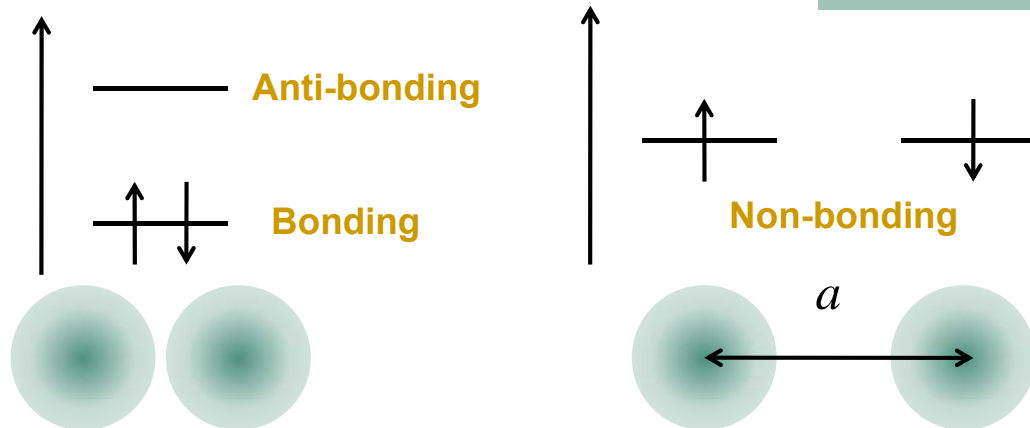The 17th CMD workshop
"Advanced study woth ES-Opt"

Multi-reference DFT

Koichi Kusakabe
Grad. Sch. Eng. Sci, Osaka University

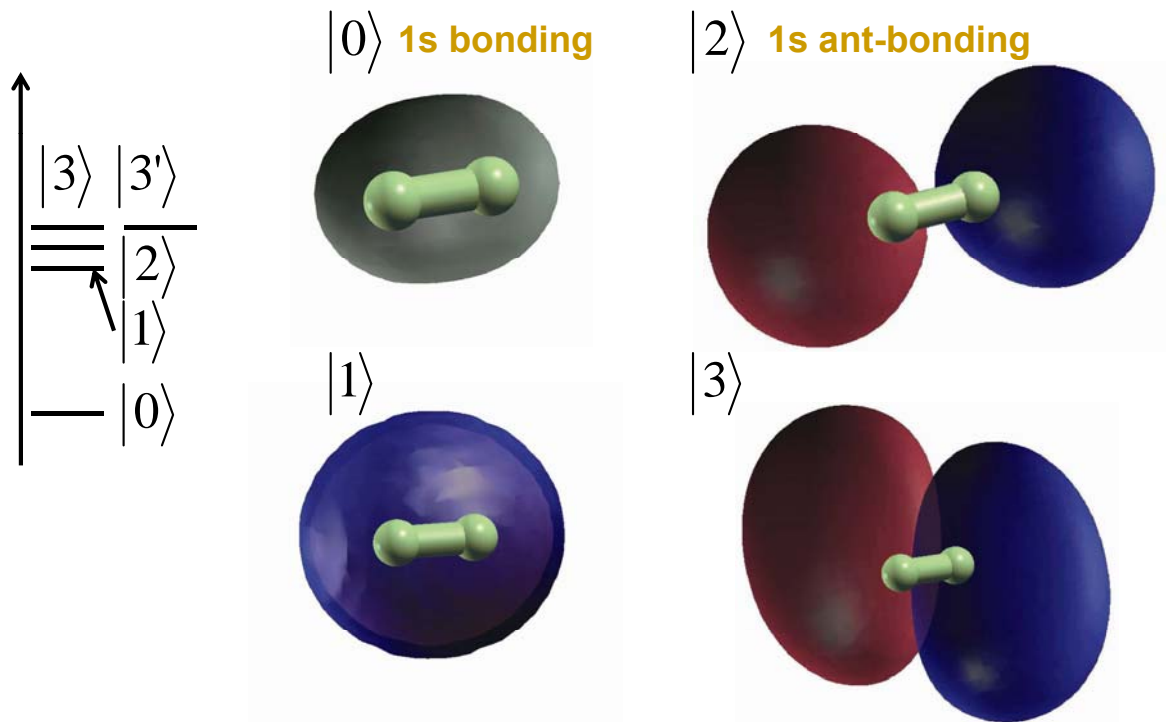# Electronic structure of diatomic molecules

Anti-bonding

Bonding

Non-bonding

a

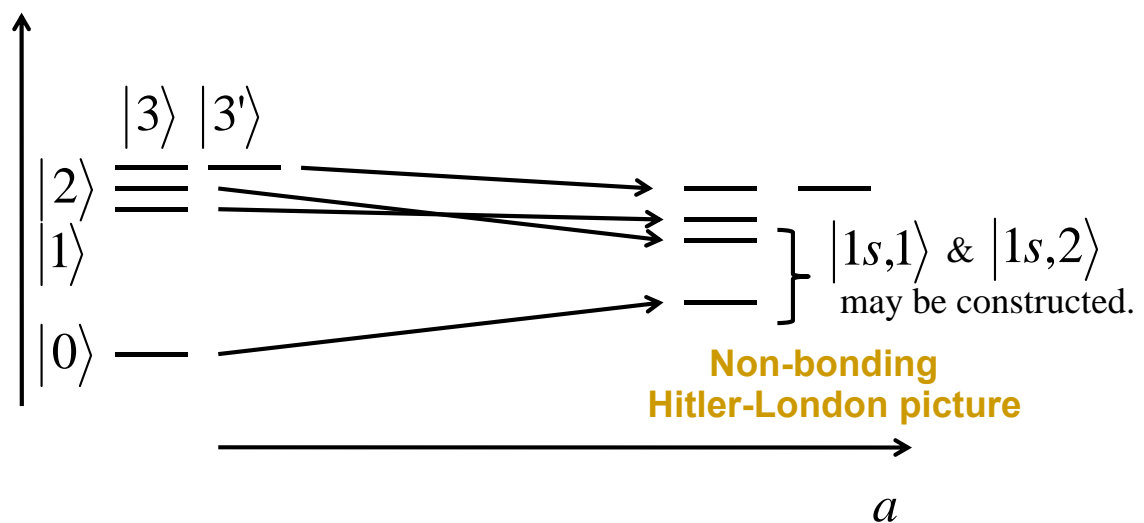**Molecular orbital picture**

Heitler-London picture

Known results in DFT-LDA
• Molecular orbital picture is given for any inter-atomic distance.
• The stable electronic state in equilibrium is well-reproduced.

Molecular orbital given by DFT-LDA

$|0\rangle$ **1s bonding**

$|2\rangle$ **1s ant-bonding**

$|1\rangle$

$|3\rangle$

$|3\rangle$ $|3'\rangle$

$|2\rangle$

$|1\rangle$

$|0\rangle$

Dependence on inter-atomic distance

$|3\rangle$ $|3'\rangle$

$|2\rangle$

$|1\rangle$

$|0\rangle$

$|1s,1\rangle$ & $|1s,2\rangle$ may be constructed.

**Non-bonding
Hitler-London picture**

a

Is there any concise method to describe this dependence?

Correlation effects

- In DFT-LDA, the Kohn-Sham orbital is determined with correlation effects included in the effective potential.
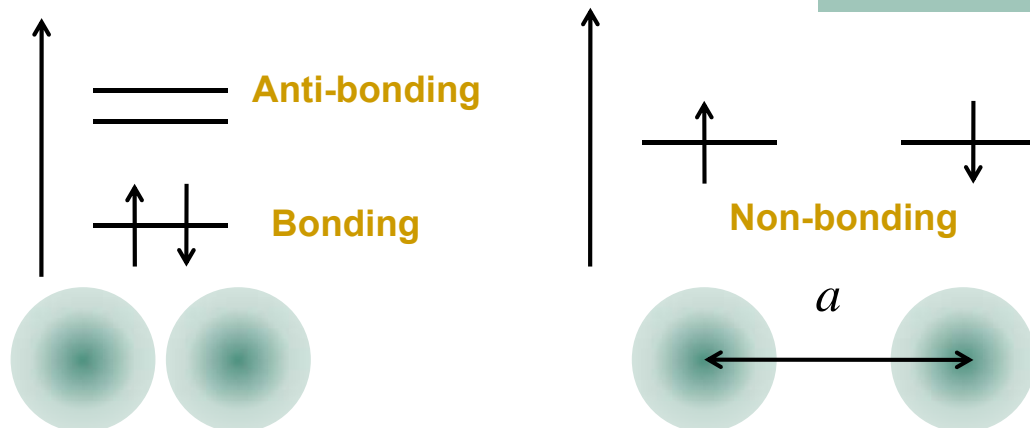- The correlation effect can behave differently depending on atomic configuration.
- A key is,

$$E_{xc}[n] = \frac{e^2}{2} \int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} n_{xc}(\mathbf{r},\mathbf{r}')$$

$$n_{xc}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}') \int_0^1 \left[g_n(\mathbf{r},\mathbf{r}',\lambda) - \delta(\mathbf{r}-\mathbf{r}') \right] d\lambda$$

$$= \int_0^1 \left[\langle \Psi_\lambda | : (\hat{n}(\mathbf{r}) - n(\mathbf{r}))(\hat{n}(\mathbf{r}') - n(\mathbf{r}')) : | \Psi_\lambda \rangle / n(\mathbf{r}) \right] d\lambda.$$
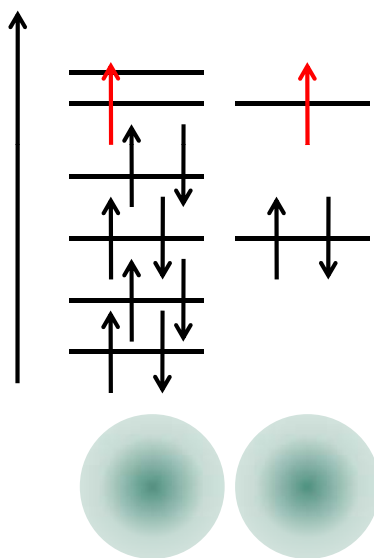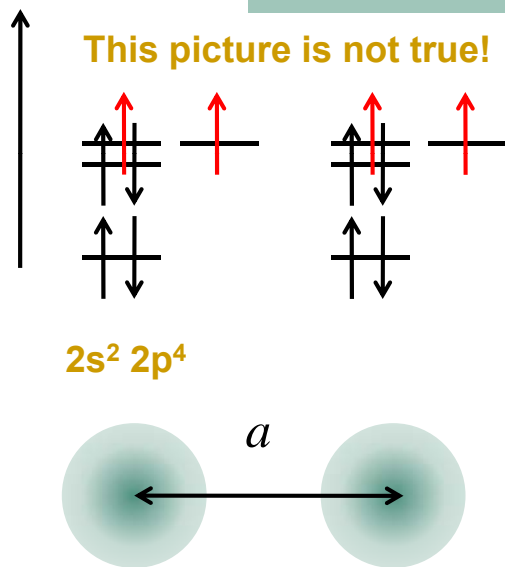
Charge fluctuation!

H$_2$

Anti-bonding

Bonding

Non-bonding

a

This is a weak correlation limit!   **This is a strong correlation limit!**

O₂

This picture is not true!

$2s^2\ 2p^4$

a

S=1 ground state!
This is a strong correlation limit!

S=1 ground state!
This is a strong correlation limit!

How the multi-reference density functional theory acts?

- The Kohn-Sham single-particle description may be used, but may not always be reliable.
- So, if a simplified description allowing a multi-Slater determinant is introduced, we may use the method as another starting point.
- A simplest case is a DFT-LDA solution for a degenerate ground state.

$S=1,\ S_z=1$

$S=0,\ S_z=0$
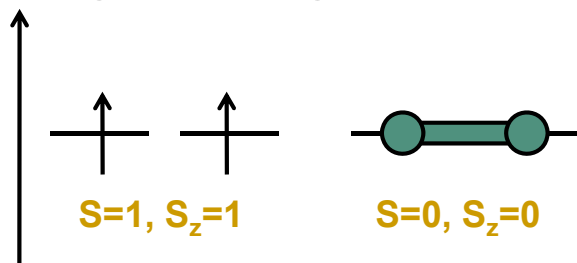
Determination of GS may be possible by looking at
• charge-charge correlation or
• variational energy.

Two physical quantities specifying correlation effects

- Density-density correlation : FRM

$$\langle \underline{n}_i^2 \rangle = \left\langle \left(n_{i\uparrow} + n_{i\downarrow} - \langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle \right)^2 \right\rangle$$

- Variational energy : DFVT

$$E_0 \leq \min_{X_i, \varepsilon_i, g_i} \left\{ \min_{\Psi} \bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] + \Delta \bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] \right\},$$

$$\bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] = \langle \Psi | \hat{T} + \hat{V}_{X_i} | \Psi \rangle + \frac{e^2}{2} \int d^3 r \, d^3 r' \frac{n_\Psi(\mathbf{r}) n_\Psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ E_{\varepsilon_i}[n_\Psi] + E_{g_i}[\Psi] + \int d^3 r \, v_{\text{ext}}(\mathbf{r}) n_\Psi(\mathbf{r}).$$

$$\Delta \bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] = \frac{e^2}{2} \int d^3 r \, d^3 r' \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

$$\times \langle \Psi | : (\hat{n}(\mathbf{r}) - n_\Psi(\mathbf{r}))(\hat{n}(\mathbf{r}') - n_\Psi(\mathbf{r}')) : |\Psi \rangle$$

$$- E_{\varepsilon_i}[n_\Psi] - E_{g_i}[\Psi] - \langle \Psi | \hat{V}_{X_i} | \Psi \rangle.$$

Fluctuation reference method

- To have a simplified description based on DFT, we need information given by another accurate electronic structure calculation.
  - Diffusion Monte-Carlo method for electron gas ⇒ LDA, GGA
  - Complete-Active-Space Configuration-Interaction method ⇒ FRM to determine *U*.

FRM : Fluctuation reference method

Two Hydrogen systems

We define ϕ_i by

$$\phi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2),$$
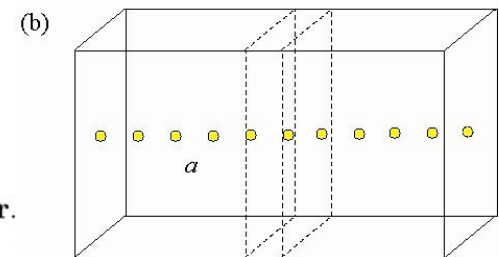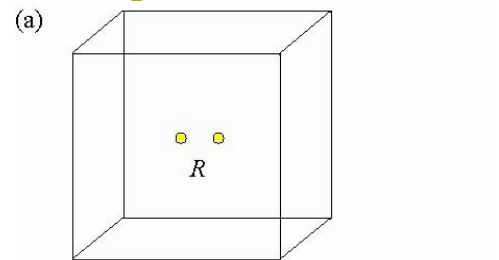
$$\phi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2),$$

for the molecule and the Wannier state

$$\phi_i = \frac{1}{\sqrt{N}} \sum_{k=1}^{N} \exp\left(i\frac{2\pi}{Na}kx_i\right) \chi_{1,k},$$

for a chain with N atoms.

$$t_{ij} = \int \phi_i^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m}\Delta_{\mathbf{r}} + v_{\text{eff}}(\mathbf{r}) \right\} \phi_j(\mathbf{r}) d\mathbf{r}.$$
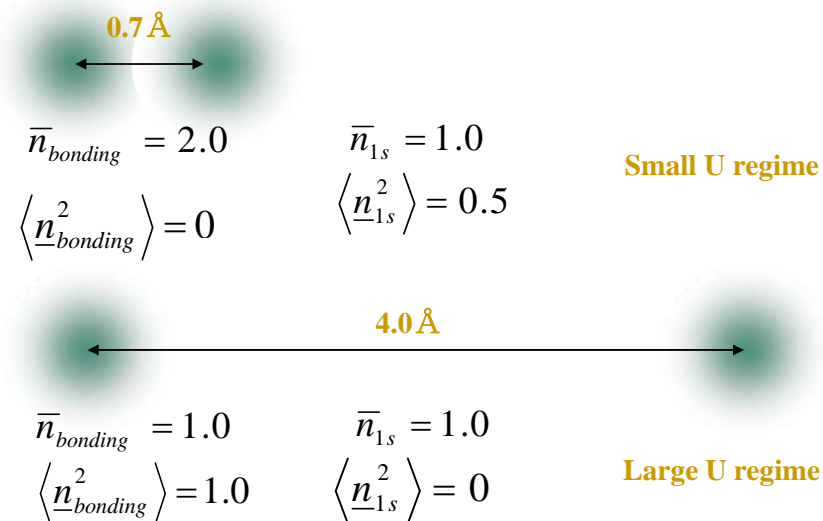
(a)

H$_2$ Molecule

(b)

Hydrogen array

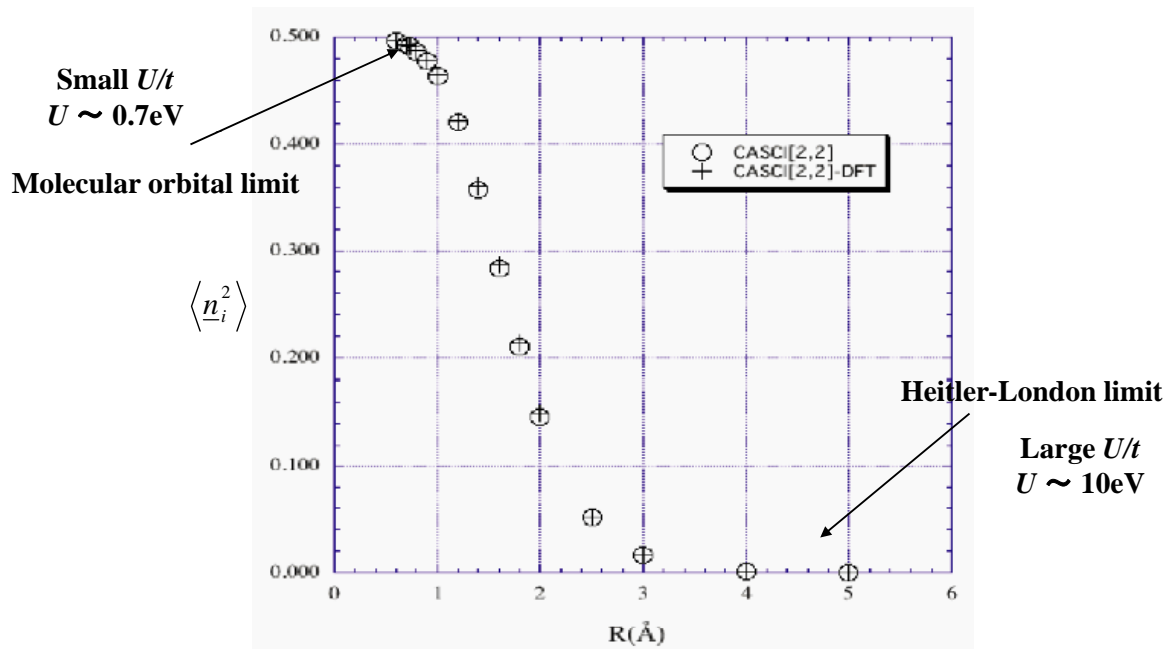# Local fluctuation on ϕ_{1s} of H$_2$

$\left\langle \underline{n}_i^2 \right\rangle = \left\langle \left(n_{i\uparrow} + n_{i\downarrow} - \langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle \right)^2 \right\rangle$ **as a function of the inter atomic distance**

0.7 Å

$\overline{n}_{bonding} = 2.0$ $\overline{n}_{1s} = 1.0$

$\left\langle \underline{n}_{bonding}^2 \right\rangle = 0$ $\left\langle \underline{n}_{1s}^2 \right\rangle = 0.5$

Small U regime

4.0 Å

$\overline{n}_{bonding} = 1.0$ $\overline{n}_{1s} = 1.0$

$\left\langle \underline{n}_{bonding}^2 \right\rangle = 1.0$ $\left\langle \underline{n}_{1s}^2 \right\rangle = 0$

Large U regime

We are able to find relevant orbitals with Coulomb suppression by
1. Finding an orbital (or a set of orbitals) on which fluctuation becomes 1.
2. Using a unitary transformation to have localized orbitals.

Orbital fluctuation in CI calculation

CAS-CI calculation for H_2 by S. Yamanaka.

Small U/t
$U \sim 0.7$eV

Molecular orbital limit

$\left\langle \underline{n}_i^2 \right\rangle$

CASCI[2,2]
CASCI[2,2]-DFT

Heitler-London limit

**Large U/t**
$U \sim 10$eV

R(Å)

In the whole range, mean occupation of 1s is 1.

A test calculation of Hydrogen systems

- $E_{xc}[n]$ is given by LDA of PW91.
- Plane-wave expansion with the Troullier-Martins soft-pseudopotential is introduced for H.
- The energy cutoff for the plane-wave is 40Ry.
- The solver of single-particle part of the extended Kohn-Sham equation is given by the "opt" code.
- Effective many-body problem is solved by the exact diagonalization with e.g. the Lanczos method.
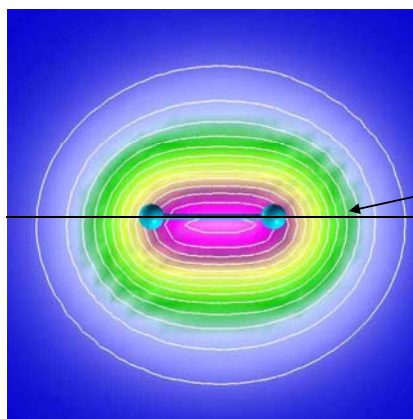
The value of U for H_2 determined by FRM

Reference calculation: CASCI method for H_2
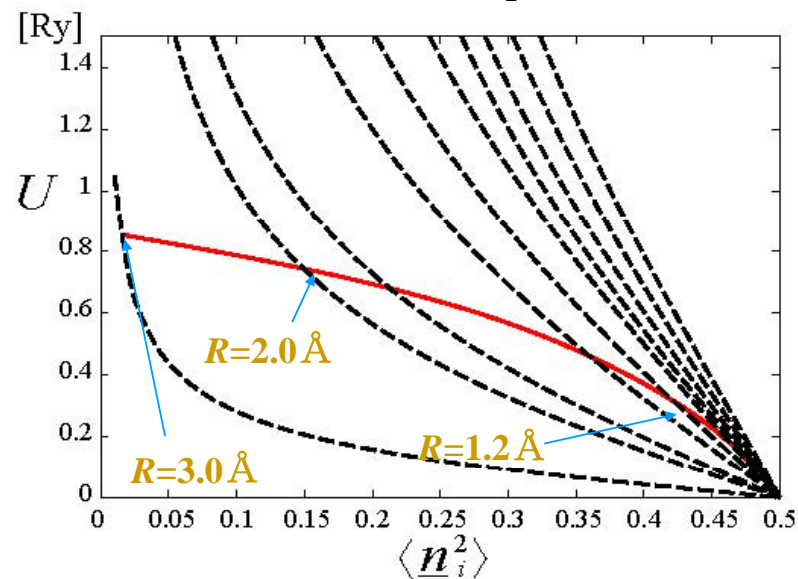
The 1st method to have U by the fluctuation reference method.

K. Kusakabe, et al. J. Phys.: Condens. Matter (2007).

# Charge density of H_2 given by MR-DFT

Weak correlation regime

This section is
Shown in the
right panels.

R=0.6 Å

U is not
needed.

Strong correlation regime
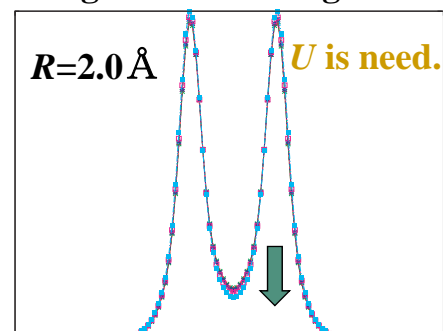
R=2.0 Å U is need.

To reproduce bonding charge in
correlated electron regime, we need to
overcome difficulty in the single-reference
description. It is achieved by using the
multi-reference description as known in
the Hybrid-DFT.
(Cf. S. Yamanaka, et al.)
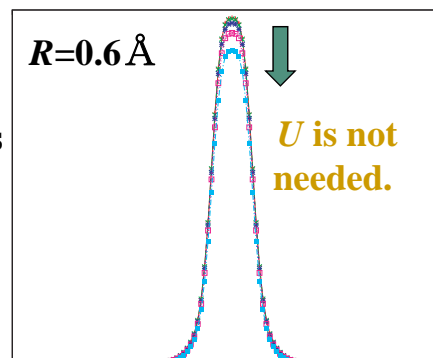
Variational method

DFVT for MR-DFT

$$E_0 \leq \min_{X_i, \varepsilon_i, g_i} \left\{ \min_\Psi \bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] + \Delta\bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] \right\},$$

$$\bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] = \langle\Psi|\hat{T} + \hat{V}_{X_i}|\Psi\rangle + \frac{e^2}{2}\int d^3r\, d^3r' \frac{n_\Psi(\mathbf{r})n_\Psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$+ E_{\varepsilon_i}[n_\Psi] + E_{g_i}[\Psi] + \int d^3r\, v_{\text{ext}}(\mathbf{r})n_\Psi(\mathbf{r}).$$

$$\Delta\bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] = \frac{e^2}{2}\int d^3r\, d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$
$$\times \langle\Psi| : (\hat{n}(\mathbf{r}) - n_\Psi(\mathbf{r}))(\hat{n}(\mathbf{r}') - n_\Psi(\mathbf{r}')) : |\Psi\rangle$$
$$- E_{\varepsilon_i}[n_\Psi] - E_{g_i}[\Psi] - \langle\Psi|\hat{V}_{X_i}|\Psi\rangle.$$

It is possible to evaluate $\Delta\bar{E}[\Psi]$.

Note: If DFVT is used in a space of single Slater
determinant, the Hartree-Fock approx. is given.
This is natural, but not so trivial.
Thanks to Dr. Maruyama & Dr. Friedlich.

DFT model formation

$$E_0 \leq \min_{X_i, \varepsilon_i, g_i} \left\{ \min_\Psi \bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] + \Delta E_{X_i, \varepsilon_i, g_i}[\Psi] \right\},$$

$$\Delta E_{X_i, \varepsilon_i, g_i}[\Psi] = F[n_\Psi] - \frac{e^2}{2}\int d^3r\, d^3r' \frac{n_\Psi(\mathbf{r})n_\Psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$- E_{\varepsilon_i}[n_\Psi] - E_{g_i}[\Psi] - \langle\Psi|\hat{T} + \hat{V}_{X_i}|\Psi\rangle.$$

PBE0+GW, PBE0+U will be refined.

To understand MR-DFT

$$E_0 \leq \min_{X_i, \varepsilon_i, g_i} \left\{ \min_\Psi \bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] + \Delta E_{X_i, \varepsilon_i, g_i}[\Psi] \right\},$$

$$\Delta E_{X_i, \varepsilon_i, g_i}[\Psi] = F[n_\Psi] - \frac{e^2}{2}\int d^3r\, d^3r' \frac{n_\Psi(\mathbf{r})n_\Psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$- E_{\varepsilon_i}[n_\Psi] - E_{g_i}[\Psi] - \langle\Psi|\hat{T} + \hat{V}_{X_i}|\Psi\rangle.$$

**This functional contains
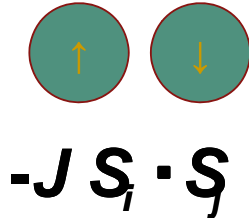the universal energy-
density functional F[n]**

**This functional should be
evaluated using a multi-
Slater description.**

$$\Delta\bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] = \frac{e^2}{2}\int d^3r\, d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$
$$\times \langle\Psi| : (\hat{n}(\mathbf{r}) - n_\Psi(\mathbf{r}))(\hat{n}(\mathbf{r}') - n_\Psi(\mathbf{r}')) : |\Psi\rangle$$
$$- E_{\varepsilon_i}[n_\Psi] - E_{g_i}[\Psi] - \langle\Psi|\hat{V}_{X_i}|\Psi\rangle.$$

Heisenberg exchange:
Introduction to the localized spin model

- Heisenberg and Dirac considered quantum mechanical origin of magnetic interaction

↑ ↓

$$-J\, S_i \cdot S_j$$

J>0 : Parallel spin configuration
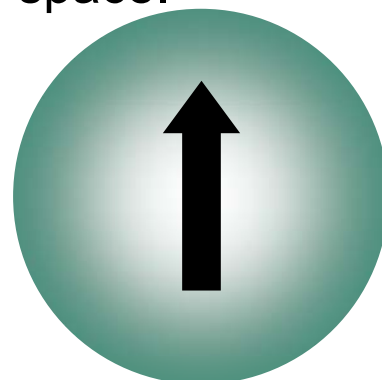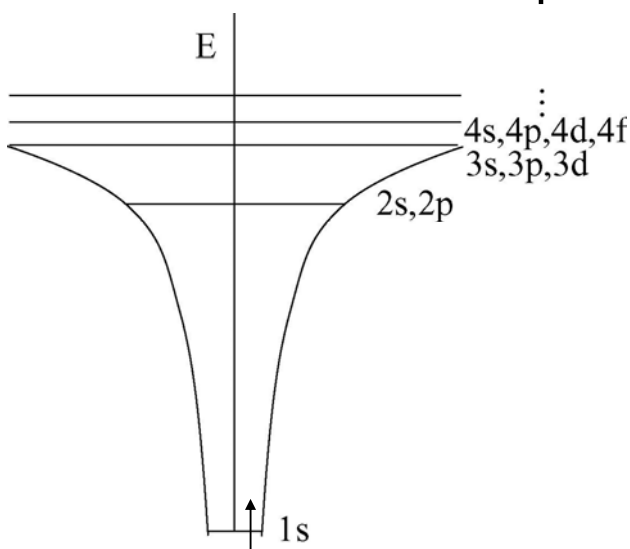**Ferromagnetic**
J<0 : Anti-parallel spin configuration
Antiferromagnetic

whose order of magnitude can be of the order of the Coulomb interaction.

Where does J come from?

Idea of restriction of the phase space

- For low-energy states, we may consider only states in a restricted phase space.
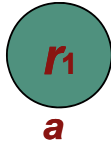
E

4s,4p,4d,4f
3s,3p,3d

2s,2p

1s

The 1s orbital of the Hydrogen atom

Let's consider the phase space spanned by spin states $|1s, \downarrow\rangle$, $|1s, \uparrow\rangle$
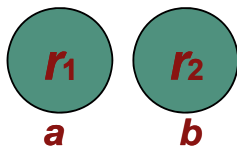
Atomic orbitals and molecular orbitals

- ## Atomic orbitals

$$\phi_a(r)\xi_\uparrow(1)$$

$$c_{a\uparrow}^\dagger|0\rangle$$

- ## Molecular orbitals (in LCAO)

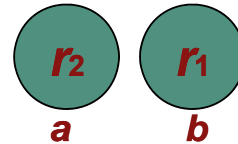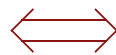$$\frac{1}{\sqrt{2}}\left(\phi_a(r) + \phi_b(r)\right)\xi_\uparrow(1)$$

$$\frac{1}{\sqrt{2}}\left(c_{a\uparrow}^\dagger + c_{b\uparrow}^\dagger\right)|0\rangle$$

The Heitler-London theory of H_2

Two electrons repel each other and each orbital ϕ_u ($u = a, b$) is occupied by an electron **A picture in the strong correlation limit!!**

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2) = \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \qquad\qquad \Psi_2(\mathbf{r}_1, \mathbf{r}_2) = \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)$$

$$\Longleftrightarrow$$
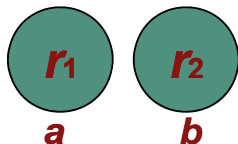
Note that there is no doubly occupied 1s orbital in this theory.

First key: Quantum states are linear combinations of Ψ_1 and Ψ_2 due to Pauli's principle.

(3) (4)

Singlet: $\Psi_+ = c_+(\Psi_1 + \Psi_2)$.
$(\mathbf{S}_1 + \mathbf{S}_2)^2 = 0$.
$E = E_+$.

Triplet: $\Psi_- = c_-(\Psi_1 - \Psi_2)$.
$(\mathbf{S}_1 + \mathbf{S}_2)^2 = 2$.
$E = E_-$.

Energy of spin states

Using following values, $E_\pm$ are obtained.

The orbital energy e_0 given by $\mathcal{H}\phi_u(\mathbf{r}) = e_0\phi_u(\mathbf{r})$. ($u = a, b$ and $\mathcal{H}$ is the Hamiltonian of an atom.)

An overlap integral $S = \int \phi_a^*(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r}$.

A Coulomb integral $U = \int \Psi_1^*(\mathbf{r}_1, \mathbf{r}_2)\left(\dfrac{e^2}{R_{ab}} + \dfrac{e^2}{r_{12}} - \dfrac{e^2}{r_{1b}} - \dfrac{e^2}{r_{2b}}\right)\Psi_1(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$.

An exchange integral $I = \int \Psi_1^*(\mathbf{r}_1, \mathbf{r}_2)\left(\dfrac{e^2}{R_{ab}} + \dfrac{e^2}{r_{12}} - \dfrac{e^2}{r_{1b}} - \dfrac{e^2}{r_{2b}}\right)\Psi_2(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$.

We have

$$E_+ = 2e_0 + \frac{U + I}{1 + S^2}, \qquad\qquad E_- = 2e_0 + \frac{U - I}{1 - S^2}.$$

Evaluation of J: Direct exchange

The triplet-singlet separation is evaluated as,

$$\Delta E = E_- - E_+ = 2\frac{US^2 - I}{1 - S^4}.$$

Second key: Energy separation between the magnetic state and the non-magnetic state can be as large as the Coulomb interaction.

The Heisenberg interaction is redescribed as,

$$H_{Heis} = -J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2 = -J_{12}\left[\frac{(\mathbf{S}_1 + \mathbf{S}_2)^2}{2} - \frac{3}{4}\right].$$

Energy of each state becomes $E_- = -\frac{1}{4}J_{12}$ for the triplets and $E_+ = \frac{3}{4}J_{12}$ for the singlet, which results $\Delta E = -J_{12}$ and thus,

$$J_{12} = -2\frac{US^2 - I}{1 - S^4}.$$

If $S = 0$, the interaction is ferromagnetic.

Ferromagnetic direct exchange I.

Consider atomic orbitals $\phi_u(\mathbf{r})$ which is real.

> "The exchange integral I is positive, *i.e.* it is ferromagnetic, when $S = 0$."

Proof: The definition of I is,

$$I = \int {}^*\phi_a(\mathbf{r}_1){}^*\phi_b(\mathbf{r}_2)\left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2b}}\right)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2 .$$

Let S=0, then we have,

$$I = \int \frac{e^2}{r_{12}}\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 .$$

Ferromagnetic direct exchange II.

- Exchange integral of two orthogonal orbitals with $S=0$ becomes ferromagnetic.

A proof: Consider the exchange integral when $S=0$.

$$I = \int dr_1 dr_2 \frac{e^2}{|r_1 - r_2|}\phi_a^*(r_1)\phi_b(r_1)\phi_b^*(r_2)\phi_a(r_2)$$

Note that the expression below.

$$\phi_a^*(r_1)\phi_b(r_1) = \mathrm{Re}\left(\phi_a^*(r_1)\phi_b(r_1)\right) + i\,\mathrm{Im}\left(\phi_a^*(r_1)\phi_b(r_1)\right)$$

$$I = \int dr_1 dr_2 \frac{e^2}{|r_1 - r_2|}\phi_a^*(r_1)\phi_b(r_1)\left(\phi_a^*(r_2)\phi_b(r_2)\right)^*$$

$$= \int dr_1 dr_2 \frac{e^2}{|r_1 - r_2|}\mathrm{Re}\left(\phi_a^*(r_1)\phi_b(r_1)\right)\times\mathrm{Re}\left(\phi_a^*(r_2)\phi_b(r_2)\right)$$

$$+ \int dr_1 dr_2 \frac{e^2}{|r_1 - r_2|}\mathrm{Im}\left(\phi_a^*(r_1)\phi_b(r_1)\right)\times\mathrm{Im}\left(\phi_a^*(r_2)\phi_b(r_2)\right)$$

To show the positivity of I, it is enough to consider an integral of real functions,

$$I = \int dr_1 dr_2 \frac{e^2}{|r_1 - r_2|}\Phi(r_1)\Phi(r_2)$$

Ferromagnetic direct exchange III.

Substitute next expressions into I.

$$\frac{e^2}{r} = \int d\mathbf{q}\frac{4\pi e^2}{q^2}\exp(i\mathbf{q}\cdot\mathbf{r}) \, ,$$

$$\Phi(\mathbf{r}) = \int d\mathbf{q}v(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}) \, .$$

Since Φ are real, $v^*(\mathbf{q}) = v(\text{-}\mathbf{q})$. Then, we can show,

$$
\begin{aligned}
I &= \int d\mathbf{r}_1 d\mathbf{r}_2 \int d\mathbf{q}\frac{4\pi e^2}{q^2}\exp(i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)) \\
&\quad \int d\mathbf{q}_1 v(\mathbf{q}_1)\exp(i\mathbf{q}_1\cdot\mathbf{r}_1)\int d\mathbf{q}_2 v(\mathbf{q}_2)\exp(i\mathbf{q}_2\cdot\mathbf{r}_2) \\
&= \int d\mathbf{q}\frac{4\pi e^2}{q^2}v(-\mathbf{q})v(\mathbf{q}) \\
&= \int d\mathbf{q}\frac{4\pi e^2}{q^2}v^*(\mathbf{q})v(\mathbf{q}) > 0 \, .
\end{aligned}
$$

Slater determinants for a system with two electrons I.

1. Triplet states   **a**   **b**

$$\langle\mathbf{r}_1,1;\mathbf{r}_2,2|S_{tot}=1,S_z=1\rangle = \langle\mathbf{r}_1,1;\mathbf{r}_2,2|\phi_a\uparrow,\phi_b\uparrow\rangle$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_a(\mathbf{r}_1)\xi_\uparrow(1) & \phi_a(\mathbf{r}_2)\xi_\uparrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\uparrow(1) & \phi_b(\mathbf{r}_2)\xi_\uparrow(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_a(\mathbf{r}_1) & \phi_a(\mathbf{r}_2) \\ \phi_b(\mathbf{r}_1) & \phi_b(\mathbf{r}_2)\end{vmatrix}\xi_\uparrow(1)\xi_\uparrow(2) \quad (1)$$

$$\langle\mathbf{r}_1,1;\mathbf{r}_2,2|S_{tot}=1,S_z=0\rangle = \langle\mathbf{r}_1,1;\mathbf{r}_2,2|S_{tot}^-|\phi_a\uparrow,\phi_b\uparrow\rangle$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_a(\mathbf{r}_1) & \phi_a(\mathbf{r}_2) \\ \phi_b(\mathbf{r}_1) & \phi_b(\mathbf{r}_2)\end{vmatrix}\frac{1}{\sqrt{2}}(\xi_\uparrow(1)\xi_\downarrow(2)+\xi_\downarrow(1)\xi_\uparrow(2))$$

$$= \frac{1}{2}\{(\phi_a(\mathbf{r}_1)\xi_\uparrow(1)\phi_b(\mathbf{r}_2)\xi_\downarrow(2) - \phi_b(\mathbf{r}_1)\xi_\uparrow(1)\phi_a(\mathbf{r}_2)\xi_\downarrow(2))$$

$$+ (\phi_a(\mathbf{r}_1)\xi_\downarrow(1)\phi_b(\mathbf{r}_2)\xi_\uparrow(2) - \phi_b(\mathbf{r}_1)\xi_\downarrow(1)\phi_a(\mathbf{r}_2)\xi_\uparrow(2))\}$$

$$= \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_a(\mathbf{r}_1)\xi_\uparrow(1) & \phi_a(\mathbf{r}_2)\xi_\uparrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\downarrow(1) & \phi_b(\mathbf{r}_2)\xi_\downarrow(2)\end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_a(\mathbf{r}_1)\xi_\downarrow(1) & \phi_a(\mathbf{r}_2)\xi_\downarrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\uparrow(1) & \phi_b(\mathbf{r}_2)\xi_\uparrow(2)\end{vmatrix}\right\} \quad (2)$$

Slater determinants for a system with two electrons II.

Thus,

$$\langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | S_{tot} = 1, S_z = 1, 0, -1 \rangle$$

$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1) & \phi_a(\mathbf{r}_2) \\ \phi_b(\mathbf{r}_1) & \phi_b(\mathbf{r}_2) \end{vmatrix} \begin{cases} \xi_\uparrow(1)\xi_\uparrow(2) \\ \frac{1}{\sqrt{2}}(\xi_\uparrow(1)\xi_\downarrow(2) + \xi_\downarrow(1)\xi_\uparrow(2)) \\ \xi_\downarrow(1)\xi_\downarrow(2) \end{cases} \tag{3}$$

2. Singlet states

We have another state which is orthogonal to $|S_{tot} = 1, S_z = 0\rangle$.

Multi Slater determinants

$$\langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | S_{tot} = 0, S_z = 0 \rangle$$

$$= \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1)\xi_\uparrow(1) & \phi_a(\mathbf{r}_2)\xi_\uparrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\downarrow(1) & \phi_b(\mathbf{r}_2)\xi_\downarrow(2) \end{vmatrix} - \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1)\xi_\downarrow(1) & \phi_a(\mathbf{r}_2)\xi_\downarrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\uparrow(1) & \phi_b(\mathbf{r}_2)\xi_\uparrow(2) \end{vmatrix} \right\}$$

$$= \frac{1}{2} \{ (\phi_a(\mathbf{r}_1)\xi_\uparrow(1)\phi_b(\mathbf{r}_2)\xi_\downarrow(2) - \phi_b(\mathbf{r}_1)\xi_\uparrow(1)\phi_a(\mathbf{r}_2)\xi_\downarrow(2))$$

$$- (\phi_a(\mathbf{r}_1)\xi_\downarrow(1)\phi_b(\mathbf{r}_2)\xi_\uparrow(2) - \phi_b(\mathbf{r}_1)\xi_\downarrow(1)\phi_a(\mathbf{r}_2)\xi_\uparrow(2)) \}$$

$$= \frac{1}{\sqrt{2}} (\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)) \frac{1}{\sqrt{2}} \begin{vmatrix} \xi_\uparrow(1) & \xi_\uparrow(2) \\ \xi_\downarrow(1) & \xi_\downarrow(2) \end{vmatrix} \tag{4}$$

Spin states in the second quantization

In the second-quantization description,

$$\langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | S_{tot} = 1, S_z = 1 \rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1)\xi_\uparrow(1) & \phi_a(\mathbf{r}_2)\xi_\uparrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\uparrow(1) & \phi_b(\mathbf{r}_2)\xi_\uparrow(2) \end{vmatrix}$$

$$\longrightarrow |S_{tot} = 1, S_z = 1\rangle = c_{a,\uparrow}^\dagger c_{b,\uparrow}^\dagger |0\rangle$$

Similarly,

$$|S_{tot} = 1, S_z = 0\rangle = \frac{1}{\sqrt{2}} (c_{a,\uparrow}^\dagger c_{b,\downarrow}^\dagger + c_{a,\downarrow}^\dagger c_{b,\uparrow}^\dagger) |0\rangle$$

$$|S_{tot} = 1, S_z = -1\rangle = c_{a,\downarrow}^\dagger c_{b,\downarrow}^\dagger |0\rangle$$

$$|S_{tot} = 0, S_z = 0\rangle = \frac{1}{\sqrt{2}} (c_{a,\uparrow}^\dagger c_{b,\downarrow}^\dagger - c_{a,\downarrow}^\dagger c_{b,\uparrow}^\dagger) |0\rangle$$

2-electrons in molecular orbitals

Let us consider two electrons in the bonding orbital.

$$\langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \uparrow, \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \downarrow\rangle$$

$$= \frac{1}{2}(\phi_a(\mathbf{r}_1) + \phi_b(\mathbf{r}_1))(\phi_a(\mathbf{r}_2) + \phi_b(\mathbf{r}_2))\frac{1}{\sqrt{2}}\begin{vmatrix} \xi_\uparrow(1) & \xi_\uparrow(2) \\ \xi_\downarrow(1) & \xi_\downarrow(2) \end{vmatrix}$$

$$\longrightarrow |\frac{1}{\sqrt{2}}(\phi_a + \phi_b) \uparrow, \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \downarrow\rangle$$

$$= \frac{1}{2}(c_{a,\uparrow}^\dagger + c_{b,\uparrow}^\dagger)(c_{a,\downarrow}^\dagger + c_{b,\downarrow}^\dagger)|0\rangle \tag{5}$$

If we expand eq. (5), we obtain,

$$|\frac{1}{\sqrt{2}}(\phi_a + \phi_b) \uparrow, \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \downarrow\rangle$$

$$= \frac{1}{\sqrt{2}}\left\{ \frac{1}{\sqrt{2}}(c_{a,\uparrow}^\dagger c_{b,\downarrow}^\dagger - c_{a,\downarrow}^\dagger c_{b,\uparrow}^\dagger)|0\rangle + \frac{1}{\sqrt{2}}(c_{a,\uparrow}^\dagger c_{a,\downarrow}^\dagger + c_{b,\uparrow}^\dagger c_{b,\downarrow}^\dagger)|0\rangle\right\} \tag{6}$$

The Heitler-London wf.   **Ionic states!**

The Heitler-London state v.s. the molecular orbitals

We can consider a trial (variational) state in which ionic states are mixed with the Heitler-London wavefunction.

$$|S_{tot} = 0; \alpha\rangle$$
$$= \frac{1}{\sqrt{1+\alpha^2}}\left\{ \frac{1}{\sqrt{2}}(c_{a,\uparrow}^\dagger c_{b,\downarrow}^\dagger - c_{a,\downarrow}^\dagger c_{b,\uparrow}^\dagger)|0\rangle + \frac{\alpha}{\sqrt{2}}(c_{a,\uparrow}^\dagger c_{a,\downarrow}^\dagger + c_{b,\uparrow}^\dagger c_{b,\downarrow}^\dagger)|0\rangle\right\} \tag{7}$$

1. $\alpha = 0$: the Heiter-London wavefunction (Localized electron picture)

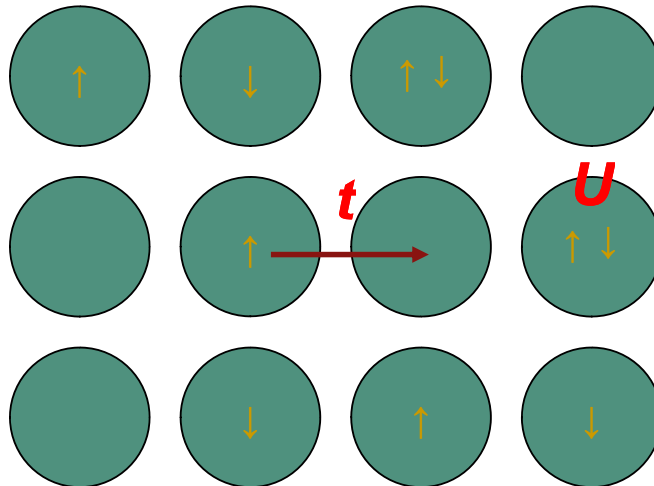2. $\alpha = 1$: the doubly-occupied bonding state (Delocalized electron picture)

The true w.f. is close to a variational state with 0<α<1.

α is dependent on the inter-electron interaction or choice of the model (interaction parameters etc.).

The Hubbard model : I.

The Hubbard model : II.

1) The Bloch function

For crystals, the single particle wave function $\phi_{i,\sigma}(\mathbf{r})$ is given in a Bloch form as,

$$\phi_{n,\mathbf{k},\sigma}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n,\sigma}(\mathbf{r}) ,$$

where n and $\mathbf{k}$ are the band index and the wave vector, respectively. $u_{n,\sigma}(\mathbf{r})$ is a function with periodicity of the lattice. $\phi_{n,\mathbf{k},\sigma}$ satisfies,

$$\left\{ -\frac{\hbar^2}{2m}\Delta_{\mathbf{r}} + v_{\text{eff}}(\mathbf{r}) \right\} \phi_{n,\mathbf{k},\sigma}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}}\phi_{n,\mathbf{k},\sigma}(\mathbf{r}) .$$

2) The Wannier function

A localized function at a lattice point $\mathbf{r}_i$ can be made as,

$$\phi_{n,\sigma}(\mathbf{r} - \mathbf{r}_i) = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{r}_i}\phi_{n,\mathbf{k},\sigma}(\mathbf{r})$$

Notes:
1) $\phi_{n,\mathbf{k},\sigma}(\mathbf{r})$ (and $\phi_{n,\sigma}(\mathbf{r} - \mathbf{r}_i)$) give an orthonormal complete set.
2) The definition of the Wannier func. has a degree of freedom.
   Cf. Marzari and Vanderbilt, PRB **56** (1997) 12847.

The Hubbard model : III.

Introduce creation (annihilation) operators $c^\dagger_{n\mathbf{k}\sigma}$ ($c_{n\mathbf{k}\sigma}$) satisfying

$$\psi^\dagger_\sigma(\mathbf{r}) = \sum_{n\mathbf{k}} \phi^*_{n,\mathbf{k},\sigma}(\mathbf{r}) c^\dagger_{n\mathbf{k}\sigma} \, ,$$

the effective Hamiltonian is written as,

$$\hat{H}_{\text{eff}} = \sum_{n\mathbf{k}\sigma} \varepsilon_{n,\mathbf{k}} c^\dagger_{n\mathbf{k}\sigma} c_{n\mathbf{k}\sigma} \, .$$

Introduce a unitary transformation,

$$c_{ni\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \sum_m e^{i\mathbf{k}\mathbf{r}_i} U^{-1}_{mn}(\mathbf{k}) c_{m\mathbf{k}\sigma}$$

$$c^\dagger_{ni\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \sum_m e^{-i\mathbf{k}\mathbf{r}_i} U_{nm}(\mathbf{k}) c^\dagger_{m\mathbf{k}\sigma} \, .$$

The effective Hamiltonian is rewritten as,

$$\hat{H}_{\text{eff}} = \sum_{nmij} \sum_\sigma t^{nm}_{ij} (c^\dagger_{ni\sigma} c_{mj\sigma} + \text{H.c.})$$

This model is called the tight-binding model, where $t^{nm}_{ij} = \frac{1}{N} \Sigma_{\mathbf{k}} \, e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} U^{-1}_{nl}(\mathbf{k}) \varepsilon_{l,\mathbf{k}} U_{lm}(\mathbf{k})$.

The Hubbard model : IV.

Consider the Hartree approximation to make an effective potential. (The method below is applicable for the Hartree-Fock approximation, but we need another formulation for DFT.)

$$\hat{H}_0 = \sum_{n,\mathbf{k},\sigma} \varepsilon_{n,\mathbf{k}} c^\dagger_{n\mathbf{k}\sigma} c_{n\mathbf{k}\sigma}$$

$$\hat{H}_1 = \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\mathbf{r}) \psi^\dagger_{\sigma'}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}') \psi_\sigma(\mathbf{r})$$

$$- \left[\int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho(\mathbf{r}) \sum_\sigma \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) - \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho(\mathbf{r}) \rho(\mathbf{r}') \right]$$

Expand $\psi^\dagger_\sigma(\mathbf{r})$ ($\psi_\sigma(\mathbf{r})$) into $c^\dagger_{n\mathbf{k}\sigma}$ ($c_{n\mathbf{k}\sigma}$), utilize the unitary transformation into $c^\dagger_{ni\sigma}$ ($c_{ni\sigma}$), then H_1 is rewritten as,

$$\hat{H}_1 = \frac{1}{2} \sum_{ijkl} \sum_{m_1 \cdots m_4} \sum_{\sigma\sigma'} (m_1 i, m_2 j | \frac{1}{r} | m_3 k, m_4 l) c^\dagger_{m_1 i\sigma} c^\dagger_{m_2 j\sigma'} c_{m_3 k\sigma'} c_{m_4 l\sigma}$$

$$- \sum_{ijkl} \sum_{m_1 \cdots m_4} \sum_\sigma (m_1 i, m_2 j | \frac{1}{r} | m_3 k, m_4 l) \nu_{m_2 j m_3 k} c^\dagger_{m_1 i\sigma} c_{m_4 l\sigma}$$

$$+ \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \rho(\mathbf{r}) \rho(\mathbf{r}')$$

where $\nu_{m_1 i m_2 j} = (1/N) \Sigma_{n\mathbf{k}} \, e^{-i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} U_{nm_1}(\mathbf{k}) \langle n_{n\mathbf{k}} \rangle U^{-1}_{nm_2}(\mathbf{k})$.

The Hubbard model : V.

Consider a single band model with well-localized Wannier orbitals. The local interactions are classified into groups. Hubbard estimated the values as follows. (Hubbard 1963)

1. Intra-orbital repulsion: $U = (ii|\frac{1}{r}|ii) \sim 20$ eV
2. Inter-orbital repulsion: $V = (ij|\frac{1}{r}|ji) \sim 6$ eV
3. Correlated hopping: $X = (ii|\frac{1}{r}|ji) \sim 1/2$ eV
4. Off-site corr. hop.: $X' = (ij|\frac{1}{r}|ki) \sim 1/20$ eV
5. Inter-orbital exchange: $J = (ij|\frac{1}{r}|ij) \sim 1/40$ eV
6. Pair hopping: $J' = (ii|\frac{1}{r}|jj) \sim 1/40$ eV

Note that we may utilize screened values, if we consider screening effects due to electrons in other bands. Usually the counter term with ν_{ij} is assumed to be irrelavant for discussion of low-energy phenomena.

Thus, we may utilize the Hubbard model

$$H = - \sum_{\langle i,j \rangle} \sum_{\sigma} t_{i,j}(c_{i,\sigma}^{\dagger}c_{j,\sigma} + \text{H.c.}) + U \sum_{i} n_{i,\uparrow}n_{i,\downarrow}$$

for the discussion of magnetism.

The Hubbard model : VI.

Introduce a creation operator (an annihilation operator) $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) for each local orbital. They satisfy commutation relation.

$$\{c_{i,\sigma}, c_{j,\sigma'}^{\dagger}\} = \delta_{i,j}\delta_{\sigma,\sigma'} .$$

The Hubbard model is given by,

$$H = - \sum_{\langle i,j \rangle} \sum_{\sigma} t_{i,j}(c_{i,\sigma}^{\dagger}c_{j,\sigma} + \text{H.c.}) + U \sum_{i} n_{i,\uparrow}n_{i,\downarrow}$$

- $t_{i,j}$: Transfer integral
- U : The Hubbard interaction parameter
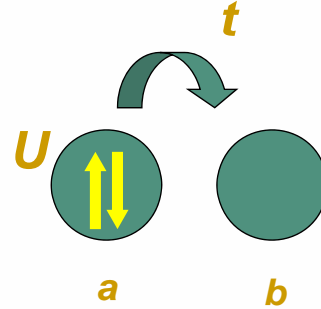
2-site Hubbard model : I.

Consider a 2-site Hubbard model.
Each site allows 4 states, $|0\rangle$, $c^\dagger_{i,\uparrow}|0\rangle$, $c^\dagger_{i,\downarrow}|0\rangle$, and $c^\dagger_{i,\uparrow}c^\dagger_{i,\downarrow}|0\rangle$. $(i = a, b)$

- States available : $4^2 = 16$

- States with 2 electrons : 6.

- States with one $\uparrow$ spin and one $\downarrow$ spin : 4.

We consider the next 4 states.

- $|a,\uparrow; b,\downarrow\rangle \equiv c^\dagger_{a,\uparrow}c^\dagger_{b,\downarrow}|0\rangle$.

- $|a,\downarrow; b,\uparrow\rangle \equiv c^\dagger_{a,\downarrow}c^\dagger_{b,\uparrow}|0\rangle$.

- $|a,\uparrow,\downarrow; b,0\rangle \equiv c^\dagger_{a,\uparrow}c^\dagger_{a,\downarrow}|0\rangle$.

- $|a,0; b,\uparrow,\downarrow\rangle \equiv c^\dagger_{b,\uparrow}c^\dagger_{b,\downarrow}|0\rangle$.

2-site Hubbard model : II.

The Hamiltonian is given by,

$$H = -t\sum_\sigma(c^\dagger_{b,\sigma}c_{a,\sigma} + c^\dagger_{a,\sigma}c_{b,\sigma}) + U\sum_{i=a,b} n_{i,\uparrow}n_{i,\downarrow} \tag{8}$$

A matrix representation of H in terms of the above 4 states are,

$$H \doteq \begin{bmatrix} 0 & 0 & t & t \\ 0 & 0 & -t & -t \\ t & -t & U & 0 \\ t & -t & 0 & U \end{bmatrix} \tag{9}$$

Using a unitary transformation U which gives spin eigen states,

- $|S_{tot} = 0, \alpha\rangle \equiv \frac{1}{\sqrt{2}}(c^\dagger_{a,\uparrow}c^\dagger_{b,\downarrow} - c^\dagger_{a,\downarrow}c^\dagger_{b,\uparrow})|0\rangle$.

- $|S_{tot} = 0, \beta\rangle \equiv \frac{1}{\sqrt{2}}(c^\dagger_{a,\uparrow}c^\dagger_{a,\downarrow} + c^\dagger_{b,\uparrow}c^\dagger_{b,\downarrow})|0\rangle$.

- $|S_{tot} = 0, \gamma\rangle \equiv \frac{1}{\sqrt{2}}(c^\dagger_{a,\uparrow}c^\dagger_{a,\downarrow} - c^\dagger_{b,\uparrow}c^\dagger_{b,\downarrow})|0\rangle$.

- $|S_{tot} = 1, S_z = 0\rangle \equiv \frac{1}{\sqrt{2}}(c^\dagger_{a,\uparrow}c^\dagger_{b,\downarrow} + c^\dagger_{a,\downarrow}c^\dagger_{b,\uparrow})|0\rangle$.

2-site Hubbard model : III.

U is defined by,

$$U \doteq \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{bmatrix} \qquad (10)$$

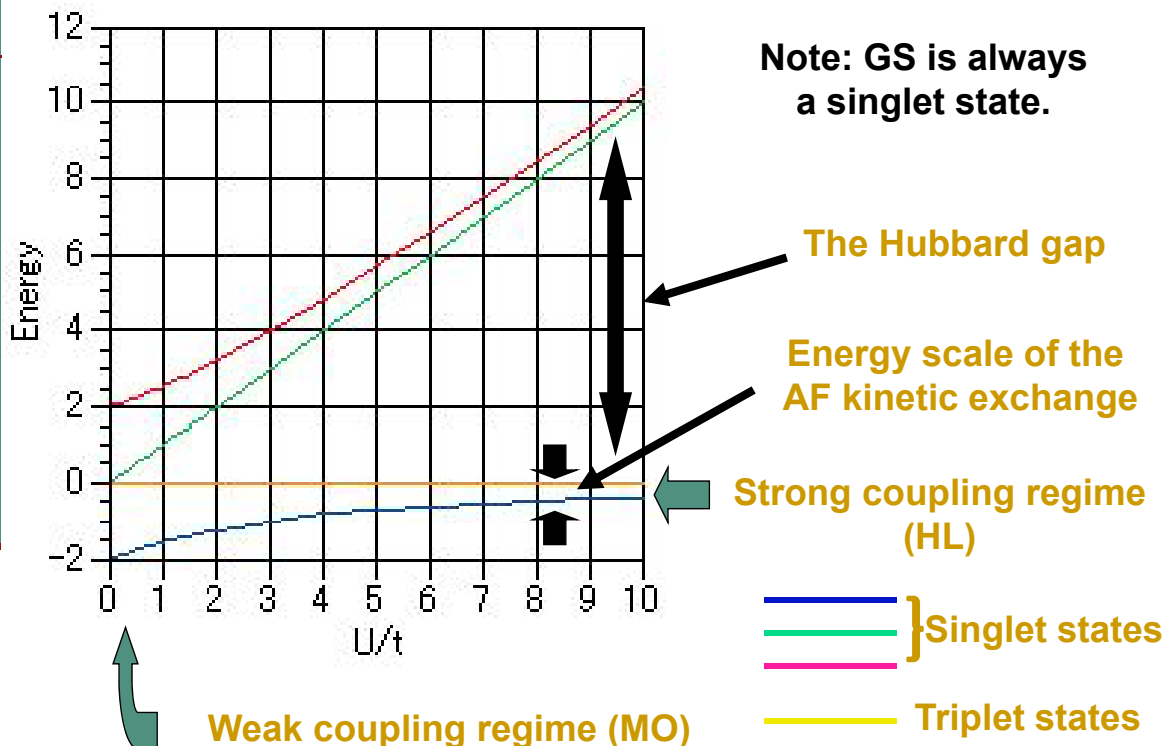Then, we have a block-diagonalized H,

$$U^{-1}HU \doteq \begin{bmatrix} 0 & 2t & 0 & 0 \\ 2t & U & 0 & 0 \\ 0 & 0 & U & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad (11)$$

and eigen values are

- $E_1 = \frac{1}{2}\left(U - \sqrt{U^2 + 16t^2}\right) \sim -\frac{4t^2}{U}$.
- $E_2 = \frac{1}{2}\left(U + \sqrt{U^2 + 16t^2}\right) \sim U + \frac{4t^2}{U}$.
- $E_3 = U$.   • $E_4 = 0$.

Crossover from weak coupling regime to strong coupling regime

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2-site Hubbard model : IV.

Note: GS is always a singlet state.

The Hubbard gap

Energy scale of the AF kinetic exchange

Strong coupling regime (HL)

Weak coupling regime (MO)

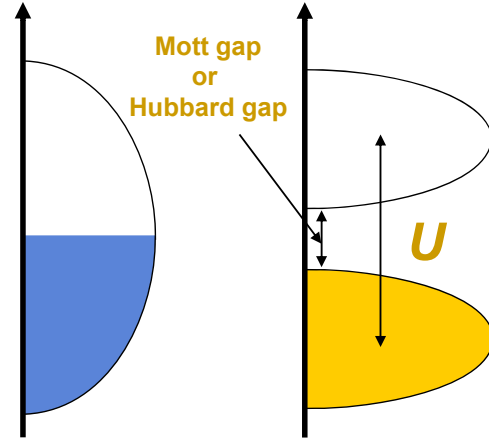**} Singlet states**

Triplet states

Concept of the Mott insulator

- Electron transfer from an orbital to an occupied orbital is prohibited by the Coulomb repulsion. This leads to an insulating state.
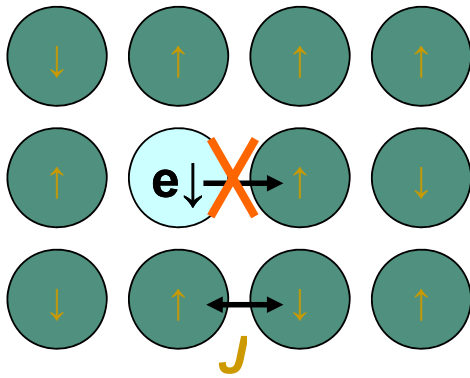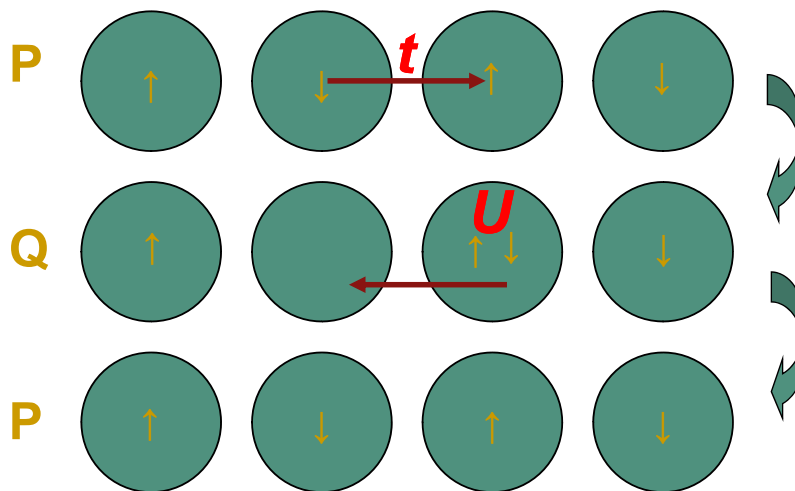

The half-filled Hubbard model shows the Mott insulating ground state.

Formation of the Mott gap in the single particle excitation.

The kinetic exchange

- Effective interaction at around $U=\infty$

We have another process starting from transfer of the up spin moving to the neighboring site.

$$H_{eff} = \frac{2t^2}{U} \sum_{\langle i,j \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4})$$

Antiferromagnetic Heisenberg model.

Superexchange interaction

- In the transition-metal oxides, there is a structure of M-O-M (M: transition metal, O: oxygen）. Along this structure, two localized spins couples via the superexchane through non-magnetic oxygen atom.

Often, Mott insulator is formed.
→ M has an open d-shell.

d_{x2-y2} @ M

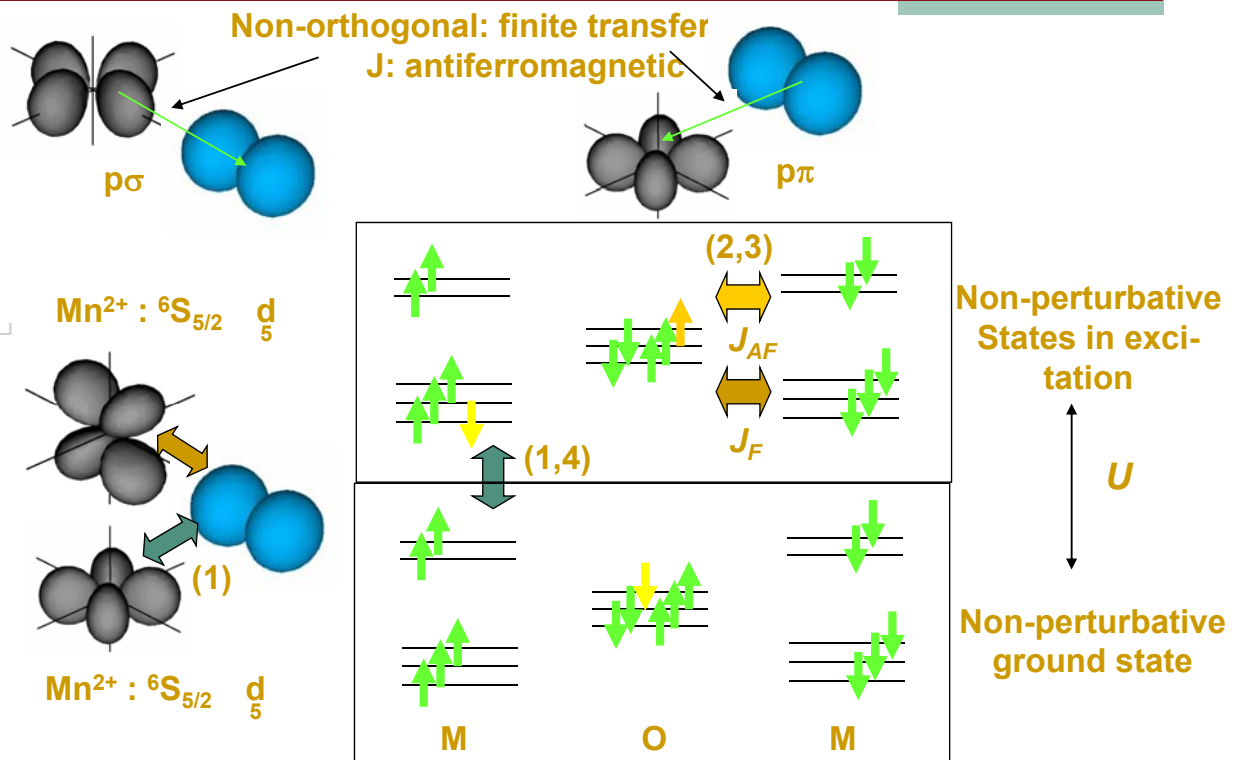p_x @ O

d_{x2-y2} @ M

J_{AF}
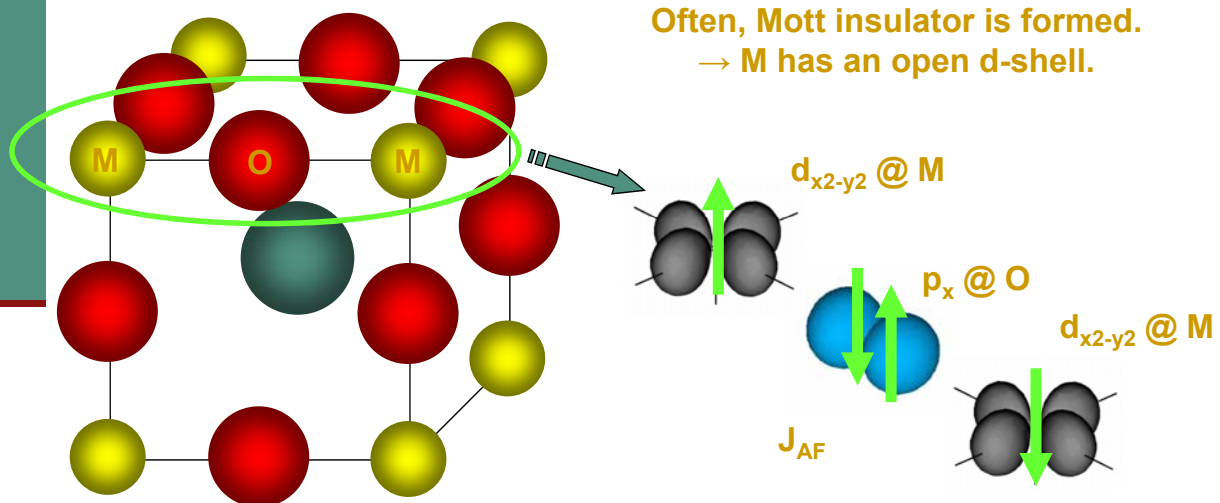
The Kanamori-Goodenough rule

- Consider description by non-orthogonalized atomic orbitals (LCAO picture)
- The electron transfer is possible from O to M when two neiboring orbitals are not orthogonal.
- The sign of exchange interaction between d and p is,
  - Ferromagnetic if two orbitals are orthogonal with each other,
  - Antiferromagnetic if two orbitals are not orthogonal
- Occupation of d-orbitals are determined by the crystal field splitting and the Hund rule.

Following the above rule, we can determine the sign of superexchange in a qualitative manner.

P.W. Anderson reformulated the rule using the orthogonalized Wannier basis allowing the second quantization scheme.

Exanple of antiferromagnetic exchange

Non-orthogonal: finite transfer
J: antiferromagnetic

$p\sigma$

$p\pi$

Mn^{2+} : $^6S_{5/2}$ d_5

Mn^{2+} : $^6S_{5/2}$ d_5

(1)

(2,3)

J_{AF}

J_F

(1,4)

M   O   M

Non-perturbative States in exci- tation

U

Non-perturbative ground state

Various types of exchange interaction

- Direct exchange : (Cf. Heitler-London theory)
- Kinetic exchange : (Cf. the Hubbard model)
- Super exchange
- Double exchange
- RKKY interaction
- Anisotropic exchange interaction
- Dzyaloshinsky-Moriya interaction

1. **Exchange interactions except for the 1st one are effective interactions.**
2. **Effective interactions can be derived from a model with local interactions.**