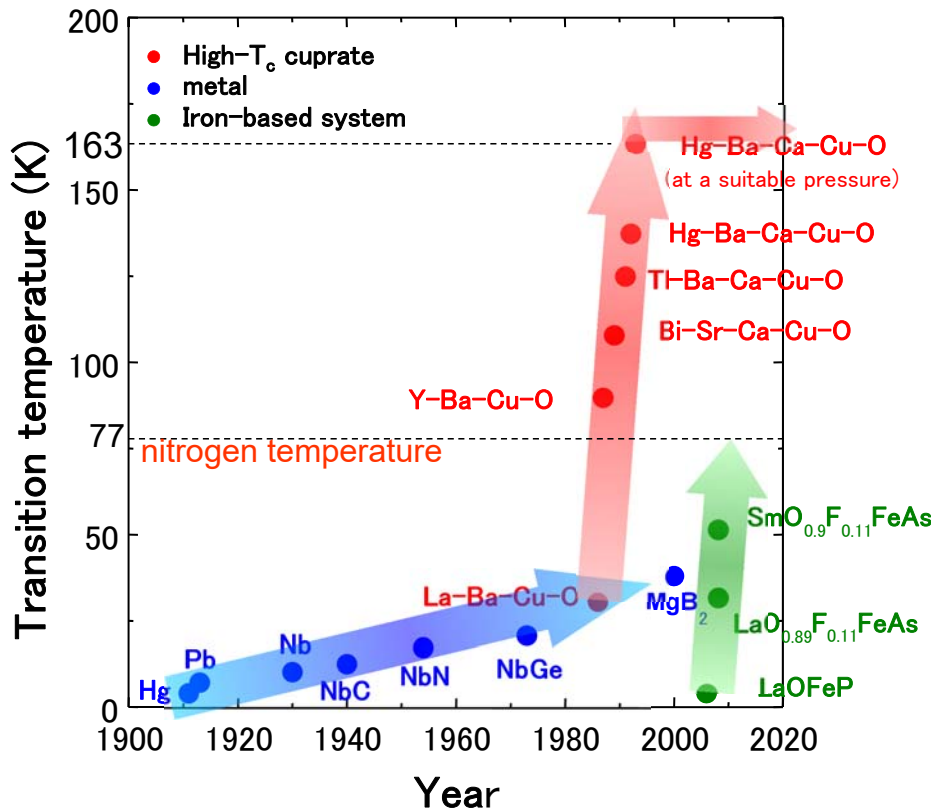# History for High-T_c Superconductivity Phenomena

1911

Superconductivity was discovered

1986

High-T_c cuprate was discovered

2006

Iron-based system was discovered
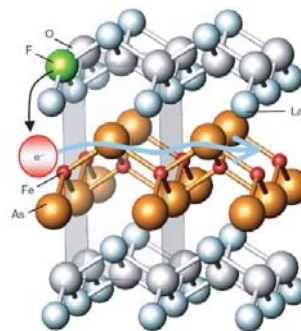
Mechanism of High-T_c Superconductivity ?

Copper oxides

Magnetic interaction
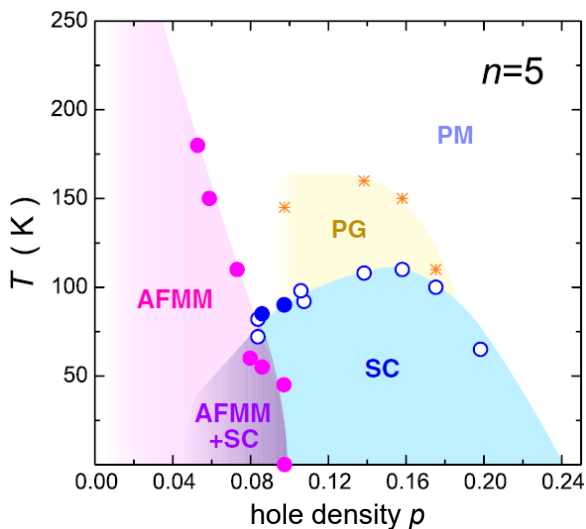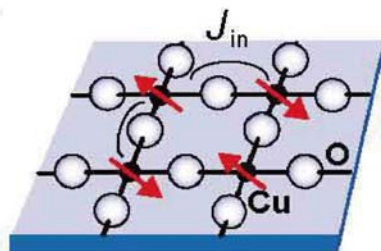
Iron pnictides

La1111:T_c=27 K

Nd1111:T_c=55 K

Spin fluctuations?
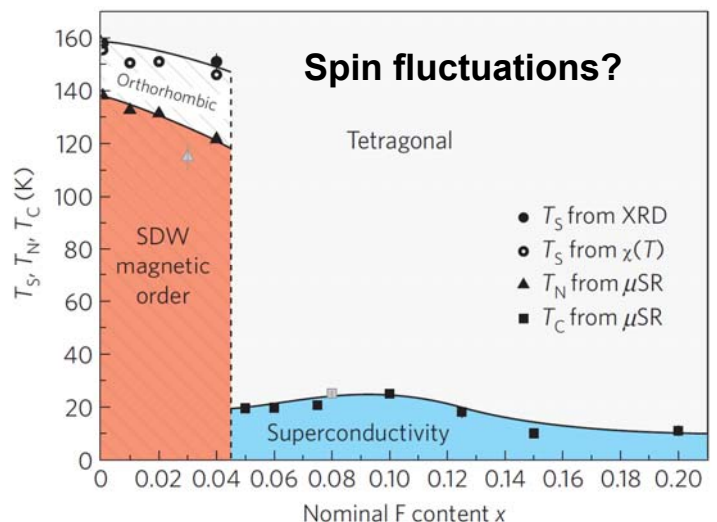
Mukuda *et al*., JPSJ 81(2012),

Luetkens *et al*., Nat. Mater. **8**,

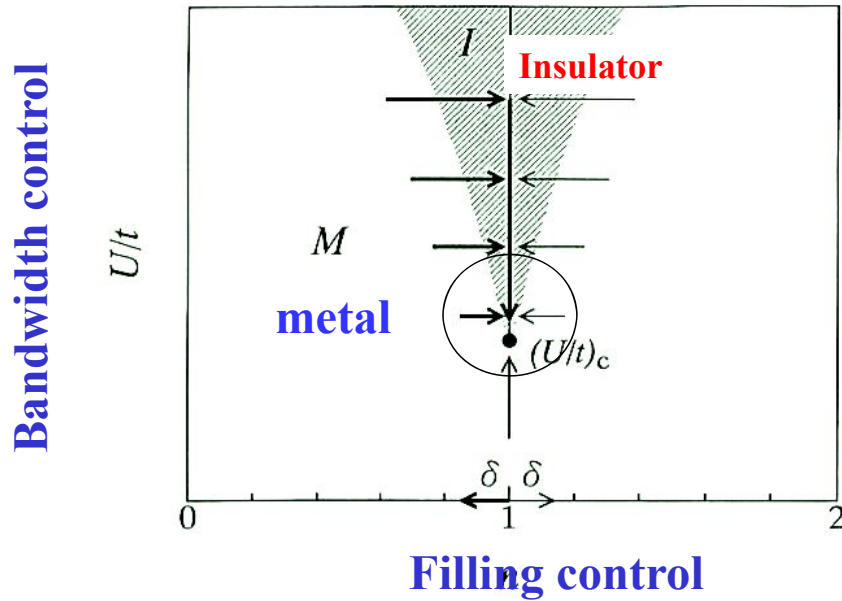# Theoretical model for correlated electron systems

Hubbard model

$$H = -t\sum a^+_{i+1}a_i + U\sum n_{i\uparrow}n_{i\downarrow}$$

Kinetic energy   **On-site Coulomb repulsive interaction**

To see outside world   Make them away from each other

Bandwidth control

U/t

I

Insulator

M

metal

$(U/t)_c$

δ δ

0   1   2

Filling control

What is the Novel Characteristics of Correlated Electrons ?

Conventional metal（itinerant electrons with no spin degree of freedom)
    Charge plays role for "Electronics"

One electron per atom

$t >> U$
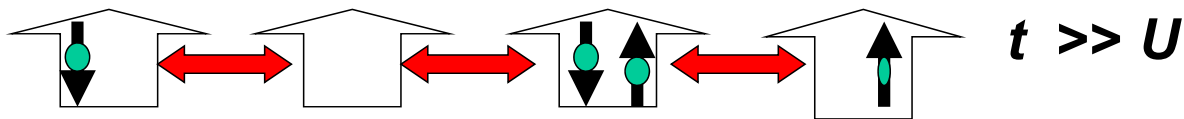
Mott Insulators (magnetism with spin degree of freedom)

$U >> t$
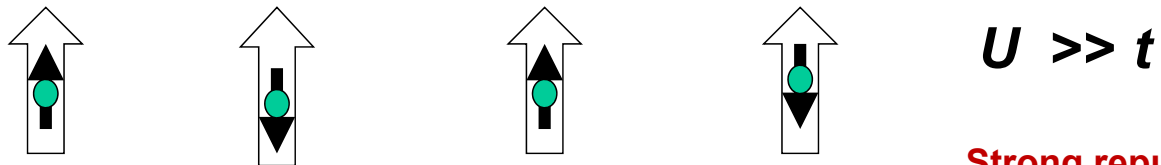
Doped Mott insulators
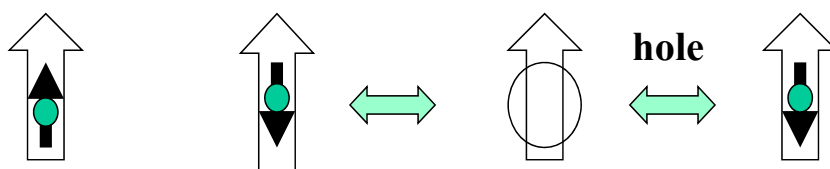
Strong repulsive Coulomb interaction on a same lattice site due to narrow 3d orbitals

hole

Spin·Charge·Orbital degrees of freedom are coupled each other

hole
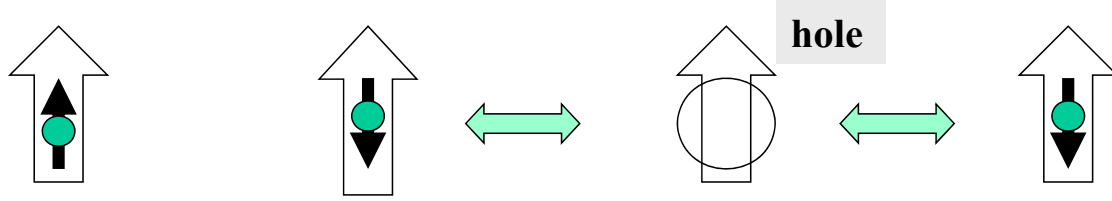
Multi-criticality of different phase yields giant response to the application of external magnetic or electric fields, and to photo irradiation.

Rich variety of ground states such as high-T_c superconductors, novel magnetism and electricity

Small number of electrons affects the Avogadro's number of electrons

Narrow spatial distribution of orbits of 3d and 4f electrons play role for emergent properties in transition metal oxides and rare earth inter-metallic compounds due to Correlation

Periodic table of elements

Li	Be									
	0.026									
Na	Mg									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
			0.39	5.3						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
			0.52	9.2	0.92	8.8	0.49			
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
		6.0	0.09	4.48	0.01	1.70	0.66	0.11		
Fr	Ra	Ac								

Ce	Pr	Nd	Pm	Sm	Eu	Gd
Th	Pa	U	Np	Pu	Am	Cm
1.37	1.4	1.8		0.79		

$n=1$ $n=2$ $n=3$

3s

$l=0$ 1s $l=0$ 2s $l=0$ 3s

$l=1$ 2p $l=1$ 3p

3d

$l=2$ 3d

r^2R^2

r/nm

(b)

Radial Distribution of Electron Density at atomic site

Hamiltonian in Magnetic Substances

$$H = -2J\Sigma_{ij} \, \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

$J < 0$ （in case of wave functions mixed ）

： Antiferromagnetism

$J > 0$ （in case of wave functions being orthgonalized ）

： Ferromagnetism

Theoretical model for correlated electron systems

Hubbard model

$$H= \ -t\sum a^{+}_{i+1}a_{i} + U\sum n_{i\uparrow}n_{i\downarrow}$$

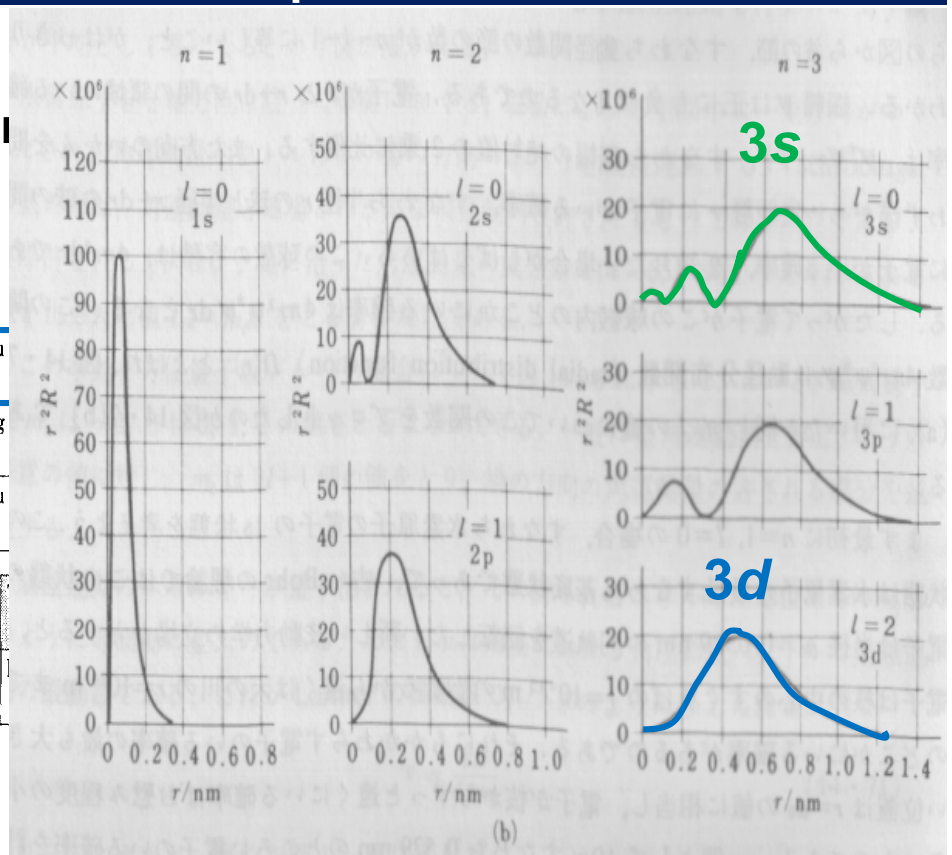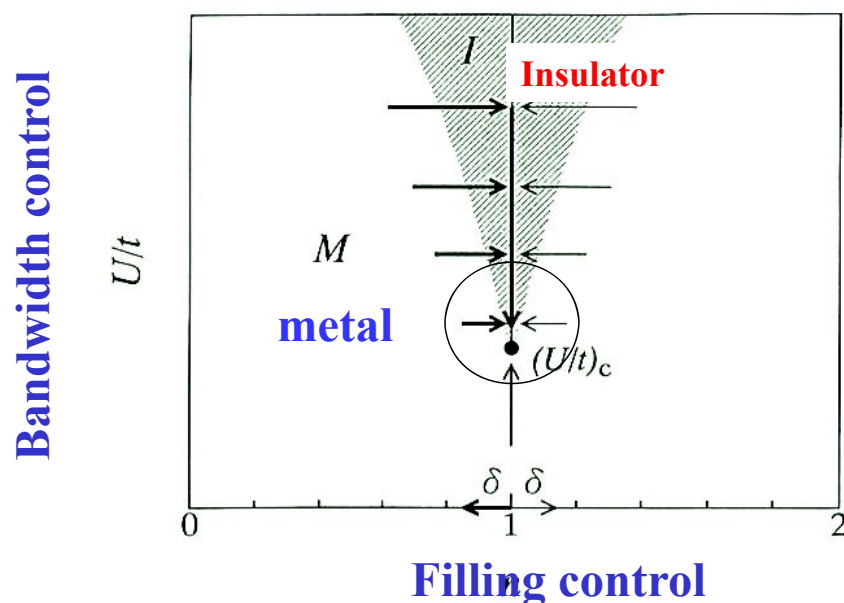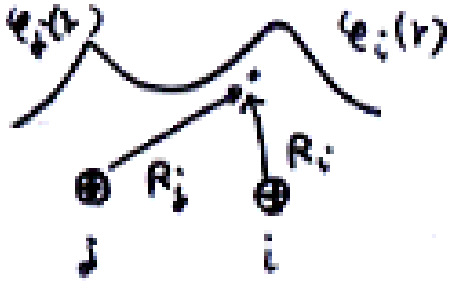**Kinetic energy**   **On-site Coulomb repulsive interaction**

To see outside world   Make them away from each other

Model Hamiltonian for Strongly Correlated Electrons Systems

$$-t_{ij} = \int \varphi_j^*(\vec{r})\left[-\frac{\hbar^2}{2m}\Delta - \frac{e^2}{R_i} - \frac{e^2}{R_j}\right]\varphi_i(\vec{r})\,d\tau$$

U : Coulomb repulsion

t : Transferred integral

$$\mathcal{H} = -\sum_{ij\sigma} t_{ij}\, a_{i\sigma}^\dagger a_{j\sigma} + U\sum_{i,\sigma} n_{i\sigma}\cdot n_{i,-\sigma}$$

$$-\,2J\Sigma_{ij}\,S_i\cdot S_j \quad \text{for } U \gg t$$

Carrier doping into Mott insulator

La$_2$CuO$_4$ La$^{3+}_{2-x}$Sr$^{2+}_{x}$CuO$_4$

charge reservoir

CuO$_2$ 面

charge reservoir

d(x^2−y^2)

Cu^{+2} (3d^9)   Cu^{2+x}

La (Sr)

- ● Cu
- ○ O
- ● La(Sr)

La-Sr-Cu-O

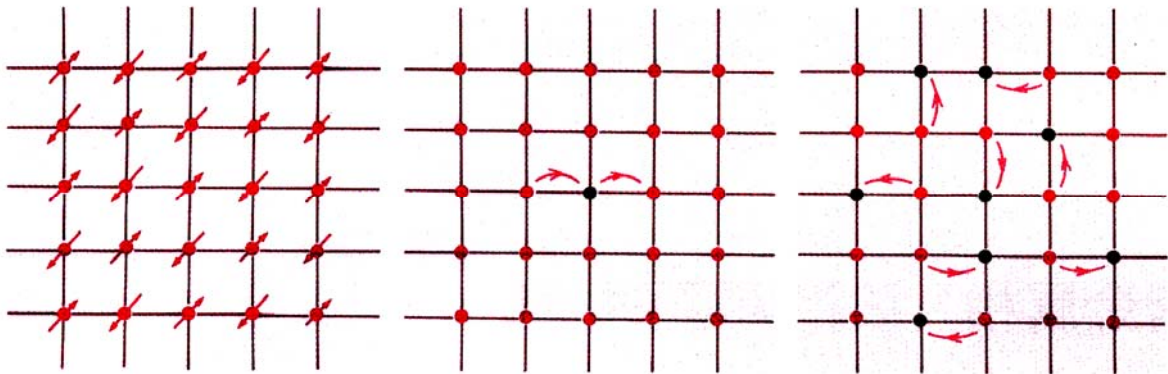● 電子   ╱ スピ

Mott insulator

Hole doping causes conductivity
Onset of high-T_c SC !

Mott Insulator and charge-carriers doped Insulator – Metal Transition

(a)	(b)	(c)
Mott Insulator	**Strongly Correlated Metal**	**Conventional Metal**

How to dope carriers
- Chemical substitution
- Photo induced carriers injection

強相関効果から生まれる

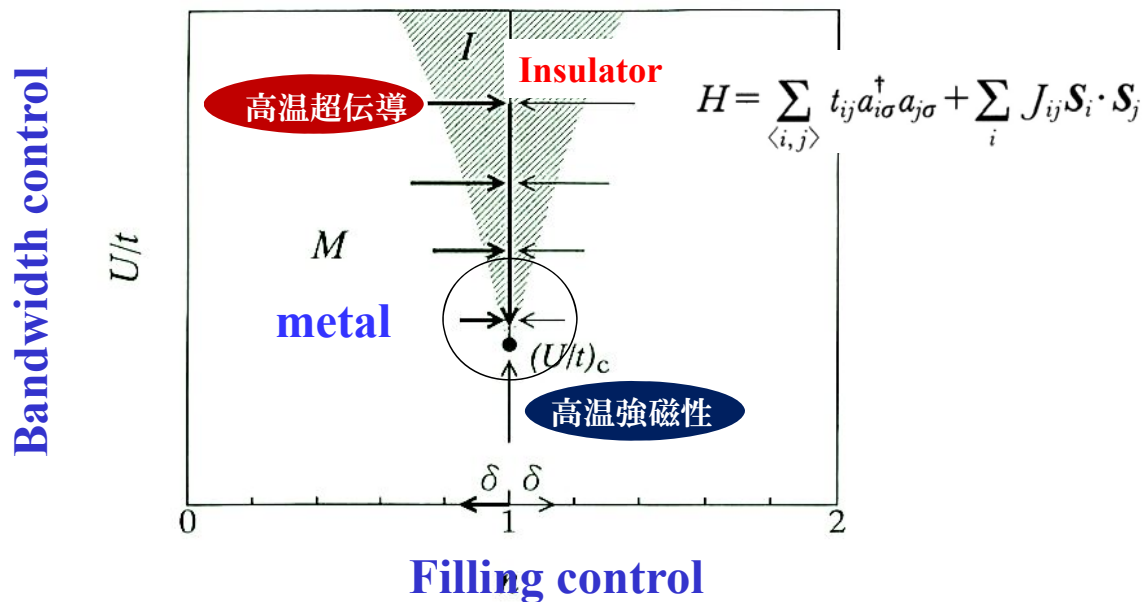高温超伝導と高温強磁性

強相関効果は機能を生み出す

Hubbard model

$$H = -t\sum a^{+}_{i+1}a_{i} + U\sum n_{i\uparrow}n_{i\downarrow}$$

Kinetic energy   **On-site Coulomb repulsive interaction**

To see outside world   Make them away from each other

Bandwidth control

U/t

Filling control

I **Insulator**

高温超伝導

M

metal

$(U/t)_c$

高温強磁性

$$H = \sum_{\langle i,j\rangle} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + \sum_i J_{ij} S_i \cdot S_j$$

$\delta \quad \delta$

0   1   2

n

強相関効果は本当に役に立ち

Ferromagnetic metal

Fe $T_c = 1053$ K

E_F

Spin Density of States

$$t \geq U_{eff}$$

$$T_c \sim 1000\text{K}$$

$$U\sum_i n_{i,\uparrow}n_{i,\downarrow} = -2U\sum_i s_{iz}^2$$

High-performance Permanet Magnet

$Nd_2Fe_{14}B$
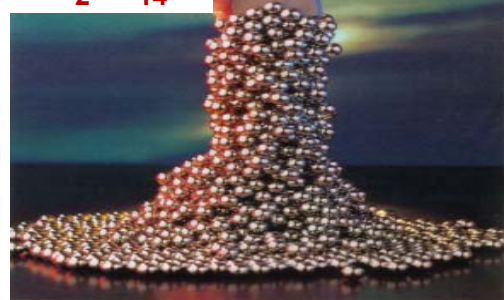
Antiferromagnetic Mott Insulator

J
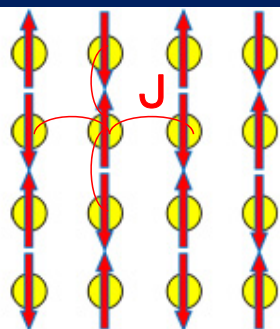
$$t \ll U$$

$$T_c \sim 150\text{ K}$$

All spins become anti-parallel
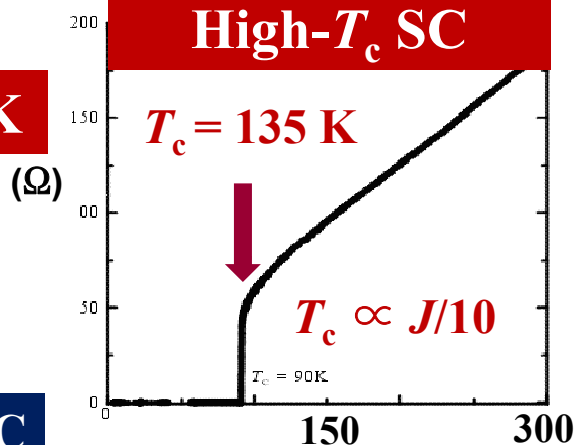
A Route to Search Room-temperature SC

High-T_c SC

200

(Ω)

$T_c = 135$ K

150

100

50

$T_c \propto J/10$

$T_c = 90$ K

0

150   300

強相関効果とは

Covalent bonding effect of H_2 molecule

図 **1.3**　２個の水素原子が近づいて水素分子を形成するようす．二つの電子は
結合軌道に収容される．

1. Electronic state of H_2^+ (Molecular Orbital Method)

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{|r-R_a|} - \frac{e^2}{|r-R_b|}$$

$$\psi = c_a\phi_a + c_b\phi_b \longrightarrow$$

Molecular orbital composed of *1s* eigen state at nuclear A and B sites

Eigen equation

$$H\psi = E\psi$$

$$\begin{vmatrix} H_{aa}-E & H_{ba}-SE \\ H_{ab}-SE & H_{bb}-E \end{vmatrix} = 0$$
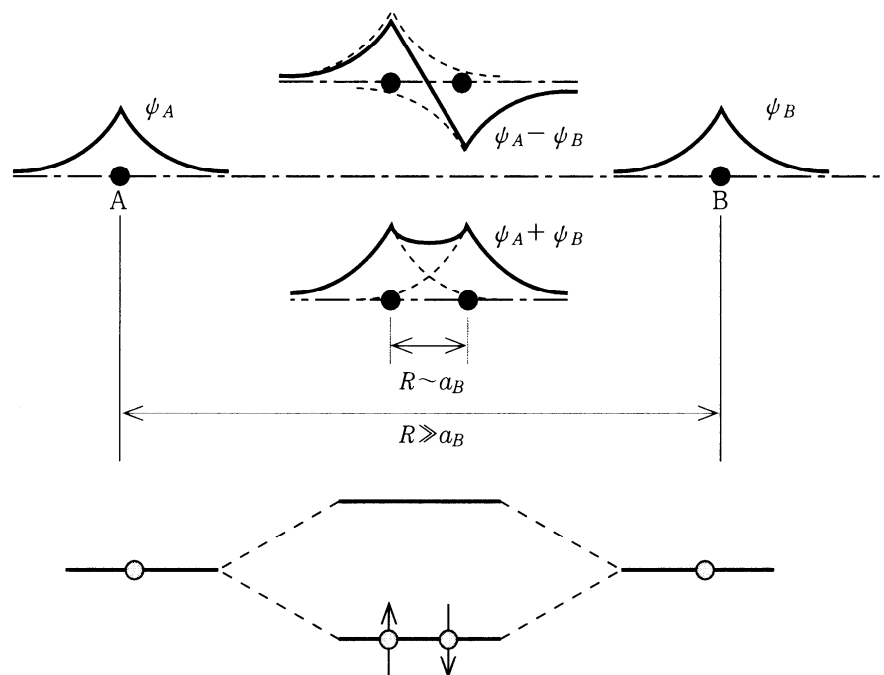
Eigen function   **Eigen energy**   **Here**

$$\phi_1 = \frac{\phi_a + \phi_b}{\sqrt{2(1+S)}}, \qquad E_1 = \frac{H_{aa}+H_{ab}}{1+S}, \qquad S = \int \phi_a\phi_b\,dv, \qquad H_{ij} = \int \phi_i H \phi_j\,dv.$$

$$\phi_2 = \frac{\phi_a - \phi_b}{\sqrt{2(1-S)}}, \qquad E_2 = \frac{H_{aa}-H_{ab}}{1-S}. \qquad H_{aa} = H_{bb}, \;\; H_{ab} = H_{ba}$$

2. Hydrogen Molecule (Molecular orbital method)

Put two electrons into the lowest bonding molecular orbital state

$$\phi_1 = \frac{\phi_a + \phi_b}{\sqrt{2(1+S)}}$$

The wave function for two electrons system should be under the constrain of anti-symmetric condition in mutual exchange of position of electrons.

$$\Phi_S = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix}$$

$$= \phi_1(1)\phi_1(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Here H'_1, H'_2 are given by

$$H = H'_1 + H'_2 + e^2/r_{12}$$

$$H' = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{|r-R_a|} - \frac{e^2}{|r-R_b|}$$

**The expectation value of eigen energy is given by**

$$E_S = 2E_1 + \int \phi_1(r_1)^2\phi_1(r_2)^2\frac{e^2}{r_{12}}\,dv_1 dv_2$$

$$E_1 = \frac{H_{aa}+H_{ab}}{1+S}$$

The Coulomb repulsive interaction energy is included.

The right figure shows the binding energy E_g as the function of distance R between the A and B nuclear. The molecular orbital approximation gives rise to E_g = 2.65 eV and R= 0.85 Å．　These values are not consistent with the respective experimental values 4.72 eV and 0.74 eV.
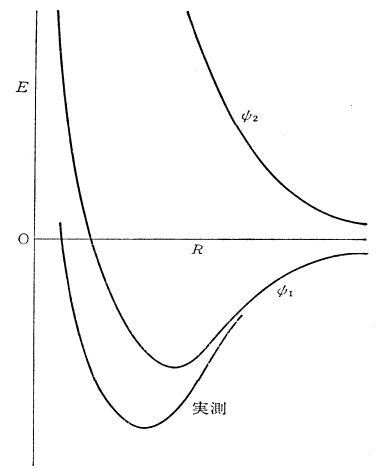
2-1 図　原子間距離の関数として H₂⁺ の
結合エネルギーを描いたもの

What is the reason why the molecular orbital method is not good approximation ?

$$\phi_1(1)\phi_1(2) \propto \phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2) + \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)$$

The first and second term correspond to the state where two electrons occupy the same site like H⁺H⁻. In the case of $R \longrightarrow \infty$,   H⁺H⁻ is unstable because two hydrogen atoms are well separated. The reason why this approach is not good is that the on-site Coulomb energy cost U is larger than the transfer integral t .

2．Atomic orbital description of hydrogen molecular （Heitler-London method)

$$\Phi_{\mathrm{HL}} = \frac{1}{\sqrt{2(1 + S^2)}}[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]$$

The expectation value of eigen energy is given by

$$\langle\Phi_{\mathrm{HL}}|H=(H'_1 + H'_2 + e^2/r_{12})|\Phi_{\mathrm{HL}}\rangle=E_{\mathrm{HL}}$$

$$E_{\mathrm{HL}} = \frac{1}{1 + S^2}\iint \phi_a(1)\phi_b(2)H[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]dv_1dv_2$$

$$E_{\mathrm{HL}} = 2E_{1s} + \frac{Q}{1 + S^2} + \frac{J}{1 + S^2}$$

$$Q = \iint \phi_a(1)^2\,\phi_b(2)^2\left(-\frac{e^2}{|r_1 - R_b|} - \frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_2$$

$$J = \iint \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(-\frac{e^2}{|r_1 - R_b|} - \frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_2$$

	Biding energy （eV）	Distance between atoms (Å)
Molecular orbital	2.65	0.85
Atomic orbital	3.14	0.87
Experiment	4.72	0.74

The atomic orbital method is better than the molecular method for hydrogen molecule. Note that the spin state of the atomic orbital is given by [α(1) β(2) −β(1) α(2)]/$\sqrt{2}$]

Consider other atomic orbital state with parallel spins as follow ;

$$\Phi_T = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2(1-S^2)}}[\phi_b(1)\phi_a(2) - \phi_a(1)\phi_b(2)]\alpha(1)\alpha(2)$$

The spin function is expressed by other two sets $\beta(1)\,\beta(2)\,(S_z=-1)$,

[α(1) β(2) + β(1) α(2)]/$\sqrt{2}$]($S_z=0$) for parallel spins (S=1).

The expectation value of energy for parallel spins ($S=1$)

$$2E_{1s} + \frac{Q}{1-S^2} - \frac{J}{1-S^2}$$

overlap integral

For anti-parallel spin ($S=0$)

$$2E_{1s} + \frac{Q}{1+S^2} + \frac{J}{1+S^2}$$

The difference between $S=0$ and $S=1$ state is 2J where

$$J = \iint \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(-\frac{e^2}{|r_1-R_b|}\right.$$
$$\left. -\frac{e^2}{|r_2-R_a|} + \frac{e^2}{r_{12}}\right)dv_1dv_1 = -2St + J'$$

Since the overlap integral between the 1s wave function S is large, J is negative. Therefore, when the spin direction at each atomic site is anti-parallel, atoms are bound. This is called as covalent bond.

$$J = \iint \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(-\frac{e^2}{|r_1 - R_b|}\right.$$
$$\left. -\frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}} + \frac{e^2}{R}\right)dv_1 dv_2$$

The difference between the $S = 0$ and $S = 1$ state is

$$E(\uparrow\downarrow - \downarrow\uparrow) - E(\uparrow\uparrow, \leftarrow\leftarrow, \downarrow\downarrow) = 2J = -4St + 2J'$$

In other context, the effective Hamiltonian is given by $-2J\, s_a \cdot s_b$.

note $S = s_a + s_b$ and $S(S+1) = S^2 = s_a^2 + s_b^2 + 2s_a \cdot s_b$

Note $s_a \cdot s_b = -3/4$ for $S = 0$ and $s_a \cdot s_b = 1/4$ for $S = 1$.

$$E(S = 0) - E(S = 1) = 2J \text{ is obtained.}$$

$-2J\, s_a \cdot s_b$ type of Hamiltonian is applicable for many-body systems and is called as the *Heisenberg Hamiltonian*.

Problem 1

Consider the electronic state of hydorgen molecule ion (H_2^+). The Hamiltonian $[\mathcal{H}(H_2^+)]$ is given by,

$$\mathcal{H}(H_2^+) = \frac{-\hbar^2}{2m}\Delta - \frac{e^2}{|\mathbf{r} - \mathbf{R_a}|} - \frac{e^2}{|\mathbf{r} - \mathbf{R_b}|}$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the differential operetor of kinetic energy and $U_0 = -\frac{e^2}{r - R_a} - \frac{e^2}{r - R_b}$ is the Coulomb attractive potential energy between electron and nuclei. $\mathbf{r}, \mathbf{R_a}, \mathbf{R_b}$ are the position vectors at electron, and neclear A and B, respectively. e and m is the charge and mass of electron. $h(\hbar = h/2\pi)$ is the Plank's constant. When E_{1s} is the eigen energy for the 1s state of hydrogen atom and $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are their eigen function for the nuclear A and B, respectively. Anser the following problems..
The transfer integral (t) and the Coulomb integral are respectively defined by

$$t = \int \psi_a(\mathbf{r})\frac{e^2}{|\mathbf{r} - \mathbf{R_a}|}\psi_b(\mathbf{r})d\mathbf{r} = \int \psi_b(\mathbf{r})\frac{e^2}{|\mathbf{r} - \mathbf{R_b}|}\psi_a(\mathbf{r})d\mathbf{r}$$

$$u = \int |\psi_a(\mathbf{r})|^2\frac{e^2}{|\mathbf{r} - \mathbf{R_b}|}d\mathbf{r} = \int |\psi_b(\mathbf{r})|^2\frac{e^2}{|\mathbf{r} - \mathbf{R_a}|}d\mathbf{r}$$

Then, the overlap integral (S) of the 1s wave function for the A and B nuclear is also defiend by $S = \int \psi_a(\mathbf{r})\psi_b(\mathbf{r})d\mathbf{r}$.

[1] Write down the following matrix elements of $\mathcal{H}(H_2^+)$, $< \psi_a(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_a(\mathbf{r}) >, < \psi_a(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_b(\mathbf{r}) >,$
$< \psi_b(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_a(\mathbf{r}) >, < \psi_b(\mathbf{r})|\mathcal{H}(H_2^+)|\psi_b(\mathbf{r}) >$ in terms of the basic functions of $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$
and express them, using E_{1s}, t, u, S.

[2] Consider the electroninc state of H_2^+ by means of the molecular orbital method. Assume that it is given by

$$\Psi(\mathbf{r}) = c_a\psi_a(\mathbf{r}) + c_b\psi_b(\mathbf{r}),$$

When this Shorendinger equation is expressed by

$$\mathcal{H}(H_2^+)\Psi = E\Psi$$

Write down the eigen energy E_1, E_2, using E_{1s}, t, u, S and expess the corresponding eigen function, $\Psi_1(\mathbf{r})$ and $\Psi_2(\mathbf{r})$ in terms of $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$, S. Here $E_1 < E_2$.

Consider the electronic state of hydorgen molecule ion (H_2^+). The Hamiltonian $[\mathcal{H}(H_2^+)]$ is given by,

$$\mathcal{H}(H_2^+) = \frac{-\hbar^2}{2m}\Delta - \frac{e^2}{|\mathbf{r} - \mathbf{R_a}|} - \frac{e^2}{|\mathbf{r} - \mathbf{R_b}|}$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the differential operetor of kinetic energy and $U_0 = -\frac{e^2}{\mathbf{r}-\mathbf{R_a}} - \frac{e^2}{\mathbf{r}-\mathbf{R_b}}$ is the Coulomb attractive potential energy between electron and nuclei. $\mathbf{r}$, $\mathbf{R_a}$, $\mathbf{R_b}$ are the position vectors at electron, and neclear A and B, respectively. e and m is the charge and mass of electron. $h(\hbar = h/2\pi)$ is the Plank's constant. When E_{1s} is the eigen energy for the 1s state of hydrogen atom and $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are their eigen function for the nuclear A and B, respectively. Anser the following problems..
The transfer integral (t) and the Coulomb integral are respectively defined by

$$t = \int \psi_a(\mathbf{r})\frac{e^2}{|\mathbf{r} - \mathbf{R_a}|}\psi_b(\mathbf{r})d\mathbf{r} = \int \psi_b(\mathbf{r})\frac{e^2}{|\mathbf{r} - \mathbf{R_b}|}\psi_a(\mathbf{r})d\mathbf{r}$$

$$u = \int |\psi_a(\mathbf{r})|^2\frac{e^2}{|\mathbf{r} - \mathbf{R_b}|}d\mathbf{r} = \int |\psi_b(\mathbf{r})|^2\frac{e^2}{|\mathbf{r} - \mathbf{R_a}|}d\mathbf{r}$$

Then, the overlap integral (S) of the 1s wave function for the A and B nuclear is also defiend by $S = \int \psi_a(\mathbf{r})\psi_b(\mathbf{r})d\mathbf{r}$.

[1] Consider the spin state for hydrogen molecule H_2. Answer the size of total number of spin, $\mathbf{S} = \mathbf{s_1} + \mathbf{s_2}$.

[2] Write down all possibe electronic states $\Psi_{H_2}(\mathbf{r_1}, \mathbf{r_2})$ for hydrogen molecule H_2 corresponding to each the spin state obtained in [1] as functions of $\Psi_1(\mathbf{r_1})$, $\Psi_1(\mathbf{r_2})$, $\Psi_2(\mathbf{r_1})$ and $\Psi_2(\mathbf{r_2})$ and describe why it is so wirtten.

[3] Answer the eigen wave function $\Psi_{H_2}(\mathbf{r_1}, \mathbf{r_2})_g$ and eigen energy E_g at the ground state as functions of E_{1s}, t, u, S, U, K, J. Here all the integrals on the Coulomb repulsive interaction are defined as follows;

$$U = \int\int |\psi_a(\mathbf{r_1})|^2\frac{e^2}{|\mathbf{r_{12}}|}|\psi_a(\mathbf{r_2})|^2 d\mathbf{r_1}d\mathbf{r_2}$$

$$K = \int\int |\psi_a(\mathbf{r_1})|^2\frac{e^2}{|\mathbf{r_{12}}|}|\psi_b(\mathbf{r_2})|^2 d\mathbf{r_1}d\mathbf{r_2}$$

$$J = \int\int \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2})\frac{e^2}{|\mathbf{r_{12}}|}\psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})d\mathbf{r_1}d\mathbf{r_2}$$

, then all other integrals are ignored. Note $\mathbf{r_{12}} = \mathbf{r_1} - \mathbf{r_2}$.

Problem 3

$$\Phi_{HL} = \frac{1}{\sqrt{2(1 + S^2)}}[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]$$

Show that the expectation value of eigen energy

$$<\Phi_{HL}|H=(H'_1 + H'_2 + e^2/r_{12})|\Phi_{HL}>=E_{HL}$$

$$E_{HL} = \frac{1}{1 + S^2}\int\int \phi_a(1)\phi_b(2)H[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]dv_1 dv_2$$

is given by

$$E_{HL} = 2E_{1s} + \frac{Q}{1 + S^2} + \frac{J}{1 + S^2}$$

where

$$Q = \int\int \phi_a(1)^2\,\phi_b(2)^2\left(-\frac{e^2}{|r_1 - R_b|} - \frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}}\right)dv_1 dv_2$$

$$J = \int\int \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(-\frac{e^2}{|r_1 - R_b|} - \frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}}\cdot\right)dv_1 dv_2$$

Problem 4

We define the following integrals

$$U = \int\int |\psi_a(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_{12}|}|\psi_a(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$K = \int\int |\psi_a(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_{12}|}|\psi_b(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$\boldsymbol{J'} = \int\int \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_{12}|}\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Other integrals are neglected. $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ とする.

Show that

$$E_{HL} + \frac{e^2}{R} + \frac{Q}{1+S^2} + \frac{J}{1+S^2} = 2E_{1s} - 2u - 2\underline{S}t + K + J'$$

$$Q = \int\int \phi_a(1)^2 \, \phi_b(2)^2\left(-\frac{e^2}{|r_1 - R_b|} - \frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}} + \frac{e^2}{R}\right) dv_2 = -2u + K$$

$$J = \int\int \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(-\frac{e^2}{|r_1 - R_b|}\right.$$
$$\left. - \frac{e^2}{|r_2 - R_a|} + \frac{e^2}{r_{12}} + \frac{e^2}{R}\right) dv_2 = -2\underline{S}t + J'$$

And then $E_g - E_{HL} = ?$

Problem 5

An energy difference between the spin-singlet (S=0) state and the spin-triplet (S=1) state is given by

$E (↑↓+ ↓↑) — E(↑↑, ←← ,↓↓) = 2J$

on the basis of the atomic orbital method. Here, $2J = -4\underline{S}t + 2J'$.

$$J' = \int\int \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(\right.$$
$$\left. + \frac{e^2}{r_{12}} \cdot \right) dv_1 dv_2$$

and $\underline{S}$ is the overlap integral.

This energy difference is described by the following effective Hamiltonian using the respective spin-operators S_a and S_b at the A and B sites.

$$H_{eff} = -2J \, s_a \cdot s_b$$

Noting that $S = s_a + s_b$ and $S(S+1) = S^2 = s_a^2 + s_b^2 + 2 s_a \cdot s_b$, when S=0 and S=1, show that $s_a \cdot s_b = -3/4$ and $s_a \cdot s_b = 1/4$, respectively, and the energy difference between S=0 and S=1 is given by 2J. The above Hamiltonian is known as the Heisenberg Hamiltonian is written by $H = -2J\sum_{ij} S_i \cdot S_j$

Problem 6

We next consider a more realistic solution of the electronic state in H_2 beyond either Heitler－London or Molecular Orbital approximations, by assuming $H(1,2)=h(1)+h(2)+V(1,2)$ as a Hamiltonian for H_2 where $h(1)+h(2)$ is the sum of one-electron Hamiltonian and $V(1,2)$ is the Coulomb repulsive interaction between electrons. Several integrals are defined as the follows;

$$\varepsilon \equiv \int \phi_a(1)h(1)\phi_a(1)dv_1 = \int \phi_b(1)h(1)\phi_b(1)dv_1$$

$$t \equiv \int \phi_a(1)h(1)\phi_b(1)dv_1 = \int \phi_b(1)h(1)\phi_a(1)dv_1$$

$$U_0 \equiv \int \phi_a(1)^2\phi_a(2)^2 V(1,2)dv_1dv_2 = \int \phi_b(1)^1\phi_b(2)^2 V(1,2)dv_1dv_2$$

$$U_1 \equiv \int \phi_a(1)^2\phi_b(2)^2 V(1,2)dv_1dv_2 = \int \phi_b(1)^2\phi_a(2)^2 V(1,2)dv_1dv_2$$

$$J' \equiv \int \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2) V(1,2)dv_1dv_2$$

Solve the next problems.

(6-1)The trial wave functions of Molecular Orbital and Heitler-London (HL) with spin-singlet and HL with spin-triplet are given by

$$\Phi_S = \phi_1(1)\phi_1(2)$$

$$\Phi_{HL} = \frac{\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)}{\sqrt{2}}$$

$$\Phi_T = \frac{\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)}{\sqrt{2}}$$

Show the respective expected eigen energies are given as follows;

$$E_S = 2(\varepsilon + t) + \frac{1}{2}U_0 + \frac{1}{2}U_1 + J'$$

$$E_{HL} = 2\varepsilon + U_1 + J'$$

$$E_T = 2\varepsilon + U_1 - J'$$

(6-2) In order to improve the HL wave function;

$$\Phi_{\text{HL}} = \frac{1}{\sqrt{2(1+S^2)}}[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]$$

We incorporate the following states, using $\phi_a(1)$ $\phi_a(2)$ and $\phi_b(1)$ $\phi_b(2)$

$$\Phi' = \frac{1}{\sqrt{2}}[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

Then, the improved trial wave function is expressed by $\Phi = c_1\Phi_{HL} + c_2\Phi'$.

Show how to get the following relation and solve an eigen energy for this state

$$\begin{vmatrix} 2\varepsilon + U_1 + J' - E & 2t \\ 2t & 2\varepsilon + U_0 + J' - E \end{vmatrix} = 0$$

If $U_0 - U_1 >> |t|$ is valid for Mott insulator, show that the eigen energy is given as the follow;

$$E_{\text{HL}} = 2\varepsilon + U_1 + \boxed{J' - \frac{4t^2}{U_0 - U_1}}$$