

Electron Correlation (電子相関)

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

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

Slater determinant

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

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 φ_1 and φ_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

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

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

One-electron part
K: # of MO

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

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 ρ_k and MO l

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

Exchange integral

Exchange 1 and 2

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

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

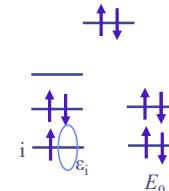
$$(2) 2 \text{ electrons in a MO} \quad E = 2H_1 + J_{11}$$

$$(3) \text{ Remove one electron from the i-th MO.}$$

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

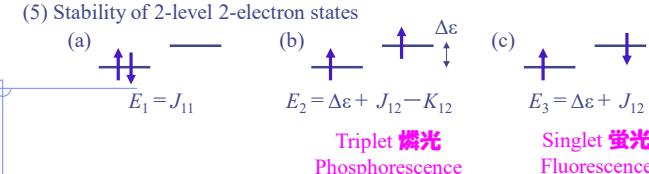
Effective energy of the i-th electron
(Koopmans' Theorem)

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



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



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

Triplet excitation is stabler than singlet excitation.

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

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

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

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

Degeneracy leads to triplet: triplet instability

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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

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

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

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

$$\rightarrow \underbrace{\chi_A(1)\chi_A(2)}_{2 \text{ electrons on hydrogen A}} + \underbrace{\chi_A(1)\chi_B(2)}_{\text{Covalent bond}} + \underbrace{\chi_B(1)\chi_A(2)}_{\text{2 electrons on hydrogen B}} + \underbrace{\chi_B(1)\chi_B(2)}_{\text{H}^- \text{H}^+ \text{ ionic}}$$

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

This comes 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 Ψ

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<p>Configuration Interaction CI (配置間相互作用)</p> <p>Linear combination of an excited state is included in order to involve electron correlation in MO:</p> $\Psi = \Psi_1 + c\Psi_2$ $= (\chi_A(1) + \chi_B(1))(\chi_A(2) + \chi_B(2)) + c(\chi_A(1) - \chi_B(1))(\chi_A(2) - \chi_B(2))$ $= (1+c)(\chi_A(1)\chi_A(2) + \chi_B(1)\chi_B(2)) + (1-c)(\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2))$	<p>反結合</p> <p>結合</p> <p>$\Psi = \Psi_1 + c\Psi_2$</p>	
Ionic		Covalent 共有結合性
$c = -1$ 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.		

Mathematical Models Representing Mott Insulator

(1) Gutzwiller 波動関数

$$\Psi_G = \prod_i (1 - \eta \underbrace{m_{i\uparrow} n_{i\downarrow}}_{\text{Subtract double occupancy (ionic state)}}) \Psi_0 = \exp(-\eta \sum_i n_{i\uparrow} n_{i\downarrow}) \Psi_0$$

Similar to CI, but the calculation is difficult.

(2) Hubbard Model

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

$$H = \underbrace{\sum_{i \neq j} t_{ij} a_i^\dagger a_j}_\text{Energy band} + U \underbrace{\sum_i n_{i\uparrow} n_{i\downarrow}}_\text{Double occupancy at the i site costs energy U.}$$

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,

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

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

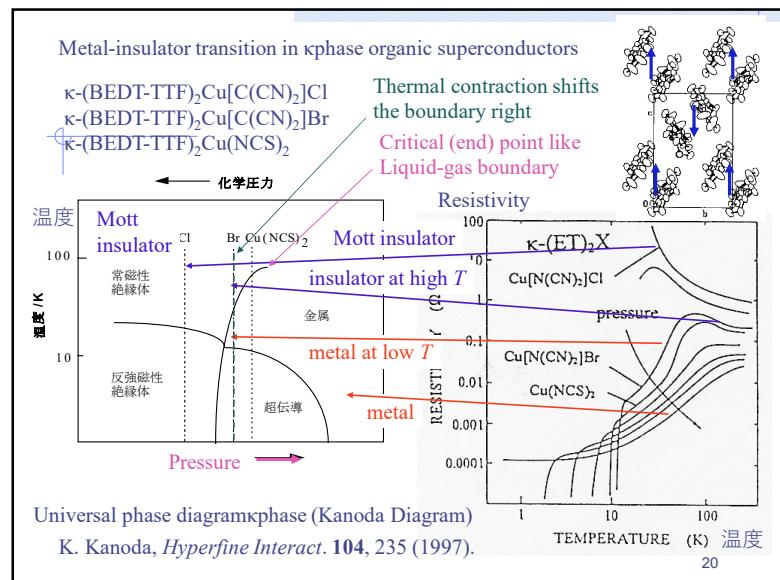
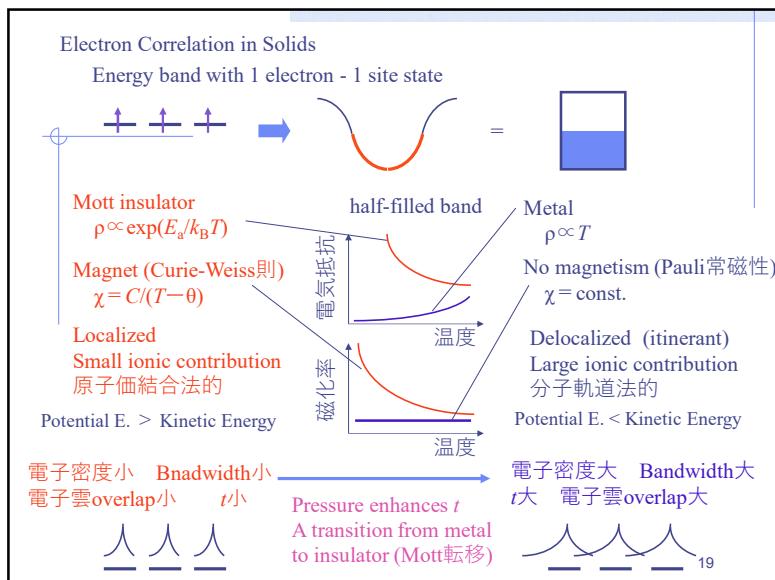
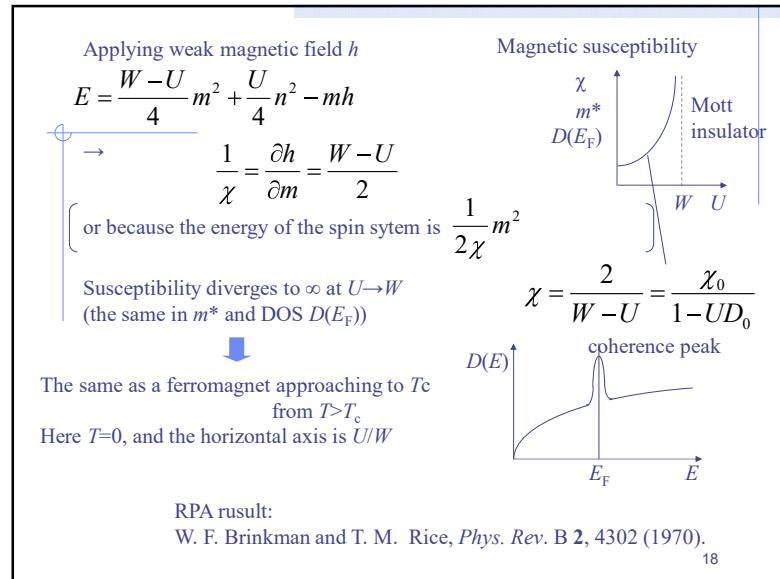
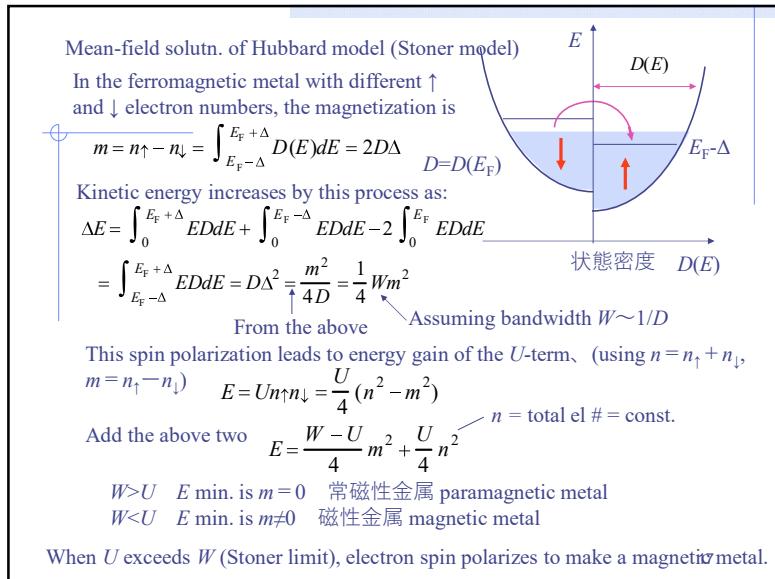
(1) $t \ll U$

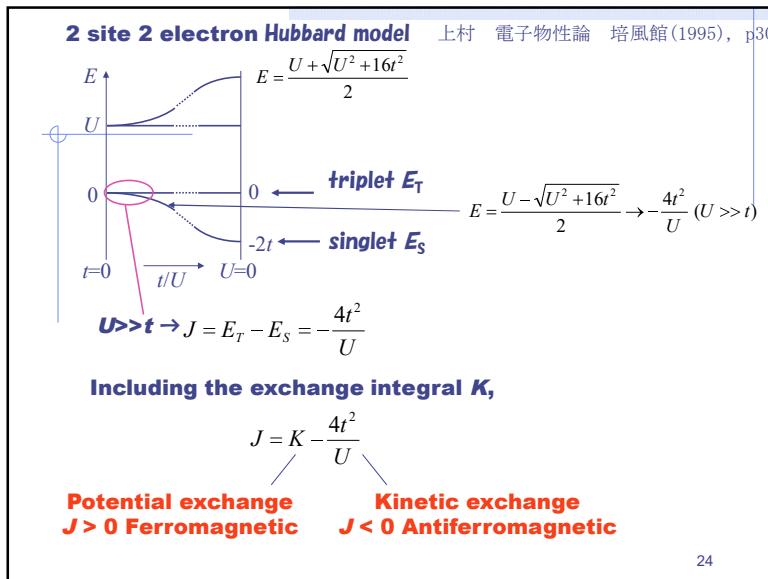
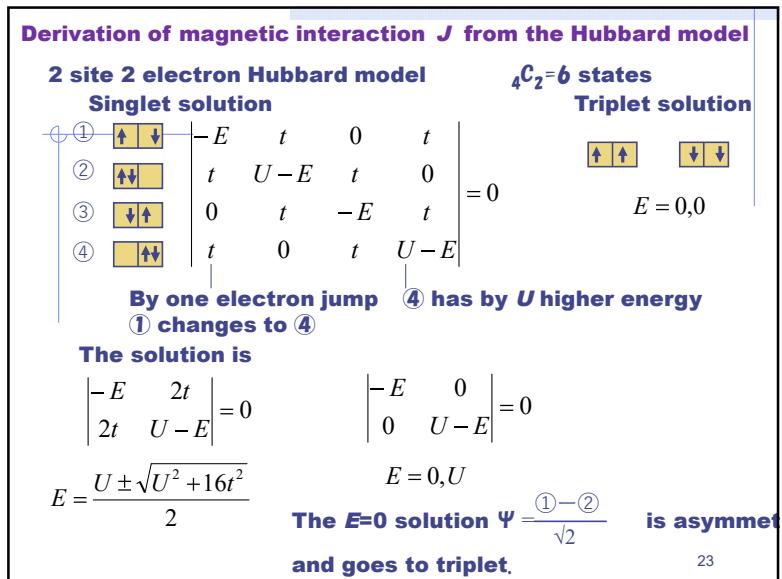
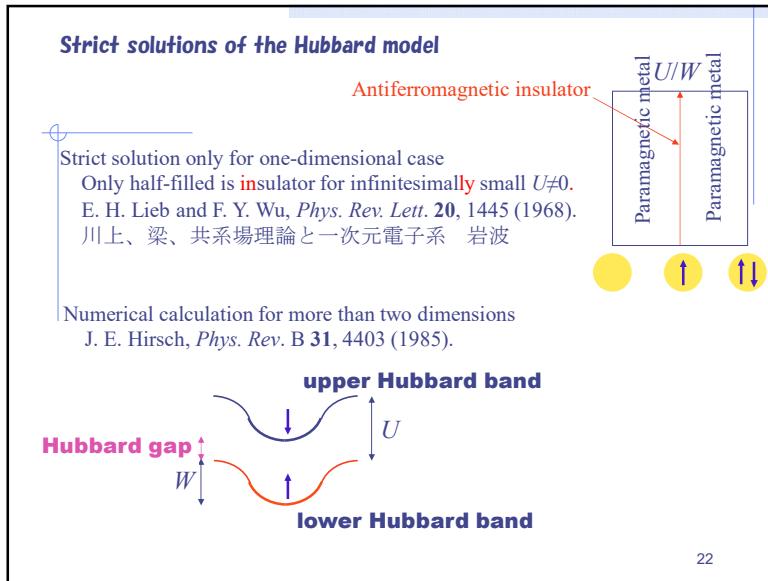
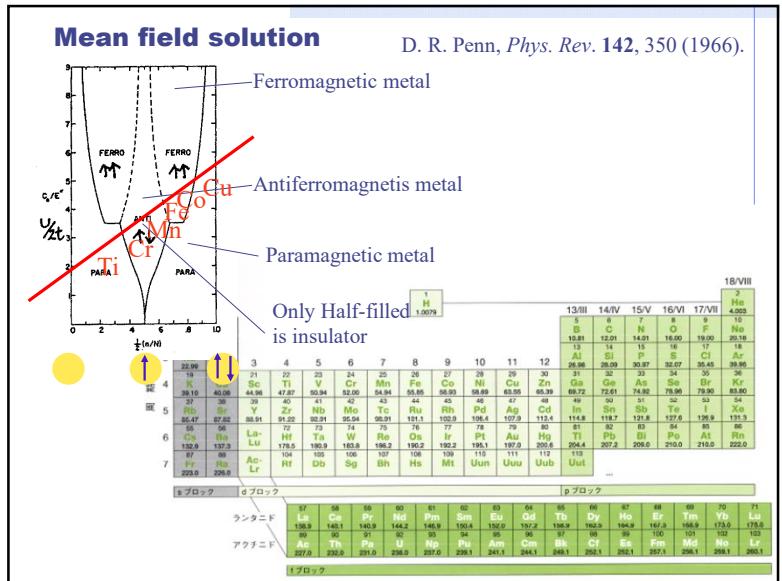
Split ↑ and ↓ energy bands by U .
 $U > W$ makes a Hubbard gap, and becomes insulating when half-filled.
Mott transition happens when U exceeds W .

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)

Fully Occupied		Insulator
Partially Occupied (less than half filled)		Metal
Half Filled		Mott Insulator ($U \neq 0$)
Partially Occupied (more than half filled)		Metal





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

(1) Potential exchange

In degenerated 2 levels, triplet is more stable by:
 $K_{12} = \int \phi_1^*(1)\phi_2^*(2) \frac{e^2}{r_{12}}\phi_1(2)\phi_2(1)d\tau > 0$ (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 ?

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

Vloss
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)

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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

$U = J_{11}$

$V = J_{12}$

2 orbitals on the same position → U

Coulomb Integral V / eV vs Intermolecular Distance ΔZ / Å

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

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

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

$n = 1/2$ $\langle n_\uparrow \rangle = \langle n_\downarrow \rangle = n/2$

(a) 金属 $n = 1/2$ スピン分極なし

(b) 電荷整列 $n = 1$ スpin分極なし

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

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

$n = 1, 0$

$\frac{U}{16} + \frac{V}{4} > \frac{U}{8}$

where charge order is more stable than uniform metal

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