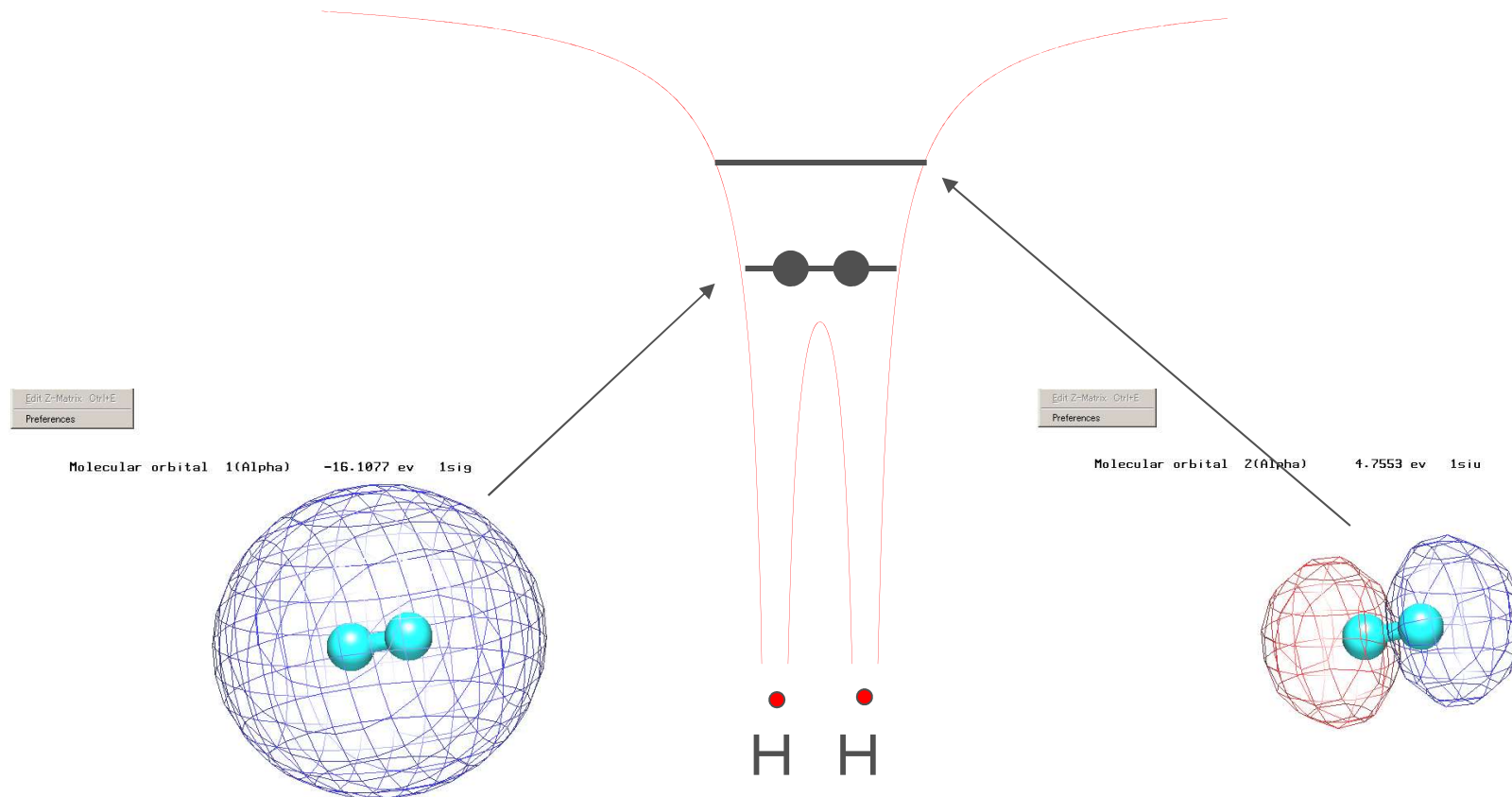
Electronic structure of hydrogen atom



In physics, the **vacuum level** refers to the energy of a free stationary electron that is outside of any material .

Electronic structure of hydrogen molecule

Vacuum level

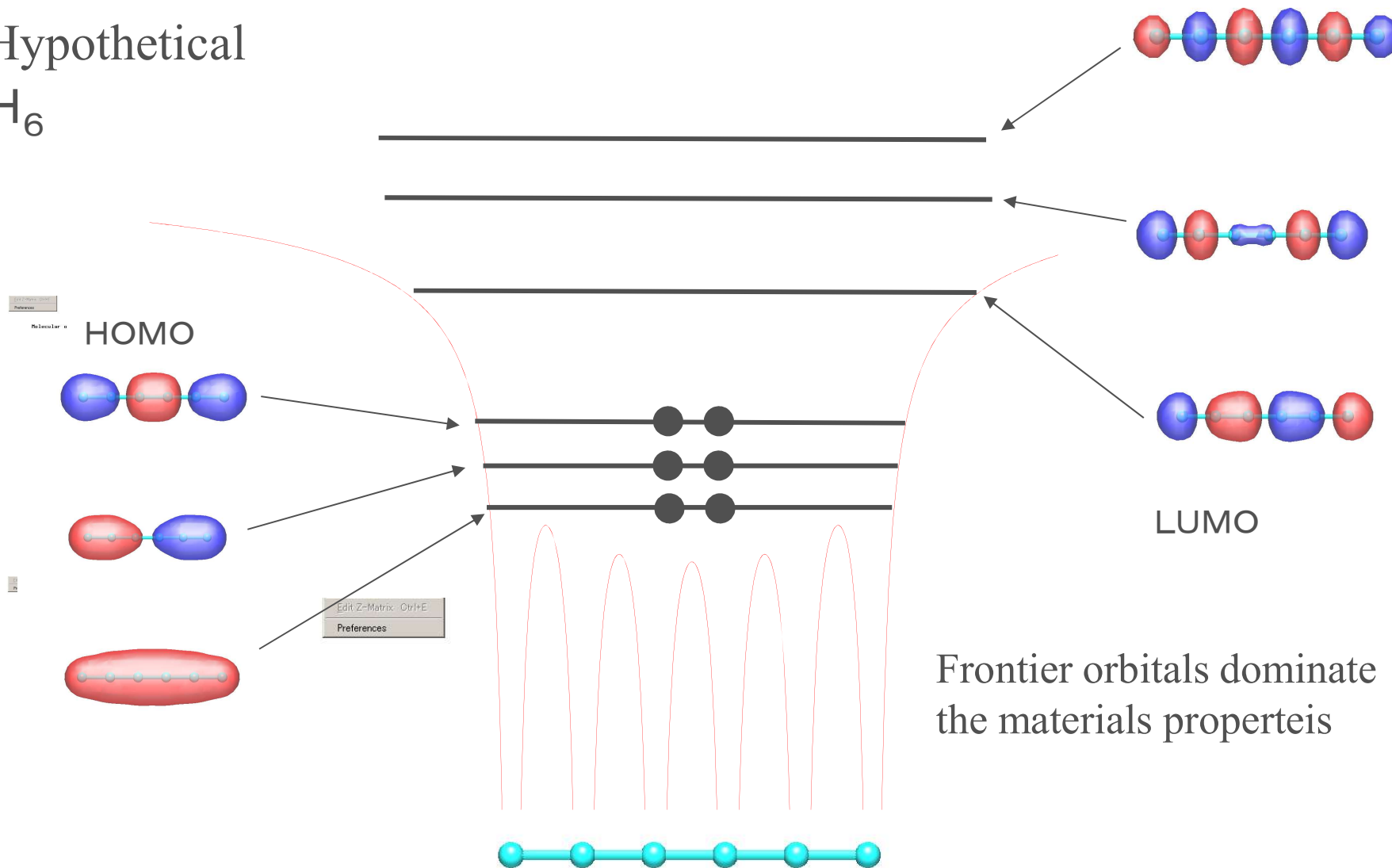


Molecular orbital

Edit Z-Matrix Ctrl+E
Preferences

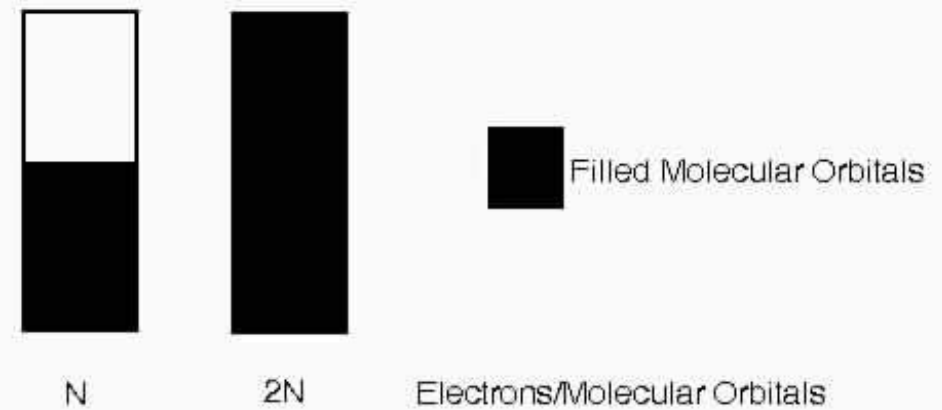
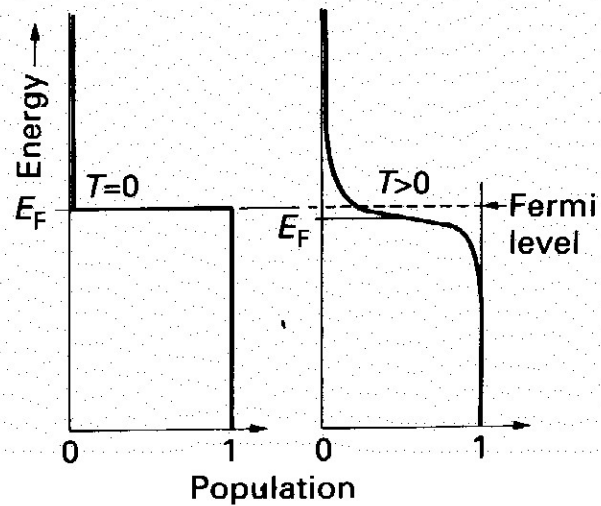
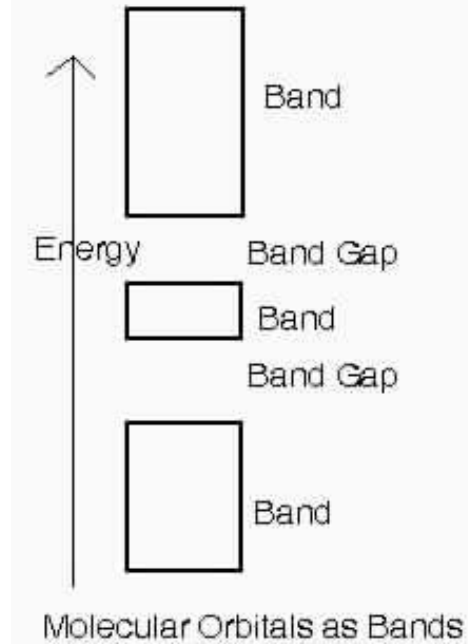
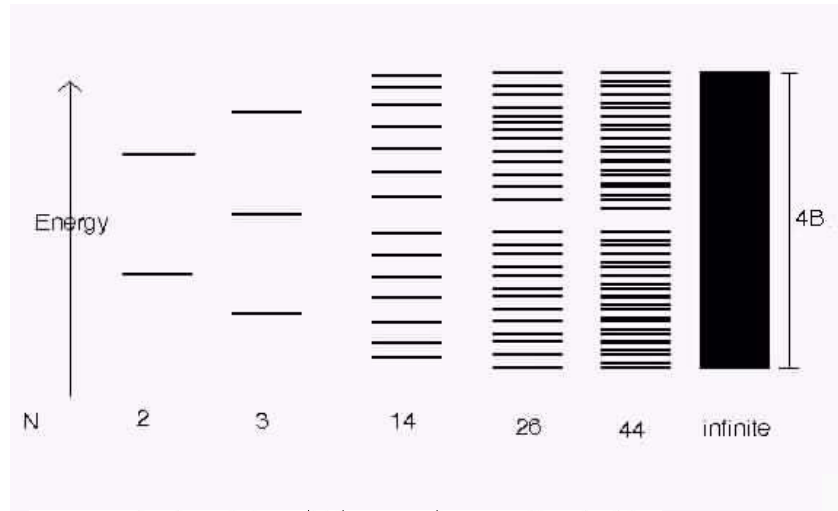
Molecular orbital 6(Alpha) 2.3123 ev 3sio

Hypothetical
 H_6

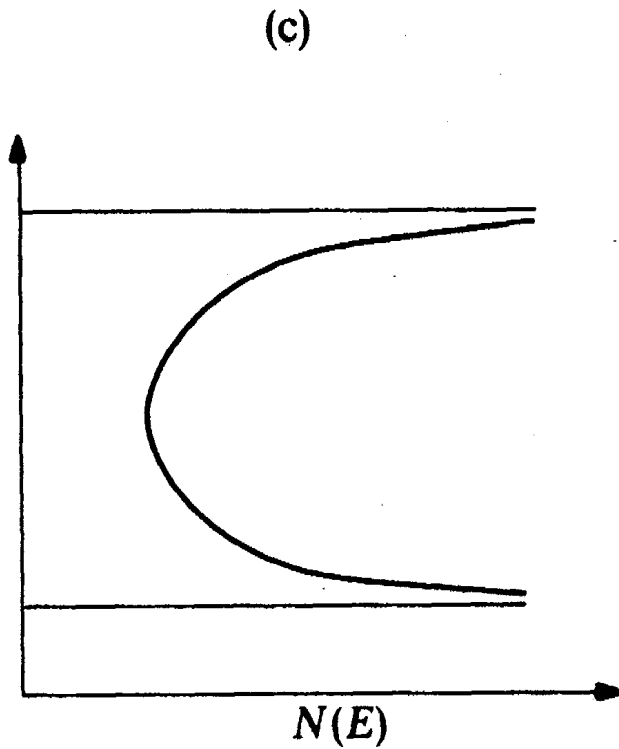
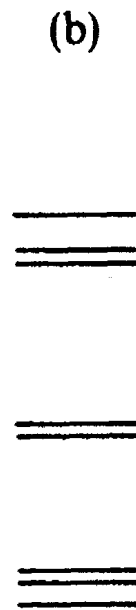
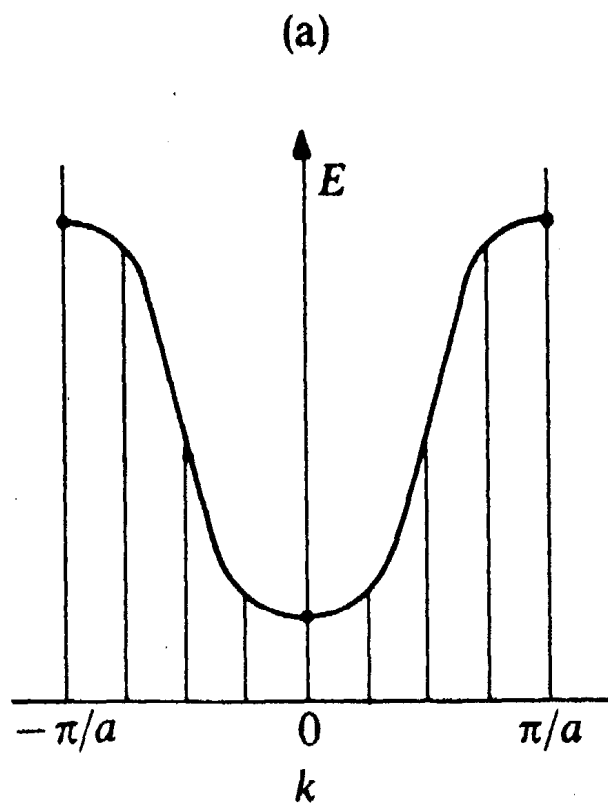


Frontier orbitals dominate
the materials properties

MO to Band



10^{21} electrons in one band



Wave function of total system

$$\Psi(x_1, x_2, x_3, \dots)$$

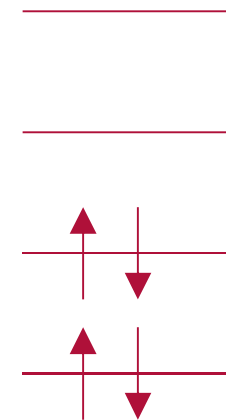
$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}.$$

$$\Psi_{MCSCF} = \sum_{k=1}^n c_k |\phi_{k1} \phi_{k2} \phi_{k3} \cdots \phi_{kn}|$$

One electron approximation

Ignoring many body effect

- each electron will occupy a one electron state independently of all the other electrons
- electrons in different one electron states do not "recognize" each other



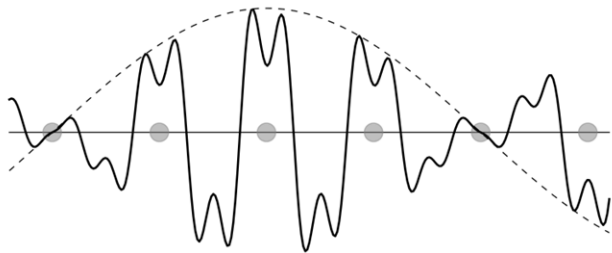
LCAO

$$\phi_i(x_i, y_i, z_i) = \sum c_{ij} \chi_j$$

$$\delta \frac{\langle \Phi | \mathbf{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = 0$$

In crystal,
Bloch Theorem

In molecule,



$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r})$$

$$\phi_i(x, y, z) = \sum_i c_{ij} \chi_j(x - x_j, y - y_j, z - z_j)$$

$$\psi_m(\mathbf{r}) \approx \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot\mathbf{R}_n} \varphi_m(\mathbf{r} - \mathbf{R}_n)$$

Delocalized states

Running wave

Localized states

Stationary wave



分子軌道のおさらい

Review of molecular orbital
interaction

$$\Delta^* - \Delta = \frac{2S(S\alpha_0 - \beta)}{1 - S^2} > 0$$

重要

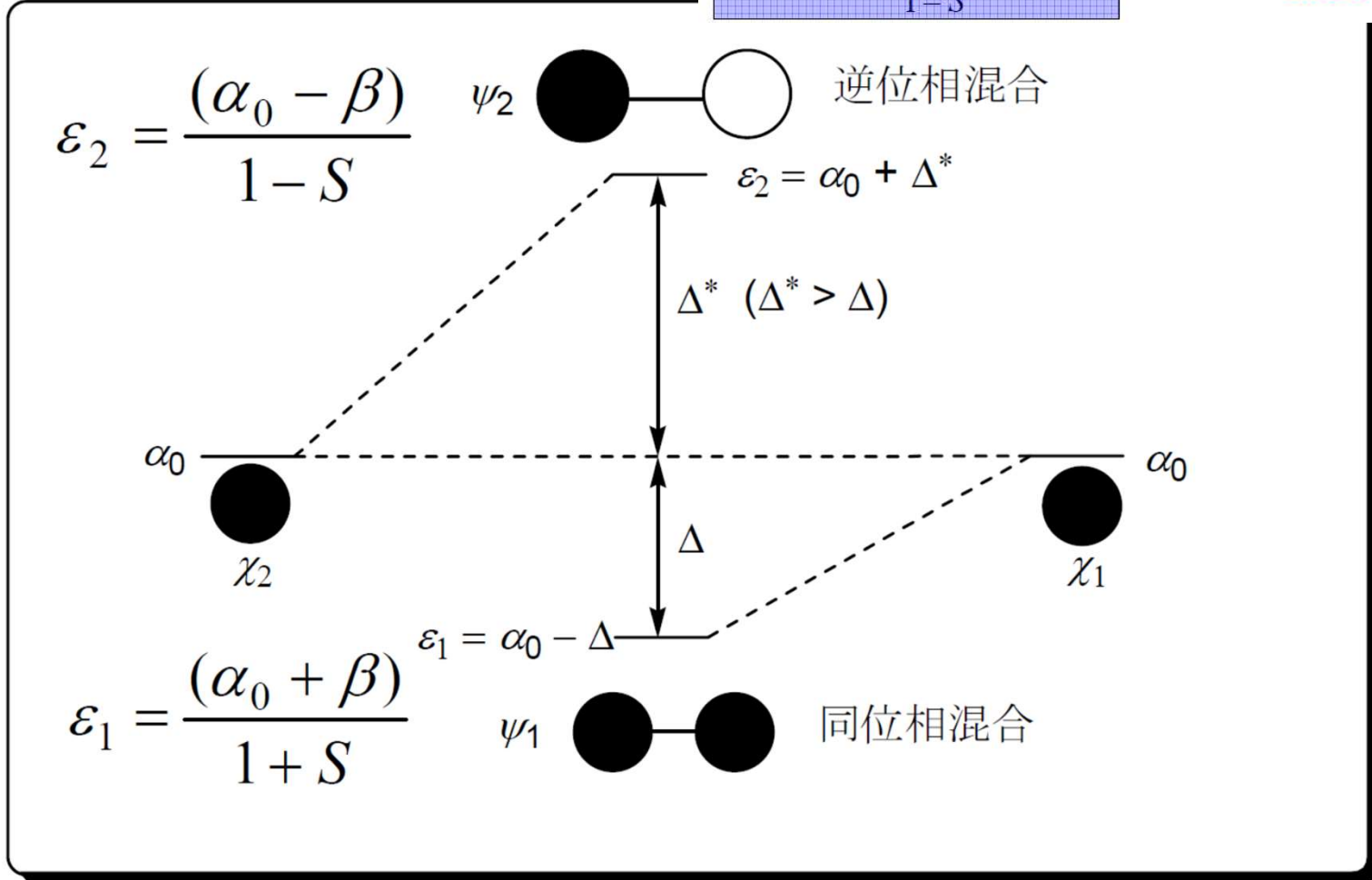


図3.3 縮重系の軌道相互作用 (2つのs軌道の場合)
Interaction between two degenerated orbitals

摂動論 Perturbation

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$$

$$\hat{H} = \hat{H}^0 + \lambda\hat{H}' + \lambda^2\hat{H}'' + \dots$$

$$\hat{H}^0|\varphi_n^0\rangle = E_n^0|\varphi_n^0\rangle \quad \langle\varphi_n^0|\varphi_m^0\rangle = \hat{O}_{mn}$$

$$|\varphi_n\rangle = |\varphi_n^0\rangle + \lambda|\varphi_n'\rangle + \lambda^2|\varphi_n''\rangle + \dots$$

$$E_n = E_n^0 + \lambda E_n' + \lambda^2 E_n'' + \dots$$

$$E_n = E_n^0 + \lambda E_n'$$

$$E_n' = \langle\varphi_n^0|\hat{H}'|\varphi_n^0\rangle$$

$$|\varphi_n\rangle = |\varphi_n^0\rangle + \sum_j' \frac{H_{jn}'}{E_n^0 - E_j^0} |\varphi_j^0\rangle$$

$$\begin{aligned} & \left(\hat{H}^0|\varphi_n^0\rangle - E_n^0|\varphi_n^0\rangle \right) + \left(\hat{H}^0|\varphi_n'\rangle + \hat{H}'|\varphi_n^0\rangle - E_n^0|\varphi_n'\rangle - E_n^0|\varphi_n^0\rangle \right) \lambda \\ & + \left(\hat{H}^0|\varphi_n''\rangle + \hat{H}'|\varphi_n'\rangle + \hat{H}''|\varphi_n^0\rangle - E_n^0|\varphi_n''\rangle - E_n^0|\varphi_n'\rangle - E_n^0|\varphi_n^0\rangle \right) \lambda^2 \\ & + \dots = 0 \end{aligned}$$

縮重系の波動関数

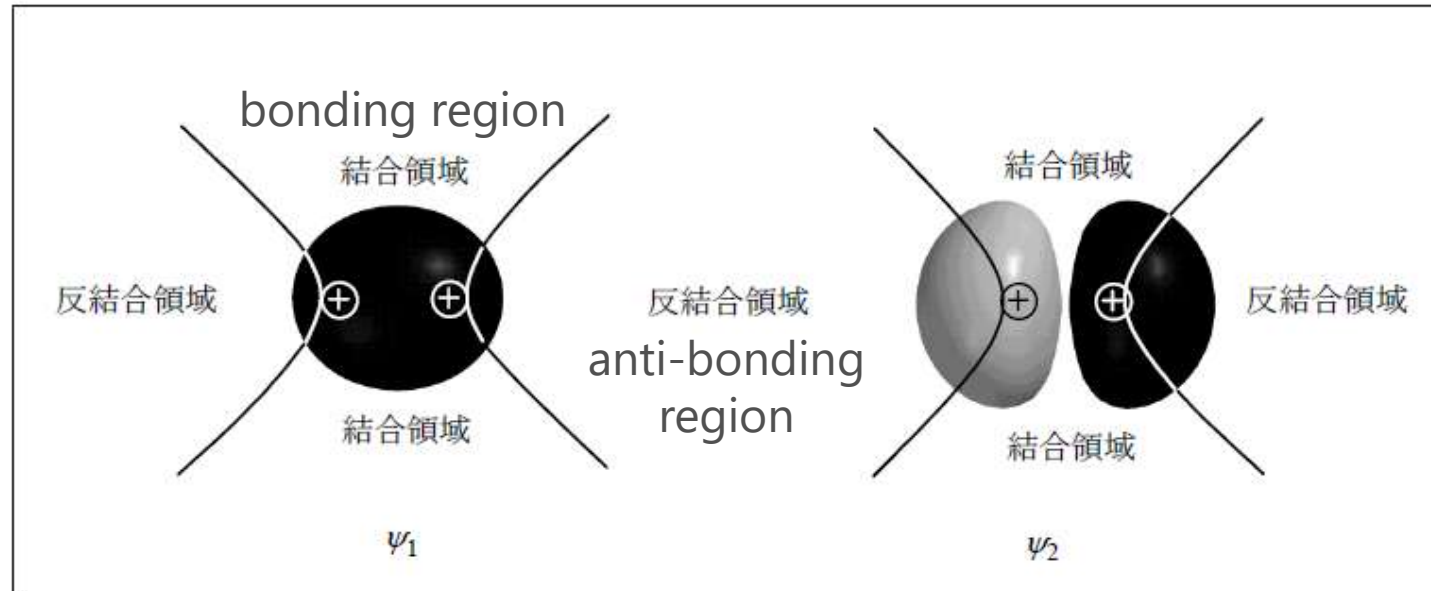
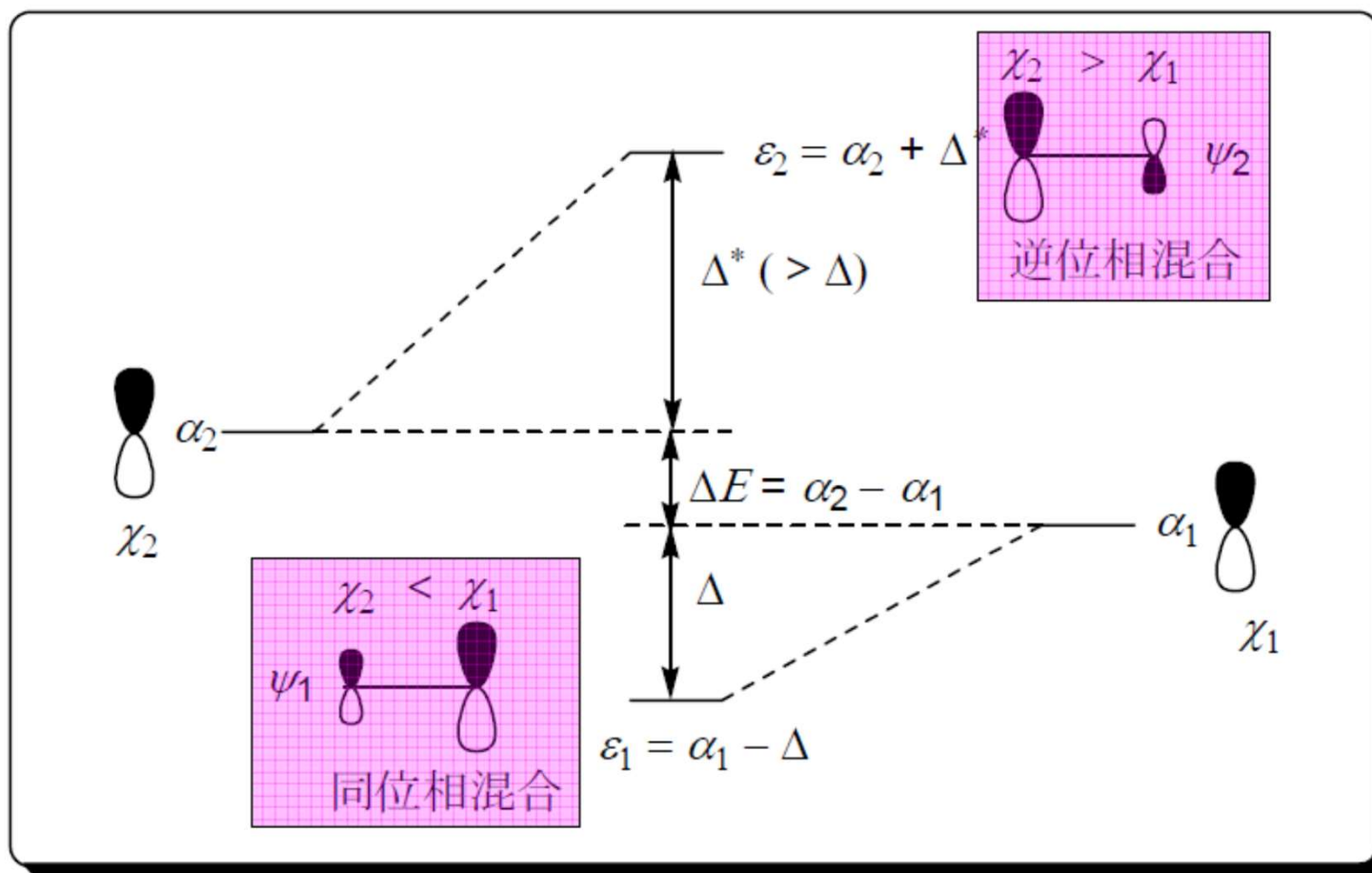


図3.4 2個の1s軌道の場合のMO(図3.2の ψ_1 と ψ_2) (\oplus は原子核)

ψ_1 : 結合性分子軌道 (bonding MO)

ψ_2 : 反結合性分子軌道 (antibonding MO)

図3.5 1 : 1 軌道相互作用 (縮重がない場合)



Interaction between two non-degenerating orbitals

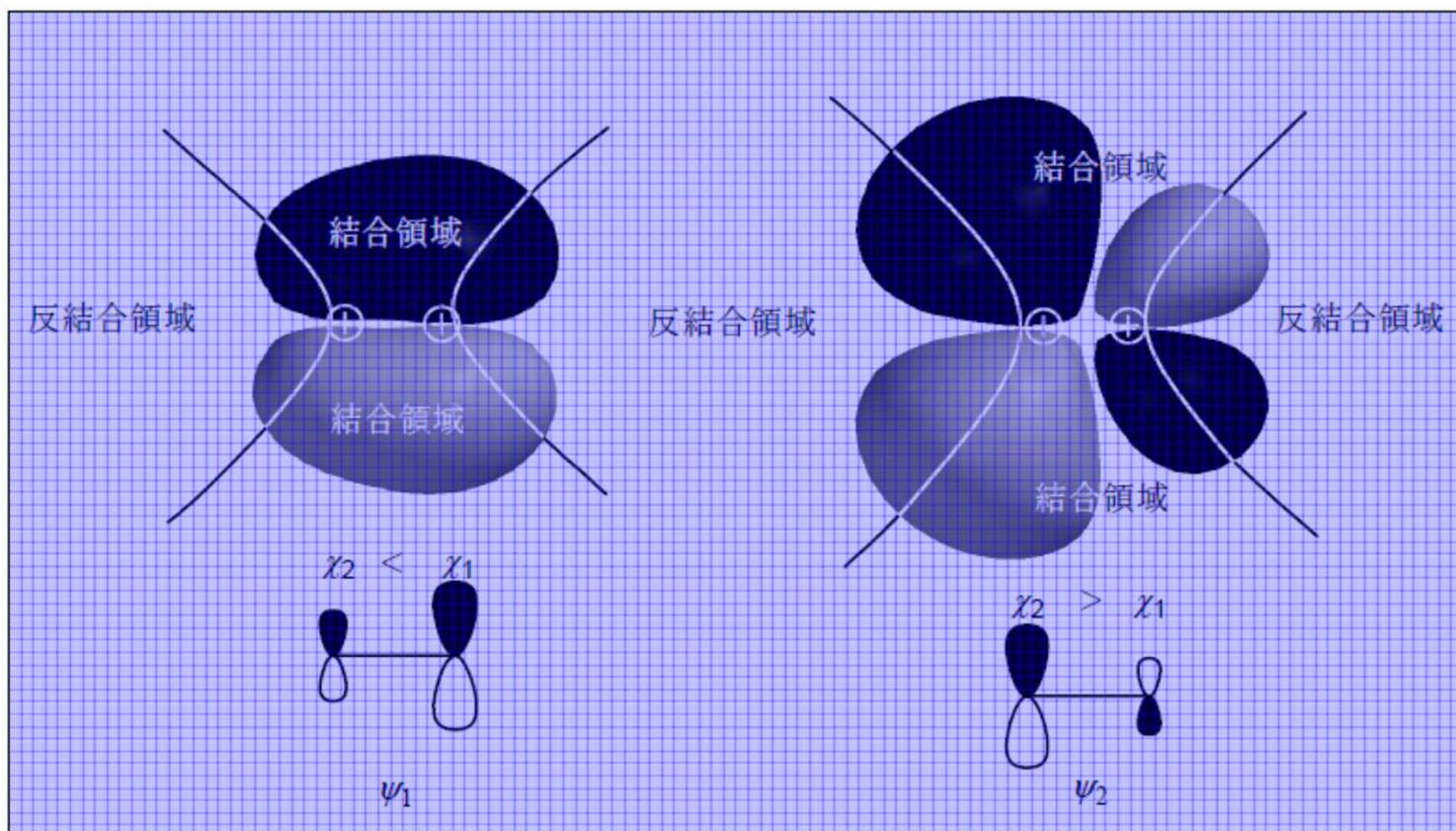


図3.6 非縮重相互作用系の分子軌道
(2p軌道の場合; +は原子核)

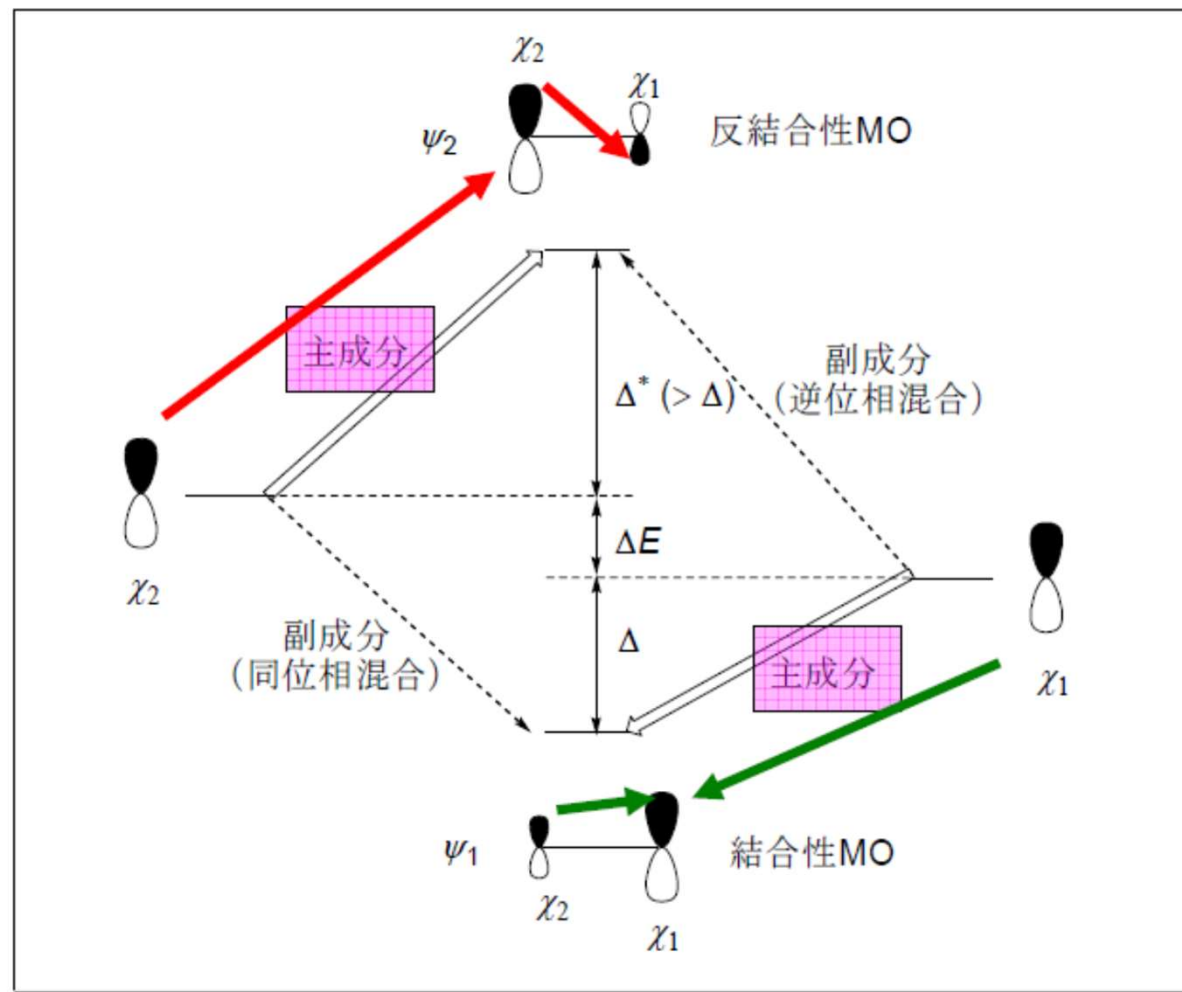
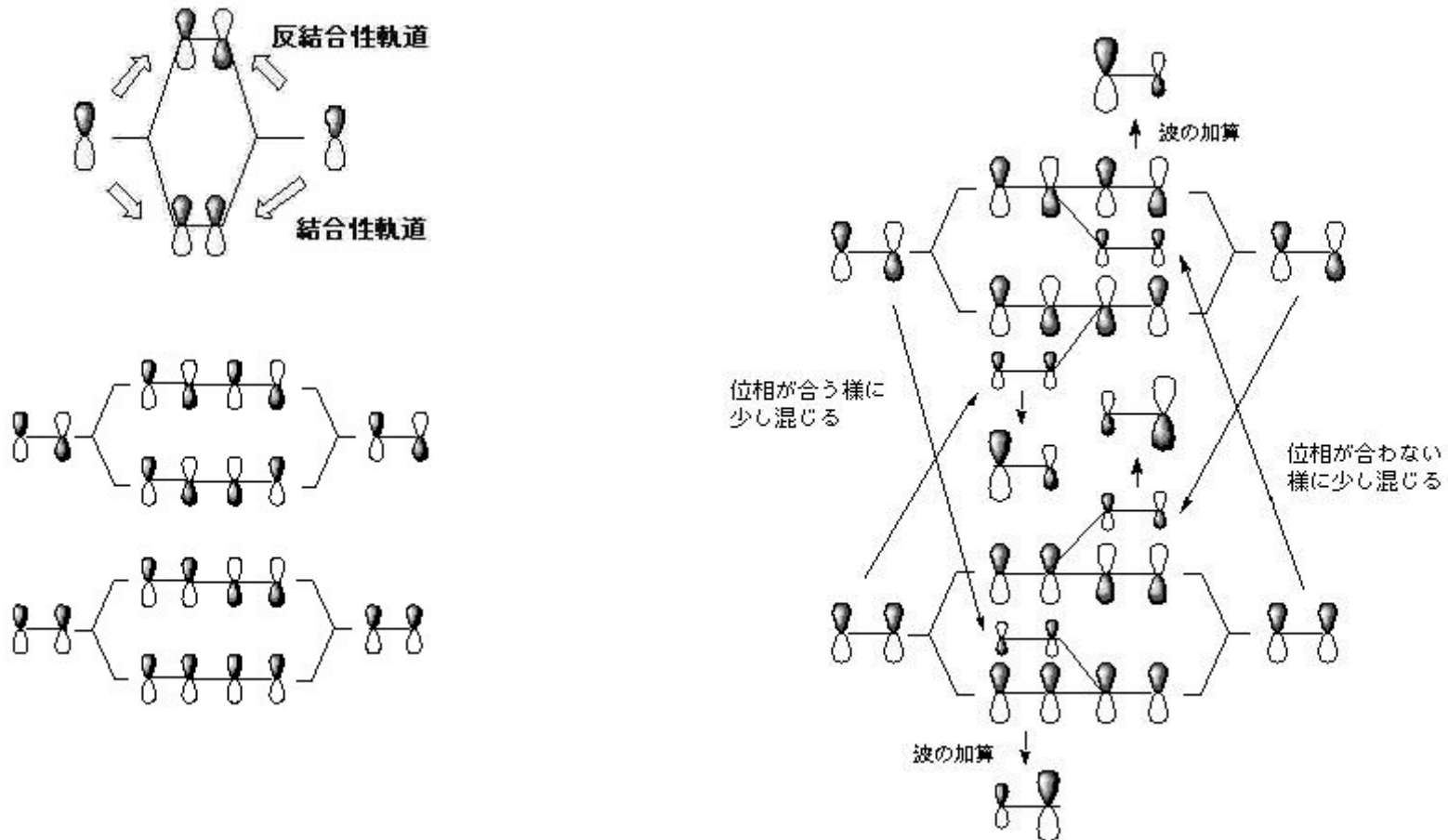


図3.7 軌道相互作用の原理(覚えよう)

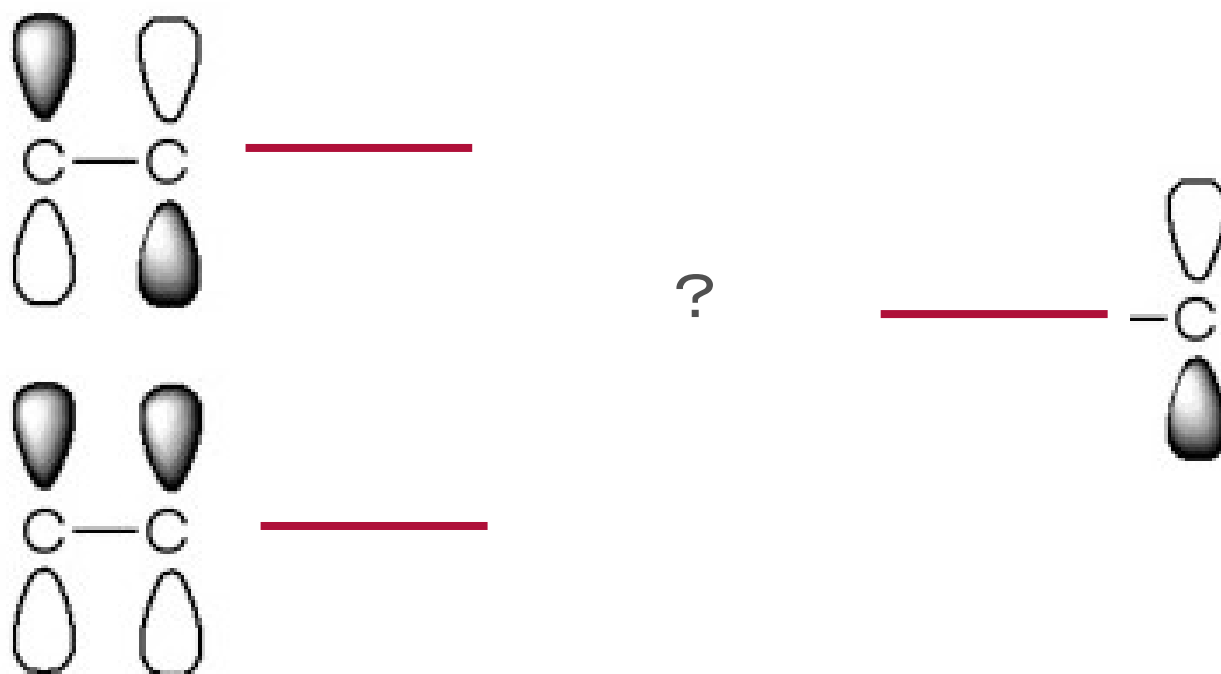
軌道混合則 Orbital mixing rule

1. When higher energy orbital mixes with lower orbital, they mix *in phase*.
2. When lower energy orbital mixes with higher energy orbital, they mix *out of phase*.



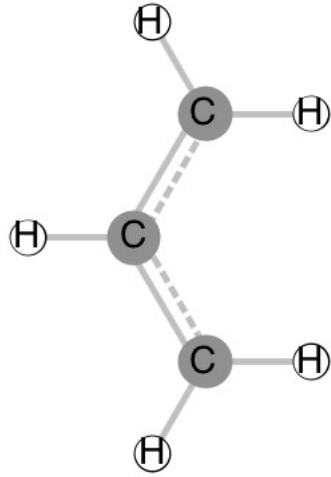
Drill

- How can you mix the HOMO and LUMO of ethylene molecule with additional carbon pi-orbital?

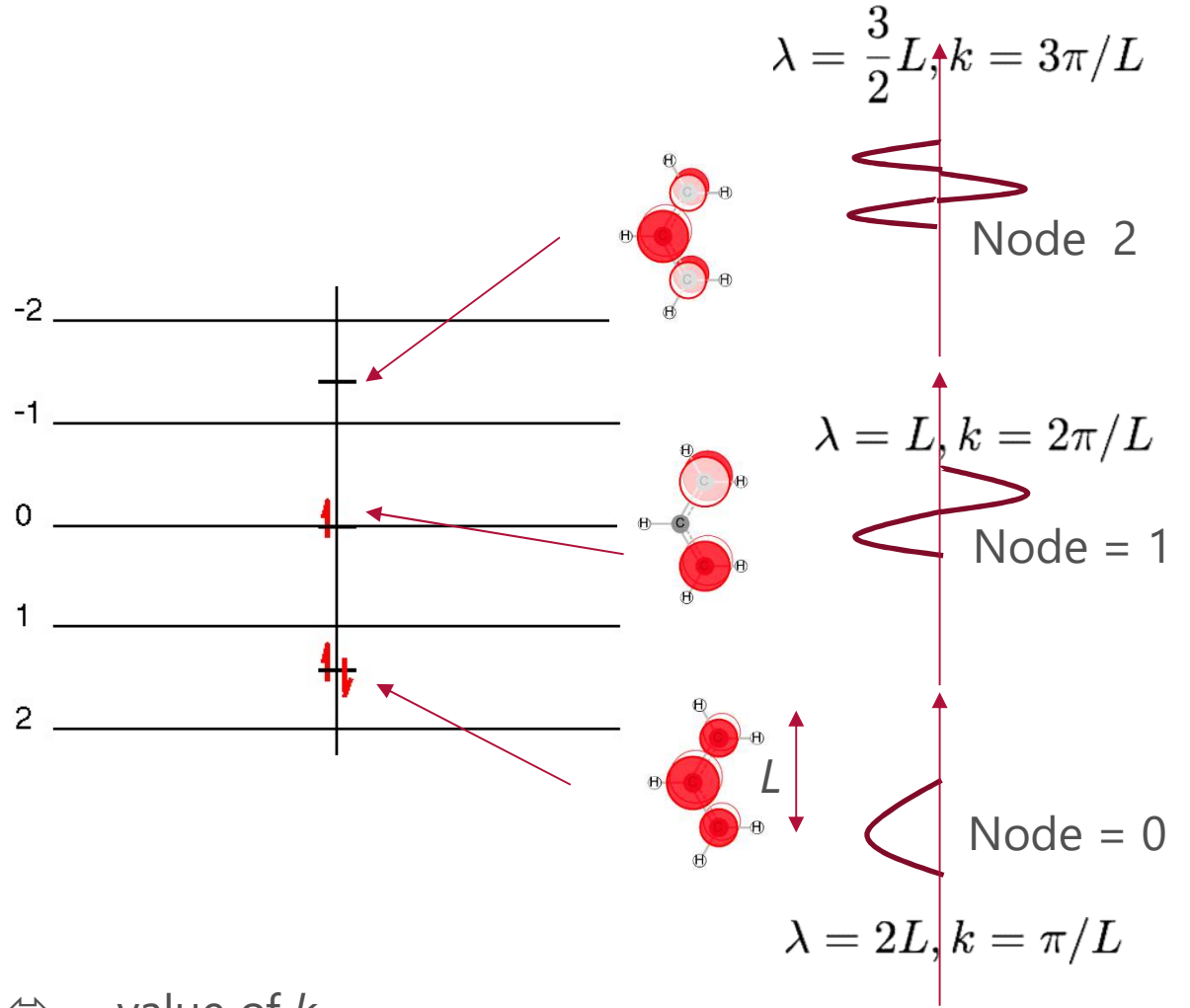




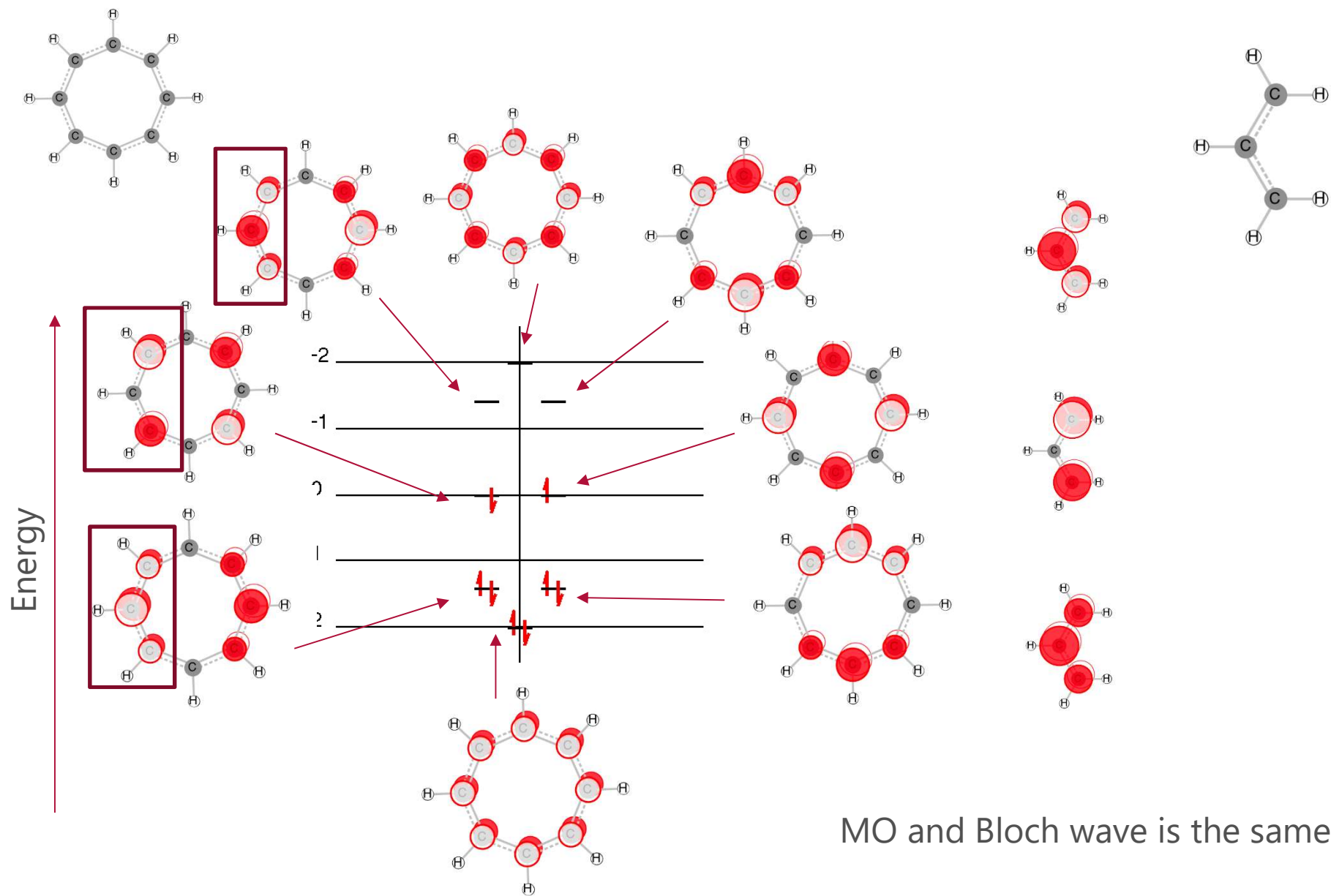
Let us play with Hückel MO Calc.



Energy ↑



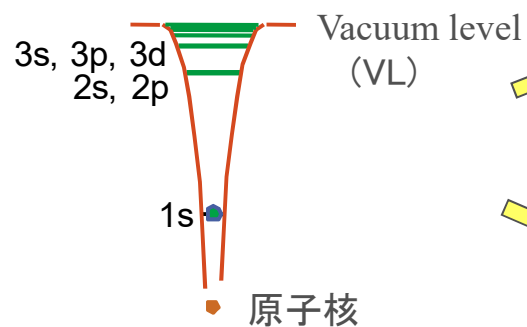
Play with MO



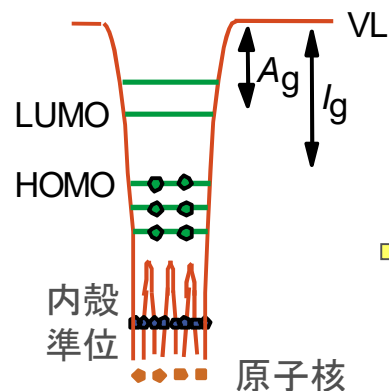
MO and Bloch wave is the same.

Electronic structures of atom, molecule, and solids

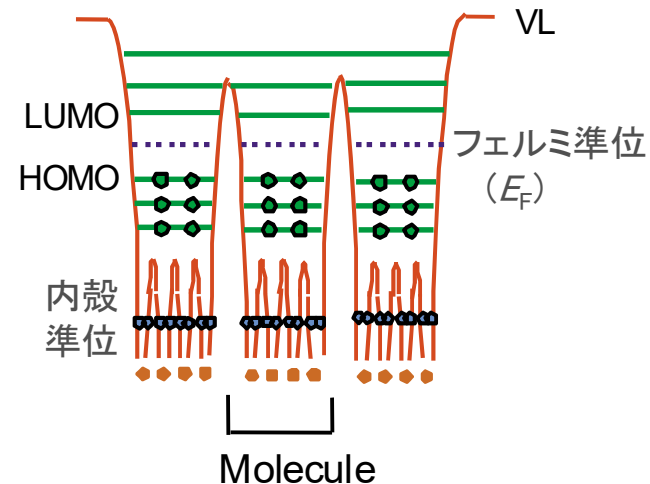
atom



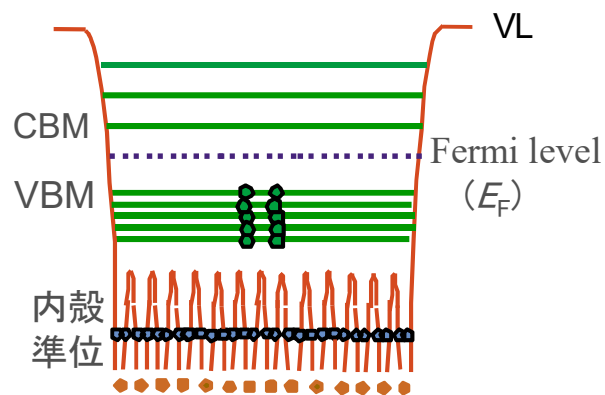
molecule



Molecular solid

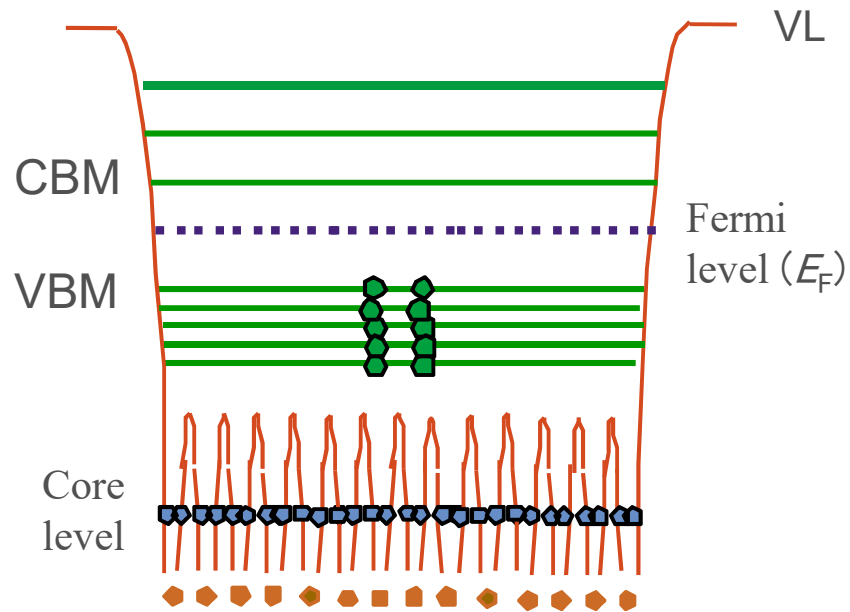


Inorganic solid



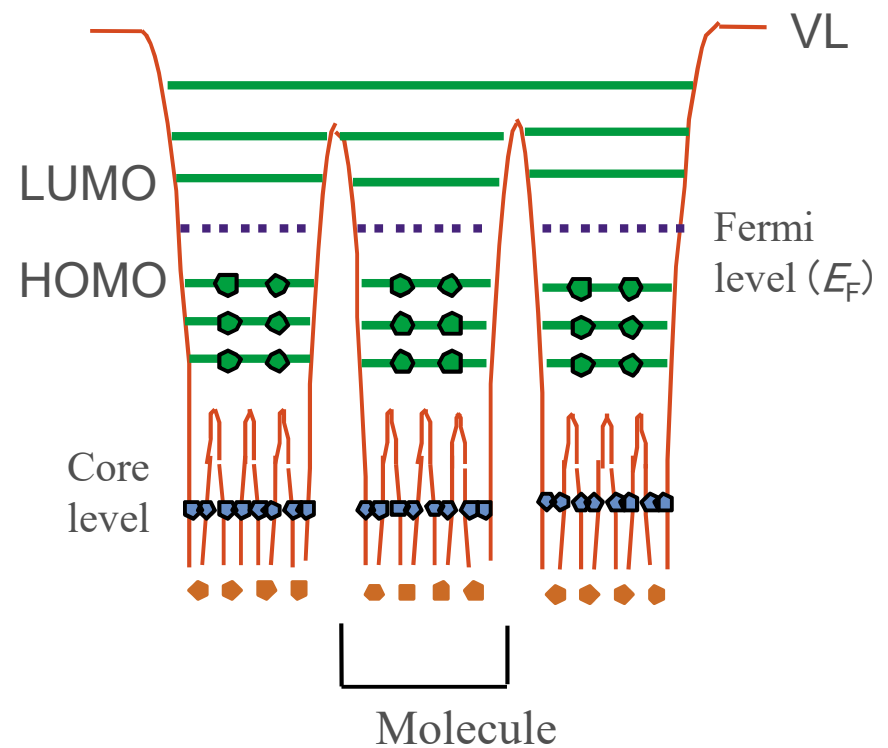
Energy diagram of inorganic and molecular solid

Inorganic solid



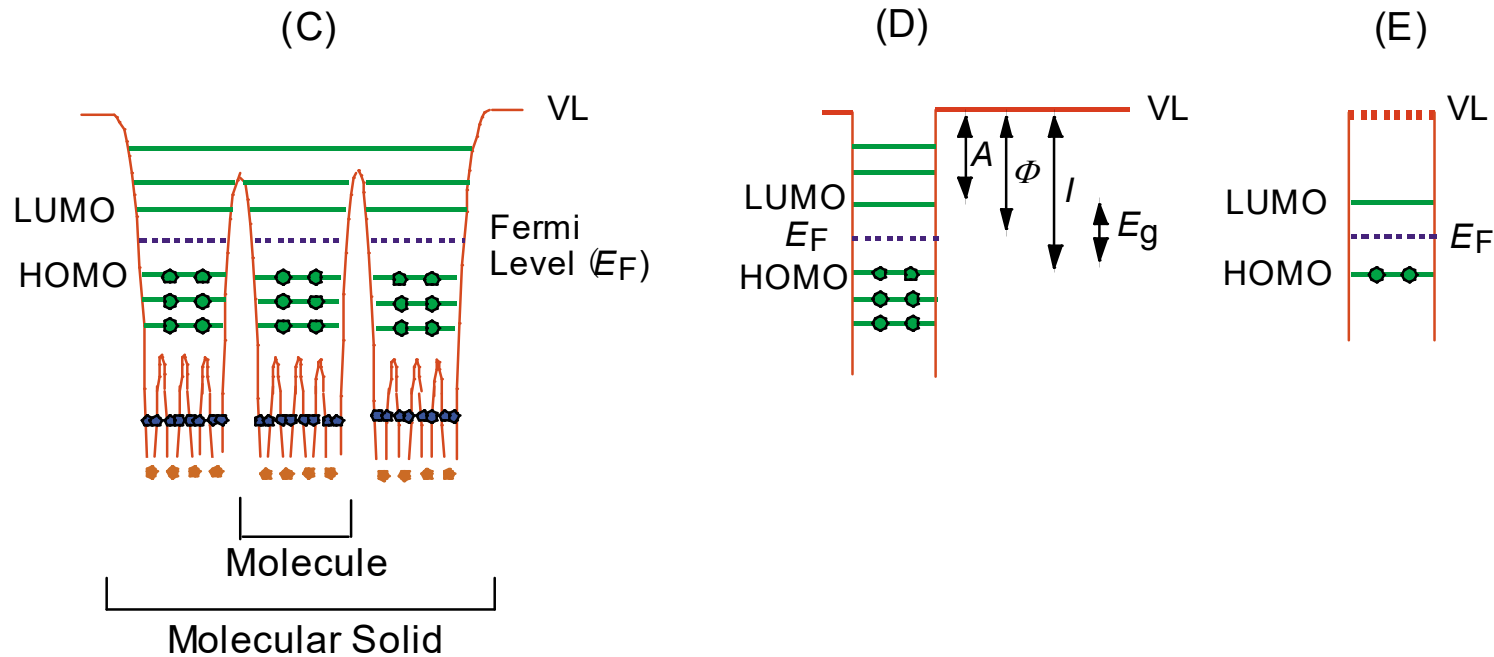
Valence electrons are delocalized

Molecular solid



Valence electrons are localized in molecule,
But delocalized within molecule.

Simplification of energy diagram



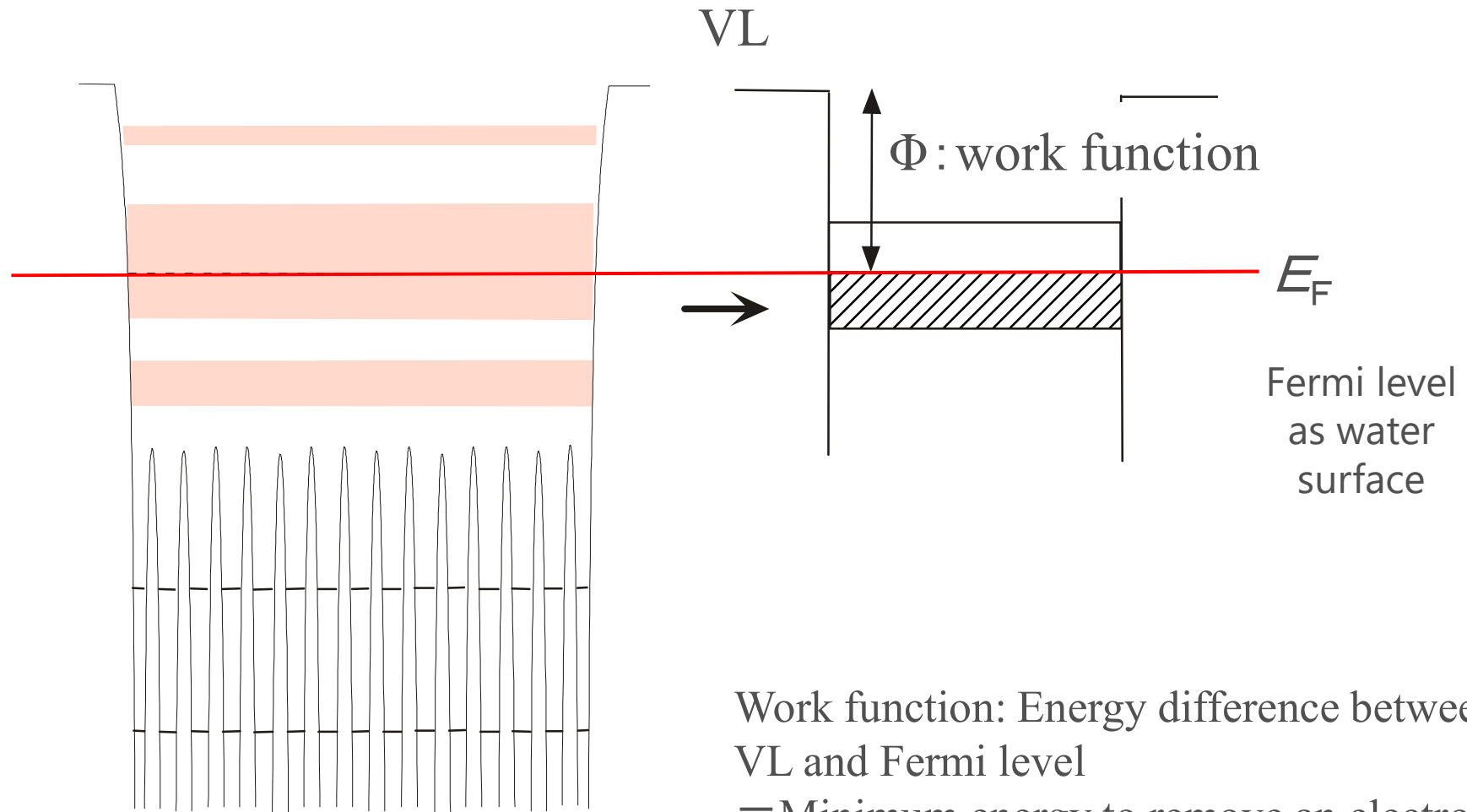
People tend to forget of “localization of electrons” in simplified diagram

I : Ionization energy (energy necessary to withdraw an electron) **定義の詳細は後で**

A : Electron affinity (Energy gain upon an electron attachment)

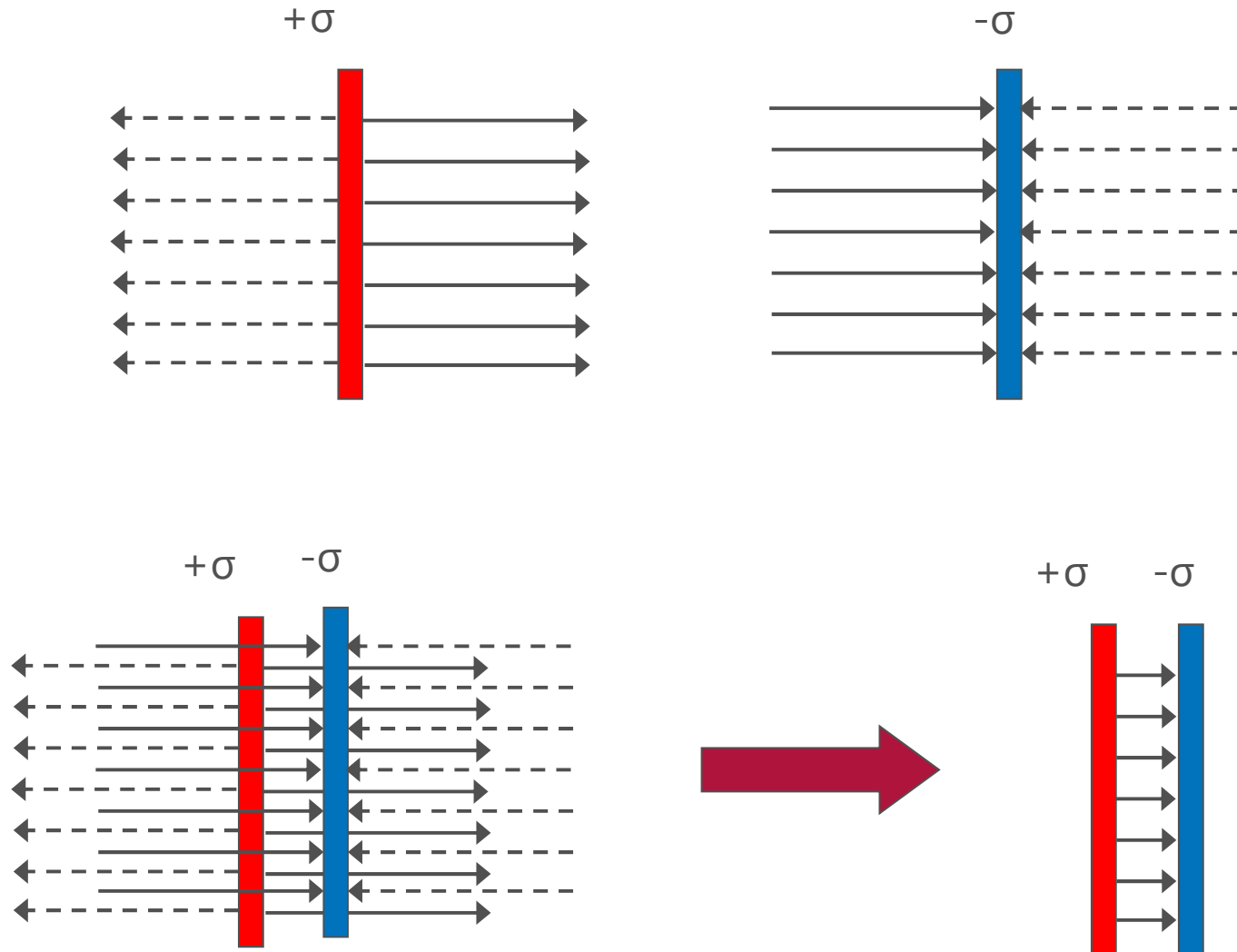
E_F : Fermi level

Electronic structure of metal

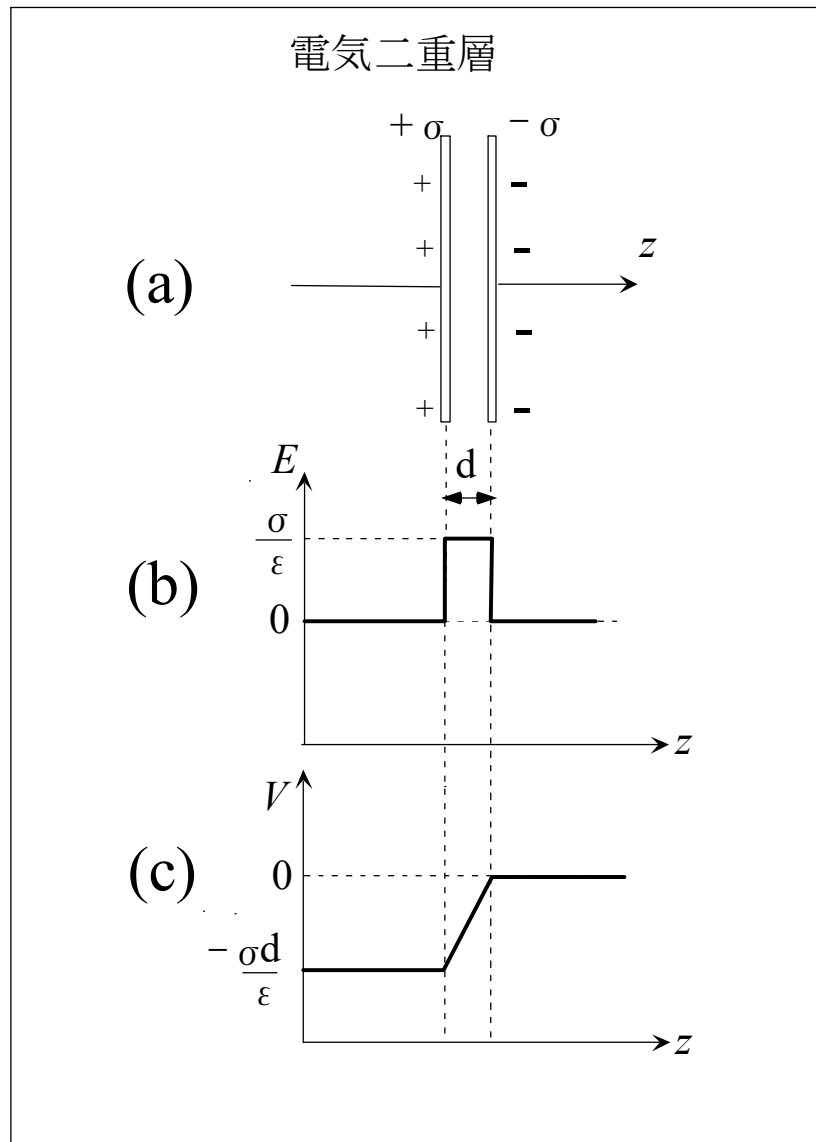


Work function: Energy difference between VL and Fermi level
= Minimum energy to remove an electron (ionization energy)

Electric Double Layer



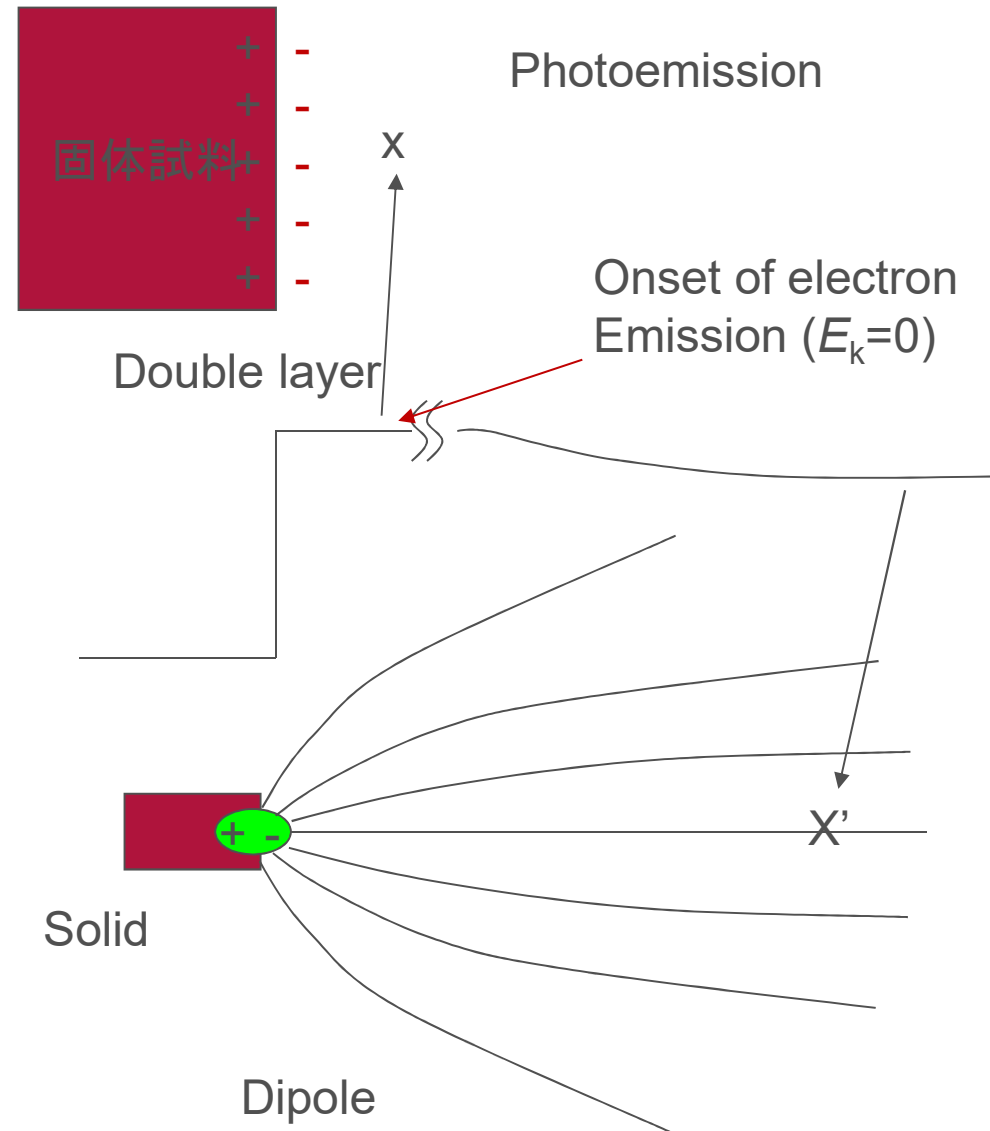
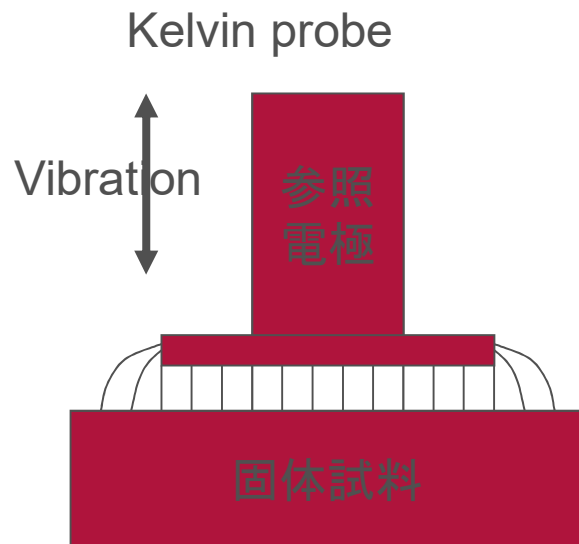
Electric double layer



Vacuum level at where?

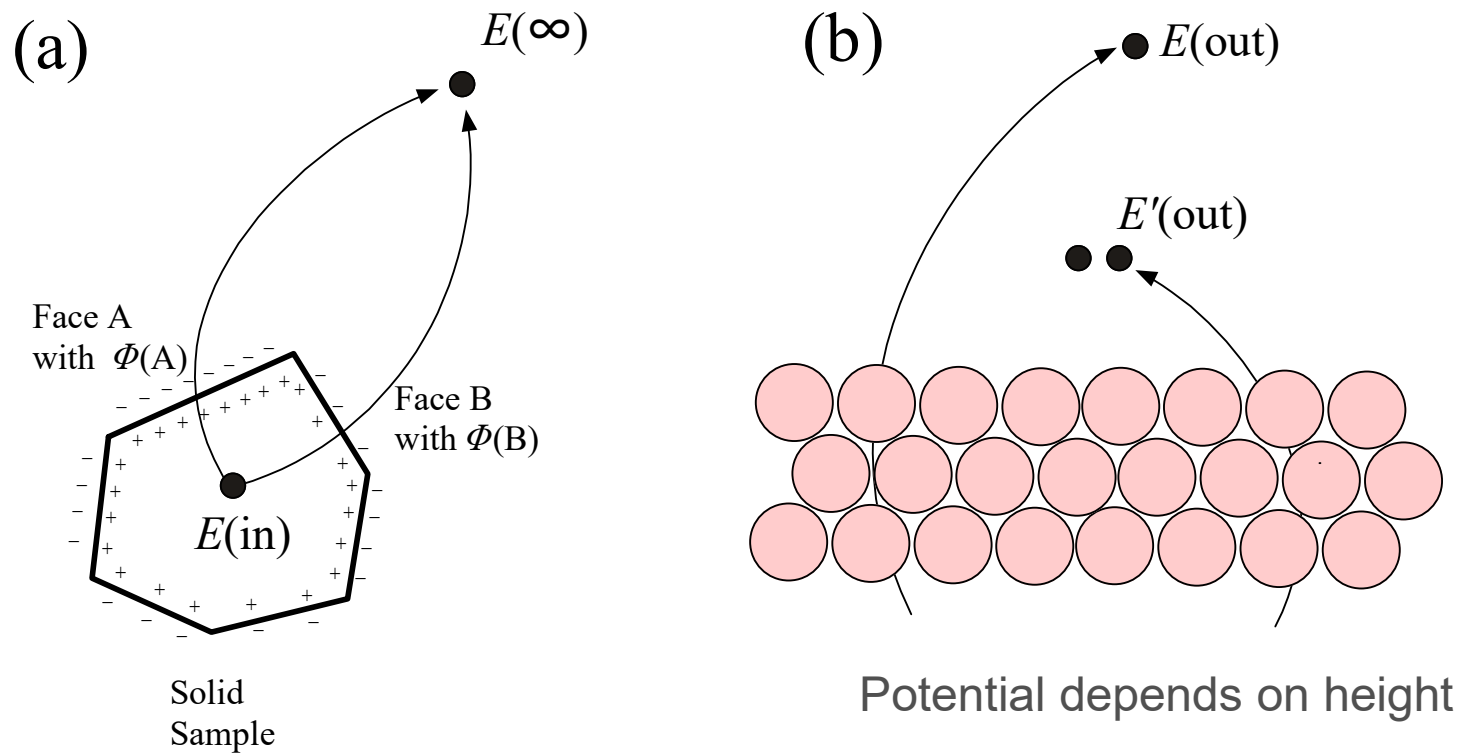
The vacuum level refers to the energy of a free stationary electron that is outside of any material (it is in a perfect vacuum). It may be taken as infinitely far away from a solid, or, defined to be near a surface.

- Where is the place of rest electron just outside solid.



Where is the reference point for vacuum level?

Closer in the scale of crystal size, but far in atomic scale



Double layer depends on face

Work function v.s. electro negativity

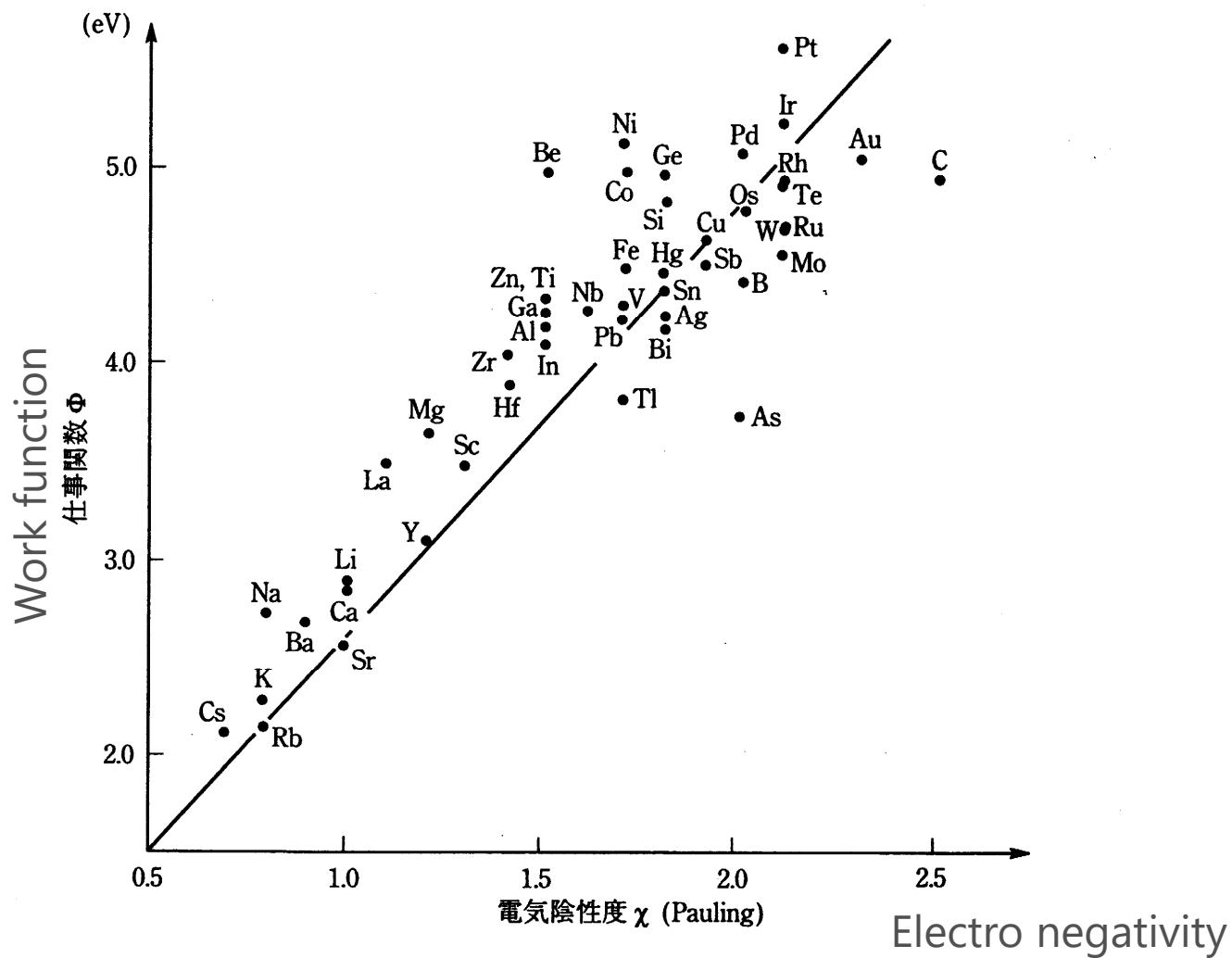


図3-11 仕事関数と電気陰性度の関係

The relation between electronegativity and work

表 5-2 元素の電気陰性度と仕事関数

| 元素 | 電気陰性度* ポーリング | 電気陰性度** マリケン | 左/2.85 | 仕事関数*** (単位 eV) |
|----|-----------------|-----------------|--------|--------------------|
| H | 2.1 | 7.15 | 2.5 | |
| Li | 1.0 | 2.95 | 1.0 | 2.9 |
| Be | 1.5 | 4.36 | 1.5 | 4.98 |
| B | 2.0 | 4.19 | 1.5 | 4.45 |
| C | 2.5 | 6.24 | 2.2 | 5.0 |
| N | 3.0 | 6.98 | 2.4 | |
| O | 3.5 | 7.96 | 2.8 | |
| F | 4.0 | 10.67 | 3.7 | |
| Na | 0.8 | 2.57 | 0.9 | 2.75 |
| Mg | 1.2 | 3.37 | 1.2 | 3.66 |
| Al | 1.5 | 3.09 | 1.1 | 4.28 |
| Si | 1.8 | 4.38 | 1.5 | 4.85 |
| P | 2.1 | 5.60 | 2.0 | |
| S | 2.5 | 6.43 | 2.3 | |
| Cl | 3.0 | 8.30 | 2.9 | |
| K | 0.8 | 2.81 | 1.0 | 2.30 |
| Ca | 1.0 | | | 2.87 |
| Sc | 1.3 | | | 3.5 |
| Ti | 1.5 | | | 4.33 |
| V | 1.7 | | | 4.3 |
| Cr | | | | 4.5 |
| Mn | | | | 4.1 |
| Fe | 1.7 | | | 4.5 |
| Co | 1.7 | | | 5.0 |
| Ni | 1.7 | 3.97 | 1.4 | 5.15 |
| Cu | 1.9 | 4.46 | 1.6 | 4.65 |
| Zn | 1.5 | | | 4.33 |
| Ga | 1.5 | | | 4.2 |
| Ge | 1.8 | | | 5.0 |
| As | 2.0 | | | 3.75 |
| Se | 2.4 | | | 5.9 |
| Br | 2.8 | 7.63 | 2.7 | |
| Rb | 0.8 | | | 2.16 |

| 元素 | 電気陰性度* ポーリング | 電気陰性度** マリケン | 左/2.85 | 仕事関数*** (単位 eV) |
|----|-----------------|-----------------|--------|--------------------|
| Sr | 1.0 | | | 2.59 |
| Y | 1.2 | | | 3.1 |
| Zr | 1.4 | | | 4.05 |
| Nb | 1.6 | | | 4.3 |
| Mo | 2.1 | | | 4.6 |
| Tc | | | | 4.4 |
| Ru | 2.1 | | | 4.71 |
| Rh | 2.1 | | | 4.98 |
| Pd | 2.0 | | | 5.12 |
| Ag | 1.8 | 4.29 | 1.5 | 4.26 |
| Cd | 1.5 | | | 4.22 |
| In | 1.5 | | | 4.12 |
| Sn | 1.8 | | | 4.42 |
| Sb | 1.9 | | | 4.55 |
| Te | 2.1 | | | 4.95 |
| I | 2.5 | 6.77 | 2.4 | |
| Cs | 0.7 | | | 2.14 |
| Ba | 0.9 | | | 2.7 |
| La | 1.1 | | | 3.5 |
| Hf | 1.4 | | | 3.9 |
| Ta | 1.5 | | | 4.25 |
| W | 1.9 | | | 4.55 |
| Re | 2.1 | | | 4.96 |
| Os | 2.0 | | | 4.83 |
| Ir | 2.1 | | | 5.27 |
| Pt | 2.1 | | | 5.65 |
| Au | 2.3 | 5.82 | 2.0 | 5.1 |
| Hg | 1.8 | 6.12 | 2.1 | 4.49 |
| Tl | 1.7 | | | 3.84 |
| Pb | 1.7 | | | 4.25 |
| Bi | 1.8 | | | 4.22 |

* W. Gordy, W.J.O. Thomas: *J. Chem. Phys.*, 24, 439 (1955) による.

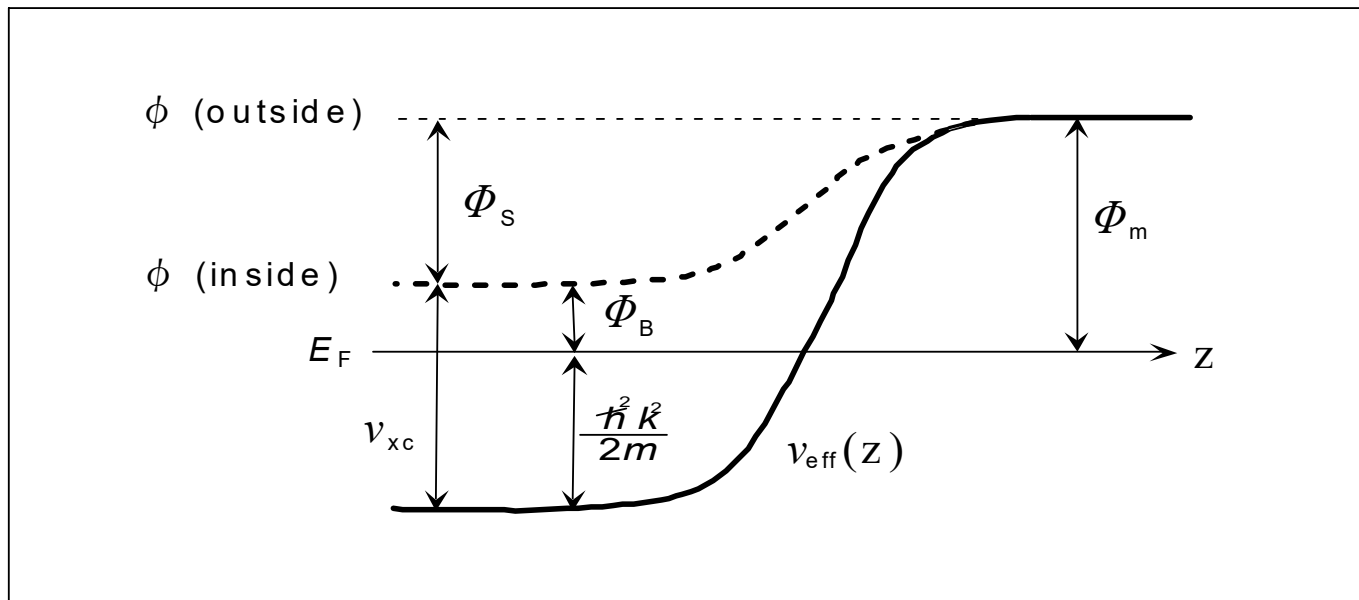
** (イオン化エネルギー+電子親和力)/2 (eV)

*** H. B. Michaelson: *J. Appl. Phys.*, 48, 4729 (1977) による.

「仕事関数」塚田 捷 著,
(物理学One Point—21), 共立出版(1983)より

Work function of metal

Bulk term (Φ_B): Exchange correlation potential 交換・相関ポテンシャル
Surface term (Φ_S) : Surface dipole

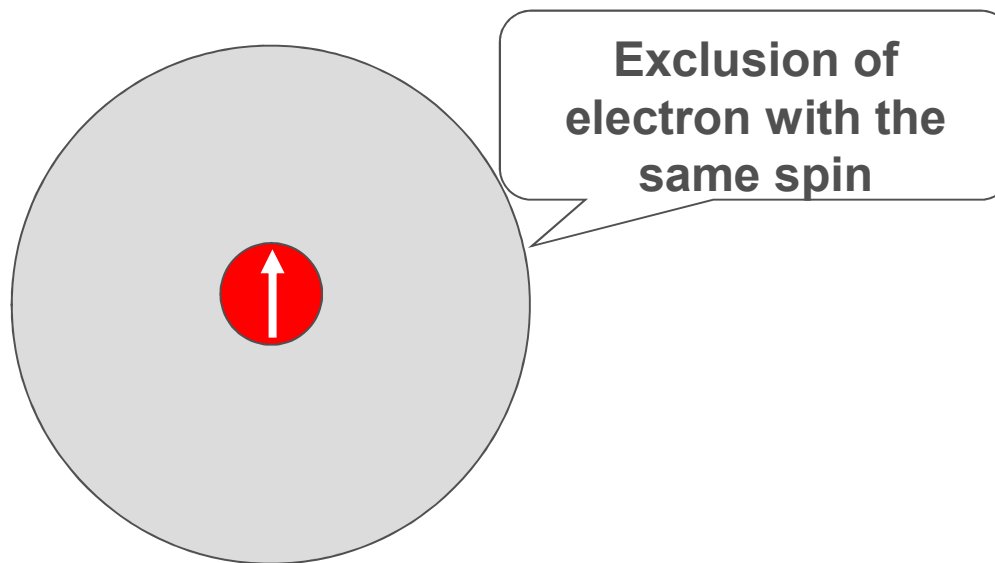


丸善 表面科学シリーズ、表面科学入門、表面における理論1など

Fermi hole

- **Exchange-correlation potential**

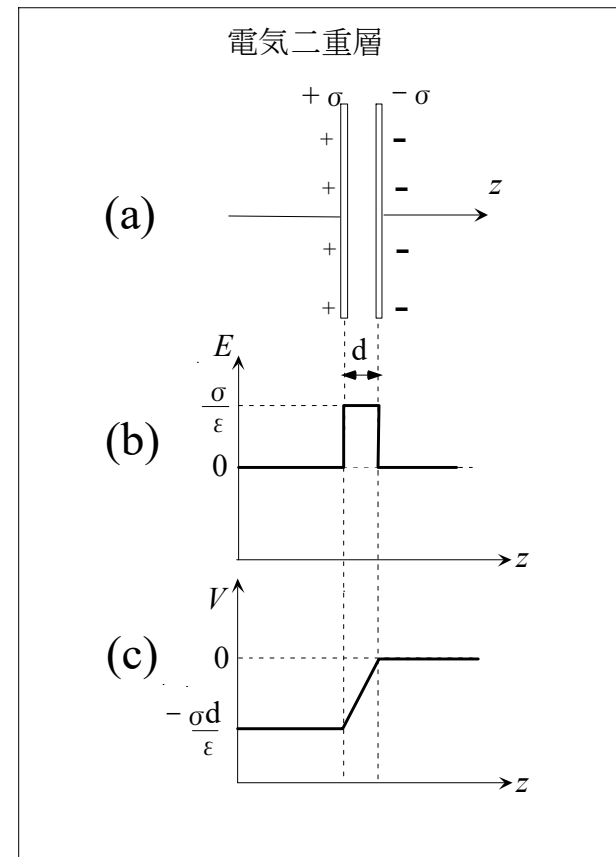
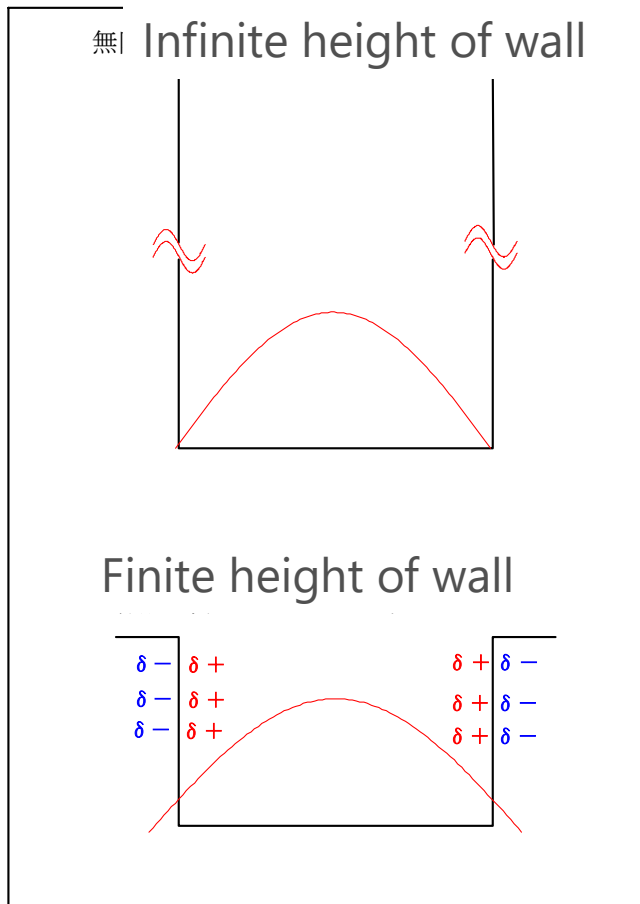
An electron feels attractive potential with its Fermi hole



Surface dipole layer of metal

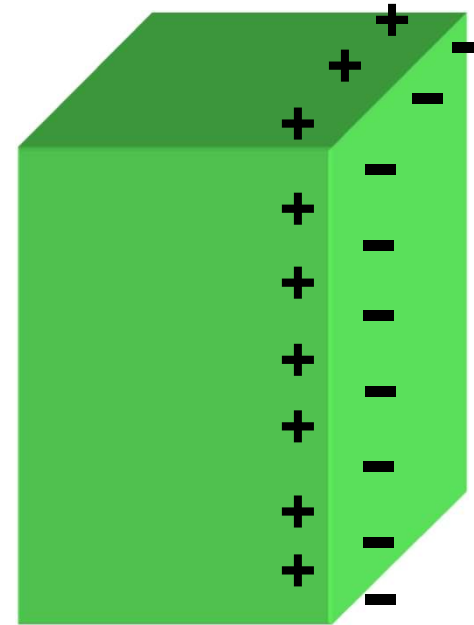
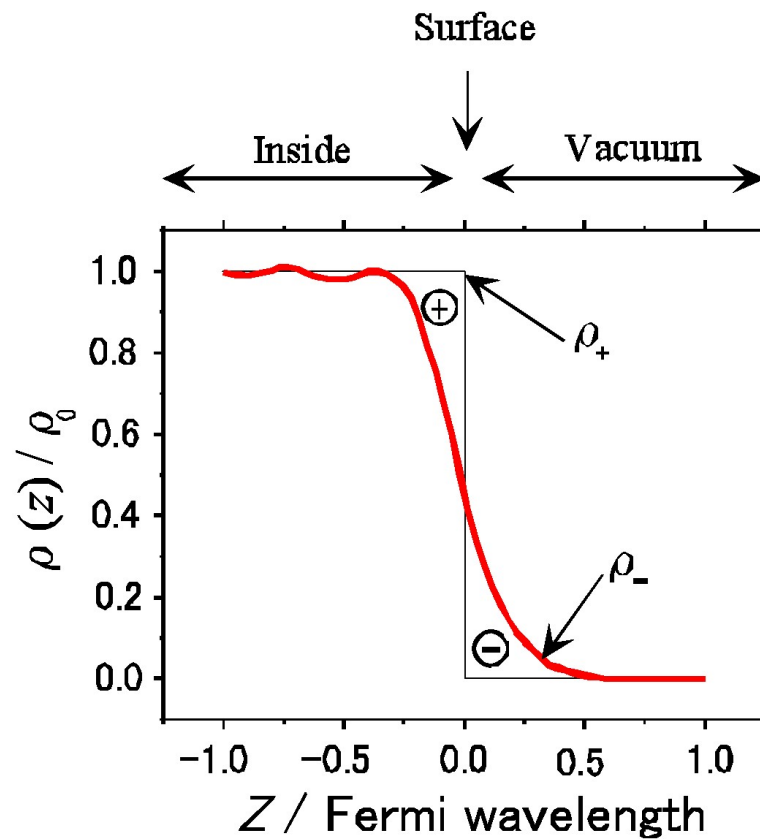
A part of electrons smears out → Double layer

→ Confinement of electrons → Surface term (Φ_B)

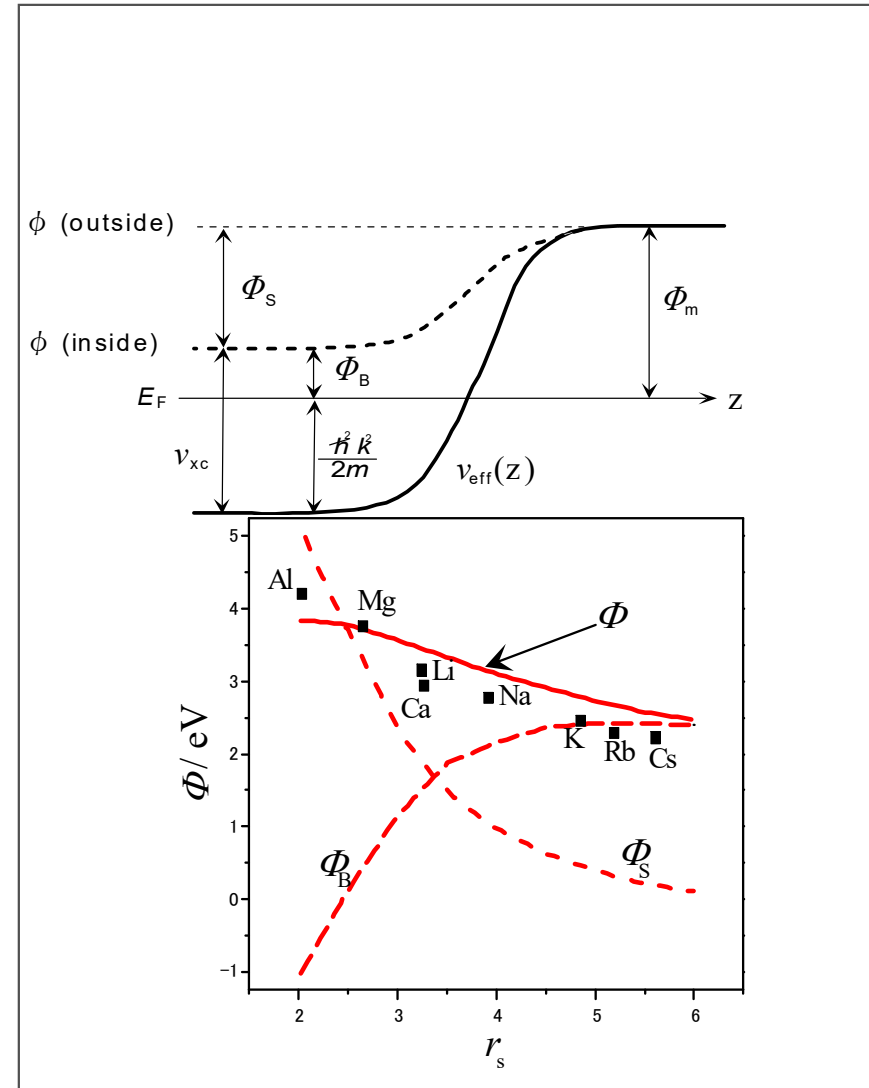
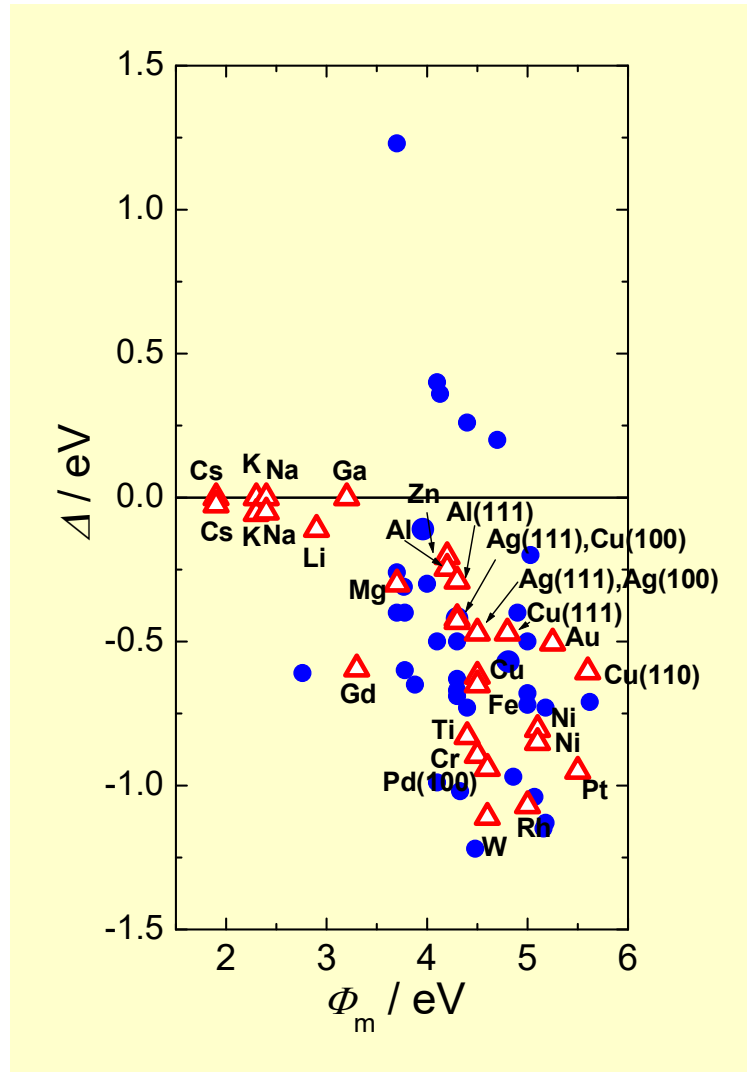


Surface dipole layer of metal

Electron smoothing effect



Surface term v.s. bulk term

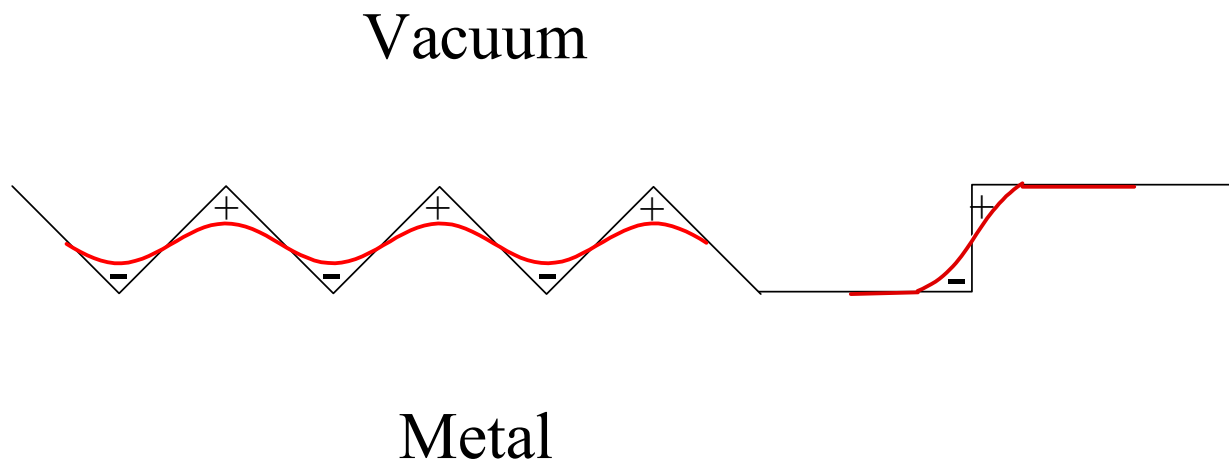


Work function of metals related to OLED


| Element | Polycrystal | (110) | (100) | (111) |
|---------|-------------|-------|-------|-------|
| Cs | 2.14 | 1.7 | 1.7 | 1.6 |
| K | 2.30 | 1.65 | 1.78 | 1.85 |
| Li | 2.9 | | | |
| Ca | 2.87 | | | |
| Mg | 3.66 | | | |
| Al | 4.28 | 4.06 | 4.41 | 4.24 |
| Ag | 4.26 | 4.52 | 4.64 | 4.74 |
| Cu | 4.65 | 4.48 | 4.59 | 4.98 |
| Pd | 5.12 | | | |
| Au | 5.1 | 5.37 | 5.47 | 5.31 |
| Pt | 5.65 | | 5.84 | 5.93 |

Depends on face UHV v.s. Atmosphere
Roughness induces the decrease of WF

Smoluchowski electron smoothing effect



Surface roughness induces the lowering of work function



P-type and n-type of organic
semiconductors

Work function of semiconductor

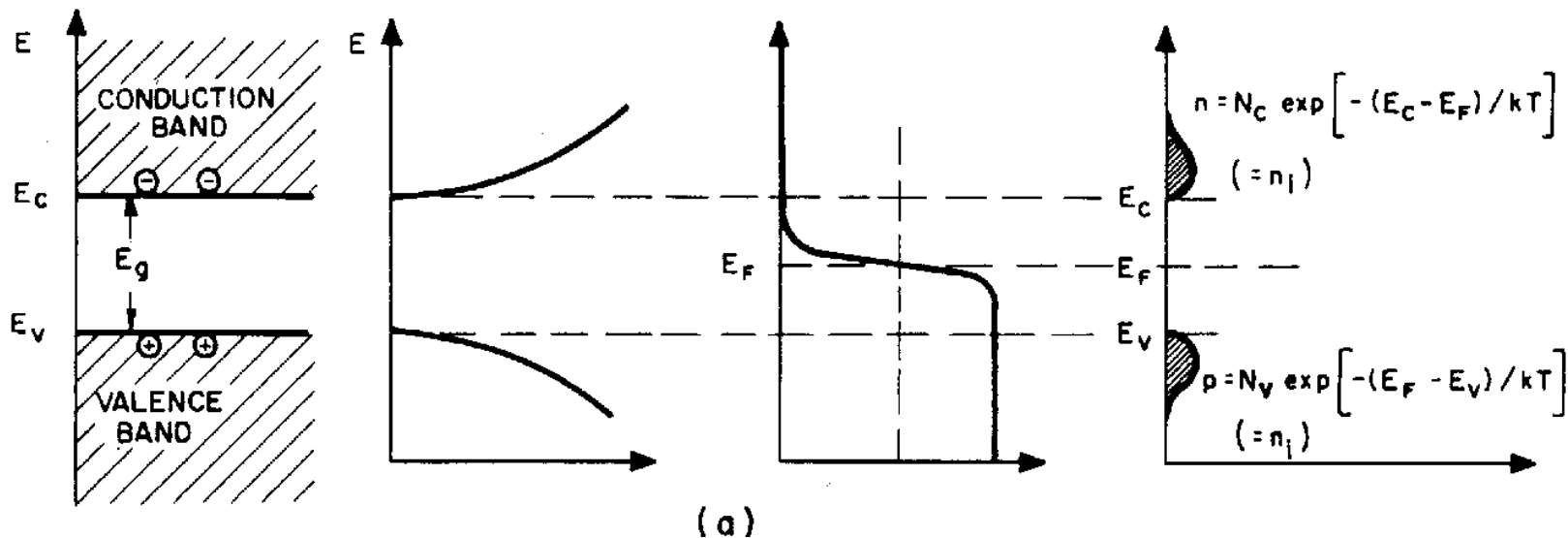
Work function = Energy difference between E_f and VL
 \neq minimum energy to remove an electron

$$e\phi = -e\Phi_0 - \bar{\mu}$$

$$\bar{\mu} = \left(\frac{\partial G}{\partial n_e} \right)_{T,P}$$

半導体の場合の仕事関数

$$E_i = (E_v + E_c)/2 - (1/2)kT \ln(N_c^{eff}/N_v^{eff})$$

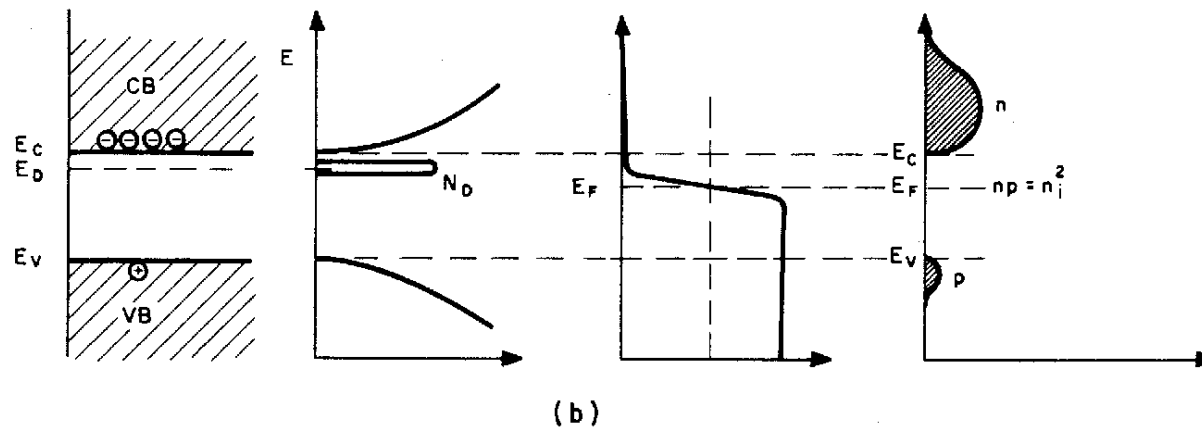


$E_f \gg$ electrochemical potential

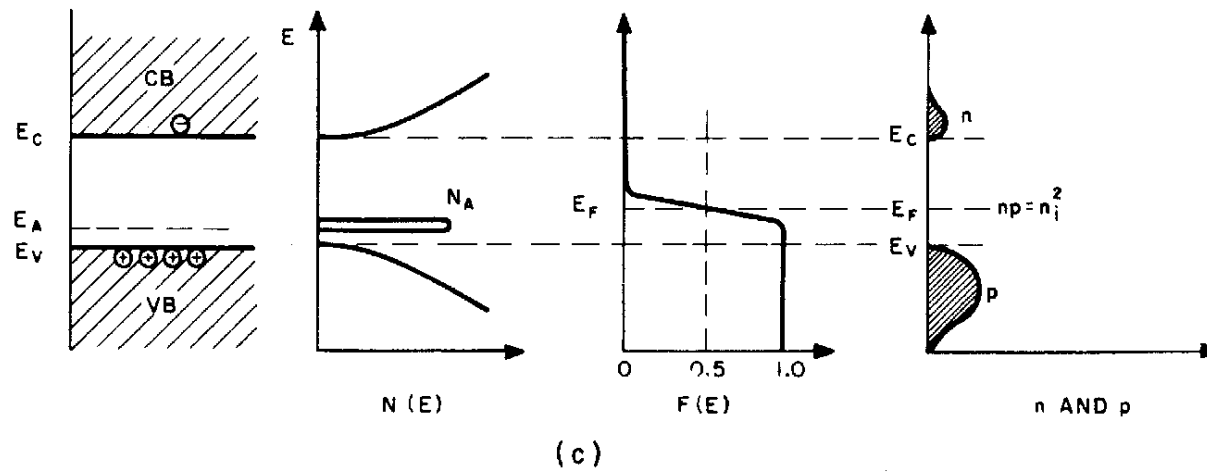
Fermi準位：電子の水面

Fermi level of extrinsic semiconductor

n型



p型



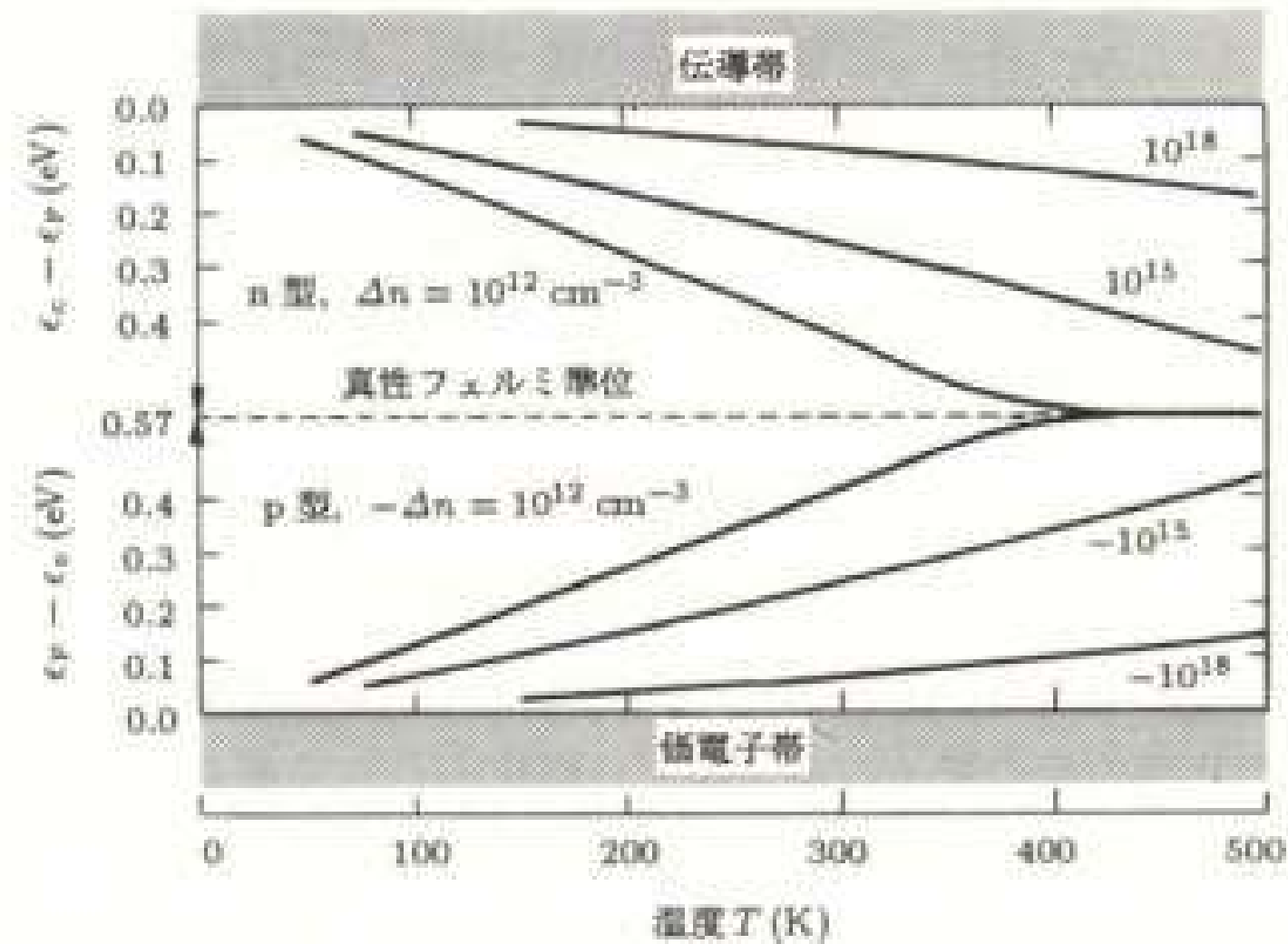


図 4.10 フェルミ準位の温度、不純物濃度による変化³⁾

P-type and n-type of semiconductor

- P or N should be defined on the basis of the type of majority carrier
 -
- In inorganic semiconductors, P or N is determined on the basis of dopant.
 -
- In organic semiconductors, p or n seems to be dependent on molecule (?)

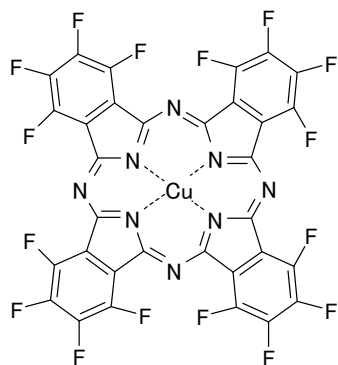
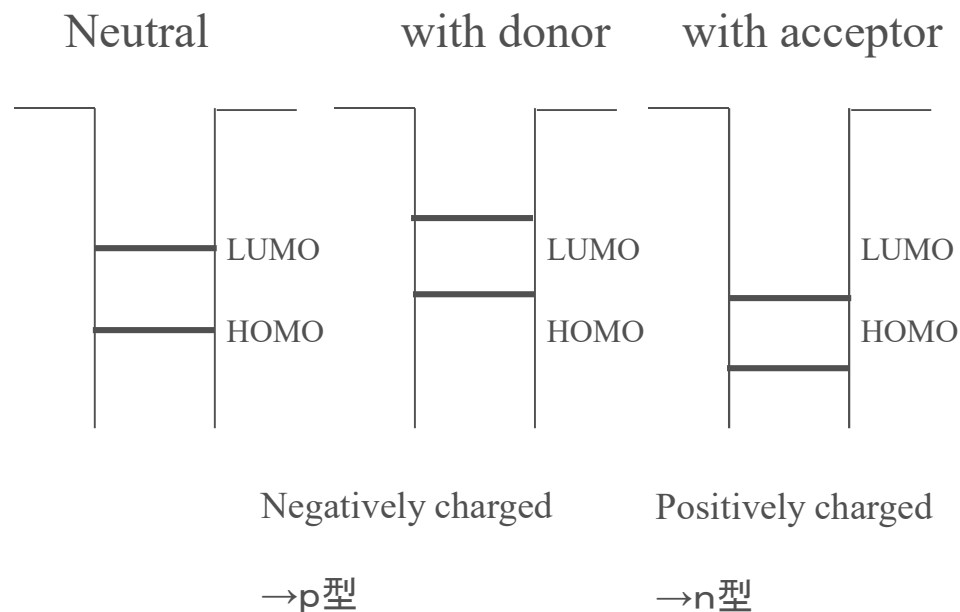
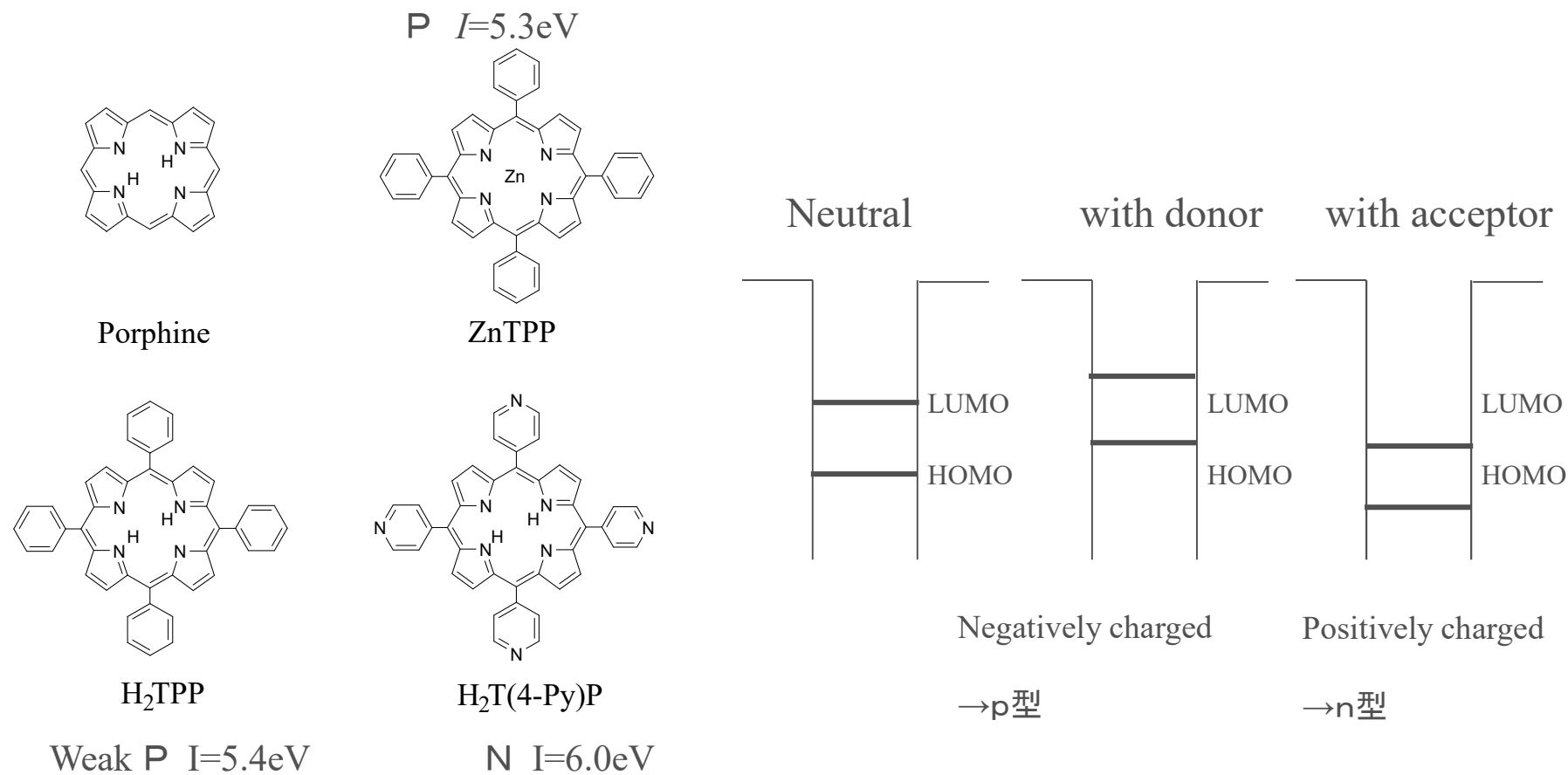
P and N in Organic Semiconductors

- 無機半導体における p 型、 n 型発現の機構が有機半導体にも適用できるかどうかは確立されていない。
 - 有機における p、 n の判定
 - 多数キャリアの直接的な同定は一般に容易ではない。
 - 何らかの電気特性を使って p、 n を判定することが多い。
 - 光起電力が、高仕事関数電極との接合で生じれば n 型、低仕事関数だと p 型など
 - ギャップ内でのフェルミ準位の位置など
 - 有機半導体は本来は真性半導体のはずだが、「意図しないドーピング」が生じている
 - p 型は大気中の酸素がアクセプターとして作用していると信じられている
 - n 型は謎. 正体不明のドナーが作用しているという説もある.
 - キャリアの発生機構が、無機半導体と有機半導体では違う可能性がある。有機材料が持つイオン化ポテンシャルや電子親和力の違いによって、キャリアの注入されやすさが電子または正孔のどちらかに偏る？

P-type organic semiconductors: Majority carrier is hole and/or hole can be easily injected.

N-type organic semiconductors: Majority carrier is electron and/or electron can be easily injected.

p,n control of organic semiconductors by substitution



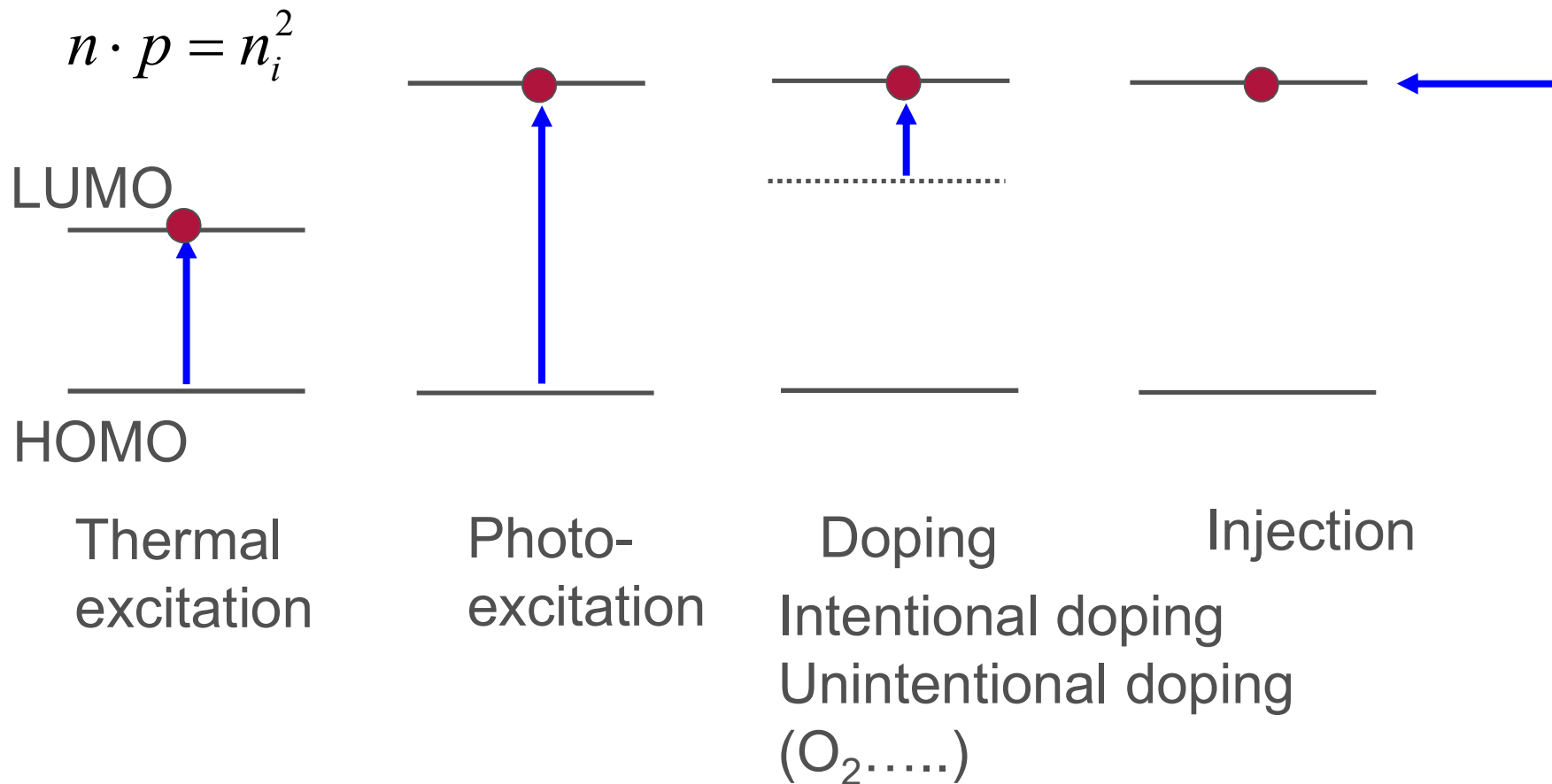
Conductivity

$$\sigma = ne\mu$$

n : carrier density

μ : mobility

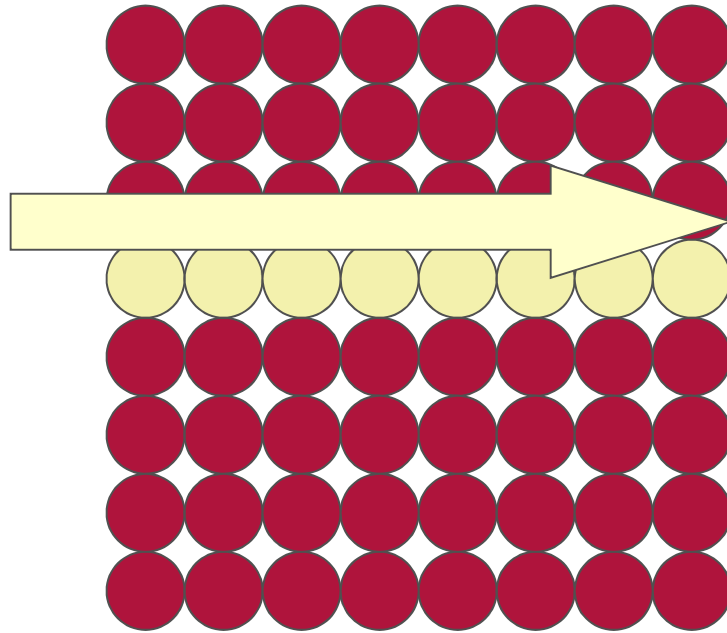
Supply of carriers in organic semiconductor



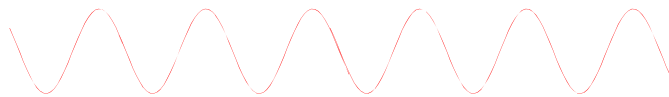
Band transport and Hopping transport

Usually, positive / negative carriers are cation radical/ anion radical in the case of organic. In the case of inorganic semiconductor, electron and hole. In the case of organic crystal, the situation may be intermediate.

電子が走る

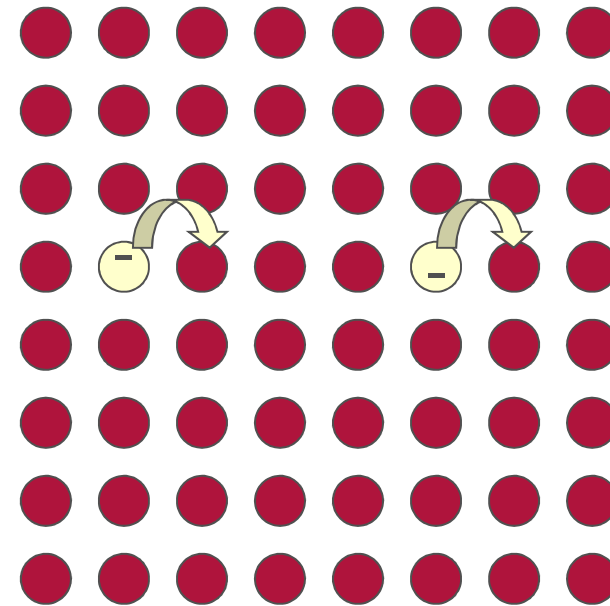


無機半導体



Delocalized
Running wave

電子がホップ



有機半導体

ψ



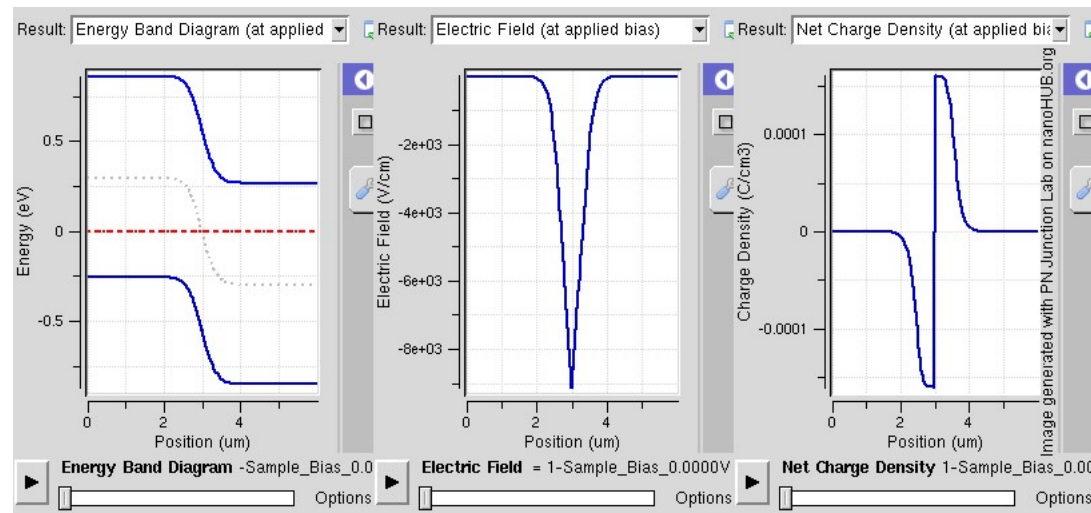
Localized
Stationary wave

v.s.

Quasi Fermi Level (imref)

We can define a quasi Fermi level and quasi temperature due to thermal equilibrium of electrons in conduction band, and quasi Fermi level and quasi temperature for the valence band similarly.

quasi thermal equilibrium.

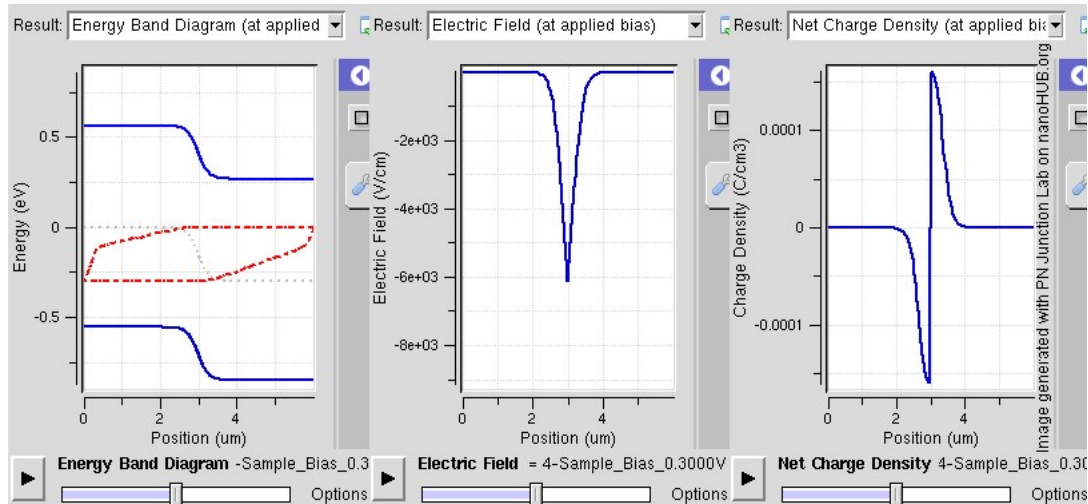


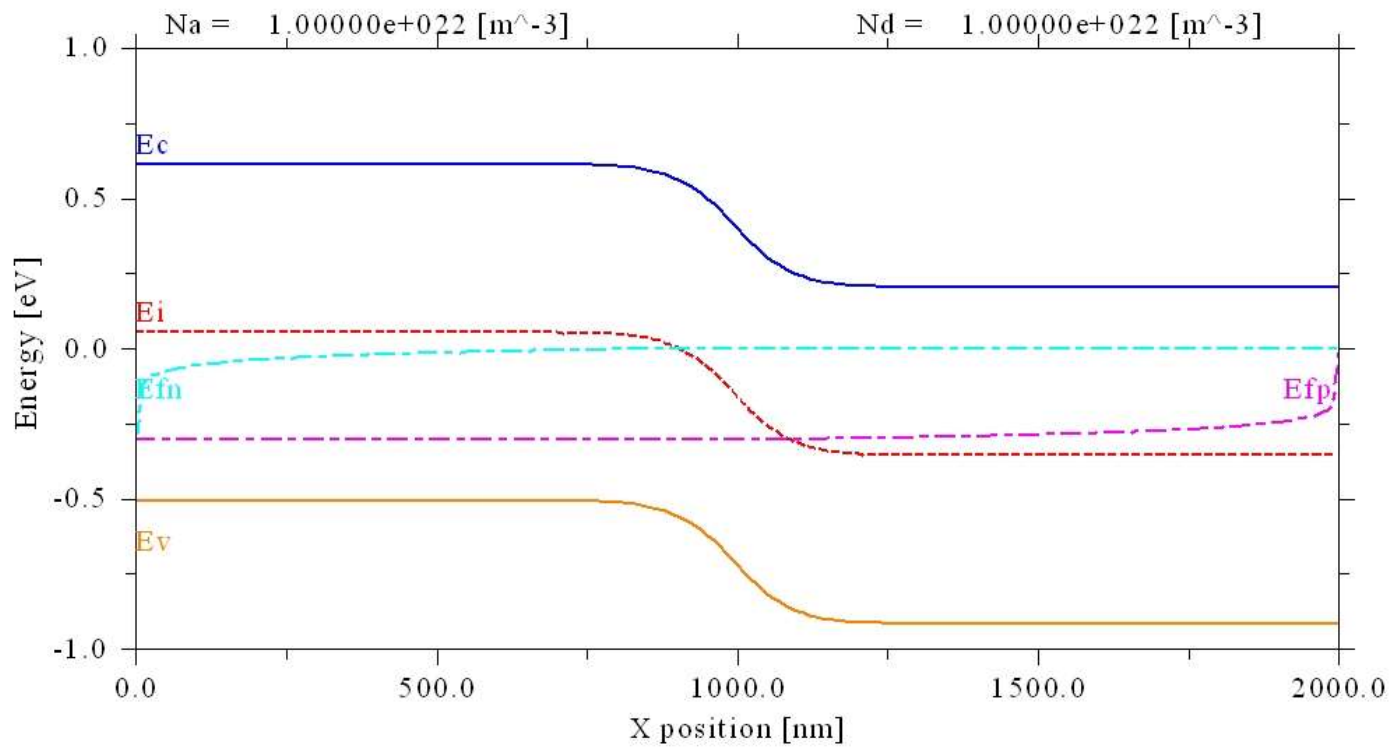
$$n = n(E_{F_c})$$

$$p = p(E_{F_v})$$

$$\mathbf{J}_n(\mathbf{r}) = \mu_n n \cdot (\nabla E_{F_c})$$

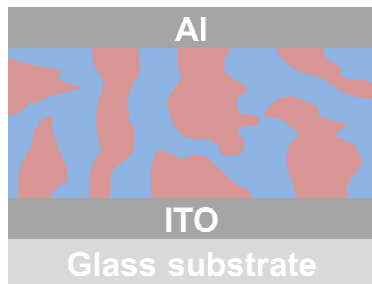
$$\mathbf{J}_p(\mathbf{r}) = \mu_p p \cdot (\nabla E_{F_v})$$



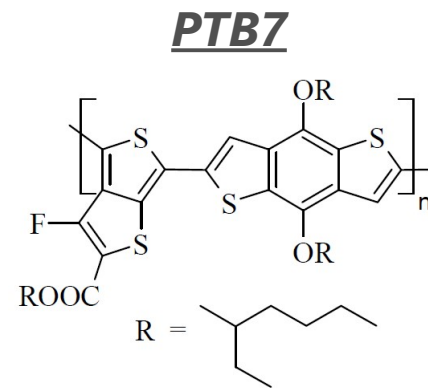


http://www2.kobe-u.ac.jp/~lerl2/j_executable_2012.html

DOS in Organic Solar Cell Material



Bulk-Hetero Junction



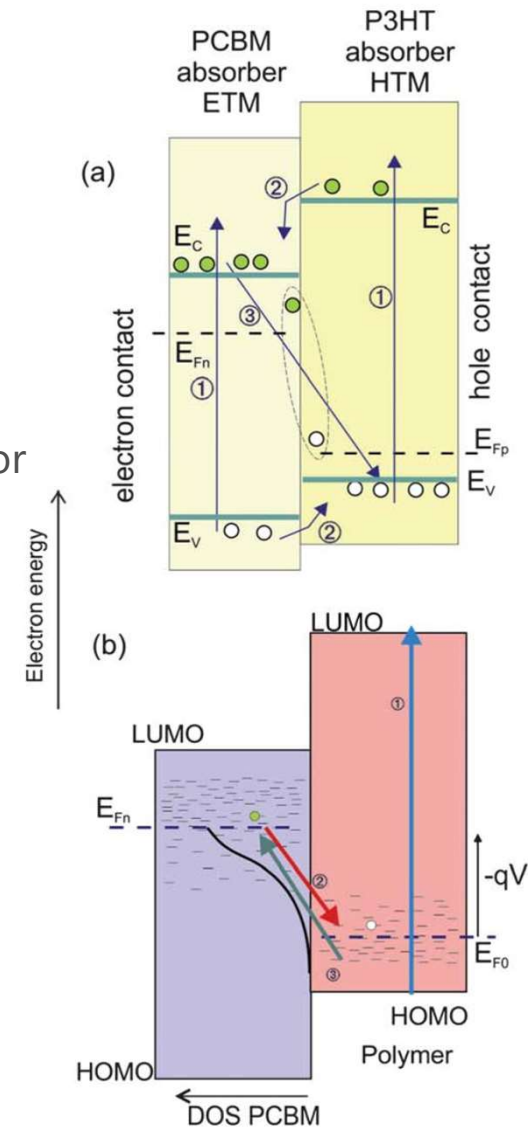
p-type organic semiconductor
(Donor material)

Gap states due to disorder are expected to modify the properties such as

- *Recombination and Trap of Carriers
- *Reduction of Voc due to change of Pseudo Fermi Level

$$V_{oc} = \frac{1}{e} (E_{fp,D} - E_{fn,D}) \approx \frac{1}{e} (I_D - A_A) - 0.3$$

M.C.Scharber et al., Adv. Mater.18, 789(2006).



0.3 eV is the difference in pseudo Fermi level of hole and electron calculated by assuming single level in 10^{19}cm^{-3} photo-carrier density.

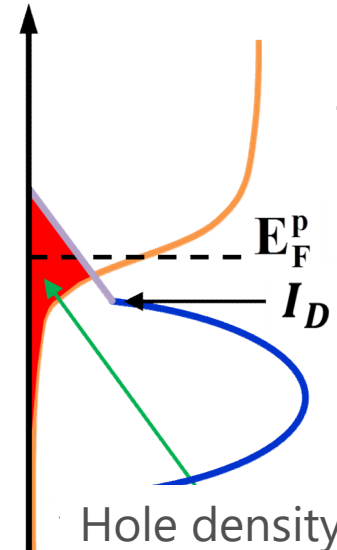
How to Determine Pseudo Fermi Level



T. Sato

Method Using Real DOS

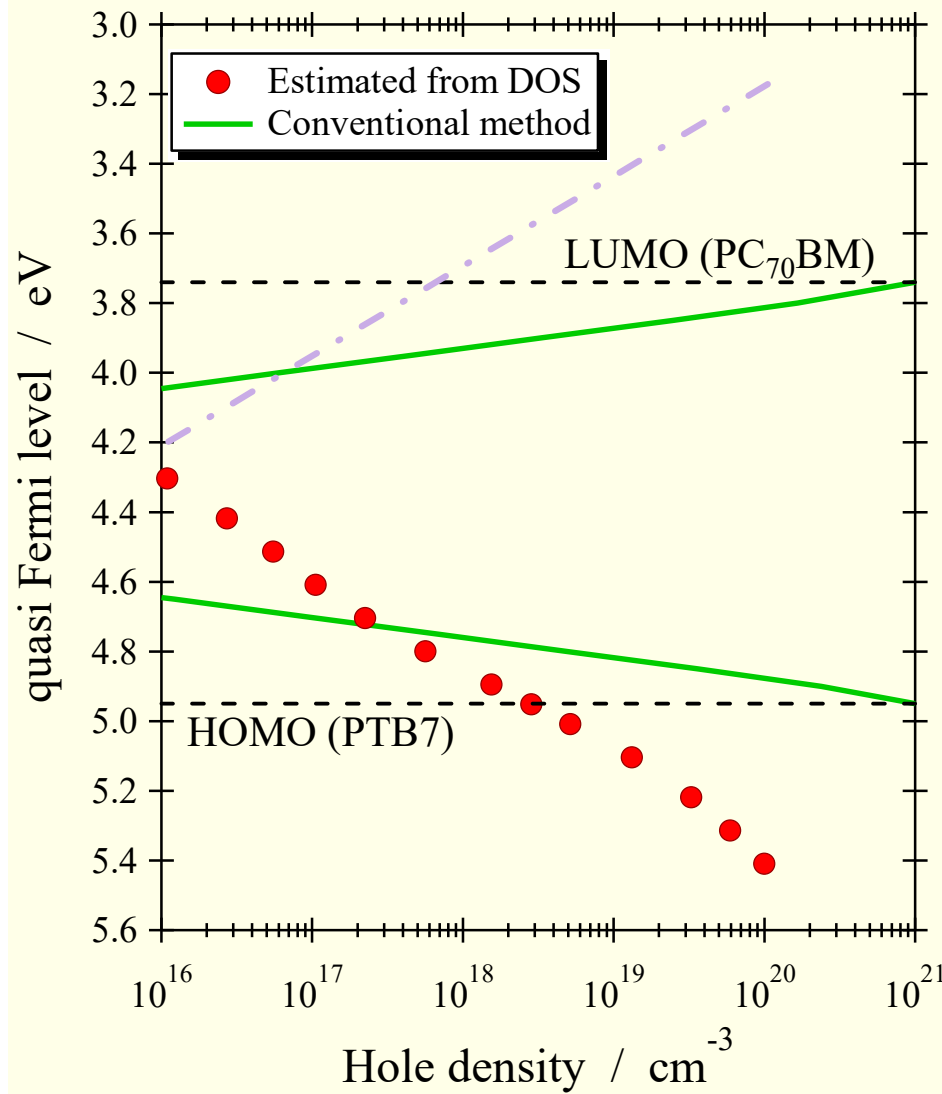
- ✓ Distribution of HOMO
- ✓ Gap states



$$p_D = \int (1 - f_{FD}(\varepsilon)) \cdot D(\varepsilon) d\varepsilon$$

$$f_{FD}(\varepsilon) \equiv \frac{1}{1 + \exp((\varepsilon - E_{fp,D}) / kT)}$$

Pseudo Fermi Level can be determined from Photo-carrier density through DOS



$$10^1 p_D \approx n_A \approx 10^2 \text{ cm}^{-3}$$

