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Resonating valence bond states in 2 and 3D – brief history and recent examples

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Abstract : Resonating valence bond states are quantum spin liquids, having low energy spin- ½ (spinon) or spin-1 excitations. Although spins are 'disordered', they possess subtle topological orders and some times chiral orders. RVB states are easily appreciated and seem natural in the quantum fluctuation dominated 1D world. In 2 and 3D, competing orders such as antiferromagnetism, charge order or even superconductivity often hide an underlying robust quantum spin liquid state. Introduction of additional spin interactions or doping of delocalized charges, or finite temperatures, could frustrate the long range magnetic order and reveal a robust RVB state. To this extent they are natural in 2D and above. We present a brief history of insulating RVB states. Then we summarise our own recent theory of RVB states for 2 and 3D systems, including some newly synthesised ones: (i) boron doped diamond, (ii) Na_xCoO_2:yH_2O , (iii) quasi 2D organic conductors and (iv) a 2D graphene sheet.

Keywords : Resonating violence bond theory, quantum spin systems, Mott insulators, high temperature superconductors

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1. Introduction

Resonating valence bond (RVB) states occupy a special position among quantum states and phases in condensed matter physics. They became popular and important, as a seat for high temperature superconductivity[1, 2] in cuprates. Subsequently, their novel quantum properties, such as quantum number fractionization, topological order and a deep connection to gauge theories, have also received a well deserving attention in the past two decades. In this article, we give a brief history of RVB theory, focussing on the insulating states, followed by a short introduction to RVB states. Then we provide some examples for RVB states from real systems in 2 and 3D, based on our own results and new understanding that have come in the last few years: (i) boron doped diamond, (ii) $NaxCoO_2$:yH_2O, (iii) quasi 2D organic conductors and (iv) a 2D graphene sheet.

2. A brief history

The idea of resonating valence bond (RVB) arose in the description of quantum mechanical resonance of covalent bonds in unsaturated $p-\pi$ bonded organic molecules such as benzene. It was soon generalised to 2D graphite and metals by Pauling[3]. The overwhelming phenomenological success of semi empirical results and reasonings of Pauling, apparently even questioned the need for notions such as Fermi surface in describing a metal. It was at this point, in 1973, Anderson [4] became enthusiastic about the idea of RVB in a Mott insulator, while he remained silent about metals. He pointed out that the idea of RVB could be really relevant to family of spin-$\frac{1}{2}$ Mott insulators, where an expected long range antiferromagnetic order was often absent. Anderson attributed this to enhancement of quantum fluctuations created by frustrated spin interactions and lower dimensionality. He elaborated this by an analysis of a 2D triangular lattice of spin-half Heisenberg antiferromagnet. His variational study showed that this system could very well have a quantum spin liquid ground state, a short range RVB state.

Very few in condensed matter community paid attention to this proposal; exceptions were Fazekas[5], Klein, Shastry, Sutherland, Caspers, some Japanese experimental groups (Hirakawa, Yamada and possibly others) and to some extent myself. I was familiar with RVB ideas, partly through Fazekas in the early 80's, at ICTP, Trieste, a wonderful meeting ground of so called third and first world. (A first rate condensed matter theory activity, that continues now, was being nurtured by the efforts of Stig Lundquist, Norman March, Paul Butcher, Eli

Burstein, Abdus Salam and faculty like Mario Tosi, Erio Tosatti, Michele Parrinello, Roberto Car and others. People like Phil Anderson, Bob Schrieffer took great interest in ICTP activities and frequented the center. My association with Anderson was made possible by ICTP and Erio Tosatti).

In the early 1986, just before Bednorz-Muller's discovery was published, I was intrigued by the question of phase relations among valence bond configurations in a short range RVB wave function, and what it really meant in a magnetic insulator. When Anderson responded[2] to Bednorz-Muller's discovery of high Tc superconductivity, with his RVB proposal, I was well prepared and was quick to appreciate it. That is how I joined Anderson in his second RVB journey, as a partner. A 20 year long journey is still continuing. Anderson's Science paper[2] and our collaborative works[6-8], interestingly, done during the very first year of this journey (1987-88), continue to light the path.

On another front, a non-trivial solution to 1D anti-ferromagnetic Heisenberg chain by Bethe[9] was drawing more and more attention; its mathematics was formidable and revealed surprises such as, absence of long range antiferromagnetic order, even at $T = 0$ and presence of gapless topological (domain wall) spin half excitations[10], which was later named[8] spinon. It is in this background, before Anderson proposed his RVB theory in 1973, Majumdar and Ghosh discovered a model[11] in 1969, a slight variant of standard Heisenberg chain, which exhibited a strikingly simple many body ground state - a valence bond solid. Valence bond resonance was completely absent.

Even these developments did not suggest an RVB description of the complicated Bethe ansatz ground state. Shastry, Sutherland[12], Klein[13] and others went for higher dimensional generalisation of Majumdar-Ghosh model and valence bond solid phases. Interestingly, recent study[14] of Klein models have given a rich possibility of quantum liquid of valence bonds, at some special lattices and for some choice of parameters. The fertile modern materials science has offered a compound [15], $SrCu_2(BO_3)_2$, where the Shastry-Sutherland model is indeed realized.

The idea of resonating valence bond was in the hands of quantum chemists for a long time, mostly studying the $p-\pi$ bonded organic systems. The richness of this novel quantum phase was yet to be unravelled. According to Anderson, when superconductivity in oxides such as $LiTi_2O_4$ and $BaBi_{1-x}Pb_xO_4$ were discovered[16] thoughts of RVB crossed his subconscious mind. Like many cases in physics, a key experimental result was necessary to open the doors and revive and flourish an old and fertile idea such as resonating valence bond. Discovery of high Tc superconductivity in an unexpected oxide $L_{a-x}Ba_xCuO_4$ by Bednorz and Muller catalysed a revolution in the RVB theory front. As mentioned earlier, it was Anderson, who was, alert and sensitive to the new oxide and the challenge from experiments. He proposed the RVB mechanism of superconductivity. His collaborators gave flesh to his proposal and offered new insights. Two key many body approaches were developed: (i) RVB mean field theory[6] (BZA theory) and (ii) a gauge theory [7, 17] (BA theory), to go beyond RVB mean fleld theory. The currently popular experimental phase diagram for cuprates was part of the RVB theory conjecture[8], before the experimental phase diagram emerged.

The RVB character of the ground state of 1D Heisenberg Chain (Bethe Ansatz wave function) was well recognised in the BZA paper. A new impetus was given by Haldane and Shastry, who showed that the Gutzwiller projected BZA mean field solution in 1D is indeed the ground state of a non-trivial 1D Heisenberg model, which has become the celebrated Haldane-Shastry model[18]. The BZA and BA theory showed a deep connection between RVB states and gauge theories; quantum number fractionization came out as a rather natural possibility. A gauge structure and dynamically generated gauge fields in a quantum spin problem was rather unexpected and opened a new field of activity. Using these insights a new mean field solution by Affleck and Marston[19] and a chiral spin liquid wave function by Kalmayer and Laughlin[20] appeared in the scene. They contained a nonzero ground state condensates of the BA gauge fields. Gauge field condensation, flux tube attachment and a consequent statistics transmutation eventually lead to Laughlin's proposal[21] of anyon superconductivity in 2 dimensions. Wen, Wilczek and Zee[22] made a key identification of the 'magnetic flux' of RVB gauge field with spin chirality, $\boldsymbol{S}_i \cdot (\boldsymbol{S}_j \times \boldsymbol{S}_k)$. Large N theories[23] that followed Affleck-Marston's work studied valence bond solid phases.

Kotliar's *d*-wave RVB meanfield solution [24], based on slave boson approach, adapted to $t - J$ model by Zou and Anderson[25], explained the *d*-wave symmetry of cuprate superconductors successfully; Fukuyama[26] school and others did extensive study on this front.

Kivelson, Sethna and Rokhsar [27] used short range RVB wave function to study cuprates and introduced the notion of 'holon', a topological excitation for charge. Other authors, including Sutherland[28] and Reed and Chakraborty[29] pursued the study of short range RVB states and the nature of spinon and holon excitations. Quantum dimer models introduced by Rokhsar and Kivelson [30], to understand short range RVB states have brought out novel topological ground state degeneracies, and some non-trivial gapless spin liquid phases; this has been developed further by Moessnerasedand Sondhi Mesmer[31], and others. The idea of topological degeneracy, that also unifies RVB states with fractional quantum Hall states, has been elevated to an interesting notion of 'quantum order' by Wen[32] and several insights have been offered.

Statistics other than fermion and boson were suggested to be possible in a 2D world by Leinaas, Myrlheim, Wilczek and Zee[33]. RVB phases and quantum Hall systems became play grounds for particles with non standard statistics. Dzyaloshinski, Polyakov and Wiegman [34], suggested interesting statistics transmutation properties for spinons, through a topological Hopf term, for the 2D spin-$\frac{1}{2}$ Heisenberg antiferromagnet. Some attempts[35, 36] to organize the sum of single spin Berry phase terms did not lead to the anticipated Hopf term. However, in a recent work[37] the present author has shown that a proper summation of the Berry phase terms leads effectively to a statistics transmutation. The Berry phase does get organized and behave like a nontrivial topological term; however, it does not have a local continuum Hopf like analytic form.

Affleck, Zou, Hsu and Anderson [38] and also Dagotto and Fradkin Moreo [39] found a $SU(2)$ description of the BA theory. However, it was realized soon that owing to the limited dimensionality of Hilbert space of our spin system, only a subgroup, the center Z_2 of the $SU(2)$ group is really necessary to describe the thermodynamic phases and dynamics, rather than the full $SU(2)$ or $U(1)$ group. This was nicely shown by an identity due to Marston[40], which showed how the dynamically generated RVB flux gets restricted to integer or half integer flux quanta rather than an arbitrary value. That is at the level of a classical action, $SU(2)$ or $U(1)$ fields exists formally. However, the quantum dynamics chooses only a limited set of the field degrees of freedom. Marston[40] incorporated the quantum kinematic restriction through a Chern-Simons term in the action, by hand. What is important is that within the subspace of zero and half flux, the Chern-Simons term retains the PT symmetry. This was soon taken further and a Z_2 gauge theory of spin system was formulated by Tosatti, Yu Lu and the present author[41]. In another work, using a similar identity due to Wen, Wilczek and Zee[22], the present author[42] reduced the famous triangular lattice problem to a Z_2 gauge theory. Zou in an insightful paper[43] discussed how Chern Simon terms could arise as a quantum anomaly in an $SU(2)$ gauge theory for spin-$\frac{1}{2}$ Heisenberg antiferromagnet in 2D. Wen[44] and Read and Sachdev[45] also developed the Z_2 gauge theory ideas and connection to topological degeneracies *etc*.

Systematic way of going beyond BZA theory for insulating and conducting spin systems using Gutzwiller approximation has become very useful for quantitative progress, in the hands of Gros, Zhang, Rice[46, 47], Ogata, Shiba, and recently Paramekanti, Randeria and Trivedi, [48], Fukhshima [49] and others. The BA gauge theory, on the other hand has been very useful in giving new qualitative insights; its full potential as a quantitative tool has not been realized, in spite of notable efforts[50] by Ioffe, Larkin, Nakamura, Matsui, Patrick Lee, Nagaosa, Wen, Dung-Hai Lee, Ng and recently Tesanovic, Franz and others.

Hsu[51], showed that the antiferromagnetic order existing in the ground state of 2D Heisenberg model on the square lattice can be viewed as a spinon density wave in an underlying quantum spin liquid. A 'bosonic' variational RVB wave function (similar to Gutzwiller projection of Arovas and Auerbach's Schwinger boson[52] type wave function) introduced by Liang, Doucot and Anderson[53] exhibited a spontaneous antiferromagnetic order in the ground state for a range of variational parameter. Outside this range, the spin correlation function decayed exponentially. However, the energy expectation value changed very little with the variational parameter, even though sub lattice magnetisation changed substantially from zero to a large value. This analysis substantiated the fact that long range antiferromagnetic order is a minor modification in an otherwise robust spin liquid state. Some of these ideas have been summarised by a principle of valence bond amplitude maximisation (VBAM)[54] by the present author.

In the recent past, quantum number fractionization and spinon deconfinement has been studied by Senthil *et al* [55]. A Z_2 gauge symmetry has been very prominent in the discussion. Possibilities of classifying RVB states into Z_2, $U(1)$ and non-abelian spin liquids have been discussed.

A recent work by the present author shows[37] a surprising result that quantum number fractionization occurs, above a finite energy gap, even in the ordered Heisenberg antiferromagnet in 2D ! That is, in addition to gapless spin wave excitations we have deconfined, freely propagating spinons above a finite energy gap. I showed that a (scale free) finite energy quantum skyrmions is made of two unbound 'chiral spinons'. Chiral spinons carry non vanishing condensed RVB magnetic flux or chiral density $\boldsymbol{S}_i \cdot (\boldsymbol{S}_j \times \boldsymbol{S}_k)$ distributed specially in a broad fashion. This result confirms and sharpens an early conjectured connection of meron with spinon by Anderson *et al* [56] and John and Berciu [57]. It will be interesting to make connection of our formally exact result with recent works of Ho *et al* [58] and others [59] on spinons.

An elegant construction by Affleck, Kennedy, Lieb and Tasaki[61] has given models with valence bond like ground states with higher spins and higher dimensions. In the process it has given a new meaning to the Haldane gap phenomenon.

On numerical front, RVB wave functions have been analysed by several authors for frustrated and nonfrustrated spin systems in great detail. Highly frustrated spin systems such as Kagome lattice has given some surprises[62].

RVB excitations, because of their topological and 'abelian' or 'non-abelian anyon' character, arising from topological degeneracy in the ground state, could have a special immunity against decoherence. They also have fascinating quantum entanglement and braiding properties. Consequently, they have

been considered as serious q-bit candidates in quantum computers by Kitaev [63] and others. RVB theory and fractional quantized Hall effects have indirectly given a new impetus to theoretical studies in quantum computers, with envisaged experimental potential [64].

This is a brief history of RVB theory, without going to the fascinating superconductivity or antiferromagnetism aspects.

3. RVB wave function, topological degeneracy and excitations

Above T_N, thermal fluctuations destroy long range antiferromagnetic order in quantum spin systems. At very high temperature the thermal state is a structureless 'classical' paramagnetic phase. What is the state we reach, when we destroy long range antiferromagnetic order, by frustrating it through additional interactions, at $T = 0$ or $k_B T << J$? The 'spin crystal' quantum melts and we get a quantum spin liquid. In this quantum spin liquid, the antiferromagnetic order decays in a power law or exponential fashion. This phase, where spins are seemingly disordered, have some special quantum coherence properties, which is what makes it a resonating valence bond state. This paramagnetic state has a special pair coherence among spins and also topological degeneracy. The special pair coherence has a natural and suggestive representation as a general RVB state, written down first by Anderson[2]. It turns out that this state has a rather natural representation, not in the standard S^z basis, but in terms of underlying electron operators c's that makeup a spin half moment:

$$\left|RV\ B;\phi\right\rangle \equiv P_G\left(\sum_{ij}\phi_{ij}b_{ij}^{\dagger}\right)^{\frac{N}{2}}\left|0\right\rangle, \qquad (1)$$

where, $b_{ij}^{\dagger}\equiv\frac{1}{\sqrt{2}}\left(c_{i\uparrow}^{\dagger}c_{j\downarrow}^{\dagger}-c_{i\downarrow}^{\dagger}c_{j\uparrow}^{\dagger}\right)$. $P_G\equiv\prod_i\left(1-n_{i\uparrow}n_{i\downarrow}\right)$, is the Gutzwiller projection, which ensures that the effective low energy electron occupancy of any site in a Mott insulator is one. Therefore, total number of electrons N in eq. (1) is the same as the number sites. The pair function ϕ_{ij} characterises the RVB state. The RVB wave function (eq. 1) is identical to, except for the Gutzwiller projection, an N particle projected BCS wave function, with ϕ_{ij} playing the role of a Cooper pair function. This is what made Andersons proposal of a (Mott) insulating RVB state becoming a superconductor, on moving away from half filling (doping), so natural and appealing.

In a 2D square lattice, the standard short range RVB corresponds to ϕ_{ij} non zero only for nearest neighbour sites and a special relation between signs of ϕ 's between neighbouring bonds, so as to satisfy Marshall sign convention. In general, for various choices of ϕ_{ij}, we get (i) the BZA state with a pseudo fermi surface, (ii) Affleck-Marston π -flux state with nodal excitations, (iii) gapful Kalmayer Laughlin's chiral spin liquid state, (iv) antiferromagnetically ordered state, (v) d, $d + id$ and s-wave superconducting state, (vi) ground state of Haldane Shastry Hamiltonian in 1D, (vii) states with charge and spin stripe correlations *etc*. The physically motivated Gutzwiller projection does wonders - it enhances antiferromagnetic correlations and even introduces strong chiral correlations, in the process of reducing the double occupancy fluctuations.

Anderson's RVB wave function and the corresponding Hilbert space of states for strongly correlated electron systems is as basic and similar to Laughlin wave function and the corresponding Hilbert space of states for quantum Hall physics. It is very different from effectively slater determinant type 'Fermi liquid Hilbert space'.

Kivelson and Rokhsar introduced and studied a quantum dimer model on a square lattice, with a view to understand short range RVB physics. This non-trivial model has given many insights. For example, the idea of topological degeneracy in the ground state was manifest. If we consider a square lattice with periodic boundary condition (torus of genus g) all dimer coverings break into 4^g distinct classes, such that they are super selected with respect to local moves of the valence bonds. In the RVB mean field theory the topological degeneracy appeared as a (PT symmetric) half flux quanta of magnetiflux of RVB gauge field, that can be thread through various holes in the torus of genus g. In this sense, there is a close connection of this topological degeneracy with corresponding one in fractional quantised Hall states, giving the possibility of non-abelian character to spinons, in some RVB states.

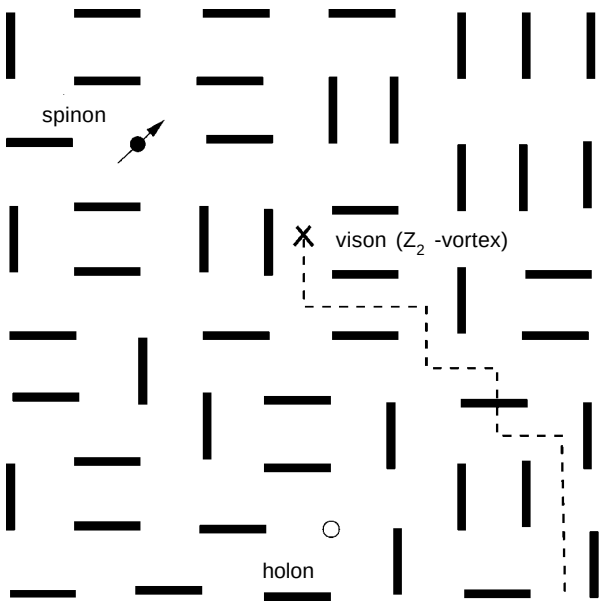

Figure 1. Schematic pictures of topological excitations, (i) spinon, (ii) holon and (iii) a Z_2 vortex (vison). The valence bonds in the background should resonate in the readers mind.

The valence bond character of the RVB wave function suggests presence of certain type of topological excitations (Figure 1) : (i) spinon: an unpaired spin in the back-ground of resonating singlets and (ii) holon or doublon: an empty site or a doubly occupied site in the background of resonating singlets and (iii) Z_2 vortices, carrying a π -flux, dubbed as 'vison' in recent works[55].

A simple way to imagine a spinon is to freeze a singlet bond and convert it into a triplet and localise one up spin at a given site and move the other upspin to the boundary. What we get is a localised spinon, an unpaired upspin in the background of resonating singlets. For some RVB systems such an unpaired spin may become freely propagating spinon excitation; examples are 1D Heisenberg chain, 2D chiral spin liquid, BZA phase with a spinon pseudo fermi surface, Affleck-Marston phase with nodal spinons *etc*. If this be the case we have quantum number fractionization and spinon deconfinement. In some cases two spinons may be bound and we may get a spin-1 low energy excitation branch. In the case of short range RVB system in 2D and 3D (without any chiral symmetry breaking) we expect spinons to be confined; however the spin-1 branch is a well defined excitation of the underlying quantum spin liquid. The Z_2 vortices are best understood as a `local defect' in the Marshal sign convention, which carries a phase string. The phase string excitation have been studied in detail by Weng and collaborators[59]. Energetic considerations and some deep issues related to confinement may force either a spinon or holon to be bound to a Z_2 excitation.

In the valence bond basis, creating a spinon at a site is a complicated non local operation, as outlined. The nonlocal and global rearrangement needed to create an isolated spinon or holon make them topological excitations. BZA theory give a simple and straightforward method to construct spinons and holons. In this approach, it is done by a local operation of creating in the mean field RVB state (that lives in an enlarged Hilbert space) a particle-hole pair excitation followed by a Gutzwiller projection:

$$\zeta^{\dagger}_{i\sigma}\zeta^{\dagger}_{i\sigma'}\left|RV\ B\right\rangle \equiv P_G c^{\dagger}_{i\sigma}c_{j-\sigma'}\left|mRV\ B\right\rangle, \qquad (2)$$

where $\left|mRV\ B\right\rangle = \left(\sum_{ij}\phi_{ij}b^{\dagger}_{ij}\right)^{\frac{N}{2}}\left|0\right\rangle$ is the unprojected RVB mean field solution. Here, $\zeta_{i\sigma}$ is a spinon operator. We note that the order of operation is important: Gutzwiller projection should be done after the creation of particle-hole pair. We can construct holon or doublon in a similar fashion.

Using the above construction, non-trivial excitations such as the spinon of the Haldane Shastry model in 1D and the Kalmayer-Laughlin model in 2D can be easily constructed. Somen Bhattacharjee's pfaffian representation[60] of RVB wave function may be useful in the study of RVB states; it remains to be explored.

4. New examples of 2 and 3D RVB states

In what follows we will summarise our recent results for certain non-cuprate systems, for which we have suggested RVB phases as the suitable reference vacuum state. We will not go to details of the theory, but will only outline the physics behind. The systems are: (i) quasi 2D organic conductors (ii) boron doped diamond, (iii) Na_xCoO_2:yH_2O and (iv) a 2D graphene sheet.

Superconductivity in organic solids :

Superconductivity in organic molecular conductors is a well developed field[65]. From a modest 1 K in Bechgard salt, the superconducting T_c has increased to a value 13 K in ET salt family. This is remarkable, considering the low carrier density, n ~ 10^{20} =cm^3 in organics. Various ideas including spin fluctuation mechanism of superconductivity has been discussed to explain superconductivity in 2D organics. In my opinion, they were unsatisfactory. One generic property of this system is that after taking care of crystallographic doubling of unit cell, it is well described[66, 67] as half filled single band system; *i.e.*, one electron per Wannier orbital. Often these systems exhibit Mott insulator to superconductivity transitions, either under external pressure or chemical pressures.

What is the physics behind these Mott insulator to a superconductor transition ? Firstly, it is a strong first order transition. A large Mott gap (comparable to band width) collapses to zero value. Long range coulomb interaction drives the transition first order. This is missing in the standard Hubbard model; consequently it predicts a continuous vanishing of the Mott Hubbard gap, across the Mott-Hubbard transition. I observed[68] that, in experiments, the optical conductivity $\sigma(\omega)$ retains the upper Hubbard band feature nearly intact across the transition. The only change is the emergence of a

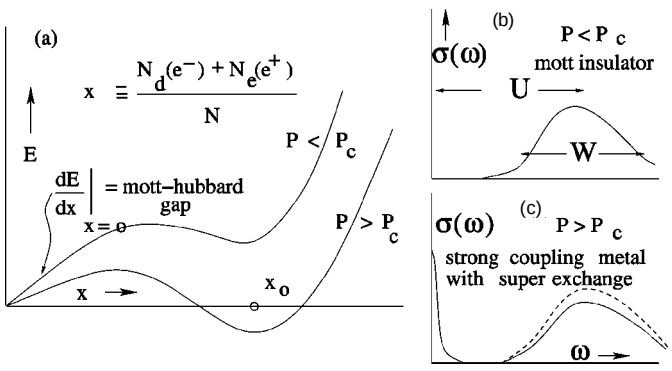

Figure 2. (a) Energy of a half filled band above and below the critical pressure P_c, as a function of $x = N_d(e^-) + N_e(e^+)/N$. Here $N_d(e^-) = N_e(e+)$ are the number of doubly occupied (e^-) and number of empty sites (e+); total number of lattice sites N = total number of electrons. Optimal carrier density $x_0 \equiv 2N_0/N$ is determined by long range part of coulomb interaction and superexchange energy. (b) and (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 band width.

Drude peak at low frequencies; the weight of the Drude peak indicates a small density of mobile carriers (often as low as 5 to 10 %).

Based on the above observation, I suggested that across the Mott transition, the Mott insulator retains its integrity, in the sense of survival of super exchange on the conducting side (Figure 2). The only new aspect is that a small and equal density of mobile positive and negative charge carriers (doublons and holons) have been spontaneously generated. These carrier density are individually conserved (Figure 3) and governed by the physics of long range coulomb interaction. In other words, I gave a new interpretation of Mott transition in theses systems as a process of self doping a Mott insulator.

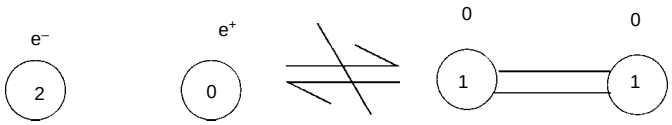

Figure 3. Forbidden hoping process, *i.e.*, absence of annihilation of $e+$ and e^- at low energies in our strong coupling metal. Double line represents a spin singlet (valence) bond.

These suggestions implied immediately a close connection of the mechanism of superconductivity to that in cuprates, where the doping is external. I developed this idea further and introduced a 2 species t–J model and discussed how superconductivity arises there. My conclusion[68] is that superconductivity in organics is based on RVB mechanism. The new feature is that preexisting neutral singlets get charged across the Mott transition and produce superconductivity, through a process of self doping rather than external doping. The superconducting T_c is determined by, apart from other factors such as superexchange, the density of self doping. As self doping increases beyond the optimal value (achieved by increasing pressure) superconductivity quickly disappears, as seen in the experiment. Recent theoretical works[69–71] essentially corroborate my view point, albeit with some minor differences.

In a very recent work, Kanoda[72] group have reported interesting results, in my opinion offering a direct support to RVB physics in one of the members of the ET salt family in the Mott insulating phase. They find evidence for a pseudo fermi surface like excitations from magnetic and specific heat measurements. This is likely to be a first example of realization of spinon pseudo fermi surface in 2D, suggested by Anderson and realized in BZA theory. This ET salt is a Mott insulator with enhanced near neighbour multi spin couplings, in view of smaller Mott-Hubbard gap. These couplings seem to frustrate antiferromagnetic order and really stabilise a quantum spin liquid with a pseudo fermi surface for spinons.

Boron doped diamond :

Diamond is known to be one of the best insulators. It has a large band gap of 5.6 eV. In a remarkable recent work Ekimov and collaborators[73] have managed to convert diamond to a superconductor by doping with boron; *i.e.*, diamond:B. It is well known that small traces of boron impurities is responsible for the captivating blue colour of diamond; however, heavy doping makes it dark and superconducting! The superconducting T_c has steadily increased from about 4 K to nearly 12 K, with increasing doping and improved material characteristics using MOCVD preparation methods[74, 75].

I have developed a theory[76], based on phenomenological and microscopic grounds that superconductivity takes place in the impurity band introduced by boron substitution, across the insulator to metal transition. Briefly, a substituted boron has a nice sp^3 tetrahedral bonding with neighbouring carbon atoms, except that there is a missing electron, *i.e.* a hole. This hole resides in one of the 3-fold degenerate impurity states, at about 0.37 eV above the top of the valence band. When the boron density is low, the holes are localised in their respective hydrogenic type of impurity states and well isolated. Holes, instead of getting delocalized into extended states, remain in their home site, because of an effective U (hole affinity - hole

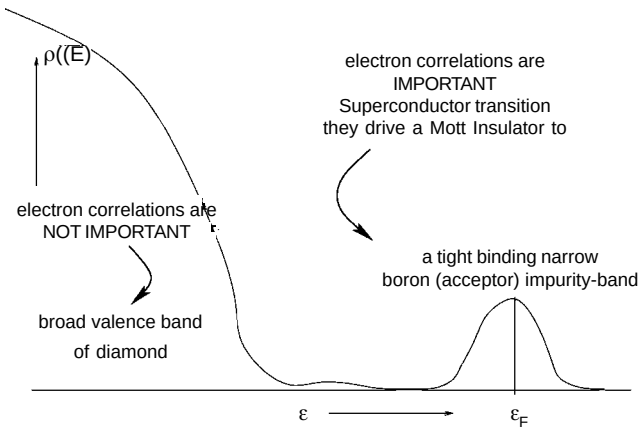

Figure 4. Hole density of states (schematic) in boron doped diamond, an uncompensated p-type semiconductor. Holes of acceptors form a strongly correlated and impurity band at commensurate filling. Anderson-Mott insulator to superconductor transition is suggested to take place in the impurity band as we increase boron density (Figure 5).

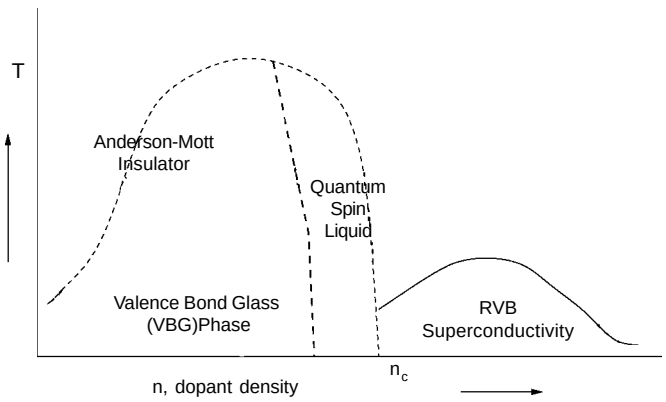

Figure 5. Schematic phase diagram as a function of dopant density in Diamond:B, an uncompensated case.

binding energy) > impurity band width W; *i.e.*, it costs energy to ionise and delocalized a hole. It is a Mott insulator formed of impurity states (Figures 4, 5). The holes stay in their impurity states and virtual fluctuations to neighbouring impurity sites leads to antiferromagnetic superexchange interaction. This leads to spin singlet coupling. Since the impurity states are randomly distributed in space, a spin finds its closest neighbour and forms a valence bond; this leads to valence bond solid (glass) phase, very similar to what has been studied for the case of Si:P. The spin half character of the hole in the impurity state and the orbital degeneracies stabilise a valence band glass phase rather than a spin glass phase.

As we increase boron concentration, we expect a Mott insulator to metal transition, in the impurity band subsystem. Since we have an uncompensated doping, randomness and Anderson localisation issues are only secondary. We can imagine the impurity state subsystem as a lattice of hydrogen atoms whose lattice parameter is decreased as increasing dopant density. As we approach Anderson-Mott transition point, the impurity state wave functions strongly overlap; *i.e.*, the inter impurity distance is comparable to the size of the impurity state wave function (effective Bohr radius a_B^*). Valence bond resonance increases and valence bond glass melts. We get a quantum spin liquid in a disordered lattice (Figure 5).

The resonating singlets are the preformed pairs. They are neutral. Across the first order Mott transition, the Mott-Hubbard gap collapses from a finite value to zero, by a process of self doping of the Mott insulator. That is, the Mott insulator continues to be a Mott insulator with valence bond resonance, except for a spontaneous creation of a small density of delocalized B^+ and B^- species. This mechanism of superconductivity is very similar to our mechanism for the organics, outlined in the previous section. In fact the carrier density and the size of the molecular orbital in organics and the impurity wave functions in diamond:B are similar in size leading to a similar value of T_c.

In the literature, at least three different phonon mechanism, which put the doped holes at the top of the valence band, in extended states have been proposed[77]. Even liberal estimates of Tc give a value small compared to experiments. Various phenomenology, particularly large value of low temperature intrinsic resistivity and recent ARPES results[78] indicate that the carrier mean free path are comparable to nearest boron-boron distance. There are also other experimental evidence[79] for the exsistence of an impurity band in the superconducting state, suggesting that the origin of short mean free path of carriers is not necessarily due to randomness. It is likely to be the effect of strong correlation within the impurity band.

Na_xCoO_2 . yH_2O, an icy superconductor :

New superconductors and novel materials continue to be discovered by Japanese groups, thanks to their concerted efforts in materials science with an eye not only on technology but also basic science. Historically, many systems exhibiting RVB physics have been discovered by the Japanese groups, including a Shastry Sutherland compound $SrCU_2(BO_3)_2$, alluded to earlier. Quickly following the footstep of discovery of superconductivity in MgB_2 by Akimitsu group, a Tsukuba group synthesized[80] a layered Na_xCoO_2 that becomes superconducting only when it is intercalated with water: Na_xCoO_2:yH_2O (Figure 6).

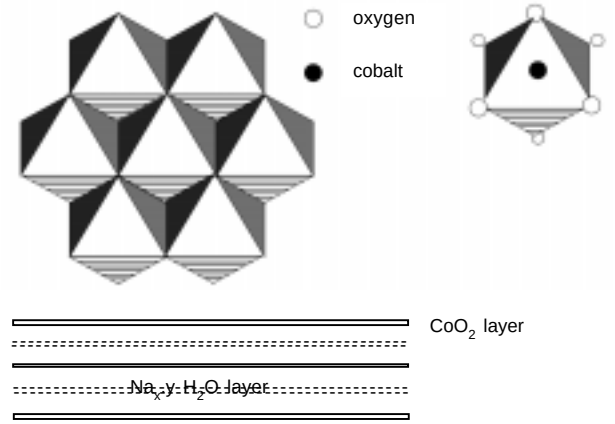

Figure 6. A triangular network of edge sharing oxygen octahedra. Co atoms are at the center of the oxygen octahedra. Each $Na_x.yH_2O$ layer is sandwitched by two CoO_2 layers.

Sitting in Chennai and I got a news of this icy superconductor by email, through a superconductivity e-group. It became clear that it is a doped spin half orbitally non-degenerate Mott insulator on a triangular lattice (Figure 7). It is indeed a long sought after, doped spin- $\frac{1}{2}$ triangular lattice system ! Absence of orbital degeneracy in Na_xCoO_2:yH_2O was my conjecture based on simple estimates: that is, the small fermi surface pockets that appeared in David Singh's electronic structure calculation[81] should infact disappear due to correlation effects, leaving a hole like band around the Γ point. It worked ! Later ARPES experiments showed[82] a single circular fermi surface, validating my single band model hypothesis and a non standard sign of the hopping integral.

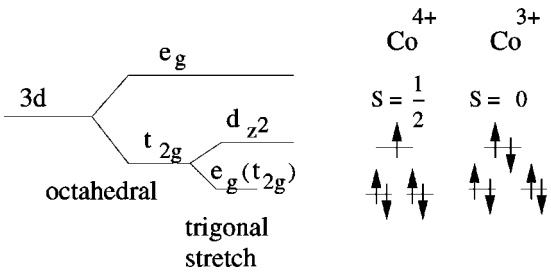

Figure 7. Crystal field split 3*d* levels of cobalt.

I worked out an RVB theory quickly[83]. What was novel was, the possibility of an important chiral RVB state as the reference Mott insulator. In an earlier work, Lee and Feng[84], inspired by Kalmayer-Laughlin's chiral spin liquid state[20], had

in fact found a PT violating RVB mean field solution, where every triangular plaquette contained a $\frac{\pi}{2}$ RVB magnetic flux. I showed that on doping, the insulating chiral spin liquid will continue into a PT violating chiral singlet superconductor, having a $d_{x^2-y^2} + id_{xy}$ (or briefly, $d + id$) order parameter symmetry (Figure 8).

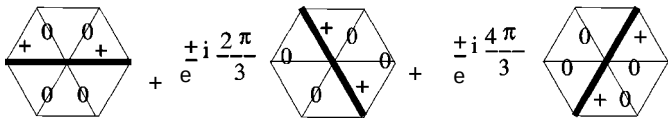

Figure 8. Relative phases of cooper pair amplitudes ($\Delta_{ij} \neq 0$ on dark bonds) in PT violating $d_1 \pm id_2$ states.

Subsequent theoretical analysis by Kumar-Shastry[85], Wang *et al* [86] have supported the above RVB scenario. Within the RVB scenario, there is a possibility of chiral p-wave superconductivity at high doping end (Figure 9). There are also other proposals of spin triplet superconductivity[87]. On the experimental front, there is an intense effort, using magnetic resonance studies, to find the order parameter symmetry by Nagoya and Kyoto and other groups. Recent results from Nagoya group[88], confirm their earlier findings and give strong evidence for spin singlet pairing. The issue of gap is still not settled. Earlier μSR studies[89] did not see any parity violating orbital magnetic field, making a PT violating state suspect. However, this result should be carefully analyzed, because of a possible invasive character of muon, through polarization of the H_2O dipoles. I have suggested [90] that a local polarization of H_2O molecules might destabilize superconductivity and stabilize a competing charge order locally.

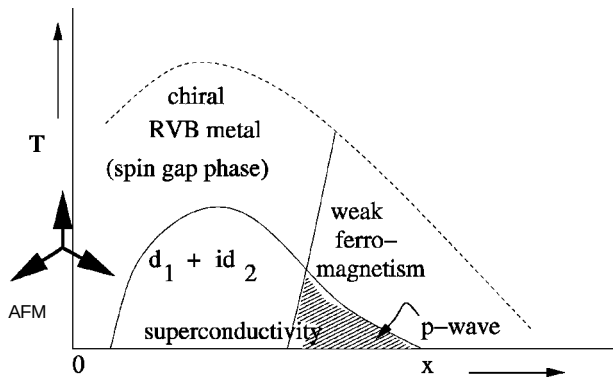

Figure 9. The schematic x - T phase diagram.

I had also suggested[83] that, in between the PT symmetric metallic state and PT violating superconducting state, an intermediate PT violating metallic (a chiral metal) phase should be present , over a finite temperature interval (Figure 9). Increase sample quality should enable one to search for this PT violating metallic state experimentally.

Heavily doped $Na_{0.5}CoO_2$, has an interesting metallic state, which exhibits a coherent charge transport, like a good metal; however spins are incoherent as seen by a non-Pauli, Curie magnetic susceptibility ! This phase has been called a Curie metal by the Princeton group[91]. Combining the above with some possible signatures of Luttinger volume anomaly seen in ARPES[82], I have suggested[92] a phase called 'Quantum Charge Liquid'. This is a natural generalization of RVB phase to heavily doped Mott insulators.

RVB and spin-1 collective mode in single graphene layer :

Graphite was a play ground for RVB ideas in the hands of Pauling. One should have expected some unique signature in low energy physical properties from RVB physics. Surprisingly no one seems to have looked for possible consequences of RVB phenomenon in graphite. Historically, with the advancement of electronic structure calculations and a variety of magnetic field dependent measurements, such as de Haas van Alfven effect, the single electron theories have been reigning supreme. One possible reason behind is that the subtle RVB effects of a 2D graphene sheet, at low energy, are being masked by the finite interlayer electron tunnelling matrix element ($t_\perp \sim$: 2eV), which gives rise to small cylindrical fermi surfaces around the K and K' points in the BZ.

In a recent paper[93], I and Jafari investigated effects of electron electron interaction in a single graphene sheet, using a simple Hubbard model. Graphene is a semi metal, where valence and conduction bands meet at K and K' points in the BZ. That is the fermi surface is shrunk to two points. Around these two points the band structure locally resembles a Dirac cone. This leads to an interesting gapless particle-hole continuum, that is very different from the standard 2D particle-hole continuum (Figure 10). In fact, the graphene particle-hole continuum (Figure 11) has a big window. It resembles particle-hole continuum of a 1D fermi gas rather than a 2D fermi gas.

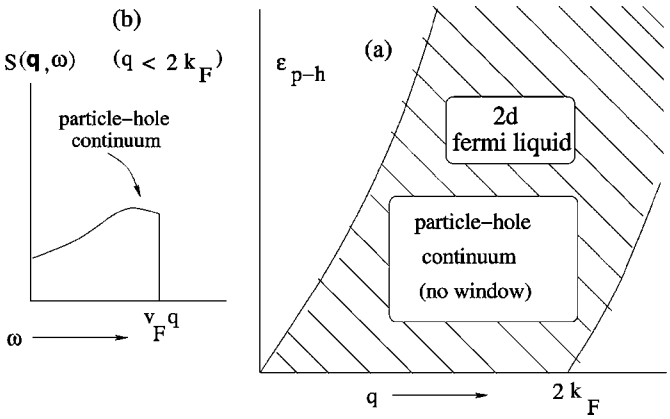

Figure 10. (a) Particle-hole continuum without a 'window' for a 2d fermi gas. (b) $S(\boldsymbol{q},\omega)$ for $q < 2k_F$.

One effect of electron electron interaction is to modify the excitation spectrum. We studied the particle-hole excitation spectrum by a straight forward RPA analysis, looking for spin-

1 collective mode or triplet exciton. Based on what happens in molecules such as benzene, anthracene *etc.*, which are finite pieces of graphene, we expected a spin-1 collective mode to emerge in some region of the window. To our pleasant surprise we found that a gapless spin-1 branch emerged in the full window, that is, all over the BZ. Thus a new spin-1 collective mode branch has been predicted for a single graphene sheet. Its energy ranged from zero to about 2 eV. In real graphite, inter layer coupling modifies the spectrum somewhat,particularly below about 0.2 eV.

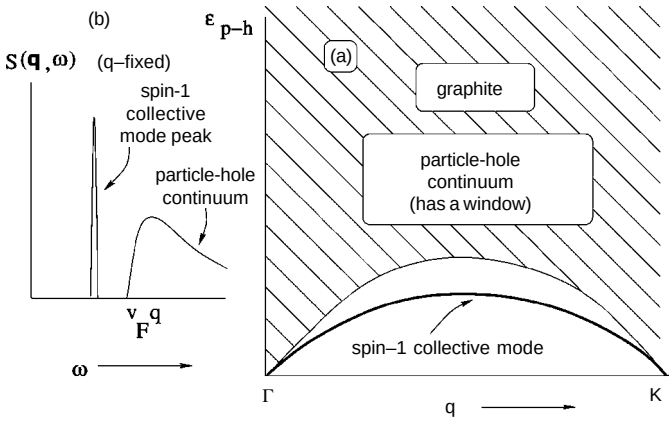

Figure 11. (a) Particle-hole continuum with a 'window' for graphite. (b) $S(\boldsymbol{q},\omega)$ for $q > q_c\left(\sim \frac{1}{50}\frac{\pi}{a}\right)$.

What is the spin-1 spectrum to do with RVB ? If electrons in a graphene sheet are non interacting, singlet correlation exists in the ground state only because of kinematics imposed by Pauli principle. That is, a Bloch state is occupied by two electrons with opposite spin, to make a spin singlet in k-space. This minimal singlet correlation is kinematic in origin. However, when one introduces finite U, repeated collisions in the spin singlet channel enforce spin singlet correlations in the ground state. If U were large compared to the band width, we would have had a Mott insulator and these collision processes would have been called superexchange processes. But graphene is not a Mott insulator. Still some kind of kinetic exchange processes continue to exist, which give an enhanced near neighbor singlet correlations in the ground state, compared to the free fermi gas.

In other words, the emergence of spin-1 collective mode indicates a coherent modification of the free fermi gas state, into an RVB state or a quantum spin liquid state. If there is an RVB physics and if it is a metal, why a finite temperature superconductivity is absent in graphite ? I have found, in a recent work[94] that the development of RVB correlation (pre existing singlet pairs) in a graphene sheet fail to make it a superconductor, because of vanishing of the single particle density of states at the fermi level.

Recently, single graphene states have been isolated and studied, from quantum Hall effect point of view[95], yielding spectacular integer quantization of Hall conductance. It will be interesting to study single graphene sheet and look for consequences of RVB correlations, including large superconducting fluctuations, spin-1 collective modes and its effects.

It is a pleasure to recall important contributions from the Chanchal Majumdar group on quantum theory of magnetism, including the Majumdar-Ghosh model, that is being celebrated in this meeting.

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