

## Electron correlation

Coulomb repulsion in molecular orbital theory

Configuration interaction

Electron correlation in solids

Hubbard model

Stoner model

Mott insulator

Strict solution of Hubbard model

Origin of magnetic interaction  $J$  from the Hubbard model

Charge order: non half-filled case

Hartree-Fock approximation of the Hubbard model

Superexchange interaction

Charge density waves

Kondo effect

Localization in a disordered system

## Electron Correlation (電子相關)

Molecular orbital theory considering inter-electron Coulomb repulsion

$$H = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_n \frac{Z_n e^2}{r_{ni}} \right] + \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{r_{ij}}$$

Sum for electrons

Attraction from nuclei

Inter-electron Coulomb repulsion

For an  $N$ -electron system, in general

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \cdots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \cdots & \varphi_N(N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum \text{P}^{(-1)} \varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)$$

Slater determinant

All permutations for electron numbers

One permutation such as  $1 \leftrightarrow 2$  generates a minus sign.

Exchange  $1 \leftrightarrow 2$  electrons  $\rightarrow$  Columns 1,2 exchange  $\rightarrow$  (Antisymmetric)

The same  $\varphi_1$  and  $\varphi_2$   $\rightarrow$  The same 1, 2 lines  $\rightarrow$   $|\text{Determinant}|=0$

$\rightarrow$  2 electrons (Fermi 粒子) cannot take the same state (Pauli's exclusion principle)

Put the Slater determinant in  $E = \int \Psi^* H \Psi d\tau$  to give

$$E = \sum_k H_k + \sum_{k \neq l} (J_{kl} - K_{kl})$$

$$H_k = \int \varphi_k^* \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \sum_n \frac{Z_n e^2}{r_n} \right] \varphi_k d\tau \quad \text{One-electron part}$$

$$J_{kl} = \int \varphi_k^*(1) \varphi_l^*(2) \left( \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{12}} \right) \varphi_k(1) \varphi_l(2) d\tau$$

Coulomb integral

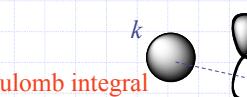
$$= \int \frac{e^2 \rho_k(1) \rho_l(2)}{4\pi\epsilon_0 r_{12}} d\tau > 0$$

Average el-el repulsion between MO  $k$  with electron distribution  $\rho_k$  and MO  $l$

$$K_{kl} = \int \varphi_k^*(1) \varphi_l^*(2) \left( \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{12}} \right) \varphi_k(2) \varphi_l(1) d\tau > 0$$

Exchange integral

Exchange 1 and 2



$$(1) \int \alpha(1) \beta(1) d\tau = 0 \quad \text{so that for opposite spins: } K_{kl} = 0$$

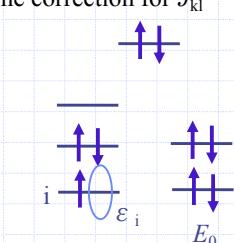
The same spin cannot come to the same place due to the Pauli 排他原理 (Fermi 子). This reduces the Coulomb repulsion. The correction for  $J_{kl}$

$$(2) 2 \text{ electrons in a MO} \quad E = 2H_1 + J_{11}$$

(3) Remove one electron from the  $i$ -th MO.

$$E = E_0 - \underbrace{\left[ H_i + \sum_k (J_{ik} - K_{ik}) \right]}_{\varepsilon_i}$$

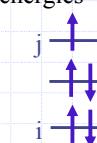
Effective energy of the  $i$ -th electron  
(Koopmans' Theorem)



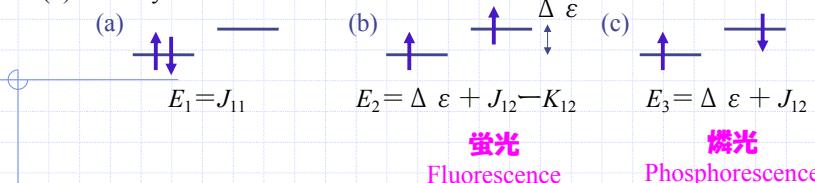
Total energy is  $E_0 + \sum_i \varepsilon_i$  : a sum of the one-electron energies

One electron is added on the  $j$ -th MO

$$E = E_0 + \left[ H_j + \sum_k (J_{jk} - K_{jk}) \right] = E_0 + \varepsilon_j$$



(5) Stability of 2-level 2-electron states



$$K_{12} > 0 \rightarrow (c) > (b)$$

**Triplet excitation is stabler than singlet excitation.**

$$(a) (b) \text{ from } H_1 + J_{11} < H_2 + J_{12} - K_{12}$$

1, 2 are MOs on the same molecule  $\rightarrow$  assuming  $J_{11} \sim J_{12}$

$$H_2 - H_1 > K_{12} \rightarrow (b) > (a) \rightarrow \text{Chemical bond leads to singlet}$$

$$H_2 = H_1 \text{ Degenerate } (a) > (b) \rightarrow \text{Triplet Hund's rule}$$

Degeneracy leads to triplet: triplet instability

Configuration Interaction

CI (配置間相互作用)

Linear combination of excited states are included in order to involve electron correlation in MO:

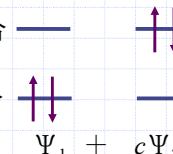
$$\Psi = \Psi_1 + c\Psi_2$$

$$= (\chi_A(1) + \chi_B(1))(\chi_A(2) + \chi_B(2)) + c(\chi_A(1) - \chi_B(1))(\chi_A(2) - \chi_B(2))$$

$$= (1+c)(\chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)) + (1-c)(\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2))$$

Ionic

反結合



$c = -1$  corresponds to the valence bond method, with no ionic contribution.

$c = 0$  corresponds to the MO method with 50% ionic contribution.

$c$  is determined so as to minimize the energy ( $-1 < c < 0$ ).

CI calculation is inevitable for the calculation of excited states in MO.

Molecular Correlation in Molecular Orbital

$$\alpha - \beta \quad \phi = \chi_A - \chi_B$$

A hydrogen atom has 2 electrons in the bonding orbitals, so that the whole wave function is

$$\alpha + \beta \quad \phi = \chi_A + \chi_B$$

$$\Psi = (\chi_A(1) + \chi_B(1))(\chi_A(2) + \chi_B(2))(\underline{\alpha(1)\beta(2)} - \underline{\alpha(2)\beta(1)})$$

Spin part in the Slater determinant is antisym.  $\rightarrow$  singlet  $\rightarrow$  omitted

$$\rightarrow \underline{\chi_A(1)\chi_A(2)} + \underline{\chi_A(1)\chi_B(2)} + \underline{\chi_B(1)\chi_A(2)} + \underline{\chi_B(1)\chi_B(2)}$$

2 electrons on  
hydrogen A  
 $H^-H^+$  ionic

Covalent bond  
 $H^-H^+$  ionic

2 electrons on  
hydrogen B  
 $H^-H^+$  ionic



Ionic contribution in MO is 50%; this is obviously too large!

This come from the averaged electron density, and electron correlation (電子相關) is not considered.

cf. Valence Bond Theory (Heitler Lindon法)

Use  $\Psi = \chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)$  instead of the above  $\Psi$

Mathematical Models Representing Mott Insulator

(1) Gutzwiller 波動関数

$$\Psi_G = \prod_i (1 - \eta \underline{n_{i\uparrow}n_{i\downarrow}}) \Psi_0 = \exp(-\eta \sum_i n_{i\uparrow}n_{i\downarrow}) \Psi_0$$



Subtract double occupancy (ionic state) from the wave function  
Similar to CI, but the calculation is difficult.

(2) Hubbard Model

Double occupancy costs energy  $U$  (on-site Coulomb repulsion).

$$H = \sum_{i \neq j} t_{ij} a_i^\dagger a_j + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

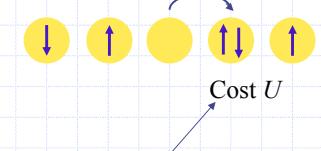
Energy band  
 $2t \cos ka$

Double occupancy at the  $i$  site costs energy  $U$ .  
Zero if either  $n_{i\uparrow}$  or  $n_{i\downarrow}$  is 0.

Secondary quantization

$a_j$  : annihilate  $j$ -site electron       $a_i^\dagger$  : create  $i$ -site electron

$n_{i\uparrow} = a_i^\dagger a_i$  :  $i$ -site electron number



When we assume  $U$  does not change the band shape,

$$E_{\uparrow} = 2t \cos ka \quad \text{Energy band of the 1-st electron}$$

$$E_{\downarrow} = 2t \cos ka + U \quad \text{Energy band of the 2-nd electron}$$

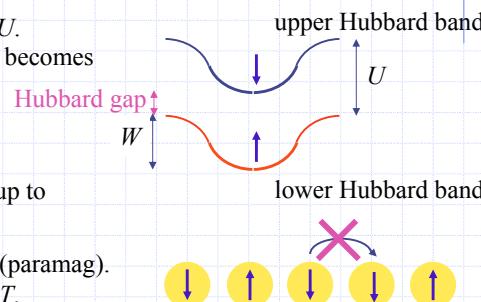
(1)  $t \ll U$

Split  $\uparrow$  and  $\downarrow$  energy bands by  $U$ .  
 $U > W$  makes a Hubbard gap, and becomes insulating when half-filled.

Mott transition happens when  $U$  exceeds  $W$ .

Lower Hubbard band occupies up to 1 electron (usually 2).

Spin orientation may be random (paramag).  
 Maybe antiferromagnetic at low  $T$ .



Hubbard model is insulating only for half-filled. (other fillings are metals)

Mean-field solutn. of Hubbard model (Stoner model)

In the ferromagnetic metal with different  $\uparrow$  and  $\downarrow$  electron numbers, the magnetization is

$$m = n_{\uparrow} - n_{\downarrow} = \int_{E_F - \Delta}^{E_F + \Delta} D(E) dE = 2D\Delta \quad D = D(E_F)$$

Kinetic energy increases by this process as:

$$\begin{aligned} \Delta E &= \int_0^{E_F + \Delta} EDdE + \int_0^{E_F - \Delta} EDdE - 2 \int_0^{E_F} EDdE \\ &= \int_{E_F - \Delta}^{E_F + \Delta} EDdE = D\Delta^2 = \frac{m^2}{4D} = \frac{1}{4}Wm^2 \end{aligned}$$

状態密度  $D(E)$

From the above      Assuming bandwidth  $W \sim 1/D$

This spin polarization leads to energy gain of the  $U$ -term, (using  $n = n_{\uparrow} + n_{\downarrow}$ ,  $m = n_{\uparrow} - n_{\downarrow}$ )  $E = Un_{\uparrow}n_{\downarrow} = \frac{U}{4}(n^2 - m^2)$

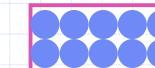
Add the above two  $E = \frac{W-U}{4}m^2 + \frac{U}{4}n^2$   $n = \text{total el } \# = \text{const.}$

$W > U$   $E$  min. is  $m=0$  常磁性金属 paramagnetic metal

$W < U$   $E$  min. is  $m \neq 0$  磁性金属 magnetic metal

When  $U$  exceeds  $W$  (Stoner limit), electron spin-polarizes to be a magnetic metal.

Fully Occupied



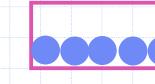
Insulator

Partially Occupied (less than half filled)



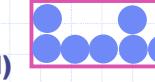
Metal

Half Filled



Mott Insulator ( $U \neq 0$ )

Partially Occupied (more than half filled)



Metal

Applying weak magnetic field  $h$

$$E = \frac{W-U}{4}m^2 + \frac{U}{4}n^2 - mh$$

$$\rightarrow \frac{1}{\chi} = \frac{\partial h}{\partial m} = \frac{W-U}{2}$$

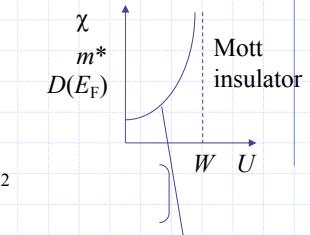
or because the energy of the spin system is  $\frac{1}{2\chi}m^2$

Susceptibility diverges to  $\infty$  at  $U \rightarrow W$   
 (the same in  $m^*$  and DOS  $D(E_F)$ )

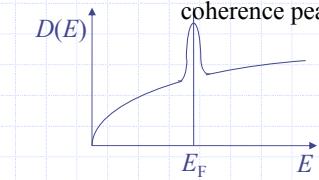
The same as a ferromagnet approaching to  $T_c$  from  $T > T_c$

Here  $T=0$ , and the horizontal axis is  $U/W$

Magnetic susceptibility



$$\chi = \frac{2}{W-U} = \frac{\chi_0}{1-UD_0}$$

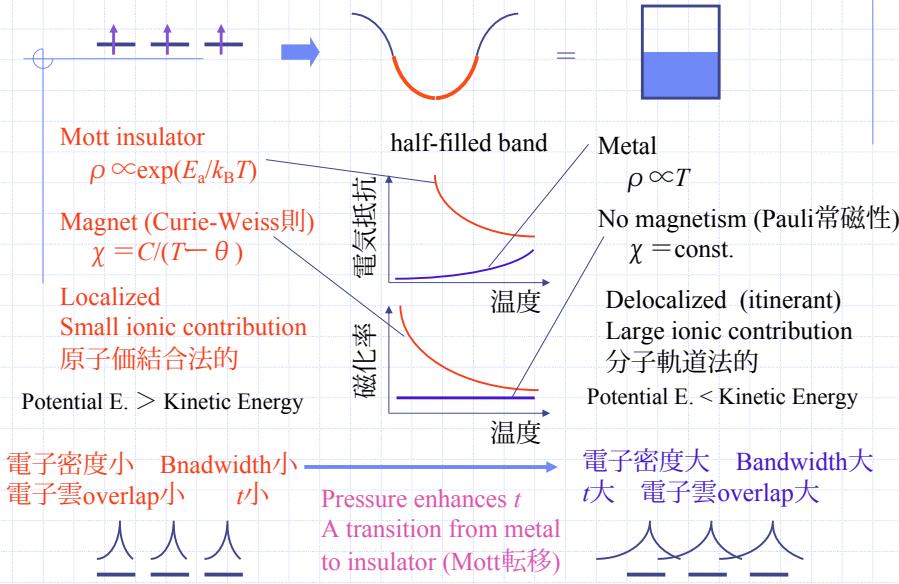


RPA result:

W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 4302 (1970).

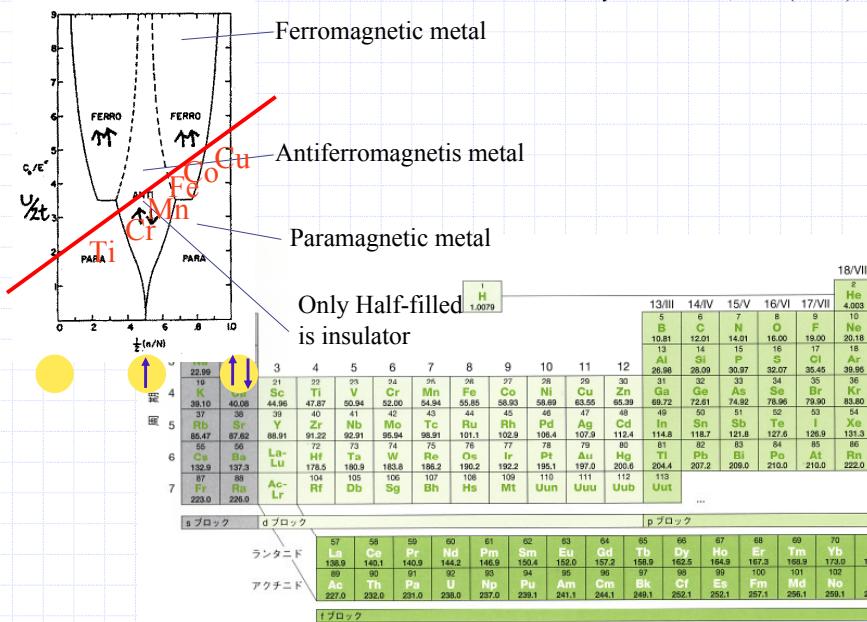
# Electron Correlation in Solids

Energy band with 1 electron - 1 site state



## Mean field solution

D. R. Penn, *Phys. Rev.* **142**, 350 (1966)



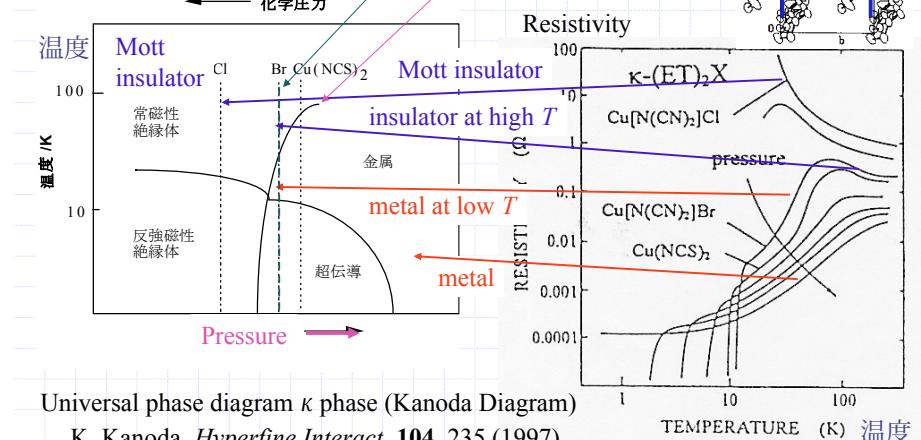
## Metal-insulator transition in $\kappa$ phase organic superconductors

## $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[C(CN)<sub>2</sub>]Cl

$\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[C(CN)<sub>2</sub>]Br the boundary right

$\kappa$  -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> Critical (end) point like

## Liquid-gas boundary



Universal phase diagram  $\kappa$  phase (Kanoda Diagram)

K. Kanoda, *Hyperfine Interact.* **104**, 235 (1997)

## Strict solutions of the Hubbard model

## Antiferromagnetic insulator

Strict solution only for one-dimensional case

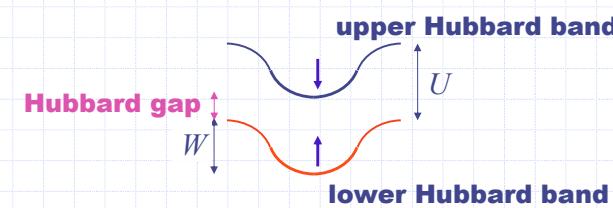
Only half-filled is simulator for infinitesimal small  $U \neq 0$

E. H. Lieb and F. Y. Wu, *Phys. Rev. Lett.* **20**, 1445 (1968)

川上、梁、共系場理論と一次元電子系 岩波

## Numerical calculation for more than two dimensions

J. E. Hirsch, *Phys. Rev. B* **31**, 4403 (1985)



## Derivation of magnetic interaction $J$ from the Hubbard model

### 2 site 2 electron Hubbard model

#### Singlet solution

$$\begin{array}{c|cccc} & \textcircled{1} & \textcircled{2} & \textcircled{3} & \textcircled{4} \\ \hline \textcircled{1} & \uparrow\downarrow & -E & t & 0 & t \\ \textcircled{2} & \uparrow\downarrow & t & U-E & t & 0 \\ \textcircled{3} & \downarrow\uparrow & 0 & t & -E & t \\ \textcircled{4} & \uparrow\uparrow & t & 0 & t & U-E \end{array} = 0$$

$E = 0, 0$

By one electron jump  
 ① changes to ④

The solution is

$$\begin{vmatrix} -E & 2t \\ 2t & U-E \end{vmatrix} = 0$$

$$E = \frac{U \pm \sqrt{U^2 + 16t^2}}{2}$$

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

$$E = 0, U$$

The  $E=0$  solution  $\Psi = \frac{\textcircled{1}-\textcircled{2}}{\sqrt{2}}$  is asymmetric  
 and goes to triplet.

### $4C_2=6$ states Triplet solution



## 2 site 2 electron Hubbard model

上村 電子物性論 培風館(1995), p30.

$$E = \frac{U + \sqrt{U^2 + 16t^2}}{2}$$

$$E = \frac{U - \sqrt{U^2 + 16t^2}}{2} \rightarrow -\frac{4t^2}{U} \quad (U \gg t)$$

$$U \gg t \rightarrow J = E_T - E_S = -\frac{4t^2}{U}$$

Including the exchange integral  $K$ ,

$$J = K - \frac{4t^2}{U}$$

Potential exchange  
 $J > 0$  Ferromagnetic

Kinetic exchange  
 $J < 0$  Antiferromagnetic

$$J = K - \frac{4t^2}{U}$$

#### (1) Potential exchange



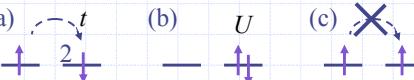
In degenerated 2 levels, triplet is more stable by:

$$J_{12} \quad J_{12} - K_{12}$$

$$K_{12} = \int \varphi_1^*(1)\varphi_2^*(2) \frac{e^2}{r_{12}} \varphi_1(2)\varphi_2(1) d\tau > 0 \quad (\text{exchange integral})$$

→ spin parallel (ferromagnetic) (=Hund's rule)

#### (2) Kinetic exchange



Electron moves from atom 1 to atom 2 by transfer integral  $t$ .

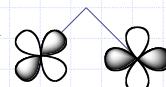
Energy increases by the on-site Coulomb integral  $U$  (b). When going back to (a) and mixing the (b) state, the (a) state is stabilized by  $J = -2t^2/U$ .

Parallel spin (c) is not stabilized due to the Pauli exclusion principle,  
 So antiparallel (a) is more stable by  $J = -2t^2/U$ .

Usually (2)>>(1) leads to antiferromagnetism, and  $J < 0$ .

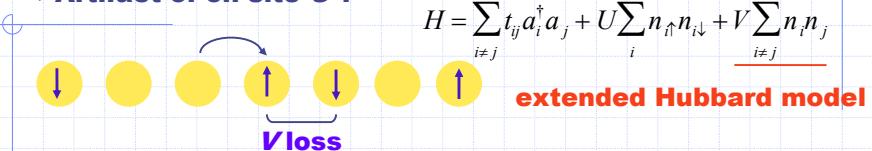
Exception : Orthogonal nearby orbitals leads to  $t \rightarrow 0$

so that (2)→0, (1) remains to result in ferromagnetism  
 $J>0$  (Kanamori-Goodenough rule).



## Charge order in non half-filled bands

Only half filled is insulating in the Hubbard model  
 → Artifact of on-site  $U$ ?



Adjacent-site electron leads to by  $V$  (off-site Coulomb repulsion) higher energy

At 1/4-filled, alternate arrangement is stable.



Charge order insulator



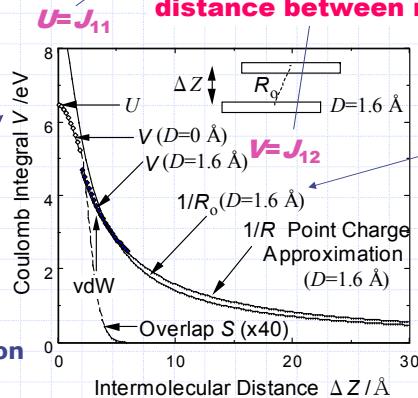
2-fold periodicity

(=  $4k_F$  CDW in a one-dimensional system)  
 (cf. no new periodicity in a Mott insulator)

## Extended Hubbard model including $V$

$$H = \sum_{i \neq j} t_{ij} a_i^\dagger a_j + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{i \neq j} n_i n_j$$

$V$  is approximately inverse of the distance between molecular centers



2 orbitals on the same position  
→  $U$

Coulomb repulsion is  $\propto 1/r$ : not only on-site  
Inverse distance in Bohr radius (0.52 Å) →  $V$  in Hartree (26.6 eV)

## In molecular orbital theory

$$E = 2 \sum_k^{occ} H_k + 2 \sum_{k \neq l}^{occ} J_{ik} - \sum_{k \neq l} K_{ik}$$

For the same spins

In solid state physics

$$U$$

$$J$$

$J_{ii}$  for the same MO

Magnetic interaction

$J_{ij}$  for different MO

Many intriguing phenomena  
in solid state physics  
emerge from these parameters.

## Charge order in 1D : atomic limit ( $t \rightarrow 0$ )

~~$$H = \sum_{i \neq j} t_{ij} a_i^\dagger a_j + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{i \neq j} n_i n_j$$~~

$$\langle n_\uparrow \rangle = \langle n_\downarrow \rangle = n/2$$

(a) 金属  $n = 1/2$  スピン分極なし



$$n = 1/2$$

$$E = U \times \frac{1}{4} \times \frac{1}{4} + V \times \frac{1}{2} \times \frac{1}{2} = \frac{U}{16} + \frac{V}{8}$$

(b) 電荷整列  $n = 1$  スpin分極なし



$$n = 1, 0$$

$$E = \frac{1}{2} [U \times (\frac{1}{2} \times \frac{1}{2} + 0 \times 0) + 2V \times 1 \times 0] = \frac{U}{8}$$

$$\frac{U}{16} + \frac{V}{8} > \frac{U}{8}$$

$$4V > U$$

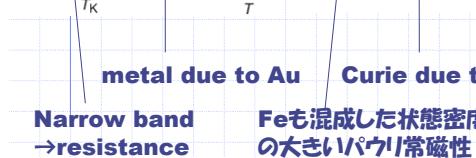
where charge order is more stable than uniform metal

## Kondo effect: magnetic impurities in metals lose spins below $T_K$

Au + several%Fe

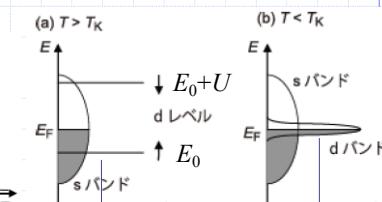


metal due to Au  
Narrow band  
→ resistance increases



Feも混成した状態密度の大きいパウリ常磁性

Curie due to Fe



Occupied lower Hubbard → localized spin  
Fe spin cancelled by the surrounding Au

DOS of narrow d band:  $D(E) = \frac{1}{\pi} \frac{1}{(E - E_0 - nU)^2 + \Delta^2}$

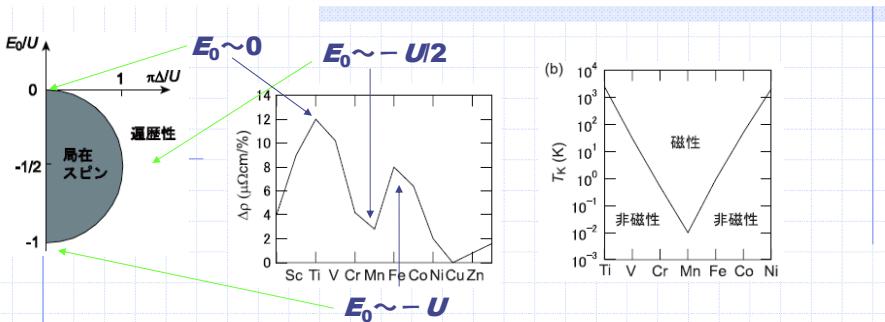
From Stoer model  $UD(E) > 1$

$$\frac{\Delta}{\pi} \frac{U}{(E_0 + nU)^2 + \Delta^2} > 1$$

$E_0 = -U/2$ : d level by  $U/2$  below  $E_F$  → Easily localize

$$k_B T_K \sim \Delta$$





After tremendous calculation **Resistance minimum**

$$R(T) = R_0 (1 + 2JD(E_F) \ln(k_B T / \Delta)) \rightarrow T_K = \Delta \exp(-1/D(E_F) |J|)$$

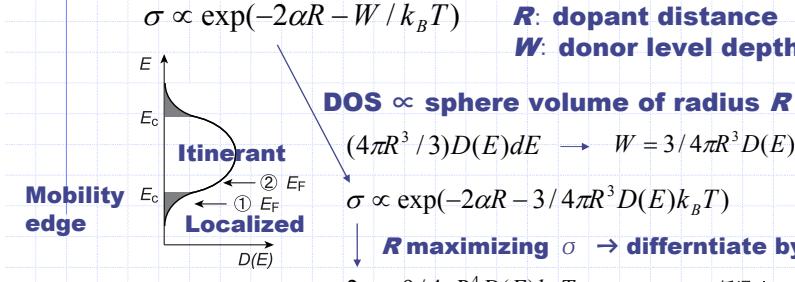
**Cu:**  $T_K \sim 1000$  K  $> rt$ : no spin at rt  $\rightarrow$  nonmagnetic metal  
**Cu<sup>4/3+</sup> in an organic conductor Cu(DMDCNQI)<sub>2</sub>**  
 is hybridized  $\rightarrow$  non magnetic (Mixed valent)

**Mn:**  $T_K \sim 0.01$  K  $\rightarrow$  magnetic metal  
 $\kappa$ -BETS<sub>2</sub>FeBr<sub>4</sub> maintains magnetism  
 (cannot cancel S=5/2)

### Variable Range Hopping in a random system

N. F. Mott, Phil. Mag., 19, 835 (1969).

**Conductor**  $\sigma \sim 1/L$   $\rightarrow$  **Localization**  $\sigma \sim \exp(-\zeta r)$



$$\text{DOS} \propto \text{sphere volume of radius } R$$

$$(4\pi R^3/3)D(E)dE \rightarrow W = 3/4\pi R^3 D(E)$$

$$\sigma \propto \exp(-2\alpha R - 3/4\pi R^3 D(E)k_B T)$$

**R maximizing**  $\sigma \rightarrow$  differentiate by **R**

$$2\alpha = 9/4\pi R^4 D(E)k_B T$$

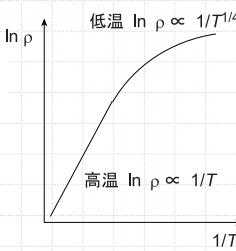
**Localized limit at  $R < R_D \rightarrow -2\alpha R$  is important**

$\rightarrow$  this **R** is inserted to give

$$\sigma \propto \exp(-a/T^{1/4}) \quad \text{3D}$$

$$\sigma \propto \exp(-a/T^{1/3}) \quad \text{2D}$$

$$\sigma \propto \exp(-a/T^{1/2}) \quad \text{1D}$$



### Anderson localization

**Ordinary conductance**  $G = \sigma L^{d-2} \rightarrow$  **3D**  $\rho = RS/L \Omega\text{cm}$   
**2D**  $\sim L^0$  sheet resistance

$L \times v$  leads to  $\frac{G(vL)}{G(L)} = f(G(L), v)$  **G(vL)** and **G(L)** comes from **v** (Scaling principle)

The logarithmic derivative is devided by  $\ln v$ , and in the  $v \rightarrow 1$  limit

$$\lim_{v \rightarrow 1} \frac{\log(G(vL)/G(L))}{\log v} = \lim_{v \rightarrow 1} \frac{\log G(vL) - \log G(L)}{\log(vL) - \log L} = \frac{d \log G}{d \log L} \equiv \beta(G)$$

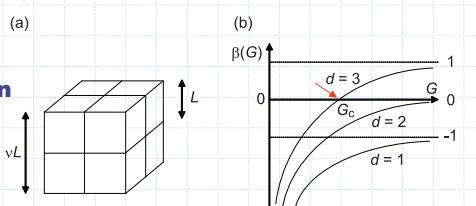
Large **G** (metal)  $\rightarrow \beta(G) = d-2$  Power of **L** in **G**

Small **G** (localized)  $\rightarrow G = G_0 e^{-\alpha L/\xi} \rightarrow \beta(G) = \log(G/G_0) = -\alpha L/\xi$

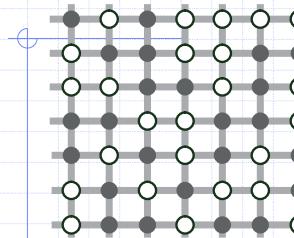
**1D**  $\beta(G) < -1$  localization

**2D**  $\beta(G) < 0$  weak localization

**3D**  $\beta(G) = 0$  crossed  
 Anderson transition



### Percolation Theory



Black ball conducting  
 White ball insulating

Connected black cluster  $\rightarrow$  conducting

Critical black ball ratio coordination#

3D Simple cubic	0.311	6
Body center cubic	0.246	8
Face center cubic	0.198	12
2D Square lattice	0.593	4
Triangular lattice	0.500	3
1D	~1.0	

Only a white ball makes insulator

Large coordination # leads to small critical values