

Quantum Percolation Theory and High-Temperature Superconductivity [and Discussion]

J. C. Phillips, A. O. E. Animalu, P. W. Anderson and E. Salje

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Quantum percolation theory and high-temperature superconductivity

BY J. C. PHILLIPS

AT&T Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.

An overall view of the methodology of quantum percolation theory as applied to high-temperature superconductivity clarifies the differences in its approach compared to others. Several crucial predictions have been confirmed by experiment, including the percolative nature of the superconductive transition itself.

1. Introduction

Many-layered cuprates (such as $\text{YBa}_2\text{Cu}_3\text{O}_7$) are superconductive with transition temperatures about five times higher than those obtainable in intermetallic compounds such as Nb_3Sn . These materials are often insulating when initially formed and become metallic and superconductive only when subjected to carefully controlled oxidation or reduction. Even then their room-temperature resistivities are usually larger (greater than $200 \mu\Omega \text{ cm}$) than the Mooji resistivity (*ca.* $100 \mu\Omega \text{ cm}$) which separates ordered 'good' metals ($d\rho/dT > 0$, with predominant scattering by phonons) from disordered 'bad' metals ($d\rho/dT < 0$, residual scattering by disorder). We may say that the highest transition temperatures are found not in 'good' metals like Al and Pb, but in oxides which are 'bad' metals, with resistivities similar to those found in metallic glasses.

Most theoretical efforts to explain this unexpected situation have focused on the search for alternatives to the electron-phonon interaction which is the basis for the bcs theory of superconductivity in intermetallic compounds (Phillips 1989*a*). The two alternatives discussed most often are electron-magnon and electron-exciton interactions. These alternatives are interesting (and perhaps even refreshing), but there are extremely persuasive reasons for excluding them at present. The strongest is probably Ockham's razor, which says that however attractive novelty may be for its own sake, we should insist that the standard electron-phonon mechanism be disproven before we discard it. The efforts to do this so far have relied mainly on naive interpretations of data from heterophase samples (where magnetism and superconductivity coexist, but in different parts of the sample) or on misassignment of infrared absorption bands (due not to excitons but to defects) or to misinterpretations of the isotope effect. Meanwhile, there is growing evidence (Phillips 1990*a*; Reichardt *et al.* 1989; Franck *et al.* 1991) for strong electron-phonon interactions from isotope effect experiments and from phonon softening at T_c . Finally there is the generic assessment (Phillips 1989*a*) which shows that one-electron-ion interactions are 10–20 times stronger than electron-magnon or electron-exciton interactions, so that the latter could never be taken seriously as a mechanism for Cooper pairing in high T_c materials.

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451

[59]

2. Quantum percolation theory (QPT)

The alternative to exotic interactions is percolation, or two-component Fermi liquid theory, which says that near a metal–insulator transition the electronic states near the Fermi energy E_F can in favourable circumstances be separated into two groups, localized and extended. The electron–phonon interaction, although not large on the average, can be large for a few extended states because it is small for many localized states.

The answer to the key question of whether Fermi energy extended and localized states can coexist and be separated into a two-component Fermi liquid in a disordered metal or in the impurity band of a semiconductor depends on dimensionality d . For $d < d_m = 2$ all states are localized, whereas for $d > d_m$ some extended states may exist. Because the marginal dimensionality $d_m = 2$, it is natural to suppose that this is the reason that the layered cuprates are both bad normal metals and high-temperature superconductivity (HTS). The derivation of the marginal dimensionality $d_m = 2$ is topological (orbital) and does not depend on the nature of the electron–electron interactions (Coulomb, exchange, excitonic, or what have you), emphasizing the same point that exotic interactions are not the key to HTS.

One of the peculiarities of localization theory is that there seem to be as many theories as there are theorists. Considering that classical percolation, a simpler situation, is always treated by numerical rather than analytic methods, it is not surprising that quantum percolation is a complex subject. Most of the final decisions must be made by experiment, but the possibilities can be listed theoretically. Some of the central issues are matters of style, and here consistency is important. For example, the main ideas of QPT have not changed since I first presented them (Phillips 1983*a, b*, 1988), and several predictions have been successful. This has not been the case for any of the theories based on exotic interactions.

The main ideas of quantum percolation theory, in addition to the separability of localized and extended states for $d > d_m = 2$, in the context of the cuprates, are the following. We are concerned with the states contained in the energy shell $|E - E_F| \lesssim E_c$, where $E_c \approx 0.1 - 0.2$ eV is only somewhat larger than the maximum vibrational energy (*ca.* 0.05 eV). In addition to the planar CuO_2 states near E_F (which would be metallic if they were three dimensional) there are defect states with energy E_d in the semiconductive layers (such as BaO in $\text{YBa}_2\text{Cu}_3\text{O}_7$) at $|E_d - E_F| \lesssim E_c$. These defect states not only pin E_F but they also act as electrical bridges between CuO_2 planes or CuO chains. Conduction in these planes is blocked by domain walls generated by residual disorder, with a typical domain wall spacing $w \approx 100 \text{ \AA}$ †. These electrical bridges generate an effective dimensionality $d = 2 + \epsilon$ associated with percolative paths of the type shown in figure 1.

Elucidation of the nature of localized and extended states is provided by spectroscopic experiments on $\text{YBa}_2\text{Cu}_3\text{O}_7$, notably Raman scattering (Cooper *et al.* 1988; Phillips 1989*b*) and single-domain polarized reflectivity studies (Schlesinger *et al.* 1990) of the electronic continuum near E_F both above and below T_c . For $T > T_c$ the continuum observed by Raman scattering for $\hbar\omega \lesssim E_c$ is somewhat enhanced near $\omega = 0$ by defects (probably oxygen vacancies O^\square on CuO chains) but it is approximately constant, which suggests that the measured scattering strength

† $1 \text{ \AA} = 10^{-10} \text{ m}$.

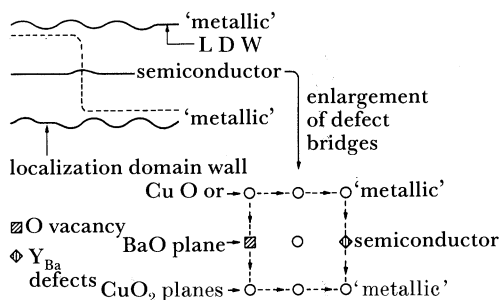


Figure 1. A sketch of interplanar current paths avoiding localization domain walls by utilizing Fermi-energy defects.

provides a faithful representation of $N(E)$. For $T \ll T_c$ this same continuum scattering is proportional to $|E - E_F|$, and in spite of superposed vibrational bands, a planar energy gap E_g is recognizable near $500 \text{ cm}^{-1} \approx 8 kT_c$. Two-component Fermi liquid theory (FLII) readily explains the observed spectral changes. For $T > T_c$ both extended and localized states contribute to the scattering. Well below T_c , according to FLII, only the extended Fermi liquid states have become superconductive and been pushed above E_g . The localized Fermi liquid states are confined to incoherent planar domains and do not become superconductive. Their density of states $N_l(E_F)$ is proportional to $|E - E_F|$ because of maximal elastic metallic hybridization (Phillips 1990*b*).

FLII immediately makes crucial predictions concerning the frequency and/or temperature dependence of the Drude currents carried by extended states. The interplanar coherence of the extended states is fragile and is destroyed by elastic scattering by residual disorder. In one-component Fermi liquids (FLI) in strongly disordered metals elastic scattering makes the residual resistivity nearly constant (within a few per cent). In FLII we have a selection rule for elastic scattering of extended states: they are always scattered into localized states. But while $N_e(E)$, the density of extended states, is nearly constant near E_F (as in a normal Fermi liquid), $N_l(E) \propto |E - E_F|$. This means that $\Gamma_e(\omega, T)$, the scattering rate for extended states, is proportional to (ω, T) , in agreement with experiment (Schlesinger *et al.* 1990). Notice that these predictions do not require any modification of the extended state Fermi surface states, whereas some other attempts using FLI to explain $\rho(\omega, T)$ require (Varma *et al.* 1989; Anderson 1990) that the renormalized quasi-particle strength $z(E_F) = 0$.

It appears then that the crucial concept which is pivotal to understanding the electronic structure of HTS is QPT or FLII. This concept originally arose (Phillips 1983*a, b*, 1988) in an effort to understand the metal-semiconductor transition in impurity bands (Si:P). In earlier work Mott assumed (Mott 1972; Cohen 1970) that localized and extended states could not coexist, and therefore that this transition was always discontinuous, whereas Anderson and coworkers showed (Abrahams *et al.* 1979) with a classical model that it could be continuous, and that in some cases the marginal dimensionality for achieving metallic conductivity might be $d = d_m = 2$. The key step which I took (Phillips 1983*a, b*, 1988) was to argue that not only could localized and extended states coexist, but that also in certain cases these coexisting states could be separated. This separation leads to the two-component Fermi liquid model (FLII) which differs drastically from the ordinary Fermi liquid model FLI

which is used to describe the normal state in conventional metallic superconductors. Although classical scaling arguments (Abrahams *et al.* 1979) were used only to guess that $d_m = 2$, I was able to derive this result from the relation $d_m - 1 = \frac{1}{2}d_m$. This relation is the quantum analogue, based on the uncertainty principle, of a similar relation derived in classical random-field Ising models (Imry & Ma 1975).

3. Some general remarks

The separation of localized and extended states in a highly disordered medium is possible only as a hypothetical process, because near the metal–insulator transition the ‘signal’ (the extended states) is very small compared to the ‘noise’ (the localized states). The possibility of such a separation varies from case to case. It cannot be proved, but must actually be decided by experiment. For instance, this separation is possible in Si:P, but only for uncompensated samples (Phillips 1983*a, b*, 1988). In axiomatic set theory (Cohen 1966; Tiles 1989) one can show that once extended states exist, they can be separated from localized states regardless of energy. (This is called the subset axiom.) The separability is a general property, and it does not require us to find a constructive algorithm, that is to say the correct unitary transformation which actually performs the separation. (If we could find such an algorithm, we would validate the axiom of choice (AC) for our disordered system. But the remaining axioms, including the subset or separability axiom, are valid independently of the AC, according to Gödel and Cohen (Cohen 1966; Tiles 1989). Such an AC algorithm is especially difficult to construct in the face of the uncertainty principle, but its absence in no way impairs the validity of the subset axiom. The AC is important if we want to impose internal order on (or alphabetize) the subset of extended states, for example, but this is not necessary in the present circumstances, where we need to know only $N_l(E)$ and $N_e(E)$.) In the case of HTS, it is just the high T_c s, together with the layered structures ($d \approx d_m$) that convinced me that a separation is possible.

At this point the reader may well wonder why such a simple construct as FLII has not already gained general acceptance. If we discount some of the obvious (but practically important) explanations, such as a deluge of theories of HTS, then we may hazard the following observations. QPT has not been generally accepted (Lakner & Löhneysen 1990) even as an explanation (Phillips 1983*a, b*, 1988) for the conductivity exponent m in the relation $\sigma \propto (n - n_c)^m$ in Si:P, where $m = 0.50$ in the uncompensated state, even though it is the only theory that explains the result. (All other theories give $m \geq \frac{2}{3}$.) Even in this more leisurely field, the separability of localized and extended states is not generally accepted (Lakner & Löhneysen 1990). Probably this comes from the reluctance of most physicists to accept as a probability the existence of the abstract unitary transformation which separates $\{l\}$ and $\{e\}$ without explicit examples. (However, when such an abstract separation into localized domains and domain walls is made in the classical random-field Ising model (Imry & Ma 1975), it is considered obvious and seminal. Mathematically the two situations are equivalent, but of course the separation is easier to visualize classically in real space than quantum mechanically in Hilbert space.)

We can understand the difference in philosophy between FLI and FLII in another way. In FLI the effects of scattering by disorder on itinerant wave functions are treated by perturbation theory, either in the one-electron approximation or by using

renormalization techniques to describe many-electron interactions. What many scientists apparently do not realize is that renormalization methods, being perturbative, are limited to the range $|1-z| \ll 1$ just like ordinary one-electron theory. The real utility of FLI lies thus in removing divergences associated with strong electron–electron long-range Coulomb repulsion, and it brings very little that is new to our understanding of the effects of short-range disorder near the metal–insulator transition where the renormalization factor $z \ll 1$.

Excellent illustrations of the difference between the set-theoretic and perturbative approaches are provided by numerical studies (Feng *et al.* 1985) of the stiffness transition of the vibrations of amorphous or glassy systems. The $N \times N$ dynamical matrices describing these systems are very complex, with *ca.* $\frac{1}{2}(1-z)N^2$ off-diagonal matrix elements. If these systems were treated in the spirit of FLI, we would construct a virtual crystal model, obtain its eigenvalues $\{\omega^2\}$, and then scale these eigenvalues by $\omega_n^2 + (1-z)\omega_{\text{od}}^2$, where ω_n^2 are the diagonal matrix elements and ω_{od}^2 represents off-diagonal effects. This gives good answers for z near 1, but near the percolation threshold $z \ll 1$ the answers are qualitatively wrong. In particular, perturbation theory will never yield the cyclical (Goldstone) modes which are found by exact matrix diagonalization. Thus the recent failures (Varma *et al.* 1989; Anderson 1990) of FLI to describe HTS are not technical in origin, and they cannot be repaired by technical refinements. The failures are conceptually intrinsic to FLI and cannot be overcome without replacing FLI by FLII.

A deeper and more fundamental objection to separability is that in any two-fluid model the entropy is lower than in a one-fluid model. By assuming separability but not actually displaying it, are we not in effect postulating a Schrödinger demon who could violate the second law of thermodynamics, which in other contexts leads to perpetual motion machines? The answer is no. Separability is important only to transport (including optical) properties and not to thermal experiments. In transport theories at some stage a relaxation time approximation is always made. This approximation is applied to diagonal elements of the density matrix and it yields different results for different basis sets. It is therefore essential that we choose the correct basis states before we discuss any transport property, including superconductivity.

I conclude by mentioning that in a recent experiment on single-crystal YBCO, Palstra *et al.* (1990) have shown that there is substantial entropy transport in crossed electronic and magnetic fields above T_c . This result can also be explained by QPT, and it provides an excellent illustration of the argument made above that FLII is internally consistent (J. C. Phillips, unpublished work).

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Phil. Trans. R. Soc. Lond. A (1991)

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Discussion

A. O. E. ANIMALU (*University of Nigeria, Nsukka, Nigeria*). Would it not be possible and even natural to replace the localized states by a narrow Cu(3d) band that crosses and hybridizes with an extended broad (2p) band, in a two-band model; in which case there may be a connection between the QPT and a two-band model?

J. C. PHILLIPS. This thought also occurred to me, but I finally abandoned it because in spatially homogeneous two-band models both bands become superconductive at a common transition temperature. In the cuprates, however, the states in the gap remain there down to $T \ll T_c$. It therefore seems natural to assume that these states are localized and that for them $\lambda_{ep} - \mu^* < 0$, where λ_{ep} is the electron-phonon coupling strength and μ^* is the renormalized Coulomb repulsion.

P. W. ANDERSON (*Princeton University, U.S.A.*). (1) The isotope effect was discussed by Fisher *et al.* They remarked that there is a relatively large contribution coming from the ‘natural’ effect of changes in hopping matrix elements, which are exponential in distance. These give us little confidence in deductions from the isotope effect.

(2) I am not aware of serious controversy in the theory of localization. It is accepted that the Si:P case is an exceptional one of strong interactions which has been explained in most features by Kotliar, di Castro and others. Localization in percolating networks was well treated by B. Shapiro and has no particular unusual

features. In no case can localized and extended régimes overlap near the Fermi energy.

(3) It is often claimed that the cuprates are poor conductors. This is far from true: their room-temperature conductivity per electron is only 2–3 less than pure copper. In particular, localization phenomena always occur close to the Mott–Yoff–Regal criterion $k_F l \approx 1$ while their number is greater than 10 in these metals.

J. C. PHILLIPS. The paper by Fisher *et al.* was never taken seriously by me for several reasons, including fudging of several parameters. In any event its relevance disappeared after large isotope shifts were found in LSCO, as I predicted, and more recently in (Y, Pr) BCO alloys, as discussed in the reply to Professor Salje.

The wide variety of viewpoints on localization is a characteristic aspect of the subject which is discussed extensively by Sir Nevill Mott in almost all of his excellent papers on this subject during the 1970s and 80s. He, himself, for example, adhered to the discontinuous model of the Si:P transition until quite recently, when he seems to have tacitly adopted the FLII model. The various scaling papers mentioned by Professor Anderson, curiously enough, seem to have regressed to the discontinuous model, a large step backwards from his own continuous (but linear rather than square root) scaling model of 1979. I have recently shown that strong interactions not only do not explain the square root dependence of σ on $(n - n_c)$ in the $T = 0$ limit, but they are also not needed to understand the cross-over from square-root to linear behaviour in partly compensated samples. Also, I have shown that strong interactions, as treated by first-order perturbation theory by Altschuler and Aronov, are not the appropriate way to explain $\sigma = \sigma(T) - \sigma(0)$ for n near n_c , but that this difference can be explained entirely by elementary fluctuation theory in the context of quantum percolation. Of course, in the end ‘forces are at work’, as someone said, and it is the competition between Coulomb repulsion and kinetic energy that is responsible for metal–semiconductor transitions in both Si:P and high T_c cuprates. However, this competition takes place in highly disordered media, and it is the disorder itself, and not the strength of the forces, which governs the functional behaviour in the critical region in Si:P and which generates the giant electron–phonon couplings in the cuprates. As for quantum percolation itself, Shapiro and others discuss only classical percolation. Quantum percolation, because of its two-component nature, is fundamentally different from classical percolation.

As for whether the cuprates are good conductors or not, experimentalists are well aware that the as-prepared samples are generally green, and that subtle oxidation or reduction procedures are required to produce materials which are ‘good’ metals in Professor Anderson’s sense. However, even then, because of marginal dimensionality, a mean free path of order 50–100 Å in a cuprate plane is no guarantee that we have a ‘good’ metal, because electrons in the absence of interplanar defect bridges will still be localized in planar domains 100 Å in diameter. It is the density of these bridges that explains why the number of effective carriers is small and why the associated mean free paths are long. All of these points are examined at length in my book.

E. SALJE (*Cambridge University, U.K.*). The arguments of Professor Phillips seem to be supported by recent experimental results. (1) The isotope effect in YBCO is finite. (2) Phonon renormalization during the superconducting phase transition is as large as 3 cm^{-1} in YBCO. (3) The corrected carrier density during condensation is *ca.* 10%

Phil. Trans. R. Soc. Lond. A (1991)

of the total carrier condensation. However, does not Co doping with increased O concentration change T_c for small doping levels?

J. C. PHILLIPS. With regards to the isotope effect, recent experiments by Franck *et al.* (1991) on the isotope shift in (Y, Pr)BCO alloys confirm that its small value in YBCO is accidental and is probably the result of anharmonic variations in domain wall width (Phillips 1990*a*), where I also discussed phonon renormalization. The reduction in the effective carrier density that he mentions is fully consistent with interlayer percolation via apical oxygen vacancy states, with the apical oxygen vacancy concentration being about 6%, as revealed by recent well-refined diffraction data on an untwinned YBCO sample. Finally, I have already discussed the effect of Co, Ni and Zn doping on T_c (Phillips 1989*a*). There I concluded that serious questions arise concerning dopant homogeneity on the appropriate length scale, which is less than 100 Å. More recent data appear to indicate better homogeneity, but it is still doubtful whether adequate levels of homogeneity have been achieved.