Lecture note：http://nmr.mp.es.osaka-u.ac.jp/

Evolutional Science and Engineering of Correlated Electrons Matter

◇ Lecturer

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講義情報（Lecture note）
強相関電子機能工学
(Evolutional Science and Engineering
of Correlated Electrons Matter)

◇ **Summary of lecture**

New types of superconducting and magnetic phenomena emerge in correlated electron matters. Strong electron-correlation effect gives rich physical phenomena and functions in condensed matters, being key-concept for heavy-electron materials, itinerant electron magnets, high-transition-temperature cupper-oxide superconductors, novel transition-metal oxides, and organic-conductors magnets and superconductors. We begin with a perspective view on these materials. An overview on experimental techniques, that are powerful tools for investigating these phenomena, are given, focusing on Nuclear Magnetic Resonance (NMR) and Neutron Scattering (NS) experiments. On the basis of microscopic information obtained by these techniques, we address intriguing properties in correlated electron matters and their physical backgrounds. The important functions and central physics of superconductivity are reviewed on conventional materials so as to be able to capture its basic concept. Strongly correlated superconductivity is also remarked for understanding of a new concept for superconductivity mediated by magnetic interactions. Potential application of correlated electron matters to technology is presented focusing on "Spintronics" or "Strongly Correlated Electronics".

Schedule of lecture：

Y. Kitaoka

Oct. ：6th, 13, 20, 27

Nov. ：10th, 17, 24

Dec. ：1th, 8, 15 (examination)

H. Mukuda

Jan. ： 5th, 12, 19, 26（lecture）

Contents

◇ **Contents**

1. Introduction to Correlated Electrons Matters （Report :1-4）

2. Introduction to Magnetism （Report :5-6）

3. Basic notion on Superconductivity （Report :7）

4. How to Probe Rich and Emergent Properties in Correlated Electron Matters

　　--Nuclear Magnetic Resonance (NMR) and Neutron Scattering Methods--

5. Frontier of Superconductivity

　5.1 High-T_c Copper Oxides and Novel superconductivity

　5.2 Spin-fluctuations mediated d-wave superconductivity

　5.3 Heavy-Electron Systems

6. Recent Topics

Why T_c is so high？

1911	Superconductivity was discovered
1986	High-T_c cuprate was discovered
2006	Iron-based system was discovered

Fe-Pnictides Superconductors – Mechanism?

iron-based system

charge reservoir layer

High-T_c cuprate

La
O
e^-
Fe
As
F

La
Cu
O
Sr^{2+}

Electron dope ($O^{2-} \rightarrow F^-$)
O^{2-} deficiencies

Hole dope ($La^{3+} \rightarrow Sr^{2+}$)
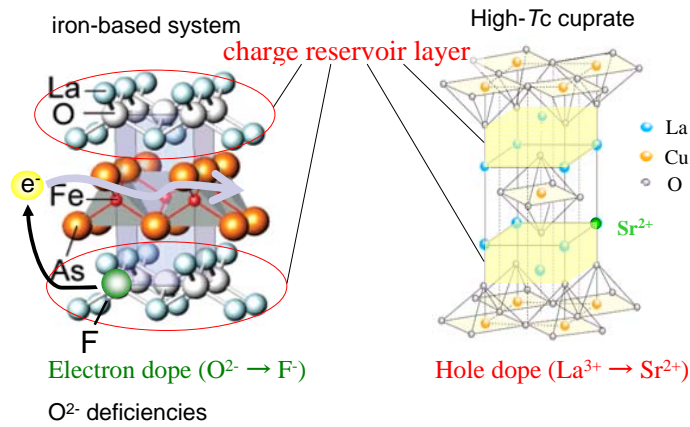
・ Layered structure (charge reservoir layer & conduction layer)

Phase diagram in FeAs and CuO systems

FeAs-based system

High-T_c cuprate

Temperature

AF?

electron density

Temperature (K)

300
250
200
150
100
50

AFMI
AFMM
SC
AFMM +SC
?

0.0   0.1   0.2   0.3
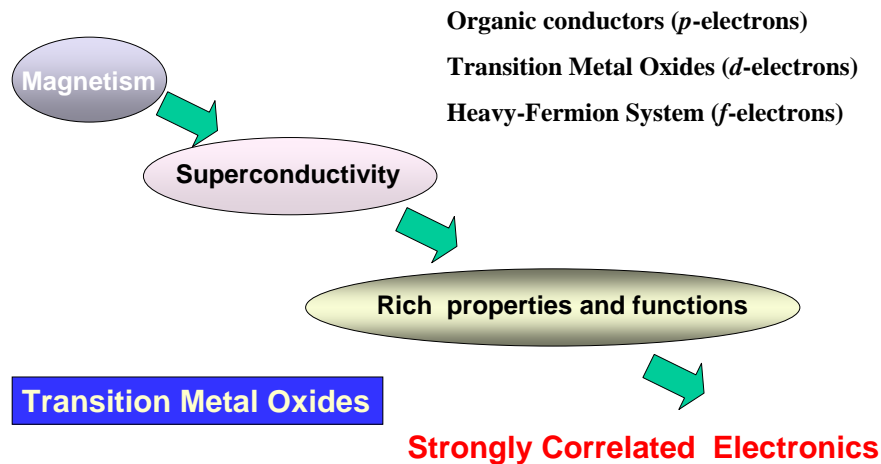Hole density /CuO$_2$ plane
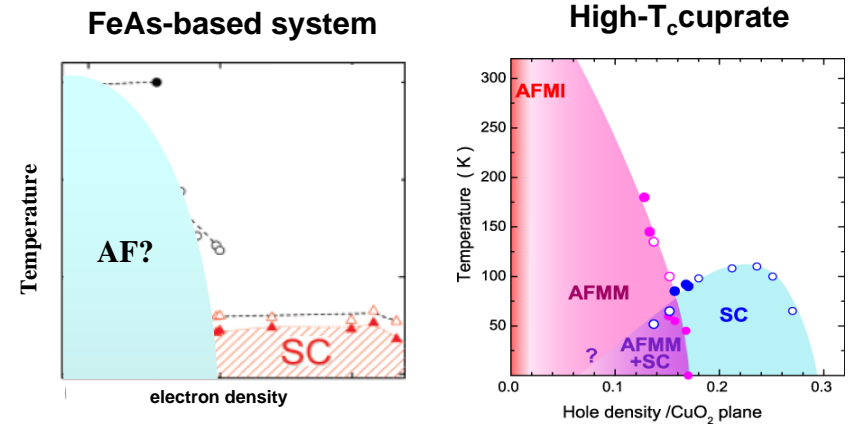
Superconductivity emerges by doping carriers？

Relation to a magnetic instability？

Physics behind Strong Electron Correlation
*and possible application to technology*

Strong correlated electron system shows a rich variety of phenomena

Organic conductors (*p*-electrons)
Transition Metal Oxides (*d*-electrons)
Heavy-Fermion System (*f*-electrons)

Magnetism

Superconductivity

Rich properties and functions

Transition Metal Oxides

Strongly Correlated Electronics

What is the Novel Characteristics of Correlated Electrons ?
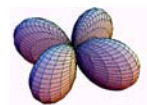
Conventional metal （itinerant electrons with no spin degree of freedom ）
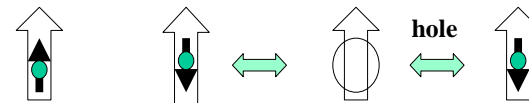*Charge plays role for "Electronics"*

One electron per atom
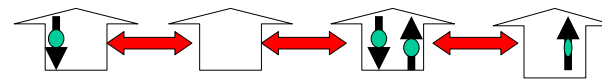
Strong repulsive Coulomb interaction on a same lattice site due to narrow 3d orbitals

Mott Insulators （magnetism with spin degree of freedom)
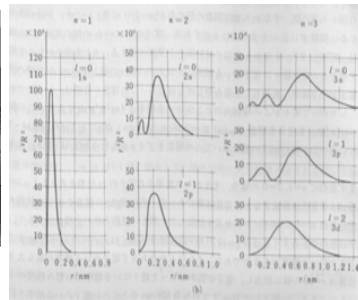
Doped Mott insulators

(quantum liquid and quantum nematics of spin and charge)

hole

Holes are traveling under restricted conditions for spin direction and whether electron is occupied or not.

Panel 1 (top-left)

Narrrow spatial distribution of orbitals of 3d and 4f electrons play role for emergent properties in transition metal oxides and rare earth inter-metallic compounds

Periodic table of elements

Radial Distribution
of Electron Density
at atomic site

Panel 2 (top-right)

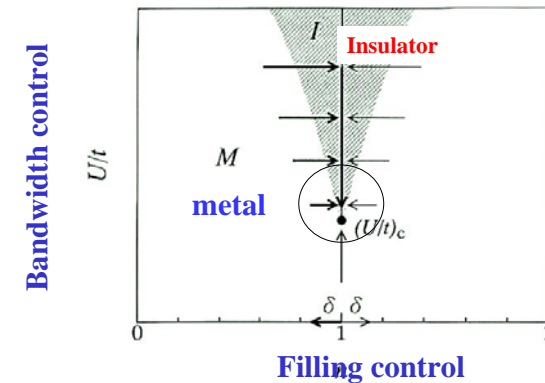**M-I (Mott) transition in correlated electron system**

Hubbard model

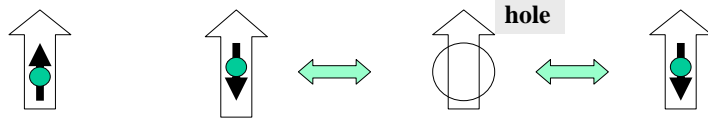$$H = -t\sum a^{+}_{i+1}a_i + U\sum n_{i\uparrow}n_{i\downarrow}$$

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

Filling control

Panel 3 (bottom-left)

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

hole

quantum liquid and quantum nematics of spin and charge

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

Panel 4 (bottom-right)

Classification of Mott Hubbard Insulator and Charge Transfer Insulator

Energy

d band

U

Δ

p band

d band
Upper Hubbard band

Δ

U

p band

Lower Hubbard band

(a)   (b)
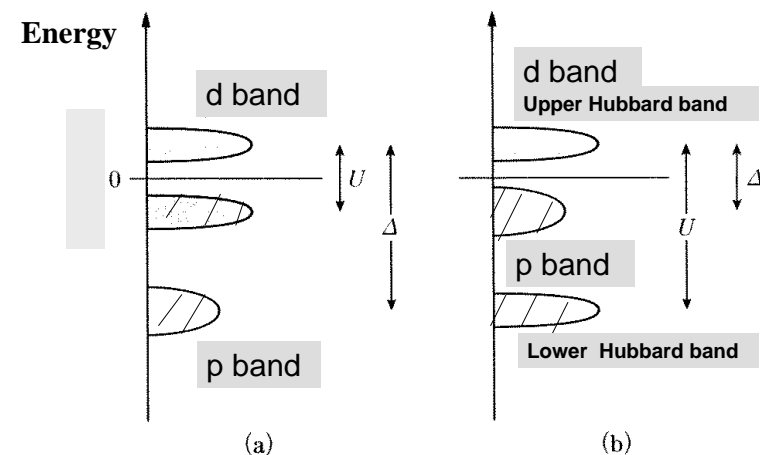
Strong Correlation Effect in Solid

Covalent bonding effect of H_2 molecule

1.2 化 学 結 合

ϕ_A ϕ_B

$\phi_A - \phi_B$

A B

$\phi_A + \phi_B$

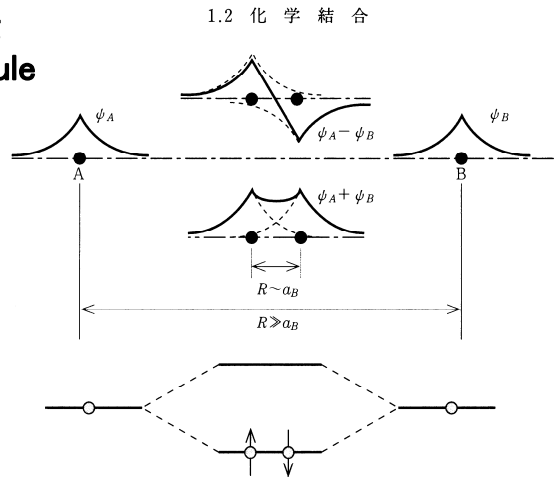$R \sim a_B$

$R \gg a_B$

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．

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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

$$H\psi = E\psi \qquad \begin{vmatrix} H_{aa} - E & H_{ba} - SE \\ H_{ab} - SE & H_{bb} - E \end{vmatrix} = 0$$

Eigen function

$$\psi_1 = \frac{\phi_a + \phi_b}{\sqrt{2(1+S)}},$$

$$\psi_2 = \frac{\phi_a - \phi_b}{\sqrt{2(1-S)}},$$

Eigen energy

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

$$E_2 = \frac{H_{aa} - H_{ab}}{1 - S}.$$

Here

$$S = \int \phi_a \phi_b \, dv, \qquad H_{ij} = \int \phi_i H \phi_j \, dv.$$

$$H_{aa} = H_{bb}, \quad H_{ab} = H_{ba}$$

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2. Hydrogen Molecule（Molecular orbital method）

Put two electrons into the lowest bonding molecular orbital state

$$\psi_1 = \frac{\phi_a + \phi_b}{\sqrt{2(1+S)}}$$

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

$$H = H'_1 + H'_2 + e^2/r_{12} \qquad H' = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{|r - R_a|} - \frac{e^2}{|r - R_b|}$$

The expectation value of eigen energy is given by

$$E_S = 2E_1 + \int \phi_1(r_1)^2 \phi_1(r_2)^2 \frac{e^2}{r_{12}} dv_1 dv_2 \qquad E_1 = \frac{H_{aa} + H_{ab}}{1 + S}$$

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.

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

E

ψ_2

O R

ψ_1

実測
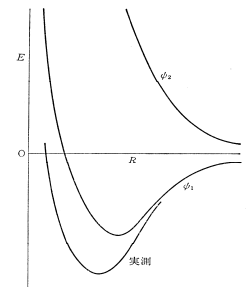
2-1 図　原子間距離の関数として H_2^+ の
結合エネルギーを描いたもの

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

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** .

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

The expectation value of eigen energy is given by

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

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

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

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

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

	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 [$\alpha(1)$ $\beta(2)$ — $\beta(1)$ $\alpha(2)$]/ $\sqrt{2}$]

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

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

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

overlap integral

For anti-parallel spin (I=0)

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

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

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

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.

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.

$E(S=0) - E(S=1) = 2J$ is obtained.

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

When **J** is negative due to the overlap of wave functions among nearest neighbor atomic sites, Spins are anti-parallel. On the other hand, if the wave function is orthogonalized, J is always positive and hence ferromagnetism is realized

Proof:

$$J_{n_1 n_1} = \int \varphi_{n_1}^*(r_1)\varphi_{n_2}^*(r_2)\frac{e^2}{r_{12}}\varphi_{n_1}(r_2)\varphi_{n_1}(r_1)d\tau_1 d\tau_2$$

1 / r is expanded in a Fourier series as

$$\frac{e^2}{r_{12}} = \frac{1}{V}\sum_k \frac{4\pi e^2}{k^2}e^{ik\cdot(r_1-r_2)}$$

$J = -2St + J' = J'$ (because of S=0)

$$J_{n_1 n_1} = \frac{1}{V}\sum_k \frac{4\pi e^2}{k^2}\int \varphi_{n_1}^*(r_1)\varphi_{n_2}(r_1)e^{ik\cdot n}d\tau_1$$
$$\times \int \varphi_{n_1}^*(r_2)\varphi_{n_1}(r_2)e^{-ik\cdot n}d\tau_2 > 0$$

のように書きかえられる. したがって $J_{n_1 n_1}$ は常に正である.

M-I (Mott) transition in correlated electron system

Hubbard model

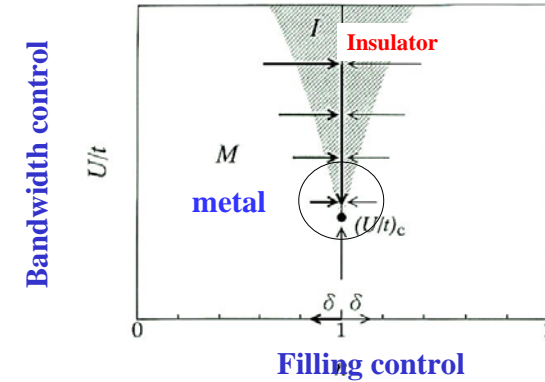$$H = -t\sum a^+_{i+1}a_i + U\sum n_{i\uparrow}n_{i\downarrow}$$

Kinetic energy　　　On-site Coulomb repulsive interaction

To see outside world　　　**Make them away from each other**

Bandwidth control (vertical axis U/t)

Filling control (horizontal axis)

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

$$E_g = 2E_1 + \frac{1}{(1+S^2)}[U/2 + K/2 + J'] \quad \Psi_{H_2}^{S=0} = \Psi_1(\mathbf{r}_1)\Psi_1(\mathbf{r}_2))$$

$$E_1 = \frac{E_{1s}(1+S)-u-t}{(1+S)}$$

$$E_{HL} = 2E_{1s} + \frac{Q}{1+S^2} + \frac{J}{1+S^2} = 2E_{1s} - 2u - 2\underline{S}t + K + J'$$
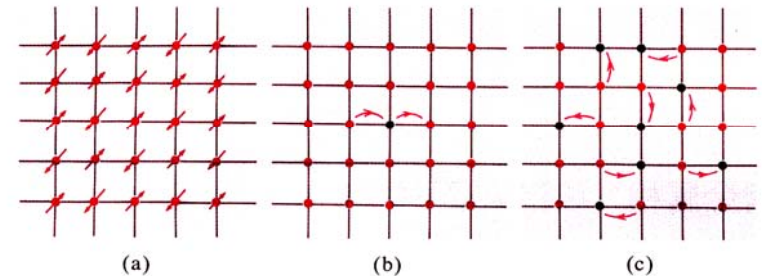
$$Q = \iint \phi_a(1)^2\phi_b(2)^2\left(-\frac{e^2}{|r_1-R_b|}-\frac{e^2}{|r_2-R_a|}+\frac{e^2}{r_{12}}\right)dv_1 dv_2 = -2u+K$$

$$J = \iint \phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)\left(-\frac{e^2}{|r_1-R_b|}\right.$$
$$\left.-\frac{e^2}{|r_2-R_a|}+\frac{e^2}{r_{12}}\right)dv_1 dv_2 = -2\underline{S}t+J'$$

Hubbard model: K=0

$$E_g - E_{HL} = [(K/2+U/2-2t) - (K+2\underline{S}t)] \sim (U-K)/2-2t = [(U-K) - 4t]/2 > 0$$

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

Mott Insulator and charge-carriers doped Insulator – Metal Transition

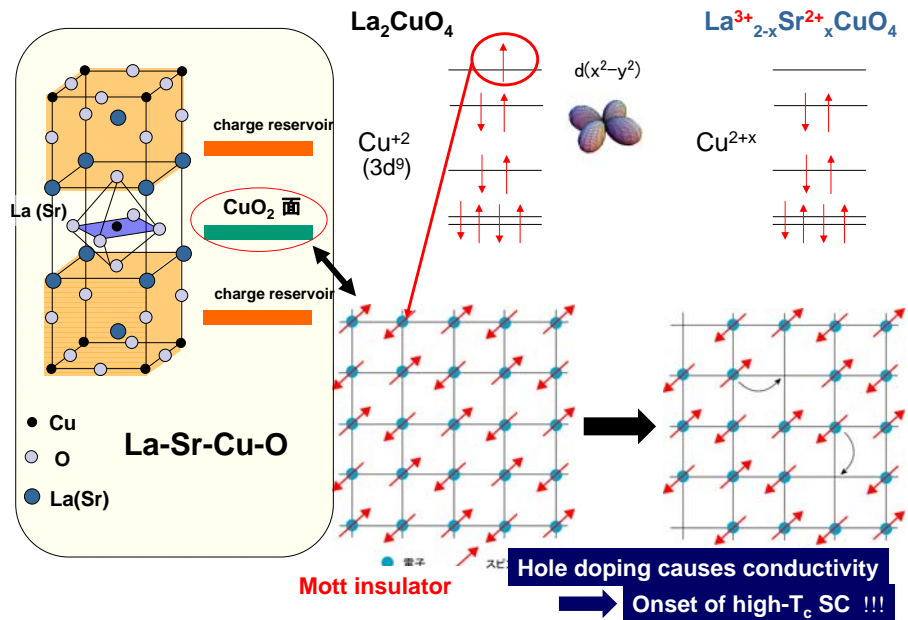(a)　　　(b)　　　(c)

Mott Insulator　　**Strongly Correlated Metal**　　**Conventional Metal**

How to dope carriers　　　·**Chemical substitution**
　　　　　　　　　　　　　　·**Photo induced carriers injection**

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 !!!

High Temperature Superconductivity in Doped Strong Correlated Oxides

Cu
Nd(Ce)
La(Sr)
Block Layer
CuO$_2$ Sheet
Block Layer

T

AF

SC

SC

0.15

0

0.15

x

La$_{2-x}$Sr$_x$CuO$_4$

Nd$_{2-x}$Ce$_x$CuO$_4$

T′
Nd$_{2-x}$Ce$_x$CuO$_4$

T
La$_{2-x}$Sr$_x$CuO$_4$

Nd^{3+}→Ce^{4+}
Electron doping

La^{3+}→Sr^{2+}
Hole doping

Hole doping

Electron doping
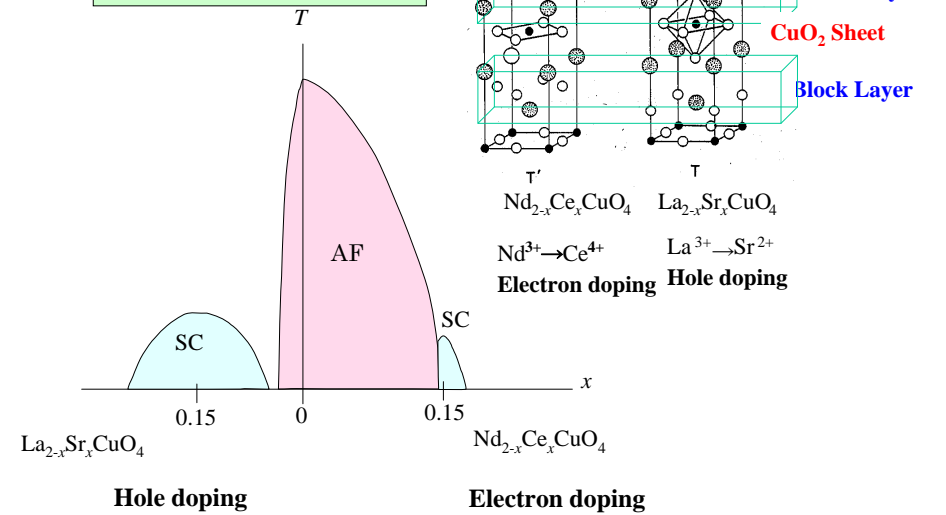
Origin of force in the Nature

Magnetic exchange interaction

$$-JS_1 \cdot S_2$$

AFM Mott Insulator

(A) Molecular
Heitler-London (1927)
Heisenberg (1932)

p　p

e$^-$

e$^-$

p　p

migrating real fermion

(B) Nuclear Force
Yukawa (1935)

n　p

π$^+$

p　n

mediating virtual boson

強い相互作用：
meson

弱い相互作用：
weak bosons

電磁相互作用：
photon

Formation of Copper pairs

mobile electrons

e$^-$　e$^-$

BCS theory：

Mediating virtual bosons: phonon
magnetic excitations

Heisenberg Model

$$H = \sum_{\langle i,\, j \rangle} J_{ij} S_i \cdot S_j,$$

AFM + Local Spin Singlet