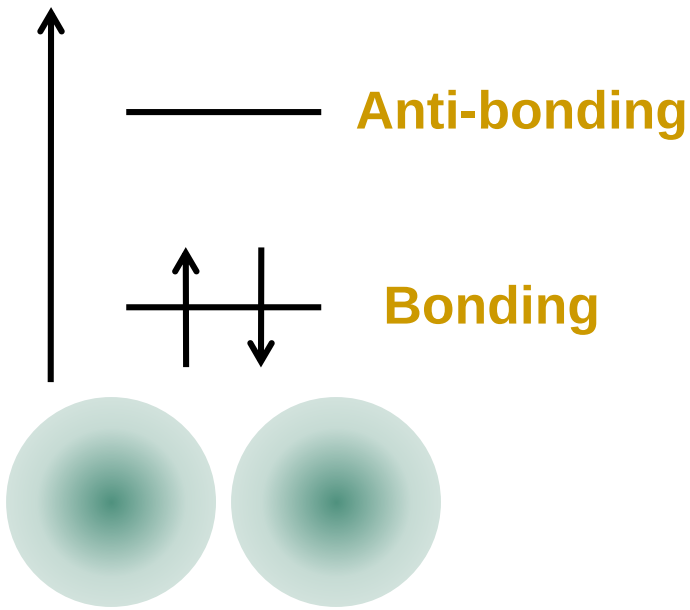
The 32th CMD workshop "Advanced study with ES-opt"

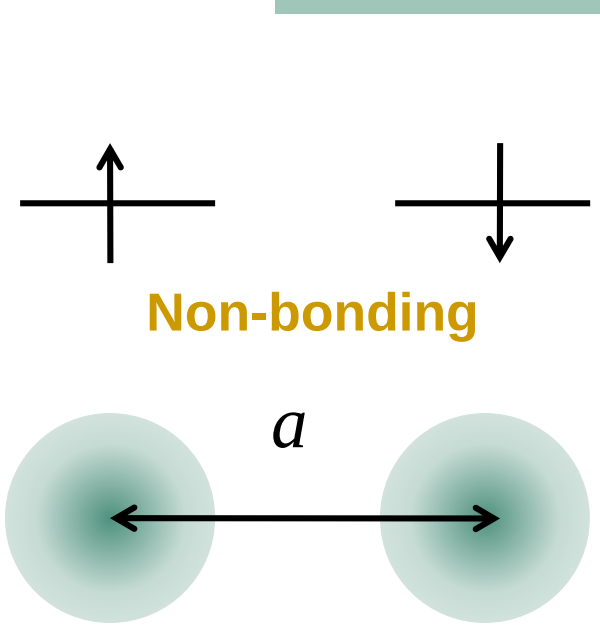
Multi-reference DFT

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

Electronic structure of diatomic molecules



Molecular orbital picture

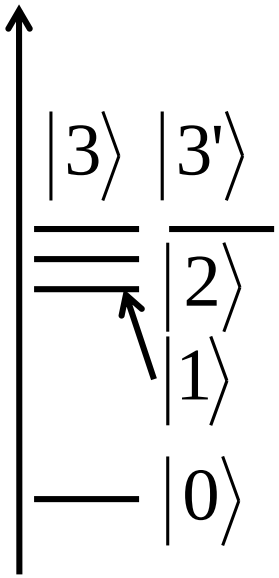


Heitler-London picture

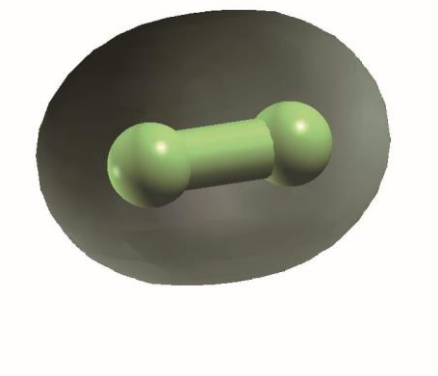
Known results in DFT-LDA

- **Molecular orbital picture is given for any inter-atomic distance.**
- **The stable electronic state in equilibrium is well-reproduced.**

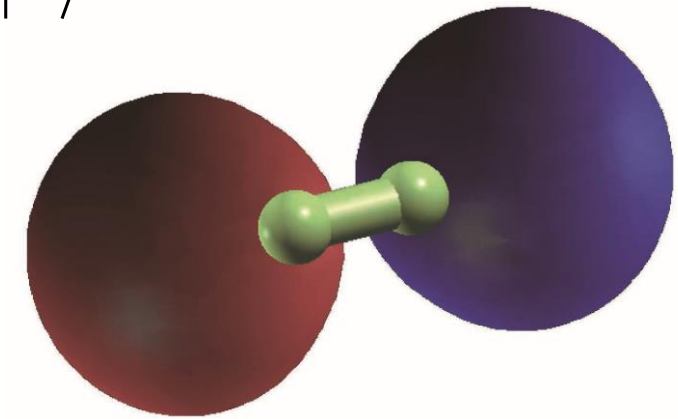
Molecular orbital given by DFT-LDA



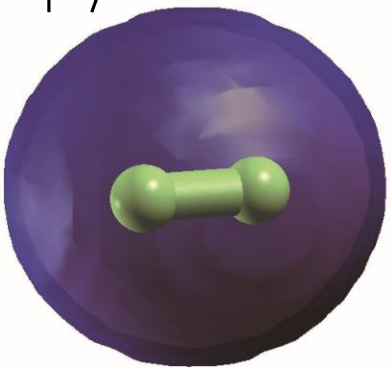
$|0\rangle$ **1s bonding**



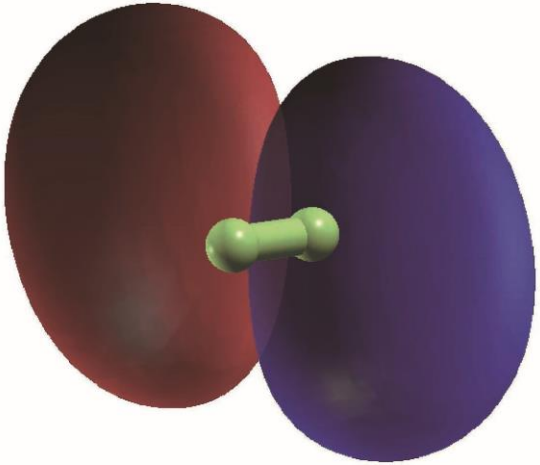
$|2\rangle$ **1s anti-bonding**



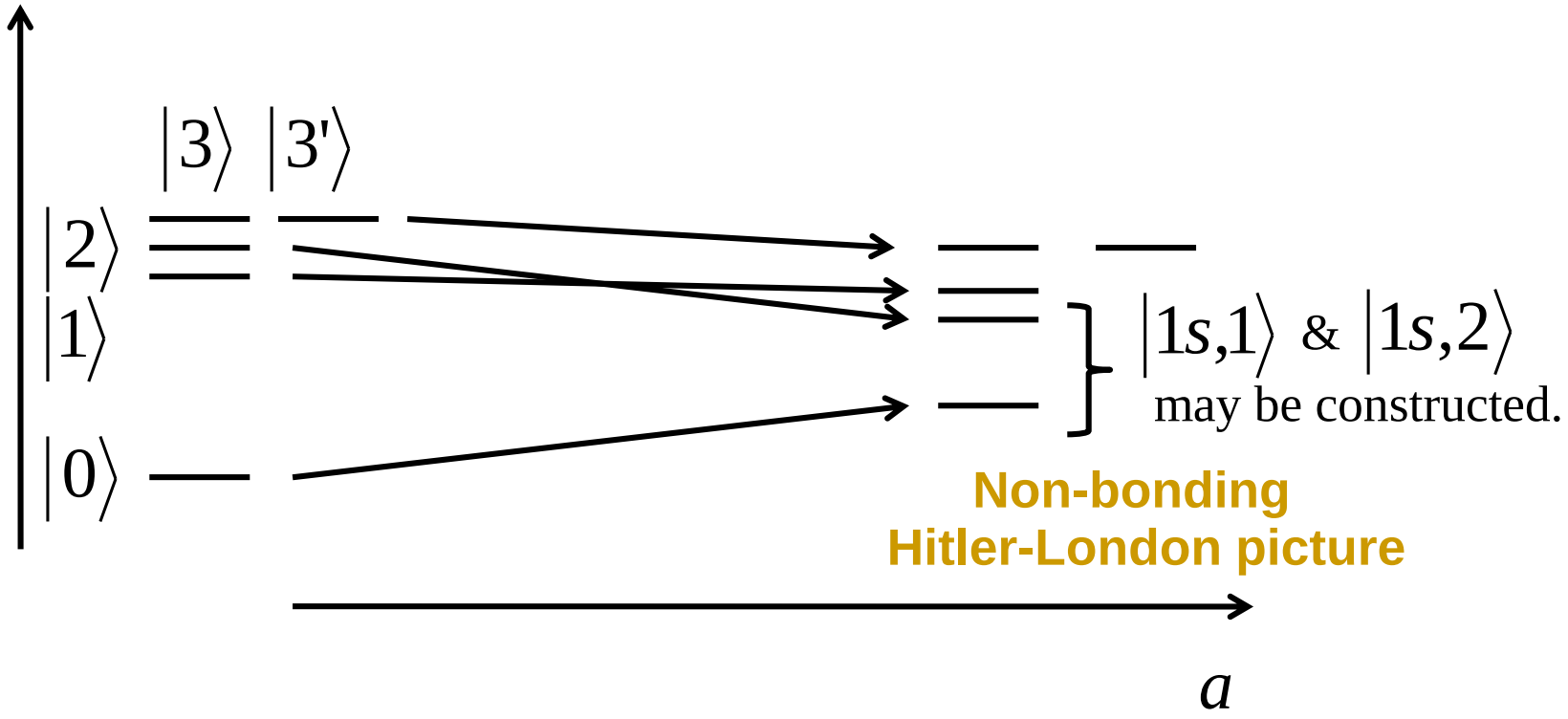
$|1\rangle$



$|3\rangle$



Dependence on inter-atomic distance



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,

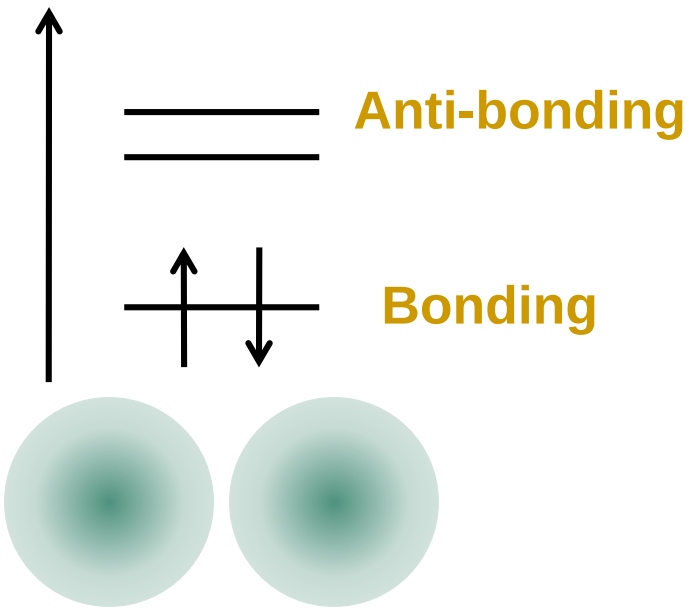
$$E_{xc}[n] = \frac{e^2}{2}\int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} n_{xc}(\mathbf{r},\mathbf{r}')$$

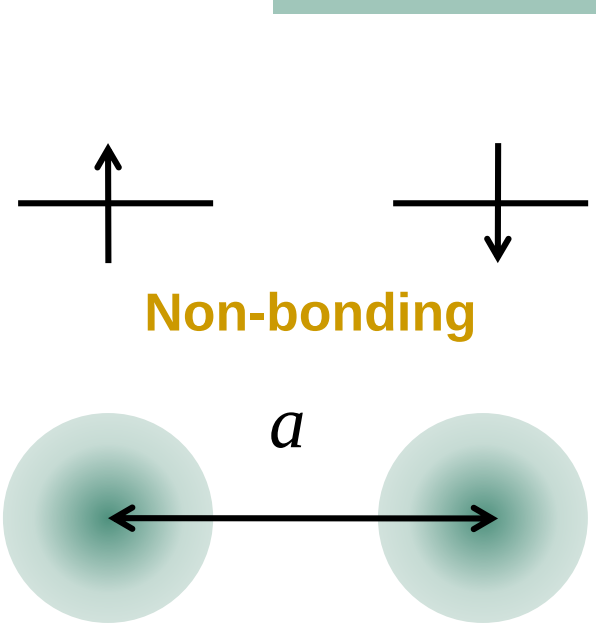
$$n_{xc}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}')\int_0^1 [g_n(\mathbf{r},\mathbf{r}',\lambda) - \delta(\mathbf{r}-\mathbf{r}')]d\lambda$$

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

Charge fluctuation!

H_2

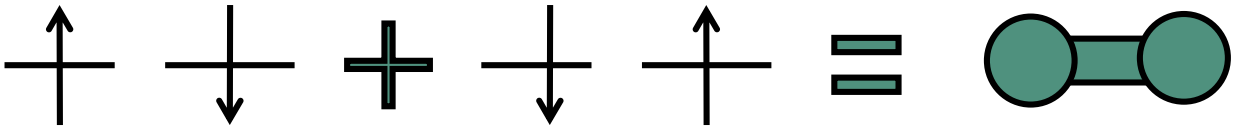




This is a weak correlation limit!

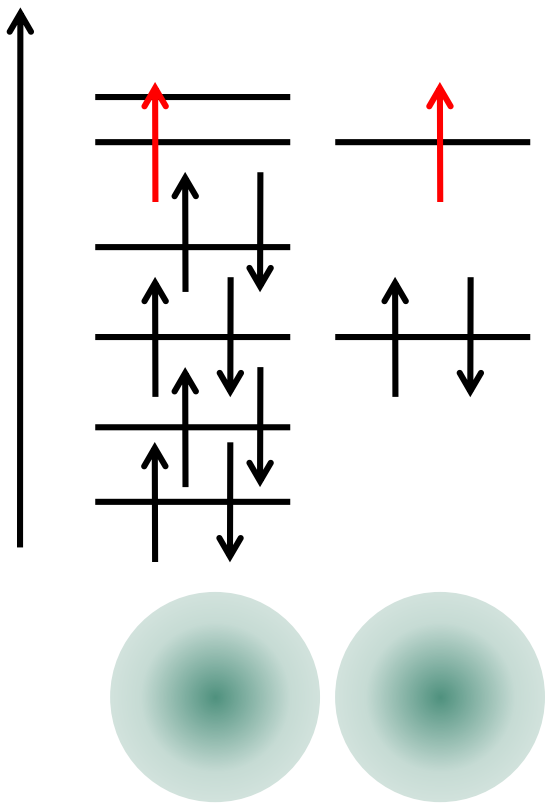
This is a strong correlation limit!

In real nature & in CI, we have

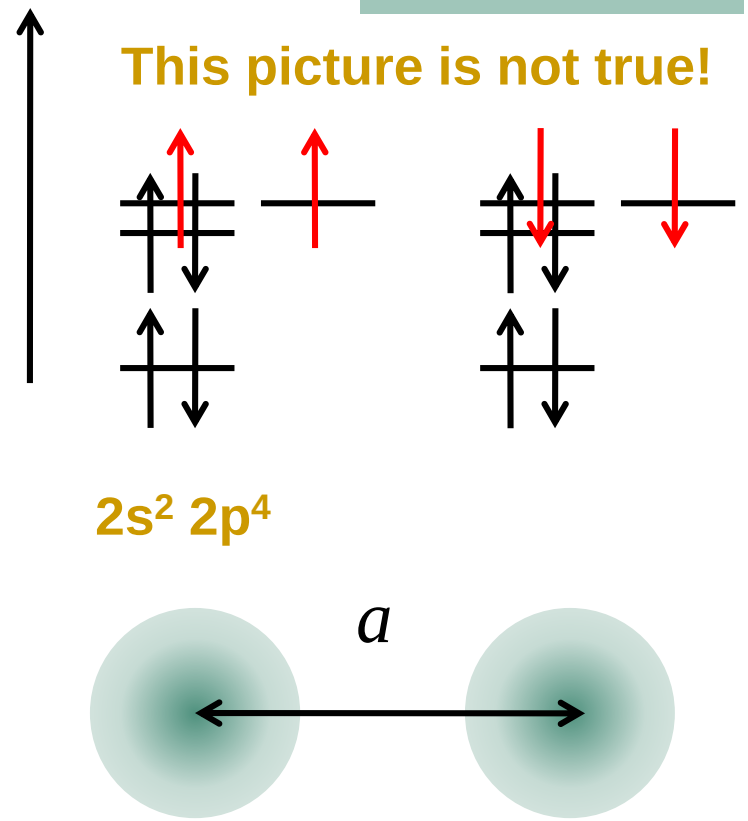


Quantum mechanical superposition

O_2



This picture is not true!



S=1 ground state!

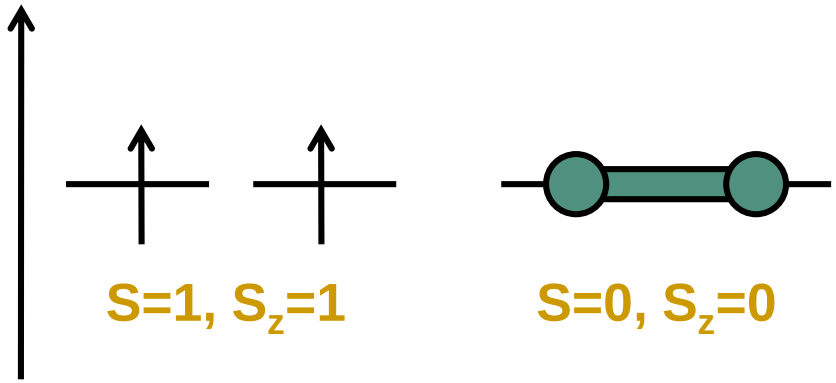
This is a strong correlation limit!

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.



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

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

- Variational energy : DFVT

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

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

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

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

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

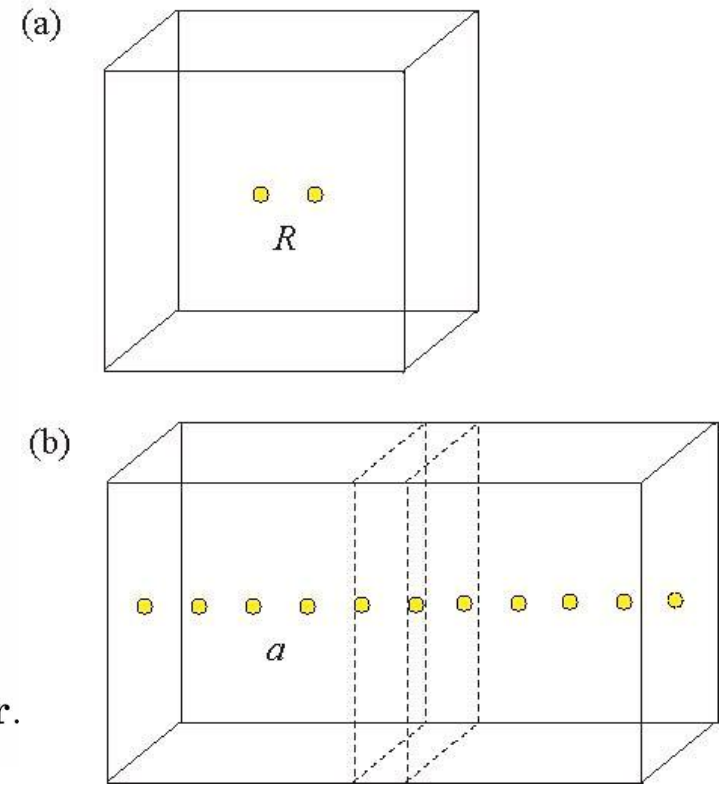
for the molecule and the Wannier state

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

for a chain with N atoms.

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

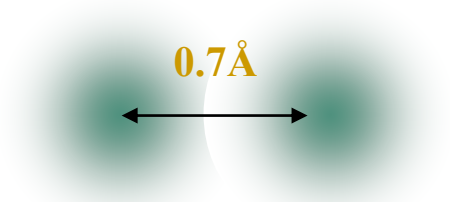
H_2 Molecule



Hydrogen array

Local fluctuation on ϕ_{1s} of H_2

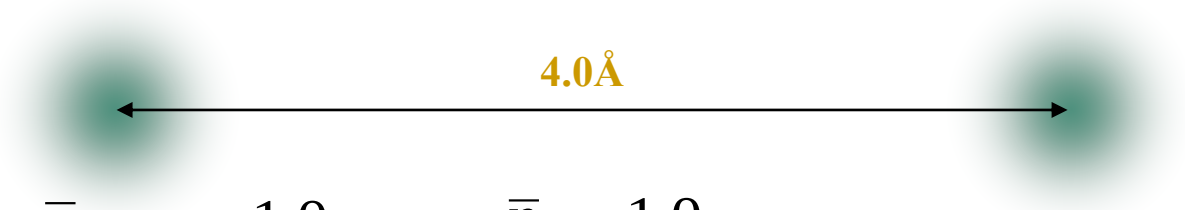
$\left\langle \underline{n}_i^2 \right\rangle = \left\langle \left(n_{i\uparrow} + n_{i\downarrow} - \left\langle n_{i\uparrow} \right\rangle - \left\langle n_{i\downarrow} \right\rangle \right)^2 \right\rangle$ **as a function of the inter atomic distance**



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

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

Small U regime



$\bar{n}_{bonding} = 1.0$ $\quad$ $\bar{n}_{1s} = 1.0$

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

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.**

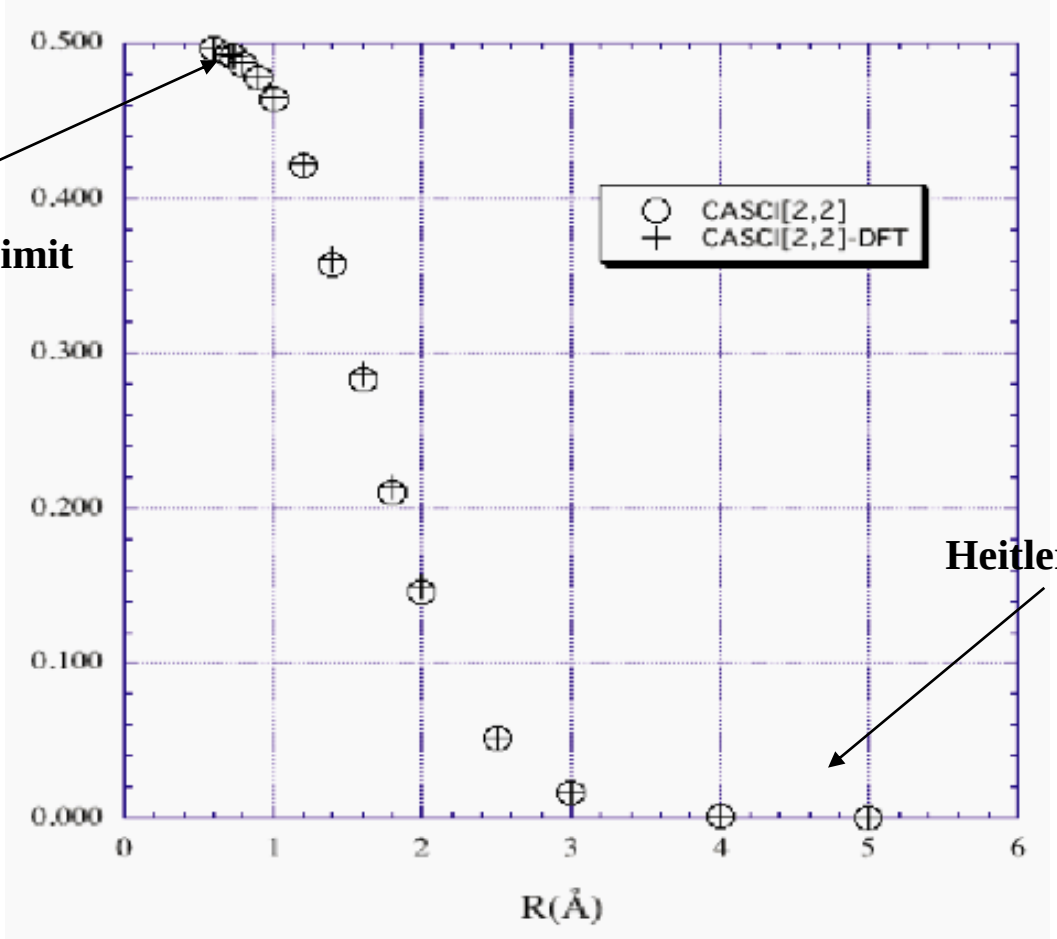
Orbital fluctuation in CI calculation

CAS-CI calculation for H_2 by S. Yamanaka.

Small *U/t*
***U* ∼ 0.7eV**

Molecular orbital limit

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



Heitler-London limit

Large *U/t*
***U* ∼ 10eV**

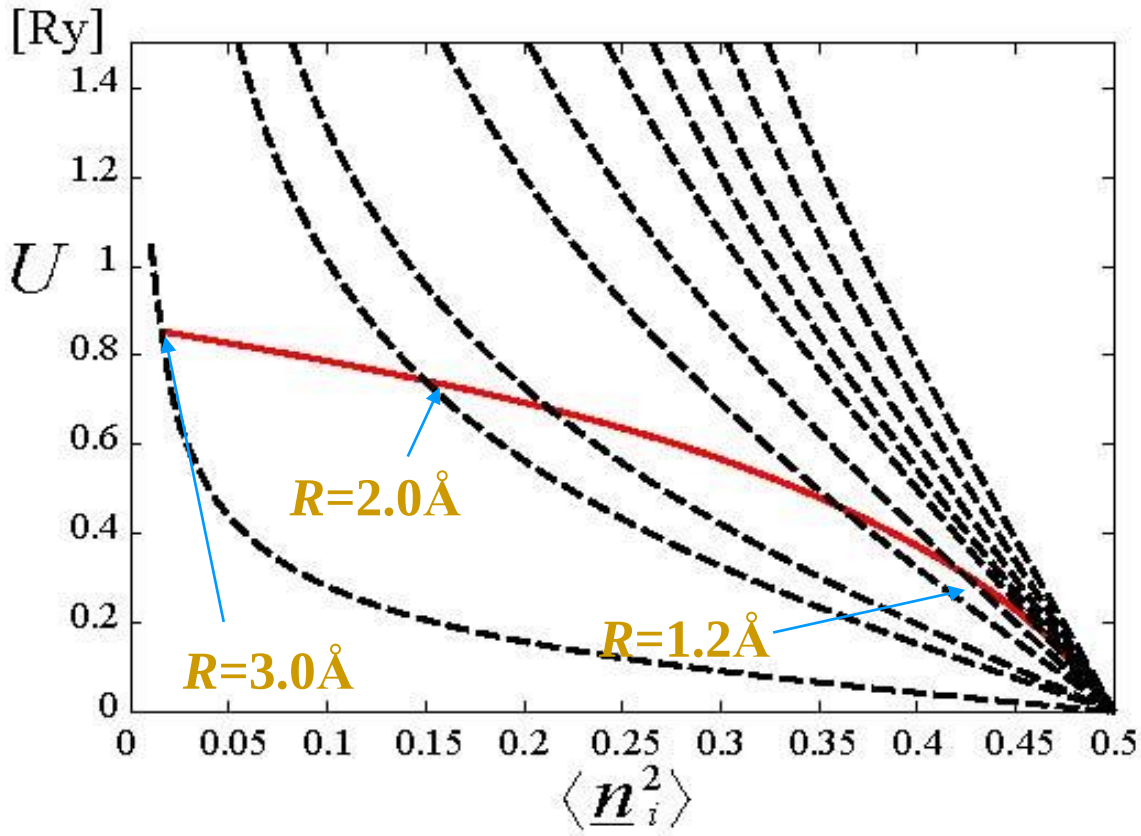
In the whole range, mean occupation of 1s is 1.

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

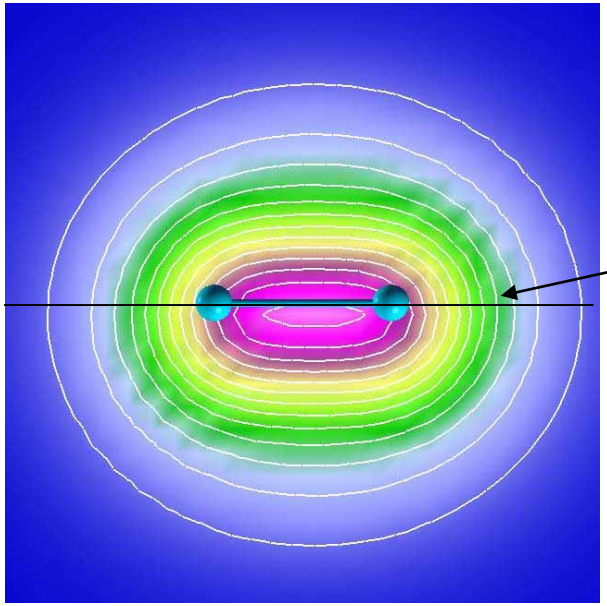
Reference calculation: CASCI method for H_2



The 1st method to have U by the fluctuation reference method.

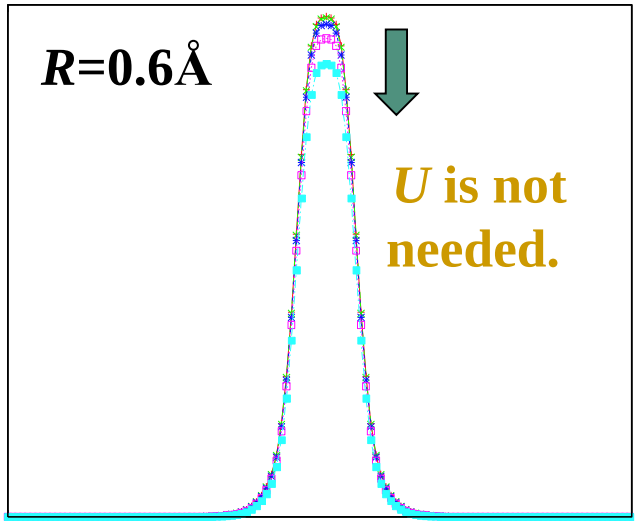
K. Kusakabe, et al. J. Phys.: Condens. Matter (2007).

Charge density of H_2 given by MR-DFT

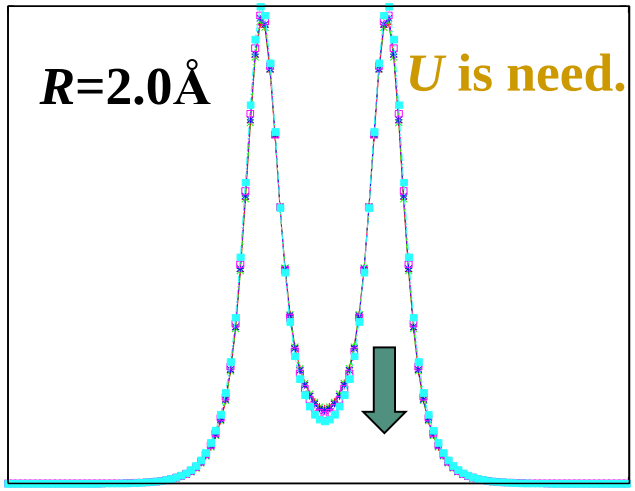


This section is Shown in the right panels.

Weak correlation regime



Strong correlation regime



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

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

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

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

DFT model formation

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

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

PBE0+GW, PBE0+U will be refined.

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.

To understand MR-DFT

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

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

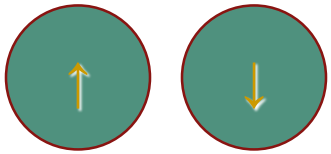
This functional contains the universal energy-density functional F[n]

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

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

Heisenberg exchange: Introduction to the localized spin model

- Heisenberg and Dirac considered quantum mechanical origin of magnetic interaction



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

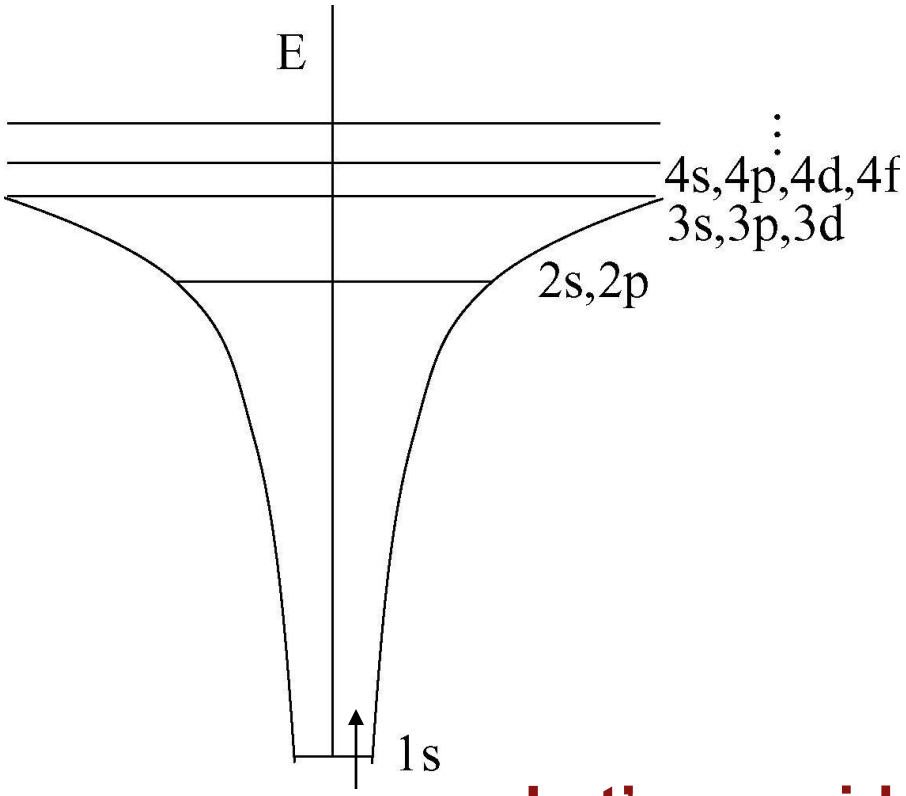
J>0 : Parallel spin configuration
Ferromagnetic
J<0 : Anti-parallel spin configuration
Antiferromagnetic

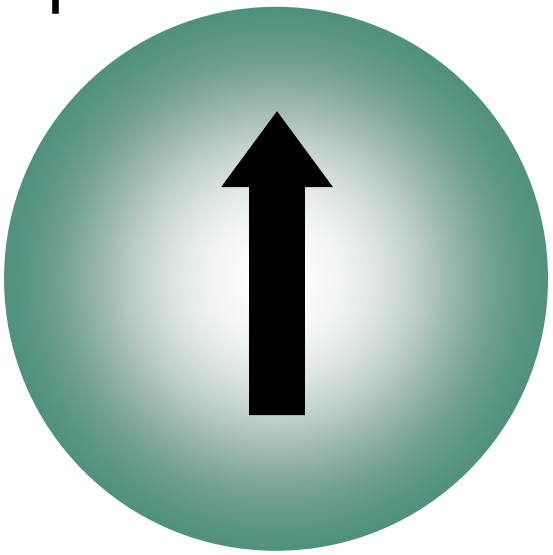
whose order of magnitude can be of the order of the Coulomb interaction.

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.



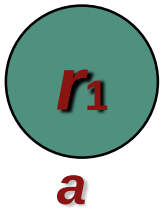


The 1s orbital of the Hydrogen atom

Let's consider the phase space spanned by spin states $|1s,\uparrow\rangle$, $|1s,\downarrow\rangle$.

Atomic orbitals and molecular orbitals

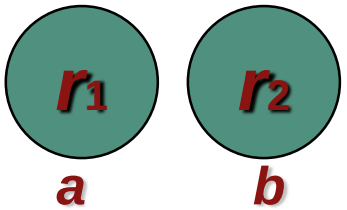
- Atomic orbitals



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

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

- Molecular orbitals (in LCAO)



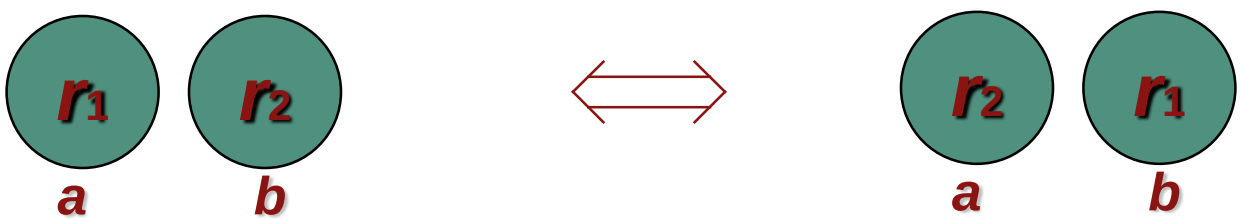
$$\frac{1}{\sqrt{2}}\left(\phi_a(r)+\phi_b(r)\right)\xi_\uparrow(1)$$

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

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!!**

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



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.

Singlet: $\Psi_+ = c_+(\Psi_1 + \Psi_2)$. **(3)**

$(\mathbf{S}_1 + \mathbf{S}_2)^2 = 0.$

$E = E_+.$

Triplet: $\Psi_- = c_-(\Psi_1 - \Psi_2)$. **(4)**

$(\mathbf{S}_1 + \mathbf{S}_2)^2 = 2.$

$E = E_-.$

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

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

We have

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

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.

$$I = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)$$

Note that the expression below.

$$\phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1) = \mathrm{Re}\left(\phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\right) + i\,\mathrm{Im}\left(\phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\right)$$

$$I = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\left(\phi_a^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)\right)^*$$

$$= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \mathrm{Re}\left(\phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\right) \times \mathrm{Re}\left(\phi_a^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)\right)$$

$$+ \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \mathrm{Im}\left(\phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\right) \times \mathrm{Im}\left(\phi_a^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)\right)$$

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

$$I = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Phi(\boldsymbol{r}_1)\Phi(\boldsymbol{r}_2)$$

Ferromagnetic direct exchange III.

Substitute next expressions into I.

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

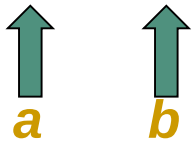
$$\mathbf{\Phi}(\mathbf{r}) = \int d\mathbf{q} v(\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}) \ .$$

Since $\mathbf{\Phi}$ are real, $v^*(\mathbf{q}) = v(-\mathbf{q})$. 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



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

$$\langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | S_{tot} = 1, S_z = 0 \rangle = \langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | S_{tot}^- | \phi_a \uparrow, \phi_b \uparrow \rangle$$
$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1) & \phi_a(\mathbf{r}_2) \\ \phi_b(\mathbf{r}_1) & \phi_b(\mathbf{r}_2) \end{vmatrix} \frac{1}{\sqrt{2}} (\xi_\uparrow(1)\xi_\downarrow(2) + \xi_\downarrow(1)\xi_\uparrow(2))$$
$$= \frac{1}{2} \{ (\phi_a(\mathbf{r}_1)\xi_\uparrow(1)\phi_b(\mathbf{r}_2)\xi_\downarrow(2) - \phi_b(\mathbf{r}_1)\xi_\uparrow(1)\phi_a(\mathbf{r}_2)\xi_\downarrow(2))$$
$$+ (\phi_a(\mathbf{r}_1)\xi_\downarrow(1)\phi_b(\mathbf{r}_2)\xi_\uparrow(2) - \phi_b(\mathbf{r}_1)\xi_\downarrow(1)\phi_a(\mathbf{r}_2)\xi_\uparrow(2)) \}$$
$$= \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1)\xi_\uparrow(1) & \phi_a(\mathbf{r}_2)\xi_\uparrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\downarrow(1) & \phi_b(\mathbf{r}_2)\xi_\downarrow(2) \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1)\xi_\downarrow(1) & \phi_a(\mathbf{r}_2)\xi_\downarrow(2) \\ \phi_b(\mathbf{r}_1)\xi_\uparrow(1) & \phi_b(\mathbf{r}_2)\xi_\uparrow(2) \end{vmatrix} \right\} \qquad (2)$$

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,

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

$$\longrightarrow \; |S_{tot} = 1, S_z = 1\rangle = c^\dagger_{a,\uparrow} c^\dagger_{b,\uparrow} |0\rangle$$

Similarly,

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

2-electrons in molecular orbitals

Let us consider two electrons in the bonding orbital.

$$
\begin{aligned}
& \langle \mathbf{r}_1, 1; \mathbf{r}_2, 2 | \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \uparrow, \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \downarrow \rangle \\
= \; & \frac{1}{2}(\phi_a(\mathbf{r}_1) + \phi_b(\mathbf{r}_1))(\phi_a(\mathbf{r}_2) + \phi_b(\mathbf{r}_2)) \frac{1}{\sqrt{2}} \begin{vmatrix} \xi_\uparrow(1) & \xi_\uparrow(2) \\ \xi_\downarrow(1) & \xi_\downarrow(2) \end{vmatrix} \\
\longrightarrow \; & | \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \uparrow, \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \downarrow \rangle \\
= \; & \frac{1}{2}(c^\dagger_{a,\uparrow} + c^\dagger_{b,\uparrow})(c^\dagger_{a,\downarrow} + c^\dagger_{b,\downarrow})|0\rangle \qquad (5)
\end{aligned}
$$

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

$$
\begin{aligned}
& | \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \uparrow, \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \downarrow \rangle \\
= \; & \frac{1}{\sqrt{2}} \left\{ \underline{\frac{1}{\sqrt{2}}(c^\dagger_{a,\uparrow} c^\dagger_{b,\downarrow} - c^\dagger_{a,\downarrow} c^\dagger_{b,\uparrow})|0\rangle} + \underline{\frac{1}{\sqrt{2}}(c^\dagger_{a,\uparrow} c^\dagger_{a,\downarrow} + c^\dagger_{b,\uparrow} c^\dagger_{b,\downarrow})|0\rangle} \right\} \qquad (6)
\end{aligned}
$$

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.

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

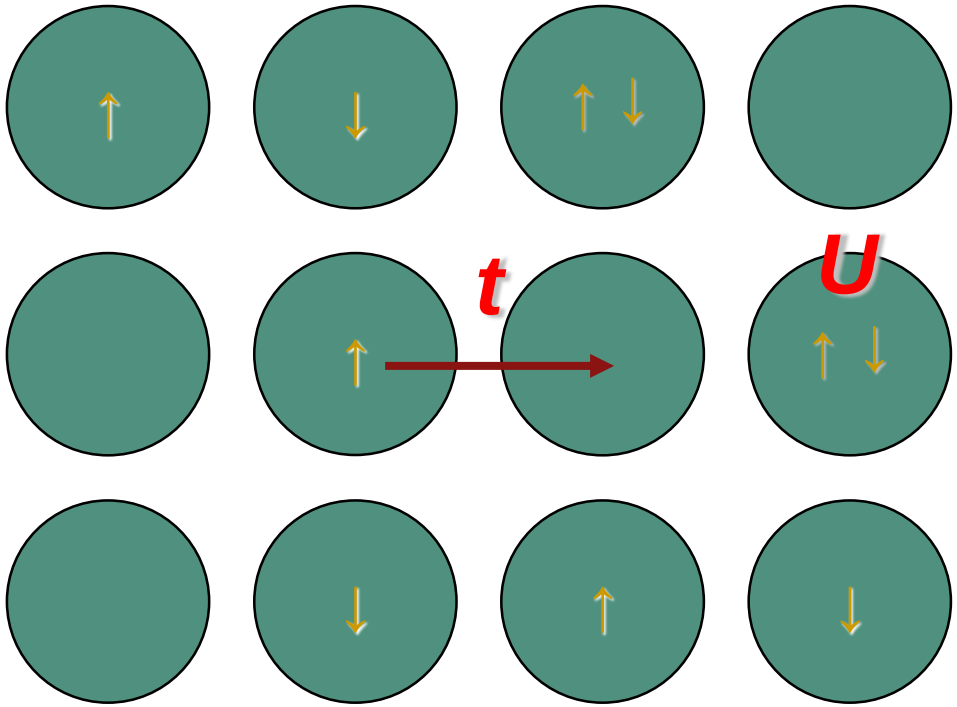
1. $\alpha = 0$: the Heiter-London wavefunction (Localized electron picture)
2. $\alpha = 1$: the doubly-occupied bonding state (Delocalized electron picture)

The true w.f. is close to a variational state with $0<\alpha<1$.

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

The Hubbard model : I.

1. Consider a system with atomic sites. Each site is assumed to have an orbital for the conduction electrons
2. Electrons can hop between neighboring sites by a transfer integral *t*.
3. Two electrons coming across at a site feels a repulsive interaction *U*.



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,

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

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,

$$\begin{aligned} c_{ni\sigma} &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \sum_m e^{i\mathbf{k}\mathbf{r}_i} U^{-1}_{mn}(\mathbf{k}) c_{m\mathbf{k}\sigma} \\ c^\dagger_{ni\sigma} &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \sum_m e^{-i\mathbf{k}\mathbf{r}_i} U_{nm}(\mathbf{k}) c^\dagger_{m\mathbf{k}\sigma} \ . \end{aligned}$$

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.)

$$\begin{aligned}
\hat{H}_0 &= \sum_{n,\mathbf{k},\sigma} \varepsilon_{n,\mathbf{k}} c^\dagger_{n\mathbf{k}\sigma} c_{n\mathbf{k}\sigma} \\
\hat{H}_1 &= \frac{1}{2}\int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\mathbf{r})\psi^\dagger_{\sigma'}(\mathbf{r}')\psi_{\sigma'}(\mathbf{r}')\psi_\sigma(\mathbf{r}) \\
&- \left[\int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}) \sum_\sigma \psi^\dagger_\sigma(\mathbf{r})\psi_\sigma(\mathbf{r}) - \frac{1}{2}\int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}')\right]
\end{aligned}$$

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,

$$\begin{aligned}
\hat{H}_1 &= \frac{1}{2}\sum_{ijkl}\sum_{m_1\cdots m_4}\sum_{\sigma\sigma'}(m_1 i, m_2 j|\frac{1}{r}|m_3 k, m_4 l) c^\dagger_{m_1 i\sigma} c^\dagger_{m_2 j\sigma'} c_{m_3 k\sigma'} c_{m_4 l\sigma} \\
&- \sum_{ijkl}\sum_{m_1\cdots m_4}\sum_{\sigma}(m_1 i, m_2 j|\frac{1}{r}|m_3 k, m_4 l)\nu_{m_2 j m_3 k} c^\dagger_{m_1 i\sigma} c_{m_4 l\sigma} \\
&+ \frac{1}{2}\int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}')
\end{aligned}$$

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

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

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

for the discussion of magnetism.

The Hubbard model : VI.

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

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

The Hubbard model is given by,

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

- $t_{i,j}$: Transfer integral
- U : The Hubbard interaction parameter

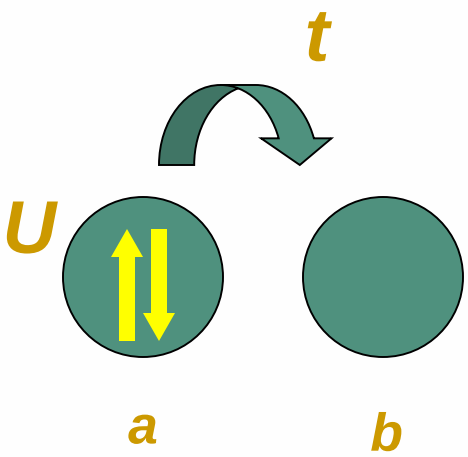
2-site Hubbard model : I.

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,

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

Then, we have a block-diagonalized H,

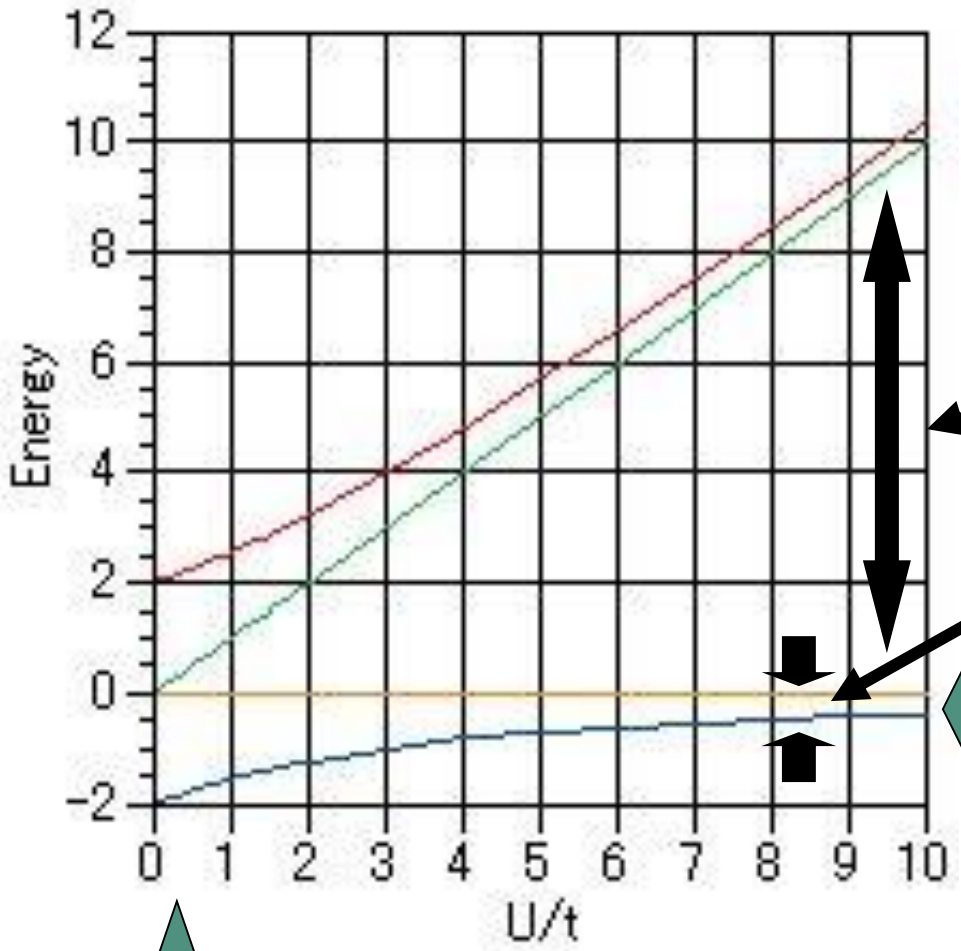
$$U^{-1}HU \doteq \begin{bmatrix} 0 & 2t & 0 & 0 \\ 2t & U & 0 & 0 \\ 0 & 0 & U & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{11}$$

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

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)

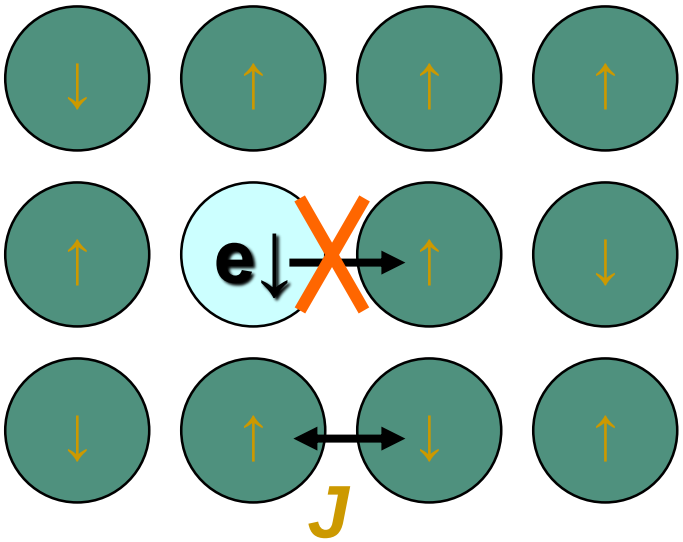
Singlet states

Triplet states

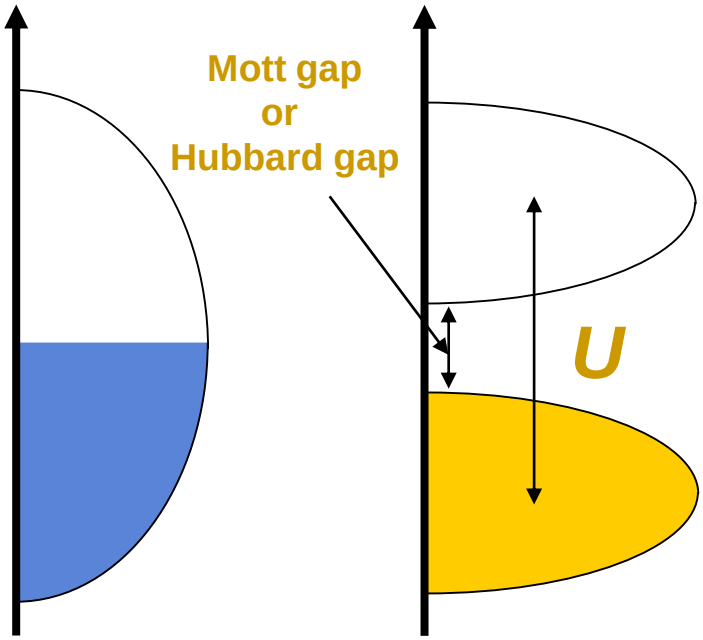
Weak coupling regime (MO)

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.



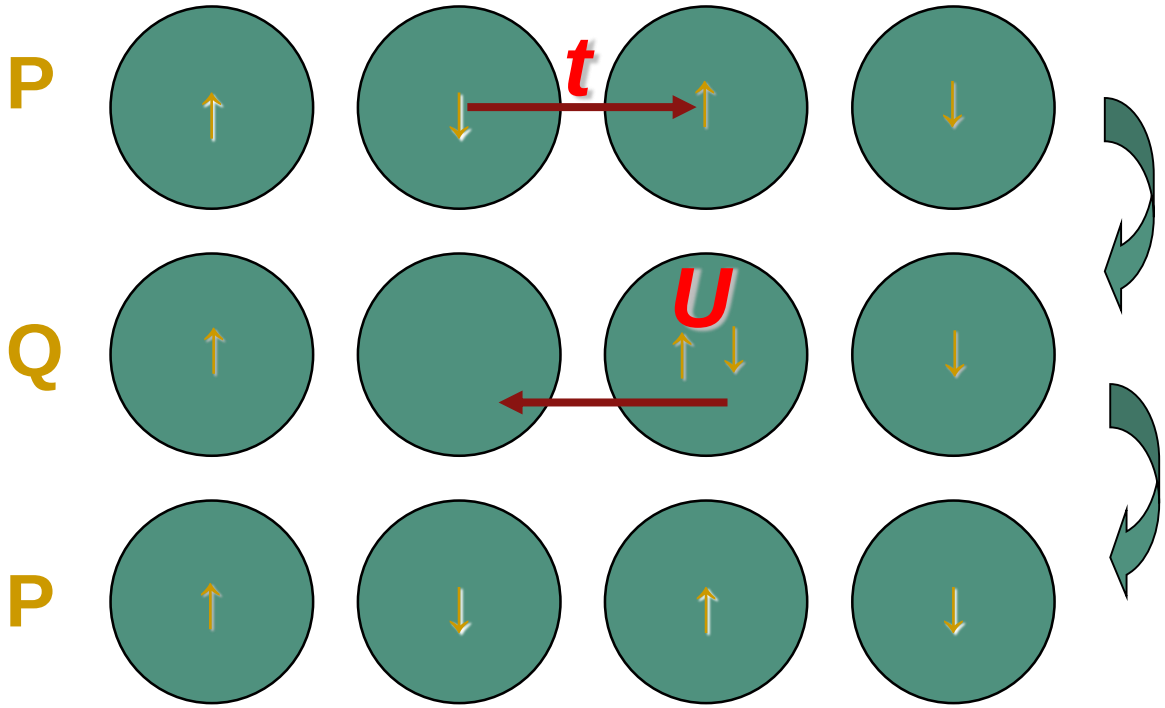
The half-filled Hubbard model shows the Mott insulating ground state.



Formation of the Mott gap in the single particle excitation.

The kinetic exchange

- Effective interaction at around $U=\infty$



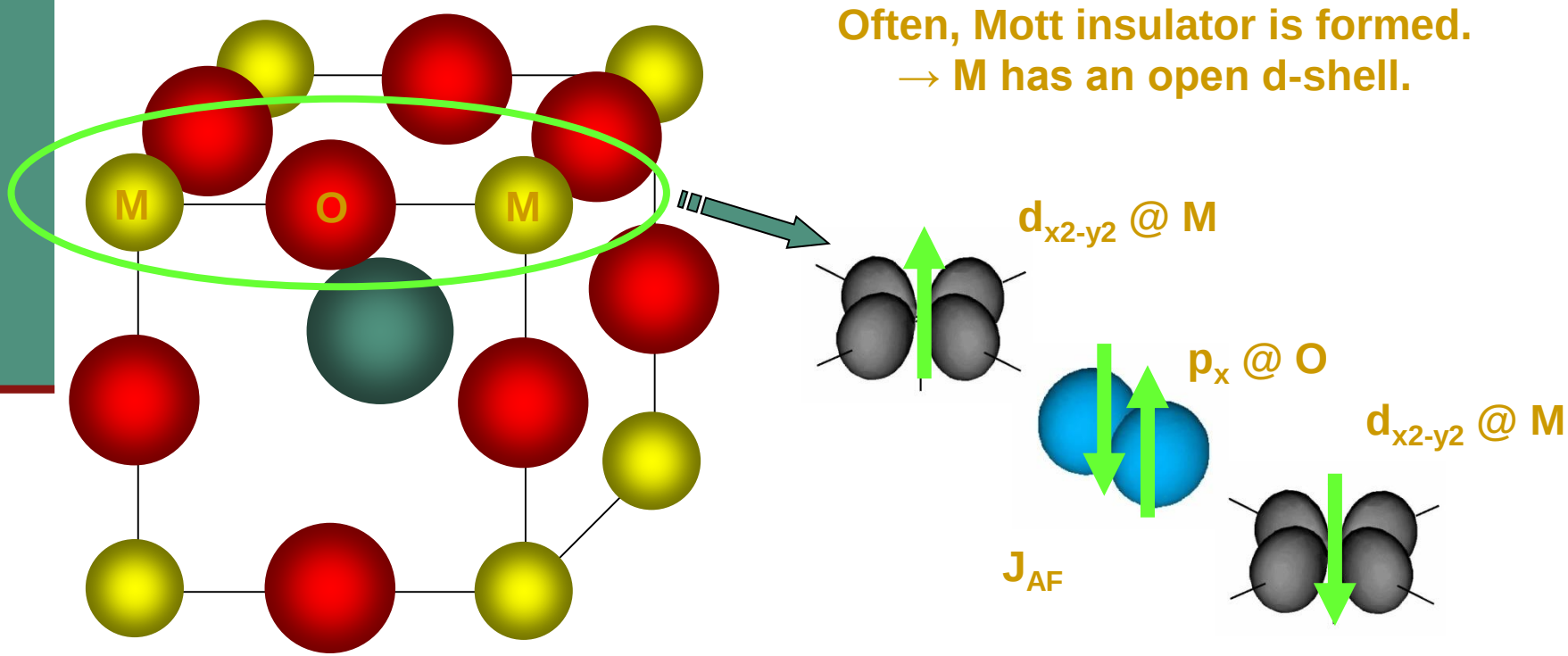
We have another process starting from transfer of the up spin moving to the neighboring site.

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

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.



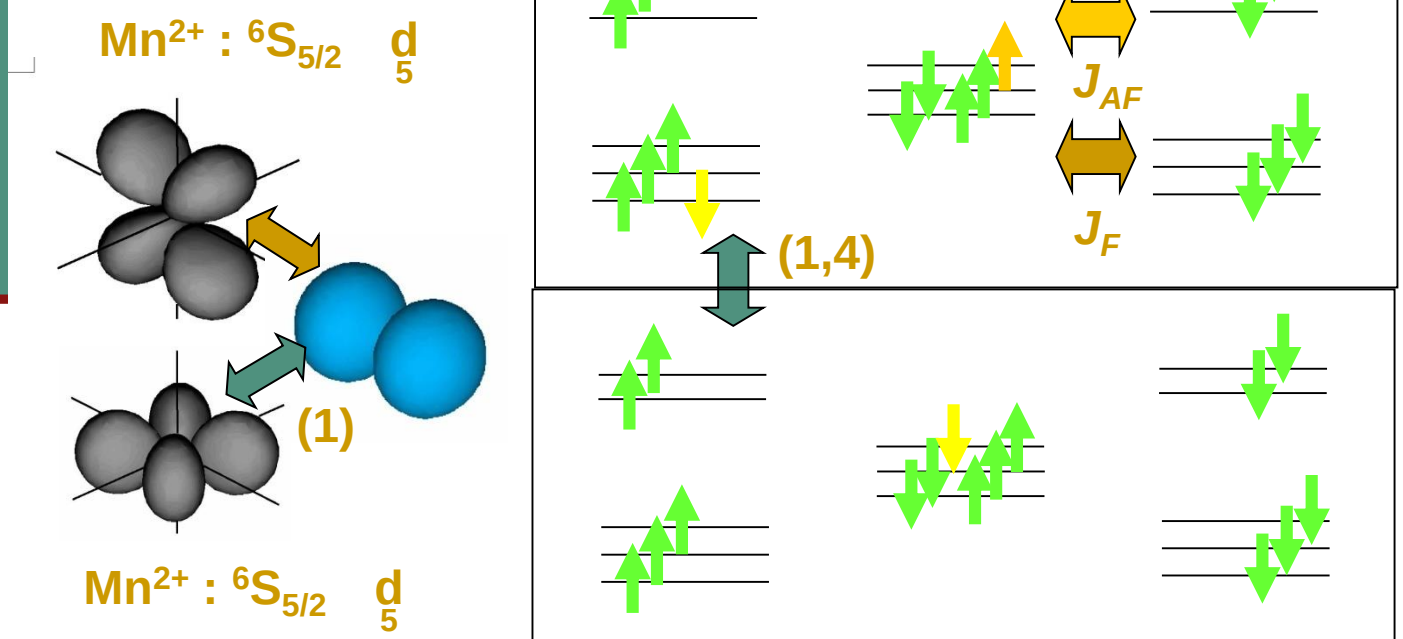
The Kanamori-Goodenough rule

- 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



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
- Dzyaloshinskii-Moriya interaction

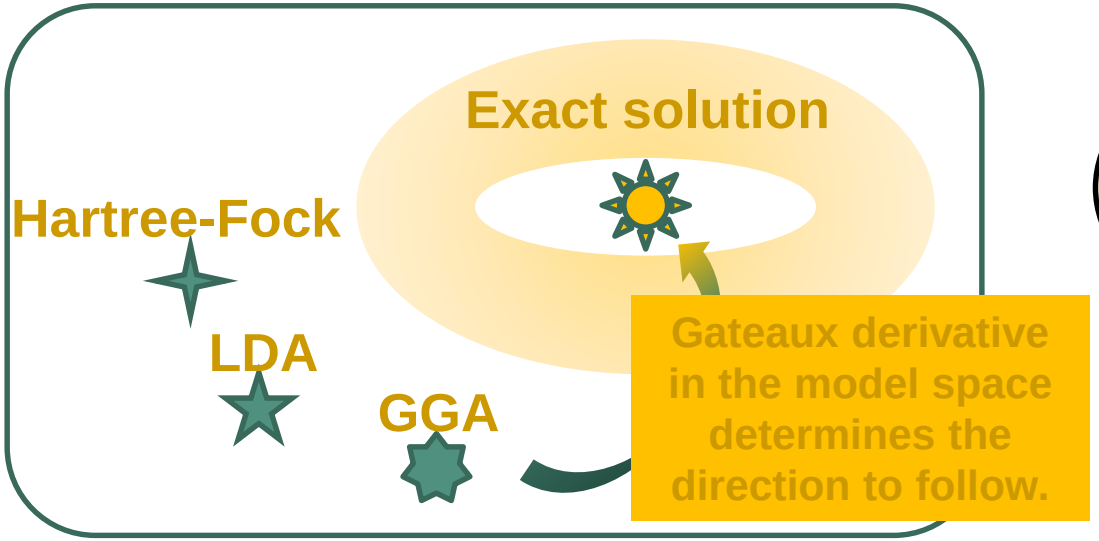
1. **Exchange interactions except for the 1st one are effective interactions.**
2. **Effective interactions can be derived from a model with local interactions.**

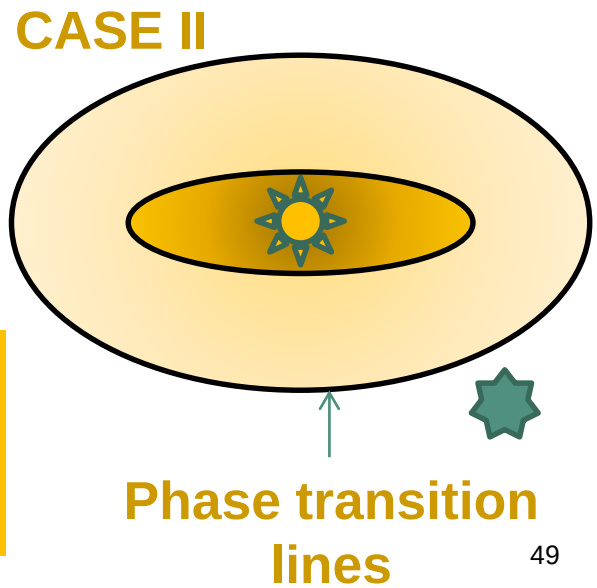
An almighty method

- Space of DFT models
  - Distance :

$$\left\| n_i - n_{i+1} \right\|.$$

  - Variational principle: DFVT by K.K. (2009).





Super processes

To have an initial state of correlated electron system, we may utilize

The upconversion Hamiltonian

$$\left(\hat{H}_{1,i} + \hat{H}_2^{A_i \to A_i} - \hat{H}_2^{A_i^c \to A_i} P_B \frac{1}{\hat{H}_{1,i} + \hat{H}_2^{A_i \to A_i} + \hat{H}_2^{A_i \leftrightarrow A_i^c} - E} P_B \hat{H}_2^{A_i \to A_i^c} \right) \left| \Psi_i \right\rangle = E \left| \Psi_i \right\rangle.$$

which leads us to the convergent model series in the DFT model space.

Cf. K. Kusakabe, I. Maruyama, "Electronic state calculation method, electronic state calculation device, computer program", PCT filed No. PCT/JP2011/068589, date 2011.8.18.

Problems in static state

Magnetism

The super-exchange process

Superconductivity

The super-pair hopping process

Semi-classical & quantum dynamics

The van-der-Waals interaction

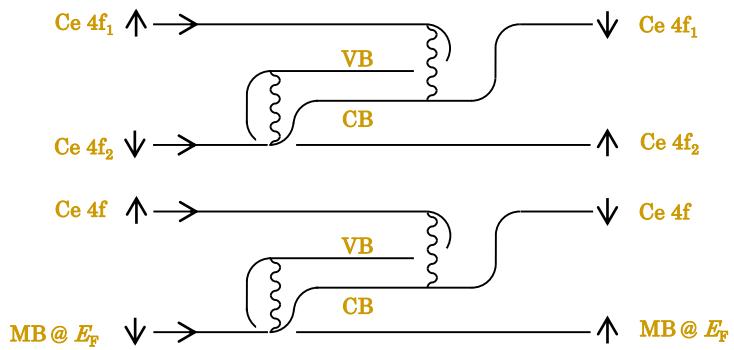
…

Quantum processes in QED!

Two & multi-photon processes

Exchange scattering

Feynman diagram of exchange



Evaluation of c-f exchange

$$\left(J_{eff-cf}\right)_{c_j f_i}$$

AF effective exchange
⇒ The Kondo Screening

Upconversion Hamiltonian with super processes

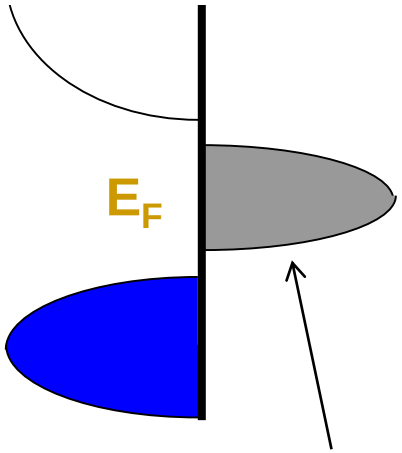
$$\left(\hat{H}_{1,i}+\hat{H}_2^{A_i\to A_i}-\hat{H}_2^{A_i^c\to A_i}P_B\frac{1}{\hat{H}_{1,i}+\hat{H}_2^{A_i\to A_i}+\hat{H}_2^{A_i\leftrightarrow A_i^c}-E}P_B\hat{H}_2^{A_i\to A_i^c}\right)\left|\Psi_i\right\rangle=E\left|\Psi_i\right\rangle,$$

$$H_{1,i}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\int d^3r\lim_{r'\to r}\hat{\psi}^\dagger(\mathbf{r}')\Delta_{\mathbf{r}}\hat{\psi}(\mathbf{r})+\int d^3r\bar{v}_{eff}(\mathbf{r})\hat{n}(\mathbf{r})+\frac{\delta}{\delta\langle\Psi|}E_{g_i}[\Psi],$$

$$\bar{v}_{eff}(\mathbf{r})=\frac{\delta}{\delta n(\mathbf{r})}\left\{\frac{e^2}{2}\int d^3rd^3r'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{\varepsilon_i}[n]+\int d^3rv_{ext}(\mathbf{r})n(\mathbf{r})\right\}.$$

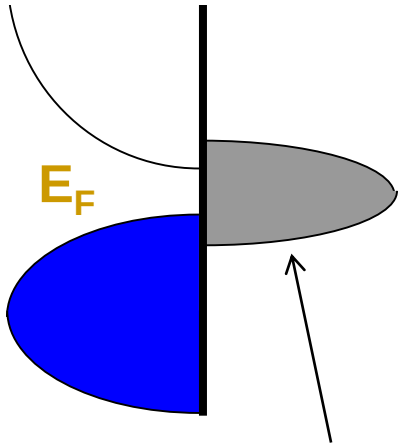
A unified picture of high-T_c materials

Isolated center band



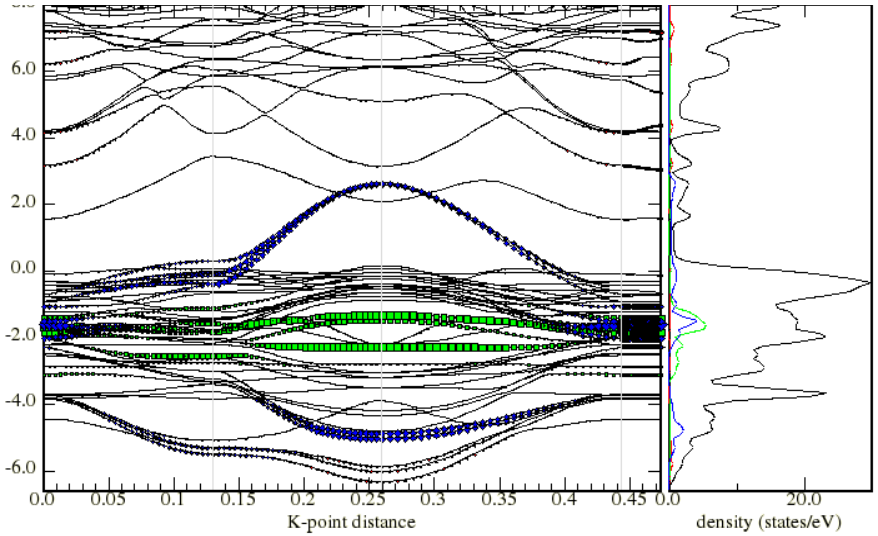
Correlation enhanced

Embedded center band



Correlation enhanced

Band structure of Tl-cuprates



Empirical rule :

1. **Embedded type preferable**
2. **Larger band width of center band preferable**
3. **Correlation induced by localized Wannier orbital preferable**