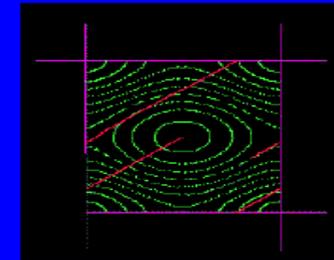
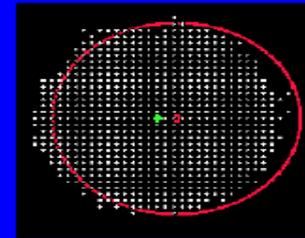
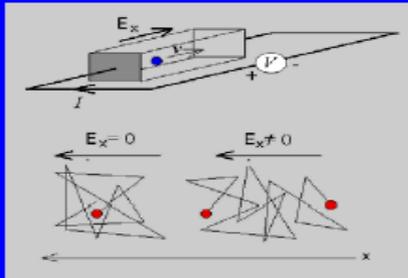


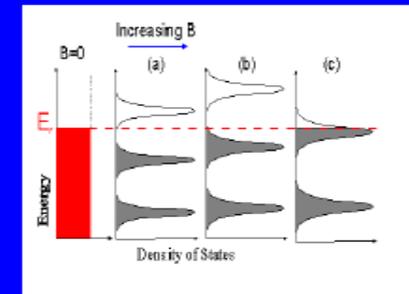
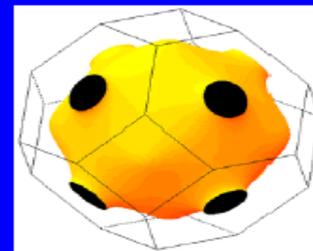
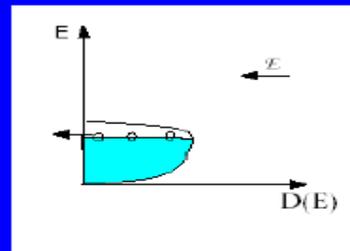
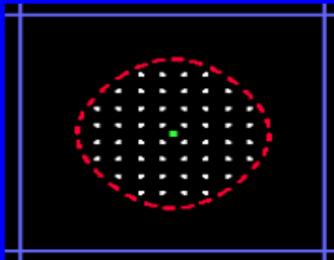
# Transport Phenomena in Solids

## Motions of electrons and transport phenomena



$$\sigma = \frac{ne^2\tau}{m}$$

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \sum_j \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}$$



# Strongly correlated electron systems

## What is it?

Systems where interaction between electrons is very large (mainly Coulomb repulsion). Electrons are usually localized at the atomic sites

This includes most transition metal oxides, typically with partially filled  $d$  or  $f$  shells

This yields a close correlation of the spin, charge, orbital and lattice degrees of freedom of the electrons.

# Strongly correlated electron systems

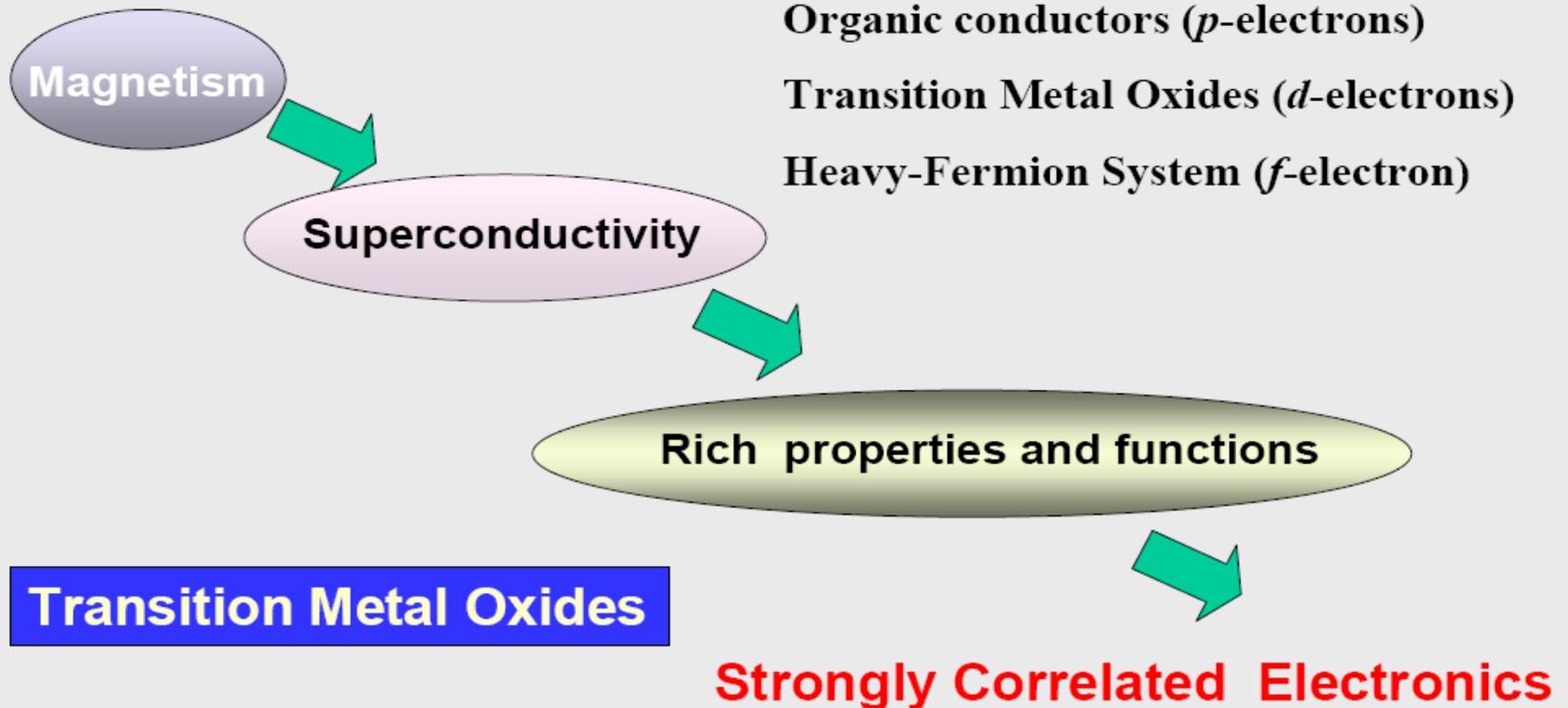
collection of many similar objects  
that mutually interact  
exhibits new properties characteristic of collection

There exists a family of solids, in which the electron–electron interaction plays so substantial a role that the one-electron approximation fails. This is known as the strongly correlated electron system. Historically, De Boer and Verwey were the first to point out, as early as in 1937, that NiO in the NaCl structure should be metallic, since the Fermi level falls in the middle of the Ni-3d band.

NiO is known to exist as a transparent insulator

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

**Strong correlated electron system shows a rich variety of phenomena**



Strongly correlated electrons: movement of one electron depends on positions of all other electrons due to long ranged Coulomb repulsion

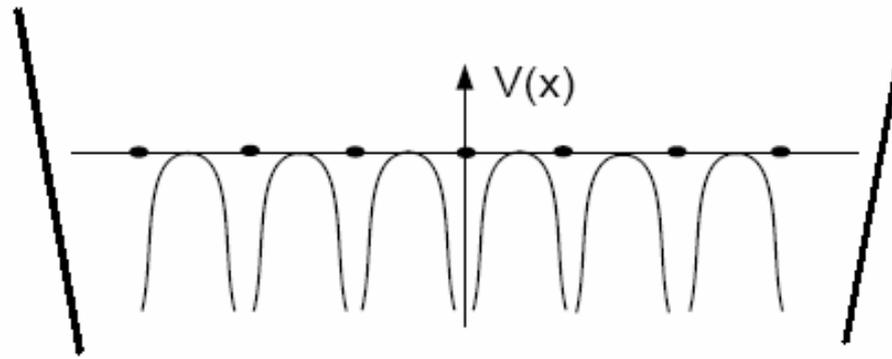
Novel Phenomena and functionalities:

- high temperature superconductivity (1986: Bednorz & Müller)
- colossal magneto resistance CMR
- magnetocaloric effect
- multiferroic effect
- metal-insulator transition
- negative thermal expansion

- Fermi gas:
  - Fermi liquid:
  - band structure:
- single  
particle  
wave  
function

- electronic correlations: strong Coulomb interaction!

- adiabatic approximation (Born-Oppenheimer)  
separates lattice and electronic degrees of freedom

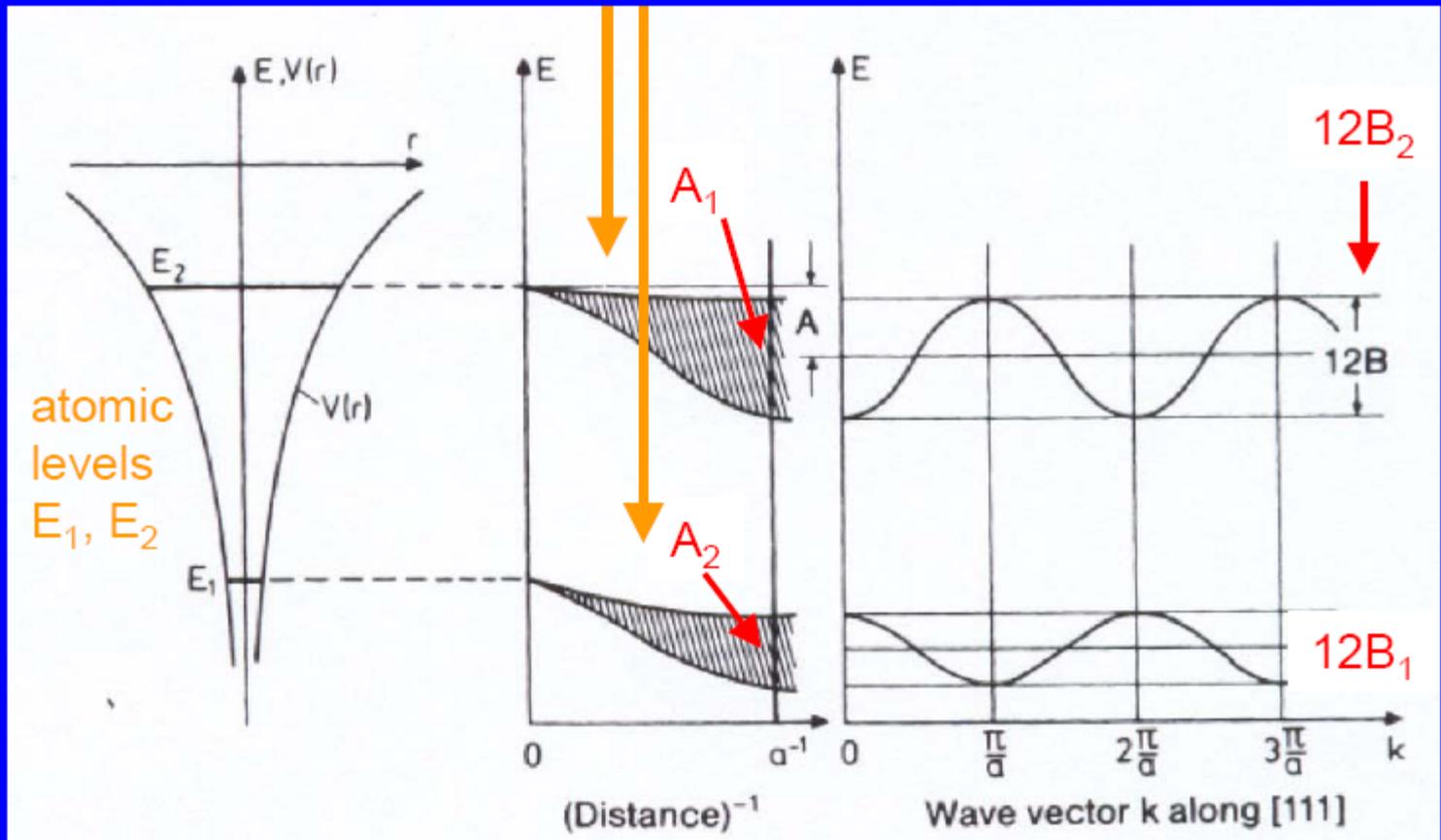


free electron model: single electron moves in 3d potential well with infinitely high walls (crystal surfaces)

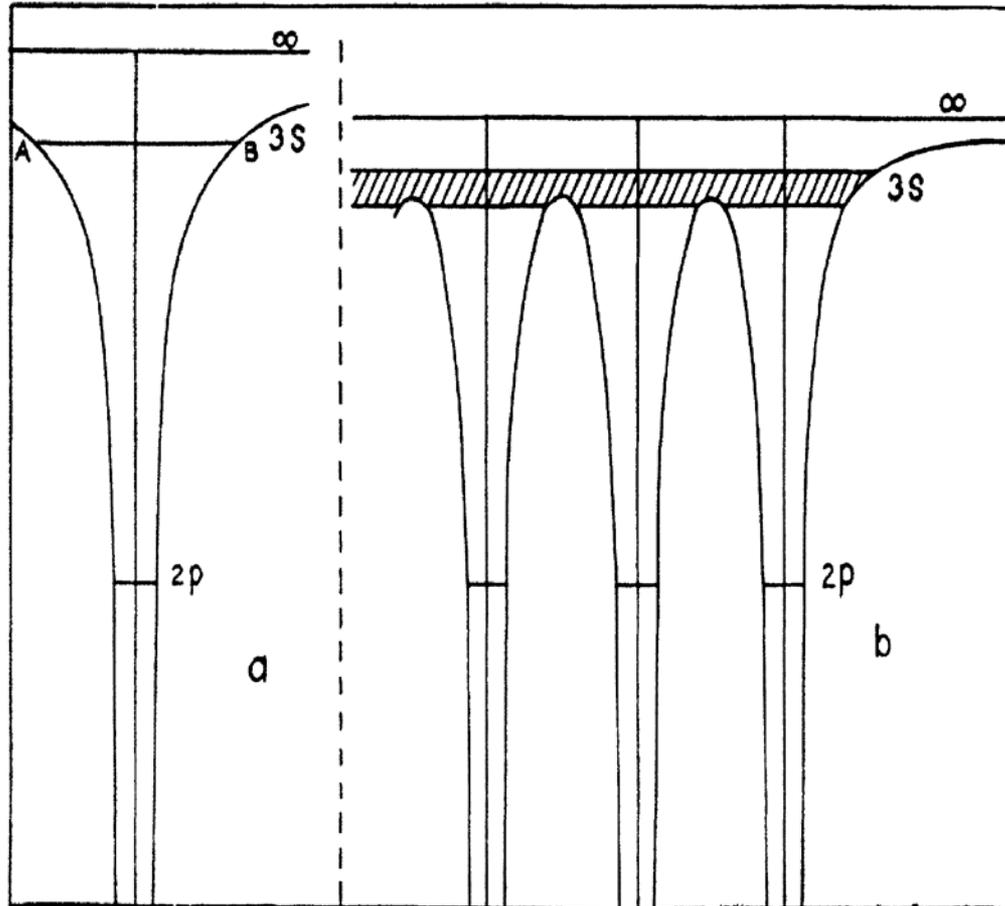
electron-electron interaction accounted for by quasiparticles “dressed electrons” with charge  $e$ , spin  $\frac{1}{2}$ , but effective mass  $m^*$

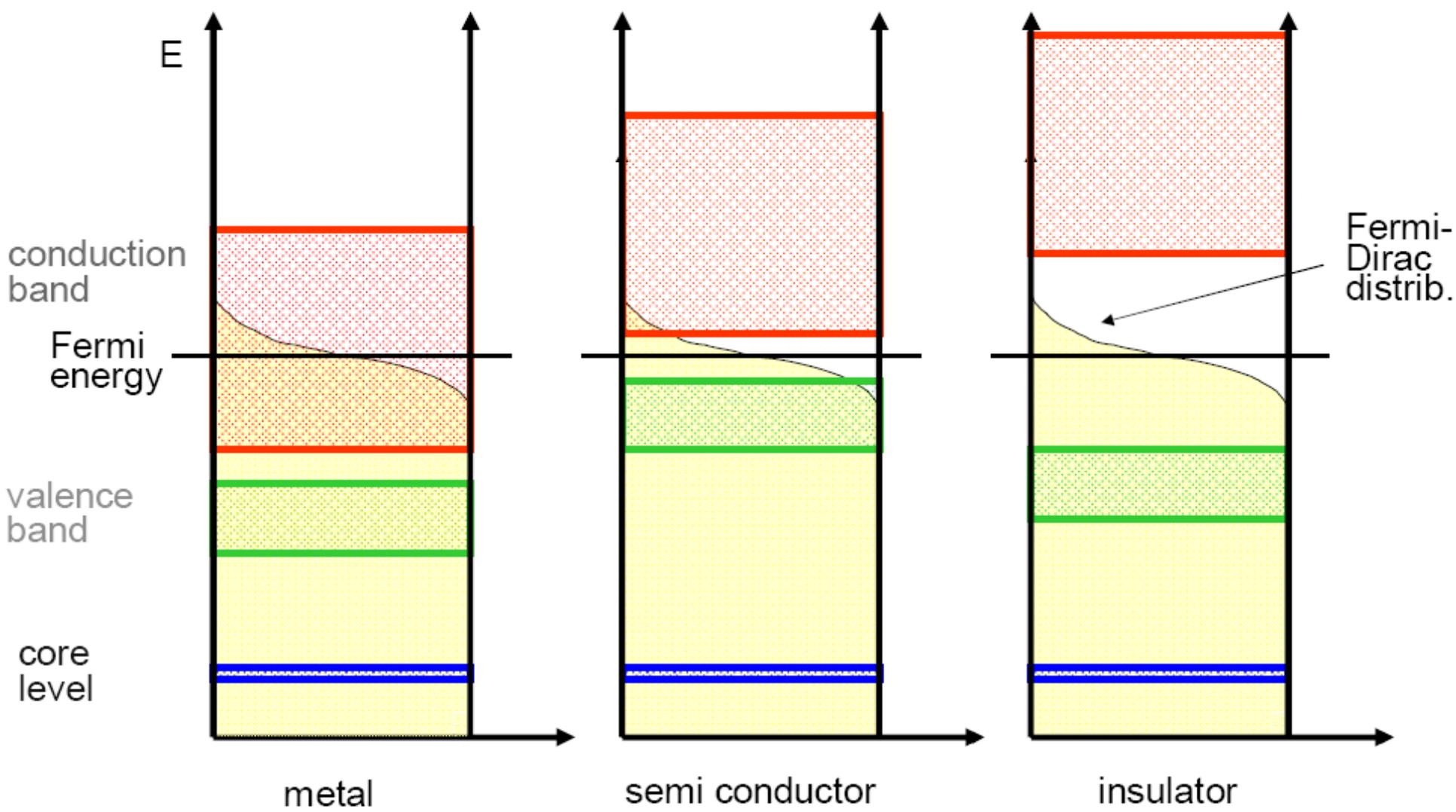
takes into account periodic potential of atomic cores at rest;  $e^-$  moves in average potential from atomic cores and other  $e^-$

## tight-binding bands



- energy width larger as overlap (hybridization) increases
- $2N$  electrons per band





... but where are the electronic correlations?

# Fermi liquid theory and quasiparticles

Landau considered that any homogeneous system composed of a large number of particles has **low-lying excited states** of waves and introduced the concept of the **quasiparticle** to describe the waves.

- A typical example is an assembly of atoms, from which **lattice waves** are excited and **phonons** are created as quasiparticles.
- The **interacting electron system** is called the electron liquid or the **Fermi liquid** in contrast to an ideal electron gas or the Fermi gas for the case of non-interacting electrons.
- The **Coulomb interaction** between electrons is included in the energy dispersion of the quasiparticle.
- one-electron approximation for electrons near the Fermi level in interacting electron systems → each conduction electron experiences an average Coulomb field created by other electrons.

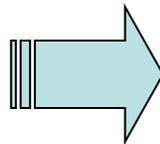
The **Coulomb interaction** between the conduction electrons in a metal is reduced to the screened short-range potential  $\exp(-\lambda r)/r$

the **Coulomb interaction** is screened at large distances and each electron effectively keeps other electrons away from its neighbors and behaves as if it carries a “positively charged” cloud along with it.

$$\varepsilon(k) = \hbar^2 k^2 / 2m^*$$

The quasiparticle is defined in such a way that the energy of each electron is modified when the interaction between electrons is gradually turned on.

**Number of quasiparticles**



$$f(\mathbf{p}, \mathbf{r}) d\mathbf{p} d\mathbf{r} / h^3$$

The quasiparticle is assumed to carry the electronic charge ( $-e$ ) in the same way as the non-interacting free-electron and to interact with the ionic potentials. In this way, the energy dispersion for the quasiparticle can be uniquely defined.

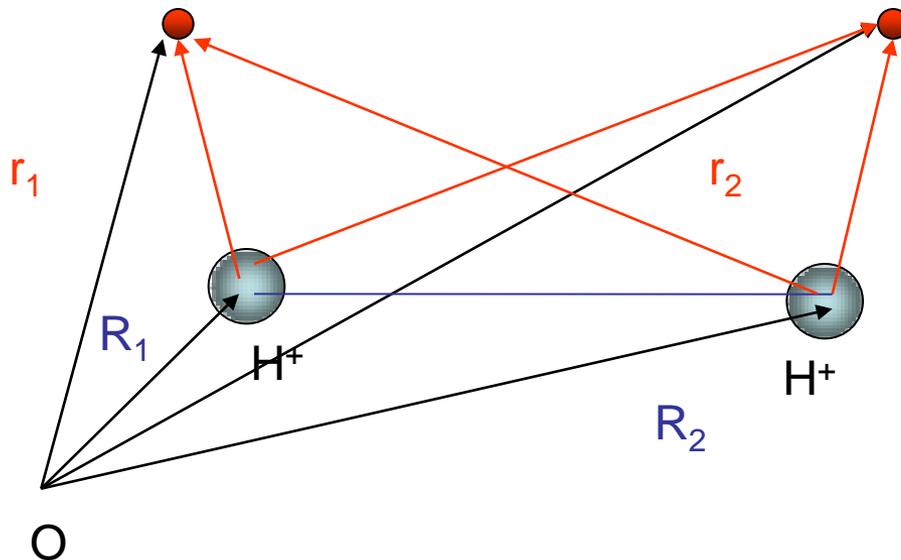
# Electronic states of hydrogen molecule and the Heitler–London approximation

Let's see the limits of one-electron approximation

See Mizutani

→we ignore electron-electron interaction

$$\left[ \sum_{i=1,2} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_2|} \right) \right] \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2),$$



$$(H_1 + H_2) \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2),$$

$$H_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_2|} \quad (i=1, 2).$$

one-electron Hamiltonian

$$H\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$\psi_0(\mathbf{r}) \text{ and } \psi_1(\mathbf{r}),$$

where

$\psi(\mathbf{r})$  is the one-electron wave function and  $\varepsilon$  is its energy in the presence of the two protons.

the lowest energy  $\varepsilon_0$  and the second-lowest energy  $\varepsilon_1$

total orbital wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  for two electrons

at the lowest energy  $E_s = 2\varepsilon_0$

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2).$$

next-lowest energy  $E_t = \varepsilon_0 + \varepsilon_1$

$$\psi_t(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1)\psi_1(\mathbf{r}_2) - \psi_0(\mathbf{r}_2)\psi_1(\mathbf{r}_1)$$

the relation  $E_s < E_t$  holds, since  $E_s - E_t = \varepsilon_0 - \varepsilon_1 < 0$ .

the total wave function  $\implies$   
must be antisymmetric

product of the orbital and spin  
wave functions

The spin states of a two-electron system like the hydrogen molecule  
linear combination of  $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle$  and  $|\downarrow\downarrow\rangle$ :

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

$$S_z = 0, 1, 0 \text{ and } -1$$

**singlet** ( $S=0$  and  $S_z=0$ )  $\implies$  symmetric orbital wave function

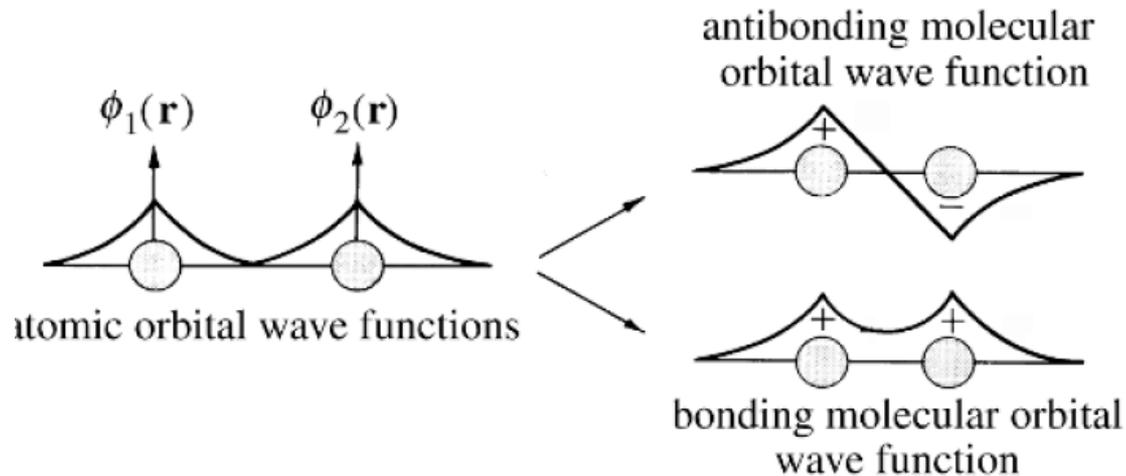
**triplet** ( $S=1$  and  $S_z=1, 0$  and  $-1$ )  $\implies$  antisymmetric

linear combination of atomic orbitals in the tight-binding method.

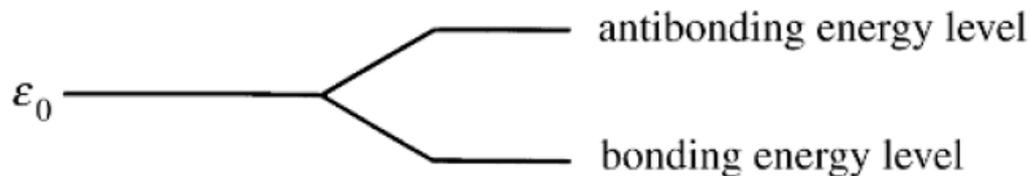
$$\psi_0(\mathbf{r}) = \phi_1(\mathbf{r}) + \phi_2(\mathbf{r}) \quad \text{bonding molecular orbital}$$

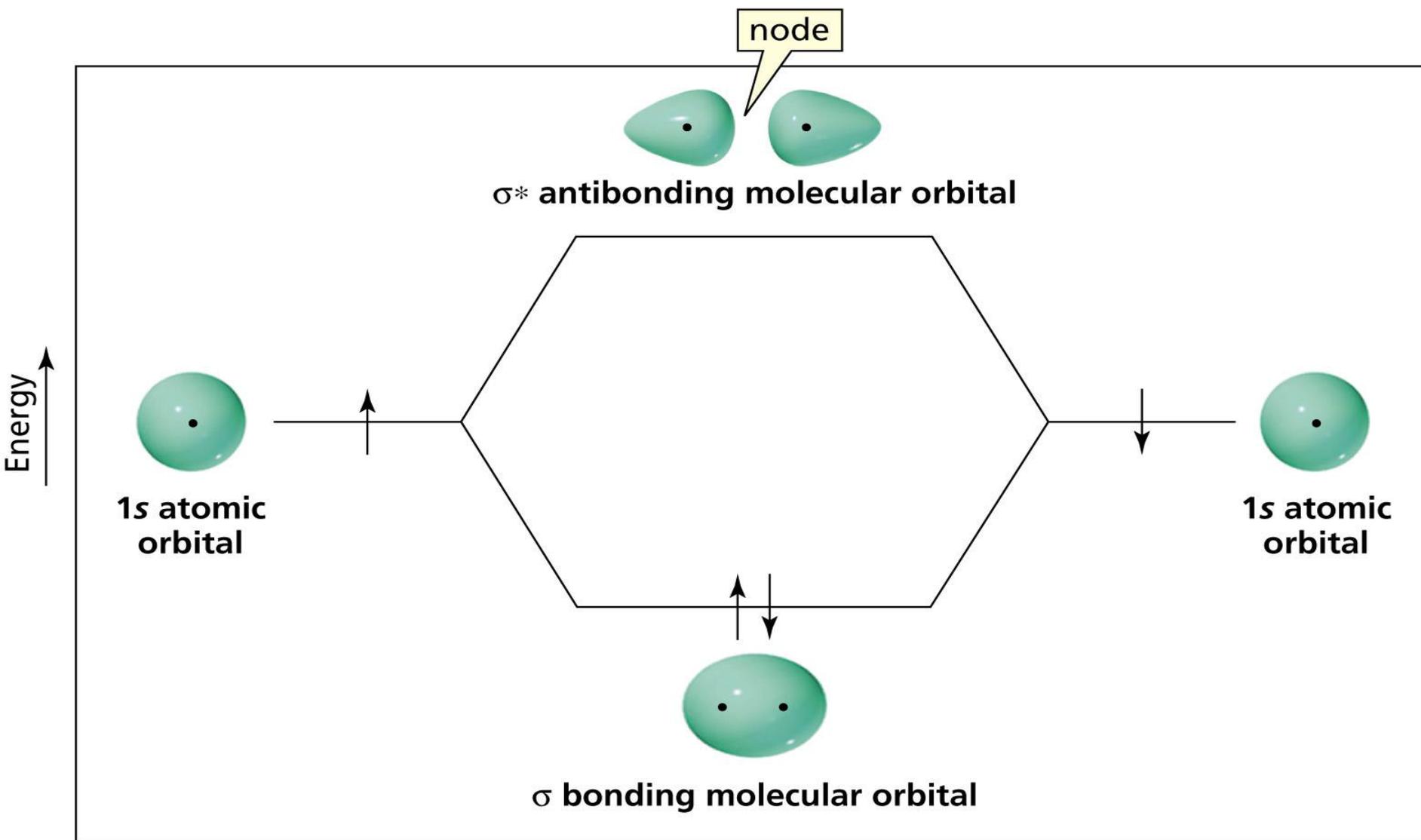
$$\psi_1(\mathbf{r}) = \phi_1(\mathbf{r}) - \phi_2(\mathbf{r}), \quad \text{antibonding molecular orbital}$$

$\phi_i(\mathbf{r})$  is the 1s atomic orbital wave function of the hydrogen atom



from Mizutani





$$\begin{aligned}\psi_s(\mathbf{r}_1, \mathbf{r}_2) &= \psi_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2) \\ &= \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\end{aligned}$$

The first and second terms the motion of each electron around the respective protons  $i=1$  and  $2$

the third and fourth  
two electrons simultaneously occupy the same orbit

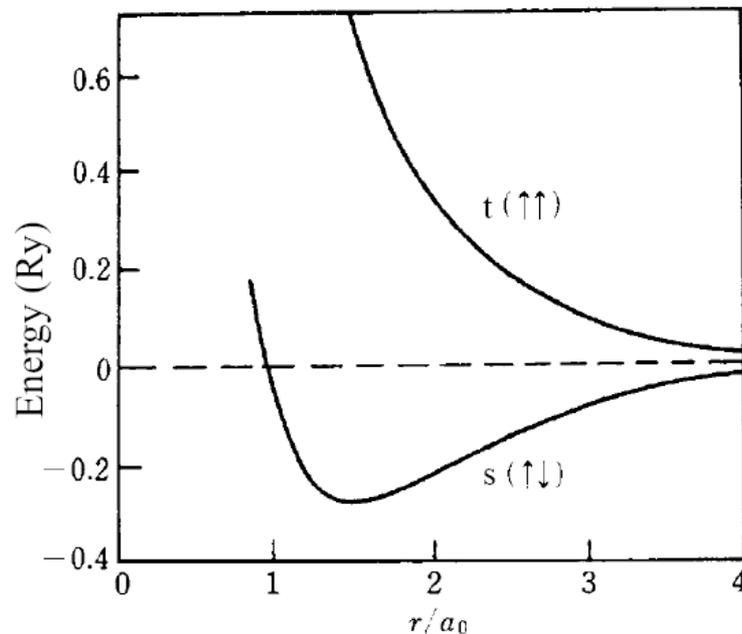
- If we were to include the electron–electron interaction in equation then the third and fourth terms should not have occurred because of an increase in the Coulomb repulsion between the two electrons.
- it is clear that this equation cannot be taken as the ground state in the hydrogen molecule, since the electron–electron interaction cannot be neglected.

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2).$$

- the energy of the system can be lowered by aligning two spins in different orbits parallel to each other
- electrons occupy orbits around different atoms as in the hydrogen molecule.

the singlet  
state becomes more stable.

$$\begin{aligned}\psi_t(\mathbf{r}_1, \mathbf{r}_2) &= \psi_0(\mathbf{r}_1)\psi_1(\mathbf{r}_2) - \psi_0(\mathbf{r}_2)\psi_1(\mathbf{r}_1) \\ &= 2[\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) - \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)].\end{aligned}$$



from Mizutani

Figure 14.2. Energy of the hydrogen molecule in the Heitler–London model. The symbols  $s(\uparrow\downarrow)$  and  $t(\uparrow\uparrow)$  refer to the symmetric and antisymmetric orbital wave functions, respectively. The energy is taken to be zero, when two hydrogen atoms are infinitely apart. The distance is normalized with respect to the Bohr radius  $a_0 = 0.053$  nm.

## Failure of the one-electron approximation in a strongly correlated electron system

We extend now the discussion from  $N=2$  to  $N = N$  in tight binding method

We now consider a cuprate compound typical of a strongly correlated electron system, which undergoes a transition to the superconducting state by carrier doping, and show how the one-electron approximation fails when applied to it. A large number of high- $T_c$  cuprate compounds crystallize into the layered perovskite structure, in which the  $\text{CuO}_2$  plane and the so-called “block layer” are stacked, as sketched in Fig. 14.3 [4]. The block layer represents an intervening layer composed of metal ions and oxygen ions.

from Mizutani

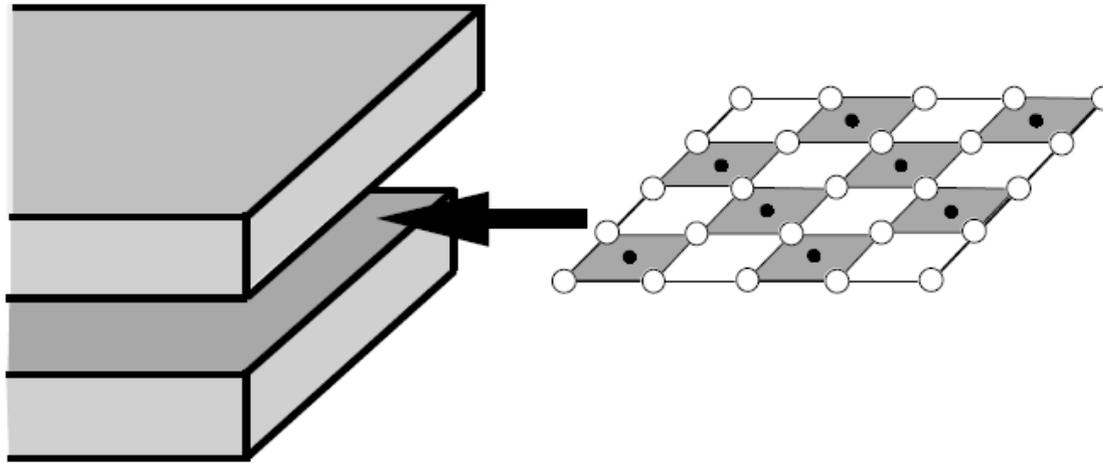


Figure 14.3. Alternate stacks of block layer and  $\text{CuO}_2$  plane of the high- $T_c$  cuprate superconductors.

from Mizutani

As a typical example, we show the crystal structure of the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  compound in Fig. 14.4. It consists of a repetition of the rock salt-type  $\text{La}_2\text{O}_2$  block layer and the  $\text{CuO}_2$  plane. The  $\text{CuO}_2$  plane per cell is charged to  $-2$ , since Cu and O atoms are ionized to  $+2$  and  $-2$ , respectively. The average charge of the block layer must be  $+2$  in order to maintain charge neutrality in the whole crystal. The replacement of  $\text{La}^{3+}$  by  $\text{Sr}^{2+}$  ions in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  compound causes the charge of the block layer to decrease to  $3(2-x) + 2x - 4 = 2-x$  and the difference  $x$  must be compensated for in the  $\text{CuO}_2$  plane to maintain charge neutrality. This means that the excess positive charge enters into the  $\text{CuO}_2$  plane and makes it to be conductive. This is called hole doping.

from Mizutani

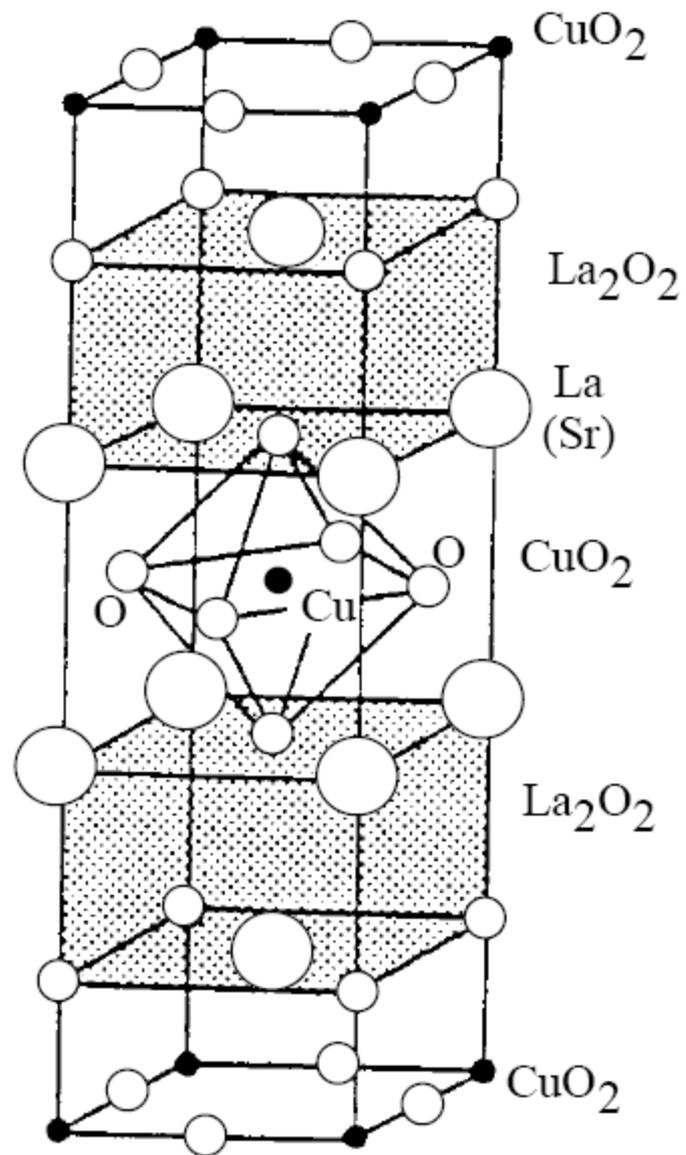
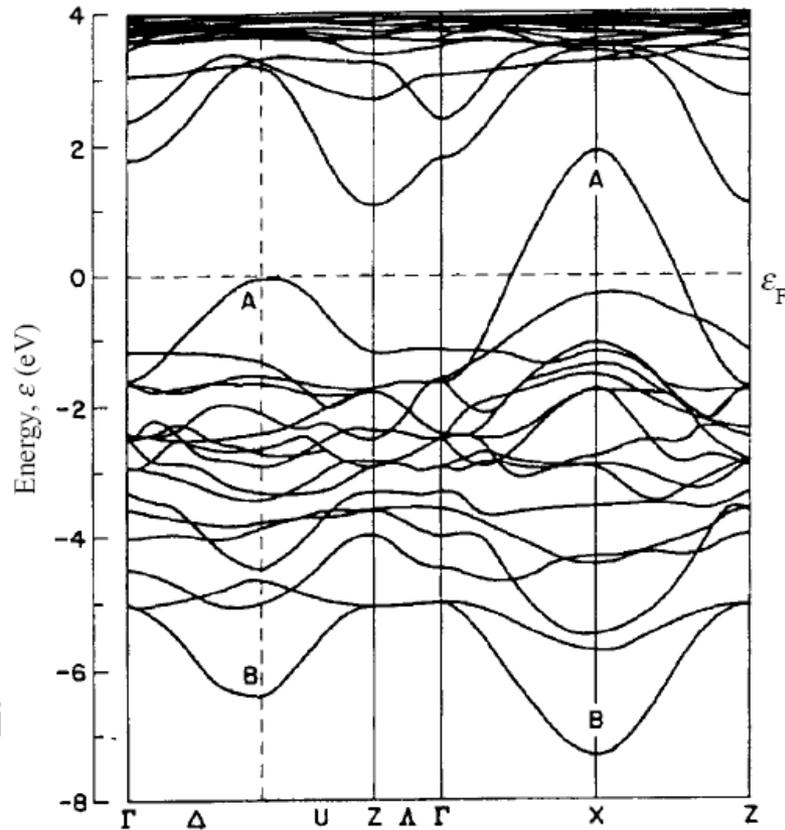


Figure 14.4. Structure of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . [Y. Tokura, H. Takagi and S. U  
*Nature* 337 (1989) 345]

The one-electron band calculations have been performed for such oxides.

A fairly large hole Fermi surface is centered at X.



This clearly indicates the formation of a metal.

•this undoped compound is an antiferromagnetic insulator.

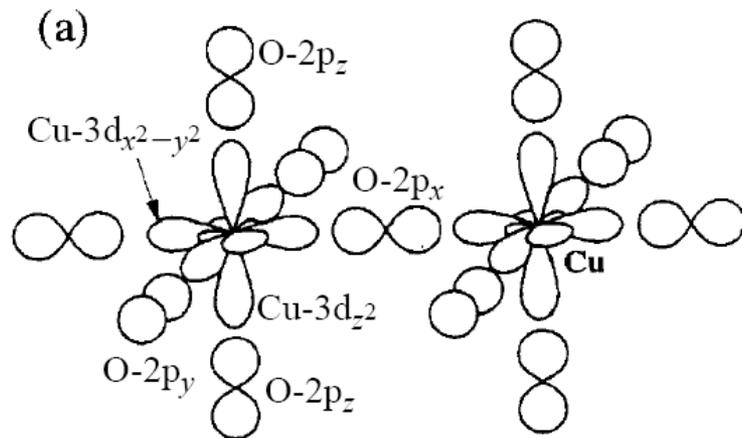
from Mizutani

Figure 14.5. Energy bands for  $\text{La}_2\text{CuO}_4$  in the bct Brillouin zone [5]. A and B represent the antibonding and bonding states between  $\text{Cu-}3d_{x^2-y^2}$  and  $\text{O-}2p_\sigma$  orbitals, respectively.

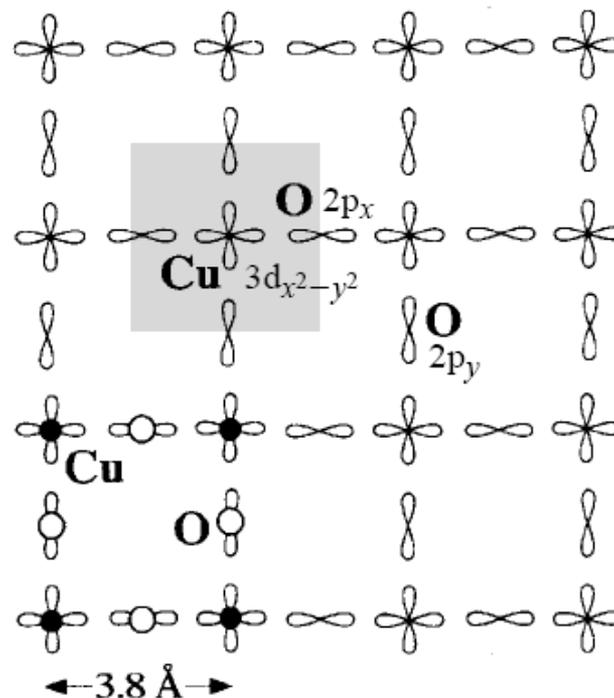
hybridization of the  $3d_{x^2-y^2}$  orbitals of Cu sites



with  $2p_{\sigma}$  orbitals of the neighboring oxygen atoms of the  $\text{CuO}_2$  plane.



(b)



This hybridization results in one hole on each Cu site, which gives rise to a large Fermi surface centered at the point X

- the failure of the one-electron band calculations stems from the difficulty in evaluating properly the Coulomb repulsive energy associated with the Cu-3d orbital

# Hubbard model and electronic structure of a strongly correlated electron system

$$H = -t \sum_{i,j} (c_{i\uparrow}^+ c_{j\uparrow} + c_{i\downarrow}^+ c_{j\downarrow}) + U \sum_i n_{i\uparrow} n_{i\downarrow},$$

where  $c_{i\uparrow}^+$  creates a spin-up electron at site  $i$ ,  $c_{j\downarrow}$  annihilates a spin-down electron at the site  $j$  and  $n_{i\uparrow} = c_{i\uparrow}^+ c_{i\uparrow}$  represents the number of spin-up electrons at site  $i$  and takes either 0 or unity.

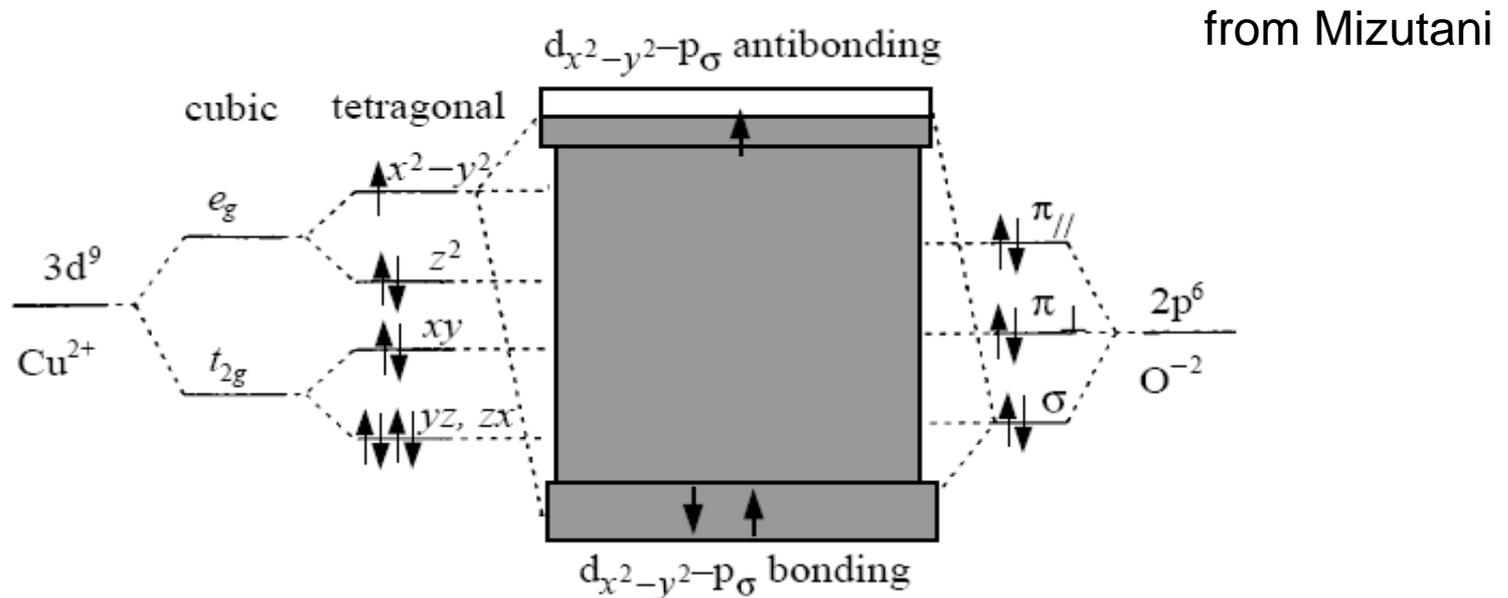
The second term indicates that the energy of the system increases by  $U$  when a spin-down electron is added to an orbit where a spin-up electron already exists.

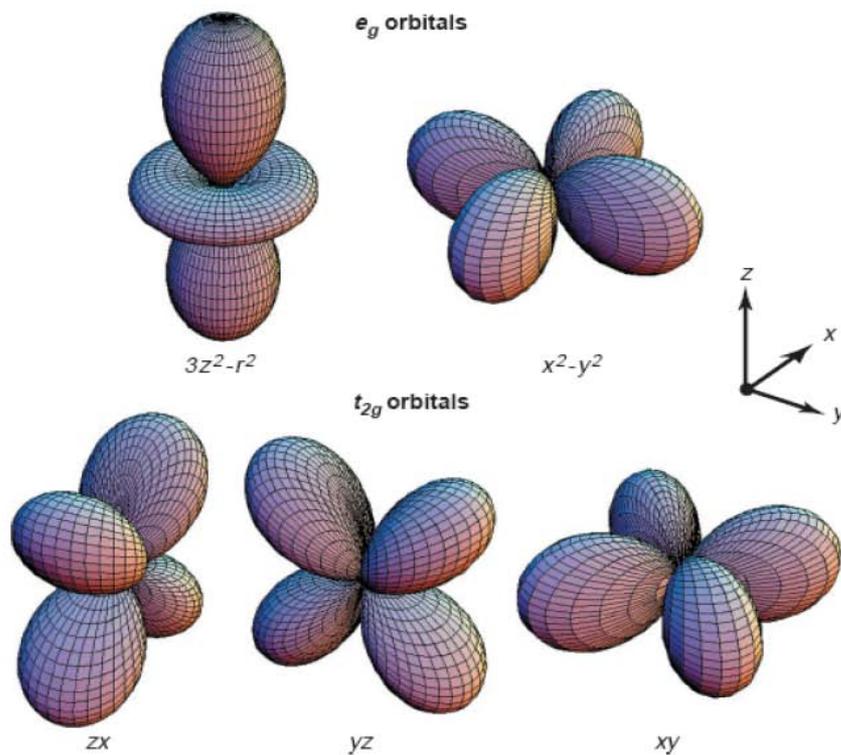
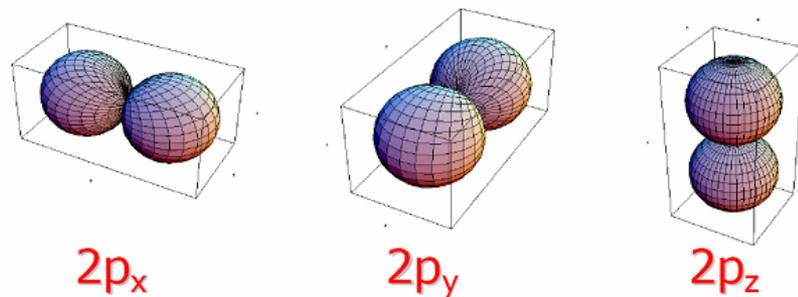
$U$  is called the on-site Coulomb energy.

The parameter  $t$  in the first term is called the transfer integral or the hopping matrix element and represents the kinetic energy involved upon the transfer of a spin-up electron at site  $j$  to a neighboring site  $i$  without changing its spin orientation.

Let us consider again the  $\text{CuO}_2$  plane in the layered perovskite cuprate compounds and apply the Hubbard model to it by focusing on the local electronic structure in the  $\text{CuO}_2$  plane. There exist two oxygen atoms per Cu atom in the  $\text{CuO}_2$  plane, and hence, the molecular wave function is constructed by a linear combination of six 2p and five 3d orbitals.

The electronic structure of the  $\text{CuO}_2$  plane exposed to a three-dimensional octahedral crystalline field of tetragonal symmetry:





**Figure 8.** Five d orbitals. In the cubic crystal field, this fivefold degeneracy is lifted to two  $e_g$  orbitals ( $(x^2 - y^2)$  and  $(3z^2 - r^2)$ ) and three  $t_{2g}$  orbitals ( $(xy)$ ,  $(yz)$  and  $(zx)$ ) from [168]. Reprinted figure with permission from AAAS.

the hybridization of the  $3d_{x^2-y^2}$  orbitals of Cu sites with  $2p_\sigma$  orbitals of the neighboring oxygen atoms in the  $\text{CuO}_2$  plane is critically important and gives rise to bonding and antibonding states.

- oxygen atom has a very high electronegativity in comparison to other atoms

Because of this nature, **two electrons**, one spin-up and the other spin-down, in the  $d_{x^2-y^2}-p_\sigma$  orbital reside exclusively on the **oxygen site** and only one spin-up electron is left in the  $d_{x^2-y^2}$  orbital on the Cu site.

Since all  $d_{x^2-y^2}$  orbitals on  $\text{Cu}^{2+}$  sites are **half-filled**, we can in principle add a spin-down electron without any violation of the Pauli exclusion principle.

$$U \gg t$$

the addition of the spin-down electron **raises the on-site Coulomb energy by  $U$**

when the condition  $U \gg t$  holds, the addition of the spin-down electron raises the on-site Coulomb energy by  $U$ .

This leads to the formation of a **new 3d band** of the spin-down electrons at the energy  $U$  above the 3d band of the spin-up electrons.

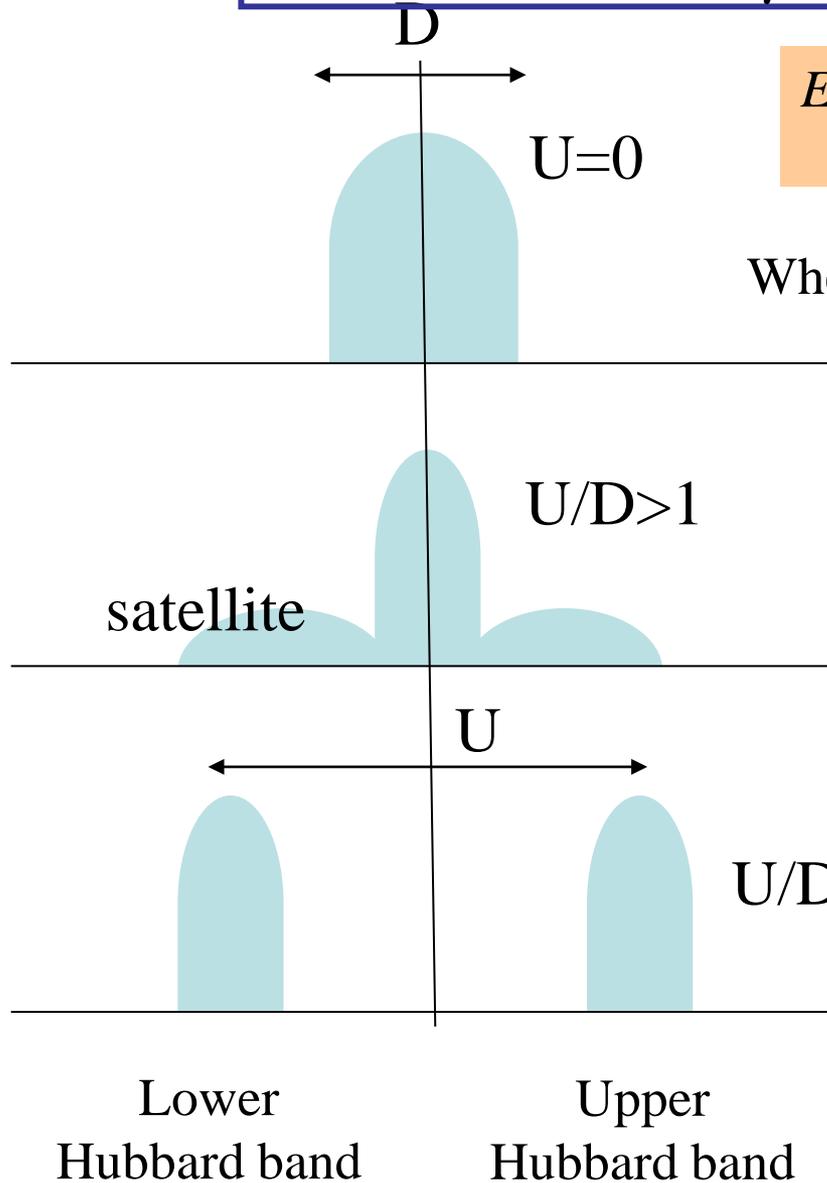
These are called the **upper** and **lower** Hubbard bands,  
which are separated by the energy  $U$ .

the band calculations based on the one-electron approximation are unable to produce this unique band structure.

The transfer of an electron from site  $i$  to its neighbors means that the system becomes an insulator in spite of the fact that the band is only half-filled.

**Mott-Hubbard insulator**

# Competition between kinetic energy and $U$ (itineracy and localisation)

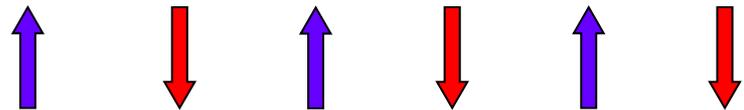


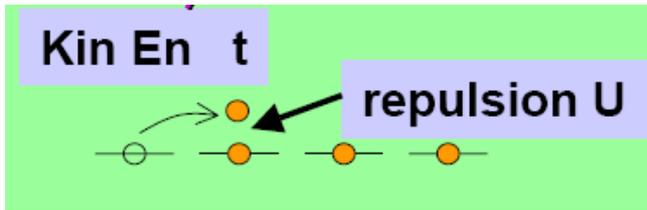
*Electrons prefer to “spread” themselves to lower their kinetic energy.*

When  $U$  is small it is preferable for the electrons to delocalise  $\rightarrow$  metal

For intermediate  $U$  it is a mixture of localised and delocalised electrons.

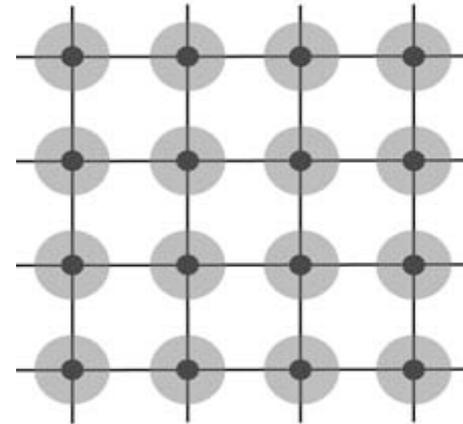
When  $U$  is large it is costly for the electrons to hop  $\rightarrow$  localised (Mott insulator)





If  $U \gg t$ , insulator occurs for a half-filled band (average of one electron per lattice site) .

- Electrons are localised on individual lattice sites



- Insulator because it is hard for charge to move through the system because of the energy cost associated with doubly occupied sites.

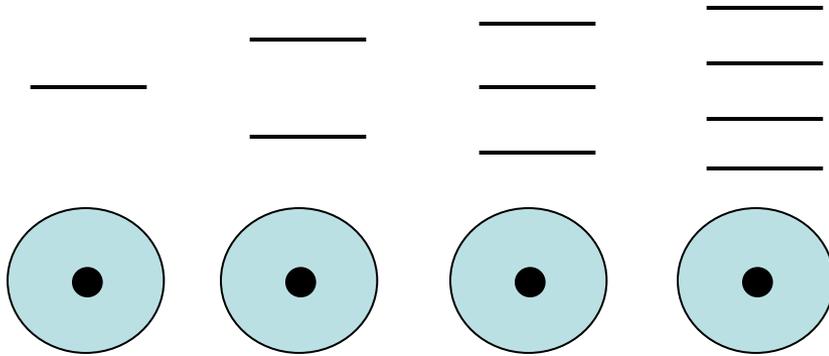
According to Mott

(1937), Peierls noted

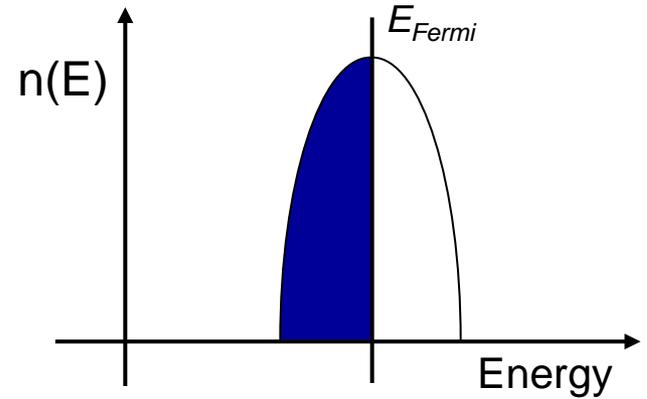
“it is quite possible that the electrostatic interaction between the electrons prevents them from moving at all. At low temperatures the majority of the electrons are in their proper places in the ions. The minority which have happened to cross the potential barrier find therefore all the other atoms occupied, and in order to get through the lattice have to spend a long time in ions already occupied by other electrons. This needs a considerable addition of energy and so is extremely improbable at low temperatures.”

These observations launched the long and continuing history of the field of **strongly correlated electrons**, particularly the effort to understand how partially filled bands could be insulators and, as the history developed, how an insulator could become a metal as controllable parameters were varied.

Band structure theory:

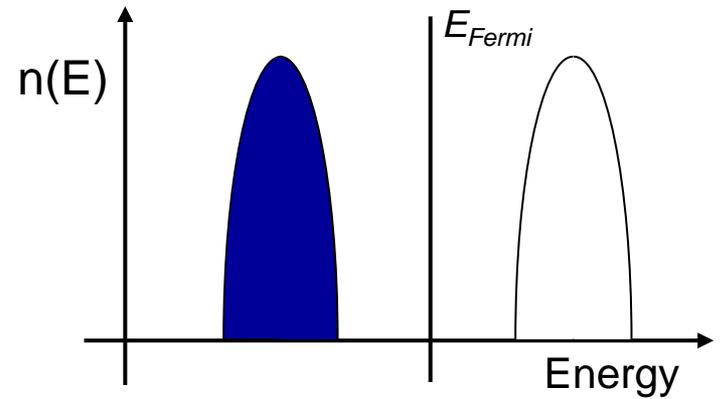
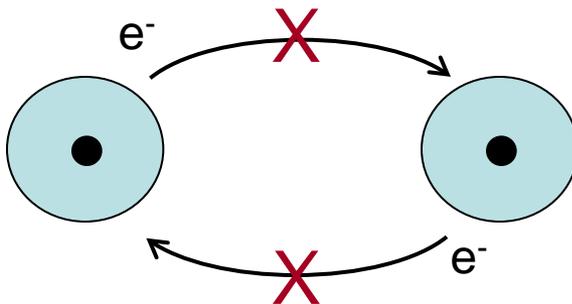


- orbitals hybridize
- electrons delocalize



With strong correlations:

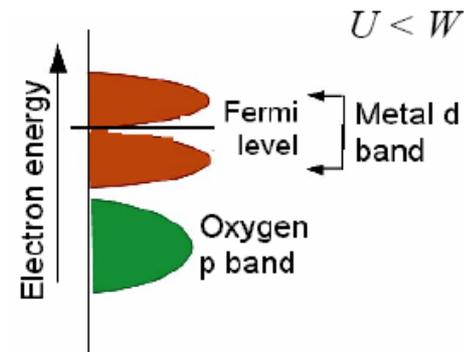
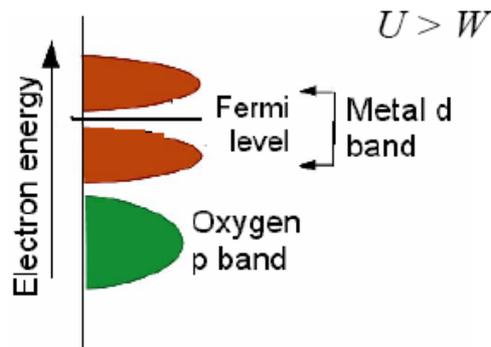
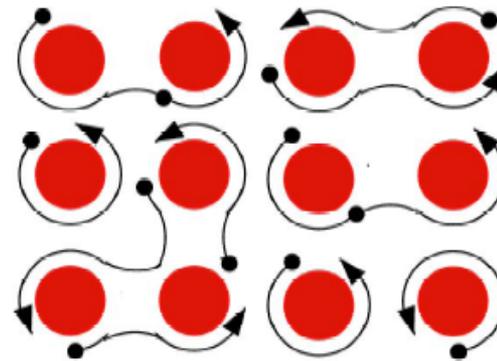
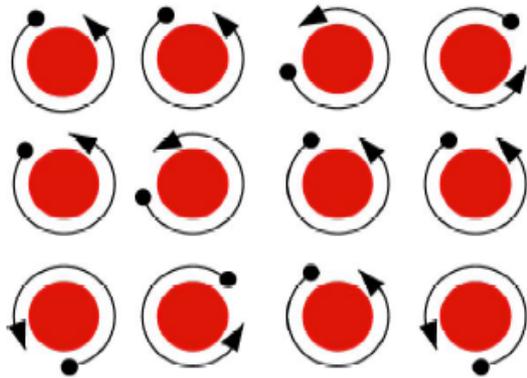
- strong on-site Coulomb repulsion prevents delocalization



- Mott-Hubbard insulator

**Strong repulsive  
Coulomb interaction  
on a same lattice  
site due to narrow  
3d orbitals**

Y. Tokura, Correlated electron physics in transition metal oxides



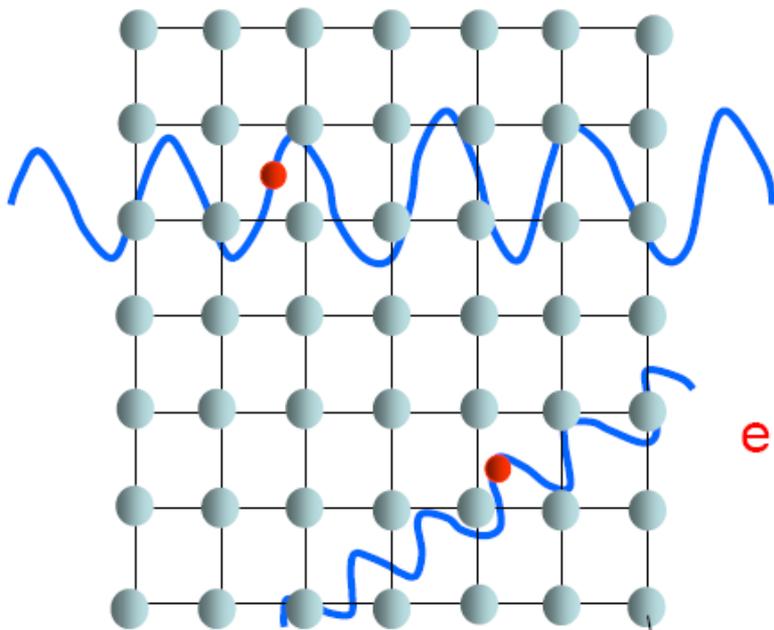
Bloch state

1nm



Mott state

Coulomb repulsion

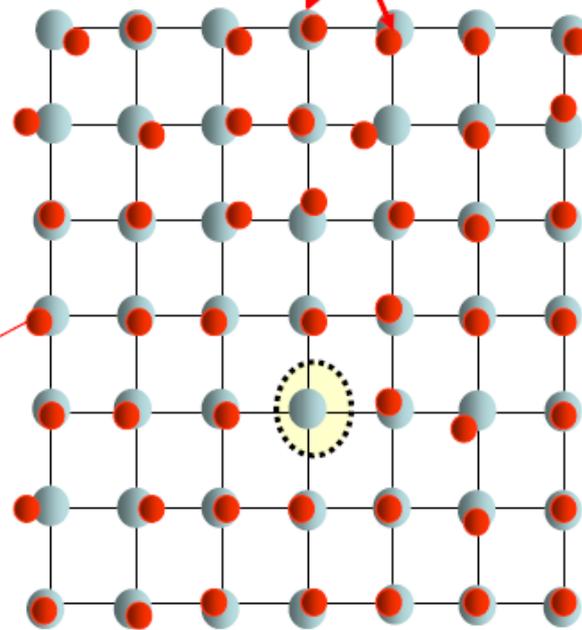


electron

wave picture

atom

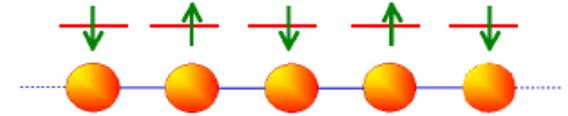
itinerant



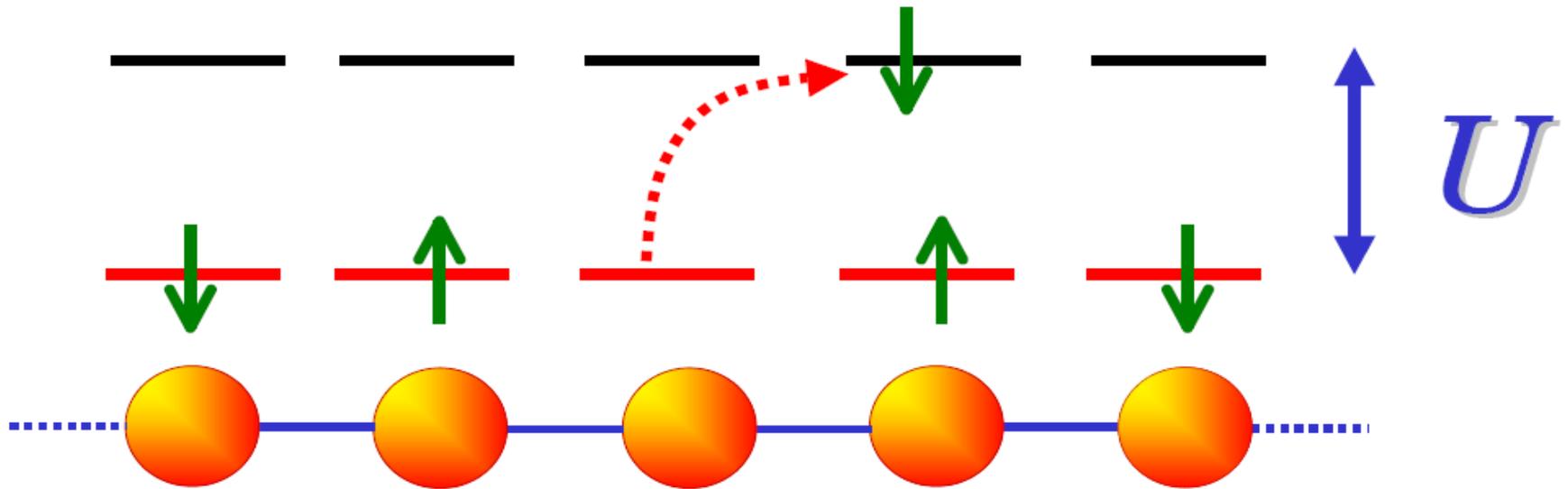
particle picture

localized

# Hubbard model



● electron repulsion leads to localisation:



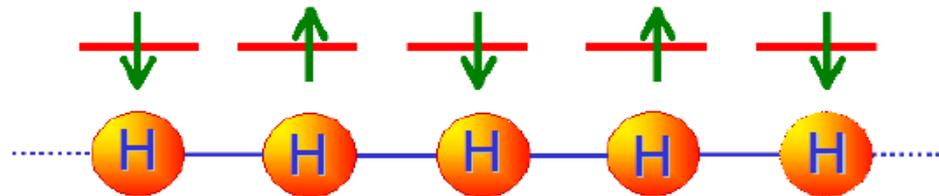
● E required to remove an electron from an orbital =  $I$ ,  
to add it to another site =  $A$

$$U = I - A$$

## Hubbard model

- $U = I - A =$  repulsion between two e in same atom

e.g.



if our atoms in the chain were hydrogen,

$$U = I - A = 13.6 \text{ eV} - 0.8 \text{ eV} = 12.8 \text{ eV}$$



repulsion drives a half-filled band insulating, when the intersite interaction (and thus  $W$ ) is small



## Hubbard model

- e.g. single band Hubbard model

$$H = -t \sum_{\langle \mathbf{i}\mathbf{j} \rangle, \sigma} c_{\mathbf{i}\sigma}^\dagger c_{\mathbf{j}\sigma} + U \sum_{\mathbf{i}} n_{\mathbf{i}\uparrow} n_{\mathbf{i}\downarrow}$$

transfer integral  
large = strong intersite  
overlap, large  $W$

Hubbard  $U$   
punishes double occupancy

competition:

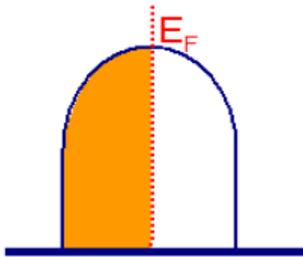
$U$  wants to localise

$t$  rewards delocalisation

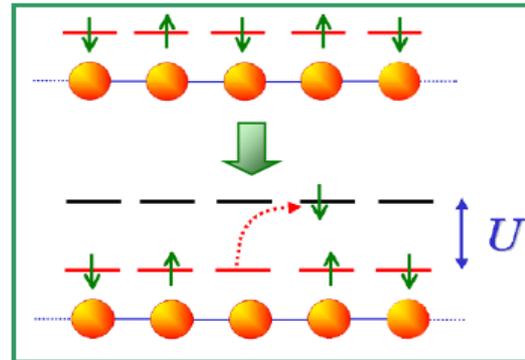
competition:

$U$  wants to localise

$W$  rewards delocalisation



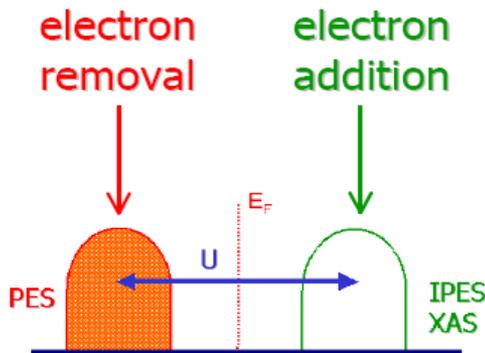
$U$  shows up when altering the occupation (e.g. transport, spectroscopy)



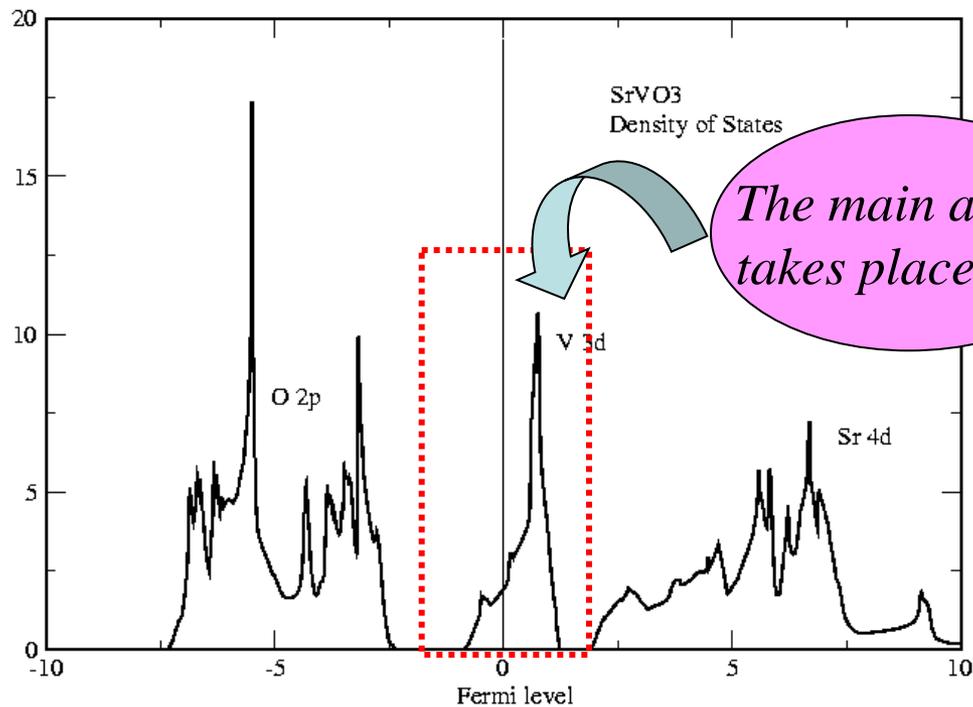
$$U = E_0(N-1) + E_0(N+1) - 2E_0(N)$$

one must pay the Mott-Hubbard gap to excite an electron into another orbital:

→ *direct relevance to transport*



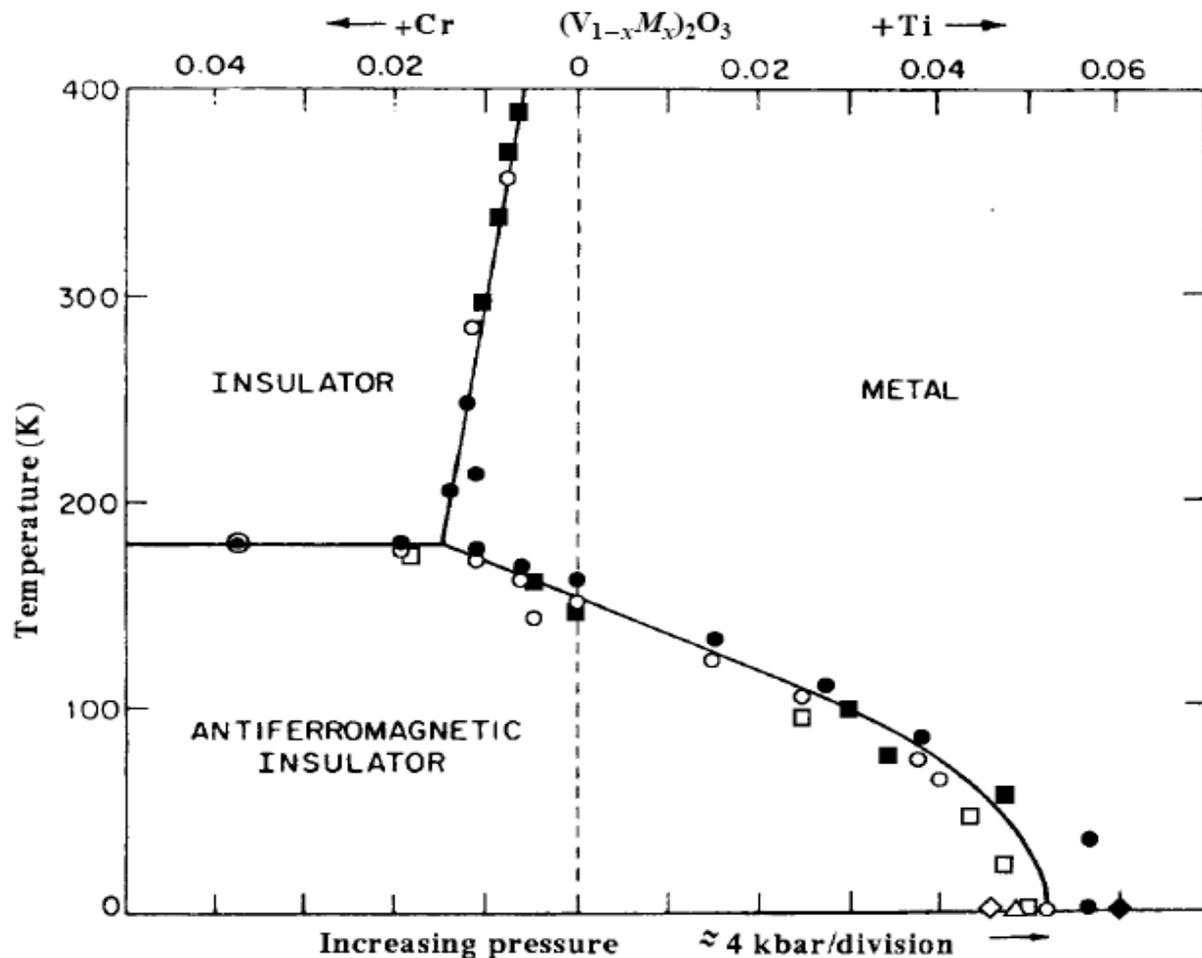
*Typical electronic structure of correlated materials:  
Partially filled narrow 3d or 4f band across the Fermi level*



By slight distortion or pressure *the ratio of  $U$ /bandwidth* changes and the materials can undergo, e.g., phase transitions (metal-insulator).  
→ competition between kinetic energy (bandwidth) and  $U$ .

## electronegativity:

Pauling [7] introduced a quantity termed electronegativity  $\chi$  to discuss the nature of bonds between unlike atoms. It represents the power of an atom in a molecule to attract an electron to itself. Electronegativity values for relevant elements are as follows: Ti (1.5), V (1.6), Cr (1.6), Mn (1.5), Fe (1.8), Co (1.8), Ni (1.8), Cu (1.9), Zn (1.6) and O (3.5). Hence, the oxygen atom attracts more electrons than transition metal atoms. The square of the electronegativity difference of the atom pair is called the ionic resonance energy  $\Delta$ . The larger the electronegativity difference or the ionic resonance energy, the stronger is the ionic character of the bond. Conversely, a bond with a small value of  $\Delta$  will be more covalent.



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Figure 14.8. Generalized phase diagram of transition temperature as a function of pressure and as a function of doping with  $M=Cr$  or  $Ti$  in  $(V_{1-x}M_x)_2O_3$  system. Solid and open circles are obtained from the temperature dependence of resistivity at 1 atm for mixed oxides on increasing and decreasing temperature, respectively. Triangles, squares and diamonds are obtained for  $x=0$ ;  $x=0.04$ ,  $M=Cr$ ; and  $x=0.04$ ,  $M=Ti$ , respectively, for increasing (*solid*) and decreasing (*open*) pressure (or temperature), respectively. The pressure was scaled to the composition, i.e., 4 kbar/division, using the difference in the critical pressure for the “ $V_2O_3$ ” and “ $x=0.04$ ,  $M=Cr$ ” samples (for more details, see ref. [9]).

Research on the metal–insulator transition induced by strong electron–electron interaction dates back many years. For instance, data of the metal–insulator transition for the  $V_2O_3$  system, which is known as a typical Mott–Hubbard insulator, are depicted in Fig. 14.8 [9]. It can be seen that the metal–insulator transition temperature systematically changes with either varying pressure or substitution of Cr or Ti for V and that the antiferromagnetic insulating phase is stable at low temperatures but transforms into the metallic phase at high temperatures.

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# Electronic structure of 3d-transition metal oxides

Typical example: transition metal oxides e. g. CoO

CoO: rock salt structure → 1 Co & 1 O per unit cell

electron configuration: Co: [Ar] 3d<sup>7</sup> 4s<sup>2</sup>

O: [He] 2s<sup>2</sup> 2p<sup>4</sup>

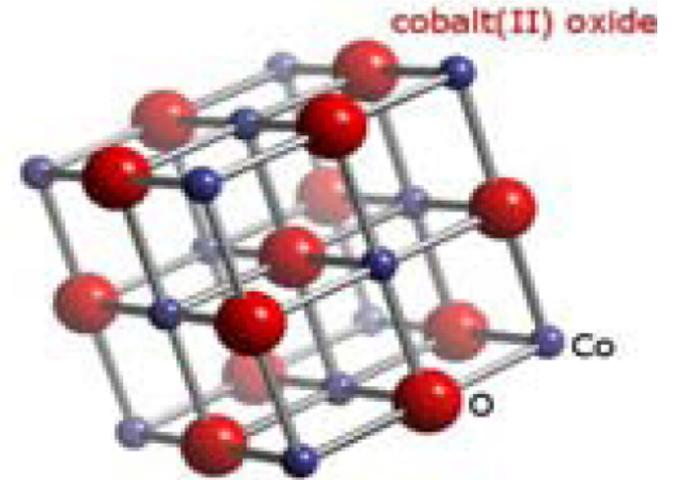
⇒ total number of electrons per unit cell: 9 + 6 = 15

uneven number of electrons → at least one partially filled band (spin up and down!)

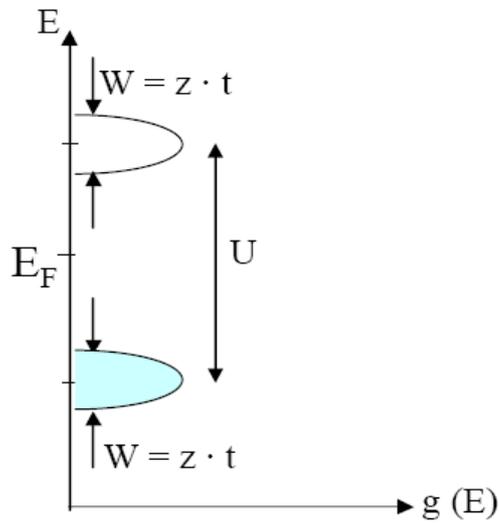
→ CoO ≡ metal !

in reality: CoO ≡ insulator ( $\rho \approx 10^8 \Omega \text{ cm}$  @ RT; compare: Fe →  $\rho \approx 10^{-7} \Omega \text{ cm}$ )

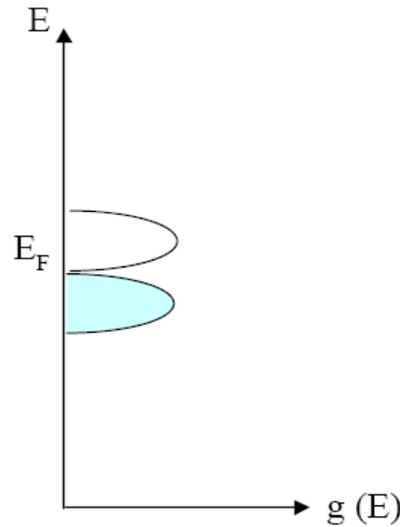
with activation energies  $\approx 0.6 \text{ eV} \approx 7000 \text{ K}$  !



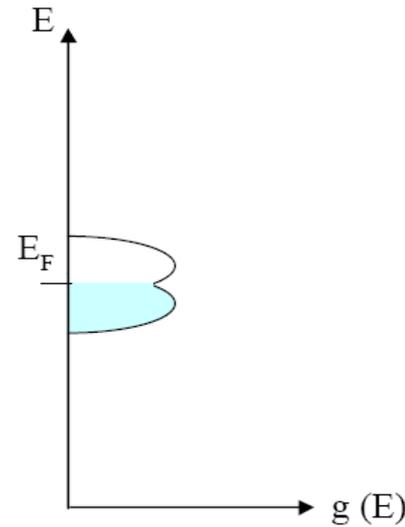
at half band filling (CoO ??)



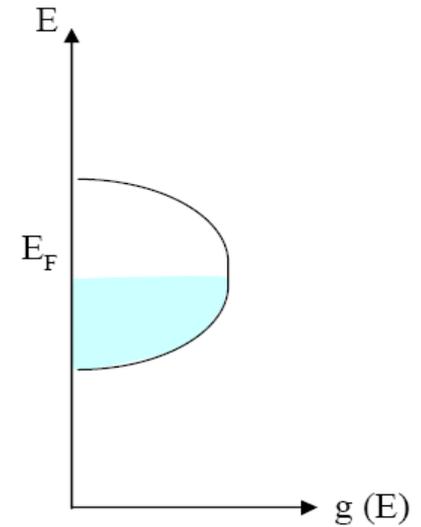
$U \gg W = z \cdot t$ :  
Mott-insulator



$U = W = z \cdot t$   
→ Metal-insulator-  
transition



$U < W$   
→ Metal



$U = 0$   
→ Band metal without  
correlations

Correlations lead  
to band splitting!

(z-coordination number of the lattice)

from Mizutani

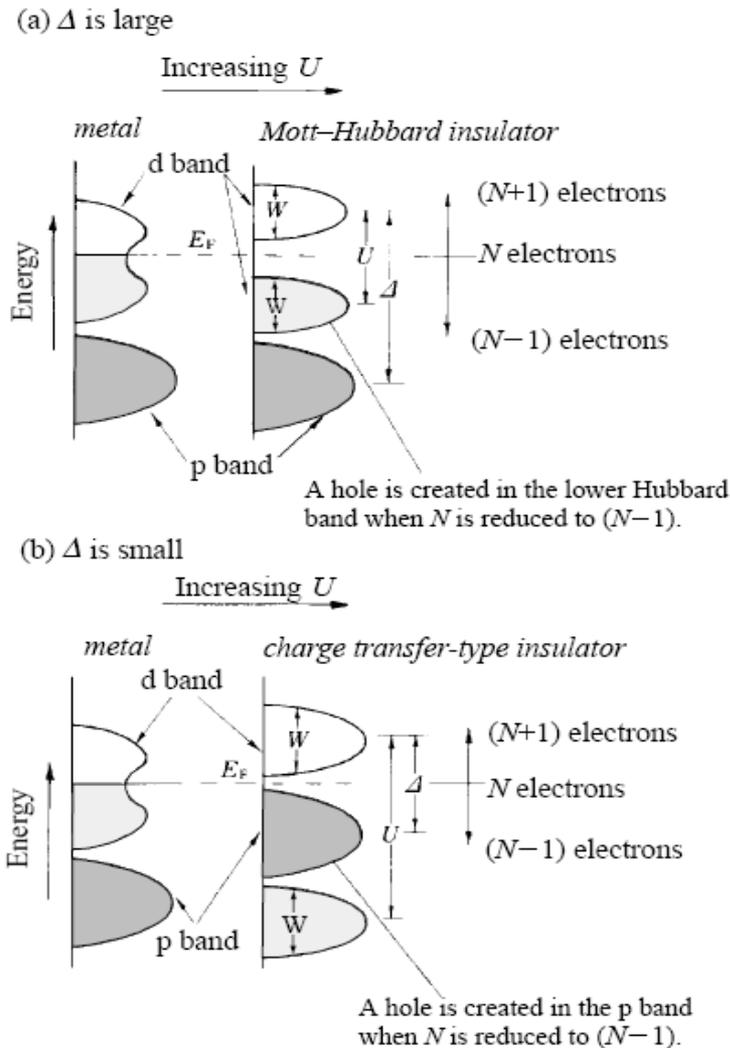
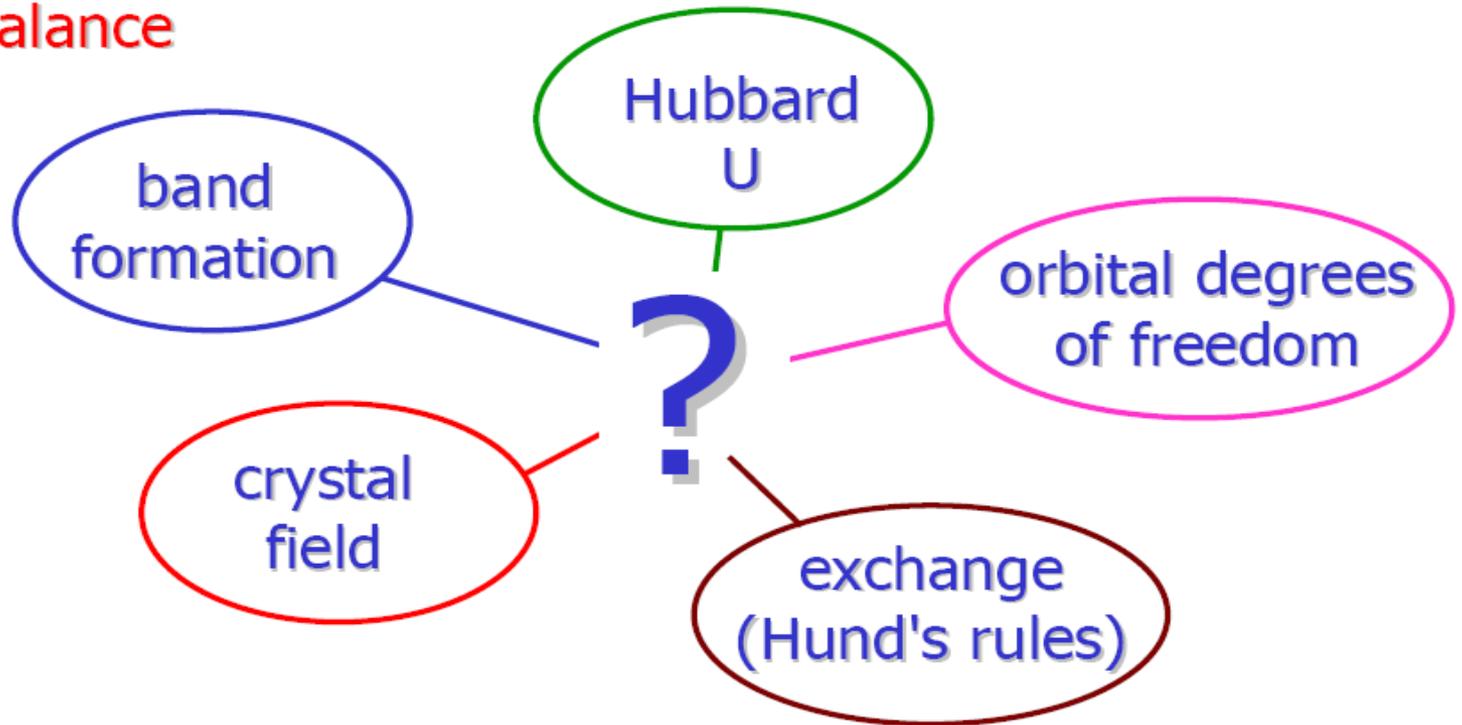


Figure 14.9. Electronic structure of (a) Mott-Hubbard insulator and (b) charge transfer-type insulator in comparison with the corresponding metals. The parameter  $\Delta$  is large in (a) but small in (b). The ground state refers to the system with  $N$  electrons. The system is excited to those with  $(N-1)$  or  $(N+1)$  electrons either by ejecting one photoelectron from the occupied states or by absorbing one electron in the unoccupied state. Both  $(N-1)$  or  $(N+1)$  states can be observed by photoemission and inverse photoemission experiments but the  $N$ -electron states cannot be observed. Contrary to normal metals, the electronic structure in a strongly correlated system depends on how many electrons are involved in the system.

# Transition metal systems and electron correlation

- delicate balance



- depending on system, can be quite close to border line

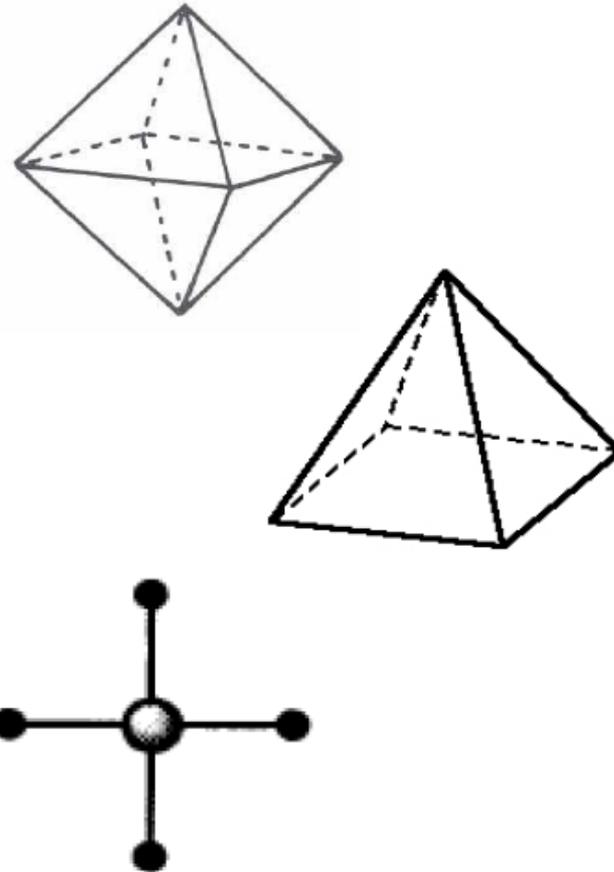
$$U \sim W$$

➡ thus many interesting (and useful) transitions can occur on changing T, P, filling, structure etc.

## TM oxides: *LEGO on atomic dimensions*

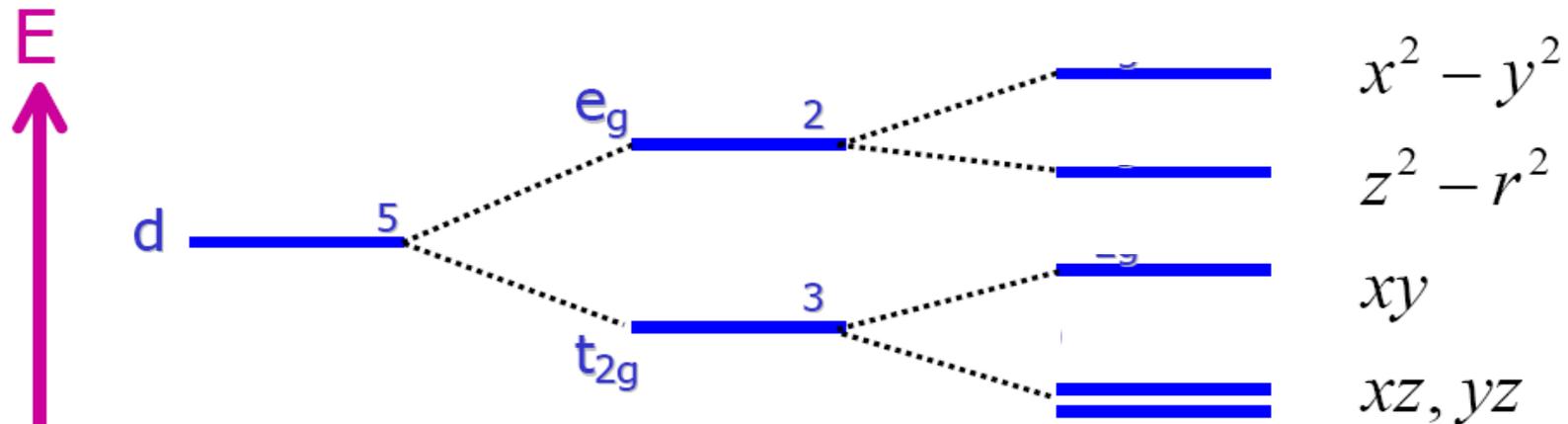
Just like all crystalline solids, TM-oxides are built up of regular repeat units such as:

- TM-O<sub>6</sub> octahedron
- TM-O<sub>5</sub> square pyramid
- TM-O<sub>4</sub> plaquette



## Effects of structure on the electronic levels

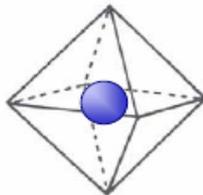
Coulomb potentials in oxides lead to lifting of the orbital degeneracy of the 3d levels:



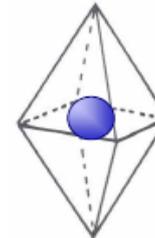
free ion



cubic



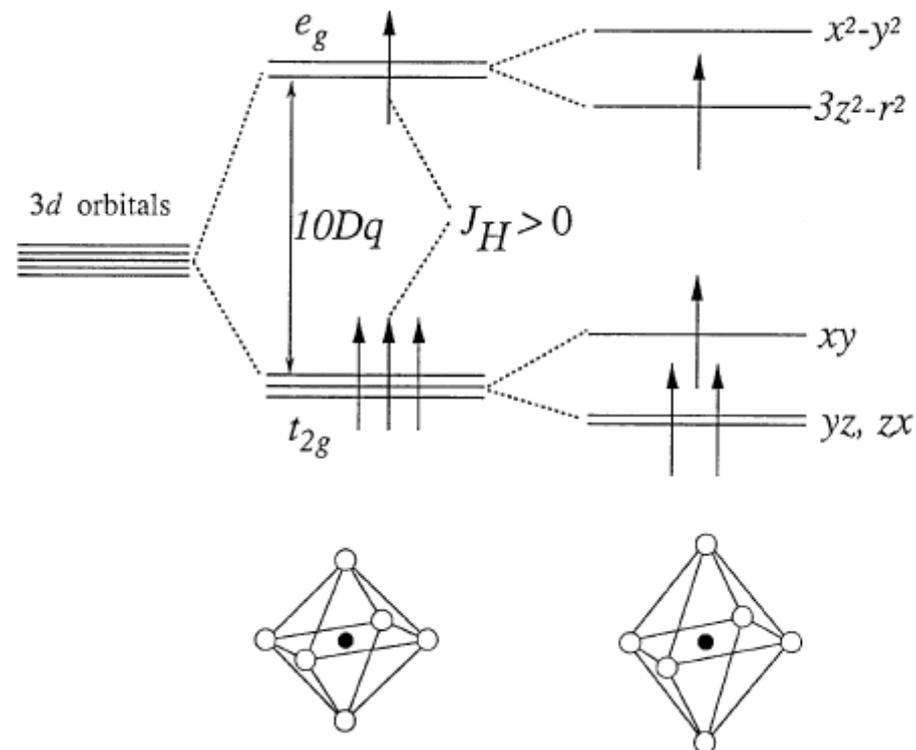
tetragonal



crystal  
field  
splitting

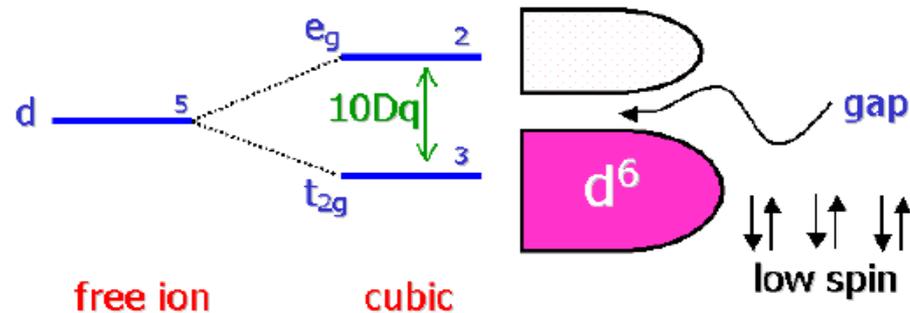
# Jahn-Teller distortion

when degenerate energy states are unequally occupied then the system will be found to distort so as to remove that degeneracy

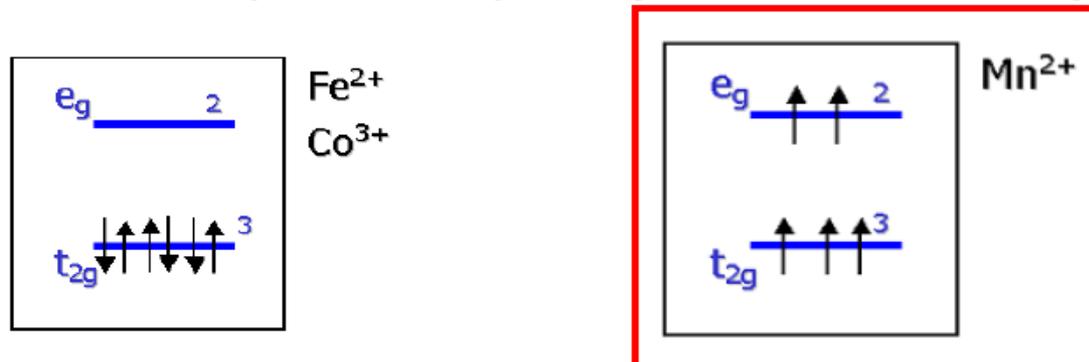


## Interplay: Hund's rules and crystal field

- competition between ligand field and exchange interaction (Hund's 1st rule)

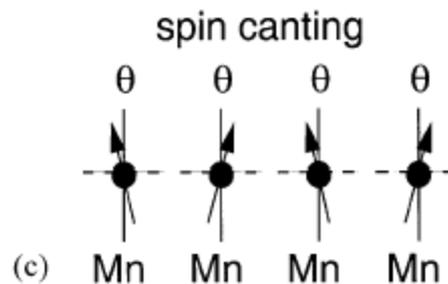
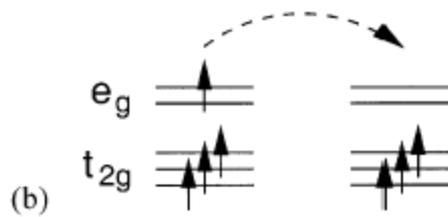
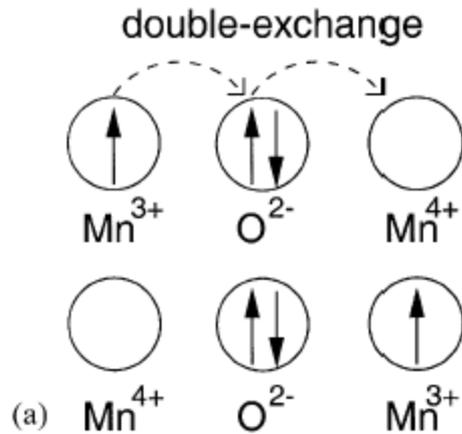


- the system *could* promote electrons to the  $e_g$  states in order to maximise no. of parallel spins (thus Hund wins):

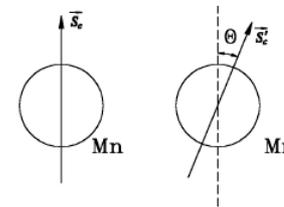


# • DOUBLE EXCHANGE INTERACTION

(Zener and de Gennes, Anderson, Hasegawa 1950')



hopping of misaligned spins

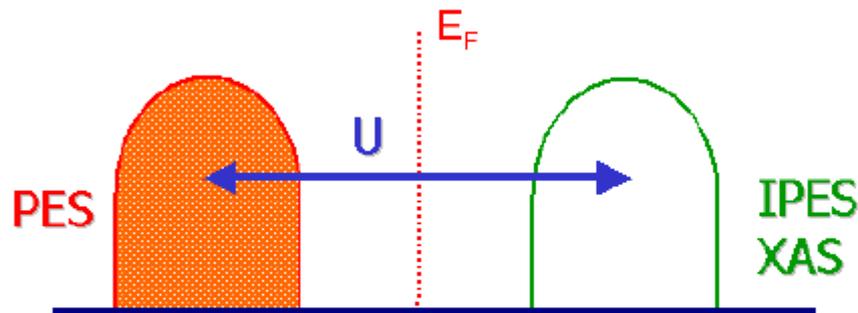


$$t_{ij} \text{ ----- } > t_{ij} \cos(\theta_{ij}/2)$$

E. Dagotto

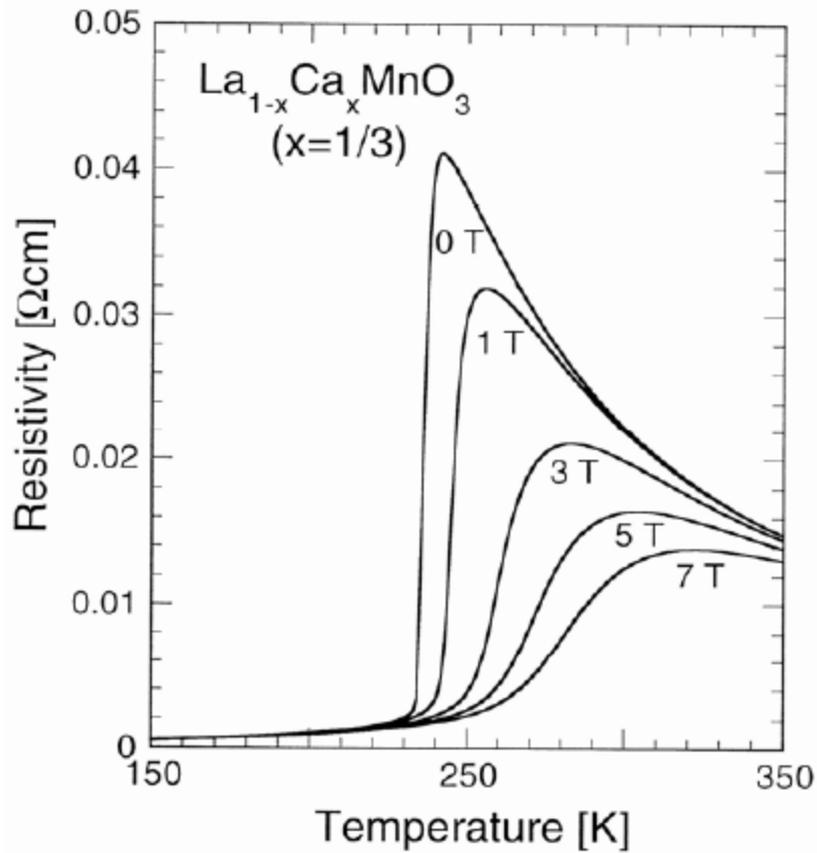
## Doping

- La = 3+, substitute by Sr = 2+ adds holes

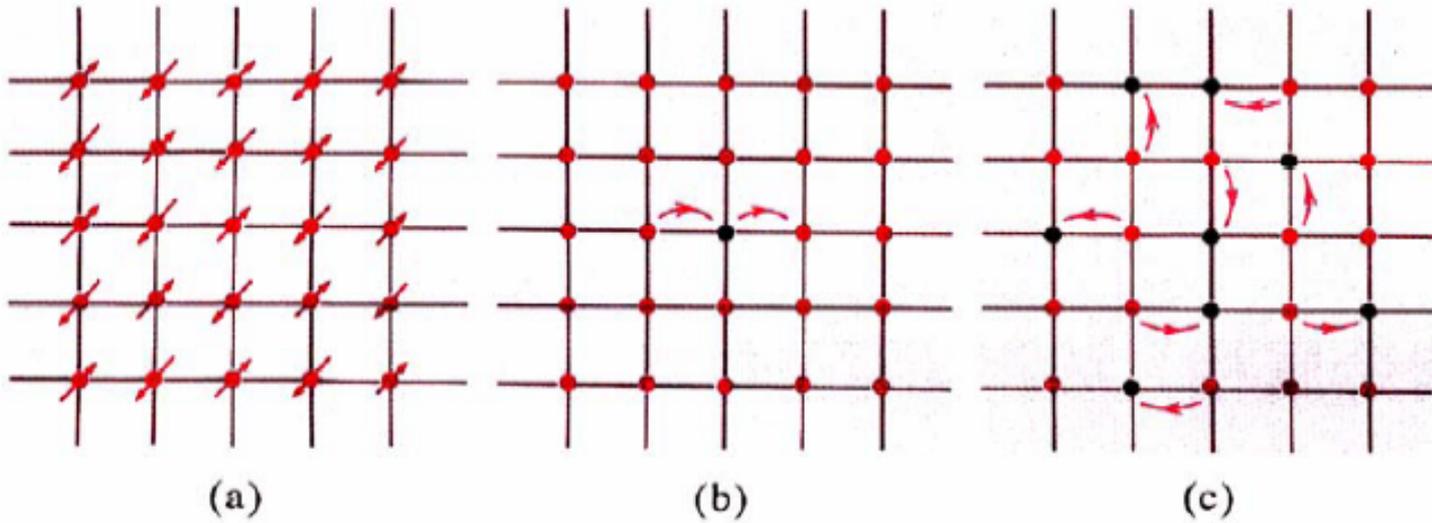


- quite large doping required to overcome charge/spin/orbital long range order
- doped carriers can self assemble

## Colossal magnetoresistance (CMR)



## Mott Insulator and charge-carriers doped Insulator – Metal Transition



Mott Insulator

Strongly Correlated  
Metal

Conventional  
Metal

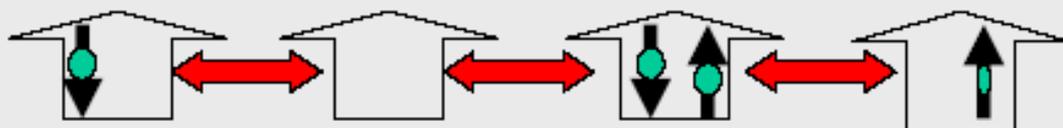
How to dope carriers

- Chemical substitution
- Photo induced carriers injection

## What is the Novel Characteristics of Correlated Electrons ?

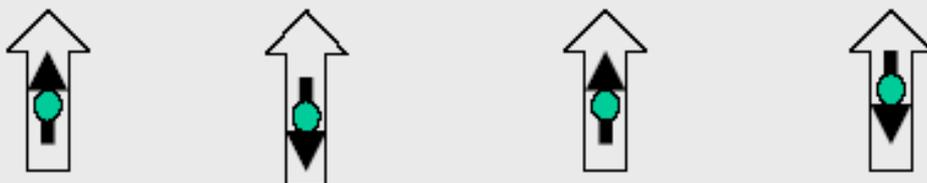
*Conventional metal (itinerant electrons with no spin degree of freedom)*  
*Charge play role for "Electronics"*

One electron per atom



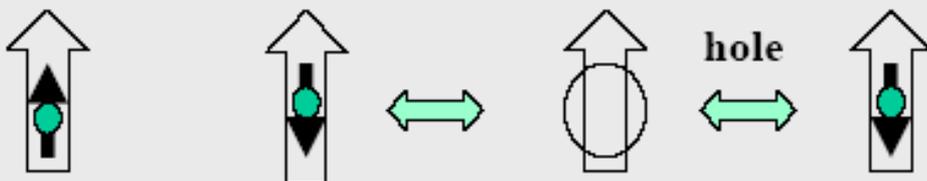
**Strong repulsive  
Coulomb interaction  
on a same lattice  
site due to narrow  
3d orbitals**

*Mott Insulators (magnetism with spin degree of freedom)*



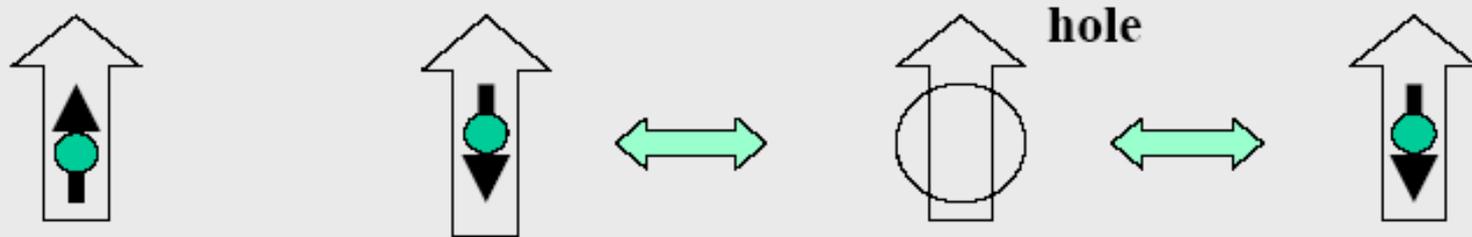
**Doped Mott insulators**

(quantum liquid and quantum nematics of **spin and charge**)



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

## Spin • Charge • Orbital degrees of freedom are coupled each other



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**

## Localisation plays a crucial role

- correlation (Mott) physics means that the electrons are localised at the atomic sites
- this means we have clear occupation of orbitals, and a clear local spin orientation (e.g. via superexchange)
- opens the door for quantum electronic texture.....  
.....with versatile ordering patterns

## Why transition metal oxides ?

### ● fundamental importance

the outstanding challenge to solid state physics and chemistry:

*understand and master strongly correlated electronic systems*

### ● technological potential

superconductors

superionic conductors

spintronic materials

catalysts (making money already)

high  $T_c$   
superconductors

CMR systems

myriad quantum  
ground states:

FM

AFM

PM

insulator

semiconductor

metal

superconductor

MITs

QPTs

CO / OO