Twenty-five Years of High-Temperature Superconductivity –
A Personal Review

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Abstract. I present a personal review of the last twenty-five years of research on high-temperature superconductivity.

Twenty-five Years

Yes, folks, it has been 25 years and a few months since most of us first learned of the existence of the cuprate superconductors. The materials meeting in Boston of Dec ’86 was the venue for the first few of a flood of confirmatory experimental papers; and the Bangalore meeting of January 1987 was the venue where theoretical ideas were first discussed among a substantial community. Is my talk there about RVB the first ever on theory of high Tc? I don’t really know.

In that rather confused talk, and the Science paper which followed in March, I made two contentions which have turned out to be extraordinarily prescient (or lucky?). The first of these was that the CuO₂ planes which are the prominent feature of this class of material would turn out to be best described by the simple Hubbard Model

\[ H = \sum_{i,j,\sigma} t_{ij} c_{i,\sigma}^* c_{j,\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]  

which is often used to model the Mott metal-insulator transition. This model and this transition were a classic unsolved problem of theoretical physics—why should not this classic problem—the doped Mott insulator, we can call it—turn out to be the source of the new, puzzling behavior? It was not just guesswork, of course—I could see how the giant Jahn-Teller distortion which creates the planes would be expected to split out the single band of the Hubbard model—but still a bit lucky. Incidentally, electron, as opposed to hole, doping, in this view, does not lead to the simple Hubbard model, but has strong polaron effects. As far as I know, all of the papers which have made any headway with the problem work with the one-band Hubbard Model, and without fear of successful contradiction I shall take this as given.

The second contention was rather more of a leap in the dark. It had two parts: one was that the pairing was due to spin interactions via the antiferromagnetic superexchange implied by equation [1]; and the second was that the superconducting pairing could grow out of a novel insulating quantum state, a liquid of pair bonds or Resonating Valence Bond (RVB) state. In the first I was certainly not original:
Scalapino and Hirsch, and Schmidt-Rink et al, had presented similar ideas over a year earlier. But they spoke in terms of “spin fluctuations” and as will be one of my main points, spin fluctuations are by definition a weak coupling phenomenon in metals, not descriptive of what’s going on here.

I surely wish that I could say “and starting from this it was all obvious!” Quite the opposite: as I have described elsewhere,[1] I almost immediately jumped off of my own bandwagon and abandoned the RVB, leaving it to be followed up by others—Maurice Rice and his group,[2] Patrick Lee et al.[3] Gabby Kotliar et al,[4] and others including Bob Laughlin, aka Hiawatha [5] -- and with my considerable group I spent a decade wandering off in obvious, though it was not until 2002, 15 years into the problem, that it began to seem so to me.

At this point I shall have to abandon the mode of personal reminiscence and go into a bit of technical discussion of the Hamiltonian in equation [1]. This is so simple that it basically has only two parameters aside from the temperature, the ratio $0 < U/t < \infty$ giving the coupling strength, and the doping $0 < x < 1$, defined as 1 - the number of electrons per site.

Fig 1. $U vs x$ diagram for Hubbard model, showing the two fundamental separators: the Mott line where spin fluctuations diverge, and the Tallon separator between large and small Fermi surface physics.

In the figure 1 I plot $U/t$ on a scale from 0 to $\infty$ vs $x$ and try to delineate boundaries between broad classes of behaviors. If $U$ is small we will just have a metal, even for small $x$; but as we increase $U$, especially at small $x$, the ladder diagrams for spin fluctuations, which I show in figure 2, begin to diverge, and the system can go unstable either to spin density waves or to singlet superconductivity. But it still remains a metal, especially above the transition temperature of whatever ordering happens.

For $x=0$, it is well-known that there is a critical $U/t$ for the Mott transition. I like to think of the Mott transition as not a transition between states, like the superconducting transition, but between models. Above it, it no longer makes sense to start from electrons near a Fermi surface; instead one thinks of spins in a Heisenberg model. The other possible view of it is that it is where the spin fluctuations diverge: they become a cloud of bound states outside of the two-Fermion continuum, and acquire their own dynamics.
Fig 2. Spin fluctuation ladders the divergence of which occurs at the Mott line and separates off the antibound subspace.

But from that point of view this transition must extend into the continuum where $x$ is finite; and I draw what to me seems the most likely trajectory for it in the $U/t$ vs $x$ space. The important point to make is that there is sound experimental evidence that the cuprates are where I have drawn them, always above this generalized Mott transition. Above this line, we must somehow eliminate the divergent bound states from our model, as was done formally by Walter Kohn in 1964 for the case $x=0$ (following my 1959 idea). What we did was to canonically transform away all of the matrix elements of the kinetic energy which led into doubly occupied hole states. This canonical transformation can be expanded in powers of $1/U$, and this expansion replaces, in principle rigorously, the Hubbard model operating in the full space with a Heisenberg model acting in a space with spins only.

Maurice Rice and collaborators, as well as a number of others, generalized this transformation procedure to a derivation of the “t-J” Hamiltonian

$$H = P \sum_{i,j,\sigma} t_{i,j} c_{i,\sigma}^* c_{j,\sigma} P + \sum_{i,j} J_{i,j} S_i \cdot S_j$$

$$= T + J$$ with

$$P = \prod_i (1 - n_{i,\uparrow} n_{i,\downarrow})$$

[2]

$P$ is the famous (or to some, notorious) Gutzwiller projector. But it is not here used as a calculational approximation, but as a rigorous constraint on the appropriate “effective low-energy theory” for the cuprate problem. Above the critical line in figure 1, in order to describe low-energy states of the Hubbard model one MUST confine them to a projected subspace if we are not to mix in very high-energy states into low-energy phenomena. If one does not do that one simply produces boring, misleading nonsense.
simple, sharp Fermi surface. It has the "strange metal" which occurs to remain only a perturbation.

Upon a thought of as the most well-known of these is the kinetic energy term $T$ vanishes and the low-energy states are those of the Heisenberg model $J$. The most well-known of these is the antiferromagnet. The states of this with added holes were studied by Shraiman and Sigija in '89 and they have a Dirac-like zero at $k=\pi/2,\pi/2$. So added holes would have a small “pocket” Fermi surface around these nodes.

An alternative state which doesn’t break translational symmetry is the RVB; as a number of us showed years ago this is not competitive with the antiferromagnet; rather the antiferromagnet can be thought of as derivative from it, a broken symmetry version of the same state. Therefore it is not at all surprising that it has the same Fermionic excitation spectrum for added holes, a set of four Dirac nodes at the $\pi/2,\pi/2$ points. Both of these insulating states, then, count their Luttinger’s sum rules from $x=0$, not $x=1$ as one has for a simple metal. (It was Maurice Rice and collaborators who first emphasized this fact.) So in this region the sensible thing to do is to start by diagonalizing “J”, and then add in “t” where the hole Fermions are in a small Fermi surface around or near the nodes.

On the other hand, when the doping is great enough we have all kinds of experimental evidence that there is a true Fermi surface, with area proportional to $n_h=1-x$. So for $x$ large enough the state is based upon a large Fermi surface, which results from starting with $T$ as one’s $H_0$ and treating $J$ as a perturbation.

So we have, as a function of $x$, another very fundamental boundary: between the states based upon a large Fermi surface, and those where the spins have already paired up at high energies and there remains only a small Fermi surface. This is marked as the heavy blue line in Fig 3. It is the locus of all kinds of physical changes, as was first noticed by Loram and Tallon.

The states to the right of the Loram-Tallon line have been studied in a sequence of papers by my student Casey and myself, and the situation there seems under control; I spoke about the explanation of the “strange metal”, which occurs there, at the Boston APS meeting. It is not a conventional Fermi liquid, but can be related to transport properties and superconductivity in a “hidden” true Fermi liquid with a simple, sharp Fermi surface. It has little to do with critical fluctuations which are often adduced for it.

Fig 3. $T - x$ diagram for cuprates showing Hidden FS to Hidden RVB separation at Loram-Tallon line. Also shown is $T^*$, where pairing occurs; a rough estimate is $T^* - J_t x$ from earlier argument. For the reader: is TRSB related to HRVB?

Therefore, when we confine ourselves to the cuprate line on this diagram, we are studying the states of the $t$-$J$ Hamiltonian. We exhibit them in the familiar “generalized phase diagram” of the cuprates in the space of $x$ vs $T$ (Fig 3).

In this diagram there is again a very important boundary which is more fundamental than a mere phase transition or a critical point. To understand this, let us again look at the Mott limit $x=0$. In this limit the kinetic energy term $T$ vanishes and the low-energy states are those of the Heisenberg model $J$. The most well-known of these is the antiferromagnet. The states of this with added holes were studied by Shraiman and Sigija in '89 and they have a Dirac-like zero at $k=\pi/2,\pi/2$. So added holes would have a small “pocket” Fermi surface around these nodes.

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\[ = \text{"s+ id"} = \cos k_x + \cos k_y + i(\cos k_x - \cos k_y) \]

Fig 4. “Portrait of an RVB” – to show extreme asymmetry of Green’s function at x – 0. (Yazdani)

Fig 5. Early Davis tunneling data showing similar abrupt dropout of electron amplitude at end of “arc”.
A second line, marked $T^*$, is drawn in Fig 3. Empirically this is the locus of indications that spin pairing effects begin below $T^*$. Theoretically, it agrees with the d-wave gap energy calculated in 1988 by Rice’s group and by Kotliar and Liu from the t-J model, the Gutzwiller approximation and renormalized MFT.

But there are still many mysteries on the underdoped side, the famous “pseudogap” problem. Here we must first diagonalize “J”, as I said, and at highish temperatures that means that the state will be an RVB: but which RVB? In the early days it was discovered, following Laughlin, that the RVB could be represented as a Gutzwiller-projected “flux phase”, the one-electron state in which the wave-functions are required to experience a phase shift of $\pi$ or $-\pi$ around each elementary plaquet in the square lattice. (this is completely equivalent, under projection, to my group’s preference: an s+id superconductor) Some authors supposed that one could accommodate holes by simply allowing this $\pi$ phase to change, but as Rice et al found, eventually, this phase is coupled to the lattice structure commensurably (they call this “umklapp”) and does not move in k-space as holes are added. It is essentially an insulator because (also) at x=0 it has no electron excitations (see figure 4), only holes.

What happens at finite x? (see figure 6) If x is pinned at zero by keeping the chemical potential within the Mott gap there are only spinons, which can only be created in pairs and form a Dirac cone with its apex at $(\pi/2,\pi/2)$. But as the chemical potential for holes reaches the edge of the Mott gap the spinon states become ordinary holes and the Dirac cone begins to accommodate a finite density of holes, making a small pocket of Fermi surface. If no superconductivity intervened, there would be an electron spectrum up to a finite energy $E_F$. But what seems to happen at low temperature is that the electrons are born paired with the holes, and that the spectrum is therefore necessarily perfectly symmetric up to $E_F$, where it breaks off in a cusp singularity on the electron side because all the states are gapped, but the gap retains the d-wave character of the RVB. I show you a number of instances of this behavior of the tunneling spectrum in figure 5, which has been emphasized by Ali Yazdani.

The further evolution of these pockets was recognized by Rice et al to lead to a crossover to the conventional Fermi surface; but because that group omitted the large contributions to the particle self-energies of the RVB, they made two unphysical predictions: at low doping, the pockets surround the nodes on the diagonals; and at near optimal doping, the n kinetic energy allows electron pockets, which are unphysical.

At this point the kinetic energy term begins to be finite because there are now a few empty sites for electron hopping. The Gutzwiller procedure refers only to the site occupancy and does not introduce in
itself any correlations at all in momentum space, so that the kinetic energy, to a very good approximation, is simply renormalized by a factor \( g = 2x/(1+x) \) proportional to the number of holes. That means that the phase rigidity of the superconductivity is very weak and the transition temperature very low (even 0 below \( x = 0.055 \)). So the system undergoes a phase transition into a state where the electrons and holes in the pockets remain paired but lose their phase coherence. This is the “vortex liquid” phase discovered by Ong and whose limits have recently been beautifully defined by c-axis infrared spectroscopy of the Fribourg group (reported at this conference). See figure 7. This phase has an upper critical temperature where pairing in the pocket-arcs gives out.

![Figure 7](image)

**Fig 7.** Delineation of 3 phases of pseudogap region: superconductivity in pocket-arcs, vortex liquid in pocket-arcs, RVB with no charge pairing. As measured by C. Bernhard group, Fribourg.

![Figure 8](image)

**Fig 8.** Pocket shapes as given by Rice et al, omitting spin pairing self energy.
Fig 9. Gap distribution if arc gap is d-wave.

Fig 10. Gap distribution measured by nonlinear diamagnetism (Li): note amplitude T-dependent, NOT max gap.

But although this phase has an upper critical temperature because the superfluid density gives out, the gap as a function of momentum does NOT appear to be at all temperature dependent. This has been demonstrated in Lu Li’s data on non-linear diamagnetism of, which can be shown to be a good measure of the gap distribution. The principle is illustrated in figure 8. We imagine the arc-pocket of Fermi surface as in the last figure, centered on the Brillouin zone diagonal where the gap is zero; so the gap as a function of k along the Fermi surface rises more or less linearly on both sides of zero as shown. If we convert that into the density of a given gap, P(Δ), that is constant as a function of delta, as shown in figure 9. Finally, we can convert gap into field by noting that the diamagnetism of electrons with a given gap disappears when H > Hc2, and Hc2 may be defined as the field where

\[ H_c^2 = \frac{\Phi_0}{B} = \frac{\zeta}{\Delta} = \frac{\hbar v_F}{\Delta} \]

so \( \sqrt{H} \propto \Delta \), since \( v_F \) is nearly constant
Fig 11. Same as Fig. 10 for a widely different x.

Fig 12. Summary of pseudogap physics.

A plot of $\rho_s$ vs square root of $H$, then, which is available from Li’s measurements for two different dopings (see figures 10 and 11) tells us the maximum value of the gap. What is noteworthy is that while the superfluid density decreases with $T$, the maximum field—and hence the maximum gap—does not. The gap is not self-consistently and cooperatively determined: it comes from outside the pocket-arc! We can conclude only that it is determined by the RVB spin pairing, which serves as a kind of Higgs-like mechanism to determine gaps for the real electrons in the pocket-arcs.

I present a summary in my final figure 12.
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