MOTT HUBBARD VS CHARGE TRANSFER INSULATORS:

IN THE CF SCENARIO, THE ROLE OF OXYGEN IS ONLY TO CAUSE THE CRYSTAL FIELD. WHEN I DRAW ENERGY LEVELS I ONLY CONSIDE THOSE OF THE TM

HOWEVER THE CF-SPLITTING IS TECHNICALLY THE RESULT OF THE HYBRIDIZATION BETWEEN 3d AND 2p ORBITALS

THIS IS OK IF THE ENERGY OF THE 2P LEVELS IS FAR FROM THAT OF THE 3d.

EXAMPLES: La_2CuO_4, $LaMnO_3$, NiO

IN THESE SYSTEMS, THE TM — O — TM BOND IS ALMOST 180°

IF I CANNOT NEGLECT THE OXYGEN 2P BANDS => THE HUBBARD MODE BECOMES:

$$H = \varepsilon_d \sum d^\dagger_{i\sigma} d_{i\sigma} + \varepsilon_p \sum p^\dagger_{j\sigma} p_{j\sigma} + \sum t_{pd,ij} (d^\dagger_{i\sigma} p_{j\sigma} + h.c.) + U_{dd} \sum n_{di\uparrow} n_{di\downarrow}$$
$$+ \left(U_{pp} \sum n_{pj\uparrow} n_{pj\downarrow} + U_{pd} \sum n_{di\sigma} n_{pj\sigma'} \right)$$

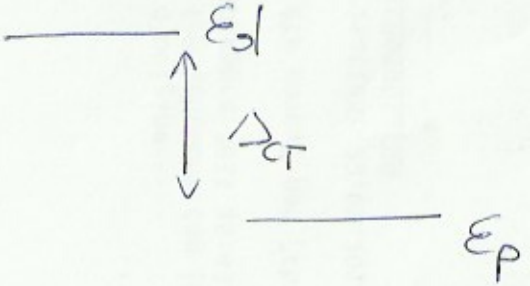
Three band model

La_2CuO_4

<u>TYPICALLY:</u>

Δ_{CT} IS THE ENERGY COST TO TAKE AN e^- FROM O AND PUT IT ON Cu

<u>NOTE</u>: IN ALL THESE COMPOUNDS O HAS VALENCE 2^- $\Rightarrow$ 2P LEVEL IS FULLY OCCUPIED ($2s^2 2p^4 + 2e^- \Rightarrow 2s^2 2p^6$)



IN THE HUBBARD MODEL $d_i^n d_j^n \longrightarrow d_i^{n-1} d_j^{n+1}$ COSTS $E = U_{dd}$

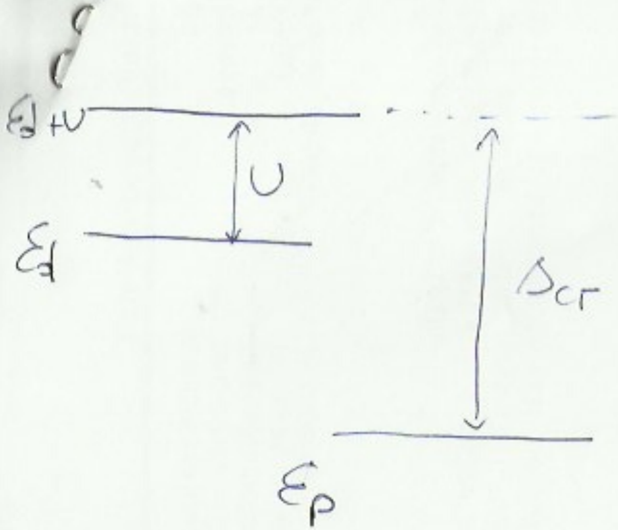
IN THE 3-BANDS HB THERE IS ALSO $d^{n} p^6 \rightarrow d^{n+1} p^5$ WHICH COSTS $E = \Delta_{CT}$

THIS PROCESS CAN ALSO BE WRITTEN AS $d^{n+1} \underline{L}$ ← HOLE IN THE LIGAND

IF THE d-SHELL IS EMPTY $\Rightarrow$ $\Delta_{CT} = \varepsilon_d - \varepsilon_p$

<u>BUT</u>

IF THE d-SHELL IS PARTIALLY FILLED $\Rightarrow$ THERE ARE STATES THAT ARE PUSHED TO HIGHER ENERGIES BY COULOMB REPULSIONS $\Rightarrow$



$$\Delta_{CT} = (\varepsilon_d + U_{dd}) - \varepsilon_p$$

U_{dd} KEEPS INTO ACCOUNT $e^- - e^-$ CORRELATIONS!

WHEN THERE ARE MANY 3d e^- IN THE SYSTEM, CALCULATING Δ_{CT} IS DIFFICULT AS ONE HAS TO FIGURE OUT ALL POSSIBLE CONFIGURATIONS AND THEIR ENERGY (AB-INITIO CALCULATION)

Cu2+ valence

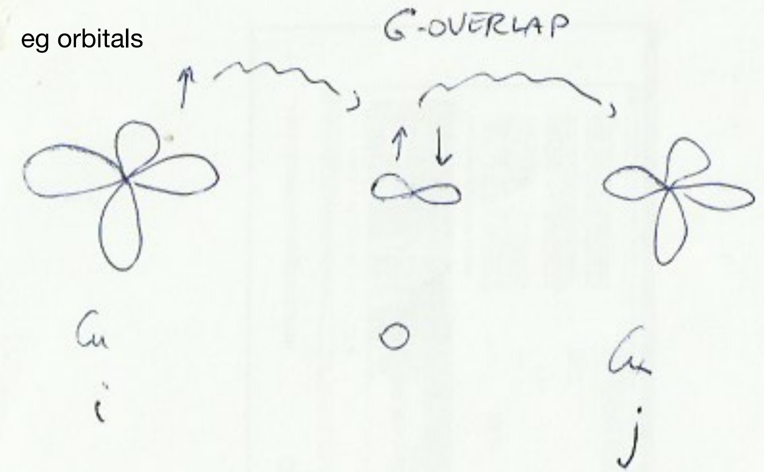
IN La_2CuO_4, SINCE WE HAVE A $3d^9$ CONFIGURATION WITH ONLY ONE ORBITAL FREE => WE CAN WORK WITH ONE HOLE AND SAY THAT FOR ONE $3d_{x^2-y^2}$ HOLE THE CT

$d^9p^6 \to d^{10}p^5$ HAS $\Delta_{CT} = \tilde{\varepsilon}_p - \tilde{\varepsilon}_d$

Energy of 1 hole on p

Energy of 1 hole on d

LET'S SEE HOW e^- CAN MOVE IN THIS SYSTEM:



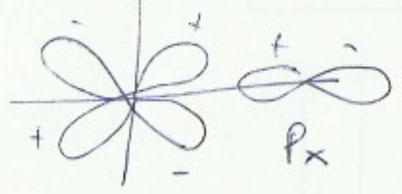
$$d_i^m p^6 d_j^m \longrightarrow \underline{d_i^m p^5 d_j^{m+1}} \longrightarrow d_i^{m-1} p^6 d_j^{m+1}$$

THIS COSTS Δ_{CT}

EFFECTIVE dd HOPPING $t_{dd}^{eff} = \dfrac{t_{pd}^2}{\Delta_{CT}}$

Larger for eg as for t2g

FOR t_{2g} ORBITALS |xy>, |xz>, |yz>



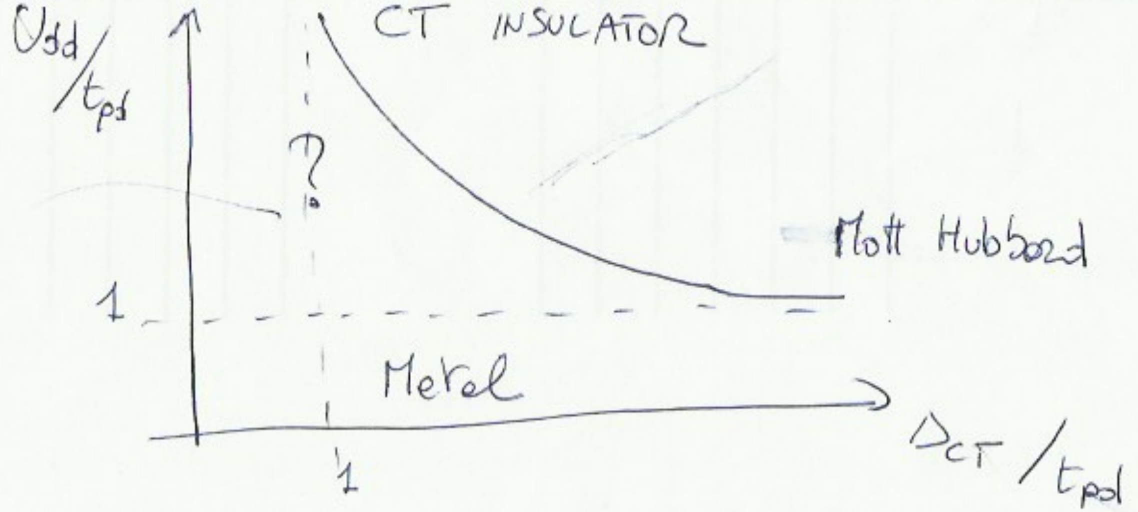
IN THIS GEOMETRY THERE IS <u>NO OVERLAP</u> WITH P_x

AND THERE IS SOME HOPPING BETWEEN

⇒ π - TYPE OF OVERLAP

WHAT IS THE DIFFERENCE BETWEEN M-H AND CT-INSULATOR?

HEAVY FERMIONS
STRONGLY CORRELATED
MATERIALS



IF $\Delta_{CT} < U_{dd}$ ⇒
CT INSULATOR

MOST TM OXYDES
EXEPT FOR V, Ti

EXCHANGE INTERACTION IN CHARGE-TRANSFER INSULATORS ⑥

IN HUBBARD INSULATORS WE HAVE SEEN THAT

$\overset{\longrightarrow}{\uparrow \quad \uparrow}$ THIS HOPPING IS FORBIDDEN BY PAULI PRINCIPLE $\Longrightarrow$ $\uparrow \quad \downarrow$ THE GS IS <u>AF</u>

IN A CHARGE TRANSFER INSULATOR THE HOPPING PROCESS IS:

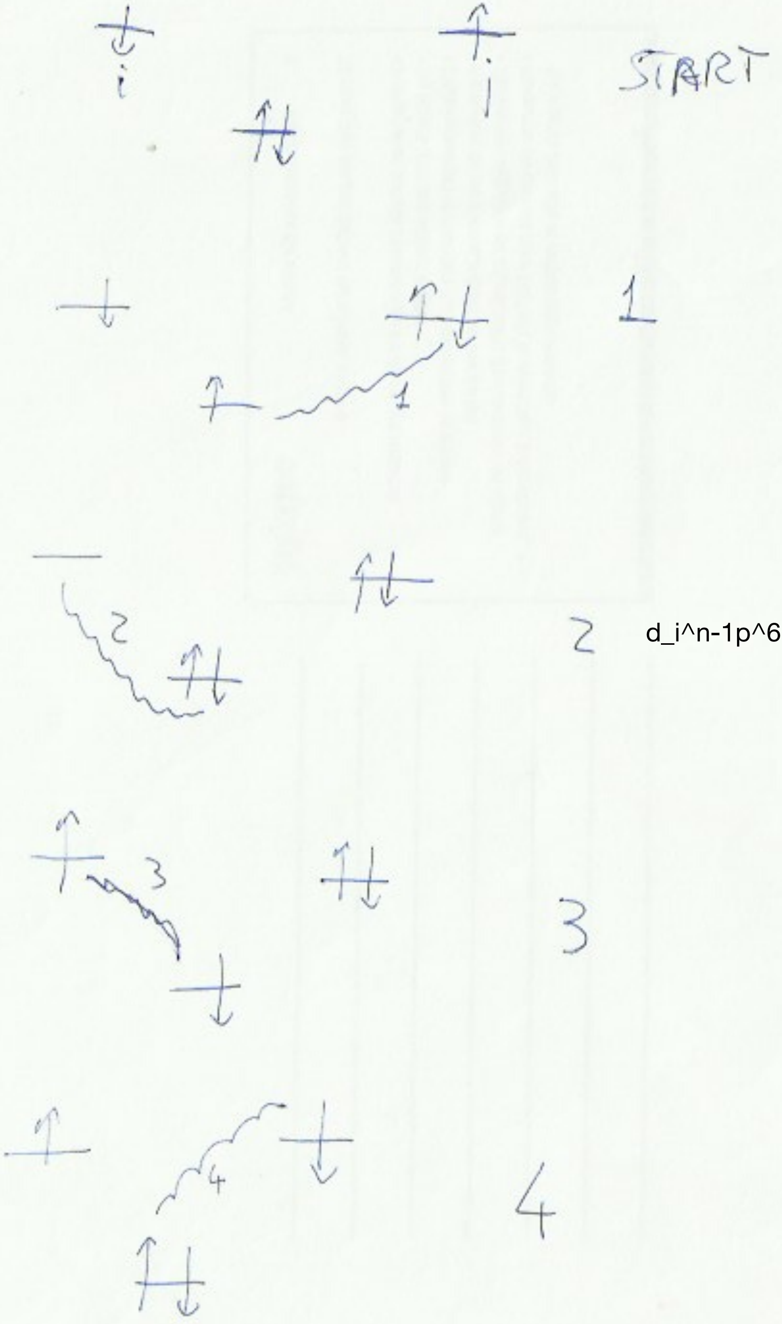
$$d_i^n p^6 d_j^n \xrightarrow{1} d_i^n p^5 d_j^{n+1} \xrightarrow{2} d_i^{n-1} p^6 d_j^{n+1}$$

$$\xrightarrow{3} d_i^n p^5 d_j^{n+1} \xrightarrow{4} d_i^n p^6 d_j^n$$

THIS ALSO GIVES AF EXCHANGE WITH EFFECTIVE HAMILTONIAN

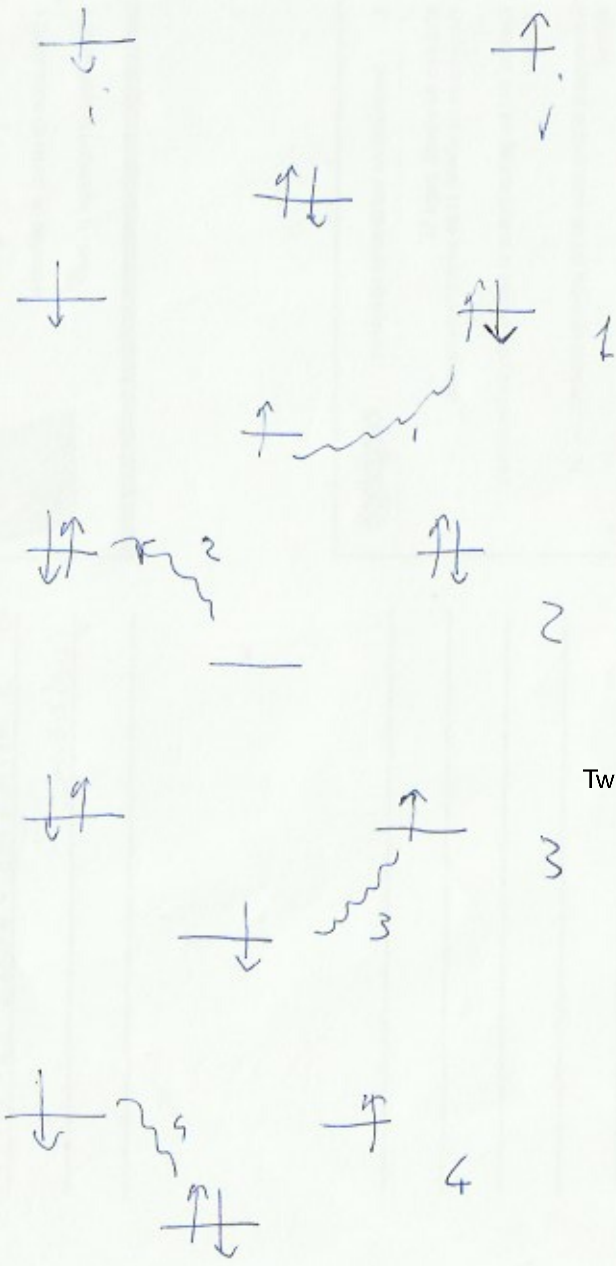
$$H = J \sum_{\langle i,j \rangle} S_i S_j \qquad \text{AND} \qquad J = \frac{2 t_{pd}^4}{\Delta_{CT}^2 U_{dd}}$$

PROCESS A



$d_i^{n-1}p^6d_j^{n+1}$

PROCESS B



$d_i^{n+1}p^4d_j^{n+1}$

This gives U_{pp}

Two possibilities: either i or j first

IN THIS CASE $J_{pd} = \frac{2t_{pd}^4}{\Delta_{CT}^2(\Delta_{CT}+\frac{1}{2}U_{pp})}$

WHICH PROCESS WILL DOMINATE?

BOTH GIVE AF GROUND STATES, THE TOTAL J CAN BE WRITTEN AS

$$J_{TOT} = \frac{2t^4_{pd}}{\Delta^2_{CT}}\left(\frac{1}{U_{dd}} + \frac{1}{\Delta_{CT}+\frac{1}{2}U_{pp}}\right)$$

Difference CTI and MHI:
-lowest charge excitation
-response to doping and moving in phase diagram
-more degrees of freedom

IF $U_{dd} \gg \Delta_{CT} \Rightarrow$ SECOND PROCESS DOMINATES

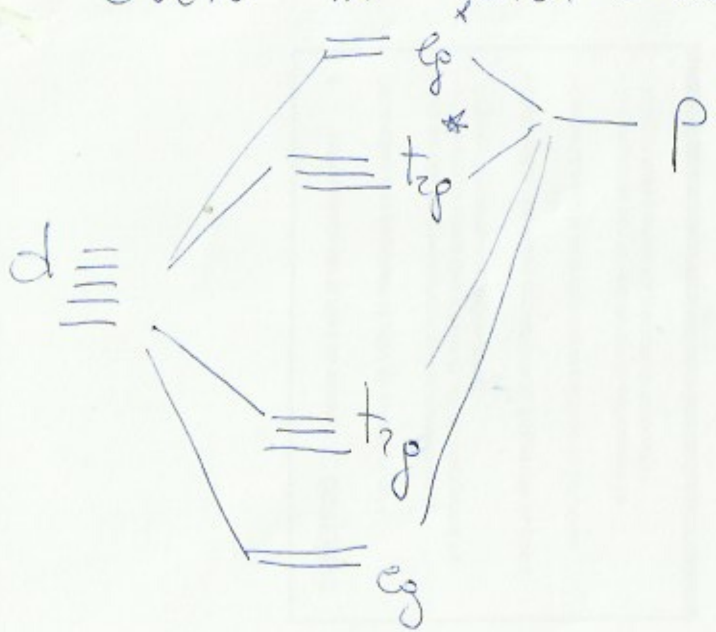
in CT state

NEGATIVE OR SMALL CT ENERGY!

FOR $\Delta_{CT} < 0$ $d^n p^6 \longrightarrow d^{n+1} p^5$ OCCURS SPONTANEOUSLY!

Sometimes referred to as self-doping (see FeO example)

EVEN IN STOICHIOMETRIC COMPOUNDS IN THE GS



CONSEQUENCES:

e_g AND t_{2g} LEVELS INVERT IN ENERGY BETWEEN BONDING AND ANTIBONDING ORBITALS

Very responsive to doping: La2CuO4 has D_CT>0
La(2-x)Sr(x)CuO4 has D_CT<0 and becomes a hight temperature superconductor

THIS SCENARIO CHANGES THE OVERLAPS BETWEEN ORBITALS →
IT ALSO CHANGES THE PROPERTIES OF THE SYSTEM

THE CT ENERGY IS TUNABLE WITH CHEMISTRY!

IT IS AN EXTRA PARAMETER FOR MATERIAL'S DESIGN

LET'S SEE AN EXAMPLE: MEASURING AND TUNING CT