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EXPERIMENTAL WORKSHOP ON
"HIGH TEMPERATURE SUPERCONDUCTORS"
(30 March - 14 April 1989)

# PHENOMENOLOGY AND THEORY OF SUPERCONDUCTIVITY
## (Lecture IV)

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(... replaces p. 5 of Lecture I)

# INTRODUCTION to HTSC

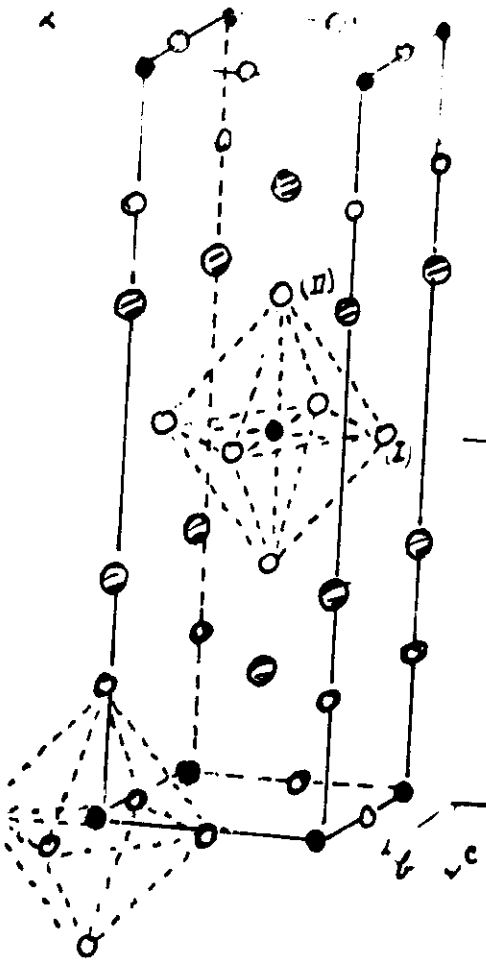
* $La_{2-\delta}(Ba,Sr)_{\delta}CuO_{4-y}$ (214), $T_c \sim 40K$ ($\delta \sim 0.15$, $y \sim 0$)
* $YBa_2Cu_3O_{7-\delta}$ (123), $T_c \sim 90K$ ($\delta \sim 0$)
* $\begin{cases} Tl_2Ca\,Ba_2Cu_2O_8 \\ Bi_2Ca\,Sr_2Cu_2O_8 \end{cases}$ $T_c \sim 80-125K$, $H_{c1} \gtrsim 10$ Oe, $H_{c2} \gtrsim 100$ T

compare: $T_c(Hg) \simeq 4K$; $T_c(Nb_3Ge) \simeq 23.2K$; $LHe \sim 4.2K$; $LN_2 \sim 77K$; $H_c \sim 10^2$ Oe; $H_{c2} \sim 10$ T

* 'Chemical' SUPERCONDUCTORS
ceramic oxides. stoichiometry important

Band Met
Intermetallics

Also $\begin{cases} BaPb_{1-x}Bi_xO_3, T_c \sim 12K, x \sim 0.3 \\ K_{1-x}Ba_xBiO_3, T_c \sim 30K, x \sim 0. \end{cases}$

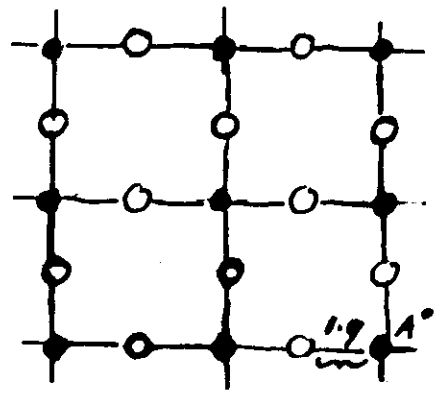



$La_2CuO_4$: Tetragonal
Layered Perovskite structure ($K_2NiF_4$)

Main Electronic feature: square planar $CuO_2$ layers

Cu-O(I): 1.9 Å
Cu-O(II): 2.4 Å
Weak inter-layer coupling
ANISOTROPIC
Layered (low dimensional)

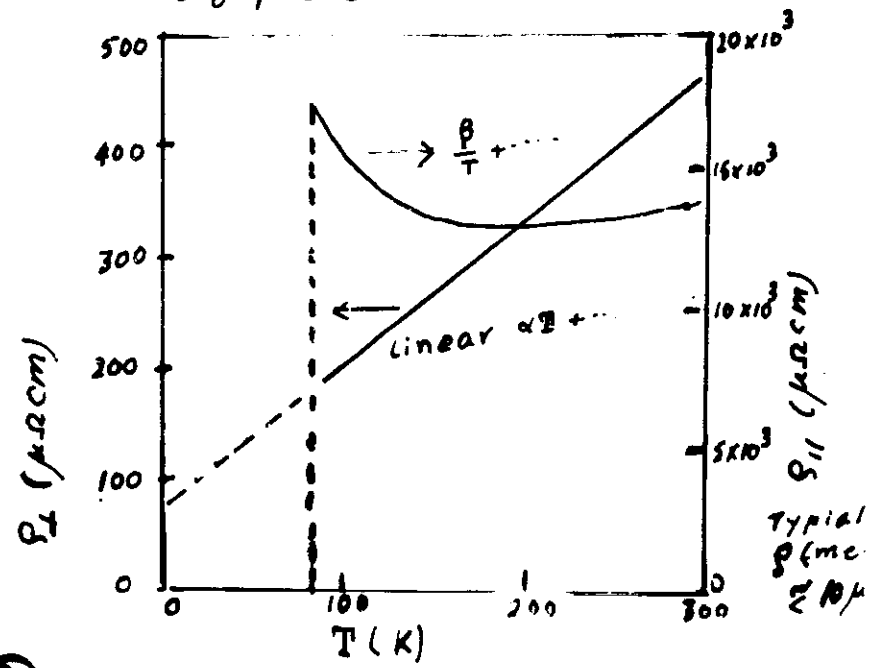
$La_2CuO_4$ undoped - Insulator
Conductivity gap 2-3 eV.




$CuO_2$ Planes
⊥ c-axis separated by ~6 Å

- ● $La^{3+}$ $a = 3.78$ Å
- ● $Cu^{2+}$ $b = a$
- ○ $O^{2-}$ $c = 13.25$ Å

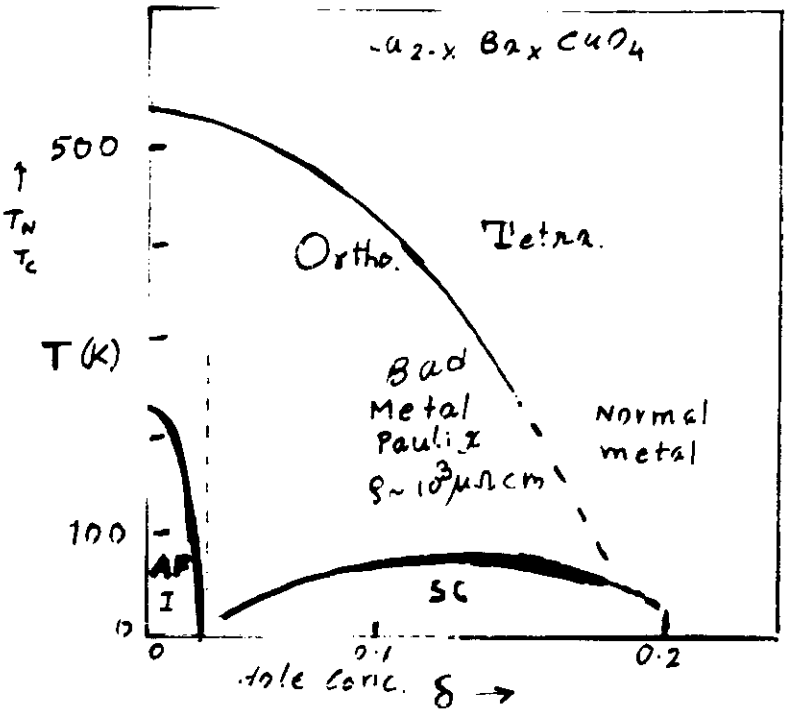
$Cu^{2+} \equiv 3d^9$ ∴ half-filled band should be a band metal. But actually an AF ($S = \frac{1}{2}$) insulator (pure)
same for $YBa_2Cu_3O_{7-\delta}$.

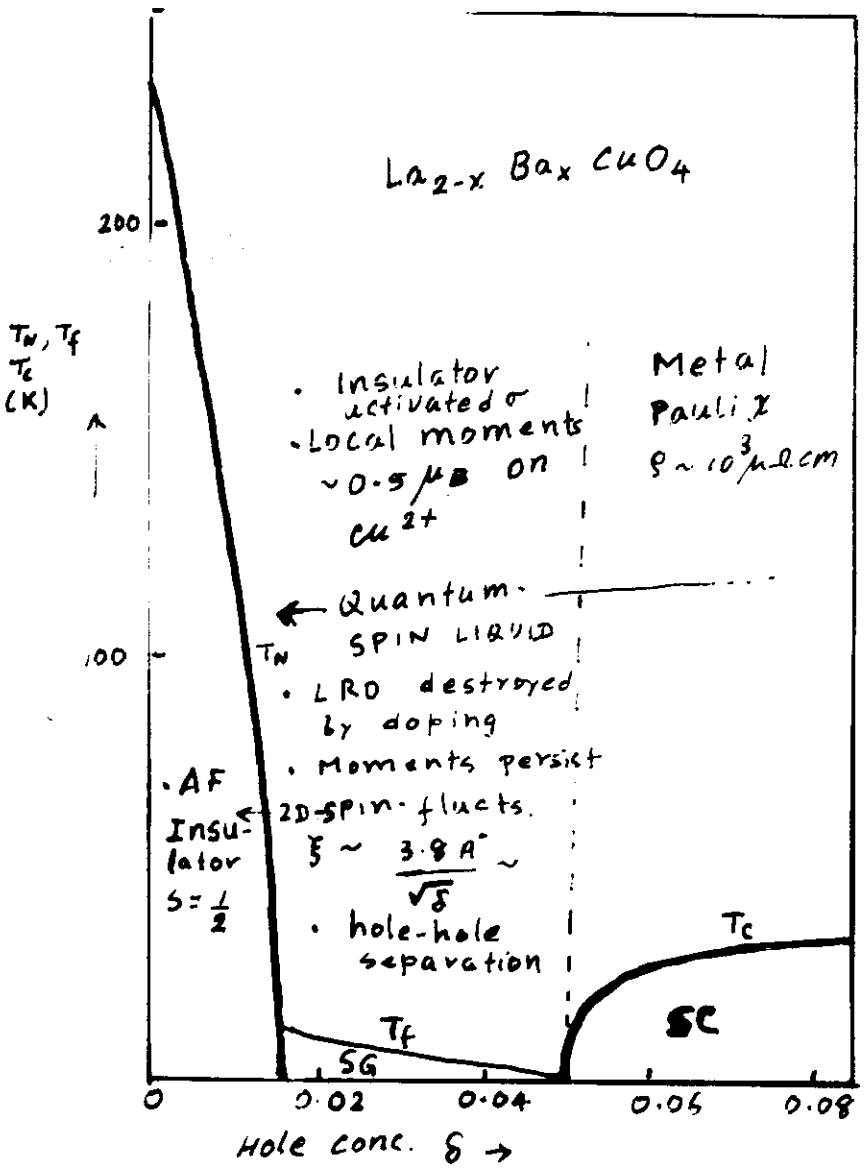



single crystal $YBa_2Cu_2O_{7-\delta}$ $\delta \sim 0$

NEUTRON scattering

- Pure $La_2CuO_4$ : AF ($T_N \sim 200$
- $T > T_N$ $Cu^{2+}$: $S = \frac{1}{2}$, $0.5 \mu_B$
  Primarily 2D spin-spin correlation $\xi \sim 200$
- At $T = T_N$ 3D ordering se
- T/O transition $\sim 550K$
- Both $T_N$, T (T/O) ↓ ... with $\delta$ ↑
- AF order lost for $\delta > 0.03$ << percolation threshold.




- spin-spin corr. length $\xi$ ↓ to ~10 A° as $\delta$ ↑ for $T > T_N$
- spins fluctuate rapid $\tau_{SF} \sim 10^{-14}$ s for $T > T_N$ (totally dynamic $S(q, \omega)$)

AF → SPINGLASS → SC
insul. insul.
as $\delta$ ↑

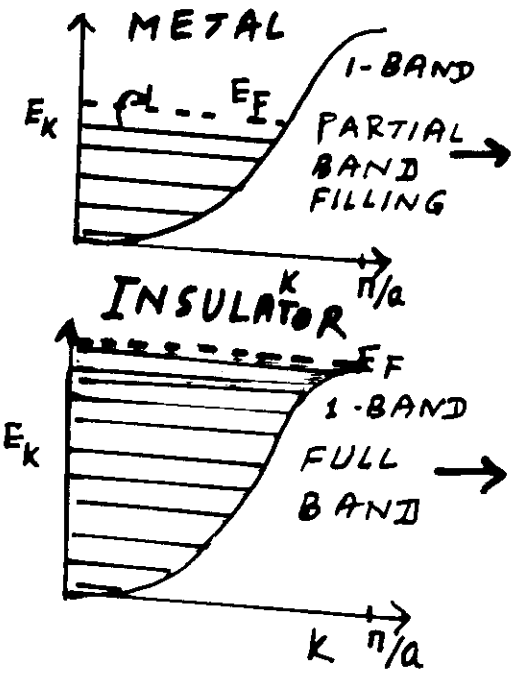
Thus unlike $S \geq 1$ syste (e.g. $La_2NiO_4$, $La_2MnO_4$) we have truly 2D - Quantum spin Liquid and AF ordering is driven by the third dimensionality.

# HIGH-TEMPERATURE SUPERCONDUCTIVITY IN CERAMIC OXIDES: DEVIATION FROM INSULATING STATE rather than a band-metallic state.

Why?

- **WHAT MAKETH A METAL → Band Theory:** PARTIALLY FILLED BAND ⇒ Empty states infinitesimally close to Fermi Level ⇒ NO GAP for CHARGE EXCITATION, hence conducts without activation.

- **WHAT MAKETH AN INSULATOR → BAND Theory:** FILLED BAND ⇒ FERMI LEVEL in the gap ⇒ CHARGE EXCITATION GAP, hence activated conduction.




- n electrons
- N orbitals > n
- Empty states ○
- singly occ. ↑, ↓
- Doubly occ. ↑↓

snap shot Real space

$n < N$ $R_H < 0$

$n > N$ $R_H > 0$

(Hall coeff.)

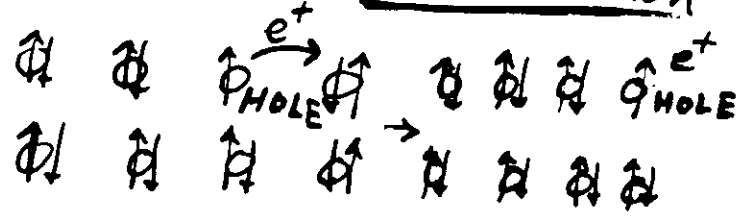
- $n = 2N$
- only doubly occ. states ↑↓.

snap shot Real space.

PAULI's Exclusion Forbids transport.

- **DOPING BAND INSULATOR → semiconduction**

Example: 1 hole ⇒




Hole: $e^+$, spin $\frac{1}{2}$ Fermion ⇒ $R_H > 0$

* $La_2CuO_4$: Parent compound (of $La_{2-x}Sr_xCuO_4$) has $\frac{1}{2}$-filled "conduction band". SHOULD be metal a la BAND THEORY BUT IS

BAND THEORY FAILS → Clue to HTSC

$La\,Cu\,O_4$ : is not a band insulator.
is Insulator because of
strong electron-electron repulsion
(on-site repulsio $U$) disfavouring
double occupancy ⇒ singly-occupied-
orbitals-only at $\frac{1}{2}$-filling ($n = N$).
Any charge transport involves
double occupancy ⇒ Coulomb gap ~ $U$
∴ Insulator (Mott-Hubbard Insulator)
→ STRONGLY CORRELATED FERMIONS

- COMPETITION between lowering of kinetic energy by delocalization ($\sim \frac{1}{2}$ BandWidth) and of potential energy ($U$) by localization determines the physics of normal & sc states.
- Deviation from $\frac{1}{2}$-filling ⇒ itinerant charge carriers (different from doped band semiconductors)

- Strong Correlation (on-site repulsion $U$)
  → Insulator at $\frac{1}{2}$-filling
  → Antiferromagnetism at $\frac{1}{2}$-filling ?
- Deviation from $\frac{1}{2}$ filling (by doping $\delta$, $La^{3+} \rightleftarrows Ba^{2+}$, or oxygen deficiency)
  → destroys AF order quickly for small $\delta$
  → conduction in normal state (Anomalous)
  → SC at low temp. & higher $\delta$.

Seems that:

- We are dealing with strongly correlated, almost localized lattice bound fermions ⇒ the charge- and the spin- degrees of freedom may get dissociated leading to unconventional Superconductivity — RVB

Non-Fermi Liquid behaviour: Absence of Fermi Surface.

Anderson (1987)

- Normal state properties reflect the unconventional sc.

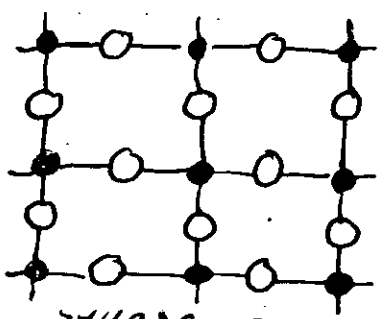
# ELECTRONIC STRUCTURE → HUBBARD MODEL (2D)

For $La_2CuO_4$

- Crystal structure (x-ray, Neutrons)
- Anisotropy $\sigma_{\parallel}/\sigma_{\perp} \sim 10^2$ (electrical)
- Magnetic correlation and dispersion (inelastic Neutron scatt
- Dispersionless Calculated band structure ∥ c-axis

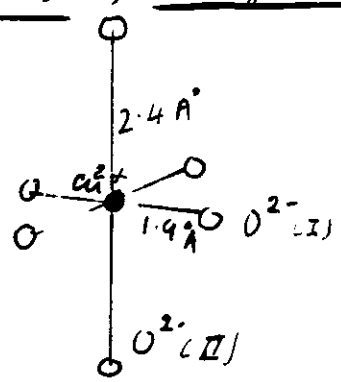
⇓

- Electronically 2D system of layers of corner-sharing elongated $CuO_6$ octahedra. layer separation ~6 Å
- Band Theory → metal. But actually Insulator ⇒ strong Correlation (like Ni



2D layers of $CuO_2$

square planar $Cu$ local symm. at $Cu^{2+}$ : $D_{4h}$



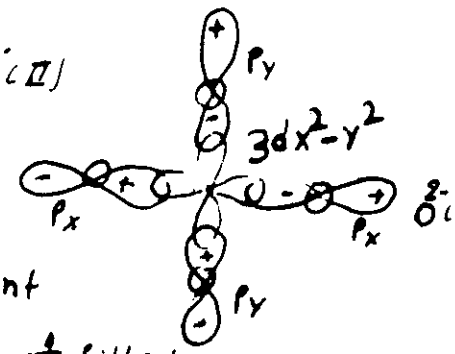

$Cu^{2+}$ site symm
$D_{4h}$
elongated
$CuO_6$

$La_2^{3+}Cu^{2+}O_4^{2-}$

$3\times2+2=2\times4$

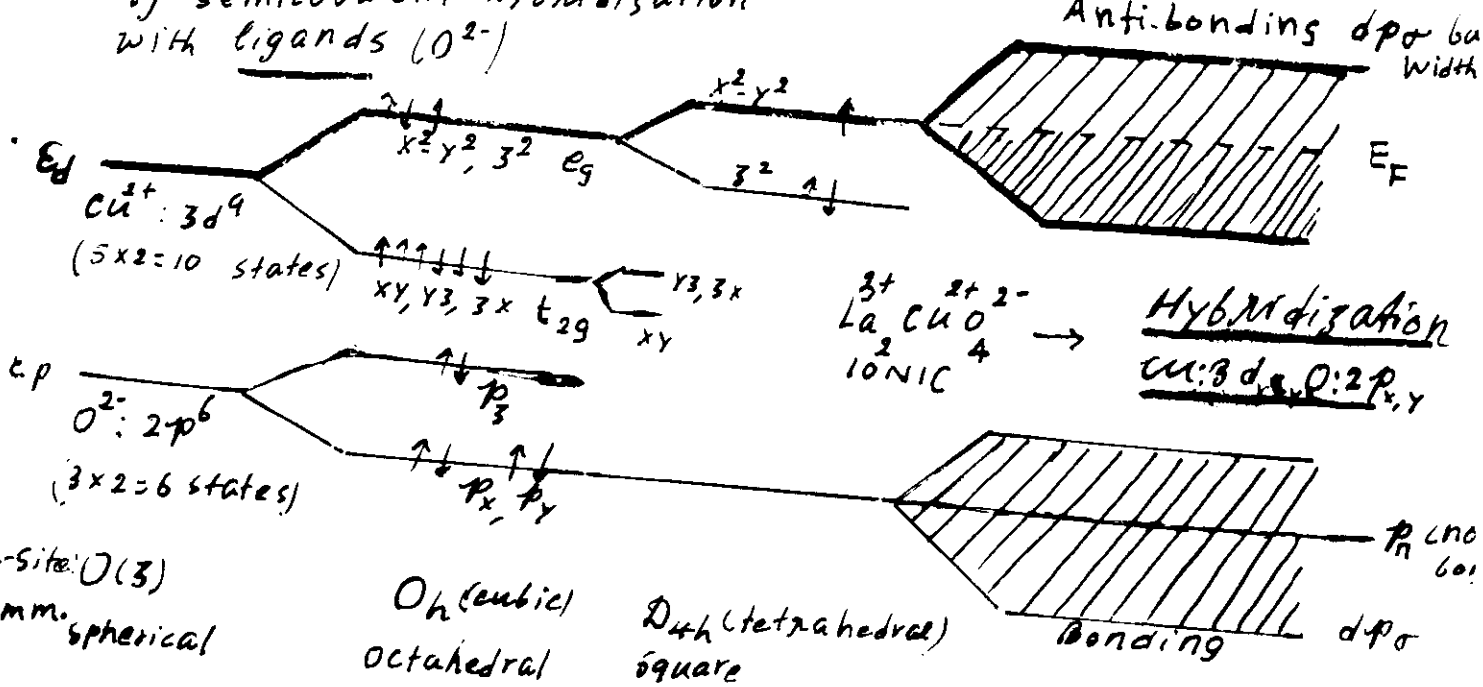
charge balance

Electron count




- Energy Level Diagram

Essentially Ionic $Cu^{2+}$ crystal field-splitting and stabilization by semicovalent hybridization with ligands ($O^{2-}$)




$La_2^{3+}Cu^{2+}O_4^{2-}$ → Hybridization

Ionic

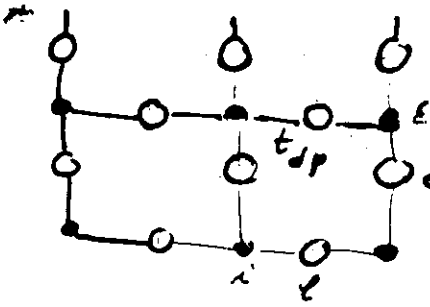
$Cu: 3d_{x^2-y^2}$ $O: 2p_{x,y}$

Cu-Site: O(3)

symm. spherical

$O_h$ (cubic) octahedral

$D_{4h}$ (tetrahedral) square

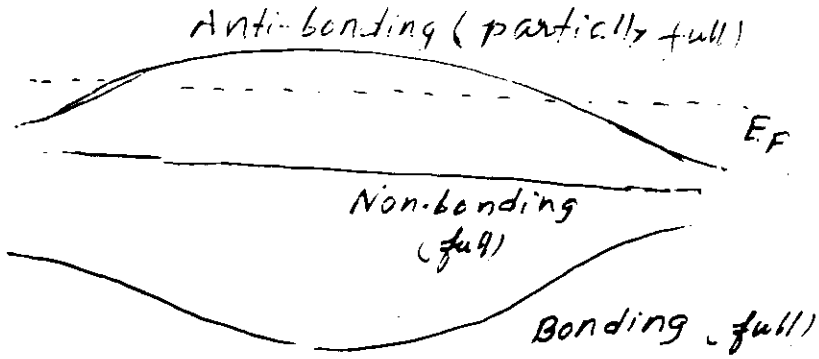



Two-band tight-binding Hamiltonian:

$$\sum_{i\in Cu,\sigma} \epsilon_d c_{i\sigma}^{\dagger} d_{i\sigma} + \sum_{\ell\in O,\sigma} \epsilon_p p_{\ell\sigma}^{\dagger} p_{\ell\sigma} + t_{dp} \sum_{\langle i,\ell\rangle} (d_{i\sigma}^{\dagger} p_{\ell\sigma} + h.c.)$$

can be diagonalized to give, non-bonding $\langle i,\ell\rangle$ Hybridized bonding and Antibonding bands:

$$\epsilon_k \begin{matrix} + \\ 0 \\ - \end{matrix} \begin{matrix} \text{Anti-bonding} \\ \text{Non-bonding} \\ \text{Bonding} \end{matrix} = \left(\frac{\epsilon_d + \epsilon_p}{2}\right) \pm \frac{1}{2}\sqrt{(\epsilon_d - \epsilon_p)^2 + 8 t_{dp}^2 (1 + \cos k_x a + \cos k_y a)}$$




For $\epsilon_d - \epsilon_p \equiv \Delta >> t_{dp}$, the high lying, partially full Anti-bond. band is well isolated, and is physically relevant.

This band can now be approximated by a one-band tight-binding Hamiltonian

$$H_0 = -t \sum_{\langle i,j\rangle \, 6\,\text{cells}} c_{i\sigma}^{\dagger} c_{j\sigma}$$

Here $|\phi_i\rangle$ effective Wannier orbital for the lattice cell i.

Now we can introduce the intra-orbital Coulomb repulsion $U \equiv$ cost of double occupancy.

$$H \equiv H_0 + H_1 = -t \sum_{\langle i,j\rangle} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$ **Hubbard Hamiltonian**

This is valid if $U << \Delta$ (Ignore configurational Interaction)

# ★ One-Band Hubbard Model in $D=2$ for strongly-correlated Electrons (tight-binding)

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

  $t$ : transfer nn matrix element $\sim 1$ eV, $W = 23t$ band width

  $U$ : Intra-orbital coulomb repulsion $\sim 10$ eV ($Cu^{2+} + Cu^{2+} \overset{U}{\rightleftharpoons} Cu^{3+} + Cu^{1+}$ Ionization − Affinity)

  $t/U \ll 1$

  $i$ : labels the Wannier (atomic) orbital at site $i$. $N$ : no. of sites

  $n$ : no. of electrons $\leq N$

  $\delta$ : $1 - n/N \ll 1$ deviation from half-filling ≡ no of holes/site created by doping ($La^{3+} \rightarrow Ba^{2+}$) or oxygen deficiency

- This is the simplest Hamiltonian → describes Narrow band transition metal oxides...

- Exactly solved for $D=1$ only

  for: Ground state Energy
  Elementary excitation spectrum
  spin-spin correlation
  Migdal discontinuity at $E_F$

- PHYSICS is determined by competition between

  delocalization ($t$) lowering kinetic energy

  localization ($U$) lowering potential energy by suppressing double ($\uparrow\downarrow$) occupancy.

  and no. of holes ($\delta$) the available free volume in the crowded condition

- control parameter appears to be $(t/U\delta)$:

  $t/U\delta > \beta$ ... Antiferromagnetism

  $t/U\delta <$ ... ferromagnetism

  $\alpha < t/U\delta < \beta$ ... non-magnetic

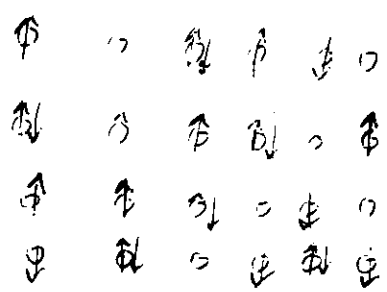
  } for $t/U \ll 1$, $\delta \ll 1$

- For Half-filled case ($\delta = 0$): Metal → Insulator transition (continuous) at $t/U$ decreases below a critical value $\sim 1$. For $\delta \neq 0$ always metallic (may not be Fermi-Liquid)

: Qualitative Picture :

at $\delta = 0$ (Half-filled) → snap-shot occupancy

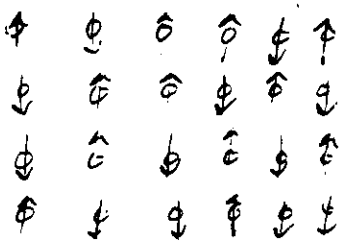
- $t/U \to \infty$ (No Corr.)



25 % double-occ.
25 % unocc. } at random
50 % single occ. } Band / Metal / Pauli paramag.

doping ($\delta > 0$) just changes $E_F$

- $t/U \to 0$ (strong corr)

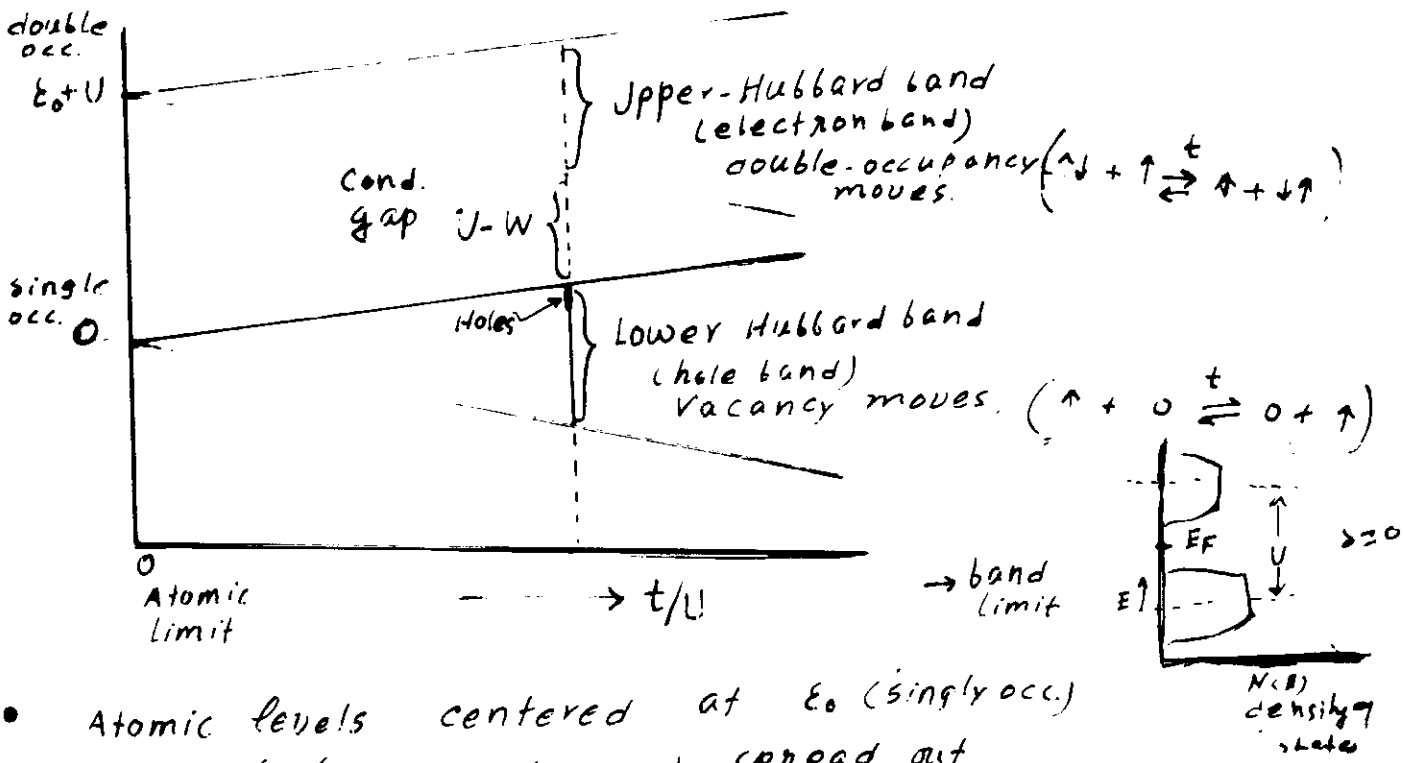


0 % double occ.
50 % single occ. (↑) } Insulator / Paramagne
50 % " " (↓) }

doping ($\delta > 0$ → finite cond. & SC ?

suppresses double occ.
∴ No transport

- Interpolation between two limits




- Atomic levels centered at $\varepsilon_0$ (singly occ.) and at $\varepsilon_0 + U$ (doubly occ.) spread out into bands by hopping matrix element ($t$) centered at $\varepsilon_0$ and $\varepsilon_0 + U$ respectively. These are many-body bands, deceptively resemble a semiconductor picture.

* HUBBARD CORRELATION ($U_d$) on Copper : $Cu^{2+} + Cu^{2+} \rightleftharpoons Cu^{1+} + Cu^{3+}$ (POLARON)

CHARGE TRANSFER ENERGY $\Delta$ ; $Cu^{2+} + O^{2-} \rightleftharpoons Cu^{1+} + O^{1-}$

BAND Energy ($-t$)

(Parameters $U, \Delta$ from Valence band Photoemission, optical absorption, **core-level shift**

- configurational Interaction (CI) Important

| | | |
|---|---|---|
| $U \ll \Delta$ | Mott-Hubbard Insulator | } for small $t$ |
| $U \gg \Delta$ | CHARGE TRANSFER INSULATORS | |

In hole representation:

Let (hole vacuum) = $|Cu^{1+}, O^{2-}\rangle$ ($3d^{10}$, $2p^6$)

$|Cu^{2+}, O^{2-}\rangle$ ... one hole on copper → Energy ... 0 (say) (undoped)

$|Cu^{3+}, O^{2-}\rangle$ ... added hole also on copper → Energy ... $U_{dd} \sim 5\text{-}10$ eV

$|Cu^{2+}, O^{-}\rangle$ ... added hole on oxygen → Energy ... $\Delta \sim 2\text{-}4$ eV

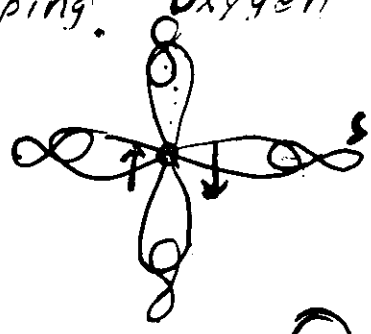
- WHERE ARE THE HOLES : (No sign of $Cu^{3+}$ in photoemission...)

The oxidation state of $Cu^{2+}$ does not change with doping ∴ Added holes go to oxygen ($O^-$), or $O_2^{2-}$

hole on $O^-$ Exchange coupled to $Cu^{2+}$ pre-existing hole → singlet.

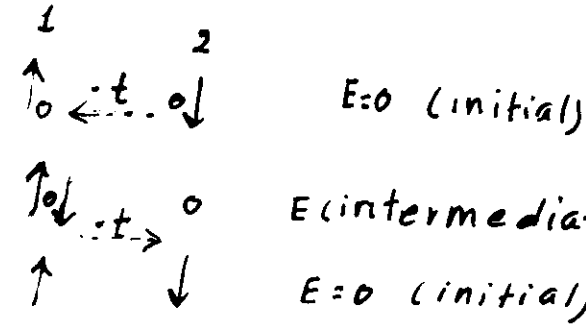
Thus moves like a hole in a one-band model.

(The main feature: Interlacing of bands. No direct O-O hopping. Oxygen holes move via copper)



Spin Singlet ($Cu^{2+}L$) hole-pair moves like a hole in one-band model. Internal structure of this singlet? A composite object.

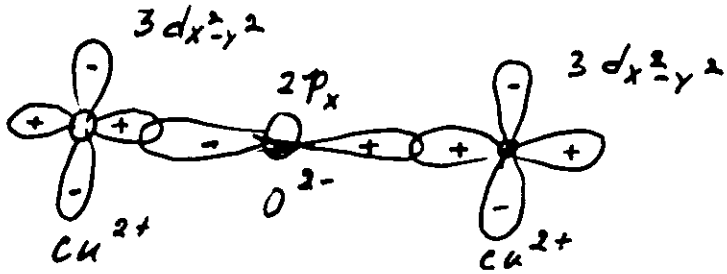
* [Note on Kinetic exchange $J = \frac{2t^2}{U}$ of Anderson.



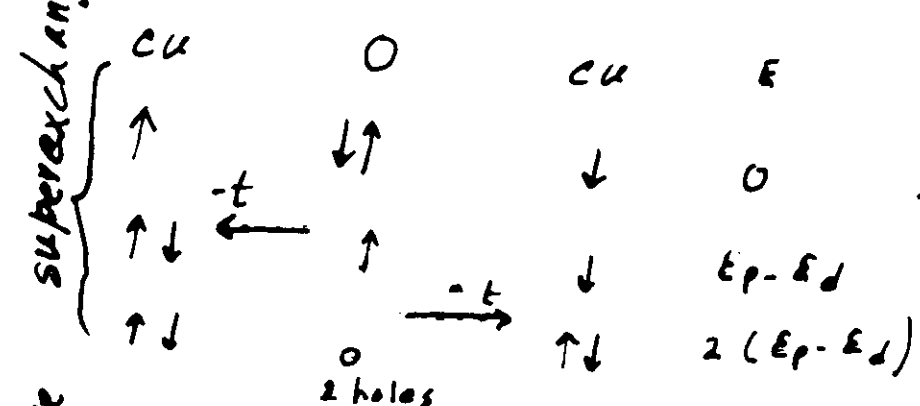

This virtual process in which the orbital 2 is virtually doubly occupied (and the conjuga process in which orbital 1 is doubly occupied) lowers the energy of antiparallel state relative to parallel-spin state by $2(-t)^2/U$. Antiferromagnetic

$\therefore J\left(\hat{S}_1 \cdot \hat{S}_2 - \frac{1}{4}\right)$, $J = \frac{4t^2}{U}$

* For the actual system spins on $Cu^{2+}$ bridged by diamagnetic $O^{2-}$, we have Super-exchange Antiferromagneti

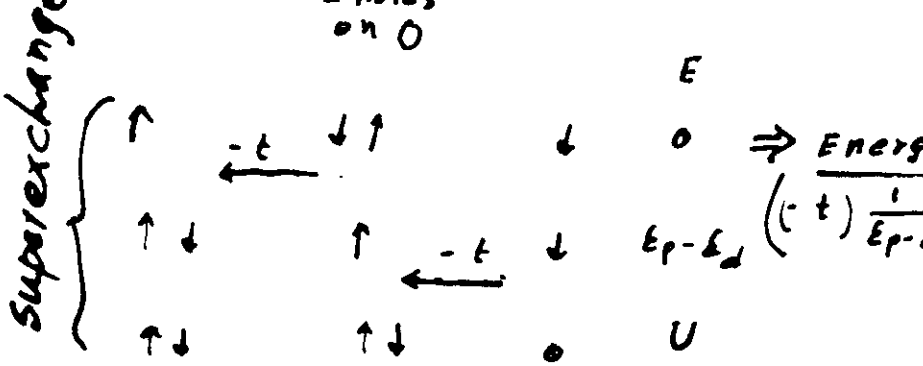



Hole representation:
$|Vacuum\rangle \equiv |Cu^{1+}, O^{2-}\rangle$
$|Cu^{3+}, O^{2-}\rangle \Rightarrow E = U+$
$|Cu^{2+}, O^{2-}\rangle \Rightarrow E = 0$, sa
$|Cu^{1+}, O\rangle \Rightarrow E = \varepsilon_p - \varepsilon$




$\Rightarrow$ energy lowering

$$\left(\frac{-t}{\varepsilon_p - \varepsilon_d}(-t)\right)^2 \frac{1}{2(\varepsilon_p - \varepsilon_d)} = \frac{t^4}{2(\varepsilon_p - \varepsilon_d)^3}$$




$\Rightarrow$ Energy lowering:

$$\left((-t)\frac{1}{\varepsilon_p - \varepsilon_d}(-t)\right)^2 \frac{1}{U} = \frac{t^4}{(\varepsilon_p - \varepsilon_d)^2 U}$$

$$\therefore J = \frac{4t^4}{2(\varepsilon_p - \varepsilon_d)^3} + \frac{4t^4}{(\varepsilon_p - \varepsilon_d)^2}$$

Here On-site Repulsion of holes on Cu is $U \sim 5$-$10$ eV

" " " " O is $\sim 0$

## 1- BAND HUBBARD MODEL in 2- DIMENSIONS AWAY FROM $\frac{1}{2}$- FILLING (STRONG COUPLING LIMIT $U/t \gg 1$)

- $n$ electrons and $N$ sites (orbitals)
  $\delta = 1 - n/N$, deviation from $1/2$ filling (by doping, oxygen stoichiometry; $\delta > 0$ hole sc, $\delta < 0$, electron sc). Consider $\delta \tilde{>} 0$.

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

  $U$: on-site repulsion $> 0$
  $2zt$: Band width
  $t/U \ll 1$, disfavours double-occupancy
  $t \sim 1$ ev, $U \sim 5$-$10$ eV.

- For $t/U \ll 1$ good approximation to project out doubly occupied configurations
  Well known transformation →

$$\tilde{H} = -t \sum_{\langle ij \rangle \sigma} \underbrace{(1 - n_{i,-\sigma})\, c_{i\sigma}^{+} c_{j\sigma}\, (1 - n_{j,-\sigma})}_{\text{hole motion}} + \underbrace{\frac{4t^2}{U}}_{J} \sum_{\langle ij \rangle} \underbrace{\left( S_i \cdot S_j - \frac{n_i n_j}{4} \right)}_{\text{spin-dynamics}} + \cdots$$

(within sub-space of non-doubly occupied states).

- The constraint of non-double occupancy $\sum_{\sigma} n_{i\sigma} \leq 1$, approximately, reduces the effective bandwidth, $t \to \delta t$. Then the control parameter is the ratio $J/\delta t \propto t/\delta U$ that determines the nature of the ground state.
- For dimensionality $\neq 1$ exact results not available.
- For $D = 3$, the ground state is AF.

TWO Scenarios suggested for ($t/U \ll 1$)

- (1) At $\frac{1}{2}$-filling, $\delta = 0$ $\Rightarrow$ AF (antiferromagnetic) ground state (Neèl like ordering with large zero-point spin fluctuations : low-dimensionality ($D=2$) and low spin ($=\frac{1}{2}$). Added holes ($\delta \gtrsim 0$) move in AF background and pairing of magnetic origin. SC due to condensation of these Bose-like compact pairs. Simple minded.

  Emery
  Hirsch (1987)
  Mohan & Kumar

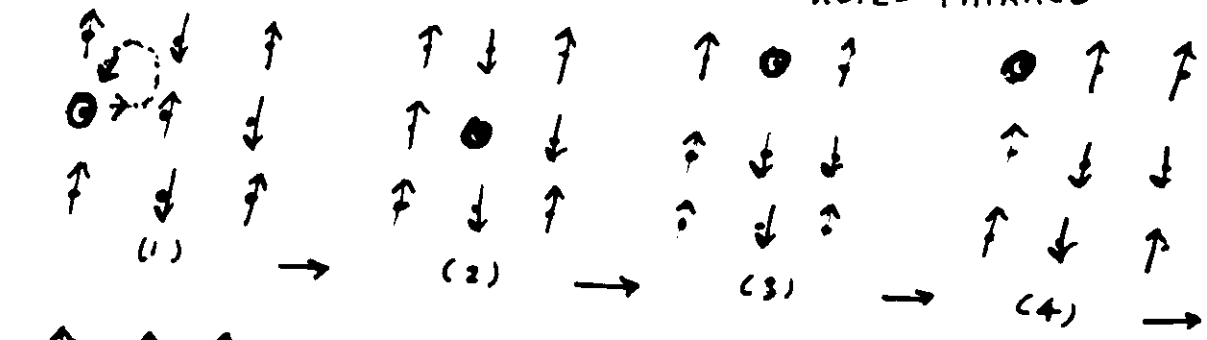
- (2) At $\frac{1}{2}$-filling (and aided by doping), the ground state is a Quantum SPIN Liquid → Resonating Valence Bond state (RVB) and doping is Solitonic, leading to Unconventional Super-conductivity — originated by Anderson (1987) and extended by Princeton group Baskaran, Zou and Santa Barbara Group Kivelson ... & Many others.

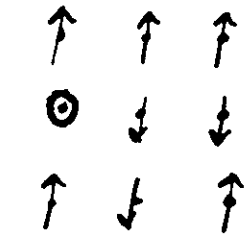
  This is the most extensively and intensively studied mechanism

- Numerical simulations tend to support the non-fermi liquid behaviour but the ground state and the possibility of SC in 1-band Hubbard model still not conclusive.
- An elementary account follows.

# BACKGROUND (Neel like)

**A** closed-loops : Confining string & hole-PAIRING



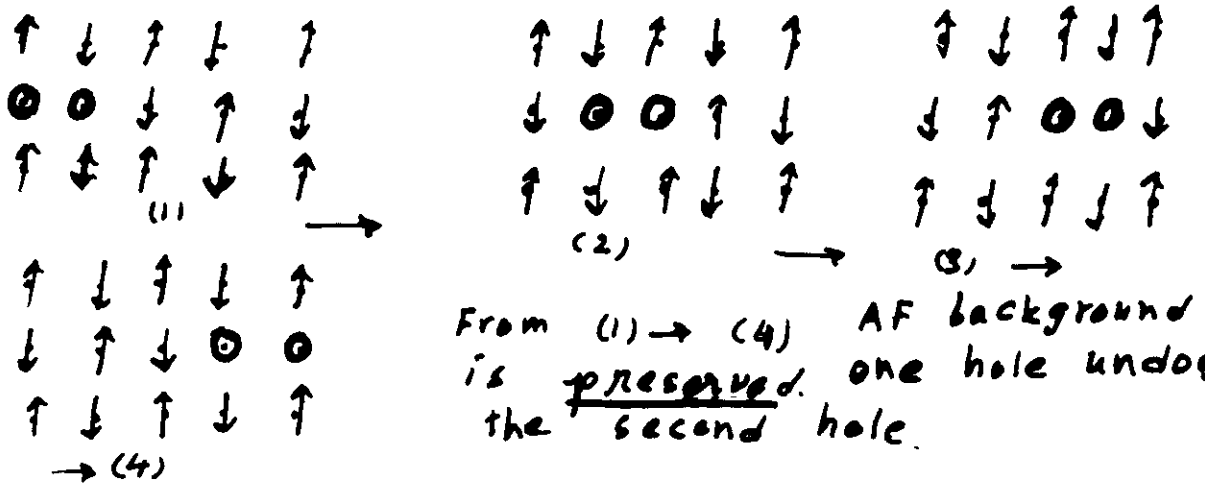

THUS (1) → (5) hole returns to original site on closed-loop but background changed ⇒ description entirely in terms of hole position alone not possible. (Unwinding possible).

Ignore these closed-loop (higher order) motion

⇒ SELF-RETRACING PATH APPROXIMATION

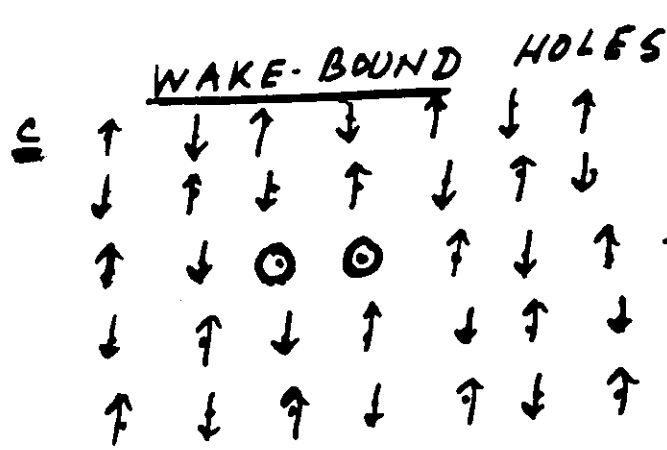
⇒ effectively Bethe lattice topology.

**B** TWO Holes can co-move without altering background : Motion of hole concomitant with spin flip ⇒ strong spin-hole coupling

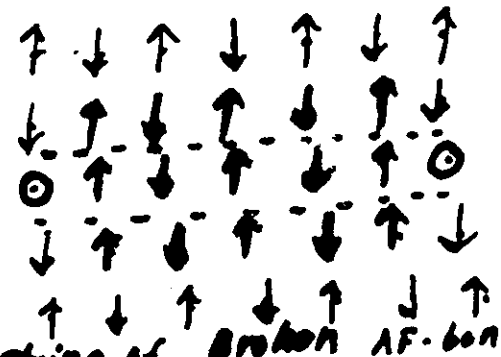



From (1) → (4) AF background is preserved. one hole undoes the second hole.

**C** WAKE-BOUND HOLES



Holes moved Apart →



String of broken AF-bonds ∴ Linear confining potential PAIRING string tension 4J ⇒

# Valence Bond & Resonating Valence Bond

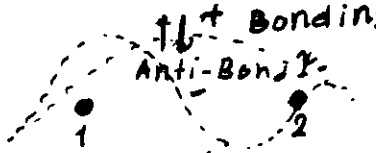
## Chemical Bond:

* **Valence Bond** ($H_2$): Two orbitals and 2 electrons (exactly solved simple case)

$$H = \epsilon_0 c_{1\sigma}^\dagger c_{1\sigma} + \epsilon_0 c_{2\sigma}^\dagger c_{2\sigma} - t(c_{1\sigma}^\dagger c_{2\sigma} + h.c.) + U n_{1\uparrow} n_{1\downarrow} + U n_{2\uparrow} n_{2\downarrow}$$

- **Molecular Orbital** : $t/U \gg 1$ Weak coupling

MIXING & COVALENCE



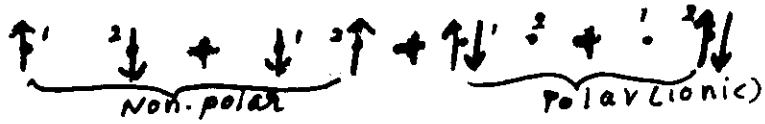

→ Ground state $= c_{+\uparrow}^\dagger c_{+\downarrow}^\dagger |0\rangle$ → Linear comb. of polar and covalent conf. → Meta limit

Singlet (Bond. state occ. Anti-bond. empty)

$$\psi_\pm = (|1\rangle \pm |2\rangle)\frac{1}{\sqrt{2}}$$

$$c_{\pm\sigma}^\dagger = (c_{1\sigma}^\dagger \pm c_{2\sigma}^\dagger)\frac{1}{\sqrt{2}}$$

(one-electron states)




- **Heitler-London** Exchange : $t/U \ll 1$, strong Coupling

Singlet state without double occupancy:

$$\frac{1}{\sqrt{2}}(c_{1\uparrow}^\dagger c_{2\downarrow} - c_{1\downarrow}^\dagger c_{2\uparrow})|0\rangle \rightarrow$$



→ Atomic limit

NO ionic config.

* **Extended System** ($t/U \ll 1$) : {singlet bond $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\frac{1}{\sqrt{2}}$ denoted by —}

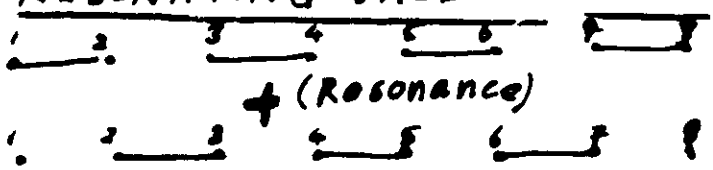
- SPIN-PEIERLS state (Jahn-Teller)


Bond Alternation frozen-in (dimerization)

≡ nn-singlet bonds (with possible bond-length contractio

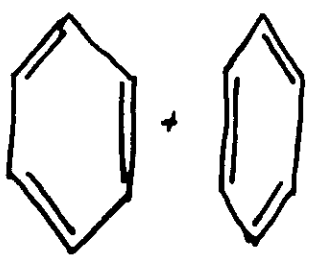
(spatially BROKEN SYMMETRY STATE Valence Bond Solid.

••• **RESONATING VALENCE BOND**



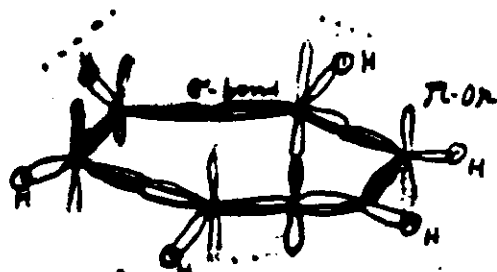

TWO degenerate bond alternation patterns and hence quantum resonance (of valence bonds).

NO dimerization, NO spatial broken symmetry.

- 

Resonance : single- and double-bond alternation patterns resonate

Benzene Ring, other aromatic and conjugated annulenes.

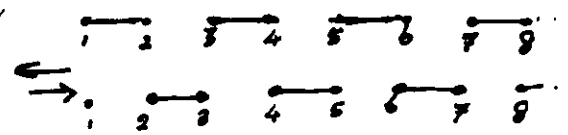



$sp^2 \rightarrow$ σ-bond

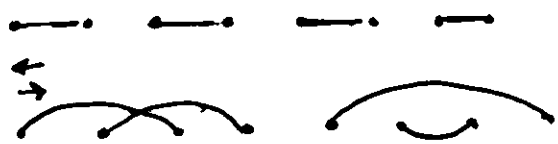
$p \rightarrow$ π bonds. Alternate

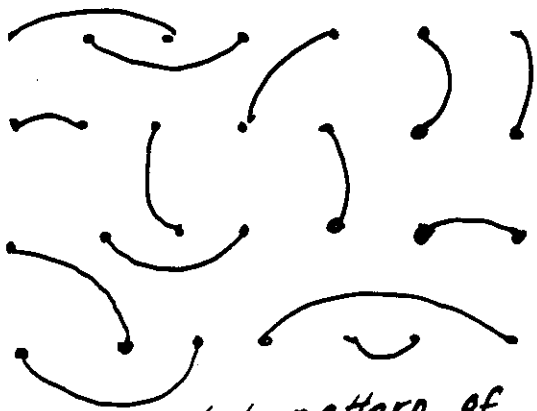
In D=1

- Nearest Neighbour (nn) Bonds can resonate only synchronously ∴ obstruction to resonance.

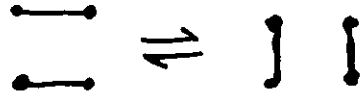


- Free asynchronous resonance requires larger range or/and higher dimensionality





A snap-shot pattern of singlet bonds in 2D.



Asynchronous resonance with nn bonds in 2D

(Not orthogonal!)

An RVB state is a coherent superposition of all possible patterns of singlet (dimer) covering of the lattice. The constraint of non-double occupancy and the singlet spin multiplicity gives RVB state a topological structure. Overcomplete

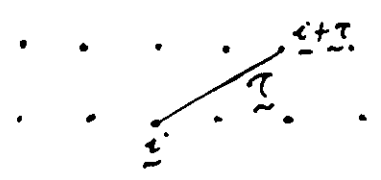
- The RVB ground state is: Spin Singlet without spatial symm. breaking (featureless). Incompressible. Quantum spin liquid (QSL) with gapless spin (covalent) excitations But charge (ionic) excitations have gap — RVB INSULATOR.
- can be made conducting by doping (removing electrons) → 'holes' moving in background of non-doubly occ. sites
- Topological excitations →
  - holons (+v charge spinless hard core bosons)
  - spinons (spin ½ neutral Fermions but have magnetic moment).

as we shall see

SPINONS →
- Pseudo Fermi surface
- Linear-Temp. Sp. heat at low temp. in normal and sc state
- Pauli like χ

Holons →
- Bose condensation → sc at low doping
- → Linear ρ-T ∴ holon spinon scattering
- → Tunneling

## Construction of RVB Ground State ($\delta=0$)




singlet valence bond $\tau$:

$$b_\tau^\dagger |0\rangle = \frac{1}{\sqrt{2N}} \sum_i \left( c_{i\uparrow}^\dagger c_{i+\tau\downarrow}^\dagger - c_{i\downarrow}^\dagger c_{i+\tau\uparrow}^\dagger \right) |0\rangle$$

↑ creates bond

General bond with bond-length distribution of weight $|a_\tau|^2$ ⇒ $b^\dagger = \sum_\tau a_\tau b_\tau^\dagger = \sum_k a(k) c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger$ ← "Cooper pair" wavefunction

- Constraint of no double occupancy ($a_{\tau=0}=0$) ⇒ $\sum_k a(k) = 0$

  [Anomalous $\langle b \rangle \neq 0$, suppressed by phase-fluctuation for $\delta=$

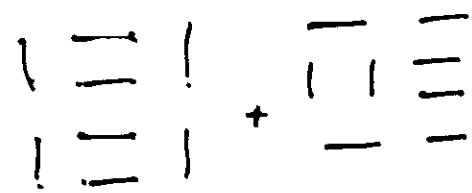
- To construct an RVB state for $N$ electrons and $N$ lattice sites ($\delta=0$):

  (i) prepare a singlet pair in zero momentum state .... $\left( \sum_\tau a_\tau b_\tau^\dagger \right) |0\rangle$

  (ii) Prepare $N/2$ singlet pairs ... $\left( \sum_\tau a_\tau b_\tau^\dagger \right)^{N/2} |0\rangle$
  $= \left( \sum_k a_k c_{k\uparrow}^\dagger c_{k\downarrow}^\dagger \right)^{N/2} |0\rangle$

  (iii) Project out states with double occupancy $\prod_i (1 - n_{i\uparrow} n_{i\downarrow}) \left( \sum_\tau a_\tau b_\tau^\dagger \right)^{N/2} |0\rangle$
  ↑ take Jastrow corr. factor
  $\equiv P_D \left( \sum_k a_k c_{k\uparrow}^\dagger c_{k\downarrow}^\dagger \right)^{N/2} |0\rangle$
  ↑ Microcanonical BCS wavefunction (incompressible) singlet valence pairs ↔ Cooper pairs.

Range of $a_\tau$ determines the nature of RVB :

Because of 'short-range' lattice structure ⇒

Possible Symm. of Valence Bond (Cooper pairs): $\Delta(k) = \sum_\tau a_\tau e^{i k \cdot \tau}$

$\Delta(k)$ = $\Delta_0$ (constant) s-wave

$\Delta(k)$ = $\Delta_0$ ($\cos k_x a + \cos k_y a$) Extended s-wave

$\Delta(k)$ = $\Delta_0$ ($\cos k_x a - \cos k_y a$) d-wave

$\Delta(k)$ = $\Delta_0$ [$(\cos k_x a + \cos k_y a) + i(\cos k_x a - \cos k_y a)$] = s + id wave (flux phase). } Anisotropic

Note on Local Gauge Invariance & RVB

- At half-filling ($\delta=0$) the Hamiltonian

$$\tilde{H} \simeq -\delta t \sum_{\langle ij\rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + \frac{4t^2}{U} \sum_{\langle ij\rangle} \left( S_i S_j - \frac{n_i n_j}{4} \right)$$

is invariant under site-dependent (Local) gauge

$$c_i \to e^{i\theta_i} c_i$$

and hence $\langle b_{ij} \rangle \equiv \langle \frac{1}{\sqrt{2}} (c^{\dagger}_{i\uparrow} c^{\dagger}_{j\downarrow} - c^{\dagger}_{i\downarrow} c^{\dagger}_{j\uparrow}) \rangle = 0$ (unlike the global gauge symm. if the Hamiltonian has local gauge symm. then only gauge-invariant quantity can have non-zero average value $\equiv$ Local gauge symm. can not be broken spontaneously — it is like a finite system!)

- Away from $\frac{1}{2}$-filling, $\delta \neq 0$, the first term destroys Local gauge symm. Then the phase for the singlet can not be varied freely — it costs torsional energy $\sim \delta t (1-\cos\theta) \sim \frac{\delta t \theta^2}{2}$

$$\langle b_{ij} \rangle \propto \langle b_{ij} \rangle_{T=0} \int e^{i\theta} e^{-\frac{\delta t \theta^2}{2 k_B T}} d\theta \propto \langle b \rangle_{T=0} e^{-\frac{k_B T}{2\delta t}}$$

Here $\theta$ is the phase of $b_{ij}$ relative to neighbouring pairs.

Thus the RVB order parameter assumes below some temp. non-zero value, to be given by a self-consistent treatment of the Hamiltonian as in Gor'kov factorization.

This however, is not quite the SC order parameter.

SC is attributed to holons that move in this featureless singlet medium.

Thus RVB state is (mathematically) like BCS-paired state but projected so as to avoid double occupancy. For exact $\frac{1}{2}$-filling, the 'incompressibility' destroys ODLRO. But doping provides the necessary free phase-space. One can think of SC resulting from these pre-existing singlet pairs (early version).

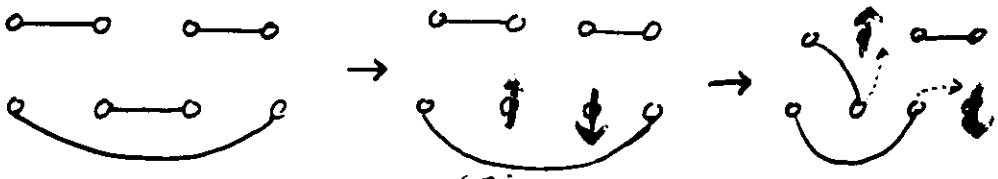
- Mean-field treatment proceeds via the anamalous expectations along the BCS line but there are important differences because of the constraint.

- The RVB theory is evolving continually with the identification of new internal symmetries.

- In the following, we concider some important aspects pictorially:
  The new topological objects →
  <u>SPINONS</u>
  <u>HOLONS</u>
  suggesting total <u>separation</u> of <u>charge</u>- and <u>spin</u>- degrees of freedom.

# Doped RVB Insulator vs. Doped Band Insulators
## SPINONS & HOLONS

- **SPINONS** (Created in pairs): $s = \frac{1}{2}$, $q = 0$, mag. moment $\neq 0$

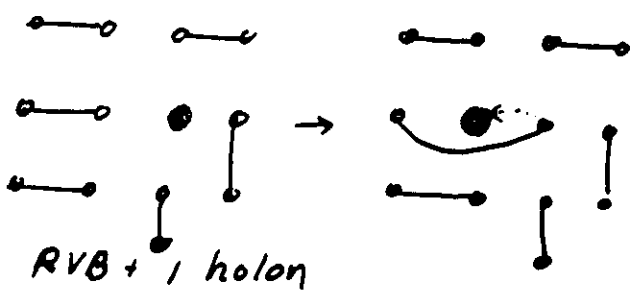


an RVB Configuration (in ground state)

spin excitation: Singlet bond admixed with triplet

The two Spinons ↑, ↓ move away
No charge fluctuation

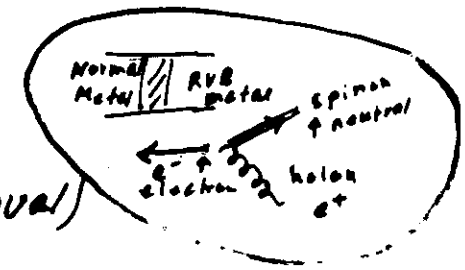
- **Holons**: $s = 0$, $q = |e|$, mag. moment $= 0$



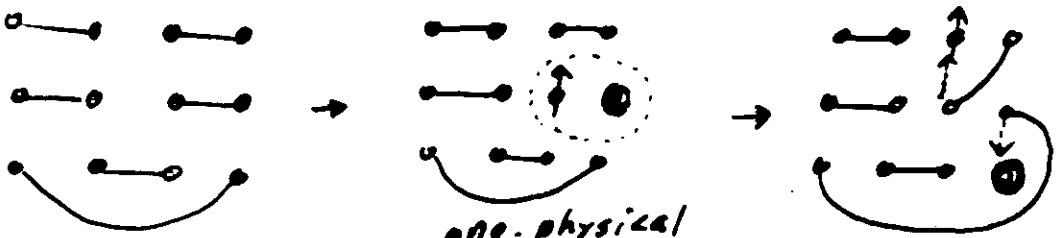
RVB + 1 holon

Holon motion → charge transport, no spin fluctuation

Ex.:




- **PHYSICAL HOLE** (DOPING: electron removal of RVB INSULATOR)

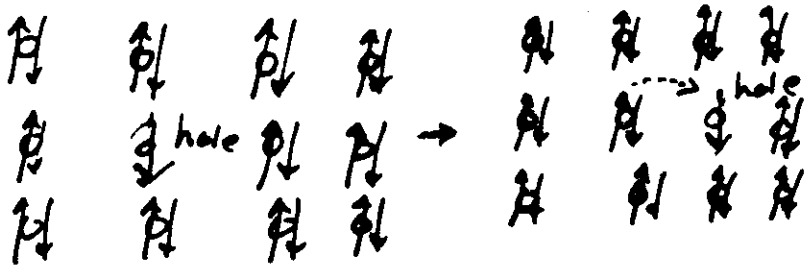


RVB config.

one physical hole by doping ≡ 1 spinon + 1 holon

spinon and holon separate out charge and spin get separated

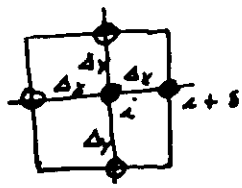
compare with:
DOPING OF BAND INSULATOR (removal of spin ↑ electron): A hole moving in background of doubly occupied sites




Hole motion transports +ve charge an spin ↓.

## RVB Order parameter:

- $\langle S_{i\uparrow}^{\dagger} S_{j\downarrow} \rangle \equiv \Delta_{ij}$




$\Delta_y = e^{i\theta} \Delta_x$

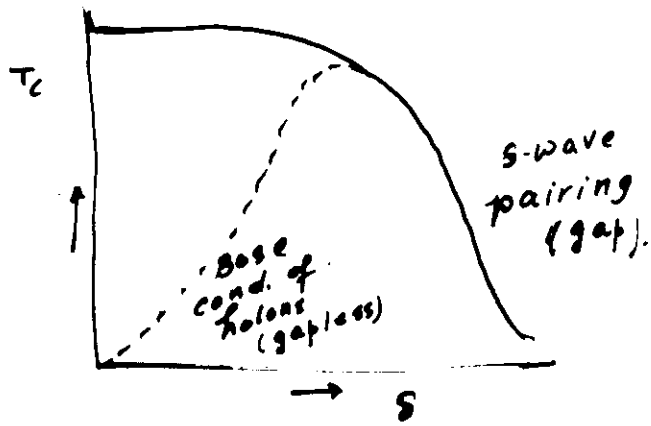
$\theta = 0 \Rightarrow$ s-wave

$\theta = \pi \Rightarrow$ d-wave

$\theta = \pi/4 \Rightarrow$ s+id-wave } lines of zero of gap. Will affect tunneling, NMR relaxation, sp. heat etc.

- supercond. Order parameter:

$\langle c_{i\uparrow}^{\dagger} c_{j\downarrow}^{\dagger} \rangle \propto \langle S_{i\uparrow}^{\dagger} S_{j\downarrow}^{\dagger} \rangle \langle b_i b_j \rangle$




- Relative stability of s, d and s+id wave phases is very controversial (d-wave appear to be favoured

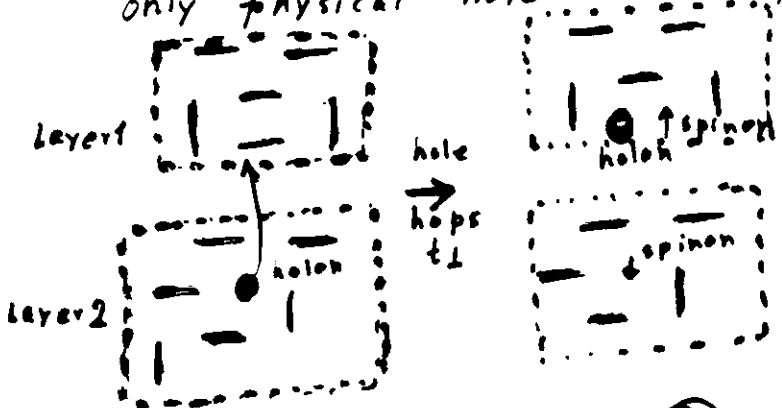
These effect: { tunneling N/s ; s/s; sp. heat - Linear; $T_1^{-1}$ NMR relaxation; $\chi \sim$ Pauli like; $\rho \sim$ temp. linear; Flux quantization ?; Andreev reflection ?; Light scattering (Raman) ? } still ?

Recent Cu & oxygen NMR results should provide crucial test of these ideas

Is RVB merely a matter of representation? overcomplete set.

* Inter-layer holon-holon pairing (exchange of spinons) :

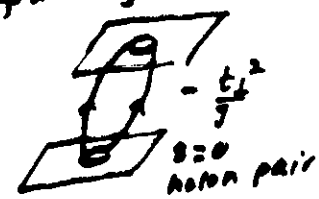
only physical hole can hop interlayer ($t_\perp$) :




$\Rightarrow$ Thus inter layer hopping $\rightarrow$ two spinons (energy cost $\sim J$)

$\therefore$ In second order $\Rightarrow$ holon-holon pairing

$k_B T_c \sim t_\perp^2 / J$



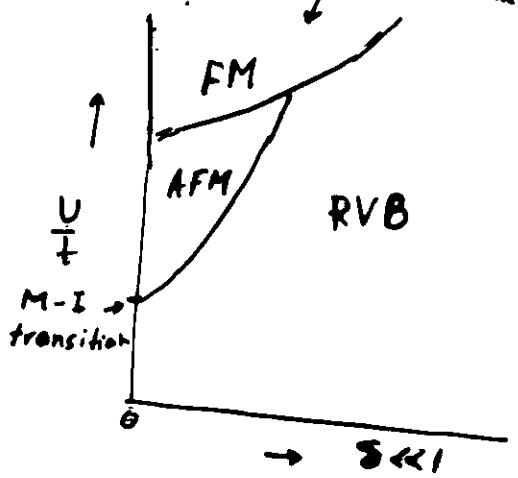
# * What Stabilizes RVB state against AF Long Range Order

1. **Low Dimensionality (D)** : • 3D systems have AF ground st
   • 2D systems are numerically found to be AF in thermodynamic limit
   • 1D system has no LRO

2. **Geometric Frustration** : nn AF coupling → $J_1$ $J_1$ $J_2$ $J_1, J_2 >$
   can not make all spins happy at the same time.
   Triangular lattice → $J$ $J$ $J$ $J>0$

3. **Low Spin (S)**
   $S = \frac{1}{2}, \frac{3}{2}$ - integral → no spectral gap, correlation decays algebraically
   $S = 1, \ldots$ integeral → spectral gap, exponential decay
   lower spin ⇒ Quantum zero-point fluctuations
   Higher Spin favours order (Hund's rule)
   $La_2 Ni O_4$, $La_2 Mn O_4$, $La_2 Co O_4$ ... AF 3D
   $S=1$ $S=$
   $La_2 Cu O_4$ ... essentially 2D spin fluids
   $S=\frac{1}{2}$ ordered by third dimension

4. **Doping δ**
   Very Rough phase diagram
   Doping stabilizes RVB ?
   " destroys AF rapidly dynamically




Competition between:
Lowering of mobile hole energy due to delocalization ($\propto \delta t$)
cost of magnetic energy ($\frac{t^2}{U}$) due to spin misalignment

Finally, a Remark : It appears that for valence bonds to resonate in an extended solid, there should be a back-bone structure that holds the solid together on its own more or less. Otherwise resonance may be blocked by spatial broken symmetry.