Superconductivity and related exotic phases in organic systems

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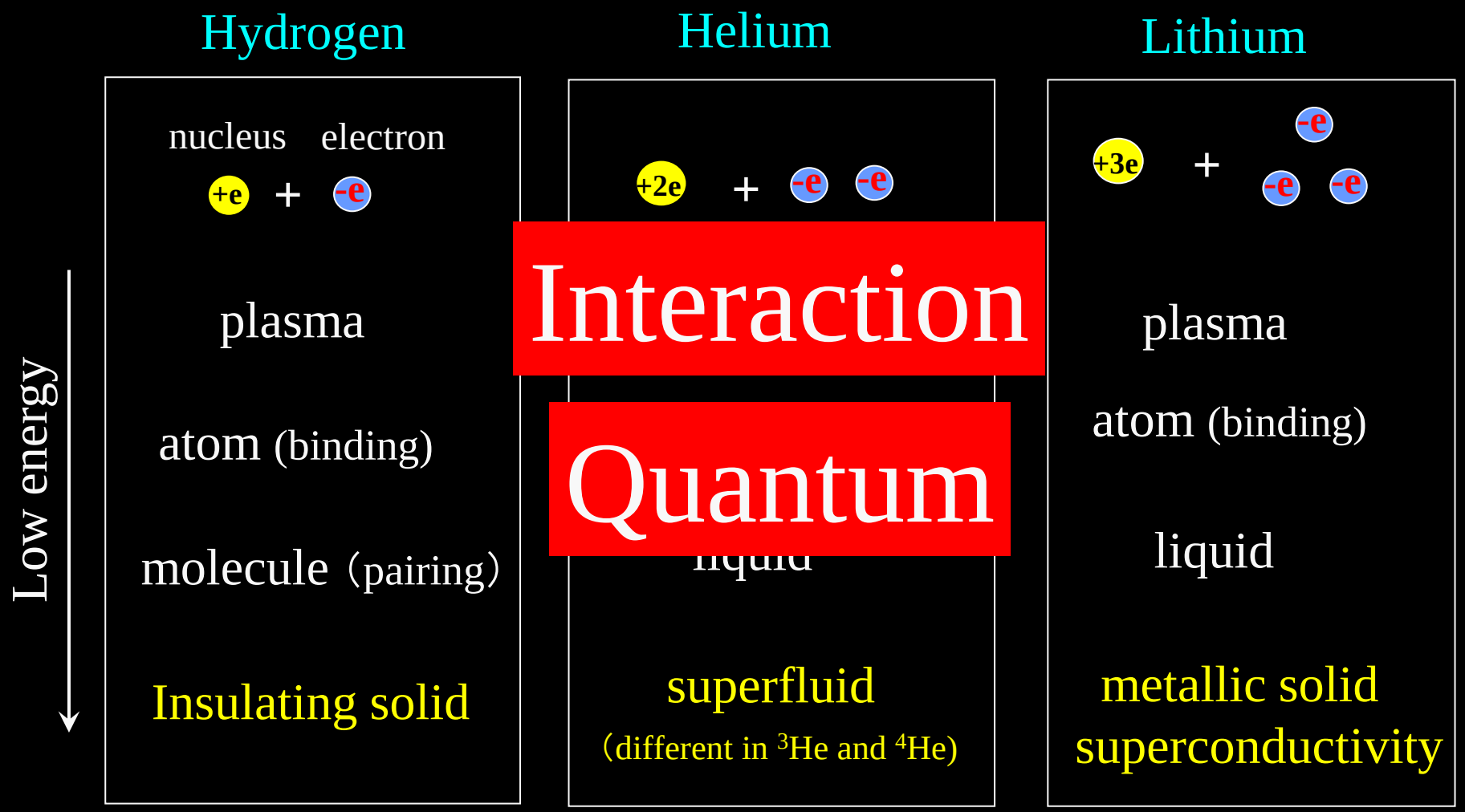
20th
1. Introduction to organic conductors
   molecular orbital, simple band structure, Fermi surface instability

21th
2. Mott transition and superconductivity
   high-energy universality vs low-energy diversity

23th
3. Spin liquid and superconductivity
   fate of unhappy electrons under triangular relations

Physics of condensed matter
Understanding low-energy state of nucleus and electron assembly

More is *differently* different.

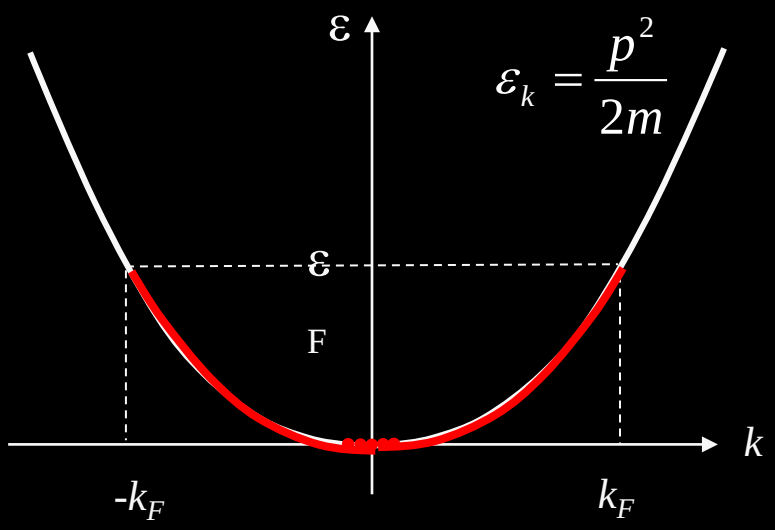


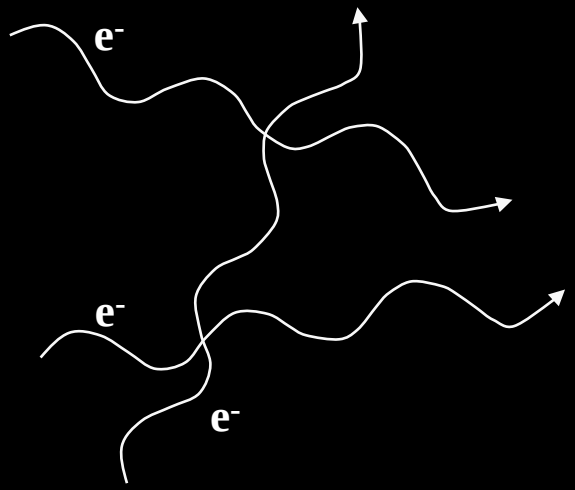
Without interaction,

electrons behave like free waves with Fermi surface.

$$e^{i\mathbf{k}\cdot\mathbf{r}}$$

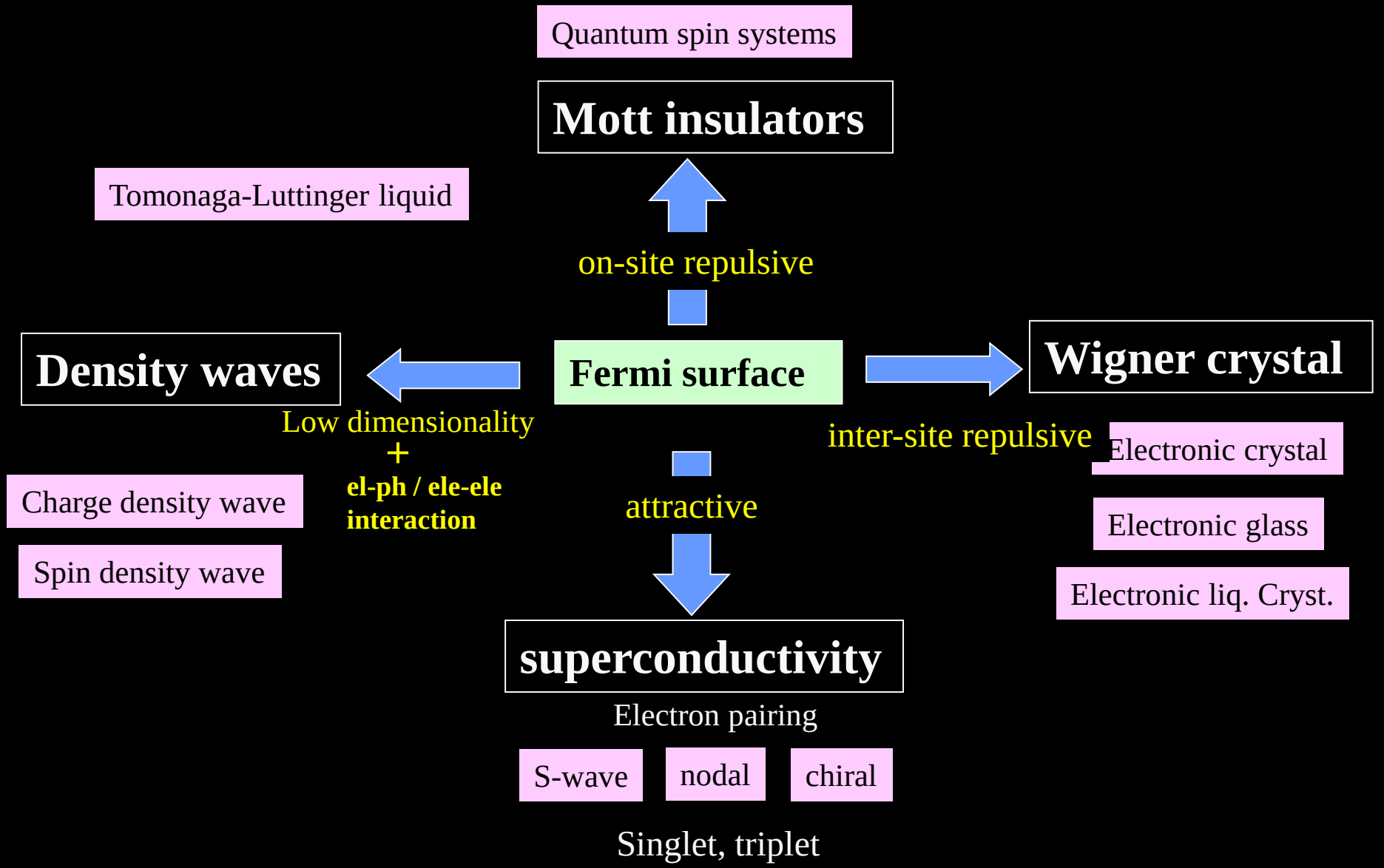
$$(p = \hbar k)$$





Fermi gas

Fermi surface is unstable to perturbation, interaction



Today

1. **Introduction to organic conductors**

   flexible lattice, molecular orbital, band structure, Fermi surface instability

2. Mott transition and superconductivity

   Mott quantum criticality, nodal superconductivity

3. Spin liquid and superconductivity

   various types of RVB, doped quantum spin liquid, BEC-BCS crossover

Structure of organic conductors

Flexible lattice geometry

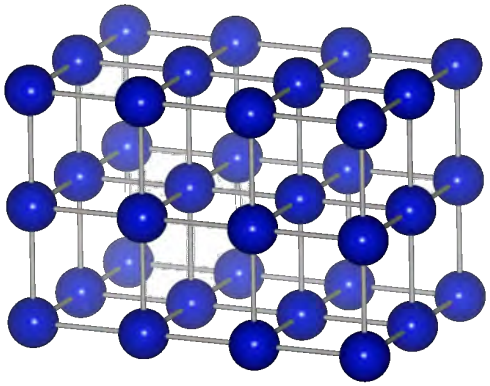
Organic materials → flexible & controllable lattice geometry

Inorganic materials

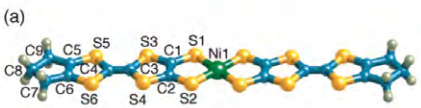
atom

Orbital degeneracy
Spin-orbit coupling
Hunt coupling
…….

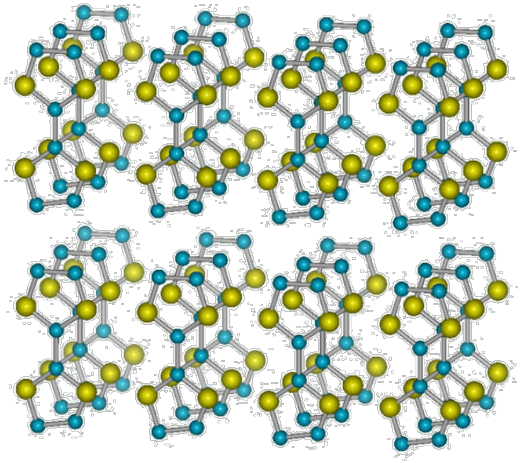
lattice



Organic materials



lattice



Organic materials → Physics of interaction and geometry

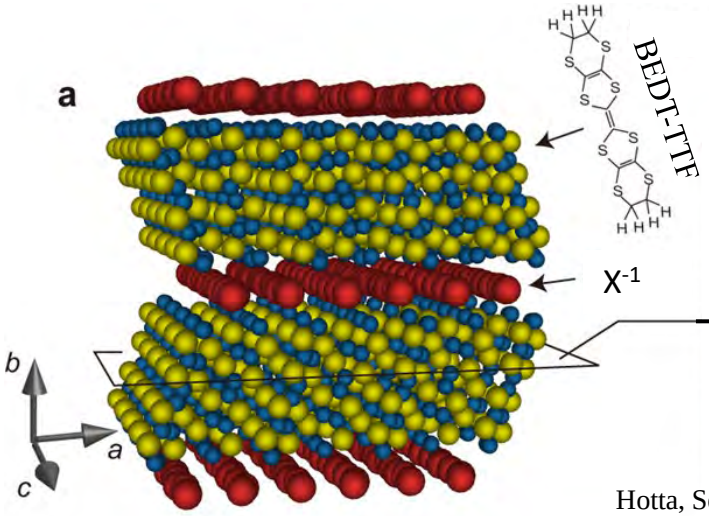
$(BEDT\text{-}TTF)_2X$

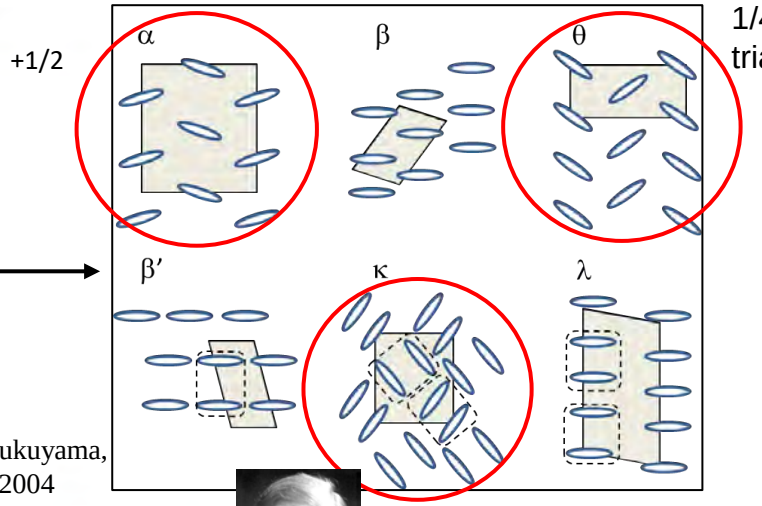
Various in-plane structures

Diverse correlation phenomena

Massless Dirac ele.

Wigner Xtal/glass





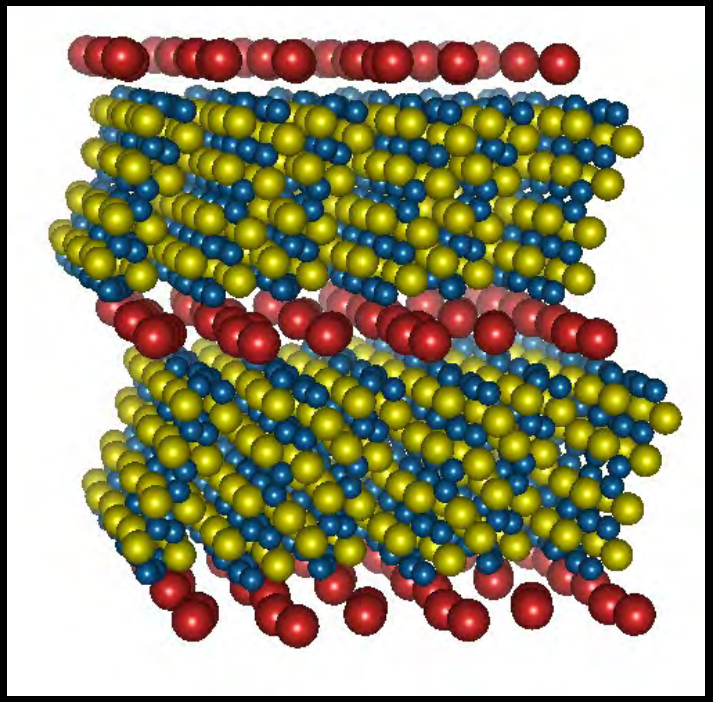
1/4-filled band
triangular lattice

Hotta, Seo, Fukuyama,
Chem. Rev., 2004

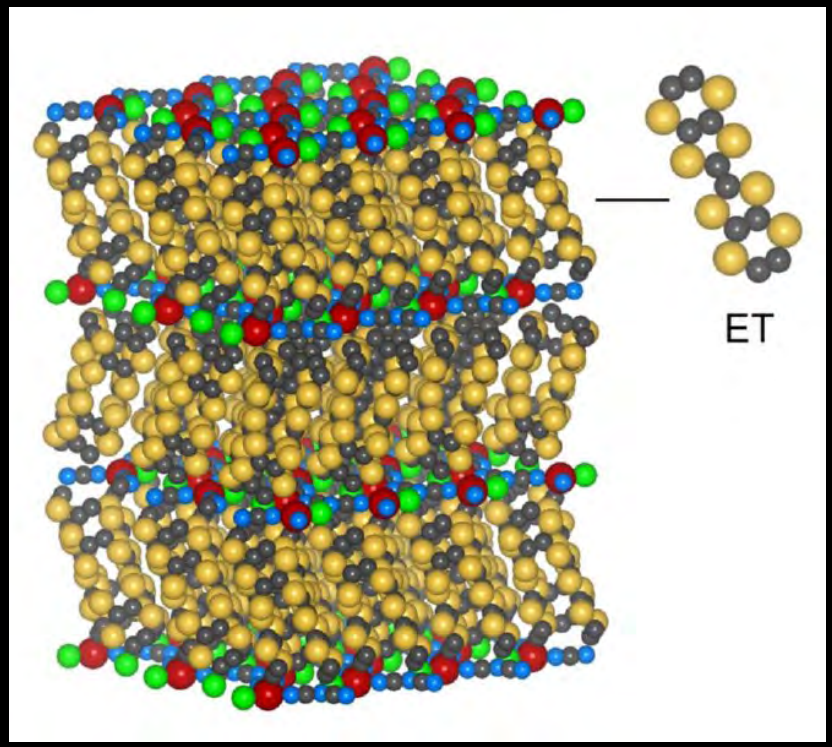
Mott physics

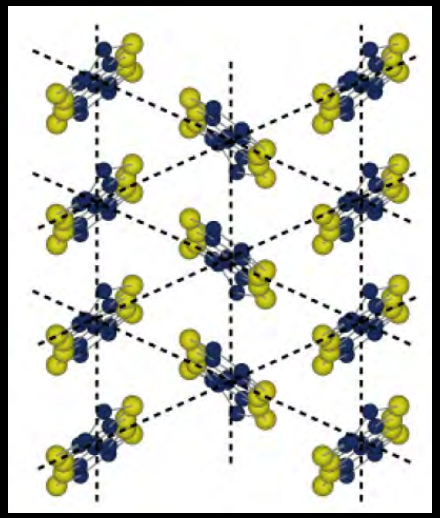
1/2-filled band
triangular lattice

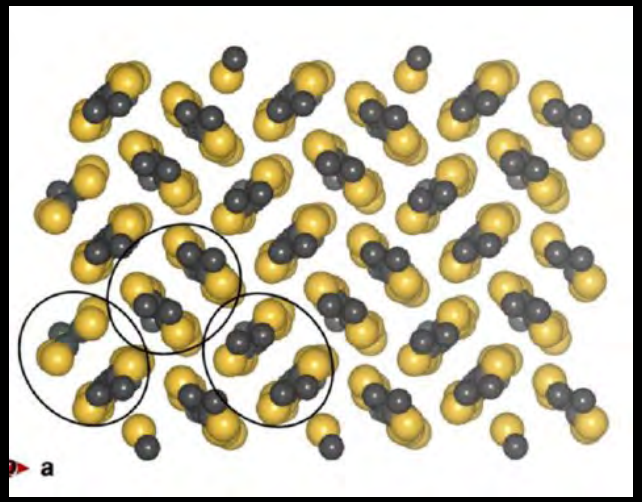
α-$(BEDT\text{-}TTF)_2I_3$



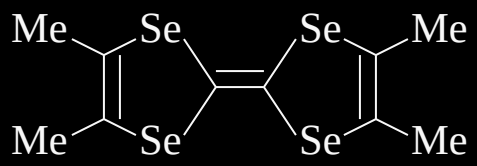
κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$



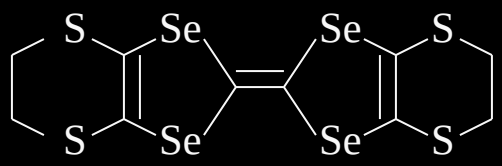




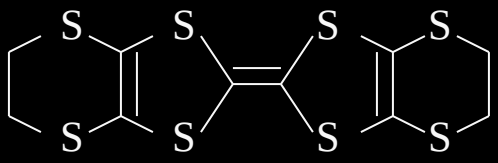
Organic molecules giving (super)conductors



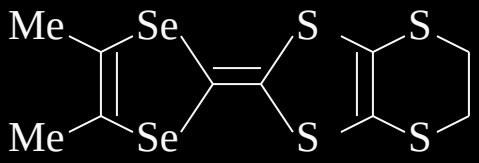
TMTSF



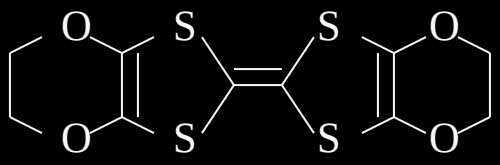
BEDT-TSF (BETS)



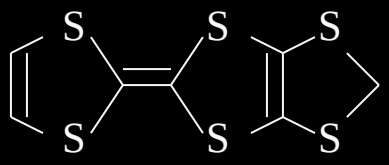
BEDT-TTF (ET)



DMET



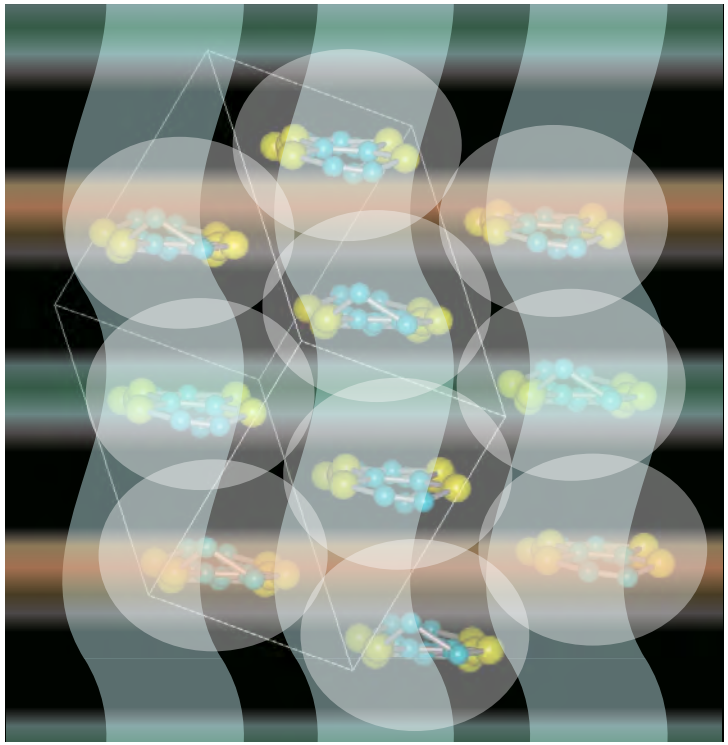
BEDO-TTF (BO)



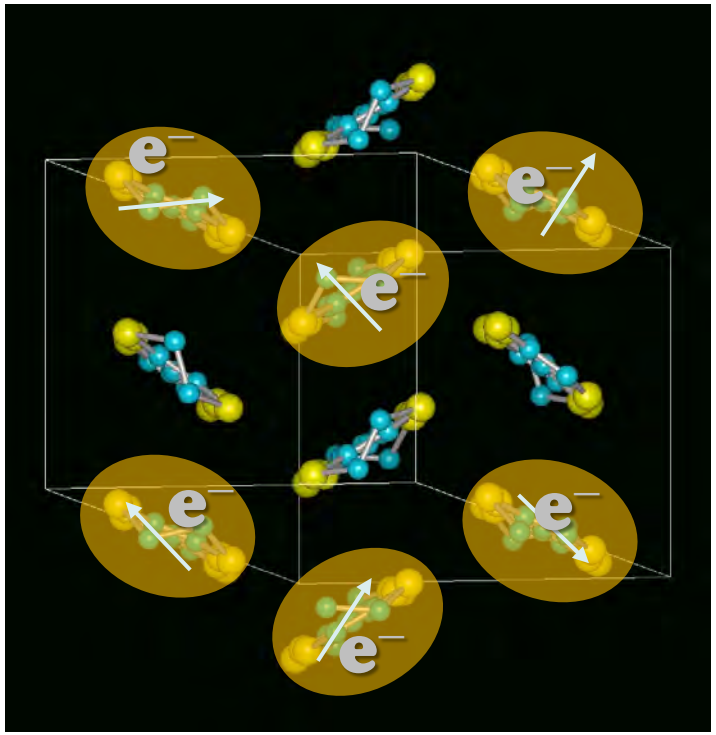
MDT-TTF

Modification of lattice geometry → drastic change in electronic state

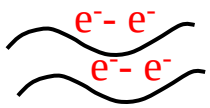
β-type arrangement



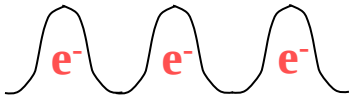
θ-type arrangement



superconductivity



Electronic crystals



Electronic structure

Crystal structure is complicated in real space,
but
electronic structure is surprisingly simple in *k-space !*

Molecular orbital is a minimum entity for electrons

No need to get back to atomic orbitals
if you work in a low energy scale

atomic orbital → **molecular orbital** → electronic band

Key concept

1) The simplest non-degenarate case; hydrogen molecule

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b} + \frac{e^2}{4\pi\varepsilon_0 R}$$

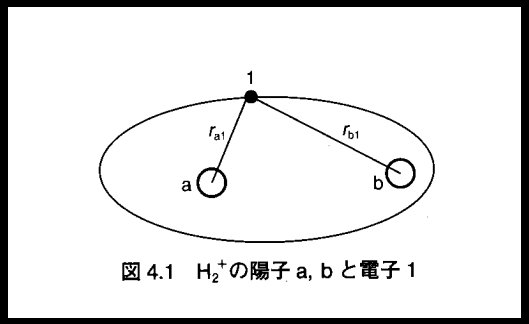


図 4.1　H_2^+の陽子 a, b と電子 1

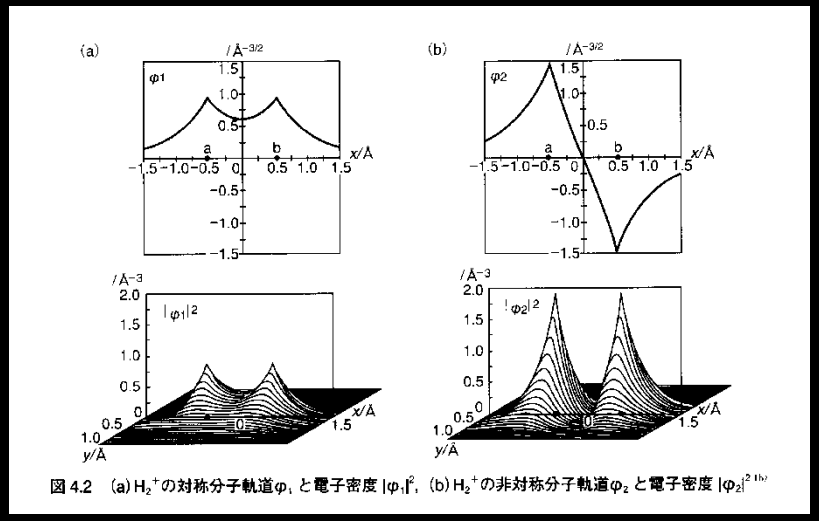
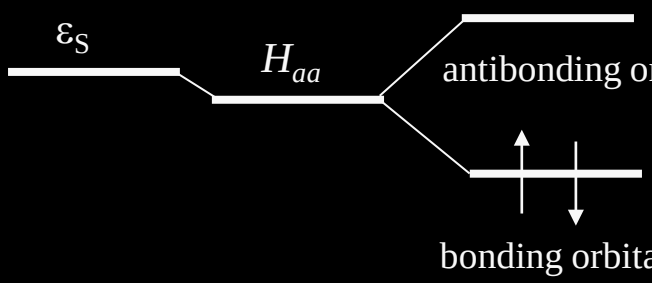


図 4.2　(a) H_2^+の対称分子軌道φ_1と電子密度 $|\varphi_1|^2$, (b) H_2^+の非対称分子軌道φ_2と電子密度 $|\varphi_2|^2$

Molecular orbital = linear combination of atomic orbitals

$$\varphi = c_a\phi_a + c_b\phi_b$$



$$\varepsilon_2 = \frac{H_{aa} - H_{ab}}{1 - S} \qquad \varphi_2 = \frac{1}{\sqrt{2(1-S)}}(\phi_a - \phi_b)$$

$$\varepsilon_1 = \frac{H_{aa} + H_{ab}}{1 + S} \qquad \varphi_1 = \frac{1}{\sqrt{2(1+S)}}(\phi_a + \phi_b)$$

$$S = \int \phi_a^* \phi_b d\tau$$

Overlapping integral

$$H_{aa} = \int \phi_a^* H \phi_a d\tau$$

$$H_{ab} = \int \phi_b^* H \phi_a d\tau$$

Transfer integral

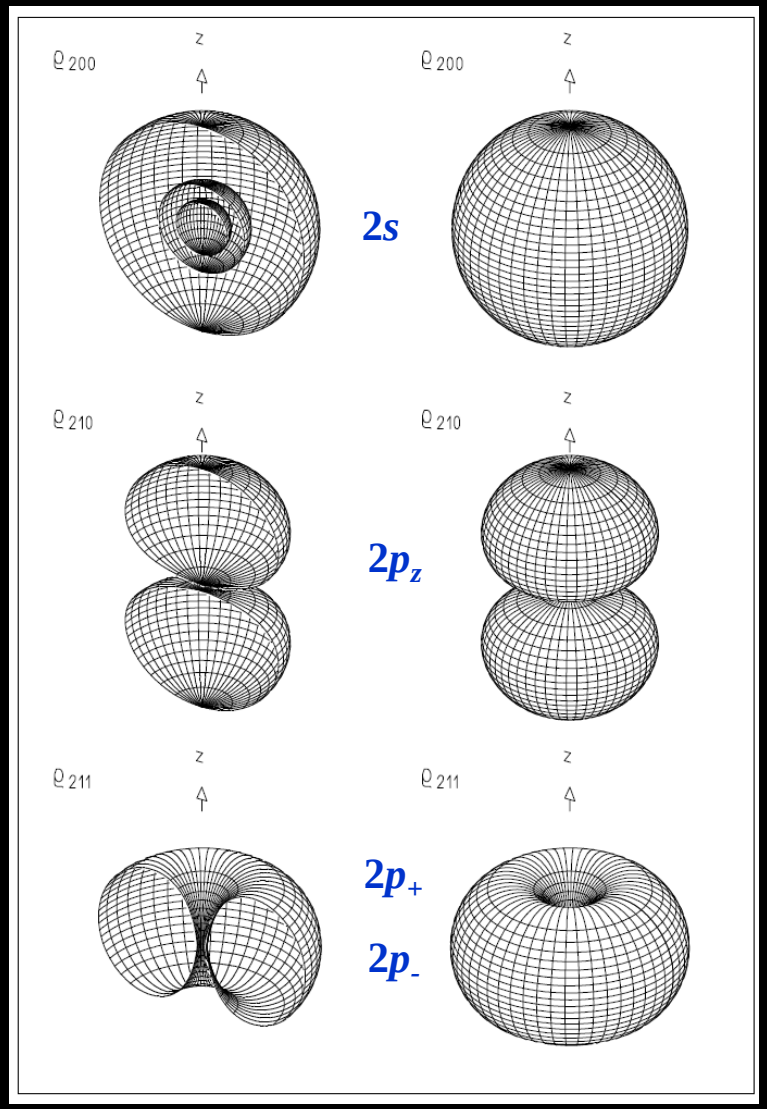
2) degenarate case: carbon atom

$\phi_{lmn} = R_{nl}(r)Y_{lm}(\vartheta,\varphi)$ For n=2, four orbitals (2s, 2p × 3) are degenarate.

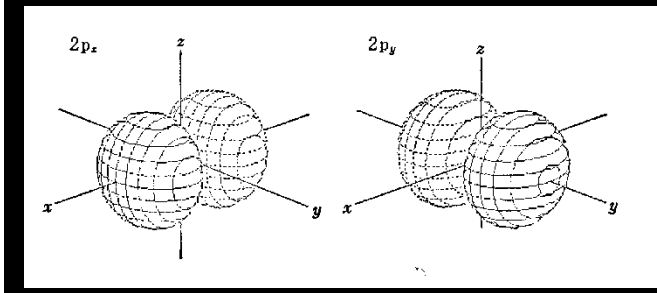
$Y_{00}(\vartheta,\phi)$

$Y_{10}(\vartheta,\phi)$

$Y_{11}(\vartheta,\phi)$
$Y_{1-1}(\vartheta,\phi)$



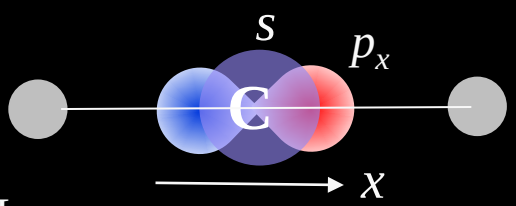
$2p_x$ $2p_y$



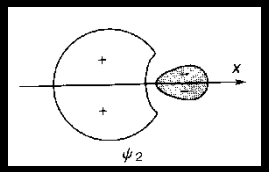
3 steps in making a molecular orbital from atomic orbitals

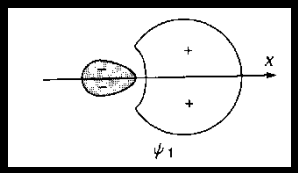
- 1st step: intra-atomic hybridization
  reconstruct orbitals to fit to symmetry of coordination
- 2nd step: inter-atomic hybridization → Chemical bond
  reconstruct orbitals between neighbors like hydrogen molecule)
- 3rd step: construct the overall molecular orbitals

i) Uniaxial 2-way coordination; ***sp* hybridization**

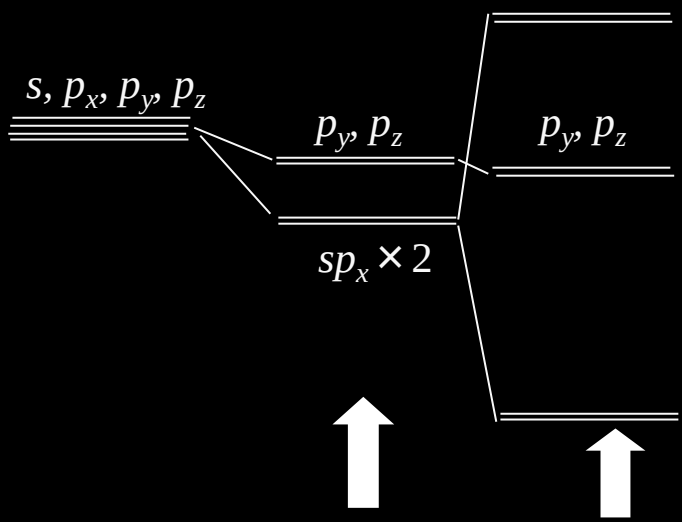


H-C≡C-H
Acetylene



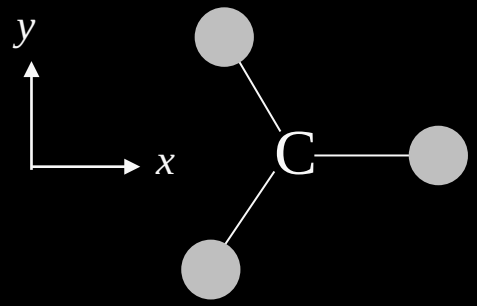


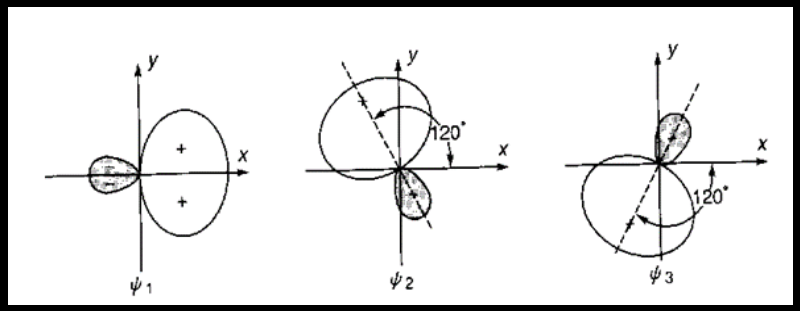
$$sp_x = \frac{1}{\sqrt{2}}(s \pm p_x)$$

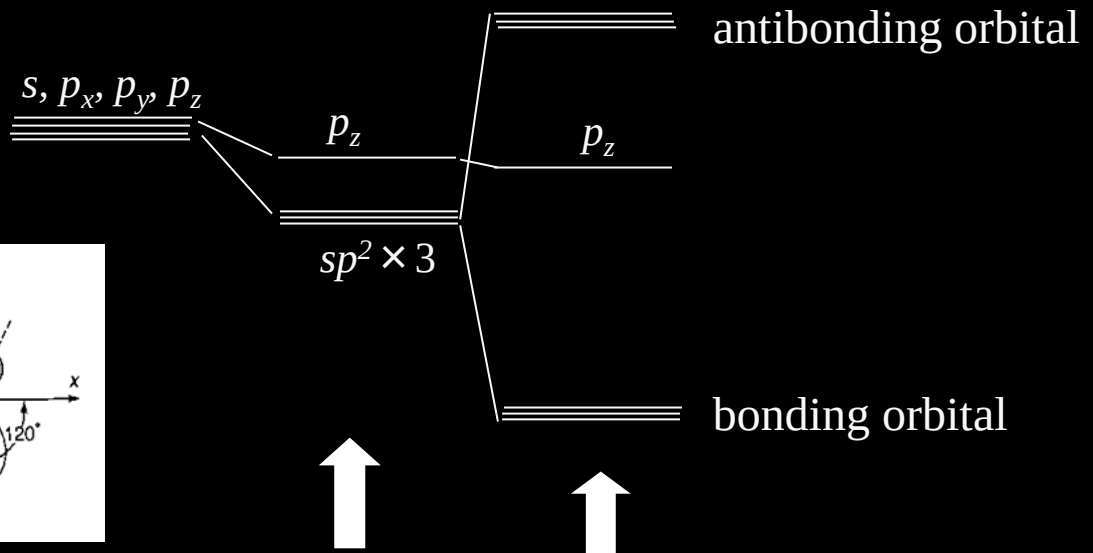


ii) Planar 3-way coordination; sp^2 hybridization

Benzene, graphene





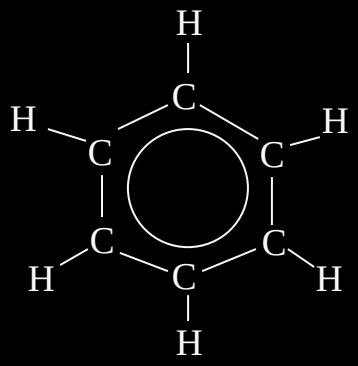


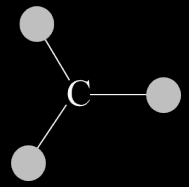
$$sp^2 = \frac{1}{\sqrt{3}}(s + \sqrt{2}p_x)$$

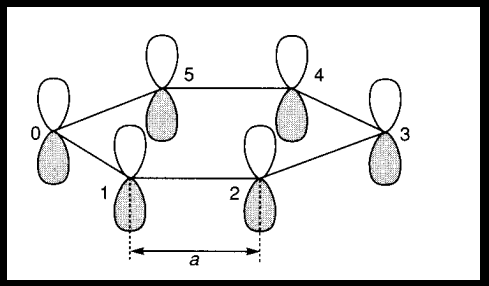
$$\frac{1}{\sqrt{6}}(\sqrt{2}s - p_x + \sqrt{3}p_y)$$

$$, \frac{1}{\sqrt{6}}(\sqrt{2}s - p_x - \sqrt{3}p_y)$$

3rd step: constructing molecular orbital; the case of benzene C_6H_6 (sp^2 and p_z)







intra-atomic hybridization

inter-atomic hybridization

1st step

2nd step

Molecular orbital

3rd step

sp^2 antibonding

s, p_x, p_y, p_z

p_z

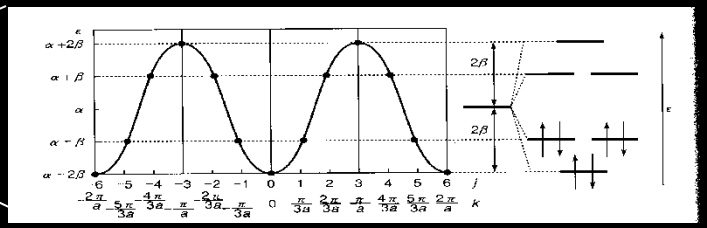
p_z

$sp^2 \times 3$

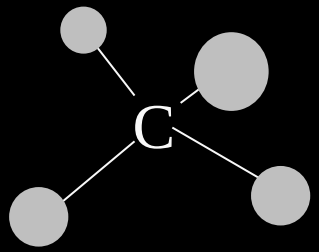
sp^2 bonding

π orbital

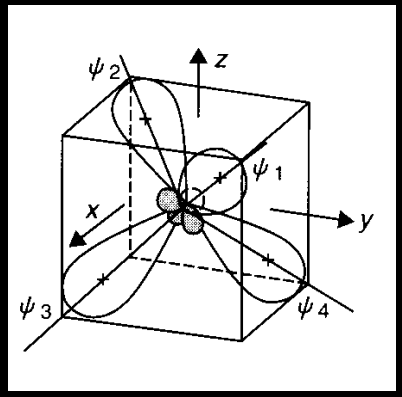
σ orbital

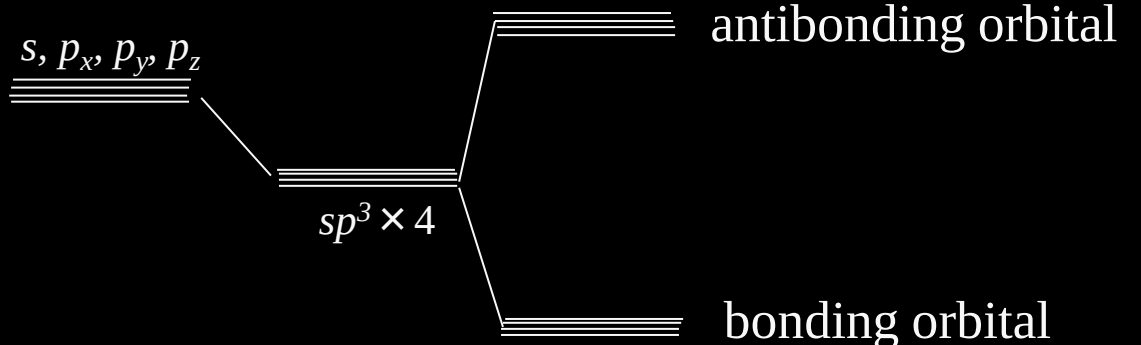


iii) Tetrahedral 4-way coordination; sp^3 hybridization



methane, diamond



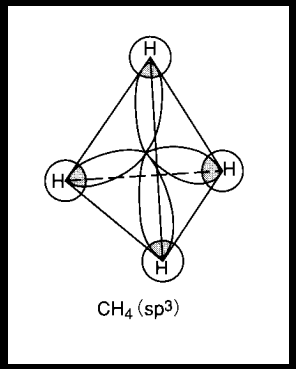


$$sp^3 = \frac{1}{2}(s + p_x + p_y + p_z)$$
$$\frac{1}{2}(s + p_x - p_y - p_z)$$
$$\frac{1}{2}(s - p_x - p_y + p_z)$$
$$\frac{1}{2}(s - p_x + p_y - p_z)$$

intra-atomic hybridization — **1st step**

inter-atomic hybridization — **2nd step**

3rd step: constructing molecular orbital; the case of methane $\mathbf{CH_4}$ (sp^3)



antibonding orbital

s, p_x, p_y, p_z

$sp^3 \times 4$

bonding orbital

1st step

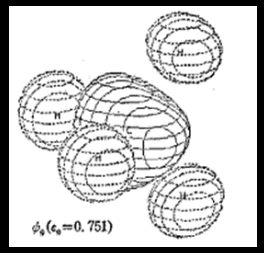
intra-atomic hybridization

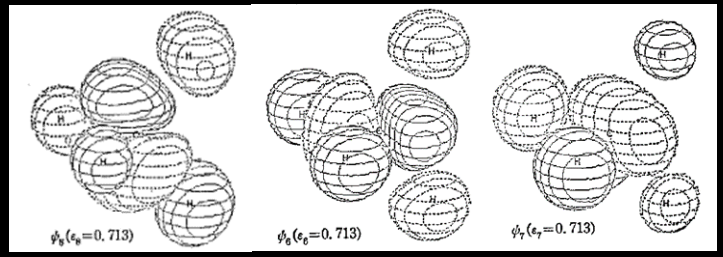
2nd step

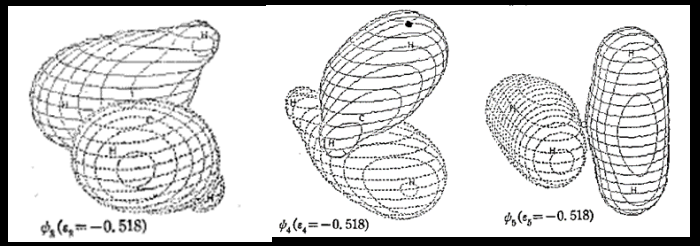
inter-atomic hybridization

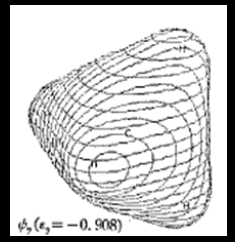
3rd step

Molecular orbital

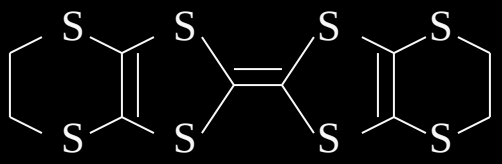




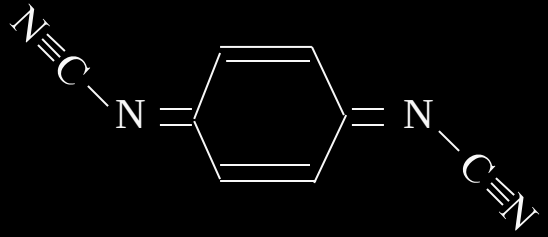




Molecular orbital in molecular conductors



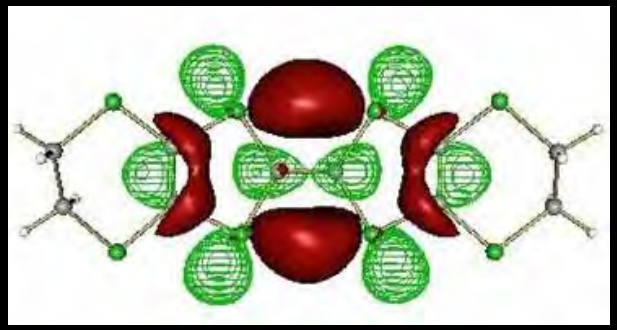
BEDT-TTF (ET)

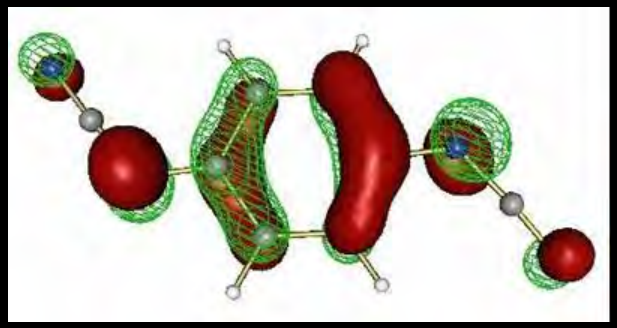


DCNQI

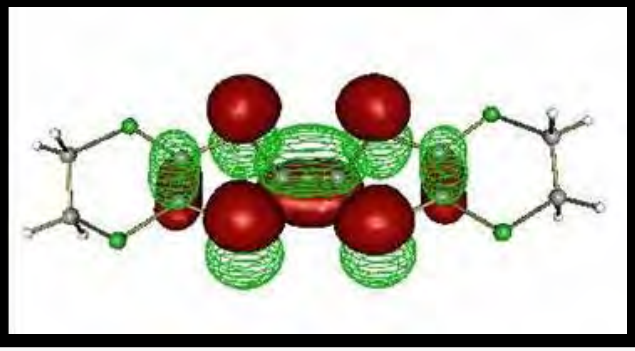
ε

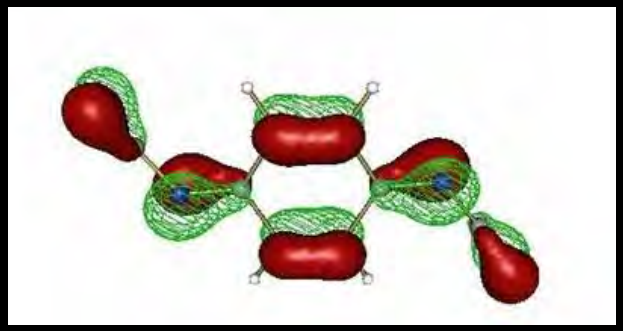
Lowest Unoccupied Molecular Orbital (LUMO)





Highest Occupied Molecular Orbital (HOMO)



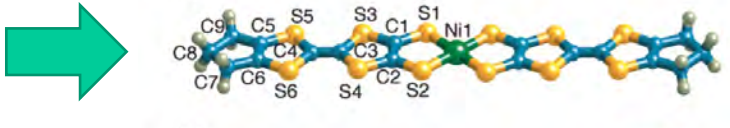


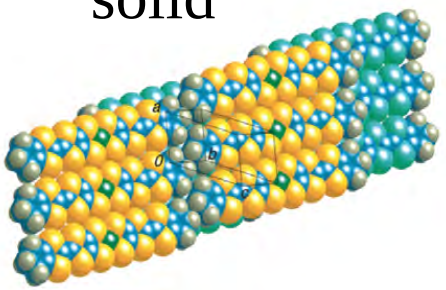
By Imamura and Tanimura

molecular orbitals (MOs)→ formation of electronic band

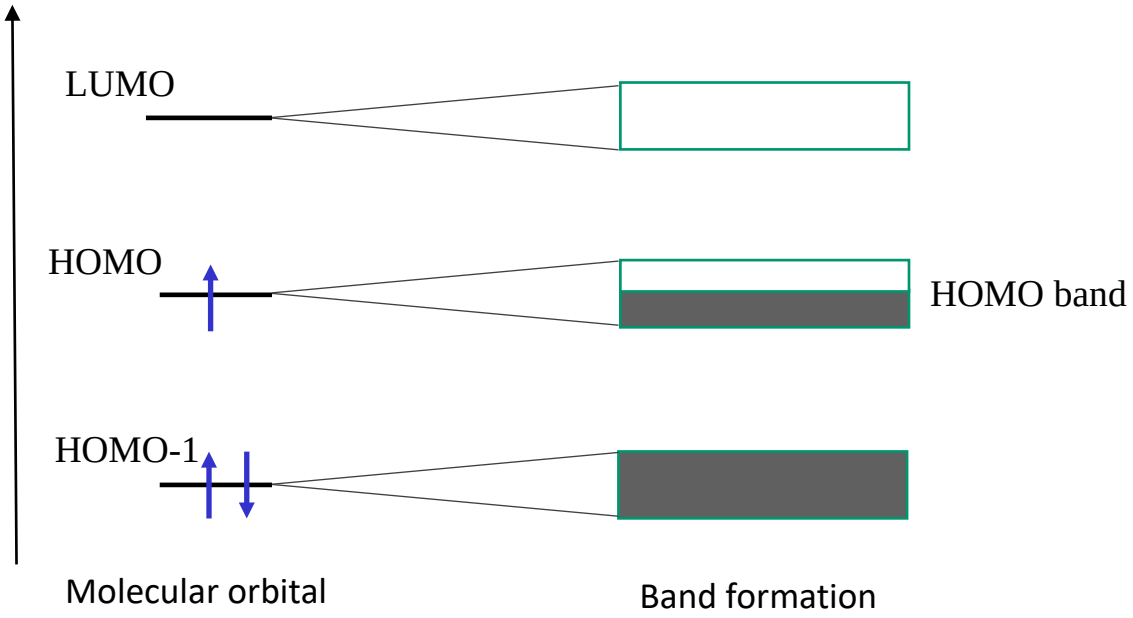
complex in real space, but ***simple band structure***

atom molecule solid



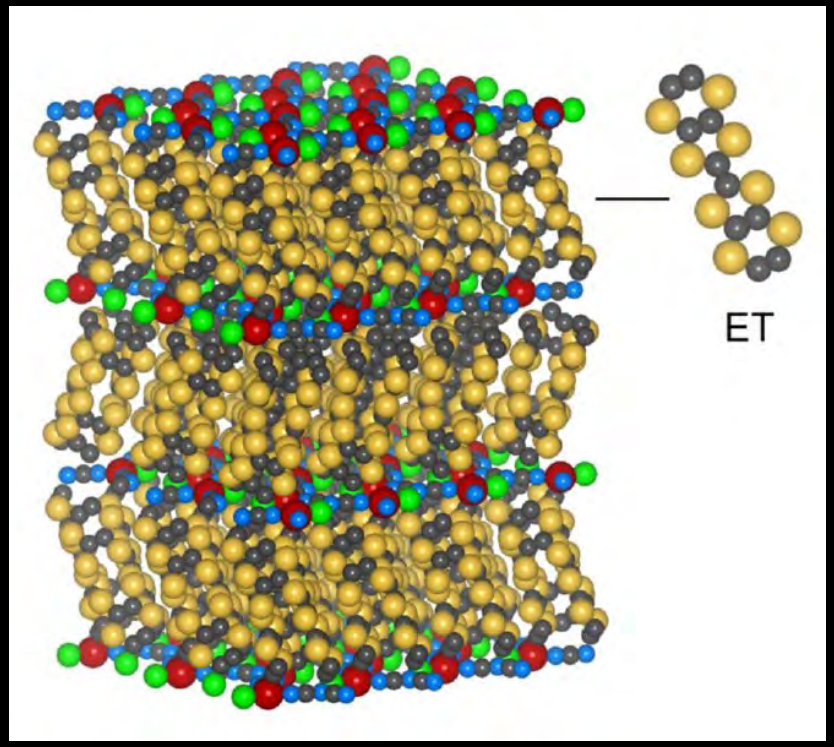


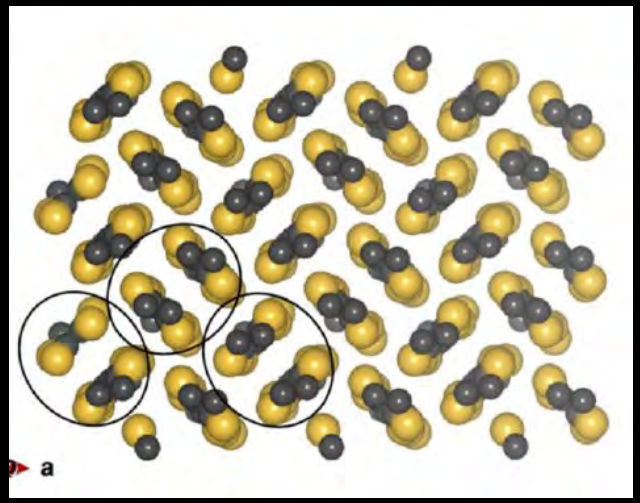
Only one or two MO(s) is responsible for conduction band!



Two methods for band-structure calculations

1) MO calculations + tight binding approx.
2) First-principles calculations

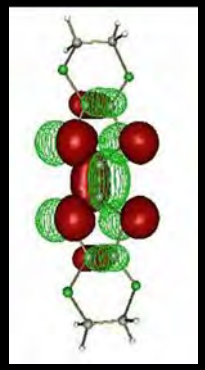




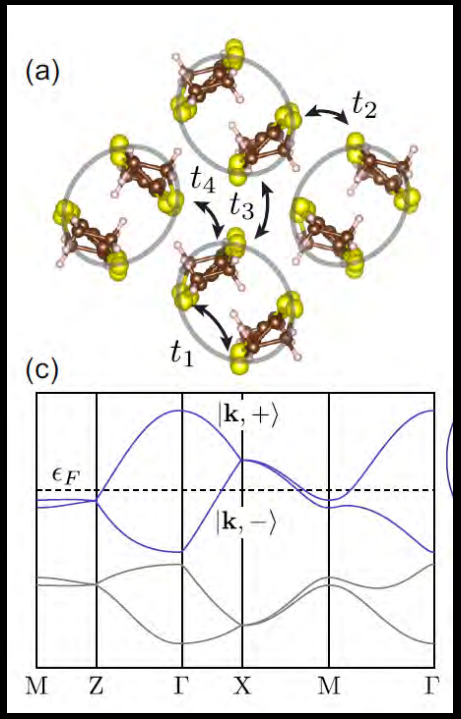
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

Band-structure calculations I; π electronic system κ-$(ET)_2Cu_2(CN)_3$

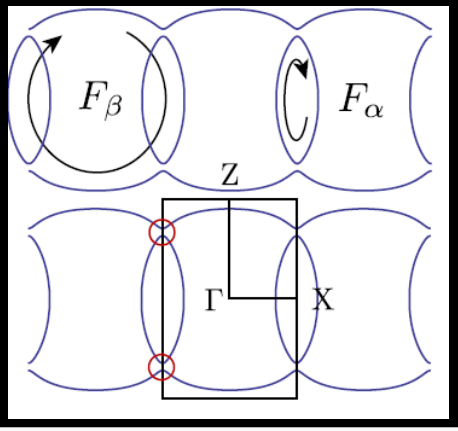
HOMO＋tight-binding approx.



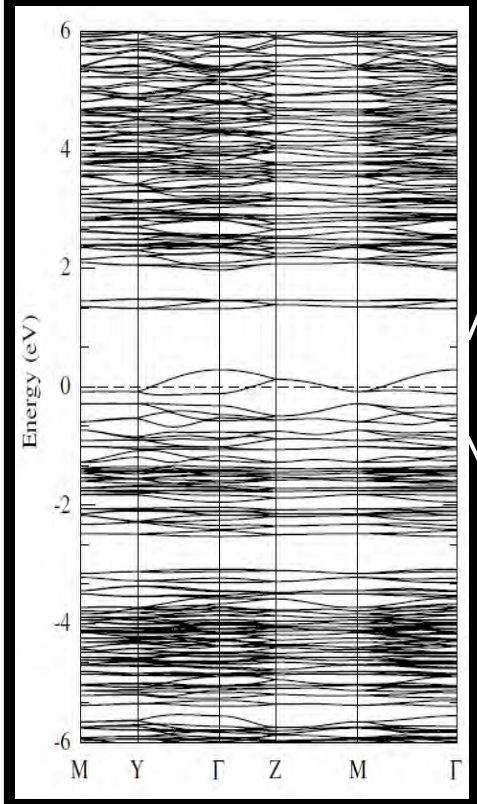
dispersion

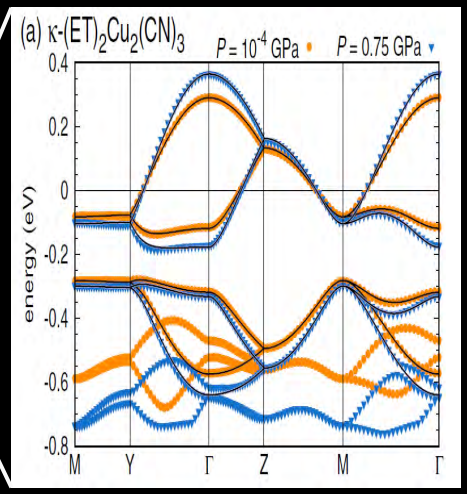


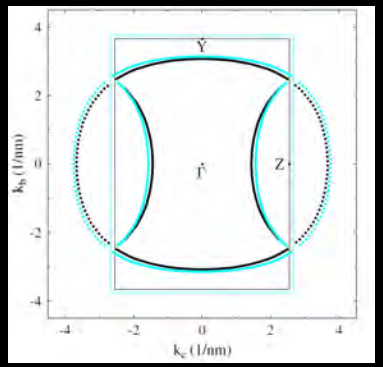
Fermi surface



First-principles calculations



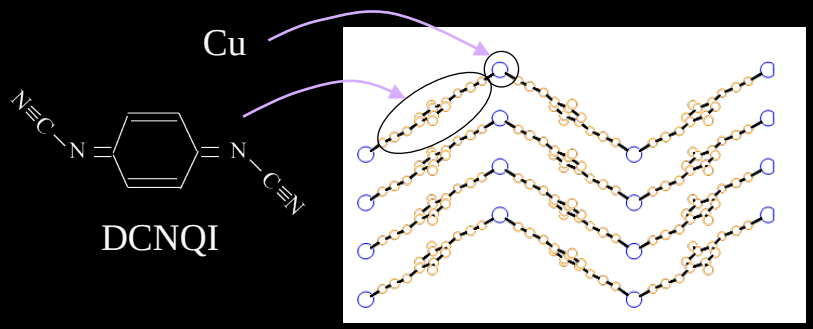


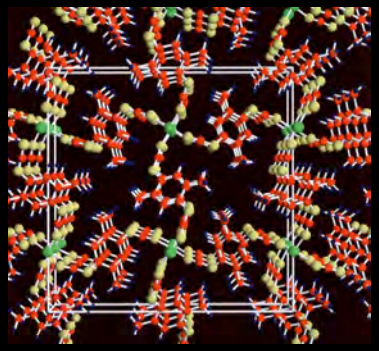


Kandpal *et al.*, *PRL 103, 067004 (2019)*

Winter *et al.*, *PRB 95, 060404(R) (2017)*

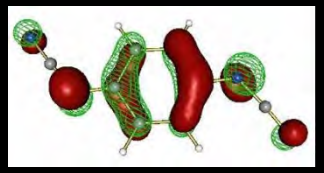
Band-structure calculations II; π-d electronic system **(DMe-DCNQI)$_2$Cu**



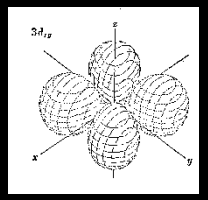


Tight-binding calc. of LUMO and d_{xy}

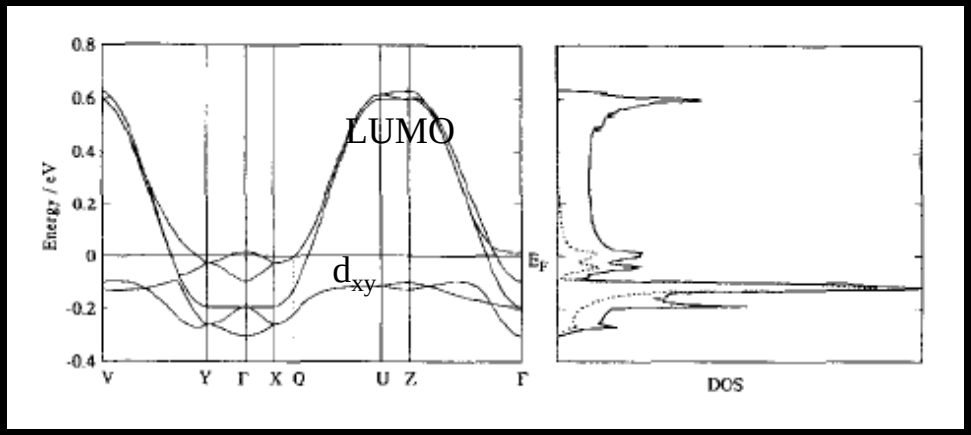
DCNQI LUMO



Cu d_{xy}

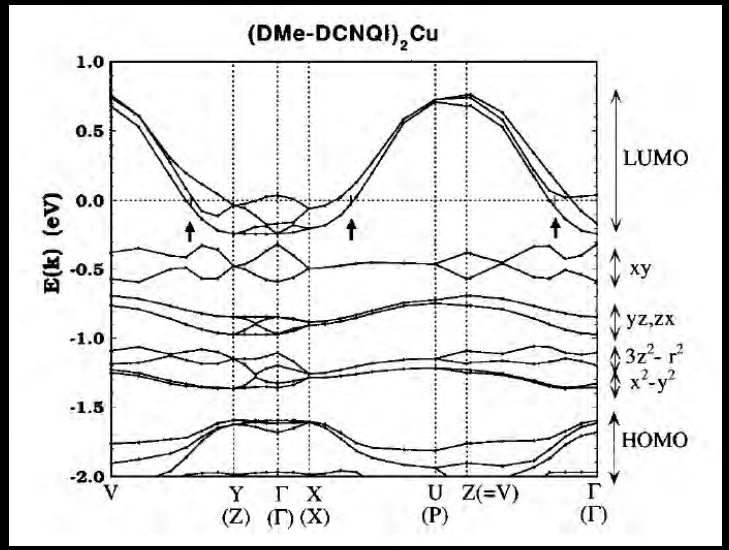


R. Kato et al.,



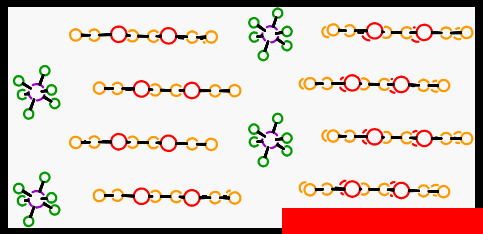
First-principles calculations

Miyazaki & Terakura,

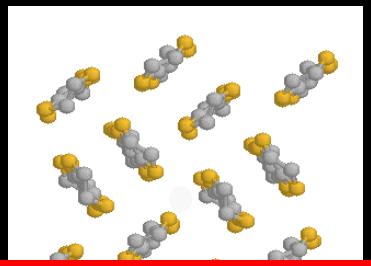


Verious kinds of Fermi surfaces → metals expected, but…….

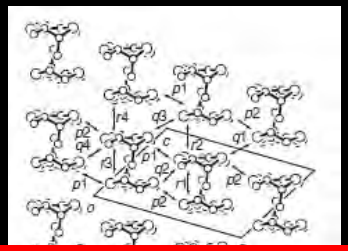
Quasi 1D 1/4-filled
$(TMTSF)_2X$



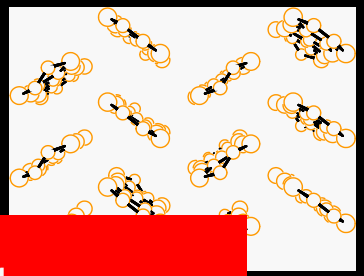
Quasi 2D 1/2-filled
κ-$(ET)_2X$



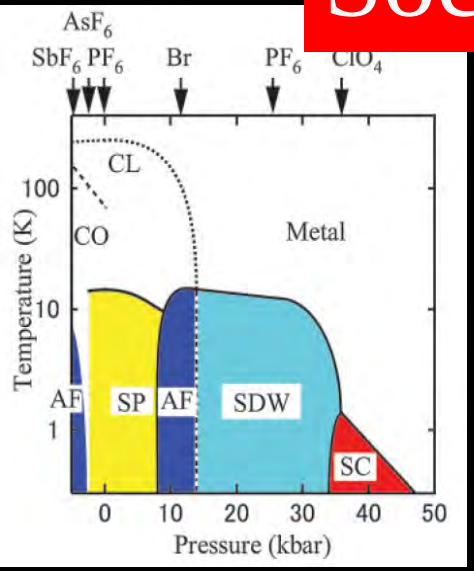
Quasi 2D ¼-filled
β-(*meso*, DMeET)$_2PF_6$

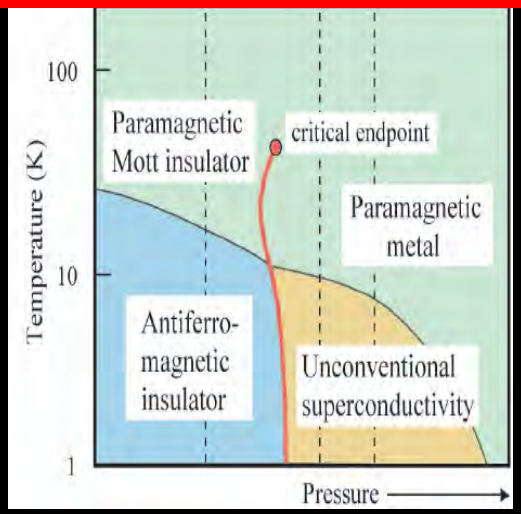


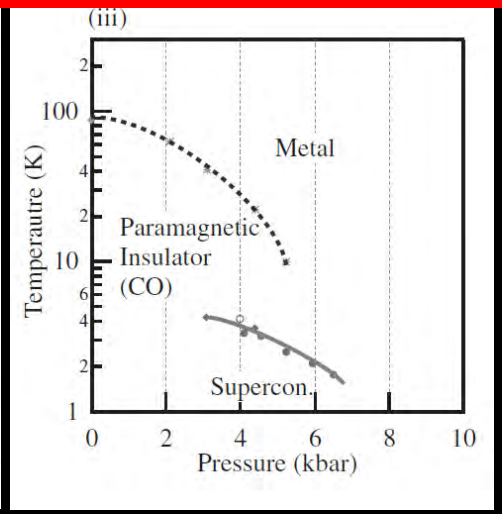
Quasi 2D ¼-filled
α-$(ET)_2X$

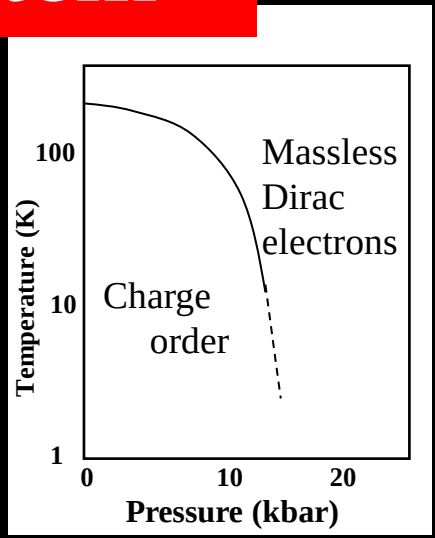


Sociology of electronic system









SDW/SC
Nesting

Mott/SC
On-site repulsion

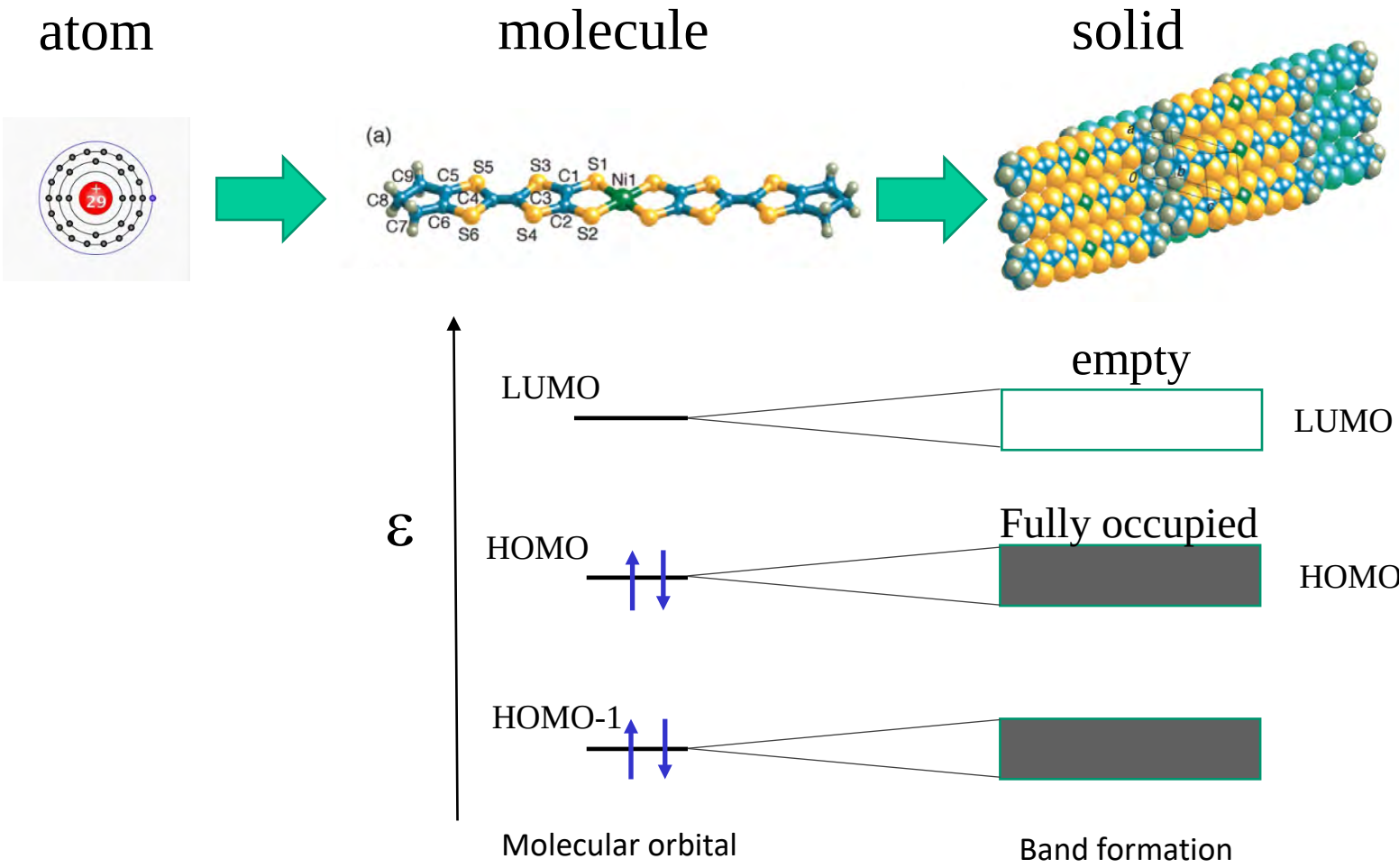
CO/SC
Inter-site repulsion

CO/DE
Inter-site repulsion

Fermi surface instability

Peierls instability

Most organic materials are insulators

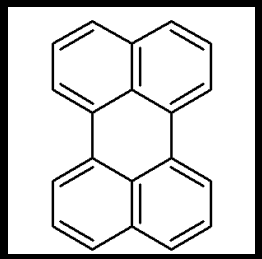


The dawn of organic conductors

Nature 173 (1954) 168

In the past, it was taken for granted that organics are insulators.

It is because conduction band is fully occupaied.



Perylene solid exposed to Br atmosphere

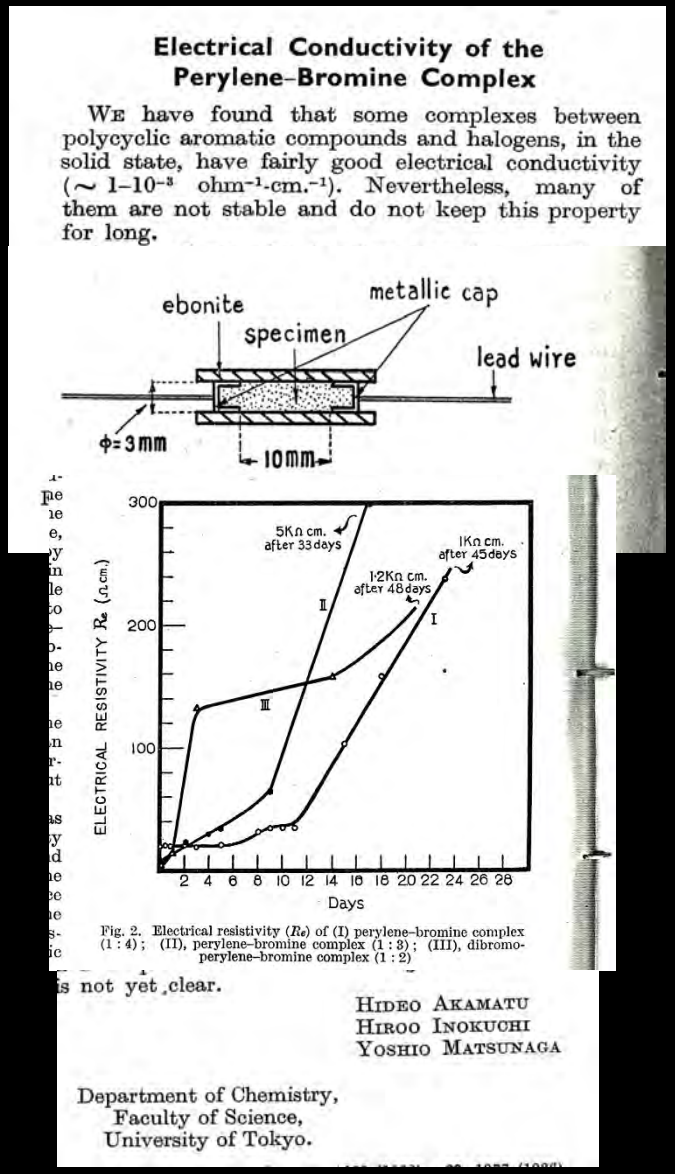
⇩

Getting highly conductive

Absorbed Br atoms extract electrons from Perylene

複合系　　A^+-B^-

Two-component systems



Electrical Conductivity of the Perylene–Bromine Complex

We have found that some complexes between polycyclic aromatic compounds and halogens, in the solid state, have fairly good electrical conductivity (~ 1–10^{-3} ohm^{-1}·cm.$^{-1}$). Nevertheless, many of them are not stable and do not keep this property for long.

Fig. 2. Electrical resistivity (R_e) of (I) perylene–bromine complex (1 : 4); (II), perylene–bromine complex (1 : 3); (III), dibromo-perylene–bromine complex (1 : 2)

…s not yet clear.

Hideo Akamatu
Hiroo Inokuchi
Yoshio Matsunaga

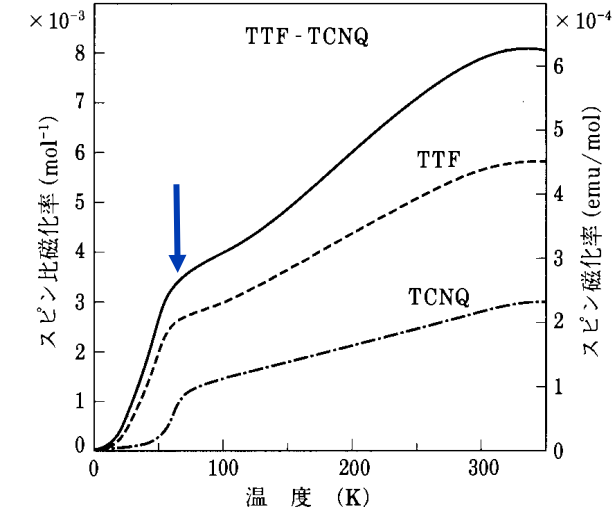
Department of Chemistry,
Faculty of Science,
University of Tokyo.

TTF-TCNQ --- epoch-making organic conductor

Coleman et al., Solid Stae Commun. 12, 1125 (1973)

Highly conductive σ_b(R.T.)=400 $(\Omega cm)^{-1}$
but
A metal-insulator transition at 58 K.

Low-T insulator is nonmagnetic.



6－7図 TTF - TCNQ のスピン磁化率 [9,10]

Conductivity
maximum at 58K

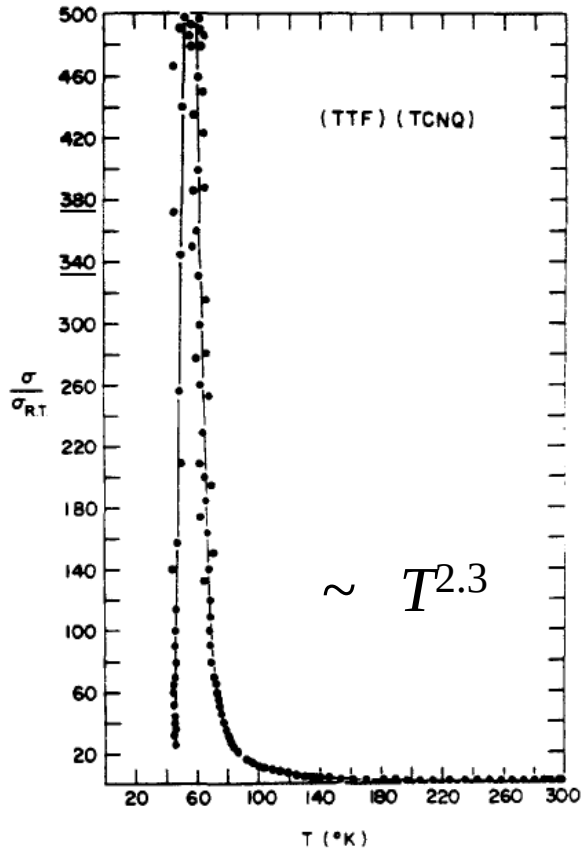


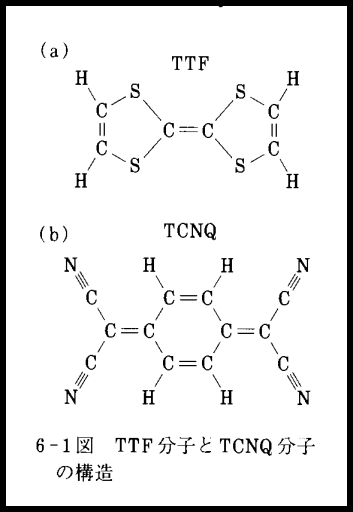
FIG. 1. Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal.

Organic conductor TTF-TCNQ

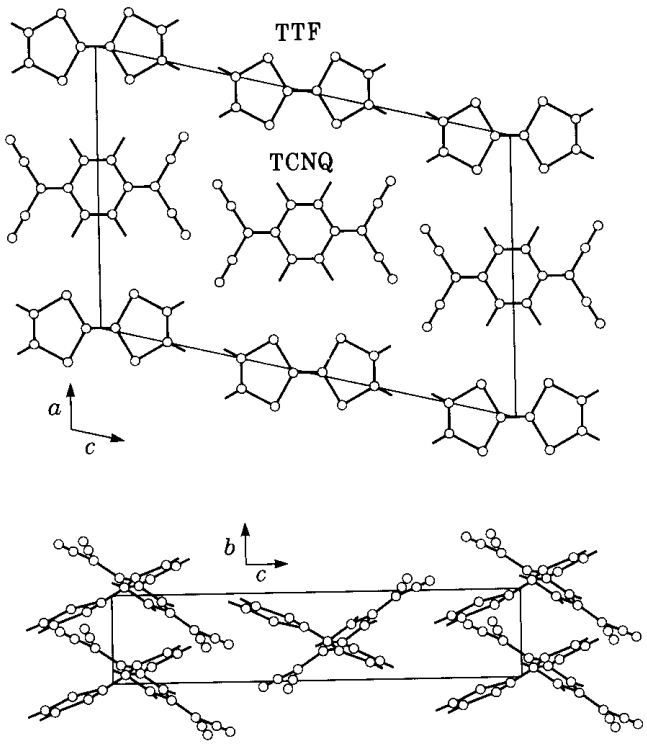
Two kinds of one-dimensional chains
（TTF column ＆ TCNQ column）

Highly one-dimensional

$\sigma_b/\sigma_a \sim 500$
$\sigma_b/\sigma_c \sim 120$

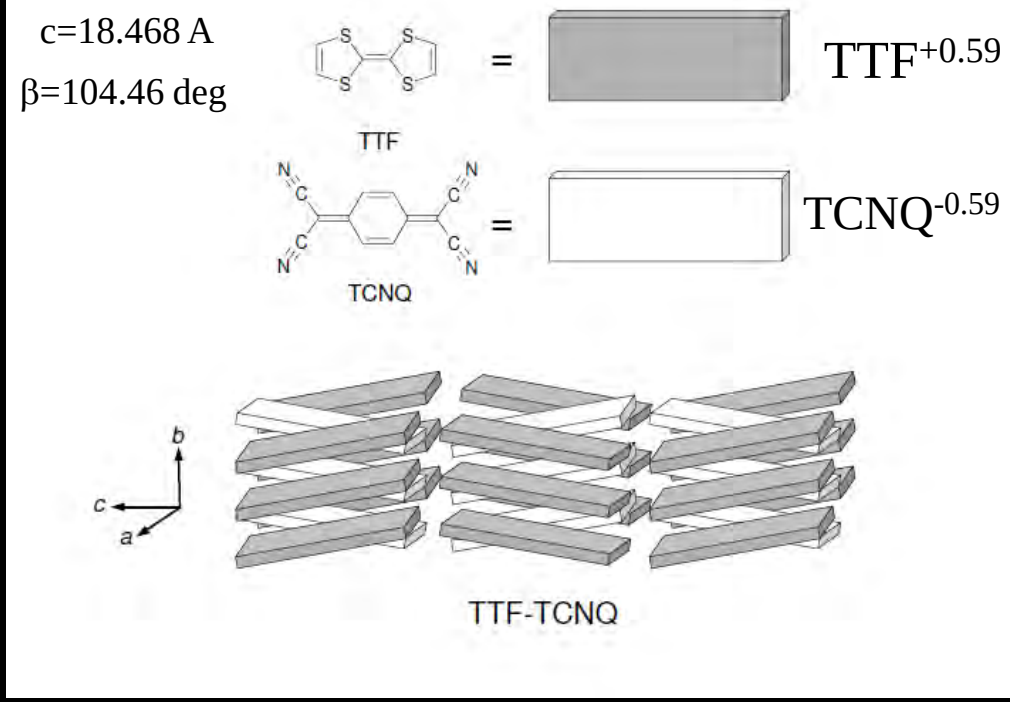


6－1図　TTF分子とTCNQ分子の構造



6－2図　TTF－TCNQ結晶の構造[1)]

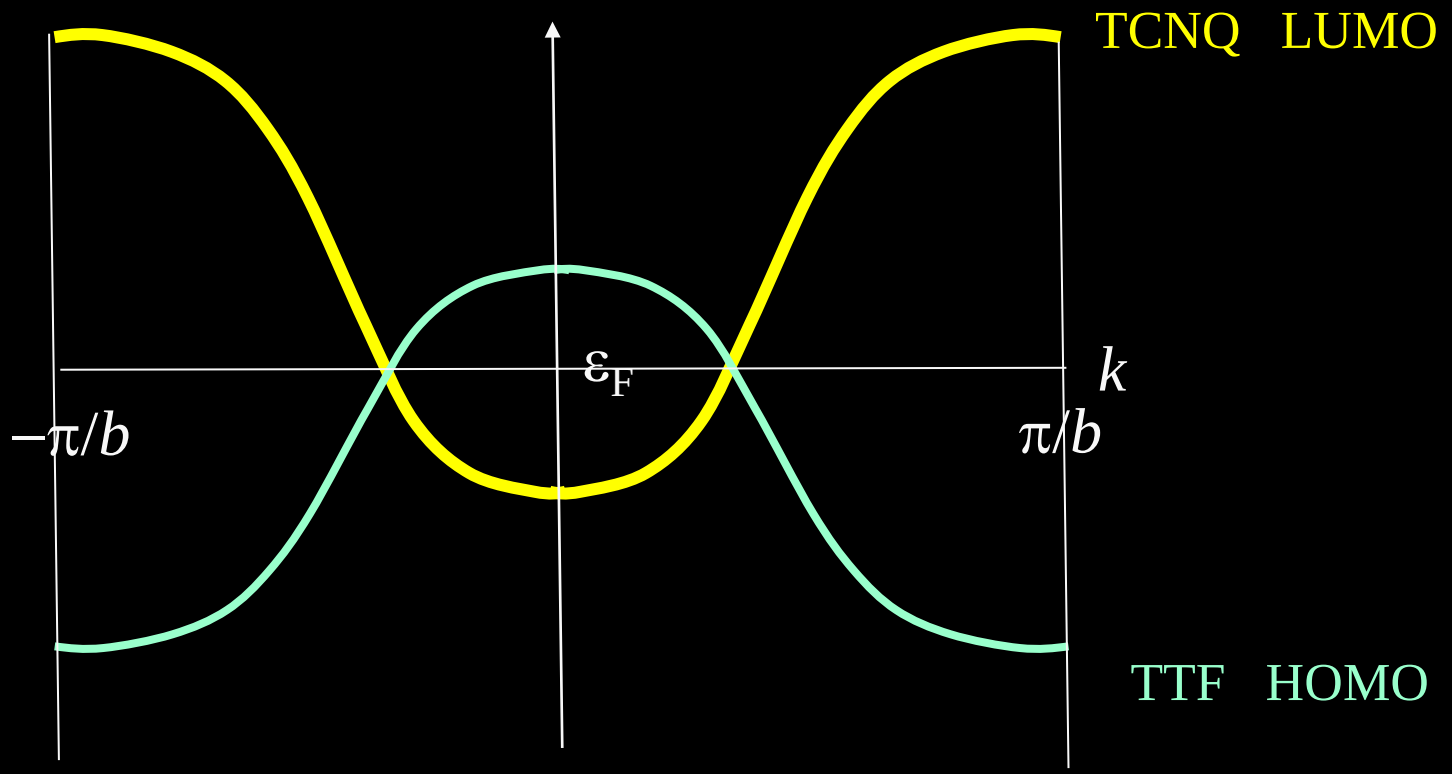
a=12.298 A
b= 3.819 A
c=18.468 A
β=104.46 deg



Two one-dimensional bands in TTF columns and TCNQ columns

Charge transfer from TTF to TCNQ

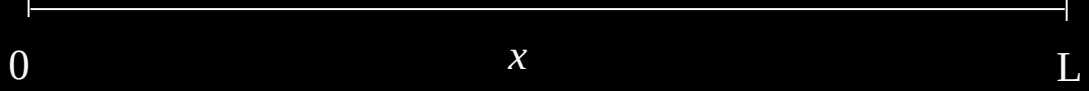
$TTF^{+0.59}$-$TCNQ^{-0.59}$



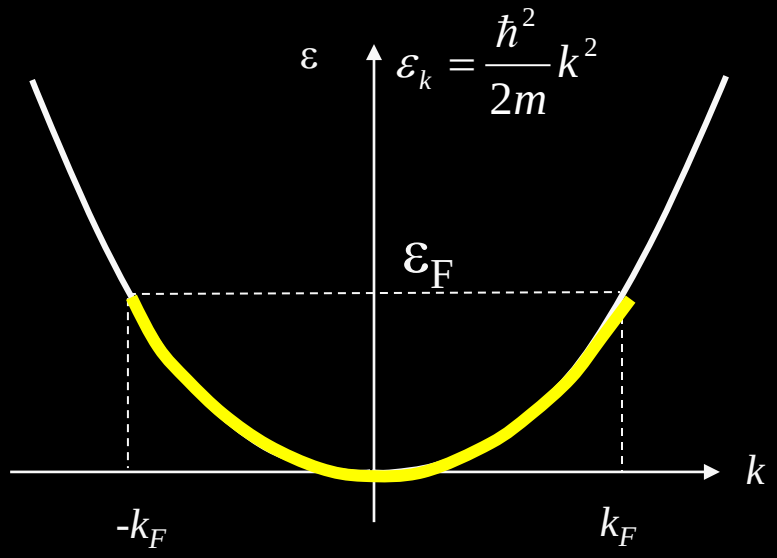
Why insulating at low temperatures ?

Free electrons in one dimension

$$-\frac{\hbar^2}{2m}\frac{\partial^2\varphi}{\partial x^2} = \varepsilon\varphi$$



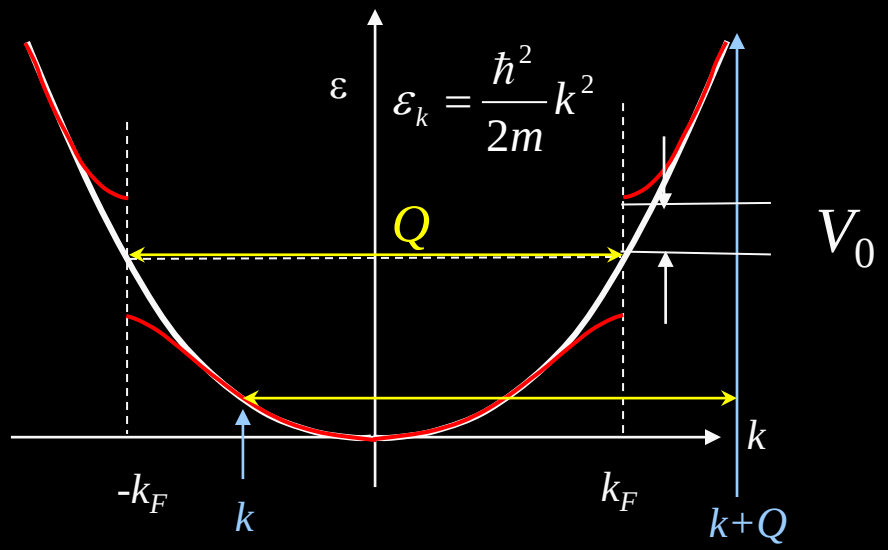
$$\varphi(x) = \frac{1}{\sqrt{L}}e^{ikx} \qquad k = \frac{2\pi}{L}\nu \quad (\nu;\ \text{integer})$$



N electrons in *L* $\qquad \dfrac{2k_F}{(2\pi/L)} \times 2 = N \qquad k_F = \dfrac{\pi}{2}\left(\dfrac{N}{L}\right) = \dfrac{\pi}{2}n$

If a periodic potential of $Q=2k_F$ is applied,

$$V(x) = 2V_0 \cos(Qx)$$



only <k | $V(x)$ |$k \pm Q$> is not vanishing

1) In case that ε_k and $\varepsilon_{k\pm Q}$ are different more than V_0, the energy correction is of 2nd order.

2) In case of $\varepsilon_k \sim \varepsilon_{k+nQ}$ (degenarate), the energy correction is of 1nd order.

$$\tilde{\varepsilon}_k = \frac{1}{2}\left\{(\varepsilon_k + \varepsilon_{k-Q}) \pm \sqrt{(\varepsilon_k - \varepsilon_{k-Q})^2 + 4V_0^2}\right\} \qquad \varepsilon_k = \frac{\hbar^2}{2m}k^2 \qquad \varepsilon_{k-Q} = \frac{\hbar^2}{2m}(k-Q)^2$$

Electronic energy gain by the periodic potential

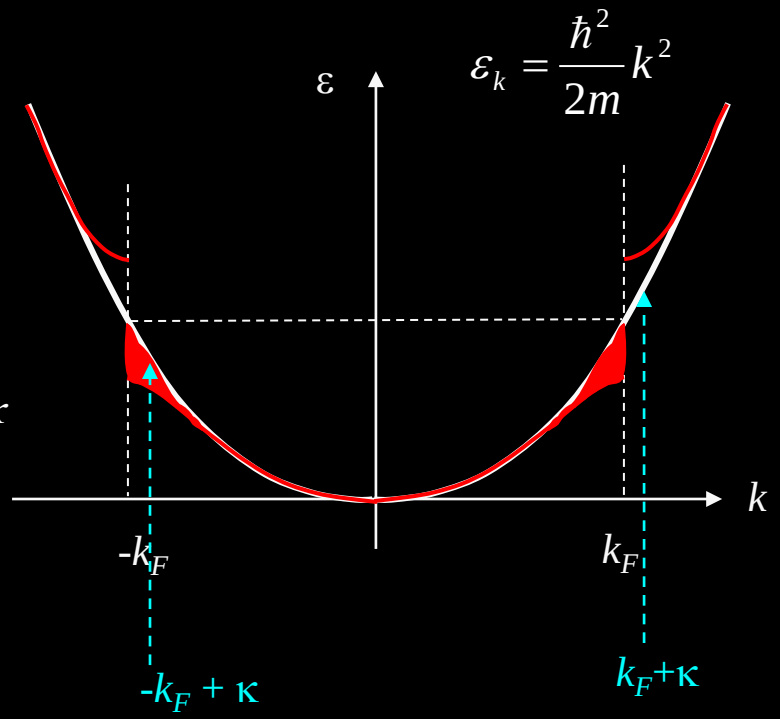
linear approximation of dispersion around k_F

In the vicinity of $k \sim k_F$

$$\varepsilon = \varepsilon_F + \frac{\hbar^2}{2m}(k^2 - k_F^2) = \varepsilon_F + \frac{\hbar^2}{m} k_F \kappa = \varepsilon_F + \hbar v_F \kappa$$

In the vicinity of $k \sim -k_F$

$$\varepsilon = \varepsilon_F + \frac{\hbar^2}{2m}(k^2 - k_F^2) = \varepsilon_F - \frac{\hbar^2}{m} k_F \kappa = \varepsilon_F - \hbar v_F \kappa$$



Thus,

$$\tilde{\varepsilon}_k = \varepsilon_F - \frac{1}{2}\sqrt{(2\hbar v_F \kappa)^2 + 4V_0^2}$$
$$= \varepsilon_F - \sqrt{(\hbar v_F \kappa)^2 + V_0^2}$$

The electronic energy gain is obtained by an integration

$$\Delta E_{el} = \sum_{\sigma, -k_F < k < k_F} (\tilde{\varepsilon}_k - \varepsilon_k) = 4 \frac{1}{(2\pi/L)} \int_0^{k_F} (\tilde{\varepsilon}_k - \varepsilon_k) dk = \frac{2L}{\pi} \int_0^{k_F} \left[(\varepsilon_F - \sqrt{(\hbar v_F \kappa)^2 + V_0^2}) - (\varepsilon_F + \hbar v_F \kappa) \right] dk$$

$$= \frac{2L}{\pi} \int_{-k_c}^{0} \left[-\sqrt{(\hbar v_F \kappa)^2 + V_0^2} - \hbar v_F \kappa \right] d\kappa = \frac{2L}{\pi} \frac{1}{\hbar v_F} \int_{-\varepsilon_c}^{0} \left[-\sqrt{\varepsilon^2 + V_0^2} - \varepsilon \right] d\varepsilon = \frac{2L}{\pi} \frac{1}{\hbar v_F} \int_0^{\varepsilon_c} \left[\varepsilon - \sqrt{\varepsilon^2 + V_0^2} \right] d\varepsilon$$

By integrating it, one gets an energy gain $\Delta E_{el} \cong -\frac{L}{\pi\hbar v_F} V_0^2 \log(\frac{\varepsilon_c}{V_0})$

To produce the periodic potential, Lattice deformation is required.

elastic deformation
$u(x)=u_0\cos(Qx)$ ⇒ Lattice elastic energy $\Delta E_{lat} = Bu_0^2$

Assuming periodic potential is proportional to elastic deformation,

$V(x) = gu(x) \longrightarrow V_0 = gu_0$

Total energy gain by lattice and potential modulations is

$$\Delta E_{el} + \Delta E_{lat} = -Au_0^2 \log(\frac{\varepsilon_c}{gu_0}) + Bu_0^2$$

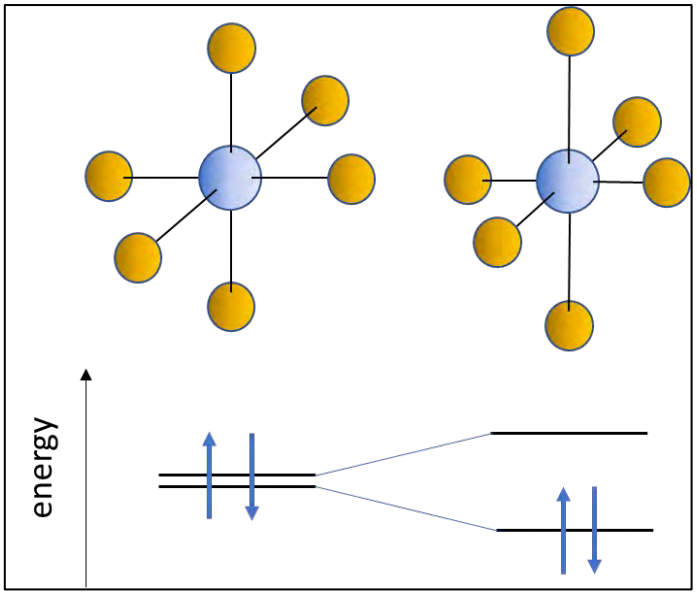
which has a minimum at $u_0 \neq 0$

Thus, lattice is spontaneously deformed to produce a periodic potential of $Q=2k_F$

→ Insulator

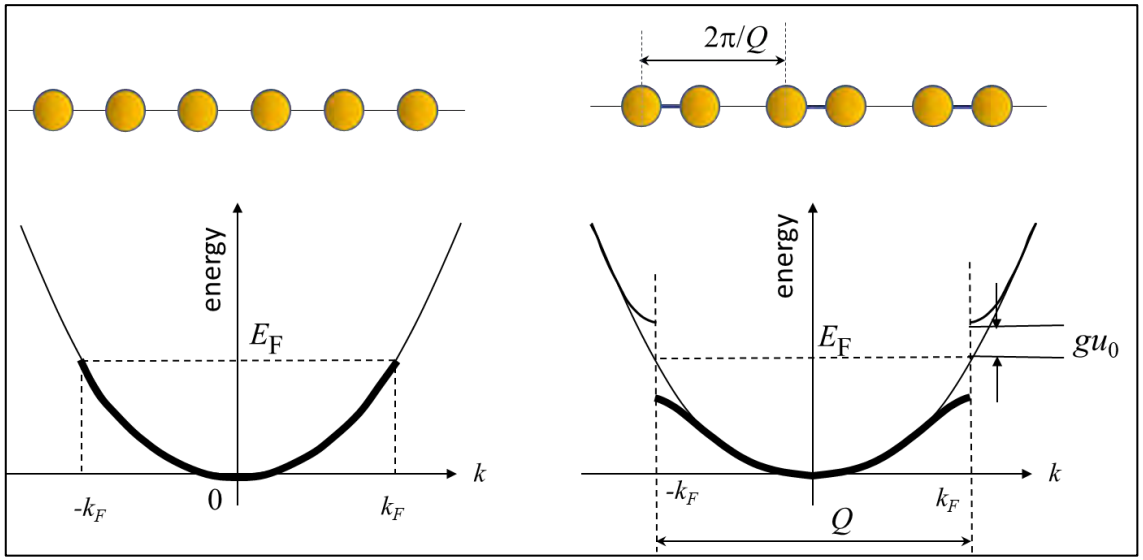
the Peierls transition!

Jahn-teller effect and Peierls transition



Jahn-Teller effect

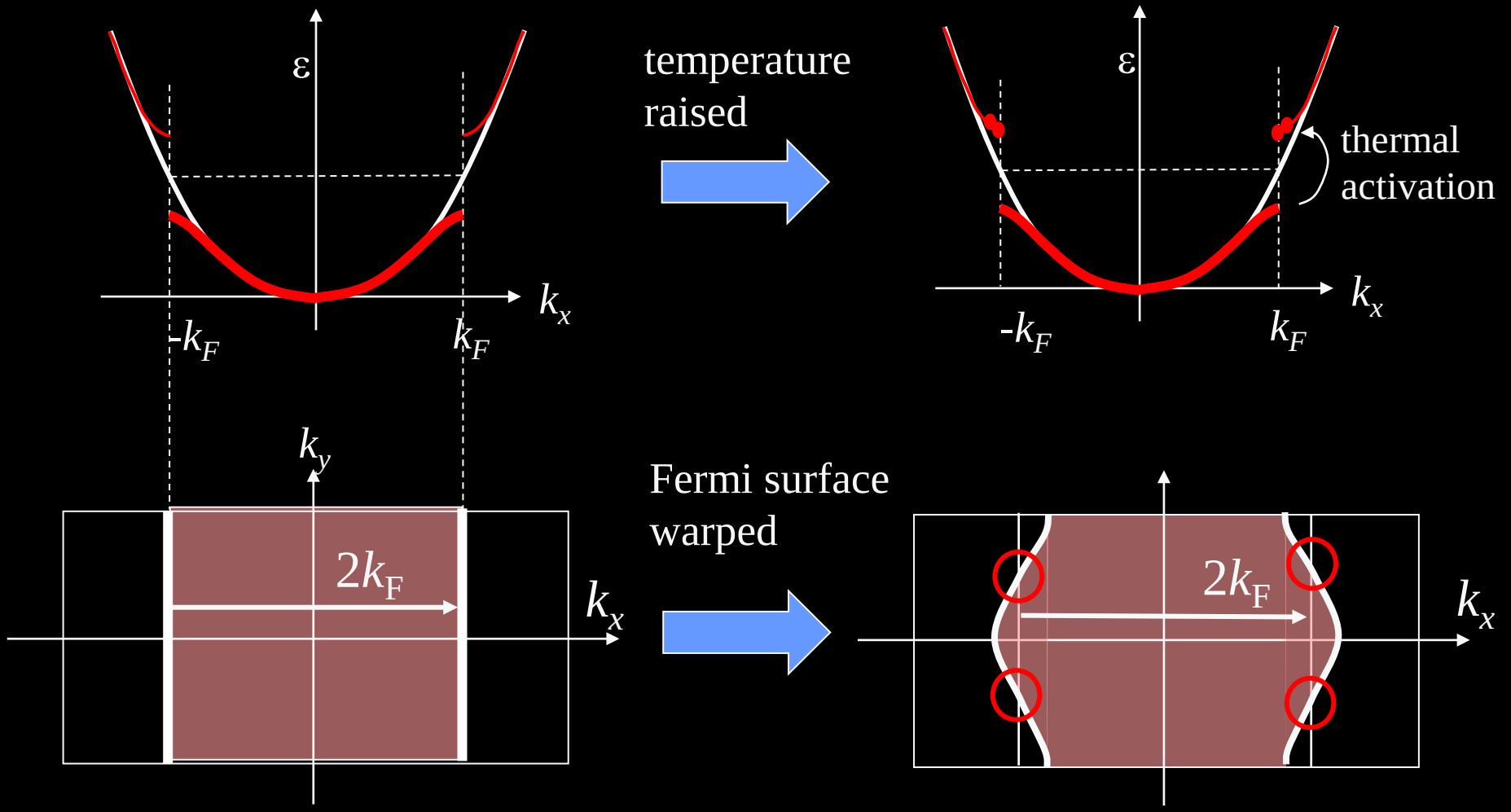
(Finite system)



Peielrls transition

(infinite system)

Peierls insulator is restored to metal when temperature is raised or FS is warped (higher dimensionality)



Whole electrons at FS participate in lowering energy

Only a portion of electrons at FS do that.