HOLE CONDUCTORS AND SUPERCONDUCTORS

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ABSTRACT

A fundamental asymmetry exists between electrons and holes in solids. Electrons at the Fermi surface give rise to high conductivity and normal metallic behavior, holes at the Fermi surface yield poor conductivity and give rise to superconductivity. We review here the theoretical basis for this assertion and its implications, particularly for the understanding of high temperature superconductivity in oxides.

I. HOLES VERSUS ELECTRONS

There exists a fundamental asymmetry in solids between electrons and holes. This fact has been largely unrecognized or neglected in theoretical solid state physics. In fact, solid state physics textbooks often emphasize the fact that electron and hole descriptions are essentially equivalent within a single particle picture.[1] In attempting to understand many-body phenomena like superconductivity, however, this asymmetry assumes foremost importance.[2]

We can understand this asymmetry in various ways. Consider the situation depicted in Fig. 1. In (a), we add an electron to a lattice of H^+ ions. As is well known, the electron goes into a "bonding state." This state is a smooth $k = 0$ wavefunction that has a large amplitude for the electron to be in the region between the positive H^+ ions. Thus it gives rise to cohesion, i.e. an attractive interaction between the H^+ ions (hence the name bonding).

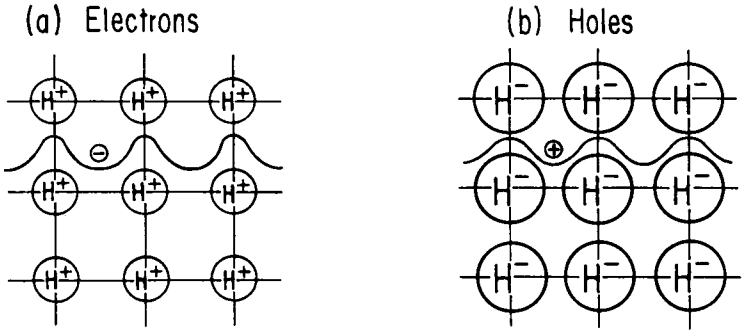

Figure 1: Schematic depiction of a bonding state for (a) an electron in a lattice of H^+ ions and (b) a hole in a lattice of H^- ions. The symmetry between electrons and holes is broken because the H^- ion deforms leading to a qualitatively different state from the one depicted in (b).

Consider now a lattice of H^- ions, as shown in Fig. 1(b), and imagine adding a positive charge, a hole (i.e., removing an electron). If particle-hole symmetry existed, the positive hole would go into a smooth bonding state with large amplitude between the H^- ions to

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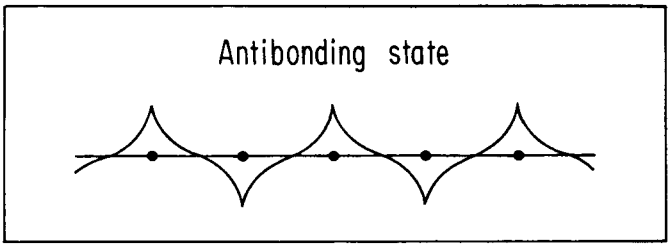

Figure 2: Schematic depiction of an antibonding state, the state of an electron at the top of the electronic band or equivalently the state of a hole at the bottom of the hole band.

provide cohesion between them, as shown in Fig. 1(b); this would be exactly the same situation as in Fig. 1(a) with the sign of the charges reversed.

However, this is *not* what happens. The reason is that it is not possible to think of the H^- ion as a rigid object, as H^+ is. The Coulomb interaction of the hole with its background, the H^- anions, causes a large disruption of this background. The end result is not a smooth bonding state for the hole as in Fig. 1(b), but instead a "bumpy" antibonding state, as shown in Fig. 2: the wave-function switches sign in going from site to site. This difference in the nature of the wavefunctions of electrons and holes has fundamental consequences for their properties, as we will see below.

These considerations may seem trivial; we emphasize them, however, because this physics is completely missed in the type of Hamiltonians that are usually considered to describe many-body effects in solids, like the extended Hubbard model:

$$H = \sum_{\substack{\langle ij \rangle \\ \sigma}} t_{ij}(c^+_{i\sigma}c_{j\sigma} + h.c.) + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij \rangle} n_i n_j. \qquad (1)$$

This Hamiltonian is particle-hole symmetric if the band structure defined by t_{ij} is so (for example, nearest neighbor hopping on a bipartite lattice). The properties of the system described by Eq. (1) with a few electrons or with a few holes are hence identical, and the asymmetry between electrons and holes is lost.

II. THE HAMILTONIAN

To recover the fundamental physical difference between holes and electrons, we have proposed a Hamiltonian for holes that includes explicitly the interaction of the hole with its background, the H^- anions in Fig. 1(b).[2] This amounts to treating the holes as if they were electrons and incorporating "by hand" the physics that makes them different. The phenomenological Hamiltonian that results is given by:

$$H = -t\sum_{\substack{\langle ij \rangle \\ \sigma}}(c^+_{i\sigma}c_{j\sigma} + h.c.) + \lambda\sum_{i\sigma} n_{i\sigma}\sigma^i_z + w\sum_i(\cos\theta\sigma^i_z + \sin\theta\sigma^i_x) + U_0\sum_i n_{i\uparrow}n_{i\downarrow} \qquad (2)$$

where the pseudospin degree of freedom σ^i describes the "deformation" of the H^- ion by the presence of the hole. (We have omitted the nearest neighbor repulsion between holes and specialized to nearest neighbor hopping for simplicity.) It was shown in Ref. 3 that hopping of a single hole from site to site results in flipping the pseudospin at the site where the hole goes through. This is a way of representing the 180° phase flip that occurs in an

antibonding state from site to site (Fig. 2). It was further found in exact cluster studies of the Hamiltonian Eq. (2)[3,4] that the interaction with this pseudospin leads to two physical effects: a band narrowing (effective mass enhancement) for hole conduction, and a pairing (attractive) interaction between holes. This pairing interaction was found to increase with the hopping amplitude t and to become weaker when too many holes were added.

It was then shown[5] that elimination of the pseudospin degrees of freedom in perturbation theory in the hopping leads to an effective Hamiltonian for the holes that accurately reproduces the properties of the original one Eq. (2), given by:

$$H_{eff} = -\bar{t}\sum_{\substack{\langle ij\rangle \\ \sigma}}(c^+_{i\sigma}c_{j\sigma} + h.c.) - \Delta t\sum_{\substack{\langle ij\rangle \\ \sigma}}(c^+_{i\sigma}c_{j\sigma} + h.c.)(n_{i,-\sigma} + n_{j,-\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow} \tag{3}$$

where in particular $\bar{t} \ll t$ and $\bar{t}, \Delta t > 0$. $c^+_{i\sigma}$ is a *hole* creation operator, and the "modulated hopping interaction" Δt gives a larger amplitude for a hole to hop if another hole is present at the site the hole is hopping to or from. This term in the Hamiltonian Eq. (3) contains the fundamental asymmetry between electrons and holes.

If one looks at the problem from the point of view of electrons rather than holes it is possible to derive the Hamiltonian Eq. (3) in a simpler way.[6] The key point is that an off-diagonal matrix element of the Coulomb interaction between electrons, that is usually neglected, needs to be kept. In deriving a single band Hubbard-like tight-binding Hamiltonian from first principles[7] the following matrix elements for the Coulomb interaction between electrons in local orbitals ϕ_i result:

$$(ij|1/r|k\ell) = \int d^3r d^3r' \phi^*_i(r)\phi^*_j(r')\frac{e^2}{|r-r'|}\phi_\ell(r')\phi_k(r) \tag{4}$$

and the largest ones involving two centers only are:

$$U = (ii|1/r|ii) \tag{5a}$$

$$V = (ij|1/r|ij) \tag{5b}$$

$$\Delta t = (ii|1/r|ij). \tag{5c}$$

The Hamiltonian that results *for electrons* if we assume only nearest neighbor interactions is:

$$\begin{aligned} H &= -t\sum_{\substack{\langle ij\rangle \\ \sigma}}(c^+_{i\sigma}c_{j\sigma} + h.c.) + \Delta t\sum_{\substack{\langle ij\rangle \\ \sigma}}(c^+_{i\sigma}c_{j\sigma} + h.c.)(n_{i,-\sigma} + n_{j,-\sigma}) \\ &+ U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j \end{aligned} \tag{6}$$

where t, Δt, U and V are all positive, and $c^+_{i\sigma}$ creates an electron at site i. The important point is that the first two terms in the Hamiltonian Eq. (6) *necessarily* have always opposite signs if the $c_{i\sigma}$ operators describe electrons.[6] Under a particle-hole transformation and a sublattice rotation the Hamiltonian takes the form Eq. (3) where the operators describe holes and the sign of the hopping interaction term is reversed.

The Hamiltonian Eq. (6) clearly displays the two physical properties that make holes different from electrons, effective mass enhancement and attractive interactions. The first is simplest seen from a Hartree decoupling of the hopping interaction term, which leads to an effective hopping:

$$\bar{t} = t - n\Delta t \tag{7}$$

with n the band occupation. The effective hopping becomes smaller as the band filling increases, leading to a larger effective mass for holes as compared to electrons. Within a standard Drude-type expression for the conductivity:

$$\sigma = \frac{ne^2\tau}{m^*} \tag{8}$$

heavy holes will give rise to poorer conductivity than light electrons.

The attractive interaction can be clearly seen by inspection of the second term in Eq. (6). At the bottom of the band the wavefunction has the same sign on neighboring sites and this term is positive (repulsive); at the top of the band the wavefunction flips its sign in going from a site to its neighbor, $c^+_{i\sigma}c_{j\sigma}$ is negative, and this interaction is attractive. The interactions U and V are of course repulsive throughout the band.

The same physics can be formulated in more general terms[8] than given by Eq. (6), which makes its universality apparent, but the Hamiltonian Eq. (6) contains the essential physics in its simplest form.

III. CONSEQUENCES

The Hamiltonian Eq. (6) gives rise to superconductivity in a conventional s-wave state but with some specific features which we now summarize. Details can be found in the references, particularly Ref. 9.

1. The pairing interaction resulting from Eq. (6) allows for superconductivity even in the presence of large Coulomb repulsion through the combination of two effects: a large "phase space" factor for the hopping interaction, and an energy dependence that helps as in the usual "pseudopotential" effect.[10] For example, in the case studied in Ref. 9 superconductivity was found for the on-site repulsion U up to 30 times larger than the hopping interaction Δt.

2. There is a characteristic dependence of T_c on carrier concentration.[9,11] T_c first increases as holes are added to a full band, due to phase space, goes through a maximum and then decreases to zero when the states at the Fermi surface have lost much of their antibonding character. Such dependence is observed in a variety of systems such as oxide superconductors[12] and transition metal alloys.[13]

3. The superconducting energy gap has an energy dependence, which is very small in the regime of "conventional superconductors" but appreciable for high T_c oxides. It leads to a dependence on carrier concentration of physical properties such as gap ratio and specific heat jump that should be experimentally observable.[9]

4. An intrinsic asymmetry of universal sign is predicted for the N-I-S tunneling characteristics of all superconductors[14]: the tunneling current should be larger when the sample is negatively biased, i.e. for hole injection. This asymmetry is very small in the conventional regime (fraction of percent) but substantial (10-30%) in the high T_c oxide regime.

5. A high sensitivity to disorder exists in the high T_c oxide regime due to the energy dependence of the gap.[9] This explains observations such as the broadening of the resistive transition in a field, the spread in gap values obtained in tunneling experiments and their larger value as compared to "bulk" measurements of the gap such as infrared, and the existence of weak links and hence low critical currents.

We next address some of the issues specific to the oxides. Superconductivity in these materials arises from hole conduction by direct hopping through the oxygen anion network, presumably through the $p\pi$ orbitals.[15] A very narrow band, relatively small Coulomb repulsions and a large modulated hopping interaction Δt lead to high T_c's and short coherence lengths; the ratio of energy gap to bandwidth is a factor of 50 or more larger than for conventional "weak coupling" superconductors. Such conditions will always occur whenever conduction occurs predominantly through holes in an anion network, which is likely also what occurs in the cases where "transient" high temperature superconductivity has been observed in the past.[16] The normal state properties can be explained from the large effective mass[17] that occurs through the hopping renormalization Eq. (7). The Cu-O planar lattice structure is favorable because it allows for close approach between $O^=$ ions in the plane, hence leading to large Δt and high T_c's. The physics is the same in the oxides with Cu, in the 30° K material $Ba_{1-x}K_xBiO_3$ [18] and in the "old" $BaPb_{1-x}Bi_xO_3$.[19] In the latter in particular, evidence has been found for heavy hole carriers at the Fermi energy from thermopower measurements.[20]

With regard to the "electron-doped" oxide superconductors,[21] our model has a specific prediction: oxygen hole carriers will be found in all the samples that go superconducting. It is easy to understand how this can come about: electrons added to Cu^{++} repel the electrons in neighboring $O^=$, pushing them onto other neighboring Cu^{++}. The very same fact that allows for electron doping in those structures, absence of apical oxygen, makes this process energetically favorable as the Madelung potential of the Cu^{++} sites is higher than it would be in the presence of apical O. The net result for each electron added to Cu^{++} is then several Cu^+ and several oxygen holes. We also remark that finding oxygen hole carriers in the electron-doped materials will not lend support to other theories that are based on these carriers.[15,22–25] This is because these theories use as the "glue" that gives rise to the oxygen hole pairing either spin[15,22,23] or charge[24,25] excitations of the Cu^{++} background, and this background is rapidly being destroyed in these oxides by the added plus induced electrons that turn Cu^{++} into Cu^+. Our theory instead will be strongly supported if oxygen hole carriers are found in these materials (and conversely it will be ruled out if it is established that no oxygen hole carriers exist).

We conclude with some general comments. Our theory provides simple answers for many long outstanding puzzles on superconductivity of "conventional" materials,[8] and in particular offers a compelling explanation for the competition found in numerous instances between lattice stability and superconductivity[26]: electrons in bonding states lead to attractive interactions between ions and repulsive interactions between electrons, and hence to lattice stability and normal metals; electrons in antibonding states lead to repulsive interactions between ions (hence their name) and attractive interactions between electrons, and hence to lattice instabilities and superconductivity. Both types are present in most materials (except in simple metals which is why they are not superconducting) and their relative weight determines both the stability and the superconductivity. We believe this model will make it possible to correlate specific aspects of the band structures of materials with the occurrence of superconductivity, and in particular to calculate superconducting T_c's from first principles given detailed information on the states at the Fermi surface. It also provides natural guidelines in the search for materials with higher superconducting transition temperatures. Lastly, it suggests that electron-phonon interactions are irrelevant for superconductivity in all materials.[27]

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