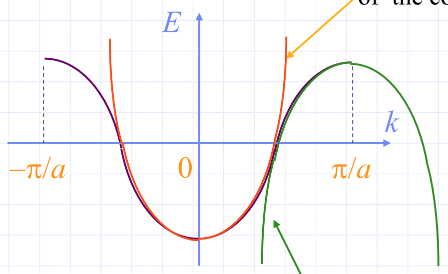
(10) Correspondence to the free electron model

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

Free electron model is the bottom parabola of the cos function.

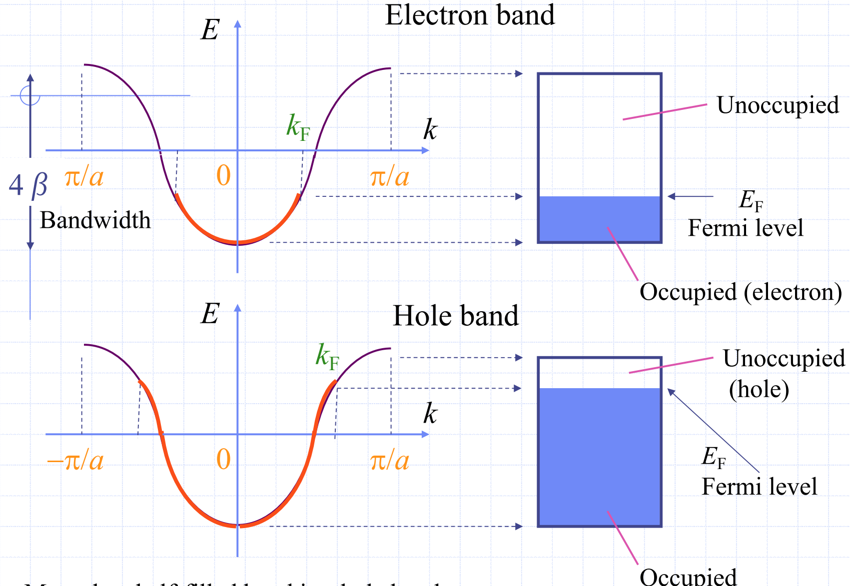


Approximated by $E = \dfrac{\hbar^2 k^2}{2m}$

m is different from the value for a real electron.
(Effective mass)
4β large → m small→ mobile
4β small → m large→ not mobile

Upper half of the band is approximated by free electron with $m < 0$.
Opposite response to electric field,
→ Hole with + charge

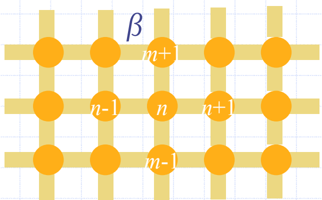
(11) Electron band



More than half-filled band is a hole band.

(12) 2-Dimensional Square Lattice

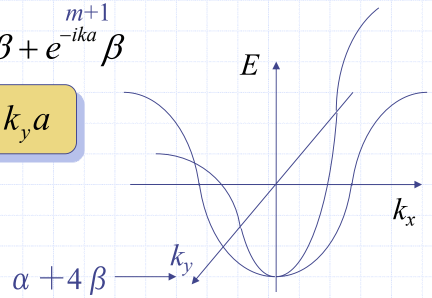
$$\phi = \sum_n \sum_m e^{inka} e^{imka} \chi_{nm}$$



$$E \propto \sum_n \sum_m \sum_p \sum_q e^{i(n-m)ka} e^{i(p-q)ka} \int \chi_m^* H \chi_n \, d\tau$$

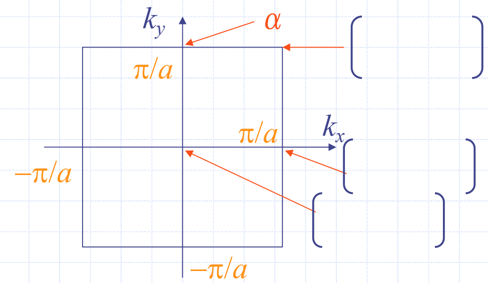
$$E = \overset{n\text{-}1}{e^{ika}}\beta + \alpha + \overset{n+1}{e^{-ika}}\beta + \overset{m\text{-}1}{e^{ika}}\beta + \overset{m+1}{e^{-ika}}\beta$$

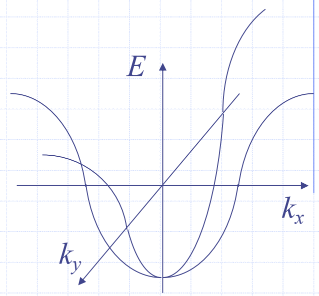
$$\boxed{E = \alpha + 2\beta \cos k_x a + 2\beta \cos k_y a}$$



(12) 2-Dimensional Square Lattice

$$\boxed{E = \alpha + 2\beta \cos k_x a + 2\beta \cos k_y a}$$

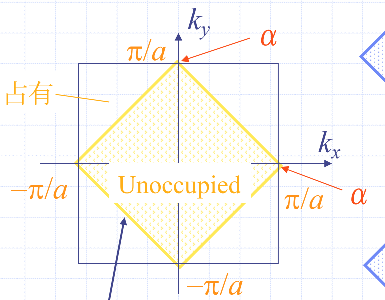


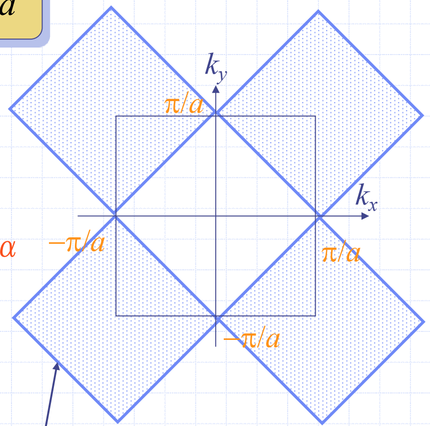


Bandwidth: 8 β
(In general, bandwidth is $2z\beta$, where z is the coordination number (the number of the nearby sites.))

(12) 2-Dimensional Square Lattice

$$E = \alpha + 2\beta\cos k_x a + 2\beta\cos k_y a$$





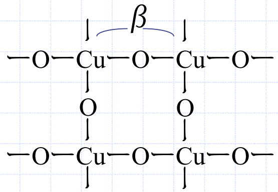
Electron-like Fermi surface
equi-energy surface for $E = \alpha$.

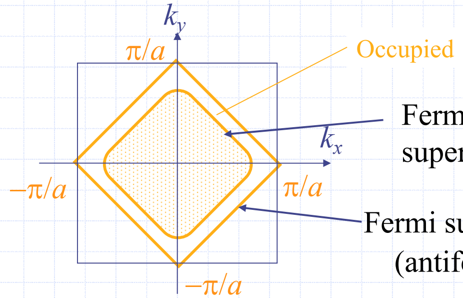
Hole-like Fermi surface

(12) 2-Dimensional Square Lattice

Cupper oxide high-temperature superconductor

$(La_{1-x}Sr_x)_2CuO_4$





Fermi surface of the hole-doped superconductor, $(La_{1-x}Sr_x)_2CuO_4$

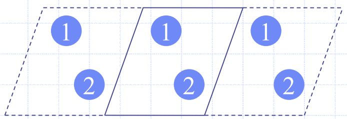
Fermi surface of the parent La_2CuO_4 (antiferromagnetic insulator)

$La_2Cu^{2+}O_4$ $\rightarrow$ Cu：d^9 $\rightarrow$ $d_{x^2-y^2}$ band has one electron (Half-filled)

(13) Tight-bonding method for more than two atoms in a cell

LCAO-MO $\phi = \sum_i c_i \chi_i$

For 2 atoms, i=1, 2



Bloch function is made from χ_i for the whole crystal.

$$\chi_i \rightarrow \sum_n e^{inka} \chi_i(n)$$

Crystal orbital is constructed instead of molecular orbital as,

$$\phi = \sum_i \sum_n c_i e^{inka} \chi_i(n)$$

Calculate $E = \dfrac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau}$ from this, and similarly to the usual Mo theory,

$\dfrac{\partial E}{\partial c_i} = 0$ leads to simultaneous equations of c_i, and the secular equation is

$$\begin{vmatrix} \alpha_{11}(k) - E & \beta_{12}(k) & \cdots\cdots \\ \beta_{21}(k) & \alpha_{22}(k) - E & \end{vmatrix} = 0$$

Since χ_i is Bloch function, the matrix elements, α and β are functions of k:

$$\alpha_{ii}(k) = \int (\sum_m e^{-imka} \chi_i^*(m)) H (\sum_n e^{inka} \chi_i^*(n)) d\tau$$

$$= \alpha_i + \sum_n \beta_{ii}(n) e^{inka} \qquad \beta_{ii}(n) = \int \chi_i^*(0) H \underbrace{\chi_i(n)}_{\text{Nearby atoms}} d\tau$$

$$\beta_{ij}(k) = \int (\sum_m e^{-imka} \chi_i^*(m)) H (\sum_n e^{inka} \chi_j^*(n)) d\tau$$

$$= \sum_n \beta_{ij}(n) e^{inka}$$

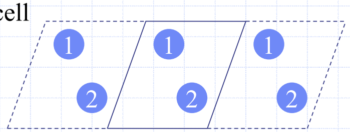
When interaction β exists in the r direction, add a term βe^{ikr}.

$$\beta_{ij}(n) = \int \chi_i^* \overbrace{(0) H \chi_j(n)}^{\text{Nearby atoms}} d\tau$$

Energy band for a system with many atomic orbitals

LCAO-MO from all atomic orbitals in a cell
(N, each atom may have more than one.)

$$\phi = \sum_i c_i \chi_i$$



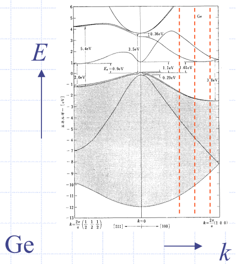
Make the Bloch function of each χ

$$\chi_i \rightarrow \sum_n e^{inka} \chi_i(n)$$ leading to an

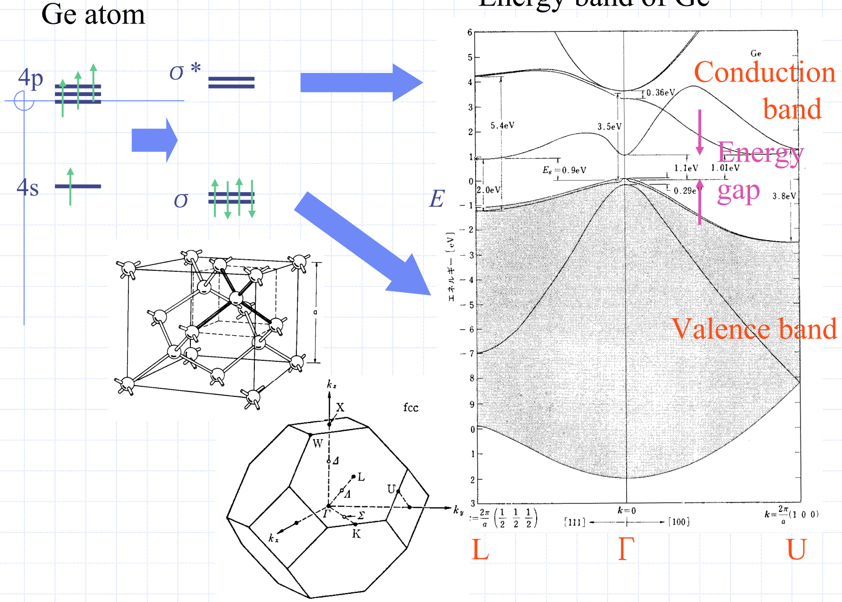
$N \times N$ secular equation

$$\begin{vmatrix} \alpha_{11}(k)-E & \beta_{12}(k) & \cdots \\ \beta_{21}(k) & \alpha_{22}(k)-E & \end{vmatrix} = 0$$

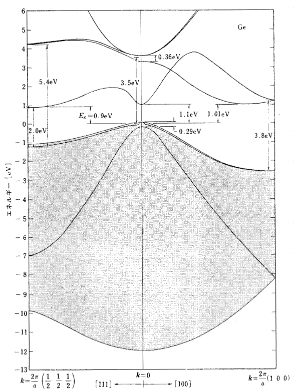
Since each element is a function of k,
this secular equation is solved at each k, to give
N energy levels.
These energy levels for different k are connected
to afford continuous energy bands (right).



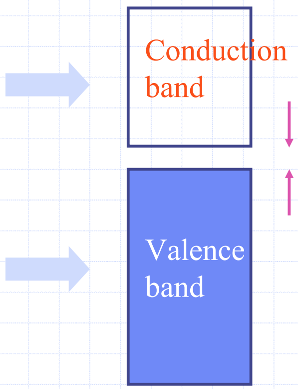
Energy band of Ge



Forgetting k



Energy band of Ge

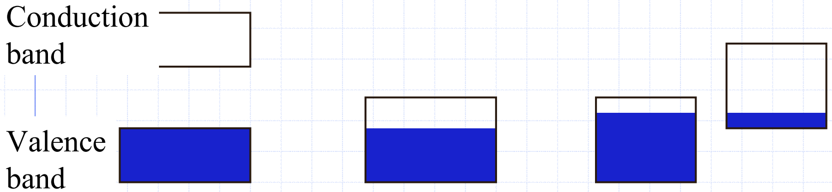


Energy gap
(Band gap)

C	5.47 eV
Si	1.12 eV
Ge	0.66 eV

Semiconductor

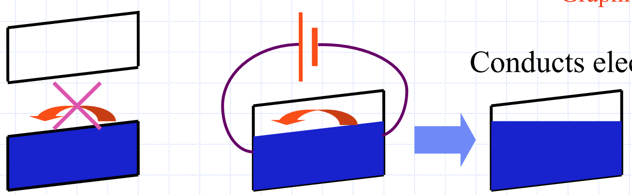
Energy bands of solids



Insulator
Completely Filled

Metal
Partially Filled

Semimetal
Bands overlap partially.
Graphite

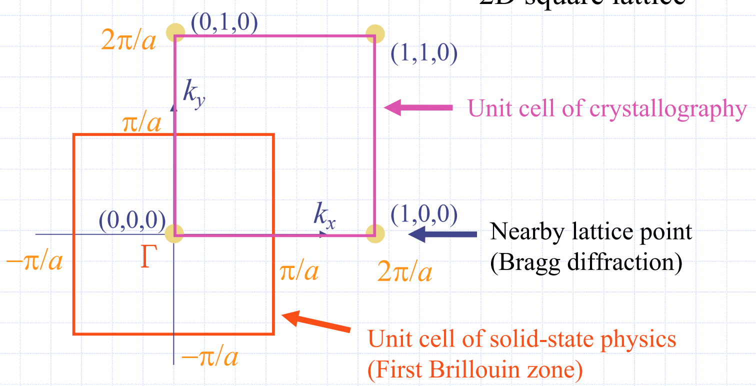


Conducts electricity

A unit of 1D energy band is $-\pi/a < k < \pi/a$

2D, 3D

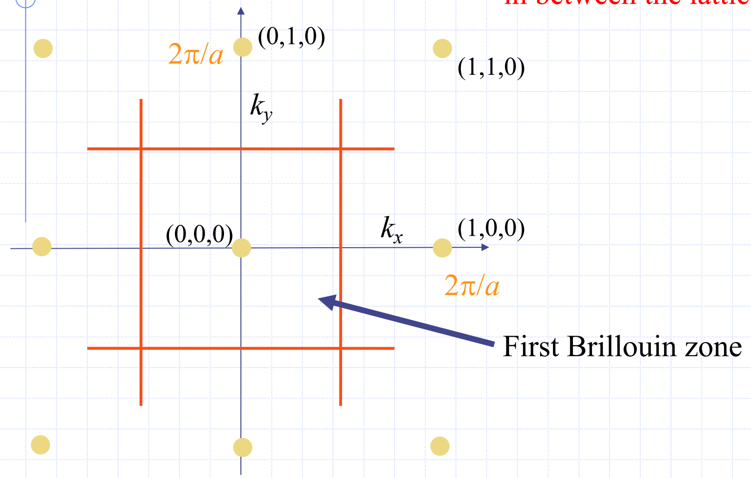
2D square lattice



Solid-state physics defines the k-space from e^{ika}: reciprocal lattice points at $2\pi/a$.
Crystallography defines the k-space from e^{2pika}: reciprocal lattice points at $1/a$.

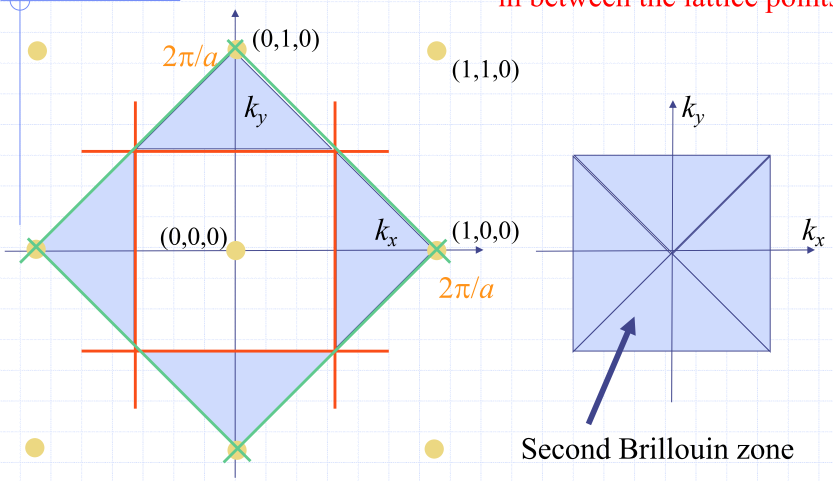
How to make the Brillouin zone.

Bordered by perpendicular bisectors in between the lattice points

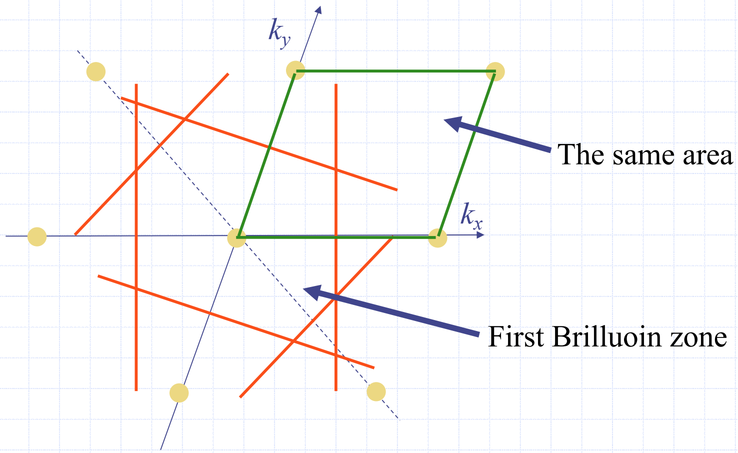


How to make the Brillouin zone.

Bordered by perpendicular bisectors in between the lattice points

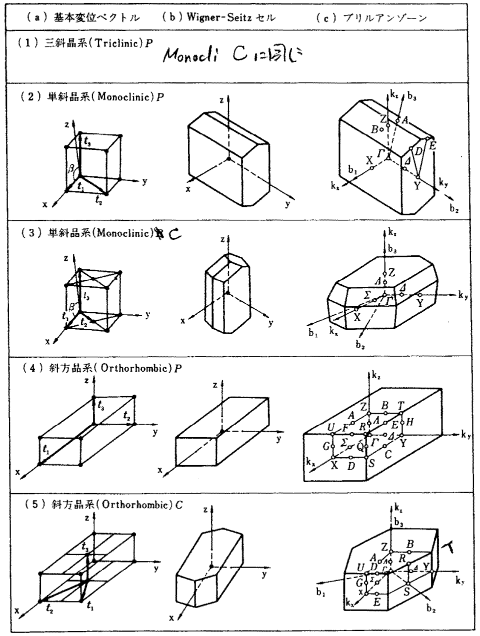


How to make the Brillouin zone for a oblique lattice.



Brillouin zone and the Bravais lattices

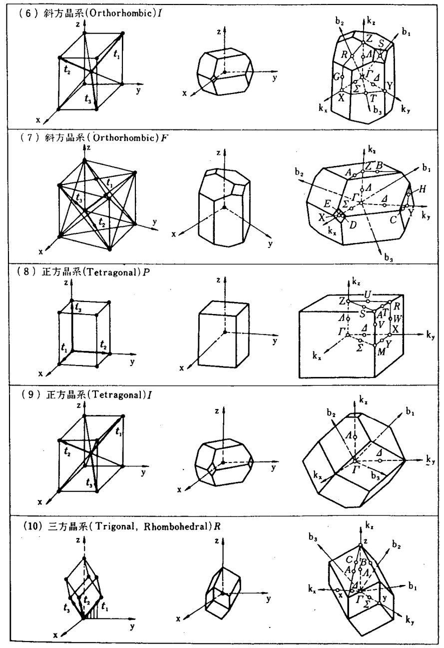
Reciprocal of centered is centered



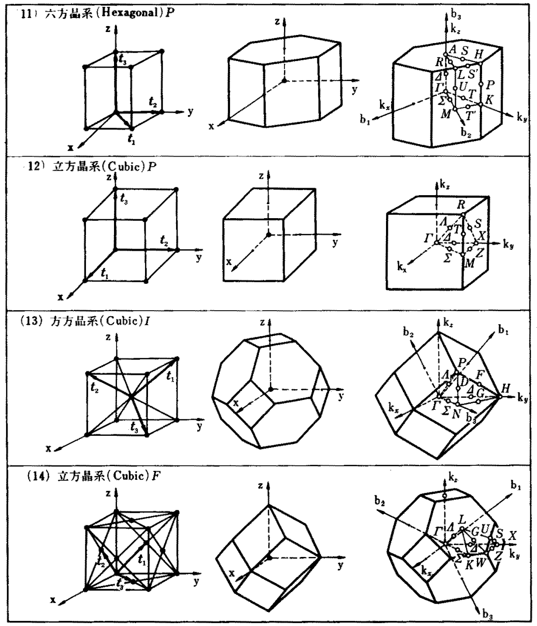
Brillouin zone and the Bravais lattices

Reciprocal of face centered is body centered

Reciprocal of body centered is face centered



Brillouin zone and the Bravais lattices



体心立方格子
bcc
body centered
cubic

面心立方格子
fcc
face centered
cubic

Fermi surface of metals

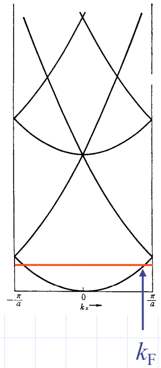
(1) Alkali metals Li, Na, K

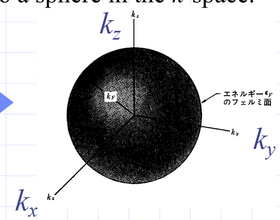
Fermi surface ⇔ trajectory of k_F ⇔ Surface at $E=E_F$ =const.

Assuming free electron

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

leads to a sphere in the k-space.





Fermi surface of alkali metals is not deviated from the perfect sphere by 1%.

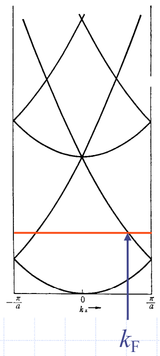
Energy interval in the k-space is $\Delta k = \dfrac{2\pi}{Na}$

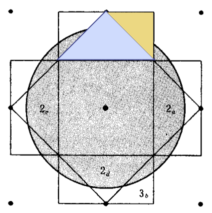
Volume of the Fermi sphere is half of the volume of the 1st Brillouin zone.

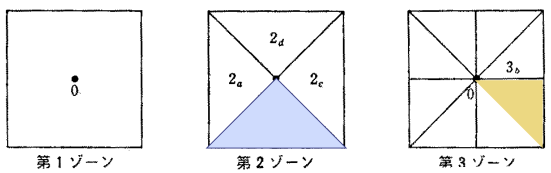
Fermi surface of metals

(1) Divalent metals Mg, Al

Volume of the Fermi sphere is the same as the volume of the 1st Brillouin zone.

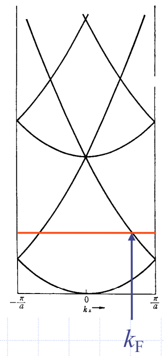


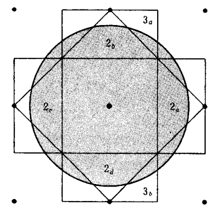


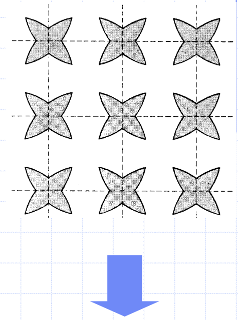


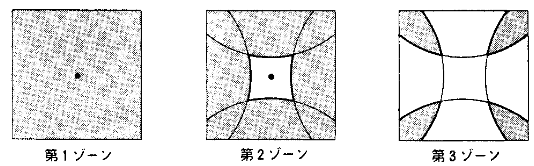
Fermi surface of metals

(2) Divalent and trivalent Mg, Al



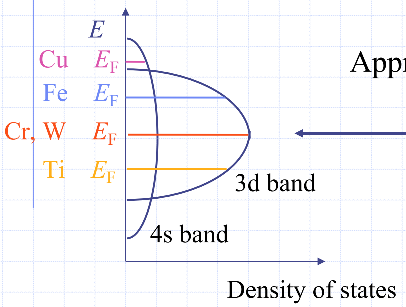






Fermi surface of metals

(3) Transition metals



3d band is narrower than the 4s band.

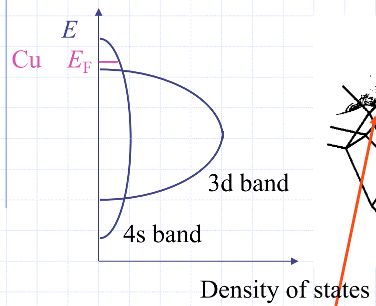
Approximately s^1d^{n-1}

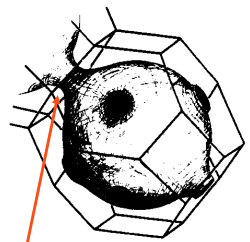
W: highest melting point (3380℃)

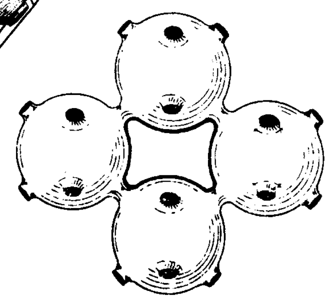
← strong bonds

Fermi surface of metals

(4) Cu, Ag, Au $s^1d^{10} \rightarrow$ close to alkali metals





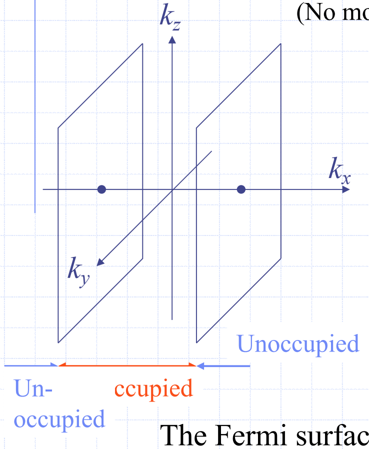


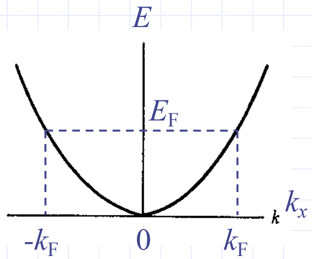
Nearly a sphere but
Partly connected.

1D metal

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

(No momentum for other k_y and k_z directions. = cannot move.)

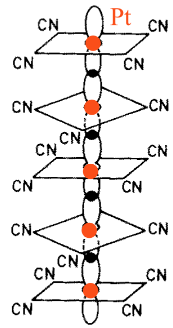


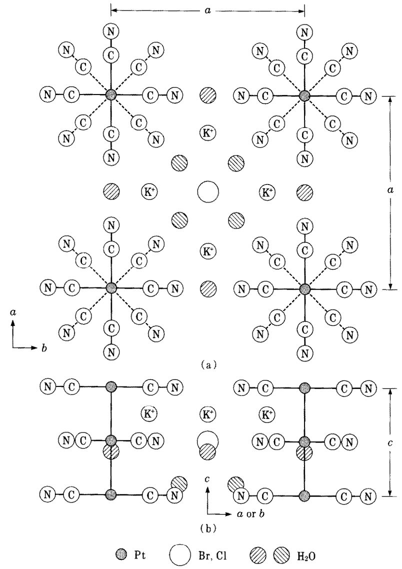


The Fermi surface consists of a pair of planes.

Examples of 1D metals

(1) 1D Platinum Complex KCP $K_2[Pt(CN)_4]Br_{0.40}xH_2O$



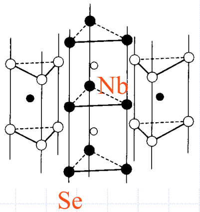


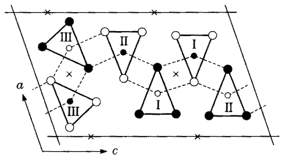
Pt surrounded by CN
Metal 1D Chain

Metal at room temp.
Insulator at low temp.

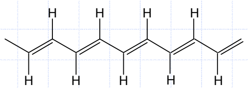
Examples of 1D metals

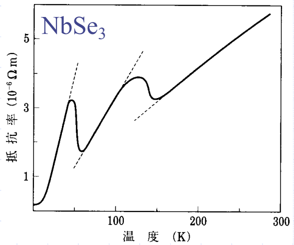
(2) $NbSe_3$





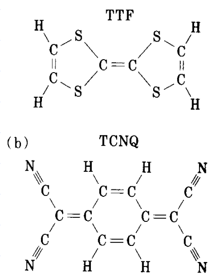
(3) Polyacetylene

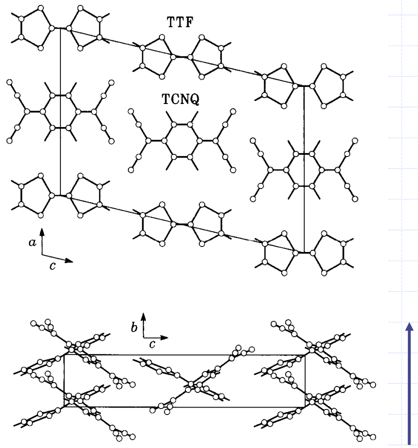




Examples of 1D metals

(4) Organic Charge-Transfer Complex (TTF)(TCNQ)



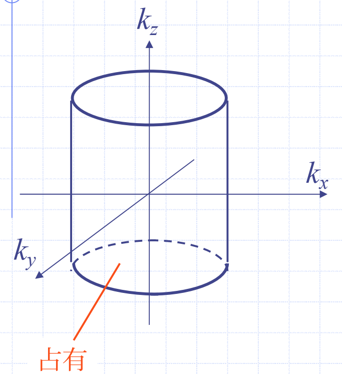


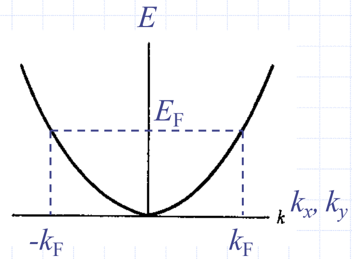
Current flow

Examples of 2D metals

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

$\rightarrow$ circle





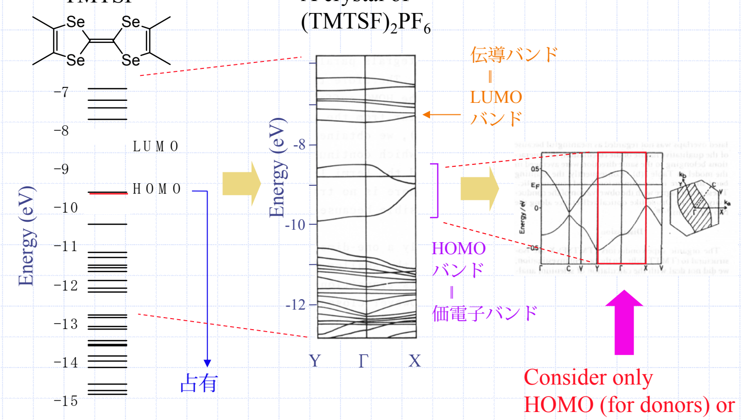
Cylindrical Fermi surface

Examples
- Graphite
- Organic superconductors

Organics：energy levels → energy bands

A single molecule of TMTSF

A crystal of $(TMTSF)_2PF_6$



Energy levels

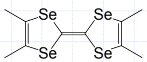
Energy bands

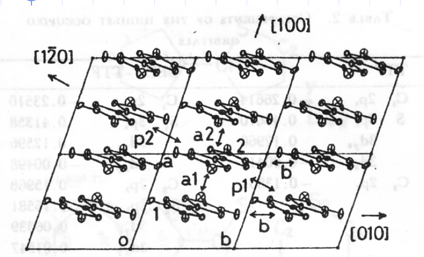
Consider only HOMO (for donors) or LUMO (for acceptors)

Energy band of organic conductors consists of only HOMOs.

Fermi surface of the first organic superconductor

$(TMTSF)_2PF_6$





	Direction	Interaction
1→1	$\pm b$	b
2→2	$\pm b$	b
1→2	$a/2$	a1
	$-a/2$	a2
	$a/2-b$	p1
	$-a/2+b$	p2

$$\beta_{11} = \beta_{22} = \beta_b e^{ikb} + \beta_b e^{-ikb} = 2\beta_b \cos(kb)$$

$$\beta_{12} = \beta_{21}^* = \beta_{a1} e^{ika/2} + \beta_{a2} e^{-ika/2} + \beta_{p1} e^{ika/2-kb} + \beta_{p2} e^{-ika/2+kb}$$

β (meV)	HOMO
a1	200
a2	230
b	35
p1	20
p2	7

Put these in $\begin{vmatrix} \beta_{11} - E & \beta_{12} \\ \beta_{21} & \beta_{22} - E \end{vmatrix} = 0$ and solve to give:

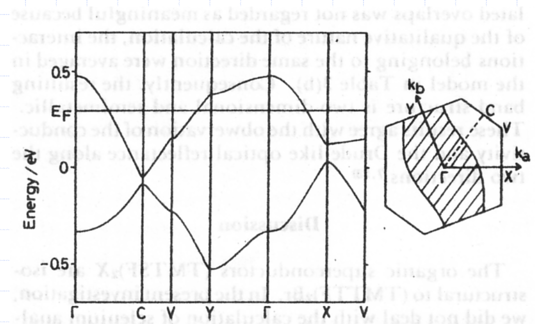
$(TMTSF)_2PF_6$

$$E(k) = 2\beta_b \cos(kb) \pm \sqrt{\Delta}$$

$$\Delta = [(\beta_{a1} + \beta_{a2})\cos(\frac{ka}{2}) + (\beta_{p1} + \beta_{p2})\cos(\frac{ka}{2} - kb)]^2 + [(\beta_{a1} - \beta_{a2})\sin(\frac{ka}{2}) + (\beta_{p1} - \beta_{p2})\sin(\frac{ka}{2} - kb)]^2$$

方向	β (meV) HOMO
a1	200
a2	230
b	35
p1	20
p2	7

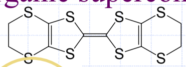
Calculated from MO

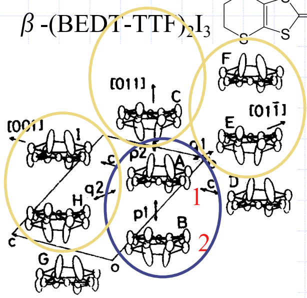


A pair of waving planes → Quasi-1D conductor
Considerable waving reflects the 2D character.

Fermi surface of organic superconductor

β-(BEDT-TTF)$_2$I$_3$



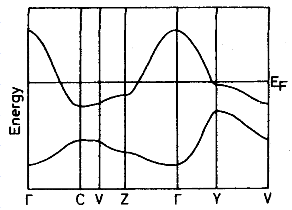


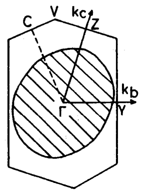
	方向	相互作用	方向	HOMO
1→1	±c	c	p1	245
2→2	±c	c	p2	84
1→2		p1	c	50
	b+c	p2	q1	127
	c	q2	q2	68
	b	q1		

Transfer integrals β (meV)

From MO calc.

$$\beta_{11} = \beta_{22} = \beta_c e^{ikc} + \beta_c e^{-ikc}$$
$$= 2\beta_c \cos(kc)$$
$$\beta_{12} = \beta_{21}^{*} = \beta_{p1} + \beta_{p2} e^{i(kb+kc)}$$
$$+\beta_{q2} e^{ikc} + \beta_{q1} e^{ikb}$$

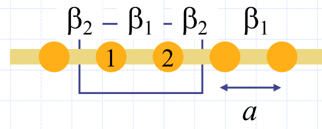




Cylindrical Fermi surface indicated 2D.

Program available from http://www.op.titech.ac.jp/lab/mori/lib/program.html

(14) Energy band of one-dimensional alternating chain



β is alternately β_1 and β_2.

→ Two atoms 1 and 2 in a cell.

For simplicity, put $\langle \chi_1|H|\chi_1\rangle = \langle \chi_2|H|\chi_2\rangle = \alpha = 0$.

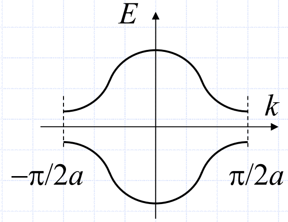
$\langle \chi_1|H|\chi_2\rangle = \langle \chi_2|H|\chi_1\rangle^* = \beta_2 e^{-ika} + \beta_1 e^{ika}$

β_2 in the $-a$ direction from 1 β_1 in the a direction from 1

Secular equation is,

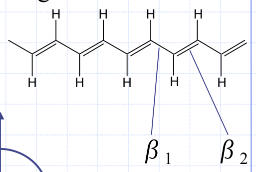
$$\begin{vmatrix} -E & \beta_2 e^{-ika} + \beta_1 e^{ika} \\ \beta_2 e^{ika} + \beta_1 e^{-ika} & -E \end{vmatrix} = 0$$

The solution is depicted in the right:

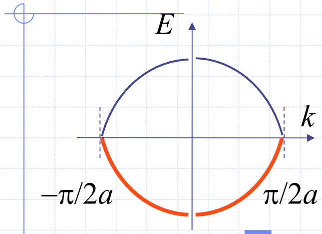


$$1 + \cos 2x = 2\cos^2 x$$

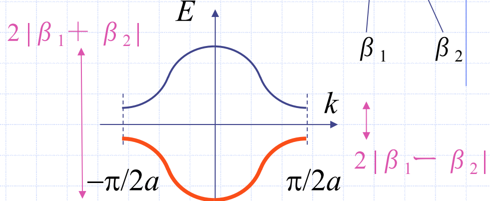
Different β for single and double bonds



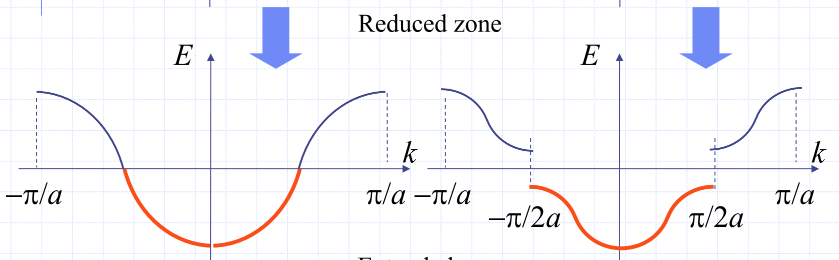
$\beta_1 = \beta_2$



$\beta_1 \neq \beta_2$

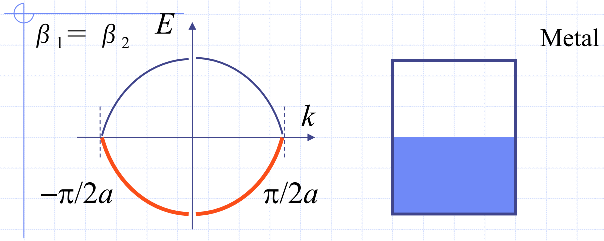


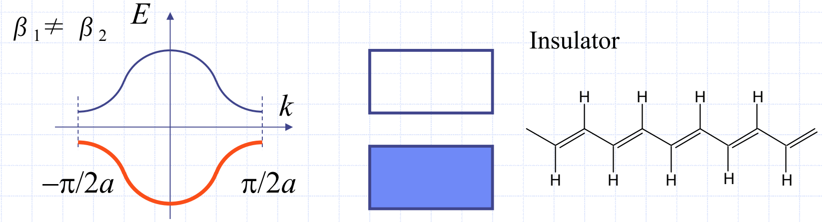
Reduced zone



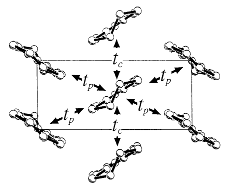
Extended zone

Peierls Insulator: Long periodicity generates a new energy gap and makes the system insulating.

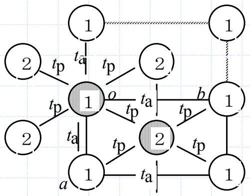




Excise Band structure of the θ -phase



This generally found structure is called herringbone structure in organic crystals or alternatively θ -phase in organic conductors. Calculate the energy bands of this structure.



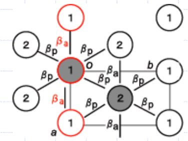
A unit cell contains two molecules, numbered 1 and 2.
Transfer t_a, running along a, is between two Molecule 1.
Transfer t_p, running diagonal ($a/2$, $b/2$) etc, is between Molecule 1 and 2.
(1) How many Molecule 1 exist near Molecule 1?
From this, obtain the diagonal element F_{11}.
(1) How many Molecule 2 exist near Molecule 1?
From this, obtain the nondiagonal element F_{12}.
(3) Solve the secular equation, and obtain an equation of $E(k_a, k_b)$ representing the energy band.

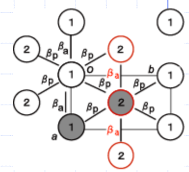
$$\cos x + \cos y = 2\cos\frac{x+y}{2}\cos\frac{x-y}{2}$$

Matrix elements are obtained from (transfer)$e^{ik(\text{vector})}$

1→1 from β_a located at ±a

$$F_{11} = \beta_a e^{ika} + \beta_a e^{-ika} = 2\beta_a \cos ka$$

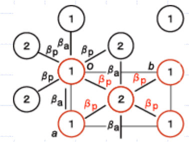




The same for 2→2

$$F_{22} = 2\beta_a \cos ka$$

2→1from β_p located at ±$a/2$±$b/2$



$$F_{21} = \beta_p e^{i\frac{ka+kb}{2}} + \beta_p e^{i\frac{ka-kb}{2}} + \beta_p e^{i\frac{-ka+kb}{2}} + \beta_p e^{i\frac{-ka-kb}{2}}$$

$$= 2\beta_p \cos\frac{ka+kb}{2} + 2\beta_p \cos\frac{ka-kb}{2}$$

The secular equation is

$$\begin{vmatrix} F_{11}-E & F_{12} \\ F_{12} & F_{11}-E \end{vmatrix} = 0 \Rightarrow E = \pm F_{11} \pm F_{12}$$

$$E = \pm 2\beta_a \cos ka \pm 2\beta_p \cos\frac{ka+kb}{2} + 2\beta_p \cos\frac{ka-kb}{2}$$

Calculate this inserting βa=101 and βp=25 meV using(tbmap)

$$E = \pm 2\beta_a \cos ka \pm 2\beta_p \cos\frac{ka+kb}{2} + 2\beta_p \cos\frac{ka-kb}{2}$$

ZX and YC degenerate due to
k_x// screw axis
k_y// glide plane
(Practical lattice periodicity is half.)