

Title: Warm Superconductors

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Abstract:

3rd July 2012



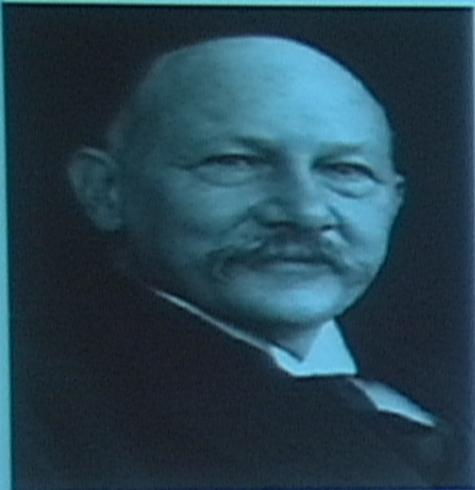
## Acknowledgement

**P W Anderson** (Princeton)  
**V Shenoy** (IISc, Bangalore)  
**S Pathak** (UC, Santa Cruz)  
**A Jafari** (Sharif)

**Superconductivity is a most remarkable  
Macroscopic quantum phenomenon**

**Macroscopic Wave function on the table top**

**Zero resistance, Meissner effect, Josephson effect ...**



Heike Kamerlingh Onnes



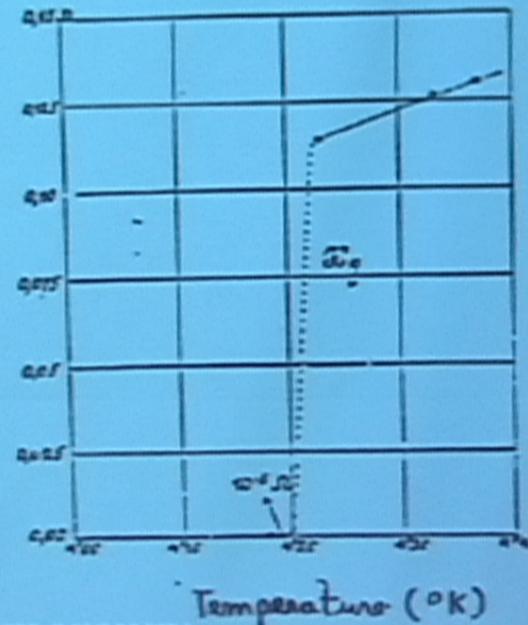
Nobel Prize 1913

1911

Perfect conductivity

Resistance of mercury

Kamerlingh Onnes 1911



Source: Carrington

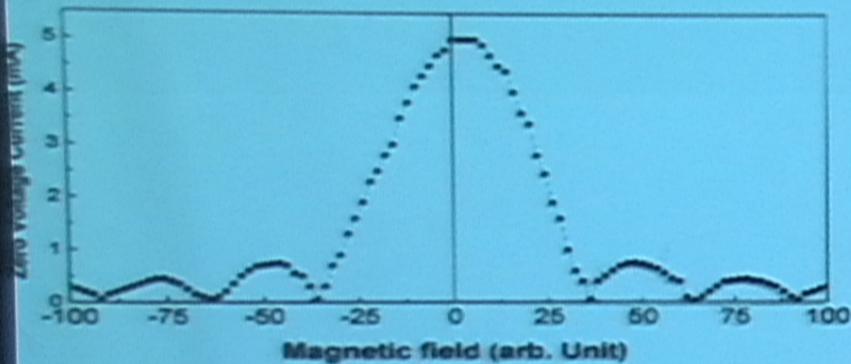
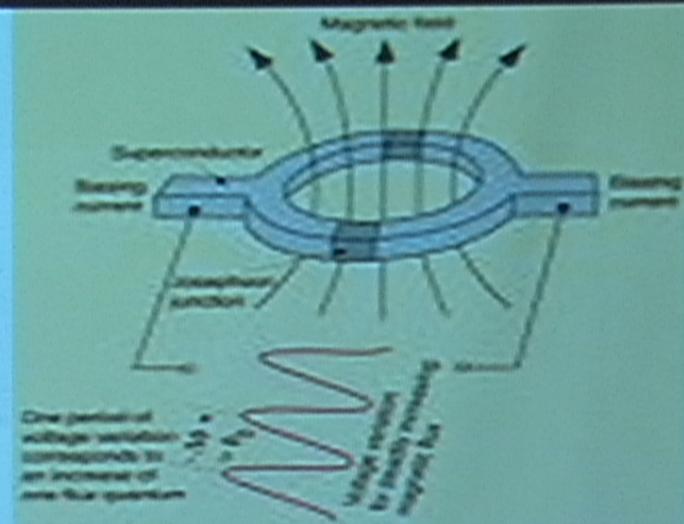


Figure 2. Dependence of critical current  $I_c$  of the junction on magnetic field.



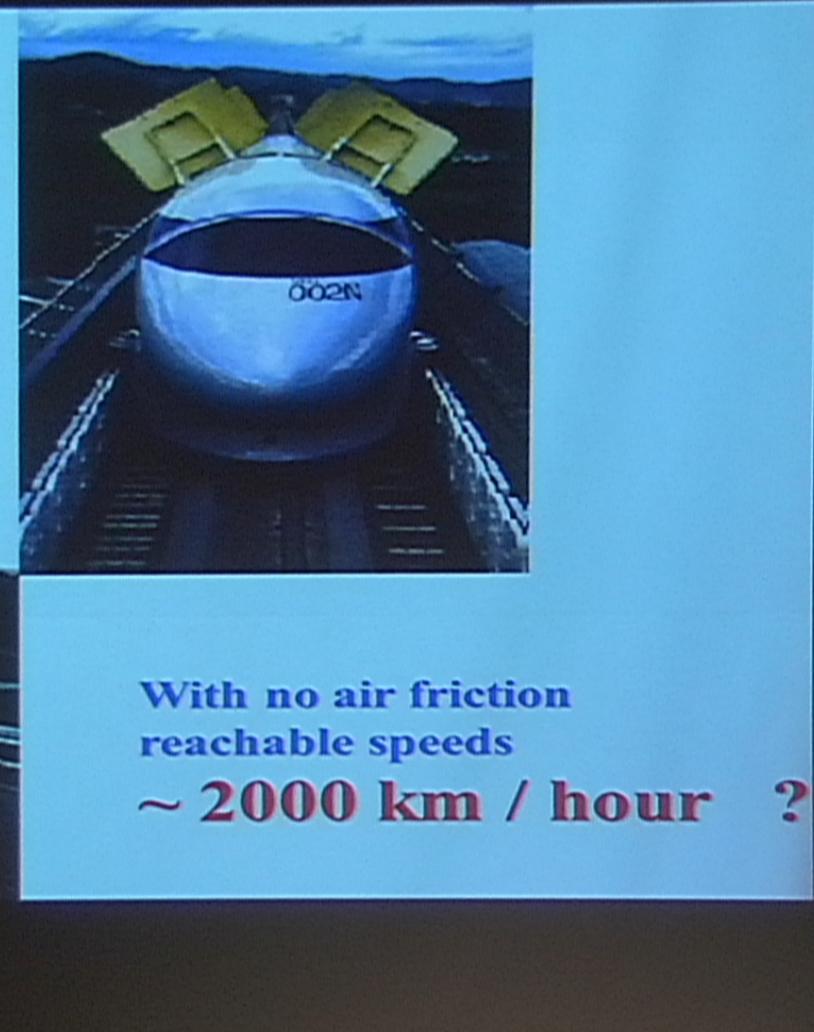
## Josephson Interferometer

### Interference of Macroscopic wave function

$$\Delta\phi = \frac{Et}{\hbar} = \frac{2eV_0t}{\hbar}$$

$$J = J_1 \sin(\phi_0 + \Delta\phi)$$

$$= J_1 \sin(\phi_0 + \frac{2eV_0t}{\hbar})$$



## **Quantum Matter is ubiquitous**

**Space and time as quantum spin system - spin network, spin foam**

**Space time and matter as Super String matter**

**Dark quantum matter, ...**

**QCD (spaghetti vacuum), color superconductor, nuclear matter**

**Cosmic ray, LHC jets, quark gluon plasma, nuclei, neutron star ...**

**Non-relativistic Quantum matter**

**Superconductivity, superfluidity, CDW, SDW, heavy fermions, Mott insulators**

**QHall States, QMagnetism ... Cold atoms, non-equilibrium QPhenomena, ...**

**QNumber fractionization, anyons, emergent gauge fields, Quantum Order, ...**

**Quantum Biology**

**Characterizing entanglement of many body, many Qubit systems, ...**

**Theoretical methods (holography, tensor network, ...) for**

**Strongly coupled Quantum fields and many body Systems**

**Solid State Qubits, Majorana Fermions, Fibonacci anyons, ...**

**Designing Room Temperature Quantum matter ...**

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## Matters of Consequence

**BCS theory of (c)old Superconductors has had a Special and Unifying Role in Physics**

**It provided key insights for unification of weak, electromagnetic and strong interactions in Standard Model of elementary particle physics**

Spontaneous symmetry breaking,

Nambu-Jona-Lasinio mechanism of mass generation, chiral symmetry breaking  
Anderson-Higgs mechanism, Higgs boson ...

Pairing in nuclei, superfluidity in neutron stars, ...

**Theory and new physics in Warm Superconductors**

**Another Special role in Physics ?**

Emergent gauge fields, quantum order, topological order,  
Novel entanglement structure ...

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# **Limiting values of Physical Properties of Non relativistic matter**

**Highest density  
melting point  
hardness  
Youngs modulus  
Tc ferromagnetism  
Tc superconductivity  
resistance  
viscosity**

**Room temperature Qubits**

**can theory help  
ab initio ? not yet**

**microscopic models  
with phenomenological inputs  
- yes, to some extent**

## **Basic input**

**Electric charge e  
Mass of electron m  
Mass of proton  $m_p$   
Atomic numbers Z  
Velocity of light c  
Planck's constant h**

# Approaches to High temperature Superconductivity

## Theoretical

Little's mechanism

Ginzburg's mechanism

Bipolaron

Pressurized Hydrogen

Doped Mott insulators  
& RVB mechanism

## Experimental

Cuprates - 32 K to 163 K

Organics - 1 K to 13 K

TM oxides,  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ,  $\text{MgB}_2$  40 K

Nickel borocarbides (TIFR) 24 K

Carbon, fullerene based 40 K

Fe Arsenide 56 K

# **B.T. Matthias\* Rules for Superconductivity**

**1960's**

- 1) cubic structures**
- 2) avoid oxygen**
- 3) avoid magnetism**
- 4) avoid insulators**
- 5) don't talk to theorists**

\* An outstanding experimentalist and discoverer  
of new families of superconductors, including  $\text{Nb}_3\text{Ge}$ ,  
a record holder for maximum  $T_c$  till 1986,  
before high  $T_c$  cuprates appeared in the scene

## Theory of Lord Kelvin (1902)

According to Rutherford model of atoms, conduction electrons in metals should get attached back to parent ions as we lower the temperatures.

**Every metal is likely to become an insulator at sufficiently low temperatures**

Kammerlingh Onnes went on to prove Lord Kelvin right

**He ended up discovering superconductivity in Hg !**

**Bednorz and Muller (1986) were inspired by**  
**a theory based on Jahn-Teller effect induced bipolaron**  
Höck, Nickisch, Thomas, Helv. Phys. Acta. 56, 237 (1983)

**They ended up discovering cuprate superconductors  
where there is no Jahn-Teller effect but  
an entirely new (RVB) mecehanism  
based on electron correlations**

## **Moral of the story (GB)**

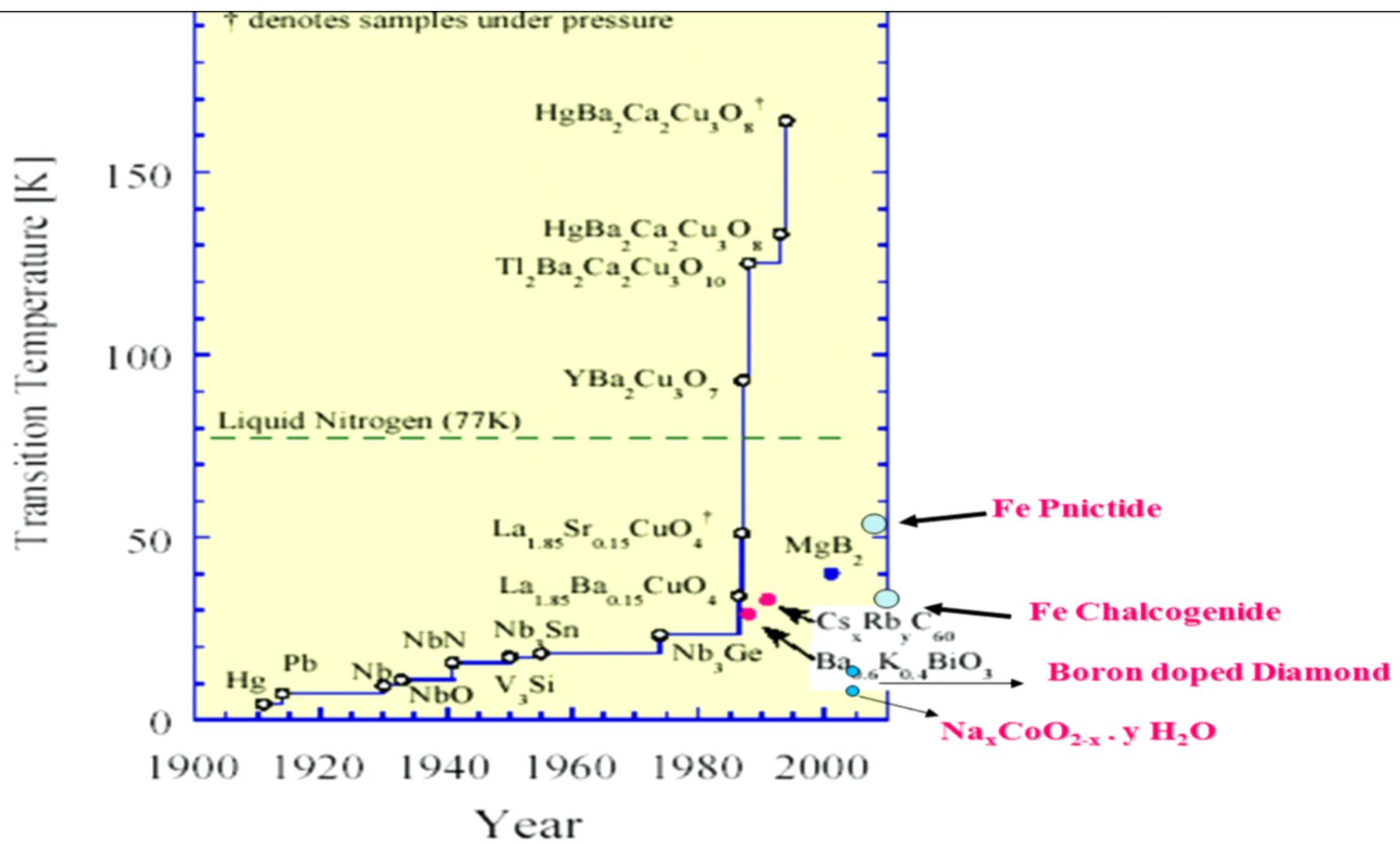
**Listen to theorists**

**They will put you in some good track**

**where things might be more interesting than one wanted !**

## Periodic Table of the Elements Showing Superconducting Transition Temperatures

A. Carrington



Source: Carrington

# **Superconductivity in Elemental Metals**

**Hg, Pb, Al, .... Ti, V, Nb, ...**

## **Model**

**Electron gas interacting with a lattice of ions,..., screening**

**A stable harmonic solid, Fermi liquid**

**Electron dynamics - Landau quasi particles (electron, hole)**

**Lattice dynamics – harmonic phonons**

## **Important energy scales are large**

**Fermi energy  $\sim 50,000$  K, Debye energy  $\sim 500$  K**

**Deformation potential  $\sim 10,000$  K**

## **Why is $T_c$ always small $< 10$ K ?**

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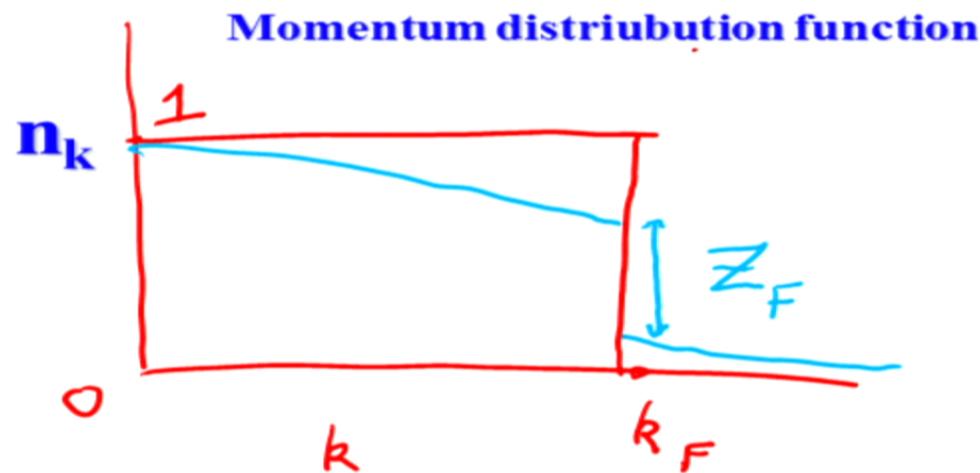
**Deformation potential  $\sim 10,000$  K**

## **Why is T<sub>c</sub> always small < 10 K ?**

**BCS theory of superconductivity**  
Needs a reference vacuum/normal state

**Fermi liquid metallic state**

**Superconductivity is a  
Minor instability of this vacuum**

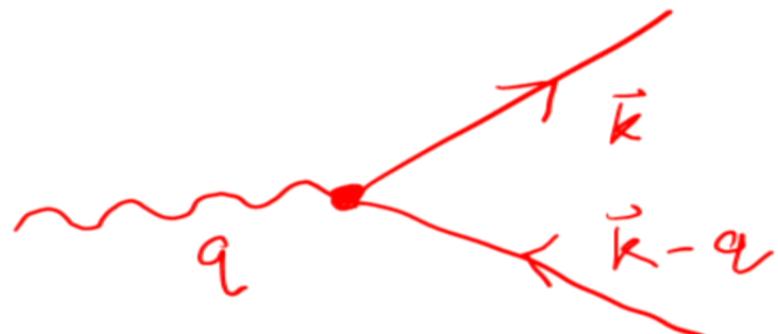


$Z_F$  : Wave Function Renormalization Constant

$$m^* \sim \frac{m_e}{Z_F}$$

# Residual interaction between electron and phonon

## Electron-phonon interaction



Electron-electron attraction  
Mediated by Phonon



BCS Hamiltonian

$$H = \sum_k \left( \frac{\hbar^2 k^2}{2m} - \mu \right) c_{k\sigma}^\dagger c_{k\sigma} - g \sum' c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger c_{-k'\downarrow} c_{k'\uparrow}$$



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$$\frac{-1}{k_B T_c = \hbar \omega_D e^{\rho \cdot g}}$$

$$\hbar \omega_D \sim \frac{1}{\sqrt{M_N}}$$

**Serious constraints from stability point of view**  
**-McMillan, Anderson, Cohen**

**Phonon mediated maximum Tc ~ 30 K**

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**-McMillan, Anderson, Cohen**

**Phonon mediated maximum  $T_c \sim 30$  K**

## **BCS theory inspired traditional route to new superconductors**

$$\frac{-1}{k_B T_c = \hbar \omega_D e^{\rho \cdot g}}$$

**Look for**

**Large Debye energy  $\hbar \omega_D$**   
**Large density of states at Fermi level  $\rho$**   
**Large electron phonon coupling constant  $g$**

# High T<sub>c</sub> Superconductivity – Copper Oxides

1986



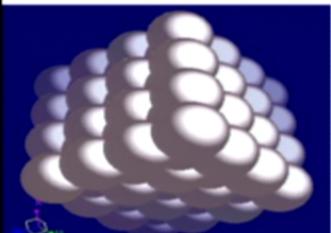
Georg Bednorz



Alex Müller



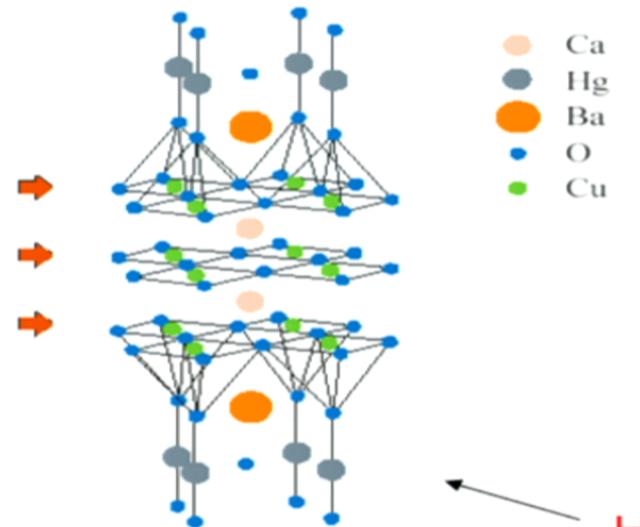
Nobel Prize 1987



Mercury

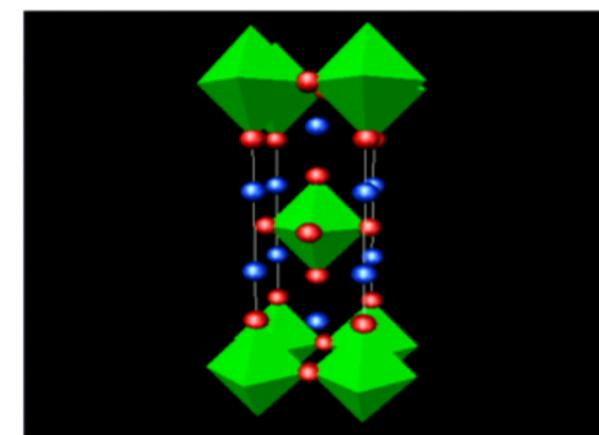
Kammerlingh Onnes  
Nobe Prize 1913

CuO<sub>2</sub>  
Planes



Hg 1223

La<sub>1-x</sub>Ba<sub>x</sub>CuO<sub>4</sub>



# High T<sub>c</sub> Superconductivity – Copper Oxides

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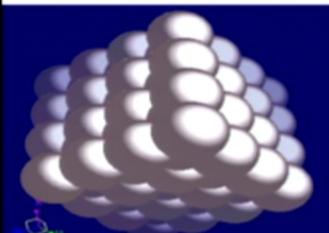
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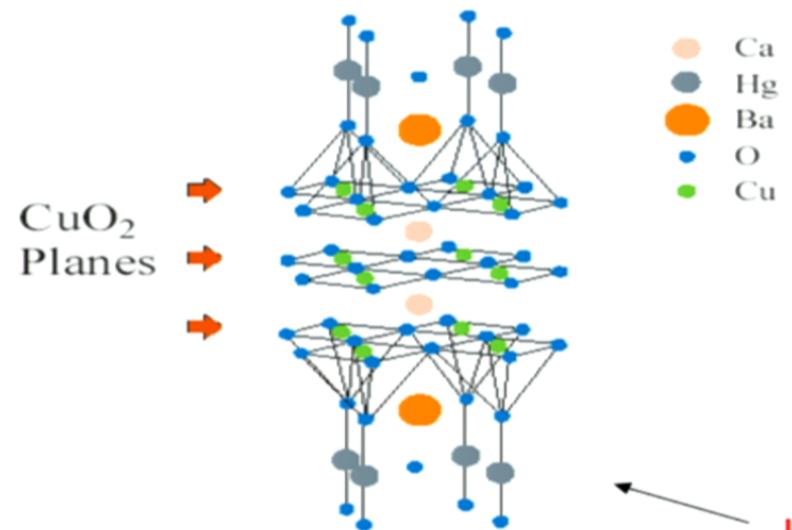


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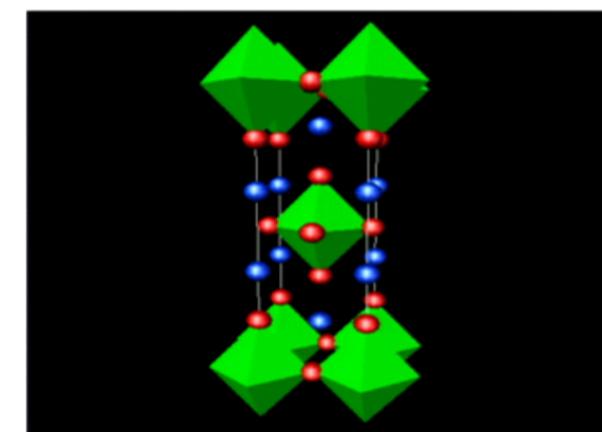


Mercury

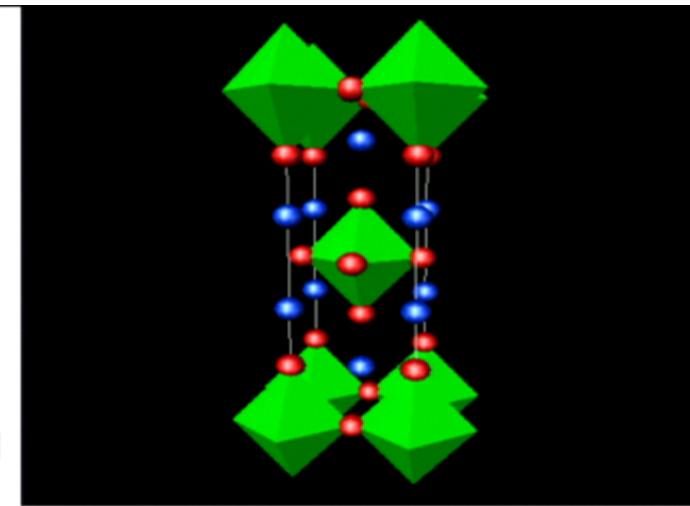
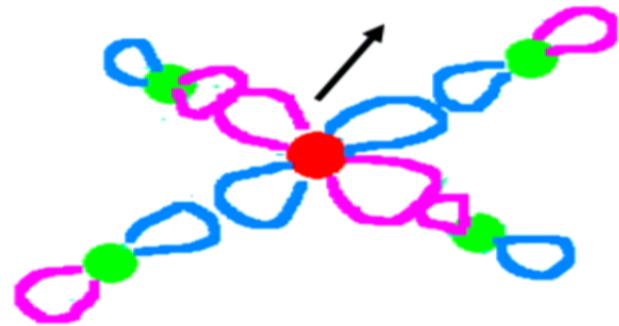
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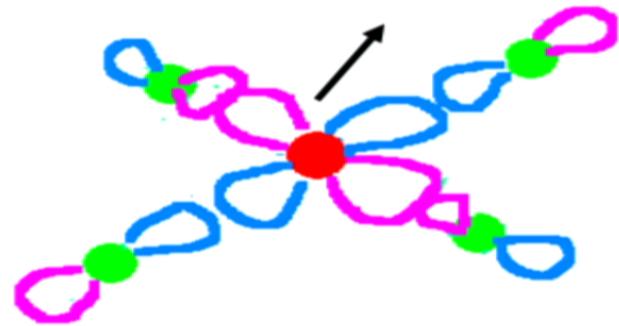


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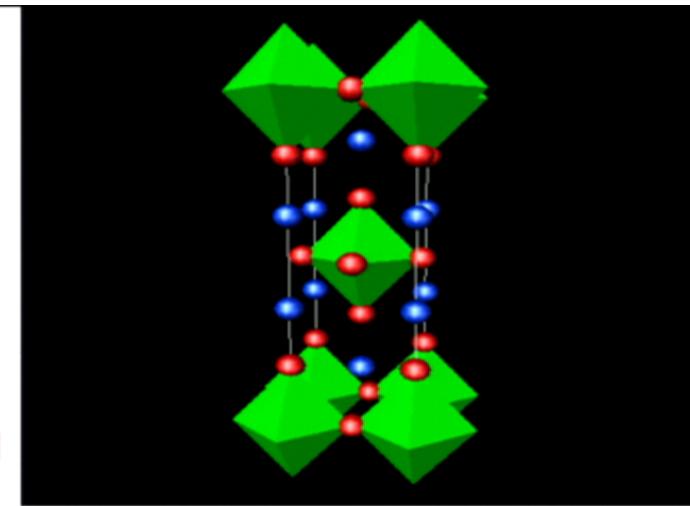


Cu 3d<sup>9</sup> Ligand

One hole per Cu cell in a molecular orbital of  $\mathbf{d}_{x^2-y^2}$  symmetry



Cu 3d<sup>9</sup> Ligand



One hole per Cu cell in a molecular orbital of  $\mathbf{d}_{x^2-y^2}$  symmetry

---

**A ray of hope came from  
Resonating Valence Bond (RVB) theory  
1987**

**Mott insulators  
as opposed to fermi liquids  
are seats of  
High Tc Superconductivity**

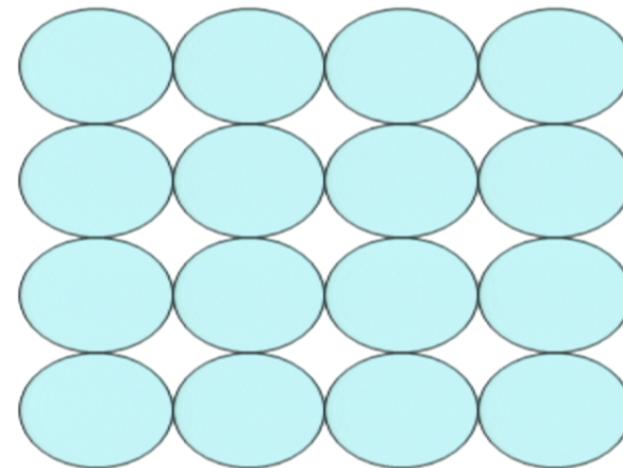
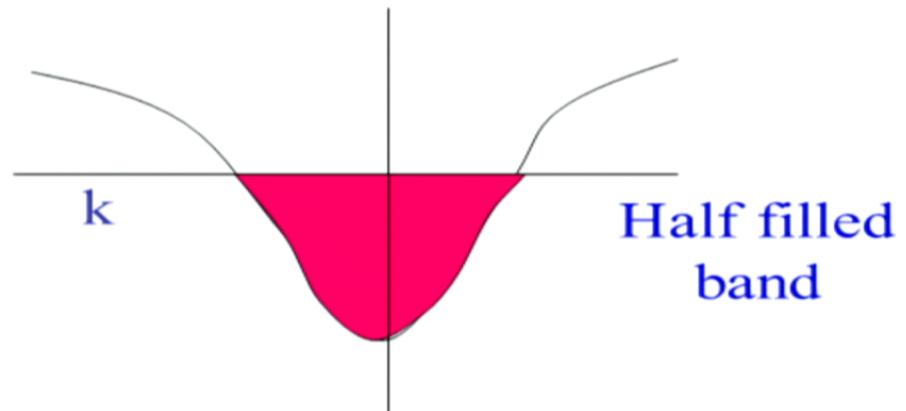
**Superexchange  
as opposed to exchange of phonon  
is the pairing GLUE**

**A collection of hydrogen atoms forming a hypothetical 3D lattice**

**1s states of individual hydrogen atoms strongly overlap and form a tight binding half filled band**

**It is a metal described by Hubbard Model**

$$H = -t \sum_{\langle i,j \rangle} C_{i\sigma}^+ C_{j\sigma} + h.c. + U \sum n_{i\uparrow} n_{i\downarrow}$$



$$\mathbf{a} \sim \mathbf{a}_B$$

$$U \ll zt$$

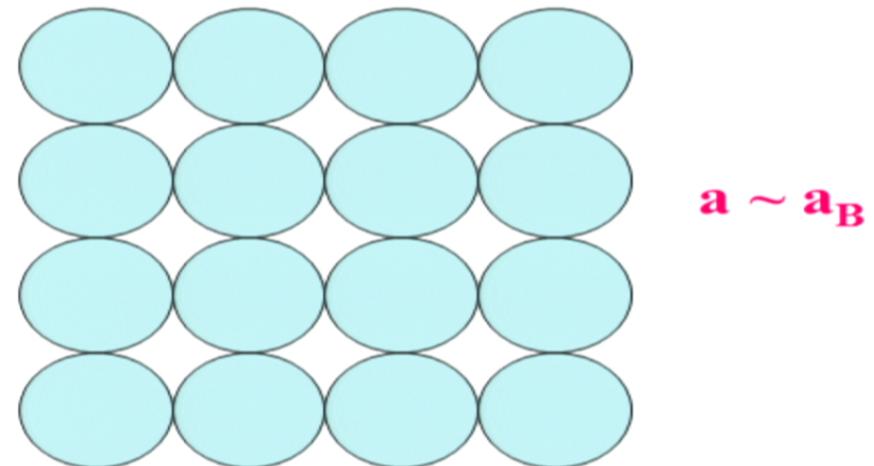
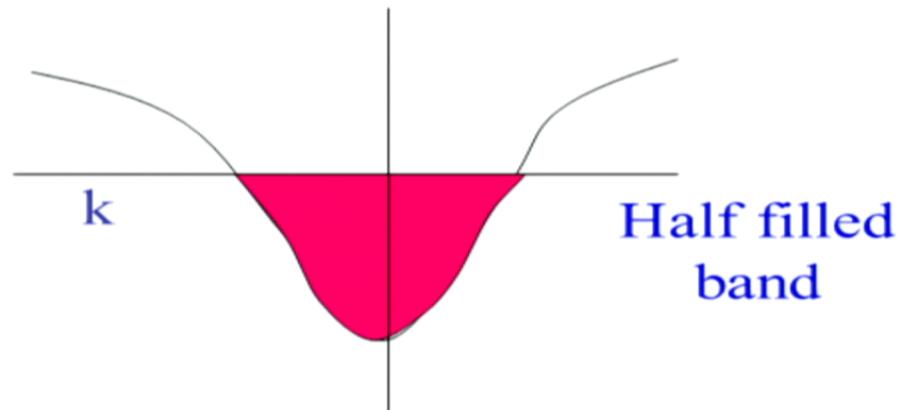
band width

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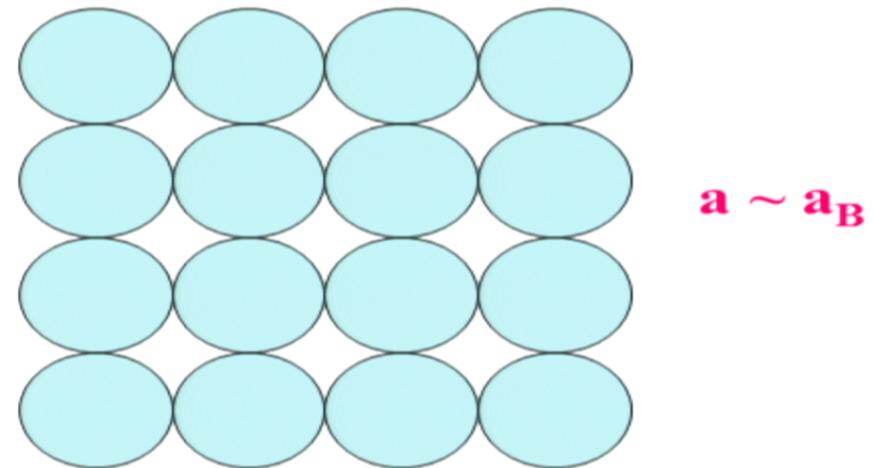
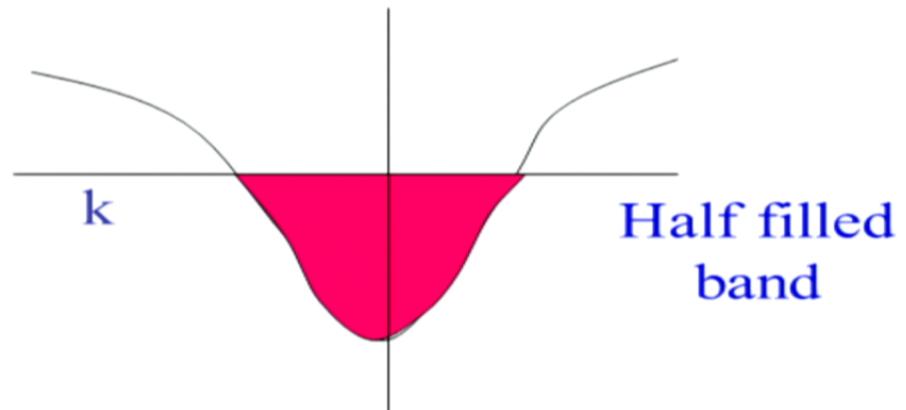
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Let us expand the lattice

For  $a \gg a_B$

we get a Mott insulator

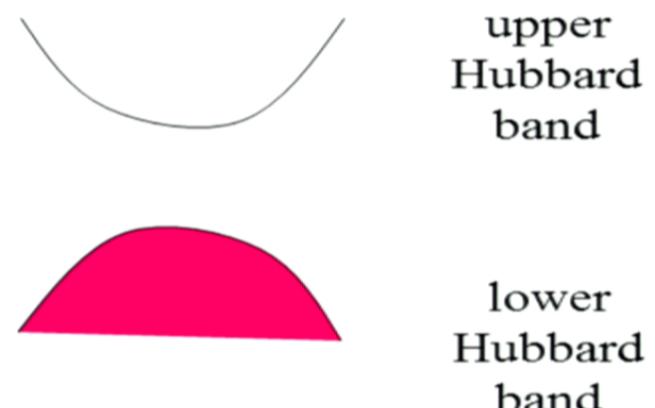
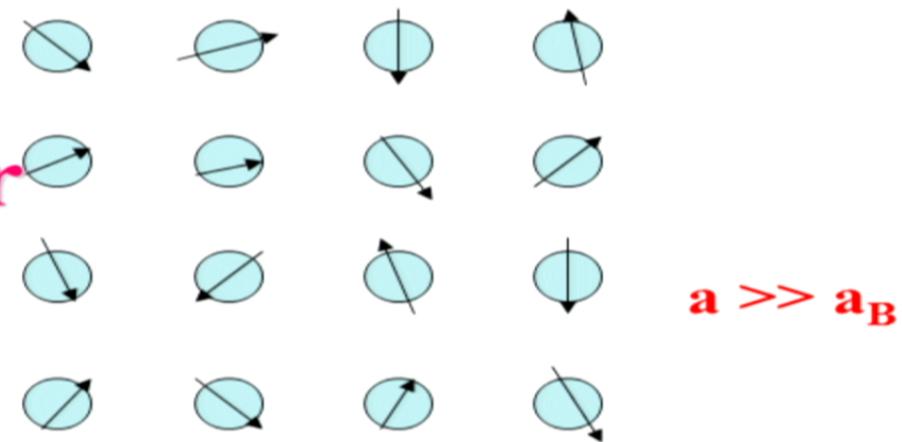
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$$U \gg t z$$

Spins are soft degrees of freedom  
while charges are frozen

A half filled band loses its  
fermi surface becomes an insulator

Not a Bragg gap but a  
Correlation gap.



Let us expand the lattice

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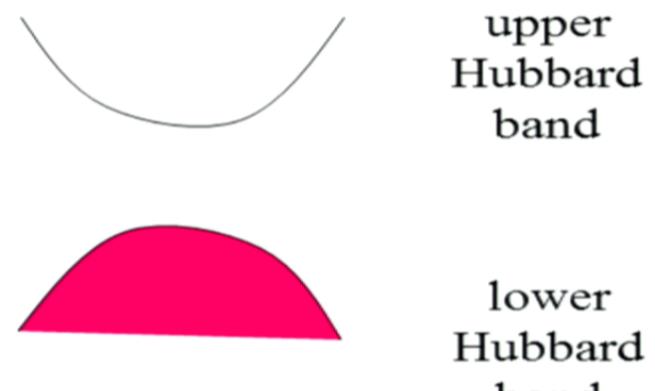
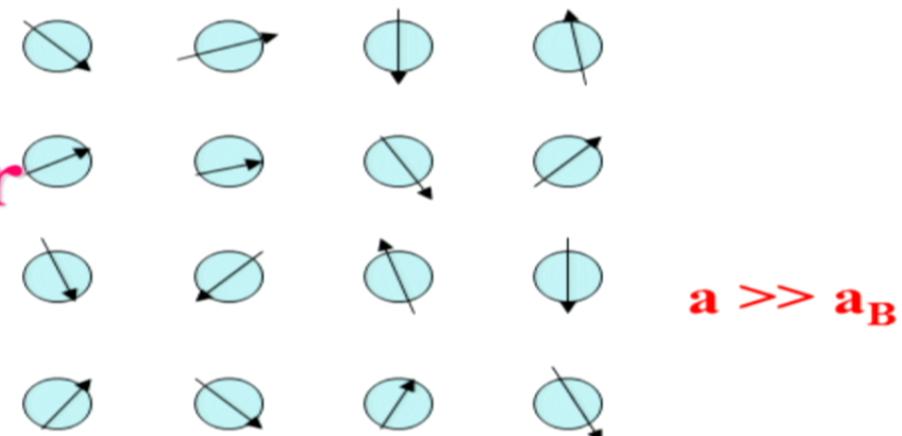
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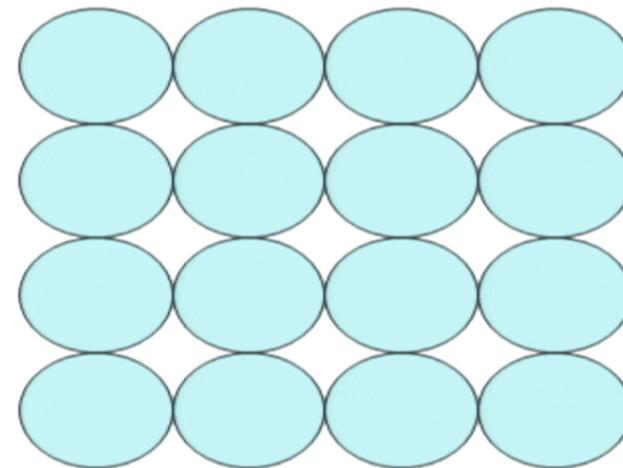
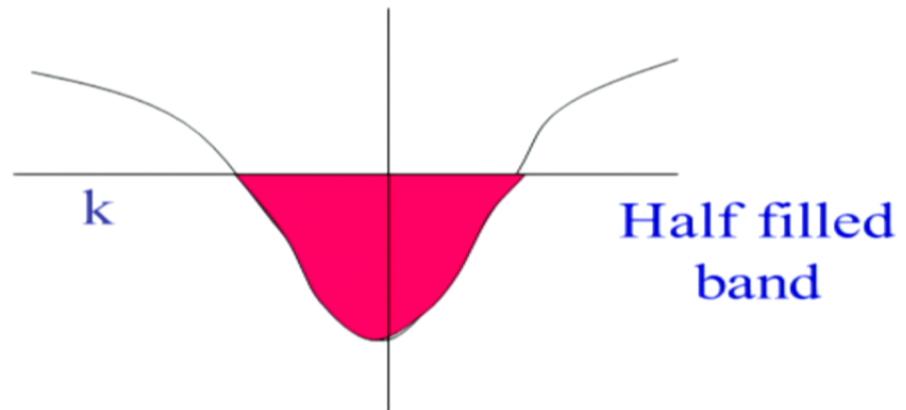


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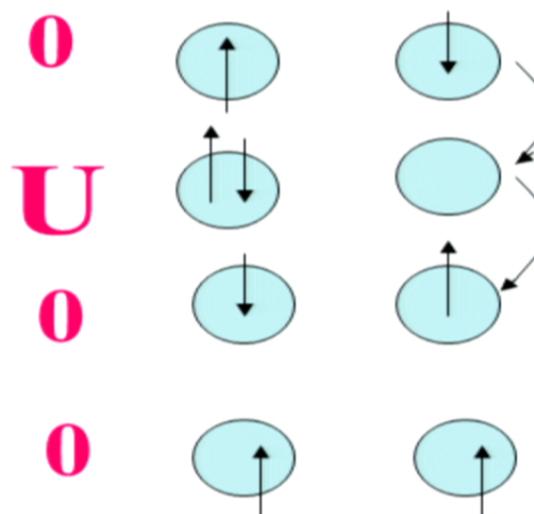
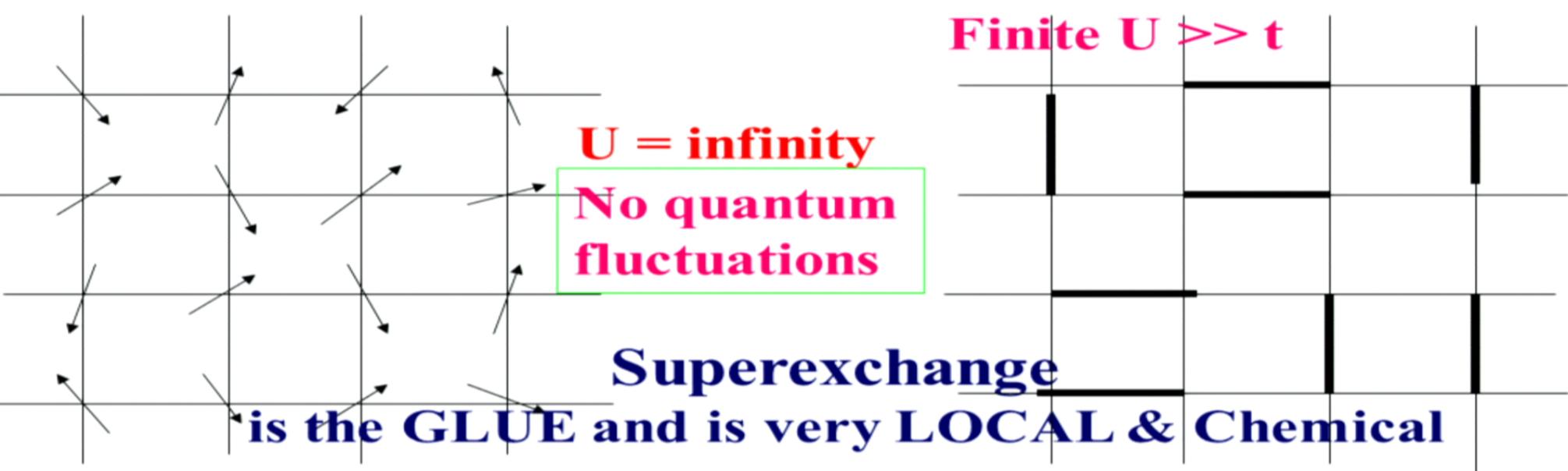
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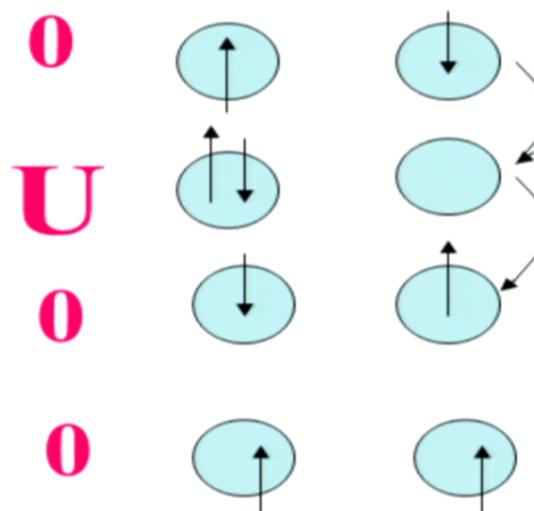
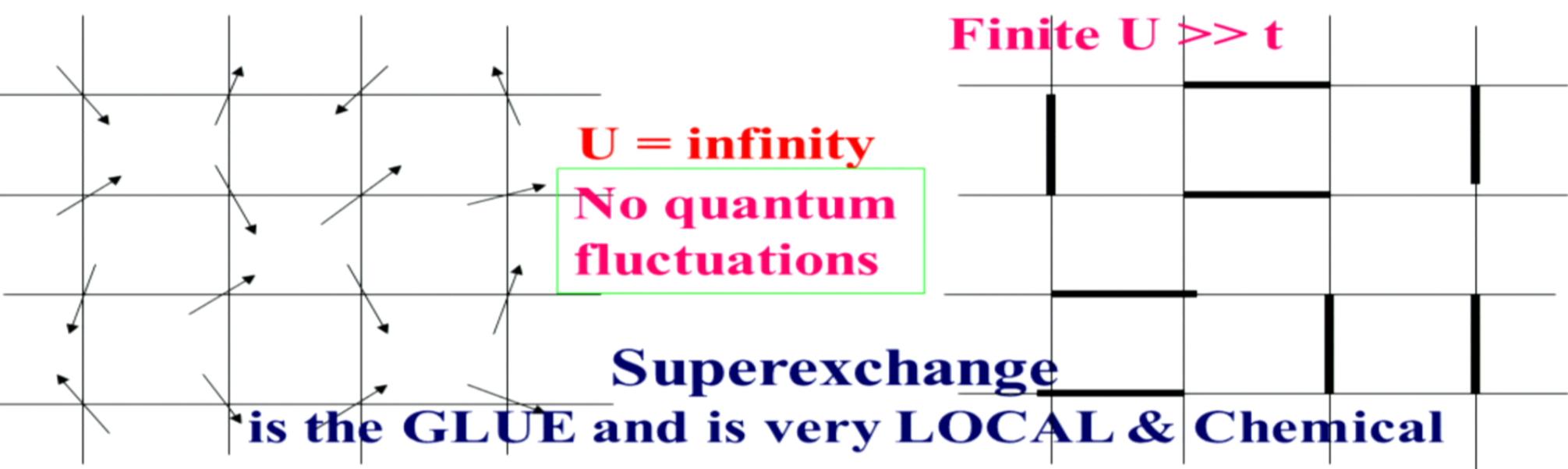
$$t \quad \text{Energy gain} = J = \frac{-4t^2}{U} \quad = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

singlet

triplet

**Energy gain = 0 !**

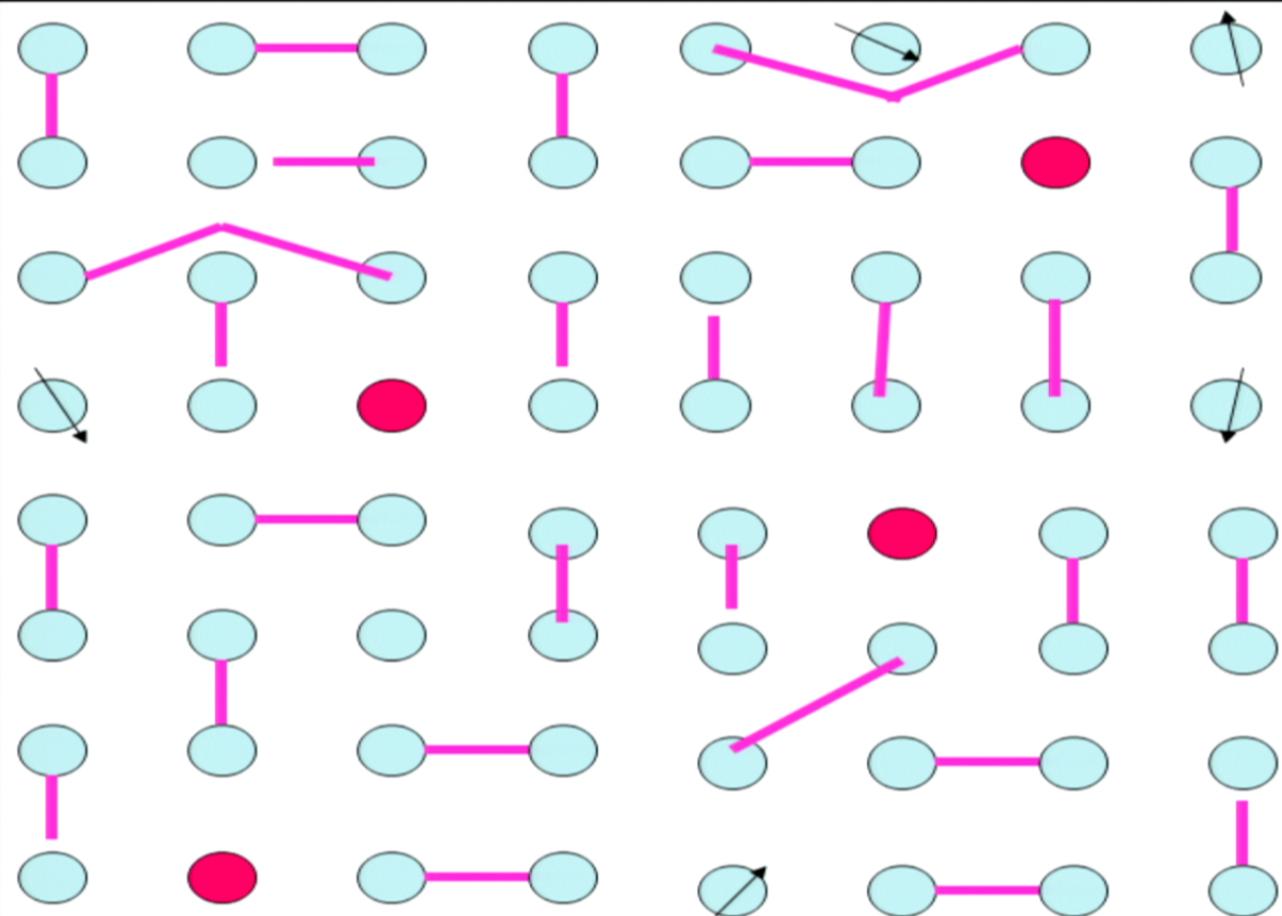
$$H = J \sum_{\langle ij \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4})$$



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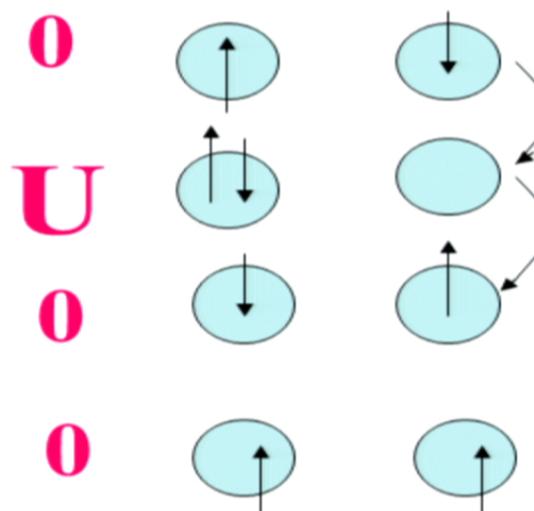
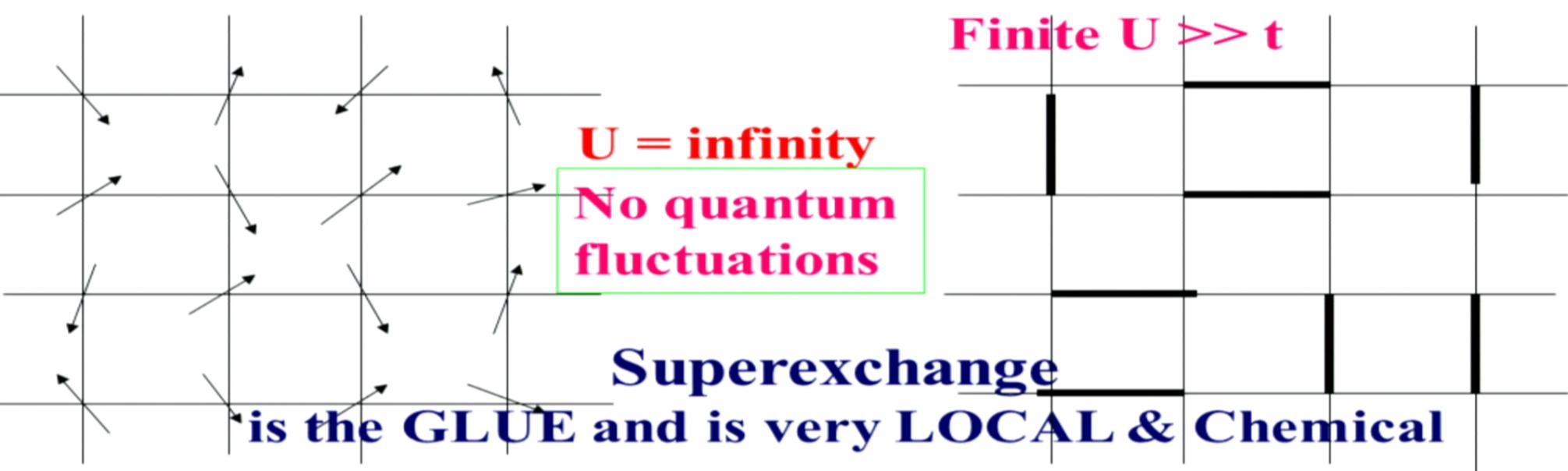
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**Energy gain = 0 !**



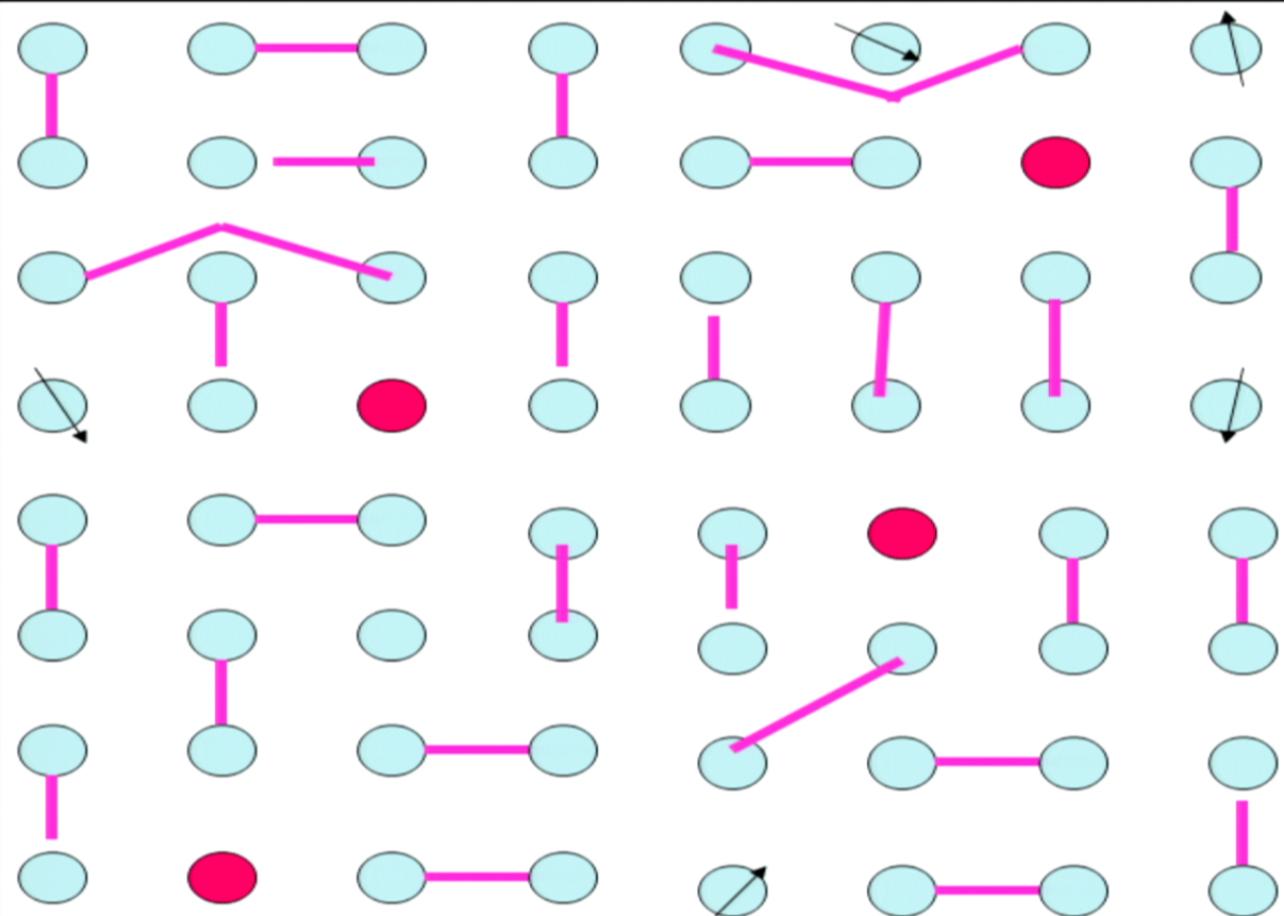
**Large positive U  
prevents fermi sea formation  
and creates local singlets**

**Nearly all electrons begin to participate in superconductivity**



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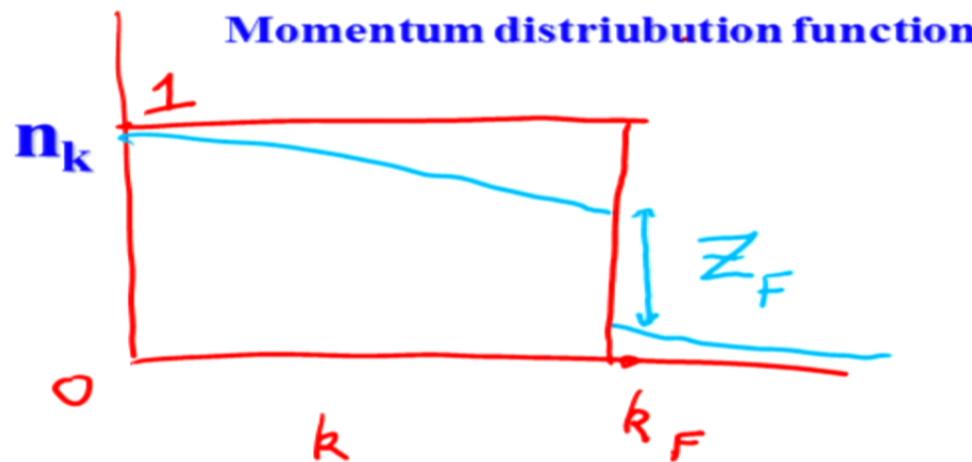
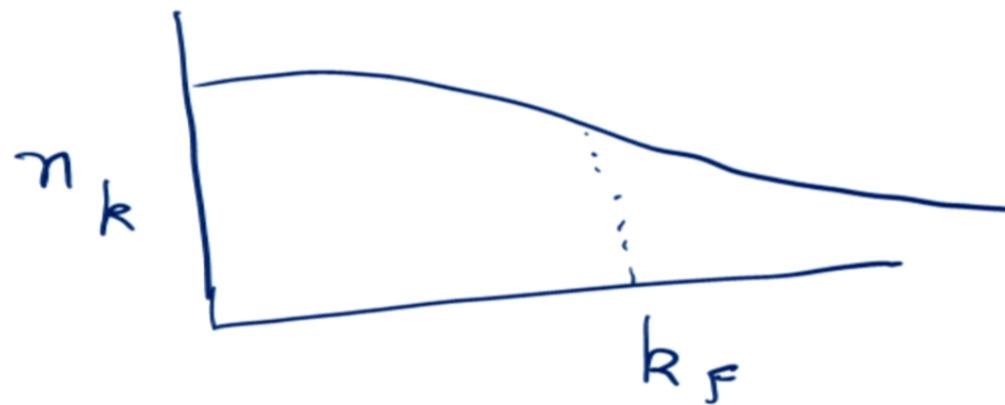
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## Non Fermi liquid metallic state ?



$Z_F = 0$   
 Luttinger Liquid  
 in 1+1 dim  
 2+1 dimension?  
 spin-charge  
 decoupling

## Fermi liquid metallic state

$Z_F$  : Wave Function Renormalization Constant

$$m^* \sim \frac{m_e}{Z_F}$$

## Message from RVB theory

**Mott insulators are seats of high Tc Superconductivity**

**Superexchange is the GLUE**

**Fraction of electrons participating in superconductivity**

**is not**

$$\frac{\hbar\omega_D}{\epsilon_F}$$

**but x**

**PW Anderson  
GB, Zou, PWA  
GB, PWA  
PWA, GB, Hsu, Zou  
1987-88**

**Therefore**  $k_B T_c \sim xt$  **(here t is the hopping parameter)**

## **Key parameters of RVB theory**

**t, U, x, lattice structure & Dimensionality**

**Superexchange J and t**  
**(Magnetism and band formation)**

**t and U known in known systems inferred from experiments puts  
Tc already above the scale of room temperature**

**Graphene is a good example**

**Cuprates are also failed room temperature Superconductors**

**Impurity band Mott insulator Nitrogen doped Diamond**

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# **Cuprate is a failed Room Temperature Superconductor**

**Intrinsic maximum  $T_c \sim 250$  K  
at optimal doping**

**G. Baskaran, Mod. Phys. Lett., 14 377 (2000)  
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# **Difficulties**

## **1 dimension**

**Fluctuations from low dimensionality**

**Competing orders – Peierls, Spin Peierls Instability**

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**Competing orders – Valence bond order**

**AFM, spin stripes**

**Charge stripes, chirality order**

**Multiple bands**

**Jahn Teller effect and polaronic localization**

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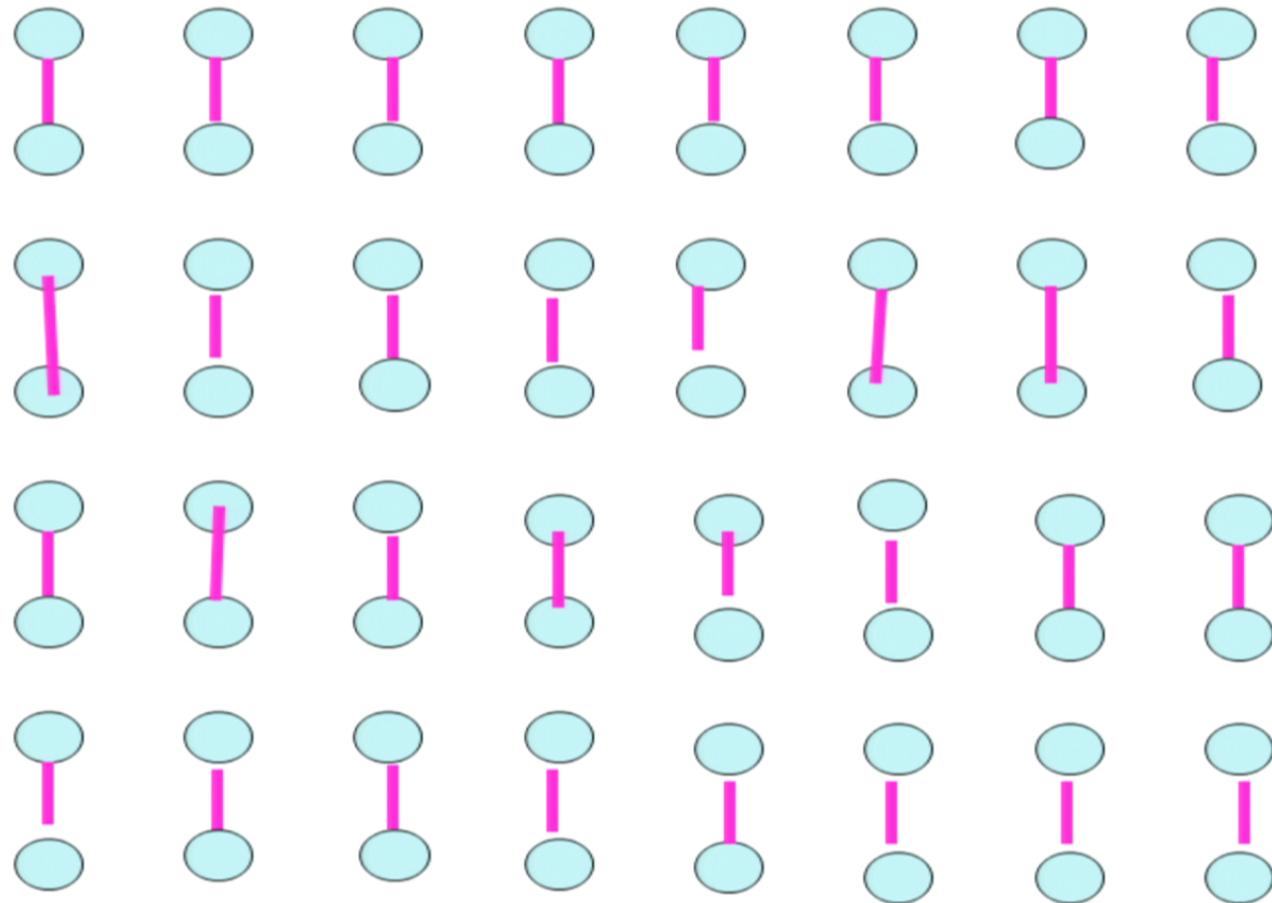
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**Multiple bands**

**Jahn Teller effect and polaronic localization**



## Theory of large U Hubbard model or tJ model

**RVB mean field theory, Emergent fermions and superconductivity  
in undoped and doped Mott insulators (GB, Zou, PWA 1987)**

**Gauge theory and emergent gauge fields (GB, PWA 1988)**

..... Many significant developments since 1987

**BCS vs RVB superconductor and Entanglement hierarchy  
(GB, unpublished)**

**We want to create a  
non Fermi liquid metallic state where  
Real Space Pairing or singlet formation  
is encouraged**

**However there are competing orders**

**Is there a clue from nature for another system ?**

**Yes !**

# P.W. Anderson, in AIP Conference Proc. Vol. 169 (1988)

156

Modern Physics in America

I emphasize that at this point everything depends on calculations of the exact low-energy spectrum of the bosons which we haven't really settled down upon. At this point we know to an gnat's eyelash what's going on in the mysterious insulator. We have a pretty good idea what's going on in the mysterious metal. We have a hypothesis for the mysterious superconductor and, just to further compound confusion we have an even wilder hypothesis for the strange unrepeatable observations that people keep seeing above the transition temperature of the normal material, starting with Paul Chu's own measurements which showed that there was something strange happening at 240  $^{\circ}\text{K}$ .

The question is, is this normal metal really a normal metal, or is it, since it's a two-dimensional layer of bosons, is it in fact a superconductor, but only a two-dimensional superconductor? Present day theory isn't capable of answering the question because it's not known what material has this. There's a state, a type of topologically ordered superconductor that does exist in other cases, and we can't exactly see why we shouldn't have a topologically-ordered superconductor in our two-dimensional sheets even up to quite high temperatures. We can see that until the pair tunneling can take place, we're not ever going to have real, or three-dimensional superconductivity.

If we had a batch of two-dimensional superconductors our vortices would be point objects in the individual planes and they would have nothing but magnetic forces coupling them between the different planes. These magnetic forces are unbelievably small, microdegrees, so the vortices are very free to move around from place to place. The only way you could actually



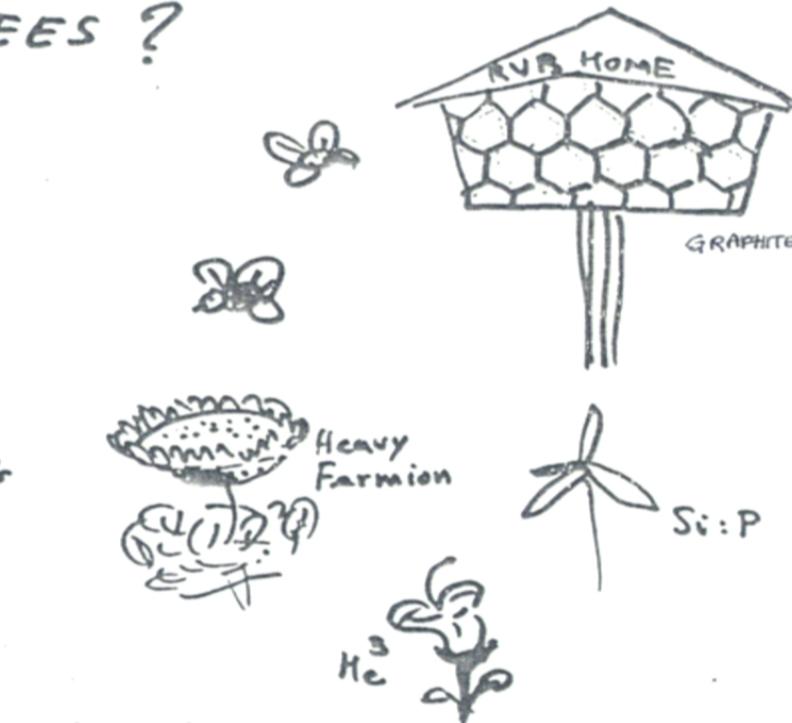
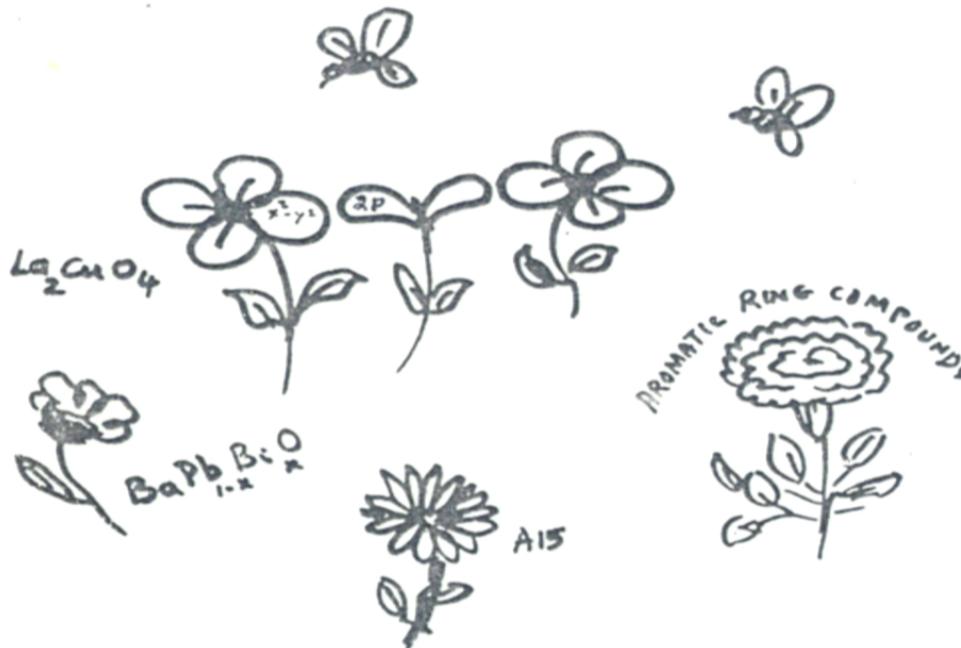
## I close with a postcard (Fig.21)

.....  
..... from Aspen. ....  
.....

**RVB's become a question – and  
this is the answer. As far as  
we know, certainly there are B's,  
but maybe there are some other  
B's hanging around in a lot of  
other interesting places**

Dear Phil,

ARE WE BEES ?

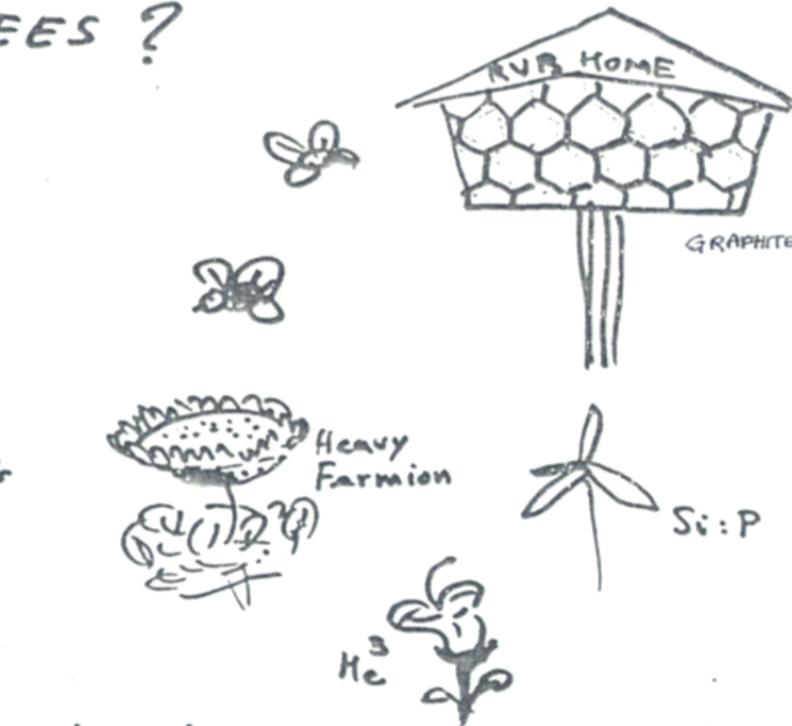
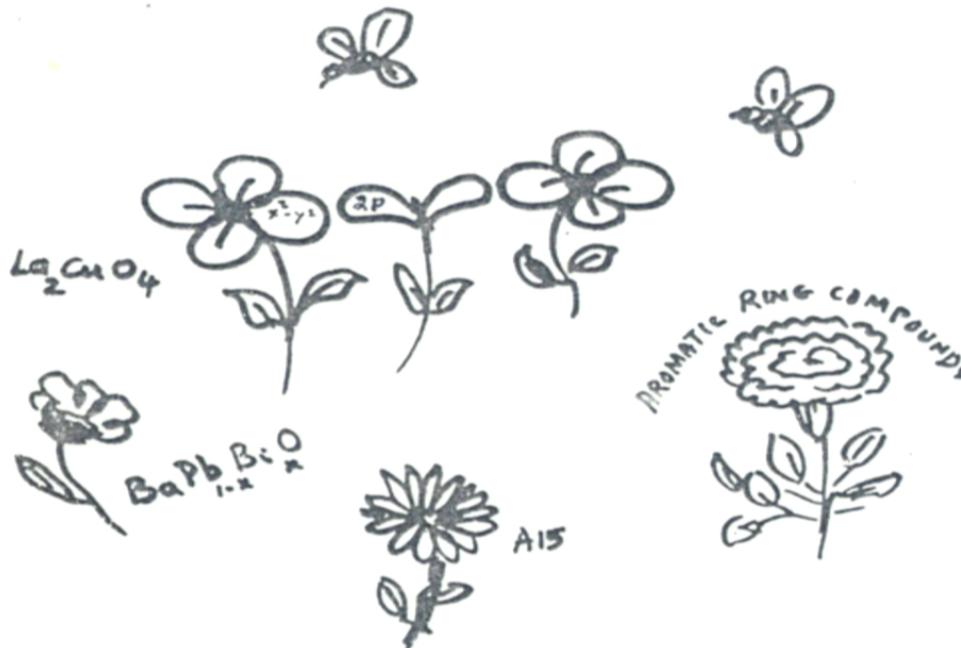


With best Regards

  
20 July '87. ASPEN

Dear Phil,

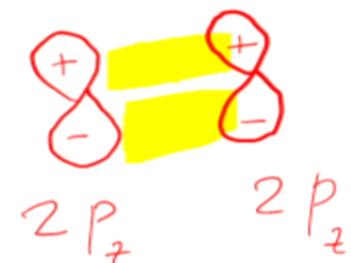
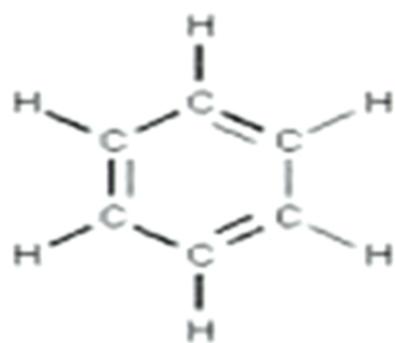
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# Benzene



Resonating valence bond

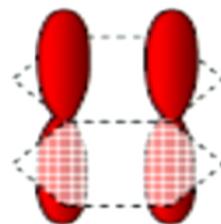
Resonance of 2 electron  
bond of valence  $\pi$  electrons



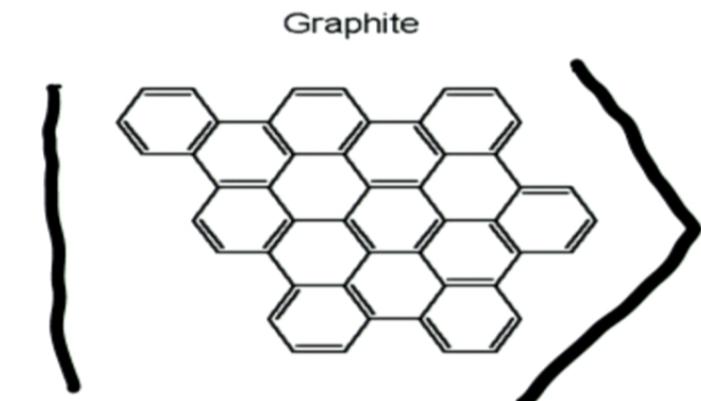
# Pauling's Idea of Resonating Valence Bond

Dominance of neutral C<sup>0</sup> configurations and C=C covalent bonds

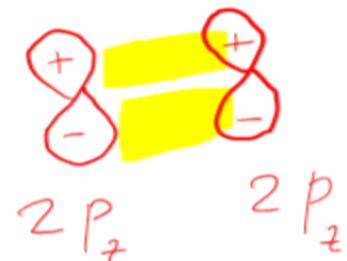
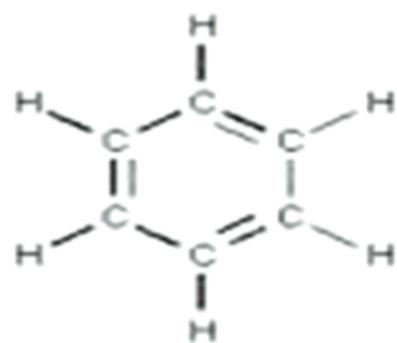
As a first approximation  
Freely propagating polar (C<sup>1+</sup>, C<sup>1-</sup>) configurations are ignored  
(there by approximating it as a Mott insulator !)



$$|RVB\rangle = \sum |$$



# Benzene



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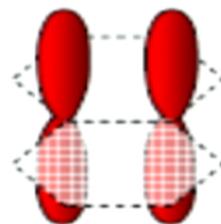
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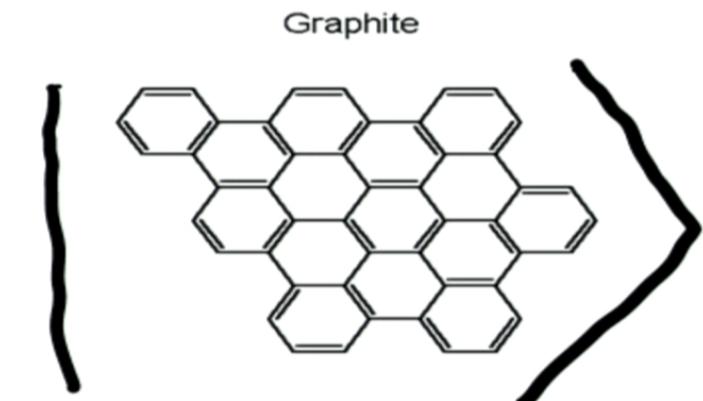
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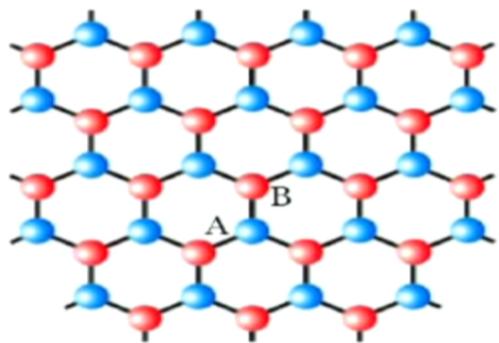
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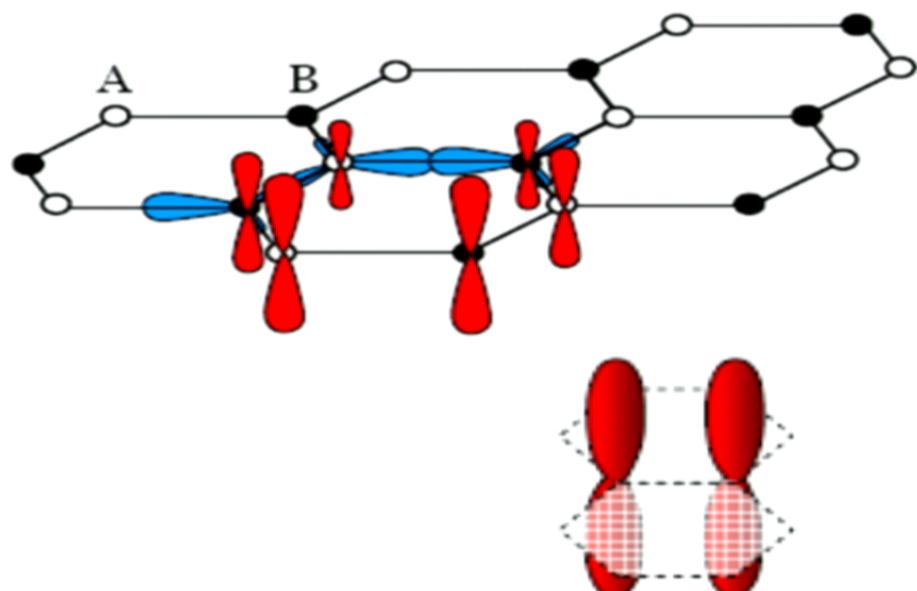


$$|RVB\rangle = \sum |$$





## Graphene



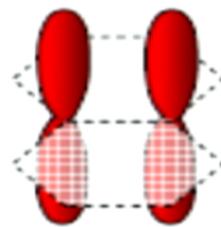
- Carbon atom  $1s^2 2s^2 2p^2$
- Three in-plane  $sp^2$  covalent bonds with N.Ns
- **One electron per  $2p_z$  orbital left for hopping**
- Tight-binding model:

$$H_t = -t \sum_{\langle i,j \rangle \sigma} (c_{i\sigma}^+ c_{j\sigma} + c_{j\sigma}^+ c_{i\sigma})$$

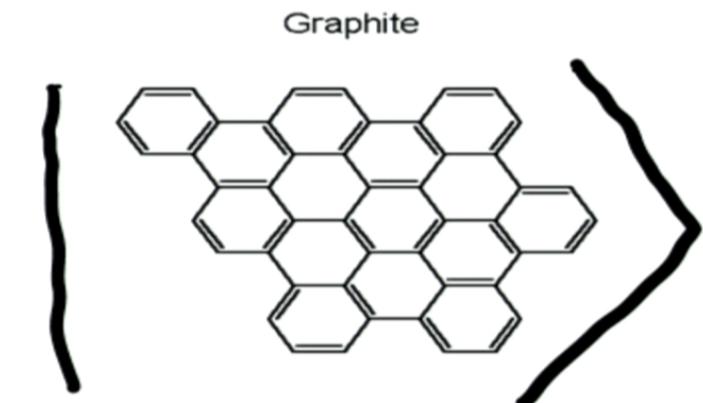
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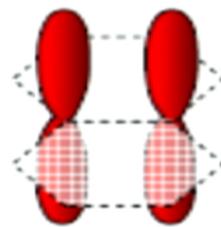
$$|RVB\rangle = \sum |$$



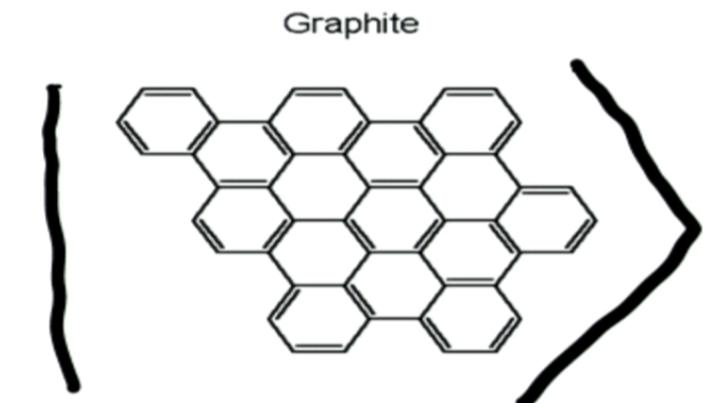
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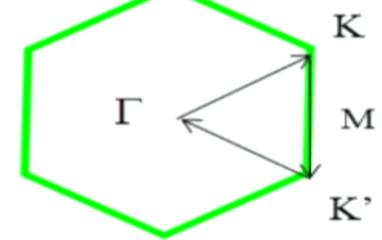
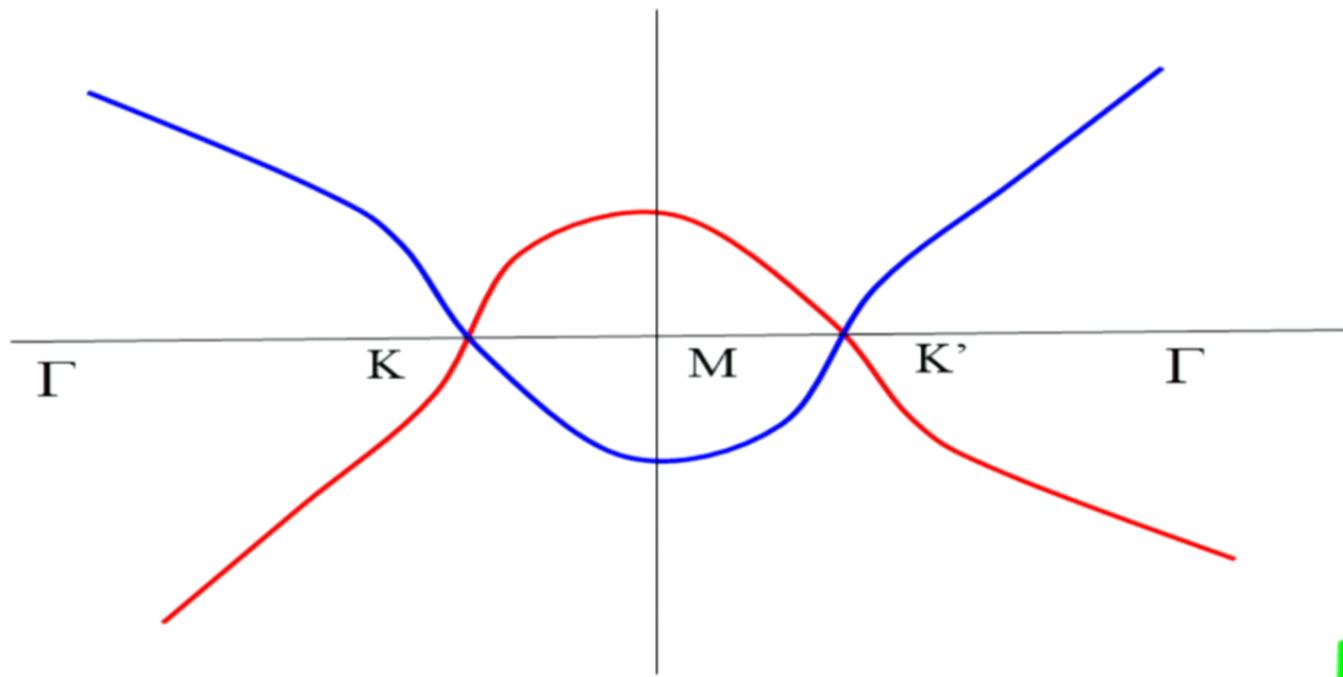
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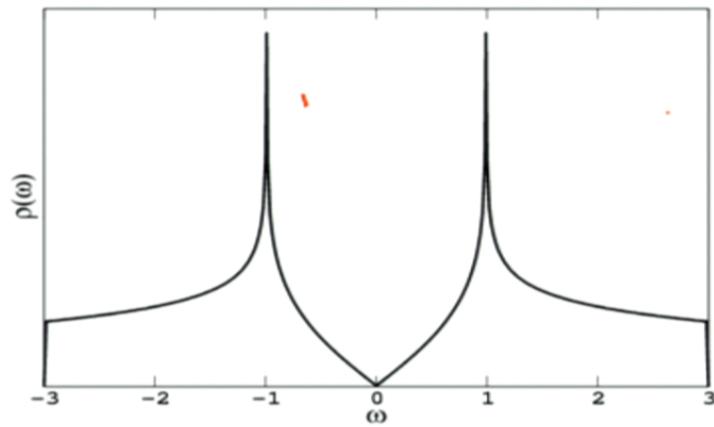


$$|RVB\rangle = \sum |$$





Will J produce  
Superconductivity  
in Neutral  
GRAPHENE ?



As  $\delta(E_F) = 0$  for  
neutral graphene  
the available J  
is below the  
critical  $J_c$  to  
produce Superconductivity!  
GB (2002)

Good !  
Graphite &  
neutral graphene  
do not superconduct at low T

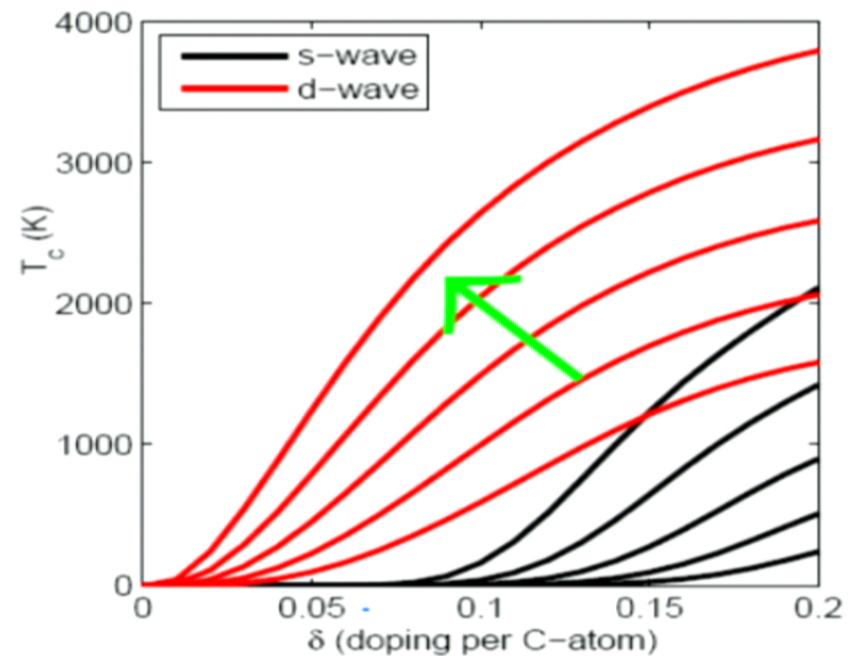
**A.M. Black-Schafer and S. Doniach, Phys Rev B 2007**

revived the GB (2002) work and performed a careful mean field theory and produced the following phase diagram.

**They also found that**

**d + id order parameter has lower energy.**

**d + id**



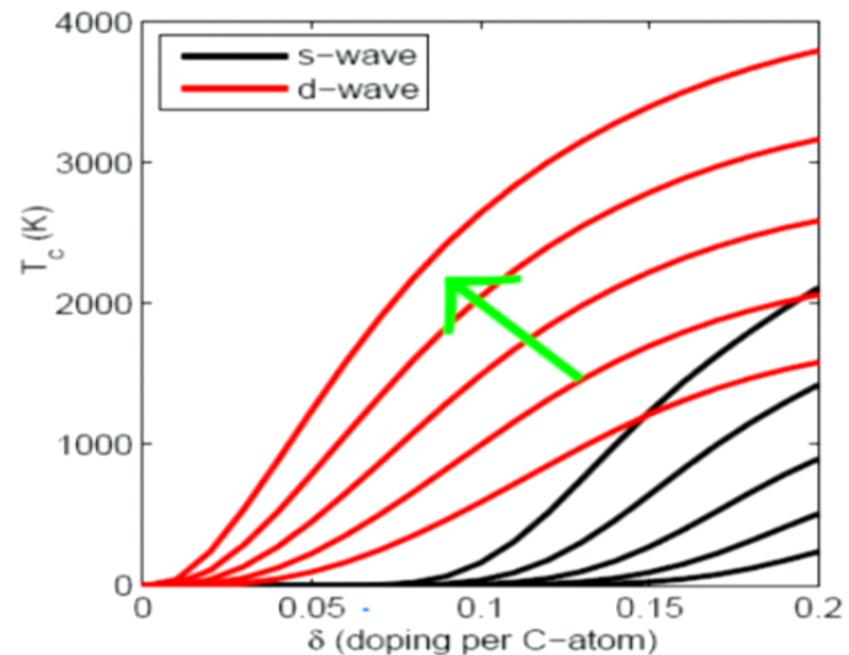
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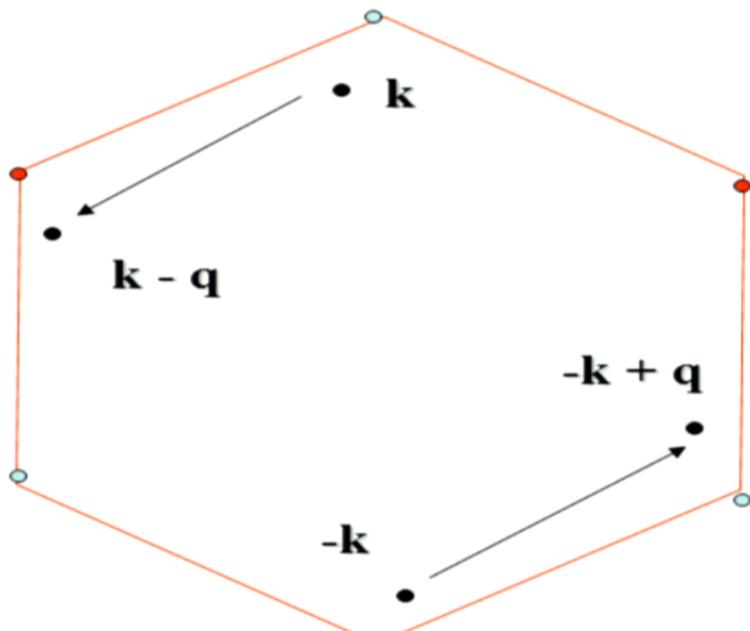
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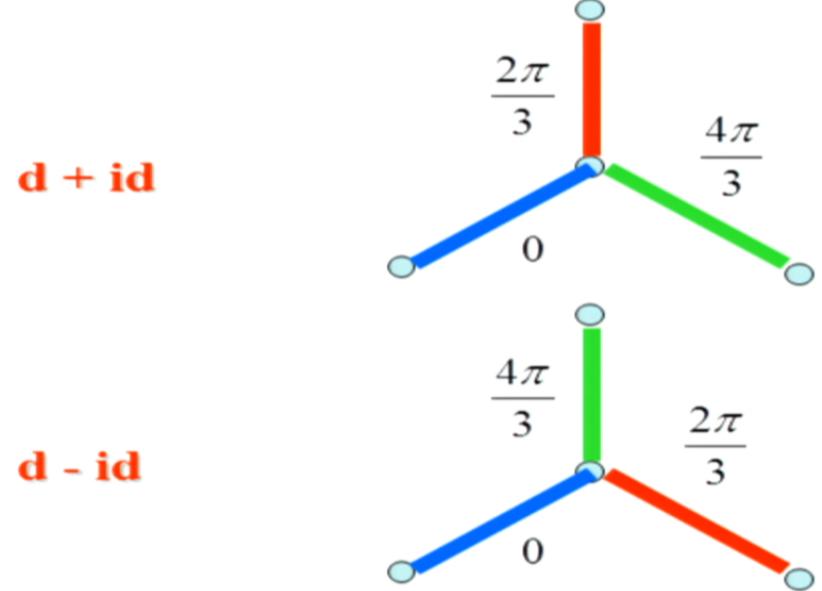
**d + id**



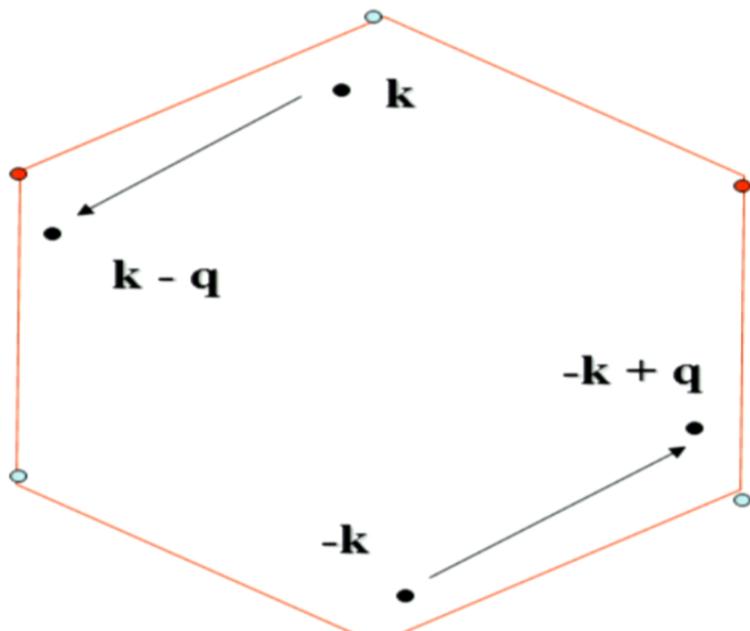
$$\Delta_\alpha = \Delta e^{\frac{i 2\pi(\alpha - 1)}{3}} \quad \alpha = 1, 2, 3$$



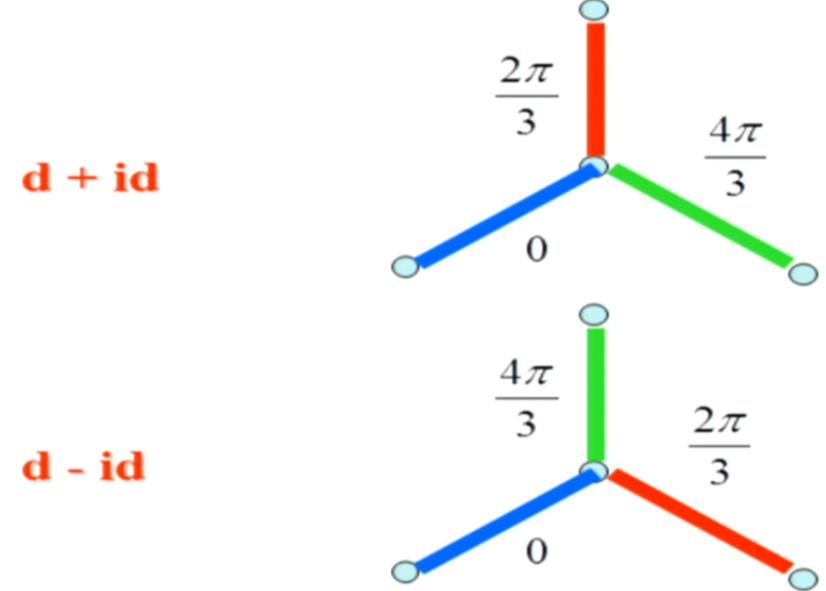
**Repulsive scattering**



$$\Delta_\alpha = \Delta e^{\frac{i 2\pi(\alpha - 1)}{3}} \quad \alpha = 1, 2, 3$$



**Repulsive scattering**



## **Instead of the model**

$$H_{eff} = -t \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^+ c_{j\sigma} + c_{j\sigma}^+ c_{i\sigma}) - J \sum_{\langle ij \rangle} b_{ij}^+ b_{ij}$$

**let us go to the more basic repulsive Hubbard model**

$$H = -t \sum_{\langle ij \rangle} C_{i\sigma}^\dagger C_{j\sigma} + \text{H.c.} + U \sum n_{i\uparrow} n_{i\downarrow}$$

$$|\Psi\rangle = g^{\mathcal{D}} |BCS\rangle_N$$

$$\mathcal{D} = \sum_i (n_i^a + n_i^b)$$

**Two variational parameters:  $g$  and  $\Delta$**

**Variational Monte Carlo  
(Pathak, Shenoy, GB)**      **13 x 13 sites (state of the art )**

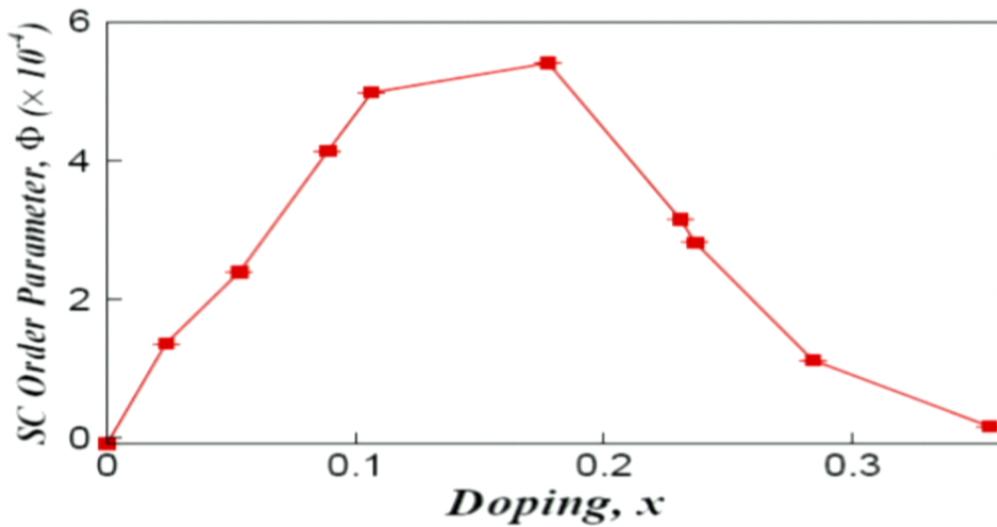


FIG. 1: Doping dependence of superconducting order parameter  $\Phi$  as obtained from VMC calculation of the Hubbard model on a honeycomb lattice for  $U/t = 2.4$ .

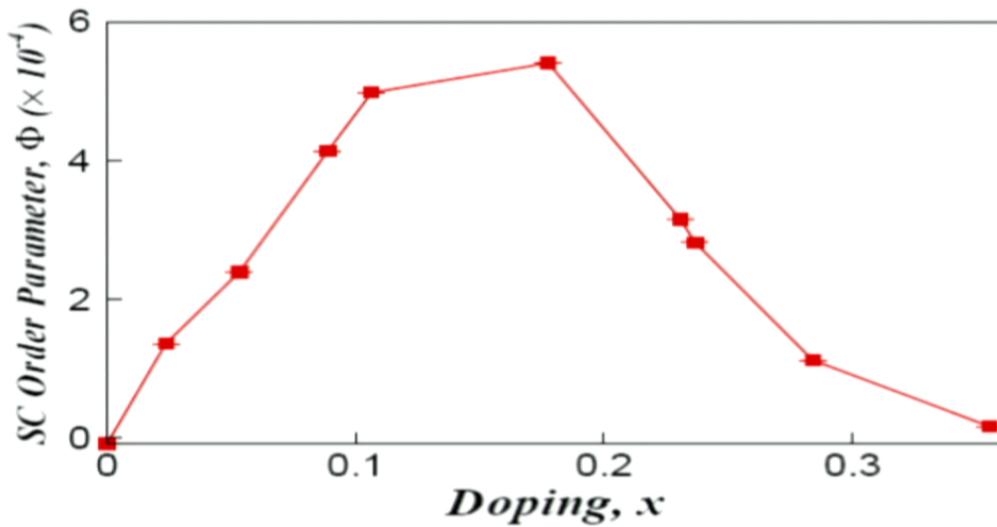


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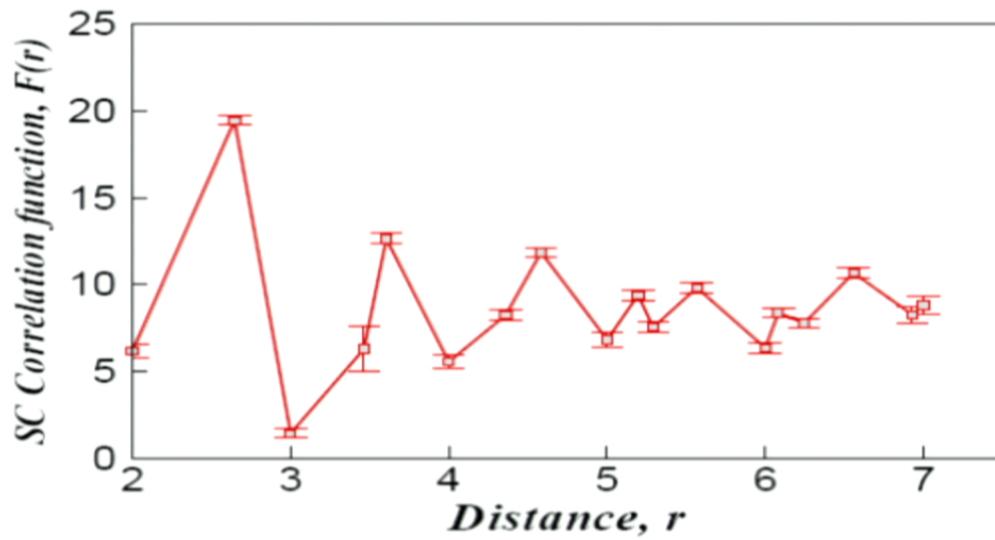


FIG. 2: Dependence of superconducting correlation function  $F(r)$  on distance  $r$  as obtained from VMC calculation of the Hubbard model on a honeycomb lattice for  $U/t = 2.4$ ,  $x = 0.2$ .

**In graphene number of C atoms/cm<sup>2</sup> ~ 2 x 10<sup>15</sup>**

**Currently available maximum doping ~ 10<sup>13</sup>/cm<sup>2</sup>**

**To see an appreciable Tc we need 3 to 5 % doping**

**We need to go to a charge transfer of  
5 x 10<sup>13</sup> to 10<sup>14</sup> /cm<sup>2</sup>**

# **How to dope ?**

**Intercalation (makes the problem 3 dimensional ...)**

**Electrical gate doping**

**Electrochemical (solid electrolyte)**

**Spraying metal atoms (?)**

**2 dimensional carbon metals with finite density of states at the fermi level  
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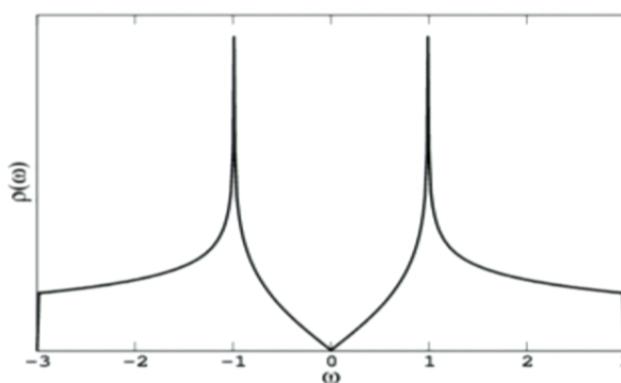
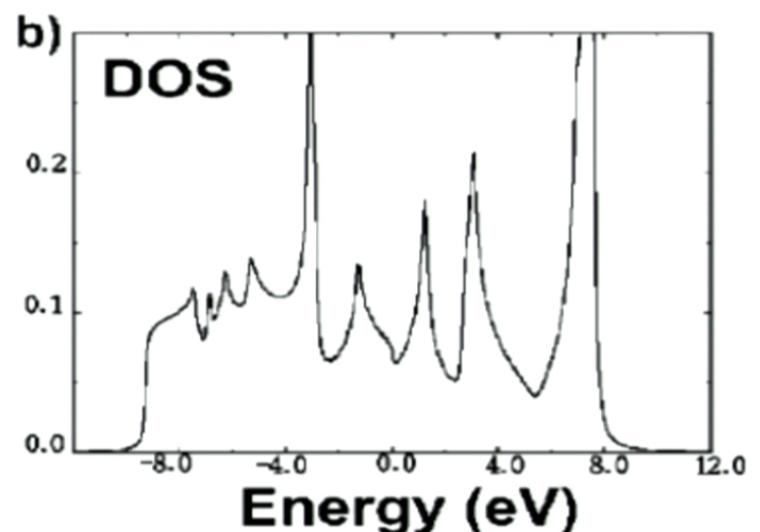
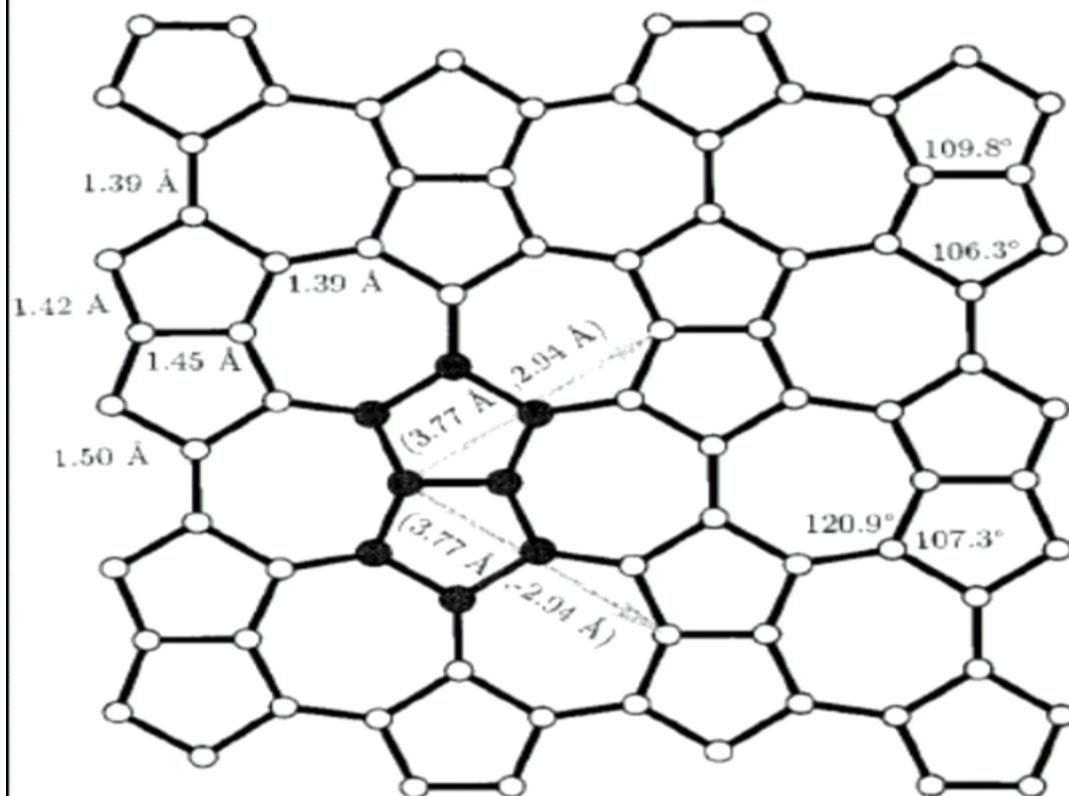
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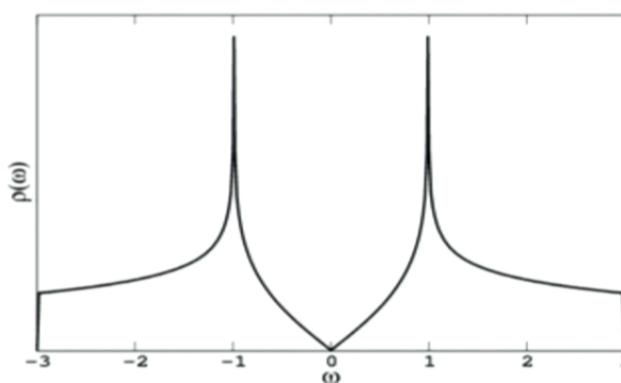
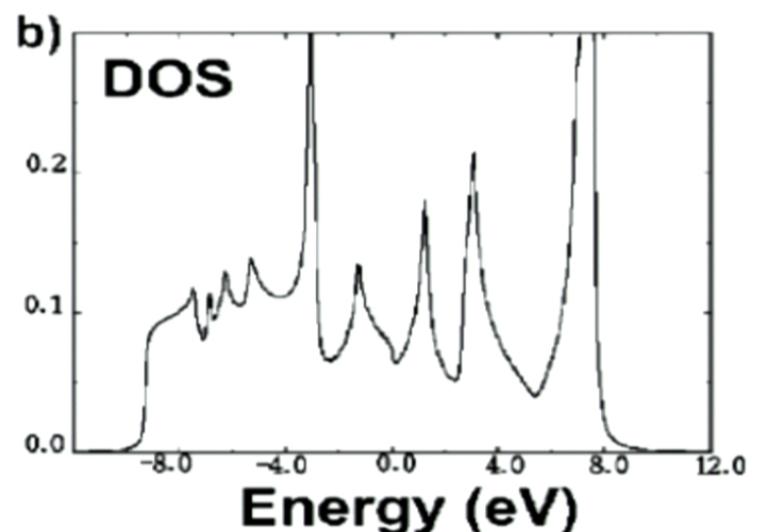
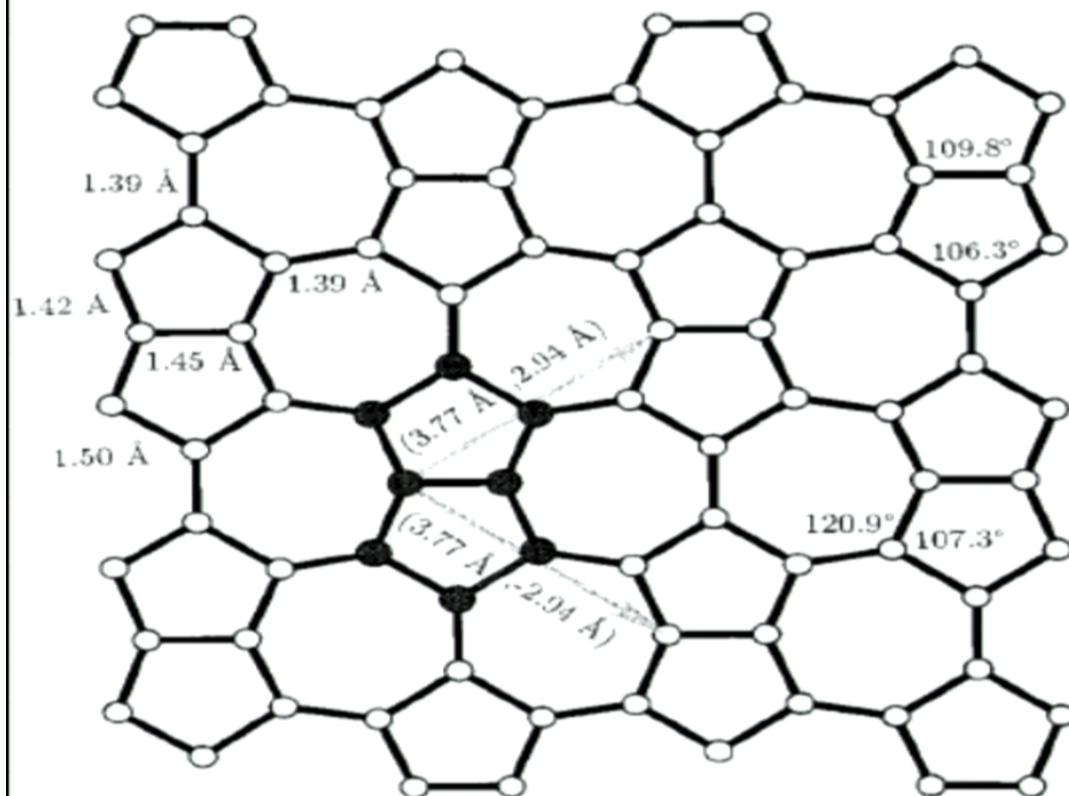
**Prediction of a pure-carbon planar covalent metal**

Vincent H. Crespi, Lorin X. Benedict, Marvin L. Cohen, and Steven G. Louie



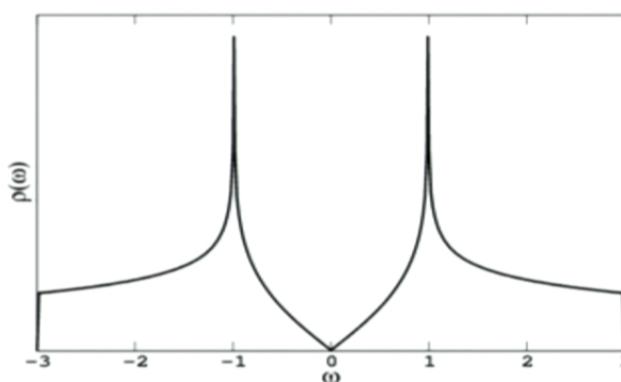
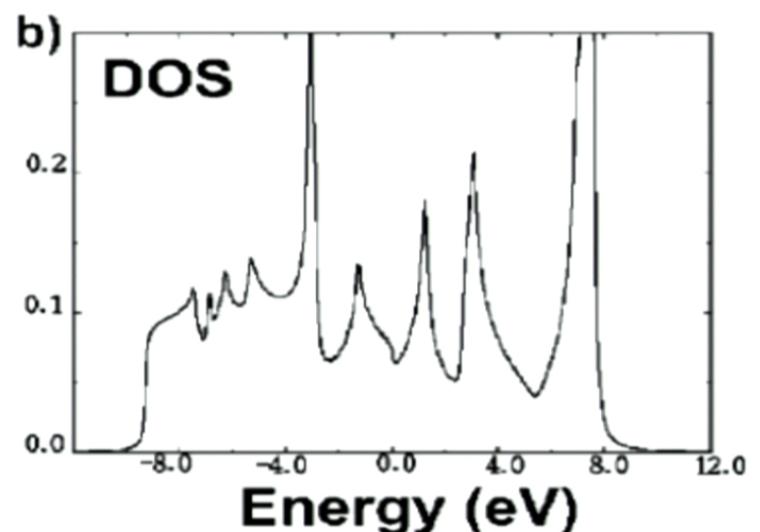
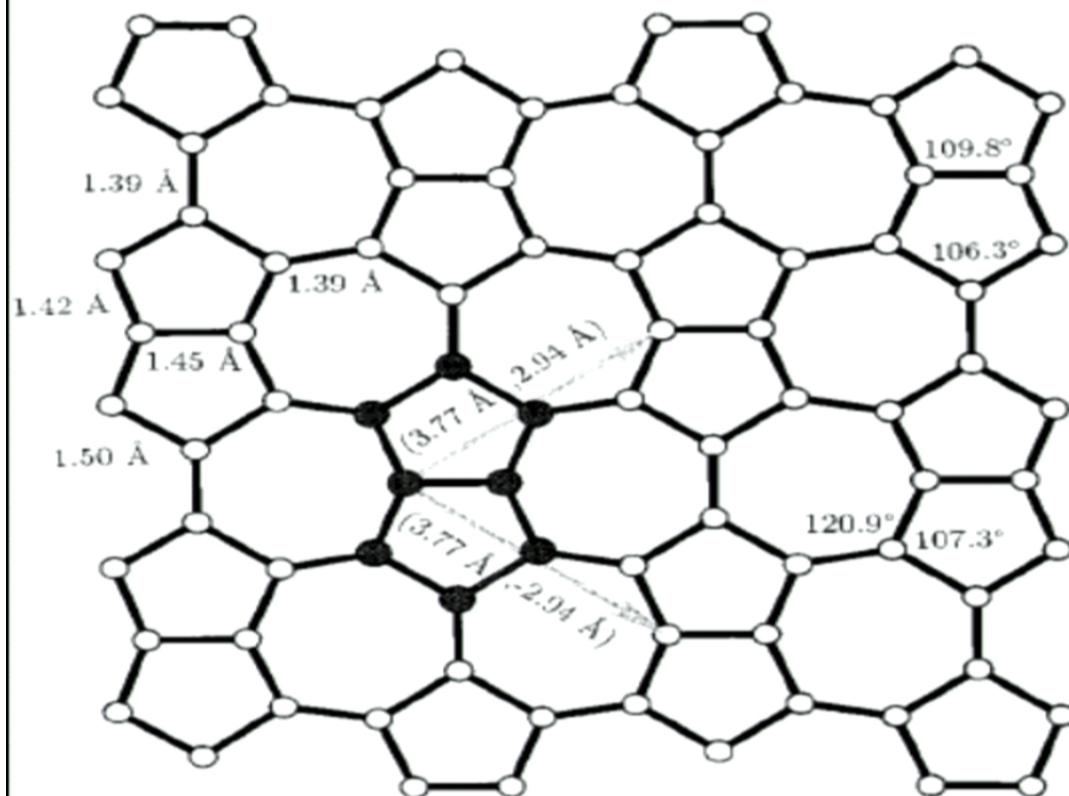
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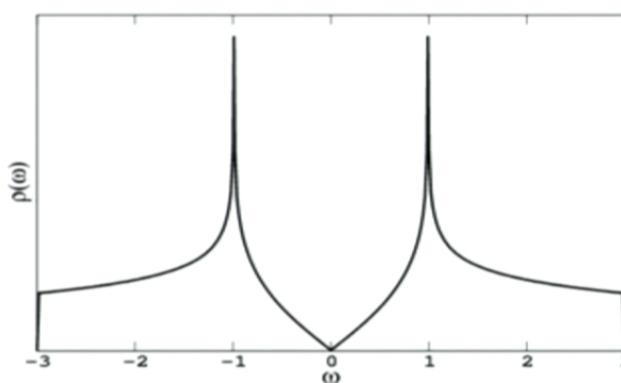
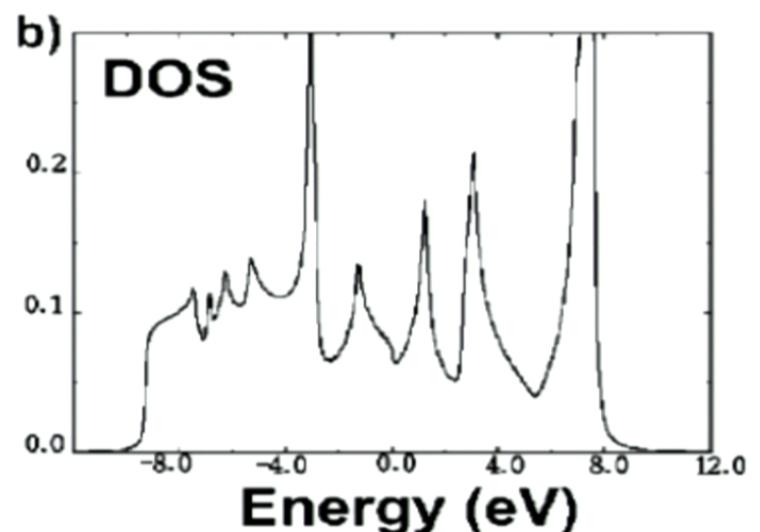
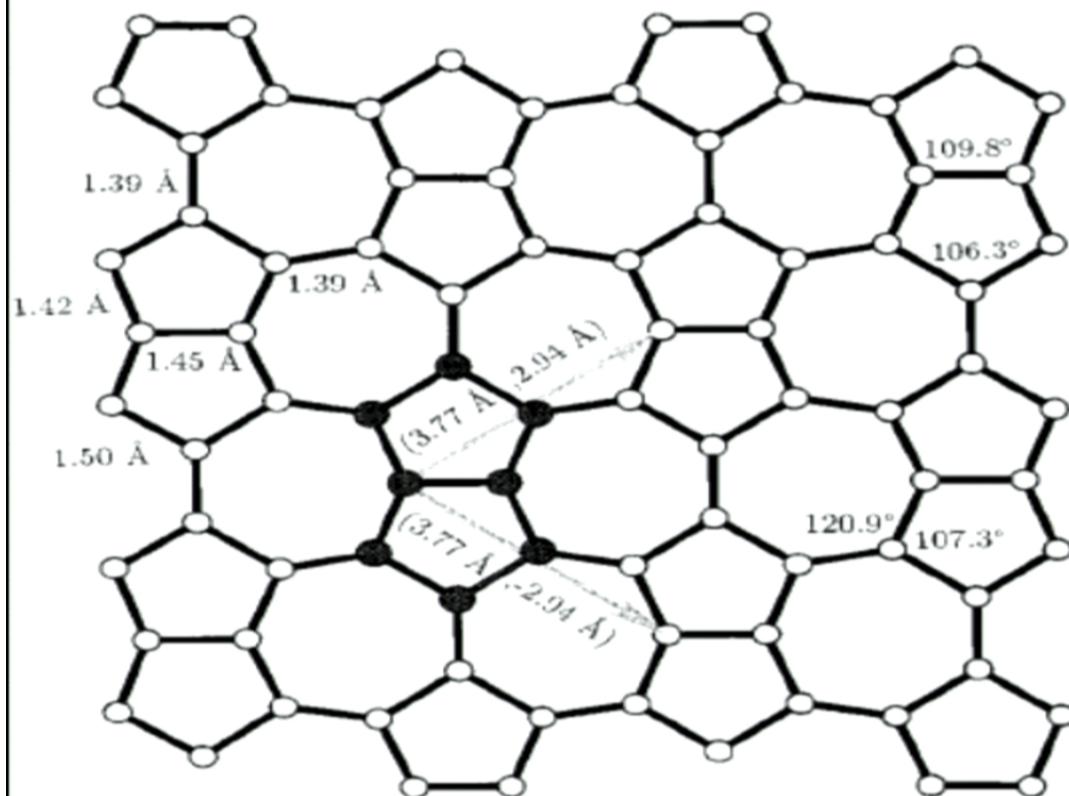
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**Signals for unstable high (including room) temperature superconductivity  
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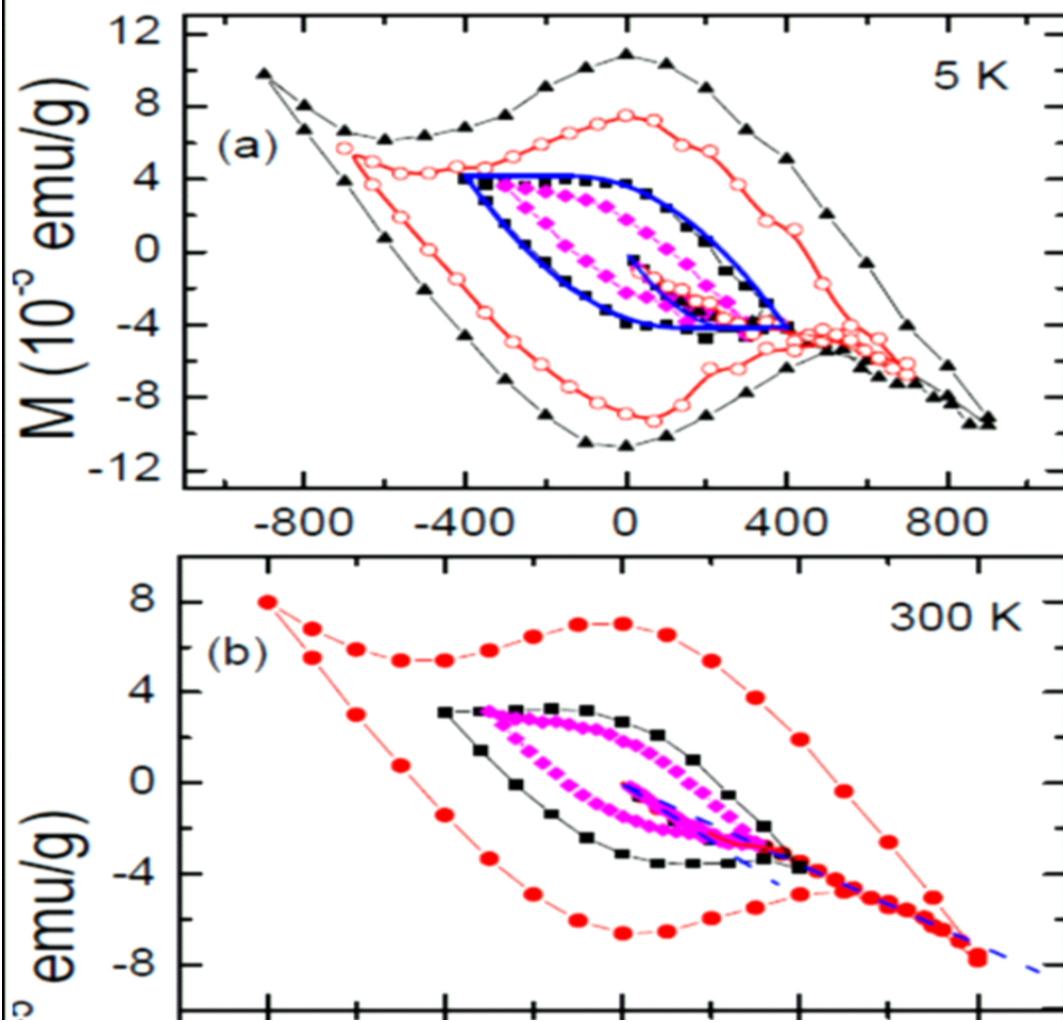
**Sept 2012**

**Can doping graphite trigger room temperature superconductivity ?  
Evidence for granular HTSC in water-treated graphite powder**

*T. Scheike, W. Böhlmann, P. Esquinazi\*, J. Barzola-Quiquia, A. Ballestar, A. Setzer*

**arXiv:1209.1938**

**<http://onlinelibrary.wiley.com/doi/10.1002/adma.201202219/abstract>**



T. Scheike et al. arXiv:1209.1938

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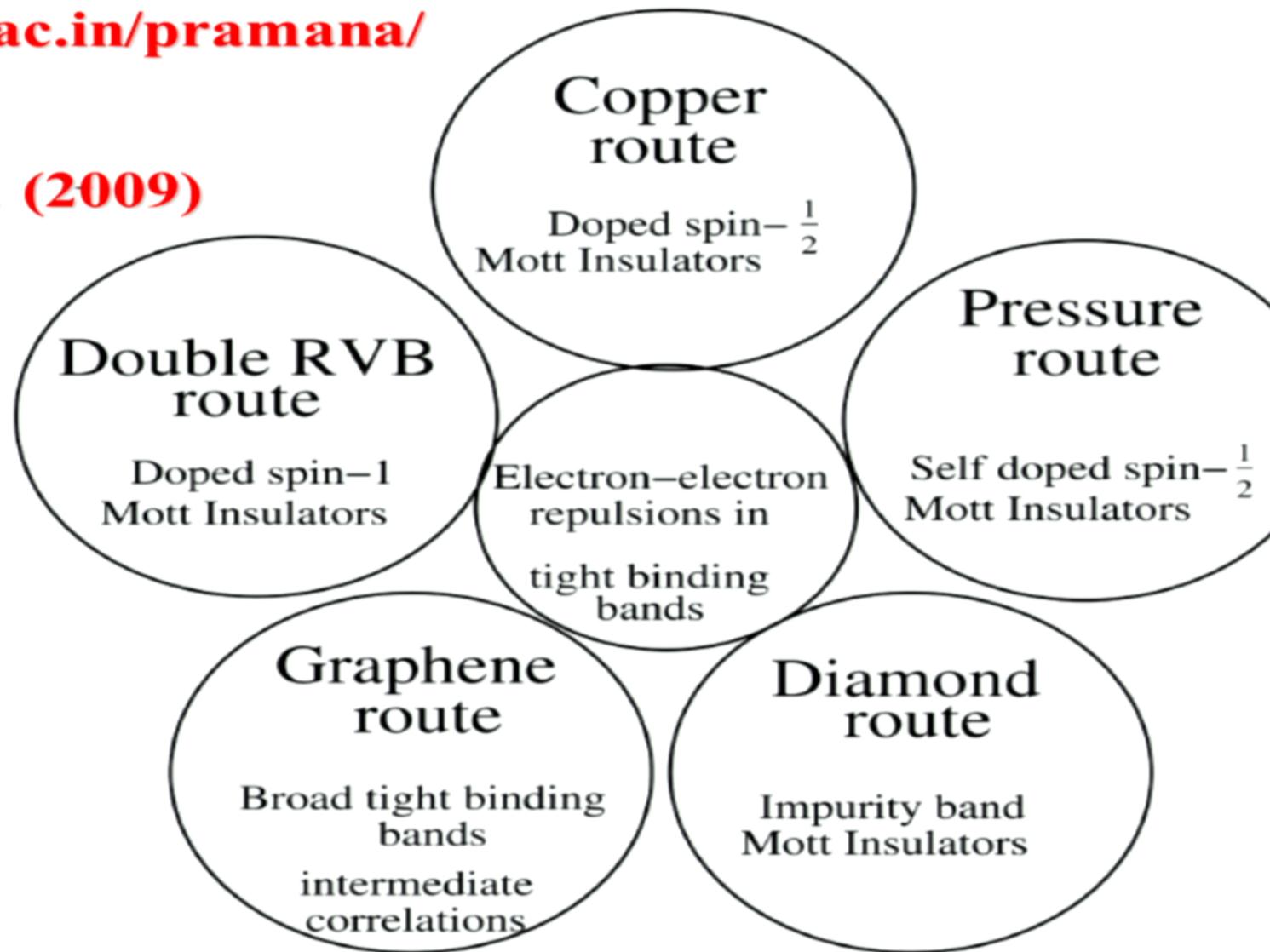


**Sahara Desert**

**10.05.2006 03:58**

G Baskaran

Pramana 73, 61 (2009)



G Baskaran

Pramana 73, 61 (2009)

