Mott Insulator to High T_c Superconductor via Pressure: Resonating Valence Bond Theory and Prediction of New Systems

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Mott insulator superconductor transition, via pressure and no external doping, is studied in orbitally nondegenerate spin-$\frac{1}{2}$ systems. It is presented as another resonating valence bond route to high T_c superconductivity. We propose a "strong coupling" hypothesis that views long range Coulomb force driven first order Mott transition as a self-doping process that also preserves superexchange on the metal side. We present a two-species t-J model where conserved N_0 doubly occupied (e^-) sites and N_0 empty sites (e^+) hop in the background of $N - 2N_0$ singly occupied (neutral) sites in a lattice of N sites. An equivalence to the regular t-J model is made. Some old and new systems are predicted to be candidates for pressure-induced high T_c superconductivity.

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Bednorz-Muller's discovery [1] of high temperature superconductivity in doped La_2CuO_4 and Anderson's resonating valence bond (RVB) theory [2] initiated a new interest in Mott insulators as a novel quantum state. In RVB theory the preexisting singlet correlations among electron spins in a spin-$\frac{1}{2}$ Mott insulator readily become the superconducting correlations on doping. The RVB mean field theory [2], gauge theory [3], and later developments [4] have given results that are in qualitative and sometimes quantitative agreement with many experimental results.

Motivated by high T_c superconductivity in cuprates, RVB theory has so far focused on the metallization of a Mott insulating state by external doping. However, we know that there are three families of "commensurate" tight binding systems that undergo Mott insulator (spin-Peierls or antiferromagnetic order) to superconductor transition under pressure or chemical pressure and no external doping: (i) quasi-one-dimensional $(TMTSF)X_2$, Bechgaard salt family [5]; (ii) quasi-two-dimensional κ-$(BEDT\text{-}TTF)X_2$, ET-salt family [6]; (iii) three-dimensional fullerites [7,8]. For ET and Bechgaard salts a single band repulsive Hubbard model at half filling is known to be a right model [9,10].

As antiferromagnetism (more correctly, enhanced singlet correlations [11]) is present in the insulating side we study Mott transition in spin-$\frac{1}{2}$ orbitally nondegenerate systems from the RVB theory point of view. By looking at a body of experimental results and theories on Mott transition [12] in real systems and using the first order character of the Mott transition, we propose a strong coupling hypothesis. This hypothesis leads to a two-species t-J model, where a fixed number of doubly occupied sites and empty sites hop in the background of $N - 2N_0$ singly occupied (neutral) sites that have superexchange interaction among themselves. Here N is the number of lattice sites. The long range Coulomb interaction determines the total number of mobile charges $2N_0$, that is the amount of self-doping.

The issue of RVB superconductivity is solved by transforming our two-species t-J model containing N_0 holes and N_0 doubly occupied sites in a Mott insulator into a regular t-J model that contains either $2N_0$ holes or $2N_0$ doubly occupied sites. So our model also exhibits superconductivity to the extent the corresponding regular t-J model exhibits superconductivity. Encouraged by our theory we make certain predictions about the possibility of pressure-induced superconductivity in a family of compounds: (i) old ones such as three-dimensional CuO, layered La_2CuO_4, infinite layer $CaCuO_2$, insulating Tl and Hg cuprates, and YBCO; (ii) new ones such as $La_2CuS_2O_2$, La_2CuS_4, $CaCuS_2$ with CuS_2 planes or their selenium analogs, to mimic chemical pressure along the ab plane.

It should be pointed out that 1D Mott transition and various Hubbard model based theories exist in the literature [9,10,13] for the Bechgaard, ET salts, and fullerites. Our viewpoint emerging from the *strong coupling* hypothesis and the resulting two-species t-J model emphasizes that the physics of the conducting state is also determined by a strong coupling physics with superexchange and the consequent RVB physics.

The standard thought experiment of Mott transition is an adiabatic expansion of a cubic lattice of hydrogen atoms forming a metal. Electron density decreases on expansion and Thomas-Fermi screening length increases; when it becomes large enough to form the first electron-hole bound state, there is a first order transition to a Mott insulating state, at a critical value of the lattice parameter $a \approx 4a_B$, where a_B is the Bohr radius. The charge gap jumps up from zero to a finite Mott-Hubbard gap across the transition [Fig. 1(a)], by a feedback process that critically depends on the long range part of the Coulomb interaction, as emphasized by Mott [12].

Experimentally known Mott transitions are first order and the insulating side close to the transition point usually has a substantial Mott-Hubbard gap; in oxides this gap is often of the order of an eV. In organics, where the

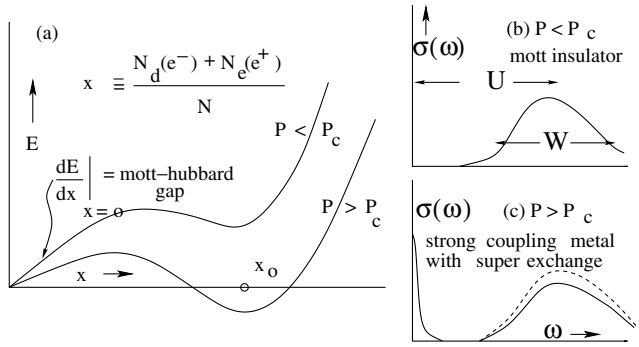

FIG. 1. (a) Energy of a half filled band above and below the critical pressure P_c, as a function of $x = \{[N_d(e^-) + N_e(e^+)]/N\}$. Here $N_d(e^-) = N_e(e^+)$ are the number of doubly occupied (e^-) and number of empty sites (e^+); total number of lattice sites N = total number of electrons. Optimal carrier density $x_0 \equiv (2N_0/N)$ is determined by long range part of Coulomb interaction and superexchange energy. (b),(c) Schematic picture of the real part of the frequency dependent conductivity on the insulating and metallic side close to the Mott transition point in a real system. W is the bandwidth.

bandwidths are narrow ≈ 0.25 eV the Mott-Hubbard gap also has a similar value. In view of the finite Mott-Hubbard gap, the magnetism on the Mott insulating side is well described by an effective Heisenberg model with short range superexchange interactions. There are no low energy charge carrying excitations; that is, we have a strong coupling situation.

What is interesting is that this strong coupling situation continues on the metallic side as shown by optical conductivity studies, for example, in Bechgaard [14] and ET salts: one sees a very clear broad peak (a high energy feature) corresponding to the *upper Hubbard band both in the insulating and conducting states*. The only difference in the conducting state is the appearance of a Drude peak, whose strength and shape gives an idea of the number of free carriers that have been liberated [Figs. 1(b) and 1(c)]. As the location and width of the Hubbard band has only a small change across the transition, one may conclude that the local quantum chemical parameters such as the hopping matrix element t's and the Hubbard U(corresponding superexchange J) remain roughly the same. This leads to our strong coupling hypothesis: *a generic Mott transition in real systems gives a metallic state where a small but conserved number of N_0 holes (empty sites) and N_0 electrons (doubly occupied sites) are self-consistently generated by the long range Coulomb interaction and delocalized in the background of singly occupied sites undergoing superexchange processes.*

Recall that in a tight binding model of noninteracting electrons at half filling, the number of doubly occupied sites and empty sites is not individually conserved since the up and down spin particles have no repulsion; i.e., a process shown in Fig. 2 freely occurs, maintaining an average total number $\frac{N}{4}$ of doubly occupied and empty

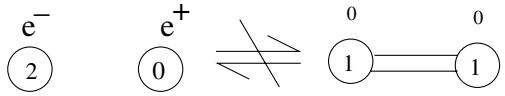

FIG. 2. Forbidden hopping process, i.e., absence of annihilation of e^+ and e^- at low energies in our strong coupling metal. The double line represents a spin singlet (valence) bond.

sites. Here N is the total number of sites. In our strong coupling metal, on the other hand, long range Coulomb interaction has self-doped a small and equal number $N_0(<\frac{N}{4})$ of individually conserved empty sites and doubly occupied sites. This means that hopping that leads to real processes shown in Fig. 2, is absent at low energies. We prove the absence of these processes by recognizing that it is precisely these processes that have been eliminated to get the superexchange interaction in the first place. We cannot include them again in our low energy Hamiltonian. In other words, the existence of superexchange and annihilation of e^+ and e^- at low energies is incompatible in our strong coupling metal.

The above arguments naturally lead to a two-species t-J model for the conducting side in the vicinity of the Mott transition point,

$$H_{t\text{-}J} = -\sum_{ij} t_{ij} P_d c^\dagger_{i\sigma} c_{j\sigma} P_d - \sum_{ij} t_{ij} P_e c^\dagger_{i\sigma} c_{j\sigma} P_e + \text{h.c.} + \sum_{ij} J_{ij}\left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j\right), \quad (1)$$

operating in a subspace that contains a fixed number N_0 of doubly occupied and N_0 empty sites. The projection operators P_d and P_e allow for the hopping of a doubly occupied and empty sites, respectively, in the background $N - 2N_0$ of singly occupied sites. Here N is the total number of electrons, which is the same as the number of lattice sites. As the Mott-Hubbard gap is the smallest at the Mott transition point, higher order superexchange processes may also become important and contribute to substantial non-neighbor J_{ij}'s.

Our t-J model adapted to the self-doped Mott insulator has a more transparent form in the slave boson representation $c^\dagger_{i\sigma} \equiv s^\dagger_{i\sigma} d_i + \sigma s_{i\bar{\sigma}} e^\dagger_i$. Here the chargeons $d^\dagger_i$'s and $e^\dagger_i$'s are hard-core bosons that create doubly occupied sites (e^-) and empty sites (e^+), respectively. The Fermionic spinon operators $s^\dagger_{i\sigma}$'s create singly occupied sites with a spin projection σ. The local constraint, $d^\dagger_i d_i + e^\dagger_i e_i + \sum_\sigma s^\dagger_{i\sigma} s_\sigma = 1$, keeps us in the right Hilbert space. The t-J Hamiltonian [Eq. (1)] takes the following form:

$$H_{t\text{-}J} = -\sum_{ij} t_{ij} (d^\dagger_i d_j s_{i\sigma}\ s^\dagger_{j\sigma} + e_i e^\dagger_j s^\dagger_{i\sigma} s_{j\sigma}) + \text{H.c.} - \sum_{ij} J_{ij} b^\dagger_{ij} b_{ij}.$$

In the slave boson representation, $\sum_{\langle ij\rangle} t_{ij} e^\dagger_i d^\dagger_j b_{ij} +$ H.c., a part of one electron hopping term representing the process shown in Fig. 2 is the one that has been eliminated to get the superexchange in our two-species

t-J model. [Here $b_{ij}^{\dagger} = (1/\sqrt{2})(s_{i\uparrow}^{\dagger} s_{j\downarrow}^{\dagger} - s_{i\downarrow}^{\dagger} s_{j\uparrow}^{\dagger})$ is a spin singlet spinon pair creation operator at the bond ij]. As the above kinetic energy piece has been eliminated in arriving at our two-species t-J model, it is easily seen that the total number operator for doubly occupied sites $\hat{N}_d \equiv \sum d_i^{\dagger} d_i$ and empty sites $\hat{N}_e \equiv \sum e_i^{\dagger} e_i$ commute with the t-J Hamiltonian [Eq. (1)]:

$$[H_{t\text{-}J}, \hat{N}_d] = [H_{t\text{-}J}, \hat{N}_e] = 0. \tag{2}$$

That is, $\hat{N}_d$ and $\hat{N}_e$ are individually conserved. In our half filled band case $N_d = N_e = N_0$. (This special conservation law is true only for our effective t-J Hamiltonian and not for the original Hubbard model.)

This conservation law allows us to make the following statement, which is *exact for a particle-hole symmetric Hamiltonian and approximate for the asymmetric case*: our two-species t-J model with a fixed number N_0 of doubly occupied sites and equal number N_0 of empty sites has the same many body spectrum as the regular t-J model that contains either $2N_0$ holes or $2N_0$ electrons. Symbolically it means that $H_{t\text{-}J}(N_0, N_0) \equiv H_{t\text{-}J}(2N_0, 0) \equiv H_{t\text{-}J}(0, 2N_0)$. This means we can borrow all the known results of t-J model, viz., mean field theory, variational approach, numerical approach, etc., and apply them to the understanding of the thermodynamic and superconductivity properties of our self-doped Mott insulator. Response to electric and magnetic field perturbation has to be done separately as the d and e bosons carry different charges, e^- and e^+, respectively.

Another consequence of the above equivalence is shown in Fig. 3, where we have managed to draw the path of pressure-induced Mott transition in a Hubbard model phase diagram, even though the Hubbard model does not contain crucial long range interaction physics. The jump from B to C is the first order phase transition,

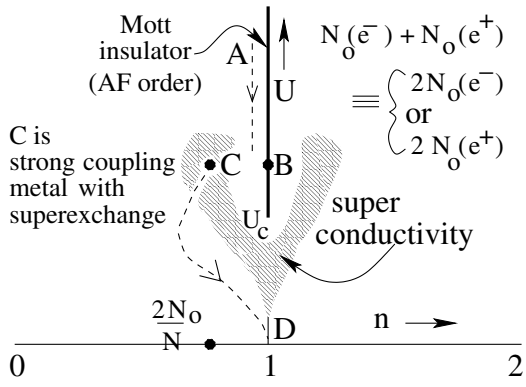

FIG. 3. Schematic U-n plane phase diagram for the Hubbard model. $ABCD$ represents the path a real system takes as pressure increases. B to C is the first order Mott transition, consistent with our *strong coupling* hypothesis. The point C, from a regular t-J model point of view, is hole doped at density $n = (2N_0/N)$; however, based on our equivalence it corresponds to a half filled band with a total of $N_0(e^-) + N_0(e^+)$ self-doped carriers.

remembering that, in the presence of our new conservation law, what decides the spectrum of our two-species t-J model is the total number of e^+ and e^- charge carriers in an equivalent regular t-J model. The horizontal jump is also consistent with our strong coupling hypothesis.

An important parameter in our modeling is the sum of self-doped e^+ and e^- carrier concentration, $x_0 \equiv (2N_0/N)$. Superconducting T_c near the Mott transition point is partly controlled by x_0. The long range part of Coulomb interaction and short range superexchange interaction determine x_0; we may estimate x_0 experimentally from Drude weight in $\sigma(\omega)$.

Since we have reduced our self-doped Mott insulator problem into a t-J model, superconducting T_c is determined by t, J, and x_0, as in the t-J model. If exchange interaction contribution is comparable to the long range Coulomb contribution, x_0 will be closer to the value that maximizes superconducting T_c. Another important point is the possibility of non-nearest-neighbor superexchange J_{ij} processes, which (i) frustrate long range antiferromagnetic order to encourage spin liquid phase and (ii) increase the superexchange energy contribution to the total energy; this could give a larger superconducting T_c across the Mott transition than expected from a t-J model with nearest neighbor superexchange. Perhaps an optimal self-doping and sufficiently frustrated superexchange interactions are realized in the $(NH_3)K_3C_{60}$ family [8], since the Néel temperature $T_n \approx 40$ K and the superconducting $T_c \approx 30$ K are comparable.

If the self-doping is small there will be competition from the antiferromagnetic metallic phase, stripes, and phase separation. For a range of doping one may also get superconductivity from interplane and/or interchain charge disproportionation. If self-doping is very large, then the effect of superexchange physics and the consequent local singlet correlations are diluted and the superconducting T_c will become low. This is the reason for the fast decrease of superconducting T_c with pressure in the organics.

In what follows we discuss some families of compounds, some old ones and some new ones, and predict them to be potentially high T_c superconductors, *unless some crystallographic transitions or band crossing intervenes* and change the valence electron physics drastically. CuO is the mother compound [15] of the cuprate high T_c family. It is monoclinic and CuO_2 ribbons form a three-dimensional network, each oxygen being shared by two ribbons mutually perpendicular to each other. The square planar character from four oxygens surrounding a Cu in a ribbon isolates one nondegenerate valence d orbital with a lone electron. This makes CuO an orbitally nondegenerate spin-$\frac{1}{2}$ Mott insulator and makes it a potential candidate for our pressure route to high T_c superconductivity. The frustrated superexchange leads to a complex three-dimensional magnetic order with a Néel temperature $\sim$230 K. These frustrations should help in stabilizing short range singlet correlations,

which will help in singlet Cooper pair delocalization on metallization.

As far as electronic structure is concerned, the CuO_2 ribbons give CuO a character of coupled 1D chains. This makes it somewhat similar to quasi-one-dimensional Bechgaard salts, which have a Mott insulator to superconductor transition, via an intermediate metallic antiferromagnetic state as a function of physical or chemical pressure. The intermediate metallic antiferromagnetic state represents a successful competition from nesting instabilities of flat Fermi surfaces arising from the quasi-one-dimensional character. Once the quasi-one-dimensional character is reduced by pressure, nesting of Fermi surface is also reduced and the RVB superconductivity takes over.

If manganite [16], a perovskite, and fullerites [8] are any guidance, metallization should take place under a pressure of $\sim$ tens of GPa's. CuO should undergo a Mott insulator superconductor transition, perhaps with an intermediate antiferromagnetic metallic state. The superconducting T_c will be a finite fraction of the Néel temperature, as is the case with Bechgaard salts or $K_3(NH_3)C_{60}$. Thus an optimistic estimate of $T_c$will be 50 to 100 K.

Similar statements can be made of the more familiar La_2CuO_4, insulating YBCO and the $CaCuO_2$, the infinite layer compound or the family of Mott insulating cuprates such as Hg and Tl based insulating cuprates. Infinite layer compound has the advantage of absence of apical oxygen and should be less prone to serious structural modifications in the pressure range of interest to us. The quasi 2D Hubbard model describing the CuO_2 planes does have an appreciable t', making nesting magnetic instabilities weaker. Thus we expect that on metallization a superconducting state to be stabilized with a small or no antiferromagnetic metallic intermediate state.

The quasi 2D cuprates have a special advantage in the sense we may selectively apply *ab*-plane pressure in thin films by epitaxial mismatch and *ab*-plane compression. Apart from regular pressure methods, this method [17] should be also tried.

One way of applying chemical pressure in cuprates is to increase the effective electron bandwidth by increasing the band parameters such as t and t' in the Hubbard model. This can be achieved by replacing oxygens in the CuO_2 planes (or in three-dimensional CuO) by either sulfur or selenium, which because of the larger size of the bridging $3p$ or $4p$ orbitals increase the bandwidth and at the same time should reduce the charge transfer or Mott-Hubbard gap. On partial replacement of oxygen, as $CuO_{2-x}X_x$ in the planes or $CuO_{1-x}X_x$ ($X = S, Se$) one might achieve metalization without doping.

Some possible new stoichiometric compounds are $La_2CuS_2O_2$, La_2CuS_4, and $CaCuS_2$ or their Se versions. Synthesizing these compounds may not be simple, as the filled and deep bonding state of oxygen $2p$ orbitals in CuO_2 play a vital role in stabilizing square planar coordination. With S or Se versions these bands will float up and come closer to the Fermi level thereby making square structure less stable. Under pressure or some other nonequilibrium conditions some meta stable versions of these compounds may be produced. One could also optimize superconducting T_c by a judicious combination of pressure-induced self-doping and external doping.

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