Advanced Course in Surface Properties of Organic Materials

1. Energy Band of Organic Crystals (Mori)
2. Organic Conductors and Organic Electronics (Mori)
3. Optical Properties of Solids (Ishikawa)
4. Liquid Crystals (Ishikawa)
5. Surface Analysis and Spectroscopy (Ouchi)
6. Surface Properties of Organic Materials (Matsumoto)
7. Organic Nanomaterials (Matsumoto)

Hydrogen Molecule

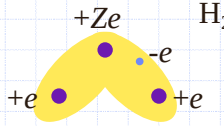
(2) LCAO-MO $\phi = c_A\chi_A + c_B\chi_B$

(4) Secular Eq. $\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$

(6)

Stabilization due to the covalent bond is ( )

Molecular orbital theory



(1) One-electron Schrödinger equation

$$[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\sum_n \frac{Z_n}{r_n}]\phi = E\phi$$

Put one electron in the arranged nuclei.

(2) LCAO-MO (Linear Combination of Atomic Orbitals)

$$\phi = \sum_i^N c_i\chi_i$$

N : total number of atomic orbitals

(3) $E = \dfrac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau}$ energy minimum $\dfrac{\partial E}{\partial c_i} = 0$ i=1∽N

(4) Secular equation $N \times N$

$$\begin{vmatrix} \alpha_{11}-E & \beta_{12} & 0 & \cdots\cdots \\ \beta_{21} & \alpha_{22}-E & \beta_{23} & \\ 0 & \beta_{32} & \alpha_{33}-E & \end{vmatrix} = 0$$

Non diagonal : resonance integrals

$$\beta_{ij} = \int \chi_i^* H \chi_j d\tau$$

$$\alpha_{ii} = \int \chi_i^* H \chi_i d\tau$$

Diagonal : Energy level of i-th AO

(5) N-order equation of E

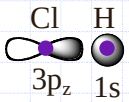
(6) N energy levels of E (固有値)

Simultaneous equation for c_i

(7) N-set of c_i (固有関数) = Molecular orbital (分子軌道)

Polar bond

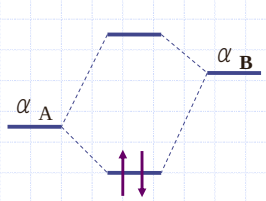
(2) LCAO-MO $\phi = c_A\chi_A + c_B\chi_B$



(4) Secular Eq. $\begin{vmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{vmatrix} = 0$

(6)

$$E = \frac{\alpha_A + \alpha_B}{2} \pm \frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2} \rightarrow \frac{\alpha_A + \alpha_B}{2} \pm \frac{|\alpha_A - \alpha_B|}{2}\left(1 + \frac{2\beta^2}{(\alpha_A - \alpha_B)^2}\right)$$



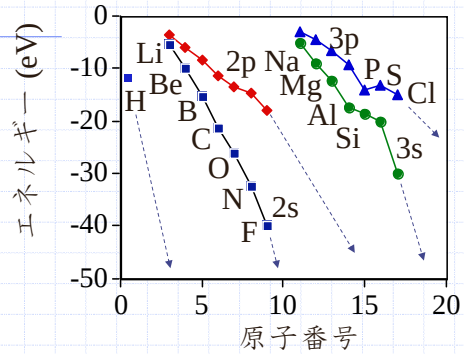
Antibonding
Large on B

Bonding
Large on A

Large α_A
→ Electronically negative atom

$Cl^{\delta-}H^{\delta+}$

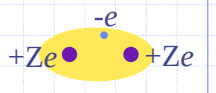
Energy of Atomic Orbital α_A = Ionization energy



$E \propto -\zeta^2$

Due to the imperfect screening, going right leads to
( ) ionization energy, and ( ) atomic orbital.
Going right leads to electronically negative.

Diatomic molecule like N_2



N 1s + 2s + 2p × 3 → 5AO × 2 = 10 AO

$$\phi = c_1\chi_{1s}^A + c_2\chi_{1s}^B + c_3\chi_{2s}^A + c_4\chi_{2s}^B + c_5\chi_{2pz}^A + c_6\chi_{2pz}^B + c_7\chi_{2py}^A + c_8\chi_{2py}^B + c_9\chi_{2px}^A + c_{10}\chi_{2px}^B$$

1s 2s $2p_z$ $2p_y$ $2p_x$

A B A B A B A B A B

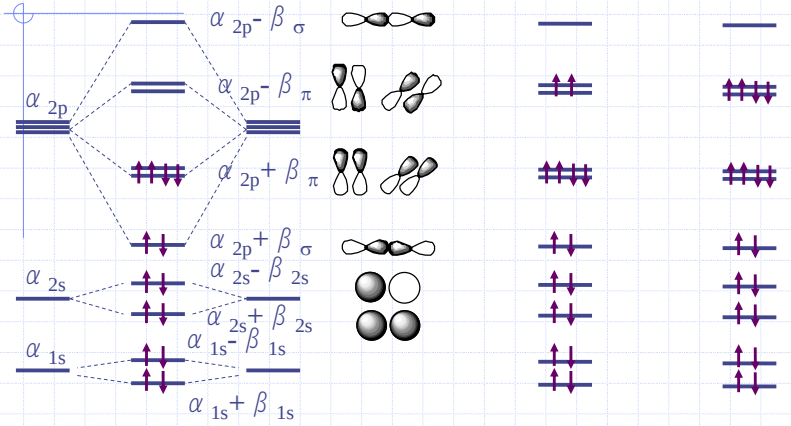
$$\begin{vmatrix}
\alpha_{1s}-E & \beta_{1s} & & & & & & & & \\
\beta_{1s} & \alpha_{1s}-E & & & & & & & & \\
 & & \alpha_{2s}-E & \beta_{2s} & & & & & & \\
 & & \beta_{2s} & \alpha_{2s}-E & & & & & & \\
 & & & & \alpha_{2p}-E & \beta_\sigma & 0 & 0 & 0 & 0 \\
 & & & & \beta_\sigma & \alpha_{2p}-E & 0 & 0 & 0 & 0 \\
 & & & & 0 & 0 & \alpha_{2p}-E & \beta_\pi & 0 & 0 \\
 & & & & 0 & 0 & \beta_\pi & \alpha_{2p}-E & 0 & 0 \\
 & & & & 0 & 0 & 0 & 0 & \alpha_{2p}-E & \beta_\pi \\
 & & & & 0 & 0 & 0 & 0 & \beta_\pi & \alpha_{2p}-E
\end{vmatrix} = 0$$

orthogonal

Electron configuration

N_2 O_2 F_2

$7 \times 2 = 14$ electrons $|\beta_\sigma| > |\beta_\pi|$



Bond order is ( ) ( ) ( )

Bond order = [(#Bonding orbital) − (#Antibonding orbital)]/2

π -Electron System Hückel Method

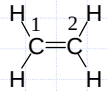
σ and π -orbitals are orthogonal.

$$\begin{vmatrix} \sigma & 0 \\ 0 & \pi \end{vmatrix} = 0$$

Consider only this part.

β for nearby C = C is nonzero. Others are zero.
All overlap integrals are S=0.

Example ethylene



$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Bonding energy is

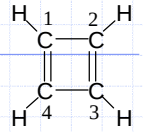
α - β —— $\phi = \chi_A - \chi_B$

α + β —— $\phi = \chi_A + \chi_B$

Hückel Method for Complicated π -Electron Sytems

Number carbon atoms with π , the total is N.
Wright a $N \times N$ secular equation, with all diagonal terms $\alpha - E$.
Nondiagonal terms are β for bonded i-th and j-th carbons, and zero for non bonded carbons.
| determinant | =0 leads to N-th equation of E, which is solved to obtain N energy levels.
Put electrons from the bottom. (#Electron)=(#Carbon)

Wright the secular equation of cyclobutadiene.



The solution is

α -2 β ——

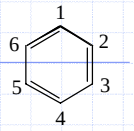
α ——

α +2 β ——

Bonding energy is

There is no energy gain compared with two double bonds
$2 \times 2\beta = 4\beta$

Wright the secular equation of benzene.



The solution

α -2 β ——

α - β ——

α + β ——

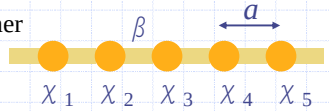
α +2 β ——

Bonding energy is

Compared with three doublebonds
$3 \times 2\beta = 6\beta$, there is 2 β energy gain (delocalization energy).
$4n$+2 membered ring delocalization aromatic
$4n$ membered ring no delocalization
(Hückel rule)

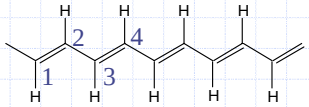
Energy Band (Tight-Binding Approximation)

LCAO-MO of a one-dimensional polymer
(Hückel MO of polyacetylene)



$$\varphi = \sum_n c_n \chi_n$$

The secular equation is

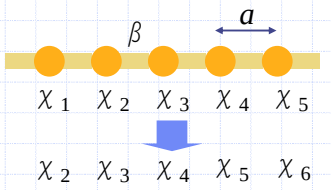


$$\begin{vmatrix} \alpha - E & \beta & 0 & \cdots \\ \beta & \alpha - E & \beta & \\ 0 & \beta & \alpha - E & \\ & & & \end{vmatrix} = 0$$

$N \times N$次

We can directly solve this, but we use another way:

$$\phi = \sum_n c_n \chi_n$$



translation by one unit cell, $\boldsymbol{r} \rightarrow \boldsymbol{r}+\boldsymbol{a}$
should not change the physics, because
it only changes the atom number.
So the electron density $\rho = \phi^* \phi$ does
not change. Accordingly, $c_{n+1}{}^* c_{n+1} = c_n{}^* c_n$,
or only the phase of c_n may change. Thus, we can put
$c_{n+1} = c_n e^{i\theta} = c_n e^{ika}$, Consequently ϕ is:

$$\phi = c_0[\chi_0 + e^{ika}\chi_1 + e^{i2ka}\chi_2 + e^{i3ka}\chi_3 + e^{i4ka}\chi_4 + \cdots]$$
$$= c_0 \sum_n e^{inka} \chi_n$$

(Bloch function)
c_0 is mere a normalization constant.

Energy of $\phi = \sum_n e^{inka}\chi_n$ is

$$E = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\int (\sum_m e^{-imka}\chi_m^*) H (\sum_n e^{inka}\chi_n) d\tau}{\int (\sum_m e^{-imka}\chi_m^*)(\sum_n e^{inka}\chi_n) d\tau}$$

$$= \frac{\sum_n \sum_m e^{i(n-m)ka} \int \chi_m^* H \chi_n d\tau}{\sum_n \sum_m e^{i(n-m)ka} \int \chi_m^* \chi_n d\tau}$$

$$= \frac{N(e^{ika}\beta + \alpha + e^{-ika}\beta)}{N}$$

n

$m = n\text{-}1 \quad n \quad n+1$

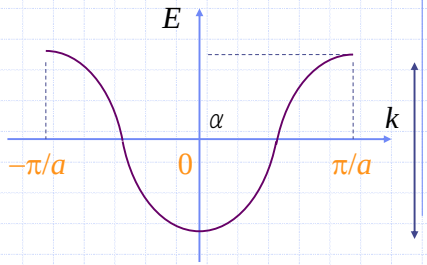
$\beta = \int \chi_{n-1}^* H \chi_n d\tau \qquad \beta = \int \chi_{n+1}^* H \chi_n d\tau$

$\alpha = \int \chi_n^* H \chi_n d\tau$

$$E = \alpha + 2\beta\cos ka$$

$$\cos ka = \frac{e^{ika} + e^{-ika}}{2}$$

$$E = \alpha + 2\beta\cos ka$$



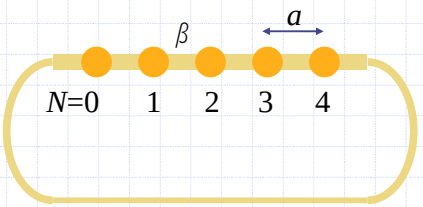
Owing to the periodicity,
we only consider
$-\pi < ka < \pi$ or
$[\ -\pi/a\ ] < k < [\ \pi/a\ ]$

(2) Owing to $\beta < 0$,
Maximum of E is (at $k = \pi/a$) $E = [\quad]$
Minimum of E is (at $k = 0$) $E = [\quad]$

(3) As a whole, the energy band has the bandwidth, $[\quad]$

$E = \alpha + 2\beta\cos ka$

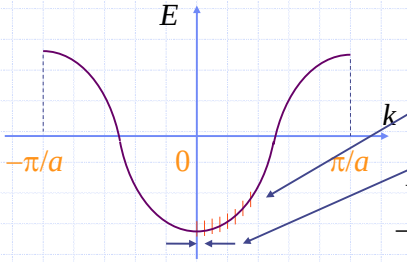
$\phi = \sum_n e^{inka}\chi_n$



(4) Make a ring.
(Otherwise, "edge state" appears.)
When the total atoms are N, N-the atom = 0-th atom, so

$e^{iNka} = 1 \rightarrow Nka = 2\pi n$ (n : integer) $k =$ ( )

Periodical boundary condition



Arranged with a fine interval

The interval is $\Delta k =$ ( )

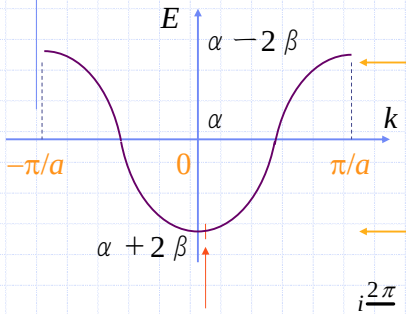
Very fine for large N.
→ Nearly continuous (Energy band)

$E = \alpha + 2\beta\cos ka$

(5) $\phi = \sum_n e^{inka}\chi_n$

$k =$ 0 leads to $\phi = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$

$k = \pi/a$ leads to $\phi =$ ( )



All intervals have nodes.
→ Completely antibonding

Completely bonding

The state next to k=0 has extra $e^{i\frac{2\pi}{N}}$ phase. When rotated around the solid, the phase shifts by 2π. So the whole solid has only one node.

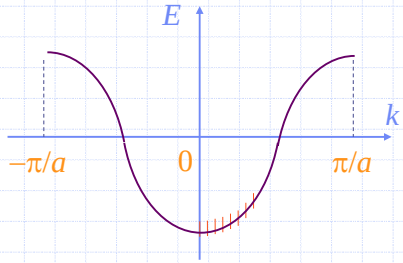
(6) Total number of levels

from $-\pi/a$ to π/a

$2 \times \frac{\pi}{a} \Big/ \frac{2\pi}{Na} =$ ( )

level interval

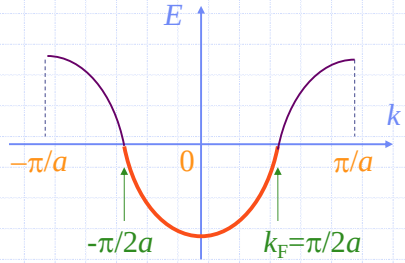
N atoms → N energy levels

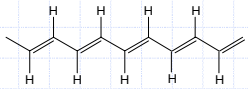


(7) For N electrons

$2\frac{2k_F}{2\pi/Na} = N \rightarrow k_F =$ ( )

for half-filled.

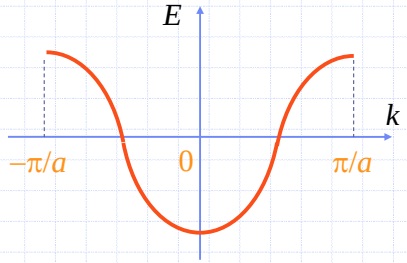




Polyacetylene without bond alternation

(8) For $2N$ electrons

$2\frac{2k_F}{2\pi/Na} = 2N \rightarrow k_F =$ ( )



All states are occupied

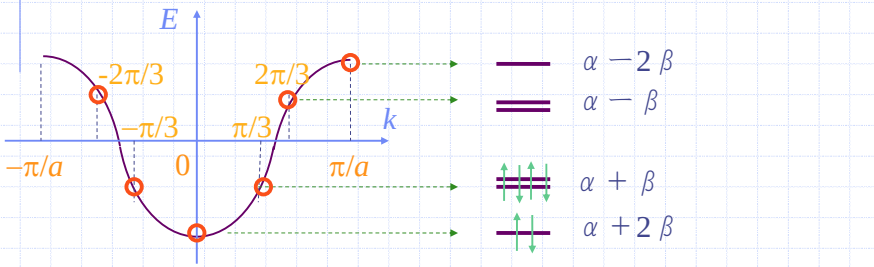
Two electrons, ↑ and ↓ , enter in one atomic orbital χ .

(9) For $N=6$

$k=\frac{2\pi n}{Na}=\frac{2\pi n}{6a}$ leads to $E=\alpha+2\beta\cos ka=\alpha+2\beta\cos\frac{2\pi}{6}n$

0 , ±π/3, ±2π/3, π

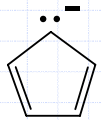
$E=\left(\alpha+2\beta\right)\left(\alpha+\beta\right)\left(\alpha+\beta\right)\left(\alpha-\beta\right)\left(\alpha-\beta\right)\left(\alpha-2\beta\right)$



π orbitals (Hückel method) for benzene

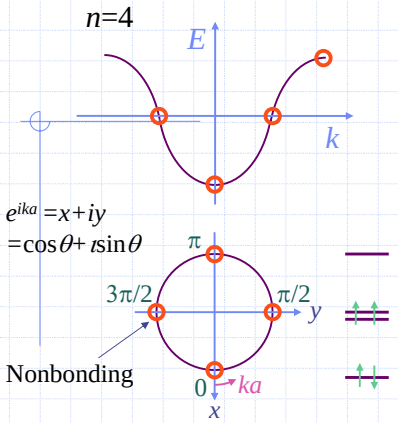
Similarly, we can calculate Hückel molecular orbitals for *N*-carbon rings.

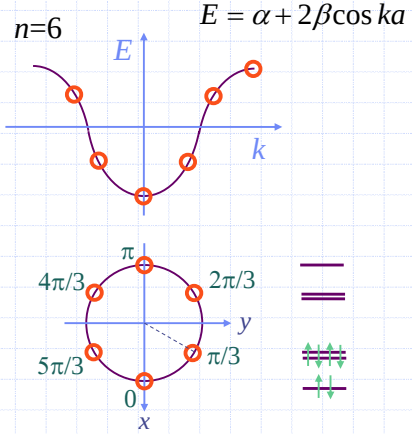
Excise Hückel Molecular Orbital of Cyclopentadienyl



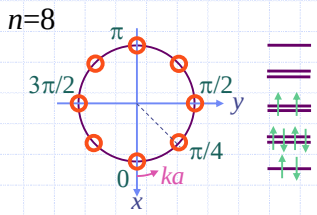
Cyclopentadienyl anion (right) is pentagon and has delocalized negative charge.
Calculate the energy levels from the equation of the tight-binding band, $E=\alpha+2\beta\cos ka$.

（1） When *N*=5, *k* takes the values of 0、±A、±B. Show A and B.
（2） Obtain the energy levels.
Use cos(2π/5) = cos72° = 0.309、 cos(4π/5) = cos144° = -0.809.
（3） Calculate energies of the anion, the radical and the cation.





$E=\alpha+2\beta\cos ka$

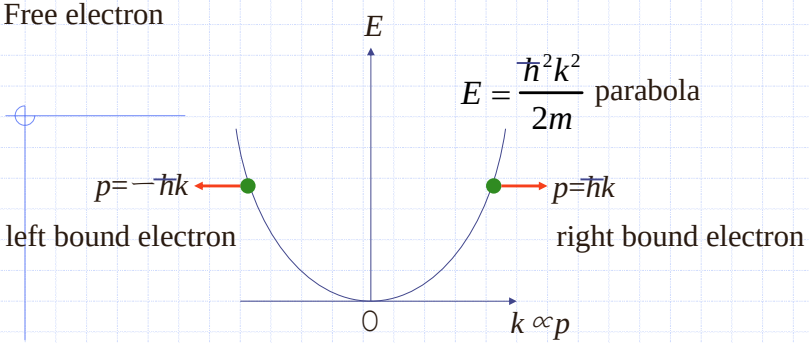


N=4*n* uses nonbonding level
→ No stabilization
N=4*n* +2 does not have nonbonding
→ stabilization → Hückel role

Free electron approximation

(1) Simple free electron approximation derived from the first principle of quantum mechanics.
(2) Electrons in metals, particularly the energy and momentum distribution, are investigated starting from a large number of free electrons.
(3) Distribution of electrons at finite temperatures are discussed in view of the Fermi statistics: statistical mechanics.

Free electron



Wave number $k=2\pi/\lambda$ is inverse of the wavelength.
The number of waves in unit $\times 2\pi$ length.

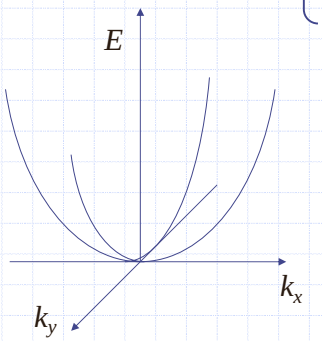
$E=\frac{p_x^2+p_y^2+p_z^2}{2m}+V$ in three dimension.

Schrödinger equation is,

$$[-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})+V]\phi=E\phi$$

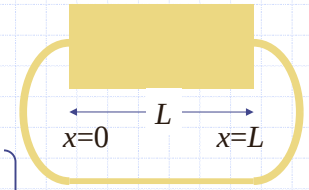
Eigenfunction (solution) for $V=0$ is $\phi(x,y,z)=e^{i(k_xx+k_yy+k_zz)}$

Eignevalue (energy) is $E=$ ( )



We cannot depict k_z at the same time.

Instead of an infinite space, consider a box with a finite length L, and the $x=L$ edge is connected to $x=0$.
(Otherwise, the edge generates a "surface" state.)
$\phi(x+L,y,z)=\phi(x,y,z)$

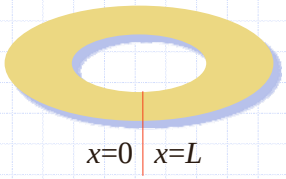


$e^{ik_xL}=1 \rightarrow k_xL=2\pi n \rightarrow k_x=$ ( )

(n : integer)

Similarly for y, z,

$k_x=\frac{2\pi}{L}n_x \quad k_y=\frac{2\pi}{L}n_y \quad k_z=\frac{2\pi}{L}n_z$



(Consider a cube with L edges.)

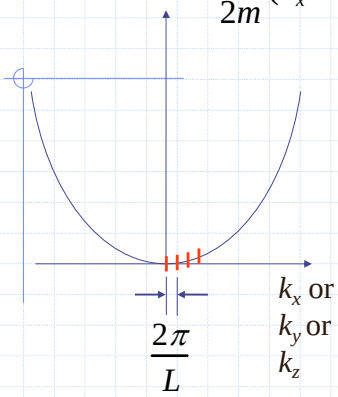
Periodical boundary condition

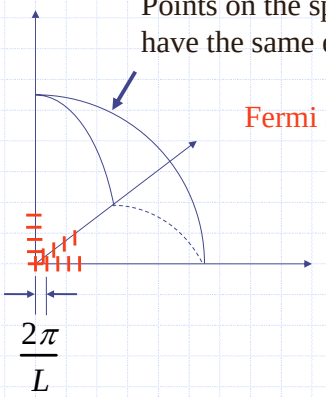
$E=\frac{\hbar^2}{2m}(k_x^2+k_y^2+k_z^2)$

Fermi energy

Points on the sphere have the same energy.

Fermi surface





Interval of energy levels
→ continuous for large L.
→ Energy band

Fill N electrons according to the Pauli's exclusion principle.
Starting from the origin with the minimum energy, to the inside of a sphere with radius $k=\sqrt{k_x^2+k_y^2+k_y^2}$

Volume of a sphere with radius k is

$$2\frac{\frac{4\pi}{3}k^3}{(\frac{2\pi}{L})^3} = N \quad \Rightarrow \quad \left(\qquad\right) = N \quad \text{where} \quad V = L^3$$

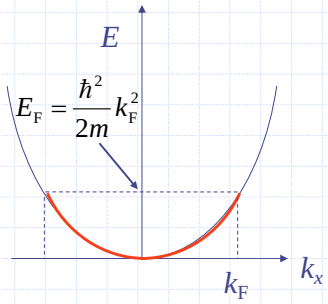
Interval of states (3D)

One energy level has two electrons with ↑ and ↓ spins

Electron with the highest energy (Fermi energy) is

$k_F^2 = k_x^2 + k_y^2 + k_y^2$

$$E_F = \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m} \times \left(\qquad\right)$$

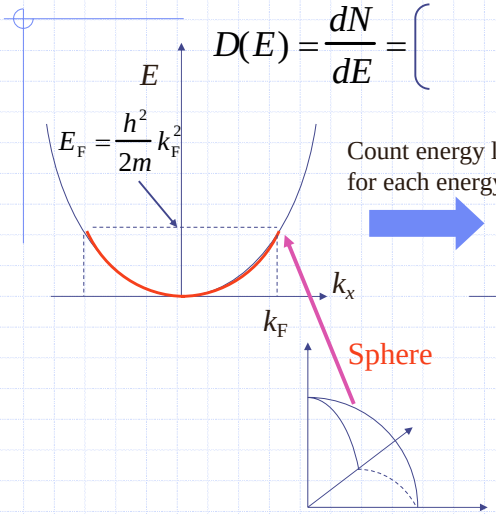


is solved as for N to give,

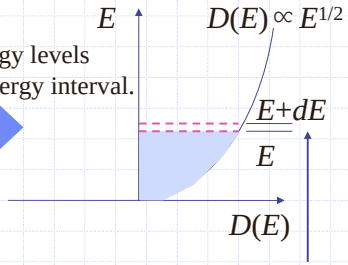
$$N = \frac{V}{3\pi^2} \times \left(\qquad\right)$$

Differentiate as for E, and the number of energy levels per unit energy (density of states or states density) is

$$D(E) = \frac{dN}{dE} = \left(\qquad\right) \quad \text{or} \quad D(E) = \frac{3}{2}\frac{N}{E}$$

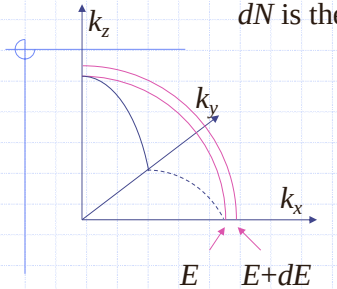


Count energy levels for each energy interval.



$D(E)$ is the number of levels in between E and $E+dE$.

Another derivation of states density



dN is the number of states in between E and $E+dE$.

Surface of the sphere

$$2\frac{4\pi k^2 dk}{(\frac{2\pi}{L})^3} = dN$$

Interval of the states in 3D

$$E = \frac{\hbar^2 k^2}{2m} \text{ より } dE = \left(\qquad\right)$$

$$D(E) = \frac{dN}{dE} = 2\frac{4\pi k^2}{(\frac{2\pi}{L})^3}\frac{1}{\frac{\hbar^2 k}{m}dk} = \frac{V}{2\pi^2}\frac{2m}{\hbar^2}k = \frac{V}{2\pi^2}(\frac{2m}{\hbar})^{\frac{3}{2}}E^{\frac{1}{2}}$$

$$k = (\frac{2mE}{\hbar^2})^{\frac{1}{2}}$$

The same conclusion

Two-dimensional metal

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) = \text{const.} \quad \text{leads to } k_x^2 + k_y^2 = k_F = \text{const.}$$

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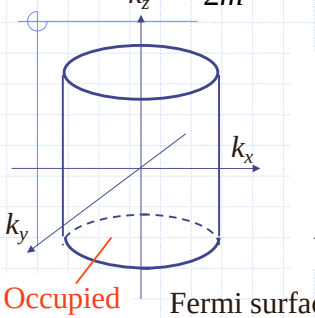
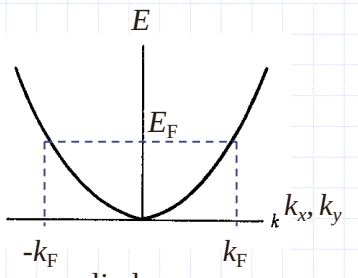
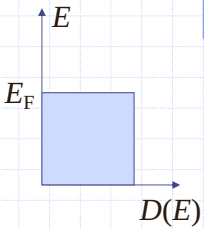


Fermi surface = cylinder

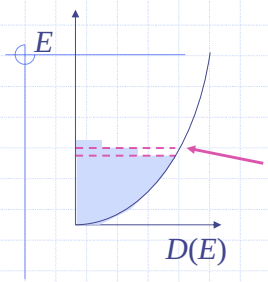


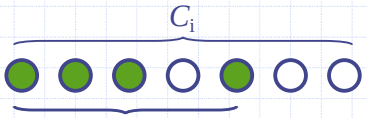


Area of the circle

$$2\frac{\pi k^2}{(\frac{2\pi}{L})^2} = N \quad \Rightarrow \quad N = \frac{L^2}{2\pi}k^2 = \left(\qquad\right) \quad \Rightarrow \quad D(E) = \frac{dN}{dE} = \left(\qquad\right)$$

Fermi statistics: only one electron can occupy a state.





Occupied by N_i electrons

N_i electrons are in the C_i states with energy E.
We cannot distinguish N_i electrons, so that the statistical weight is the number to choose N_i from C_i:

$$W_i = \frac{C_i!}{N_i!(C_i - N_i)!}$$

The definition of entropy in statistical mechanics is

$$S = k_B \ln W = k_B \ln \prod_i W_i = k_B \sum_i \ln W_i = k_B \sum_i \ln \frac{C_i!}{N_i!(C_i - N_i)!}$$

$$= k_B \sum_i (C_i \ln C_i - N_i \ln N_i - (C_i - N_i)\ln(C_i - N_i))$$

Stirling' equation $\ln N! = N \ln N - N$

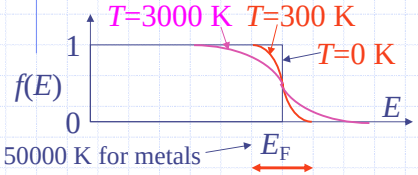
The realized distribution of N_i minimizes the Gibbs free energy
$F = E - TS - \mu N$ where $E = \Sigma N_i E_i$, $N = \Sigma N_i$.
So differentiation of F as for N_i is zero to give,

$$\frac{\partial F}{\partial N_i} = E_i + k_B T(\ln N_i - \ln(C_i - N_i)) - \mu = 0$$

$$\frac{C_i - N_i}{N_i} = \left(\quad \right)$$

Occupation

$$f(E_i) = \frac{N_i}{C_i} = \left(\quad \right)$$



Fermi-Dirac distribution

When $T \neq 0$, $f(E)$ changes continuously from 1 to 0 with the width of $k_B T$.

When T=0:

$E < \mu$ $f(E) = \frac{1}{e^{-\infty} + 1} = \left(\quad \right)$

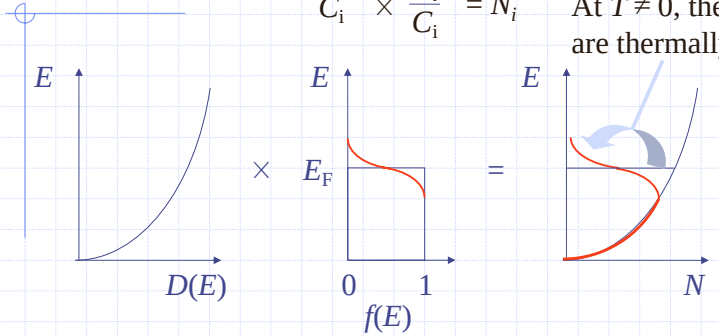
$E > \mu$ $f(E) = \frac{1}{e^{+\infty} + 1} = \left(\quad \right)$

$E_F = \mu$: chemical potential

The real electron number is $D(E) \times f(E)$

$$C_i \times \frac{N_i}{C_i} = N_i$$

At $T \neq 0$, these electrons are thermally excited.



$$\frac{E_F}{k_B T} \approx \frac{50000\text{K}}{300\text{K}} > 100$$

→ Only <1% electrons are thermally excited.

Internal energy of metal electrons

$$U(T) = \int_0^\infty (E - E_F) D(E) f(E) dE$$

Measured from E_F = 0.

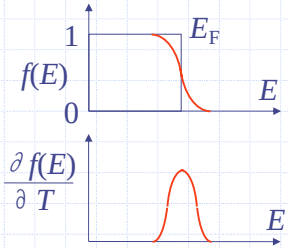
Specific heat

$$C_V = \frac{\partial U}{\partial T} = \int_0^\infty (E - E_F) D(E) \frac{\partial f(E)}{\partial T} dE$$

T appears only in $f(E)$.

where $f(E_i) = \frac{1}{e^{\frac{E_i - \mu}{k_B T}} + 1} = \frac{1}{e^x + 1}$ $x = \frac{E - \mu}{k_B T}$ gives

$$\frac{\partial f}{\partial T} = \left(\quad \right) \quad dx = \frac{dE}{k_B T}$$



$\frac{\partial f(E)}{\partial T}$ is nonzero only near E_F.

so that approximated to be $D(E) \backsim D(E_F)$.

$$C_V = D(E_F)\int_0^\infty (E-E_F)\frac{\partial f(E)}{\partial T}\,dE$$

$$= D(E_F)\int_0^\infty (k_B T x)\frac{x}{T}\frac{e^x}{(e^x+1)^2}k_B T dx$$

$$= k_B^2 T D(E_F)\int_0^\infty x^2\frac{e^x}{(e^x+1)^2}dx$$

$\pi^2/3$ from table of integrals

$$= \left(\qquad\right) T$$

$C_v = \gamma T$

γ

Specific heat of metal electrons

or using $D(E_F) = \frac{3}{2}\frac{N}{E_F} = \frac{3}{2}\frac{N}{k_B T_F}$ T_F: Fermi temperature

$$C_v = \frac{\pi^2}{3}\frac{3}{2}\frac{N}{k_B T_F}k_B^2 T = \frac{\pi^2}{2}Nk_B\frac{T}{T_F} = \frac{\pi^2}{2}nR\frac{T}{T_F}$$

Gas constant

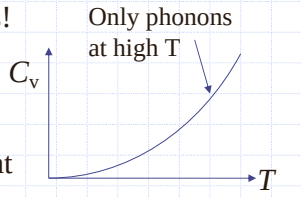
If free electron is an ideal gas, according to the Dulong-Petit theorem, the specific heat is $C_v = 3R$. However, it is less than

$$\frac{T}{T_F} \approx \frac{300\,\mathrm{K}}{50000\,\mathrm{K}} \approx 10^{-2}$$

➡ Owing to the Fermi distribution, only $k_B T$ electrons near E_F are excited, and contribute to the specific heat.

➡ Metal electrons are "Fermi" particles!

➡ Fermi gas cf. Classical gas



At low temperatures (<50 K), the lattice vibration (photon) decays as $C_v \propto T^3$ so that

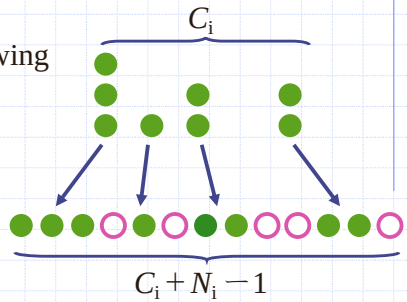
$C_v = \gamma T + \beta T^3$ ➡ $\frac{C_v}{T} = \gamma + \beta T^2$

free electron phonon

Experimental estimation of $\gamma \rightarrow D(E_F)$ from the low-temperature (<4 K) specific heat. γ {

Bose-Einstein statistics

Insert N_i particles in C_i levels, allowing any particles in the same level.



The number to arrange N_i particles and C_i-1 partitions.

$$W_i = \frac{(C_i + N_i - 1)!}{N_i!(C_i - 1)!}$$

C_i-1 → C_i gives

$$\ln W_i = (C_i + N_i)\ln(C_i + N_i) - N_i \ln N_i - C_i \ln C_i$$

Put this in $F=E-TS-\mu N$, and differentiation as for N_i is put zero to

$$\frac{\partial F}{\partial N_i} = \left(\qquad\right) = 0$$

$$\frac{C_i + N_i}{N_i} = e^{\frac{E_i - \mu}{k_B T}}$$

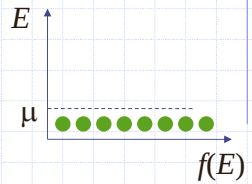
$$f(E_i) = \frac{N_i}{C_i} = \left(\qquad\right)$$ Bose-Einstein statistics

$T \rightarrow 0$

$E_i - \mu > 0$ $e^{+\infty} \rightarrow +\infty$ $f(E) \rightarrow 0$

$E_i - \mu = 0$ $e^0 \rightarrow 1$ $f(E) \rightarrow +\infty$

All particles go to the lowest level.



$E_i - \mu \rightarrow \hbar\omega$ gives $f(E_i) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$ Planck distribution

Phonon (lattice vibration) is Bose-Einstein particle.

Photon (light) is the same → black body

$$f(E_i) = \frac{1}{e^{\frac{E_i - \mu}{k_B T}} \pm 1}$$

$+$ { }

$-$ { }

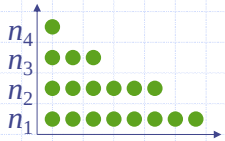
Quantum statistics

E-μ>>$k_B T$ leads to e^{large}>>1 $\quad f(E_i) = e^{-\frac{E_i-\mu}{k_B T}}$

Boltzmann (classical) distribution

Classical distribution

Each i-th state has n_i particles, with the total $N = \Sigma\, n_i$ particles.
The statistical weight is



$$W = \frac{N!}{n_1! n_2! n_3! \cdots}$$

$\ln N! = N \ln N - N$ Stirling's equation

so

$$\ln W = \ln \frac{N!}{n_1! n_2! n_3! \cdots} = N \ln N - \sum_i n_i \ln n_i$$

Put this in $F = E - TS - \mu N$ $\quad (S = k_B \ln W)$

$$F = \sum_i E_i n_i - k_B T (N \ln N - \sum_i n_i \ln n_i) - \mu \sum_i n_i$$

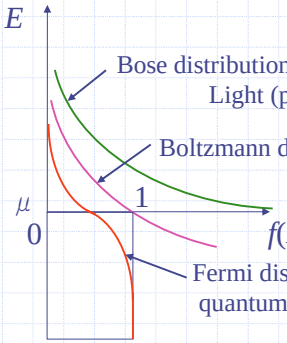
Differentiation as for n_i is zero to give,

$$\frac{\partial F}{\partial N_i} = \left(\qquad \right) = 0$$

so

$$f(E_i) = n_i = \left(\qquad \right)$$ Boltzmann sidtribution

$$f(E_i) = \frac{1}{e^{\frac{E_i-\mu}{k_B T}} - 1}$$



Bose distribution : Particles with integer spin quantum number : Light (photon), Lattice vibration (phonon), ^{4}He

Boltzmann distribution : classical particles

$f(E_i) = e^{-\frac{E_i-\mu}{k_B T}}$ $\qquad f(E_i) = \frac{1}{e^{\frac{E_i-\mu}{k_B T}} + 1}$

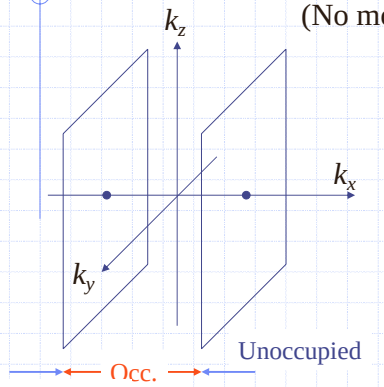
Fermi distribution : Particles with half-integer spin quantum number : electron, proton, neutron, ^{3}He

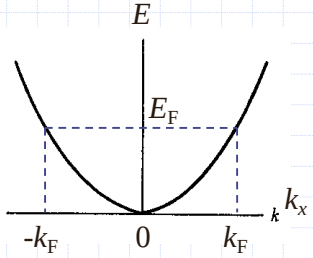
Everything approaches to Boltzmann at $E_i - \mu >> k_B T$.

One-dimensional metal

$$E = \frac{\hbar^2 k_x^2}{2m} = \text{const. leads to} \quad k_x = k_F = \text{const.}$$

(No momentum for k_y, k_z = does not move)





Fermi surface consists of a pair of planes.